



Sorption of ⁶⁰Co onto bentonite clay

Master's thesis in Innovative and Sustainable Chemical Engineering

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Images are created by the author unless stated otherwise Cover image: scintillation vials with radioactive water and fluor that are to be analysed through liquid scintillation counting.

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Abstract

Spent nuclear fuel is highly radioactive, warranting adequate methods of disposal. In Sweden, SKB is constructing a final repository in Forsmark, which utilises several barriers to prevent any radioactive material from reaching nature or society. The spent fuel, held in place by ductile iron cartridges, is placed inside copper canisters, which are surrounded by bentonite clay in bedrock tunnels situated 500 metres underground. In the event of a canister breaking, it is important to know the behaviour of the radioactive material as it spreads. Earlier experiments, performed by SKB and at Chalmers University of Technology have studied the diffusion of the radionuclide ⁶⁰Co in bentonite to find the rate of spread of the active substance. One aspect of the diffusion process is the amount of cobalt that sorbs onto the clay. By studying the sorption through the distribution coefficient, R_d , the diffusion mechanism can be better understood.

In this thesis, the distribution coefficient has been studied for 60 Co onto bentonite clay, by means of batch sorption in simulated groundwater, as well as water with NaClO₄ and Ca(ClO₄)₂, at 25 °C, 50 °C and 75 °C for a period of circa two months. Samples were prepared at a solid to liquid ratio of 1:20 and the activity of the samples was measured with increasing time intervals through liquid scintillation counting. Long-term equilibrium was reached after approximately 30 days for all samples. The studied parameters, temperature and water composition, were determined to both have a significant impact on the sorption process, where temperature and ion diversity displayed positive and negative correlation, respectively, to 60 Co-sorption onto bentonite. Distribution coefficient values at room temperature ranged between approximately 0.28-0.63 m³/kg at 25 °C, 1.04-2.97 m³/kg at 50 °C and 2.87-7.41 m³/kg at 75 °C.

Keywords: Cobalt, Bentonite, Batch sorption, Repository, Distribution coefficient

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Glossary

Abbreviations

ANOVA	Analysis of variance
BET	Brunauer, Emmett and Teller (surface area analysis model)
BJH	Barrett, Joyner and Halenda (pore size analysis model)
DFT	Density functional theory
KBS-3	Nuclear fuel safety (Kärnbränslesäkerhet-3)
LOT	Long term test of buffer material
LSC	Liquid scintillation counting
MOX	Mixed oxide (fuel)
SKB	Svensk Kärnbränslehantering AB

Glossary

Isotope	Refers to the atomic variant with the same amount of protons as a certain chemical element, but varying number of neutrons.
Neutrino	Neutrinos and their corresponding antimatter components, antineutrinos, are subatomic particle without electrical charge and very light weight that are a part of radioactive decay.
Nucleus	The core of the atom constituted by protons and neutrons.
Positron	Antiparticle of the negatively charged electron. Identical in mass, but the exact opposite in charge.
Radionuclide	An unstable isotope undergoing radioactive decay by emission of e.g. α , β , or γ radiation.

1

Introduction

1.1 Background

According to the International Energy Agency (IEA), nuclear power is a low-carbon electricity producer, which produces approximately 10 % of the world's total electricity supply. In 2018, this amounted to 2700 TWh. Nuclear energy has in recent years receded in usage in many countries where nuclear power plants have been shut down and investments in the energy source have been reduced. While there are countries still expanding their nuclear power capacity, the general trend is on a downward trajectory in favour of other renewable energy sources (IEA, 2019). In Sweden, nuclear power accounted for approximately 39 % of the generated electricity in 2019, making it the largest source of energy along with hydropower (SCB, 2021). There are six nuclear reactors currently in operation in Sweden in Forsmark, Oskarshamn and Ringhals, with two other reactors having shut down in 2017 and another two in 2019 and 2020, respectively. However, the operating reactors are set to cease energy production in around year 2040 (Strålsäkerhetsmyndigheten, n.d).

Waste from nuclear power plants can be sorted into long or short-lived and low, intermediate or high activity categories. Short-lived waste is described by the Swedish National Council for Nuclear Waste (Kärnavfallsrådet) as having lost its radioactivity after a few hundred years and may come in the form of low or intermediate activity level, such as contaminated garbage, used radiation protection clothing, filters, etc. Low or intermediate activity long-lived waste mainly consists of the inner parts of the reactor that have been heavily neutron-activated, whereas highly radioactive waste is composed primarily of spent nuclear fuel, which needs to be isolated from the biosphere for at least 100 000 years (Kärnavfallsrådet, n.d.). Between 15-25 tonnes of spent nuclear fuel is produced every year in Sweden (SKB, 2020). Today, Sweden has about 7000 tonnes of spent nuclear fuel.

The main constituents of spent nuclear fuel are a variety of radioactive isotopes that emit ionising radiation, which can cause damage to living cells and DNA, and as such require appropriate disposal management to avoid contact with living organisms for as long as the waste remains radioactive. In the current method, bundles of spent nuclear fuel rods, fuel assemblies that have been used in the reactor are transported under water to so called spent fuel pools at the nuclear power plant (USNRC, 2020). After allowing the activity of the spent fuel to subside for at least a year, the fuel is eventually moved, as the pool capacity is finite. In Sweden, the fuel is moved to an intermediate storage in Oskarshamn known as Clab (*Centrala mellanlagret för använt kärnbränsle*), where it is stored for 30 years in pools situated in cave rooms in order to reduce the radioactivity further (Strålsäkerhetsmyndigheten, 2018) As the

spent fuel still contains long-lived highly radioactive isotopes, such as ²³⁸Pu, ²³⁹Pu and ²⁴¹Am (Choppin et al., 2013), the SKB company is planning to construct a final repository close to the Forsmark nuclear power plant in Sweden. The methodology behind the repository, denominated KBS-3 (Kärnbränslesäkerhet-3), involves the storage of nuclear fuel inside ductile iron cartridges that are placed within a five meter tall copper canisters, which are subsequently stored in tunnels built in the bedrock, 500 metres underground. The copper canisters are to be surrounded by rings and blocks of a barrier material, bentonite clay, which in turn is enclosed by the bedrock. Once the canisters are installed in the tunnels, the repository will be closed off and groundwater allowed to flow into the area. Using bentonite clay as a barrier material is desirable as it will attenuate the spread of radionuclides in case of a defective canister as they will sorb onto and diffuse through the pores of the material. The clay also absorbs water, causing it to swell, which protects the copper canisters from movements in the rock, while also preventing corrosive substances in the groundwater from reaching the canisters. The KBS-3 method is designed to prevent any migration of radioactive material to where it may cause harm to the environment and human life for at least 100 000 years (SKB, 2016). A schematic image of the SKB repository barriers can be found in figure 1.1.



Figure 1.1. The proposed barriers involved in the final repository SKB is constructing. Spent nuclear fuel, is placed inside ductile iron cartridges encased by a copper capsule, surrounded by bentonite clay inside the bedrock 500 metres underground. Figure is based on (SKB, 2016).

In a scenario where a copper canister would be damaged and break, causing the radioactive substances to leak out and potentially come into direct contact with groundwater, via the bentonite clay, it is important to be able to estimate the release rate from the bentonite. The radionuclide ⁶⁰Co is used in research performed by SKB for studying the integrity of bentonite as a buffer material over an extended time (about 20 years) at Äspö, near Oskarshamn (Karnland et al., 2009). Those results have been reported elsewhere, for example in the work by Beckius (2020). In the project presented here, the sorption of ⁶⁰Co onto bentonite over a limited time (about 1 month) is studied experimentally, using bentonite from the Äspö experiments, in order to find the distribution coefficients (*R*_d-values) for some different experimental conditions, which describe to what extent sorption has occurred. In order to measure *R*_d-values, the adsorbing medium must initially be free from the adsorbing substance.

This thesis can therefore be seen as complementary to the testing at Äspö (Karnland et al., 2009), as well as a master's thesis on the evaluation of diffusion of ⁶⁰Co in the Äspö tests conducted at Chalmers University of Technology (Beckius, 2020).

1.2 Purpose

This thesis aims to study the sorption of ⁶⁰Co to bentonite clay from different types of simulated groundwater, by finding the distribution coefficients at different temperatures and studying how it changes over time. The purpose is to be able to better understand the diffusion process of cobalt radionuclides in the water saturated bentonite clay, which have been evaluated by Beckius (2020). The latter work evaluated the apparent diffusivity (D_a) of ⁶⁰Co from the long-term Äspö in-situ experiments, but due to the experimental design, gave no value for the sorption coefficient. The present work utilises instead the traditional batch sorption laboratory method and can therefore be seen as a complementary study to Beckius (2020).

1.3 Delimitation

The project is limited to analysis of the sorption with variation in mainly two parameters 1) the type of dominating cationic ions in the water solutions, Na or Ca, and 2) temperature. The experiments were conducted at 25 °C, 50 °C and 75 °C. Three types of water solutions were used, firstly a water solution in accordance with data on the water composition around Äspö Hard Rock Laboratory. The other two solutions were Na and Ca perchlorate electrolytes of corresponding ionic strength. The total time for testing each batch was limited to a maximum of three months, but for some batches the test period was shorter.

2

Theoretical background

2.1 Bentonite

Bentonite is a type of rock, containing high amounts of swelling clay minerals, belonging to the group of phyllosilicate mineral species known as smectites. Smectites swell when exposed to water and subsequently shrinks once dried. The mineral consists of a 2:1 layer structure, which involves repeating sheets of the pattern T-O-T, where a sheet that is octahedrally (O) coordinated by an aluminium cation (Al³⁺) is enclosed by two, by silicon cations (Si⁴⁺), tetrahedrally (T) coordinated sheets, connected through oxygen atoms. The silicon and the aluminium may be substituted by other cations with valence of lower positive charge, resulting in a net negative charge of the layers and in turn, the bentonite surface. This charge is balanced by cations, generally K⁺, Na⁺ or Ca²⁺ being inserted in between the T-O-T layers, in the so called interlayer region. The swelling properties of bentonite clay, however, is associated with sodium ions being the predominant cation in the interlayer region. The layers are held together by weak van der Waals forces, which allows for a distance to be asserted by water molecules entering the interlayer region, thus causing swelling (Nesse, 2000). This swelling ability, as well as the general inexpensiveness of bentonite clay makes it a desirable material for various engineering purposes, including as an adsorbent for nuclear fuel repositories.

Dry bentonite has an interlayer distance of 10 Å, whereas bentonite with two layers of water molecules, displays an interlayer distance of 15.2 Å (Nesse, 2000). The clay particles are separated by free pores, with a diffuse double layer of high cation concentration located close adjacent to the clay particle surface (Appelo, 2013). A representative overview of the bentonite structure with regard to the layers, interlayer and pore structure is given in figure 2.1.



Figure 2.1. Representative overview of bentonite clay particles with tetrahedral (T) and octahedral (O) layers, as well as the diffuse double layer and free pore system.

The predominant cation in the interlayer region is used to denominate the type of bentonite, i.e. bentonite with high amounts of sodium cations between the layers is called Na-bentonite. The main type of smectite in bentonite is called montmorillonite. Other components of the bentonite may be other clay minerals, quarts, gypsum, pyrite, feldspars and amorphous and organic compounds, of which prevalence and quantity varies by geography due to the geochemical conditions that affected the formation of the bentonite (Jönsson et al., 2009). The general structure for montmorillonite, the main constituent responsible for the swelling properties in bentonite, can be described by the following formula:

$$M_{y}^{+} \cdot nH_{2}O\left(Al_{2y}Mg_{y}\right)Si_{4}O_{10}(OH)_{2}$$

where M is the balancing cation in the interlayer region and n the amount of water molecules between the layers (Odom, 1984).

