The Capital Region of Denmark

March 2017

Pilot test of Electrokinetically Delivered Thermally Activated Persulfate, EK-TAP™ Final Report

Ballerup Denmark

PROJECT

Pilot test of Electrokinetically Delivered Thermally Activated Persulfate, EK-TAP^{TM}. Final Report

The Capital Region of Denmark

Project No. 215445
Document No. 1223009824
Version 2
Prepared by HENK, D. Reynolds, & D. Gent
Verified by HES, E. Cox
Approved by CER

NIRAS A/S
Sortemosevej 19
3450 Allerød, Denmark

Reg. No. 37295728 Denmark
FRI, FIDIC
www.niras.com

T: +45 4810 4200
F: +45 4810 4300
E: niras@niras.dk

D: +45 4810 4323
M: +45 2373 9691
E: cer@niras.dk

Appendices

1. **Site plan**
    - **1 A.** Well placement – April 2015
    - **1 B.** Well placement – September 2015
    - **1 C.** Well placement – October 2015
    - **1 D.** Well placement – November 2015
    - **1 E.** Well placement – February 2016

2. **Geological cross sections**

3. **P&ID diagram**

4. **Operational data**
    - **4 A.** Buffer consumption
    - **4 B.** pH graph from PLC

5. **Temperature data**

6. **Water sample results**

7. **HPT logs**

8. **Soil sample results**

9. **Well logs**

10. **Analytical reports**
    - **10 A.** Soil samples
    - **10 B.** Groundwater samples

11. **Simulation of electrical field**
    - **11 A.** Cross section: Electrodes at original depth
    - **11 B.** Cross section: Electrodes at elevated depth (“tip effect”)
    - **11 C.** Plan view
    - **11 D.** Modelled migration at days 30, 45, 60, 75 and 90

12. **Overview of EK-TAP^{TM} pilot test area**

13. **Conceptual layout EK-TAP^{TM} operational system**

14. **Electrode in well construction**

15. **Field notes**

1 DANSK RESUMÉ

På vegne af Region Hovedstaden har NIRAS A/S i fællesskab med Geosyntec Consultants udført et pilotforsøg med Elektrokinetisk Termisk Aktiveret Persulfat (EK-TAP^{TM}) i en lav permeabel morænelersaflejring. Pilotforsøget er udført i perioden april 2015 til marts 2016 på Region Hovedstadens innovationsgarage, Skovlunde Byvej 96A i Ballerup.

Konceptet med teknologien indebærer elektrokinetisk transport af persulfat ved jævnstrøm ud i den lavpermeable moræneler samt efterfølgende opvarmning ved vekselstrøm for at aktivere den tilsatte persulfat, hvorved en oxidationsproces af chlorerede opløsningsmidler igangsættes. EK-TAP^{TM} er en ny metode til oprensning af forurenede grunde med chlorerede opløsningsmidler i lav permeable aflejringer.

EK-TAP^{TM} pilotforsøget udgøres af følgende tre faser:

1. EK persulfat ($S_2O_8^{2}$) migrationsfase (jævnstrøm), hvor persulfat distribueres i den lav permeable moræneler med udgangspunkt i katodeboringen (*7+14 uger*).

2. Opvarmningsfase (vekselstrøm), hvor jordpakken indenfor testfeltet opvarmes til en ”target” temperatur på minimum 30°C. Herved sker der en aktivering af det tilsatte persulfat til sulfat radikaler (SO_4^-), hvilket igangsætter en kemisk oxidation af chlorerede opløsningsmidler (*9½ uge*).

3. Nedkølingsfase, hvor temperaturudviklingen efter endt opvarmning følges for at vurdere hvor lang tid det tager at køle jorden indenfor testfeltet ned til baggrundsniveau (*11 uger*).

Fordelen ved EK-TAP^{TM} er, at den samme infrastruktur kan bevares gennem hele oprensningsforløbet, både under jævnstrøm- og vekselstrømsfasen. Endvidere er temperaturen lavere (ca. 30°C) end typiske elektriske opvarmningsmetoder (ca. 90°C), og forureningen fjernes ved ”in situ” oxidation i stedet for ved fordampning . Sammenlignet med EK-BIO, der primært retter sig mod chlorerede ethener, vil EK-TAP^{TM} metoden også kunne anvendes til oprensning af fx TCA og 1,4-dioxan.

Det overordnede formål med den gennemførte single dipol EK-TAP^{TM} test har været at demonstrere og evaluere anvendeligheden af EK-TAP^{TM} metoden til at distribuere persulfat i lavpermeable morænelersaflejringer og efterfølgende aktivere persulfat ved opvarmning. Formålet var yderligere at afklare, hvorvidt den samme infrastruktur (elektrodeboringer etc.) kunne bibeholdes gennem hele oprensningsforløbet, at evaluere den optimale temperatur til at aktivere og fastholde aktiveringen af persulfat under feltforhold, samt at evaluere hvor effektiv en fordeling af persulfat, der kunne opnås med det valgte testlayout.

Det udførte EK-TAP^{TM} single dipol felt pilotforsøg har demonstreret, at det er muligt at transportere persulfat igennem lavpermeable morænelersaflejringer, samt efterfølgende at aktivere persulfat ved opvarmning resulterende i kemisk oxidation af PCE i grundvandet inden for testområdet. Koncentrationsniveauet i grundvandet inden for testområdet blev reduceret fra over 100 mg/l til vel under 50 mg/l under migrations- og opvarmningsfasen.

Dog syntes de delvist umættede forhold i den øverste del af jordpakken at udgøre en hæmmende faktor for udbredelsen af persulfat, hvorfor udbredelseshastigheden af persulfat var mindre end forventet.

Den målsatte temperatur på 30°C blev nået i hele testfeltet i løbet af 30 dage af opvarmningsfasen. Den tilsatte persulfat blev aktiveret både af jordens naturligt forekommende jern og af opvarmningen. Data viser, at opvarmningen spillede en central rolle for fuldstændigt at aktivere det tilsatte persulfat og for at oxidere PCE i grundvandet.

Pilotforsøget viste endvidere, at de anvendte MMO-belagte titanium-elektroder såvel som de installerede elektrode- og monitoreringsboringer kunne anvendes både i jævnstrøms- og vekselstrømsfasen. Dette er netop et centralt karakteristikum ved EK-TAP^{TM}-metoden.

2 INTRODUCTION

At many contaminated sites in Denmark, and in the Capital Region especially, the source area of the contamination is located in low permeable deposits, often in clayey till deposits. So far only few remediation methods have proven effective at remediating such source areas. There is thus a need to develop and demonstrate new remedial methods to assess their capability of meeting this challenge.

Electrokinetically Delivered Thermally Activated Persulfate, EK-TAP^{TM}, is one such method. It combines the delivery enhancement capabilities of electrokinetics, that are independent of soil hydraulic properties, with minimal electrical resistance heating of the soil, using the same infrastructure for both stages of the remediation. Distribution of persulfate in low permeable deposits and subsequent heat activation of persulfate for degradation of chlorinated solvents is an emerging technology and has been successfully demonstrated in laboratory tests but has not previously been tested at the field scale.

Based on laboratory tests with EK-ISCO and EK-TAP^{TM} carried out with soil and groundwater from Skovlunde Byvej 96A along with knowledge and experience from the successful pilot study and full-scale remediation with EK-BIO at the site in Skuldelev, the Capital Region of Denmark has decided to conduct a pilot test of Electrokinetically Delivered Thermally Activated Persulfate, EK-TAP^{TM}. The pilot test was designed and conducted by NIRAS and Geosyntec.

The present report describes the overall design, the installation and operation of the EK-TAP^{TM} system as well as the monitoring and documentation of the field pilot test. The report is prepared by NIRAS and Geosyntec Consultants in collaboration.

2.1 Pilot test site

The EK-TAP^{TM} single dipole pilot test was conducted at the Skovlunde Byvej 96A site in Ballerup, Denmark. The site is currently owned by the Capital Region of Denmark and is being used as a demonstration site for innovative investigation and remediation methods for soil and groundwater contamination.

At the site Skovlunde Byvej 96A, dry cleaning activities have taken place from 1960 to 1987, resulting in soil and groundwater contamination with dominantly chlorinated solvents. From 1997 to 1999 soil and groundwater investigations have been conducted at the site. Remedial activities have been initiated in 1999.

The pilot test area is located on the northern side of the building at Skovlunde Byvej 96A as seen in Figure 2.1.

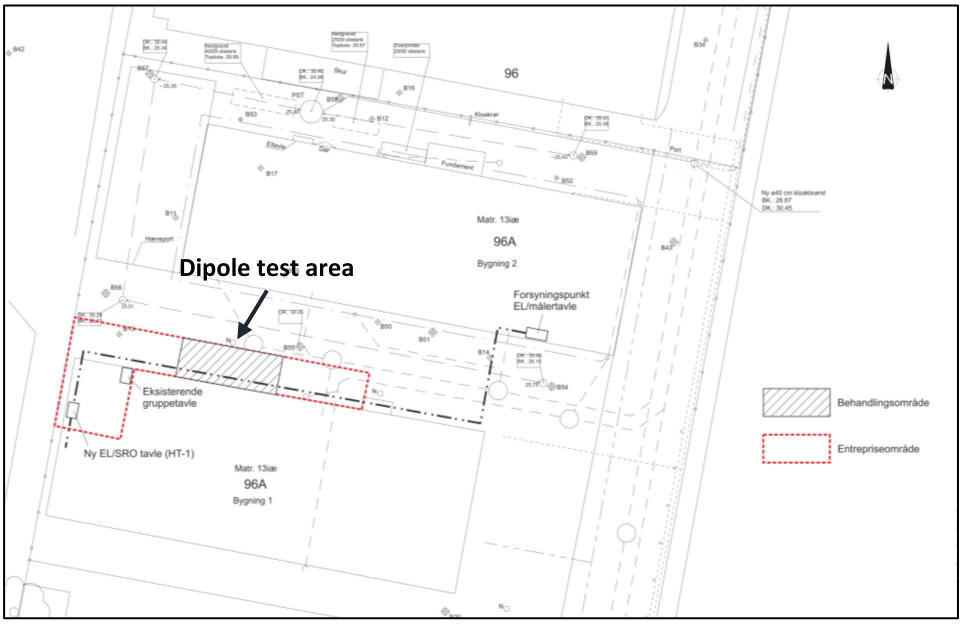

Figure 2.1: Overview of the location of the EK-TAP^{TM} dipole pilot test area. (See appendix 12 for higher resolution)

2.1.1 Geological setting

Regional geological setting

The regional geological setting and the geology at the site are described in more detail in /4/ and summarized below.

The Ballerup area is located in the eastern part of Zealand, a Quaternary glacial landscape, geologically characterized by a layer-cake structure, with sandy meltwater plain sediments both overlain and underlain by glacial clay tills of different Quaternary origin. In the Ballerup area the glacial tills rest on Quaternary meltwater deposits which is overlying a Danien limestone formation.

Glacial till is sediment composed of a large variety of grain sizes, which has been deposited in a glacial environment that does not provide any sorting of the material. In all glacial tills the grain size fractioning can vary significantly and unsystematically within very short distances, both horizontally and vertically. Clay till deposits in Zealand generally appear as unsorted silty, sandy, calcareous clay of low plasticity with variable amounts of gravels, cobbles and stones. Clay contents of 12-15 % are common and water content typically approaches 8-14% /1/. Danish clay tills typically exhibit fractures due to subglacial shear and extension and in their upper portions also exhibit contraction fractures due to a period of late glacial freeze-thaw and subsequent desiccation.

Local geological setting, Skovlunde Byvej

The Ballerup test site at Skovlunde Byvej comprises two formations. The upper formation is a glacial till, overlying a (glacial) sand formation.

The first meters below ground level (m bgl) consist of top soil followed by a partly saturated sandy/silty clay for another approximately 3 meters. From approximately 3,5-8,5 m bgl an underlying partly saturated clay till is deposited on top of an unsaturated sand formation starting at approximately 8,5 m bgl.

A geological cross section of the treatment area is shown in Figure 2.2. A well-drained till on partly unsaturated sand, as seen at the site, is commonly intensely fractured. Till texture sometimes become fissile in the upper 2-3 m bgl due to frequent fractures.

The upper approximately 3 meters of the glacial till are relatively uncompacted and water rich, whereas the lower 3-9 m of till are more compact and water deprived /4/. Porewater has been recorded at 1-2 m below surface, but has occasionally been observed at 4-5 m below surface, suggesting that the pore water observations are not hydraulically interconnected. It is assumed that temporal and spatial variations in perched secondary water levels are present on the site. A formation of silty fine sand is found at 9-20 m depth. The sand formation becomes gradually coarser at approx. 20-27 m depth. The upper 5-6 meters of the sand formation is unsaturated. A regional chalk basement was expected below the sand formation, at approx. 27 m depth, but was not reached when drilling /4/. The primary aquifer comprises the deeper part of the glacial sand formation and the limestone formation. It is unconfined and starts at a depth of approx. 13 m bgl (corresponding to local reference primary aquifer water level of +17DVR90) /4/.

