

MITIGATING THE RELEASE OF ACIDITY AND METALS FROM AN ACID SULFATE SOIL

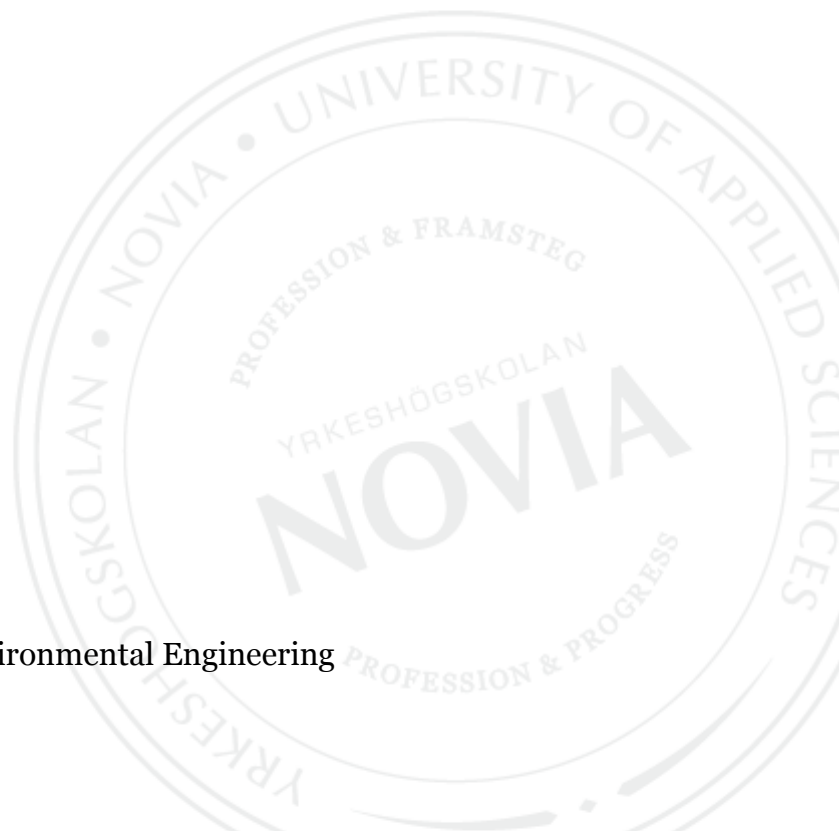
A study using column experiments

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Abstract

Acid sulfate soils are soils containing rich sulfide minerals found mostly in low-lying coastal areas. Upon exposure to atmospheric oxygen, these sulfide minerals oxidize, producing more sulfuric acid than can be neutralised by the buffering capacity of the soil.

This thesis aimed at developing and testing methods to mitigate the release of acidic and metals from acid sulfate soils, which will be used as a study case at Risöfladan experimental field in Vaasa, using column leaching test as experimental technique. The column test were carried out in NOVA University of Applied Sciences laboratory using CaCO_3 (Enrich C and FC 2.5) and peat suspensions as treatment chemicals.

During the initial flushing of all the acid sulfate samples with autoclaved water, the pH of the permeate was at a value of circa four. During CaCO_3 (Enrich C and FC 2.5) treatments, the pH of the permeate increased to a value of circa 7 and remained at this value even after switching to autoclaved water. In contrast to CaCO_3 treatments, treatment with peat suspension had little or no effects on the pH.

All treatments on the other hand, had significant effects on the temperature-corrected conductivity and redox potential of the permeate leached from the acid sulfate soil samples.

Language: English

Key words: Permeate, Redox Potential, pH

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1 Introduction

The internship with the PRECIKEM II project in NOVIA University of Applied Sciences during the summer of 2016, gave an overview about acid sulfate soils. The project aimed at studying the impact of the mitigation strategies on acid sulfate soils and microbial activities. In the course of the training, the topic was found interesting and chosen as a focus area for this thesis because it helps to achieve goals of sustainable development, which has become an important issue both on the local and international scene in this era. The world is currently faced with issues concerning population increase with the UN projecting the population of the world to exceed 8 billion by the year 2030. The increase in population simultaneously gives rise for demand in resources like land for agricultural and infrastructural activities. Currently, with pressures on land reaching its critical point, doubts have been raised on whether lands available now can suffice the demands of the population increase. Old marine sediments now available due to land uplift and climate change especially in the coastal areas have been reclaimed to satisfy the needs of the people. However, some of these old marine sediments are potential acid sulfate soils containing sulfide rich sediments.

Disturbances such as land uplift and drainage activities expose these sulfide sediments to atmospheric oxygen leading to the oxidation of these sulfide rich sediments and as a result acid sulfate soils are formed [1]. Acid sulfate soils pose as a real and imminent threat to the environment because they release high amount of acids and metals (aluminum, nickel, cadmium, manganese) into ecosystems such as rivers etc. and as a result destroy those habitats.

2 Thesis Objective and Methodology

The objective of this thesis is to develop and test methods to mitigate the release of acidic and metals from acid sulfate soils, which will be used as a study case at Risöfladan experimental field in Vaasa, using column leaching test as experimental technique.

To achieve this objective, the thesis consists of both theoretical and practical parts. The theoretical part covers an overview of acid sulfate soils, formation and impacts. This part was done by reviewing some literature materials relating to the subject. The practical part

contains laboratory experiments done during internship with the PRECIKEM II project to mitigate the impacts.

3 Theoretical Background

3.1 Acid Sulfate Soil

According to Joffe (1936) [2]; *“soil is a natural body, differentiated into horizons of mineral and organic constituents, usually unconsolidated, of variable depth, which differs from the parent material below in morphology, physical properties and constitution, chemical properties and composition and biological characteristics.*

Various types of soils obtained are classified using this definition or knowledge. However, using this classification scheme to differentiate between soils universally can be very tedious and complex [3] because the formation of soil is hinged on the following factors; parent material, topography, climate, biota and time [4] which differ universally. Human activities also have an influence [5], as seen in many places. Acid sulfate soil can be classified in two groups namely, potential acid sulfate and actual acid sulfate soils.

Potential acid sulfate soil is a term given to rich sulfide sediments that have not been oxidized by exposure to atmospheric oxygen [1]. Potential acid sulfate soils can be identified by their dark-grey color which is often associated with a rotten egg smell [6]. The pH of potential acid sulfate soil ranges from 6.5 to 7.5 and has unoxidized iron sulfides [7] which upon exposure to atmospheric oxygen or disturbed which could be in the form of excavation, leads to the oxidation of the iron sulfides and as a result actual acid sulfate soils are formed. Actual acid sulfate soils are very acidic with their pH often below 4 and often contain jarosite as a byproduct of their oxidation [1].

3.2 Formation and Development of Acid Sulfate Soil

Acid sulfate soils are formed due to specific environmental conditions [3]. Acid sulfate soils are mostly found at coastal regions [8] where pressures from population and infrastructural activities are at its peak. In Finland, acid sulfate soils contains anoxic layers which lies below the groundwater table, in which sulfur is stored in the form of sulfide.

The anoxic layer is formed as a result of the microbial decomposition of organic carbon. The sulfur stratum of the acid sulfate soils came about 10000 years ago during the Littorina Sea period which took place during 7500- 1500 BC after the ice age. Littorina Sea which was rich in organic matter, more saline than the Baltic sea and containing significant amount of dissolved iron and sulfur as sulfate. Some of the sulfur was also derived from microorganisms in the Littorina Sea whose microbiological decomposition consumes the oxygen in the lower stratum as a result reducing the sulfate into sulfide. The sulfide formed then combines with iron from the sediments to produce iron sulfides in the lower sediments [9].

Natural phenomena such as postglacial land uplift [5] of about 8 mm/year [9] and human activities have exposed these sulfide sediments to atmospheric oxygen as a result forming acid sulfate soils [6]. Oxidization of the sulfide occurs in one the following equations according to [10].



3.3 Geographical Distribution of Acid Sulfate Soils

Acid sulfate soils are widespread across the world. Global estimates of potential acid sulfate soils and actual acid sulfate soils are about 17 million ha [8], which accounts for about one percent of the cultivated land in the world [3].

Acid sulfate soil has the highest occurrence in Asia and the Far East followed by West Africa and Latin America. In a review on the global distribution of acid sulfate soils, it was estimated that about 10 million ha of the world's acid sulfate soils are found in the tropical regions [8]. Most of these tropical regions have high temperatures, protected mangroves and marches, with large amount of tidal exchange, which helps in accumulating much pyrite. In Europe, Finland has the highest occurrence of potential and actual acid sulfate soil. An extensive survey on Finnish acid sulfate soils published in 1991 shows that , there are about 3360 km² of acid sulfate soils in Finland, this represents 16 % of its field areas and more than 20 % of its cultivated land area in the coastal environment [9]. Table 1

below shows the global distribution of potential acid sulfate soil (PASS) and actual acid sulfate soil (ASS).

Table 1: World distribution and extent of potential and actual acid sulfate soils

Source: [8]

	Area(million ha) per length of growing period 2002
Continents	Area estimated for PASS & ASS
Africa	4.5
Asia	6.5
Latin America and the Caribbean	2.8
Europe	0.24
Australia	3
North America	0.1
Total	17.14

4 Impact of Acid Sulfate Soils

When potential acid sulfate soils are not disturbed, that is if they are in reducing conditions below the water table they pose no threat to the environment [10]. However, upon exposure to atmospheric oxygen these soils oxidize and as an outcome large quantity of acid and metals [6] are released into the environment. Some of these impacts will be discussed in the subsequent subchapters.

4.1 Agricultural Activities

Acid sulfate soils reduce the productivity of a land [11] and to be able to cultivate on a potential acid sulfate soil, the land has to be drained effectively. This drainage activity causes the sulfide sediments of the soil to acidify and in order for cultivation to be possible, lime has to be applied to the top soil of the acid sulfate soil to neutralize it. Large amount of lime is needed for the neutralization, about 30 tons of lime per hectare [9]. Lime application can have economic impact on the farmer because large quantity of lime is

needed. Moreover, shallow roots crops or plants can only be cultivated on the land since neutralization with lime only raises the pH of the top soil.

In addition, pastures used for grazing will be reduced [3] because of the acidic conditions. As a result, decreasing animal productivity and exposing the top soil to erosion [11].

4.2 Watercourses

When oxidation products from acid sulfate soils are leached into watercourses, they causes significant problems to the waterbody and its aquatic life activities. Aluminum which occurs in most acid sulfate soils as aluminosilicate [12], when leached into watercourses hydrolyses and precipitates as aluminum hydroxide which increases the acidity of the water [7] endangering most aquatic species who can't survive in acidic waters. Increased amounts of iron in watercourses particularly affected by acid sulfate soils decreases water quality. Furthermore, waters with high levels of aluminum decreases the turbidity of the watercourse making it possible for the waterbed to be seen from few depths [13]. This is because aluminum can cause flocculation of particles on the surface of the watercourse to sink to the bottom of the watercourse [13]. In 1937, a case of this sort was recorded at the Kyrö river in Finland where at a depth of two meters the riverbed could be clearly seen [9]. Decrease turbidity of watercourses have significant impact on the feeding behavior, health and distribution of fishes thus altering the predator-prey ratio and food chain of the aquatic species [14].

4.3 Aquatic Organisms

During the wet seasons, high amount of sulfuric acid and metals such as aluminum and iron are leached into nearby waters. This gives rise to an increase in acidity of the water and thus affecting aquatic life. Most aquatic organisms thrive in waters with minimum pH of about 6 and waters particularly those affected by acid sulfate soils has pH of about 4 or less [13]. Aquatic plants and organisms such as fish which cannot tolerate these acidic and metallic conditions often die. As seen in various places where massive amount of fish were killed in acid sulfate soil areas [12]. These fish kills are often seen and noticed as effects of acidification [3] particularly in acid sulfate soils areas. However, studies have shown also less obvious but significant effects on fish in acidified waters. An evident problem is the decline in growth rate of fishes [13] which is due to reproductive disturbances such as yolk and sperm formation and lessen the hatching of young ones since the hatching period is

mostly during the wet season where water acidity is at its peak [12]. Disturbances in the yolk and sperm formation and spawning behavior [12] of fish begin when the pH of the water is below 5.5 [9].

The fish skin and gill can be infected or damaged when the water becomes acidic. Damages to the skin makes osmoregulation much more difficult and increases the chances of fungal and bacteria attacks [13]. When the gill of a fish is damaged it lessens the ability of the fish to take up oxygen.

The habitat of aquatic life is affected due to the precipitation of iron oxyhydroxide [3] which occurs when acidic water mixes with less acidic, that is waters of high pH [13]. Iron oxyhydroxide smothers the streambed sediments and plants and thus life threatening pH can be formed [13]. Many aquatic plants are also affected by acid water since only few aquatic plants can tolerate waters with high acidity [9].

4.4 Human and Infrastructure

Recent studies shown that acid sulfate soils in areas used for agricultural activities like dairy cattle production, have been linked with high concentration of metals (Al, Fe, Zn) in their dairy products. This case was recorded at the basin of the Kyrö river in Finland which has acid sulfate soils in the area used for dairy farming [12]. High concentration of acid and metals leached from the acid sulfate soils [1] into the river decreases the water quality and harm fishes as discussed earlier. Recreational activities such as fishing and swimming is affected as a result of this [15]. Moreover, high concentration of metals in dairy products, water and crops can cause potential health risks to people.

