Sorption Reactions between Ionic Species and Magnetite in Aqueous Solution.

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Abstract

The surface chemistry of inorganic materials is of great significance in a number of industrially important processes such as separation of ore by flotation, catalysis, water purification, leaching, as well as in the formulation of some pharmaceutical preparations. This thesis deals with magnetite and its sorption properties. Especially it was focused on the sorption of ions present in the process water and possibly affecting the balling properties of the magnetite concentrate in the pelletizing process. It is well-known that these properties become deteriorated if the magnetite surface becomes less hydrophilic, which motivated the use of an amphiphilic adsorbate (sodium oleate) in this study.

The magnetite nano-particles were synthesized and subsequently characterized by X-ray, electron microscopy, and infrared spectroscopy. The mechanisms of magnetite formation from co-precipitation of Fe (II) and Fe (III) as well as oxidation of ferrous hydroxide were evaluated using iron isotope fractionation measurements (Paper I).

Since magnetite pellets are heated during the sintering process and also may contain small amounts of the hydrophobic collector used in the flotation process, it was interesting to follow what happened with a model collector such as sodium oleate upon heating the magnetite/oleate system. This was studied using a combination of thermal analysis and FTIR spectroscopy. It was found that the oleate molecules were bonded to iron atoms by predominantly a bidentate mononuclear complex and formed essentially a single layer with a surface density of ~36 Å²/molecule of the oleate. Thermogravimetric analysis indicated double bond cleavage that yielded products enriched in oxygen and also capable of forming hydrogen bonds (Paper II).

To study how the magnetite surface might be modified caused by process water, the magnetite nano-particles were evenly distributed over an internal reflection element and this combination was used to study the adsorption of ions present in the process water in-situ. The ionic system included the model collector (oleate) in stead of the collector used in practise (Atrac) to separate apatite from magnetite.

Among ions in the process water, the adsorption properties of sulphate, silicate, and carbonate were studied as well as the effect of calcium ions on the adsorption properties and the competition between silicate and oleate for the magnetite surface. Paper III focused on the effect of Ca (II) on the adsorption of sulphate and it could be concluded that this effect was of minor importance. On the other hand, calcium ions in solution had a large effect on the adsorption of carbonate ions onto magnetite (Paper VII). During the flotation process, silicate is added to the pulp in order to disperse the magnetite particles and make the reverse flotation of apatite from magnetite more efficient. Accordingly, the adsorption of silicate onto magnetite as well as maghemite was investigated as a function of pH (Papers IV and V).

Finally, the kinetics of oleate adsorption onto magnetite and competition between sodium oleate and sodium silicate for the magnetite surface was studied. Of particular interest was to which extent oleate could possibly be substituted for silicate and vice versa. These studies are elaborated in Paper VI.

Keywords: Magnetite, Maghemite, Inorganic Oxoanions, Sodium oleate, ATR-FTIR Spectroscopy, Sorption.
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Introduction
1. Introduction

1.1. Background
Magnetite, one of the important iron ores, can be found in igneous and metamorphic rocks. As the major source of iron ore in the northern part of Sweden, magnetite plays a vital role for the Swedish economy, and of course, for the economy of the Norrbotten province. A large amount of this iron ore is shipped to the iron and steel-making industries in Sweden and other countries every year. Prior to transport to the market, a series of pre-treatments must be performed on the ore in order to meet the customer requirements. Flotation, pelletization, pulverization and sintering are common ore processing methods to upgrade and produce higher quality products. Not long ago, a collaboration programme between Luleå University of Technology and LKAB was established (Hjalmar Lundbom Research Centre, HLRC) aiming at the development of knowledge and scientific background for iron ore processes including the production of high quality pellets. In the pelletization process very finely ground particles of ore are mixed with additives such as limestone, bentonite, olivine and dolomite and shaped into centimetre sized balls in a pelletizer. These balls, now called green pellets, are finally sintered at high temperature to produce pellets for the market.

Pelletization of iron ore is a complex process with many components interacting in a more or less unknown manner. Probably the best approach to improve the knowledge about these interactions is to divide the complex system into simplified models. The understanding of the reactions occurring in the simplified systems is a prerequisite for the possibility to eventually improve the production of customer-adapted pellets.

1.2. Scope of the thesis
The scope of this thesis is first and foremost to elucidate some of the adsorption behaviour of magnetite particles with respect to its properties to adsorb collectors and ions from aqueous solutions. However, the thesis work was commenced with an attempt to get a clue to the mechanism of magnetite formation (paper I).

It is obvious that adsorption at mineral surfaces is a complex phenomenon and can be affected by various parameters. One important issue in surface adsorption studies of minerals is that the adsorption process occurs only at the surface and hence, it is advantageous from an experimental point of view if the mineral has a high surface area. Thus, first of all, one usually should synthesize pure and small size mineral particles in order to increase the
specific surface area and get a better control of its surface composition and properties. This
was done by synthesizing nano-sized magnetite particles using the co-precipitation method
and different techniques were used to characterize the synthesized magnetite particles. Iron
isotopic measurement was applied to study the mechanism of magnetite formation. The
results of iron isotopic measurement on the synthesized magnetite using co-precipitation was
compared with magnetite produced from oxidation of ferrous hydroxide (paper I).
The synthesized magnetite particles were then used to study adsorption of organic collectors
and inorganic anions at its surface. Paper II deals with adsorption and characterization of
oleate on magnetite. Oleate is a well-known collector used in flotation, as well as in a large
number of other applications for surface modifications of iron oxides. FTIR and TGA were
used to characterize the surface of magnetite coated oleate and to identify the structural layers
and surface density of oleate at the magnetite surface.

Attenuated total reflection infrared spectroscopy (ATR-FTIR) was utilized to investigate the
adsorption behaviour of sulphate (paper III), silicate (paper IV and V), oleate/silicate (paper
VI) and carbonate (paper VII) at the magnetite surface. The advantage of this in-situ
technique is that the speciation and kinetics of the adsorption reaction can be probed in-situ,
while the mineral is in direct contact with the adsorbate.

Sulphate and carbonate ions are among those found in the process water. Sulphate is one of
the major constituents present in the process water at LKAB. Carbonate is also present in this
water either through dissolution of carbon dioxide from atmospheric air or from carbonato
minerals. Water glass or sodium silicate solution is also added to the system as a dispersant.
Adsorption of these anions on iron oxides can alter their surface chemistry; affect the surface
charge and the reactivity of the oxide, as well as the interaction with other components in the
system, such as cations. The effect of charge at the surface may influence the efficiency of
agglomeration process which is a key factor for pelletization.

Na⁺ salts of anions of interest were used throughout the thesis works. However, Ca²⁺ was also
added to the system, where carbonate and sulphate adsorption were studied. The presence of
Ca ions adsorbed at the magnetite surface can decrease the effectiveness of benonite binder in
the pelletization process. Oleate was selected as a model collector for Atrac, which is a multi-
component collector used by LKAB in the reverse flotation process to separate apatite from
magnetite.

Another important approach in this thesis was to take a further step toward the real system,
where a multi-component system of ions and collector are present. To achieve this objective,
Ca²⁺ was added to the system to investigate the effect of Ca²⁺ on sulphate and carbonate
adsorption onto magnetite (paper III and VII). Furthermore, water glass and oleate were studied in a mixed system and the competition between oleate and sodium silicate for the magnetite surface was evaluated (paper VI). The later is important for a better selectivity in the reverse froth flotation of fluorapatite from magnetite ores.
Theoretical
Background
2. Theoretical background

2.1. Magnetite

Magnetite is ubiquitous in nature. It is found in ocean floor, soils, rocks, meteorites, atmospheric dust, bacteria and other living organisms. It is also a common corrosion product of iron and steel.

2.1.1. Crystal structure

The crystal structure of magnetite is inverse spinel with a unit cell consisting of 32 oxygen atoms in a face-centred cubic structure and a unit cell edge length of 0.839 nm [1]. In this crystal structure Fe(II) ions and half of the Fe(III) ions occupy octahedral sites and the other half of the Fe(III) occupies tetrahedral sites. Divalent iron atoms prefer to occupy octahedral sites to have a higher Crystal Field Stabilization Energy (CFSE), whilst the trivalent iron atoms has a CFSE=0 in both octahedral and tetrahedral sites. The schematic representation of the unit cell is shown in Figure 2.1 and 2.2.

![Figure 2.1](image)

**Figure 2.1.** Crystal structure of magnetite showing the arrangement of oxygen and iron atoms [2].
2.1.2. Laboratory synthesis of magnetite:

A number of methods have been developed to synthesize magnetite with specific characteristics i.e. shape, size, magnetic property etc. Some of the common methods are coprecipitation [4], oxidation of ferrous hydroxide Fe(OH)$_2$ [5], reduction of hematite at 400 ºC and in H$_2$/Ar as reducing atmosphere, alkaline hydrolysis of ferrous sulphate followed by calcination at 500 ºC, and oxidation of ferrous sulphate at alkaline condition by potassium nitrate [6].

2.1.3. Characterization

Magnetite is usually characterized by several methods. Some of the most important characterization methods for magnetite are infrared spectroscopy, ultraviolet and visible spectroscopy (UV-VIS), X-ray diffractometry (XRD), thermal analysis, magnetometry and Mössbauer spectroscopy, each of which gives certain information about the chemical and crystal structure of magnetite. In addition, microscopy methods such as TEM and SEM are applied to examine size and shape of the particles. The surface area can be measured with
2.2. Mechanism of magnetite formation in aqueous solution

2.2.1. Overview
Generally, Fe(III) ions are unstable in a wide pH range in aqueous solution and they may hydrolyze and precipitate. The product of hydrolysis, depends highly on a number of parameters e.g. pH, temperature, Fe(II) concentration, oxidation-reduction condition etc. The interdependency of these parameters also should be considered when one is preferably synthesizing a desired iron oxide, e.g. magnetite.

The mechanism of magnetite formation in a mixed aqueous solution of Fe(II) and Fe(III) ions is started with formation of tetramers such as \([\text{Fe}_4\text{(OH)}_{10}\text{(OH}_2)_6]^{3-}\) [7]. Chains and planes rapidly grow via olation and the excess octahedral ferric ions form Fe-O-Fe bridges between planes by oxolation. The ferric ions in the bridges should switch to coordination four to decrease imposed steric constraints. As it was explained in section 2.1.1, the CFSE=0 for Fe(III) ions, so that the coordination can easily change to four. The role of Fe(II) is necessary for a spinel structure to be formed through electron transfers between Fe(II) and Fe(III). The electron transfer is allowed in a compact structure of the tetramer where the distance between Fe(II) and Fe(III) is short and d-orbitals can overlap.

Oxidation of a suspension of Fe(OH)_2 in water also leads to formation of iron oxides. Some factors governing the oxidation rate are pH, temperature [8], presence of anions, concentration of dissolved oxygen, and ionic strength. It is believed that green rust complexes are initially formed as intermediates which can be then transformed to iron oxides. In transformation of the green rust to iron oxide, dehydroxylation and oxidation are competing processes. Magnetite is the predominant phase when a slow oxidation takes place. This means that when dehydroxylation occurs prior to oxidation, the green rust will transfer to magnetite.
2.2.2. Application of iron isotope fractionation in the mechanistic study
Isotopes of a certain atom in a reactant molecule can influence both the equilibrium reaction constant and the rate of reaction, especially if the atom is involved in a bond formation or bond breakage. In equilibrium condition, the heavier isotopes are concentrated in those chemical compartments, i.e., elemental species, in which the element forms the strongest bonds. The effect is generally larger when the mass ratio between isotopes is larger as for $^1\text{H}$ and $^2\text{H}$ (D).
Iron has four stable isotopes, among them; $^{54}\text{Fe}$ and $^{56}\text{Fe}$ have the highest natural abundances. By the recently introduced new generation of mass spectrometric techniques, a small isotope variation of Fe isotopes can be measured [9-11]. The measurement of partitioning of isotopes in different products or solution-precipitates allows us to predict a reaction pathway [paper I]. Examples of application of iron isotopic ratio data in mechanistic study can be found in the literature [e.g. 12, 13]

2.3. Adsorption onto mineral surfaces
Adsorption on mineral surfaces is a very important phenomenon in both environmental and technical related processes. For instance, many geochemical processes on the Earth, such as weathering, dissolution, sedimentation and crystallization can be influenced by or is a result of adsorption on minerals [14]. Likewise in industry, adsorption is a crucial factor in ore processing, catalysis and corrosion. The basis for this change in the properties of mineral particle systems by adsorption is due to alteration or modification of the minerals surface chemistry. Therefore, having knowledge about the surface chemistry is a prerequisite for the change of these properties in a desirable direction. Figure 2.3 is a schematic representation of the interrelationships between factors determining surface properties and possible applications of the results in various areas.
2.3.1. Surface chemistry of iron oxides

In aqueous systems, iron oxides act as Lewis acids and adsorb/coordinate water or hydroxyl groups. A secondary water molecule also can be hydrogen-bonded to the surface hydroxyl groups. The hydroxyl group at the surface may be coordinated to more than one Fe atom, so that there are singly, doubly and triply coordinated Fe atoms. Further, two OH groups can coordinate to one iron atom. The coordination of hydroxyl groups and the number of active surface sites depend on both the crystal structure and morphology of the iron oxide.
These surface hydroxyl groups are, indeed, the reactive sites, which can react with both acids and/or bases. They can be replaced by other organic or inorganic anions, they can adsorb more protons or cations, release water upon heating etc.

Potentiometric titrations and spectroscopic methods (UV-Vis, IR, XPS) are among the techniques used to characterize the surface of these oxides e.g. their acidity, surface reactions, bonding coordination and adsorption properties.

### 2.3.2. Models of adsorption

There are a number of models developed to describe the adsorption mechanisms and to fit the experimental adsorption isotherm data. Probably the most often used model is the Langmuir isotherm. The mathematical expression for the Langmuir isotherm can be written as:

\[
\theta = \frac{KC}{1 + KC} \quad (2.1)
\]

In this equation \(C\) is the bulk concentration of adsorbate in solution, \(K\) is an affinity constant, and \(\theta\) is defined as the fraction of the surface sites covered by the adsorbate:

\[
\theta = \frac{A}{A_{\text{max}}} \quad (2.2)
\]

where \(A\) is the amount of the adsorbate, which is adsorbed at equilibrium concentration \(C\) and \(A_{\text{max}}\) is the amount that is necessary to cover the surface by a monolayer of the adsorbate.

In this adsorption isotherm, the assumption is that the energy of adsorption is constant at all concentrations up to the full coverage of the surface.

The Langmuir equation can be written in the linear form as:
So, $C/A$ versus $C$ should result in a straight line. Anion adsorption on iron oxides has previously been described by the Langmuir model [1].

Another type of equation that has been used to fit the adsorption data is the Freundlich equation, which can be written as:

$$q = K_d C^{1/n}$$  \hspace{1cm} (2.4)

In this equation, $q$ is the amount of species adsorbed at the surface, $C$ is the equilibrium concentration of the adsorbate in solution, $K_d$ is the distribution coefficient and $n$ is a correction factor related to the heterogeneity of the surface. Taking the logarithm of either sides of this equation, it can be rewritten as:

$$\log q = 1/n \log C + \log K_d$$  \hspace{1cm} (2.5)

A plot of $\log q$ versus $\log C$ will give rise to a straight line with the slope of $1/n$ and intercept of $\log K_d$ if the adsorption follows a Freundlich isotherm. This equation has been used for fitting data related to adsorption of cations on iron oxides [1].

Still another type of equation, which has sometimes been applied to adsorption data is the Temkin equation. It uses a logarithmic relationship between the amount of species adsorbed and their concentration in solution:

$$q = \alpha \ln C$$  \hspace{1cm} (2.6)

where $\alpha$ is a constant. Similar to the Freundlich equation, the Temkin model takes into account the heterogeneity of the surface [1].

2.3.3. Prerequisite for flotation

Surface chemistry and surface modification play a key role in ore processing, particularly in separation of an ore from gangue minerals using the froth flotation.

Flotation is a separation technique, by which a mixture of fine solids dispersed in a liquid suspension is separated into desired components. In mineral industry, flotation is widely used to separate a desired mineral from gangue minerals and other undesired materials. The
process is based upon the differences in surface properties of individual components in the mixture. A surfactant or collector is preferentially adsorbed on one component and makes its surface more hydrophobic. Small particles of this mineral with the modified hydrophobic surface are then attached to the air bubbles and rise to the top of the flotation pulp. Long chain carboxylic acid derivatives are usually used for flotation of iron oxides. For instance, oleic acid is a common collector for flotation of hematite. In flotation of fluorapatite from magnetite, a composed collector (Atrac) is used as surfactant, selectively adsorbing on fluorapatite which is floating up and separating from magnetite (reverse flotation).

2.4. Surface science techniques

The surface is the outermost layer of a bulk material and can be considered as a break in periodicity of a solid network in one direction, therefore leading to structural changes as well as localized electronic and vibrational states.

Nowadays, study of surfaces is essential in a large number of scientific and industrial applications. Thus, the number of available surface techniques has been growing over the last decades [15] and enormous amount of literature has been devoted to the study of surface properties of different minerals and materials. Description of all available surface techniques in detail is out of the scope of this thesis. Here, the techniques used in this thesis as well as the most relevant techniques for sorption from aqueous solution, including the widely used technique in mineral processing and environmental science are briefly introduced.

The analytical procedure for measuring sorption of an adsorbate to the surface can be divided into two categories.

1) The first category includes methods that are measuring the quantity of adsorbate in solution and the data, which are obtained in this way can be used to estimate the amount of sorbed species at the surface. All types of analytical methods applicable for liquid solutions can be used. Some examples of these methods are; atomic absorption, ICP-MS, classical titration techniques, spectroscopic techniques (e.g. UV-Vis, IR, etc.), electrochemical (conductometry, voltametry etc.), gravimetric and other methods.
One of the frequently used methods to study the acidity (basicity) of the surface, and type and amount of surface active sites as a function of pH is potentiometric titration. It is based on adsorption and/or desorption reactions involving protons at the mineral surface determined by measuring pH i.e. concentration of H$_3$O$^+$ in solution. These data can be used to obtain the Point of Zero Charge (PZC) value of the surface, as well as concentration of the active surface site [16, 17]. These data are of great value for surface characterization of minerals.

2) This category includes methods that probe the surface directly and give information on quality and/or quantity of the surface structure and composition, as well as the chemical composition and structure of the adsorbed species at the surface. A variety of methods has been developed for both surface and adsorbate characterization [18, 19].

Short descriptions and applications of some of the most common methods used for surface characterization of minerals are listed below:

- **BET (Brunauer, Emmett, and Teller) surface area measurements**

This method involves measuring the extent of adsorption of N$_2$ (at the boiling temperature of liquid N$_2=77$ K) on the outgassed solid as a function of the relative pressure P/P$_0$, where P is the adsorption isotherm representing the partial pressure of N$_2$ and P$_0$ is its equilibrium vapour pressure. In case, where very small surface area is to be measured, Ar gas instead of N$_2$ gas can be used, which has a lower saturation vapour pressure.

Knowing the average dimensions of the crystals of a crystalline material and the density of the material, the surface area may also be calculated. For example, assuming either spherical or cubic shape for the crystallite particles, the specific surface area can be calculated according to the following equation:

\[
S = \frac{3}{(d \cdot r)} = \frac{6}{(d \cdot l)}, \quad (2.7)
\]

where d is the sample density, r is the particle radius for spherical shape and l is the particle side length for cubic shape.
- *ζ*-Potential:
Zeta potential is the electrostatic potential difference at the shear plane, *i.e.* the plane formed between the attracted water molecules at the mineral surface and the stationary water molecules in the liquid phase. By determining the *ζ*-Potential at different pH, the isoelectric point (IEP) of the particles can be determined. At IEP, the particles in suspension have zero mobility in the electric field. The difference between IEP and ZPC (the zero point of charge) values, show the presence of ionic species other than H⁺ and OH⁻ on the surface [20].

- Contact angle measurement
The contact angle is the angle, at which a liquid/vapor interface meets the solid surface. It is illustrated with a small liquid droplet resting on a flat horizontal solid surface.

![Figure 2.5](image.png)

*Figure 2.5.* Liquid droplets on a rigid solid surface showing the angle $\theta$ as defined in Young’s relation. The angle $\theta$ depends on the hydrophobicity of the drop and/or the solid.

The shape of the droplet is determined by the Young relation as follows:

$$\gamma_{SG} - \gamma_{SL} = \gamma_{LG}\cos\theta$$ (2.8)

where $\gamma$ is the surface tension and indices S, G and L are solid, gas and liquid phases, respectively.

The measured contact angle is an indication of the hydrophobicity of the surface, which is related to the interaction of the collector with the mineral surface.

- X-ray Photoelectron Spectroscopy (XPS)
XPS also called Electron Spectroscopy for Chemical Analysis (ESCA) is one of the so-called core level spectroscopies among other electron spectroscopies [18, 19]. It is rather a surface
specific technique, which may probe any given spot across the surface at a depth of approximately 10 nm or less and may be applied to a wide range of materials. The principle of XPS is based on interaction of an X-ray photon with the sample surface and ejection of photoelectrons (Fig. 2.6). The energy analysis of electrons emitted from the solid surface is used to gain information on the electronic energy levels in the surface region.

![Figure 2.6. Schematic of the photoemission process (adapted from [18]).](image)

The kinetic energy ($E_K$) of the ejected photoelectron and the electron binding energy ($E_B$) have the following relationship:

$$E_B = h \cdot \nu - E_K - \Phi \quad (2.9)$$

where $h \nu$ is the photon energy of the X-rays and $\Phi$ is the spectrometer work function which is about 4-5 eV and is induced by the analyser. The binding energy is characteristic of the atom but also depends on the chemical environment of the atom. The analysis is performed in ultra-high vacuum.

- **Auger Electron Spectroscopy (AES)**

AES is also an electron spectroscopy, which can be categorized as a core electron level spectroscopy. It is a common surface analytical tool for probing chemical and compositional
surface environments and provides both qualitative and quantitative information from the outermost layer of the surface. This technique involves ionization of electron from core levels by a relatively high energy electron (or X-ray) beam and detection of emitted by atoms Auger electrons with a low kinetic energy (~10 eV – ~2 keV). The physical principle behind it is the relaxation of an atom with a hole in one of its inner shells, which may lead to radiationless Auger process or to emission of a photon in a process called X-ray fluorescence. In the Auger process the hole in the inner shell of an excited atom is filled by an electron from the outer shell while a second outer shell electron is emitted and carries the energy as kinetic energy. The advantages of AES over XPS is faster scanning and higher sensitivity due to more readily available more dense electron beams relative to X-ray sources. AES also produces higher spatial resolution. XPS, on the other hand, has a better detection limit for quantitative measurement. AES should also be run in ultra-high vacuum [19].

- **Scanning Electron Microscopy (SEM)**

  Scanning electron microscopy is a type of microscopy, in which a high energy beam of electrons is used to scan the specimen (sample surface) and to produce an image. To date, resolution of the most advanced SEM instruments is about 1 nm. In SEM, the electron beam from an electron gun is focused by means of condenser lenses at a certain spot of interest at the surface. The interaction of electrons with atoms of the sample produces several types of signals, which are detected. Both Back-Scattered Electrons (BSE) and Secondary Electrons (SE) detectors are most commonly used in SEM for imaging and gaining topographic information of the surface sample. Characteristic X-rays emitted from the sample can be detected if the instrument is equipped with an EDS detector. EDS (Energy Dispersive X-ray Spectroscopy) is used to identify the composition and the distribution of elements on the surface of the sample.

  With respect to the powder samples, shape, size and size distribution of particles may be obtained.

- **Atomic force Microscopy (AFM)**

  Atomic force microscopy [21] or scanning force microscopy is a very high resolution (up to fractions of a nanometre) technique for imaging and force spectroscopy/measurement at the sample surface. It consists of a cantilever with a sharp tip or probe for scanning the specimen.
surface. The sharp tip mounted on the cantilever is moved across the sample surface and the
deflection of the tip is monitored to produce an image with structural information. One of the
most important advantage of AFM over SEM is that AFM can work quite well under air and
liquid (e. g. aqueous solution) environment so that in-situ examination of a specimen is
possible. Generally, a higher resolution and an improved 3-D image could be obtained by
AFM rather than SEM. On the other hand, a scanning rate and an image size, i. e. an area and
a height that can be imaged, are smaller than those in SEM. These are some of the
disadvantages of AFM.

- **Solid state Nuclear Magnetic Resonance (NMR) spectroscopy**

Solid state NMR has not commonly been used for surface studies. Nevertheless, a
considerable amount of efforts has been devoted at the Division of Chemistry, Luleå
University of Technology, to apply solid state NMR spectroscopy to study surface adsorption
and surface active sites of minerals [17, 22-24].

The majority of elements in the periodic table of the elements have at least one magnetic
isotope, which can, in principle, be studied using NMR spectroscopy. However, iron oxides
contain iron atoms, which are paramagnetic, because of the electronic structure of the iron
atom. In practice, NMR spectroscopy on samples with iron oxide is difficult because of a
severe line broadening and large paramagnetic shifts. On the other hand a small amount of
iron in a sample under study (mmol/dm³) enhances intensities of the spinning sidebands in
MAS (magic angle spinning) NMR spectra that provide additional information on the
chemical structure of a mineral. This property, for example, has been utilized for investigation
of both interaction and adsorption of Fe²⁺ and maghemite nanoparticles onto fluorapatite [17,
24].

- **X-ray Absorption Spectroscopy (XAS)**

XAS is a type of X-ray absorption spectroscopy, which is widely used for determining the
local structure of matter [18, 25]. It uses synchrotron radiation sources to provide intense and
tuneable X-ray beams. In XAS the radiation photo-ionizes the core electrons of the atoms.
When the energy of the incident beam matches with the binding energy of a core electron in
the atom of a sample, it will be absorbed and show up as a peak in the transmitted spectrum
versus energy. The fine structure arises from interaction of the ejected electron with electrons
in the surrounding non-excited atoms, resulting in modulation of the absorption coefficient. XAS includes X-ray Absorption Near Edge Structure (XANES) and Extended X-ray Absorption Fine Structure (EXAFS) which together, provide a complementary information. They can be used to probe the local structure around a specific element within the material. Such information as the bond length (inter-atomic distances) and the chemical coordination environment around the original absorbing atom as well as the adsorption site may be obtained. EXAFS has been for example, used to study Pb and carbonate adsorption on goethite and uranium carbonato adsorption complexes on hematite [26, 27]. The XAS technique can be used in-situ, i.e., to study surfaces in aqueous solution [28].

- **Molecular Orbital/Density Functional Theory (MO/DFT):**
  Quantum mechanical calculation and theoretical modelling such as MO/DFT is another way of retrieving information and estimating bond length, vibration frequencies and configurations of the adsorbed species at the surface [29-31]. The MO/DFT method is usually combined with EXAFS and FTIR and a good match between the calculated, optimized geometry and experimental observation is expected. In such theoretical methods, the optimal geometry and conformation of a molecule at the surface is obtained by calculating the minimum total energy of the system. The adsorbent surface property i.e., surface site, crystal face etc. is included in the calculation. The geometry and conformation of the adsorbate as well as the hydration effect are among parameters to be optimized.

- **Thermogravimetric Analysis (TGA)**
  Thermogravimetric analysis is widely used in surface sciences [32-35] for instance for measuring the amount of water, hydroxyl groups or organic adsorbates at the mineral surfaces. It can also be used to measure the thermal stability of the adsorbate at the surface and/or monitor the enthalpy change and temperature, at which a surface reaction occurs. Thus, TGA may provide a useful information on the structure of organic layers on the surfaces. Both kinetic and thermodynamic information can be achieved using this technique. The weight change of about 1 µg can be recorded with an extremely sensitive balance hanging inside a furnace. There is a possibility for running experiments under air, inert gas or reactive gas conditions.
- Infrared spectroscopy (IR)

Undoubtedly, infrared spectroscopy has been one of the most widely used spectroscopic techniques in chemical analysis in general, and for surface studies. The main reason is the high sensitivity of IR spectroscopy on the molecular level. Moreover, the instrumentation is relatively cheap and easy to operate, so a spectrum is easily recorded, although its full explanation is a much more difficult task.

Applications of IR spectroscopy in surface science are particularly useful for obtaining information on the nature of adsorbed molecules, rather than on the elemental composition of surfaces as is the case in many other surface methods. Due to versatility of the technique, the application of IR spectroscopy is not limited to low temperature (e.g. room temperature), but also high temperature and high pressure applications are also common. Both adsorptions of organic and inorganic substances from solutions and gaseous molecules on various substrates can be studied. For example, many studies have been carried out on adsorption of CO, CO₂, NO, NH₃ etc., as well as organic molecules on metal and metal oxide substrates at room and elevated temperatures (36-38). The purpose of these investigations were to find the catalytic activity and reaction mechanism on catalysts.

A number of sampling techniques are available in IR spectroscopy among which Diffuse Reflectance Infrared Fourier Transform (DRIFT) spectroscopy is more appropriate for adsorption on dried powders of fine particles, whilst Attenuated Total Reflectance (ATR) is advantageous where in-situ adsorption from aqueous solutions is aimed to be investigated. Thus, these two techniques have more frequently been utilized in mineral processing and environmental science. Reflection- Absorption (R-A) spectrometry is another surface sensitive technique, which may be used for both detection and characterization of a thin layer on a flat and reflective surface of a metallic substrate [38].
2.5. IR spectroscopy

2.5.1. Vibrational motions in a molecule

This one and the following four sections are included in the thesis for those who are not familiar with infrared spectroscopy in order to give a short introduction to the field of IR spectroscopy.