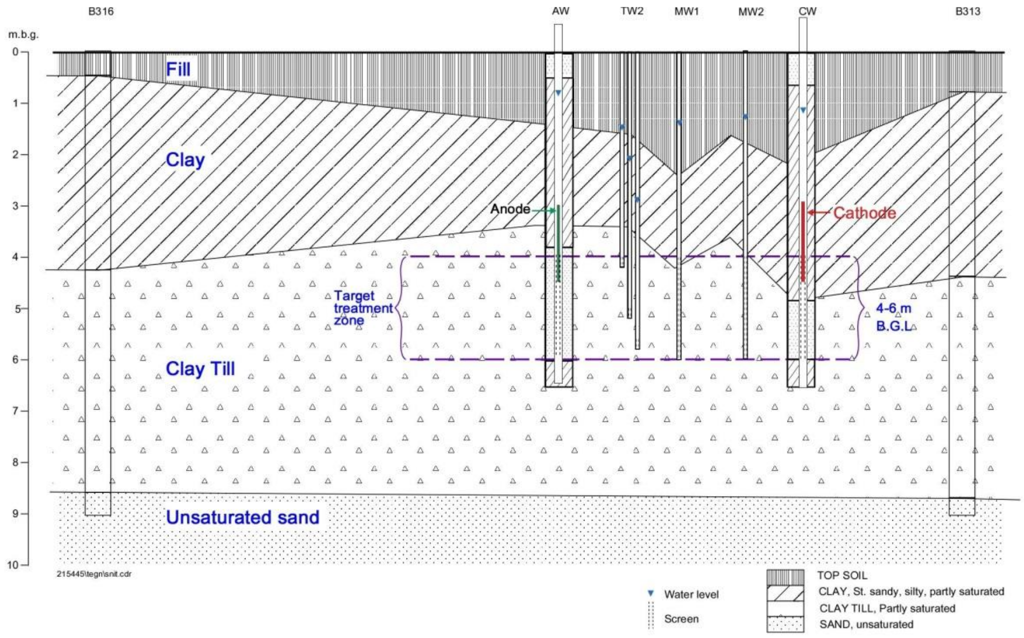

Figure 2.2: Geological cross section of treatment area at the test site Skovlunde Byvej, Ballerup. (See appendix 2 for higher resolution)

2.1.2 *Contamination*

The test site is heavily contaminated by chlorinated solvents in both the overburden and in the primary aquifer as shown in Figure 2.3 and Figure 2.4. Investigations indicate that there is approximately 2 tons of PCE at this site /2/.

In general, the highest concentrations of chlorinated solvents are found in the surface fill at the hot spot and between 2.5 – 4.0 m bgl outside the hot spot area.

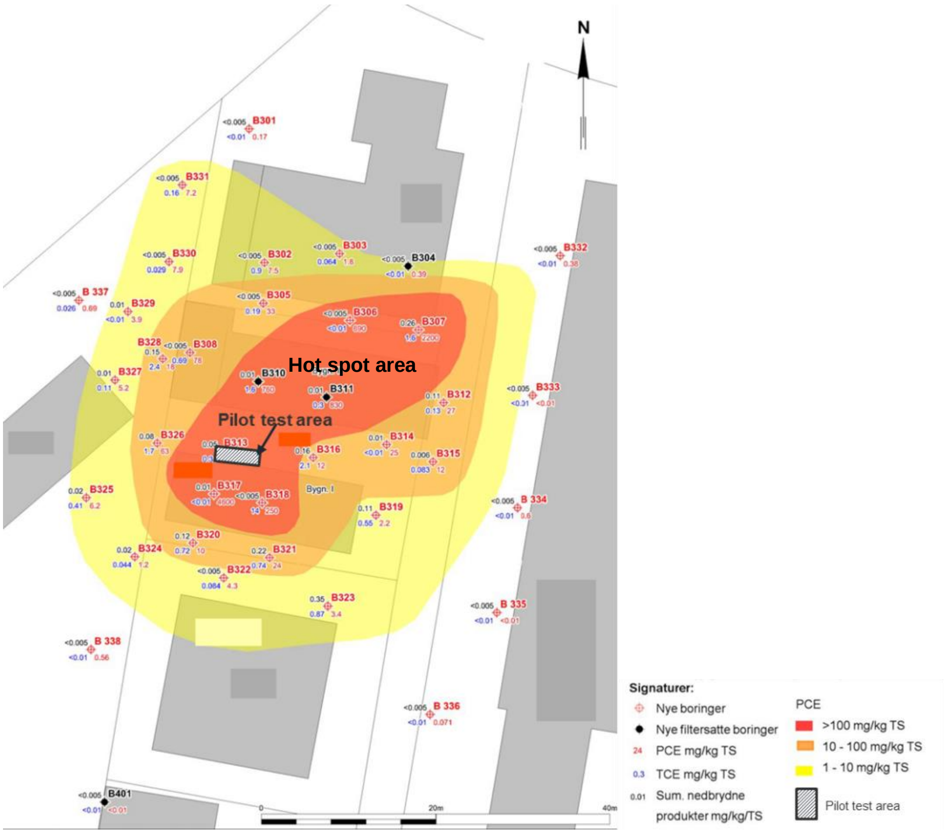

Figure 2.3: Horizontal distribution of contamination at test area. Modified from /3/.

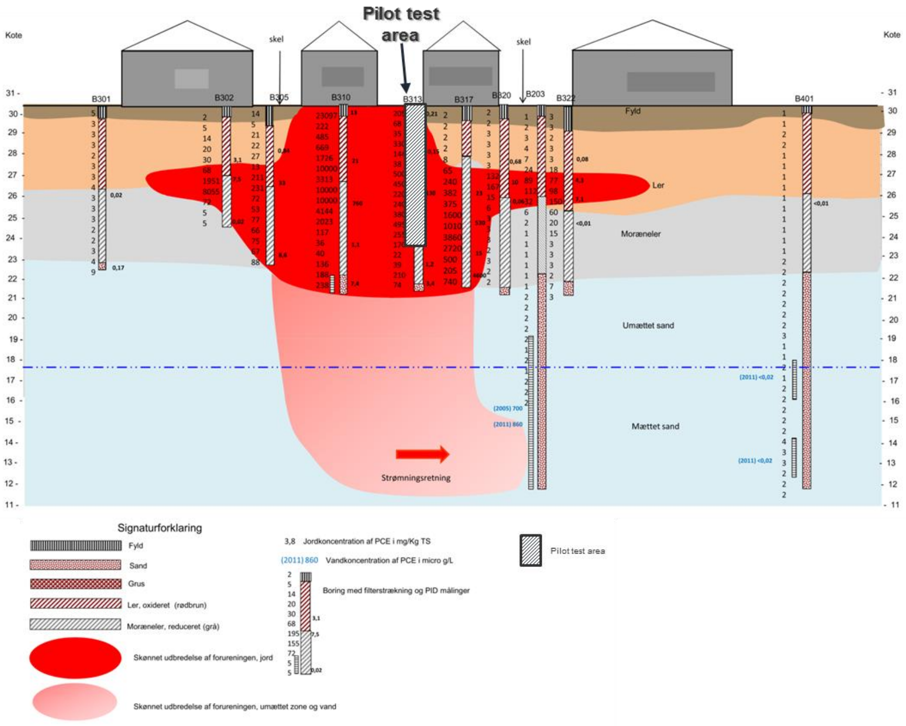

Figure 2.4: Geological cross section illustrating vertical distribution of contamination at Skovlunde Byvej 96A. Modified from /3/.

3 BACKGROUND

3.1 EK-TAP^{TM} Technology Overview

The Electrokinetic Thermally Activated Persulfate (EK-TAP^{TM}) technology is intended to distribute the chemical oxidation sodium persulfate (NaPS) throughout low permeability materials, through the establishment of an electrical field in the subsurface. The process is conducted by applying direct current (DC) current to promote electromigration of the persulfate, followed by heating of the soil package through application of AC current, based on electrical resistance heating (ERH), to activate the persulfate and oxidize the chlorinated solvents /5/.The electrical field is established by applying a low-voltage DC to electrodes installed within the targeted subsurface materials. The established subsurface DC electric field facilitates efficient transport and mixing of specific remediation reagents through 3 transport mechanisms: electroosmotic advection (electroosmosis), ion migration (electromigration), and electrophoresis, as depicted in Figure 3.1. Electroosmosis is bulk transport of the pore fluid in the soil; usually the flow direction is from the anode toward the cathode. Electromigration refers to the movement of anions (negative ions) and cations (positive ions) to the anode and cathode, respectively. Electrophoresis describes the transport of charged particles, such as clay particles, under the applied electric field to the electrodes of opposite polarity. Typically, electrophoresis is expected to contribute less to remediation in the subsurface because soil tends to act as a filter to retard the movement of solid particles. For the EK-TAP^{TM} technology, electroosmosis and electromigration are anticipated to be the two primary mechanisms for delivery of chemical oxidation reagents in the subsurface /5/.

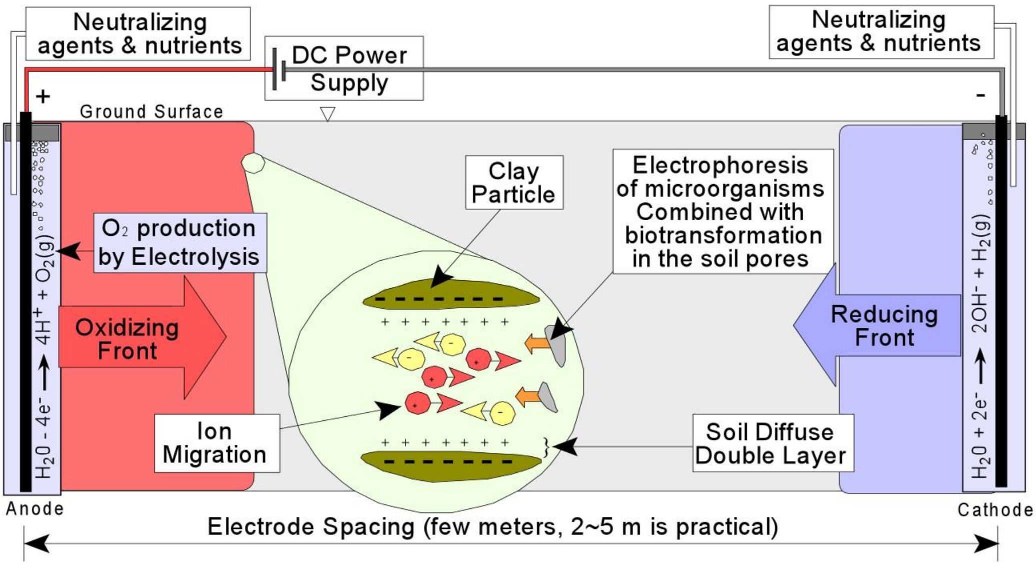

Figure 3.1: Schematic illustration of electrochemical processes of EK technology /5/.

The theoretical transport rate for a chemical oxidant reagent achievable under EK processes can be calculated as:

$$J_i = c_i \; u_i \; i_e + c_i \; k_e \; i_e \qquad \textbf{(1)}$$

where J_i ($MT^{-1} L^{-2}$) is the flux of species i due to electromigration and electroosmosis; c_i (ML^{-3}) is the concentration of i; u_i ($L^2T^{-1} V^{-1}$) is the effective ionic mobility of i; k_e ($L^2T^{-1} V^{-1}$) is the coefficient of electroosmotic permeability; and i_e (VL^{-1}) is the electric gradient.

The rate of electroosmotic flow is controlled by k_e, which is a measure of the rate of fluid flow per unit area under a unit electrical gradient. The value of k_e is widely accepted as a function of zeta potential of the soil particle surface, viscosity of the pore fluid, porosity, and electrical permittivity of the medium. The value of zeta potential is dependent on the pore fluid's ionic strength and pH. The impact of electrochemical changes (e.g., pH and ionic strength) during application of electric currents on zeta potential and electroosmotic permeability has been demonstrated. A careful measurement of pH dependence of the zeta potential in Kaolinite clay showed a zero isoelectric point (and therefore minimal electroosmosis) when the pH approached a value of 4.0. Therefore, proper control of electrolyte strength and pH at the electrodes and within the treatment area are important considerations for achieving efficient electroosmotic flow.

EK technology has been used previously for electroosmotic extraction of organic contaminants from soils. A team evaluated the use of electric fields for electroosmotic extraction of TCE from a site in Paducah, Kentucky, with the application of layered horizontal electrodes, or the "Lasagna™" process. The Lasagna™ process relied on electroosmosis for extraction of target contaminants from the soil into electrode treatment wells. The time estimated for 99% electroosmotic extraction of benzene, TCE, toluene, m-Xylene, and hexane was on the order of several years (depending upon electrode spacing). In contrast to the Lasagna™ process, the EK-TAP^{TM} technology is designed to use EK as an enhanced delivery process to help promote in-situ chemical oxidation directly within low permeability zones.

The application of electric current will also result in electrolytic reactions at the electrodes. If inert electrodes (such as graphite or ceramic-coated electrodes) are used, water oxidation produces oxygen gas and acid (H_3O^+) at the anode (positive electrode), while water reduction produces hydrogen gas and base (OH^-) at the cathode (negative electrode). Electrolytic reactions are shown below in Equations 2 and 3,

$$2H_2O \implies 4e^- + 4H^+ + O_2 \qquad \text{at Anode} \qquad \textbf{(2)}$$

$$2H_2O + 2e- \implies 2OH^- + H_2 \qquad \text{at Cathode} \qquad \textbf{(3)}$$

Faraday's law for equivalence of mass and charge can be used to calculate the rate of redox reactions that will occur at the electrodes. Therefore, it is possible to engineer and control the processes at electrodes to produce the desired amendments, such as H_2 and O_2, depending on the system design objectives.

To date, there have been relatively few field demonstrations of EK delivery of amendments into low permeability subsurface materials. A pilot and full-scale implementation designed to distribute electron donor (lactate) and dechlorinating biomass (KB-1^{TM}) has been performed at Hot Spot IV in Skuldelev, Denmark.

Chemical oxidants, such as persulfate will migrate into and across low permeability zones along the electric field lines that are established between the electrodes. Because the transport is designed to occur principally in the form of ion migration, soil pore size and porosity will have little effect on transport rates. This migration will be relatively independent of the hydraulic conductivity and flow of water due to hydraulic gradients. A comparison of typical transport rates in clay and sand under hydraulic and electric gradients shows that although hydraulic transport rates in sands can be orders of magnitude higher than in clays, transport rates by ion migration are relatively similar in clays and sands. While hydraulic delivery techniques are limited by the preferential flow through the high permeability areas (bypassing low permeability zones), an electric field will produce uniform delivery of oxidants through low and high permeability zones of heterogeneous deposits /5/.