Due to pressures from population, especially in the coastal lands where acid sulfate soils are mostly found, have been used for infrastructural activities (buildings, roads etc.). This has resulted in oxidation and structural changes of the soils, which affects these buildings. Sulfuric acid leached from acid sulfate soil [16] can cause cracks and loosen the bonds in the concrete and mortar which can lead to the collapsing of the buildings. Pipes and steels in acid sulfate soils areas corrode at much higher rate due to the sulfuric acid, thus creating an extra maintenance cost [16].

5 PRECIKEM I Project (2010 – 2014)

PRECIKEM (chemical precision treatment of acid sulfate soils to prevent acid formation) I project, which took place from 2010 to 2014 aimed at mitigating the acidic and metal rich drainage from an acid sulfate soil in an experimental field at Risöfladan in Vaasa. In the subsequent chapters, the experimental field used in this project, the treatment method used, why this treatment method was chosen and the outcome of the project will be discussed. The project was funded by the European Agricultural Fund for Rural Development via the Rural Development Programme for Mainland Finland 2007-2013.

5.1 A Study Case at Risöfladan Finland

As discussed earlier, Finland has the largest area of potential and actual acid sulfate soils in Europe. Based on the extensive survey published by [17] the areas with most potential and actual acid sulfate soils in Finland are Southern and Central Ostrobothnia and Southwestern Finland [9].

The experimental field used for this project is an agricultural field in Vaasa, western Finland. The field is divided into 9 subfields which each subfield a hectare wide as shown in Fig. 1. Each subfield has its own drainage system, consisting of subsurface drainpipes, a collection pipe and a control well [9]. Each subfield has plastic sheets that extends to a depth of 1.8 meters separating it from the other subfields [18]. This allows each subfield to be treated differently from the other and makes monitoring easy. In Fig.1, the red lines represent the plastic sheets used in separating each subfield. The blue lines in Fig. 1 represent collection pipes installed in each subfield. The collection pipes are connected to the control well on each subfield used for sampling drainage water and applying treatments. On each subfield, leveloggers and barologger purchased from Solinst have been installed. The loggers are installed at a depth of 10 cm above the bottom of the 2.5 m deep groundwater pipes. The leveloggers are used in measuring continuous groundwater level while the barologger is used in measuring pressure. Also in Fig.1, three GR signs can be seen on each subfield. These are groundwater pipes placed at a depth of 2.5 m used for sampling the groundwater of each subfield.

The parent material of the field consists of Holocene estuarine clay and silt with the field pH varying with depth just as acid sulfate soils used in cultivation. The top soil (c. 0-30

cm) is just weakly acid because of the large amount of lime applied to it before cultivation. Below the top layer is the acidic layer and the pH of this layer ranges from 3 to 4.5. This layer extends to depth of 120 cm, underneath this layer lies the unoxidized sediments having a pH between 6.5 to 7.5 [19].

Each subfield was treated with different amounts of ultrafine-grained suspensions of calcium carbonate or calcium hydroxide mostly in slurry form using water from the Toby river nearby. Subsurface drainage system was the treatment method used in treating or applying treatment chemicals into the field. Treatment of the field was done during the dry period when oxidation of the sulfide sediment is most significant and the groundwater table is below drainage depth. Therefore, during the wet periods when oxidation products are leached, the effects are minimized.

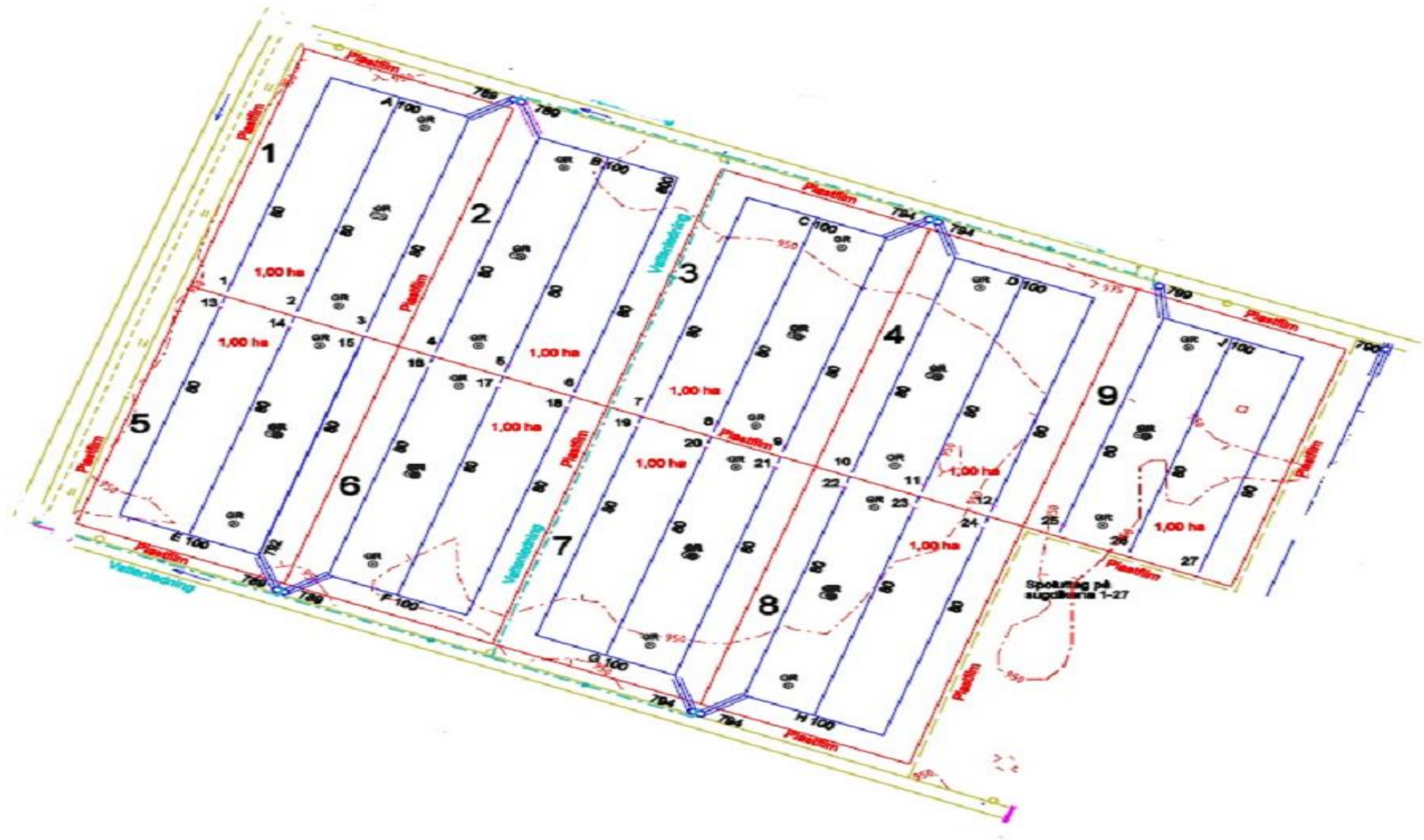


Fig.1 A map of the experimental field at Risöfladan.

5.2 Subsurface Chemical Treatment

When sulfide rich sediments are disturbed by human activities such as drainage, atmospheric oxygen gains access through the macropores in the soil to the sulfide sediments. As a result an actual acid sulfate soil is formed by chemical and microbiological process that takes place upon oxidation. To restrain further oxidation of the sulfide sediments by the microorganisms along the hydrologically active macropores, the soil is treated by pumping suspension of fine-grained (2.5 μm) calcium carbonate or calcium hydroxide through these macropores. The fine-grained calcium carbonate adheres to the macropores of the soil. Ultra fine-grained particles is used in order to avoid clogging of the drainage system and also facilitate the breaking and dispersion of chemicals in the acidic layer of the soil [20]. On the experimental field, suspensions are pumped through the control well in each subfield.

5.3 Why this Type of Treatment was Chosen

Applying lime to the surface of soil or land only neutralizes the acidity of the top soil (0-30 cm) hence making the top soil favorable to cultivate crops or plants with shallow roots. The acidic layer of the soil is left untreated and the problem is left unsolved.

Subsurface chemical treatment was chosen to (1) neutralize the acidity, (2) immobilize metals in the soil macropores, and (3) hinder the microorganisms that causes oxidation of the sulfide sediments [22].

5.4 Outcome of the Project

After treating the soil with calcium carbonate, the effects of the treatment were monitored by sampling both ground and drainage water [20]. The following effects were observed; (1) an instant increase in pH indicating the neutralization of recently formed sulfuric acid and causing the precipitation of some metals. (2) The fine grind (2.5 μm) acts as a barrier blocking the passage of atmospheric oxygen through the macropores hence inactivating the microorganisms, which facilitates the oxidation of the sulfide sediments [22].

The treatment had significant impact on the pH and metal concentration of the soil drainage water but the redox condition was affected only to a smaller extent [22].

6 PRECIKEM II Project

The PRECIKEM II project is an ongoing (1.7.2015 – 30.6.2018) research project at NOVA University of Applied Science's research and development unit, a follow up to PRECIKEM I. The following institutions; Vaasa University of Applied Sciences, Abo Akademi University and YA! participates in the project [23]. The aim of the project is to further develop effective methods to mitigate acid and metal of acid sulfate soils at Risöfladan experimental field. The aim of this project will be achieved by making column-leaching experiments using various chemical treatments in NOVA University of Applied Sciences laboratory using ASS samples taken from the experimental field. Successful treatments will be used as in situ treatment at the experimental field [23]. The European Agricultural Fund funds PRECIKEM II project via the Rural Development Programme for Mainland Finland 2014-2020.

7 Laboratory Procedures

7.1 Soil Sampling

Acid sulfate soil samples were collected at Risöfladan experimental field. To obtain the acidic layer (actual acid sulfate soil), a pit of 6 m in length and 2 m wide was dug and about 50 cm of the top soil was taken off [24]. Polyethylene tubes with each length about 1.5 m were pushed into the soil using an excavator. After the soil samples were collected the polyethylene tubes were sealed to prevent air from accessing the soil [1]. The tubes were later delivered to the laboratory for treatment.

7.2 Column Experiment

Upon delivery, the soil horizon from 70 to 85 cm (15 cm) was obtained by cutting the tube based on how deep each tube was inserted [1]. The desired 15 cm of the actual acid sulfate sample was inserted into a cylindrical rubber membrane which was pressed against the soil by being submerged in water. External pressure about one bar was applied to the experiment to avoid flow between the membrane and the soil sample [1] and a pump was used to maintain a constant flow rate of treatment chemicals through the soil column.

In this experiment, five acid sulfate soil samples were used. During treatment with peat and FC 2.5 Calcite suspension, two-replicate test were run simultaneously on separate soil samples. Experiment R and G from each treatment will be showed and analyzed. Data from the replicate set (experiment S and H) can be found in appendix. The experiment was set up in a refrigerator with a temperature about 10 degrees Celsius.



Fig 2. *Experimental set-up for peat suspension test with propellers. Peat suspension was pumped from the canister through the soil column into the flow through cell where in situ pH, temperature-corrected conductivity and redox potential are measured every 15 minutes. Permeate from each experiment is collected in their respective measuring cylinders where the ex situ pH and temperature- corrected conductivity will be measured. The samples are collected and stored for further analyses.*

7.3 Chemical Treatment and Instrumentation

During the column experiment, the acid sulfate soil samples were treated with FC 2.5 calcite suspension, Enrich C calcium carbonate suspension and peat suspension. The table below shows the experiment name and the treatment used.

Table 2: Experimental name and Treatment chemical used

Experiment Name	Treatment
R	Peat suspension
S	Peat suspension
G	FC 2.5 calcite suspension
H	FC 2.5 calcite suspension
DEF	Enrich C CaCO ₃ suspension

In the experiment, each acid sulfate soil sample was leached with about 10 liters of autoclaved water before and after treatment with either FC 2.5 calcite, Enrich C calcium carbonate and peat suspensions. Autoclaved water (AC water) was used in flushing in order not to introduce any microorganisms into the soil samples because of the microbial study of the soil sample after treatment [25]. The treatment chemical, FC 2.5 Calcite has a median particle diameter of 2.5 μm and was purchased from Nordkalk [1]. The concentration of the FC 2.5 calcite suspension was 8 g/l and had an initial pH of 9.6 and temperature-corrected conductivity of 51 $\mu\text{S}/\text{cm}$.

The peat used for this experiment was obtain from VAPO Fibers Oy in Finland. Fig. 3 shows the particle size distribution of the peat. The concentration of the peat solution was 4 g/l. The pH and temperature-corrected conductivity of the peat suspension after the experiment was 4.0 ± 0.1 and 35 $\mu\text{S}/\text{cm}$. Enrich C CaCO₃ suspension used for experiment was obtained from Nordkalk and the concentration of the CaCO₃ of the final suspension was 8 g/l.