Generally speaking, a molecule consisting of N atoms has 3N degrees of freedom due to 3N coordinates needed to specify the locations of N atoms. Three of these degrees of freedom are translational motion in x, y, z directions. For a monatomic gas there will be only 3 degrees of freedom, all related to the translational motion. If the molecule is diatomic, there exist 6 degrees of freedom, from which 3 are translational, 2 rotational and 1 representing the vibration. For polyatomic molecules consisting of N atoms, the number of vibrational degrees of freedom can be found as follows [39]:

\[
\text{Vibrational degrees of freedom} = \begin{cases} 
3N-5 & \text{for linear molecules,} \\
3N-6 & \text{for non-linear molecules,}
\end{cases} \quad (2.10)
\]

Each degree of freedom is associated with an energy expression, for example, the kinetic energies of the molecule travelling in three dimensions or rotations of the molecule about 3 axes (2 for linear molecules). Each degree of freedom in vibration represents a mode of vibration i.e. for a non-linear molecule with N atoms there exist 3N-6 (3N-5 for linear) normal modes of vibration. There are different types of vibrations in molecules; i.e. vibration could be bond-stretching or bending motions. The stretching and bending vibrations can be symmetric or asymmetric. Bending vibrations can also be symmetric or asymmetric in-plane or out-of-plane (also called scissoring, rocking, twisting and wagging). Figure 2.7 shows different vibrational modes of CH2 groups as an example:
2.5.2. The energy levels of vibration

As a solution of Schrödinger equation for a harmonic oscillator, the permitted energy levels can be expressed as:

\[ E_v = (\nu + 1/2) \hbar \omega \quad , \quad \nu = 0,1,2... \]  \hspace{1cm} (2.12)

where \( \omega = \{k/m_{\text{eff}}\} \) and \( m_{\text{eff}} \) is effective mass of the molecule.

This equation works well for low vibration energy states, where the variation of the potential energy with displacement resembles a parabola. At higher vibrational states, the Morse potential energy should be used which includes the anharmonicity constant and the dissociation energy. Figure 2.8 shows the Morse potential energy, the harmonic oscillator potential, and vibrational energy levels.
2.5.3. Infrared absorption and selection rules

The atoms in a molecule are connected through chemical (covalent) bonds. A molecular vibration occurs when atoms in a molecule are in periodic motion while the molecule as a whole has constant translational and rotational motion. The frequency of the periodic motion is known as a vibration frequency. The vibration frequency is usually expressed as wavenumber ($\bar{v}$), which has the following relation with wavelength ($\lambda$) and energy ($E$) of the electromagnetic radiation:

$$\bar{v} = \frac{1}{\lambda} = \frac{E}{hc} \quad (2.13)$$

Depending on the atomic masses, force constants between atoms, the vibrational mode involved, as well as the chemical environment around the atoms, there are characteristic frequencies which may be used in IR spectroscopy to identify vibrating entities in a molecule. The interpretation of infrared spectra involves the correlation of absorption bands in the
spectrum of an unknown compound with the known absorption frequencies for a certain entity. Significant for the identification of the source of an absorption band are intensity (weak, medium or strong), shape (broad or sharp), and position (cm\(^{-1}\)) in the spectrum.

Energy in the infrared region of the electromagnetic radiation may be absorbed by a molecule under certain conditions. First, the energy of the photon must be equal to the energy gap between excited state and ground state of a mode of vibration in the molecule. Second, for a vibration to be infrared active i.e. an IR band appears in the spectrum, the electric dipole moment of the molecule must change when the atoms are displaced relative to one another. This can be written as:

\[
\left( \frac{\partial \mu}{\partial q} \right)_0 \neq 0
\]  

(2.14)

where \(\partial \mu\) is the change in molecular dipole moment and \(\partial q\) is the displacement of atoms from equilibrium during a vibrational motion expressed in normal coordinates.

2.5.3.1. Degeneracy

When two or several vibrational modes correspond to the same energy (have the same vibrational transition energy), they are degenerate. Occurrence of degeneracy is related to the symmetry of the molecule. For example, H\(_2\)O with a C\(_2v\) symmetry has no degeneracy in vibrational energies while NH\(_3\) with a C\(_3v\) symmetry has one doubly degenerate energy. Whenever the symmetry of a molecule is lowered, the degeneracy decreases and more IR bands will appear in the spectrum. This fact will be used later in the results and discussion section.

2.5.3.2. Overtones and combination bands in IR spectra

Other than the fundamental vibrations, which are usually the most intense bands in the IR spectra of a molecule, there may be overtones and combination bands. Overtones are the result of excitations from the ground state (\(v=0\)) to higher energy levels (\(v=2, 3, \ldots\)). Since these transitions are forbidden by the selection rule for harmonic oscillations (\(\Delta v= \pm 1\)), the intensities of these bands are usually weak. The combination bands are also sometimes
observed in the infrared region. These bands are absorption bands observed at frequencies such as \((v_i + v_j)\) or \((v_i - v_j)\), where \(v_i\) and \(v_j\) refer to fundamental frequencies.

2.6. ATR-FTIR spectroscopy

2.6.1. Theory
When the infrared radiation propagates through an optical element in contact with a sample having lower index of refraction, the IR beam is totally reflected at the interface, when the angle of incidence \(\theta\) exceeds the critical angle. The critical angle is defined as:

\[
\theta_c = \sin^{-1} \frac{n_2}{n_1} \tag{2.15}
\]

where \(n_{21} = n_2/n_1\); \(n_2\) and \(n_1\) are the refractive index of rare and denser medium, respectively.

The attenuated total reflection spectroscopy is based on the exponentially decaying evanescent field, established at the IRE surface in the rarer medium (Figure 2.9).

\[
E = E_0 \exp \left\{ -\frac{2\pi}{\lambda_1} \left( \sin^2 \theta - n_{21}^2 \right)^{1/2} z \right\} \tag{2.16}
\]
where $\lambda_1 = \lambda/n_1$ is the wavelength of radiation in the denser medium and $\lambda$ is the wavelength in free space. $Z$ is the distance from the surface [40].

### 2.6.2. The penetration depth ($d_p$) and the effective thickness ($d_e$)

The penetration depth was initially defined by Harrick as the depth at which the electric field amplitude falls to half of its value at the surface [40]. This definition was later modified to the depth at which the amplitude $E$ decays to a value of $E_0 \exp(-1)$ i.e. at $Z = d_p = 1/\gamma$ where $\gamma$ is expressed as:

$$
\gamma = \frac{2\pi}{\lambda_1} \left( \sin^2 \theta - n_{21}^2 \right)^{1/2} Z 
$$

(2.17)

The actual depth sampled is always greater than this value, since $E > 0$ at $d_p$. The penetration depth $d_p$ depends on the refractive indices of the internal reflection element and the sample (denser and rarer medium), wavelength of the IR beam, and the incident angle, $\theta$ (equation 2.18).

$$
d_p = \frac{1}{\gamma} = \frac{\lambda_1}{2\pi(\sin^2 \theta - n_{21}^2)^{1/2}}
$$

(2.18)

It turns out from this equation that the following condition should be met, to have a penetration of the IR beam into the rarer medium:

$$
\sin^2 \theta - n_{21}^2 \geq 0
$$

(2.19)

In case, when a film of smaller particles than the wavelength of the IR beam is in contact with an aqueous solution, the refractive index of the rarer medium ($n_2$) is defined as a volume weighted average of the refractive index of the particles and aqueous solution [41].

Another important parameter in ATR-FTIR is the effective thickness. The effective thickness $d_e$ is defined as the thickness required to give the same absorbance in reflection spectroscopy as it would be in transmission spectroscopy. The effective thickness for a thick medium e.g. a bulk sample where thickness $d \to \infty$ is written as [40]:

26
\[ d_s = \frac{1}{\cos \theta} \frac{n_2}{n_1} \frac{d_p}{2} E^2 \]  

(2.20)

In this equation E stands for relative electric field in the sample, which could be either parallel-polarized or perpendicular-polarized.

As it was stated earlier, the depth of penetration is a function of refractive indices of the rarer medium and the internal reflection element. For a ZnSe internal reflection element at \( \theta = 45^\circ \) in contact with water, the penetration depth can be calculated to be 1.53 \( \mu \)m at the wavelength of 1000 cm\(^{-1}\). This value is even larger when a film of magnetite is deposited on the ZnSe crystal element. Since the whole film should be probed by the evanescent IR light, the thickness of the film should be smaller than the actual depth sampled, which is ca 3\( d_p \).

2.6.3. Choice of internal reflection element

When choosing an internal reflection element, a number of characteristics should be taken into consideration. Some of the main characteristics, which are of great importance for selection of an IRE crystal are shown in Table 2.1.
### Table 2.1. Some of the most common IRE crystals (data from PIKE Technologies)

<table>
<thead>
<tr>
<th>Crystal Material</th>
<th>n₁</th>
<th>LWL (cm⁻¹)</th>
<th>dₚ (μm)</th>
<th>Water solubility, g/100g</th>
<th>pH range</th>
<th>Hardness, Kg/mm²</th>
</tr>
</thead>
<tbody>
<tr>
<td>AMTIR</td>
<td>2.5</td>
<td>625</td>
<td>1.46</td>
<td>Insoluble</td>
<td>Low and mid pH range</td>
<td>170</td>
</tr>
<tr>
<td>Diamond/ZnSe</td>
<td>2.4</td>
<td>525</td>
<td>1.66</td>
<td>Insoluble</td>
<td>All pH range</td>
<td>5700</td>
</tr>
<tr>
<td>Diamond/KRS-5</td>
<td>2.4</td>
<td>250</td>
<td>1.66</td>
<td>Insoluble</td>
<td>All pH range</td>
<td>5700</td>
</tr>
<tr>
<td>Germanium</td>
<td>4</td>
<td>780</td>
<td>0.65</td>
<td>Insoluble</td>
<td>All pH range</td>
<td>550</td>
</tr>
<tr>
<td>KRS-5</td>
<td>2.37</td>
<td>250</td>
<td>1.73</td>
<td>0.05 Mid pH range</td>
<td>40</td>
<td></td>
</tr>
<tr>
<td>Silicon</td>
<td>3.4</td>
<td>1500</td>
<td>0.84</td>
<td>Insoluble</td>
<td>Low and mid pH range</td>
<td>1150</td>
</tr>
<tr>
<td>Silicon/ZnSe</td>
<td>3.4</td>
<td>525</td>
<td>0.84</td>
<td>Insoluble</td>
<td>Low and mid pH range</td>
<td>1150</td>
</tr>
<tr>
<td>ZnS</td>
<td>2.2</td>
<td>850</td>
<td>2.35</td>
<td>Insoluble</td>
<td>Mid pH range</td>
<td>240</td>
</tr>
<tr>
<td>ZnSe</td>
<td>2.4</td>
<td>525</td>
<td>1.66</td>
<td>Insoluble</td>
<td>Mid pH range</td>
<td>120</td>
</tr>
</tbody>
</table>

n₁= refractive index of the ATR crystal  
LWL= long wave length cut-off  
dₚ= the depth of penetration in microns at 1000 cm⁻¹

The following items must be regarded upon choosing an ATR crystal:

1) **Refractive index:** the refractive index of the IRE has to be larger than the sample. For studying dilute aqueous solutions, the refractive index of the solution is close to that of water, which is approximately equal to 1.34. Therefore, most of the ATR crystals can be used. On the other hand, if an oxide is deposited on an IRE crystal, the refractive index of the IRE should be larger than the average refractive index of the deposited film and inter-particle solution (see equation 2.19).

2) **Depth of penetration:** the optimal condition is when the actual depth sampled is close to the thickness of a porous film, so that, the evanescent light probe the whole film with minimum absorbance from the bulk. For a dense film not allowing the adsorbate to penetrate the film volume, the film thickness should be much less than the penetration depth and the absorbance due to the bulk should be corrected for.

3) **Transmission range:** the characteristic IR absorption bands of the sample should be in the transmission range of the IRE. For example, A ZrO₂ IRE crystal (LWL ~ 1800 cm⁻¹) is not a good choice for studying sulphate adsorption.
4) **Chemical resistance and hardness:** the mechanical property and chemical resistance of IRE elements is also of great importance. The IRE should not be attacked by acid/alkali or oxidizing/reducing agent if the experimental conditions are such. The solubility of the IRE in the solvent of interest is also important. When the solvent is water, it should not be dissolved in water.

5) **Specific adsorption of the sample on IRE:** When a thin layer of a mineral deposited on IRE *i.e.* the IRE itself is not the mineral of interest (see section 2.6.5), the sample should not be specifically adsorbed at the IRE surface.

### 2.6.4. Applications

A wide range of applications of ATR can be found in the literature. In addition to qualitative and quantitative measurements of chemical structure similar to other IR techniques, it has been used *e.g.* to investigate molecular orientation, semiconductor properties, membranes, biological systems and optical properties of samples (such as the refractive index of the material) [40].

In this thesis, ATR spectroscopy was mainly used to study adsorption kinetics, adsorption isotherms as well as the speciation of surface complexes, in single and multi-component systems.

### 2.6.5. Application of ATR to study sorption on mineral surfaces

Due to a high sensitivity of IR spectroscopy to small changes in the chemical structure and the environment around molecules and the advantage of ATR spectroscopy in probing and monitoring the surface of minerals in contact with water, this method has been widely used to study solid/liquid interface phenomena, *i.e.* adsorbate orientation [*e.g.* 42], adsorption/desorption equilibria, mechanisms and kinetics [*e.g.* 43, 44], speciation [*e.g.* 45, 46] etc.

This section illustrates how ATR spectroscopy technique can be utilized to study mineral/water interfaces by referring to some of the earlier works focusing on sorption on iron oxide.
2.6.5.1. Film

ATR spectroscopy of minerals in contact with solution can be applied in three ways:

1) Manufacturing an internal reflection element of the mineral of interest [47-49]. This is sometimes possible depending on the mineral of interest.

2) Controlled synthesis of a film on the IRE [50, 51].

3) Deposition of a thin layer of minerals on an appropriate IRE [45, 46].

4) Spreading a paste or concentrated suspension of already equilibrated mineral and adsorbate over the IRE crystal [29, 52-55].

These four methods are ordered according to their capability to be used in quantitative measurements, i.e. in case of the mineral being the IRE, the absolute quantification of adsorbate is possible, whilst in the 4th method (suspension) almost only qualitative information is retrievable. In the 3rd method (particle deposition), in principle, quantification is possible through calculation of $d_e$ value [41, 45], though in practice this method is semi-quantitative, i.e. the quantification is possible on a film within one experiment. However, reproducing the same film every time with exactly the same thickness and smoothness is difficult.

In case of iron oxide, the two later techniques have been used. Hug deposited a thin layer of hematite on ZnSe IRE and studied sulphate adsorption [45], and Peak et al. studied sulphate adsorption at goethite deposited on ZnSe crystals [46], whilst Su and Suarez [55] used a suspension of iron and aluminium oxide and studied carbonate adsorption.

2.6.5.2. Electrolyte solutions

NaCl has frequently been used as inert electrolyte to keep the ionic strength constant in solution. Cl$^-$ has the advantage that it has no IR absorption and thus it has been used in many ATR studies [56]. NO$_3^-$ and ClO$_4^-$ however are more inert compared to Cl$^-$ but they have IR bands in the mid-IR region which may sometimes complicate the spectral evaluation. Na$^+$ and K$^+$ are appropriate counter-ions and they are preferred over NH$_4^+$ for the same reason.

2.6.5.3. Oxoanion adsorption and symmetry

The speciation of sorbed oxoanions onto iron oxide is usually determined by utilizing the symmetry change upon sorption. If the symmetry is lowered, as compared with the species in solution, the number of visible infrared active bands will increase due to decreased
degeneracy. Figure 2.10 illustrates this concept for sulphate as a free ion and as sorbed with different possible coordinations.

![Figure 2.10](image)

Figure 2.10. Different sulphate species and their representative symmetries together with infrared spectrum they produce. Adapted from Hug and Peak [45, 46].

Among oxoanions, sorption of sulphate [45, 46], carbonate [26, 27, 29, 55, 57, 58], arsenate [59, 60], and phosphate [54, 61, 62] on iron oxide using ATR spectroscopy have attracted more attentions, partly due to the importance of these species in the environment.

### 2.6.5.4. Cation-anion Co-adsorption on iron oxide

Formations of a number of ternary complexes and co-adsorption of metal-ligand on iron oxide surface have been reported. Ostergren et al. studied effects of carbonate and sulphate on Pb(II) sorption to goethite [26]. Elzinga et al. studied interaction of sulphate and Pb(II) at the goethite-water interface [63]. They concluded that in addition to the formation of ternary complexes with SO₄, adsorption of Pb(II) promotes sulphate sorption to goethite surface by
formation of both inner- and outer-sphere sulphate surface complexes which are not coordinated by Pb.

Zhang and Peak [64] studied Cd(II)-sulphate interactions at the goethite water interface. They also found that Cd-SO₄ ternary complexes are formed on goethite in addition to an increase in sulphate adsorption to goethite. These authors observed that the effect of Cd on sulphate adsorption to goethite is larger at higher pH (6>5>4). Barger et al. used ATR and EXAFS spectroscopy to investigate adsorption of U(VI)-carbonato complexes on hematite [27]. The results obtained by these spectroscopic methods convinced them that the ternary complexes formed should have compositions similar to $\text{FeO}_2\text{UO}_2-(\text{CO}_3)_x$, where 0<x<2.

2.6.5.5. Collector adsorption on iron oxides

Although there are quite a number of ATR studies on adsorption of organic molecules onto iron oxides [e. g. 65-71], to the author’s knowledge, there are only a few publications regarding the adsorption of collectors on iron oxides using ATR spectroscopy. Bai and coworkers used ATR technique to study the mechanisms of sodium dodecyl sulphate (SDS) adsorption onto hematite in order to find the optimum condition for the froth flotation [72]. They claimed that the mechanism of SDS adsorption on hematite is mostly governed by a physical interaction. They also found that the optimum pH for this system is pH 5 and a partial monolayer coverage is sufficient for a good recovery in the flotation. Silvester and Hao [73] studied the environmental fate of some flotation collectors in mineral processing operations. They reported that the ethyl perxanthate (ROC(=S)SO$^-$), one of the products of decomposition of ethyl xanthate, interacts with the goethite surface which catalyzes the decomposition process of this reagent.
Experimental
3. Experimental

3.1. Preparation of magnetite
Magnetite was synthesized via two different ways; described below in 3.1.1 and 3.1.2.

3.1.1. Coprecipitation
The synthesis of magnetite was carried out by coprecipitation of Fe(II) and Fe(III) [74, 75]. A solution of Fe(II) and Fe(III) chloride (molar ratio 1:2) in deoxygenated Milli-Q water and at a total concentration of 1.2 M was slowly added into a solution of 0.9 M NH₄OH. The solution was kept under argon atmosphere at room temperature and was vigorously stirred. The precipitated magnetite was washed, separated by centrifugation and dried in a vacuum desiccator.

3.1.2. Oxidation of Fe(OH)₂
Fe(OH)₂ was obtained by mixing 2.8 g NaOH and 6.96 g FeCl₂·4H₂O with 70 cm³ deoxygenated Milli-Q water. The gel formed was placed in a water bath preheated to 70 °C and agitated vigorously in the presence of air for 30 hours. The precipitated magnetite was washed and dried in a vacuum desiccator.

3.2. Characterization of magnetite
The synthetic magnetite samples prepared either by coprecipitation or oxidation of Fe(OH)₂ were characterized by X-ray powder diffraction, electron microscopy, infrared spectroscopy in Far- and Mid- infrared regions, and chemical analysis (Paper I). The specific surface area of the magnetite sample synthesized by coprecipitation was determined by the BET (Brunauer, Emmett and Teller) method (Paper II-VII).
3.3. Determination of oxidation state of iron in magnetite samples
The magnetite samples were dissolved in concentrated HCl under argon and Fe (II) was
titrated with $\text{K}_2\text{Cr}_2\text{O}_7$ in presence of an indicator. At the titration endpoint, all the Fe$^{2+}$ ions
were reduced back to Fe II using SnCl$_2$ as a reducing agent and titrated again with $\text{K}_2\text{Cr}_2\text{O}_7$ in
the same way (Paper I).

3.4. Particle deposition
The main deposition method applied in this thesis is the same as previously described by other
authors (e.g. 45). A few drops of an as-synthesized magnetite suspension were evenly spread
over the internal reflection element (IRE) and dried in a vacuum desiccator. After that, the
IRE (ZnSe, ZnS) was thoroughly rinsed with ethanol and Milli-Q water. The weight of
deposited magnetite was calculated from the weight difference before and after the deposition.

3.5. Solutions
All solutions were prepared by dissolution of analytical grade reagents (if not otherwise
stated) in Milli-Q water (Millipore corp.). The solutions were freshly prepared and used just
before the experiment. NaOH and HCl were used for pH adjustments where needed.

3.6. Instrumentations

3.6.1. MC-ICPMS
Fe isotope ratio measurements were performed with a double focusing high resolution
Multiple Collector Inductively Coupled Plasma Mass Spectrometry (MC-ICPMS) instrument
(Neptune, Thermo Finnigan, Germany). MC-ICPMS uses an array of Faraday cups as detector
to precisely measure the isotope ratio of small mass differences. The cups are positioned
along the focus plane of the mass spectrometer, so that mass separated ion beams can be
simultaneously detected.
First of all, plasma has to be generated. Plasma is a gas in which atoms are present in an
ionized state. The plasma is formed by means of a radio frequency (r.f.) generator. The ions
enter the mass spectrometer through a skimmer cone at the plasma interface positioned just before the transfer lens system and the electrostatic analyzer. The ion beam is focused by two devices; an electrostatic analyzer and a magnetic sector analyzer, in forward geometry. In the electrostatic analyser module, ions are accelerated and dispersed with respect to the ion energy. On the other hand, dispersion of the ion beam is based on energy and mass in the magnetic sector. The ion beam focused in this way along the focal plane of the mass spectrometer is then detected.

3.6.2. XRD
The crystal structure of magnetite samples were analyzed by X-ray powder diffraction. X-ray diffractograms were recorded at room temperature on a Siemens 5000 powder X-ray diffractometer in 2θ range 20-70° and φ= 0° with Cu Kα radiation.

3.6.3. SEM
Scanning Electron Microscopy (SEM) was carried out to observe the particle morphology and their size. SEM was run on a Philips XL 30 equipped with a LaB₆ source and using SE (secondary electron) detector and accelerating voltage of 20 kV.

3.6.4. Surface area measurements
The specific surface area of the magnetite sample was determined by the BET nitrogen adsorption/desorption method on a dried powder sample with a surface area analyzer from Micrometrics ASAP 2000.

3.6.5. Thermal analysis
TG (thermogravimetry), DTG (derivative thermogravimetry), DSC (differential scanning calorimetry) and MS (mass spectroscopy) curves were recorded on a Netzsch STA 409/QMS equipped with a Quadruple mass-spectrometer. This instrument provides thermogravimetric and differential scanning calorimetric data, derivatives of each data set, and mass
spectroscopic analysis of evolving gas, simultaneously on a single sample. It is possible in this instrument to run the experiment under oxidizing, reducing and inert atmosphere.

### 3.5.6. IR spectroscopy

The IR spectra were recorded on a Bruker IFS 113V equipped with DTGS (Deuterated Triglycine Sulfate), DTGS-PE and MCT (Mercury, Cadmium, Telluride) detectors. Table 3.1 shows the auxiliary optics and measurement parameters used for FTIR spectroscopy.

**Table 3.1. Auxiliary optics and set up parameters used in IR spectroscopy**

<table>
<thead>
<tr>
<th></th>
<th>Far-IR</th>
<th>MID-IR</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Transmission</td>
<td>Transmission</td>
</tr>
<tr>
<td>Source</td>
<td>Globar</td>
<td>Globar</td>
</tr>
<tr>
<td>Detector</td>
<td>DTGS-PE</td>
<td>DTGS</td>
</tr>
<tr>
<td>beamsplitter</td>
<td>Mylar</td>
<td>KBr</td>
</tr>
<tr>
<td>Resolution</td>
<td>2 cm⁻¹</td>
<td>4 cm⁻¹</td>
</tr>
<tr>
<td>Zero-filling factor</td>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td>Temperature</td>
<td>~ 22 °C</td>
<td>~ 22 °C</td>
</tr>
<tr>
<td>Apodization function</td>
<td>Four point</td>
<td>Blackman-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Harris 3-term</td>
</tr>
<tr>
<td>Scanner velocity</td>
<td>2; 3 kHz</td>
<td>6; 10 kHz</td>
</tr>
<tr>
<td>Acquisition mode</td>
<td>Double sided</td>
<td>Double sided</td>
</tr>
<tr>
<td>Background</td>
<td>Single beam</td>
<td>Single beam</td>
</tr>
<tr>
<td>Number of scans</td>
<td>128</td>
<td>100-200</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

All the measurements were performed at room temperature (~ 22°C). The scanner velocity was selected depending on the frequency (mid or far-IR) and detector response time. Apodization function is a weighting function which is used to change the input intensity profile, *i. e.* to change the line shape in such a way that the peak foot approaches zero at the edges. A zero-filling factor of 2 is used in our experiments implying that the number of data points in the spectrum is doubled by interpolation resulting in smoother spectrum.
3.5.6.1. Transmission
A small drop of neat liquid oleic acid and Atrac were carefully spread between CaF$_2$ windows assembled in a vacuum cell and the spectra were recorded in the range 1000-4000 cm$^{-1}$ at a resolution of 4 cm$^{-1}$ (Paper II).
A Nujol mull on polyethylene plate method was used for magnetite sample and data were recorded in the Far-IR region (Paper I).

3.5.6.2. DRIFT
In Diffuse Reflectance Infrared Fourier Transform (DRIFT) spectroscopy technique the diffusely scattered IR radiation from a sample is collected, and refocused to the detector through mirrors. This modification of the IR technique can be employed for a high surface area samples that are not sufficiently transparent to be studied by transmission IR spectroscopy. Since the IR beam in DRIFT is reflected from the sample surface, it may be more surface sensitive compared to the transmission IR technique. The reflection may occur many times in the sample, which increases the pathlength.
A powder sample is usually mixed and grinded with a non-absorbing powder such as KBr. Although quantitative measurements may be carried out with DRIFT technique with a proper calibration [76, 77], still it is more suited for obtaining qualitative information. This is due to the lack of reproducibility of band intensities arising from variations in the scattering coefficient each time the sample is loaded into the cell. For quantitative work, the spectrum recorded is transformed to Kubelka-Munk units.
In this thesis, DRIFT spectroscopy technique with KBr as diluent was used for characterization of dried powder samples of oleate and heated oleate adsorbed on magnetite. All spectra were collected in the range 1000-4000 cm$^{-1}$ at a resolution of 4 cm$^{-1}$ using an MCT detector cooled by liquid nitrogen (Paper II). DRIFT spectroscopy was also used for carbonate adsorption onto magnetite (Paper VII).

3.5.6.3. ATR set up
Both ZnSe (Crystran Limited UK) and ZnS prisms (Spectroscopy Central LTD, UK) 50x20x2 mm, 45 degree trapezoid were used as internal reflection elements. Spectra were recorded in the Mid-IR region at a resolution of 4 cm$^{-1}$ using MCT or DTGS detectors. A single beam
background spectrum was recorded every time before collecting the sample spectra in order to get a good signal to noise ratio.

A sketch of the experimental setup is shown in Figure 3.1. A single sided rectangularly shaped flow through cell made of stainless steel was sealed to the IRE crystal via a Viton O-ring and mounted on the ATR accessory (Specac England). This arrangement provides 10 reflections inside the cell where the crystal is in contact with the solution.

![Figure 3.1. Experimental design for ATR in-situ adsorption measurements.](image)

The cell was connected to the reservoir via Viton tubings and the sample solutions were circulated by a Watson Mallow, Bredel pump (Spiram-Sarco engineering group, England). All experiments were conducted at room temperature and under argon flow. The pH value was probed during the experiment using a glass electrode and adjusted using NaOH or HCl solutions.

Data acquisition as well as data processing and analysis were carried out by means of the OPUS software.
Results & Discussion
4. Results & Discussion

4.1. Synthetic magnetite; characterization and mechanism

The structural properties of the synthetic magnetite samples were obtained by X-ray powder diffraction (XRD), scanning electron microscopy (SEM) and FTIR spectroscopy (Paper I).

The XRD pattern of both samples prepared by coprecipitation and oxidation of Fe(OH)$_2$ showed characteristic reflections of spinel phase crystallites. The magnetite synthesized by coprecipitation showed a peak broadening, which was due to the smaller crystallite size, whilst magnetite obtained by oxidation of Fe(OH)$_2$ had larger crystallites and showed sharper peaks in XRD pattern.

Scanning Electron Microscopy (SEM) also revealed that the magnetite synthesized by coprecipitation was smaller (~10 nm) and had spherical shape, whilst the samples produced from oxidation of ferrous hydroxide had larger crystallite size (~100 nm) with a considerable portion of cornered structures.

FTIR spectroscopy recorded in the Mid-Far infrared region showed broad bands around 570 and 360 cm$^{-1}$ corresponding to vibrational modes of Fe-O entities typical for the crystalline lattice of magnetite [1, 78]. No OH infrared bands (stretching or bending) due to FeOOH were observed.

In Table 4.1 data on iron isotope fractionation are presented together with the chemical analysis of magnetite synthesized by the coprecipitation method. Table 4.2 provides data for magnetite synthesized by the oxidation method. Analyzing the data in Table 4.1, it can be concluded that there is no significant variation in the $\delta$-value of magnetite sample and initial reagents; Fe(II) and Fe(III). Neither substituting NH$_4$OH for NaOH nor changing the addition rate affected the result. This may be explained with respect to the role of Fe(II) concentration on the mechanism of magnetite formation [79-81].

On the other hand, as shown in Table 4.2, the formed magnetite is enriched in the lighter isotope in the initial stage of the oxidation reaction. It is believed that the magnetite formation starts with oxidation of Fe(OH)$^+$ which is formed in water [82] as follows:

$$\text{Fe(OH)}_2\text{(solid)} \leftrightarrow [\text{Fe(OH)}]^+ (\text{aq}) + \text{OH}^- \quad (4.1)$$
Subsequently, oxidation takes place leading to the formation of the intermediate entity \([\text{Fe}_2(\text{OH})_3]^{+3}\) (aq), which can be combined with another \([\text{Fe(OH)}]^+\) (aq) to form \(\text{Fe}_3\text{O(OH)}_4^{2+}\) (aq). This intermediate entity has the same Fe(II)/Fe(III) ratio as magnetite which under slow oxidation transforms into crystalline magnetite.