2.2 Radioactivity

Radioactive decay is a phenomena displayed by certain unstable isotopes of elements that have unstable nuclei and thereby emit particles or electromagnetic waves from the nucleus in order to reach a lower, and thus more stable, energy state. The three main modes, by which this decay occurs, are through α -, β - and γ -decay. α -decay entails the emission of a helium nucleus, i.e. two protons and two neutrons, see the reaction in equation 2.1.

$${}^{A}_{Z}X \to {}^{A-4}_{Z-2}Y + {}^{4}_{2}He$$
 (2.1)

Where *X* is the original isotope, *Y* is the isotope product, *A* represents the mass number and *Z* the number of protons. The second type of decay, β -decay, occurs by three modes: 1) electron emission, in which a neutron is converted to a proton by the emission of an electron and an antineutrino, 2) positron emission, whereby a proton is turned into a neutron by emittance of a positron and a neutrino and 3) electron capture (EC), whereby a proton captures an electron from the electron shell, turning into a neutron and sending out a neutrino. The two first modes involves the emittance of a high energy particle (electron or positron) known as a β -particle (Choppin et al., 2013), while the EC mode usually only emits X-rays from the rearrangements within the electron shell. The three modes can be viewed in the three reactions in equations 2.2, 2.3 and 2.4, respectively.

$${}^{A}_{Z}X \to {}^{A}_{Z+1}Y + {}^{0}_{-1}e + \overline{v_{e}}$$
 (2.2)

$${}^{A}_{Z}X \to {}^{A}_{Z-1}Y + {}^{0}_{+1}e + v_{e}$$
(2.3)

$$e^- + {}^A_Z X \to {}^A_{Z-1} Y + \nu_e \tag{2.4}$$

 γ radiation is electromagnetic radiation of high energy, emitted from the nucleus as a result of de-excitation that has taken place by e.g. α - or β -decay. The energy of the emitted γ -ray(s) thus make up the remaining difference in energy between the high and low energy states of the nucleus (see figure 2.2). As different isotopes decay by different modes, which display different energies (commonly measured in electronvolt (eV)), these modes can form a decay pattern characteristic of the specific isotope. Furthermore, as unstable isotopes may decay into other unstable this can form distinctive chains of radioactive decay. One such example is the decay chain of ²³⁸U, where it, in many steps, decays until it reaches the stable isotope ²⁰⁶Pb. Another characteristic feature for a particular unstable isotope is its half-life, denoted *t*_{1/2}, which is the time required for the isotope to decay to the point where only half the original amount is remaining.

2.2.1 Cobalt radionuclide

Cobalt (Co) is the 27th element in the periodic table. It has one stable isotope, ⁵⁹Co, and several unstable radioisotopes, where ⁶⁰Co has the longest lifetime, with a half-life of 5.27 years. ⁶⁰Co is not present to any larger extent in spent nuclear fuel. In nuclear waste, it is mainly present as a neutron activation product from the metallic walls of the nuclear reactor (Carbol et al., 1997). It has been used as the tracer radionuclide of choice in the SKB *long term test of buffer material* (LOT) experiments, carried out by Karnland et. al. (2009) because of its easily detected gamma radiation and its convenient half-life.

The decay pattern of ⁶⁰Co can be seen in figure 2.2 and involves a β^{-} decay of relatively low energy to an excited state of ⁶⁰Ni, followed by a subsequent cascade of two high-energy γ -emissions of characteristic energy (Choppin et al., 2013)



Figure 2.2. Decay pattern of ⁶⁰Co to ⁶⁰Ni, characterised by a β -decay, succeeded by two γ -decays.

2.3 Sorption

Sorption is the process by which one substance attaches itself to another. The mode of sorption will fall under the category of either absorption or adsorption. Absorption involves a substance (absorbate) entering the bulk phase of a different substance (absorbent), e.g. a liquid entering a pore system of a solid or a water-soluble pollutant in air dissolving in water when contacted. Adsorption, however, refers to particles (adsorbate) attaching specifically to the surface of a material (adsorbent) (Atkins, 2013). The opposite of sorption is desorption, the process of one substance detaching from the other.

2.3.1 Batch adsorption

As described by the United States Environmental Protection Agency (1992), batch adsorption, or static-equilibration technique, is a method used to study the capacity of soils or to remove components from a solution by means of a soil. The experimental method is simple as it merely involves the mixing of a solution of known parameters with the adsorbent for a time period. The two phases may then be separated through centrifugation, whereupon the remaining concentration of solutes in the solution can be used to determine how much sorption has occurred. Ratio between soil and solution should be appropriate for the studied system, i.e. adhere to the adsorption capacity of the adsorbent or to the desired conditions to study. Additionally, despite the experimental simplicity of the batch adsorption method, there are a bevy of experimental parameters to consider, e.g. temperature, manner of phase contacting, moisture content of the adsorbent, equilibrating of adsorbent, pH of the solution, solute concentration, other solutes present in the solution, contact time, etc. (EPA, 1992)

2.3.2 Sorption mechanisms

This thesis exclusively studies sorption of cobalt onto bentonite. Khan (2003) details that the mechanisms by which Cobalt may sorb to bentonite clay are twofold: 1) ion exchange in the interlayer region and 2) by complex formation with the bentonite surface edge sites. The ion exchange mechanism involves exchanging another ion, e.g. Na^+ with Co^{2+} , this reaction can be explained by equation 2.5.

$$2(\equiv S - O^{-})(M^{+})_{hyd} + (Co^{2+})_{hyd} \leftrightarrow (\equiv S - O^{-})_{2}(Co^{2+})_{hyd} + (M^{+})_{hyd}$$

$$(2.5)$$

Where *S* is the silicon or substituted atom in the second outermost layer of the bentonite and *M* is the cation in the interlayer region. The index "*hyd*" indicates that the cations retain their hydration shell and are thus not chemically bonded to the surface group(s). As cobalt is a divalent ion it will bind also to a second surface site in to the layer. Potentially, this physical form of sorption could be reduced by increasing the ionic strength or diversity of cations in the water solution, as it would increase the competition between the cobalt and the other present ions. Yu et al (2006) studied the impact of the ionic strength of Co sorption onto bentonite in a sodium nitrate (NaNO₃) water solution with regard to cobalt sorption. This study yielded that the sorption, was higher at NaNO₃ concentrations of 0.01-0.1 M, but essentially independent of ionic strength between 0.5 and 2 M. Additionally, Ozsoy et al. (2015) found that sorption of NaCl from 0-0.1 M, likely due to cation competition increasing from nil to 0.1 M. A certain pH dependency of this mode of Co²⁺ binding onto bentonite surface is also expected, but only at very low pH values. Protons will then be in such abundance that they can compete with Co²⁺ for the ion exchange sites.

The second form of sorption according to Yu et al. (2006) and Khan (2003) is surface complexation, which involves direct chemical complexation between the clay mineral surface edge sites and Co, which can be described by the reactions in equations 2.6 and 2.7.

$$(\equiv S - O^{-})_{2} + (Co^{2+})_{hyd} \leftrightarrow (\equiv S - O)_{2} - Co + xH_{2}O$$

$$(2.6)$$

$$(\equiv S-OH)_2 + (Co^{2+})_{hyd} \leftrightarrow (\equiv S-O)_2 - Co + 2H^+ + xH_2O$$

$$(2.7)$$

Equation 2.6 corresponds to higher pH circumstances, where surface groups are de-protonated. Khan (2003) and Yu et al. (2006) found that, at high pH, an addition of a hydroxide group from water from the hydration shell to the cobalt may also occur in accordance with the reactions in equations 2.8 and 2.9 in sequence.

$$(\mathrm{Co}^{2+})_{\mathrm{hyd}} + \mathrm{H}_{2}\mathrm{O} \rightarrow (\mathrm{Co}\mathrm{O}\mathrm{H}^{+})_{\mathrm{hyd}} + \mathrm{H}^{+}$$

$$(2.8)$$

$$\equiv S - O^{-} + (CoOH^{+})_{hyd} \leftrightarrow \equiv S - O - CoOH + xH_2O$$
(2.9)

It was found by Khan (2003), through studying the sorption at varying pH, that surface complexation (equation 2.6 and 2.7) is predominant at pH higher than 6-7, and that the ion exchange (equation 2.5) was the main form of sorption at pH below 6-7. Equation 2.7 shows that an increased proton concentration will desorb Co from the surface complexation sites. This is in contrast with the ion exchange type of reaction in equation 2.5, which is essentially pH-independent in normal groundwater pH range (pH 6-9) and only desorb Co at very low pH. It was also determined by Khan (2003) that complexation through addition of a hydroxide group

(equations 2.8 and 2.9) is predominant at pH 10 and above. Altogether, this indicates that a high pH-dependency is involved in the sorption of cobalt to bentonite.

2.3.3 Sorption coefficient

The fundamental basis for deriving the sorption coefficient, R_d , is the equilibrium reaction describing a certain species, A, adsorbing onto a solid, S, to form the adsorbate-adsorbent complex, AS, as portrayed in equation 2.10.

$$A + S \leftrightarrows AS \tag{2.10}$$

The reaction in equation 2.10 yields the equilibrium constant, K, as following:

$$K = \frac{[AS]}{[A][S]} \tag{2.11}$$

If the number of sorption sites on the adsorbent are assumed to be limited, described by S_0 , and that no more than a monolayer is allowed to adsorb onto it, the expression in 2.11 can be expressed as in equation 2.12, which is equivalent to the Langmuir isotherm.

$$K = \frac{[AS]}{[A]([S]_0 - [AS])}$$
(2.12)

From this, Andersson et al. (2008) defines the distribution constant, K_d , through equation 2.12, under the assumption that $[S]_0 \gg [AS]$, i.e. that the number of sorption sites are in excess compared to the number of adsorbed species, which yields equation 2.13.

$$K_d \equiv K \cdot [S]_0 = \frac{[AS]}{[A]} \tag{2.13}$$

 K_d is, as such, an expression for how much adsorbent is located in the solid phase versus in the liquid phase. However, as a sorption process, for a species diluted in an aqueous phase, generally involves more than the direct sorption of the free species A onto the solid as other species also contain A, such as the reaction described in equation 2.9, they also need to be taken into account. Therefore, a distribution coefficient, R_d , can be defined in accordance with equation 2.14 (Andersson et al., 2008).

$$R_{d} \equiv \frac{[A]_{ads}}{[A]_{aq}} = \frac{[AS] + [AXS] + [AYS] + \dots}{[A] + [AX] + [AY] + \dots}$$
(2.14)

Where $[A]_{ads}$ is the total concentration of species A in the solid, $[A]_{aq}$ is the total concentration of A in the aqueous phase and the components *X* and *Y* are other species which have reacted or aggregated with A. Furthermore, the distribution coefficient is commonly described in terms of m³/kg as the concentration in the solid phase is measured indirectly, based on how much of A is left in the aqueous solution. Hence, *V*, which is the volume of the solution and the mass of the solid, *m*, must be included. As such, R_d can be described by the following equation (Andersson et al., (2008))

$$R_d = \frac{A_{ads}}{A_{aq}} \frac{V}{m}$$
(2.15)

As the batch sorption is, in this thesis project, carried out in centrifugation tubes, the walls of the tubes act as secondary solid material to which the cobalt may sorb onto. Therefore, reference samples without bentonite must be used and a term accounting for this sorption must be added into the calculations. For this purpose, the L_d values is used.

$$L_d \equiv m_{wall} R_{d,ref} \tag{2.16}$$

Note that the L_d value, which has the unit of volume, is collected in the separate wall sorption experiments, and it is not necessary to know m_{wall} and R_{ref} separately.

A reference without the wall sorption being a factor is also needed, which is accomplished by the addition of acid to another sample without solid material present. The concentration of this acidic reference, C, can then be used to determine the concentration in the stock solution. Andersson et al (2008) develops an equation for R_d expressed in measurable variables. The starting point is the two mass balances for a tube with solid phase and a tube without solid phase, the latter called (wall) reference:

$$C \cdot V_{stock} = A_{aq} + A_{solid} + A_{wall} + \sum_{i=1}^{n-1} A_{sample,i}$$

$$(2.17)$$

$$C \cdot V_{stock,ref} = A_{aq,ref} + A_{solid,ref} + A_{wall,ref} + \sum_{i=1}^{n-1} A_{sample,ref,i}$$
(2.18)

 V_{stock} is the volume of radioactive nuclide added to each tube, A_{aq} , A_{solid} and A_{wall} is the amount of A in aqueous, solid and wall phase, respectively. The summation term accounts for the mass loss at sampling occasion *n* because of the samples taken out from all previous *n*-1 sampling occasions. After some algebra, Andersson et al. (2008) arrives at the following equation for R_d

$$R_d = \left(\frac{C \cdot V_{stock} \cdot V_{sample,n}}{A_{sample,n}} - \left(V_0 - \sum_{i=1}^{n-1} V_{sample,i}\right) - L_d - \frac{V_{sample,n} \cdot \sum_{i=1}^{n-1} A_{sample,i}}{A_{sample,n}}\right) \frac{1}{m}$$
(2.19)

 L_d is the wall sorption term defined in equation 2.16. The term should give an appropriate correction for wall sorption, granted that the pH is exactly the same in tubes with and without solid sample. The other variables in the equation are directly measurable: V_0 is the starting total volume in tubes with solid, which may be slightly more than the added volume of radioactivity V_{stock} . $V_{samples,i}$ and $A_{samples,i}$ are the volume and measured radioactivity, respectively, of sample taken out at sampling occasion, *i*. The wall sorption factor L_d can also be expressed in measurable quantities

$$L_{d} = \frac{C \cdot V_{stock,ref,V_{sample,ref,i}}}{A_{sample,ref,i}} - (V_{0,ref} - \sum_{i=1}^{n-1} V_{sample,ref,i}) - \frac{V_{sample,ref,n} \sum_{i=1}^{n-1} A_{sample,ref,i}}{A_{sample,ref,n}}$$
(2.20)

The quantities are defined just as in the equation 2.19 for the main experiment with solid phase, but here with the index *ref* indicating the wall reference experiment, without solid phase

According to equation 2.14, R_d -values are coefficients and not like K_d , which are constants, the latter which, under ideal conditions, only depend on temperature. R_d values are therefore highly dependent on the experimental conditions (pH, ionic strength, other elements and ligands in solution, etc.). Moreover, the R_d values are highly dependent on the available surface area of the sorbent. If the sorbent is porous, which is the case with most rock types and minerals, the absorbing substance must first diffuse into the pore system until it has distributed itself in all the pores. Therefore, the initially measured R_d -values are apparent R_d -values and are expected to vary through the course of the batch sorption experiments, but eventually settle at a long-term stable value reached equilibrium.