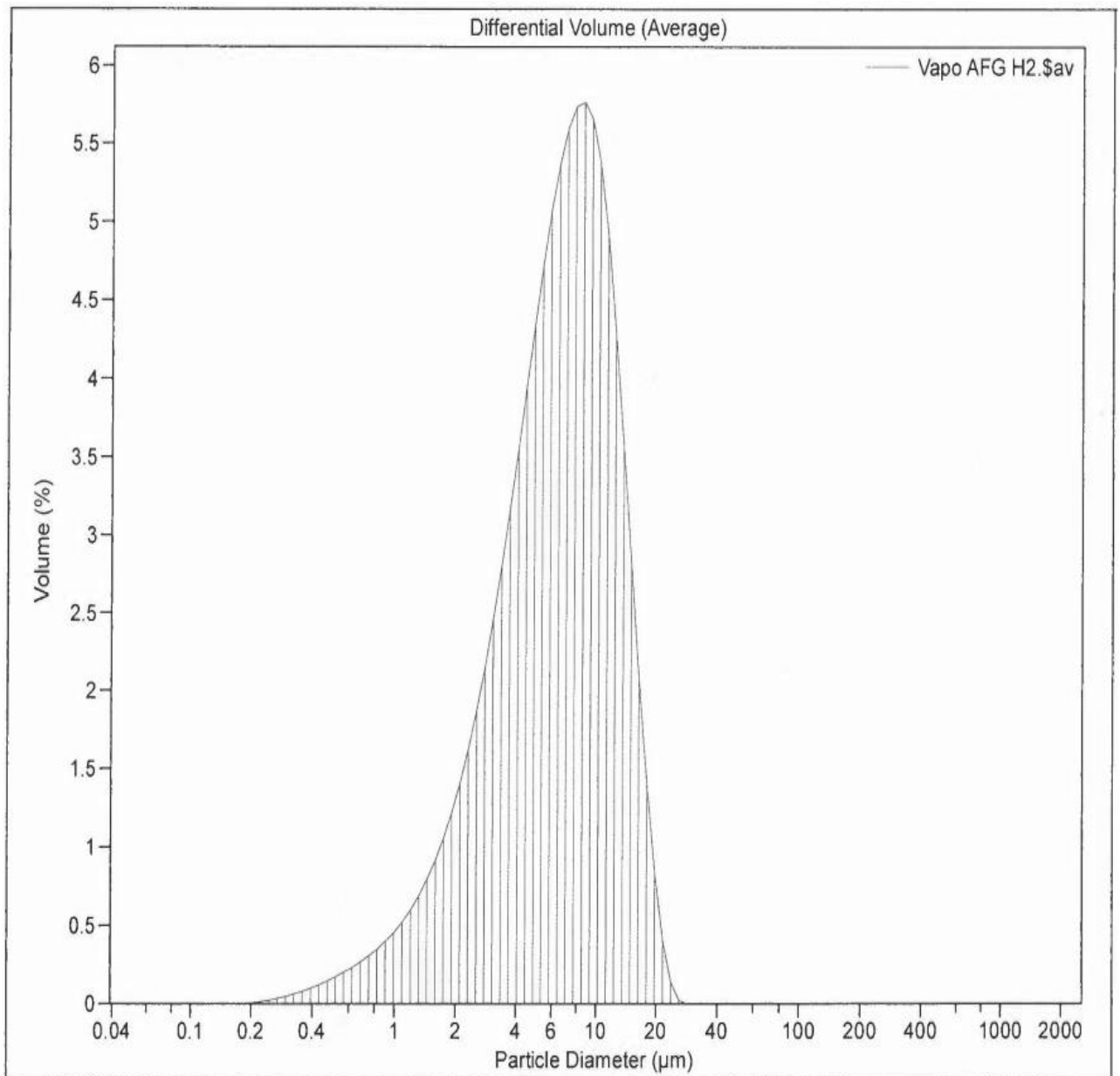


Fig 3. Particle size distribution of peat from VAPO Fibers

According to [1] leaching the soil sample with 10 liters of autoclaved water is equivalent to 1 to 2 years of percolation in the field. With 1 to 2 years of percolation on the field occurring in a much shorter time, this period was not enough for all chemical reactions that would have taken place to increase acidity and metal release. However, the results obtained suggested that it was enough for an amount of acid and metals release which typically occurs in a year.

During the experiment, in situ pH, temperature-corrected conductivity and redox potential (ORP) were measured using the YSI Professional Plus instrument (YSI Inc., Yellow Springs, OH 45387, U.S.A) shown in Fig. 4. Treatment chemicals are pumped from the

canisters shown in Fig. 2 through the soil column. As permeate fill up the flow through cell, the pH, temperature-corrected conductivity and the redox potential were measured and stored every 15 minutes. An online monitoring system, YSI data manager program was installed on a computer with the YSI Professional Plus instrument connected to it. This enable the measured in situ pH, temperature-corrected conductivity and redox potential to be monitored easily. The YSI data manager backs up to the YSI Professional Plus instrument in case of crashes and also draws the pH, temperature-corrected conductivity and redox potential diagrams. Permeate were collected in measuring cylinders in Fig. 2 twice a day. The volume of the amount of permeate collected was measured and both ex situ pH and temperature-corrected conductivity was measured. Ex situ pH was measured using pH electrode and pH meter PHM210. Temperature-corrected conductivity was measured using a radiometer cell with conductivity meter CDM210. All ex situ measurements were done at room temperatures (20 - 23°C) with the temperature of the permeate being about 13- 15°C.



Fig 4. *YSI Professional Plus meter*

8 Results Interpretations

8.1 Treatment with Peat Suspension

During this treatment (Experiment R), the soil column was initially leached with 9452 ml of autoclaved water (AC water). After leaching with water, the soil column was treated with 9064 ml of peat suspension and finally leached again with 8918 ml of autoclaved water. During the first leaching with autoclaved water, an initial flow rate of 99 ml/h. was used and was later reduced to an average of 48 ml/h. after introducing peat using the pump.

8.1.1 Effect on pH

During leaching with autoclaved water, the initial pH 3.95 decreased slightly to a value of 3.86 (Fig. 5). The slight change in pH can be attributed to leaching out of hydrogen ions in the soil column. When autoclaved water was replaced by peat suspension, the pH increased from 3.86 to circa 4.45 within some few hours. Ion exchange can be attributed to the sharp change in pH. The pH decreased and stabilized at a value circa 3.83 as shown in Fig. 5. During the treatment, some peat suspension did not adhere to the macropores of the soil column and as a result got into the flow-through cell and came in contact with the pH electrode thus causing a dip in pH.

After peat suspension was replaced by autoclaved water, during flushing we had a slight increase in pH from 3.97 to 4.09.

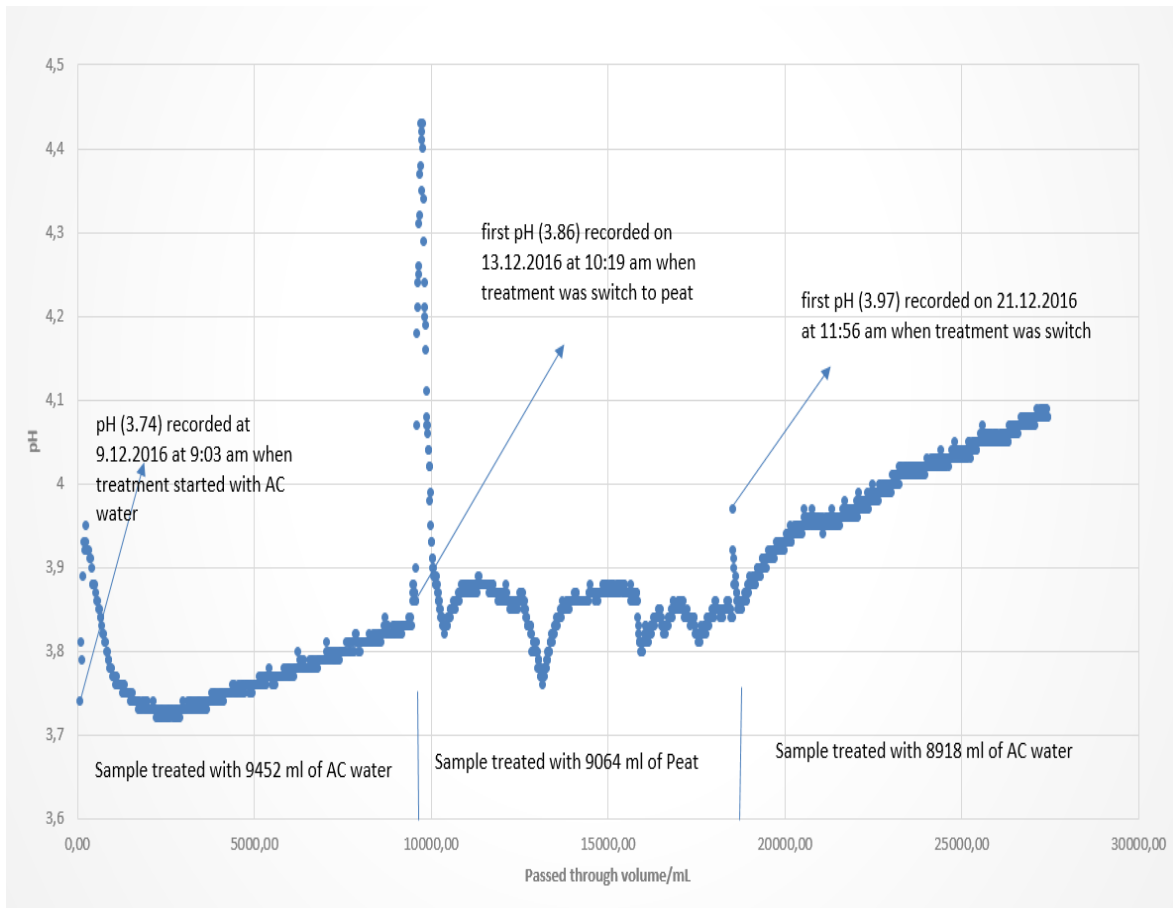


Fig. 5 pH as a function of passed-through volume in experiment R

8.1.2 Effect on Temperature-Corrected Conductivity

During leaching of the soil column with autoclaved water, the temperature-corrected conductivity (SPC) decreased sharply from 874 $\mu\text{S}/\text{cm}$ to 159.5 $\mu\text{S}/\text{cm}$ as shown in Fig. 6. This decrease was mainly due to the leaching out of sulfate ions from the oxidation of iron sulfides currently in the soil, chloride ions, nitrate ions from fertilizers and calcium and magnesium ions from the dissolution of traces of calcareous minerals [1].

When autoclaved water was replaced by peat suspension, the temperature-corrected conductivity increased slightly from 166.6 $\mu\text{S}/\text{cm}$ to 262.2 $\mu\text{S}/\text{cm}$. The temperature-corrected conductivity further decreased to 154.4 $\mu\text{S}/\text{cm}$. The slight increase in temperature-corrected conductivity could be mainly due to ion exchange which took place during the switch [18].

Before the switch to autoclaved water occurred, the pump was stopped for sometime and hence new channels could have been opened up in the soil column creating a drop in temperature-corrected conductivity from 144 $\mu\text{S}/\text{cm}$ to 126 $\mu\text{S}/\text{cm}$ when treatment began.

During the final flushing with autoclaved water, the temperature-corrected conductivity decreased further to 83.9 $\mu\text{S}/\text{cm}$ leaching out further ions.

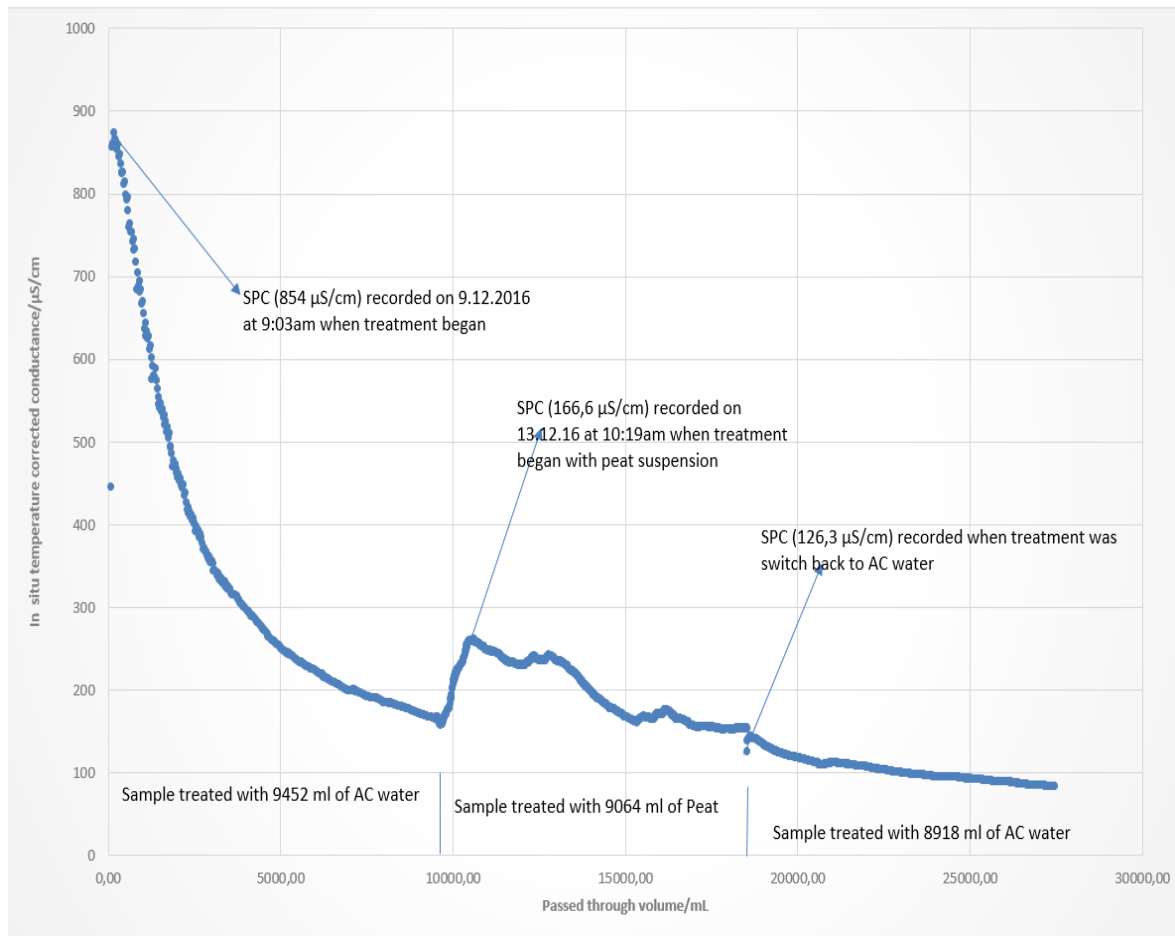


Fig. 6 *In situ* temperature-corrected conductivity as a function of passed-through volume in experiment R