The results obtained in this work suggest that Eq. 4.1 has a significant effect on fractionation of iron, since it was shown that oxidation of the Fe(II) solution leads to partitioning of \(56\text{Fe}\) into oxy-hydroxide [13]. The higher abundance of \(^{54}\text{Fe}\) compared to \(^{56}\text{Fe}\) in the \([\text{Fe(OH)}]^+\) entity is probably because of a higher lability of the lighter isotope, indicating that \(^{56}\text{Fe}\) forms stronger bonds, and therefore tends to remain in the \(\text{Fe(OH)}_2\) phase.

**Table 4.1.** \(\delta^{56}\text{Fe}/^{54}\text{Fe}\) of magnetite and Fe(II) and Fe(III) chloride; the coprecipitation method

<table>
<thead>
<tr>
<th>Sample</th>
<th>(\delta^{56}\text{Fe}/^{54}\text{Fe})</th>
<th>(\text{Fell}/\text{Fe(tot)})*</th>
</tr>
</thead>
<tbody>
<tr>
<td>source-Fe(III)</td>
<td>0.09±0.05</td>
<td>-</td>
</tr>
<tr>
<td>source-Fe(II)</td>
<td>0.00±0.05</td>
<td>-</td>
</tr>
<tr>
<td>magnetite</td>
<td>-0.05±0.07</td>
<td>31.0±0.1%</td>
</tr>
</tbody>
</table>

*Fe(tot) = Fe(II) + Fe(III), The data is expressed as: “Average ± Standard Deviation”

**Table 4.2.** \(\delta^{56}\text{Fe}/^{54}\text{Fe}\) of magnetite and Fe(OH)_2; Oxidation of ferrous hydroxide.

<table>
<thead>
<tr>
<th>Sampling time (hour)</th>
<th>(\delta^{56}\text{Fe}/^{54}\text{Fe})</th>
<th>(\text{Fell}/\text{Fe(tot)})*</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>-0.09±0.07</td>
<td>30.2±0.3%</td>
</tr>
<tr>
<td>6</td>
<td>-0.17±0.06</td>
<td>n.d.</td>
</tr>
<tr>
<td>7</td>
<td>-0.38±0.10</td>
<td>29.9±0.2%</td>
</tr>
<tr>
<td>13</td>
<td>-0.16±0.03</td>
<td>n.d.</td>
</tr>
<tr>
<td>18</td>
<td>0.04±0.02</td>
<td>n.d.</td>
</tr>
<tr>
<td>24</td>
<td>0.03±0.03</td>
<td>27.4±0.2%</td>
</tr>
<tr>
<td>30</td>
<td>0.08±0.04</td>
<td>24.8±0.3%</td>
</tr>
<tr>
<td>source-Fe(II)</td>
<td>-0.01±0.03</td>
<td>-</td>
</tr>
</tbody>
</table>

*Fe(tot)=Fe(II) + Fe(III), n.d.=not determined, The data is presented as: “Average ± Standard Deviation”

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4.2. Adsorption of oleate on magnetite surface

The oleate adsorbed on magnetite was analysed by FTIR spectroscopy and the thermal analysis (Paper II). The DRIFT spectrum of oleate adsorbed on magnetite (Fig. 4.1) showed CH₂ and CH₃ stretching bands in the spectral region 2800-3000 cm⁻¹ and the vinlylic =C-H band at 3006 cm⁻¹ together with the two bands at 1529 and 1430 cm⁻¹ assigned to asymmetric and symmetric stretching of the carboxylate group, respectively. Based on the frequency difference (Δν) between the symmetric and asymmetric carboxylate modes, a bidentate mononuclear complex was proposed to be the main surface complex formed [34].

Figure 4.1. DRIFT spectrum of the oleate adsorbed on magnetite particles before heating.
The surface excess of the adsorbed oleate and the surface area occupied by an oleate molecule at the surface of magnetite can be calculated using the total amount of oleate per surface area (11% by weight oleate; Figure 4.2) and the specific surface area of magnetite (97.7 m²/g), to be $4.6 \times 10^{-6}$ mol/m² and ~36 Å², respectively. The latter value is in good agreement with literature values [83, 84].

**Figure 4.2.** DTG and DSC diagram of the oleate on magnetite heated at a rate of 20 °C/min in 100 ml/min air flow.
4.3. Kinetics of oleate adsorption onto magnetite

The kinetics was studied using ATR spectroscopy and by in-situ monitoring of adsorption of the oleate from solution onto the magnetite surface with time (Paper VI). The integrated absorbance over the CH stretching range was assumed to be proportional to the amount of oleate adsorbed. Assuming pseudo-first order kinetics, the following equation can be derived:

\[
\ln\left(\frac{A_m}{A_m - A_t}\right) = k_1 t, \quad (4.2)
\]

where \(k_1 = k_2 C_b\) is the pseudo-first order rate constant, \(C_b\) is the concentration of the oleate in the bulk, \(t\) is time, and \(A_m\) and \(A_t\) are absorbances at equilibrium and at time \(t\), respectively [43, 49].

According to Eq. 4.2, a plot of \(\ln(A_m/(A_m-A_t))\) versus time might confirm the first-order behaviour and from the gradient of the straight line, \(k_1\) can be determined. As shown in Fig. 4.3, the reaction was confirmed to be first-order with \(R^2=0.9961\), which demonstrates a good correlation with the first-order kinetics. An apparent rate constant of \(k_1 = 0.030 \pm 0.002\) min\(^{-1}\) was obtained, which was the same rate constant (within experimental error) for all concentrations studied (0.01, 0.02, 0.05, and 0.1 mM).

![Figure 4.3. A plot of \(\ln(A_m/(A_m-A_t))\) versus time showing that the rate of adsorption of the oleate onto magnetite followed a pseudo first order reaction. The straight-line is a linear least square fit of the experimental points.](image-url)
The rate of collector adsorption, in addition to the thermodynamic considerations, is important in selective flotation. For instance if the adsorption rate of collector on both minerals (magnetite and fluorapatite) is comparable (not very different), it might be more efficient to add the collector step by step since this would reduce high local concentrations of the collector in the flotation pulp.

4.4. Adsorption of sulphate on magnetite
Adsorption of sulphate on magnetite at different concentrations, pH, and ionic strength was studied in-situ using ATR-FTIR spectroscopy (Paper III). Figure 4.4 shows IR spectra of sulphate adsorbed from aqueous solutions of different sulphate concentrations at pH 4 onto a magnetite layer deposited on IRE. Three absorbance maxima at 1115, 1044 and 979 cm\(^{-1}\) indicated a monodentate adsorption in which the \(T_d\) symmetry of \(SO_4^{2-}\) was lowered to the \(C_{3v}\) symmetry. On the other hand, from the spectra of sulphate adsorbed on magnetite at pH ≥6.5, it was inferred that adsorption in this pH range is mostly due to the formation of outer-sphere complexes.

![Figure 4.4. Adsorption of sulphate ions on magnetite from 5, 10, 20, 70, 100, 500, 1000, 2000, and 5000 μM aqueous sulphate solutions at pH = 4 and ionic strength I = 0.01 M.](image)
It was also revealed that adsorption of sulphate on magnetite reaches its saturation and the adsorption curve can be fitted into a Langmuir adsorption isotherm (see Eq. 2.3). Thus, a plot of C/A versus C (Fig. 4.5) resulted in a straight line with 1/Aₘ as the slope of the line and 1/(kAₘ) representing the intercept. Knowing Aₘ from the slope, the Langmuir affinity constant (K) of adsorption could be calculated.

![Figure 4.5. Adsorption isotherm fitted with the Langmuir model for the adsorption of sulphate onto magnetite from sulphate solutions (raw data are taken from Figure 4.4).](image)

From plot in Fig. 4.5, the Langmuir affinity constant and the free energy of adsorption at pH 4 and 298 K were estimated to be 1.2344 x 10⁴ M⁻¹ and -33.3 kJ/mol, respectively.

The rates of sulphate adsorption onto magnetite from sulphate solution concentrations of 10, 50 and 100 μM are depicted in Figure 4.6. The experimental data were fitted well into a pseudo first order reaction, however, the rate constant was increased with an increase of the concentration of sulphate in solution. The increasing rate constant with concentration might at least partly be due to the time it takes for the anions to migrate into the porous magnetite layer to eventually be adsorbed, i.e. being shorter at a higher concentration of sulphate ions.

It was observed that the spectral pattern did not vary with time for all concentrations of sulphate used in the kinetic measurements at pH 4, indicating that a single mechanism is responsible for adsorption of sulphate on magnetite at this pH.
In addition, the effect of Ca$^{2+}$ ions on sulphate adsorption was also studied. IR spectra showed a similar band shape for the sulphate adsorption both when Ca$^{2+}$ ions were added to the reaction solution and when only Na$^+$ ions constituted the ionic medium, indicating an outer-sphere sulphate adsorption at pH≥6.5. It was shown that Ca$^{2+}$ ions slightly promoted adsorption of sulphate at alkaline pH. An increase in sulphate adsorption was attributed to an increase in the positive charge at the surface due to specific adsorption of Ca$^{2+}$ at high pH. Since sulphate ions were weakly adsorbed on magnetite at pH 8.5 and Ca$^{2+}$ ions did not show a dramatic effect on its adsorption at this pH, it may be concluded that sulphate ions although a major constituent of the process water at LKAB, have only a small effect on the surface property of magnetite under the process conditions.
4.5. Adsorption of silicate on magnetite

4.5.1. Speciation of silicate in solution

The calculated equilibrium distributions of silicate anion species in sodium silicate solutions as a function of pH and at room temperature are plotted in Figure 4.7 (Paper IV).

![Figure 4.7](image)

**Figure 4.7.** A speciation diagram of silicate anions as a function of pH in (a) 1 and (b) 10 mM aqueous sodium metasilicate solution.

As seen from diagram in Fig. 4.7, at 1 mM silicate concentration, the dominant species in equilibrium are $\text{SiO}_2\text{(OH)}_2^{2-}$, $\text{SiO(OH)}_3^-$, and $\text{Si(OH)}_4$ with protons transferred between the different species as pH was changed. At 10 mM silicate concentration amorphous silica is predominant at low pH values (pH< 9) while when the pH increases, e. g. between pH 9 to 13, there are monomers, dimers, trimers and even oligomers formed in solution. This implies
that the pH and concentration of sodium silicate in solution determine the silicate anion speciation at a certain temperature. Moreover, the rate of dissolution/condensation of water glass in solution should be taken into account whenever water glass is used for surface modification, e.g. in a flotation process; because it is known that the equilibrium in solution is reached relatively slow.

4.5.2. Effect of pH on sorption of silicate onto magnetite

The effect of pH on water glass adsorption onto magnetite, shown in Figure 4.8, revealed an increased amount of sorbed silicate species with decreasing pH, in particular from 11 to 9 (paper IV). At pH 11.2, the maximum absorbance was located at 955 cm\(^{-1}\). However, as solution pH was lowered to 9.3, the band at ~1020 cm\(^{-1}\) increased in intensity, becoming the strongest band in the spectral region (800-1200 cm\(^{-1}\)) and simultaneously intensity of the band at 1120 was also increased. No remarkable change in the line shape was observed between pH 8.3 to 7. It was suggested that the increase in intensity at 1120 cm\(^{-1}\) and 1020 cm\(^{-1}\) are possibly due to the condensation of the silicate monomers at the magnetite surface.

Figure 4.8. Infrared spectra of silicate adsorbed on magnetite from a 1 mM aqueous solution at different pH. Spectra are plotted in the same order as the indicated pH values.
The band around 950 cm\(^{-1}\) might be assigned to bidentate monomeric surface species, \((\mathrm{FeO})_2\mathrm{Si(OH)}\mathrm{OH}\) or \((\mathrm{FeO})_2\mathrm{Si(OH)}\mathrm{O}^\(-\), whilst the band at ~1020 cm\(^{-1}\) could be attributed to oligomeric surface silicate species. The shoulder above 1100 cm\(^{-1}\) is consistent with a three-dimensional polymeric structure such as colloidal silica, implying polymerization of silica at the magnetite surface (Paper IV-VI).

4.5.3. Effect of silicate concentration on sorption
Spectra of the sorbed silicate onto magnetite from 0.1, 0.4, 1, and 5 mM aqueous silicate solutions at pH 8.5 is presented in Figure 4.9 (Paper VI). As evident from these infrared spectra, the absorption bands typical for adsorbed silicate species shift to higher frequency with increasing concentration of silicate in solution.

![Figure 4.9](image)

**Figure 4.9.** ATR-FTIR spectra of silicate adsorbed on magnetite from aqueous solution. The insert to the right shows the bulk silicate concentrations in mM. Spectra were recorded after equilibration for 100 minutes.

Adsorption of 0.1 mM silicate at pH=8.5 shows its maximum at ~950 cm\(^{-1}\), which was assigned to FeO-Si stretching in inner-sphere bidentate monomeric surface complexes. With increasing concentration, the peak maxima shifted to higher frequency. The frequency shift of sorbed silicate to higher wavenumber with increasing silicate concentration had a similar trend as decreasing pH from 11 to 9 (section 4.5.2). With reference to the spectral assignment
of sodium silicate in solution at different concentrations and pH values that was supported by thermodynamic modelling, the shift to higher frequency is an indication of increased polymerization at the magnetite surface resulting in oligomeric species. At 5 mM silicate concentration and pH 8.5, the broad shoulder appearing at about 1120 cm⁻¹ showed much higher intensity than at lower silicate concentration, which was assigned to an increasing number of Si-O-Si units in a three dimensional silica framework structure.

The intensity grow of the silicate band with increasing concentration and decreasing pH value (to around 9) implied that the largest amount of sorbed species and also the strongest adsorption took place at moderate pH and high silicate concentration where more oligomerized/polymerized silicates form at the surface.

According to the literature [Paper V, 85], the formation of such species has a stronger affinity for the iron oxide surface due to contribution from many Fe-O-Si segments to the strength of adsorption.

4.5.4. Kinetics of silicate sorption onto magnetite

Figure 4.10 shows the development of the IR spectral features upon adsorbing silicate onto magnetite from a 0.4 mM aqueous silicate solution. A growth in intensity of the band at ~1000 cm⁻¹ is prominent and eventually this band became the strongest one in this spectral region after 100 minutes. A similar trend occurred at higher concentration viz., 1 and 5 mM, and was described as oligomerization or polymerization of silicate at the surface with time.
Adsorption of silicate on magnetite was fast within the first 30 minutes for silicate concentrations of 0.1, 0.4, 1 and 5 mM in solution. However the adsorption equilibria were not reached within several hours, independent of pH and silicate concentrations. The increase in band intensity with time was pronounced at higher concentrations, which was suggested to be due to polymerization of silicate at the magnetite surface. This implies that both concentration and time are two important factors in condensation of silicate at the magnetite surface i.e. if the magnetite is stored for a longer time in a solution containing a certain concentration of silicate, it is finally coated with a polymerized silica layer which may change its surface properties.

4.5.5. Effect of a silicate addition on adsorption of the oleate onto magnetite
The integrated absorbance of the oleate in the C-H stretching region was plotted versus the bulk silicate concentration used to modify the magnetite surface (Fig. 4.11). Clearly, the amount of adsorbed oleate decreased with an increasing amount of silicate on the magnetite surface, especially for silicate concentrations higher than 0.4 mM.
This result indicates that the extent of oleate adsorption is considerably lower above the bulk concentration where silicate species at the magnetite surface are supposed to form oligomers or polymers. The oligomerization and polymerization of silicate at the magnetite surface seems to strengthen the attraction between silicate and iron oxide, although increased surface coverage and thickness of the adsorbed silica layer may also be important. It has been shown that both pH and silica concentration are two important factors affecting the efficiency of water-glass as a depressant in selective separation of apatite from iron oxide [Paper V, 85, 86]. However, at sodium silicate concentrations lower than 0.4 mM, the adsorbed silicate species seemed to work mainly as a dispersing agent [87]. Already at this low concentration, the adsorbed silicate species tend to take part in condensation reactions at the magnetite surface. It seems that condensation of adsorbed silicate species is more efficient in order to avoid adsorption of oleate although adsorption was strongly prohibited already for magnetite treated with 0.1 mM silicate solution (Paper VI).
4.6. Carbonate adsorption onto magnetite

Adsorption of carbonate on magnetite was studied by ATR-FTIR spectroscopy at slightly alkaline to neutral pH viz. pH 8.5-6.5 at which bicarbonate (HCO$_3^-$) is the dominant species in aqueous solution (Paper VII). As seen in Figure 4.12, three regions in the frequency range 1000-1600 cm$^{-1}$ are discerned in the IR spectrum of adsorbed carbonate, i.e. 1000-1100, 1300-1400, and 1400-1600 cm$^{-1}$.

![Figure 4.12. ATR-FTIR spectra of carbonate adsorbed from 5 mM NaHCO$_3$ aqueous solution onto magnetite surface at pH 8.5-6.5.](image)

The band at ~1070 cm$^{-1}$ was assigned to the symmetric stretching ($\nu_3$) vibration of carbonate which has become IR active because of interaction with the magnetite surface. A relatively broad band at ~1335 cm$^{-1}$ with a shoulder at the high frequency side (~1375 cm$^{-1}$) is arising from the splitting of the $\nu_3$ vibration and so are the band at ~1485 cm$^{-1}$ and the shoulder at ~1545 cm$^{-1}$. All four bands were assigned to asymmetric stretching vibration of surface-associated carbonate species. The presence of the asymmetric bands observed in this study at ~1480 and 1545 cm$^{-1}$ may therefore indicate the existence of at least two different carbonate species co-adsorbed at the magnetite surface.

Figure 4.12 also shows the effect of pH on carbonate adsorption onto magnetite. The band intensity of adsorbed carbonate species increased with decreasing pH and shifted slightly in frequency resulting in a larger $\Delta\nu_3$. Addition of CaCl$_2$ brought about an increase of all
carbonate bands at ~1070, ~1335, ~1375, ~1480, and 1545 cm\(^{-1}\) proportional to Ca\(^{2+}\) concentration.

With reference to previous reports [29, 88], it was suggested that the 1545/1335 cm\(^{-1}\) pair is due to an inner-sphere bidentate binuclear complexation of carbonate ions with iron atoms whilst the 1480/1375 cm\(^{-1}\) pair is caused by a complexation with iron or calcium atoms, which are influenced by the hydrogen bonding and is more loosely bonded to the magnetite surface.

Upon adding of sodium silicate to carbonate adsorbed on magnetite, either in the presence or the absence of Ca\(^{2+}\) ions, the band intensity of carbonate at ~1480 cm\(^{-1}\) (representing more loosely bound carbonate) was reduced more strongly than the intensity of the band at ~1545 cm\(^{-1}\) implying that silicate ions might more readily desorb the loosely bound carbonate.

The presence of calcium and carbonate in the process water and strong co-adsorption of these ions at the magnetite surface indicate that the surface of magnetite is probably coated by a calcium carbonate layer which may affect the surface property of magnetite i. e. change its surface behaviour with respect to interaction with water glass or collector adsorption.
Conclusions
5. Conclusions
In paper I, it was concluded that $^{56}\text{Fe}^{54}\text{Fe}$ data can be used in the study of mechanism of magnetite formation. The magnetite particles synthesized by two different methods showed different sizes and morphologies. Mechanisms for these two synthetic methods were also suggested.

In paper II, a single layer of the oleate on the magnetite particles was detected by IR spectroscopy and thermal analysis. Molecules in this layer were preferentially bonded to iron atoms at the magnetite surface by a bidentate mononuclear complexation. The surface density of the oleate was estimated to be $4.6 \times 10^{-6}$ mol/m$^2$, implying a surface density of $\sim 36$ Å$^2$/molecule. It was also indicated that the decomposition of oleate on magnetite under argon atmosphere initially involves the formation of species capable to exhibit hydrogen and carbon bonding structures.

In paper III, three absorbance maxima at 1115, 1044 and 979 cm$^{-1}$ were observed for sulphate adsorbed at pH 4, indicating a monodentate adsorption. At pH 6.5, however, sulphate was adsorbed on magnetite via outer-sphere complexation. It was indicated that sulphate interaction with magnetite could be classified as an intermediate to weak and the tendency of sulphate in solution to be adsorbed on magnetite decreased with an increase of pH.

In paper IV, ATR-FTIR spectra of sorbed silicate in the pH range of 11 to 7 indicated the presence of different types of surface species at the magnetite surface. The proposed sorption mechanism indicated a ligand exchange reaction, where both monodentate and bidentate complexes may co-exist at a low surface loading level. A subsequent adsorption/polymerization of silicate took place on magnetite surface with lowering of pH and further surface accumulation.

In paper V, it was concluded from infrared spectral data that both pH and the silicate concentration has a prominent influence on the interfacial reaction between a soluble silicate and the iron oxide surfaces, regarding both the amount of silicate adsorbed per unit mass of iron oxide and the surface species formed. The maximum adsorption of silicate from aqueous solution onto magnetite was detected between pH 7.0 and pH 9.5. A rapid initial increase in
the absorption intensity was observed, followed by a slower sorption stage, which was strongly dependent on the concentration of silicate in solution and the pH value.

In paper VI, it was concluded that sorption of the oleate from an aqueous solution onto magnetite surface is preferentially chemisorption. The oleate adsorption on magnetite was described by the pseudo first-order kinetics. With respect to sorption of silicate, the frequency shift toward a higher frequency as a function of both time and concentration of silicate was attributed to oligomerization of silicate at the magnetite surface, which might affect the depressive properties of silicate. It was also shown that magnetite surface modified by silicate, even at low concentration, effectively reduced adsorption of the oleate from aqueous solution.

In paper VII, two co-existed carbonate species were found at the magnetite surface. It was noted that lowering pH from 8.5 to 6.5 as well as the presence of Ca$^{2+}$ ions increased adsorption of carbonate onto magnetite surface. Moreover, it was observed that silicate in competition with carbonate facilitates desorption of loosely bound carbonate. It was also speculated that the presence of both Ca$^{2+}$ and CO$_3^{2-}$ in the process water at LKAB will certainly influence the surface properties of the magnetite particles.

**General conclusion**

In general, ATR-FTIR spectroscopy seems to be an excellent method for *in situ* analysis, which is important in mineral processing systems. Using this technique, sorption mechanisms, interface species formed, and sorption kinetics, can be studied.
Future works
6. Future works

- It is of a great interest to perform contact angle measurements, in particular on magnetite samples modified with silicate and oleate. Measurements should be carried out on both natural and synthetic samples for comparison.

- The effect of Ca ions on the interaction between sorbed silicate and bentonite used as binder is an important issue that should be evaluated, since it may offer some clues to the magnetite agglomeration process.

- Magnetite pelletization involves a multi-component system containing compounds not studied in this thesis. For example, olivine and dolomite are used in separate processes. These compounds should also be studied with respect to their influence on magnetite agglomeration properties. The effect of other components in the system, such as Mg$^{2+}$ ions and olivine, of course, would be necessary.

- Other in-situ and ex-situ techniques such as EXAFS, AFM, XPS, etc. may reveal further information on the structure and properties of the magnetite surface reacted with various reagents present in the process water.

- It also seems important to utilize theoretical methods such as density functional theory (DFT) calculations on the samples studied by different spectroscopy techniques. A combination of DFT and spectral data may be used to more precisely assign the bands to each species and accordingly be a valuable tool in the interpretation of infrared spectra.

- The author believes that Ca$^{2+}$ ions may influence adsorption of collector on magnetite as well. This deserves more extensive studies.

- Finally, the subdivision of the real multi-component system into subsystems facilitating the interpretation of experimental results should end up with experiments on the system encountered in practice. Such experiments should focus on the kinetics of adsorption of all species in solution simultaneously and be performed on both natural and synthetic magnetite making it possible to validate the usefulness of the synthetic iron-oxide in laboratory experiments.
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A STUDY ON THE MECHANISM OF MAGNETITE FORMATION
BASED ON IRON ISOTOPE FRACTIONATION

Payman Roonasi, Allan Holmgren
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A STUDY ON THE MECHANISM OF MAGNETITE FORMATION
BASED ON IRON ISOTOPE FRACTIONATION

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Keywords: synthetic magnetite, mechanism, iron isotope fractionation, phase transactions

Abstract
Having knowledge of mechanism of magnetite formation is essential in a number of industrial processes including magnetite synthesis and corrosion of iron. In this study, magnetite nanoparticle was synthesized via two different ways; coprecipitation of iron (II) and (III) and oxidation of ferrous hydroxide. The samples were characterized using X-ray diffraction (XRD), Mid-Far IR spectroscopy, scanning electron microscopy (SEM), chemical analysis for determination of Fe II/Fe III ratio and ICP-MS for iron isotopic ratio (\(^{56}\text{Fe} / ^{54}\text{Fe}\)) measurement. Since fractionation of iron isotopes depends on reaction rate and bonding strength, interpretation of the isotopic data with respect to the possible mechanisms is discussed. No fractionation of iron isotopes was observed for the magnetite synthesized by coprecipitation, whilst magnetite formed from ferrous hydroxide showed higher abundance of \(^{54}\text{Fe}\) compared to \(^{56}\text{Fe}\) in the beginning of reaction, implying the significance of the following reaction:

\[
\text{Fe (OH)}_2 \text{(solid)} \leftrightarrow [\text{Fe (OH)}]^+_{(aq)} + \text{OH}^- 
\]

Introduction
Magnetite, Fe\(_3\)O\(_4\), one of the important iron ores, is ubiquitous in nature. It is a common constituent of igneous and metamorphic rocks. Due to its black colour, surface chemistry and strong magnetic property, it has found a great number of applications in industry [1-5]. Synthetic magnetite, particularly, can be tailored for specific applications. Numerous factors such as purity, particle size and shape etc. have considerable effect on its application and in this regard, the mechanism of formation plays an important role. Moreover, the mechanism of formation of magnetite as one of the corrosion products of iron and steel in industry is also of great interest.

The recently introduced new generation of mass spectrometric techniques, in particular multi-collector inductively coupled plasma mass spectrometry (MC-ICPMS), allows reliable detection of minor natural variations in the isotopic composition of transition metals, including iron [6-10]. One of the applications of the isotopic fractionation data is to use them as evidence to verify and elucidate a specific reaction pathway [9, 10]. For example, Bullen et al. studied \(\delta^{56}\text{Fe}\) fractionation in the ferrihydrate-solution system and suggested that the heavier iron isotope is enriched in Fe II(OH)\(_{3\text{(aq)}}\) in comparison to other iron species in the solution.

The aim of this study was to investigate the possible occurrence of iron isotope fractionation in synthetic magnetite manufactured by two different ways, namely, coprecipitation of Fe II and Fe III in an alkali solution and oxidation of ferrous hydroxide. The isotope fractionation data obtained were utilized in an effort to understand the mechanism of magnetite formation.
Experimental Procedure

Reagents:
All reagents were of analytical grade (purity >99%) and used without further purification. Milli-Q water (Millipore corp.) was used in the synthesis and rinsing. Single element standard solutions (SPEX plasma standards, Edison, NJ, USA) were used as internal standard for calibration. Analytical grade hydrochloric acid (30% Fluka, Steinheim, Germany) was used to dissolve the magnetite samples. The standard for iron isotope ratio measurement, IRMM-014, was obtained from Institute of Reference Material and Measurement, Geel, Belgium.

Instrumentation
Mass Spectrometry Fe isotope ratio measurements were performed with a double focusing high resolution MC-ICPMS instrument (Neptune, Thermo Finnigan, Germany). High resolution mode of the instrument was used throughout this study allowing to resolve completely all spectral interferences on Fe isotopes from argide and oxide species originated in the plasma during the measurements. Nickel was used as normalising element for instrumental mass bias correction of the Fe isotopes using the $^{62}$Ni/$^{60}$Ni ratio. The analyses were made in the following sequence; isotope standard, sample, isotope standard etc. All samples and standards were analysed in duplicate. More details on the operating conditions of the instrument can be found in reference 6 (Malinovsky et al.).

As iron was a major constituent of the solutions in this study and other elements were present at negligible concentrations relative to Fe, no chemical purification of Fe was used prior to the isotopic analysis. The sample solutions were diluted to a Fe concentration of 5±0.5 µg/ml with 0.33 M HNO₃, spiked with Ni at 5 µg/ml and subsequently the isotope ratio was measured using MC-ICPMS. Results are presented using the $\delta$-notation, defined as:

$$\delta^{56}Fe = \left[ \frac{\left(^{56}Fe/^{54}Fe\right)_{sample}}{\left(^{56}Fe/^{54}Fe\right)_{stand}} - 1 \right] \cdot 1000 \%$$

where $\left(^{56}Fe/^{54}Fe\right)_{stand}$ is the ratio for IRMM-014, corrected for instrumental mass discrimination using Ni, and used as the standard. The similar notations are also used for $^{57}Fe/^{54}Fe$ ratios. As the samples and standard were doped with Ni having $^{58}Ni$ isobar with $^{58}Fe$, attempts to measure isotope ratios including $^{58}Fe$ were abandoned.

IR Spectroscopy The IR spectrum was recorded on a Bruker IFS 113V equipped with DTGS detector. A Nujol mull on a polyethylene plate was used in the Far-IR region (200-700 cm⁻¹, No. of scans = 128, Res. = 2 cm⁻¹). In the Mid-IR range, the samples were mixed with KBr powder as diluent and the data were collected using DRIFT (Diffuse Reflectance Infrared Fourier Transform) technique (400-4000 cm⁻¹, No of scans= 128 and Res. =4cm⁻¹).

XRD and SEM The x-ray diffractogram was recorded at room temperature on a Siemens 5000 powder x-ray diffractometer in 2θ range 20-70° and φ= 0° with Cu Ka radiation. Scanning Electron Microscopy (SEM) was run on a Philips XL 30 equipped with a LaB₆ source and using SE (secondary electron) detector and accelerating voltage of 20 KV.
Synthesis

A- Coprecipitation: Magnetite synthesized by coprecipitation of Fe II and III [2, 11] in the following three alternative ways in order to check the effect of given parameter on the fractionation and oxidation state of iron in the resulting magnetite samples.