2.4 Analytical methods

In this thesis, two analytical methods are used. The first method, utilising gas adsorption, is used for the bentonite specific surface area (in m^2/kg) and porosity. The second analytical method is liquid scintillation counting, which is utilised to determine the count rate of the radioactivity in the ⁶⁰Co sorption experiments. The knowledge of the sorbents specific surface area and porosity is important for normalising the results from the sorption experiments, in order to make them comparable to other studies.

2.4.1 Surface area & porosity measurements by gas adsorption

A common method of measuring the surface area, S_g , of an adsorbent is through the adsorption of nitrogen gas onto the adsorbent. Usually, this follows a model, put forth by Brunauer, Emmett and Teller (BET), which accounts for the formation of multilayers of gas molecules in the adsorption process. The equation for the BET model is shown in equation 2.21, as described in Seader et al., 2010), and it operates under the assumption that the adsorption heat of forming a monolayer on the adsorbent is constant, while the heat of condensation is related to the following layers.

$$\frac{P}{v(P_o - P)} = \frac{1}{v_m c} + \frac{(c - 1)}{v_m c} \left(\frac{P}{P_o}\right)$$
(2.21)

Where P_0 is the vapor pressure of the adsorb ate at the test temperature, P is the total pressure, v is the total gas volume adsorbed at 0 °C and 760 mmHg (standard room temperature, STP), c is the constant accounting for the heat of adsorption and v_m is the volume of one monolayer gas adsorbed at STP.

Instruments testing according to BET theory generally operates at the boiling point of N_2 (-195.8 °C. The BET area is evaluated at relative pressures from 0 to 0.2. Experimental values

for adsorbed gas volume is plotted as a function of P through equation 2.21 whereupon v_m and c are determined from the slope and intercept. From v_m the surface area can then be calculated according to equation 2.22 (Seader, et al., 2010).

$$S_g = \frac{\alpha v_m N_A}{V} \tag{2.22}$$

The volume of gas per mole at STP is, in the equation, represented by *V* and is equal to 22400 cm³/mol. *N*_A is Avogadro's number, equal to $6.023*10^{23}$ molecules/mole and α is the mean surface area per adsorbed molecule, which is calculated according to equation 2.22 if the assumption that spherical molecules are arranged in close two-dimensional packing is applied.

$$\alpha = 1.091 * \left(\frac{M}{N_A \rho_L}\right)^{\frac{2}{3}}$$
(2.22)

M is the molecular weight of the adsorbate and ρ_L is the density of the adsorbate. For N₂ the commonly used value for α is 16.2 Å². However, Thommes et al. (2015) recommends caution using BET, especially in the presence of micropores in the material and emphasises that it should be used as a "fingerprint" of a certain material rather than the actual accessible area for sorption. Regarding the measuring of pore size, Thommes et al. (2015) describes the usage of the modified Kelvin equation, as proposed by Barrett, Joyner and Halenda (BJH), for measuring the pore size in a mesoporous (pore width between 2 and 50 nm) material. The modified Kelvin equation is shown, for cylindrical pores, in equation 2.23.

$$\ln\left(\frac{p}{P_o}\right) = -\frac{2\gamma V_m}{RT(r_p - t_c)} \tag{2.23}$$

 V_m is the molar liquid volume and γ , is the surface tension of the bulk fluid, which are properties of the condensing gas in question, usually N₂. r_p , is the pore radius and t_c is the thickness of the adsorbed multilayer film formed before condensation. As the gas pressure is increased up to complete saturation, the Kelvin equation will be fulfilled for gradually increasing pore sizes r_n . The porosity can also be evaluated from desorption of gas by decreasing pressure from the saturation. The film thickness parameter t_c must be estimated beforehand, utilising a theoretical thickness equation. It is however pointed out that the BJH model, and other models based on the modified Kelvin equation underestimate the size of mesopores to a relatively large extent. A suggested reliable method for overcoming the limitations of the BJH procedure, for determining surface area and porosity, especially if micropores (pore width smaller than 2 nm) are present in the material, is through density functional theory (DFT), which is based on the statistical behaviour of the microscopic properties of confined fluids. Several models, based on the appearance and shape of the pores (i.e. cylindrical pores, slit pores, etc.), have been developed for DFT and the accuracy of the results will depend largely on the veracity of the pore shape for the given material (Thommes et al, 2015).

2.4.2 Liquid scintillation counting

Liquid scintillation counting (LSC) is an analysis method used to determine the count rate (cps or cpm) from the α and/or β radioactivity of a sample. Unlike γ detectors, LSC instruments are seldom efficiently calibrated with standard sources for measuring the radioactivity in Bq. The method exploits the characteristic light pulse produced by deexcitation of certain molecules, called scintillator molecules that have been excited by incoming α - and β - particles. These scintillators are present in a so called cocktail, where solvent in the form of e.g. organic aromatic molecules is then contacted with the radionuclide sample. Energy from the emission of α - or β -particles will be absorbed by the π -cloud of the aromatic molecules of the solvent, causing excitation, which will transfer this energy to other solvent molecules and eventually to a scintillator molecule, producing excited electron states. Once deexcitation of the scintillator occurs, light will be produced which can be detected and amplified by the photomultiplier tube in the liquid scintillation counter. It is possible for quenching to occur, i.e. no light is produced to be detected, because of physical phase separation, interference by quenching agents that absorbs the β -particle or partial colour quenching after scintillator deexcitation. Quenching, as well as other phenomena, such as chemiluminescence, can be compensated for by the counting instrument. (PerkinElmer, n.d.).

This analytical method is suitable as ⁶⁰Co is a β -emitter, although an alternative approach to tracking the change in activity could be through the usage of a HPGe detector, which is capable of measuring γ -radiation. The main advantage of using LSC for the present study is the much better efficiency of detection for LSC over a HPGe detector. This is especially critical when sorption is strong, leaving very little radioactivity to be measured. The samples will, through LSC, be measured over a predetermined period of time and the obtained results are measured in cpm. An overview of the LSC process can be found in figure 2.3.



Figure 2.3. Overview of the liquid scintillation counting analysis method in which a radionuclide triggers the excitation and de-excitation of a scintillation molecule, which can then be analysed, through a solvent medium.

3

Method

3.1 Raw material

Wyoming MX-80 sodium bentonite from the American Colloid Company and previously used in the SKB LOT experiment, was used as the raw material for this project (Eriksen et al., 1999) Particular pieces of the bentonite that were located far from the 60 Co source used in the LOT were cut away (fig 3.1a). These cm-sized pieces of bentonite were dried in a fume hood during 94 hours to remove easily accessible free moisture. After drying, the rocks were taken out and milled to a fine powder by mortar and pestle (fig 3.1b). The powder was placed in a sieve series, with openings in the order of 250, 125, 63 and 36 µm. The sieves were put in a shaking tower Retsch AS200 for 30 minutes, with an amplitude of 1.68 mm/'g' (fig 3.1c). Each particle fraction was weighed, the main yield of 19.22 grams was of the 63-125 µm fraction, which was then dried further in a vacuum oven at 30 °C. The mass of the sample was regularly measured and was noted to stop decreasing after 164 hours, when it was considered to have maximum achievable dryness with that drying method. The bentonite was kept in the vacuum oven to avoid the material absorbing moisture from the air.



Figure 3.1. The process of a) drying, b) grounding and c) sieving the bentonite.

For measuring the porosity and surface area of the bentonite, approximately 0.3 grams of the dry bentonite powder was dried further through degassing in a surface area and porosity analyser Micrometrics ASAP 2020 until no more gas could be evacuated from the sample. The sample was then weighed to determine the degassed, dry weight, whereupon it was placed in the instrument for porosimetry and BET surface area measurements. This procedure was done for samples in triplicate of 0.279 (BENT1), 0.281 (BENT2) and 0.298 (BENT3) grams degassed weight, respectively. Results were noted with regard to surface area, pore volume, pore size and porosity distribution by Density Functional Theory (DFT) for models " N_2 at 77

K, *Cylindrical Pores in an Oxide Surface*" and "*N*² *at* 77 *K on Carbon, Slit Pores*", according to the instrument software.

3.2 Water preparation

Four types of water to be used for the batch samples were prepared by mixing different chemicals with *Millipore Milli-Q*-purified water. All vessels were washed with 5 M HNO₃ and milli-Q water before usage. The different types of water compositions were: one resembling groundwater, two NaClO₄ solutions of differing ionic strength (one with the same ionic strength as the groundwater and one with higher ionic strength), and one Ca(ClO₄)₂-solution with similar ionic strength as the groundwater solution. Perchlorates were the chemicals of choice because the perchlorate ion was believed to be less likely to interfere with the sorption when compared with other anions, such as chloride or nitrate. The sodium and calcium ions were the main interest in varying, since these cations may affect Co sorption in different ways. pH was measured with a Radiometer pHM240 pH Meter and pHC3006 pH electrode. All prepared solutions were adjusted to 7.8 ± 0.1 through 0.1 M HCl and 0.1 M NaOH additions.

3.2.1 Groundwater solution

One litre of groundwater (henceforth denominated GW) was prepared with ion concentration resembling concentrations found in a groundwater sample taken near Äspö Hard Rock Laboratory. The expected composition of ions is shown in table 3.1.

Ion	Concentration [mmol/L]
Ca ²⁺	37.7
\mathbf{K}^+	0.17
Mg^{2+}	1.4
Na ⁺	75.1
Sr ²⁺	0.32
Cl-	144.6
HCO3 ⁻	0.13
SO 4 ²⁻	4.7

Table 3.1. Expected composition of ions based on data near Äspö Hard Rock Laboratory

From this, the ionic strength for the solution was determined to be 0.25 M. The chemicals used and the amounts in grams are found in table 3.2. The CaSO₄ was purchased from *Fluka*, SrCl₂ from *Merck*, NaCl from *Analar NormaPur* and the remaining chemicals from *Sigma-Aldrich*.

 Table 3.2. Purity and amounts of the chemicals used to mix the groundwater.

Chemical	Amount [g]
CaCl ₂ anhydrous, 96 %	3.825
CaSO ₄ dihydrate \geq 99 %	0.809

KCl anhydrous \geq 99.5 %	0.014
MgCl ₂ anhydrous \geq 98 %	0.134
NaCl anhydrous \geq 99.7 %	4.396
SrCl ₂ hexahydrate >99 %	0.085
NaHCO ₃ anhydrous \geq 99 %	0.011

3.2.2 Sodium perchlorate solutions

Two 0.25 litre solutions were prepared with different ionic strength of sodium perchlorate (NaClO₄). The first solution, *J1*, was made with the purpose to have a similar ionic strength as the groundwater solution (0.25 M), whereas the second solution, *J2*, was to contain a higher ionic strength (1 M) in order to study whether the increased ionic strength had an impact on the results. The measured amounts for each solution can be found in table 3.3. The NaClO₄ was purveyed from *Sigma-Aldrich*.

 Table 3.3 Amount and purity of NaClO4 weighed for the two solutions J1 and J2.
 Image: Comparison of the two solutions (Comparison of the two solutions)

Solution ID	Chemical	Amount
		NaClO ₄ [g]
J1	NaClO ₄ anhydrous \ge 98 %	7.34
J2	NaClO ₄ anhydrous \geq 98 %	31.23

3.2.3 Calcium perchlorate solution

For the final type of water solution, 0.3 litres of water was mixed with $Ca(ClO_4)_2$ to an ionic strength of 0.25 M. The amount of calcium perchlorate added to the water as well as chemical purity and solution ID can be seen in table 3.4. The $Ca(ClO_4)_2$ was purchased from *Sigma-Aldrich*.

Table 3.4. Amount added and purity of $Ca(ClO_4)_2$ added to the water solution CA.

Solution ID	Chemical	Amount
		Ca(ClO ₄) ₂ [g]
CA	Ca(ClO ₄) ₂ tetrahydrate \geq 99 %	7.91

3.2.4 Radionuclide

The radionuclide was supplied by *Eckert & Ziegler Analytics* in a 5.0258 g 0.1 M HCl solution containing 30 μ g Co carrier per gram HCl solution, with an activity of 3.739E+6 Bq at the reference date 11/4-2013. 4.9137 g had since been withdrawn from the solution and diluted with 0.9945 g 0.1 M HCl, giving it a cobalt mass concentration of 2.495E-5 g per gram HCl solution, or a molar concentration of 423 μ M. For the room temperature samples, 51.2 μ L of radionuclide solution was added to the water solutions GW, J1 and J2, giving cobalt concentration of 1.205E-7 M. Due to the margin of detectable radioactivity above background for the initial samples of the series at 25 °C being rather slim a reinforcement of the solutions

was made for the 50 °C and 75 °C samples, as well as the Ca(ClO₄)₂ room temperature samples. Therefore, 94.5 μ L of radionuclide solution were added to the CA water and an additional 27.5 μ L added to the already prepared GW and J1 radioactive solutions, resulting in a cobalt concentration of 20E-7 M in each type of water. The volume, amount added cobalt radionuclide stock solution and final concentrations before sampling for each water and temperature is made visible in table 3.5.