8.1.3 Effect on Redox Potential

During flushing with autoclaved water, the redox potential increased from 477.8 mV and attained a maximum value of 509.6 mV during the earlier part of treatment. The increase was the introduction of oxygenated water which mops up electrons. Later the redox potential (ORP) decreased slowly to a value of 476.2 mV when flushing was brought to an end as seen in Fig. 7. When peat was introduced, there were some fluctuations in redox potential as seen in Fig. 7. Compared with the parallel experiment which can be seen in the appendix 3, the redox potential decreases slightly with time. The main reason for the fluctuation during 5,792 ml of the treatment was that the peat suspension which could not adhere to the macropores of the soil hence getting into the flow through cell. As a result getting in contact with the redox potential electrode in the flow through cell. Whenever

peat gets into the flow through cell a sharp decrease in redox potential is obtained as seen in Fig.7.

After treating the soil column with about 5,800 ml of peat suspension, there was no peat suspension flowing into the flow through cell and there was a sharp decrease in redox from 422.3 mV to 273 mV when the treatment ended. This sharp decrease can also be seen in the parallel experiment in the appendix 1 Fig. 3. The decrease in redox potential was mainly caused by the oxidation of peat in the soil consuming oxygen in the process. When treatment with peat was brought to an end, the tubes and flow through cells were rinsed. While rinsing took place pumping was shut down.

When flushing with water began, there was a sharp increase in redox potential from 347 mV to 427 mV during the first 3000 ml of treatment with autoclaved water. The can be attributed to the introduction of oxygenated water. Later the redox potential was very stable to the end of the experiment stabilizing around a value of circa 435 mV.

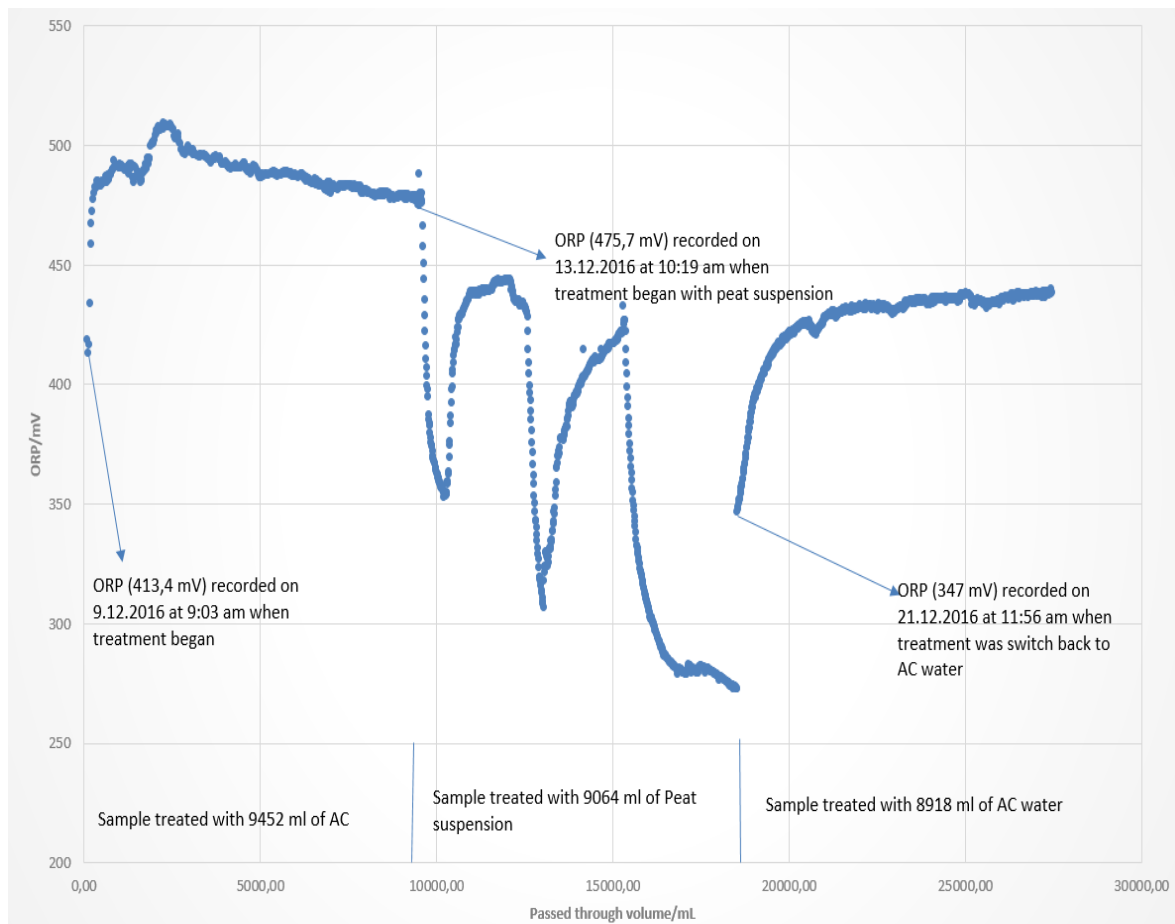


Fig. 7 Redox potential as a function of passed-through volume in experiment R

8.2 Treatment with FC 2.5 CaCO₃ Suspension

Results from experiment G will be analyzed and the other (experiment R) will be in appendix. 17921 ml of CaCO₃ was used as neutralization agent after the soil column was leached with 9972 ml of autoclaved water and further leached with 11588 ml of autoclaved water after treatment. An average flow rate of 105 ml/h. was used. There was slight differences in rate of suspension through the soil columns due to the different pumps used.

8.2.1 Effect on pH

During leaching with autoclaved water, the pH of the permeate was very constant lying between 3.8 and 4.08. According to [1] this indicates that jarosite dominates the soil column. When FC 2.5 calcite suspension was introduced, the pH increased slowly from 3.8 to 5.03 but compared to the parallel experiment in appendix 6 there was a sharp rise from 4.07 to 6.76. The slow increase, seen in Fig. 8, was due to clogged channels and thus a poor permeability of the soil [1]. The pH later rose from 5.03 to 7.63 when new channels opened up in the soil column. The increase in pH can be attributed to decrease in hydrogen ions when CaCO₃ was introduced. In similar experiment done by PRECIKEM I, an increase in nitrate concentrations and chloride anions was noticed when CaCO₃ was introduced.

When FC 2.5 calcite suspension was replaced with autoclaved water, the pH was largely constant lying between 6 to 6.5. From Fig. 8 it can be seen that we had some pH measurements below 4.5. Those were artefacts because the flow through cell was not fully filled with permeate.

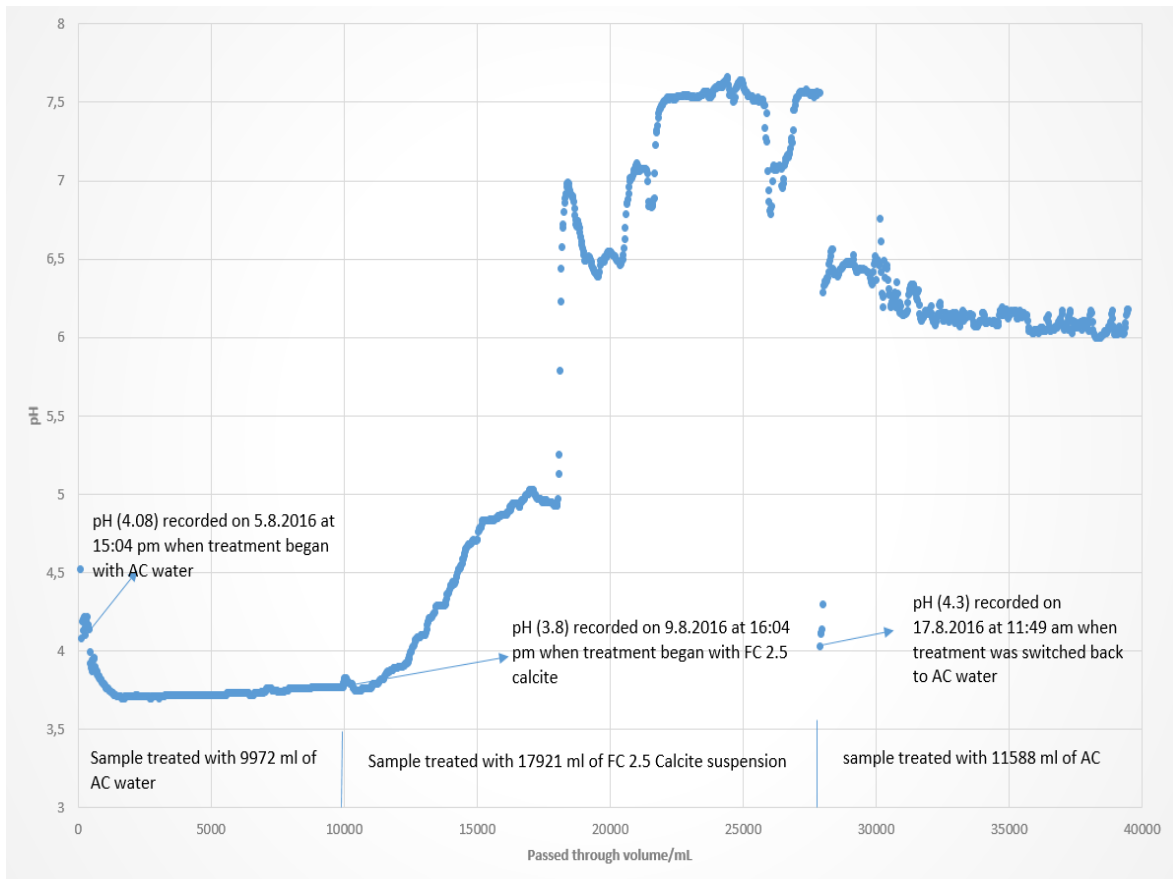
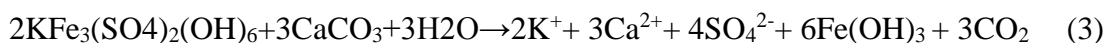


Fig.8 pH as a function of passed-through volume in experiment G

8.2.2 Effect on Temperature-Corrected Conductivity

During flushing with autoclaved water, temperature-corrected conductivity decreased sharply from 1081 $\mu\text{S}/\text{cm}$ when leaching began to 171 $\mu\text{S}/\text{cm}$ when leaching ended. In an earlier study done by PRECIKEM I similar behavior was attributed was to the flushing out of sulfate, chloride, nitrate anions and base cations [1].

When CaCO_3 was introduced, there was an increase in temperature-corrected conductivity from 171 $\mu\text{S}/\text{cm}$ to 525 $\mu\text{S}/\text{cm}$ as seen in Fig. 9. According to [1] the increase in temperature-corrected conductivity was accompanied by an increase in sulfate and potassium ion concentrations. This may be due to dissolution of jarosite (Eq. 3)[25].



When the soil column was flushed with autoclaved water after treatment with FC 2.5 calcite suspension, temperature-corrected conductivity further decreased from 537 $\mu\text{S}/\text{cm}$

to 90.4 $\mu\text{S}/\text{cm}$. Similar behavior in earlier studies attributes the decrease to the leaching out sulfate, chloride and nitrate anions [1].