“A-a”: 10 cm³ Fe II and Fe III Chloride solutions (molar ratio 1:2) with total concentration of 1.2 M were dissolved in deoxygenated Milli-Q water and added dropwise (2 cm³/min) into 80 cm³ of 0.9 M NH₄OH solution. The reaction was carried out in a three-neck flask under argon atmosphere at room temperature and was vigorously stirred during the chemical reaction. After addition of the iron salts, the mixture was stirred for another 10 minutes and then the precipitated magnetite was separated from the supernatant by decantation under argon. The solid was washed 3 times with deoxygenated Milli-Q water and separated by decantation under argon. Finally, the suspension was centrifuged at 3500 rpm and the remaining solid was dried in a vacuum desiccator.

“A-b”: the same as “A-a” but replacing NH₄OH by NaOH as alkali reagent.

“A-c”: the same as “A-a” but at an addition rate of 1 cm³/min.

B- Oxidation of Fe(OH)₂: Fe(OH)₂ was obtained by mixing 2.8 g NaOH and 6.96 g FeCl₂, 4H₂O with 70 cm³ deoxygenated Milli-Q water in a three-neck bottom-rounded flask equipped with a condenser and mechanical agitator. The flask containing the NaOH solution was placed in a water bath preheated to 70 °C and degassed by argon bubbling through the solution. Having the FeCl₂ solid added to this solution, an Fe(OH)₂ gel was formed immediately after the mixing. The gel formed was agitated vigorously in the presence of air for 30 hours. During the reaction, samples were taken at certain intervals (see Table II) and magnetite was separated each time by treating the mixture with 1 M HNO₃ and subsequent centrifugation.

The samples synthesized via this method are throughout this report referred to as O-t, where O stands for the method (oxidation of Fe(OH)₂) and t is the time of sampling in hour.

Determination of Oxidation State of Iron in Magnetite Samples

The ratio Fe II/Fe (tot) was measured for magnetite samples by chemical analysis. The magnetite samples were dissolved in concentrated HCl under argon and Fe II was titrated with K₂Cr₂O₇ in presence of barium diphenylamine sulfonate indicator. The experimental details can be found in Vogel [12]. At the titration endpoint, all the Fe ions were reduced back to Fe II using SnCl₂ as reducing agent and titrated again with K₂Cr₂O₇ in the same way. The titrations were repeated 3 times on each magnetite sample.

All the results in Table I and II (both chemical analysis and isotopic data) are the average of at least two different batches.

Results and Discussion

The structural properties of the synthetic magnetite samples were obtained by X-ray powder diffraction (XRD), scanning electron microscopy (SEM) and FTIR spectroscopy. The XRD pattern of sample A-a and O-7 are illustrated in Figure 1 and 2, respectively. Both XRD patterns are characteristic of spinel phase crystallites where the peaks from left to right are assigned to 220, 311, 400, 422, 511 and 440 reflections [13]. The peak broadening in Figure 1 is due to the
smaller crystallite size [14] of the magnetite synthesized by coprecipitation, whilst magnetite obtained by oxidation of Fe(OH)₂ has larger crystallites (sharper peaks).

Scanning Electron Microscopy (SEM) carried out on these two samples (A-a and O-7) to observe the particle morphology and size. Figure 3 is an image of the sample A-a, and Figure 4a and 4b are images of sample O-7 in two magnifications. The SEM shows the magnetite synthesized by coprecipitation has smaller size which is in consistent with the peak broadening of XRD. The images also demonstrate almost spherical shape for sample A-a, whilst sample O-7 shows a considerable portion of particles grown as orthogonal or cornered (angular shaped).

FTIR spectroscopy which is a useful technique to differentiate between different iron oxide crystals as well as between magnetite and maghemite phase [1, 5] was carried out to characterize the synthesized magnetite. Figure 5 a-b and 6 a-b depict the Mid-Far infrared spectra of samples A-a and O-7 respectively. The broad bands around 570 and 360 cm⁻¹ correspond to vibrational modes of Fe -O bonds typical for the crystalline lattice of magnetite [1, 15]. The number of bands and band positions of other iron oxide phases such as goethite, hematite, ferrihydrate and maghemite in Mid-Far IR region differ from what is observed in the IR spectra of these samples, implying formation of magnetite as the dominant phase.

The chemical analysis was performed to check the variation of Fe II in the samples (Table I and II). The chemical analysis of magnetite also confirmed the result of IR and XRD, showing the ratio Fe II/Fe III is close to the theoretical value of ½ for magnetite.

The iron isotope data are presented together with chemical analysis in Table I for the coprecipitation method and Table II for the oxidation of ferrous hydroxide. From Table I, it is seen that there is no significant variation in the δ-value among the 3 magnetite samples and Fe II and Fe III sources. This is reasonable considering the mechanism of magnetite formation in a mixed solution of Fe III and Fe II as described by Jolivet [16] and Tronc et al [17].
emphasized on the role of ferrous ions as dehydrating and structuring agent and its essential presence for a spinel structure to be formed. The overall reaction can be written as:

$$\text{Fe}^{2+} + 2 \text{Fe}^{3+} + 8\text{OH}^- \rightarrow \text{Fe}_3\text{O}_4 + 4\text{H}_2\text{O}$$  \hspace{1cm} (2)

The reaction is fast with very high yield (negligible residual of iron ions in solution remains after precipitation) and magnetite crystals are seen instantaneously after addition of iron source. This can also be deduced from the chemical analysis of magnetite samples produced via this method, where the magnetite has almost the same ratio of Fe II/Fe III as the source.

Faivre \textit{et al.} [18], in a similar work, prepared magnetite from a mixed solution of ferrous and ferric ions and concluded that Fe II concentration has a great effect on the mechanism of magnetite formation. They showed that the iron oxide form only the spinel structure where ferrous ion concentration is above a certain threshold and also that the rate of reaction depends only on Fe$^{2+}$ activity (concentration). In lower ferrous ion concentration than that threshold, ferric-oxyhydroxide is also formed.

Table I. δ $^{56}\text{Fe}/^{54}\text{Fe}$ of magnetite and Fe (II) and Fe (III) chloride; Coprecipitation method

<table>
<thead>
<tr>
<th>Sample</th>
<th>δ $^{56}\text{Fe}/^{54}\text{Fe}$</th>
<th>δ $^{57}\text{Fe}/^{54}\text{Fe}$</th>
<th>δ $^{57}\text{Fe}/^{56}\text{Fe}$</th>
<th>FeII/Fe(tot)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>source-Fe(III)</td>
<td>0.09±0.05</td>
<td>0.17±0.08</td>
<td>0.08±0.07</td>
<td>-</td>
</tr>
<tr>
<td>source-Fe(II)</td>
<td>0.00±0.05</td>
<td>0.05±0.08</td>
<td>0.00±0.07</td>
<td>-</td>
</tr>
<tr>
<td>A-a</td>
<td>-0.05±0.07</td>
<td>-0.07±0.1</td>
<td>-0.05±0.07</td>
<td>31.0±0.1%</td>
</tr>
<tr>
<td>A-b</td>
<td>0.10±0.05</td>
<td>0.16±0.08</td>
<td>0.05±0.07</td>
<td>30.3±0.2%</td>
</tr>
<tr>
<td>A-c</td>
<td>0.07±0.05</td>
<td>0.09±0.08</td>
<td>0.02±0.07</td>
<td>30.8±0.1%</td>
</tr>
</tbody>
</table>

*Fe(tot) = FeII + FeIII in the sample as described in the chemical analysis under “methods” section.

The data is presented as: “Average ± Standard Deviation”
Table II. δ 56Fe/54Fe of magnetite and Fe(OH)₂;
Oxidation of ferrous hydroxide.

<table>
<thead>
<tr>
<th>Sample</th>
<th>δ 56Fe/54Fe</th>
<th>δ 57Fe/54Fe</th>
<th>δ 57Fe/56Fe</th>
<th>Fe II/Fe (tot)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>O-3</td>
<td>-0.09±0.07</td>
<td>-0.11±0.06</td>
<td>0.05±0.07</td>
<td>30.2±0.3%</td>
</tr>
<tr>
<td>O-6</td>
<td>-0.17±0.06</td>
<td>-0.23±0.02</td>
<td>-0.06±0.04</td>
<td>n.d.</td>
</tr>
<tr>
<td>O-7</td>
<td>-0.28±0.10</td>
<td>-0.27±0.02</td>
<td>-0.04±0.08</td>
<td>29.9±0.2%</td>
</tr>
<tr>
<td>O-13</td>
<td>-0.16±0.03</td>
<td>-0.22±0.01</td>
<td>-0.03±0.01</td>
<td>n.d.</td>
</tr>
<tr>
<td>O-18</td>
<td>0.04±0.02</td>
<td>0.12±0.03</td>
<td>0.08±0.01</td>
<td>n.d.</td>
</tr>
<tr>
<td>O-24</td>
<td>0.03±0.03</td>
<td>0.1±0.11</td>
<td>0.07±0.09</td>
<td>27.4±0.2%</td>
</tr>
<tr>
<td>O-30</td>
<td>0.08±0.04</td>
<td>0.1±0.03</td>
<td>0.11±0.04</td>
<td>24.8±0.3%</td>
</tr>
<tr>
<td>source-Fe(II)</td>
<td>-0.01±0.03</td>
<td>-0.05±0.01</td>
<td>-0.02±0.01</td>
<td>n.d.</td>
</tr>
</tbody>
</table>

*Fe(tot)=FeII + FeIII in the sample as described in the chemical analysis under “methods” section.

n.d.=not determined. The data is presented as: “Average ± Standard Deviation”

In line with previous studies and considering nucleation and crystal growth theory, here the solution all the way to magnetite is supersaturated with Fe²⁺ and Fe³⁺ through iron salt supply. The iron ions precipitate in the form of magnetite almost immediately after entering the solution. On the other hand, the reverse reaction (dissolution of magnetite) is extremely slow at low temperature [19] and high pH to cause any fractionation. The latter is due to the high surface energy of magnetite and the small or even negative interfacial surface energy [16] of the magnetite-water system at our experimental condition. Therefore, no iron isotope fractionation was expected in this synthetic method.

The data in Table II shows that in the initial stage of the reaction, the magnetite formed is enriched in the lighter isotope. On the other hand, close to the end of the reaction, the isotopic composition of the magnetite approaches the isotopic composition of the source (FeCl₂). The later could be explained partially by depletion of the lighter isotope from the non-magnetite phase. Since the higher percentage of the lighter isotope now is in the magnetite phase, thus the isotopic ratio of non-magnetite residue is enriched in the heavier isotope after a certain time and consequently the probability to precipitate the heavier isotope is increased.

The reaction begins with rapid precipitation of Fe(OH)₂ after addition of the iron (II) chloride to the sodium hydroxide solution. It is believed that the magnetite formation then starts with oxidation of Fe(OH)⁺ (the dissolved form of Fe(OH)₂) in water [20]:

\[
\text{Fe(OH)₂ (solid)} \leftrightarrow [\text{Fe(OH)}⁺]_{(aq)} + \text{OH}⁻
\]  

(3)

It can also be inferred from the particle shape of the sample O-7 (Figure 4) that the mechanism proceeds through solution rather than the solid state reaction. Subsequently, the oxidation takes place as follows:

\[
2[\text{Fe(OH)}⁺]_{(aq)} + \frac{1}{2} \text{O}_2 + \text{H}_2\text{O} \rightarrow [\text{Fe}_2(\text{OH})_3]^{3⁺}_{(aq)} + \text{OH}⁻
\]  

(4)

The intermediate entity \([\text{Fe}_2(\text{OH})_3]^{3⁺}_{(aq)}\) can be combined with another \([\text{Fe(OH)}⁺]_{(aq)}\) entity to form \(\text{Fe}_2\text{O(OH)}_4^{2⁺}_{(aq)}\), which has the same Fe II/Fe III ratio as magnetite (equation 5).

\[
[\text{Fe}_2(\text{OH})_3]^{3⁺}_{(aq)} + [\text{Fe(OH)}⁺]_{(aq)} + 2\text{OH}⁻ \rightarrow \text{Fe}_2\text{O(OH)}_4^{2⁺}_{(aq)} + \text{H}_2\text{O}
\]  

(5)
At high oxidation rate or low pH value, it will further oxidize to goethite (or other Fe III oxy-
hydroxide), however, if the concentration of dissolved oxygen in water is low and the pH is high
(such as in our experimental condition), slow oxidation takes place, and dehydroxylation occurs
prior to oxidation, so that the intermediate transfers to crystalline magnetite according to the
following reaction:

\[
\text{Fe}_3\text{O} (\text{OH})_4^{2+} (\text{aq}) + 2\text{OH}^- \rightarrow \text{Fe}_3\text{O}_4 (\text{solid}) + 3 \text{H}_2\text{O} \tag{6}
\]

The results obtained in this work suggest that equation 3 has significant effect on fractionation of
iron, since it was shown that oxidation of the Fe II solution leads to partitioning of \(^{56}\text{Fe}\) into
oxy-hydroxide [10]. The higher abundance of \(^{54}\text{Fe}\) compared to \(^{56}\text{Fe}\) in the \([\text{Fe (OH)}]\) entity is
probably because of higher lability of the lighter isotope, indicating that \(^{56}\text{Fe}\) forms stronger
bonds and therefore tends to remain in the Fe(OH)\(_2\) phase.

**Conclusion**

In this report, we showed that iron isotopic data can be used in the study of mechanism of
magnetite formation. Magnetite synthesized by the coprecipitation method did not lead to
partitioning of the iron isotopes, however, oxidation of ferrous hydroxide to magnetite at
Fe\(^{2+}/\text{OH}^- \sim 0.5\) and 70 °C produced magnetite that was enriched in the lighter iron isotope in the
beginning of the reaction.

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A Fourier infrared (FTIR) and thermogravimetric analysis (TGA) study of oleate adsorbed on magnetite nano-particle surface.

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A Fourier transform infrared (FTIR) and thermogravimetric analysis (TGA) study of oleate adsorbed on magnetite nano-particle surface

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A B S T R A C T
Magnetite nano-particles were coated with sodium oleate and the spectral behaviour of the coating layer was studied by FTIR spectroscopy after the particles had been heated in air and argon. Magnetite was synthesized by controlled co-precipitation and subsequently coated with sodium oleate. Thermal analysis in combination with mass spectroscopy was carried out to support the FTIR spectroscopic interpretations, but also to monitor the decomposition and surface reaction of oleate adsorbed on the magnetite surface. It was deduced from FTIR and TGA results that the oleate molecules are bonded to iron atoms by a bidentate mononuclear complex and form essentially a single layer with a distance between oleate molecules of ~36 Å. It was shown by IR as well as Raman spectroscopy that oleic acid, when heated in air, undergoes decomposition implying that new carbon–oxygen bonds are formed. Heating the iron oxide–oleate system in air also implies oxidation of the double bond at the C:9 position of the alkyl chain and formation of intermediate oxygen-rich molecules. An enthalpy change of ΔH = 49.86 J/g was obtained for oleate desorption/decomposition at ~350 °C under argon atmosphere and a carbonaceous graphic species resulted from this decomposition.

1. Introduction

Oleic acid has been used frequently for surface modification and coating of magnetite and maghemite because of interesting applications utilizing the magnetic property of the iron oxides and their biocompatibility [1,2]. A vital factor in the surface modification is the amount and structure of the oleic acid adsorbed on the surface. The coating is performed either by adsorption of oleate molecules on the surface of already prepared iron oxide particles or simultaneously as the magnetic crystallites are forming, e.g. in thermal decomposition of iron oleate or iron carbonyl compounds in presence of oleic acid and in air or inert atmosphere [3,4]. According to O’Brien and coworkers [5], the structure of the oleate molecule, having a double bond at the C:9 position of the C18 alkyl chain, is also important in the synthesis of stable monodisperse iron oxide nano-crystals. Even organic products formed upon heating oleate adsorbed on iron oxide may be important depending on what kind of final product is in demand. Recently, Kim et al. [6] synthesized hollow iron nano-frames and suggested that the reducing agents generated from the thermolysis of oleic acid are responsible for the formation of metallic iron nano-spheres.

It has been shown that the interaction between oleate molecules (and organic intermediates produced from oleate upon heating) and the iron oxide surface has a remarkable effect on the magnetic properties and stability of the nano-particles [4,7,8]. The oleate ligands may act as tuneable magnetic spacers between the adjacent magnetic particles. Thus, the thickness and chemical structure of the organic shell is important for the magnetic properties of the particle system.

All these efforts to understand the interaction between magnetite particles and surfactants is of course very important to the application and synthesis of these particles. However, despite the fact that some research is devoted to the interaction between oleate and iron oxides there seem to be different opinions about the interpretations of infrared spectroscopic and TGA data of adsorbed oleate, especially whether a monolayer or a bilayer of oleate is formed on the maghemite surface [9] or if the oleate molecules are chemically bonded to the surface with two different bonding strengths [8].

The purpose of this study was therefore to characterize the surface of magnetite coated oleate and to identify the structural layers and surface density of oleate at the magnetite surface. It was noticed that an understanding of the thermal events at the surface was essential. Argon or nitrogen atmosphere is commonly used for TGA analysis, whilst air is used here because it represents more practical circumstances and it is also more convenient for the determination of the amount of adsorbed oleate. For the
mentioned purpose, chemical reactions and structural changes of oleate adsorbed on magnetite were detected using FTIR and Raman spectroscopy in combination with a thermal analysis instrument equipped with DSC (differential scanning calorimetry) and QMS (quadrupole mass spectroscopy).

2. Experimental

2.1. Reagents

All the reaction reagents were of analytical grade (purity > 99%) and used without further purification. Sodium hydroxide, ammonia/C0 resolution of 4 cm

Experimental settings shown below (a and b):

- TG, DSC at a rate of 5

- DTG, DSC and MS curves were recorded on a Netzch STA 409/QMS equipped with a Quadruple mass-spectrometer. This instrument provides thermogravimetric and differential scanning calorimetric data, derivatives of each data set and mass spectroscopic analysis of evolving gas simultaneously on a single sample.

- Two runs were performed on a 20–40 mg powder sample with experimental settings shown below (a and b):
  - (a) TG, DSC, MS at a rate of 5 °C/min from room temperature up to 500 °C in an argon atmosphere (100 ml/min argon flow).
  - (b) TG, DSC at a rate of 20 °C/min and from 20 °C to 600 °C in air (100 ml/min).

- TG, DTG, DSC and MS curves were recorded on a Netzch STA 409/QMS equipped with a Quadruple mass-spectrometer. This instrument provides thermogravimetric and differential scanning calorimetric data, derivatives of each data set and mass spectroscopic analysis of evolving gas simultaneously on a single sample.

- The specific surface area of the magnetite sample was determined by the BET (Brunauer, Emmett and Teller) nitrogen adsorption/desorption method on a dried powder sample (before coating) with a surface area analyzer from Micrometrics ASAP 2000. The surface area was 97.7 m²/g.

- Magnetite synthesis

The synthesis of magnetite was carried out by controlled coprecipitation of Fe (II) and Fe (III) when added to an aqueous alkaline solution [10]. Fe (II) and Fe (III) chloride solutions were prepared by dissolving the salts in deoxygenated Milli-Q water. 5 cm³ of the mixture (molar ratio 1.2: 1.2 M total iron chloride concentration) was added drop-wise (0.5 cm³/min) to a reaction vessel containing 40 cm³ of 0.9 M NaOH solution. The reaction mixture was kept under argon atmosphere at room temperature and was vigorously stirred. After addition of the iron salts, the mixture was stirred for another 20 min and then the precipitated magnetite was separated from the supernatant by decantation under argon. The solid was washed 4 times with deoxygenated Milli-Q water and separated by decantation.

The as synthesized magnetite particles were examined by XRD (X-ray powder diffraction), mid and far IR spectroscopy, and TEM (transmission electron microscopy) showing pure and well-crystallized magnetite with spherical shape and an average size of 9.5 ± 2.4 nm.

Coating was performed by adding 4 portions of sodium oleate, each portion containing 0.1 g at 80 °C. The time interval between each addition was 15 min and after the last oleate addition the adsorption reaction was allowed to proceed for another 30 min. Subsequently, the suspension was cooled to ambient temperature and 2 M HCl was added drop-wise until a black solid settled over the Teflon coated magnet bar. The excess oleate was decanted and the precipitate rinsed several times with deoxygenated Milli-Q water. A warm mixture of acetone and ethanol was used to remove physically adsorbed oleate. Finally, the residue was dried in a vacuum desiccator.

3. Results and discussion

3.1. Heating of oleic acid in air

To get information about the effect of the magnetite surface on the decomposition of oleate upon heating, the effect of temperature on oleic acid itself was used as reference. Accordingly, oleic acid was stored in an oven at 110 °C under ambient atmosphere for 1 week. The heated oleic acid and oleic acid before heating were both analysed by IR and Raman spectroscopy to identify structural changes as the result of heating (Figs. 1 and 2).

The broad feature from 3500 to 2500 is characteristic of the O–H stretching band of the acid which is known to be in dimeric form due to hydrogen bonding. The carboxyl band appears at ~1711 cm⁻¹. The CH₂ and CH₃ symmetric and asymmetric stretching vibrations are detected from 2800 to 2950 cm⁻¹ and a weak vinyl C=C–H stretch appears at 3006 cm⁻¹ (Fig. 1, dashed dotted line). Methylene groups exhibit their symmetric bending mode at about 1465 cm⁻¹. However, this band is split into two bands, the second one 1458 cm⁻¹, which is usually the case when alkyl chains are closely packed together. The spectrum of heated oleic acid (Fig. 1, continuous line) is clearly different from the spectrum of the unheated acid. The former one shows new bands at 1736 cm⁻¹ and 1171 cm⁻¹ and the absorbance of the carboxylic group is strongly reduced. In addition, the weak band due to the C–H stretch appears at 3006 cm⁻¹ and used without further purification. Sodium hydroxide, ammonia/C0 resolution of 4 cm

![Fig. 1. IR transmission spectra of heated and unheated oleic acid.](image)
H stretch at 3006 cm\(^{-1}\) has almost disappeared. The latter result strongly indicates that the C:9/C:10 positions of the molecule are attacked by oxygen. The resulting loss of unsaturation may imply that a mixture of various products is formed \([5,11]\). However, it seems that the appearance of the new band at 1736 cm\(^{-1}\) may due to the formation of ester carbonyls since this type of carbonyl function is often found around 1740 cm\(^{-1}\). This suggestion was supported by the band appearing at 1171 cm\(^{-1}\), which may be assigned to the C–O stretch of the ester moiety. Furthermore, the OH band shifts to higher frequency upon heating the sample, which was expected.

Although the loss of unsaturation is evident from the IR spectrum (Fig. 1), it is even more obvious in the Raman spectrum, where C=C bonds have a strong absorption due to its large change in polarizability during vibration (Fig. 2). The intensity of C–C at 1655 cm\(^{-1}\) drastically decreases after heating. This was accompanied by reduced intensity at 3006 cm\(^{-1}\) (vinyl C–H stretch).

When oleic acid was subjected to higher temperature (e.g. 220 °C) in air, the carbonyl absorption band was broadened and a weak shoulder appeared at ~1850 cm\(^{-1}\) in addition to a distinct shoulder at 1780 cm\(^{-1}\) indicating formation of carbonyl functions belonging to other types of chemical substances e.g. anhydrides \([12]\) (Fig. 3). This might be one of the species that gave rise to such uniform and monodisperse iron oxide nano-crystals described by O’Brien et al. \([5]\). Furthermore, the hydrogen bonding region of the spectrum shows an increased intensity relative to the methylene stretching vibrations. This should be due to the formation of new species eager to establish hydrogen bonds.

3.2. Oleate on magnetite particles heated in air and argon

The IR spectrum of oleate adsorbed on magnetite nano-particles (before heating) is shown in Fig. 4. The \(\text{CH}_2\) and \(\text{CH}_3\) stretching bands in the spectral region 2800–3000 cm\(^{-1}\) and the vinylic –C–H at 3006 cm\(^{-1}\) are the most prominent bands above 2000 cm\(^{-1}\). No free oleic acid physically adsorbed on the magnetite surface could be detected. The two bands at 1529 cm\(^{-1}\) and 1430 cm\(^{-1}\) are assigned to asymmetric and symmetric stretching of the carboxylate group, respectively, although the latter band is strongly overlapped by the symmetric bending of the methylene entities on the high frequency side of the band. This overlapping might shift the \(\nu(COO^-)\) band to slightly higher frequency. Rocchiccioli-Delcliff et al. \([13]\) proposed that the carboxylate adsorbs mainly via a bidentate mononuclear complex to a single Fe ion on the surface, whilst a small amount of oleate adsorbed was in the bridging bidentate configuration. Considering the small frequency difference between the symmetric and anti-symmetric carboxylate modes observed here (~100 cm\(^{-1}\)), a bidentate mononuclear complex seems plausible. A difference less than the one obtained for non-adsorbed oleate, viz. ~135 cm\(^{-1}\) supports this conclusion \([14]\). Zhang et al. arrived at a similar conclusion \([8]\), although the assignments of infrared bands in that paper is doubtful and the scheme showing the surface complex concluded is wrong.

A sample from the same batch was used in the following experiments described under Sections 3.2.1 and 3.2.2. The surface excess of adsorbed oleate and the surface area occupied by an oleate molecule at the surface of magnetite can be calculated using...
the total amount of oleate per surface area (11% by weight oleate; Fig. 5) and the specific surface area of magnetite (97.7 m²/g), to be
4.6 \times 10^{-6} \text{ mol/m}^2 \text{ and } 36 \text{ Å}^2, \text{ respectively. This value is in good agreement with the value of 38 Å}^2 \text{ reported by Wooding et al. [15] and the molecular area of oleate in the liquid crystal state (35 Å}^2 \text{)} [16].

3.2.1. Samples heated in air
A fraction of the batch mentioned above was stored at 150 °C for 3 h. The DTG and DSC curves of this sample are shown in Fig. 5. Two DTG peaks representing weight loss appeared at ~240 °C and at ~315 °C and were associated with two corresponding exothermic peaks on the DSC curve. There is also a third exothermic peak at ~520 °C on the DSC curve at which temperature phase transition occurred. The phase transition temperature detected here is in agreement with the phase transition for nano-crystalline magneticite to hematite also observed by Xisheng et al. [17]. The energy of this transition was calculated to be ~95.88 J/g, which is the energy of recrystallization and rearrangement of the ions in the crystal.

To evaluate thermo-chemical changes of the sample after each of the first two DSC peak temperatures, FTIR spectroscopy was utilized. The experimental results are shown in Figs. 6 and 7 showing spectra recorded at 280 °C and 450 °C. At 280 °C, the carboxylate bands (1430 cm\(^{-1}\) and 1530 cm\(^{-1}\)) are still present and a new broad feature appeared from 1690 cm\(^{-1}\) to 1860 cm\(^{-1}\). The \text{-C-H} vinylic stretching vibration is missing at 3006 cm\(^{-1}\). Comparing this spectrum with the spectrum of heated oleic acid (Fig. 3), the new carbonyl bands and the \text{C-C-O} stretching vibration (the band at 1170 cm\(^{-1}\)) could be attributed to the oxidation of oleate at the double bond. It was also evident from the

Fig. 5. DTG and DSC diagram of oleate on magnetite heated at a rate of 20 °C/min in 100 ml/min air flow.

Fig. 6. DRIFT spectrum of oleate on the magnetite heated to 280 °C in air.

Fig. 7. DRIFT spectrum of oleate on magnetite heated to 450 °C in air.

Fig. 8. TG, QMS pattern of magnetite-oleate heated to 500 °C at a rate of 5 °C/min under 100 ml/min argon flow.

TG curve that no weight loss occurred until 240 °C. Weight loss at this temperature was associated with a large exothermic energy (~818.8 J/g). This was somewhat different from the decomposition pattern of the sample under argon considering both the energy release (exothermic reaction) and amount of weight loss (Section 3.2.2). Thus, it seems that the weight loss at this temperature was related to the double bond cleavage and formation of intermediate products rich in oxygen.

At 450 °C, IR spectra show a very strong band with several shoulders in the range 3700-2500 cm\(^{-1}\) due to the stretching of hydrogen bonded O-H groups as well as methylene stretching vibrations. However, the OH stretching clearly dominates the spectrum in this region with only weak contributions from CH\(_2\) entities. All other bands from the absorption at ~1630 cm\(^{-1}\) and down to the fingerprint region are hazardous to assign because of broad features with extensively overlapped band structures. The new absorbances at 2200 cm\(^{-1}\), 2330 cm\(^{-1}\) and 2259 cm\(^{-1}\) are assigned to complexes of CO\(_x\) bound to Fe ions at the surface [18].

3.2.2. Samples heated in argon atmosphere
To another fraction of the batch sample, online mass spectroscopy was applied together with thermogravimetric analysis of the sample under argon atmosphere. The results of mass spectroscopy and the TG curve are both shown in Fig. 8. The TG measurement exhibits a continuous weight loss (0.6%) as soon as the temperature increased to above 100 °C followed by a small weight drop (2.5%) from 140 °C to 280 °C with the peak value at 200 °C and a larger one (7.5%) from 280 °C to 450 °C with the peak at 331 °C. Sahoo et al. [9] similarly found two steps of weight loss, one small drop at 240 °C and a larger one at 378 °C, and attributed the first peak to the adsorbed oleate in a second layer (physically adsorbed oleate). Zhang et al. [8] attributed the two weight losses to chemically bonded oleate with two different binding energies.
However, the mass spectroscopy investigation of our sample showed that the first drop in the TG curve corresponds essentially to water as hydrogen bonded water or surface hydroxyl groups. The second drop in the TG curve is associated with release of CO$_2$ and dehydrogenation (CO$_2$ and H$_2$ curve in Fig. 8), corresponding to desorption/decomposition of oleate at the surface. Additionally, DSC analysis of the sample showed an endothermic reaction at 350 °C associated with the second weight loss. The endothermic heat of reaction was 49.86 J/g.

