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STUDY OF THE REDUCTION OF FLUORIDE CONTENT IN GHANA'S GROUNDWATER

Sara Noriega Oreiro

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Sara Noriega Oreiro

Abstract

In 2015 it was estimated that 663 million people worldwide were subjected to the consumption of drinking water from unsafe sources, most of them living in developing countries and rural areas. Although groundwater is in general a good option due to its good microbiological and chemical quality, still elevated concentrations of elements that can have negative impact on human health may happen, and one of the parameters of concern is fluoride. According to the World Health Organization (WHO) the guideline limit for this element in drinking water is 1.5 mg/L and chronic consumption of water with bigger concentration may lead to several problems related with bone and teeth mineralization, even changes in the DNA structures or interfering kidney functioning.

Many methods have been developed for the defluorination of water, outstanding precipitation, adsorption and membrane techniques. However, the search of an appropriate technology is still a critical matter, as a lot of difficulties are present at the time of the actual implantation in certain areas, highlighting the economic reasons.

The simulation analysis carried out with *PHREEQ-C* for the study of the removal of fluoride up to 1.5 mg/L through precipitation, was favorable with the addition of $CaCl_2$ and $CaOH_2$. However, the pure addition of these compounds leads to the exit of other parameters out of the limits established by the WHO for drinking water. It is therefore necessary, to work at a temperature of 2 °C in the first case, favoring the precipitation of fluorite and requiring less amount of the added chemical, or to add carbonic acid in the second case, to regulate the pH and calcium concentration. The experimental study corroborates the values obtained by *PHREEQ-C* for pure water with added fluoride, but it is not as accurate in the presence of other ions.

Preface

This report is the result of a project carried out during the 10th semester of Chemical Engineering Master at Aalborg University as the Master Thesis Project that would complete the studies. It explores the fluoride removal from drinking water, specifically in the country of *Ghana (Africa).* The origin of high fluride contents present in many areas of the world is studied, highlighting the most influencing parameters, and focus is made on Ghana's groundwater. The different and main methods available to date for defluorination are stated in the review of the state of the art.

Initially, this project was supposed to be experimental, studying some of the techniques available on the reduction of fluoride in a replica of water from the B*ongo region (Ghana).* However, due to the situation lived with COVID-19 and the closure of the laboratories, a change in the objectives had to be made.

Through aqueous geochemical simulations (*PHREEQ-C)* precipitation of fluoride was attempted with the addition of different chemicals that would provide the best removal efficiency. Only one day access to the laboratory was provided, so the experimental part was reduced to the study of the precipitation of the best simulations through Isothermal Titration Calorimetry (ITC) and the measurement of the fluoride content through ion chromatography. Although a recreation of the Ghana's groundwater of study was intended, the limitations in the availability of chemicals made impossible its full reproduction.

I would like to thank my supervisor, Erik Gydesen Søgaard for his ideas and help for the development of this project, as well as for reviewing my work and drafts during its development.

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List of abbreviations and acronyms

- **AMMT** - Annual Mean Maximum Temperature
- **EPA** - Environmental Protection Agency
- **HRTEM** – High Resolution Transmission Electron Microscopy
- **ISE** - Ion-Selective Electrode
- **IC** - Ion Chromatography
- **ITC** – Isothermal Titration Calorimetry
- **RO** – Reverse Osmosis
- **SI** - Saturation Index
- **WHO** – World Health Organization

1. INTRODUCTION

Fluorine is an essential element naturally found in almost all food, drinking water and ocean water. When ingested in the specific dose, it brings a lot of benefits to human beings for the normal mineralization of both bones and teeth [1].

Fluoride intake from food in an average diet is estimated in around 0.3-0.5 mg/L [2]. The World Health Organization (WHO) recommends the consumption of water with a concentration in the range of 0.5-1 mg/L [3]. The amount of fluoride that is naturally found in drinking water in some countries does not reach these values. In the early 1900s, the policies of a lot of governments introduced the mandatory fluoridation of drinking water, as sodium fluoride or hexafluorosilicic acid. However, since 1994, when the WHO declared the water fluoridation as a measure of oral health protection, a lot of regulation have been revised or removed [4].

Currently, the WHO recommends the usage of only one type of systematic fluoridation per community, combining it with the use of fluoride toothpastes. The available fluoridation techniques are fluorinated water, fluorinated salt and fluorinated milk, the latter two being up to the consumer to choose their consumption, whereas in water, the consumer is forced to the intake, as it is introduced into the public water supply [5].

Despite the huge benefits associated with fluorine consumption, at higher concentrations this element is toxic. High intakes of fluoride provoke teeth mottling (dental fluorosis) and other associated problems, increasing in severity at higher consumption. The chronic endemic fluorosis, which arise due to the continued consumption of high fluorine contents, may cause limitations in the movement of joins *(Figure 1.1)* or neurological problems [6][7].

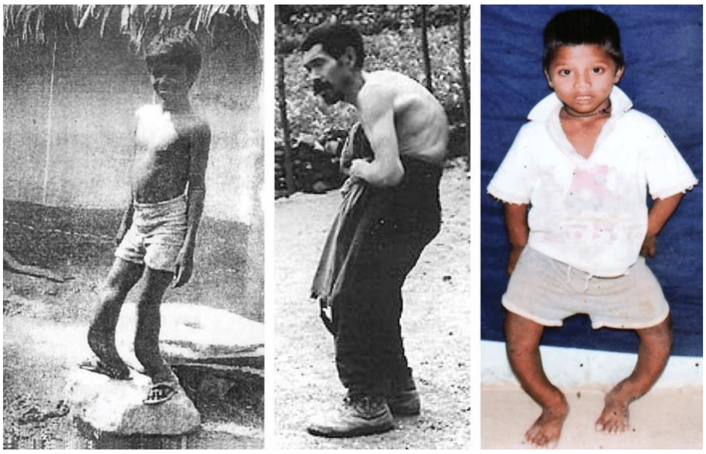


Figure 1.1 – Patients suffering from skeletal fluorosis [8]

Drinking water is very sensitive in this respect, as great deviations in concentration take places from place to place, and when fluoride content is high it has a huge effect in human diet. The concentration in natural waters can occur from trace to concentrations as high as 2800 mg/L, being the usual range from 0.1 to 10 mg/L [9][10].The WHO has set a guidance level of 1.5 mg/L, as the maximum amount of fluoride permissible in drinking water. However, a lot of countries such as China, India and some parts of Africa, especially those in the Rift Valley, have documented concentrations of this pollutant above the limit [11] and it is estimated that around 260 million people worldwide are subjected to have chronic fluorosis [12].

For this fluorine endemic areas, the WHO recommends the following hierarchical measures: (1) to find a substitute drinking water source, (2) to dilute the water with a high fluoride content with another with a lower one, in order to reach a mass balance of 1.5 mg/L, (3) to introduce diets with a high content of calcium, magnesium and vitamin c, and (4) to apply some technique of fluoride removal [13].

The presence of fluorine in groundwater (the main source in nature, although it can also be found in surface water) is due to the weathering and leaching of minerals bearing fluoride [14]. About 170 minerals are known to contain fluorine, the most abundant being fluorite (CaF_2) and apatite $Ca_5(PO_4)_3(F,Cl,OH)$, [5] and the geogenic sources are found mainly in volcanic, granitic and gneissic rocks [15]. The concentration of fluoride in water is the result of an equilibrium between the F-bearing minerals and this fluid, being dependent of the capability of ion release of each mineral and several other factors, such as the presence of precipitating ions, the contact time in a particular formation, the pH… [10]

The presence of fluoride in water cannot be determined by physical examination, and it does not have any color, smell or taste. Its concentration in groundwater can only be determined through chemical analysis, usually through colorimetry with SPADNS *(Figure 1.2)* or the complexone method, through ion chromatography or through fluoride-selective electrodes [16]. Some proxy indicators of the presence of high levels of fluoride in groundwater are, in general terms: small contents of calcium and magnesium, big contents of bicarbonate ions and sodium and an alkaline pH (which helps the mobility of the fluoride ion from fluorite) [13][14].

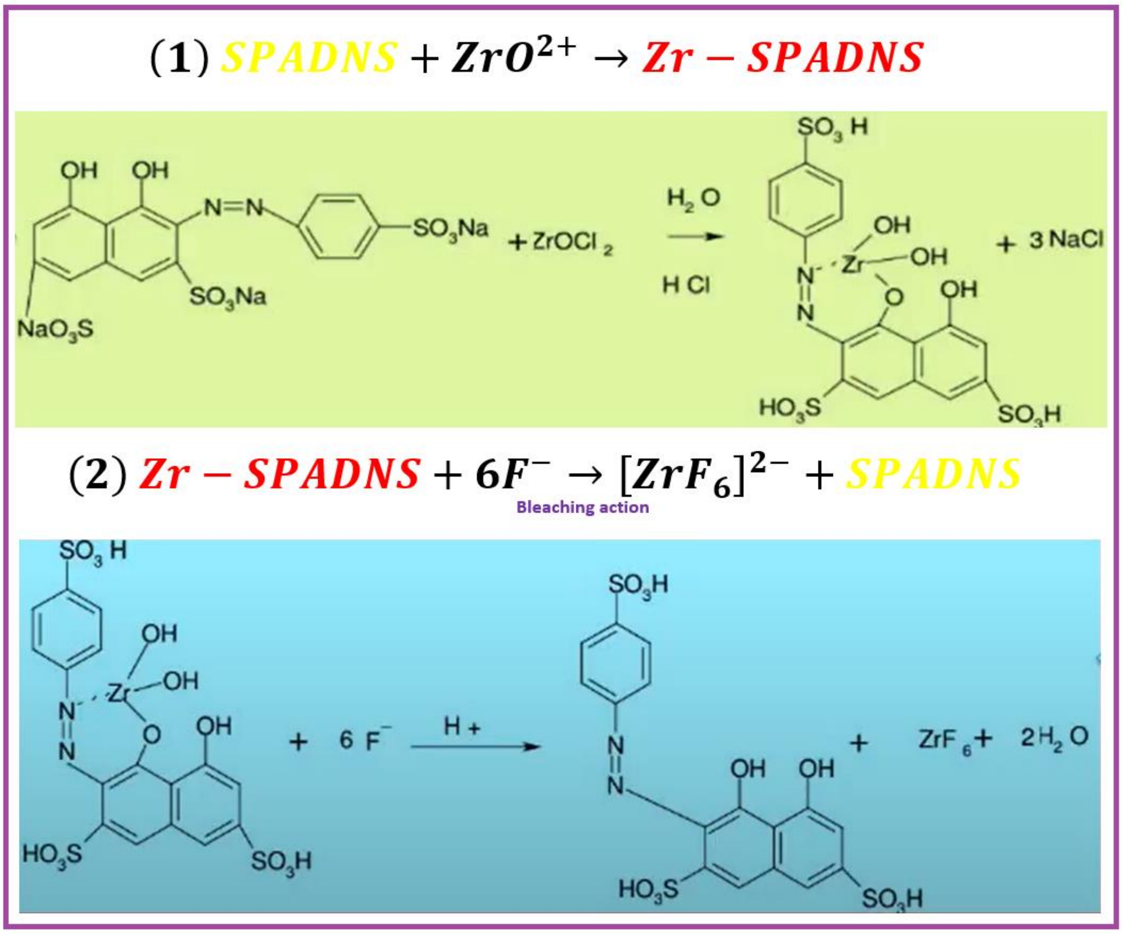


Figure 1.2 – Mechanism of colorimetry with SPADSN for fluoride concentration determination. The reagents needed are SPADNS, zirconyl ion (ZrO^{2+}), a standard fluoride solution and sodium arsenite ($NaAsO_2$) to prevent the bleaching action of the chloride ion. The sample of water with fluoride content (colorless) is made to react with Zr-SPADNS complex (red coloration). The fluoride ions form a colorless complex with the zirconyl lion leaving a yellow colour SPADSN. Thus, the stronger the bleaching action, the higher the fluoride content, which can be numerically determined through the Beer-Lamberts law [17] Figure modified from [17]

Globally, in areas of arid climate, groundwater is essentially and an inevitable resource [15]. In Africa, groundwater is a primary source of drinking water, especially in the rural communities [13]. Several methods have been developed for the fluoride removal such as membrane or adsorption techniques [18]. However, as many of the regions with high groundwater consumption are located in developing countries, the treatments for fluoride removal differ from place to place and in many, high fluoride content waters are consumed without any removal of this pollutant [9]. Many techniques have been developed but they have not reached the rural affected population due to different limitations [14].

One of the places affected by the elevated levels of this element is Ghana, specifically in the northern regions and it is the case of study of this project. The fluoride content in groundwater ranges from 0.11 mg/L to 4.60 mg/L. In an investigation done in 1994, in the *Bongo district (Ghana),* 62% of the school children suffered from dental fluorosis [10].

2. OBJECTIVES

This project is based on the study of fluoride removal from groundwater. The excess of fluoride present in the drinking water of many parts of the world have converted it in an endemic health problem, which is especially noticeable in developing countries. Different methods have been investigated and applied for the reduction in the content of this pollutant, but there is need of finding an easy and economically affordable technique that could be implemented worldwide, including the most disadvantaged areas.

This project is divided in three parts. The first consists of a theoretical approach to the problem, identifying its sources and parameters of importance. In turn, focus will be on the study of groundwater in Ghana, and on the origin of the problem in this region. By last, a review of the different methods currently available for fluoride removal, the different researches and investigations carried out to date, as well as the measures that have been tested specifically in Ghana will be pointed out.

The second part consists on a computational study using aqueous geochemical calculations with *PHREEQ-C software* for fluoride removal. With the usage of the software attempts will be made to precipitate fluoride from groundwater in the form of fluorite, simulationally.

The third part consists on the experimental reproduction of the results that have given the best results during the simulations, thus, allowing the observation of whether *PHREEQ-C* works correctly in the modelling of this reactions.

3. THEORETICAL CONSIDERATIONS

3.1 Fluoride excess in drinking water

Fluoride can occur in drinking water naturally, or by artificial fluoridation, being one of the essential trace elements [15]. There is need of a minimum fluoride concentration in the public water supply for healthy teeth and bones growth (dental enamel formation and normal bone mineralization) but a chronic consumption of too high concentration leads to several serious health issues for the consumer [19][20][16].

The WHO has set a fluoride permissible limit of 1.5 mg/L, being the recommended for artificial fluoridation in the range between 0.5 mg/L and 1 mg/L. Above this limit, the risk of dental and skeletal fluorosis is increased [3]. However, high fluoride concentrations, above 30 mg/L occur in many parts of the world [18] and it is estimated that around 260 million people worldwide are dependent on drinking water with fluoride content over the guideline standard limit [12].

Fluorine is monovalent and it is the most electronegative element, therefore, it is very reactive. Although fluorine is one of the few elements that can form diatomic molecules (F_2), it does not usually occur in elemental state rather found in the form of its anion, F^-, due to this high electronegativity [21]. It reacts producing ionic or polar substances (e.g. HF or NaF) that dissociate and produce solvated negatively charged F^- ions in water [16]. In highly acidic aquatic environments ($pH < 5$) the tendency is to form complexes with metal ions, whereas with more alkaline pH it is characteristic to find it in the form of single ion [7].

3.1.1 Causes for fluoride contamination

The presence of fluoride in the environment (including raw drinking water) can be due to natural factors or due to human activity (agricultural and industrial activities) (*Figure 3.1).*

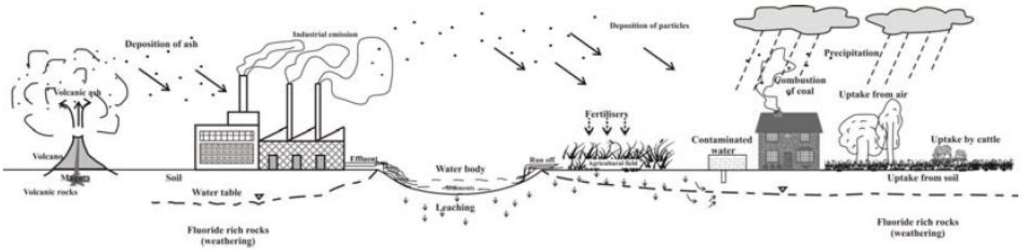


Figure 3.1 – Possible causes of fluoride in the environment [22]

There are three natural sources of fluoride. The main route of entry is the water enrichment with fluoride due to rock alteration, evaporation and geothermal mixing [16], having the rock geochemistry a great control on the contamination. Examples of natural sources of fluoride are the minerals fluorite, fluorapatite and cryolite, representing fluoride compounds around a 0.06 – 0.09 % of the Earth's crust composition (13th most common element) [23][24]. The presence of high concentrations of fluoride in the water is dependent on a big number of factors, such as the geology, the chemical and physical characteristics of the aquifer, the contact time, the pH… [25]. It is alkaline water that with the biggest tendency to solubilize the fluoride bearing materials [26]. Fluoride is found in seawater with concentrations between 1.2 and 1.4 mg/L, in groundwaters with concentrations up to 67 mg/L and in surface water bodies usually with concentrations below 0.1 mg/L [24]. The general trend of a presence of higher fluoride levels in groundwaters is reasonable since a greater interaction between geological substrates and water occurs. However, some exceptions to the rule take place, as *Malago et al.* [7] collect that through the study on fluoride levels in different African countries in the Rift Valley, higher concentrations of this pollutant were obtained in surface water bodies. A deeper explanation of the natural sources, influencing factors and mechanisms involved for the rock dissolution and water fluoridation will be carried out in the next *section 3.2.* The second contribution of fluoride from natural sources comes from the volcanic activity, through volcanic aerosols and ashes emitted during eruptive episodes. The released fluoride is mainly in the form of hydrogen fluoride (HF). This substance is highly soluble in the magma, so only around a 20% is emitted in gaseous form. It has been estimated that ~60-6000 kt (kilotonnes) are released annually worldwide through this source [25] (both atmospheric emissions and high fluoride containing magma)[25][27]. Finally, the third source consists on marine aerosols (~20 kt).

The other of the fluoride sources is related with anthropogenic events, such as the usage of phosphate fertilizers and insecticides or the discharge from several industrial activities such as burning of coals, brick-making industries, aluminum smelting, steel production or clays used in ceramic industries [28][23][29]. Fluorides can be dissolved in the groundwater bodies, released in gaseous form or in form of ashes [22][25]. However, it is believed that although the greatest source of fluoride to the environment is anthropogenic, the presence of this contaminant in the groundwater has mainly a geological origin [28].

3.1.2 Health effects of fluoride

Fluoride is an essential microelement for human health, but the continued intake of great quantities can lead to health problems, beginning with teeth mottling and followed by dental or skeletal fluorosis. Reason for this is the high electronegativity of this element, getting attached to the calcium cations that are presented in tooth and bones [28].

In small quantities (<1.5 mg/L) fluorine intake is a preventive method of dental caries. Tooth decay occurs as a consequence of bacterial action on teeth. Bacteria form a covering on the tooth, called plaque. Some oral bacteria form acids as the end product of carbohydrate metabolism (mainly sugars). When enough acid is produced making the pH go below 5.5, the calcium phosphate mineral in tooth enamel (carbonated hydroxyapatite) is dissolved. This process, called demineralization, unless retained, leads to cavity formation. It can only be recovered, or remineralized through ions dissolved in saliva. Fluorides inhibit caries formation through three mechanisms: increased dental mineralization (process in which minerals are returned to the molecular structure of the tooth itself), reversal of demineralization, and inhibition of cariogenic acid-producing bacteria [30][31][32].

Demineralization and remineralization is a dynamic process, being the balance between them, the only or natural way to keep teeth strong. When a fluoride is present in low concentrations in saliva and is concentrated in the plaque, remineralization increases and demineralization is inhibited, since fluorides contribute to the incorporation of calcium and phosphate ions in the enamel. When fluoride ions are present in the plaque fluid together with the dissolved hydroxyapatite and the pH is higher than 4.5, a remineralized fluorapatite-like veneer is formed, being this fluoride-containing enamel constituted by bigger crystals, harder and less acid soluble than the original enamel it replaces (as shown in *Equation (1)*). Besides, it is formed much faster than ordinary remineralized would. Therefore, when an enamel is been frequently subjected to the demineralization and remineralization processes with a consequent repair, the tissue will be much more resistant than normal enamel to acid attacks [30][31][32][7].

$$Ca_5(PO_4)_3OH + F^- \rightarrow Ca_5(PO_4)_3F + OH^- \qquad (1)$$

In addition, it also participates in the formation and strengthening of bones, increasing apatite crystals and reducing their solubility, playing a stabilizing role for bone tissue in certain pathologies, such as osteoporosis (it has been scientifically proven as the contribution of fluoride to patients with said disease, increased bone density in the spinal area, therefore reducing the risk of injury) [30][33][34].