When persulfate migration across the dipole has been achieved, soil heating can be conducted by applying AC power to the electrodes for a period, in order to increase subsurface temperatures within the target treatment interval of persulfate migration. By applying AC power resulting in heating of the soil package, activation of the sulfate free radical SO_4^- and subsequently chemical oxidation of chlorinated solvents can be achieved.

3.2 Advantages of EK-TAP^{TM}

- The infrastructure can be kept constant throughout the entire remediation and the same electrodes can be applied for both phases (i.e. AC/DC).
- Temperature can be kept lower (30-35^{o}C) than other typical electrical resistance heating approaches (90^{o}C) and contamination is oxidized in situ instead of evaporated.
- No need for a SVE system for collection of VOC gases.
- EK-TAP^{TM} can treat a wider range of contaminants than EK-BIO, such as TCA and 1,4 dioxane.

3.3 Laboratory Tests

Prior to initiating the field EK-TAP^{TM} dipole test, laboratory experiments were carried out from November 2013 to June 2014 and in November – December 2014. Five types of experiments were performed:

- Characterization of the soil, including measurement of zeta potential, mineralogical evaluation by X-ray analysis and measurement of natural oxidant demand (NOD) for both the oxidized and reduced till.

- Batch experiments with contaminated soil from the site that were spiked to a higher PCE content. The experiments were performed with persulfate at different concentrations.

- Column experiments (1D) testing EK-TAP^{TM} using polluted soil from the reduced zone. The column experiments included short initial tests of the transport potential under electrokinetic conditions for obtaining an initial understanding of the system before the larger (2D) experimental reactor experiments were set up.

- Reactor experiment (2D) testing of EK-TAP^{TM} using contaminated soil from the reduced zone. Reactor experiments were long term studies (14-21 days), simulating field conditions.

- Optimization batch testing to identify the optimal design parameters for field testing of EK-TAP^{TM}. PCE degradation was evaluated at three persulfate concentrations at each of three temperatures with two different application durations.

Subsequently modeling was performed in order to design a test layout for a EK-TAP^{TM} field pilot test. The modeling was performed using measured values from the laboratory tests and used to simulate persulfate distribution and PCE degradation by EK-TAP^{TM} laboratory experiments. The conducted laboratory testing and the results hereof are described in more detail in /4,5/.

Based on results of the laboratory optimization batch testing and preliminary cost-benefit analysis, Geosyntec suggested that an in-situ persulfate amendment concentration of 20 g/L would be a suitable target for the pilot test. To achieve this in-situ concentration, a feed concentration of 54 g/L was required based on the modeling work of Wu et al. /8/.

Based on the electron donor transport rates observed at the Skuldelev field site and in the EK-TAP^{TM} bench-scale testing and modeling /4/, /5/, it was assumed that persulfate transport rates greater than 5 cm/day could be achieved. The overall duration of the EK persulfate migration stage of the pilot test would be a function of the achievable transport rate. For design purposes, a transport rate of 5 cm/day or more was targeted.

Results of the laboratory optimization batch testing suggest that at a persulfate amendment concentration of 20g/L, the temperature of the site soils needed only to be increased to 30 ^{o}C in order for PCE to be oxidized to below its detection limit /5/.

4 OBJECTIVE

The overall objective of conducting a single dipole pilot test of EK-TAP^{TM}, was to demonstrate and evaluate the applicability of the method (proof of concept) to distribute persulfate in low permeable clayey till and to subsequently activate the delivered persulfate by heat.

More specifically, the objectives of the EK-TAP^{TM} pilot test were to;

- Prove the EK-TAP^{TM} concept.
- Determine how far persulfate can be distributed under real-world field conditions, and what spacing is appropriate for electrode wells for persulfate delivery.
- Evaluate if the same infrastructure (wells, electrodes) can be effectively used for both persulfate migration (using DC current) and soil heating (using AC current) as the technology is conceptualized, and to identify any specific implementation and/or operational issues that need to be resolved.
- Assess oxidation rates of PCE inside the test field and within the timeframe of the pilot study.
- Evaluate the optimum temperature to activate and sustain activation of persulfate under field conditions.

5 STRATEGY

The pilot test comprised a simple single dipole field test (1 anode and 1 cathode) to sequentially assess persulfate migration, soil heating, PCE oxidization, and soil cooling under real-world field conditions. The dipole test was performed according to /7/ with follow-on adjustments.

5.1 Well layout

The conceptual layout for the single dipole test is shown in Figure 5.1. Two electrode wells (i.e., an anode well, AW, and a cathode well, CW,) were installed approximately 3 m apart. This spacing is based on the persulfate migration rate achieved during bench-scale testing (5 cm/day) and a target maximum EK migration stage duration of 60 days. Two pilot test groundwater monitoring wells were installed between the electrode wells; one monitoring well, MW1, was installed approximately equidistant between the anode and cathode wells, while the second monitoring well, MW2, was installed approximately 60 cm from the cathode well. The wells were screened within the target treatment interval (4-6 m bgl).

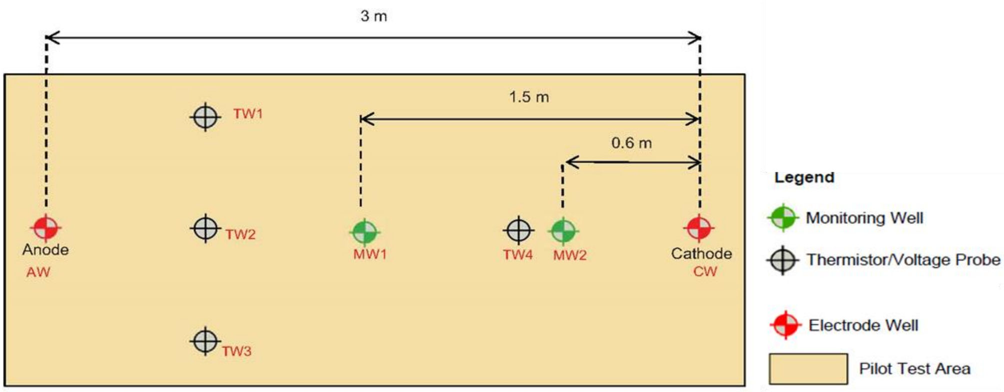

Figure 5.1: Well layout at EK-TAP^{TM} test site (plan view).

A total of four multi-level (3 depth intervals per location) thermistor probes, TW1-TW4, were installed within the test site, as shown in Figure 5.1, to measure temperatures during the heating stage as well as voltage during the migration stage.

5.2 Mode of operation

The single dipole pilot test was planned to be conducted using a 4-stage operational approach as outlined in Figure 5.2.

Figure 5.2: Overview of intended stages during EK-TAP^{TM} pilot study.

- Stage 1, pre-heating stage: AC power supplied to the electrodes for a period to reach a target temperature of 15 ^oC (i.e., as much as 5 ^oC higher than the expected background soil temperature of 10 ^oC). Stage 1 was scheduled for a period of up to 10 days.

- Stage 2, EK persulfate ($S_2O_8^{2-}$) migration stage: DC current supplied to the electrodes in order to facilitate transport of persulfate into the low permeable clayey till formation. Stage 2 was scheduled to operate for a period of up to 60 days. However, it could be extended if oxidant transport rates in the field were lower than observed in the bench-scale testing.

- Stage 3, post-migration soil heating: AC power supplied to the electrodes in order to heat the soil package within the target treatment area to a temperature of 30-35 °C, once persulfate migration across the test area was achieved. The heating stage was designed to activate the sulfate free radical SO_4^- and subsequently oxidize chlorinated solvents. Stage 3 was scheduled for a period of up to 60 days in order to allow subsurface temperatures in the target treatment interval of the pilot test area to reach and maintain the target persulfate activation temperature of minimum 30 ^oC for a minimum of 7 days.

- Stage 4, cooling phase: soil temperatures monitored in order to evaluate the time for the soil package to reach background temperatures in order to estimate the duration of a full treatment cycle as an input to the design of potential future full scale field applications.

6 INSTALLATION OF THE EK-TAP^{TM} SYSTEM

6.1 Installation of wells

A complete overview and location of all the installed wells at the pilot test area during the entire pilot study period are shown at the site plan in Figure 6.1 and in appendix 1. Well logs of all installed wells, borings and cores are attached in appendix 9.

Installation of the electrode wells, the two first monitoring wells and the temperature monitoring wells were conducted by Arkil. Installation of the remainder of the monitoring wells and soil borings as well as sampling of the soil cores were conducted by NIRAS.

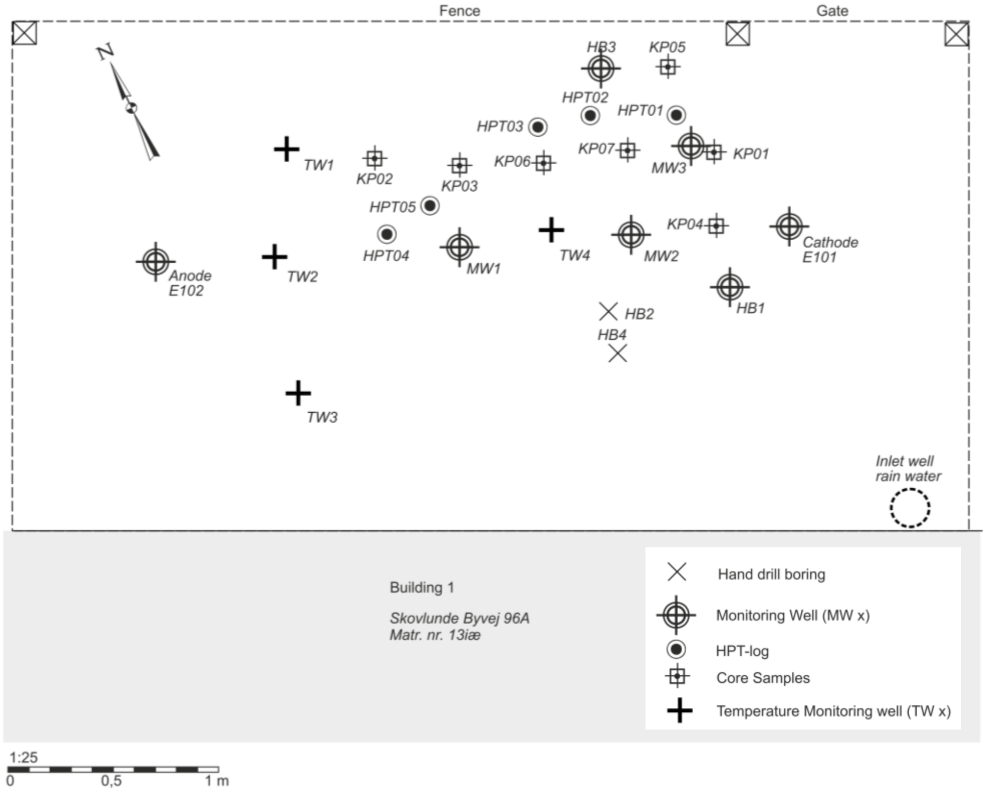

Figure 6.1: Well placement of all the installed wells, core samples and HPT-logs at the pilot test area.

6.1.1 *Electrode wells*

Electrode wells CW and AW were installed in April 2015 to 6.5 m depth and screened in the interval from 4 – 6 m bgl. During execution of the drilling, soil samples were taken every half meter for geological assessment and PID readings. Well layout and specifications are provided in Table 6.1 and appendix 14. Well logs are presented in appendix 9.

Well	Borehole dimension (mm)	Screen dimension (mm)	Well depth (m bgl)	Screen interval (m bgl)
Anode well	300 (12")	200	6.5	4.0 - 6.0
Cathode well	300 (12")	200	6.5	4.0 - 6.0

Table 6.1: Well specifications for electrode wells.

6.1.2 *Monitoring wells*

Monitoring wells MW1 and MW2 were installed in April 2015 to a depth of 6 meters and were screened from 4 to 6 m bgl. During execution of the drilling, soil samples were taken every half meter for geological assessment, PID measurement and chemical analysis serving as soil baseline data.

Monitoring well MW3 was installed in October 2015 during stage 2 (DC migration). Well specifications are provided in Table 6.2. Well logs are presented in appendix 9. Analytical reports are attached in appendix 10.

Well	Borehole dimension (mm)	Screen dimension (mm)	Well depth (m bgl)	Screen interval (m bgl)
MW-1	200 (8")	125	6	4.0 - 6.0
MW-2	200 (8")	125	6	4.0 - 6.0
MW-3	Hand drilled Ø25		6	4.0 - 5.7

Table 6.2: Well specifications for monitoring wells.

6.1.3 *Temperature monitoring wells*

A total of four temperature monitoring wells were installed in April 2015 within the pilot test area to monitor subsurface temperatures during the soil heating stage and the cooling stage. Each well was screened at the top, middle, and bottom of the target treatment interval within a single borehole. Each well was drilled to 6 m bgl. During execution of the drilling, soil samples were taken every half meter for geological assessment and PID readings.

Well specifications for the temperature monitoring wells are provided in Table 6.3. Well logs are presented in appendix 9.

Well	Borehole dimension (mm)	Screen dimension (mm)	Well depth (m bgl)	Screen interval (m bgl)
TW1	200 (8")	3 x 25	6	Screen 1: 5.67 - 5.92
				Screen 2: 4.83 - 5.08
				Screen 3: 3.88 – 4.13
TW2	200 (8")	3 x 25	6	Screen 1: 5.60 – 5.85
				Screen 2: 4.95 – 5.20
				Screen 3: 3.90 – 4.15
TW3	200 (8")	3 x 25	6	Screen 1: 5.37 – 5.62
				Screen 2: 4.67 – 4.92
				Screen 3: 4.00 – 4.25
TW4	200 (8")	3 x 25	6	Screen 1:5.63 – 5.88
				Screen 2: 4.83 – 5.08
				Screen 3: 3.90 – 4.15

Table 6.3: Well specifications for temperature monitoring wells.