The IR spectrum of the sample at 550 °C (Fig. 9) exhibits a very strong broad feature in the hydrogen bonding region in addition to the bands below 1600 cm$^{-1}$. There are also several broad and intense bands below 1600 cm$^{-1}$ discussed in Section 3.2.1. Weak CH stretching bands still appear. It was shown by Raman and FTIR spectra that decomposition/oxidation of oleic acid heated at 110 °C for 1 week under ambient atmosphere, occurred at the C–H position and the reaction proceeded with an increased amount of oxygen containing species as the temperature raised to 220 °C. Thermogravimetric analysis showed a weight loss of adsorbed oleate on the surface under ambient atmosphere, also indicating double bond cleavage that yielded products enriched in oxygen. It was also observed that the transformation to hemimicropore occurs at 520 °C.

Mass spectroscopy together with DSC and TG indicated that the first weight loss of the sample heated under argon was predominantly water which exists as hydrogen bonded water or hydroxyl functions at the surface. A second weight loss included desorption/decomposition of oleate on the magnetite surface and was associated with CO$_2$ and dehydrogenation. The enthalpy of desorption/decomposition was calculated to be 49.86 J/g. Furthermore, according to the infrared spectra, it seems that the decomposition of oleate on magnetite under argon atmosphere initially involves the formation of species capable to exhibit hydrogen and carbon bonding structures.

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**References**

An ATR-FTIR study of sulphate sorption on magnetite; rate of adsorption, surface speciation, and effect of calcium ions.

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An ATR-FTIR study of sulphate sorption on magnetite; rate of adsorption, surface speciation, and effect of calcium ions

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**A B S T R A C T**

The adsorption of sulphate on magnetite was studied in-situ using ATR-FTIR spectroscopy. Synthetic magnetite particles were deposited on a ZnSe internal reflection element and the spectra of sulphate adsorbed at pH 4–8.5 were recorded. Two different ionic strengths were used viz. 0.01 M and 0.1 M NaCl. The spectra of adsorbed sulphate on magnetite coated ZnSe were compared with the spectra of sulphate solutions at the same pH values and in contact with uncoated ZnSe. The spectrum of adsorbed sulphate at pH 4 showed three maxima at 979, 1044, and 1115 cm⁻¹ indicating a monodentate adsorption in which the Td symmetry of SO₂⁻ is lowered to C₃v. At pH 6.5, sulphate adsorbed as an outer-sphere complex with two weak bands appearing at 1102 and 980 cm⁻¹. Moreover, spectra of the adsorbed sulphate at pH 4 were recorded as a function of time and sulphate concentration. The equilibrium absorbance at different concentrations fitted a Langmuir type adsorption isotherm. The Langmuir affinity constant K at pH 4 was determined from the slope and intercept of the Langmuir plot to be $K = 1.2344 \times 10^6$ M⁻¹ and the Gibbs free energy of adsorption $\Delta G_{ads}$ was estimated from this value to be $–33.3$ kJ/mol. Kinetic analysis indicated that adsorption at pH 4 is fast, whilst the desorption kinetic at the same pH is very slow. In addition, the effect of Ca ions on sulphate adsorption was also studied. It was shown that Ca ions increased the sulphate adsorption on magnetite at pH 8.5.

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1. Introduction

Surface and interfacial chemistry of minerals in water is a base for many research efforts because of its importance in a variety of applications such as water management, soil chemistry, and mineral processing. There have been a variety of methods developed to study surfaces of particulate solids in water as dispersion medium. One of the methods that have become increasingly popular is infrared spectroscopy, which gives information on chemical bonds and structure of molecules. However, application of infrared spectroscopy to aqueous systems requires a modified technique due to the strong absorption of water, which can mask the spectrum of interest if not properly subtracted. If subtraction of water is needed, it is usually suitable only at an absorbance less than one. Thus, the in-situ technique can be used to monitor the adsorption while the mineral is in contact with the solution. This advantage not only allows one to investigate the nature of bonding and speciation, but also the kinetic of adsorption can be studied in-situ i.e. in real time.

The ATR spectroscopy technique has been applied to study adsorption of sulphate, carbonate and phosphate on the surface of iron oxides [1–5]. The majority of these studies have been focused on the surface speciation of adsorbate on hematite, goethite and ferrous hydroxide, at different pH and ionic medium. However, there are a number of studies concerned with the co-adsorption and competitive adsorption of cations with oxyanions at the surface of iron and aluminium oxides/hydroxides, including studies using ATR FTIR of particle films [6–8].

Sulphate is widely found in soils and water and it has profound effect in environmental systems and technical applications, e.g., it can alter the surface chemistry and crystal growth of iron oxides [9], poison catalysts, and affect the surface charge and reactivity of minerals such as sorption of anions and cations.

In mineral processing ions in the process water may affect the pelletization of the mineral slurry and possibly imply weaker green pellets. In this work, we studied adsorption of sulphate on magnetite, in order to shed light on the thermodynamic and kinetic behaviour of sulphate adsorption on magnetite. There is no in-situ ATR measurement of sulphate adsorption study on magnetite in the literature to our knowledge. Magnetite is the major iron oxide...
phase in ores found in the northern part of Sweden. It is separated from gangue minerals by magnetic separation and from apatite by inverse flotation using a collector. Other than being used in steel making industries which are using magnetite pellets, owing to the magnetic property, small size magnetite (magnetite nanoparticle) has been used as sorbent and carrier agent for different purposes such as drug delivery [10] and water cleaning [11]. The pH values, 4-9 were selected to detect the surface speciation of adsorbed sulphate on magnetite. This range was chosen to avoid either etching of ZnSe IRE or formation of HSO$_4^-$ from SO$_2^-\text{d}$ at very low pH which may complicate the interpretation of the results. The isotherm and kinetic studies were performed at pH 4 in order to get strong IR absorption bands. In addition, the effect of Ca ions on sulphate adsorption was also investigated. The latter study was important because in a real system the re-circulated process water may contain a significant amount of Ca ions, e.g. in the inverse flotation of apatite from magnetite.

2. Methods and materials

2.1. Reagents

Sodium hydroxide, ammonium hydroxide (25%), FeCl$_2$·4H$_2$O and FeCl$_3$·6H$_2$O (> 99%) were purchased from Merck, Darmstadt, Germany). Anhydrous sodium sulphate pro analysi (> 99%) and NaCl pro analysis (> 59.5%) were also purchased from Merck, Milli-Q water (Millipore Corp.) was used in all steps of synthesis, washing, and preparation of solutions.

2.2. Synthesis of magnetite particles

The synthesis of magnetite was carried out by coprecipitation of Fe (II) and Fe (III) [12]. A volume of 5 cm$^3$ solution of Fe (II) and Fe (III) chloride (molar ratio 1:2) in deoxygenated Milli-Q water at a total concentration of 1.2 M was added drop-wise into a three-neck flask reaction vessel containing 40 cm$^3$ of 0.9 M NH$_4$OH solution. The solution was kept under argon atmosphere at room temperature and was vigorously stirred. After addition of the iron salts, stirring the mixture continued for another 20 min and then the precipitated magnetite was separated from the supernatant by decantation under argon. The solid was washed 4 times with de-oxygenated Milli-Q water and separated by decantation and was finally centrifuged.

Powder X-ray diffraction (XRD), chemical analysis and Far-Mid infra-red spectroscopy confirmed the magnetite structure and transmission electron microscopy (TEM) images showed spherical particle with a mean diameter of ~10 nm. Great care was taken to avoid oxidation of magnetite by deoxygenation and argon bubbling in all stages of the synthesis, film deposition and adsorption measurement, however, partial surface oxidation could occur. Nevertheless, the surface oxidation is a matter of fact for all other magnetite sources.

2.3. Particle deposition

Two methods for deposition of particles on ATR crystals were applied in this work. The first method is similar to the method previously described by other authors [1,2] and corresponds to evenly spreading a few drops of an as-synthesized magnetite suspension over the ATR crystal and drying it in a vacuum desiccator. At the end, the ZnSe IRE was thoroughly rinsed with ethanol and Milli-Q water. Suspension concentration and ethanol/water ratio are parameters that can be changed to optimize the thickness of the deposited layer. A 1.5 mg/mL suspension of magnetite with a water/ethanol volume ratio of 4 was used to get ~0.5 mg of magnetite particles spread over the ZnSe crystal (50 mm × 20 mm × 2 mm).

The second method was the dip-coating technique in which a substrate (ATR crystal) is immersed in a colloidal suspension of particles and withdrawn with a well-defined withdrawal velocity. Again, suspension specifications i.e. concentration, viscosity, and surface tension are the determining factors for the thickness of the layer in addition to withdrawal speed. The principle of this technique is based on drying a wet layer formed upon withdrawing the substrate and gelation of the layer by solvent evaporation.

The dip coating was performed using a Nima dip coater (Nima Technology Ltd., the Science Park, Coventry, England) with two beakers containing a 5 mg/mL suspension of magnetite at pH 4 in beaker 1 and a 50% methanol/water mixture in beaker 2 to rinse away the particles not adhering to the substrate. The dipping speed (immersing and raising) was set at 60 mm/mm and the total number of cycles at 20. Each cycle comprised the following sequence; immersing the substrate (ZnSe crystal) in beaker 1, waiting in the bottom for 30 s, raising it out of the beaker, waiting 120 s at the top, and then this procedure was repeated with beaker 2. Finally it was repeatedly rinsed with ethanol and Milli-Q water.

Both methods produced smooth layers of particles which were stable against circulation of the sample solution at all experimental conditions applied in this work.

2.4. Adsorption measurements

The IR spectra were recorded on a Bruker IFS 113v equipped with an MCT detector cooled by liquid nitrogen. All spectra were collected in the range 800–4000 cm$^{-1}$ at a resolution of 4 cm$^{-1}$. The number of co-added scans to produce each spectrum for the isotherm study was 1362 and for kinetic studies 136.

A sketch of the experimental setup is shown in Fig. 1. A single sided rectangularly shaped flow through cell with a volume of ca. 5 ml (40 mm length) and made of stainless steel was sealed to a ZnSe prism with a 45 degree bevel (Crystanal Limited, UK) via a Viton o-ring and mounted on the ATR accessory (Specac, England). This arrangement provides 10 reflections inside the cell where the crystal is in contact with the solution.

The cell was connected to a 250 ml reservoir containing 150 ml solution via Viton tubings and the solutions were circulated by a Watson Mallow, Bredel pump (Spiram-Sarco engineering group, England) at a rate of 5 ml/min (10 ml/min for some of the kinetic experiments). All experiments were conducted at room temperature and under argon flow. The pH value was probed during the experiment using a glass electrode and adjusted using 0.1 M NaOH or HCl solutions.

Data acquisition as well as data processing and analysis were carried out by OPUS software.
2.5. Adsorption isotherm

The electrolyte solution (0.01 M NaCl at pH 4) was continuously circulated through the cell with a flow rate of 5 ml/min for 30 min before the single beam background spectrum was recorded for 15 min (4086 scans). The experiments were carried out under argon atmosphere and the pH was controlled during the experiment as described above. Afterwards, a known volume of stock sulphate solution was added to the electrolyte solution to acquire the desired spectra. The same procedure was repeated for all concentrations between 5 μM and 5 mM to obtain the adsorption isotherm.

2.6. Adsorption kinetics

In kinetic measurements, first a background spectrum of the magnetite layer in ionic medium was collected in the same way as described for the isotherm measurements. The cell was then emptied and a sulphate solution at a given concentration and ionic medium (0.01 M NaCl at pH 4) was pumped through the cell. The time zero was set to the time when the solution entered the cell. The sample spectra were recorded at certain time intervals with the intervals measured from the middle of successive scanning times. All the kinetic experiments were carried out using a new magnetite film.

The possible effect of the flow rate on adsorption rate was examined by using two flow rates viz. 5 and 10 ml/min.

Desorption of sulphate was evaluated by rinsing the adsorbed sulphate with Milli-Q water at the same pH and flow rate as the sample solution, but the effluent was collected as waste instead of being circulated back into the system.

2.7. Effect of Ca ions on sulphate adsorption

To evaluate the effect of Ca²⁺ and Na⁺ on sulphate adsorption, CaCl₂ or NaCl was added to a solution of sulphate ions already adsorbed to equilibrium on the magnetite surface. The general experimental procedure is similar as the adsorption measurements. First the magnetite film was put in contact with a solution of sodium sulphate with known pH and ionic strength, adjusted with HCl/NaOH and NaCl, respectively. Subsequently, the system was allowed to reach adsorption equilibrium. Then, NaCl or CaCl₂ was added to this system to detect possible changes in the IR absorption band of sulphate around 1100 cm⁻¹.

3. Results and discussion

3.1. Infrared absorption of sulphate

The IR spectra of sulphate adsorbed from aqueous solutions of different sulphate concentrations at pH 4 are shown in Figs. 2 and 3. In Fig. 2 an uncoated ZnSe crystal was used, whereas Fig. 3 shows spectra upon adsorption onto a magnetite layer deposited on the IRE. In both cases the ionic medium was 0.01 M NaCl. As is clear from a comparison of these two figures, the peak positions, the line shapes, and the intensities are completely different.

Sulphate as adsorbed and the free ions exhibit different peak positions. This is easily explained by molecular symmetry. The symmetry of dissolved sulphate ions (SO₂⁻⁴) is tetrahedral (T_d) with a triply degenerated ν₃ band at ~1100 cm⁻¹ (Fig. 2), which is due to the asymmetric stretching vibration.

When sulphate ions are adsorbed on magnetite particles, three maxima at 1115, 1044 and 979 cm⁻¹ and a shoulder at 1070 cm⁻¹ are observed (Fig. 3). The peak positions shown are based on second derivative analysis [13] resulting in 4 sub-bands (see supporting materials). The curve fitting resulted in a RMS error of 0.00056, which is a very low value. At pH 6.5 (Fig. 4) sulphate is only bound as outer-sphere complexes and the recorded infrared intensity is only about 10% of the corresponding intensity of adsorbed sulphate at pH 4, although the number of hydrogen bonding sites should be more frequent close to the IEP (pH 6.5). It might be that Cl⁻ ions from the ionic medium partly prohibit outer-sphere sulphate complexes to form since chloride is a hydrogen bonding acceptor itself. These findings also indicate that sulphate ions prefer positive sites on the magnetite surface, which seems reasonable. It should be no-
ted here that the symmetry of a hydrogen bonded outer-sphere complex should be similar to the symmetry of the inner-sphere complex, as pointed out by Majzlan and Myneni [14]. However, the outer-sphere complexes at pH 6.5 do not show any splitting of the triply degenerate asymmetric stretching band of sulphate and making the symmetric band infrared active (Fig. 4). This lack of splitting might be due to the hydrogen bond being too weak.

The band at 979 cm⁻¹ is assigned to the symmetric stretching band (ν3) which becomes IR active when the symmetry is lowered. The other two peaks at 1115 and 1044 cm⁻¹ are assigned to asymmetric stretching (ν1) vibrations.

Since the symmetry is lowered upon coordination of sulphate ions to magnetite, the ν3 band is split into 2 peaks. The resulting symmetry is C2v and corresponds to monodentately coordinated sulphate species. This was further confirmed by adsorption of 100 μM sulphate solution at pH 4 using 0.1 M NaCl as ionic medium. At both ionic strengths, viz. 0.01 M and 0.1 M NaCl, the peak frequencies and line shapes were identical. As evident from the second derivative function, no negative antinode is visible around 1170 cm⁻¹, implying that the presence of a bidentate coordination of sulphate is excluded.

It is also clear that the spectra in Figs. 2 and 3 exhibit differences concerning in the absorbance of the sulphate species. The absorbance of adsorbed sulphate on the magnetite coated IRE is several magnitudes larger than the absorbance of sulphate in bulk solution. This is clear evidence that the absorbance observed in Fig. 3 is mainly due to the sulphate adsorbed on magnetite. At very low sulphate concentrations (e.g., <100 μM), the sulphate is not detectable on a bare (uncoated) IRE.

In addition, there is another difference in the recorded spectral intensity of sulphate adsorbed on the magnetite coated IRE and sulphate detected using an uncoated IRE, namely the absorbance increment observed by increasing the sulphate concentration. Increasing sulphate concentration (up to 10 mM was tested here) causes a linear enhancement in absorbance for the uncoated crystal, whilst a magnetite coated crystal exhibited a dramatic initial increase in absorbance. Eventually the absorbance approaches an equilibrium plateau value in the latter case. The adsorption of sulphate on magnetite evidently shows a saturation behaviour, which will be further explored in Section 3.2 below.

Adsorption of sulphate on magnetite at pH 6.5 (0.01 M NaCl as ionic medium) is shown in Fig. 4. From this spectrum it was inferred that the adsorption at this pH is mostly due to the formation of outer-sphere complexes since the spectrum was very much like a spectrum of sulphate in the bulk and the intensity was much less as compared with the adsorption at pH 4. This seems reasonable with respect to the fact that the point of zero charge (PZC) of magnetite is slightly above 6 so the surface charge is close to neutral. Therefore, replacing hydroxyl groups by SO$_2^-$ is not as spontaneous as expected.

Similar results were obtained by Hug [1] for sulphate adsorption on hematite implying 3 bands at 976, 1060, and 1128 cm⁻¹. He concluded that sulphate adsorb on hematite as a monodentate inner-sphere complex at pH 3–5 and a contribution of an outer-sphere coordination at pH 6 and 7. However, Lefevre et al. [3] observed a small shoulder at 1165 cm⁻¹ in addition to the three bands at 975, 1065 and 1115 cm⁻¹ in their study of sulphate adsorbed on hematite at pH 4 and interpreted this result as being due to a mixture of monodentate (dominating) and bidentate complexes. As discussed earlier in this section, we did not observe a band at ~1165 cm⁻¹ for the sulphate/magnetite system. This might be due to the distance between adjacent active surface sites of the magnetite being larger than the distance between O–O atoms in SO$_2^-$ (2.45 Å).

3.2. Adsorption isotherm

Probably the most often used adsorption model is the Langmuir isotherm which has also been used to describe anion adsorption on iron oxides [15, p. 255]. A modified mathematical expression of the Langmuir isotherm can be written as:

$$C_i = \frac{1}{K \cdot A_m} + \frac{1}{A_m} C_v,$$

where $C_i$ is the initial concentration of adsorbate in solution, $K$ is the affinity constant, $A$ is the amount of adsorbate that is adsorbed in equilibrium with concentration $C_i$, and $A_m$ is the amount that is necessary to cover the surface by a monolayer of adsorbate. In an experiment using ATR, the amount of sulphate adsorbed at a given concentration, $C_i$, is assumed to be proportional to the integral absorbance between 900 cm⁻¹ and 1250 cm⁻¹. Since the surface excess, $\Gamma$, is too small compared to the concentration in solution, we can assume that $C_i = C_{eq}$ i.e. the adsorbed amount does not affect the bulk concentration. Thus, a plot of $C/A$ versus $C$ (Fig. 5) should give a straight line with $1/A_m$ as the slope of the line and $1/(k \cdot A_m)$ representing the intercept. Knowing $A_m$ from the slope, the Langmuir affinity constant ($K$) of the adsorption can be calculated.

From sulphate adsorption onto magnetite at pH 4, the band area between 900 cm⁻¹ and 1250 cm⁻¹ was integrated after baseline corrections. The integrated absorbance was corrected for bulk contribution (notice that the bulk contribution to the absorbance is ≤5% in the concentration range applied in this work) using the data obtained from sulphate absorbance on uncoated ZnSe. A plot of $C/A$ versus $C$ is shown in Fig. 5.

From this plot, the Langmuir affinity constant can be estimated to be $1.2344 \times 10^5$ M⁻¹. Using the affinity constant, the free energy of adsorption at $T = 298$ K can be calculated according to:

$$\Delta G_{ads}^0 = -RT \ln(K \times 55.5) = -33.3 \text{ kJ/mol}.$$
were measured. The sulphate absorption between 900 cm⁻¹ and 1250 cm⁻¹ was integrated and plotted versus time. The adsorption kinetics showed similar results at both 5 and 10 ml/min flow rate, implying that the mass transport from bulk solution to the porous layers is very complicated and needs further studies.

As evident from the curves in Fig. 6, the adsorption is fast during the first five minutes and increasingly so at higher concentrations. However, the spectral pattern did not vary with time and concentration in the range of concentrations studied (Fig. 7). As shown in Fig. 8, the experimental data indicate a pseudo first order reaction as expected. However, the rate constant increased with NaCl concentration. A difference in concentration gradient within the magnetite layer would imply a larger rate constant at higher concentration. A difference in concentration gradient within the magnetite layer to eventually be adsorbed, this time being shorter at higher concentration since the electric field increases towards the crystal surface. As pointed out by others [3], the kinetics of adsorption in porous layers is very complicated and needs further studies.

The desorption kinetics is very slow and when the adsorbed sulphate was rinsed with Milli-Q water at the same pH and flow rate, only a negligible decrease in absorption intensity was observed during 30 min of desorption (see supporting materials).

The rate of sulphate ion adsorption onto magnetite seems to be governed by a number of factors of which the bulk concentration of sulphate is the most important one at least at a fixed temperature. It was observed that NaCl concentration had an effect on the adsorption kinetics. The higher the NaCl concentration, the slower was the initial adsorption rate. This is probably due to a screening of the predominantly positively charged magnetite surface at pH 4 from the negatively charged sulphate. However, the NaCl concentration had no effect on the position and number of the infrared absorption bands.

Similar to our result (Fig. 7), Lefevre et al. [3] observed that the band shape of sulphate adsorbed on hematite at pH 4 does not evolve as a function of time. We also observed that for all concentrations of sulphate used in the kinetic measurements at pH 4, the absorptions showed the same line shape. This indicates that a single mechanism is responsible for adsorption of sulphate on magnetite at pH 4.

Sun et al. [20] studied the surface characteristics of magnetite (synthesized in the same way as in this work) in aqueous suspension using potentiometric titration and zeta-potential measurements and concluded that the surface of magnetite contains surface hydroxyl groups, which are protonated at pH below the PZC of magnetite and deprotonated above this pH:

\[
\begin{align*}
&\text{Fe(II,III)OH}^+ \equiv \text{Fe(II,III)OH} + \text{H}^+ & \text{pH} < \text{PZC}, \\
&\text{Fe(II,III)OH} \equiv \text{Fe(II,III)OH}^+ + \text{H}_2\text{O}^- & \text{pH} > \text{PZC}.
\end{align*}
\]

The protonated hydroxyl functions at the surface could readily be exchanged by a sulphate ligand. The adsorption studied here may take place at the sites that are more prone to sulphate adsorption viz. already protonated sites.

It is therefore suggested that the Fe(II,III)OH⁺ sites predominate in the initial adsorption. In the course of time and adsorption of sulphate, the charge and available sites on the surface decreases eventually resulting in a slower reaction rate.

### 3.4. Effect of calcium ions on sulphate adsorption on magnetite

The effect of Ca ions on sulphate adsorption on magnetite was investigated at acidic and alkaline pH (pH 4 and 8.5) and in the concentration range 3 mM < Ca²⁺ < 6 mM. No increase in sulphate adsorption was observed at pH 4 when Ca²⁺ ions were
also to coadsorption of Ca\(^{2+}\) to the increase in positive surface charge caused by Ca ions, but between calcium and sulphate adsorption in soils containing Fe and Al hydrous oxides [21]. The effect of Ca ions was attributed mostly to the increase in positive surface charge caused by Ca ions, but also to coadsorption of Ca\(^{2+}\) and SO\(_4^{2-}\) as CaSO\(_4^{2-}\) ion pairs at higher concentration of Ca\(^{2+}\) and SO\(_4^{2-}\). Rahnemaie et al. [22] suggested a combination of outer-sphere and inner-sphere monodentate or bidentate surface complexation of Ca ions on the goethite surface based on a CD (charge distribution) model. They concluded that there was an increase of outer-sphere Ca adsorption with decreasing pH and Ca concentration.

The spectroscopic study carried out here, showed similar band shape for the sulphate adsorption both when Ca ions were added to the reaction solution and when only Na ions constituted the ionic medium, indicating an outer-sphere sulphate adsorption. It also showed that Ca increased the adsorption of sulphate at alkaline pH. In the concentration range of Ca\(^{2+}\) and SO\(_4^{2-}\) used in these experiments, the increase in adsorption should mostly be attributed to the increase in positive charge at the surface due to specific adsorption of Ca\(^{2+}\) at high pH.

4. Conclusions

Adsorption of sulphate on magnetite was studied using in-situ ATR-FTIR spectroscopy. Three absorbance maxima at 1115, 1044 and 979 cm\(^{-1}\) were observed for sulphate adsorbed at pH 4 based on the second derivative analysis. This indicated a monodentate adsorption at pH 4 in which the Td symmetry of SO\(_4^{2-}\) was lowered to C\(_{3v}\). At pH 6.5, however, sulphate adsorbed on magnetite via outer-sphere complexation. It was also shown that adsorption of sulphate onto the magnetite surface at pH 4 followed the Langmuir adsorption isotherm and the Langmuir affinity constant and the free energy of adsorption at this pH and 298 K were estimated from the Langmuir plot to be 1.2344 ± 10 M\(^{-1}\) and 33.3 kJ/mol, respectively. The data indicated that sulphate interaction with magnetite could be classified as intermediate to weak and the tendency of sulphate in solution to adsorb on magnetite decreased with increasing pH.

Regarding the adsorption kinetics, the experimental data indicated a pseudo first order reaction with a rate constant increasing with concentration. This implies that the kinetics of adsorption in porous layers is very complicated and needs further studies. It was also shown that the Ca ions slightly increased the adsorption of sulphate at pH 8.5 probably caused by an increase of the surface charge.

Figure 9 illustrates the effect of Ca ions on the adsorption of sulphate when 3.3 mM CaCl\(_2\) was added to a solution of 700 μM sulphate at pH 8.5 using NaCl as ionic medium (the ionic strength was 0.01 M).

**Fig. 9.** The influence of Ca ions on sulphate adsorption onto magnetite at pH 8.5.

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Supporting material

The online version of this article contains additional supporting material.


References

A study of sodium silicate in aqueous solution and sorbed by synthetic magnetite using in situ ATR-FTIR spectroscopy.
X. Yang, P. Roonasi, A. Holmgren.
A study of sodium silicate in aqueous solution and sorbed by synthetic magnetite using in situ ATR-FTIR spectroscopy

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ABSTRACT

The sorption of sodium silicate by synthetic magnetite (Fe3O4) at different pH conditions (pH 7–11) and initial silicate concentrations (1 × 10−4 and 10 × 10−4 mol L−1) was studied using in situ attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy. The analysis of infrared spectra of sodium silicate in solution as well as adsorbed on magnetite nano-particles clearly showed the evolution of different silicate species depending on pH and silica concentration. The silicate concentration studied (10 × 10−4 mol L−1) contained polymeric or condensed silicate species at lower pH as well as monomers at high pH, as evident from infrared spectra. Condensation of monomers resulted in an increased intensity of absorptions in the high frequency part (>1050 cm−1) of the spectral region, which contains information about both silicate in solution and sorbed silicate viz. 1300 cm−1–850 cm−1. In the pH range studied, infrared spectra of sorbed silicate and sorbed silicate during desorption both indicated the presence of different types of surface complexes at the magnetite surface. The sorption mechanism proposed is in accordance with a ligand exchange reaction where both monodentate and bidentate complexes could exist at low surface loading level, the relative proportion of the complexes being due to both pH and concentration in solution. Oligomerization occurred on the magnetite surface at higher surface loading.

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1. Introduction

Soluble sodium silicates are probably one of the oldest and most widely used industrial chemicals. Because of its unique chemical properties, e.g. buffering ability, surface charges modifying ability, heat and chemical stability, polymerizing capability, and viscosity regulating ability, sodium silicates have been used as cleaners and detergents, modifying reagents in flotation, and binders in agglomeration just to name a few applications [1,2]. Among a wide variety of applications where these properties are utilized, an important one is the use of sodium silicate as a deflocculation agent in clay mining processes and ore flotation. In ore flotation, sodium silicate is often used as depressant or dispersant to improve the selectivity in the flotation of salt-type minerals such as apatite, calcite and fluorite, from sulfides and oxides, siliceous minerals, and also other salt-type minerals [3]. It is already known that in the flotation process soluble sodium silicates, also known as ‘water-glass’, can adsorb onto the target particle surfaces and disperse the agglomerates into fine particles by charging the surfaces. However, sodium silicates showed different selectivity, dispersing activity, and efficiency depending on the mineral system and silicate dosage. In the flotation of apatite from calcite, Rao et al. [4] found for example that at pH 8 and 9 sodium silicate at concentrations higher than 1.3 × 10−3 mol L−1 exhibited a certain depression effect on calcite, but had no such effect at lower concentration. At higher pH values, however, polymeric silicates selectively adsorbed onto calcite surfaces rather than on apatite even at this low silicate concentration (1.3 × 10−3 mol L−1). Gong et al. concluded that the role of sodium silicate (10−3 to 10−4 mol L−1) in the selective flotation of apatite from iron oxides was attributed to the adsorption of moderately polymerized silicate species, which were responsible for the depression of the iron oxide [5,6]. However, in the reversed flotation of apatite from magnetite, Su et al. observed that the selectivity of sodium silicate as depressant decreased when the dosage increased from 300 g t−1 (2.4 × 10−4 mol L−1) to 500 g t−1 (4 × 10−4 mol L−1) resulting in a less efficient dephosphorization of magnetite fines and proposed that the dispersion effect of sodium silicate played a key role at such a low concentration rather than the depressant effect [7]. Knowledge about silicate–metal oxide reactions is of course also important to better understand other industrial applications than
flotation such as the synthesis of zeolites and iron oxide-silicate composites as well as interfacial reactions in environmental systems [8–10].

During the past decades, a lot of experimental work was performed to specify silicate anion species in aqueous solution. These efforts were based on potentiometric titrations as well as infrared, Raman and 29Si NMR spectroscopy [11–17]. From these studies, it became clear that aqueous silicate solutions is a mixture of anions and that the distribution of various silicate species mainly depended on the SiO2:Na2O ratio, SiO2 concentration, pH, temperature and aging. Combining results from 29Si NMR and infrared spectroscopy, Bass et al. [17] confirmed that more of polymeric silicates were present in the silicate solutions at higher SiO2:Na2O ratios [18].