Solution	Temperature of	Volume	Volume cobalt	Со
ID	samples	[L]	stock solution	concentration
			added [µL]	before sampling
				[M]
GW(1)	25 °C	0.18	51.2	1.24E-7
GW(2)	50 and 75 °C	0.1465	51.2+27.5	2.0E-7
J1(1)	25 °C	0.18	51.2	1.24E-7
J1(2)	50 and 75 °C	0.1465	51.2+27.5	2.0E-7
J2	25 °C	0.18 L	51.2	1.24E-7
CA	25, 50 and 75 °C	0.20 L	94.5	2.0E-7

Table 3.5. Volume, amounts of added cobalt to the water types GW, J1, J2 and CA for different temperatures and their final concentration.

3.3 Sample preparation

All samples except the acidic reference samples (AR) were prepared in 10 mL PPCO centrifuge tubes (Nalgene Oak Ridge Centrifuge Tubes 3119-0010). The samples were made in triplicate with two wall reference samples, without bentonite (R) in accordance with the schematic in table 3.6 and labelled by indices using letters A-F and numbers 1-10.

0 71	5 I I	1 5	1 1
Solution ID \ Temperature	25 °C	50 °C	75 °C
GW	3 + 2R + 1AR	3 + 2R	3 + 2R
J1	3 + 2R + 1AR	3 + 2R	3 + 2R
J2	3 + 2R + 1AR		
СА	3 + 2R + 1AR	3 + 2R	3+2R

Table 3.6. Schematic detailing the types and number of samples prepared for the sorption experiments.

The wall references and acidic references were made for the sole purpose of calculating R_d by equation 2.19. The experimental design used in this thesis, with regard to the obtained results, as well as for the study of the chosen parameters, temperature and ion type, is made visible in table 3.7, which corresponds to a two-stage nested design as outlined by Montgomery (2012).

Temperature	Room temperature		50 °C			75 °C			
Ion type	GW	J1	CA	GW	J1	CA	GW	J1	CA
Observations	R d,111	Rd,121	R d,131	Rd,211	Rd,221	Rd,231	R d,311	Rd,321	R d,331
	R _{d,112}	R _{d,122}	R _{d,132}	R _{d,212}	R _{d,222}	R _{d,232}	R _{d,312}	R _{d,322}	R _{d,332}
	R _{d,113}	R _{d,123}	R _{d,133}	R _{d,213}	R _{d,223}	R _{d,233}	R _{d,313}	R _{d,323}	R _{d,333}

 Table 3.7. The main experimental setup in terms of the distribution coefficients received.

In table 3.7, J2 is not included as the impact of ionic strength is not a main parameter studied in this thesis. The distribution coefficients for J2 conditions were also measured in order to indicate whether or not the ionic strength could be influential.

Before addition of water and bentonite to the centrifuge tubes, they were washed with 5 M HNO₃, followed by milli-Q water and were allowed to dry. Vacuum-dried bentonite clay was then added to the non-reference sample tubes in a ratio of 1:20, with 0.4 grams of bentonite and 8 mL of water. Before testing, all samples with bentonite were equilibrated for seven days with 8 mL of respective non-radioactive water solution in order to saturate the bentonite with water. They were then centrifuged and approximately 6 mL of the supernatant was removed from the samples. Sample indices, water type and temperature, as well as data regarding tube weights, added bentonite and weight before and after addition of radioactive water can be found in Appendix A.

3.4 Radioactivity measurements

Each experiment was started by the addition of approximately 6 mL of radionuclide-spiked water to the samples with bentonite and 7.5 mL to the wall reference samples. The acidic references were comprised of 1 mL 1 M HCl added to 1 mL of radioactive water. The samples were divided into three test series, A, B and C for room temperature, 50 and 75 degrees C respectively. During the course of the test period, all samples were kept in a radioactive fume hood, where the 50 and 75 °C samples were heated in Dry Block Heaters (Fisherbrand Isotemp, Digital). A photo of the sample setup is shown in figure 3.2.



Figure 3.2. The block heaters and sample tube setup used for the duration of the testing.

For the first sampling campaign, after one day, the bentonite samples were centrifuged in a high speed centrifuge (Beckman Coulter Avanti J-26S XP with rotor JA-20.1) at 20000 rpm (47 900 x g) and 15 °C, whereupon approximately 1 % of the volume (0.08-0.1 mL) of each sample was transferred to a 7 mL liquid scintillation vial. About 7 mL of LSC cocktail (PerkinElmer Hionic-Fluor) was added to the vials and the β radiation of the samples were counted for 30 minutes with a LSC detector (PerkinElmer/Wallac 1414). At each sampling occasion, blank samples were also counted for the background rate.

After centrifugation and sample outtake, the centrifugation tubes were shaken with a vortex mixer (Fisons Whirlimixer). The tests were conducted in repetition with approximately doubling intervals in days, i.e. the first measurement 1 day after test start, second after 3 days, third after 8 days, etc. This procedure was repeated for six iterations. The acidic references were measured on four occasions each and their respective measured activity (in β -radiation) was taken on average.

Results from the LSC were received in counts per minute (cpm), which were subtracted by the measured background radiation and divided with the extracted volume from each test sample in order to get concentration values. The data was then used to find the R_d and L_d values in accordance with equations 2.19 and 2.20 respectively, and the results over time were plotted and analysed. As the samples were produced in triplicate, the average R_d -values of each sample group (GW, J1, J2 and CA) were taken as an aggregated representative distribution coefficient value. Additionally, the results were analysed by ANOVA to verify whether the two main varied parameters, temperature and ion type, caused a statistically significant impact on the distribution coefficients.

4

Results

4.1 Surface area and porosimetry

The results for three bentonite samples, labelled BENT1, BENT2 and BENT3, with regard to BET surface area, BJH adsorption cumulative surface area of pores and BJH desorption cumulative surface area of pores are presented in table 4.1.

Sample	BET	BJH adsorption cumulative	BJH desorption cumulative
	surface area	surface area of pores	surface area of pores
	[m ² /g]	[m ² /g]	[m ² /g]
BENT1	15.37	14.51	32.56
BENT2	21.65	20.96	37.61
BENT3	20.95	20.63	37.28
Average	19.32	18.70	35.82
Standard deviation	3.44	3.63	2.83

Table 4.1. BET, BJH adsorption and desorption surface area results, measured in m^2/g .

The samples display a variance in surface area, mainly between BENT1 and the remaining two, implying some inhomogeneity in the material. Furthermore, the BET surface area is larger than the BJH <u>adsorption</u> cumulative surface area of pores, which was expected since BET also takes the external surface area of the bentonite particles into consideration, not just the "inner" pore surface area. It can be noted that the BJH <u>desorption</u> surface areas of pores are actually larger than the corresponding BET areas, which makes an evaluation of porosity based on the desorption branch seem to be less trustworthy. The recommendation is also to use the adsorption and desorption pore volume measurements for samples BENT1, BENT2 and BENT3 are shown in table 4.2 and BJH adsorption and desorption average pore width results are displayed in table 4.3

Sample	BJH adsorption cumulative volume	BJH desorption cumulative volume of
	of pores [cm ³ /g]	pores [cm ³ /g]
BENT1	0.077	0.071
BENT2	0.084	0.078
BENT3	0.085	0.079
Average	0.082	0.076
Standard deviation	0.0044	0.0042

Table 4.2. BJH adsorption and desorption volume for the pores of the three samples.

Sample	BJH adsorption	BJH desorption	Adsorption average
	average pore width	average pore width	pore width (4V/A by
	(4V/A) [Å]	(4V/A) [Å]	BET) [Å]
BENT1	213.03	87.41	200.75
BENT2	160.83	82.93	155.23
BENT3	165.50	84.45	162.40
Average	179.79	84.93	172.79
Standard deviation	28.88	2.28	24.47

Table 4.3. Width of the pores according to BJH adsorption and desorption as well as average pore width.

In the same vein as with the surface area, the values for BENT1 differs to some extent from BENT2 and BENT3, which are more similar. Pore width measured according to BET is similar to that measured in the BJH adsorption procedure. There are some concerns about the theoretical weaknesses of the BJH method. Therefore, results according to DFT, were also calculated through two models, the first assuming cylindrical pores in an oxide surface and the second assuming adsorption on carbon with slit pores and based on the same gas adsorption datasets that were used for the BJH method. Both the DFT models uses nitrogen gas at 77 K. The pore volume and area results for BENT1, BENT2 and BENT3, using each model, are presented in tables 4.4 and 4.5.

Table 4.4. Pore volume and area, as well as standard deviation of fit according to DFT cylindrical pores model

Sample	Volume in	Volume in Total volume		Total area in	Model
	pores	in pores	pores	pores	standard
	< 20.23 Å	≤ 387.34 Å	> 387.34 Å	≥ 20.23 Å	deviation of
	[cm ³ /g]	[cm ³ /g]	[m ² /g]	[m ² /g]	fit [cm ³ /g]
BENT1	0.0024	0.020	8.38	10.33	2.47
BENT2	0.0029	0.022	9.17	11.46	2.003
BENT3	0.0031	0.020	9.78	11.62	2.09
Average	0.0028	0.021	9.11	11.14	
Standard deviation	0.00041	0.0010	0.70	0.70	

Table 4.5. Pore volume, area and standard deviation of fit according to DFT adsorption on carbon with slit pores.

Sample	Volume in	Total volume	Area in pores	Total area in	Model
	pores	pores in pores		pores	standard
		≤ 1265.80 Å	> 1265.80 Å	≥15.91 Å	deviation of
	< 15.91 Å	$[cm^{3}/g]$	[m ² /g]	[m ² /g]	fit [cm ³ /g]
	[cm ³ /g]	_		_	
BENT1	0.0017	0.068	2.46	7.87	0.21
BENT2	BENT2 0.0022		6.17	11.30	0.19
BENT3	0.0020	0.065	5.90	11.15	0.204
Average	0.0020	0.065	4.85	10.11	
Standard deviation	0.00025	0.0023	2.07	1.94	

In tables 4.4 and 4.5 BENT1 exhibits more divergent values, except for total pore volume, from the other two samples, once more implying inhomogeneous material. The standard deviation of the values based on slit pores in table 4.5 are considerably lower than from the cylindrical pore model in table 4.4, which implies that the pore type is better approximated as slits rather

than cylinders. In comparing the DFT data in table 4.5 with the BJH data in table 4.2, the total volume in the pores from DFT for all samples are lower than that of the BJH cumulative pore volume. The same is true for the total pore area, when comparing table 4.5 and table 4.1.

According to Thommes et al. (2015), the BJH method has a tendency to significantly underestimate the pore-size of the material. Smaller pores mean a larger total surface area for a given total volume of pores, and the results here are in fact at least partly in accordance with the stated difference between the two methods. The DFT model with slit pores gives a comparable specific pore volume ($0.065 \text{ cm}^3/\text{g}$) to the BJH model, adsorption branch ($0.085 \text{ cm}^3/\text{g}$) but the specific area is about half with the DFT model ($10 \text{ m}^2/\text{g} \text{ vs } 19 \text{ m}^2/\text{g}$), implying that the BJH average pore width in table 4.3 may have been underestimated by the method. Apart from the BJH desorption branch results, which are non-compatible with the measured total BET specific area, it is hard to say which model gives the best estimation of the specific surface area of the pores. I seems that the DFT model with slit-shaped pores fits the data well and in addition the DFT model should have a better theoretical foundation than the BJH model. Measurements on reference material with precisely defined pore size and external area of the material, have confirmed that the DFT method gives better results than the BJH method (see references in Thommes, (2019)).

4.2 Distribution coefficients

In this section the distribution coefficients (R_d values), calculated from the raw data according to equation 2.19 from the tests will be presented, sorted by test series A, B and C (25 °C, 50 °C and 75 °C, respectively). The complete set of raw data for the six tests conducted at all temperatures, with count rates, the extracted sample amounts and the amount of days from test commencement, as well as acidic reference data, is given in Appendix B

4.2.1 Test Series A (25 °C)

The temporal (apparent) distribution coefficient results of samples with different water solutions GW, J1, J2 and CA, kept at room temperature (25 °C) for the duration of the test period are presented in figure 4.1 and table 4.6.



Figure 4.1. Apparent R_d -values as for samples in the four different water solutions at 25 °C as they progressively change over time.

Table 4.6. All values for apparent R_d for the different wate	r compositions at 25 °C ove	er time, along with averages
and standard deviations.		