6.1.4 *Hand drilled borings*

Hand drilled borings were installed during stage 2, in October and November 2015. Two of the borings, HB1 and HB3, were screened to enable subsequent water sampling. During construction of the hand drilled borings soil samples were taken every half meter for geological assessment, PID readings and chemical analysis. Well specifications of hand drilled borings are provided in Table 6.4. Well logs are presented in appendix 9. Analytical reports are attached in appendix 10.

Boring	Established	Screen dimension (mm)	Well depth (m bgl)	Screen interval (m bgl)
HB1	06 Oct. 2015	25	5	3.65 – 4.75
HB2	02 Oct. 2015		5	
HB3	19 Nov. 2015	25	6	3.70 – 6.00
HB4	24 Nov. 2015		6	

Table 6.4: Hand drilled boring specifications.

6.2 Installation of EK-TAP^{TM} operation system and system components

Installation of the EK-TAP^{TM} operation system was conducted by the contractor ARKIL, while PLC-operation/programming and electrical setup was conducted by JES-TEC according to tender documents of 3 March 2015 /6/. The EK-TAP^{TM} system was installed during March and April (week 12-18), 2015.

A conceptual layout of the EK-TAP^{TM} operation system is shown in Figure 6.2.

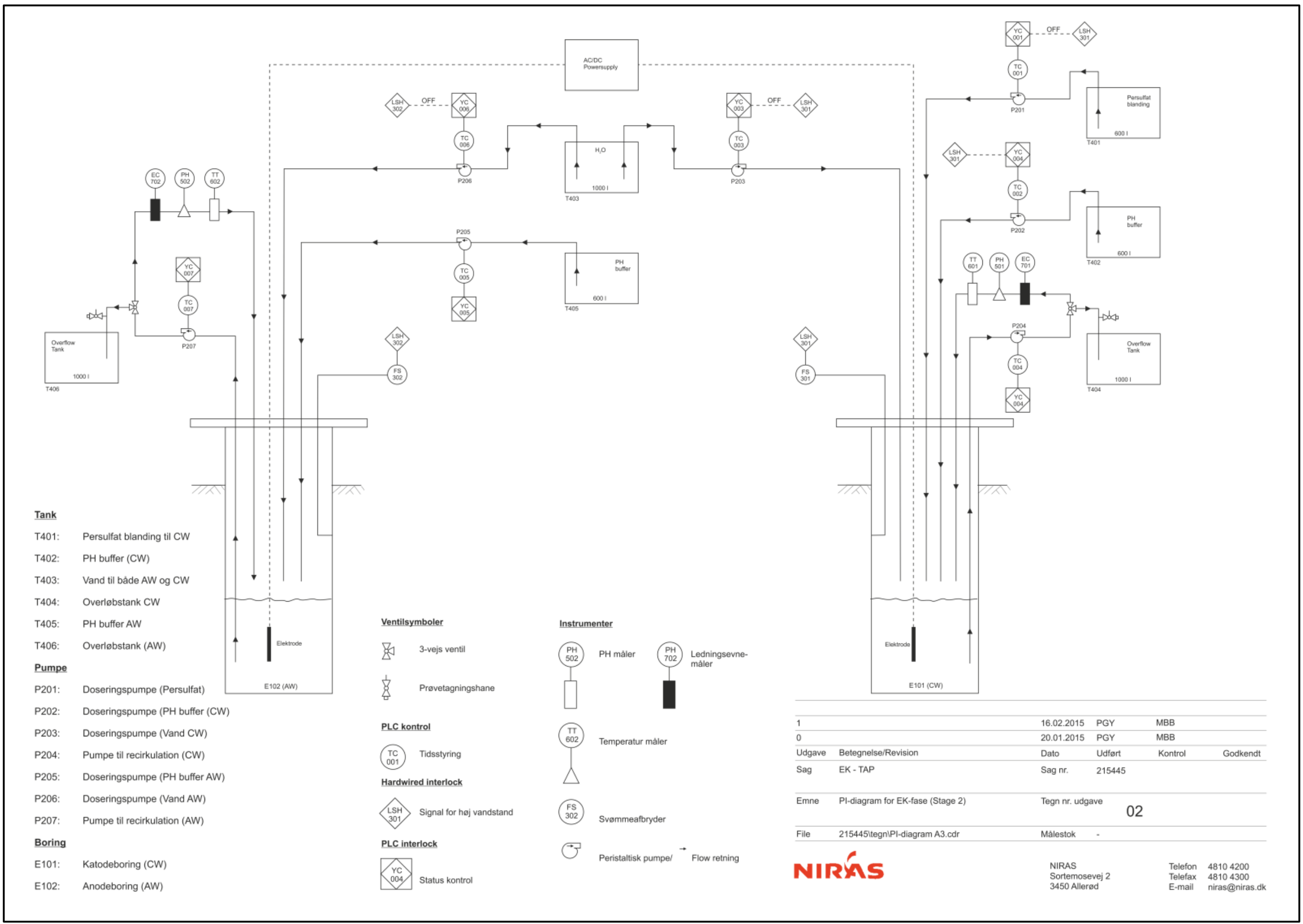

Figure 6.2: Conceptual layout of the installed EK-TAP^{TM} operational system (See Appendix 12 for higher resolution).

6.2.1 *Electrodes*

The anode and cathode electrodes consisted of a 1.5 m long, 6.35 cm (2.5”) diameter titanium tube coated with a MMO coating to prevent passivation and corrosion of the electrodes. The electrodes were connected to the power supply unit at ground surface with a cathodic protection cable. Electrodes were purchased pre-connected to the cable, and all cables were of equal length.

6.2.2 *Programmable Logic Controller (PLC)*

The EK-TAP^{TM} system included instrumentation and controls to monitor and operate the system automatically using a PLC, which was capable of alarm notification and remote monitoring. Overall operation of the persulfate and buffer metering pumps was controlled by timers in the PLC. Solenoid valves controlled the supply of oxidant and buffer to the cathode well and of buffer to the anode well on a timer during metering pump operation. A high pressure condition in the wells beyond the setting could cause the PLC to close the solenoid valve, and a pressure safety valve (PSV) would relieve buildup of pressure in the well. A flow measuring device was used to measure the instantaneous and total flow of each amendment to the electrode wells.

6.2.3 *Power Supply*

The EK-TAP^{TM} system required both AC and DC power for operation. For the single dipole pilot test, a 120/240 V single phase AC power source (minimum 200 A service) was considered suitable, however for expansion to a larger system, a 3-phase power source will be required. DC power was provided by a Magna Power SL 160-9/VI (160 VDC, 9A, 120V AC in). AC power was provided by a variable autotransformer rated to approximately 10 A. An isolating transformer was subsequently installed by Arkil due to differences between the US and DK power supply in order to power the dipole test system.

Jes-Tec inspected all electrical wiring and connections as well as all relays and controls within the system prior to commencing system start-up.

6.2.4 *pH Control*

Monobasic and dibasic potassium phosphate buffers were supplied to the cathode and anode wells to buffer the pH change in the electrode wells in order to keep pH neutral. When combined in equal portions, these two buffers create a dual purpose buffer that buffer against increases in both H^+ and OH^-. The buffer dosage rates and volumes were assessed during system start up and initial operation and were targeted to maintain a pH between 6 and 8 in the electrode wells. During stage 2 operation buffer dosing was adjusted in response to the inline pH readings in CW and AW.

Monitoring of pH in the electrode wells was accomplished using a closed-loop recirculation system, whereby water within each electrode well was pumped from the well, through a pH analyzer, and then re-introduced into the well via the water addition drop tube.

6.2.5 *Persulfate and Buffer Supply*

The pilot test used the following chemical amendments: sodium persulfate (NaS_2O_8) and potassium phosphate (KH_2PO_4 and K_2HPO_4). Each chemical was procured by NIRAS and permits needed to apply these chemicals were obtained by NIRAS. The chemical amendments were diluted in the field using tap water, to achieve the desired target concentrations.

Chemical oxidant was originally bought as potassium persulfate (KPS), but was replaced with sodium persulfate (NaPS) as the oxidant, due to the higher solubility of the NaPS at the operation temperatures of the injectate.

The buffer system comprised a mixture between (DKP) and (MKP) in equal molar proportions.

6.2.6 *Security and Storage*

The power supply unit, amendment supply units and manifolds, and PLC system were housed within the nearby house (building 1, Figure 2.1) which was found appropriate for equipment enclosure.

6.3 Sealing of the dry well

During the DC migration stage a nearby rainwater inlet well installed in order to drain off rainwater from the rooftop of building 1 (see Figure 2.1) was suspected of letting rainwater drain into the pilot test area, possibly influencing migration of persulfate. It was therefore decided to seal the well. The sealing was conducted 18 Sep. 2015.

7 SAMPLING

At the completion of system installation, and prior to commencing the pre-heating stage of the pilot test system, baseline groundwater samples were collected from the anode well (AW) and the monitoring wells (MW-1 & MW-2) for measurements of field parameters (pH, dissolved oxygen [DO], oxidation-reduction potential [ORP], conductivity, temperature), as well as for laboratory analysis of VOCs, sulfate, persulfate, and chloride. At the time of the baseline groundwater sampling the cathode well was dry, thus no water sample was extracted from this well at that time. It is important to note that this pilot test was conducted in a clay zone containing perched water, and as a result water levels and saturations may not be uniform across the pilot test area. Parameters are presented in Table 7.1.

Sulfate, chloride and VOC's were analyzed by ALS, persulfate was analyzed by NIRAS.

Soil samples were collected during installation of monitoring wells MW-1 and MW-2 in April 2015 for baseline analysis of volatile organic compounds (VOCs), sulfate, total sulfur, chloride and chlorinated solvents. Parameters are presented in Table 7.2.

Well	CW	AW	MW-1	MW-2
Screen interval (m bgl)	4.0 – 6.0	4.0 – 6.0	4.0 – 6.0	4.0 – 6.0
Sulfate, SO$_4^-$ (mg/l)	DRY	280	26	56
Chloride Cl$^-$ (mg/l)		240	81	100
PCE (µg/l)		160000	170000	110000
TCE (µg/l)		21000	16000	11000
cis-1,2-DCE (µg/l)		13000	19000	19000
VC (µg/l)		500	1200	1200
Persulfate (mM PS)[a]		<0.008	<0.008	<0.008
Temperature (° C)		12	11.82	11.89
pH		7.6	7.7	7.6
Conductivity (µS/cm)		1414	831	833
ORP (mV)		176	184	174
DO (mg/l)		4.3	7.6	8.7

Table 7.1: Measured baseline water sample parameters. Samples taken April 29, 2015. ([a] Persulfate measured 16 July 2015)

Well	**Depth** (m bgl)	**Chloride** (mg/kg TS)[a]	**Sulfur** (mg/kg TS)	**Sulfate** SO_4^{2-} (mg/kg TS)	**PCE** (mg/kg TS)	**TCE** (mg/kg TS)	**cis-1,2-DCE** (mg/kg TS)	**VC** (mg/kg TS)
MW-1	2.5	<100	158	<50	0,042	<0,010	0,087	0,029
	3.0	<100	89	<50	16	0,17	1	0,076
	3.5	<100	113	<50	390	4,8	0,66	0,028
	4.0	100	100	<50	97	0,83	0,71	0,019
	4.5	250	2.230	<50	430	1,2	1,2	0,041
	5.0	200	1.820	54	110	1,6	1,7	0,087
	5.5	220	2.630	<50	7.200	6,4	1,1	0,085
	6.0	170	2.330	77	210	2,6	0,66	0,087
MW-2	2.5	<100	118	<50	0,52	0,092	1,1	0,18
	3.0	<100	108	<50	15	0,67	1,2	0,022
	3.5	<100	135	<50	39	1,6	0,81	0,017
	4.0	<100	104	<50	8	0,37	0,52	<0,010
	4.5	<100	100	<50	120	2	0,58	0,014
	5.0	150	2.050	<50	260	2,6	1	0,037
	5.5	250	2.310	63	110	2,6	1,2	0,065
	6.0	190	1.950	68	420	0,75	0,26	0,02

Table 7.2: Measured baseline soil sample parameters. Samples were taken April 13, 2015. PCE concentrations are visualized in cross section Figure 7.1 ([a] Chloride baseline are measured with another method and analytical lab than subsequent chloride measurements).

A geological cross section with the measured PCE concentrations in the soil at baseline is presented in Figure 7.1.

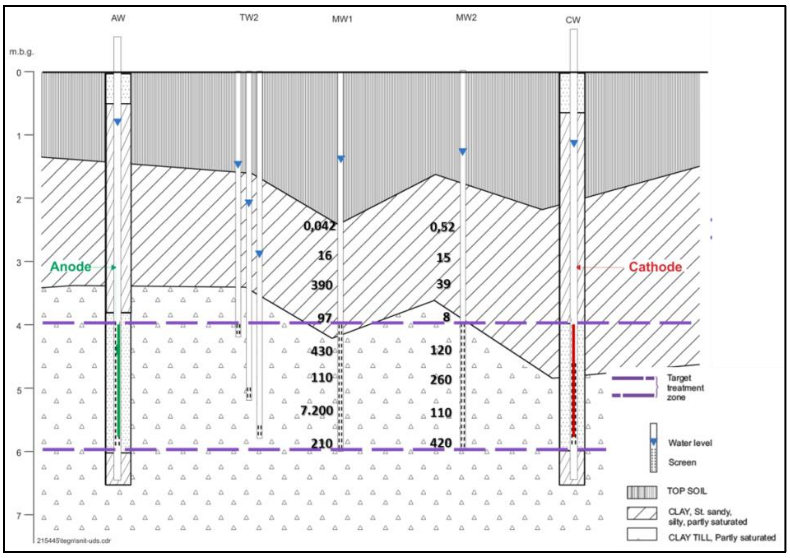

Figure 7.1: Baseline PCE vertical distribution in soil samples (mg/kg dry matter) for MW-1 & MW-2.

8 OPERATION

Figure 8.1 and Figure 8.2 illustrates the actual durations of the operational stages of the pilot test.

Figure 8.1: Overview of conducted stages and durations. Note that the electrodes were raised after 7 weeks of the DC migration stage and stayed elevated through the rest of the pilot test.