On the other hand, as it has been said, excess consumption causes the opposite effect, weakening the enamel (causing more cavities) and weakening our bones (more decalcification and osteoporosis). In this case, the reaction that is taking place is as shown in *Equation (2)* [7].

$$Ca_5(PO_4)_3F + 9F^- \rightarrow Ca_5F_{10} + 3PO_4^{3-} \qquad (2)$$

Once fluorapatite is formed, it continues to react with an excess of fluoride ions, giving place to the formation of calcium decafluoride, very hard and brittle material, not suitable for skeletal structure [7].

Depending on the level of fluoride (C_F) present in the drinking water, the possible symptoms after chronic consumption are:

- **1.5 mg/L < C_F < 3 mg/L: Dental fluorosis** *(Figure 3.2).* It is mainly characterized by the appearance of stains on the teeth. Moderately or intensely affected teeth may show a tendency to wear or fracture the enamel, weakening teeth and causing a permanent physical damage [7] [35].

Figure 3.2 – Dental fluorosis [36]

- **4 mg/L < C_F < 8 mg/L: Skeletal fluorosis.** It has an effect on bone growth and remodeling, causing diffuse densification of bones. The changes in the bone structure make them harder and thus brittle and less elastic. Some of the early symptoms are stiffness and pain in the joints, due to the thickening of the bone structure and accumulation of bone tissue [37] [38] [39] [40].
- **C_F > 10 mg/L: Crippling fluorosis.** It is the most severe way of skeletal fluorosis. Causing serious problems as limitation of joint movement due to its calcification, muscle wasting or several neurological problems due to compression of the spinal cord to the extent that the patient can become paralyzed [7] [38] [39].

The three diseases stated are the ones drawing the most attention, however, other health effects associated with the consumption of elevated fluoride levels are red blood cell deformities, reduced immunity, nausea…

3.1.3 Fluoride occurrence in the world

Geogenic occurrence in areas of high fluoride content are usually linked with volcanic activity, geothermal waters, shallow aquifers in desert areas with strong evaporation, sedimentary aquifers experiencing ion exchange and fumaric gases [13] [41].

In *Figure 3.3*, the main documented occurrences of fluoride levels bigger than 1.5 mg/L (maximum level recommended from the WHO for safe consumption of drinking water) in groundwater worldwide can be seen.

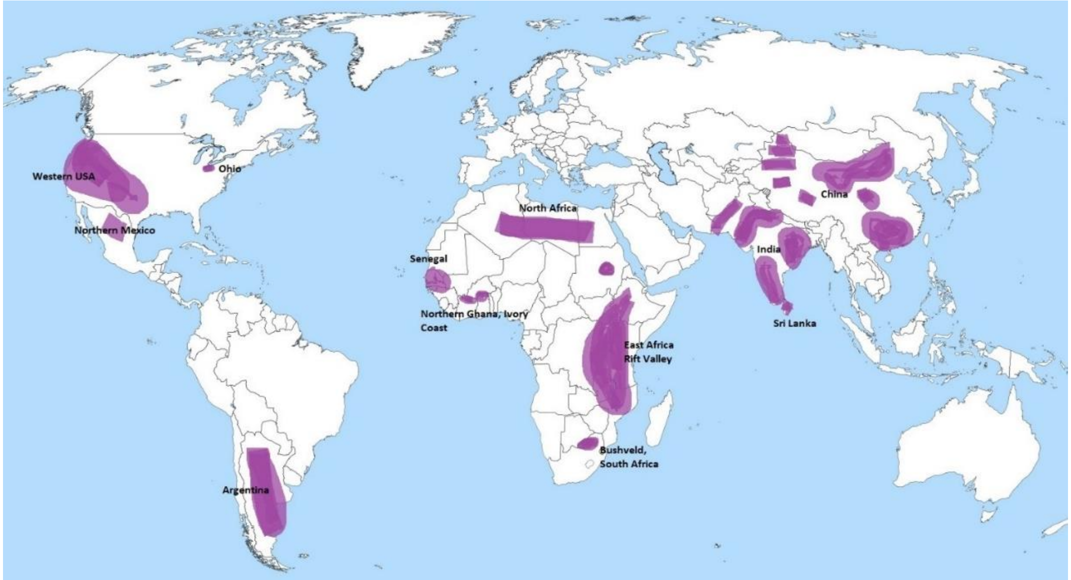


Figure 3.3 – Documented main worldwide fluoride occurrence in groundwater – purple areas showing fluoride concentrations > 1.5 mg/L (based on [41])

It has been reported that in 2017 in 6 American continental countries, 8 Asian and Middle East countries, as well as in 14 African countries, water was being consumed with a fluoride level higher that 1.5 mg/L [7]. Some examples are some regions of Brazil where concentrations of up to 4.97 mg/L were found due primarily to phosphate fertilizer production emission, Malawi with a range between 0.5 and 6.98 mg/L because of the presence and weathering of rocks containing biotite, hornblende, fluorite and amphiboles, or Kenya, where contents of up to 25 mg/L are related with the volcanic activity and chemical weathering [22].

In some of the countries, fluoride removal techniques are being applied, but the techniques vary widely and in many parts the water is consumed without any treatment, suffering the population from chronic endemic fluorosis [9].

3.2 Sources of fluoride in water, influencing parameters and release mechanism

As it has been said, the main reason for the natural presence of fluoride in water is the result from water-rock interaction by weathering of rocks containing high fluoride rich minerals [7][25]. Weathering consist on the disintegration and decomposition of a rock. The physical weathering is the fragmentation of a rock into different smaller pieces and the chemical one is the change of the internal structure by addition or removal of some or various elements [42]. Therefore, fluoride is leached out (extracted from the carrier into the liquid [43]) and dissolved into thermal gases and groundwater.

3.2.1 Influencing parameters in the presence of fluoride in water

The natural occurrence of high fluoride concentrations in both superficial and groundwater is dependent on a series of factors, outstanding the geology, the contact time, the climate and the chemical composition of the water itself [29].

- Geology: The presence of fluoride is a result from the interaction between the water and fluoride rich rocks, through weathering and circulation processes. Fluorine can be leached out from the minerals with high concentration of natural origin (up to 6 ppm) [44] and dissolved in the groundwater or in thermal gases. The geology is therefore one of the key factors on this occurrence, being some of the most common fluoride-bearing minerals fluorite (CaF_2) *(Figure 3.4)* , fluorapatite ($Ca_5(PO_4)_3F$), cryolite (Na_3AlF_6), topaz ($Al_2SiO_2(F,OH)_2$) and hornblende (whose general formula can be given as $(Ca,Na)_{2\text{-}3}(Mg,Fe,Al)_5(Al,Si)_8O_{22}(OH,F)_2$) [29] [7] [45][22].

Figure 3.4 - Fluorite [46]

The F-bearing minerals can be divided into three main categories [47]:

(1) Those in which F^- is a must component, an essential anion (e.g. fluorides, complex halides)
(2) Those in which F^- replaces an OH^- ion (phosphates and silicates)
(3) Those in which F^- substitutes an O^{2-} ion (oxides and some silicates)

The ionic radii of the F^- (1.33 Å) and OH^- (1.40 Å) ions are very similar and although F^- can be the predominant anion of certain minerals, such as fluorite, being an essential constituent, it can also be part of some F-bearing minerals by isomorphous replacement (substitution in the hydroxyl position)[48] [47]. The concentration range for some of these minerals is significantly large. The facility for F^- substitution for OH^- ion during mineral formation is observed from the huge amount of OH^-bearing materials where F^- is highly concentrated, as most of the silicate rock-forming materials (mainly biotites ($K(Mg,Fe)_3AlSi_3O_{10}(F,OH)_2$) and amphiboles such as tremolite ($Ca_2Mg_5Si_8O_{22}(OH,F)_2$)). To a lesser extent, sometimes fluorine can substitute the O^{2-} (ionic radii 1.32 Å), under high temperature and pressure conditions [47]. Reason for the preference in the substitution with the hydroxyl ion may be due to its facility to escape from the mineral lattice and combine with a H^+ ion [47]. During weathering, these isomorphous materials are the ones from which fluorine is released preferentially. So, when biotites and amphiboles are abundant, for example in granites, they constitute a major source of fluoride in water bodies [9].

Thus, fluoride can be presented in many minerals either as a must component or camouflaged by isomorphic constitution.

In *Figure 3.5* are shown some photomicrographs of typical crystalline rocks (the upper one obtained in the *Bongo region (*Ghana*)*, and the lower one in *Anuradhapura* (Sri Lanka)) with high content of fluorine-bearing minerals.

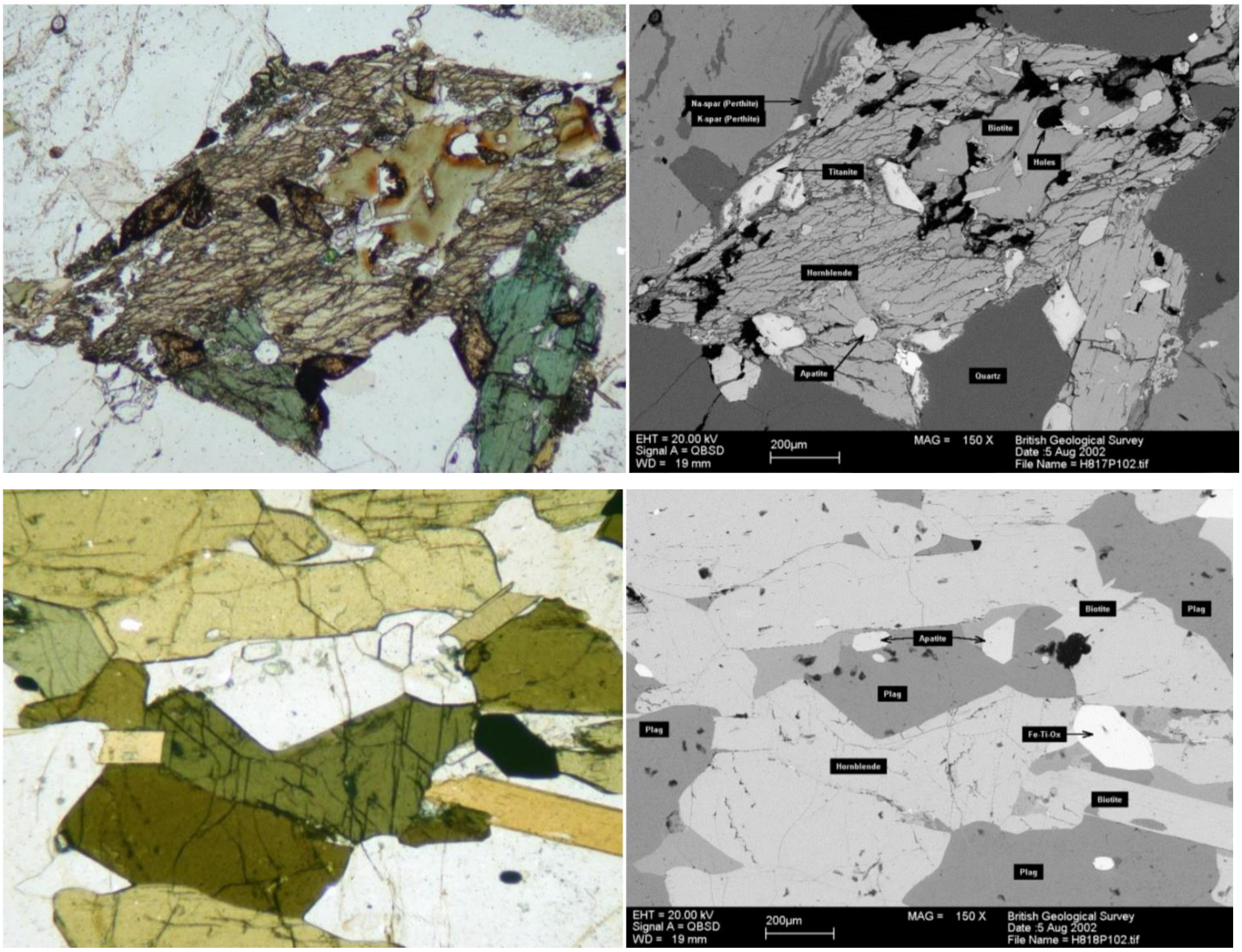


Figure 3.5 - Photomicrographs of typical crystalline rocks pointing out the high content of fluorine-bearing minerals [9]

The most important fluoride bearing minerals are found into the main three rock types: igneous, sedimentary and metamorphic. Most fluorine comes from acidic igneous formations, sedimentary rocks that have been subjected to biochemical reactions and mineralized veins [9].

- **Igneous rocks (magmatic rock):** *(Figure 3.6)* They are formed through the cooling and subsequent solidification of the magma or lava. They can be of two types, intrusive and extrusive. The intrusive ones are characterized by their crystallization below the Earth's surface, therefore having a very slow cooling rate that allows the formation of large crystals. On the other hand, the extrusive igneous rocks erupt onto the surface, having a fast cooling and giving place to small crystals or even amorphous glass when the cooling is even faster [49] [50].

Figure 3.6 – Granite (igneous rock) [52]

Most igneous rocks are formed by silicate materials. Thus, an early classification was made according to the weight percentage of SiO_2 in the rock: acidic (>66 % SiO_2), intermediate (52-66 % SiO_2), basic (45-52 % SiO_2) and ultrabasic (<45 % SiO_2) [51].

Fluorine is present both in the intrusive and extrusive types of magmatic rocks [7]. Fluoride generally accumulates during the magma crystallization process as well as during igneous differentiation (various processes which encompass the bulk chemical change of the magma during the partial melting, cooling, eruption or emplacement) [53][29].

The major fluoride bearing minerals presented in these rocks are fluorite and apatite. Fluorite is frequently presented in most common igneous rocks and found in hydrothermal veins, although in small quantity [48]. When fluorine cannot be incorporated in the crystalline phase during the crystallization and differentiation processes, it is accumulated in the hydrothermal solutions. In these type of solutions the transport of fluorine is mainly driven by the solubility of fluorite [29].

Apatite is more bountiful in basic rocks than in acidic, but higher concentration of fluorine is presented in the acidic ones [48].

Actually, the biggest proportion of fluorine in igneous rocks comes from minerals where the OH^- has been substituted by a F^- ion, and there is a bigger amount of fluorine in acidic rocks (~800-1000 ppm, whereas intermediate rocks present an average fluorine content of 400 ppm and basic and ultrabasic ~100 ppm) [48].

Groundwaters in contact with crystalline igneous rocks are very sensitive to have high fluoride concentrations, specially, those in contact with alkaline granites (with low calcium content) [29].

- **Sedimentary rocks:** *(Figure 3.7)* Sedimentary rocks are those formed by pre-existing rocks and also parts of living organisms that accumulate in deposits on the surface of the Earth (existing up to a depth of 10 km in the Earth's crust). They often have a distinctive layering or bedding [54]. They are formed, consequently, by accumulation of sediments, which are particles of various sizes that are transported by water, ice or wind and are subjected to physical and chemical processes (diagenesis), which give rise to consolidated materials [55].

Figure 3.7 – Clastic sedimentary rock [54]

Fluorine is the most copious halogen in sedimentary rocks, but the concentration is commonly low, except in certain areas with specific mineralization [7].
Both rock's chemical and mechanical weathering gives place to the release of fluorine and ensuing to its deposition in sedimentary basins [47]. Sedimentary rocks have a fluorine concentration ranging from 200 ppm to 1000 ppm [29]. The lowest concentration is associated with carbonate sedimentary rocks (those composed mainly by calcium carbonate, $CaCO_3$, or other carbonate materials), such as limestone, dolomite and marl [56]. In this type of sedimentary rocks fluoride is present as fluorite [29]. Fluoride occurs in greater amounts in argillaceous deposits, as the fluorine is concentrated in illites and micas in the clay fractions [29] [57].

However, it is apatite *(Figure 3.8)* the only mineral presented in sedimentary rocks that contains more than 1% fluoride by weight [48]. High concentrations can be found too in phosphate sedimentary beds, bentonite (very fine-grained clay containing bases and iron) [58] and volcanoclastic deposits [29] [7].

Figure 3.8 – Fluorapatite [59]

- **Metamorphic rocks:** *(Figure 3.9)* Metamorphic rocks result from the transformation of pre-existing rocks that have undergone structural and mineralogical adjustments under certain physical or chemical conditions, or combination of both, such as the temperature, pressure and/or chemical activity of the fluids that cause metamorphism. These adjustments, commonly imposed below the surface, transform the original rock without losing its solid state, generating a metamorphic rock [60].

Figure 3.9 – Examples of schistose metamorphic rocks [61]

The generated rock depends on the composition and texture of the original rock, on the agents of metamorphism, as well as on the time that the original rock was subjected to the effects of the so-called metamorphic process [60]. Metamorphic rocks can be divided into two types: the foliate ones, which visually present a series of layers produced by exposure to directed heat and pressure (e.g. slate), and the non-foliate ones, that do not have this aspect (e.g. marble) [62]. Another division within metamorphic rocks can be made depending on the metamorphism process: contact or regional metamorphism. The contact metamorphism is generated by a large increase in the temperatures of the rocks adjacent to a magma. Around the magma an area called halo is generated, where contact with adjacent rocks occurs, increasing their temperature and therefore, being both minerals and texture modified. In contrast, regional metamorphism, that is in a larger scale than the contact one, may be due, for example, to the collision of two lithospheric plates which gives rise to a lifting and corresponding crushing of the rocks, or due to rocks that over time deposit one on another and therefore increase the pressure of those below [63].

Fluorine plays an important role in both contact and regional metamorphisms, especially in the first one. The concentration ranges between 100 ppm (regional) up to 5000 ppm or more (contact). The rocks are enriched with fluorine through metasomatic process (geological process corresponding to the subtraction or addition, as in this case, of chemical components to a rock by means of aqueous fluids keeping the rock its solid state) [7] [64].

During metamorphism fluoride is a mobile element. Due to the high P-T conditions generating instability and the water interaction promoting the hydrolysis, fluoride leaks as hydrogen fluoride, that moves along the chemical potential gradient until a sink, for example a reactive rock (e.g. limestone) or until it is released to the surface (where a lot of fluoride is lost) [47].

The main F-bearing minerals that are presented in this type of rocks are biotite, amphibole (isomorphous substitution) and apatite (having this last one less effect than in the igneous and sedimentary rocks) [47].

- <u>Contact time:</u> It is another parameter of vital importance. The longer the reaction time between the water and the rocks, the higher fluoride concentration that will be reached. In general, high residence times are often associated with deep aquifers and slow water movement. On the contrary, usually in shallow groundwaters the amount of fluoride is relatively small, since rainwater is constantly infiltered. The exception could be a shallow aquifer in areas with high volcanic activity, where big fluoride concentrations could be found due to the increase in the solubility of fluorite with the increase of temperature and to the dissolution of gaseous hydrogen fluoride [29].
- <u>Climate:</u> In arid regions the tendency is the presence of high levels of fluoride, as groundwater flow is slow and therefore, the contact time long. Due to high temperatures and evaporation, the fluoride content may be increased if there is an equilibrium between the solution and calcite, and the hardness is lower than the alkalinity. In tropical areas, with a large volume of precipitation, rainwater act as a natural diluent, reducing fluoride concentration [29].
- <u>Chemical composition of groundwater:</u> The places where a high concentration of fluoride have been found are usually characterized by carbonated sodium-type water and have low values of magnesium and calcium (usually alkaline water pH ~7.6-8.6) [29] [47]. In some cases, there is also high nitrate contents in water where high fluoride content has been found [47]. For example, *Singh et al.* [65] evaluated a total of 100 samples of groundwater in western India, a country where fluorosis has become a major public health issue. In a 63% of the samples the fluoride concentration exceeded the limit established by the WHO, and sodium and bicarbonate where the major components in all the samples. This experimental study is showing the tendency from fluorite and other F-bearing minerals to solubilize with increasing alkalinity, existing a noticeable correlation between fluoride and pH. Reason for this is that the

OH^- presented in the water can be exchange with the F^- presented in minerals, fluoridating groundwater. In another study *Singh et al*. [66] suggest that based on the thermodynamic considerations the fluoride concentration seems to be governed by the Ca^{2+} activity. When calcium ions are in excess and given certain characteristics of the water matrix the concentration of fluoride is controlled by CaF_2 (technique used for the removal of fluoride ions in precipitation water treatment). Therefore, it seems than in the absence of Ca^{2+} ions in the solution, higher concentrations of F^- will be stable (however, also precipitation of carbonates can reduce the fluoride content) [9].

3.2.2 Release mechanism of fluoride in water

Usually, only a small fraction of the fluoride present in the soil is very soluble (e.g. <10 mg/kg) [9]. For example, an study made on Argentinian soils reveled that out of 26 samples, the fluoride concentration in the soil was in a range between 24 and 1220 mg/kg, but the water soluble fraction was between 0.53-8.33 mg/kg (being these values greater than the typically found, probably due to the fine grain-size of the soils) [67].