Many publications about the adsorption of silicate anions on iron oxides have used batch experiments and ex situ spectroscopy methods. Stumm and colleagues were among the pioneers, who elaborated a ligand-exchange model to explain and predict the adsorption of H4SiO4 on goethite [8]. Other authors [10,19,20] have used but also developed this ligand-exchange model. Very recently, Hiemstra et al. modelled silicate sorption onto goethite from 1.0 × 10−4 to 1.0 × 10−3 mol L−1 solutions using a modified surface complex model (CD-MUSIC distribution model) [21]. They concluded that a bidentate surface complex ([FeH2SiO3]−) is favoured at low surface loading while at high surface loading polymerized species are more likely. Jordan et al. [22] used titration and sorption data along with the FitEq 4.0 code to model the surface complexes formed when dilute silicate solutions (<2.0 × 10−4 mol L−1) were sorbed on three different iron oxides, viz. goethite, hematite, and magnetite. Their results indicated the formation of two types of monodentate surface complexes, [FeH2SiO3]− and [FeH4SiO4]−. Attenuated total reflection Fourier transformed infrared (ATR-FTIR) spectroscopy has been proven to be a powerful in situ technique to study solid–liquid interface reactions, where various inorganic anions (such as arsenate, sulfate, phosphate) and organic compounds interacts with metal oxides and minerals [23–26]. Although there are some IR, XPS and EXAFS studies on the interaction of silicate with iron oxides or polymers [27,28], no in situ spectroscopy study monitoring the sorption of silicate from dilute solutions, viz., the concentrations used in mineral flotation (<10 mmol L−1), onto the surface of magnetite could be found in the literature. The one most closely resembling our study is an investigation by Gong et al. who applied ATR-IR spectroscopy to study silicate solutions and used XPS to analyse the adsorbed species on hematite after drying. Their results show that polymerized silicate species were formed at the hematite surface [6].

Therefore, in the present paper, the ATR-FTIR technique was used to obtain molecular information about sodium silicate in solution as well as adsorbed onto magnetite particles in situ. The effects of pH and concentration of silicate in solution on silicate species distribution and adsorption characteristics was monitored. Possible interfacial reactions and formed surface complexes were analyzed by comparing the spectra of silicate adsorbed on the magnetite particles with those of silicate in solution.

2. Experimental

2.1. Materials

Two types of sodium silicates were used. Stock solutions of sodium metasilicate (Na2SiO3·9H2O) from J.T. Baker were prepared with Milli-Q water as solvent. Silicate 3.25 was an industrial water glass reagent with a SiO2:Na2O weight ratio of 3.25 and obtained from Luossavaara–Kirunavaara AB (LKAB) in Kiruna, Sweden. The pH of the stock solutions was ~11.5 and sample solutions were prepared just before the in situ measurements. To avoid the ionic strength effects, no extra ionic medium was used. All other reagents were of analytical grade, and all solutions were prepared with Milli-Q water as solvent. NaOH and HCl solutions were used for pH adjustments.

2.2. Preparation of magnetite films

Magnetite films were prepared from the colloidal dispersion of fresh made magnetite which was synthesized by coprecipitation of Fe(II) and Fe(III), a method described by Julivet et al. and Kim et al. [29,30]. Briefly, 5 mL deoxygenated FeCl2 and FeCl3 solution (molar ration 1:2) at a total iron concentration of 1.2 mol L−1 was added to 40 mL 0.2 M NH3·OH solutions. All solutions were carefully kept under argon atmosphere at room temperature, and vigorously stirred. The precipitation was separated from the supernantant by decantation after stirring for 20 min, and then rinsed 4 times with deoxygenated Milli-Q water. Finally, the resulting magnetite paste was dispersed again and kept in a closed vessel. Although all possible precautions were taken to avoid the oxidation of the magnetite particles, a partial oxidation of the particle surfaces to maghemite cannot be completely excluded.

Powder XRD pattern confirmed the crystal structure as magnetite and the broad lines indicated small particle size. TEM images showed aggregated spherical particles with an average size of 10 nm. The specific surface area estimated from particle size was around 115 m2 g−1 (assuming a model surface area of 97.7 m2 g−1). By spreading a certain amount of magnetite suspension over the substrate with a pipette, magnetite was evenly deposited onto the ZnSe crystals and subsequently dried in a vacuum desiccator. After rinsing the deposit with Milli-Q water and allowing it to dry again, the weight of deposited magnetite was calculated from the weight difference.

2.3. ATR-FTIR measurements

All spectra were recorded on a BrukerIFS 66/s FTIR spectrometer equipped with a DTGS detector and a vertical ATR accessory. The vertical ATR accessory consisted of a trapezoidal-shaped ZnSe IRE (45°, 50 mm × 20 mm × 2 mm) with totally 25 internal reflections mounted in a −3.5 mL flow-through stainless steel cell. Spectra of aqueous silicate and of silicate adsorbed on magnetite were recorded by averaging 200 scans at a resolution of 4 cm−1. Data evaluation and spectra simulation were performed with OPUS software from Bruker Optics.

2.4. Spectra of sodium silicate in solution and on magnetite

In situ ATR infrared measurements were performed using the flow cell technique described elsewhere [23,24,26]. The pH of the reaction solutions were monitored by a combined pH electrode and adjusted when needed. A peristaltic pump was used to pump reaction solution through the flow cell at a flow rate of ~4.7 mL min−1.

A calculated amount of silicate stock solution was added to the MilliQ-water after solvent (water) background spectrum was
recorded. The diluted silicate solution was then adjusted to desired pH using NaOH. All experiments were commenced at pH 11. After the spectrum of silicate in solution at a desired pH has been collected, the pH was lowered to next level by addition of HCl, and the spectrum at the new pH was recorded.

Spectra of adsorbed silicate were recorded with ZnSe, magnetite deposit and water as background. After the background spectrum had been recorded, sodium silicate was added to the reaction vessel and adjusted to highest pH studied before begin the adsorption experiment. The effect of pH on sorption was measured by collecting spectra of silicate sorbed on magnetite at each pH step during about 30 min. All experiments were performed under ambient temperature (22 ± 1°C).

3. Results and discussion

3.1. Spectra of aqueous sodium silicate

Fig. 1 shows the spectrum of 10 mmol L\(^{-1}\) sodium metasilicate in aqueous solution at different pH. Due to the transmission limit of the ZnSe crystal and the strong absorption of water, the infrared absorption bands of sodium silicate are shown between 1300 cm\(^{-1}\) and 850 cm\(^{-1}\). For a 10 mmol L\(^{-1}\) solution at pH 11.5, spectrum showed two prominent absorption bands at 885 and 1023 cm\(^{-1}\), and a shoulder at ~1060 cm\(^{-1}\). Lowering the pH to 9.7, the bands at 885 and 1023 cm\(^{-1}\) decreased in intensity whereas the shoulder at 1060 cm\(^{-1}\) grew in intensity accompanied by a new broad band emerging at higher frequency. In addition, a weak band emerged with peak frequency at 945 cm\(^{-1}\) at the lowest pH studied (~7.5), the line shape of the spectrum was similar to the spectrum at pH 8.6 with the dominant band at 1122 cm\(^{-1}\) and shoulders at 1090 and 1175 cm\(^{-1}\). As expected, the spectra show that the distribution of silicate species is pH dependent. The shift to higher frequency upon lowering the pH indicates the formation of polymeric species.

Although there are a number of studies on the assignments of vibration bands of silica solids, glasses and gels [31,32], the assignments related to the distribution of anionic species in sodium silicate solution, especially very dilute solutions, are still unclear and some even incompatible [16–18]. To obtain the distribution of silicate species with pH and concentration, a silicate speciation model was set up using WinSGW program [33]. Formation constants are given by Sjöberg et al. [34] for dilute solution ([Si]<48×10\(^{-3}\) mol L\(^{-1}\)) and also by Felmy et al. [35]. Constants given by Sjöberg et al. are valid at 25°C and 0.6 M NaCl medium but since the silicate speciation is influenced by ionic strength, the thermodynamic constants given by Felmy et al. were preferred.

In the modeling the precipitation of amorphous silica under thermodynamic conditions was included. In this context it should be mentioned that the kinetics of the formation of silica precipitate is rather slow especially at high pH, low ionic strength, and high silica concentration, as shown by Icopini et al. [36]. The half-life of molybdate-reactive silica was >2700 h at a silica concentration of 4.2 mM at pH 8–9 and silicate concentration of 12.5 mM at pH 11 with ionic strength of 0.01 M. Starting at pH 11, would therefore imply that the formation of amorphous silica precipitate during the period of solution spectra collection or sorption can be ignored. The formation of nanocolloidal silica is strongly limited at high pH although at pH 7 and 10 mM silicate concentration about 10% of the silicic acid could be formed to nanocolloidal silica after 1 h [36], since the solution becomes supersaturated when pH is lowered [13]. Equilibrium protonation/deprotonation parameters and the formation constants are shown in Table 1 along with the chemical formula of each species and the calculated equilibrium distributions are plotted in Fig. 2. Below 2 mmol L\(^{-1}\) (the solubility limit of amorphous silica [34]), the monomers SiO(OH)\(^{2-}\), Si\(_2\)O\(_3\)\(^{2-}\), and Si(OH)\(_4\) are dominant with protons transferred between different species as pH was changed. The distribution of silicates becomes more complex when the concentration of silicate in solution increases, because dimers, trimers, oligomers and higher aggregates will form by condensation of monomers at high concentration. In 10 mmol L\(^{-1}\) solution, more dimers and trimers

---

### Table 1

<table>
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</tr>
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</table>
but even tetramers and polymers are formed between pH 9 to 13, and at low pH colloidal SiO₂ might be formed. The distribution diagram in Fig. 2 is a support in our interpretation of infrared spectra of silicate species in solution.

Curve fitting of the absorption bands was utilized in an attempt to distinguish the spectral features of the various silicate anions from each other. Considering the spectral intensity and signal to noise problems at low concentrations only spectra in Fig. 1 (10 mmol L⁻¹) were curve fitted using the OPUS program (Fig. 3).

Each spectrum was resolved into six or seven component bands. It is clear that the variation of spectral features in the wavenumber region 1250–850 cm⁻¹ can be explained by the change in relative contributions from component bands at different pH. As shown in Fig. 3, the most intense component band at 1020 cm⁻¹ (pH 11.5) together with the band at ~890 cm⁻¹ decreased in intensity with decreasing pH, whilst the intensity of the bands at ~1065, 1122, and 1180 cm⁻¹ showed a significant increase becoming the three most intense bands at low pH. An additional band showed up at 945 cm⁻¹ as pH was changed to lower values than 9.7.

Halasz et al. reported infrared spectra of sodium silicate solutions dissolved from Na₂SiO₃ and Na₂SiO₃ · 9H₂O at pH > 13 [18]. The spectral features of 0.05 mol L⁻¹ Na₂SiO₃ were similar to our spectrum of a 0.01 mol L⁻¹ solution at pH 11.5 where bands at ~1020 and ~890 cm⁻¹ are the most prominent ones. They assigned these two bands to the fully dissociated SiO(OH)₂⁻ species. However, according to the distribution diagram in Fig. 2, the prominent species in 10 mmol L⁻¹ solution at pH 11.5 is SiO(OH)₃⁻ rather than SiO(OH)₂⁻. Accordingly, the bands observed here at 1020 and 890 cm⁻¹ are assigned to SiO(OH)₃⁻ species. Apparently, this assignment seems also to be consistent with the spectra reported by the same authors concerning a 0.2 mol L⁻¹ solution of Na₂SiO₃ · 9H₂O. However, when the alkaline condition changed by adding NaOH to the latter system (0.2 mol L⁻¹ Na₂SiO₃, 0.4 mol L⁻¹ NaOH), the two bands at 1020 and 890 cm⁻¹ shifted to 1001 and 934 cm⁻¹ caused by undissociated Na-silicate species, although a shoulder still appeared at 890 cm⁻¹. In another study, Bass and Turner also observed a similar shift of infrared bands from 1020 and 890 cm⁻¹ to 1000 and 930 cm⁻¹, respectively (0.4 mol L⁻¹ sodium silicate solution), when the ratio of silica to alkali decreased from 3.3 to 0.2 [17]. Considering the two main factors determining the properties of sodium silicate solutions, namely silica to alkali ratio and silicate concentration, a solution with lower ratio of silica to alkali should imply a higher pH value. Thus, it seems clear that the bands at ~1000 and ~930 cm⁻¹ correspond to partly undissociated SiO₂(OH)₂⁻.

Since the concentration of silica in the present study is much lower (10 mM), the effect of undissociated sodium silicate species can be omitted indicating that the wavenumber distance between these two bands become larger when SiO₂(OH)₂⁻ anions are forming SiO(OH)₃⁻ species through protonation.

Based on the fractional distribution of silicate anions in aqueous solution (Fig. 2), analysis of our infrared spectra, and comparison with previous studies, the infrared bands at ~890 and 1020 cm⁻¹ could be assigned to Si–O stretching vibration of SiO(OH)₃⁻ species. The band at ~945 cm⁻¹ seems to mainly involve the stretching of Si–OH in Si(OH)₄ monomers, since it appears at low pH, whereas the band at 1070 cm⁻¹ may originate from stretching vibrations involving the Si–O–Si entity. With decreasing pH of the silicate solutions, the SiO(OH)₃⁻ ions tend to be protonated and possibly further condensed since more OH function groups are available. Hence the bands appearing in the 1050–1200 cm⁻¹ range and showing an increased intensity upon lowering the pH are assigned to stretching vibrations involving the Si–O–Si entities.

3.2. The effect of pH on sorption and desorption of the silicates

The effect of pH on the amount of silicate adsorbed on magnetite is shown in Fig. 4, where the integrated intensity of the absorbance from 1300 to 800 cm⁻¹ was plotted versus pH and time. As a first approximation, it may be assumed here that the integrated absorbance in the 1300–800 cm⁻¹ region is proportional to the amount of adsorbed silicate [37]. This assumption is reasonable as long as surface species formed at different pH are similar or exhibit transition dipole moments of similar numerical value. If not so, there is no simple linear relation between the integrated absorbance at different pH and the amount of adsorbed species. However, this difficulty does of course not exclude qualitative interpretations of Fig. 4.
As evident from Fig. 4, the adsorption equilibrium was not reached after 30 min independent of pH value although the increase in intensity per minute was considerably lowered with time. However, there was no significant change in the spectral line shape with time, which implies that the same types of surface complexes are formed at a certain pH. Therefore, only the last spectrum at each pH value is shown in Fig. 5 and used in the following discussion about formed surface complexes on magnetite at different pH, but at constant silicate concentration in solution. As shown in Fig. 4, the integrated intensity for silicate adsorbed from 1 mmol L\(^{-1}\) metasilicate and Silicate3.25 solutions (Figs. 4b and 4c) were about the same, whilst the adsorption from 10 mmol L\(^{-1}\) metasilicate solution was 4 to 5 times larger. A considerable increase in the adsorption of silicate occurred from pH 11 to 9, whereas a decrease in pH from 9 to 7 only contributed a minor change in spectral intensity. It is well known that silicate sorption onto iron oxyhydroxides has a maximum at a pH value around 9\(^{[8,10,21,22]}\), but this is not reflected in our spectra. The observed sorption should already have passed its maximum when reaching pH 7. However, sorption at pH 7 for 30 min was not enough time to desorb the silicate from the surface. Probably this is reflecting a non-equilibrium situation where both the silicate species sorbed at the magnetite surface and the protonation state of the surface itself must change as pH is lowered.

In the pH range 11–9, the magnetite surface should be dominated by both negatively charged surface sites and neutral surface hydroxyl groups as the point of zero charge of magnetite is about 6\(^{[38]}\). In solution silicate exists as negatively charged anions. Despite this, the silicate anions are readily adsorbed at the magnetite surface, as evident from the fast and large increase in the surface concentration of silicate. At lower pH values, neutral surface hydroxyl groups become predominant on the magnetite surface and neutral silicate species begin to dominate in solution as well (pH < 9.5). Therefore, the negatively charged silicate anions (SiO(OH)\(_3^-\)) and neutral Si(OH)\(_4^−\) species both are active adsorbate species. The observed pH dependent adsorption properties are consistent with the ligand exchange of protonated as well as deprotonated surface hydroxyl groups with SiO–H groups having Lewis base properties\(^{[39]}\).

To further assess the properties of the adsorbate, desorption experiments were performed by flushing the flow-cell with Milli-Q water at a certain pH. It can be seen from Fig. 4 that the extent of silicate desorption from magnetite was influenced by pH. Higher pH implied that more of the surface species were desorbed and the desorption curve exhibits an initial fast decrease in spectral intensity followed by a slower desorption step. A higher desorption rate and extent of desorption under alkaline conditions is reasonable considering the nature of a ligand-exchange reaction. Even after long desorption time, it was a significant amount of surface species left, which indicates that a certain amount of surface species are firmly attached to the magnetite surface by covalent bonds implying that inner-sphere complexes are formed between magnetite and silicate species.

3.3 Spectra of sodium silicate at the magnetite surface

Figs. 5a, 5b, and 5c show the spectra of silicates on magnetite sorbed from 10 mmol L\(^{-1}\) and 1 mmol L\(^{-1}\) sodium metasilicate solution (Figs. 5a and 5b) and 1 mmol L\(^{-1}\) Silicate3.25 solution (Fig. 5c) at different pH. A comparison of the spectra of sorbed silicates with those of silicate in aqueous solution (Fig. 1) shows that the absorbance of the surface species is significantly higher. This is because of the strong affinity of magnetite for the silicate species resulting in a higher concentration of these species at the magnetite surface. The spectral line-shape for silicates sorbed from 1 mmol L\(^{-1}\) solutions (Figs. 5b and 5c) is similar, whilst the line-shapes obtained from 10 mmol L\(^{-1}\) solution are clearly different changing with pH (Fig. 5a).

It can be seen from Figs. 5b and 5c that the spectra of sorbed silicate from 1 mmol L\(^{-1}\) sodium silicate solutions are similar although they have different silica to alkali ratio. In Fig. 5b, at pH 11.2, the maximum absorbance is located at 955 cm\(^{-1}\) and the peak frequency remained constant in position with decreasing pH. However, as solution pH was lowered to 9.3, the band at ~1020 cm\(^{-1}\) increased in intensity becoming the strongest band in the spectral region (800–1300 cm\(^{-1}\)) and simultaneously an ap-
parent increase in the intensity of the band at 1120 cm\(^{-1}\) can be observed. When pH was decreased from 8.3 to 7.0, there was no remarkable change in the lineshape. Similarly, spectra of sorbed Silicate3.25 on magnetite (Fig. 5c) at pH 9.9 to 6.6, were dominated by a sharp band centred at 1020 cm\(^{-1}\) with shoulders on each side, viz. at ~930 and ~1120 cm\(^{-1}\).

The broad absorption at pH 11.1 (Fig. 5a) is apparently composed of three broad bands at ~955, 1029, and ~1120 cm\(^{-1}\) with the most intense band at 1029 cm\(^{-1}\) shifting to 1060 cm\(^{-1}\) as pH was decreased to 7. Simultaneously, the infrared band at 1120 cm\(^{-1}\) became much stronger. The only experimental difference between Figs. 5a and 5b is the concentration of the aqueous silicate solution. A higher concentration should facilitate the conversion between Figs. 5a and 5b by increasing the amount of additional silicate species attached to the magnetite surface. The following ligand-exchange reactions are proposed:

\[
\text{Fe(OH)}_3\text{Si(OH)}_2\text{O} + \text{Na}_2\text{SiO}_3 \rightarrow \text{Fe(OH)}_3\text{Si(OH)}_2\text{O} + 2\text{Na}^+ + 2\text{OH}^-
\]

\[
\text{Fe(OH)}_3\text{Si(OH)}_2\text{O} + \text{H}_2\text{O} \rightarrow \text{Fe(OH)}_4\text{Si(OH)}_2\text{O} + 2\text{H}^+
\]

where X represents a negative charge or proton. Comparing with FTIR and EXAFS data on the iron(III)-silica coprecipitate [9, 28], the infrared band at ~950 cm\(^{-1}\) in the present work would be related to the Fe–Si stretching in the bidentate surface complex \(\langle=\text{FeO}≡\text{Si})\text{O}X\), whilst at lower pH oligomeric surface species should be formed. The latter species corresponds to the increase in intensity of the infrared band observed at ~1020 cm\(^{-1}\), an assignment that is supported by thermodynamic modelling [21].

Fig. 6 shows the resolved component bands from spectra of sorbed silicate on magnetite. Each spectrum of sorbed silicate was curve fitted using a minimum of component bands. For the two 1 mmol L\(^{-1}\) silicate solutions, the position of component bands was similar as shown in Figs. 6b and 6c, even though pH was changed. Figs. 6b and 6c also show that the absorbance at ~1020 cm\(^{-1}\) is the most intense band in the pH range 10–7.

In contrast to the situation in solution, this band continued to be the strongest one also at low pH. The possible surface complexes can be postulated to be \(\equiv\text{Fe}≡\text{Si}O\text{O}X\) or \(\equiv\text{FeO}≡\text{Si})\text{O}X\) for the reactions between silicate monomers and the magnetite surface. The following ligand-exchange reactions are proposed:

\[
\text{FeO}X + \text{Si(OH)}_2\text{O} \rightarrow \text{FeO}X + \equiv\text{Si}O\text{O}X
\]

\[
\text{FeO}X + \text{Si(OH)}_2\text{O} \rightarrow \text{FeO}X + \equiv\text{Si}O\text{O}X + \text{H}_2\text{O}
\]

where X represents a negative charge or proton. Comparing with FTIR and EXAFS data on the iron(III)-silica coprecipitate [9, 28], the infrared band at ~950 cm\(^{-1}\) in the present work would be related to the Fe–Si stretching in the bidentate surface complex \(\langle=\text{FeO}≡\text{Si})\text{O}X\), whilst at lower pH oligomeric surface species should be formed. The latter species corresponds to the increase in intensity of the infrared band observed at ~1020 cm\(^{-1}\), an assignment that is supported by thermodynamic modelling [21].

Fig. 6 shows the resolved component bands from spectra of sorbed silicate on magnetite. Each spectrum of sorbed silicate was curve fitted using a minimum of component bands. For the two 1 mmol L\(^{-1}\) silicate solutions, the position of component bands was similar as shown in Figs. 6b and 6c, even though pH was changed. Figs. 6b and 6c also show that the absorbance at ~1020 cm\(^{-1}\) is the most intense band in the pH range 10–7. In contrast to the situation in solution, this band continued to be the strongest one also at low pH. The possible surface complexes can be postulated to be \(\equiv\text{Fe}≡\text{Si}O\text{O}X\) or \(\equiv\text{FeO}≡\text{Si})\text{O}X\) for the reactions between silicate monomers and the magnetite surface. The following ligand-exchange reactions are proposed:

\[
\text{FeO}X + \text{Si(OH)}_2\text{O} \rightarrow \text{FeO}X + \equiv\text{Si}O\text{O}X
\]

\[
\text{FeO}X + \text{Si(OH)}_2\text{O} \rightarrow \text{FeO}X + \equiv\text{Si}O\text{O}X + \text{H}_2\text{O}
\]

where X represents a negative charge or proton. Comparing with FTIR and EXAFS data on the iron(III)-silica coprecipitate [9, 28], the infrared band at ~950 cm\(^{-1}\) in the present work would be related to the Fe–Si stretching in the bidentate surface complex \(\langle=\text{FeO}≡\text{Si})\text{O}X\), whilst at lower pH oligomeric surface species should be formed. The latter species corresponds to the increase in intensity of the infrared band observed at ~1020 cm\(^{-1}\), an assignment that is supported by thermodynamic modelling [21].

4. Conclusions

In situ ATR-FTIR spectroscopy was used to monitor the silicate species in solution as well as sorbed on magnetite surfaces. The spectral changes observed for sodium silicate solutions at different pH were analyzed in detail and showed the variation of dominating silicate anions in solution. As evident from infrared spectra, the silicate concentration studied (10 \(^{-3}\) mol L\(^{-1}\)) within a reaction time of 30 min, the sorption of silicate onto magnetite from 1 mmol L\(^{-1}\) solutions was significant at each pH step from 11 to 7. At lower pH, the reaction slowed down and only a minor amount of additional silicate species were attached to the magnetite surface in the pH range studied (11–7). Infrared spectra of sorbed silicate indicated the presence of different types of surface...
species at the magnetite surface, whereas desorption of sorbed silicate indicated species firmly attached to the magnetite surface. At least for dilute silicate solutions, the value of pH seems to be a more useful parameter rather than the silica to alkali ratio in order to reveal information about species distribution facilitating the interpretation of infrared spectra. The adsorption mechanism proposed is in accordance with a ligand exchange reaction where both monodentate and bidentate complexes could exist simultaneously at low surface loading level. Subsequent polymerization occurred on surface with pH lowering and further surface accumulation.

Acknowledgments

This work was financially supported by funds donated by LKAB to the Hjalmar Lundbohm Research Centre (HLRC) at Luleå University of Technology. Xiaofang Yang appreciates the National Natural Science Foundation of China (Grant No. 20537020) for providing the possibility to perform this work in Sweden within a visiting Ph.D. student program.

References

Kinetics of silicate sorption on magnetite and maghemite. An ATR-FTIR study.
Kinetics of silicate sorption on magnetite and maghemite: An in situ ATR-FTIR study

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Abstract

Attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy was used to monitor the in situ sorption of sodium metasilicate from aqueous solution onto synthesized magnetite and maghemite particles in the pH range of 10.8–7.0 using silicate concentrations between 0.1 mM and 5 mM. The spectral data showed that both pH and silicate concentration had great influence on the interfacial reaction between soluble silicate and the iron oxide surfaces, regarding the amount adsorbed per unit mass of iron oxide and the surface species formed. A pH dependent sorption of silicate on iron oxides was observed, implying that a maximum sorption took place in the pH range of 9.5–7.0. All experiments showed a fast initial increase in the absorption intensity followed by a slower sorption stage which was strongly dependent on the concentration of silicate in solution and the pH value. The amount of sorption onto maghemite was 3–5 times larger than onto magnetite, but there was no significant difference in the line shape of corresponding absorption bands. At pH 8.5 and low concentration (<0.1 mM), the silicate monomers dominate in solution and on the iron oxide surface also monomeric species were dominating as evident from the infrared band at 950 cm⁻¹. However, at higher concentration (0.4–5.0 mM), the dominating absorption band at about 1000 cm⁻¹ shifted to higher frequency during the sorption indicating that oligomeric surface silicate species were formed on the iron oxide surface. Desorption of silicate from the surface of the iron oxides was easier to accomplish at low silicate concentration, whilst the highest concentration showed a comparatively low relative amount of desorbed silicate, suggesting that polymerized species had a stronger affinity for the iron oxide surface as compared to monomeric species.

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1. Introduction

Interfacial reactions between soluble silicates and iron oxide surfaces are of great importance in the natural environment considering the content of dissolved silicate in natural waters from mineral weathering [1–3] as well as in industrial applications, e.g., flotation of salt-type minerals from metal oxides and other salt-type minerals where sodium silicate is usually used as dispersion or depressant agent [4]. Concretely, in the dephosphorizing flotation of magnetite particles, sodium silicate with modulus 3.25 (weight ratio of SiO₂ to NaO₂) is used mainly to disperse the agglomerated particles [5], whereas in the flotation of apatite from hematite sodium silicate may be utilized as a selective depressing agent to reduce the flotation of the gangue mineral (hematite) [6]. It is well known that the concentration, modulus, and pH of sodium silicate solutions are the main factors determining selective silicate sorption on mineral surfaces and that the properties of the modifying agent is strongly influenced by the distribution of silicate species in solution viz. monomers, oligomers, higher polymers, and colloidal silica [6–9].

During the past decades, the study of interaction between silicate and iron oxides as well as other minerals was mainly carried out by batch adsorption experiments, modeling methods, and ex situ spectroscopy techniques [1,3,7,10–12]. However, there are very few if any in situ studies on the sorption of silicate species onto magnetite showing the formation of surface complexes with time. Another topic is the often appearing question whether the surface of the magnetite particles, which during experimental handling may be exposed to air, represents magnetite or to some extent are oxidized to maghemite although the structure of the two iron oxides is similar both representing a spinel structure with tetrahedral and octahedral sites [13]. In maghemite, all or most of the octahedral Fe(II) in magnetite are oxidized to trivalent implying a Fe(II)-deficient structure with a slightly smaller unit cell volume as compared with magnetite. From a surface chemical point of view, the important question is whether the sorption behaviour of sodium silicate onto...
the two mentioned iron oxides is the same or if the oxidation state of the iron atoms has a significant influence on the affinity of the surfaces for silicates. Moreover, a molecular level investigation of silicate species sorbed on iron oxide surfaces and especially the time dependence of the sorption is critical in industrial processes with limited conditioning times but also important in geochemical systems.

Accordingly, in the present study attenuated total reflection Fourier transform infrared (ATR-FTIR) spectrocscopy was utilized to monitor the sorption of sodium silicate onto a thin layer of synthetic magnetite (Fe₃O₄) nanoparticles as compared with the sorption onto a corresponding layer of synthetic maghemite (γ-Fe₂O₃). The study encompassed different pH and silicate concentration. Of special interest here was the possible change of sorbed species at the iron oxide surfaces with time and the possible difference in the amount sorbed under similar experimental conditions. In addition, desorption of the already adsorbed silicate species was studied, possibly revealing the type of surface complexes formed and the affinity of different silicate species for the surfaces.