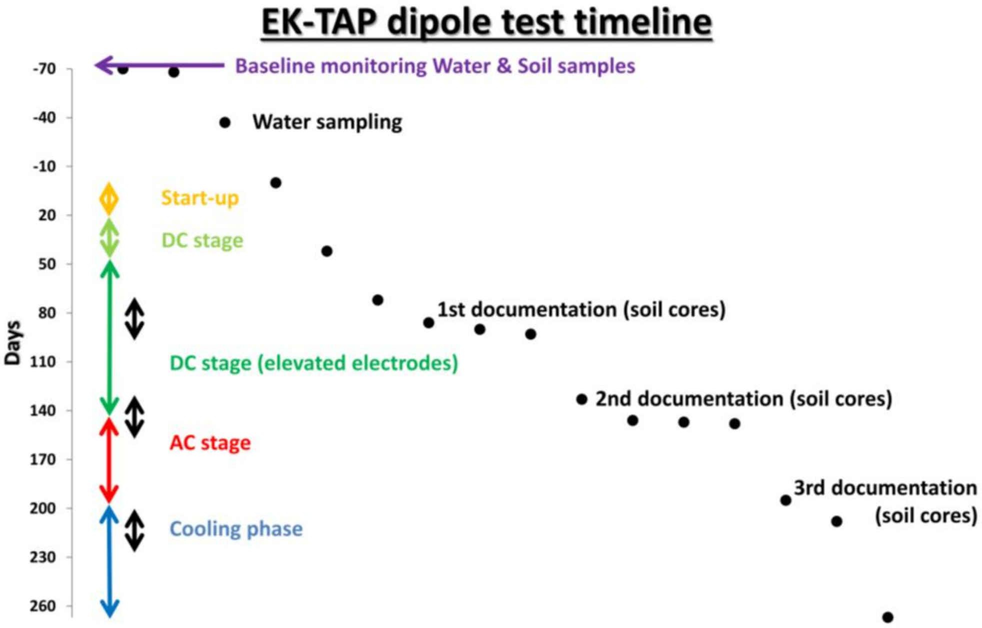

Figure 8.2: Timeline of EK-TAP^{TM} single dipole test including water sampling (monitoring) and soil sampling (documentation).

8.1 Pre-heating, Stage 1 – Preliminary Heating Assessment

During the pre-heating stage, AC power was supplied to the electrodes between 4 May 2015 – 10 May 2015, prior to the EK persulfate migration stage. The target temperature for this stage was 15 ^{o}C (i.e., as much as 5 ^{o}C higher than the expected background soil temperature of 10 ^{o} C). The target temperature was low enough to not result in activation of persulfate and thus a cool-down period would not be required following the stage. Soil and electrode well temperatures were closely monitored during this preheating stage. This stage was conducted to provide field data that could be used to assess the potential for elevated temperatures near the electrode wells (and thus the need for potential contingency measures) and to plan the duration of the post-persulfate migration heating stage. Temperatures were recorded by the PLC at an appropriate interval, once every hour, during this stage of the testing. For monitoring of temperatures by the PLC via the thermistors, externally applied electric fields (both AC and DC) was temporarily removed for the duration of monitoring (likely less than 5 minutes).

Recirculation of liquid in CW, AW and MW1 was temporarily stopped during the pre-heating stage.

8.2 Operational parameters

Table 8.1 lists the operational parameters and target range of operational conditions during Stages 1-3.

Operational Stage	Operational Parameter	Target Conditions[a]
Pre-heating	Target current	10 A
	Target Subsurface Temperature	15 ^{o}C
EK Persulfate Migration	Target voltage between cathode & anode (Target voltage gradient between electrode wells)	150 V (0.5 V/cm) and/or 0.5 A/m^2
	Target pH in electrode wells	pH 6-8
	Water levels in electrode wells	Maintain steady water levels
	Target in situ persulfate concentration	20 g/L
	Target persulfate feed concentration	54 g/L
Soil Heating	Target current	10 A
	Target subsurface temperature	30 ^{o}C

Table 8.1: Pilot test operation parameters and ranges /5/.
Notes: A – amperes, ºC - degrees centigrade, V – volts,
V/cm - volts per centimeter, g/L - grams per liter.

8.3 Initial Operation and adjustments

Some minor adjustments and changes were made to the system during start-up and initial operation (and are shown in an updated PI diagram in figure 8.5):

- KPS (potassium persulfate) was replaced by NaPS (sodium persulfate) as the oxidant due to the higher solubility of NaPS in water. With the necessary (cool) temperatures of the oxidant solution it was not possible to achieve the target feed concentration of persulfate using KPS.

- Temperature was measured in the CW tank through connection to the PLC, in order to avoid activation of the persulfate at raised temperatures.

Furthermore temperature was measured in the CW and AW wells. Air condition was installed in the storage tank room and kept constant at 18 °C, in order to prevent heating of water within the tank system recycled to the wells.

- Water mixing pumps were installed in the tanks in order to help dissolve the added sodium persulfate and buffers.
- Buffer tank and persulfate tank were originally planned to be separated, but due to the slow recharge of the wells, the buffer tank and persulfate tank were connected to reduce the volume of fluid required to be added to the wells. To further prevent well overflow, the closed-loop recirculation between the CW and the measuring probes (pH, EC & temp.) was expanded to include the persulfate/buffer amendment from the CW tank (Figure 8.3).
- Conductivity measurement in AW was moved to MW-1 to be able to measure persulfate breakthrough without the EC measurements being influenced by the added buffer solution in AW.

Figure 8.3: Connection of the buffer tank and the persulfate tank recycling content to CW.

- Adjustments in the concentration feed of persulfate were made during the DC stage. The system setup was able to regulate both amount and frequency of persulfate feed. Adjustments were conducted according to the concentration of persulfate in the tank and to keep a steady level of solution in the cathode well.

Figure 8.4: Overview of installations and recycling pumps.

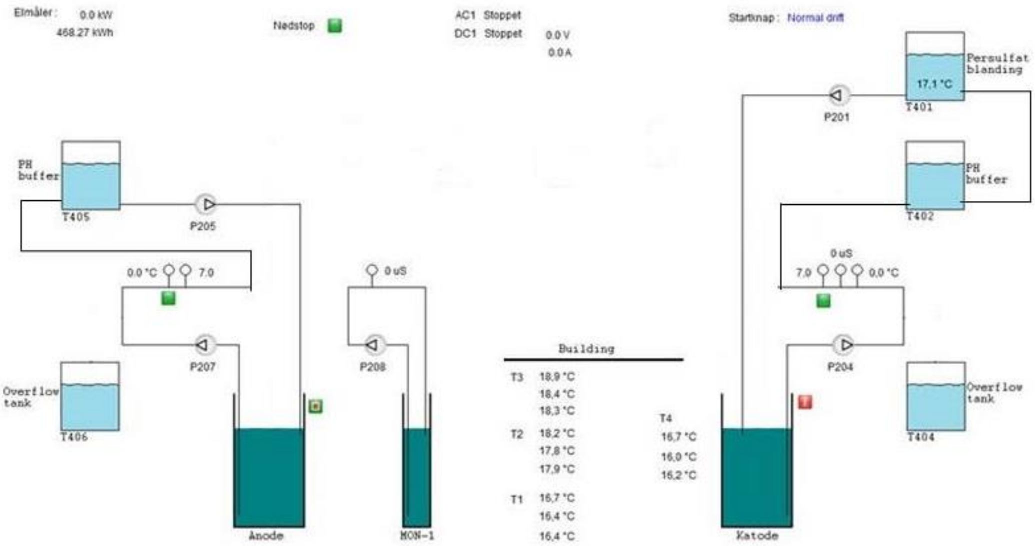

Figure 8.5: PI diagram with adjustments conducted during start-up and initial operation.
For higher resolution see Appendix 3.

8.4 DC-stage, Stage 2 – EK Persulfate Migration

During the EK persulfate migration stage, power was applied to the electrodes using a DC power supply, and persulfate and potassium phosphate buffers were introduced into the subsurface via the cathode well. The anode well was periodically amended with potassium phosphate buffers to control the pH change at this well. Electrodes (1,5 m long) were hung in each well, in the middle of the screen (i.e., 4.25 – 5.75 m bgl) (Figure 8.6). Electrodes were raised 1,5 m (2.75 - 4.25 m bgl) on 19 Aug. 2015 (day 42 after start-up) to offset tip effects of the electrodes driving the electric field below the target treatment zone. Electrical field lines are simulated for before and after elevation of electrodes in Figure 8.6. The EK migration stage with elevated electrodes was run for 15 weeks until November 30, 2015. This EK stage was operated for a total period of 21 weeks.

The distribution of the electric field within the target treatment interval of the pilot test area was monitored by determining the voltage gradient between a passive electrode inserted in each of the monitoring well screens and the electrode wells. Electrical potential measurements were conducted from CW, MW2, TW4, TW1/TW2/TW3 to AW. Process control parameters (i.e. voltage, pH, and electrical conductivity) were monitored to evaluate process control requirements. In addition, the total volume and flow rate of persulfate and pH buffers into the system were monitored and recorded.

Table 8.1 lists the operational parameters and target range of operational conditions during Stage 2.

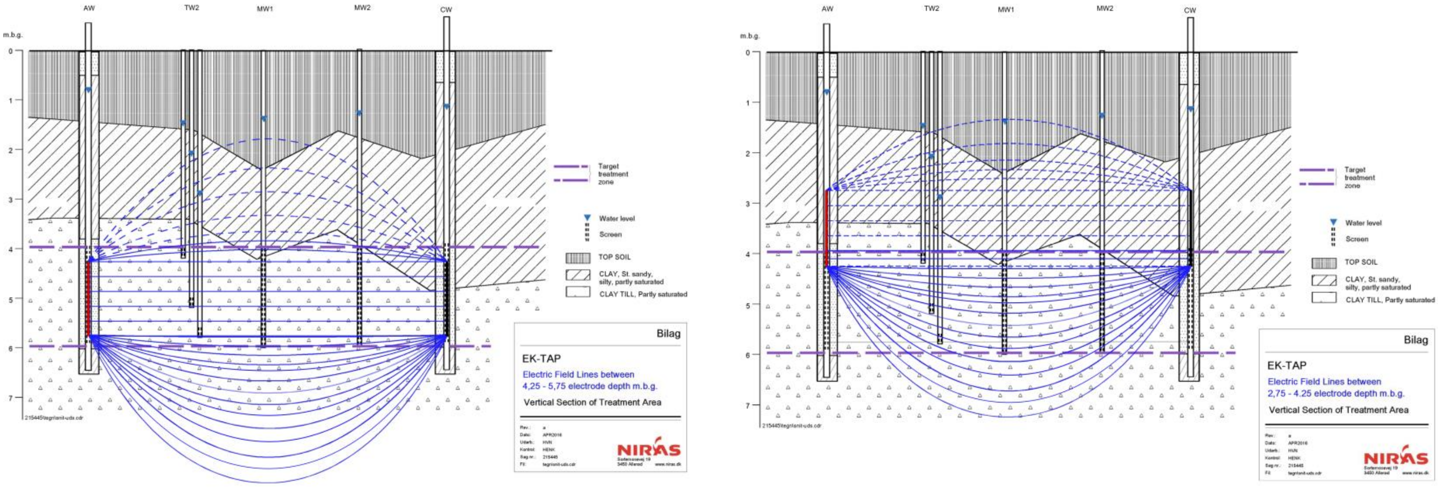

Figure 8.6: Conceptual depiction of electrical field during pilot test study before (4.25-5.75 m bgl, left figure) and after elevation (2.75-4.25 m bgl, right figure) of electrodes (Elevated 19 Aug. 2015). For higher resolution see Appendix 11.

8.4.1 *Injection of persulfate*

The persulfate injection solution was prepared in batches by mixing the required amount of persulfate with a specific amount of water to achieve the target feed concentration. The persulfate solution was then added to the cathode tank along with the buffer solution, from which its content was pumped to the cathode well. Table 8.2 presents the amount of NaPS used during the pilot test.

Date	NaPS (kg)
12.08.2015 – 29.09.2015	10
29.09.2015 – 19.10.2015	10
19.10.2015 – 19.01.2016	25
TOTAL	**45**

Table 8.2: Amounts of added persulfate to cathode tank.

8.4.2 *Setup - Persulfate Concentration*

Based on results of the laboratory optimization batch testing and preliminary cost-benefit analysis, an in-situ persulfate amendment concentration of 20 g/L was recommended to be targeted for the pilot test. To achieve this in-situ concentration, a feed concentration of 54 g/L was required.

8.4.3 *Persulfate Transport Rate vs. Electrode Well Spacing*

Based on the electron donor transport rates observed at the Skuldelev field site and in the bench-scale testing and modeling /4/, it was assumed that persulfate transport rates greater than 5 cm/day could be achieved. The overall duration of the EK persulfate migration stage of the pilot test was based on the achievable transport rate. Transport rates were intended to be monitored by measuring breakthrough at both monitoring wells and the anode well, but due to a lower transport rate than expected, HPT logs and soil coring were conducted in order to document persulfate breakthrough close to the injection point (CW) (Se section 9).

8.4.4 *Persulfate Dosing Schedule*

Persulfate loading to the cathode well was a function of the mass flux of persulfate into the pilot test area delivered by the cathode well. The dosing rate to the cathode well required tuning in the field during system start-up. The dosing rate was changeable via the PLC. Based on laboratory studies /4, 5/, the initial target dosing rate of persulfate was 1.3 kg per day and this was originally attempted to be maintained during the persulfate migration stage. The actual dosing rate was limited by the low permeability of the soil near the CW (slow return of the water level in the well to equilibrium following dosing) and by the actual solubility of persulfate at operating temperatures. The actual average dosing rate of NaPS was 0.4 kg per day. The transition from stage 2 (EK migration stage) to stage 3 (heating stage) was intended to be triggered by observed breakthrough of persulfate in both monitoring wells and the anode well /7/.