CO_2 plays an important role in the release of fluorides. Rainwater is enriched with CO_2 as it falls, and afterwards on the surface with soil air and as it percolates, due to the aerobic respiration of the bacteria. When CO_2 is dissolved in the groundwater, the concentration of hydrogen ions tends to increase [7]. When the dissolved CO_2 reacts with water, it dissociates into the bicarbonate ion and a hydrogen ion, according to the following reaction: $CO_{2(aq)} + H_2O \rightarrow HCO_{3(aq)} + H^+{}_{(aq)}$. In the case of alkaline waters, this balance will be almost completely shifted to the right.

These hydrogen ions have a great effect on the weathering of silicates (as can be seen in *Equation (3)*) and consequently, in their accessory minerals (*Equation (4)*) [7], as during the weathering and circulation processes the fluorine can be reached and dissolved:

$$2NaAlSi_3O_{8(s)} + 2H^+ + 9H_2O \rightarrow Al_2Si_2O_5(OH)_4 + 4H_4SiO_4 + 2Na^+ \qquad (3)$$

$$CaF_{2(s)} + H_2O \rightarrow Ca^{2+}_{(aq)} + 2F^-_{(aq)} \qquad (4)$$

As it has been said in the previous section a lot of parameters take place in the dissolution of F-bearing materials, and whereas in alkaline condition the fluoride desorbs and is released into water, in the acidic ones it tends to be adsorbed on clays [7]. It has also been commented how the presence of excess of ionic concentration of HCO_3^- and Na^- favors the release. In the case of fluorite, when it reacts with sodium carbonates or bicarbonates, it increases its dissociation activity giving rise to a precipitate of calcium carbonate ($CaCO_3$), as can be seen in *Equations (5)* and *(6)* [7].

$$CaF_2 + 2NaHCO_3 \rightarrow \downarrow CaCO_3 + 2Na^+ + 2F^- + H_2O + CO_2 \qquad (5)$$

$$CaF_2 + Na_2CO_3 \rightarrow \downarrow CaCO_3 + 2Na^+ + 2F^- \qquad (6)$$

3.3 Fluoride presence in African drinking water

The resources to access clean drinking water in the African continent are scarce, and the main drinking water source, especially in rural communities, comes from groundwater. Surface water bodies have the problem of being, in general, highly polluted; in addition to the great cost that would be required to install the transport structure needed to pipe the water from a potentially clean source to the arid rural areas. Some of the advantages of the usage of groundwater is that apart from being a reliable source during droughts, it has good microbiological and biological properties, being naturally protected from bacteria. However, groundwater is not a fail-save resource, as it can also be contaminated by natural pollutants as it is the case of fluoride [7][68].

3.3.1 Fluoride distribution in the African continent

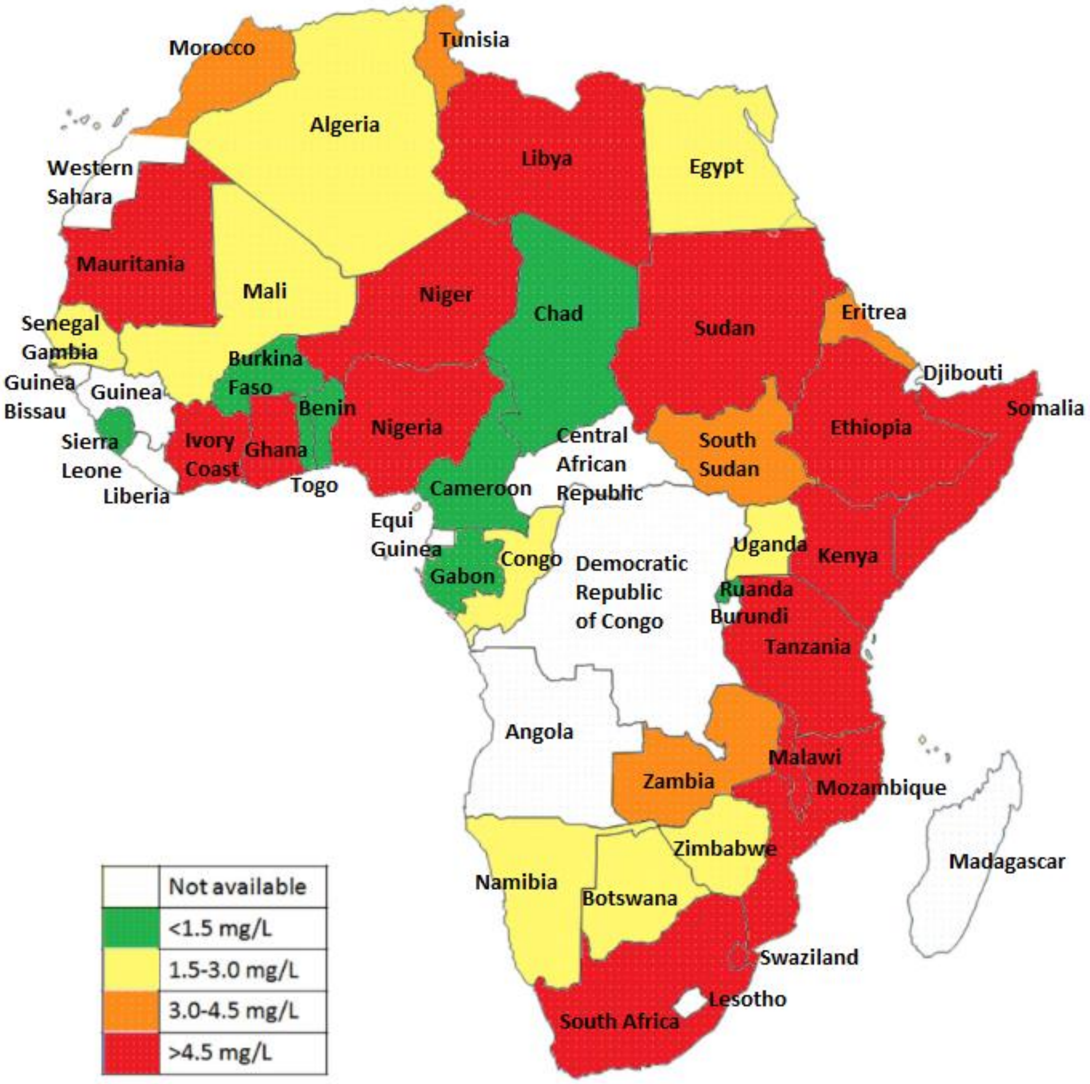


Figure 3.10 – Reported fluoride levels in selected African groundwaters (modified from [16])

As it can be seen from *Figure 3.10*, most of the African continent is affected by fluoride levels above the recommended limit.

One of the areas with the biggest content is that of the East Africa Rift Valley (encompassing countries such as Ethiopia, Kenya, Tanzania, Malawi and Mozambique) [69]. This region is characterized for its alkaline volcanic character [16]. Although there is not available information on the global amount of people in Africa suffering from fluorosis, only in the East Africa Rift Valley more than 80 million citizens are subjected to these symptoms in different degrees [70].

This project is based on the specific problem of fluoride removal in Ghana, so, from now on, we will focus on the actual situation of this country.

Figure 3.11 – Ghana [73]

The Republic of Ghana *(Figure 3.11)* is located along the Atlantic Ocean and the Gulf of Guinea, in West Africa. It has a population of around 30 million inhabitants [71], with a ~43.94 % (in 2018) living in rural areas and being a ~ 24.3% of the total population below the poverty line [72].

The access to water and sanitation facilities is very poor, especially in rural areas. Only around a 50% of the rural population has access to water [74], being the traditional source open ponds and wells, usually polluted [75]. More than 5 million people (~18%) are dependent on surface water (like the *Oti river*, the main one crossing the district [76]), being vulnerable to water-related diseases [77]. For the rest, groundwater is a key resource, especially in the dry seasons and in the northern part [78]. As it has been said, apart from the weather conditions, the preference for groundwater is due generally to presenting a better quality, being less contaminated and requiring little bacteriological treatment before consumption [79].

The most affected areas by fluoride are the Upper East, Upper West and northern regions, ranging the content of fluoride in groundwater between 0.11 and 4.60 ppm in general (although outliers of up to 282.29 ppm have been found [80]). The several studies that have been carried out through bareholes show that the proportion of water sources with a fluoride level above the one recommended by the WHO is around 20-30 % and dental caries, especially in minors, cause a serious health problem in the country, affecting more than 60% of the population [81][82][10][47]. Besides, the risk of fluorosis is also increased in this country due to the high consumption of water because of the climate. People consume in average 3-4 L of water per day, which is higher than the consumption estimated by the WHO of 2 L per day (for adults) [22]. In fact, *Galagan et al.* [83] developed an equation to establish the optimal upper fluoride limit according to the water daily consumption and temperature of each region (*Equation (7)):*

$$Optimal\ upper\ level\ of\ F^{-} concentration\ \left(in \frac{mg}{L}\right) = \frac{0.022}{0.0104 + 0.000724 * AMMT} \qquad (7)$$

Being AMMT the Annual Mean Maximum Temperature over a 5-year period (in order for this figure to be representative) in Celsius degrees.

In the north of the country, where the fluorine concentrations are the highest, the AMMT is 34ºC [84]. By applying *Equation (7)* the optimal limit in this case would be around 0.63 mg/L, a 42% smaller than the one recommended by the WHO.

3.3.2 Geology and hydrogeology of Ghana

Ghana present different soil compositions from part to part. The South West of the country is characterized by the presence of the alisols. These are very acidic soils, prone to aluminum and manganese toxicity. They are characterized by a dense subsurface layer formed by accumulated clay that present mixed minerology [78][85][86].

The North and East of the country presents soils of lixisol and plinthosol character. Lixisols are developed mainly on unconsolidated materials, with a fine texture that have undergone a strong alteration and washing. They predominate in oil soils subjected to strong erosion or deposition, in tropical, subtropical or warm climates with a pronounced dry season [87]. They are usually clay rich. Plinthosols, on the contrary, are iron-rich soils [78].

As it has been discussed in previous sections, the presence of high concentrations of fluoride is highly dependent on the geology. In *Figure 3.12* are shown the main lithostratigraphic regions in Ghana.

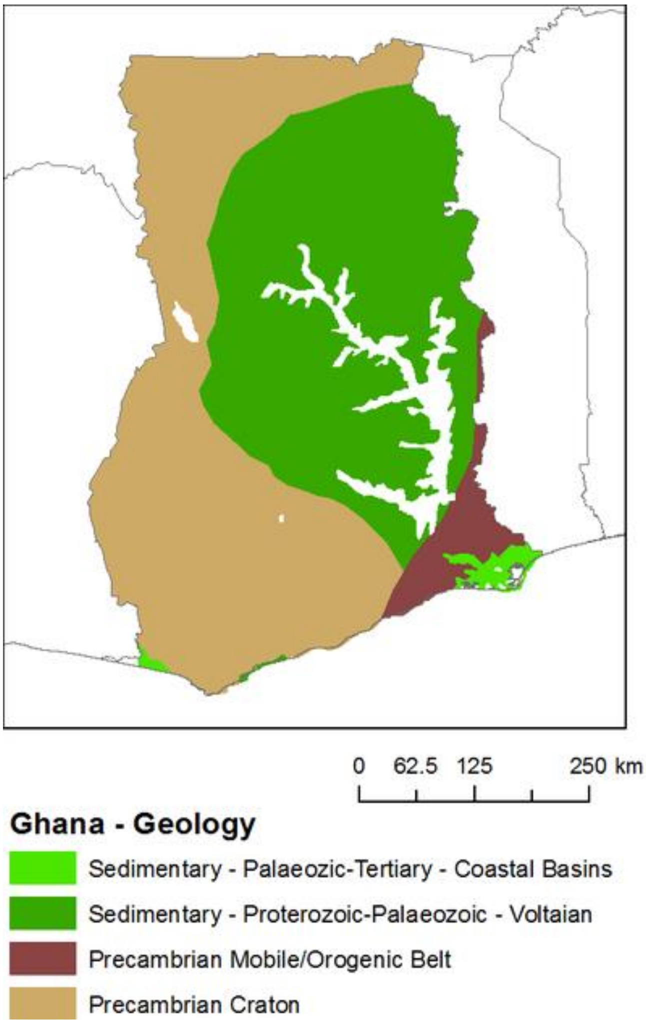


Figure 3.12 – Simplified map of Ghana's geology [78]

It is basically formed by ancient crystalline rocks, with great abundance of granite and granodiorites and metamorphic sediments (e.g. gneiss, a metamorphic rock composed from the same minerals than granite [88]) [82]. In the Precambrian Craton (North and South West) are found ancient crystalline rocks with big granite intrusions. The South East is formed by a mixture of both metamorphosed sedimentary rocks and igneous rocks. On the other hand, the middle region (colored green in *Figure 3.12)* is characterized by sandstones, mudstones and limestones [89].

It has been said that the main areas affected by fluoride contamination are the Upper East, Upper West and North. Taking a look at the map it can be seen how they mainly correspond to the Precambrian Craton, where the bedrock geology is dominated by granite. In the South (South West) this type of geology is also predominant. However, the northern regions are more arid, and in the south, the increase in rainfall have a diluting effect in the groundwater composition [89].

It is known that a large amount of the population is dependent on groundwater. In Northern Ghana there are about 5,000 hand pump boreholes supplying the population [79], most of them untested and not hygienic for consumption [82]. Certain regions suffer from high concentrations of fluoride, but the main problem is located in the *Bolgatanga* and *Bongo* districts. In the second one, in 1994 a 62% of the school children suffered from dental fluorosis. In an study developed by *Apambire et al.* [10] in 1997 in the Bongo region (whose geology is characterized for coarse-grained hornblende granite), 49% of the wells in the area where showing a fluoride level lower than 0.5 mg/L (contraindicated due to the risk of dental caries), a 28% where in the interval between 0.5 and 1.5 mg/L (recommended by the WHO for good dental health) and a 23% of the wells where showing a concentration exceeding the guideline limit.

Relative to hydrology, due to the abundance of crystalline silicate rocks and derivatives, groundwater is usually characterized by low salinity (low Na^+ content), and in general by an acidic pH (which in principle are not the most optimal conditions for fluoride dissolution) [80]. In the upper regions, the aquifers are developed due to the weathering and fracture of the bedrock of crystalline and metamorphic rocks from the Precambrian age due to overburden [90]. The presence of water is therefore dependent on the thickness of the load, the extent of decomposition and intensity of the rock cracking [10]. According to *Wright et al.* [91], the African Basement aquifers are made up of two parts. One consists of a surface layer of homogeneous composition (from clay to clayey sand) with low permeability in most cases (container function). The other one corresponds to the fractured bed rocks, where there is great permeability, allowing therefore in general a strong flow. The recharge in the groundwater takes place thought the rainwater infiltration and also, though in a lower degree, due to the rivers and influent streams [10].

3.4 State of the Art on fluoride removal from drinking water

In order to overcome the hazardous impact of fluorosis, different techniques have been developed that achieve the defluorination of the drinking water of purpose, decreasing concentration to acceptable limits. The main defluorination methods employed worldwide encompass adsorption techniques, ion exchange, coagulation/precipitation, membrane separation processes, etc. Each technique has its own advantages and limitations and behave appropriately, at least under ideal conditions [13][16][18][92]. In this section a brief explanation of the main techniques that are being used and studied is introduced.

3.4.1 Precipitation/coagulation

The most widely used coagulation/precipitation technique for the decreasing of the fluoride content in water is known as the *Nagolda technique* (method discovered in 1975 [16]). It is based on the addition of lime and aluminum sulfate. The alum salt (hydrated aluminum sulfate $[Al_2(SO_4)_3 \cdot xH_2O]$ is the most used coagulant for the flocculation of fluoride. The lime, is used to increase the pH

(~11-12), and achieve the fluoride precipitation as calcium fluoride (also it has a coagulant effect) [13] [16] [92].

The *Nagolda technique* is carried out in a batch reactor and it involves the following steps: fast mixing, coagulation/flocculation, sedimentation, filtration, disinfection (with bleaching powder) and sludge concentration for the regained of the water and aluminum salts [16].

The first step is the addition of the lime, which causes a part of the fluoride to precipitate (*Equations (8) and (9))*, followed by the addition of the alum salt, which achieves coagulation [13] [16].

$$CaO + H_2O \rightarrow Ca(OH)_2 \qquad (8)$$

$$Ca(OH)_2 + 2F^- \rightarrow CaF_2 + 2OH^- \qquad (9)$$

The following reactions take place [13] [92]:

First, the aluminum salt reacts with the alkalinity portion, giving rise to a precipitate of aluminum hydroxide *(Equation (10)):*

$$Al_2(SO_4)_3 + 6H_2O \rightarrow 2Al(OH)_{3(s)} + 3SO_4^{2-} + 6H^+ \qquad (10)$$

Thereafter, co-precipitation and sorption takes place on the insoluble aluminum hydride, reacting with the fluoride ions in water *(Equation (11)):*

$$Al(OH)_3 + F^- \rightarrow Al - F\ complex + undefined\ product \quad (11)$$

The dosage of aluminum is dependent on the amount of fluoride presented, and the lime is in general a twentieth part of the one of aluminum. The best removal takes place at the pH interval 5.5-7.5.

Among the advantages of this technique is that it is very used and common, practical and easy to understand. However, very big amounts of chemicals are needed, there is a big sludge production, the release of aluminum can cause health problems on the population and it is not possible to reduce the fluoride concentration below 1.5 mg/L, so it is mainly used for wastewater treatment [93] [92].

Another technique, which avoids the generation of a sludge, is the contact precipitation. In this case, for example, calcium or phosphate compounds are added to the water before its entrance in a catalytic filter bed. Theoretically, it is possible the removal of fluride by precipitation of fluorite or fluorapatite, however, it is a very slow kinetically process. Thus, there is need of a catalyst in the contact bed, which besides, acts as a filter for the precipitate generated. The reactions are shown in *Equations (12), (13), (14) and (15)*. Firstly, calcium chloride ($CaCl_2$) and sodium dihydrogen phosphate (NaH_2PO_4), are dissolved in water, and the ions released react with the fluoride in excess, precipitating as fluorite and fluorapatite [13].

$$CaCl_{2\,(aq)} \rightarrow Ca^{2+}_{(aq)} + 2Cl^{-}_{(aq)} \qquad (12)$$

$$NaH_2PO_{4(aq)} \rightarrow Na^{+}_{(aq)} + 2H^{+}_{(aq)} + PO^{2-}_{4(aq)} \qquad (13)$$

$$Ca^{2+}_{(aq)} + 2F^{-}_{(aq)} \rightarrow CaF_{2(s)} \qquad (14)$$

$$10Ca^{2+}_{(aq)} + 6PO^{2-}_{4(aq)} + F^{-}_{(aq)} \rightarrow Ca_{10}(PO_4)F_{2(s)} \qquad (15)$$

The third method that deserves a mention is the precipitation using purely calcium salts (e.g. $CaCo_3$, $CaCl_2$ or $Ca(OH)_2$). However, this technique is also mainly used for the precipitation of fluoride in groundwater and industrial effluents containing very high contents of fluoride (~30 mg/L), as in most cases is not possible to bring down the concentration for the limits stablish by the WHO for drinking water by pure precipitation (in the general industrial wastewater discharge standards the guideline limit for fluoride is 15 mg/L [94]). Also magnesium and barium hydroxides are used rejecting the fluoride as MgF_2 and BaF [95] [18]

Although these are the most common and traditionally used techniques, many studies are continuing to take place on the improvement of the different methods.

3.4.2 Adsorption and ion exchange

Adsorption refers to the adhesion of a thin layer of molecules from the bulk solution to the solid surfaces they are in contact with, by physical or chemical forces. It is a technique used widely in the drinking water industry, especially for the removal of organic substances [92] [96]. Adsorption involves the entry of water through a contact bed, being fluoride removed by surface chemical reaction with the solid bed matrix. It is a technique that has an important role for the research in drinking water defluorination as it is an effective method with a great accessibility and a lower cost compared to other methods. Besides, there is a wide variety of adsorbents available, that expand the field of study [18] [13] [92] [16]. The most used adsorbents for fluoride removal are activated alumina and activated carbon, but among the others that can be used appear, for example, bone charcoal, coated silica gel, magnesium oxide, calcite, activated saw dust… [13] However, as fluoride concentration is decreased, many of the adsorbents lose the removal capacity, and many of them have a maximum removal of up to 2 mg/L, not enough for drinking water purposes [97]

Theoretically, the adsorption of fluoride onto solid particles involves the following steps [18] [97]:

(1) Diffusion or fluoride ions transport from the bulk solution to the surface of the adsorbent material, across the boundary layer (external mass transfer)
(2) Adsorption of the ion into the surface

(3) Transference of the adsorbed fluride ions into the internal surface for porous materials or in many cases exchange with the structural elements of the adsorbent, depending on the specific chemistry

The adsorption is usually controlled by the pH, the temperature, the co-existing ions, the sorption kinetics, the particle size of the adsorbent, the concentrations and the surface area [16]. The pH is usually a key factor, being its value dependent on the adsorbent used but usually found in a range between 4 and 9. However, for example, the absorbance on activated carbon is only feasible at a pH lower than 3, disabling the removal method [97].