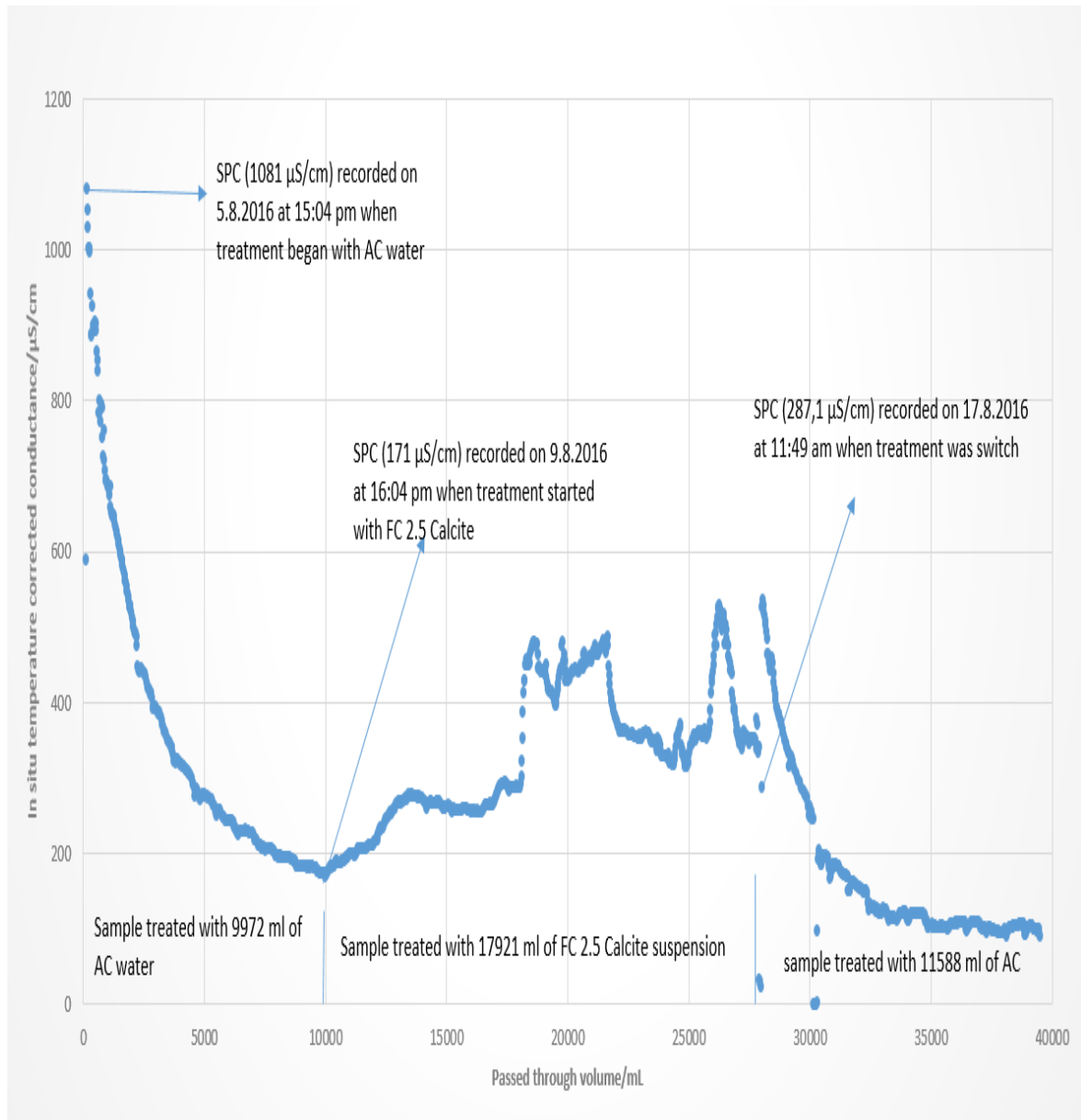


Fig. 9 *In situ* temperature-corrected conductivity as a function of passed-through volume in experiment G

8.2.3 Effect on Redox Potential

During flushing with autoclaved water, the redox potential was largely constant lying between 482.5 mV and 506.9 mV. This indicates, that the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio of the soil was not altered. When calcite suspension was introduced, the redox potential decreased sharply from 474.3 mV to 269 mV after the soil column was treated with 11640 ml of calcite

suspension. The cause for the decrease in redox potential was the removal of an important electron acceptor such as Fe^{3+} , which precipitate due to the sharp increase in pH [17]. The redox potential increased from 269 mV to 310 mV, indicating the attainment of a steady state. The redox potential was fairly constant at a value circa 327 mV until the treatment was brought to an end.

When flushing with autoclaved water began, the redox potential rose sharply from 240.9 mV and stabilized at approximately 434 mV. The increase in redox potential was as result of the introduction of oxygenated water. Before the switch to autoclaved water the flow through cells and tubes were rinsed. While rinsing took place the pump was shut, this might influence the usage of oxygen by microorganisms in the soil hence creating a drop in redox when flushing with autoclaved water began as shown in Fig. 10.

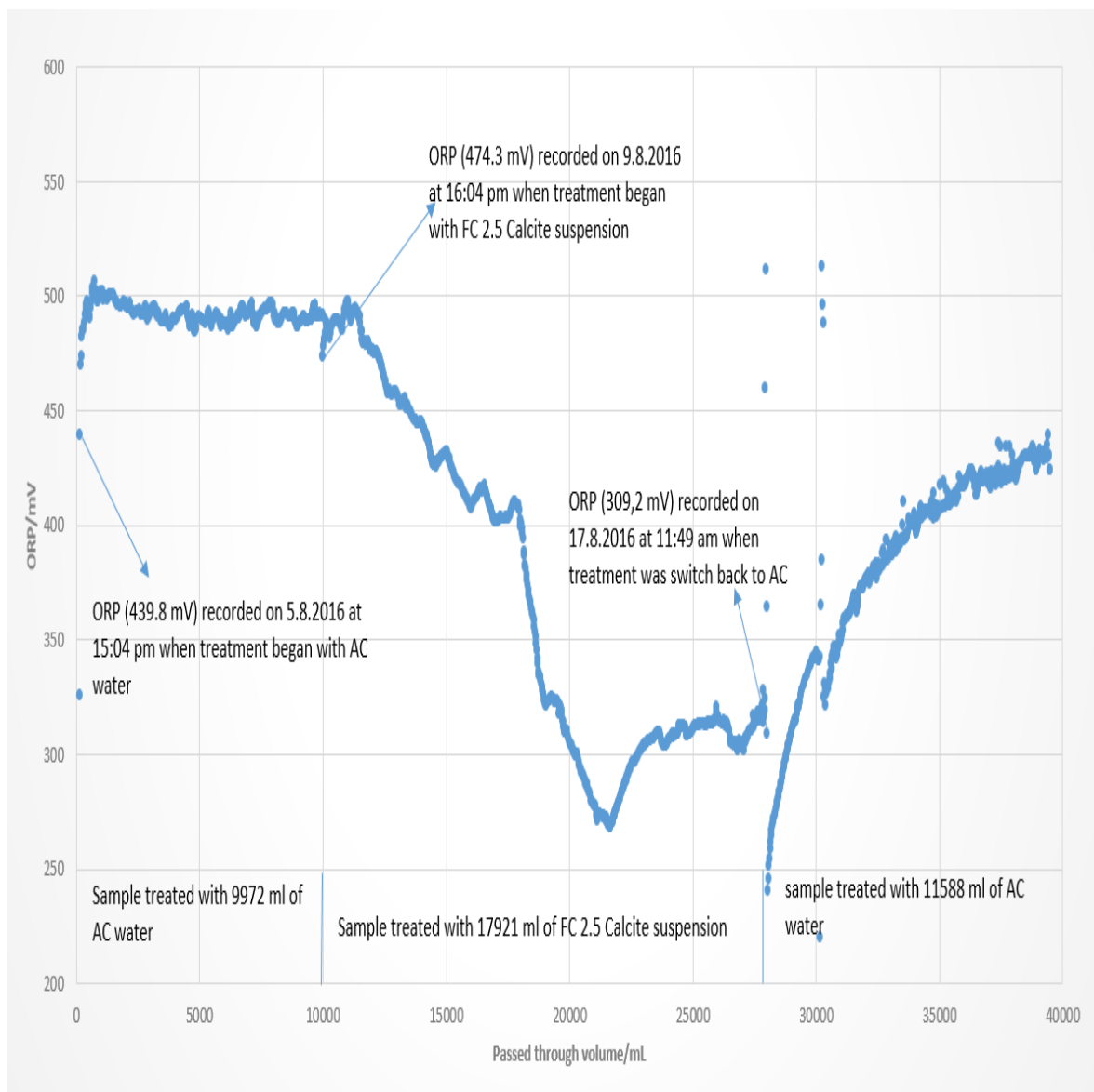


Fig. 10 Redox potential as a function of passed-through volume in experiment G

8.3 Treatment with Enrich C CaCO₃ Suspension

During treatment with Enrich C calcium carbonate suspension, the soil column was leached with 10691 ml and 12787 ml of autoclaved water before and after treatment. The soil column was treated with 7550 ml of Enrich C CaCO₃ suspension. An average flow rate of 115 ml/h was used during this experiment.

8.3.1 Effect on pH

When flushing with water began, a pH of 4.22 was recorded but as flushing continued, there was a slight change in pH, decreasing and stabilizing around a value circa 3.86 until flushing with water was brought to an end as seen in Fig. 11. When Enrich C CaCO₃ suspension was introduced, the pH of the permeate increased sharply from 3.86 to 6.32 as shown in Fig. 11. A slow rise in pH was obtained during the course of treatment with the pH stabilizing around a value circa 7.34.

Before switching to autoclaved water, the tubes and flow-through cell were rinsed. During rinsing, the pump was stopped for almost two hours. This may lead to the opening up of new channels in the soil releasing sulfuric acid. This accounts for the drop in pH (7.39-6.88) in Fig. 11 when flushing with autoclaved water began. During flushing, the pH increase slowly from 6.88 to 7.7 after pumping about 5 liters of autowater water. The reason for the rise in pH can be attributed to the washing away of CaCO₃ on the baseplate and in the soil column. The pH of the permeate decreased gradually and stabilized around a value circa 6.8.

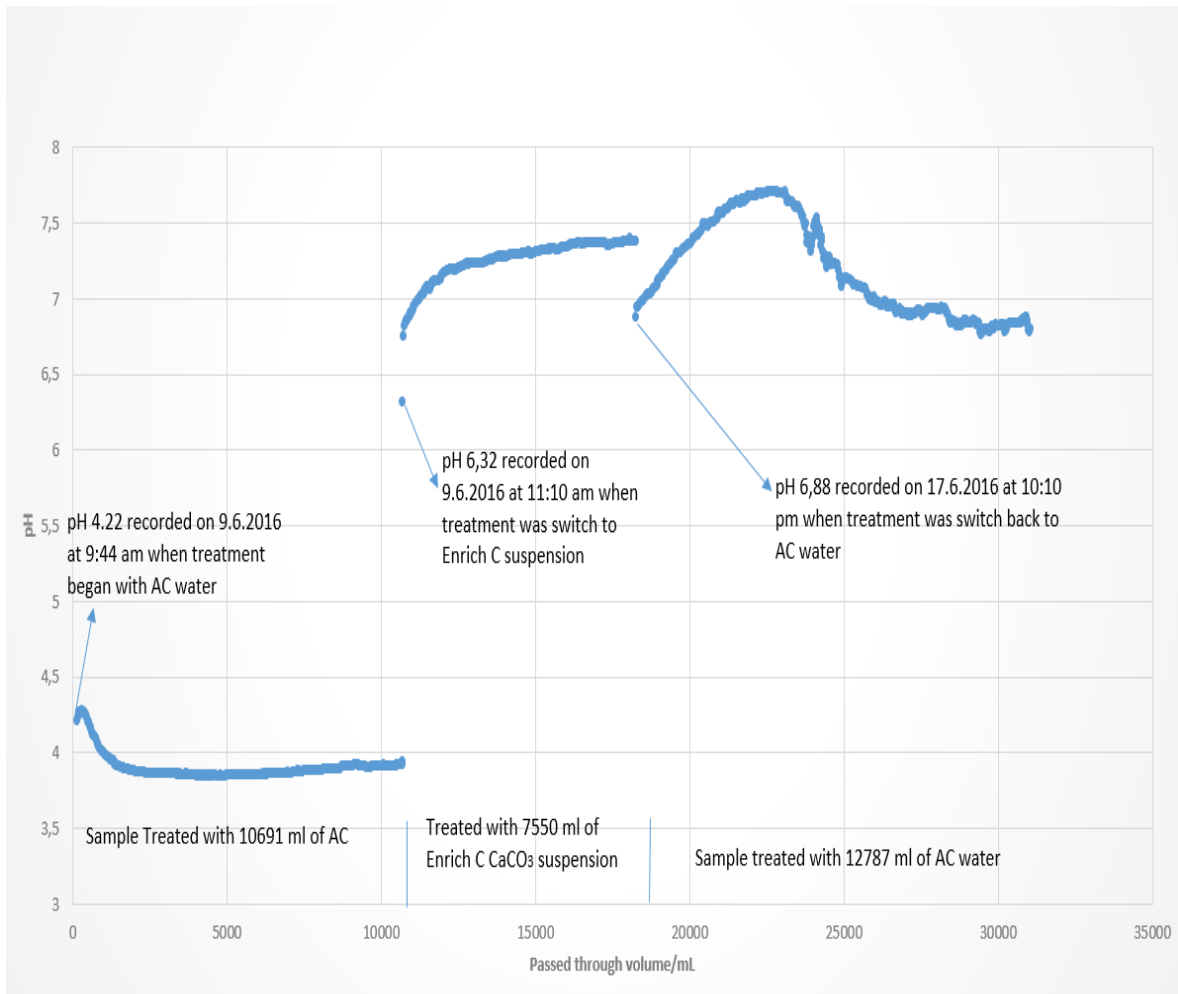


Fig. 11 In situ *pH* as a function of flow through volume in experiment DEF

8.3.2 Effect on Temperature-Corrected Conductivity

When flushing with autoclaved water began, the temperature-corrected conductivity decreased sharply from 840 $\mu\text{S}/\text{cm}$ to 134.2 $\mu\text{S}/\text{cm}$ as shown in Fig. 12. The reason the sharp decrease is mainly due to the flushing out of the sulfate, nitrate anions, chloride and base cations based on similar behavior in an earlier study [1].