Given that the actual migration was slower and more laterally widespread than assumed the transition from stage 2 to stage 3 was initiated when persulfate distribution from CW to MW1 was documented.

8.5 AC-stage, Stage 3 – Soil Heating

Once persulfate migration across at least half of the test area was achieved (based on soil and groundwater data), a third stage of operation (soil heating stage) was carried out, in which AC power was supplied to the electrodes for a period of 9½ week in order to allow subsurface temperatures in the target treatment interval of the pilot test area to reach and maintain the target persulfate activation temperature of 30 ^{o}C for a minimum of 7 days. Temperatures were recorded by the PLC at an appropriate interval, once every hour, during this stage of the testing.

The amendment supply units and manifolds were disconnected during this part of the testing.

Table 8.1 lists the operational parameters and target range of operational conditions during Stage 3.

8.6 Cooling stage, stage 4

Following the heating stage, the AC power source was disconnected and the system allowed to cool back to ambient levels. Temperatures were recorded by the PLC at an appropriate interval, once every hour, during this stage of the testing.

8.7 Power consumption and essential changes

8.7.1 Voltage and Amperage

The target voltage gradient between the electrodes during the EK persulfate migration stage was planned to 0.5 V/cm. The system was intended to be operated in constant current mode (estimated at 0.5 A/m^2), similar to the operational parameters at the Skuldelev field site, with a PLC-controlled limiter such that the voltage gradient did not exceed 0.5 V/cm. The actual electrical gradient achievable depends on the electrical properties of the soil, such as electrical conductivity, and as such was to be assessed during system start-up. Current adjustments during operation are summarized in Table 8.3.

Date	Voltage
17 Aug. 2015	Increase in current from 2 to 2.5 A
25 Aug. 2015	Increase in current from 2.5 to 3 A. (Start voltage 56.4 V)
30 Nov. 2015	Wiring changed to AC power supply

Table 8.3: Table of voltage adjustments during EK-TAP^{TM} system operation.

The design current for the soil heating stage was supplied to the electrodes in a similar manner as the DC stage. During the heating stage, the current was increased from 6 A initially to 10 A at the end of this stage.

8.7.2 *Power consumption heating stage*

Total power consumption from startup date to 27 May 2016 amounts to 5,466.52 kWh.

During the heating stage a total of 4,710 kWh were used for heating the soil. In Figure 8.7 the hourly distribution of power consumption is shown.

The gradual increase in power consumption is likely a result of the manual increases in current, and the resultant increase in voltage.

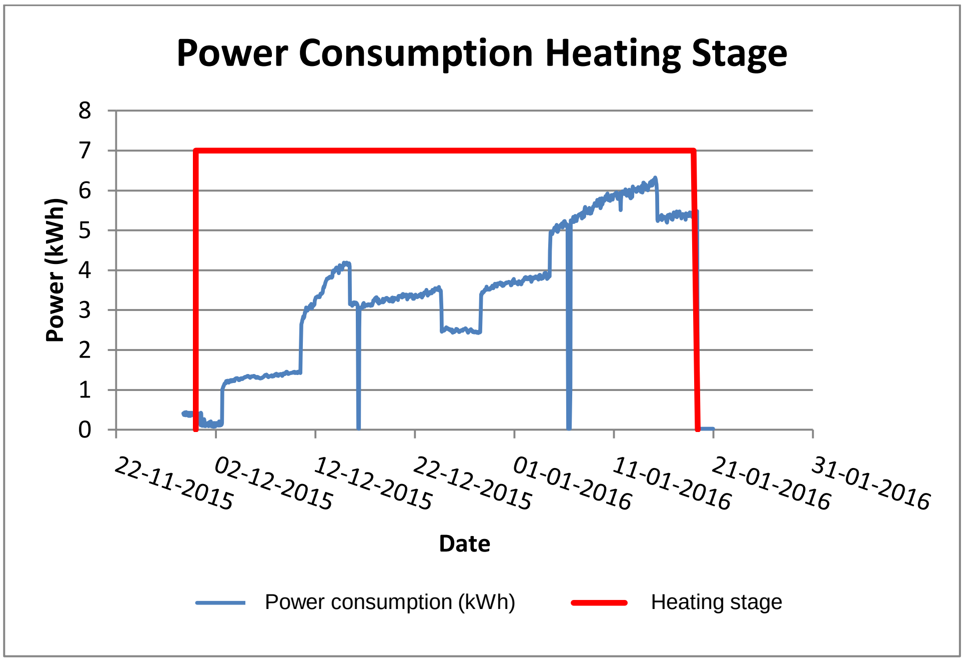

Figure 8.7: Power consumption during the heating stage.

9 MONITORING AND DOCUMENTATION

9.1 Process monitoring

Table 9.1 summarizes the monitoring elements related to system operational parameters. Table 9.2 summarizes the groundwater and soil performance monitoring program elements. The actual sampling events and extent for water and soil samples can be seen in Appendix 6 (water) and Appendix 8 (soil).

The electrical potential and current were measured manually, the current with a current clamp.

Temperatures within the target treatment interval were recorded continuously by the PLC during the AC stage of the testing and by hand through field measurements during the DC stage of the testing.

The concentration of NaPS was measured in the CW tank during each visit to the site (approx..weekly) to determine the mass used as well as the dosage.

EC (Electrical conductivity) was measured continuously in CW and MW1 using a closed-loop recirculation system, whereby water from each of the two wells was pumped from the well, through an EC analyzer and then re-introduced into the well via the water addition drop tube. EC-measurements were recorded by the PLC.

Parameter	Frequency
Power supply voltage & current	Continuous
Electrical potential	Weekly (DC)
pH in electrode wells	Continuous
Thermistors	Continuous (AC)
Fluid levels in electrode wells	Continuous
All mechanical components	Weekly (DC) / Bi-weekly (AC)
Amendment supply & replenishment	Weekly (DC)

Table 9.1: Pilot test process monitoring program.

Operational Stage	Media	Location	Sample Type	Parameters	Frequency
EK Persulfate Migration	Groundwater	Electrode & monitoring wells	Groundwater sample	Field parameters[a], VOCs, sulfate, persulfate[b], chloride	Bi-weekly[c]
	Soil	Soil borings	Soil sample	VOCs, sulfate, total sulfur, chloride	Post-EK persulfate migration[d]
Soil Heating	Groundwater	Electrode & monitoring wells	Groundwater sample	Field parameters[a], VOCs, sulfate, persulfate[b], chloride	Bi-weekly[c]
	Soil	Soil borings	Soil sample	VOCs, sulfate, total sulfur, chloride	Post-soil heating

Table 9.2: Performance monitoring program.

(a): Field parameters include pH, dissolved oxygen, oxidation reduction potential, electrical conductivity & temperature

(b): Persulfate laboratory analysis using method described by Huang et al. 2002.

(c): Once every second week

(d): Soil samples were collected once sulfate breakthrough was observed (based on groundwater data)

Electrical potential

Electrical potential measurements were conducted from AW to each of CW, MW2, TW4, TW1/TW2/TW3. Electrical potential measurements were conducted 17 times during a period between 31 July 2015 – 30 Nov. 2015. Figure 9.1 presents selected electrical potential measurements.

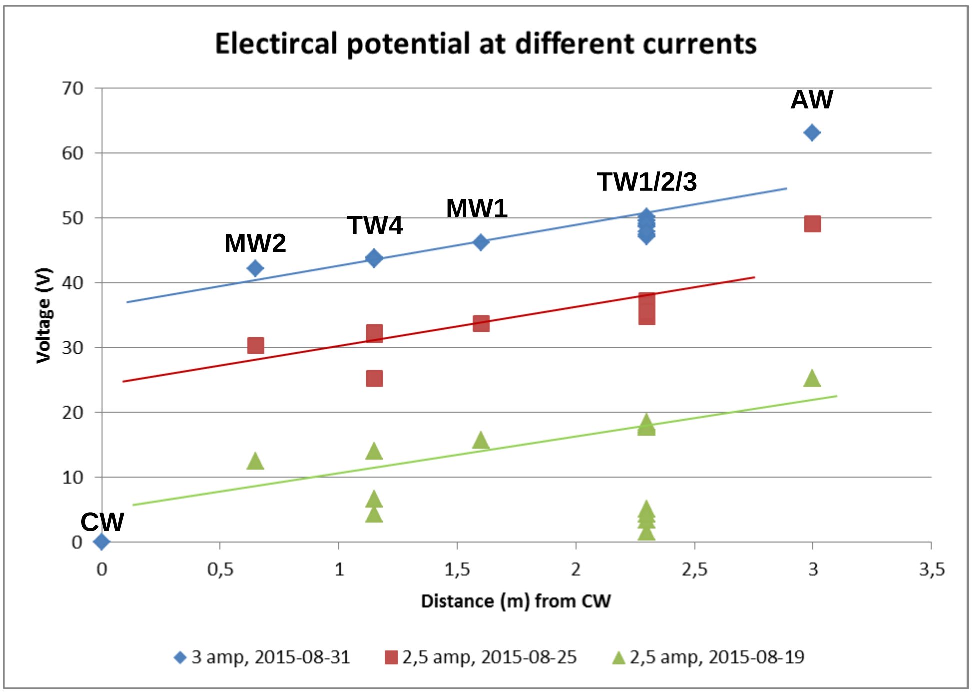

Figure 9.1: Selected electrical potential measurements. 2015-08-19 data is from before elevation of the electrodes.

The voltage gradient across the majority of the system was linear and equal to approximately 0.4 V/cm at the end of the migration stage (stage 2). The majority of the voltage loss in the system, particularly at higher applied currents occurred in the vicinity of the cathode well, likely due to lower water saturations in this region (as was seen during well installation). Elevating the electrodes within the wells changed the in-situ voltage gradient from 0.06 V/cm to 0.16 V/cm after which the voltage gradient gradually increased to 0.4 V/cm during the remainder of stage 2. The voltage step changes in the vicinity of the cathode well increased in proportion to the increased amperage, indicating that the majority of the current loss (highest soil resistance) is in the vicinity of the cathode well. This may be due to a lower water content or differences in the soil structure in the vicinity of the cathode well. Raising the electrodes likely resulted in a more effective distribution of the electric potential field within the target treatment area.

9.2 Performance monitoring and documentation

During the EK persulfate migration and soil heating stages (stages 2 and 3), bi-weekly (i.e., once every two weeks) collection of groundwater samples from the monitoring wells and the anode well (see Figure 9.2. for locations) was performed and samples were analyzed for field parameters (pH, DO, ORP, conductivity, temperature), sulfate and persulfate, VOCs and chloride.

During sampling of water and soil samples both AC and DC power was temporarily shut-off for the duration of the sampling.

The monitoring program was adjusted several times during the DC stage in response to changes in the understanding of the system as new results came in and as new monitoring wells were installed. Water and soil samples for chloride and VOC analysis taken during and post operation were preserved with ascorbic acid in order to prevent oxidation of VOC’s after sampling. Subsequently the chloride analyses were performed by Højvang, a different laboratory, using a different analytical method than the one who performed the baseline analysis (ALS).

Due to an apparent slower persulfate migration rate than anticipated and lack of persulfate and EC breakthrough in MW1, the performance monitoring was extended to include HPT logs, soil cores, and hand drilled borings during stage 2. Once sulfate breakthrough was observed (based on groundwater data collected during stage 2 operation), HPT logs were carried out to investigate alternate pathways for persulfate migration. As part of the HPT program, soil cores were collected and analyzed for total sulfur and sulfate soil concentrations, as well as VOCs and chloride. Each soil core was collected from a location that was evaluated at appropriate distance from the cathode and the central monitoring well. At each location, soil samples were collected from 2.5 m bgl up to maximum 7.7 m bgl. Installation of hand drilled borings (MW3, HB1-4) is described in section 6.1.2 and 6.1.4.

Following the soil heating stage, soil cores (Table 9.3) were collected from locations adjacent to baseline soil sampling locations to document persulfate migration and VOC oxidation. Soil samples were collected in the depth interval 4-6 m bgl from each location and submitted for laboratory analyses for the same parameters as those of baseline sampling.

Following the soil heating stage, temperatures within the pilot test area were continuously monitored until they declined to approximately 15 °C.

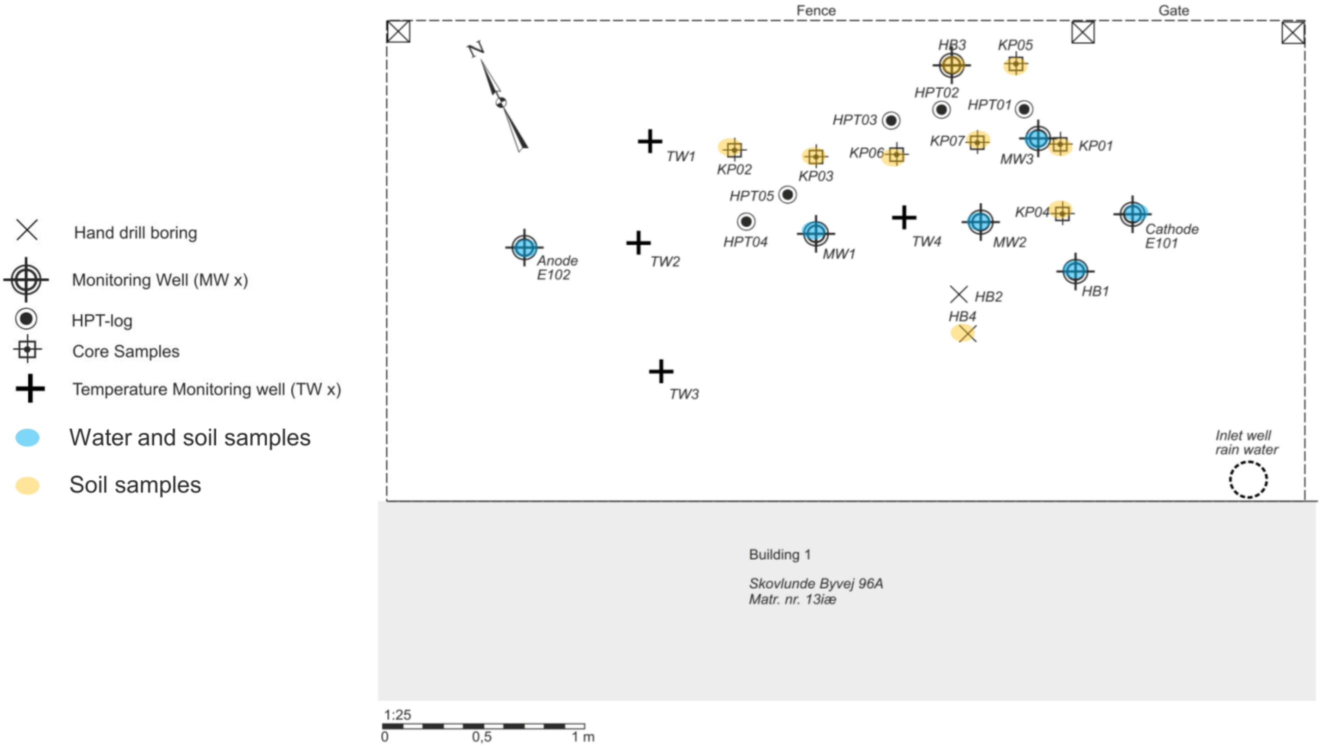

Figure 9.2: Overview of documentation points during EK-TAP^{TM} pilot test study.