2. Experimental

2.1. Chemicals and materials

Sodium metasilicate (Na₂SiO₃·9H₂O) from Sigma was dissolved in Milli-Q water and prepared as a stock solution (0.5 M, pH = 11.5). Magnetite used in this study was synthesized based on a coprecipitation of Fe (II) and Fe (III) chlorides method described by Jolivet et al. and Jarlbring et al.[14,15]. Briefly, Fe (II)/Fe (III) chloride salt mixture (1:2 molar ratio) was hydrolyzed using NH₄OH, purified with deoxygenated Milli-Q water, and stored under argon atmosphere. Maghemite was prepared by heating magnetite in an oven at 240 °C overnight. The BET surface area of magnetite was 97.7 m² g⁻¹ and that of maghemite was 87.3 m² g⁻¹. All other reagents were of analytical grade and all solutions were prepared from Milli-Q water as solvent. NaOH and HCl solutions were used for pH adjustments.

2.2. FTIR measurements

Spectral data were acquired with a BrukerIFS 66v/S FTIR spectrometer equipped with a deuterium triglycine sulphate (DTGS) detector and a vertical ATR accessory. The vertical ATR accessory consisted of a trapezoidal-shaped 25x25 mm internal reflection element (45°, 50 mm × 20 mm × 2 mm, totally 25 reflections) and a single-chamber (∼3.5 mL) flow-through stainless steel cell. Spectra of silicate sorbed on iron oxide were recorded by averaging 100–200 scans at a resolution of 4 cm⁻¹. All spectral data evaluations were performed with the OPUS program from Bruker Optics.

2.3. Preparation of iron oxide films on the ATR crystal

A visually evenly distributed magnetite or maghemite film was deposited on one side of the ATR crystal by spreading a certain amount of the iron oxide dispersion on the crystal surface and subsequently evaporate the dispersion medium in a desiccator under vacuum. After rinsing the deposited film gently with Milli-Q water and let it dry in the desiccator again, the mass of deposited film was weighted. Since the dispersion was allowed to stand for a while after stirring to let the larger particles settle down, the concentration of the dispersion dispensed using a pipette varied to a certain extent. Thus the mass of the film was not exactly controlled but only weighted and amounted to generally less than 1 mg. Accordingly, the bulk silicate concentration can be assumed to be effectively constant during the experiments.

2.4. ATR-FTIR spectra of sorbed silicate

In situ ATR infrared measurements were performed using the flow-cell technique described by Peak and others [16,17]. The small amount of iron oxide used (<1 mg) assures that the depth of penetration is much larger than the thickness of the evenly distributed oxide layer. The pH of the silicate solution was monitored by a combined pH electrode and adjusted when needed. The solution (100 mL) was pumped from a beaker into the flow-cell by a peristaltic pump at a flow-rate of ∼4.7 mL min⁻¹. Single beam background spectra of the solvent (Milli-Q water) were recorded at each pH. Sodium silicate was added into the vessel at a desired concentration and pH adjusted with NaOH/HCl. Spectra of sorbed silicate were recorded as a function of time. Desorption experiments were carried out by flushing flow-cell with Milli-Q water at desired pH. All experiments were performed under ambient temperature (22 ± 1 °C).

3. Results and discussion

3.1. pH dependent silicate sorption/desorption kinetics onto maghemite

According to Fig. 1a and b, infrared spectra recorded upon sorption from a 1 mM sodium silicate solution at pH 10.8 is quite different from corresponding spectra at pH 8.5. At pH 10.8 the strongest absorption had its peak position at 952 cm⁻¹ with a shoulder at ∼1020 cm⁻¹. This shoulder is hardly detected at the beginning of the sorption reaction but grows in intensity with the time of reaction. At this pH value, the dominant species in solution is Si(OH)₃⁻ (Fig. 2, Table 1) [18] and the magnetite surface should be negatively charged since its point of zero charge is ∼6.0 [19]. These spectral changes indicate different inner-sphere surface complexes appear at the magnetite surface during sorption. Comparing the sorption and the desorption it also seems that the absorbance at ∼1020 cm⁻¹ upon sorption increases faster relative to the 952 cm⁻¹ band than the absorbance at ∼1020 cm⁻¹ decreases relative to the 952 cm⁻¹ band during desorption. These in situ ATR-FTIR results were compared with EXAFS results of Pokrovski et al. [20] on iron(III)–silica coprecipitate, strongly indicating that the 952 cm⁻¹ band should be assigned to the bidentate monomeric surface species, [FeO]₂–Si(OH)₂OH or (Σ)O₂=Si(OH)₂⁻, whilst the shoulder at ∼1020 cm⁻¹ should be assigned to oligomeric surface silicate species which desorbed slower than monomeric species.

At pH 8.5, it is interesting to notice that the oligomeric species is dominating already at the beginning of the sorption reaction although the peak frequency of the absorption band appears at lower wavenumber (1000 cm⁻¹). This might indicate a difference in the degree of oligomerization with fewer monomer units in the oligomer at the beginning of the sorption reaction. Since these oligomers do not dominate in aqueous solution at this low concentration (1 mM, Fig. 2), it further indicates that the polymerization occurs at the magnetite surface. This latter suggestion is in accordance with results from the literature [27], showing that polymerization of silicic acid on an iron oxide surface is promoted at lower pH. At longer sorption times, it is also evident from the experiments at pH 8.5 that an infrared absorption at wavenumbers >1100 cm⁻¹ evolves. This absorption band is consistent with a three-dimensional polymeric structure such as colloidal silica [21] and would imply that the polymerization of silica occur at the magnetite surface also at this low concentration of silica in solution (1 mM).

The pH dependence of silicate sorption from 1 mM sodium silicate solution onto magnetite was determined by collecting ATR-FTIR spectra of sorbed silicate with time at the pH values: 10.8, 9.5,
Fig. 1. ATR-FTIR spectra of silicate sorbed onto magnetite from 1 mM sodium metasilicate aqueous solutions. The time dependence of the sorption is shown for (a) pH 10.8 and (b) pH 8.5.

8.5, and 7.0 (Fig. 3). In Fig. 3, the infrared absorbance caused by silicate was integrated between 1300 cm\(^{-1}\) and 800 cm\(^{-1}\) and divided by the mass of magnetite deposited as a thin layer on the ATR crystal and then this ratio was plotted versus the reaction time. It can be clearly seen that from pH 10.8 to pH 8.5, the integrated intensity of sorbed silicate increased with decreasing pH. However, when pH was lowered to 7.0 the integrated intensity decreased implying that there is a maximum in the amount of sorbed silica. This pH dependent silicate sorption behaviour of magnetite is consistent with previous studies\(^{[1,7,11,12]}\) where thermodynamic models have been used to explain the observed maximum. The decreased amount of sorbed silicate between pH 8.5 and pH 7.0 occurred in a pH interval where the charge of the silicate species in solution is neutral (Fig. 2) and that of the magnetite surface is still negative although decreasingly so with pH. However, the condensation of silicate monomers is promoted at the magnetite surface at lower pH\(^{[2,7,22]}\). The decreased sorption of silicate from pH 8.5 to pH 7.0 could therefore be attributed to the decreased availability of surface sites caused by condensation reactions masking otherwise available Fe–OH sites and/or the decrement of ionic silicate species which are essential to the sorption reaction. The measured absorbance of the infrared spectrum is proportional to the square of the vector product between the electric field vector of the evanescent field (\(E\)) and the transition dipole moment (\(M\)), which should relate to the structure of formed surface silicate species. Using an equation proposed by Dobson et al.\(^{[23]}\), the absorption may be described as:

\[
A_i = \varepsilon_i \frac{t}{\delta} \frac{I_i}{\tau}
\]

where \(A_i\) is the measured absorbance of the \(i\)-species, \(\varepsilon_i\) is the molar absorption coefficient of sorbed silicate species, \(I_i\) is the apparent surface loading concentration, \(t\) is the thickness of the deposited layer on the crystal, \(\delta\) is the effective path length determined by the refractive indices of the internal reflection element and the medium outside, by the thickness of the layer, angle of incidence, and the wavelength of the infrared radiation.

As a first approximation, it is assumed that the molar absorption coefficients of sorbed silicate species formed at different pH are not changing with the amount sorbed or are experienced to the same relative change. This assumption is reasonable, at least for pH 9.5–7.0, considering the similarities in line shapes of the infrared spectra of sorbed silicate within this pH range (not shown here, but in [22]). Except at extremely high pH (pH 10.8), showing a different line shape, the spectral line shapes recorded at pH 7.0, 8.5, and 9.5 were very similar indicating similar silicate species on the iron
oxide surface at each pH value and that the relative amount of these species were also similar. Between different series of spectral data at a certain pH, the mass of the deposited magnetite layer varied from 1.0 mg to 0.3 mg. For the experiments at pH 7.0 and pH 8.5, the mass of the magnetite layer was close to 0.3 mg, and at pH 9.5 and pH 10.8 the amount of magnetite was close to 1.0 mg. However, the integrated intensity of infrared absorption should be proportional to the mass of the magnetite layer. Despite of the uncertainty of the ratio in Eq. (1) that restricted the application of accurate quantitative comparison between different experimental series, the time dependent trend of silicate sorption onto magnetite, as shown in Fig. 3, should be true in this pH range. It should be noticed that the line shape and peak frequency position of the absorption bands at pH 10.8 is different from the ones at lower pH (Fig. 1) and therefore a direct comparison of sorbed amounts between high (10.8) and low (9.5–7.0) pH values in Fig. 3 is more uncertain. However, it seems still plausible to suggest that the highest pH value implies a lower amount of sorbed silica, which is also supported by results from others [1,7,11,12]. Desorption experiments carried out directly after sorption at a certain pH were used to assess the sorption affinity of silicate for the magnetite surface. The residual silicate on the magnetite surface was monitored during the time the flow-cell was flushed with Milli-Q water. ATR-FTIR spectra are shown in Fig. 4 and desorption results are plotted in Fig. 3. During the time of desorption used here (2 h) it is clear that silicate is more easily desorbed at high pH than at low pH. This might be caused by the formation of oligomeric surface silicate species at low pH. Formation of such species would imply stronger interaction with the magnetite surface since each species may offer many Fe–O–Si bonds with the surface and therefore it takes longer time to desorb these species. On the other hand high pH would imply an enhanced detachment of sorbed silicate as ions in accordance with the silica dissolution mechanism and an increased electrostatic repulsion between magnetite surface and silicate species which should facilitate the desorption and inhibit the resorption as well. Although the desorption rate seemed to be higher in the beginning of the desorption reaction, an equilibrium plateau value was not reached within 2 h.

3.2. Effect of silicate concentration on sorption

In Figs. 4 and 5, the sorption of silicate from aqueous solution onto magnetite (Fig. 4) and maghemite (Fig. 5) is shown at pH 8.5 and different silicate concentration. Clearly, the concentration as well as pH is important for the type of surface complexes formed. At the lowest concentration (0.1 mM, Fig. 4), the recorded spectra reminds very much of spectra recorded at pH 10.8 but for a higher silicate concentration (1 mM, Fig. 1a). Accordingly, the 950 cm\(^{-1}\) band is due to bidentate monomeric surface species, whilst the shoulder at the high frequency side of this band demonstrates the formation of oligomeric species. At the highest silicate concentration (5 mM), the dominant band at ∼1020 cm\(^{-1}\) for a 1 mM solution is shifted to ∼1050 cm\(^{-1}\) upon increased surface loading. This is an interesting spectral shift because a higher silicate concentration is expected to result in more of polymeric species. Accordingly, the shift from 1020 cm\(^{-1}\) to 1050 cm\(^{-1}\) is an indication of increased polymerization at the magnetite surface resulting in oligomeric species with a higher degree of polymerization but may simultaneously reflect a change of the structure of the oligomers since infrared spectra are well-known to be sensitive to changes in molecular structure. Sorption from a 5 mM aqueous silicate solution also imply a much higher intensity at 1100–1150 cm\(^{-1}\), which was assigned to a three-dimensional framework such as amorphous silica. However, the broadness of this band is significantly larger than the half-width of a spectrum of amorphous silica particles (not shown) although the peak frequency is almost the same. This might imply that the three-dimensional silica framework structure eventually will form a silica layer which infrared spectrum is similar to the spectrum of amorphous silica particles. It might be speculated that the appearance of such a broad band in this region could be due to the number of Si–O–Si units exposed to different environments such as in cyclic trimers, mono-substituted cyclic tetramers, cyclic tetramers, bridged cyclic tetramers etc. If these units represent slightly different vibrational potentials with low activation energy between them, the result should be a broadening of the absorption band caused by Si–O vibrations. Fig. 5 shows that vibrational spectra of silicate sorbed on a maghemite surface at pH 8.5 are very similar to the correspond-
The sorption reaction, relative to the absorption at ∼3450 cm⁻¹ of silicate on surface during desorption. Infrared spectra were integrated between 900 and 1100 cm⁻¹ and 1000–1050 cm⁻¹. The absorbance ratio of sorbed silicate per mg magnetite; open circles, integrated absorbance of resid-
ual silicate on surface during desorption. Infrared spectra were integrated between 1300 cm⁻¹ and 800 cm⁻¹.

Fig. 6. Sorption and desorption of sodium silicate at pH 8.5 and different silica concentration: (a) magnetite and (b) maghemite. Filled circles; integrated absorbance of resid-
ual silicate on surface during desorption. Integrated absorbance of resid-
ual silicate on surface during desorption. Infrared spectra were integrated between 1300 cm⁻¹ and 800 cm⁻¹.

Table 1

<table>
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<th>Chemical Formula</th>
<th>log (K)</th>
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<tr>
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</tr>
<tr>
<td>2</td>
<td>Si(OH)₃⁻</td>
<td>−2.27</td>
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<td>3</td>
<td>Si(OH)₂⁻</td>
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<td>−2.91</td>
</tr>
<tr>
<td>5</td>
<td>Si⁺</td>
<td>−3.21</td>
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</table>

The sorption of silicate from aqueous solution onto magnetite and maghemite was monitored by in situ ATR-FTIR spectroscopy. From the infrared absorption of silicate species versus time it was concluded that the maximum sorption appeared between pH 7.0 and pH 9.5. Below pH 9.5, a sorption equilibrium value could not be reached within 2 h. Desorption of already sorbed silicate on a magnetite surface was easier to accomplish at high pH (10.8) than at low pH (9.5–7.0). One reason could be the more extensive for-
ation of oligomeric surface silicate species at low pH. At high pH or low silicate concentration, the dominant surface species were a bidentate monomeric surface complex assigned to the infrared band at 950 cm⁻¹. Decreasing pH or increasing the concentration of silicate implies more of oligomeric surface silicate species assigned to the infrared absorption at 1000–1050 cm⁻¹. At the highest sil-
icate concentration (5 mM) this band shifted from 1020 cm⁻¹ to 1050 cm⁻¹ as the surface loading increased with the time of reac-
tion. Simultaneously, a broad band at 1150 cm⁻¹ grew in intensity, a band that was assigned to a three-dimensional silica framework. The gradual shift from 1000 cm⁻¹ to higher frequency indicated that the degree of polymerization increased with the sorption time and silicate concentration.

4. Conclusions

The sorption of silicate from aqueous solution onto magnetite and maghemite was monitored by in situ ATR-FTIR spectroscopy. From the infrared absorption of silicate species versus time it was concluded that the maximum sorption appeared between pH 7.0 and pH 9.5. Below pH 9.5, a sorption equilibrium value could not be reached within 2 h. Desorption of already sorbed silicate on a magnetite surface was easier to accomplish at high pH (10.8) than at low pH (9.5–7.0). One reason could be the more extensive for-
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The main difference between magnetite and maghemite con-
cerning silicate sorption was the amount sorbed. The amount of
silicate sorbed onto magnetite was 3–5 times larger than the corresponding sorption onto maghemite.

Acknowledgments

This research was financially supported by funds donated by LKAB to the Hjalmar Lundbom Research Centre (HLRC) at Luleå University of Technology. Xiaofang Yang thanks the National Natural Science Foundation of China (Grant No. 20537020) for providing the possibility to perform this work in Sweden within a visiting PhD student program.

References

Competition between sodium oleate and sodium silicate for a silicate/oleate modified magnetite surface studied by in-situ ATR-FTIR Spectroscopy.

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Submitted
Title: Competition between sodium oleate and sodium silicate for a silicate/oleate modified magnetite surface studied by in-situ ATR-FTIR Spectroscopy.

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Abstract

Attenuated Total Reflection (ATR) IR spectroscopy was utilized to monitor adsorption of sodium oleate and sodium silicate onto synthetic magnetite at pH=8.5, both individually and in a competitive manner. Oleate was adsorbed within a concentration range of 0.01 mM-0.5 mM. It was observed that adsorption of oleate increased linearly with increasing concentration of oleate in solution up to a concentration of 0.1 mM. The infrared spectrum of oleate showed a broad single band at 1535 cm⁻¹ assigned to the asymmetric stretching vibration of carboxylate, implying chemisorption of oleate to the magnetite surface. The kinetics of oleate adsorption followed a pseudo first-order reaction with an apparent rate constant of \( k_1 = 0.030 \pm 0.002 \text{ min}^{-1} \). Competitive adsorption of silicate and oleate was performed either by adding silicate solution to a magnetite film initially equilibrated with 0.1 mM oleate or adding oleate solution to magnetite treated with silicate solutions in the concentration range 0.1 mM - 5mM. It was shown that silicate, within reasonable time, had only minor effect on the amount of oleate already adsorbed on magnetite. On the other hand, oleate did not efficiently compete with silicate if the latter substance was already adsorbed on the iron oxide.

Keywords: ATR-FTIR spectroscopy, magnetite, oleate, silicate, depressive effect, adsorption kinetics
1. Introduction

The agglomeration of finely ground iron ore concentrates into magnetite pellets is a complex surface chemical process involving a mixture of various components such as magnetite, bentonite, water-glass, olivine, as well as ions dissolved in the process water. In addition it may be necessary to use a collector for reversed flotation of apatite from magnetite, as is the case at Luossavaara-Kirunavaara AB (LKAB) in Sweden. This reagent is applied to minimize the apatite content by froth flotation, but a small amount of the collector may also adsorb at the magnetite particle surfaces and such a wetting modification was recently shown to affect the strength of the green pellets formed in the pelletizing process [1]. Thus, it is important to reduce the adsorption of this collector in order to further improve the strength of the pellets.

Although the chemical structure of the collector is unspecified by the manufacturer, from NMR and IR spectra of this compound it was clear that the collector contains a number of carbonyl groups, double bond(s), methyl (CH₃) and methylene (CH₂) entities (Ref. Mathias Jarlbrik´s Thesis). In this study we have used sodium oleate as a model collector molecule.

Oleate, which is a well known surfactant and collector, consists of a carboxylate head group, a hydrocarbon chain, and a double bond at the C:9 position of the C 18 alkyl chain. Attenuated total reflection (ATR) infrared spectroscopy was utilized, a technique that has been widely applied to study surface adsorption from aqueous solution onto finely dispersed solids including metal oxides [e.g. 2-8]. ATR spectroscopy has also been used to study surface reactions related to flotation [9-15]. Especially the in-situ method is advantageous since it admits the adsorbed species to be monitored while the mineral is in contact with the solution. This advantage not only allows one to acquire information regarding the nature of the species, but also the rate of adsorption can be studied in-situ i.e. in real time [3, 8-10].

The aim of the present study was primarily to investigate the adsorption properties of oleate on the magnetite particle surfaces including the adsorption kinetics and the competition
between oleate and sodium silicate for the magnetite surface. Silicate species adsorbed at magnetite will make the iron oxide surface hydrophilic, which is advantageous for the particle agglomeration process, whilst adsorbed collector would have the opposite effect. Sodium silicate (known as water glass) is one of the mostly used modifying reagents in flotation. It is well known that the speciation of silicate species in aqueous solution depends on SiO$_2$:Na$_2$O ratio, SiO$_2$ concentration, pH, temperature, and aging [16-20]. These parameters therefore play a significant role in its application in surface modification processes. Here pH was adjusted to intermediate values (8.5), close to the pH of the process water at LKAB. Polymerization of silicate is known to be more extensive at intermediate pH values than at higher pH [20].

2. Materials and methods

2.1. Materials and Reagents

Magnetite was synthesized as previously described [3, 20, 21]. The small magnetite particles implied a high surface area (97.7 m$^2$/g), which is advantageous for spectroscopic measurements and these particles were used as a model system for magnetite from the iron ore.

Sodium oleate (~99%) was obtained from Sigma. Fresh solutions of oleate were prepared by dissolving sodium oleate in water. Water glass reagent with a modulus (SiO$_2$/Na$_2$O ratio) of 3.3 was used as the silicate solution source. The water glass solutions were diluted to a desirable concentration just before the experiment. The water glass solutions were diluted to a desirable concentration just before the experiment. Analytical grade of NaOH and HCl were used for pH adjustment. Milli-Q water (Millipore corp.) was used in all stages for preparation of sodium oleate and water glass solutions and adsorption measurements.
2.2. ATR-FTIR measurements

2.2.1. Instrumentation and experimental set up

The internal reflection element (IRE) was thoroughly rinsed with ethanol and Milli-Q water before deposition of a magnetite layer. The magnetite particles were deposited over the ZnS-IRE (50 mm × 20 mm × 2 mm) by evenly spreading a few drops of an as-synthesized magnetite suspension over the crystal and drying it in a vacuum desiccator. A single sided rectangularly shaped flow through cell, made of stainless steel, was used. The cell was connected to a 250 ml reservoir containing 150ml solution via Viton tubings and the solutions were circulated through the cell at a rate of 5 ml/min [for further details, see Ref. 3]. All experiments were performed at room temperature and the reservoir was protected from air by a flow of argon. The pH value was probed during the experiment using a glass electrode. The IR spectra were recorded on a Bruker IFS 66v/S equipped with a DTGS detector and typically 350 co-added scans were recorded at a resolution of 4 cm⁻¹. Data acquisition as well as data processing and analysis were carried out by means of the OPUS software.

2.2.2. Adsorption measurements

2.2.2.1. Oleate adsorption

Milli-Q water at pH=8.5 was continuously circulated through the cell for 30 minutes before the background spectrum was collected. Afterwards, a known volume of the freshly prepared sodium oleate solution was added to the reaction vessel to acquire the desired spectra. The sample spectra were recorded using the repeated measurements facility until no significant increase in intensity of the C-H stretching frequency was observed. This was assumed to represent the adsorption maximum at the given concentration. The same procedure was repeated for oleate concentrations between 0.01 mM and 0.5 mM. Although the reported critical micellization concentration (CMC) of aqueous sodium oleate solutions varies a lot in
the literature (0.7 mM - 4.8 mM), [22, 23] the concentration range used should be below the CMC value.

A new magnetite film was deposited on the IRE for each kinetic experiment and after the background spectrum had been recorded. The background solution (Milli-Q water at pH = 8.5) was then replaced by oleate solution [further details can be found in Ref. 3].

Experiments were also performed using aqueous oleate solutions in the concentration range 0.05 mM- 0.5 mM and a bare ZnS crystal (without deposited magnetite) to make sure the observed intensity was not due to oleate adsorbed onto the bare ZnS-IRE or from oleate in aqueous solution. Only negligible IR absorption, due to oleate, was detected in these experiments.

2.2.2.2. Adsorption of water glass on oleate modified magnetite

The effect of water glass on oleate adsorption at the magnetite surface was performed as follows:

An aqueous solution of 0.1 mM oleate was equilibrated with the magnetite surface and spectra were recorded until adsorption equilibrium (ca. 80 min.), in the same way as described in section 2.2.2.1. Then, a given amount of water glass was added to obtain a silicate concentration of 0.01 mM and subsequently spectra of adsorbed silicate were monitored with time. The experiment was continued by increasing the concentration of silicate to 0.06 mM, 0.2 mM, 1 mM, and 5 mM. Spectra were recorded 75 minutes after each addition. The pH of the aqueous solutions (milli-Q water) was 8.5

2.2.2.3. Adsorption of oleate on silicate modified magnetite

A 0.1 mM aqueous silicate solution was prepared (pH = 8.5). This silicate solution was circulated for 100 minutes in contact with the magnetite surface while the spectra were collected in the same way as described under section 2.2.2.1. Subsequently, sodium oleate
was added to this solution to obtain a 0.1 mM solution with respect to oleate. This procedure was repeated with initial silicate concentrations of 0.4 mM, 1 mM, and 5 mM before adding sodium oleate (0.1 mM). The latter sequence of silicate/oleate addition is natural since silicate work both as a depressor and as a dispersing agent.

3. Results and discussion

3.1. Adsorption of oleate onto magnetite

Figure 1 shows IR spectra of oleate adsorbed on magnetite at different concentrations and Fig. 2 depicts the plot of integrated absorbance in CH stretching region (2800-3000) versus equilibrium oleate concentration in solution. As evident from Figs. 1 and 2 the adsorption increases proportionally to oleate concentration in solution. It should be noticed that the observed intensity is due to oleate adsorbed on magnetite since the adsorption onto the ZnS crystal is negligible (section 2.2.2.1) and so is absorption due to oleate in solution. A similar trend in oleate adsorption onto hematite was observed by Ofor [24], who studied oleate concentrations up to 1.07 mM. Likewise, Shibata and Fuerstenau [25] found increased oleate adsorption with increasing concentration up to $10^{-4}$ M.

The band assignments of oleate and oleic acid are well established in the literature [26]. There are four main regions in the IR spectrum of oleate which are commonly considered to determine and characterize the nature of adsorbed oleate at mineral surfaces:

Region I comprises CH stretching including symmetric and asymmetric stretching of CH$_2$ and CH$_3$ entities between 2800 cm$^{-1}$ and 3000 cm$^{-1}$ and the vinylic =C-H band above 3000 cm$^{-1}$.

The bands in this region (either the integrated absorbance over the whole CH range or only the CH$_2$ asymmetric stretching intensity) are frequently used for quantitative measurements of adsorbed organic substances [11, 27-29]. The frequency position of the asymmetric CH$_2$ stretch has also been used as indicator of the conformation of the alkyl chains [e.g. 30-33].
Figure 1. Infrared spectra of oleate adsorbed on magnetite from 0.01 mM- 0.5 mM aqueous oleate solutions. The insert shows the bulk oleate concentration in mM and spectra were shifted along the absorbance axis for clarity.

Figure 2. A plot of the integrated absorbance in the CH stretching region (2800-3000 cm⁻¹) versus equilibrium oleate concentration in solution showing a nearly linear correlation with adsorbed oleate.
Regions II, III and IV comprise the carboxylic function, where the carbonyl vibration appears around 1710 cm$^{-1}$ (II), the carboxylate asymmetric (III), and the symmetric (IV) stretching frequencies are located at about 1550 cm$^{-1}$ and 1420 cm$^{-1}$, respectively. Within the latter region (region IV) also bands due to the symmetric and asymmetric bending of methylene and methyl groups appear. The frequency distance between the two carboxylate vibrations has been proposed as an aid to distinguish between the structure of the surface complexes formed between organic acids and metal oxides [34, 35].

The CH$_2$ and CH$_3$ stretching bands are the most intense (Fig. 1) at all concentrations studied. A closer look at the frequency position of the asymmetric and symmetric CH$_2$ stretching bands at different concentrations demonstrates a shift toward lower frequency with increasing concentration up to 0.1 mM ( ~ 2 cm$^{-1}$) but becomes nearly constant at higher concentrations (Fig. 3). This behaviour indicates a decrease in the number of gauche conformers up to 0.1 mM, where after the alkyl chain packing becomes almost constant. The transfer of the alkyl chain from an aqueous environment at low concentration to a hydrocarbon environment at higher concentration could be responsible for the frequency shift.

![Figure 3. The methylene stretching region of oleate adsorbed on magnetite illustrating the shift in the position of the CH$_2$ asymmetric stretching band towards lower frequency with increasing oleate concentration.](image)
The single broad feature at 1535 cm\(^{-1}\) (Fig. 1) was assigned to the asymmetric carboxylate stretching vibration. The presence of a single broad band at this frequency is an evidence for chemisorbed oleate on metal oxide surfaces [13, 26, and 36]. The fact that significant adsorption occurs at alkaline pH (pH=8.5 in this case) which is higher than the PZC of magnetite (~6.5) support this conclusion, although PZC varies somewhat in the literature with \(pK_{a1} \sim 5\) and \(pK_{a2} \sim 8\) [37]. The weak band at 1711 cm\(^{-1}\) is assigned to the carbonyl vibration of oleic acid which is more prominent in the spectra at higher oleate concentrations. Thus, the IR band assignments together with other facts (see the next sections) provide compelling evidence that oleate at lower concentration forms mainly a chemisorbed monolayer at the magnetite surface with minor contribution from physisorbed oleate or oleate forming aggregates at the surface of the metal oxide. The latter should be more probable at oleate concentrations approaching the CMC value.

The configuration of carboxylate bonded to magnetite is determined using the frequency difference between symmetric and asymmetric COO stretching vibrations (\(\Delta\nu\)) [34, 35, and 38]. In our previous work on oleate adsorbed on magnetite using DRIFT spectroscopy [21], it was concluded that the configuration of adsorbed oleate at the magnetite surface is predominantly a chelate with a small contribution from bidentate bridging. The observed \(\Delta\nu=110\) cm\(^{-1}\) in this work (1425-1535 cm\(^{-1}\)) is less than 135 cm\(^{-1}\) obtained for non-adsorbed oleate, which supports this conclusion.

The majority of sodium oleate in solution is in the form of \(\text{Ol}^-\) at the pH and concentrations used here although other species such as \(\text{Ol}^2^-\), \(\text{HOl}^-\) and \(\text{HOl}\) may also coexist but in non-detectable concentration. However, the magnetite surface is negatively charged at this pH implying that the surface sites represent a distribution of (=FeO\(^+\)) and neutral entities (=FeOH). Oleate is therefore assumed to replace surface hydroxyl groups. The reaction might be expressed as follows:
\[ \text{[Fe(II,III)-OH]} + \text{OL}^- \leftrightarrow \text{[Fe(II,III)-OL]} + \text{OH}^- \quad (\text{OL}=\text{oleate}), \quad (1) \]

3.1.2. Kinetics of oleate adsorption onto magnetite

The kinetics was studied by in-situ monitoring the adsorption of oleate onto the magnetite surface with time. The integrated absorbance over the CH stretching range was assumed to be proportional to the amount of oleate adsorbed. Figure 4 shows the increase in adsorption with time. Assuming pseudo-first order kinetics, the following equation can be derived:

\[
\ln \left( \frac{A_m}{A_m - A_t} \right) = k_1 t, \quad (2)
\]

where \( k_1 = k_2 C_b \), is the pseudo-first order rate constant, and \( C_b \) is the concentration of oleate in the bulk, \( t \) is time, \( A_m \) and \( A_t \) are absorbances at equilibrium and at time \( t \), respectively [9, 39].