When autoclaved water was replaced by Enrich C CaCO_3 suspension, the temperature-corrected conductivity increased sharply from 134 $\mu\text{S}/\text{cm}$ to 1040 $\mu\text{S}/\text{cm}$. This increase can be attributed to an anion exchange as an increase in *pH* was also seen in Fig. 11 [21]. During treatment, the temperature-corrected conductivity decreased from 1040 $\mu\text{S}/\text{cm}$ to 476 $\mu\text{S}/\text{cm}$. Thus indicating further leaching of metals in the soil column.

Before the switch to autoclaved water, the tubes and flow-through cell were rinsed. During rinsing, the pump was shut down, with CaCO_3 in the macropores of the soil column and on

the base plate. This is probable the reason for the increase in temperature-corrected conductivity from 476 $\mu\text{S}/\text{cm}$ to 795 $\mu\text{S}/\text{cm}$ when flushing with water began. This indicates leaching of CaCO_3 from the soil column during the early stage of flushing. Metal were also leached out as shown in Fig. 12.

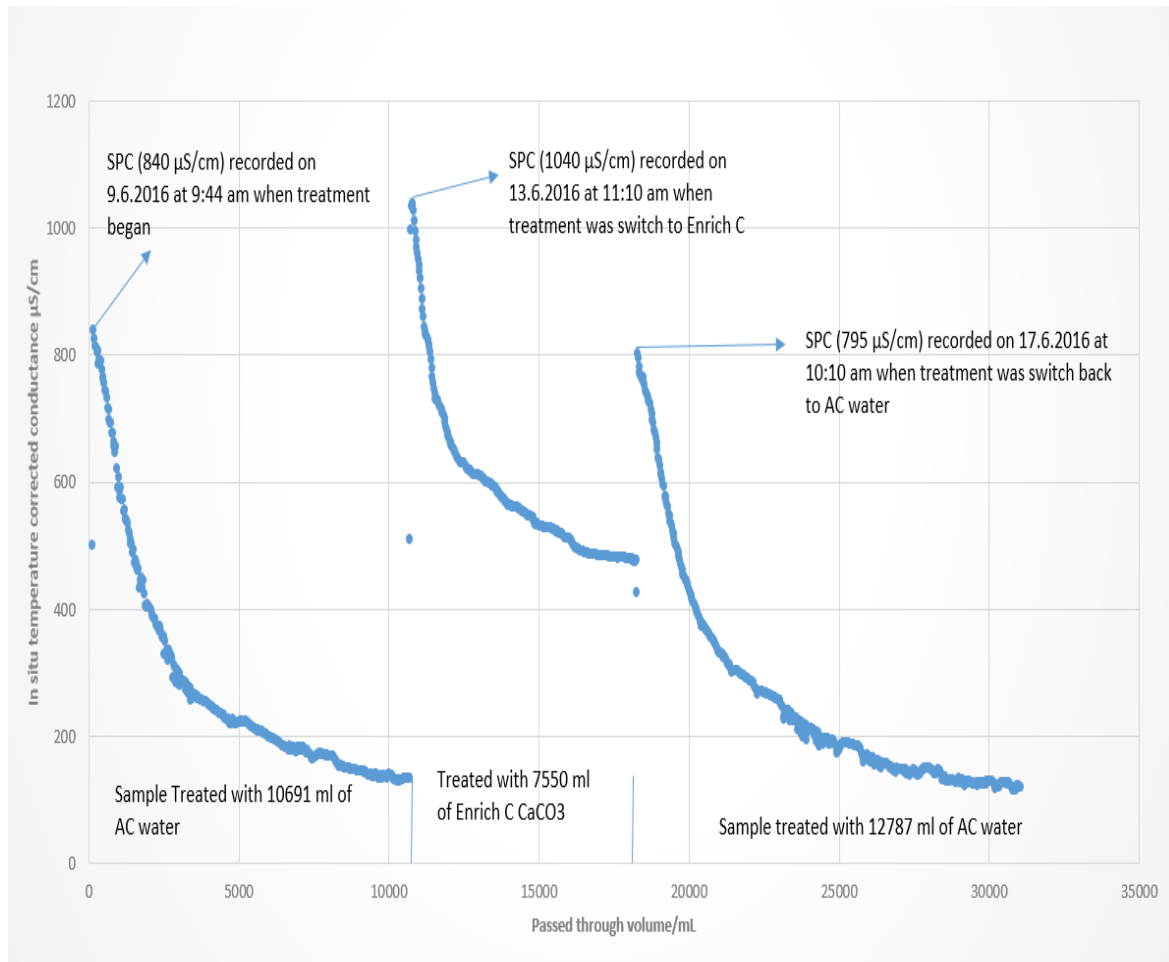


Fig. 12 Temperature-corrected conductivity as a function of passed through volume in experiment DEF.

8.3.3 Effect on Redox Potential

During flushing with autoclave water, the redox potential was largely constant between 480 mV and 490 mV until flushing was brought to an end. This shows that $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio was not altered during flushing with autoclaved water. When autoclaved water was replaced by Enrich C CaCO_3 suspension, the redox potential decreased sharply from 497 mV to 274 mV. This is due the removal of Fe^{3+} which precipitates due to the sharp increase in pH [18].

When Enrich C CaCO_3 suspension was replaced by autoclaved water, an increase in redox potential from 274 mV to 386 mV was obtained as seen in Fig. 13. This increase in redox potential was due to the introduction of oxygenated water. The redox potential slowly decreases to 318 mV when flushing was brought to an end as seen in Fig. 13.

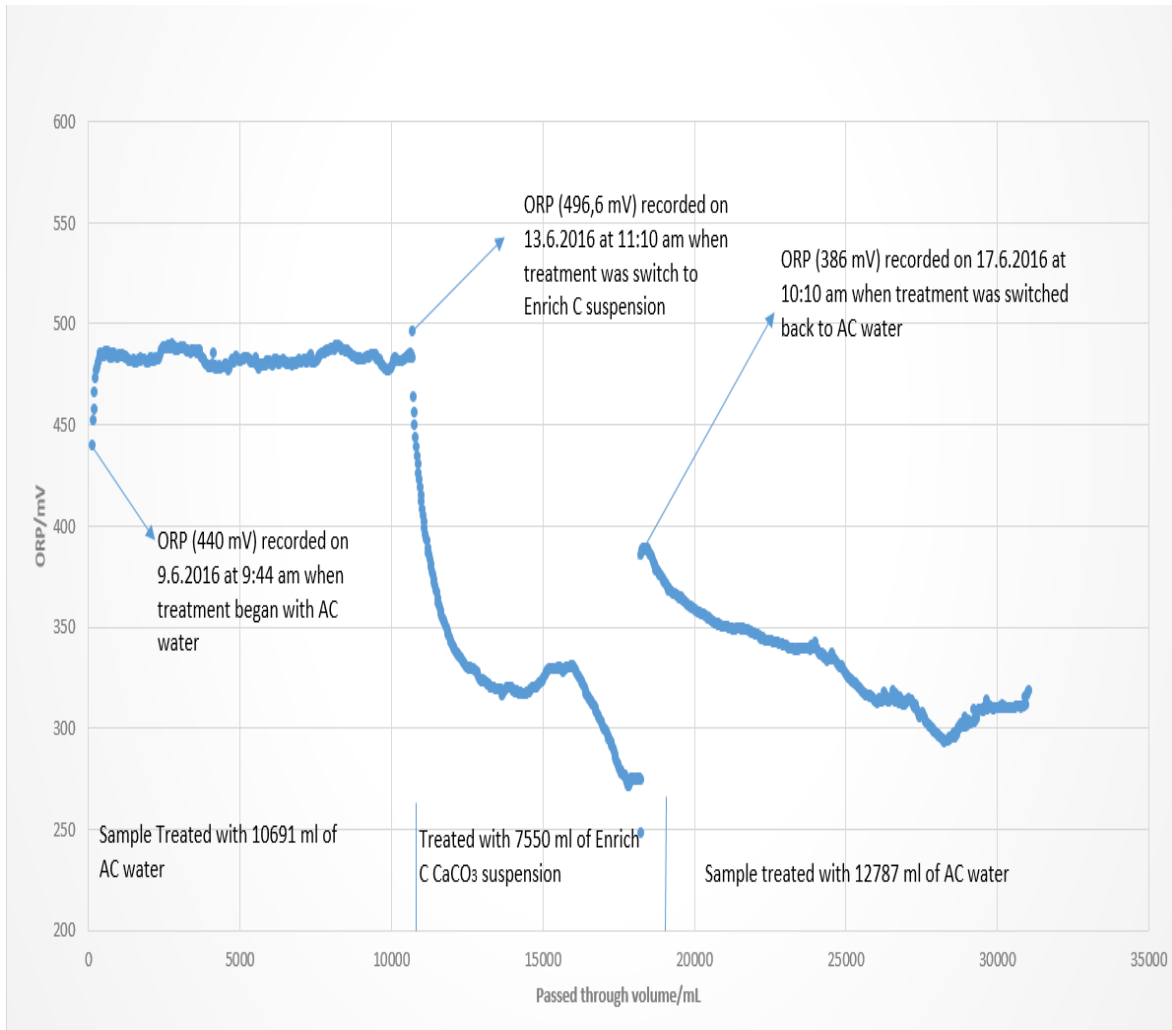


Fig. 13 Redox potential as a function of passed through volume in experiment DEF

9 Conclusions

This thesis was aimed at mitigating the acid metal- containing drainage waters from acid sulfate soils using peat suspension, CaCO₃ suspension (Enrich C and FC 2.5 quality from Nordkalk). Initial leaching of the acid sulfate samples with water resulted in permeate with pH values of circa 4. According to [1] this indicates that jarosite dominated the existing solution chemistry. Both Enrich C CaCO₃ and FC 2.5 calcite suspensions treatments raised the pH of the permeate to a value of circa 6, mitigating acid discharge from the acid sulfate soil sample. After treating the acid sulfate soil samples with Enrich C CaCO₃ and FC 2.5 calcite suspensions, the pH of the permeate during the final flushing with autoclaved water was higher than during initial flushing. The final flushing had permeate with pH value of circa 6 while the initial flushing was at a value of circa 4. In using peat as treatment, there was no much difference between the initial pH of the permeate before and after treatment hence having less effect on the pH.

However, all treatments (both CaCO₃ and peat suspensions) had strong effects on the redox potential of the acid sulfate soil samples. During treatment of the acid sulfate samples with both CaCO₃, the redox potential decreased to a value of circa 275 mV. Even after treatment, when the final flushing with autoclaved water began the redox potential was considerably lower at a value of circa 330 mV than during the initial flushing with autoclaved water which was at value of circa 500 mV. This indicates mitigated levels of Fe³⁺ in the soil column during treatments (CaCO₃ and peat suspensions) and final flushing with autoclaved water.

The subsequent increase in pH and decrease in metal concentrations will potentially inactivate microorganisms which facilitates acidification of the acid sulfate soil. As a result, mitigating the impact on watercourses and organisms.

The results obtained indicates that the treatments were successful and will be deployed as mitigating strategy at the experimental field in Risöfladan, Vasa. Further research is necessary to analyze the metal concentrations of the permeate during treatment with peat. Also subsequent treatments will involve treating each acid sulfate samples with peat followed by CaCO₃ suspension and monitor the effects.