Water	Rd	Rd	Rd	Rd	Rd	Rd
conditions	1 day	4 days	8 days	15 days	29 days	77 days
	[m ³ /kg]					
	0.075	0.15	0.20	0.23	0.21	0.27
GW	0.11	0.17	0.22	0.23	0.23	0.27
	0.10	0.16	0.21	0.26	0.22	0.28
Average	0.094	0.16	0.21	0.24	0.22	0.28
Standard deviation	0.017	0.009	0.014	0.017	0.012	0.007
	0.55	1.77	1.66	0.84	0.41	0.58
J1	0.74	2.30	1.26	0.75	0.47	0.65
	0.33	0.76	0.82	0.66	0.42	0.62
Average	0.54	1.61	1.25	0.75	0.44	0.62
Standard deviation	0.21	0.79	0.42	0.091	0.035	0.032
	0.23	1.33	3.33	3.70	0.68	0.60
J2	0.31	0.98	3.02	7.31	0.78	0.58
	0.67	1.97	2.45	5.25	0.99	0.70

Average	0.41	1.43	2.93	5.42	0.81	0.63
Standard deviation	0.23	0.50	0.45	1.81	0.16	0.061
Water	R _d	R _d	R _d	Rd	R _d	R _d
conditions	1 day	4 days	7 days	14 days	27 days	55 days
	[m ³ /kg]					
	0.25	0.47	0.42	0.24	0.21	0.36
CA	0.26	0.53	0.58	0.46	0.27	0.35
	0.22	0.37	0.47	0.34	0.25	0.37
Average	0.24	0.46	0.49	0.35	0.025	0.36
Standard deviation	0.019	0.077	0.084	0.11	0.028	0.013

In figure 4.1 and from the values in table 4.6 it can be seen that the groundwater solution samples (GW) display a clear increase and subsequent stabilisation in R_d , with low error margins, over the duration of the experiments. In contrast, the other three solution types mark a sharp rise in sorption to the bentonite within the first 20 days of the experiment, with the most extreme case being J2 (1 M NaClO₄), where the count rate in the extracted samples at the fourth measurement approached background count rate during the LSC measurements. By the fifth measurement, however, the count rate in the samples had increased, yielding again lower R_{d-1} values, possibly indicating that desorption had occurred. The samples seem to have stabilised around this lower R_d value in the final measurement. Also notable is that the GW (simulated groundwater) solution yielded the lowest sorption of the group, followed by the Ca(ClO₄)₂solution and the two NaClO₄-solutions resulting in approximately the same final value. The two different NaClO₄ solutions show distinct difference in apparent R_d values between the first and fifth measurements, which indicates that the ionic strength had a transient effect on the results, but it did not affect the final R_d values, which are identical for J1 and J2 when considering error margins. The Ca(ClO₄)₂-solution appears to still be rising to some extent through the sixth measurement, which might indicate it had not yet reached equilibrium, although for the purpose of analysis, this R_d -value will be assumed to be at equilibrium. The approach to a stable apparent R_d -value is used to signify that a long-term equilibrium with respect to diffusion and sorption have been reached and that a "true" R_d value is measured. The final R_d values are shown in table 4.7.

Aggregated sample	Туре	Long-term R _d
ID		[m ³ /kg]
GW-Room temp.	0.25 M simulated groundwater	0.28±0.01
J1-Room temp.	0.25 M NaClO4	0.62±0.03
J2-Room temp.	1 M NaClO4	0.63±0.06
CA-Room temp.	0.25 M Ca(ClO ₄) ₂	0.36±0.01
	Average	0.47

Table 4.7. Long-term distribution coefficient values for experimental samples kept at 25 °C.

Standard deviation 0.18

From table 4.7. it can be concluded that R_d varies between approximately 0.28-0.63 m³/kg depending on the water composition.

4.2.2 Test Series B (50 °C)

The apparent R_d values over time for the Groundwater, sodium perchlorate and calcium perchlorate samples kept at 50 °C are shown in figure 4.2 and table 4.8.



Figure 4.2. Apparent R_d -values for samples in the four different water solutions at 50 °C as they progressively change over time.

Table 4.8. All values for apparent R_d for the different water compositions at 50 °C over time, along with averages and standard deviations.

Water	Rd	Rd	R _d	Rd	R _d	R _d
conditions	1 day	4 days	7 days	14 days	27 days	55 days
	$[m^3/kg]$	$[m^3/kg]$	[m ³ /kg]	[m ³ /kg]	$[m^3/kg]$	[m ³ /kg]
	0.074	7.81	0.50	0.78	0.93	0.95
GW	0.078	7.81	0.36	0.58	0.99	1.23
	0.084	7.81	0.34	0.59	0.99	0.99
Average	0.079	0.24	0.40	0.65	0.038	1.06

Standard deviation	0.005	0.002	0.086	0.11	0.97	0.15
	0.098	0.36	0.65	1.30	1.51	2.09
J1	0.064	0.20	0.34	0.92	1.30	3.89
	0.026	0.24	0.40	1.03	1.38	2.46
Average	0.063	0.27	0.46	1.08	1.39	2.81
Standard deviation	0.036	0.081	0.17	0.19	0.11	0.95
	0.30	0.88	1.27	1.94	1.52	1.62
СА	0.27	0.92	1.23	2.09	1.58	1.97
	0.40	0.87	1.13	1.67	2.21	2.13
Average	0.32	0.89	1.21	1.90	1.77	1.91
Standard deviation	0.069	0.027	0.073	0.22	0.39	0.26

According to table 4.8 and in figure 4.2 the results for all solutions, with an exception of a slight downwards jump for CA conditions between the second and fourth measurement, show a clear and steady increase in sorption in the first 20 days, followed by a stabilisation in R_d . However, samples with solution J1 continued to rise slightly throughout the final measurement. As is also the case in figure 4.1 for 25 °C, the sorption is lowest in the groundwater solution and highest in the NaClO₄-solution, with the samples with Ca(ClO₄)₂-water having an R_d -value between the two. All R_d -values, once stabilisation has occurred, are higher than at the corresponding point in time for the room temperature samples, which all were below 1 m³/kg. The final distribution coefficients are given in table 4.9.

Aggregated sample	Туре	Long-term R _d
ID		[m ³ /kg]
GW-50 °C	0.25 M simulated groundwater	1.06±0.15
J1-50 °C	0.25 M NaClO4	2.81±0.95
CA-50 °C	0.25 M Ca(ClO ₄) ₂	1.91±0.26
	Average	1.93
	Standard deviation	0.88

Table 4.9. Equilibrium R_d -values for tests conducted at 50 °C.

From table 4.9. it can be concluded that R_d varies between approximately 1.06-2.81 m³/kg depending on the water composition.

4.2.3 Test Series C (75 °C)

The development of apparent R_d values over time for samples being heated to 75 °C for the duration of the experiments can be viewed in figure 4.3 and table 4.10.



Figure 4.3 Apparent R_d -values for samples in the four different water solutions at 75 °C as they progressively change over time.

Table 4.10. All R_d -values for 75 °C experiments over time,	negative values (gro	ay) are not accoun	ted for in the
average and standard deviation to avoid distortion.			

Water	R _d					
conditions	1 day	4 days	7 days	14 days	23 days	49 days
	[m ³ /kg]					
	0.089	0.55	1.63	4.98	5.07	3.82
GW	0.062	0.42	1.43	7.67	10.30	3.94
	0.058	0.39	1.36	3.37	7.79	2.95
Average	0.070	0.45	1.47	5.34	7.72	3.57
Standard deviation	0.017	0.090	0.14	2.17	2.62	0.54
	0.087	0.89	3.84	19.47	8.43	7.88
J1	0.021	1.08	13.12	67.03	8.80	6.98
	0.086	1.21	8.99	-17.25	-68.47	3.47
Average	0.13	1.06	8.65	43.25	8.62	7.43
Standard deviation	0.069	0.17	4.65	33.63	0.27	2.33
	0.44	2.72	2.06	5.16	4.31	3.17
СА	0.40	1.37	1.85	4.76	2.89	3.13
	0.41	1.27	1.87	3.19	2.63	2.37

Average	0.42	1.79	1.93	4.37	3.28	2.89
Standard	0.020	0.91	0.12	1.04	0.00	0.45
deviation	0.020	0.81	0.12	1.04	0.90	0.43

Figure 4.3 and table 4.10 show the data for the three different water types increasing through the course of the measurements, with J1 at the fourth measurement indicating sorption to the extent where the ⁶⁰Co concentration being so low that the count rate is actually at background levels, followed by a desorption from the bentonite, raising the count rate slightly for the final two measurements. This approaching to the background level of count rate is shown by the high standard error indicated by the error bars for J1 and is clear in table 4.10. The distribution of Co between the solid and liquid phase seem to stabilise in the final two measurements. As a departure from the 25 °C and 50 °C-experiments, the sorption in the Ca(ClO₄)₂-solution is now slightly lower than in the simulated groundwater solution, whilst the samples where sodium is the competing ion are once again yielding the highest sorption. In comparison to figures 4.1 and 4.2, the level of sorption is pushed further to a higher level, indicating that sorption increases with temperature. This is also shown by the long-term R_d -values in table 4.11, which are all higher than in the previous two cases (tables 4.7 and 4.9)

Aggregated sample	Туре	Long-term R _d
ID		[m ³ /kg]
GW-75 °C	0.25 M simulated groundwater	3.57±0.54
J1-75 °C	0.25 M NaClO4	7.43±2.33
CA-75 °C	0.25 M Ca(ClO ₄) ₂	2.89 ± 0.45
	Average	4.63
	Standard deviation	2.45

Table 4.11. Long-term distribution coefficient results from the experiments at 75 °C.

Table 4.11 shows that the sorption distribution coefficient ranges from approximately 2.89-7.43 m^3/kg .

4.2.4 Distribution coefficients per water composition

In sections 4.2.1-4.2.3, the resulting temporal plots of the distribution coefficients were made for the different test series, in which the temperature was varied. For an overview picture of the difference between results from the <u>same</u> water composition, but at different temperatures for GW, J1 and CA, see the figures 4.4, 4.5 and 4.6, respectively.



Figure 4.4. Apparent R_d values for the groundwater solution at different temperatures as they vary over time.



Figure 4.5. Apparent R_d values for the NaClO₄-solution at different temperatures as they vary over time.



Figure 4.6. Apparent R_d values for the groundwaterfor the $Ca(ClO_4)_2$ - solution at different temperatures as they vary over time.

From figures 4.4 through 4.6 it appears that the bulk of the sorption occurs within the first ten to twenty days of the experiments. In some cases a peak is reached at this point, followed by desorption to some extent. Increasing the temperature seems to favour the sorption and it also looks to determine the sorption degree both in the initial and the final stages of cobalt sorption onto bentonite. The desorption effect is most evident in CA at 25 °C (figure 4.6) and J1 at 25 °C and 75 °C (figure 4.5). The most stable increase is displayed by GW at room temperature and 50 °C, as well as in J1 at 50 °C.

4.2.5 Effect of temperature and ionic type.

There are visible differences between the results obtained, both between the water solutions within each series as well as between different series', where the temperature is varied. Generally, it appears that sorption increases with increasing temperature and that the sorption is lower in the groundwater solution and higher in the sodium perchlorate solution. A completed version of table 3.7, with filled in final values of R_d , and the resulting ANOVA-table, calculated according to Montgomery (2012), are shown in tables 4.12 and 4.13, respectively. The calculations from R_d -values used to construct the ANOVA-table can be found in Appendix C.

Temperature	Room temperature			50 °C			75 °C		
Ion type	GW	J1	CA	GW	J1	CA	GW	J1	CA
Observations	0.27	0.58	0.36	0.95	2.09	1.62	3.82	7.88	3.17
	0.27	0.65	0.35	1.23	3.89	1.97	3.94	6.98	3.13
	0.28	0.62	0.37	0.99	2.46	2.13	2.95	3.47	2.37

Table 4.12. The experimental setup as it pertains to the variation of ion type and temperature, with filled in long-term R_d -values in m^3/kg .

 Table 4.13. ANOVA-table constructed from the obtained distribution coefficients in table 4.12.
 Image: Construct of the obtained distribution coefficients in table 4.12.

Source of Variation	Sum of Squares	Degrees of Freedom	Mean Square	Fobs	Fstat(0.95,6,18)
Temperature	64.86	2	32.43	8.81	5.14
Ion type (within temperatures)	22.08	6	3.68	4.79	2.66
Error	13.83	18	0.77		
Total	100.76	26			

The F_{stat} -value, taken at 95 % confidence level, being smaller than the observed, F_{obs} , for both the temperature and ion type means that the difference in variance between the different sample grouping is significant. The implications of these results are that <u>both</u> the temperature and the ion types have a <u>significant</u> effect on the sorption of ⁶⁰Co to bentonite.