![Figure 4. Kinetics of oleate adsorption on magnetite shown as a plot of integrated absorbance in the 2800-3000 cm\(^{-1}\) region versus time.](image)

According to eq. 2, a plot of \( \ln(A_m/(A_m-A)) \) versus time might confirm first-order behaviour and from the gradient of the straight line, \( k_1 \) can be determined. As shown in Fig. 5, the reaction was confirmed to be first-order with \( R^2=0.9961 \), which demonstrates a good
correlation with first-order kinetics. An apparent rate constant of $k_1 = 0.030 \pm 0.002$ min$^{-1}$ was obtained, which was constant within experimental error for all concentrations studied (0.01 mM, 0.02 mM, 0.05 mM, and 0.1 mM).

Figure 5. A plot of $\ln(A_{\max}/(A_{\max}-A_t))$ versus time showing that the rate of adsorption of oleate onto magnetite followed a pseudo first order reaction. The straight-line is a linear least square fit of the experimental points.

It has been shown that adsorption of a number of collectors on mineral surfaces follows (pseudo)first-order kinetics with respect to availability of surface sites. Drelich et al. [13] modelled the adsorption of 10-undecenoic acid and 10-undecyionic acid on fluorite as pseudo-first-order kinetics. Free and Miller [14] used this kinetic model to fit their data on oleate adsorption onto fluorite. Fredriksson et al. [11] showed that the adsorption of heptyl xanthate on a layer of zinc sulphide also followed pseudo first-order behaviour. A similar model was used by Chiem et al. [10] for adsorption of polyacrylamide on a talc surface. Ofor studied adsorption of oleate on hematite and reported that the reaction was first order with respect to oleate concentration in bulk solution and considering the high activation energy, the chemical process was the rate determining step [40].
The good correlation between experimental data for different concentrations and pseudo-first order kinetics presented here indicates that the adsorption process at the surface controls the rate of adsorption. In this process the oleate molecules replace surface hydroxyl groups and also associated water molecules, so hydrogen bonding interaction should play an important role in the initial step. However, van der Waals interactions between hydrocarbon chains may also affect the reaction rate since already adsorbed oleate molecules should facilitate the adsorption of the next molecule close to the first one thereby possibly building islands of oleate at the surface, islands that grows with time and eventually forms a monolayer. The rate of collector adsorption is of course important in selective flotation. Since the separation of apatite from magnetite seems to work well in practice, the rate of collector adsorption onto apatite should be much larger. However, in the real process it might be more efficient to add the collector step by step since this would reduce high local concentrations of the collector in the flotation pulp. A high local concentration might imply that more of the collector is first adsorbed on magnetite and redistribution of the collector from magnetite surfaces to apatite is probably a comparatively slow process. This will be the subject of further investigations.

3.2. Adsorption of silicate onto magnetite

Figure 6 shows spectra from the adsorption of sodium silicate onto magnetite from 0.1 mM, 0.4 mM, 1 mM, and 5 mM silicate solutions at pH=8.5. As evident from these infrared spectra, the absorption bands typical for adsorbed silicate species shift to higher frequency with increasing concentration of silicate in solution. This shift caused by higher concentration was recently ascribed to the formation of condensation products between silicate species at the mineral surface [20].
Figure 6. Infrared spectra of silicate adsorbed on magnetite from aqueous solution. The insert to the right shows the bulk silicate concentrations in mM. Spectra were recorded after equilibration for 100 minutes.

The pH and concentration of silicate in addition to SiO$_2$/Na$_2$O ratio (modulus of sodium silicate), temperature, and aging are the main factors determining the properties of silicate species in solution. The distribution diagram of silicate anions in solution as a function of concentration and pH is available [20, 41, and 42]. According to equilibrium calculations at various pH, the monomers SiO$_2$(OH)$_2$$^{2-}$, SiO(OH)$_3^-$, and Si(OH)$_4$ are dominant at concentrations below 2 mM. At pH < 9, the monomer Si(OH)$_4$ is the major specie in solution. At concentrations higher than 2 mM and moderate pH (7<pH<9), however, amorphous silica will start to precipitate.

In previous contributions we studied the silicate adsorption on magnetite at different pH and concentrations [20, 43]. It turned out that the highest and strongest adsorption took place at moderate pH and high silicate concentrations where more oligomerized/polymerized silicates form at the surface. According to the literature [20, 43, 44], the formation of such species has a stronger affinity for the iron oxide surface due to contribution from many Fe-O-Si segments to the strength of adsorption.
Upon adsorption of silicate onto magnetite from a 0.1 mM solution, a prominent IR band appeared at ~950 cm\(^{-1}\). This band was assigned to FeO-Si stretching in inner-sphere bidentate monomeric surface complexes, \((\text{FeO})_2\text{Si(OH)}_2\) or \((\text{FeO})_2\text{Si(OH)}\text{O}^-\) \[20\]. Increasing the silicate concentration in aqueous solution from 0.4 mM to 5 mM implied that this band was shifted to higher wave numbers. At 0.4 mM, a new band appeared above 1000 cm\(^{-1}\), a band that grew in intensity with time. At 1 mM the strongest band was located at ~1020 cm\(^{-1}\) with two distinct shoulders at ~955 cm\(^{-1}\) and ~1120 cm\(^{-1}\). The band at ~955 cm\(^{-1}\) was attributed to bidentate monomeric surface species, whilst the bands at higher frequency viz. 1020 cm\(^{-1}\) and 1120 cm\(^{-1}\) were assigned to oligomeric and/or polymeric surface species. At 5 mM, the latter band was strongly enhanced and shifted to still higher frequency. The latter infrared absorption was suggested to be related to a three dimensional silica framework such as amorphous silica particles.

Figure 7 shows the development of the spectral feature upon adsorbing silicate onto magnetite from 0.4 mM silicate solution. The growth in intensity of the band above ~1000 cm\(^{-1}\) is clear and eventually this band became the strongest one in this spectral region. A similar trend occurred at higher concentration \(\text{viz.}\), 1 mM and 5 mM, and was described as oligomerization or polymerization of silicate at the surface with time \[43\].
3.3. Competitive adsorption between oleate and silicate for magnetite.

In the reversed flotation of apatite from magnetite, silicate is used as a dispersing agent i.e. to hinder agglomeration. The collector is preferentially adsorbed by apatite, but a small fraction is also adsorbed by magnetite. Since silicate and collector will modify the magnetite surfaces differently, the former making the surface hydrophilic whereas the latter makes it hydrophobic, it is interesting to know whether one of the species already adsorbed can be substituted for the other one. This is interesting because it is known in practise that in the agglomeration of magnetite it is advantageous to have hydrophilic magnetite surfaces. In a process such as pelletizing, the rate of substitution is also very important. To obtain information about such competitive adsorption, the influence of already adsorbed oleate on silicate adsorption was studied in order to evaluate the possibility of substitution of oleate for silicate anions. Subsequently, the substitution of already adsorbed silicate for oleate was investigated.
3.3.1. Substitution of oleate for silicate

Figure 8 shows the effect of addition of water glass to magnetite initially equilibrated with an aqueous solution of 0.1 mM oleate. It is clear from Fig. 8-a that the intensity of the methylene stretching vibrations only decreases a little upon increase of the silicate concentration, implying that silicate can not easily replace oleate at the magnetite surface. This result also supports the conclusion that oleate is chemisorbed at the magnetite surface, which was suggested in a previous section. Notice that the aqueous solution is all the time 0.1 mM with respect to oleate in these experiments.

The peak intensity due to silicate adsorption also increased with increasing silicate concentration (Fig. 8-b), which shows that an increased amount of silicate was adsorbed although magnetite had been made more hydrophobic by oleate. However, the band shape and peak positions are slightly different as compared with spectra recorded for the same time and concentration of silicate in the bulk, but adsorbed onto non-modified magnetite. This is reasonable since the environment of the adsorbed silicate species is different. For 1 mM and 5 mM silicate solutions, the peak position for the Si-O stretch at ~1020 cm⁻¹ and ~1040 cm⁻¹ from adsorbed species at the non-modified magnetite surface, is detected at about 6 cm⁻¹ to lower frequency at the modified surface, although a high frequency shift should be expected because of the hydrophobic environment. However, simultaneously the intensity of the shoulder at ~1120 cm⁻¹ is strongly diminished relative to the intensity of this shoulder for a non-modified surface. This difference in band shape and intensity of silicate absorption indicates less extensive or slower rate of polymerization of silicate when the surface of magnetite was treated with oleate. In addition, the results indicate that Si(OH)₄ units (pH 8.5) have reached adsorption sites at the magnetite surface although it was first modified by equilibration with a 0.1 mM oleate solution.
Figure 8. Addition of water glass to magnetite initially equilibrated with an aqueous solution of 0.1 mM oleate (see text): a) A plot of CH absorbance integrated between 2800 and 3000 cm\(^{-1}\) versus the bulk silicate concentration. b) Infrared spectra of silicate at different concentrations, adsorbed on magnetite pre-treated with 0.1 mM oleate solution. The insert to the right in Figure 8 b shows the bulk silicate concentration in mM. Each spectrum was recorded after equilibration for 75 minutes.
3.3.2. Substitution of silicate for oleate

Sodium silicate was first allowed to adsorb onto magnetite from various concentrations of aqueous silicate solutions for 100 minutes. For each of the so prepared magnetite-silicate surfaces, the solution was made 0.1 mM with respect to sodium oleate and this solution was continuously circulated through the flow cell monitoring the infrared spectra of oleate in situ.

Figure 9 shows the integrated absorbance of oleate in the C-H stretching region vs. the bulk silicate concentration used to modify the magnetite surface. Clearly, the amount of adsorbed oleate decreased with increasing amount of silicate on the magnetite surface, especially for magnetite prepared using silicate concentrations higher than 0.4 mM. As mentioned earlier, the pH of all solutions investigated was 8.5. The results show that oleate can adsorb on the silicate modified magnetite surface, but the extent of oleate adsorption is considerably lower above the bulk concentration where silicate species at the magnetite surface is supposed to form dimers or possibly polymers. The dimerization and polymerization of silicate at the magnetite surface seems to strengthen the attraction between silicate and iron oxide although increased surface coverage and thickness of the adsorbed silica layer may also be important.

Figure 9. Effect of water glass on oleate adsorbed onto magnetite (see text). A plot of the integrated absorbance for the CH region between 2800 and 3000 cm\(^{-1}\) versus the bulk silicate concentrations used to modify the magnetite surface.
It has been shown by others that pH and silica concentration are two important factors affecting the efficiency of water-glass as depressant in selective separation of apatite from iron oxide [44, 45]. However, at lower sodium silicate concentrations than 0.4 mM, the adsorbed silicate species seemed to work mainly as a dispersing agent [46]. Already at this low concentration, the adsorbed silicate species tend to take part in condensation reactions at the magnetite surface (Fig. 7). Increasing the silicate concentration in the bulk from 0.1 mM to 0.4 mM strongly reduced the amount of adsorbed oleate (Fig. 9), whilst the intensity from C-H stretching was only slightly reduced upon increasing the silicate concentration to 1 mM. Condensation of adsorbed silicate species seems therefore to be more efficient in order to avoid adsorption of oleate although adsorption was strongly prohibited already for magnetite treated with 0.1 mM silicate solution.

Conclusions

Competition between sodium oleate and sodium silicate for a silicate/oleate modified magnetite surface was studied at pH=8.5 using in-situ ATR-FTIR spectroscopy. This technique allowed the detection of the adsorbate from low concentrations in milli-Q water as solvent. Adsorption of oleate and silicate from aqueous solution was first studied separately. When oleate was adsorbed on magnetite, a broad infrared band was observed at 1535 cm\(^{-1}\) due to the asymmetric stretching of carboxylate, although the surface of magnetite is negatively charged at this pH (PZC \(~6.5\)). This indicated preferentially chemisorption of oleate onto the magnetite surface. The adsorption was shown to increase linearly with oleate concentration in the bulk up to 0.1 mM, with a contribution of physisorbed oleate at higher concentrations. The rate of oleate adsorption on magnetite showed a good correlation with pseudo first-order kinetics at all concentrations studied with an apparent rate constant of \(k_1=0.030 \pm 0.002\) min\(^{-1}\).
The IR spectra of silicate adsorbed on magnetite showed a continuous shift to higher frequency with increasing concentration of silicate in the bulk. At a silicate concentration of 0.4 mM, a new band appeared above ~1000 cm\(^{-1}\), a band that grew in intensity and shifted to higher frequency with time. The shift toward higher frequency was assigned to oligomerization of silicate at the magnetite surface, which might affect the depressive properties of silicate. It was shown that silicate in solution could not easily replace oleate already adsorbed at the surface although silicate was clearly adsorbed, but the polymerization/oligomerization of these silicate units were less extensive on magnetite initially treated with oleate as compared to an untreated magnetite surface. It was also shown that magnetite modified by silicate, even at low concentration, effectively reduced the adsorption of oleate from aqueous solution. Already at a silicate concentration of 0.4 mM, the amount of adsorbed sodium oleate was reduced to 10% of the amount adsorbed on a non-modified magnetite surface.

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An ATR-FTIR study of carbonate sorption onto magnetite.
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An ATR-FTIR study of carbonate sorption onto magnetite.

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Carbonate is one of the most abundant anions in ground water. It is also appearing at saturated concentration in the process water at LKAB, a mining company in the northern part of Sweden. Sorption of carbonate on magnetite (the major source of iron ore in this company) may affect the surface chemistry of the iron oxide by forming a carbonate surface instead of an oxide surface. This would affect the interactions between magnetite particles and other species dissolved in the process water. Attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) has appeared to be a useful technique to study adsorption/desorption properties of ions in mineral processing and environmental science. Magnetite was synthesized by co-precipitation of Fe II and Fe III in alkaline solution and deposited on a ZnS internal reflection element. Adsorption of carbonate on magnetite and the effect of pH, Na, Ca, and silicate ions on the amount and speciation of adsorbed carbonate was monitored in-situ. Adsorption of carbonate onto magnetite was found to increase with the acidity of the solution from pH 8.5 to pH 6.5 and increased also with increasing calcium concentration from 0 to 1.0 mM. The spectroscopy results were discussed and compared with previous findings in the literature.

Keywords: Carbonate sorption, Magnetite, ATR-FTIR, Ca ions, Silicate ions, pH, and Surface chemistry.
Introduction

Sorption of ions on iron oxide surfaces is an important phenomenon in a number of environmental and technically related processes. In aqueous systems, the surface hydroxyl groups, which indeed are the reactive parts at the iron oxide-water interface, can be replaced by other organic or inorganic anions, form hydrogen bonds, adsorb protons or cations etc. Anions and cations in turn, may have significant effect on adsorption depending on pH and concentration of metal cations and anion ligands in solution [1]. There are number of in-situ ATR spectroscopy studies on co-adsorption of anions and cations to iron oxides in the literature [2-7]. The vibrations of polyatomic anions are usually sensitive to the structure and coordination of the ion and the in-situ method is advantageous since it admits the adsorbed species to be monitored while the mineral is in contact with the solution. Calcium and carbonate ions are common constituents of industrial and natural water. Carbonate is present in the water either through dissolution of carbon dioxide from atmospheric air or from carbonate minerals. Despite the adsorption of carbonate is considered to be weak [8], at high concentration which is common in many industrial and environmental processes, it may compete with other anions for surface sites. A decrease in the isoelectric point (IEP) and a reversal of electrophoretic charge at lower pH values has been observed upon adsorption of carbonate implying specific adsorption [8, 9]. Carbonate can also affect the surface adsorption of cations and/or cosorb with dissolved metals [3, 7]. Calcium, on the other hand, may provide additional positive surface charge at the metal oxide surface, improving anion adsorption [10, 11]. Silicate and/or silicic acid are formed upon mineral weathering in most natural environments. It is also often used as surface modifying reagent in flotation processes, acting as a dispersing and/or depressing agent. The surface chemistry of magnetite, the major source of iron ore in the northern part of Sweden, has less been studied. In ore processing, magnetite undergoes a number of processes e.g. flotation and pelletization in order to produce high quality products. The water used in the process, so called process water, contains a number of inorganic ions including calcium, carbonate and silicate ions. Adsorption of these ions onto the iron oxide may alter its surface chemistry; affect the surface charge and the reactivity of the oxide as well as interactions with other components in the system, such as bentonite, which is used as binder in the pelletization process. It is well known that presence of calcium in process water could impair the swelling properties of sodium bentonite by transforming it into calcium bentonite. In order to improve the agglomeration process knowledge about the speciation in solution as well as the surface chemistry of magnetite is essential. The objectives of this study were to provide further insight into the carbonate adsorption mechanism on magnetite and the effect of pH, Na, Ca, and silicate ions on the amount and speciation of adsorbed carbonate using in situ ATR-FTIR spectroscopy. DRIFT spectra of carbonate adsorbed on magnetite were recorded ex-situ in order to compare with the in situ measurements.

Experimental

Magnetite was synthesized as previously described [2]. NaHCO₃, NaCl and CaCl₂ were of analytical grade purchased from Merck. Water glass reagent was obtained from Luossavaara-Kirunavaara AB (LKAB) in Kiruna, Sweden and used as the silicate solution source. Analytical grades of NaOH and HCl were used for pH adjustment. Milli-Q water (Millipore corp.) was used as solvent for all solutions prepared. The magnetite particles were deposited over a clean ZnS-IRE (50 mm × 20 mm × 2 mm) by evenly spreading a few drops of an as-synthesized magnetite suspension over the crystal and
drying it in a vacuum desiccator. The pH value was probed during the experiment using a glass electrode. The IR spectra were recorded on a Bruker IFS 66v/S equipped with a DTGS detector and typically 350 co-added scans were recorded at a resolution of 4 cm⁻¹. Further details and the experimental set up can be found in Ref.2. The adsorption measurements were always carried out in a closed system and by collecting a single beam background spectrum of Milli-Q water in contact with magnetite at room temperature. Subsequently, a known amount of NaHCO₃ was added to the reaction vessel to acquire the single beam sample spectra. The sample spectra were recorded continually until no further increase in intensity in the frequency range of 1000-1600 cm⁻¹ was observed. In separate experiments, a known amount of HCl, NaCl, CaCl₂ and water glass was added to examine the effect of pH, Na, Ca, and silicate ions, respectively. Data acquisition as well as data processing and analysis were made by means of the OPUS software. For comparison, a sample of magnetite powder was treated ex-situ with 10 mM aqueous NaHCO₃ solution at pH=8 for 30 minutes in a closed vessel. The suspension was then centrifuged, rinsed with Milli-Q water, and dried in a vacuum desiccator. A DRIFT (diffuse reflectance infrared Fourier transform) spectrum of this sample was recorded and subtracted from a DRIFT spectrum of untreated magnetite.

Results and Discussion

Carbonate adsorption and effect of pH

Figure 1.a shows ATR-FTIR spectra of carbonate adsorbed on magnetite from a 5 mM aqueous NaHCO₃ solution at pH=8.5-6.5 and in absence of other ions (i.e. no NaCl or CaCl₂ added). In this pH range, bicarbonate (HCO₃⁻) is the dominant specie in aqueous solution. As can seen in this figure, three regions in the frequency range 1000-1600 cm⁻¹ can be discerned in the IR spectrum of adsorbed carbonate i.e. 1000-1100 cm⁻¹, 1300-1400 cm⁻¹, and 1400-1600 cm⁻¹. According to molecular symmetry and vibrational spectroscopy, CO₃²⁻ ion has D₃h symmetry and show a doubly degenerate single band at ~1400 cm⁻¹ in the IR spectrum, assigned to CO asymmetric stretching (v₃) vibration. The symmetric stretching vibration (v₁) around 1050 cm⁻¹ is IR-inactive for a free CO₃²⁻ ion. When the D₃h symmetry is broken, for instance upon metal or H⁺ coordination, the doubly degenerate CO stretching vibration (v₃) splits into two bands and the symmetrical stretching vibration (v₁) becomes IR active [12]. The degree of splitting (Δv₁) is usually larger for a bidentate complex (C₂v) than for a monodentate complex (C₃v) and depends on the polarizing power of the cation, which is proportional to z/r² where z is the charge of the cation and r its ionic radius and therefore the polarizability is larger for Fe(II) than for Ca(II). It is also influenced by the coordination sphere of carbonate (type and number of bonds formed) [13]. It has been proposed that electric fields due to H₂O dipoles and cations external to the coordination sphere have an effect on the Δv₁ value of the carbonate ligand in metal-carbonate complexes and also that CO₃²⁻ is a highly versatile ligand which can give more complicated polydentate structures [13-15]. Based on the above discussion, the band at ~1070 cm⁻¹ was assigned to the symmetric stretching (v₁) vibration of carbonate which has become IR active due to interaction with the magnetite surface. The relatively broad band at ~1335 cm⁻¹ with a shoulder at the high frequency side (~1375 cm⁻¹) is arising from the splitting of the v₁ vibration and so are the band at ~1485 cm⁻¹ and the shoulder at ~1545 cm⁻¹, all four of them assigned to asymmetric stretching vibration of surface-associated carbonate species. The two latter bands indicate that two different carbonate-surface complexes are formed at the magnetite surface, both most likely influenced by hydrogen bonding.
It should be mentioned here that in the absence of deposited magnetite (viz. a bare ZnS crystal), no significant peaks in these regions were observed at the highest carbonate concentration used (5 mM). Moreover, the positions of the bands caused by adsorbed species differ from those in aqueous carbonate solution implying that the structure of carbonate was perturbed by surface chemical interaction. According to Yates and Dobson et al., two bands at 1560-1540 cm\(^{-1}\) and 1360-1300 cm\(^{-1}\) were observed for carbonate and carbon dioxide adsorbed on ZrO\(_2\) and TiO\(_2\) and assigned to carbonate forming a bidentate coordination \[16, 17\]. Wijnja and Schulthess \[18\] reported two bands at 1510 and 1390 cm\(^{-1}\) for carbonate adsorbed at aged \(\gamma\)-Al\(_2\)O\(_3\)/water interface, whilst Su and Suarez \[9\] attributed two bands at 1420 and 1490 cm\(^{-1}\) to carbonate adsorbed onto amorphous Al(OH)\(_3\) by forming a mono-dentate inner-sphere complex. In an extensive study of carbonate adsorption onto hematite, Barger et al. \[12\], using ATR-FTIR spectroscopy and MO/DFT (hybrid molecular orbital/density functional theory) frequency calculations, found evidence of different coexisting carbonate species at the surface. They assigned a pair of \(\nu_3\) bands at \(\sim 1477/1354\) cm\(^{-1}\) to outer-sphere hydrogen bonded carbonate species and the other pair at \(\sim 1546/1321\) cm\(^{-1}\) to inner-sphere bidentate species. A similar conclusion was made by Rahnemaie et al. \[19\] using the charge density (CD) model and MO/DFT calculations on carbonate adsorbed onto goethite, however they suggested that both the surface carbonate species were inner-sphere bidentate binuclear complexes, having two different geometries. The presence of the asymmetric bands observed in this study at \(\sim 1480\) and 1545 cm\(^{-1}\) may therefore indicate the existence of at least two different carbonate species co-adsorbed at the magnetite surface. This will be further discussed in the following sections. Moreover, the evolution of the infrared bands of adsorbed carbonate with pH was also studied (Fig. 1a). The band intensity of adsorbed carbonate increased with decreasing pH and shifted slightly in frequency resulting in a larger \(\Delta\nu_3\). With lower pH proton sorption increases thereby reducing the negative charge of the magnetite surface and hence results in a stronger interaction between carbonate and the surface. No bicarbonate (HCO\(_3^{-}\)) was detected in this pH range. Figure 1.b shows the DRIFT spectrum of carbonate adsorbed on magnetite (see also experimental section). The distinct bands at 1050, 1310, and 1545 cm\(^{-1}\) are very similar in frequency position to the ATR bands at 1070, 1335, and 1545 cm\(^{-1}\). No band corresponding to the one at \(\sim 1480\) cm\(^{-1}\) in the ATR spectrum was detected in the DRIFT spectrum although a weak band seemed to appear at lower frequency (\(\sim 1450\) cm\(^{-1}\)). This band might therefore be due to more loosely bound carbonate which had been affected by the rinsing and drying the sample before DRIFT measurement. The band at \(\sim 1155\) cm\(^{-1}\) was assigned to surface-OH functions \[12\].

**Effect of Ca on carbonate adsorption**

The effect of Na (spectra not shown) was found to be negligible or very small (compare to Ca) even up to concentrations as high as 0.1 M NaCl and at pH=8.5. In contrast, Ca ions considerably enhanced carbonate adsorption onto magnetite at pH=8.5. Fig. 2 presents ATR-FTIR spectra of carbonate adsorbed onto magnetite from aqueous 1 mM NaHCO\(_3\) solution at pH=8.5 and without CaCl\(_2\) as well as in presence of 0.1, and 1mM CaCl\(_2\). All carbonate bands at \(\sim 1070, \sim 1335, \sim 1375, \sim 1480,\) and 1545 cm\(^{-1}\) increased in intensity with Ca concentration. At 1 mM CaCl\(_2\) the intensity of the carbonate band was about the same as for a 5 mM aqueous NaHCO\(_3\) solution without Ca ions. However, the band intensity at \(\sim 1545\) cm\(^{-1}\) was more strongly enhanced compared to the other \(\nu_3\) bands, which indicates that the fraction of carbonate complexes causing this band increased. It was also noticed that the \(\nu_3\) bands at 1335 and 1473 cm\(^{-1}\) shifted to 1345 and 1495 cm\(^{-1}\), respectively, with increasing Ca concentration. Depending on pH, Ca\(^{2+}\) has been proposed to adsorb as a combination of outer-
and inner-sphere bi- or mono-dentate complexes on iron oxide [20]. Furthermore, it seems reasonable to assume that Ca sorption reduces the negative surface charge of magnetite at pH=8.5, which is above the PZC of magnetite (~6.5), and therefore creates more favourable condition for carbonate ions to approach the magnetite surface. Calcium ions are supposed to preferentially attach at Fe-O\(^{2-}\) sites of the surface. In addition, interaction between carbonate adsorbed on magnetite and Ca ions at adjacent surface sites as well as adsorption of calcium carbonate ion pairs may form ternary complexes at the iron oxide surface [see e.g. 3, 5, and 7]. Irrespective of the exact mechanism by which Ca enhances carbonate adsorption on magnetite, the presence of Ca\(^{2+}\) and CO\(_3^{2-}\) in the process water at LKAB will certainly influence the surface properties of the magnetite particles. With reference to previous work (see references above) it seems reasonable to suggest that the 1545 cm\(^{-1}\)/1335 cm\(^{-1}\) pair is due to inner-sphere bidentate binuclear complexation with iron atoms whilst the 1480/1375 cm\(^{-1}\) pair is caused by complexation with iron or calcium atoms although carbonate should prefer Fe because of lower solubility product and its higher polarizability and electronegativity. The latter structure seems to be influenced by hydrogen bonding and is more loosely bonded to the magnetite surface.

**Effect of silicate on carbonate adsorption**

Figure 3 shows the effect of sodium silicate (water glass) addition on the infrared spectra of adsorbed carbonate on magnetite in presence and absence of Ca ions. Water glass was added to aqueous solutions of 5 mM NaHCO\(_3\) (the results of adding 0.5 mM CaCl\(_2\) to this solution is shown in Fig. 3 d, e) and allowed to be equilibrated with magnetite at pH=8.5. With increasing concentration of silicate from 0-0.1 mM (Fig. 3 a-c), the band intensity of carbonate at ~1480 cm\(^{-1}\) (representing more loosely bound carbonate) was reduced more strongly than the intensity of the band at ~1545 cm\(^{-1}\). Interestingly, a similar trend occurred when 0.1 mM silicate was added under the same conditions but in presence of 0.5 mM CaCl\(_2\) (Fig. 3d-e). This might imply that silicate ions more readily desorb the loosely bound carbonate. Barger et al. [12] assigned the “loosely bound carbonate” to outer-sphere complexes. In an alternative approach using the CD model [19], accumulation of negative charge near the surface was proposed to favour inner-sphere bidentate carbonate complexes on goethite. However, in those approaches Ca ions were not included in the system.

**Conclusion**

ATR-FTIR spectroscopy was utilized to study carbonate adsorption onto magnetite. The asymmetric stretching CO bands at ~1485 and 1545 cm\(^{-1}\) in the spectrum of carbonate adsorbed onto magnetite were assigned to two different carbonate species coexisting at the surface. It was noted that lowering pH from 8.5 to 6.5 increased carbonate adsorption. Besides, addition of Ca was shown to significantly enhance carbonate adsorption at pH=8.5. On the other hand, competition between silicate and carbonate for the surface sites resulted in a decrease of the band at ~1485 cm\(^{-1}\), indicating desorption of loosely bound carbonate.

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References

Figure Captions

Figure 1. a) ATR-FTIR spectra of carbonate adsorbed from 5 mM NaHCO₃ aqueous solution onto magnetite surface at pH=8.5-6.5. b) DRIFT spectrum of adsorbed carbonate on magnetite.

Figure 2. Infrared spectrum of adsorbed carbonate as a function of Ca concentration. The CO₃²⁻ solution concentration was 1 mM at pH=8.5 in all three cases and Ca concentrations are shown in the figure.

Figure 3. ATR-FTIR spectra showing the effect of SiO₂ addition on carbonate sorption onto magnetite at pH=8.5. The CO₃²⁻ solution concentration was 5 mM in all cases and a) 0 mM, b) 0.01 mM, and c) 0.1 mM sodium silicate; d) 0.5 mM CaCl₂ e) 0.5 mM CaCl₂ and 0.1 mM sodium silicate.
Fig. 1
Fig. 2

Fig. 3