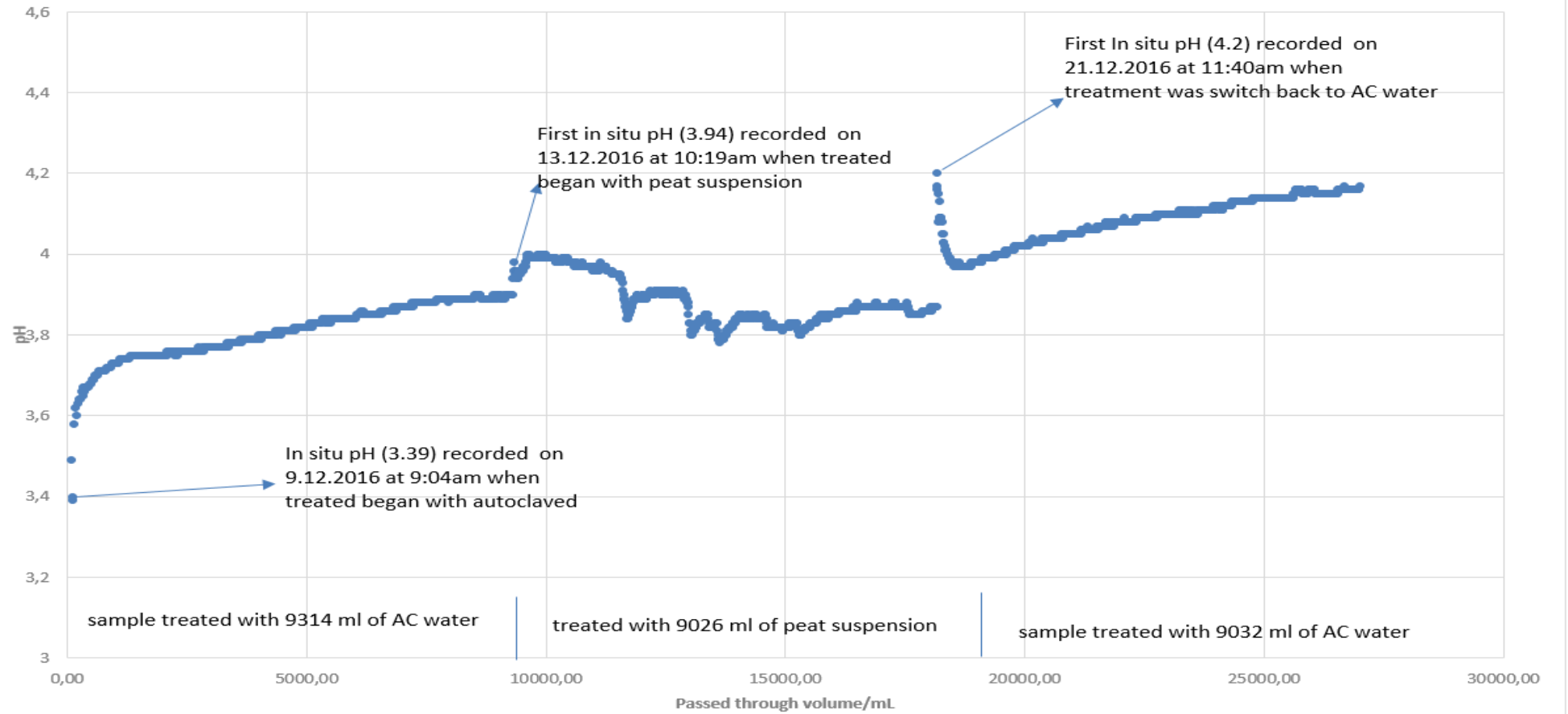
10 References

- [1] Xiaofen Wu, Pekka Stén, Sten Engblom, Pawel Nowak, Peter Österholm, Mark Dopson, *Impact of Mitigation Strategies on Acid Sulfate Soil Chemistry and Microbial Community*, *Science of the Total Environment*, 526 (2015) 215–221
- [2] Hanrahan, G. (2012). *Key Concept in Environmental Chemistry*. Waltham, MA: Elsevier.
- [3] Ronni, M. (2012). *An investigation about neutralisation rates of acid sulfate soil extracted as sediment from flood mitigation channels on the shoalhaven flood mitigation system*. Sydney : University of Wollongong
- [4] Van Breeme, N., & Peter, B. (2002). *Soil formation*. Kluwer Academic Publisher.
- [5] Young, A., Young, R. (2001). *Soils in the Australian Landscape*. South Melbourne, Vic: Oxford University Press.
- [6] *Queensland government*. Retrieved from Queensland government web site, [Online] Available: www.qld.gov.au/environment/land/soil/acid-sulfate/identified/ [Assessed 10 2 2017]
- [7] *Government of western Australia*. Retrieved from Department of of environment and conservation, [Online]. Available: www2.landgate.wa.gov.au/c/document_library/get_file?uuid=5dc8c72e-68da-48b6-8fd4-4583af6b14de&groupId=10136 [Assessed 2 11 2016].
- [8] Adriesse, W., van Mensvoort, M. (2006). Acid sulfate soil: distribution and extent Volume 1. *Encyclopedia of soil science*, 14-19.
- [9] Weppling, Kjell, Innanen, Marja, Jokela, Sinikka, (1999). *Life Lestijoki - managing acid sulphate soils*. Helsinki: Keski-Pohjanmaan liitto, WWF Finland, Länsi-Suomen ympäristökeskus.
- [10] Nicholas, J. W. (2004). *Sulfide oxidation in some acid sulfate soil materials*. Lismore, NSW: Southern Cross University.
- [11] *Australia Government*. Retrieved from Australia Online Coastal information, [Online] Available: www.ozcoasts.gov.au/indicators/econ_cons_acid_sulfate_soils.jsp [Assessed 4 11 2016].
- [12] Fältmarsch, R. M., Åström, M. E., Vuori, K.-M. (2008). *Environmental risks of metals mobilised from acid sulphate soils in Finland: A literature review*. *Boreal Environmental Research* 13, 444- 456.
- [13] *Department of Primary Industries*. Retrieved from NSW Government, [Online] Available: www.dpi.nsw.gov.au/land-and-water/soils/ass [Assessed 8 11 2016].
- [14] Madej Ann, M. *USGS*. Retrieved from Sound Waves, [Online] Available: soundwaves.usgs.gov/2004/11/research2.html [Assessed 22 2 2017].

- [15] *Envirolab Group*. Retrieved from Envirolab, [Online] Available: envirolab.com.au/sydney/news-68/the-impact-of-acid-sulphate-soil-sediments-and-rock.htm [Assessed 9 11 2016].
- [16] *Understanding cement*. Retrieved from Understanding cement webpage, [Online] Available: www.understanding-cement.com/sulfate.html# [Assessed 9 11 2016].
- [17] Puustinen, M., Palko, J. (1991). Suomen Peltojen Kuivatustilatutkimus-Tutkimussuunnitelma. *Vesi ja ympäristöhallinnon julkaisuja* 78 , 81.
- [18] Engblom, S. Column experiment. (B. Klu, Interviewer) 17 January 2017.
- [19] Åström, M., Österholm, P., Bärlund, I., Sirkka, T., (2007). *Hydrochemical effects of surface liming, controlled drainage and lime filter drainage on boreal acid sulfate soils*. *Water, Air and soil pollution*, 107- 116.
- [20] Engblom, S., Stén, P., Österholm, P., Rosendahl, R., Lall, K.-E., *Subsurface chemigation of acid sulfate soils – a new approach to mitigate acid and metal leaching*. An oral presentation by Engblom at the 20th World Congress of Soil Science (WCSS), Jeju, South Korea, June 8–13 2014.
- [21] Österholm, P., Nystrand, M., Engblom, S., Sten, P. Nowak, P., *Subsurface chemigation of acid sulfate soils – effects on water quality*. A poster presented at the 20th World Congress of Soil Science (WCSS), Jeju South Korea, June 8–13 2014.
- [22] Engblom, S., Sten, P., Österholm, P., Rosendahl, R., Grannas, A. (2015). *Precision chemical treatment of acid sulfate soils for the protection of waters in environmentally sustainable agriculture*. Vaasa.
- [23] Stén, P. *Vaasan Ammattikorkeakoulu*. Retrieved from, [Online] Available: www.puv.fi/en/com/projects/precikem_ii/ [Assessed 12 12 2016].
- [24] Stén, P. Risöfladan soil samples. (K. Bernard, Interviewer) 30 December 2016.
- [25] Stén, P. Column experiments. (K. Bernard, Interviewer) 19 January 2017.
- [26] Evangelou, V. P. (1995). *Pyrite oxidation and its control*. Florida: CRC Press.

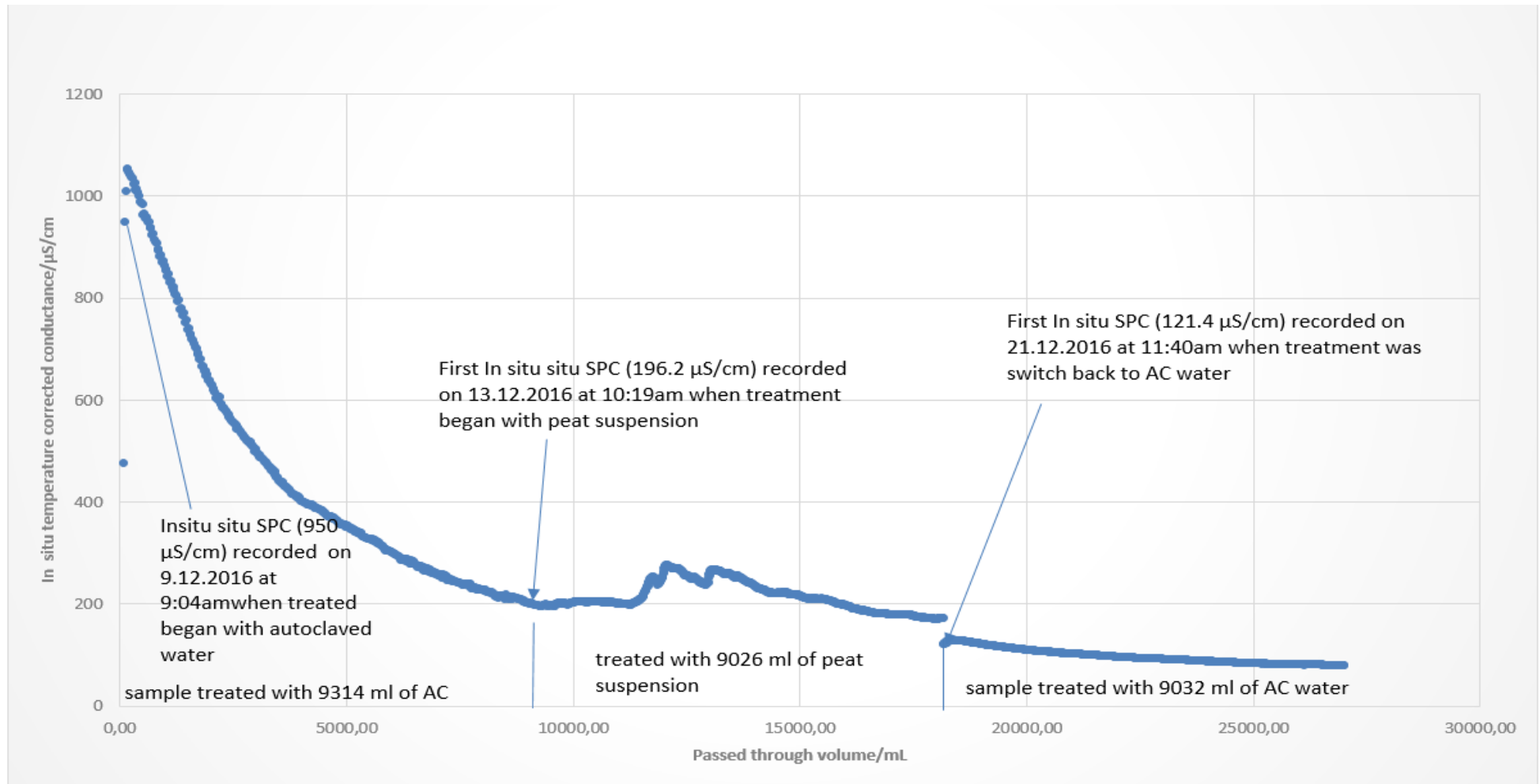
Appendix 1

(1)



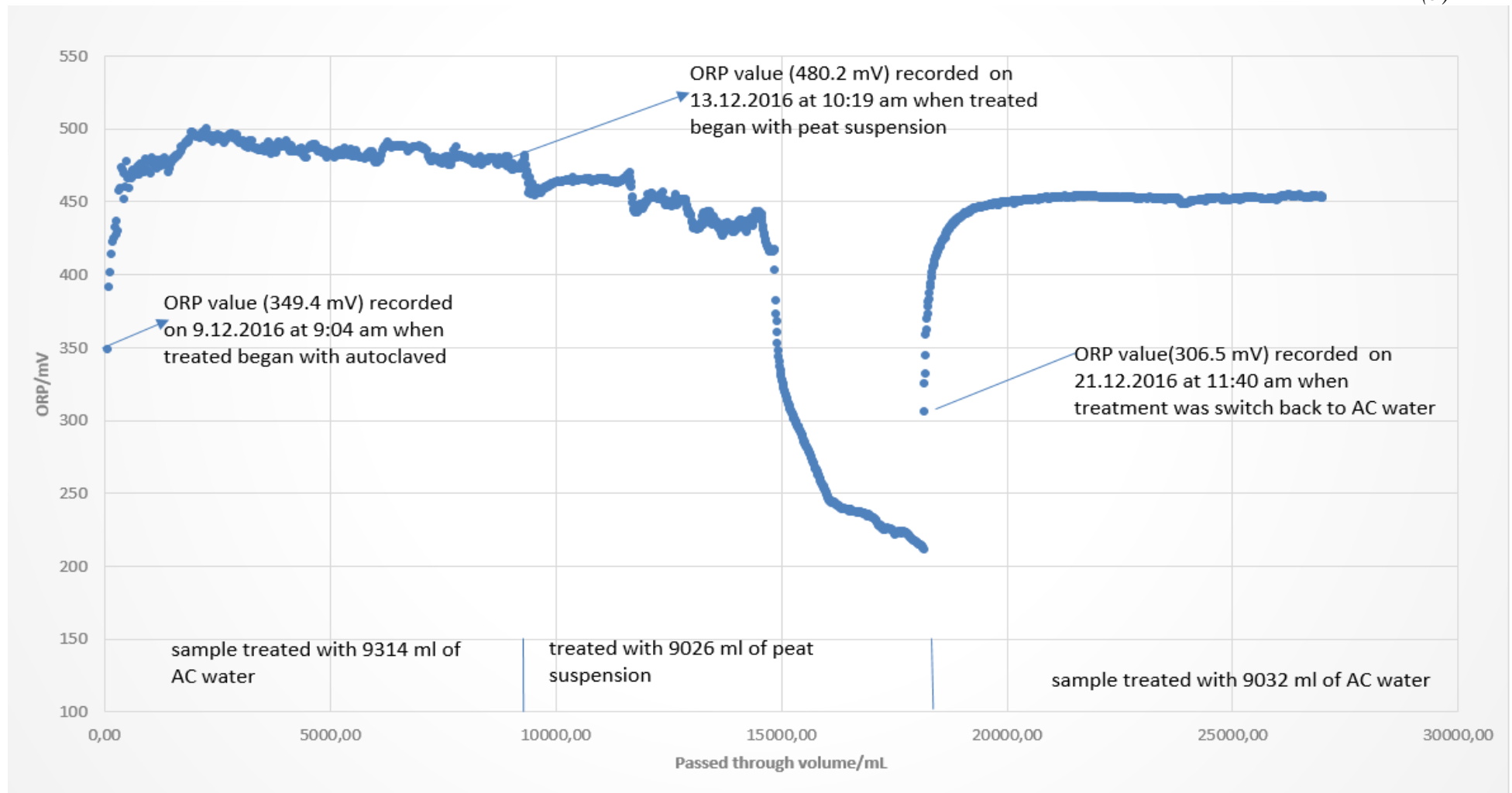
pH as a function of passed-through volume in experiment S