Tests for the water solution with 1 M NaClO₄ were not conducted at different temperature levels, but it was present in the room temperature experiments. As its final R_d-values overlap that of J1, it is likely that the difference between the two would not be statistically significant. To be able to confirm this, the final R_d -values from sample groups J1 and J2, visible in table 4.14, were compared statistically to verify or reject that these two groups were significantly different at a 95 % or 90 % confidence level. The resulting ANOVA table is shown in table 4.15. The calculations underpinning these results can be found in Appendix C.

Table 4.14. R_d -values at assumed equilibrium for the two NaClO₄ solutions used in the experiments.

Ion type	J1	J2
	0.57	0.60
Observations [m ³ /kg]	0.62	0.58
	0.59	0.70

Source of Variation	Sum of Squares	Degrees of Freedom	Mean Square	Fobs	Fstat(0.95,1,4)	Fstat(0.90,1,4)
Ion type	1.96E-04	1	1.96E-04	0.081	7.71	4.54
Error	0.0096	4	0.0024			
Total	0.0098	5				

Table 4.15. ANOVA-table comparing the two test groups J1 and J2.

Based on the results from the analysis of variance in table 4.15, since $F_{obs} < F_{stat}$ for both F_{stat} -values, it can be stated that there is no statistical indication the observations originates from different sample groups at neither a 95 % or 90 % confidence level. Therefore, the difference in results between J1 and J2 are not significant, and the impact on the long-term R_d -values with regard to ⁶⁰Co sorption to bentonite, is negligible when comparing NaClO₄-solutions of 0.25 M and 1 M ionic strength at room temperature.

5

Discussion

The results found in this work indicate that both the water type and the temperature play important roles in the sorption of ⁶⁰Co onto bentonite clay. What may be the reason for the types of ions in the solution having such an effect on the results could be that different ions compete with cobalt for the sorption sites in different ways. For example, in the groundwater solution, there were several ions present with differing valence, the cations were Mg^{2+} , Sr^{2+} , K^+ , Na⁺ and Ca²⁺, whilst the anions were Cl⁻, SO₄²⁻ and HCO₃⁻. As the surface of the bentonite is negatively charged, the sorption competitors are expected to be the cations. In the other solutions, the cations were either Ca^{2+} or Na^+ , with the only significant anion being ClO_4^- . Furthermore, the sorption was the lowest in the groundwater solution and the highest in the NaClO₄-solution. It is also known that the bentonite was of the type Na-bentonite, meaning the main cation in the interlayer region was Na⁺, causing this ion to be present in all solutions. It therefore stands to reason that there is a link between the variety of the present ions and the sorption of cobalt, i.e. by increasing the number of different ions, besides the main Na⁺ ion already present in bentonite, the sorption decreases. The question is if this decrease in sorption is due to e.g. mono and divalent ions competing differently or perhaps because the sodium, as it was present in the bentonite already, is more easily exchanged in favour of a more even distribution of different ions in the bentonite. Khan et al. (1996) found that the order of effectiveness in impeding cobalt sorption to bentonite was $K^+ > Ca^{2+} > Mg^{2+} > Na^{2+}$ at the same ionic strength. Their theory as to why potassium ions would be a more effective competitor with cobalt than calcium was that the size of the hydrated potassium ion (i.e. $K^{+}(H_2O)_x$) is smaller than the corresponding hydrated calcium ion and would thereby perform better when competing with cobalt in the ion exchange reactions outlined in equations 2.6 and 2.7. Table 5.1 shows the hydration radii for the aforementioned cations and Co²⁺ (Israelachvili, 2011, Zola et al., 2012), as well as ionic radius and calculated charge density of the hydration shell.

Cation	Ionic radius	Hydration radius	Charge density of
	[nm]	[nm]	the hydration shell
			[C/m ³]·10 ⁻⁸
Na ⁺	0.102	0.358	8.52
Mg^{2+}	0.072	0.428	9.79
Co ²⁺	0.074	0.420	10.4
Ca ²⁺	0.100	0.412	11.1
K ⁺	0.138	0.330	11.5

Table 5.1. Ionic, hydration radii and calculated charge density of hydration shell for the discussed cations.

According to the table, hydrated Ca^{2+} is smaller than hydrated Mg^{2+} which would explain why it is more effective, but it does not explain why Na⁺ would less effectively depress the cobalt sorption, as this hydrated ion is smaller than both hydrated Ca^{2+} and Mg^{2+} . The radius of hydrated Co^{2+} is larger than the other cations, with the exception of Mg^{2+} , although the difference is very small between hydrated Ca^{2+} , Co^{2+} and Mg^{2+} . If the theory holds true that K⁺ is the most competitive cation due to its smaller hydration size, this would mean a solution with Mg^{2+} , having the largest hydration radius, would be the least competitive ion, but this is not what was found by Khan et al (1996) where instead Na⁺ is the least competitive ion. Here we instead suggest an alternative approach, where the <u>calculated average charge densities</u> of the hydration shells are compared instead of hydration radii. These values are derived from the charge of ion (in the unit C) divided by the hydration shell volume. This places the Co^{2+} ion in the middle of the series and thus it predicts that it will bind stronger than Na⁺ and Mg²⁺ ions, but weaker than Ca^{2+} and K⁺ ions. Also, when comparing the ions in the order of effectiveness for impeding Co^{2+} sorption, as suggested by Khan et al. (1996), the correct order is now <u>followed.</u>

The results in this work with regard to ion selectivity are nevertheless in line with the results obtained by Khan et al. (1996). In this work the GW solution, which contained <u>all</u> the aforementioned cations, had generally the lowest sorption of Co, then followed by the Ca^{2+} solution and finally Na⁺ solution, which gave the highest sorption. The actual reason behind the different ions affecting Co sorption in this way may need to be investigated further, but the calculated charge densities may give a hint to the answer. It should also be noted that the competition of these cations discussed above is only valid for ion-exchange type of sorption, where the hydration shells in fact take part in the binding to the surface. For the surface-complexation mode of sorption, where the hydration shell of the cation is shed when binding to the surface, this type of competition is not valid. Instead, one can expect that the <u>ability of a cation to form hydroxide complexes</u> in solution will give a hint of the complexation strength with the hydroxyl group of the surface. The Co-hydroxide complexes are much stronger than any of the alkaline or alkaline-earth cations and one can therefore predict with a certain confidence that the alkaline or alkaline-earth cations <u>will not</u> compete with Co for the surface complexation sites, but only for the ion-exchange sites.

Samples with NaClO₄ were conducted at two ionic strength levels in the room temperature series, 0.3 M (J1) and 1 M (J2). While the two displayed temporal differences in sorption, the long-term values were not significantly different. This finding that ⁶⁰Co sorption was fairly independent of ionic strength is in line with Yu et al. (2006), Ozsoy and Bekbolet (2015) and Khan et al. (1996), who all found that it had an impact on the sorption only at ionic strength levels lower than 0.1 M.

With regard to the temperature of the solutions, it is clear that higher temperatures promotes the sorption of radionuclide to the adsorbent. Compare, for example, the aggregated distribution coefficients for groundwater at 25 and 75 °C, which were 0.2568 m³/kg versus $3.5504 \text{ m}^3/\text{kg}$, where the latter value is more than one order of magnitude larger than the former.

These results are in agreement Ozsoy and Bekbolet (2015), studying surface interactions of Co^{2+} with bentonite, who found that increasing the temperature from 288 to 338 K (~15 to 65 °C) caused a substantial rise in Co^{2+} adsorption to bentonite, leading them to conclude the adsorption was <u>endothermic</u> in nature. Shahwan et al. (2006) also noted that the affinity of the clay toward cobalt increases as temperature rises. Khan et al. (1995) similarly found Sr²⁺ sorption on bentonite to increase with increasing temperature. Perhaps increasing the temperature will only promote sorption to a certain point and then cause it to either stabilise or decrease. Whether 75 °C is within or past such a point of promoted sorption is uncertain, but it yields higher sorption than at 50 °C. Heat produced by spent nuclear fuel, if it is in the region of 75 °C, therefore ought to improve the affinity of bentonite to radionuclides it may encounter, provided that the structural integrity of the barrier is intact, resulting in a better barrier to radionuclide transport compared with conditions closer to the ambient temperature.

It was found that the time for relatively stable equilibrium to be reached in the experiments were approximately 20 days. This is a long time compared to Ozsoy and Bekbolet (2015), who concluded that only 30 minutes were enough time to reach adsorption equilibrium, or Yu et al. (2006), who found that the time for equilibrium was approximately 15 hours. Khan et al. (1996) reached equilibrium within 4 hours, although this experiment was performed with constant shaking of samples. The reason for the longer time to reach equilibrium is likely due to factors such as differing ratios between solution and adsorbate, agitation, different particle size, surface area or different concentrations of solute in solution. A constant agitation was not used in this work as the experimental conditions were meant to resemble those of the stagnant water zone expected close to the repository copper canisters.

According to Jansson and Eriksen (2001), the distribution coefficient value for Co²⁺ at Äspö in-situ experiments was estimated to be $0.7 \pm 0.4 \text{ m}^3/\text{kg}$ (assumedly not under heated conditions). This conforms somewhat with the samples conducted at 25 °C in this work, ranging from approximately 0.28-0.63 m³/kg, with the groundwater solution falling short of the suggested span, even though it was meant to correspond with the conditions at Äspö. The pH-value stated by Eriksen and Jansson (2001) was 7.2, whilst the solutions used in this test, at least initially, had a pH of 7.8. It was shown by Eriksen et al. (1999), that the distribution coefficient for cobalt to bentonite <u>increased</u> by almost two orders of magnitude when the pH increased from 6 to 8, which would imply that the Co sorption in this work would be higher than the ones measured by Eriksen and Jansson (2001). Perhaps the difference could be explained by carbonate from air interfering with the sorption or by other factors as explained in section 2.3.1 on batch sorption. On the other hand, Xu et al. (2006) found the distribution of cobalt onto bentonite in 0.01 M KNO₃ solution to be 2.4 ± 0.3 m³/kg at a pH of 6.8 ± 0.2, which is considerably larger than the other aforementioned results, and this at a lower pH.

Khan et al. (1996) reported a distribution coefficient of approximately 0.6 m³/kg at pH 7.8 and 25 °C, for cobalt sorption to bentonite in a solution of presumably 0.5 M NaNO₃. This compares well with the 0.3 M NaClO₄-solutions at room temperature in this thesis, where the suppression of cobalt sorption from other cations would be low, which yielded an R_d of about 0.62 m³/kg. However, it was also found by Khan et al. (1996) that if 0.25 M of sodium or calcium ions

were added, R_d of around 1.0 and 0.20 m³/kg respectively, would be attained. These values can be compared to the values found in this thesis of approximately 0.63 and 0.36 m³/kg for 1 M NaClO₄ and 0.3 M Ca(ClO₄)₂, respectively. Obviously, the distribution coefficient values varies in the literature, but the values presented in this work are, in comparison with Jansson and Eriksen (2001) as well as Khan et al. (1996), within the same order of magnitude. However, these values are only comparable in a very approximate sense. If the values are to be directly comparable, these have to be given as BET-surface corrected R_d values (or R_a) to compensate for bentonite properties.

For those references which also give a measured BET surface area of the bentonite used in their sorption studies and that was performed at room temperature, surface-corrected distribution coefficients can be calculated, see Table 5.2, below.

Table 5.2. Comparison in R_a between results for 0.3 M NaClO₄ in this work with those of references providing both R_d values and BET surface area.

Water type	pН	BET area of	\mathbf{R}_{d} (m ³ /kg)	R _a (m)	Ref.
		bentonite			
		(m^2/g)			
0.3M NaClO ₄	7.8	19.32	0.62	3.2.10-5	this work
0.5M NaNO ₃	7.8	34.0	0.6	1.8.10-5	Khan et al
(presumed)					(1996)
0.01-0.1M	7.7	38.5	5.8	$1.5 \cdot 10^{-4}$	Chen and
KNO ₃					Lu. (2008)

Despite the correction for surface area and also very similar pH in solutions, when comparing the R_a values for Co sorption onto bentonite from different works they seem not to agree any better than the corresponding R_d values. One can therefore suspect that this can be due to the fact that the gas adsorption methods <u>do not measure the interlayer surface area of the bentonite</u>, but only the free pore volume (cf figure 2.1). Hence, the BET area will only act as a proxy parameter for the surface complexation capacity and not for the ion-exchange capacity. A separate measurement of the total Cation Exchange Capacity (CEC) with an established methodology is therefore also relevant, but was not included for the present work.

The mechanisms for Co sorption onto bentonite are not entirely clear, but based on what was found by Khan (2002) and also what is reported in the review by Appelo (2013), there are two main types of sorption above pH 6-7: 1) surface complexation (equations 2.6 and 2.7) and 2) ion exchange (equation 2.5). At lower pH ion exchange should be dominant since protons will compete for surface complexation. At higher pH surface complexation should be dominant since this mechanism of sorption is far stronger than the ion-exchange mechanism, at least for Co which forms strong hydroxide complexes in solution and can consequently be expected to bind strongly to surface hydroxyl sites.. Hydroxide in the solution will remove any protons from surface complexation of Co can be expected to compete for Co ions with surface complexation of Co can be expected to compete for Co ions with surface complexation and Co may therefore adsorb less.