Budyanto et al. [95] studied the removal of fluoride with calcite nanoparticles, which take place by a combination of adsorption and precipitation. From their results they state that the surface precipitation is dominant when the fluoride content is greater than 40 mg/L, the transition from adsorption to precipitation is in the range of 5 to 20 mg/L and when fluoride is at low concentrations, it is eliminated mainly by adsorption.

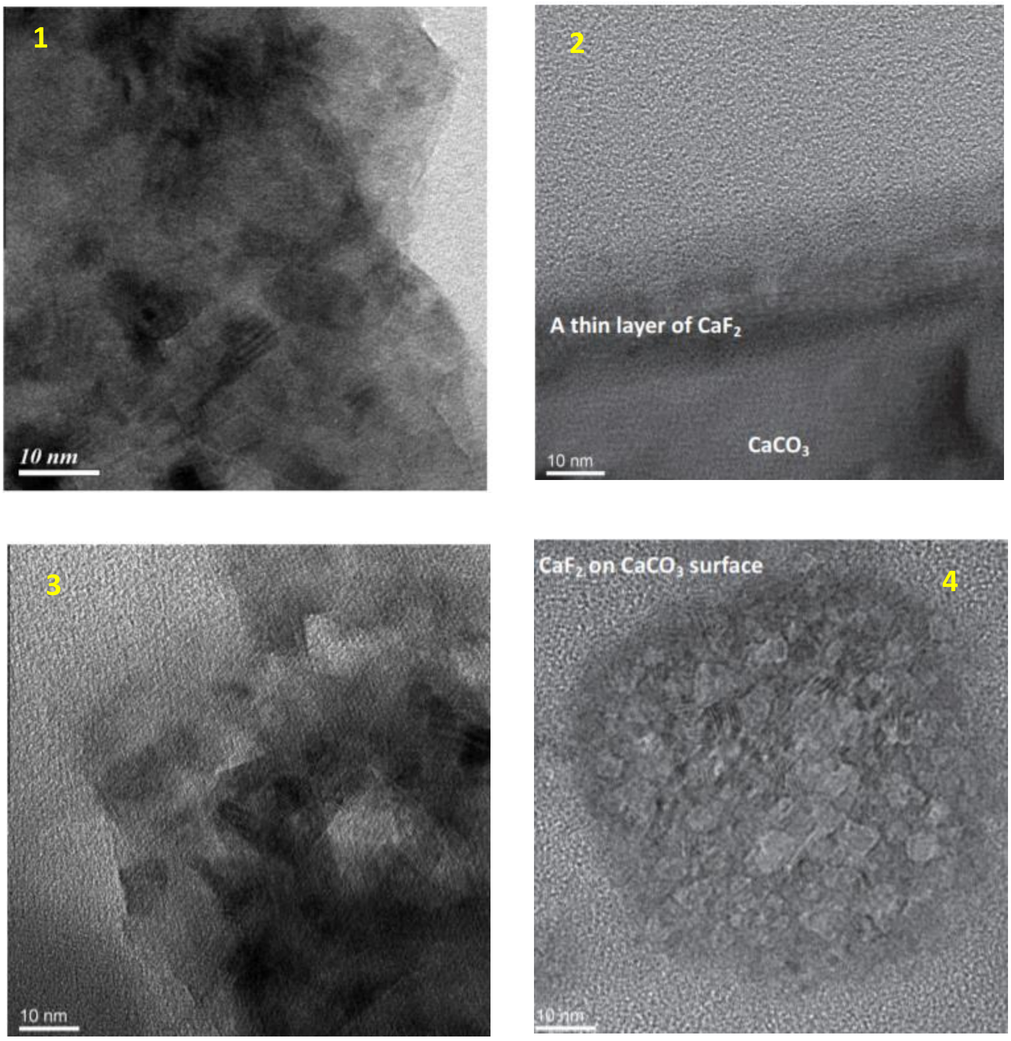


Figure 3. 13– HRTEM images (1) original single $CaCO_3$ *nanoparticle (2) single* $CaCO_3$ *nanoparticle after reaction with 40 mg/L* F^- *(pH 7.2) (3) single* $CaCO_3$ *nanoparticle after reaction with 10 mg/L* F^- *(pH 7.2) (4) single* $CaCO_3$ *nanoparticle after reaction with 100 mg/L* F^- *(pH 7.2) [95]*

The binding of the calcite nanoparticles was studied through High Resolution Transmission Electron Microscopy (HRTEM) (*Figure 3.13)*. From the different images it can be seen that between (1) and (3) (original particle and in contact with 10 g/L fluoride solution, respectively) no difference in the surface was observed. When the calcite nanoparticles where set to react with a solution of 40 mg/L F^- (2), a thin layer of fluorite appeared on the surface and when the interaction was with a solution of 100 mg/L, a lot of precipitated grains of calcium fluoride can be seen, which resulted in the damage of the calcite nanoparticles.

The study of the zeta potential (*Figure 3.14)* also corroborated these results. Originally the particles were positively charged. A decreased was seen with a 5 mg/L concentration of fluoride, that could be due to the adsorbance of the ions on the surface, resulting in a charge reversal. Then, an increase in the zeta potential appears with higher fluoride concentration, probably attributed to the precipitation of fluorite on the surface.

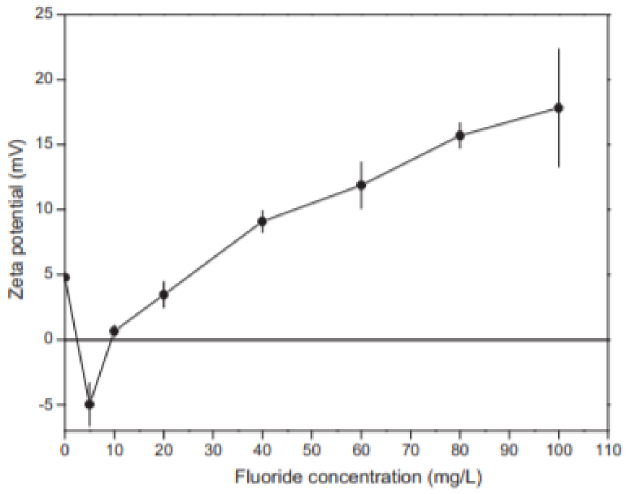


Figure 3.14 – Variation of the zeta potential of the calcite nanoparticles with the increase in fluoride concentration [95]

When studying the kinetics of the reactions, it was found that with a calcite dose of 5 g/L and a concentration of fluoride of 10 mg/L, after 60 minutes, the fluoride uptake capability is ~1 mg F^-/g $CaCO_3$, and for 100 mg/L of fluoride, ~18 mg/L.

Therefore, this method showed the capability of fluride removal from drinking water with calcite nanoparticles, based on adsorption and precipitation.

A recent study has been published by *Borgohain et al.* [98] about fluoride adsorbance on porous magnesium oxide nanoparticles, being the most effective method reported until date. In their research, the MgO nanoparticles were prepared both through the sol-gel synthesis method and the hydrothermal method, and the concentration was measured by evaluating the remaining fluoride in the solution with the SPADNS method. The generated nanoparticles resulted porous and highly crystalline, as checked in the microscopic and diffractometric studies. The results related to adsorbance show a fluoride uptake capability in the range of 5,716 mg F^-/g MgO to 15,691 mg F^-/g MgO. In *Table 3.1* can be seen the comparison in these values with some other different adsorbance methods:

Table 3.1 – Comparison of fluoride uptake capability with different adsorbents

Adsorbents	**Surface area (m^2/g)**	**Initial fluoride concentration (mg/L)**	**pH**	**Adsorbant concentration (g/L)**	**Fluoride uptake capability (mg/g)**	**Time of contact (min)**
Porous Mg nanoparticles [98]	10.5 – 171.2	10	6.7	0.2	5,716 – 15,691	~ 5
Calcite nanoparticles [95]	20.5	10	7.2	5	1	~ 5
		100			18	~ 20
Hydrous aluminum oxide in a water hyacinth bead [11]	--	10	5	1	4.43	120
Ceramic oxides ($Ce(OH)SO_4$) nanoparticles [99]	109.34	10	7	0.2	16	15
MgO mesoporous nanofibers [100]	194.17	300	6.89	0.6	237.49	-

The big advantage of this method can be seen by comparison with the other methods shown in *Table 3.1.* Besides, it is very fast, moderate amounts of adsorbent are needed and fluoride can be removed in a very big pH range (2-10).

Therefore, this method is proposed as a strong candidate in fluoride removal from drinking water due to its efficiency, having an economically affordable cost and being eco-friendship.

Ion exchange and adsorption are two very similar techniques, usually not differentiated in practical operations, but they also have some significant differences. In ion adsorption, the ions of interest are replaced by ions that are bounded by the solid phase through electrostatic interactions, in order to achieve electroneutrality [101]. One of the methods consist on the usage of an anion exchange region resin containing quaternary ammonium functional groups (*Equation (16)):*

$$(Matrix - NR_3 + Cl^-) + F^- \rightarrow (Matrix - NR_3 + F^-) + Cl^- \tag{16}$$

Therefore, the fluoride ions in the water are exchanged with the chloride ones in the resin, until full occupation. The driving force is the bigger electronegativity of the fluoride ions compared with the chloride ones. Then, the resin is washed with water supersaturated in NaCl salt, being now the fluoride ions substituted by new chloride ones. Although high efficiencies are achieved with this method, it involves a big cost and high concentration of chloride in the later drinking water [92].

3.4.3 Membrane processes

The most normally used membrane techniques comprise reverse osmosis (RO), nanofiltration, dialysis and electrodialysis.

RO is the process used for the demineralization or deionization of water by applying a pressure in excess the osmotic pressure and forcing the solvent through a semi-permeable membrane. The pressure is applied in the solution with the high concentration and the desired ions, molecules or others are rejected [102] [103]. The ions are rejected according to its size and electrical charge [16]. RO produces water of very high purity [18]. *The Environmental Protection Agency (EPA)* of the USA, stated RO as one of the best technologies for fluoride removal in 2003 [104]. Among the different studies performed, *Ndiaye et al.* [105] studied the reduction on fluoride levels from industrial wastewater with this method, achieving a rejection of fluoride typically higher than 98 % (with fully regeneration of the membrane after each set of experiments). *Assefa et al.* [106] studied the defluorination through RO membranes of constituted fluoride water with concentrations from 6 to 60 ppm, and permeates concentration were lower than 1 ppm, thus below the stablished guideline limit from fluoride in drinking water.

Among the advantages of this technique are the great efficiencies observed for the removal of fluorides, the working possibility in a wide pH range, the allowance of removal of other dissolved solids or the assurance of a constant quality of water. However, its use in rural areas is not possible, it is very costly, certain necessary minerals are removed from the water and remineralization is needed, the pH is usually lowered so there is need of afterwards remediation… [92]

Nanofiltration is another membrane technique which filtrates the solution by passing it through a membrane with nanometer-sized cylindrical pores [16]. As well as the RO, this method is very effective for defluorination and produces water of big quality [13]. In nanofiltration the pores are slightly bigger than for RO, and the pressure needed to pass the solution is therefore smaller. This implies less energy and less compaction of impurities [18]. The solute retention of the fluoride in this process is due to steric blocking and charge effects. Although fluoride is a small ion, its high charge density makes it more exothermically hydrated that other anions. Thus, it is the steric effect the one that retains the fluoride ions in the membrane, whereas chloride or nitrate, for example, can go through [18][16].

This method has a great effectiveness on fluoride removal, and at the same time it is an active barrier against suspended solids, microorganisms… Besides, no chemicals are used, and is effective on a big pH range. However, it is also a costly method in comparison with other techniques such as precipitation. Membrane degradation is a risk as well as fouling, and as RO - although in a lower degree - remineralization is needed afterwards [92].

An interesting research about the usage of nanofiltration in drinking water, is the one developed by *Bouhadjar et al.* [107]. They investigated a solar power nanofiltration drinking water pilot plant for the removal of fluoride in drinking water in the rural areas of Tanzania, being the groundwater in the studied region contaminated with up to 60 mg/L fluoride. The efficiency of the membrane was more than 98% and the final concentration of fluoride in the water was in all the cases lower than 1 mg/L. In *Figure 3.15* is shown a simplified flow diagram of the pilot plant.

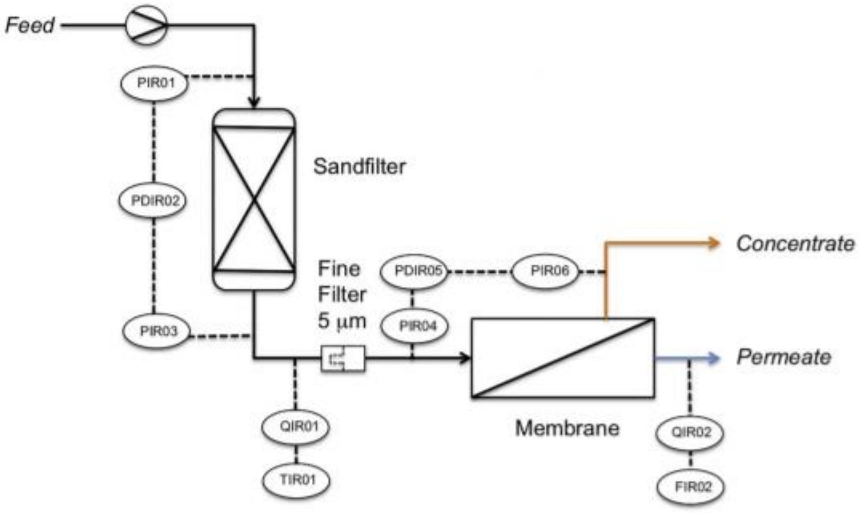


Figure 3.15 – Simplified flow diagram of the pilot nanofiltration plant [107]

The pilot plant was working for 10 months since June 2015, from 10 minutes to 7.5 hours depending on the demand, having in total 500 hours of working time and treating 953 m^3 of groundwater with high fluoride content. The cleaning of the membrane was done once a week with 60 L of permeate. The measurements of fluoride content were done both off and online, by cell test and Ion-Selective Electrode (ISE) respectively.

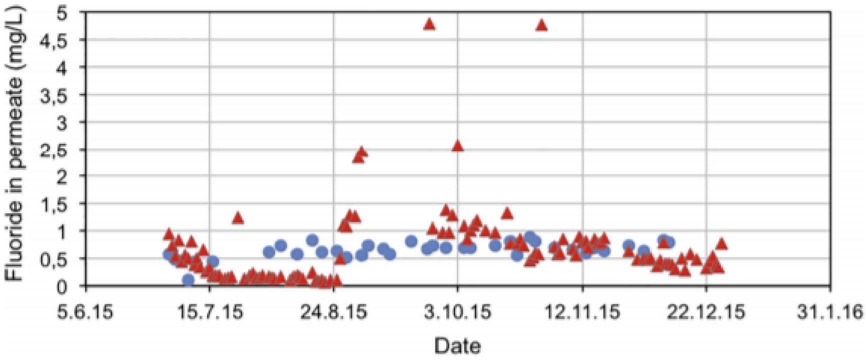


Figure 3.16 – Fluride concentration in the permeate (red triangles showing measurements through ISE and blue spots those measured through the cell test) [107]

From *Figure 3.16* it can be seen that the ISE measurements show greater fluctuations and there is also presence of several outliers. However, later recalibration was performed to the ISE measurements and the results were more in agreement with those measured with the cell test, that are in all cases lower than 1 mg/L.

The groundwater was extracted with the use a well pump powered with 6 solar photovoltaic panels, and the nanofiltration plant was equipped with 9 of them, providing a total of 2.25 kW_p. Therefore, the usage of solar power panels for around 2.5 hours per day allowed the production of around 240 L/h permeate.

Dialysis is the third membrane method. In this case, the solute is transported through a membrane, contrary to the other two previous techniques, where the membrane was used to retain the solutes. The solute is driven through the *Donnan effect* [92]. The *Donnan effect* is achieved due to the presence of impermanent ions (they cannot go thought a semipermeable membrane) in one side of the boundary from solute. In equilibrium, the ions that have the same charge polarity (co-ions) will have a lower concentration in the side of the membrane where the impermanent ions are, whereas there will be more presence of the counterions (opposite charge polarity) [108] [109]. *Durmaz et al.* [110] studied the removal of fluoride from water using anion-exchange membrane under the *Donnan effect.* The exchange membrane was of the type AHA (ammonium-type anion exchange membrane) and it was found that in order to increase the flux of fluorides, the best counterions were HCO_3^- > Cl^- > SO_4^{2-}. Few studies are found about this technique, but the concentration can be brought to less than 1.5 mg/L, as in some tests made in African groundwaters [18].

Electrodialysis is a technique for the removal of ionic compounds from aqueous solutions, by an ion exchange membrane and the application of a directed electric field. *Adhikary et al.* [111] studied the functioning of this method on water with a fluoride concentration of up to 10 ppm and total dissolved solids up to 5000 ppm. The concentrations were brought down to 1.5 ppm and 600 ppm, respectively.

However, both dialysis and electrodialysis are not so extended methods. Although they are flexible and have a low chemical request, only separation of ionic compounds is possible, they have an specific power consumption for the pump, and it is a costly method that has not been as studied and tested as the previous ones [92].

3.4.4 Electrocoagulation

Electrocoagulation is a technique that consists on applying a steady electric current to an aqueous solution through some electrodes that are submerged on it. For fluoride removal, iron or aluminum electrodes are used. When using aluminum electrodes, the reactions taking place are as shown in *Equations (17), (18) and (19)* [92] [16].

$$Al_{(s)} \rightarrow Al^{3+}{}_{(aq)} + 3e^- \qquad (17)$$

$$3H_2O + 3e^- \rightarrow {}^{3}\!/_{2}\, H_{2(g)} + 3OH^-{}_{(aq)} \qquad (18)$$

The aluminum cationic species are dissolved together with the hydrogen gas released from the interaction between electrode and water. Then, they react giving rise to aluminum hydroxide.

$$Al^{3+}{}_{(aq)} + 3OH^- \rightarrow Al(OH)_3 \qquad (19)$$

The same reactions take place when the iron electrodes are used (*Equations (20), (21) and (22)).*

$$Fe_{(s)} \rightarrow Fe^{3+}{}_{(aq)} + 3e^- \qquad (20)$$

$$3H_2O + 3e^- \rightarrow {}^{3}\!/_{2}\, H_{2(g)} + 3OH^-{}_{(aq)} \qquad (21)$$

$$Fe^{3+}{}_{(aq)} + 3OH^- \rightarrow Fe(OH)_3 \qquad (22)$$

In *Figure 3.17* is shown a schematic of the pollutant separator reactor using electrocoagulation.

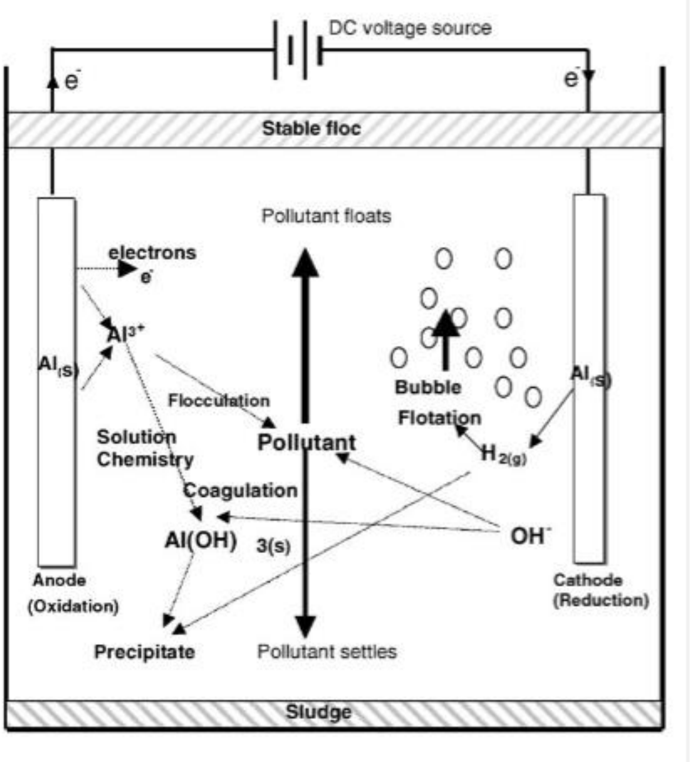


Figure 3.17 - Pollutant separation reactor of fluoride by electrocoagulation using aluminum electrodes [112]

As it can be seen from the figure, electrocoagulation generates the corresponding coagulant. In the case of aluminum, the aluminum oxide flocs contain Al-F bonds, and they act mainly as adsorbents or traps for metal ions [92] [16].