(2)



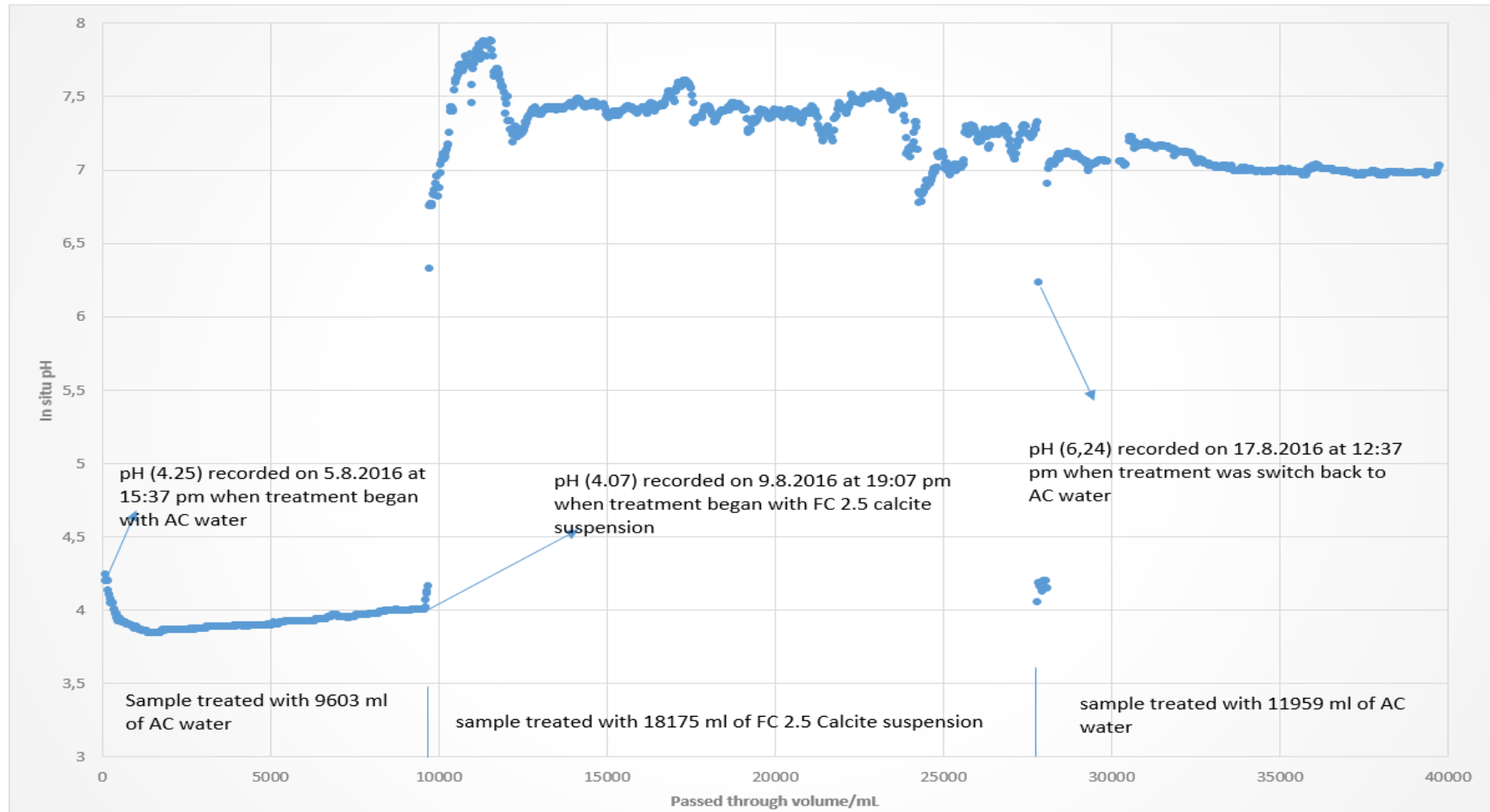
In situ temperature-corrected conductivity as a function of passed-through volume in experiment S

(3)



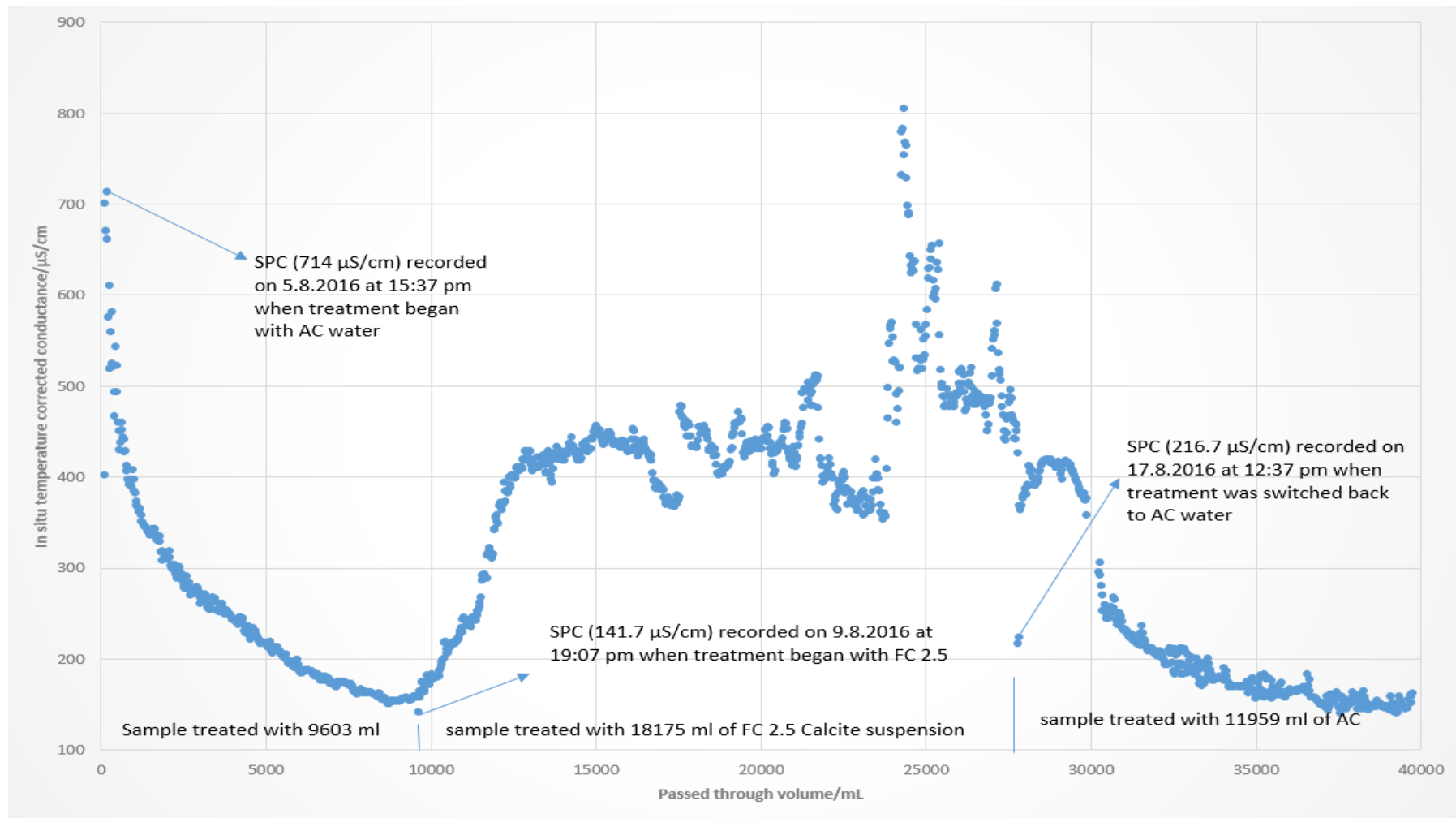
Redox potential as a function of the passed-through volume in experiment S

(4)



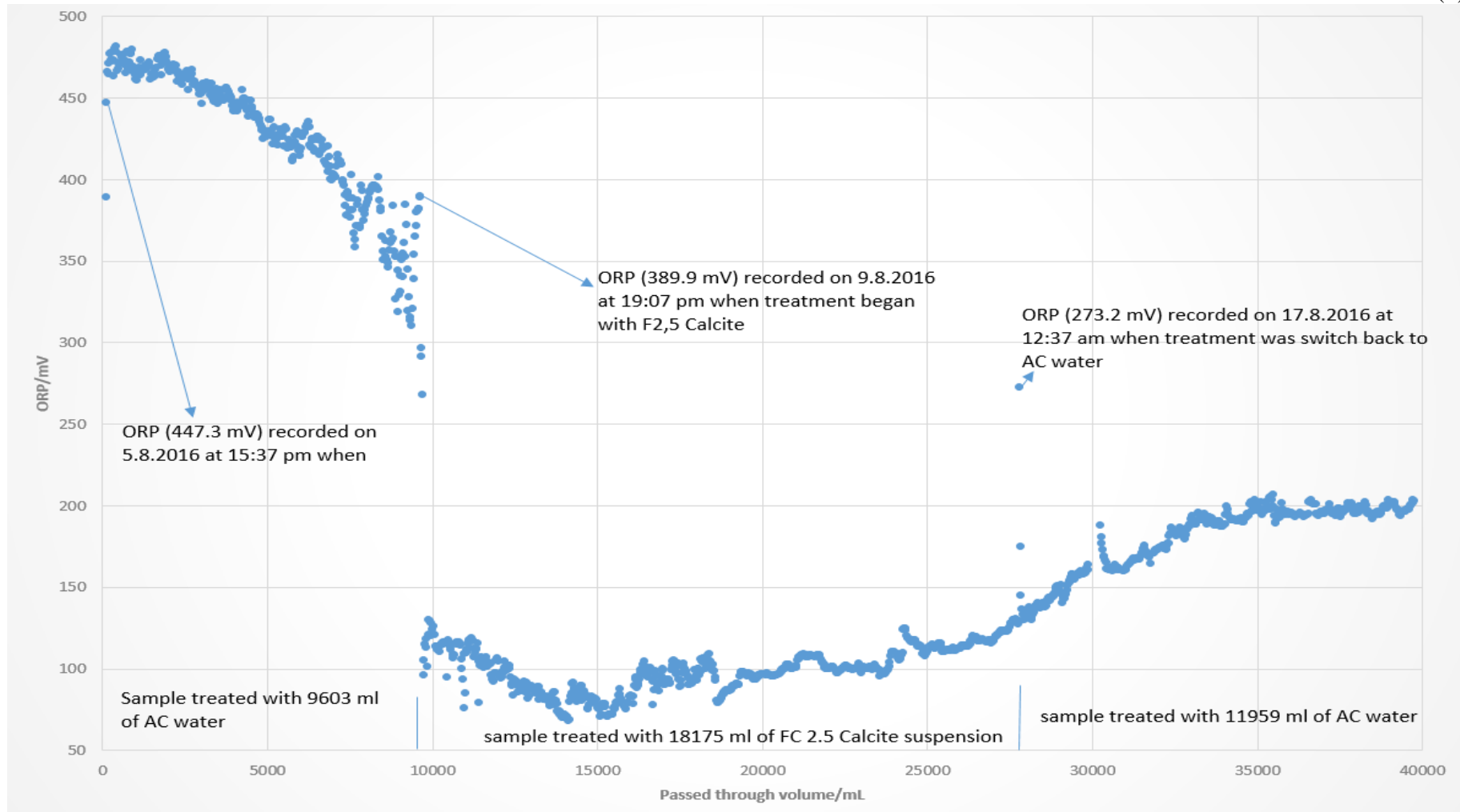
In situ pH as a function of passed-through volume in experiment H

(5)



In situ temperature-corrected conductivity as a function of passed-through volume in experiment H

(6)



Redox potential as a function of passed-through volume in experiment H