It can thus be assumed, since the solutions were prepared at pH 7.8 ± 0.1 , that both surface complexation and ion exchange were the governing sorption mechanisms. The temporal variations shown especially in the NaClO₄ experiments in this work may indicate that there are indeed two competing processes for Co sorption onto bentonite. Also, since effects on sorption were noted for both the type of background cations, which can influence ion-exchange but not surface complexation, and temperature, which mainly should influence a chemical binding like the surface complexation, one must assume that both mechanisms are participating in overall sorption.

The distribution coefficient values displayed an interesting temporal behaviour, mainly in samples with NaClO₄-water, where apparent desorption occurred after a period of increasing sorption in the first ten to twenty days of the experiment. Similar phenomena was reported by Dong et al. (2000), where a maximum distribution coefficient value was found early, followed by a lowering of R_d . Possibly, since the number of sites for ion exchange far outnumbered the amount of cobalt ions, this led to an initial high ion exchange sorption of cobalt, which was then followed by desorption in favour of the much stronger chemical sorption. This could explain the apparent desorption occurring prevalently in e.g. the NaClO₄-samples where Na⁺ eventually would re-replace cobalt in the ion exchange sites, causing a net effect of cobalt returning to the solution.

With the results of this thesis taken into consideration, in the scenario of a spent nuclear fuel copper canister breaking, with radionuclides coming into contact with groundwater and bentonite, 1) at higher temperatures, as would be expected from highly radioactive spent nuclear fuel, sorption would be favourable, 2) a groundwater consisting of a mix of different ions, especially those competing for ion exchange sites, would be unfavourable, leading to further spread of radionuclide in the clay, compared to in water with more homogeneous composition, 3) finally, the distribution coefficient for Co at typical GW would end up being in orders of magnitude close to 0.28-3.57 m³/kg, the value depending on the temperature, and granted it does not exceed 75 °C and pH is not radically different from 7.8.

6

Conclusions

Because of the results attained in this thesis, conclusions could be drawn regarding the effect temperature and differing water compositions have on the sorption of cobalt onto bentonite in water of pH 7.8.

Sorption showed a definite increase with increasing temperature, at least within the studied bounds of room temperature to 75 °C. Preferable water composition conditions for promotion of Co-sorption to bentonite were found to be ones with as few competing cations as possible, with sodium ions depressing the sorption the least. Calcium ions impeded the sorption significantly and other cations, such as potassium, magnesium and strontium, appeared to further limit sorption.

The effect of each of these individual ions remains somewhat unclear, but could be related to the charge density of the hydration shell. The literature point to K^+ being the most effective competing ion for ion-exchange sites and disruptive to cobalt sorption. However, thanks to the additional surface complexation sites in the bentonite and provided that the pH is high enough, there is always a minimum Co sorption capacity present, irrespective of the presence of alkali or alkaline earth cations which do not compete with Co for these type sorption sites. The effect of pH was not studied in this work but according to literature, the maintaining of a pH>7 seems to be essential for surface complexation of Co to be effective.

Through studying the distribution coefficients over time, a sharp rise in cobalt attachment to bentonite occurred within the first twenty days, followed by a period of stabilisation or desorption until equilibrium had been reached. Long-term distribution coefficient values were determined to be approximately 0.28-0.63 m³/kg at 25 °C, 1.06-2.99 m³/kg at 50 °C and 2.89-7.43 m³/kg at 75 °C, with the higher values corresponding to high sodium ion concentration and the lower values to groundwater circumstances or high calcium ion concentration.

7

Outlook

The results yielded differences in the distribution coefficient values when compared to the literature. As this possibly could be a result of air interfering with the samples and their pH, performing an identical experiment, with the changed variable of keeping the samples in a vacuum chamber to the extent it is possible, would yield interesting results for comparison in this aspect. This would also help reduce concentration occurring in the heated samples due to evaporation of liquid, which also could have affected the results. Alternative experiments could also involve the study of 60 Co sorption to bentonite in other types of water, e.g. using K⁺ as the primary cation to study whether the valence of the competing ions are highly influential, or another divalent ion such as Mg^{2+} or Sr^{2+} to investigate if they yield significantly different results from Ca^{2+} and how this correlates with the hydration shell charge density. More data on the distribution coefficient as temperature increases above 75 °C, as well as if a sorption vertex is reached in the region 50-75 °C should be obtained to better outline the sorption behaviour as a function of temperature. The impact of higher temperature, which would be expected at 500 metres underground, might also be of interest to study. Literature results compared in this thesis determined a considerably shorter time for reaching equilibrium. As such, more experiments ought to be conducted studying sorption over longer periods of time to investigate whether that yields similar results to the ones found in this thesis.

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Sample tube and bentonite data

Table A.1. Information about each sample in terms of its type, as well as the different weights involved up until test commencement.

Index	Water	Temperature	Туре	Tube	Bentonite	Weight	Added	Weight at
	type	[°C]		weight	added	before	radionuclide-	test start
				[g]	[g]	sampling	spiked water	[g]
						[g]	[g]	
A1	GW	25	1	3.961	0,4007	5.614	6.613	12.228
A2	GW	25	2	3.934	0.401	5.641	6.586	12.227
A3	GW	25	3	4.057	0.400	5.767	6.584	12.351
A4	GW	25	Ref1	4.061	0	4.061	8.090	12.150
A5	GW	25	Ref2	4.058	0	4.058	8.062	12.120
A6	GW	50	1	4.055	0.399	6.459	5.911	12.370
A6.2	GW	50	2	4.070	0.401	6.469	5.912	12.381
A7	GW	50	3	3.946	0.400	6.350	5.910	12.260
A8	GW	50	Ref1	4.024	0	4.024	7.738	7.738
A9	GW	50	Ref2	4.010	0	4.010	7,731	7.731
A10	GW	75	1	3.963	0.400	6.364	5.928	12.292
B1	GW	75	2	4.059	0.400	6.457	5.952	12.409
B2	GW	75	3	4.066	0.400	6.467	5.957	12.424
B3	GW	75	Ref1	3.964	0	3.964	7.700	11.664
B4	GW	75	Ref2	3.964	0	3.964	7.693	11.657
B5	J1	25	1	3.956	0.400	5.942	6.658	12.600
B6	J1	25	2	3.946	0.400	5.792	5.987	11.779
B7	J1	25	3	3.947	0.400	5.928	6.635	12.563
B8	J1	25	Ref1	4.005	0	4.005	8.195	12.200
B9	J1	25	Ref2	3.947	0	3.947	8.173	12.120
B10	J1	50	1	4.051	0.400	6.459	5.989	12.448
C1	J1	50	2	3.956	0.400	6.363	6.007	12.370
C2	J1	50	3	4.054	0.401	6.461	5.993	12.455
C3	J1	50	Ref1	3.960	0	3.960	7.798	7.798
C4	J1	50	Ref2	4.057	0	4.057	7.837	7.837
C5	J1	75	1	3.965	0.400	6.378	6.035	12.413
C6	J1	75	2	3.964	0.400	6.374	5.927	12.301
C7	J1	75	3	4.075	0.400	6.480	6.036	12.515
C8	J1	75	Ref1	3.950	0	3.950	7.700	11.650
С9	J1	75	Ref2	3.995	0	3.995	7.717	11.712
C10	J2	25	1	3.963	0,401	6.492	7.038	13.530
D1	J2	25	2	4.060	0.400	6.223	7.227	13.450
D2	J2	25	3	4.055	0.400	6.067	6.723	12.790
D3	J2	25	Ref1	4,088	0	4.088	8.632	12.720
D4	J2	25	Ref2	4.000	0	4.000	8.620	12.620

D5	CA	25	1	4.054	0.401	6.451	5.979	12.430
D8	CA	25	2	3.966	0.402	6.353	5.985	12.338
D9	CA	25	3	4.053	0.401	6.461	5.968	12.429
D10	CA	25	Ref1	3.934	0	3.934	7.743	11.677
E2	CA	25	Ref2	4.107	0	4.107	7.738	11.845
E3	CA	50	1	4.058	0.399	6.458	5.930	12.388
E4	CA	50	2	4.049	0.401	6.441	5.943	12.384
E5	CA	50	3	3.998	0.402	6.397	5.926	12.323
D6	CA	50	Ref1	3.962	0	3.962	7.739	7.739
D7	CA	50	Ref2	3.963	0	3.963	7.760	7.760
E6	CA	75	1	3.961	0.401	6.365	6.034	12.399
E7	CA	75	2	4.070	0.407	6.467	5.989	12.456
E8	CA	75	3	3.995	0.401	6.385	5.982	12,367
F1	CA	75	Ref1	4.089	0	4.089	7.770	11.860
F2	CA	75	Ref2	4.074	0	4.074	7.739	11.813

Table A.2. Information about the acidic references with regard to how much radionuclide-spiked water and hydrochloric acid were added.

Index	Water type	Туре	Added radionuclide-spiked water	Added 1 M HCl [g]
			[g]	
SGW	GW	ARef	1.010	1.021
SJ1	J1	ARef	1.023	1.023
SJ2	J2	ARef	1.081	1.022
SCA	CA	Aref	1.018	1.024

B

Liquid scintillation counting data

B.1 Test group A

Table B.1. Test series A data on the extracted sample volumes in mL for liquid scintillation counting for each measurement moment, where the extracted volume was increased after measurement A-1 for GW, J1 and J2 due to low margins of counts per minute.

Sample	Туре	A-1	A-2	A-3	A-4	A-5	A-6
ID		[mL]	[mL]	[mL]	[mL]	[mL]	[mL]
A1	GW-1	0.079	0.096	0.097	0.102	0.099	0.098
A3	GW-2	0.080	0.097	0.098	0.101	0.098	0.097
A3	GW-3	0.079	0.095	0.099	0.101	0.098	0.098
A4	GW-R1	0.080	0.130	0.097	0.101	0.102	0.098
A5	GW-R2	0.080	0.097	0.098	0.095	0.102	0.098
B5	J1-1	0.08	0.095	0.100	0.104	0.100	0.101
B6	J1-2	0.08	0.099	0.100	0.102	0.099	0.100
B7	J1-3	0.078	0.099	0.099	0.103	0.099	0.100
B8	J1-R1	0.08	0.098	0.097	0.104	0.104	0.099
B9	J1-R2	0.08	0.099	0.098	0.103	0.102	0.099
C10	J2-1	0.084	0.101	0.105	0.117	0.105	0.107
D1	J2-2	0.082	0.102	0.105	0.108	0.105	0.106
D2	J2-3	0.081	0.104	0.106	0.107	0.105	0.106
D3	J2-R1	0.08	0.103	0.105	0.109	0.107	0.106
D4	J2-R2	0.09	0.106	0.103	0.116	0.108	0.105
Sample	Туре	A-1	A-2	A-3	A-4	A-5	A-6
ID		[mL]	[mL]	[mL]	[mL]	[mL]	[mL]
A1	GW-1	0.101	0.099	0.098	0.096	0.099	0.100
A3	GW-2	0.101	0.101	0.099	0.100	0.096	0.100
A3	GW-3	0.100	0.101	0.100	0.101	0.098	0.100
A4	GW-R1	0.102	0.102	0.102	0.101	0.098	0.099
A5	GW-R2	0.100	0.102	0.099	0.095	0.098	0.100

Sample	Туре	A-1	A-2	A-3	A-4	A-5	A-6
ID		1 day	4 days	8 days	15 days	29 days	77 days
		[cpm/mL]	[cpm/mL]	[cpm/mL]	[cpm/mL]	[cpm/mL]	[cpm/mL]
A1	GW-1	867.7	465.3	373.3	317.0	353.5	273.3
A3	GW-2	647.5	419.6	330.6	324.4	318.8	274.1
A3	GW-3	669.6	441.9	341.8	287.1	335.4	262.5
A4	GW-R1	5811.3	5604.6	5698.9	5562.3	5550.3	5603.9
A5	GW-R2	5746.3	5619.6	5748.5	6009.4	5653.5	5636.4
B5	J1-1	165	52.5	55.9	109.3	219.9	153.1
B6	J1-2	111.3	36.4	66.1	110.6	171.9	128.1
B7	J1-3	266.7	120.7	111.4	138.3	211.9	149.9
B8	J1-R1	5722.5	5649.0	5591.4	5463.0	5401.9	5478.9
B9	J1-R2	5682.5	5625.3	5591.4	5532.9	5578.2	5465.3
C10	J2-1	336.0	69.0	27.6	24.8	138.1	148.2
D1	J2-2	288.8	95.1	31.3	13.0	127.1	156.5
D2	J2-3	127.8	44.4	35.8	16.8	94.3	123.0
D3	J2-R1	5782.5	5354.4	5373.3	5212.9	5194.8	5175.5
D4	J2-R2	5135.6	5360.4	5346.9	4933.6	5160.9	5140.1
Sample	Туре	A-1	A-2	A-3	A-4	A-5	A-6
ID		1 day	4 days	7 days	14 days	27 days	55 days
		[cpm/mL]	[cpm/mL]	[cpm/mL]	[cpm/mL]	[cpm/mL]	[cpm/mL]
D5	CA-1	501.0	272.7	302.6	515.6	565.0	347.3
D8	CA-2	473.7	244.1	220.3	279.8	456.8	363.7
D9	CA-3	544.2	337.6	269.8	366.1	487.8	339.7
D10	CA-R1	8214.8	8060.5	8070.5	8038.6	8016.3	8066.8
E2	CA-R2	8254.7	8070.9	8222.8	8267.0	8056.9	8200.6

Table B.2. Liquid scintillation counting results in cpm/mL at each measuring moment for test series A, as well as the days since test start.