HPT conductivity profiles

HPT/electrical conductivity logs were conducted at 6 locations, HPT01-HPT05 and a reference HPT outside the test area. Results are presented in Figure 9.3 and Appendix 7. The location of the HPT profiles is shown in Figure 9.2 and Appendix 1. HPT conductivity profiles were conducted during the pilot test study in order to document breakthrough of persulfate as well as evaluation of locations for core sampling and selection of soil plugs from soil cores for laboratory analysis.

Initial HPT tests were conducted halfway through the migration stage (HPT01, HPT02 and reference test and core sample KP01). HPT03, HPT04 and HPT05 were conducted together with core samples KP03 and KP04 at the end of the migration stage.

Figure 9.3 presents HPT conductivity profiles 1-5 overlain on the background reference. Within the target treatment zone (4-6 m bgl) electrical conductivity is increased for HPT01 and HPT04 in comparison to background reference conductivity. EC reaches approximately 550 mS/m in HPT01 within the target treatment zone, while HPT04 reaches approximately 100 mS/m (Figure 9.3). At HPT02 and HPT03, smaller but significant increases in conductivity as compared to the background values can be seen at 5.5 and 6.2 m bgl in HPT02 and at 4.4 m bgl in HPT03. At HPT05, the conductivity approaches background levels, except for slightly elevated levels at 5.5-6.0 m bgl and 6.4-6.6 m bgl.

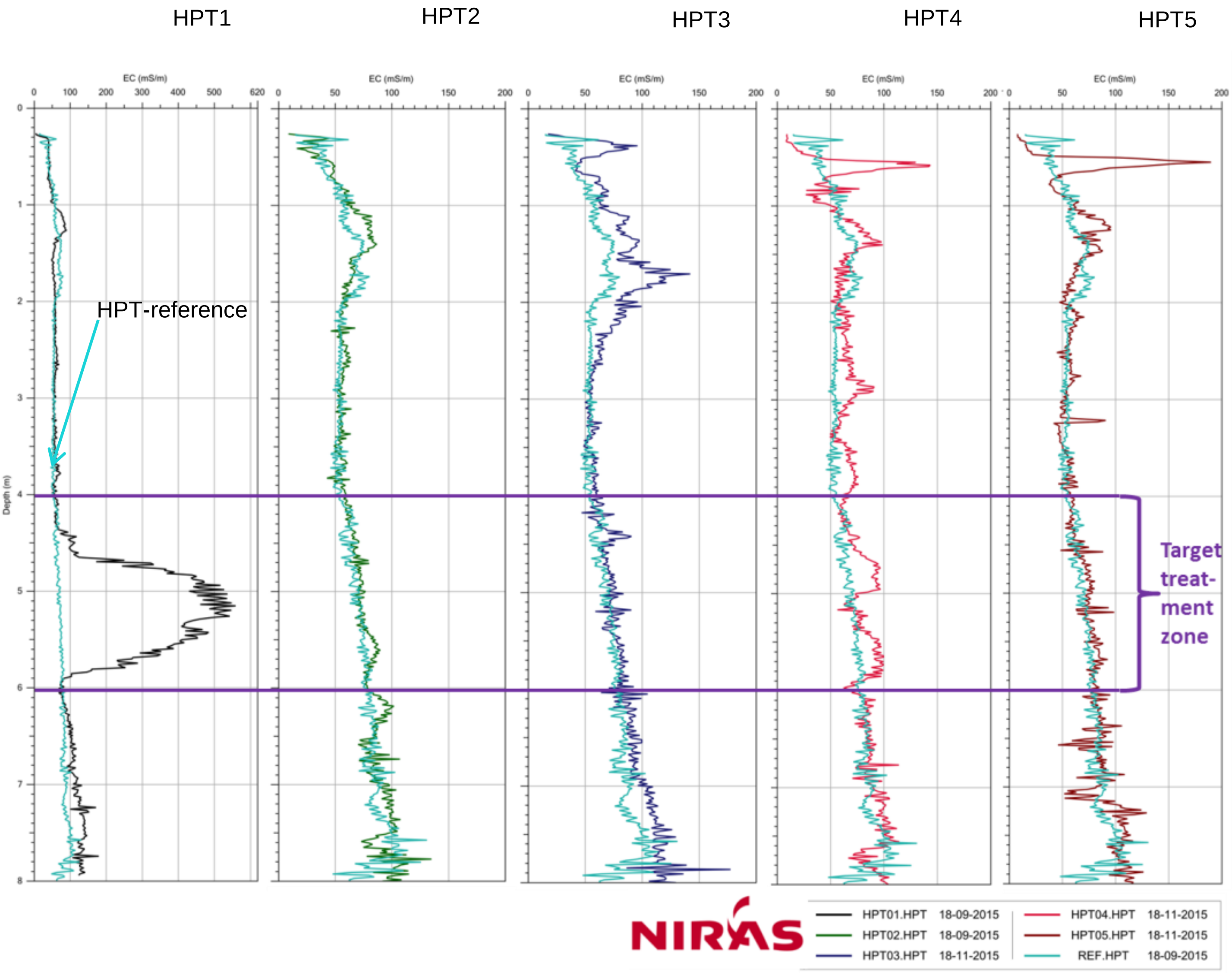

Figure 9.3: HPT conductivity profiles HPT01-HPT05 compared to background reference HPT.

When comparing the EC profile from HPT01 with concentrations of sulfate and total sulfur (Figure 9.4 & Appendix 7) a correlation between EC, sulfate and total sulfur is clearly present indicating that the increased conductivity is due to the presence of persulfate and/or sulfate.

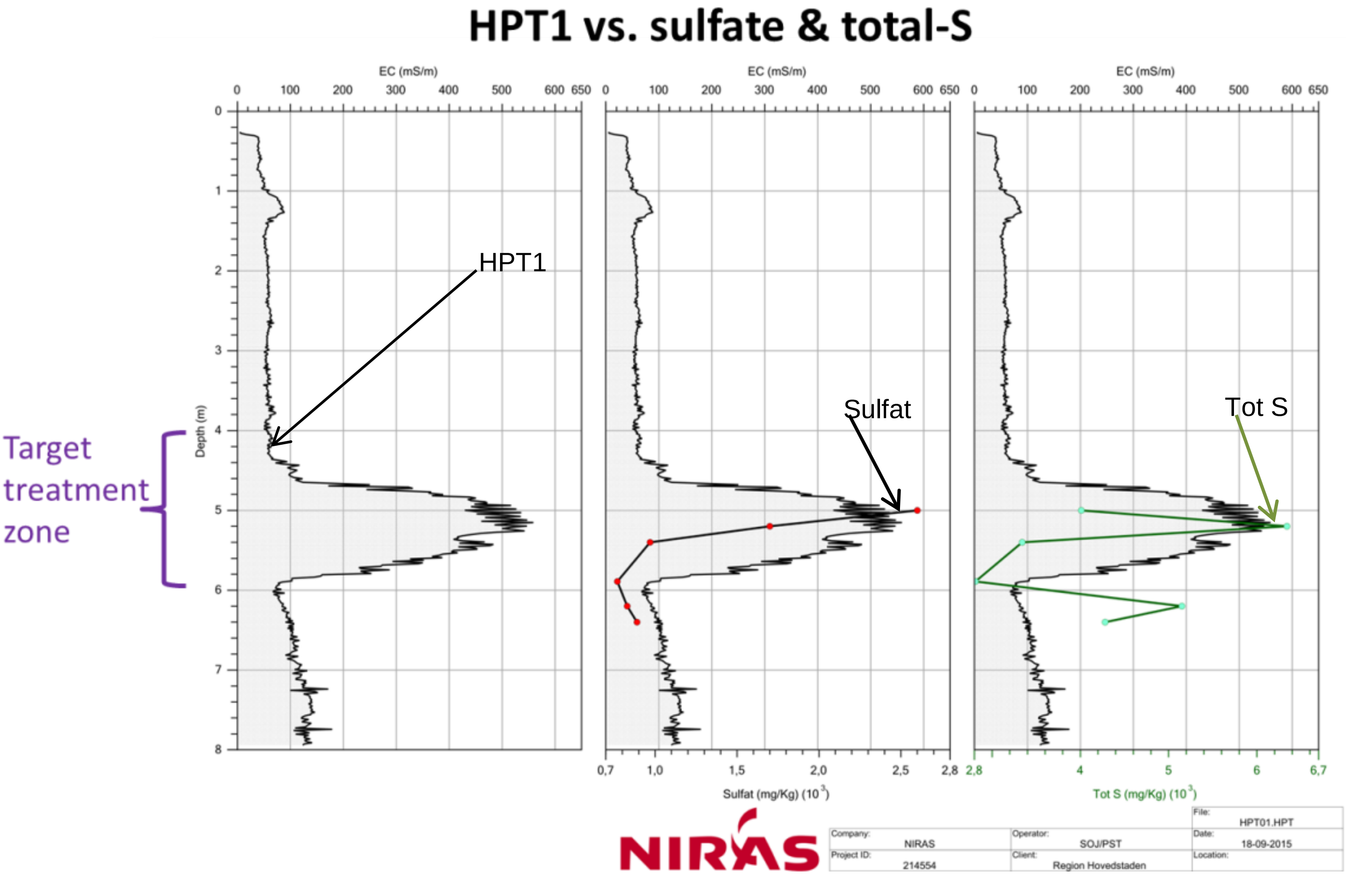

Figure 9.4: HPT01 log compared with sulfate concentrations and total sulfur concentrations within target treatment zone.

Core samples

Soil core samples (KP01-KP07) were collected using NIRAS' GeoProbe system. NIRAS performed cutting of the cores (KP01-KP07), conducted a geological assessment, took PID readings and subsequently soil extractions for lab analysis and photographed the drilled cores. The location of the soil cores is shown in Figure 9.2.

Core samples were taken at three times in September 2015 and November 2015 (during migration stage), and February 2016 (post-heating), respectively. The soil core samples were cut open in NIRAS' lab where geological assessment and PID measurements were conducted as well as measurement of electrical resistance in order to target subsampling for chemical analysis at depths with potentially high concentration of persulfate. Soil core sampling was mainly conducted within the target treatment area from 4–6 m bgl. Specifications of core samples are given in Table 9.3. Well logs are presented in appendix 9. Analytical reports are attached in appendix 10.

Core	Sampled	Cored interval (m bgl)	Core length (m)
KP01	21 Sep. 2015	4.5 – 6.5	2
KP02	19 Nov. 2015	4.3 – 6.3	2
KP03	19 Nov. 2015	4.0 – 8.0	4
KP04	27 Jan. 2016	4.0 – 6.0	2
KP05	27 Jan. 2016	4.0 – 6.0	2
KP06	27 Jan. 2016	4.0 – 6.0	2
KP07	05 Feb. 2016	4.0 – 6.0	2

Table 9.3: Soil core specifications.

10 RESULTS

10.1 Water samples

Analytical results of water samples from monitoring wells, Cathode (CW) and Anode (AW) wells are tabulated in appendix 6. Analytical reports are presented in appendix 10.

10.1.1 Field parameters

Due to the injection of buffer in AW and buffer + persulfate in CW, both wells exhibit very high conductivity and as a result measurements of conductivity in the electrode wells are not considered as representative for the conditions within the soil formation. AW and CW are therefore excluded from the graphs to better focus on in situ measurements of conductivity, pH and temperature. Therefore only the monitoring wells MW1 – MW3 are used as indicators of the conditions regarding field measurements within the soil formations.

- Electrical Conductivity (EC): In general the inline data supports the manual field measurements. For monitoring wells MW1 and MW2, slight increases in EC are observed during the migration and heating stages (Figure 10.1). EC in MW3 decreases during the migration stage and increases during the heating stage. Data for MW3 begins at its installation in October 2015.