Emamjomeh et al. [112] studied the removal of fluoride from an aqueous solution using monopolar aluminum electrodes. From the results, the removal efficiency was increased with higher values of the current, and optimal operation time was set in 55 minutes when the initial concentration of fluoride was 10 mg/L and the current was set at 1.5 A. The concentration was reduced bellow 1.5 mg/L, showing that although it is a treatment mostly used in wastewater treatment, its usage is also feasible for drinking water purposes.

In *Table 3.2* is collected a brief summary of the explained techniques with their advantages and disadvantages.

Table 3.2 – Advantages and disadvantages of the main technologies for drinking water defluorination

Technology	Advantages	Disadvantages
Precipitation / coagulation (Nagolda technique)	- Simple technology - Same chemicals than ordinary water treatment	- Concentration reduction difficult below 1.5 mg/L - High chemical dose - Sludge
Adsorption	- Widely used technique - Moderate cost - High efficiency - Great variety of adsorbents	- Depends on the specific material e.g. adjustment and readjustment of pH, water ions can interfere F^- adsorption
Ion exchange	- High efficiency	- High cost - Vulnerable to interfering ions - Increase of other components in the generated water
Membrane processes	- Very high efficiencies	- High cost - Remineralization needed for some techniques - Need for special training
Electrocoagulation	- High efficiency - High selectivity	- High cost - Need for special training - Not very developed for drinking water purposes

3.5 Local remediation methods for the fluoride removal in Ghana

In the previous section we have reviewed the main different technologies that have been developed for defluorination of drinking water. However, in Africa and other developing countries, these techniques are not widespread. In the case of large scale, some water purification plants that cover big cities have successfully decreased the fluoride level to the healthy limit using the different above methods. However, these techniques have not reached smaller communities, because of a lower degree of development, lack of suitable infrastructure and other inconveniences relating cost, taboos and culture.

At domestic level, the technique that is considered most appropriated is adsorption, due to its great efficiencies even for small concentrations, the cost, the ease of operation, the flexibility… [113]. However, it all depends on the efficiency of the adsorbent used. A good option, which has been put into practice in many African regions, Thailand or Sri Lanka, is the treatment with bone char (*Figure 3.18)* as adsorbent [107] [114]. This method is actually one of those recommended by the American EPA and the Water Quality Association. This technique is based on the charring of animals to remove all organic matter.

The way of preparation of bone char is essential to obtain a product that has high adsorption capacity and that does not provide odor or flavor to the water. Different treatments are usually used, mainly alkaline and thermal. The alkaline consists of degreasing the bone first, covering it with sodium hydroxide and heating it at around 50 ºC for 30 minutes. Then, it is washed and neutralized with dilute hydrochloric acid and this operation is repeated if necessary. 70% of the material is often lost and a large volume of sodium hydroxide is required. In the thermal one, the synthesis temperature plays a critical role in terms of crystallinity, surface and chemical characteristics of the material. The bone is subjected to incineration by pyrolysis in a temperature range of 300 to 800 ºC in an inert atmosphere or under CO_2. If the synthesis is carried out at a higher temperature, it can alter the physicochemical structure of the material, losing the active groups. In a study carried out by *Mayorga et al.* [115], they synthesized modified bone chars with metaling dropping of aluminum and ion salts Thanks to the surface modification by aluminum sulfate, the adsorption capacity was raised 600 % in comparison with the raw bone char.

Figure 3.18 – Bone char particles

This carbonized is essentially composed of 70-76% of hydroxyapatite, 9 to 11% of carbon and 7 to 9% of calcium carbonate (losing fats, oils and meat remains). Therefore, hydroxyapatite is the main inorganic component of bone char and the mechanism of fluoride adsorption on hydroxyapatite has been found to be due to electrostatic attractions and ion exchange processes. It is supposed to be mainly because of a replacement of one or the two hydroxyl groups by a fluoride ion ($Ca_{10}(PO_4)_6(OH)_2 + 2F^- \rightarrow Ca_{10}(PO_4)_6F_2 + 2OH^-$), but it is also thought that the fluoride removal is due to a reaction between the calcium carbonate and fluoride, replacing this last the carbonate and forming insoluble fluorite. Regeneration of this material can be accomplished by rinsing with 2% sodium hydroxide and a backwash cycle. Fluoride reduction using this material is somewhat pH dependent; the pH of the water must be less than 6.5 to suppress any ion competition. Generally, the fluoride adsorption capacity of bone char has been reported to vary between 1.33 and 11.9 mg/g [116] [117] [118] [113].

However, this method although promising have several limitations, many related to local taboos and in many societies (e.g. Muslims, Hindus) the method is not culturally acceptable. Also, it depends on the availability of the raw material and the preparation must follow the specific guidelines to achieve good adsorbance and to avoid bad taste and smell in the water [113].

Ayamsegna et al. [119] studied the removal of fluoride from Ghana drinking water sources using different geomaterials (bauxite and laterite tailings) of the region, being potentially easy to replicate and manage in the rural communities. Both materials were tested successful for defluorination purposes, but it was raw bauxite the one showing a higher removal capacity. Experiments were also carried out heating up the material, obtaining the optimal removal when it was heated at 6000 ºC. The optimal results were obtained with 3 g/L of adsorbent, at the said 6000 ºC, lowering fluoride concentration from 10.31 g/L to below 1.5 g/L. They suggest that one solution for the fluoride problem in the country could be the manufacture of different filters made of the corresponding ceramic material (e.g. clay), that when combined with the heated bauxite tailing granulates in the right proportions, could eliminate both microbes and the fluoride present. However, in a different study by *Craig et al.* [120] the adsorption capacities were compared to those of activated alumina, and still this one has a higher fluoride uptake per unit weight.

4. MATERIALS AND EXPERIMENTAL METHODOLOGY

In order to accomplish the objectives of this project and study fluoride removal from drinking water, three procedures were used: aqueous geomechanical simulation with *PHREEQ-C*, in order to study computationally the interaction between the different ions and the reactions arising with the mixing of the water with different chemicals, trying to reduce the fluoride content below the guideline limit set by the WHO, and to study experimentally the best results obtained through simulations. For this, precipitation attempts were carried out in the laboratory and the fluoride content was measured through Ion Chromatography (IC). Also, some of the solutions were analyzed with Isothermal Titration Calorimetry (ITC) in order to study the behavior of the reactions taking place with each injection.

4.1 Materials

4.1.1 Chemical reagents

Below are introduced the materials used in this work. All the chemicals were of reagent grade and were used without any further purification.

- Sodium fluoride (NaF) – Mw = 41.99 g/mol
- Calcium chloride ($CaCl_2$) – Mw = 110.98 g/mol
- Calcium hydroxide ($Ca(OH)_2$) – Mw = 74.09 g/mol

4.1.2 Equipment

- *PHREEQ-C version 3* – Software for aqueous geomechanical simulations
- *NOTEPAD++ user interface*
- *IC 820* ion chromatographer (*Metrohm AG)*
- *Metrodata 2.3* – Software for IC analysis
- TAM IV *(TA Instruments)* – ITC equipment
- Launch NanoAnalyze – Sofware for ITC results analysis

4.2 Experimental methodology

4.2.1 Aqueous geomechanical simulations

This study is based on the computational study of the removal of fluoride from groundwater. For this, *PHREEQ-C version* 3 was used, which allows the aqueous geochemical modelling. The graphical user interface used was *NOTEPAD++.*

PHREEQ-C is a program written in C and C++ that can simulate chemical reactions and transport processes both in natural or polluted waters, in industrial processes or in laboratory experiments.

The basis of the program lies in the analysis of the equilibrium chemistry of aqueous solutions with minerals, solids, gases, exchanges, and different sorption surfaces. Among the different functionalities of *PHREEQ-C* can be found:

- The calculation of the concentrations and distribution of the species of an element in a system
- The calculation of saturation indices (SI) as well as the prediction of precipitation or dissolution of minerals
- The calculation of the distribution of redox species of an element
- The calculation of reversible and irreversible batch reactions for homogeneous and heterogeneous systems.

Although in this project we will be working in some cases with heterogeneous reactions (e.g. incorporation of adsorbed ions into a mineral lattice), the geochemical models such as *PHREEQ-C* use thermodynamic data that are developed from homogeneous reactions and aqueous phase equilibria. However, they are still widely used for the modelling of heterogenous systems. In this case we have used *WATEQ4F* model as its database is the only that contains F-bearing minerals [121][122][123].

The specific characteristics of each simulation are specified in *Chapter 5 – Results and discussion*, and the main scripts are collected in *Appendix 1.*

4.2.2 Precipitation and measurement of the fluoride content

The results that showed better behavior with the simulation study where performed and studied experimentally. In *Table 4.1* are shown the experiments performed.

Table 4.1 – Attempts of fluoride removal through fluorite precipitation

	Water sample	**Volume water sample**	**Chemical addition**	**Volume chemical addition**
1	Ultrapure water (2.29 mg/L F^-)	20 mL	$CaCl_2$ (3.3 g/L)	20 mL
2	Ultrapure water (2.29 mg/L F^-)	20 mL	$Ca(OH)_2$ (3.7 g/L)	20 mL
3	Drinking water (+2.29 mg/L F^-)	20 mL	$CaCl_2$ (3.3 g/L)	20 mL
4	Drinking water (+2.29 mg/L F^-)	20 mL	$Ca(OH)_2$ (3.7 g/L)	20 mL

The solutions were mixed and left under magnetic stirring for 1 hour each (the necessary reaction time is unknown but the time for laboratory usage was limited). The fluoride content of the samples was then analyzed using IC, as well as that in the samples before calcium chloride and calcium hydroxide addition, in order to know in a precise way the initial amount of fluoride.

IC is a technique used for water analysis that allows the measurement of the major ions and polar molecules presented in a liquid sample (fluoride, chloride, nitrite, calcium...). In this case, the measurements were only performed for fluoride as it is the element of study in this project. The concentrations of the different elements are measured based on the interaction that they have with an ion-exchange resin, as the ionic species separate differently based on their type and size [124][125].

Further explanation of the solutions chosen and their actual concentration is collected in *Chapter 5 – Results and discussion.*

4.2.3 Experimental study of fluoride removal with ITC

Some of that samples were analyzed with ITC to study, continuously, the reactions taking place.

ITC is a technique used for the determination of thermodynamic properties of a physical or chemical equilibria, as in this case [126][127].

This technique is based on the measurement of the heat absorbed or released by the system, as this heat is equal to the enthalpy if the system is at constant pressure (*Equations (23) and (24))* [126][128].

Enthalpy (H) is the internal energy (E) of the system plus pressure (P) times volume (V). Therefore, the variation of the enthalpy can be expressed as in *Equation (23)*:

$$\Delta H = \Delta E + \Delta(P \cdot V) \qquad (23)$$

If system is kept at constant pressure and the first law of thermodynamics is applied: $\Delta E = q + w$, being (q) the heat added to the system and (w) the work performed by the system. Assuming the work is only work of expansion, it can be replaced by $w = -P \cdot \Delta V$. *Equation (24)* is then reached.

$$\Delta H = q - \cancel{P \cdot \Delta V} + \cancel{P \cdot \Delta V} = q \qquad (24)$$

The instrument consists of two cells. One is the reference cell, an ampoule made of stainless steel and the other is the sample cell *(Figure 4.1)*. They are kept in an adiabatic jacket and must be at the same temperature (25°C in this case). The difference in temperature between the cells is detected by a thermoelectric device (sensitive to very small temperature changes) and this gives feedback to the heater, which compensates this difference by increasing or reducing the power and returning to the equilibrium state.

Figure 4.1 – Sample ampoule

Figure 4.2 is showing the ITC equipment with main parts highlighted:

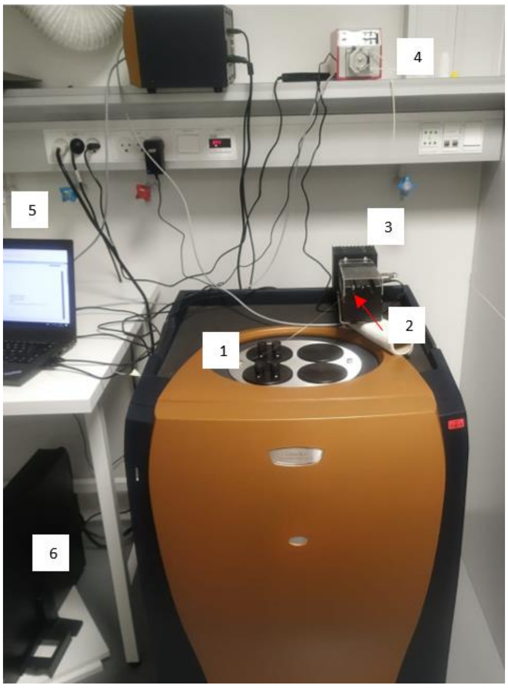


Figure 4.2 – ITC equipment – (1) Microcalorimeters with sample and reference ampoule (2) Syringe (3) Syringe support for automatization (4) Pump (5) Software for parameters setting and results collection (6) UPS

In the two different experiments carried out the same procedure was followed.

First, the operating temperature is set (25 °C). Once steady state is achieved, 250 µL of the fluid to be analyzed (the water with fluoride content) are introduced into the sample ampoule. Ampoule is placed in the ITC equipment. A syringe is filled with the liquid whose injection is studied and it is automated to introduce microaliquots of the titrant, as it is connected to a pump. The syringe is connected to a small tube that is inserted into the ampoule.

All the experiments were carried out with 10 injections, of 25 µL each and with a duration of 25 s (injection velocity : 1µL/s) The interval time was set to 12 minutes.

In *Table 4.2* are collected the experiments carried out with indication of the liquid presented in the sample ampoule, and the titrant.

Table 4.2 – Sample and titrated fluid for ITC

	Sample ampoule	**Injection**
1	Ultrapure water (2.29 mg/L F^-)	$CaCl_2$ (3.3 g/L)
2	Drinking water (+2.29 mg/L F^-)	$CaCl_2$ (3.3 g/L)

Further explanation on the experiments carried out and their reason is collected in *Chapter 5 – Results and discussion.*

5. RESULTS AND DISCUSSION

As it has been said, the objective of this project is the study of fluoride removal in groundwater, by means of simulations and the testing of the best results experimentally. Focus is on Ghana's groundwater, a country battered by the high concentrations of this pollutant, which have caused a large part of the population to suffer from chronic fluorosis.

In the absence of our own data, this project has been based on the data supported by *Apambire et al.* [10] on their study on the quality of the groundwater in the different parts of the country presenting different geology. In this case, we are going to focus on the data from the *Bongo* region, characterized for its granitoid terranes and with a tendency for presenting high fluoride levels. During their study, 109 samples from different boreholes in the community where taken, and the statistical summary (mean and range) is shown in *Table 5.1*.

Table 5.1 – Statistical summary of the main parameters in groundwater in the Bongo region (Ghana) and WHO guideline values for each [10] [129]

Parameters	**Minimum**	**Maximum**	**Mean**	**Guidelines values (WHO)**
pH	5.95	7.80	6.94	6.5- 8.5
Electric conductivity (µs/cm)	80	630	298	-
Na^+ (mg/L)	13.0	65.0	23.9	200
K^+ (mg/L)	0.7	5.7	2.0	30
Mg^{2+} (mg/L)	2.3	25.0	11.5	150
Ca^{2+} (mg/L)	7.8	50.0	25.3	200
F^- (mg/L)	0.61	4.60	2.29	1.5
Cl^- (mg/L)	1.1	31.0	6.7	250
NO_3^- (mg/L)	0.1	60.3	18.4	50
SO_4^{2-} (mg/L)	0.6	49.3	4.8	250
HCO_3^- (mg/L)	61	336	156	384
SiO_2 (mg/L)	16.0	41.0	30.3	-

From the statitistical results it can be seen how the fluoride is the only parameter whose mean is above the value recommended by the WHO. In their research, *Apambire et al.* [10] studied the Pearson correlation coefficients between the fluoride and the other parameters. They have pointed out that the correlation with calcium (r=0.273), despite being very moderate, it is positive (unlike in the rest of the terrains studied), so it seems to suggest that the main source of fluoride is, in this case, fluorite (CaF_2). However, fairly low sodium values have been detected, making it unlikely that this element has a big influence in the solubility of this material.

5.1 Geomechanical simulation of the release mechanism and water speciation of Ghana's groundwater sample

5.1.1 Geomechanical simulation of the fluoride release mechanism

First, *PHREEQ-C* was run in order to check the chemistry giving rise to the high presence fluoride in the water of certain regions.

As it has been commented in *section 3.2.2,* CO_2 plays an important role in the release of fluoride, increasing hydrogen ions concentration. The hydrogen ions have a big effect on the weathering of silicates. When Na^+ and HCO_3^- groups are liberated, the ionic excess favors fluoride release. Therefore, for the simulation an initial solution of water at neutral pH (although allowing its adjustment to charge balance by the presence of the other elements), containing CO_2 gas at a partial pressure of 0.1 atm, and with Ca^{2+} and F^- ions in equilibrium with calcite and fluorite, respectively, was set. Then, the solution was made to react with albite ($NaAlSi_3O_8$) (1.84 g/L in 30 steps), a feldspar silicate, that would release Na^+ ions. Calcite and fluorite are defined allowing its dissolution and precipitation, and quartz and kaolinite are allowed to precipitate if supersaturation happens.

The results of the simulation are shown in *Figure 5.1.*

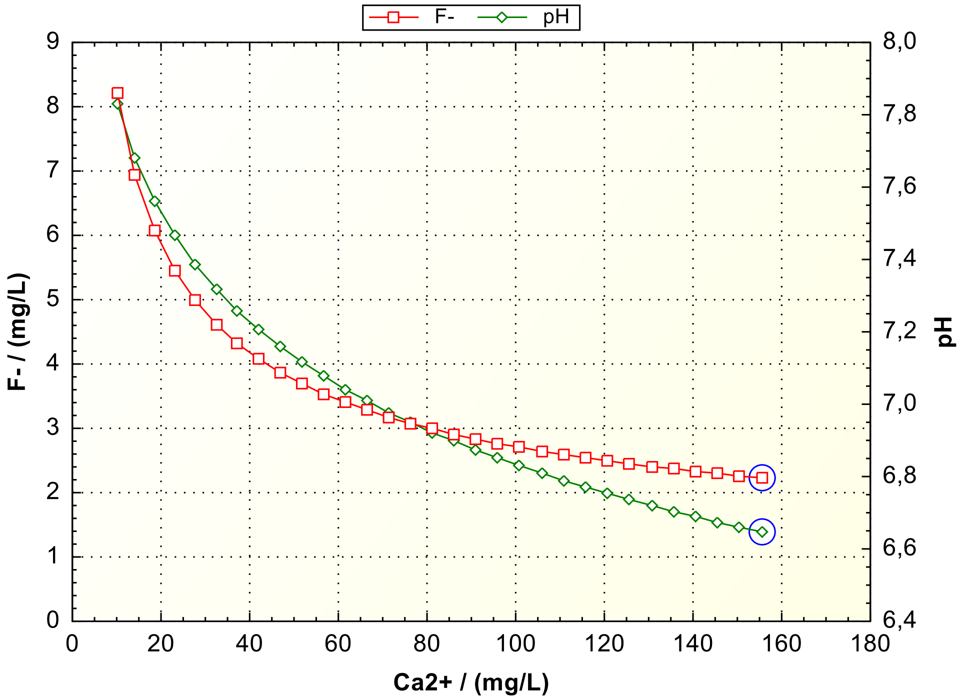
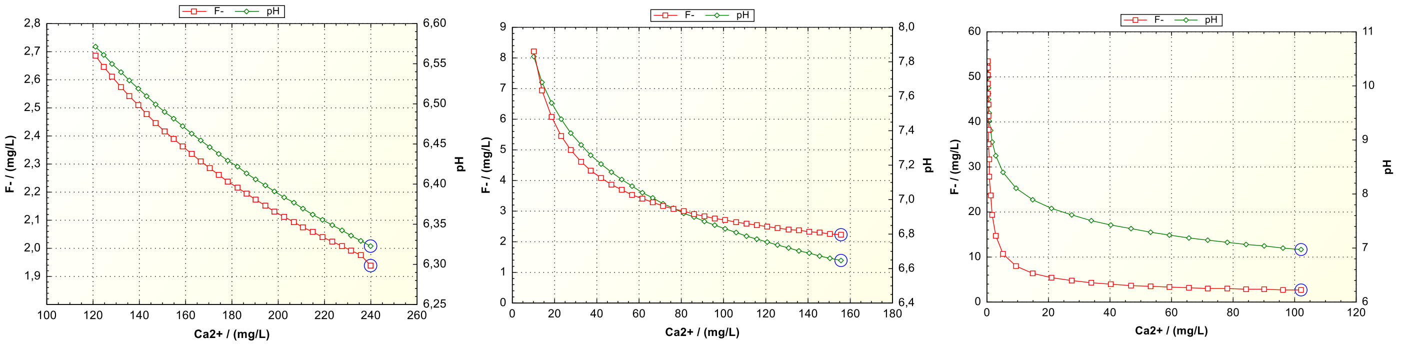


Figure 5.1 – Fluorite equilibrium while albite dissolution

From the figure the expected results are seen. The pH is increased due to the loss of hydrogen ions in the reaction with albite ($2NaAlSi_3O_8 + 2H^+ + 9H_2O \rightarrow Al_2Si_2O_5(OH)_4 + 4H_4SiO_4 + 2Na^+$). The bicarbonate ion from the dissolution of CO_2 ($CO_2 + H_2O \rightarrow HCO_3{}^- + H^+$), due to the reaction of albite, is triggered to dissociated ($HCO_3^- \rightarrow CO_3^{2-} + H^+$), giving rise to carbonate ions that react with the calcium ions in the solution precipitating calcite ($Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3$). Therefore, the initial concentration is the one showed in the blue circles in *Figure 5.1* (2.218 mg/L F^-; 155.7 mg/L Ca^{2+}, 6.644 pH) and as the reaction takes place, the calcium content decreases and the fluoride one and the pH increases.