B.2 Test group B

 Table B.3. Extracted volumes for each sample in mL for test series B.

Sample	Туре	B-1	B-2	B-3	B-4	B-5	B-6
ID		[mL]	[mL]	[mL]	[mL]	[mL]	[mL]
A6	GW-1	0.099	0.096	0.098	0.095	0.097	0.100
A62	GW-2	0.100	0.098	0.099	0.097	0.098	0.100
A7	GW-3	0.101	0.099	0.099	0.101	0.100	0.100
A8	GW-R1	0.103	0.100	0.100	0.103	0.096	0.105
A9	GW-R2	0.105	0.091	0.099	0.103	0.099	0.102
B10	J1-1	0.101	0.098	0.099	0.100	0.100	0.101
C1	J1-2	0.102	0.098	0.099	0.101	0.100	0.102
C2	J1-3	0.102	0.100	0.072	0.101	0.100	0.102

C3	J1-R1	0.105	0.103	0.101	0.087	0.101	0.104
C4	J1-R2	0.104	0.102	0.102	0.104	0.098	0.103
E3	J2-1	0.099	0.097	0.098	0.100	0.098	0.100
E4	J2-2	0.100	0.099	0.098	0.101	0.098	0.101
E5	J2-3	0.101	0.093	0.104	0.100	0.098	0.101
D6	J2-R1	0.107	0.104	0.102	0.107	0.100	0.103
D7	J2-R2	0.106	0.105	0.103	0.111	0.105	0.104

Table B.4. Liquid scintillation results in counts per minute per millilitre for test series B, along with how many days since sampling the measurements were taken.

Sample	Туре	B-1	B-2	B-3	B-4	B-5	B-6
ID		1 day	4 days	7 days	14 days	27 days	55 days
		[cpm/mL]	[cpm/mL]	[cpm/mL]	[cpm/mL]	[cpm/mL]	[cpm/mL]
A6	GW-1	1387.5	499.0	255.6	166.0	140.1	136.6
A62	GW-2	1324.6	498.5	348.8	219.4	130.2	105.7
A7	GW-3	1259.4	503.0	366.2	216.3	130.7	130.6
A8	GW-R1	8251.5	8520.0	8549.6	8316.1	8205.0	7950.2
A9	GW-R2	8327.9	8471.6	8426.6	8375.9	8385.9	8256.1
B10	J1-1	1108.9	355.7	198.4	101.8	87.6	63.5
C1	J1-2	1548.8	605.5	368.3	142.9	101.9	34.4
C2	J1-3	2716.3	510.5	320.8	127.1	95.4	53.9
C3	J1-R1	7941.0	7706.1	7533.6	8566.0	7519.4	7251.9
C4	J1-R2	7551.4	8373.3	8023.5	8115.9	7321.7	8222.4
E3	CA-1	415.2	147.0	103.1	67.9	86.4	80.8
E4	CA-2	460.8	140.4	105.9	60.5	83.0	66.6
E5	CA-3	314.5	148.1	114.9	70.1	59.2	61.4
D6	CA-R1	7690.1	7530.8	7610.8	7517.3	7587.6	7373.1
D7	CA-R2	7845.9	7545.7	7602.7	7061.5	7670.5	7754.6

B.3 Test group C

Table B.5. Data on extracted volumes for each sample before measurement included in test series C in mL.

Sample	Туре	A-1	A-2	A-3	A-4	A-5	A-6
ID		[mL]	[mL]	[mL]	[mL]	[mL]	[mL]
A10	GW-1	0.099	0.095	0.098	0.098	0.0997	0.0983
B1	GW-2	0.098	0.096	0.099	0.098	0.1006	0.0979
B2	GW-3	0.099	0.097	0.097	0.099	0.0994	0.0979
B3	GW-R1	0.101	0.098	0.1	0.099	0.0972	0.1008
B4	GW-R2	0.102	0.103	0.101	0.103	0.0956	0.1008
C5	J1-1	0.097	0.1	0.1	0.101	0.1001	0.0994
C6	J1-2	0.099	0.098	0.099	0.101	0.0997	0.1002
C7	J1-3	0.101	0.096	0.1	0.102	0.1013	0.0981
C8	J1-R1	0.104	0.101	0.104	0.105	0.1076	0.1131

C9	J1-R2	0.103	0.103	0.103	0.110	0.1043	0.1038
E6	J2-1	0.098	0.11	0.099	0.100	0.0996	0.0995
E7	J2-2	0.099	0.099	0.098	0.100	0.0979	0.0987
E8	J2-3	0.098	0.1	0.099	0.101	0.0973	0.1005
F1	J2-R1	0.1	0.099	0.102	0.105	0.0995	0.1021
F2	J2-R2	0.103	0.099	0.101	0.103	0.1022	0.1028

Table B.6. Experimental series C results in counts per millilitre, as well as the number of days since test commencement the measurement was made.

Sample	Туре	C-1	C-2	C-3	C-4	C-5	C-6
ID		1 day	3 days	7 days	14 days	23 days	49 days
		[cpm/mL]	[cpm/mL]	[cpm/mL]	[cpm/mL]	[cpm/mL]	[cpm/mL]
A10	GW-1	1200.6	229.3	90.4	30.5	26.1	34.6
B1	GW-2	1598.2	303.0	102.0	21.4	12.9	33.7
B2	GW-3	1675.4	328.5	106.6	43.5	17.1	44.9
B3	GW-R1	8382.9	8058.0	8551.9	8020.7	8908.4	8659.7
B4	GW-R2	8222.0	8262.2	8405.6	8213.9	8609.8	8242.1
C5	J1-1	1242.3	150.1	44.9	10.9	16.0	17.1
C6	J1-2	582.3	120.2	20.2	5.9	15.0	19.0
C7	J1-3	1263.1	109.5	25.0	-3.9	-2.0	38.7
C8	J1-R1	8398.3	8599.6	8381.4	8466.8	8303.0	7461.5
C9	J1-R2	8368.0	8552.2	8472.2	8077.5	8370.1	8625.2
E6	CA-1	293.5	49.2	74.6	29.9	31.1	42.2
E7	CA-2	318.8	95.8	81.1	31.8	46.0	42.6
E8	CA-3	309.5	102.9	80.7	45.5	50.4	55.7
F1	CA-R1	7910.5	8236.7	8089.2	8038.4	8220.1	8340.8
F2	CA-R2	8018.4	7937.4	8002.0	8095.7	8070.5	8232.5

B.4 Acidic references

Table B.7. Extracted volumes for each of the four times measurements were made on the four acidic references.

Sample ID	Туре	Test 1	Test 2	Test 3	Test 4
		[mL]	[mL]	[mL]	[mL]
SGW	GW-AR	0.108	0.106	0.167	0,167
SJ1	J1-AR	0.112	0.079	0.079	0,106
SJ2	J2-AR	0.086	0.111	0.109	0,109
SCA	CA-AR	0.105	0.11	0.099	0.112

 Table B.8. Results in cpm/mL for the acidic references and their combined average.

Sample ID	Туре	Test 1	Test 2	Test 3	Test 4	Average
		[cpm/mL]	[cpm/mL]	[cpm/mL]	[cpm/mL]	[cpm/mL]
SGW	GW-AR	2853.7	2976.5	1803.8	1897.7	2382.9
SJ1	J1-AR	1993.8	3727.6	2788.1	2780.8	2822.6

SJ2	J2-AR	2666.7	2687.4	2728.2	2739.2	2705.4
SCA	CA-AR	4120.6	4224.5	4342.8	4113.0	4200.2

C

Analysis of variance calculations

C.1 Temperature and ion type

Each value in table 4.7 can be described using the index *ijk*, where *i* represents the different temperature columns (i = 1,2,3 corresponds to room temperature, 50 °C and 75 °C respectively), *j* describes the ion types (j = 1,2,3 are GW, J1 and CA respectively) and *k* is the specific observation of the samples in triplicate. The temperature, ion type, total and error sums of squares are then calculated for according to equations C.1, C.2, C.3 and C.4, respectively. The calculations in this appendix follows the methods described in Montgomery (2012).

$$SS_{temperatures} = \frac{1}{bn} \sum_{i=1}^{a} y_{i..}^2 - \frac{y_{..}^2}{abn}$$
(C.1)

$$SS_{ion \, types} = \frac{1}{n} \sum_{i=1}^{a} \sum_{j=1}^{b} y_{ij.}^{2} - \frac{1}{bn} \sum_{i=1}^{a} y_{i..}^{2}$$
(C.2)

$$SS_{total} = \sum_{i=1}^{a} \sum_{j=1}^{b} \sum_{k=1}^{n} y_{ijk}^{2} - \frac{y_{..}^{2}}{abn}$$
(C.3)

$$SS_{error} = \sum_{i=1}^{a} \sum_{j=1}^{b} \sum_{k=1}^{n} y_{ijk}^{2} - \frac{1}{n} \sum_{i=1}^{a} \sum_{j=1}^{b} y_{ij.}^{2}$$
(C.4)

Where *a*, *b* and *n* corresponds to the number of temperatures, ion types per temperature and observations per ion type, all equal to 3. The degrees of freedom are calculated according to equations C.5, C.6, C.7 and C.8.

$$DoF_{temperatures} = a - 1$$
 (C.5)

$$DoF_{ion types} = a(b-1)$$
 (C.6)

$$DoF_{error} = ab(n-1)$$
 (C.7)

$$DoF_{total} = abn - 1 \tag{D.8}$$

The mean square for the temperatures, ion types and error are calculated by division of the respective sum of squares with their specific degrees of freedom. This is detailed in equations C.9, C.10 and C.11.

$$MS_{temperatures} = \frac{SS_{temperatures}}{DoF_{temperatures}}$$
(C.9)

$$MS_{ion \ types} = \frac{SS_{ion \ types}}{DoF_{ion \ types}} \tag{C.10}$$

$$MS_{error} = \frac{SS_{error}}{DoF_{error}}$$
(C.11)

In order to perform the F-test for the variance of the temperatures and ion types, the F_{obs} is calculated using equations C.12 and C.13.

$$F_{obs,temperatures} = \frac{MS_{temperatures}}{MS_{ion\,types}}$$
(C.12)

$$F_{obs,ion \ types} = \frac{MS_{ion \ types}}{MS_{error}} \tag{C.13}$$

These values are then compared with the statistical values for F-distribution, F_{stat} , at a certain confidence level and for the relevant degrees of freedom. If $F_{obs} > F_{stat}$, this means that the variance is significant and implies the studied parameter influences the results. The values are presented in the ANOVA-table in table 4.8.

C.2 Comparison of J1 and J2

From table 4.9, with two variable factors and three observations, it can be stated that a = 2 (*i* = 1,2) and b = 3 (*j* = 1,2,3). The sum of squares for the two ion types, error and the total sum of squares are calculated according to C.14, C.15 and C.16, respectively.

$$SS_{ion \ types,2} = \frac{1}{b} \sum_{i=1}^{a} y_{ij}^2 - \frac{y_{..}^2}{ab}$$
(C.14)

$$SS_{error,2} = \sum_{i=1}^{a} \sum_{j=1}^{b} y_{ij}^2 - \frac{1}{b} \sum_{i=1}^{a} y_{ij}^2$$
(C.15)

$$SS_{total,2} = \sum_{i=1}^{a} \sum_{j=1}^{b} y_{ij}^2 - \frac{y_{..}^2}{ab}$$
(C.16)

Subsequently, the degrees of freedom are calculated according to equations C.17, C.18 and C.19 for the ion types, error and total sum of squares.

 $DoF_{ion\ types,2} = a - 1 \tag{C.17}$

 $DoF_{error,2} = ab - a$ (C.18)

$$DoF_{total,2} = ab - 1 \tag{D.19}$$

The mean of squares for ion types and error are calculated through division of equations C.14 with C.17 and C.15 with C.18. The observed F-statistic is then calculated by division of the mean of squares for the ion types with the mean of squares for the error. It is then compared with the statistical F-value at a chosen confidence level and degrees of freedom corresponding to the ion type and error. If F_{obs} is smaller than F_{stat} , then the compared observations can not be said belong to significantly different groups.