The influence on the dissolution of CO_2 can be seen from *Figure 5.2*



CO₂ PARTIAL PRESSURE: 0.05 atm

CO₂ PARTIAL PRESSURE: 0.1 atm

CO₂ PARTIAL PRESSURE: 0.15 atm

Figure 5.2 – Change in the fluorite equilibrium graphs with increasing CO_2 concentration

It can be seen than when the CO_2 content is increased, there is an increase in the pH. Although in normal conditions this behavior would be opposite (as H^+ ions concentration is increased), the weathering of albite grabs these protons, increasing pH, and therefore, increasing the solubility of fluorite and the concentration of F^- ions.

5.1.2 Water speciation of the sample of groundwater from the *Bongo region (Ghana)*

PHREEQ-C was also used to determine the ion speciation and mineral equilibria calculations. Based on the aqueous content distribution of the Ghana's groundwater, the water speciation was calculated relative to a set of minerals. Whereas a chemical analysis provides the total concentration of elements that are present in a solution, in the speciation calculation these elements are distributed between different aqueous species that are likely to be formed, based on an aqueous model (*WATEQ4F* in this case) [122].

The results obtained with aqueous speciation modelling are shown in *Table 5.2.*

Table 5.2 – Aqueous speciation modelling from the sample of groundwater in the Congo region

Phase	**SI**
Anhydrite ($CaSO_4$)	-3.53
Aragonite ($CaCO_3$)	-1.01
Calcite ($CaCO_3$)	-0.87
Chalcedony (SiO_2)	0.25
Chrysolite ($Mg_3Si_2O_5(OH)_4$)	-7.53
Dolomite ($CaMgCO_3$)	-1.74
Fluorite (CaF_2)	-0.65
Gypsum ($CaSO_4 : 2H_2O$)	-3.23
Halite (NaCl)	-8.34
Quartz (SiO_2)	0.68
Sepiolite ($Mg_2SI_3O_7 \cdot 5OH : 3H_2O$)	-4.81
Sepiolite (d) * ($Mg_2SI_3O_7 \cdot 5OH : 3H_2O$)	-7.71
SiO_2 (a) *	-0.59
Sylvite (KCl)	-8.98
Talc ($Mg_3Si_4O_{10}(OH)_2$)	-3.33

** referring (a) to amorphous silica and (d) to the disordered form of sepiolite, being much more soluble*

The saturation index is showing whether the water will tend to dissolve or precipitate a certain mineral. Negative saturation indices would mean that, theoretically, the solution is capable of dissolution of a certain compound (undersaturation), whereas positive would mean that theoretically it would be capable of precipitation (oversaturation). Taking a look at the results it can be seen that the only two minerals that are oversaturated are chalcedony and quartz. However, the other silicates are all undersaturated. Both aragonite and calcite (crystal forms of calcium carbonate [130]) as well as the other minerals containing calcium ions are undersaturated too. It has been said that in their report, *Apambire et al.* [10] suggested that the main source of fluoride was coming in this case from the dissolution of fluorite, due to the positive correlation between calcium ion and fluoride ion. However, the reported Pearson coefficient was very moderate. On the one hand, the results of water speciation seem to match this, as although fluorite is undersaturated, the saturation index is quite small. However, if fluorite is the majority source, we would expect saturation indices positive or closer to zero in the minerals containing calcium ions. Therefore, we can intuit that it is possible that the granitoid terrain contained both fluorite and other F-bearing materials (by isomorphous substitution) that during weathering would leach out the fluoride ions from the minerals phase.

For contrasting, the study of water speciation was also carried out using data from one study in *Kenya*, specifically in the area of the *Rift Valley* [131]. The chemical composition of the water and all the saturation indices are collected in *Appendix 2 (Tables 10.1 and 10.2)* However, the main results are shown in *Table 5.3.*

Table 5.3 – Calcium carbonate minerals and fluorite saturation indices from a sample of Kenyan water [131]

Phase	**SI**
Aragonite ($CaCO_3$)	-0.08
Calcite ($CaCO_3$)	0.06
Fluorite (CaF_2)	0.13

The sample had a fluoride concentration of 9.3 mg/L. In the area, both sedimentary, volcanic and metamorphic rocks are found, belonging the oldest one to the Basement Systems of Precambrian age and abundant fluorite mineralization is present. In this case, silica was not present in the water content analysis and from the water speciation it can be seen how both fluorite and calcite (*Table 5.3)* are oversaturated or very near to equilibrium. Besides, the pH was higher (8 vs 6.94 in Ghana's) as well as the sodium concentration (170 mg/L vs 23.9 mg/L in Ghana), parameters that increase the solubility of fluorite. These results, contrary to the case of Ghana, do seem to show that the main and majority source of fluoride ions comes from fluorite.

5.2 Simulation on the addition of different chemicals for fluoride removal

In this section, *PHREEQ-C* was used to study the behaviour of different chemicals in the precipitation of fluorite. Fluoride was attempted to be removed in the form of said mineral due to its low solublity, making the process easier.

5.2.1 Addition of calcite to the groundwater

Although the final purpose is the study of fluoride removal from the specific case of Ghana’s groundwater, initially some pre-simulations were carried out to study the influence of several parameters, in some more generic conditions. For calculation simplification, pure water was used (which does not contain any of the aqueous phase contaminants). 5 ppm of fluoride were included.

- **Influence of the pH on the precipitation of fluorite**

As it has been said in the theoretical part, the presence of high contents of fluoride is usually associated with alkaline water, where the fluorite and other F-bearing materials are more soluble. As an initial step *PHREEQ-C* was used to study the influence of the pH on it. Beginning from the pure water with 5 ppm fluoride, calcite was added until chemical equilibria, varying the pH ($Ca^{2+} + F^{-} \rightarrow CaF_2$).

In *Figure 5.1* is shown the saturation index of the fluorite from acidic to alkaline environment.

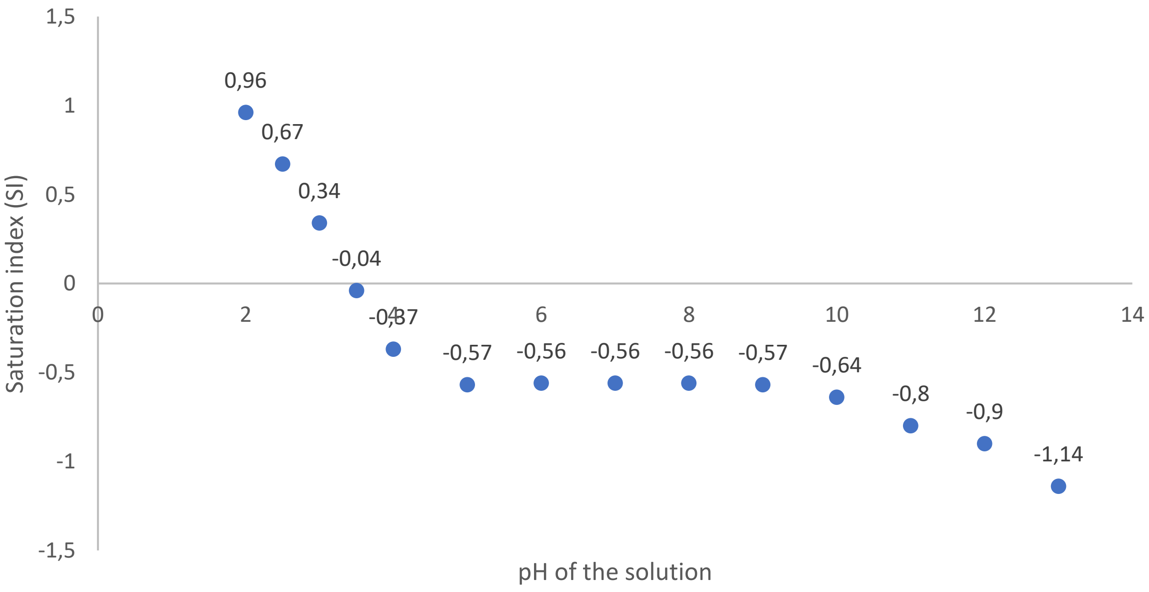


Figure 5.3 – Variation of the saturation index of the fluorite with increasing pH at 25 °C

As it can be seen the fluorite precipitation when calcite is added until equilibrium (saturation index=0) is computationally possible until a pH of ~3.5 and the tendency to decrease the solubility with increasing pH is seen (another calculation was performed with the fluoride concentration of 2.29 ppm (Ghana’s groundwater of study) and the equilibrium was achieved at a pH of ~2.4).

However, acidity not only favors the reduction of the solubility of fluorite, but also calcite is insoluble in water under normal conditions. A certain amount of acid is needed to dissolve calcite, giving rise to the calcium ions that interact with the fluoride ones. In the previous section, calcite was added to previously acidified water. It results not viable to reduce the pH of drinking water to levels where the precipitation would be feasible as a lot of chemicals would be involved. Anyway, the addition of calcite also increases the pH due to the reaction of the carbonate ions with the hydrogen cations giving rise to bicarbonate. In this specific case, if the pH is reduced to 3, the addition of calcite until equilibrium causes an increase in pH up to 7.9, that is within the limits established by the WHO (pH from 6.5 to 8.5) [132].

First, we have performed a study to see how the solubility of the calcite is dependent on the pH. Calcite was added until reaching equilibrium to a sample of pure water. The results are shown in *Figure 5.4.*

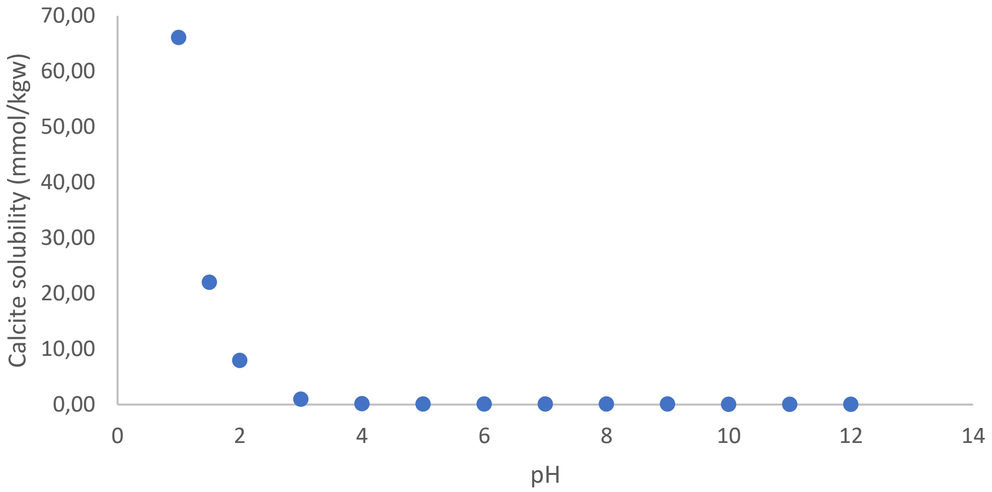


Figure 5.4 -Variation in the solubility of calcite with pH

From the results it can be seen how the solubility reduced to minimum values from pH 2.5, being 66.15 mmol/kgw for pH 1, 22.06 mmol/kgw for pH 1.5 and 7.981 mmol/kgw for 2. Usually, it is considered that a substance is soluble in a given solvent, when the solubility is bigger than 0.1 M, so only the solubility at pH 1 is more or less near to this value [133]. It seems that the calcite solubility is a very influencing factor.

The next simulation was performed by adding to the F-bearing solution, not the calcite itself, but a dissolution of it in acidic water (pH=2), limiting the amount of chemicals needed and also the problem of lowering too much the pH of the drinking water. These results (*Figure 5.5)* try to prove if it is possible to obtain fluorite precipitation under the said conditions, varying the proportion between both solutions.

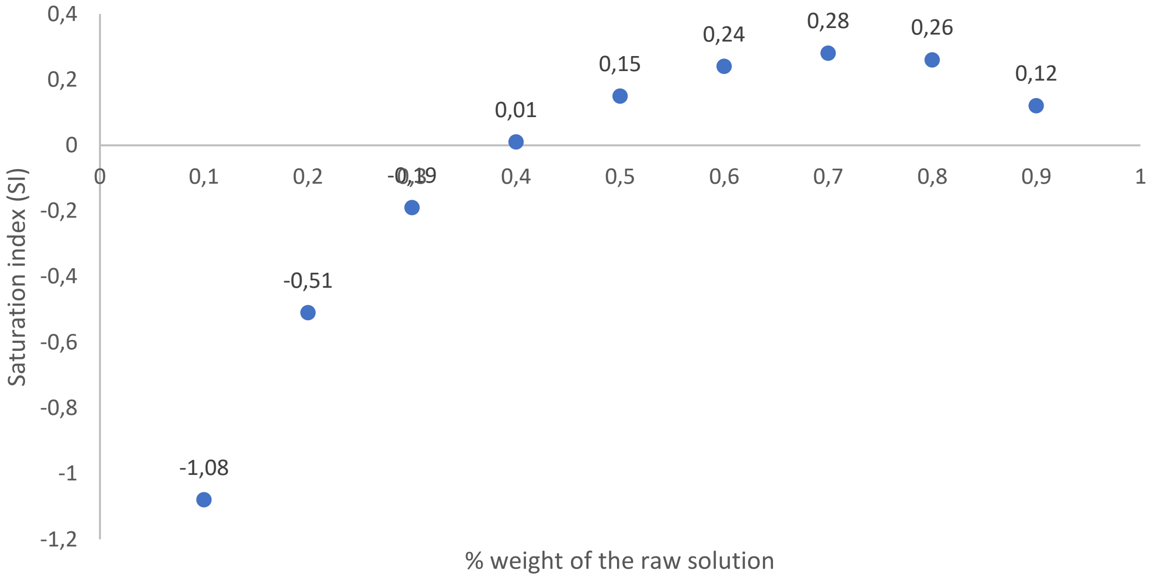


Figure 5.5 – Variation of the fluorite SI with the weight proportion of the solution with fluoride with respect to the added one of calcite (Pure water with pH 7 and 5 ppm fluoride, and calcite solution with pH 2 at 25 ºC)

It can be seen how the SI is favorable for precipitation in many cases, being the optimal solution that one obtained with 70% drinking water and 30% calcite solution (by weight). The SI are lower than those obtained with acidification of the drinking water.

- **Influence of the temperature on the precipitation of fluorite**

In *Figure 5.6* is shown how the temperature at which the reactions take place influences the precipitation. In the previous section the analysis of the pH was performed at a temperature of *25 ºC.* In this case, the same solution was used (pure water with 5 ppm F^-), but the pH was fixed at 2 and the temperature was ranged.

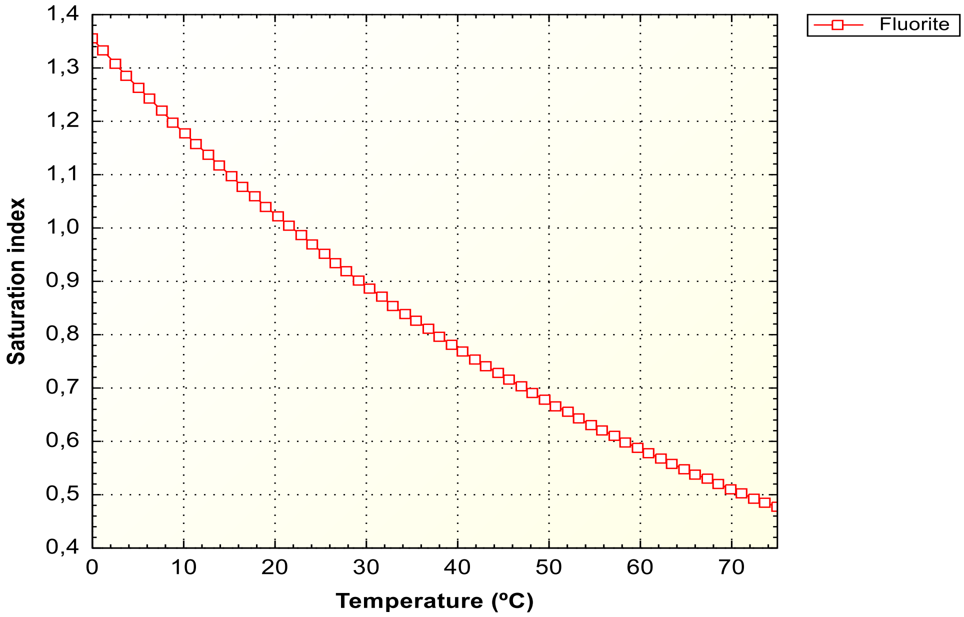


Figure 5.6– Variation of the saturation index of the fluorite with increasing temperature at pH 2

It can be seen how fluorite saturation index is decreased with increasing temperature. However, the following simulations will be made at 25 °C (assuming ambient temperature) in order to avoid the economic expense that refrigeration would entail in real life operations.

- **Calcite addition to groundwater from the *Bongo region***

Based on the previous simulations a solution with calcite in equilibrium at pH 2 was added to a solution with the composition of the groundwater from the *Bongo region*. The reactions took place at 25 °C and the weight proportion was 70% drinking water : 30 % calcite solution. According to the results the precipitation of the fluoride is not possible (SI: -0.39). Other proportions were tested in this specific case, but still 0.7 : 0.3 (water : calcite) was the one showing the best of the results.

Table 5.4- Molalities and pH of the initial groundwater solution and the simulated values after mixture with a solution saturated in calcite at 0.7 : 0.3 weight proportions

	Molality initial solution (groundwater) (mol/kg solvent)	**Molality final solution (after mixture with $CaCO_3$ solution) (mol/kg solvent)**
Alkalinity	2.557e-03	-
Ca^{2+}	6.314e-04	2.836e-03
Cl^-	1.890e-04	1.323e-04
F^-	1.206e-04	8.440e-05

K^+	5.116e-05	3.581e-05
Mg^{2+}	4.731e-04	3.312e-04
NO_3^-	1.314e-03	9.198e-04
Na^+	1.040e-03	7.279e-04
$SO4^{2-}$	4.998e-05	3.499e-05
C^{4+}	-	4.607e-03
pH	6.940	6.727

In *Table 5.4* are shown the molalities of each element in the initial groundwater solutions and the one after the mixture with calcite solution. Fluoride concentration goes from 2.29 mg/L to 1.60 mg/L. However, as can be checked from the SI obtained when running the software, no precipitation is achieved, and this fluoride reduction is due only to the dilution when mixed (70% of 2.29 mg/L gives a concentration of 1.60 mg/L)

In the theorical part we have seen a study of removal of fluoride with calcite nanoparticles, which was suitable for removal of fluoride in drinking water. The removal took place by surface adsorption at concentrations lower than 10 mg/L of fluoride, and from 40 mg/L fluoride the main process was surface precipitation. However, *PHREEQ-C* is only modeling the reactions of mixture, and its corresponding dissolution and precipitation due to the ion interaction in the aqueous solution. Therefore, the results cannot be conclusive. However, based on other studies and reports it is believed that the decrease to the desired levels is not possible with the pure addition of this component.

5.2.2 Addition of $CaCl_2$ to the groundwater

When carrying out a research in the literature on fluoride removal methods, it has been said that pure precipitation is generally only possible for its usage at industrial level, when the concentration of fluoride is very high. This process requires the addition of a great quantity of calcium, and the most economical ways are the addition of calcium chloride or lime (calcium hydroxide). Calcium chloride is usually more favorable as lime is more difficult to handle and can plug pipes, pumps or settle in the tanks. Besides, the necessary amounts of $Ca(OH)_2$ cause the pH to rise above the allowed limit, requiring subsequent treatment. This does not happen in the case of $CaCl_2$ [134].

However, the behavior of these two compounds in our specific case for drinking water purposes was studied, simulationally, starting with $CaCl_2$.

Simulations were carried out directly with Ghana's water composition at a temperature of 25 °C. The pH was not previously adjusted. The optimal concentration of $CaCl_2$ was manually checked and the one for the correct reduction to a level of 1.5 mg/L was 14 mM (1.55 g/L) (at 20 °C $CaCl_2$ has a solubility in water of 745 g/L [135]). Calcium chloride was added in 30 steps and the results are shown in *Figure 5.7.*

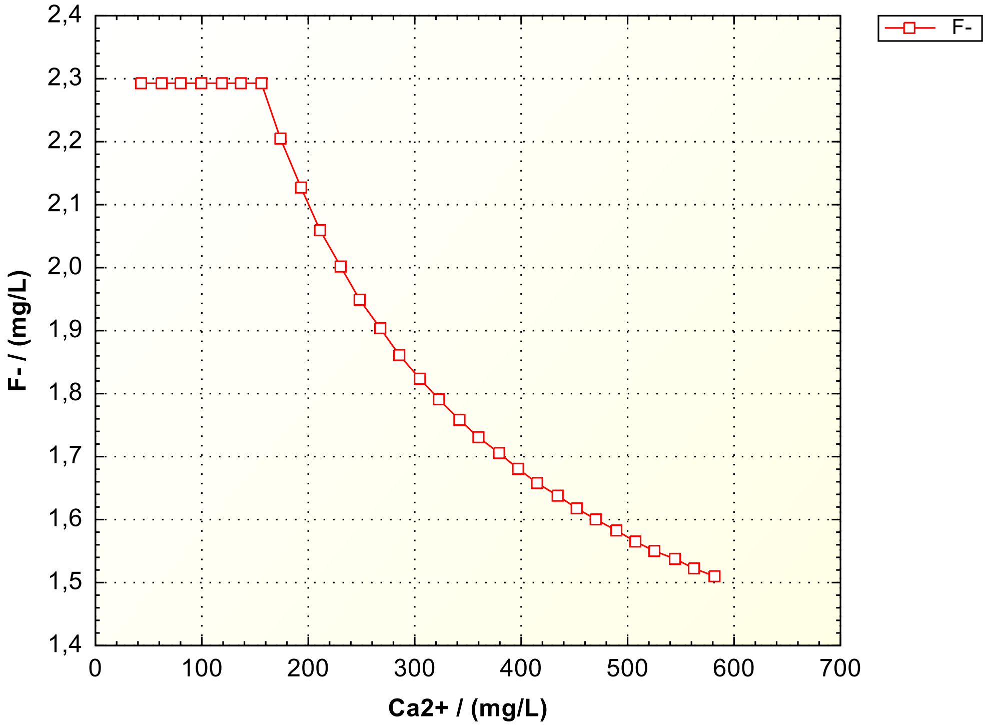


Figure 5.7 – Fluoride removal with 1.55 g/L $CaCl_2$ at 25 °C

It can be seen how this addition results effective for fluoride concentration. However, other problems arise *(Table 5.5).*

Table 5.5 – Calcium and chloride ions concentration in the water sample after $CaCl_2$ addition

	Initial (raw water)	**Final (after addition)**	**Guideline limit (WHO)**
Ca^{2+} concentration (mg/L)	25.3	580.8	200
Cl^- concentration (mg/L)	6.7	1000	250

As it can be seen, both the calcium and chloride concentrations, double and quadruple, respectively, the maximum value allowed for drinking water.

As stated, the addition of a large amount of product is necessary to reach the desired fluoride limits.

The only way in which by means of simulations it is possible to reduce the necessary fluoride content by the solely addition of $CaCl_2$, and being the rest of the parameters within the recommended values, would be by carrying out the reaction at a temperature of 2 °C. In this case, the addition of 3.5 mM $CaCl_2$ (0.39 g/L) is required for a fluoride concentration of 1.5 mg/L, giving rise to a final calcium concentration of 164 mg/L and a chloride concentration of 250 mg/L.

Another solution would be the increase in the pH of the water, reducing the amount of compound needed, however, the great decrease in the pH that is needed is not feasible. Also, calcium could be precipitated but the problem with the chloride ion would not be solved in this way.

5.2.3 Addition of $Ca(OH)_2$ to groundwater

In the case of $Ca(OH)_2$ addition, the same steps were followed. The results are shown in *Figure 5.8.*

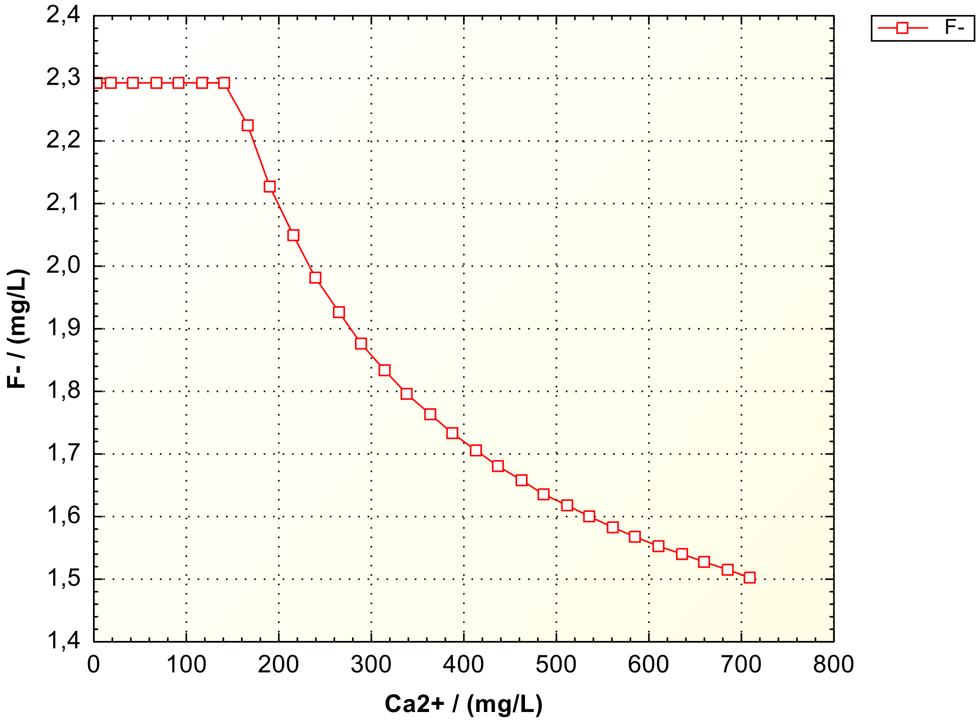


Figure 5.8 – Fluoride removal with 1.56 g/L $Ca(OH)_2$ at 25 °C

The amount of $Ca(OH)_2$ required to reduce the fluoride concentration to 1.5 mg/L at 25 °C is 21 mM (1.56 g/L) (being the solubility in water 1.85 g/L at 20 °C) [136]. However, as in the previous case, the reduction of fluoride leads to non-compliance with the recommended values of other parameters (*Table 5.6)*.

Table 5.6 – Calcium ion concentration and pH in the water sample after $Ca(OH)_2$ addition

	Initial (raw water)	**Final (after addition)**	**Guideline limit (WHO)**
Ca^{2+} concentration (mg/L)	25.3	732	200
pH	6.94	12.43	6.5 - 8.5

A solution could be the water acidification before $Ca(OH)_2$ addition. This way, due to the lower solubility of fluorite in acidic media, a lesser amount of hydroxide would be necessary, reducing the calcium present, and also the pH would be compensated. However, despite the fact that fluorite has been experimentally proven to be more soluble in alkaline medium [137], *PHREEQ-C* does not perform this calculation correctly, as it can be seen in *Appendix 2 (Figure 10.1).*

Therefore, the new simulation performed consisted on first the addition of 1.56 g/L $Ca(OH)_2$ at 25ºC, followed by the acidification of the generated solution. Carbonic acid (H_2CO_3) was used, as besides reducing the pH to appropriate values, it also reduces calcium ions concentration by the precipitation of calcium carbonate.

Different concentrations and combinations were analyzed but the best results were those shown in *Table 5.7* with the addition of 1.56 g/L of $Ca(OH)_2$ and 0.69 g/L (11 mM) of H_2CO_3.

	Initial (raw water)	**Intermediate (after Ca(OH)2 addition)**	**Final (after acidification with H2(CO)3)**	**Guideline limit (WHO)**
Ca^{2+} concentration (mg/L)	25.3	732	25.5	200
pH	6.94	12.43	7.53	6.5 - 8.5

Other simulations were performed with the addition of different chemicals such as belite (Ca_2SiO_4) or hydroxyapatite ($Ca_5(PO_4)_3OH$) for the precipitation of fluorapatite ($Ca_5(PO_4)_3F$) but did not lead to satisfactory results and they are therefore not included in the report.

5.3 Experimental study of fluoride removal by precipitation

In the objectives it was defined that in the experimental section those simulations in which the best results were obtained would be reproduced, to check their actual viability. However, due to the current situation and the permission to access the laboratory for only 8 hours, it required many simplifications.

Firstly, due to the availability of chemicals, it was not possible to prepare a solution with a composition similar to that studied in the simulations, so the experiments were carried out with ultrapure water (to which the fluorine content was increased, to equal the one present in Ghana's groundwater) or tap water (to which fluorine was also added).

Based on the simulations, the addition of calcium chloride and calcium hydroxide was decided. In the case of calcium chloride, it was defined as simulationally optimal to carry out the reactions at 2 °C. For hydroxide, the subsequent acidification of the water was required. However, all of these variants required time that was not available. That is why, the experimental part consisted purely on the addition of the calcium compounds, to compare the simulation with the experimental results and check if *PHREEQ-C* is effective in simulating the fluoride removal in the form of fluorite.

5.3.1 Precipitation and measurement of the fluoride content

As explained in the experimental methodology and found in *Table 4.1,* the removal of fluoride from the water was measured through IC. The results are shown below, as well as those modeled by *PHREEQ-C* in each case. Although the desired concentrations are those found in *Table 4.1*, the current concentration of the initial sample was also measured by IC, and therefore different values are shown here. Initial fluoride and initial pH were introduced in the simulations according to the measured values.

- **<u>Sample 1:</u> Ultrapure water (~2.29 mg/L F^-) + 3.3 g/L $CaCl_2$ in 1:1 volume proportion**

	Initial fluoride content (mg/L)	Final fluoride content (mg/L)	Initial pH	Final pH
Experiment	2.446	1.224	5.58	6.17
Simulation	2.446	1.245	5.58*	5.72

- **<u>Sample 2:</u> Ultrapure water (~2.29 mg/L F^-) + 3.7 g/L $CaOH_2$ in 1:1 volume proportion**

	Initial fluoride content (mg/L)	Final fluoride content (mg/L)	Initial pH	Final pH
Experiment	2.446	1.254	5.58	12.28
Simulation	2.446	1.256	5.58	12.80

- **Sample 3: Drinking water (+ 2.29 mg/L F^-) + 3.3 g/L $CaCl_2$ in 1:1 volume proportion**

	Initial fluoride content (mg/L)	Final fluoride content (mg/L)	Initial pH	Final pH
Experiment	3.592	1.688	7.08	7.01
Simulation	3.592	1.248	7.08	6.99

- **Sample 4: Drinking water (~2.29 mg/L F^-) + 3.7 g/L $CaOH_2$ in 1:1 volume proportion**

	Initial fluoride content (mg/L)	Final fluoride content (mg/L)	Initial pH	Final pH
Experiment	3.592	1.693	7.08	12.33
Simulation	3.592	1.257	7.08	12.80

As can be seen in the results, the simulated values and those obtained experimentally are very similar in the case of ultrapure water (sample 1 and 2). However, with a greater number of ions influencing the process, it appears that the simulations do not work as accurately. In any case, it should be noted that for the simulation with tap water, values have been taken from a Danish drinking water plant [138], but the exact composition of the water used is unknown. Also, it should be noticed that to carry out the experimental studies, higher concentrations were used than those that had been defined as optional simulationally (*sections 5.2.2 and 5.2.3*). In the case of $Ca(OH)_2$, the concentration used exceeded the solubility limit, and the sample was supersaturated. As mentioned, *PHREEQ-C* does not take this supersaturation into account, but even so, the results obtained are very similar, probably due to the fact that an adsorption on said material also takes place in the experimental exercises.

5.3.2 Experimental study of fluoride removal with ITC

ITC was carried out on a sample of ultrapure water with 2.446 mg/L of F^- (from NaF dissolution), and on a sample of tap water, to which also NaF was added, achieving a concentration of 3.592 mg/L of F^- (concentrations calculated through IC). In both cases, the chemical titrated was a 30 mM $CaCl_2$ solution. $Ca(OH)_2$ was not injected because it was not completely soluble at the concentration studied and could have plugged the injection needle.

- **ITC on ultrapure water**

In *Figure 5.9* is shown the heat flow signal versus time through the different injections, in demineralized water.

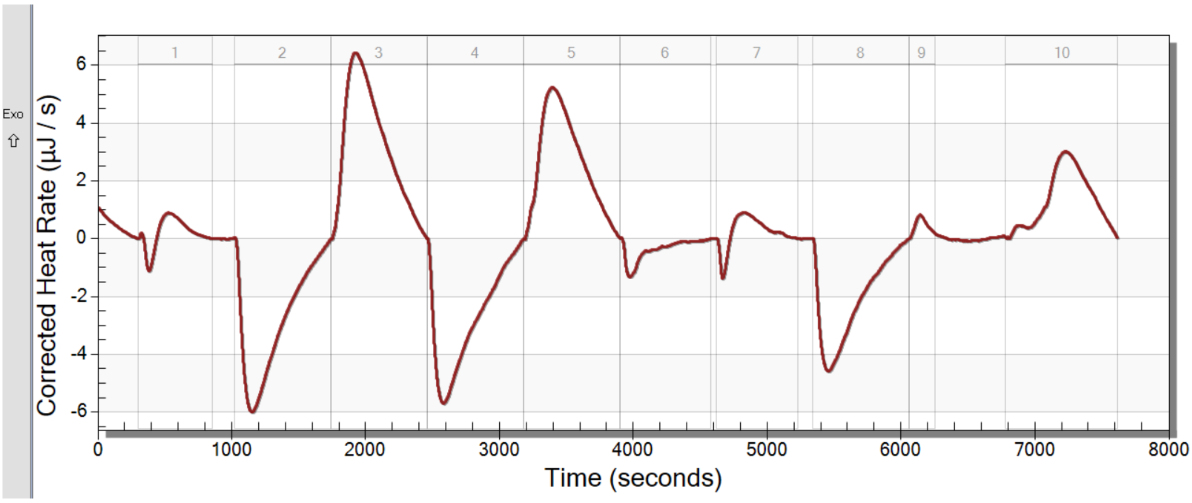


Figure 5.9 - Corrected heat rate vs time while ultrapure water with 2.446 mg/L F^- and 2.78 mg/L Na^+ is titrated with 30 mM $CaCl_2$

The thermograms are shown in the "exo up" mode, thus, the peaks are showing endothermic events when they are negative and exothermic when positive. In this case, a pattern behavior that remains constant cannot be seen.

Enthalpy change

Enthalpy of the reaction can be calculated from the heat developed with each titration (Q_{inj}) - calculated as the value of the area between peaks and the baseline shown in the heat rate thermograms-, the molar concentration of the fluid that is injected in the sample ampoule (C) and the volume of each injection (V_{inj}), as shown in *Equation (25)* [139]:

$$Q_{inj} = \Delta H \cdot [C] \cdot V_{inj} \quad \rightarrow \quad \Delta H = \frac{Q_{inj}}{[C] \cdot V_{inj}} \qquad (25)$$

The values of the heat developed with each injection (obtained with *NanoAnalyze Software)* and the calculated enthalpy changes are collected in *Appendix 2 (Table 10.3).* Shown below, in *Figure 5.10*, the final enthalpy changes.

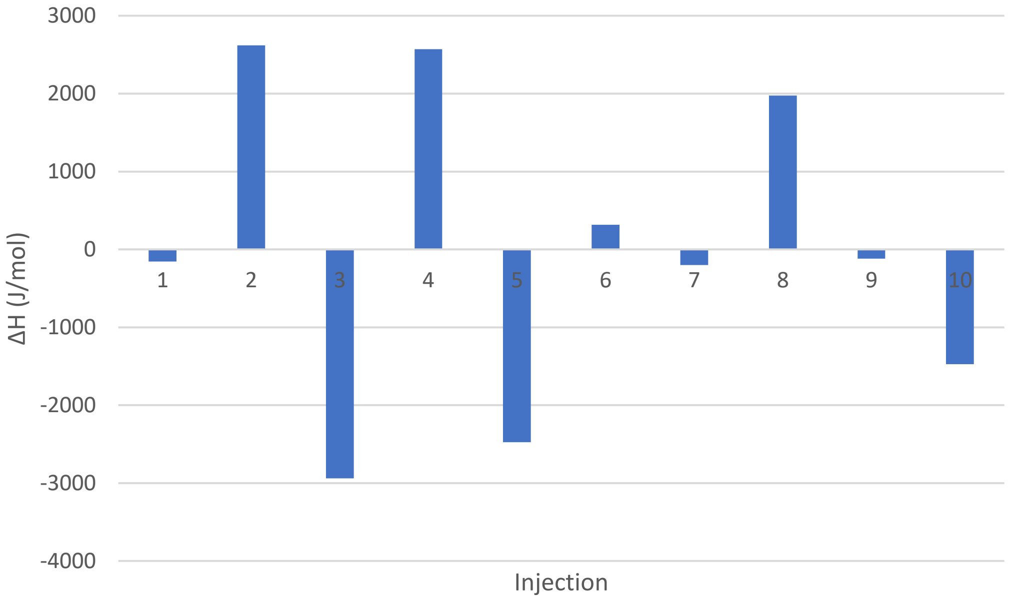


Figure 5.10 – Enthalpy change for each injection of $CaCl_2$ solution in ultrapure water solution

Taking into account the overall heat released or absorbed in each injection, 6 of them were exothermic and 4 endothermic.

The results do not have a clear analysis. We would expect exothermic peaks. Both solutions are prepared on ultrapure water, which by definition contains only H_2O molecules, H^+ ions and OH^- ions. To the base solution, NaF is added, and to the titrant $CaCl_2$. Both compounds are previously dissolved, so the only heat released or absorbed by the system would be due to interaction or dilution of ions. Calcium fluoride is precipitated, being its formation enthalpy negative, therefore exothermic (-1225.91 kJ/mol at 25 °C) [140]. The hydration enthalpy (arises when new bonds appear between ions and water molecules) is also exothermic (for the calcium, chloride, fluoride and sodium ions ~ -1650 KJ/mol, -346 kJ/mol, -505 kJ/mol and -406 kJ/mol, respectively).

These are the main sources of heat that may take place. The enthalpies obtained are also lower (in absolute value) with respect to the expected values.

The experiments were carried out at 25 °C, which is approximately the room temperature, so an endothermic evaporative influencing reaction is not expected.

In *Appendix 2 (Figure 10.2)* is shown the simulation for this exact composition. In the initial steps of the reaction more precipitate is obtained, and as the reaction is continuously more diluted, we would also expect a tendency in the decrease of the peaks with successive steps.

- **ITC on tap water**

In *Figure 5.11* is shown the heat flow signal versus time through the different injections, in tap water.

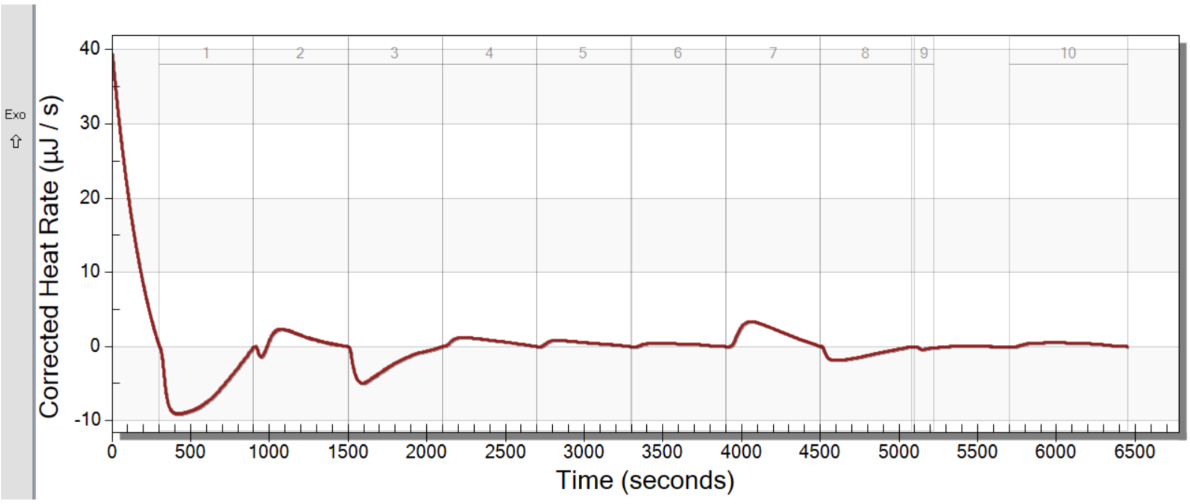


Figure 5.11– Corrected heat rate vs time while tap water with 3.592 mg/L F^- and 2.78 mg/L Na^+ is titrated with 30 mM $CaCl_2$

In this case we can see a bigger endothermic peak during the first injection for a later more or less constant heat flow.

Enthalpy change

The values of the heat developed with each injection and the calculated enthalpy changes are collected in *Appendix 2 (Table 10.4).* Shown below, in *Figure 5.12*, the final enthalpy changes

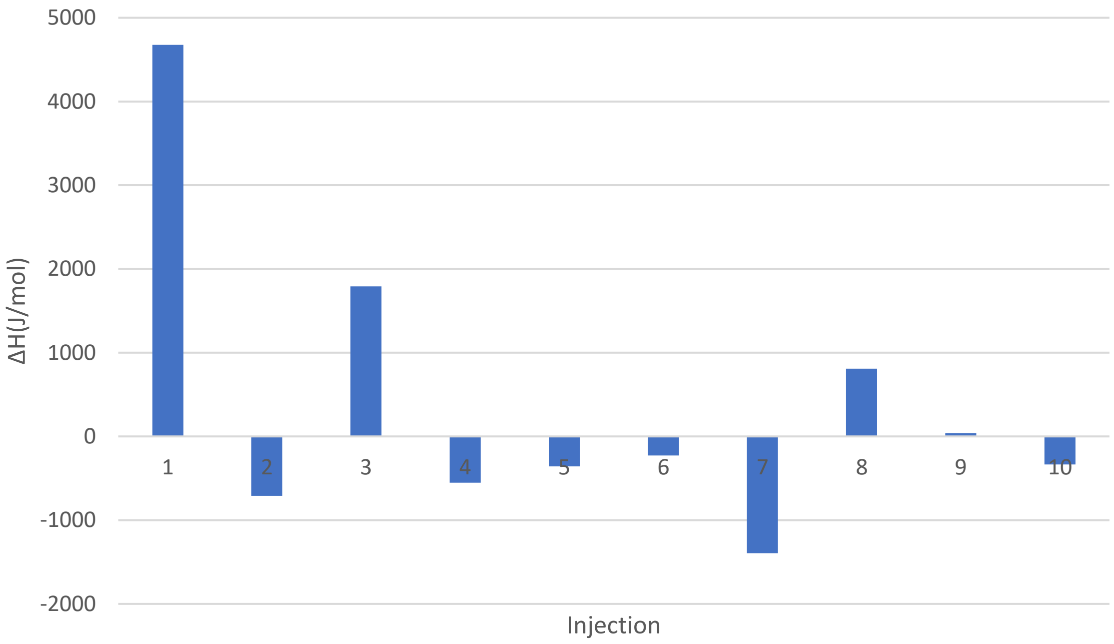


Figure 5.12 – Enthalpy change for each injection of $CaCl_2$ solution in tap water solution

As in the previous case, the results do not correspond with the expected ones. The first peak could be due to a lack of stabilization of the system during the first injection. Due to the unknowledge about the kinetics of the process, it could be thought that precipitation of fluorite is not taking place during the duration of the experiment. Also, because there was no visible precipitate. However, neither when carrying out the reactions before IC analysis was precipitate observed, despite being larger volumes (and this technique assured that the fluoride has been precipitated). Although the reaction time necessary for the precipitation is unknown, the samples were analyzed for two hours in ITC while for IC only stirred for one hour, so the precipitate had to have formed. Although it was not a fast reaction, at some point during the injections these exothermic peaks should occur. The reason for the results may be due to the interaction of ions that are present in the water, but still, ITC does not allow the analysis for the best understanding of the reaction taking place in our case.

6. CONCLUSIONS

The presence of fluoride in groundwater has been briefly reviewed with focus on Ghana, where a big part of the population is dependent on this source of drinking water. The granitoid terrains found in the northern region present a high fluoride mineralization, affecting health problems associated with high fluoride levels, such as dental fluorosis, to more than 60% of the population.

Many techniques have been developed for fluoride removal in drinking water (mainly adsorption and membrane techniques), being the main weaknesses their high operational and upkeep cost, as well as associated contamination due to other chemicals involved in the process or the need to operate at specific pH ranges. Because of this, their implementation in developing countries is difficult.

One of the best techniques studied to date is the adsorption on magnesium oxide particles, achieving an uptake capacity of between 5,716 and 15,691 mg/g. Besides, it is a fast process than works in a wide pH range. Specifically, the usage of bauxite as adsorbent have a huge potential in Ghana's north community, due to the availability of this material and therefore facility in its reproduction.

For the simulation study, it has been worked with data from the *Bongo region* (Ghana). The simulation of the fluoride release system, using water with calcite and fluorite in equilibrium and making it react with albite (a feldspar silicate) allowed the observance of the influence of the CO_2 dissolved in the solution, since, with its increase, the concentration of hydrogen ions increases, favoring albite weathering, which increases the pH and therefore fluorite solubility, at the same time that calcium carbonate is precipitated.

In the study of the water speciation of the sample of study it was verified as in this case, the amount of fluoride seems to come from both fluorite and other minerals subjected to isomorphous substitution.

Through the review of the state of the art, it was observed that pure precipitation methods are not used in general for drinking water purposes, but rather for wastewater discharge. The addition of certain chemicals to the specific case of study was checked to be feasible for fluoride removal in the form of fluorite. The addition of calcite is highly dependent on pH. In order to avoid the usage of large quantities of chemicals, an attempt was made to reduce the fluoride content by adding a solution saturated in calcite with a pH of 2, to the water sample, in a weight ratio of 0.3: 0.7 (calcite:water), but fluorite precipitation does not occur.

The study was favorable with the addition of 0.39 g/L of calcium chloride at a temperature of 2ºC. Refrigeration was necessary, to favor the reaction and reduce the amount of calcium chloride needed, since carrying out the reaction at room temperature (25 °C) both the concentration of calcium and chlorine ions exceed the limits set by the WHO for drinking water.

Reduction of fluoride to a level of less than 1.5 mg/L was also possible by adding 1.56 g/L calcium hydroxide, and subsequently, 0.69 g/L of carbonic acid, reducing the excess of calcium ions and pH generated.

These last two cases were studied experimentally. However, due to limitations, laboratory exercises were reduced to the solely addition of calcium chloride and calcium hydroxide at 25ºC, in ultrapure water and drinking water with previously increase of the fluoride content. The results of the final concentration of fluoride obtained by IC in the samples, show that the simulation results are very close to reality in samples carried out in ultrapure water, but with tap water, where a greater number of ions are involved, the accuracy is decreased. In any case, the possibility of reducing fluoride to the desired levels is confirmed.

A solution of calcium chloride was injected into both fluorinated ultrapure and tap water using ITC, in order to observe the development and behavior of the reactions. However, unfortunately, no conclusion can be withdrawn.

7. FURTHER RESEARCH

Below is stablished further research that could be undertaken to better accomplish and complete the objectives studied in this project.

It is recommended to carry laboratory experiments under the studied conditions without taking simplifications: elaborating a water solution with a composition equivalent to that of the *Bongo region* of study, and carrying out the precipitations at 2°C in the case of the calcium chloride and with subsequent acidification in the case of the calcium hydroxide. Besides, it would also be favorable the measurement in IC of the concentration of the rest of the components, not only fluoride, to completely verify the effectiveness of the suggested methods.

It would be also convenient to vary the amounts of some of the ions presented and in a wider pH range, doing both the aqueous geomechanical simulations and the corresponding lab experiments to check the accuracy of *PHREEQ-C* in the different cases and check the viability of the process in slightly different conditions.

It is suggested to repeat the ITC experiments, carrying out a previous calibration to the apparatus and perhaps decreasing the operating temperature or increasing the time between injections.

Finally, the precipitation method is attractive as it is a simple method that could be applied in developing countries. However, an economic evaluation is necessary, taking into account the needed equipment, amount of chemicals required to treat the desired volumes of water and other operational costs associated. It would be interesting an economical comparison between these precipitation methods and the adsorption on bauxite, as has been stated as a potential technique in the region of Ghana.

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9. APPENDIX 1

9.1 Main PHREEQ-C scripts

9.1.1 Release mechanism of fluoride in water

```
DATABASE C:\Program Files\USGS\phreeqc-3.6.2-15100-x64\database\wateq4f.dat
TITLE Fluoride increase with albite weathering
SOLUTION 1
 pH 7 charge
 C 1 CO2(g) -0.5
 F 1 Fluorite
 Ca 1 Calcite
REACTION
 NaAlSi3O8 1
 7e-3 in 30
 EQUILIBRIUM_PHASES 1
 Fluorite 0
 Calcite 0
 Kaolinite 0 0
 Quartz 0 0
USER_GRAPH
 -headings Ca2+  F-  pH
 -chart_title "Fluoride release while albite weathering"
 # -axis_scale x_axis 0 160
 # -axis_scale y_axis 0 10
 # -axis_scale sy_axis 6.5 7.5
 -axis_titles "Ca2+ / (mg/L)"  "F- / (mg/L)" "pH"
 -initial_solutions true
 -start
 10 graph_x tot("Ca") * 40e3
 20 graph_y tot("F") * 19e3
 30 graph_sy -la("H+")
 40 if step_no = 0 then plot_xy tot("Ca") * 40e3, tot("F") * 19e3, symbol = Circle, symbol_size = 15, color = Blue
 50 if step_no = 0 then plot_xy tot("Ca") * 40e3, -la("H+"), y_axis = 2 symbol = Circle, symbol_size = 15, color = Blue
end
end
```

9.1.2 Influence of pH in the precipitation of fluorite

```
DATABASE C:\Program Files\USGS\phreeqc-3.6.2-15100-x64\database\wateq4f.dat
TITLE Influence of pH
SOLUTION 1  Pure water with fluoride

units   ppm

    pH     x

     F       5

EQUILIBRIUM_PHASES 1 Calcite addition

   Calcite 0.0

end
```

9.1.3 Temperature influence on the precipitation of fluorite

```
DATABASE C:\Program Files\USGS\phreeqc-3.6.2-15100-x64\database\wateq4f.dat
TITLE Dependence of fluorite precipitation with temperature
SOLUTION 1  Pure water with fluoride

    units   ppm

     pH            2

     F          5

EQUILIBRIUM_PHASES 1

    Calcite 0.0

REACTION_TEMPERATURE 1

    0.0 75.0 in 50 steps

SELECTED_OUTPUT

   file temp.sel
   temperature
   si Fluorite

USER_GRAPH 1 Solubility

   headings Temperature Fluorite
   chart_title “Fluorite stability”
   axis_scale x_axis 0 75
   axis_scale y_axis 0.4 1.4
   axis_titles “Temperature (°C)” “Saturation index”
   initial_solutions false
   start

10 graph_x TC
20 graph_y SI(“Fluorite”)
end
end
```

9.1.4 Calcite addition to groundwater from the Bongo region

```
DATABASE C:\Program Files\USGS\phreeqc-3.6.2-15100-x64\database\wateq4f.dat
TITLE Fluoride removal from groundwater in Ghana
SOLUTION 1  GROUNDWATER FROM GHANA
    units   ppm
    pH     6.94
    Ca          25.3
    Mg           11.5
    Na          23.9
    K          2.0
    F          2.29
    Cl         6.7
    N(5)         18.4
    S(6)         4.8
   Si          30.3
    Alkalinity     156 as HCO3
SAVE solution 1
end
SOLUTION 2 Acidic water with calcite
        pH 2
EQUILIBRIUM_PHASES 1 Calcite addition
        Calcite 0.0
save SOLUTION 2
end
mix 1
        1 0.7
        2 0.3
end
end
```

9.1.5 $CaCl_2$ addition at 2° C to groundwater from the Bongo region

```
DATABASE C:\Program Files\USGS\phreeqc-3.6.2-15100-x64\database\wateq4f.dat
TITLE Fluoride reduction with CaCl2 addition GHANA
SOLUTION 1
units mg/L
 pH      6.94
```

```
 S(6)     4.8
 Ca       25.3
 Mg       11.5
 Na       23.9
 K        2
 N(5)     18.4
 Cl    6.7
 F     2.29
 Si       30.3
Alkalinity 156 as HCO3
Temperature 2
REACTION
Ca(Cl)2 1
3.5e-3 in 10
 EQUILIBRIUM_PHASES 1
 Fluorite 0 0
 Calcite 0 0
USER_GRAPH
-headings Ca2+ F-
-chart_title “Addition of CaCl2 to the solution”
-axis_titles “Ca2+ (mg/L)” “F- (mg/L)”
-start
10 graph_x tot(“Ca”) *40e3
20 graph_y tot(“F”)*19e3
30 if step_no=0 then plot_xy tot(“Ca”)*40, tot(“F”)*19e3,symbol=Circle, symbol_size=15, color=Blue
end
end
```

9.1.6 $Ca(OH)_2$ and carbonic acid addition to groundwater from the Bongo region

```
DATABASE C:\Program Files\USGS\phreeqc-3.6.2-15100-x64\database\wateq4f.dat
TITLE Fluoride reduction with CaOH2 addition GHANA
SOLUTION 1
units mg/L
```

```
 pH      6.94
 S(6)    4.8
 Ca      25.3
 Mg      11.5
 Na      23.9
 K       2
 N(5)    18.4
 Cl   6.7
 F    2.29
 Si      30.3
Alkalinity 156 as HCO3
REACTION 1
Ca(OH)2 1
21e-3 in 10
 EQUILIBRIUM_PHASES 1
 Fluorite 0 0
 Calcite 0 0
save solution 2
end
USE SOLUTION 2
REACTION 2
H2(CO)3 1
 1.1e-2 in 10
EQUILIBRIUM_PHASES 2
 Calcite 0 0
 Aragonite 0 0
end
```

10. APPENDIX 2

10.1 Kenya's groundwater composition

Table 10.1 – Chemical composition of groundwater from a borehole in Naivasha (Rift Valley area, Kenya) [131]

Chemical	Concentration (mg/L)
pH	8
Total alkalinity ($CaCO_3$)	324
Hardness ($CaCO_3$)	31
Ca^{2+}	11
Mg^{2+}	0.6
Na^+	170
K^+	27
Mn^{2+}	0.01
SO_4^{2-}	30
F^-	9.3
Cl^-	29
NO_3^-	0.2

10.2 Results from water speciation in Kenya's groundwater

Table 10.2 – Aqueous speciation modelling from the sample of groundwater in Naivasha (Rift Valley area, Kenya)

Phase	SI
Anhydrite ($CaSO_4$)	-3.18
Aragonite ($CaCO_3$)	-0.08
Calcite ($CaCO_3$)	0.06
Dolomite ($CaMgCO_3$)	-0.79
Fluorite (CaF_2)	0.13
Gypsum ($CaSO_4 : 2H_2O$)	-2.87
Halite ($NaCl$)	-6.87

Hausmannite (Mn_3O_4)	-10.93
Manganite (MnOOH)	-4.65
Pyrochroite ($Mn(OH)_2$)	-6.51
Pyrolusite ($MnO_2 : H_2O$)	-8.69
Rhodochrosite ($MnCO_3$)	-0.83
Sylvite (KCl)	-7.23

10.3 Fluorite solubility by PHREEQ-C

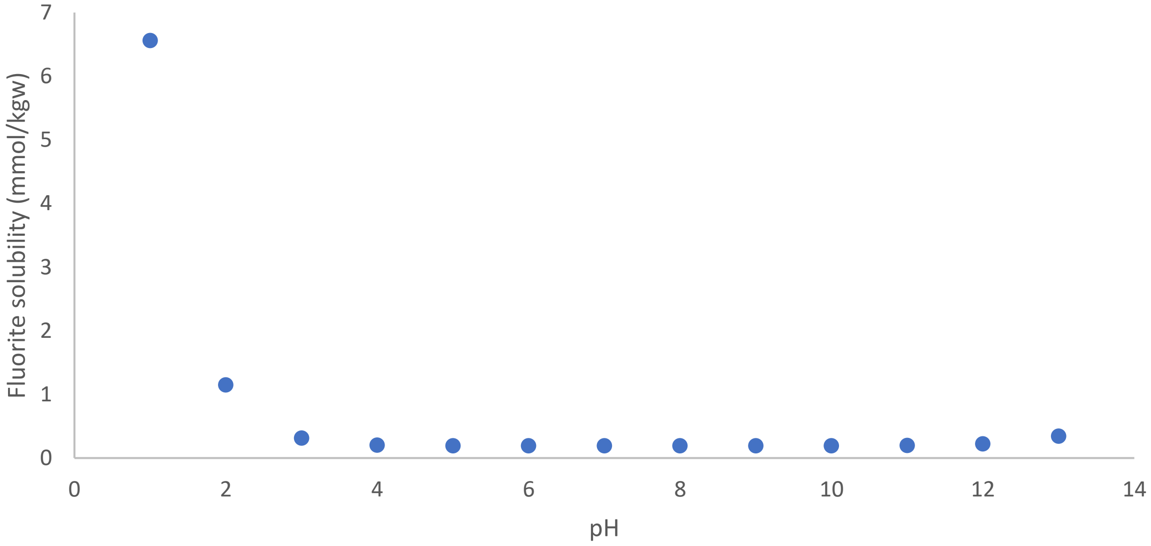

Figure 10.1 -Variation in the solubility of fluorite with pH obtained by PHREEQ-C

The results obtained by the simulation are quite surprising. Even the solubility of fluorite is very low, the different publications state that its solubility is greater in alkaline pH. In this case we can see how the bigger values are those corresponding to the lowest pHs, keeping then more or less a constant value.

10.4 ITC heat developed and enthalpy change

Table 10.3 – Heat developed and enthalpy change with each injection of $CaCl_2$ solution in the pure water sample

Injection	**Q_{inj} (µJ)**	**ΔH (J/mol)**
1	-117.8	-157.1
2	1965	2620

3	-2203	-2937.7
4	1928	2570.7
5	-1857	-2476
6	238.4	317.9
7	-149	-198.7
8	1481	1974.7
9	-90.41	-120.5
10	-1106	-1474.7

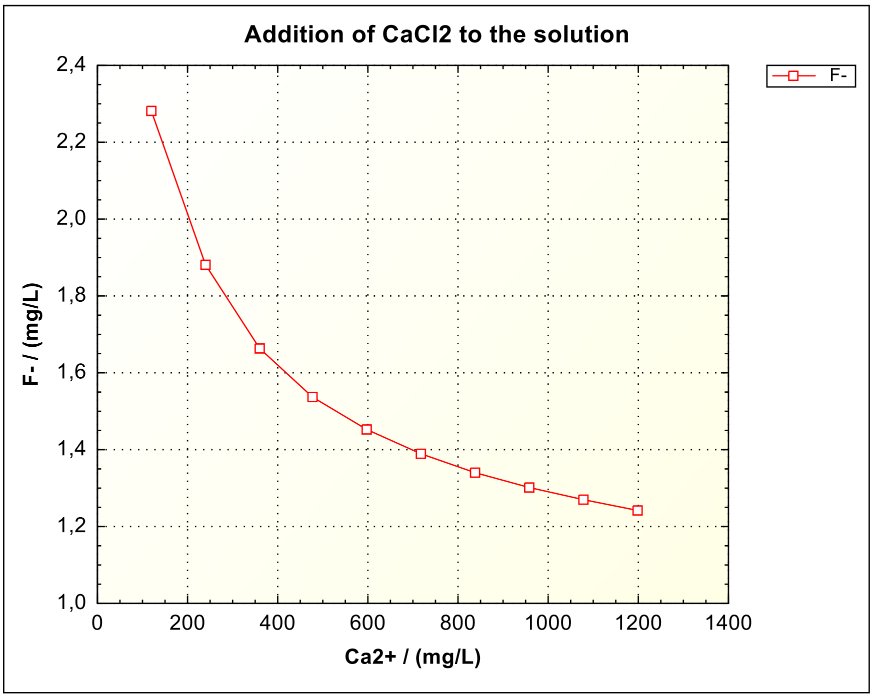

Figure 10.2 – Simulation with the characteristics ITC experiment (1)

Table 10.4 – Heat developed and enthalpy change with each injection of $CaCl_2$ solution in the tap water sample

Injection	Q_{inj} (µJ)	ΔH (J/mol)
1	3506	4674.7
2	-532.9	-710.5
3	1344	1792
4	-413.6	-551.5
5	-268.6	-358.1
6	-169.3	-225.7

7	-1047	-1396
8	606.1	808.1
9	29.21	38.9
10	250.5	-334