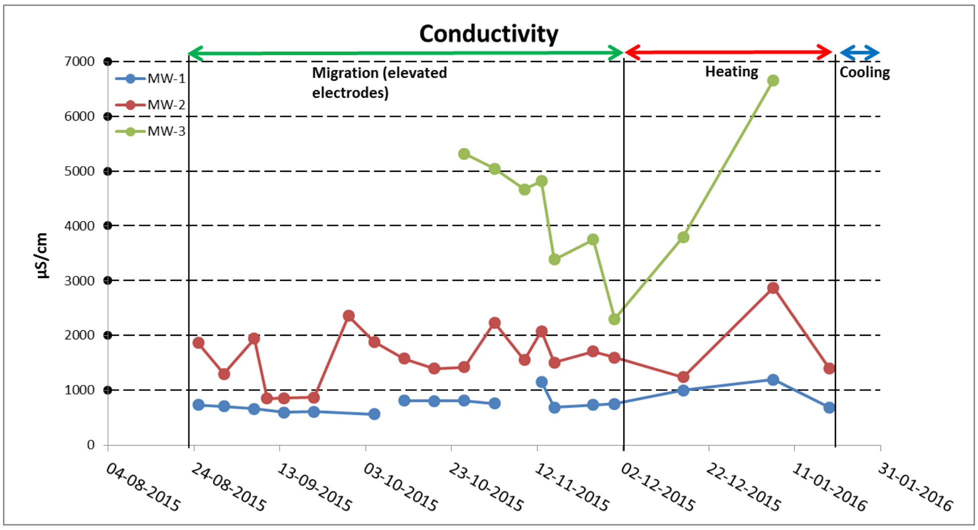

Figure 10.1: EC measurements in monitoring wells MW1-MW3.

- pH levels were well controlled by the buffer system in the electrode wells (AW & CW), which were measured continuously in response to maintain desired neutral pH levels (6 – 7). pH data from the PLC are shown in appendix 4.

- pH readings from monitoring wells MW1 and MW2 are presented in Figure 10.2 and are seen to fluctuate during the DC migration stage, but are overall at neutral to slightly basic levels ranging between 7.0 – 8.3. In general pH, measurements are higher in MW1 than in MW2. A decrease in pH during the heating stage was observed for both MW1 and MW2 to a minimum of 7.1 for MW1 and 6.8 for MW2 (Figure 10.2).

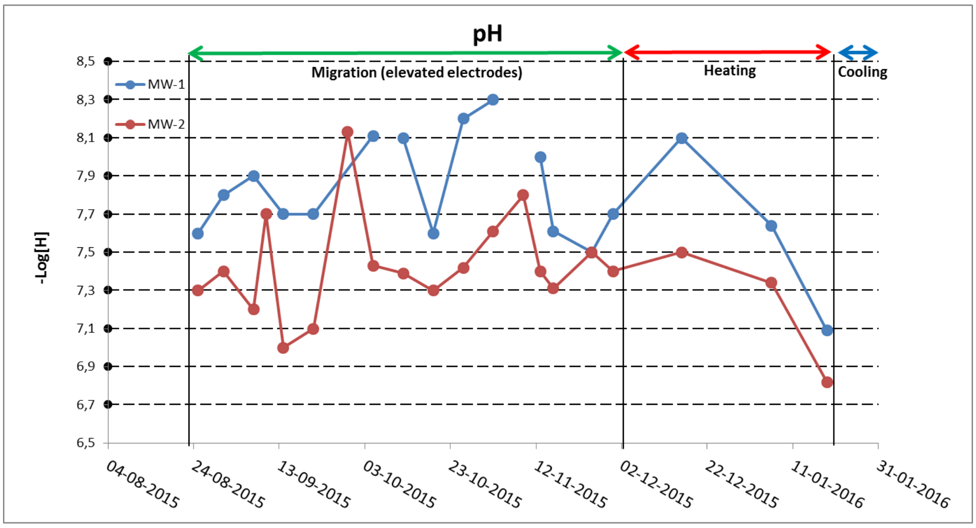

Figure 10.2: pH field measurements for monitoring wells MW1 and MW2.

- Temperatures of water samples are seen to fluctuate during the DC migration stage, with fluctuations being more pronounced in MW2 than in MW1. Temperatures for MW1 ranged from 13.2 – 16.2 °C, while MW2 ranged from 12.8 – 17.9 °C during the DC migration stage (Figure 10.3). The slightly decreasing temperature during the migration stage is probably due to the natural change in temperature throughout the year.

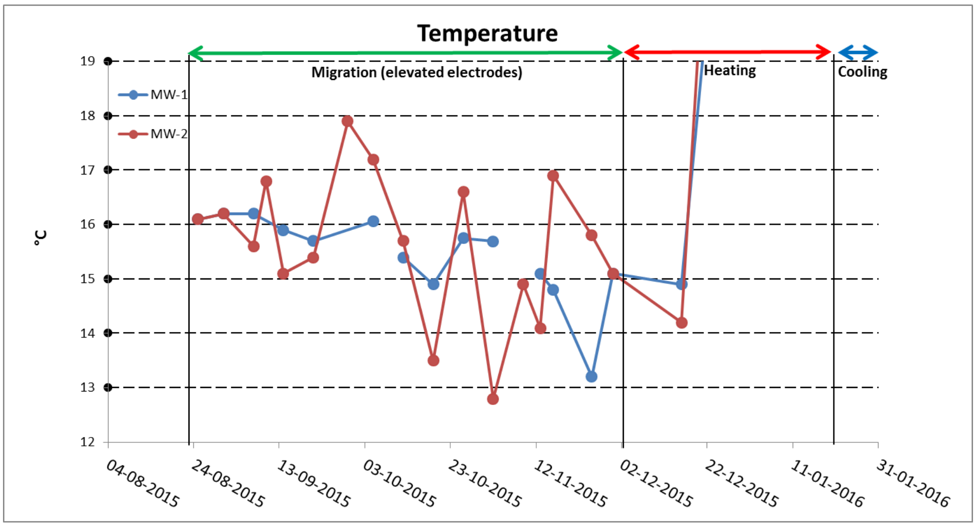

Figure 10.3: Field temperature measurements for monitoring wells MW1 and MW2.

10.1.2 *Distribution of sulfate and NaPS*

NaPS (persulfate) concentrations in groundwater measured during the pilot test are presented in Figure 10.4. Background (baseline) concentrations of persulfate were non-detect. An increase in persulfate was observed at MW2 8 weeks after the start of the DC migration stage following the elevation of the electrodes (Elevated 19 Aug. 2015). Persulfate was present at high concentrations in MW3 immediately following its installation in October 2015 (Figure 10.4). The concentration trend of persulfate in MW3 is generally decreasing within the DC migration stage, although a peak is observed at the end of the stage. During the heating stage there is an increase of NaPS followed by a decrease to non-detect levels. It is of note that MW3 is hand drilled and of small diameter resulting in very small purge volumes during water sampling, which potentially could influence the results.

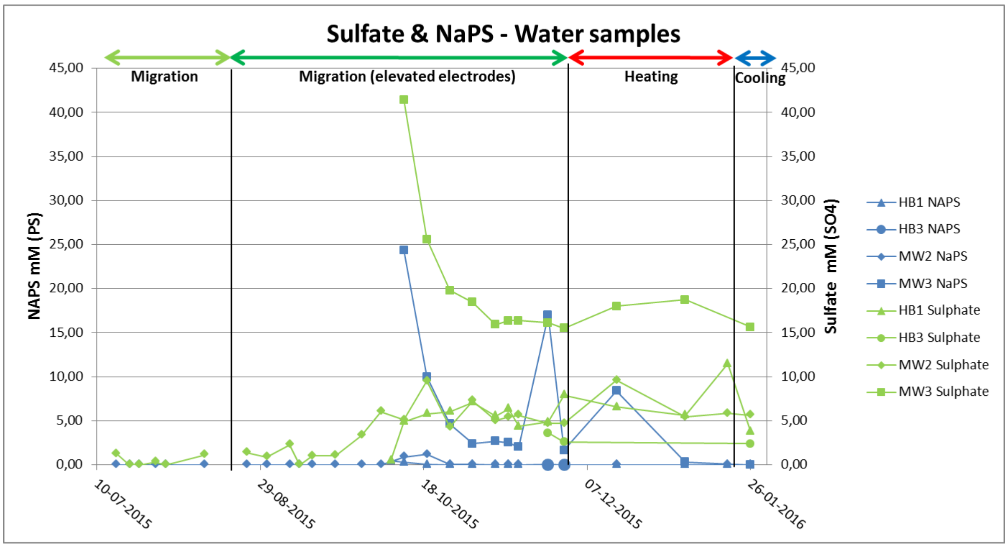

Figure 10.4: Distribution of sulfate and NaPS in water samples during the pilot test.

In general, sulfate concentrations were higher than NaPS concentrations at the monitoring wells. Given that 1 mole of NaPS contains 2 moles of SO_4, this is expected, and the molar ratio of sulfate to NaPS in the samples is close to this 2:1 ratio. Increasing concentrations of sulfate are observed for HB1, HB3 and MW2 during the migration stage (once elevation of electrodes was performed). The sulfate concentration in MW3 rapidly dropped from the levels seen immediately following its installation before levelling off during the heating stage.

10.1.3 *Distribution of PCE*

PCE baseline concentrations in water from MW1 and MW2 were measured at 170.000 and 110.000 µg/l respectively (Appendix 6). Overall, a decrease in PCE concentrations was observed during the DC migration stage followed by an increase/rebound at the end of the heating stage and cooling stage (Figure 10.5). Water sampling data are presented in appendix 6. It should be noted that DNAPL PCE was detected in MW1 during water sampling on January 26, 2016.

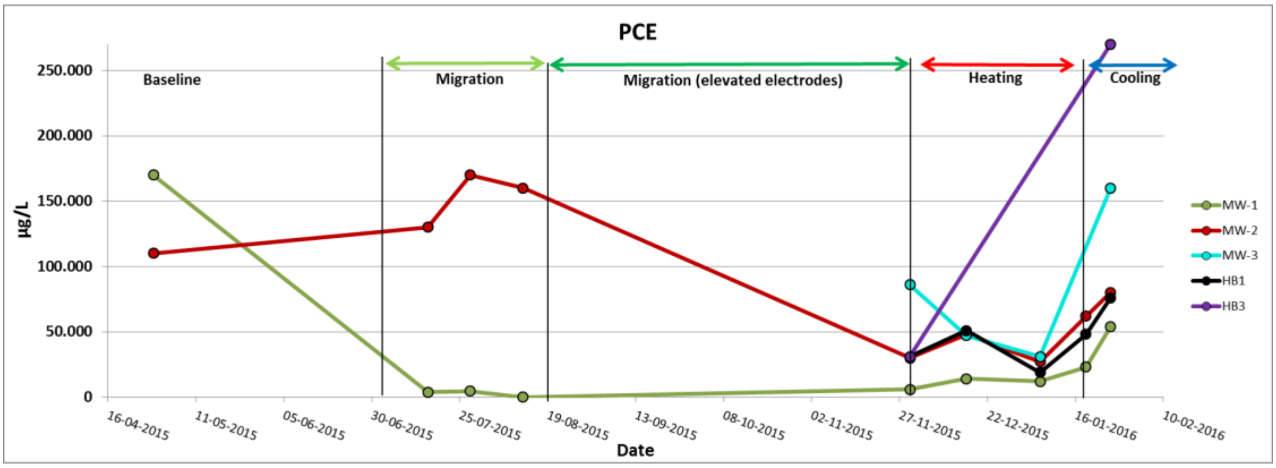

Figure 10.5: Distribution of PCE in water samples during the pilot test.

10.1.4 *Distribution of Chloride*

The concentrations of chloride in groundwater were measured during the pilot study and observed to increase in CW, MW1 and HB1, while a more steady-state or decreasing trend was observed in MW2 and MW3 (Figure 10.6). Concentrations of chloride in water samples ranged from 0 – 210 mg/L, with highest concentrations measured in the cathode well during the cooling stage. Water sampling data are presented in appendix 6.

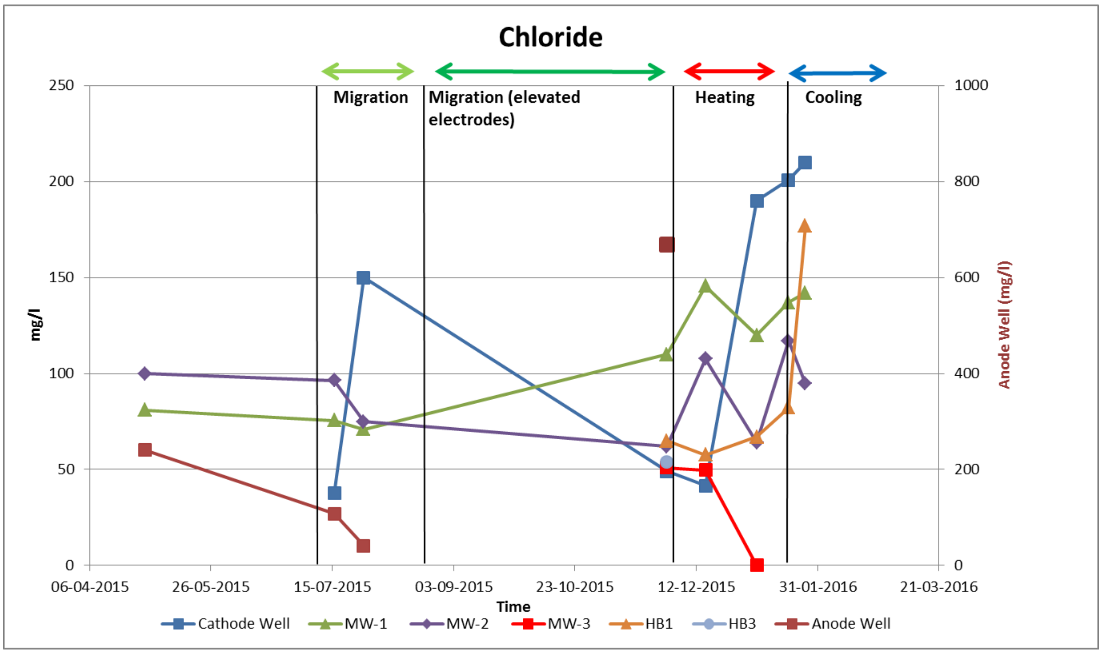

Figure 10.6: Chloride concentrations measured in water samples during the pilot test.

Figure 10.7 presents the maximum concentration of chloride in soil and groundwater measured over time and depth during the pilot study and reflects the spatial distribution of chloride within the test area. There appears to be a trend consisting of higher chloride concentration measured in soil in the middle of the test field, and decreasing chloride to both the north (HB3) and south side (HB4), however data to the south are fairly sparse.

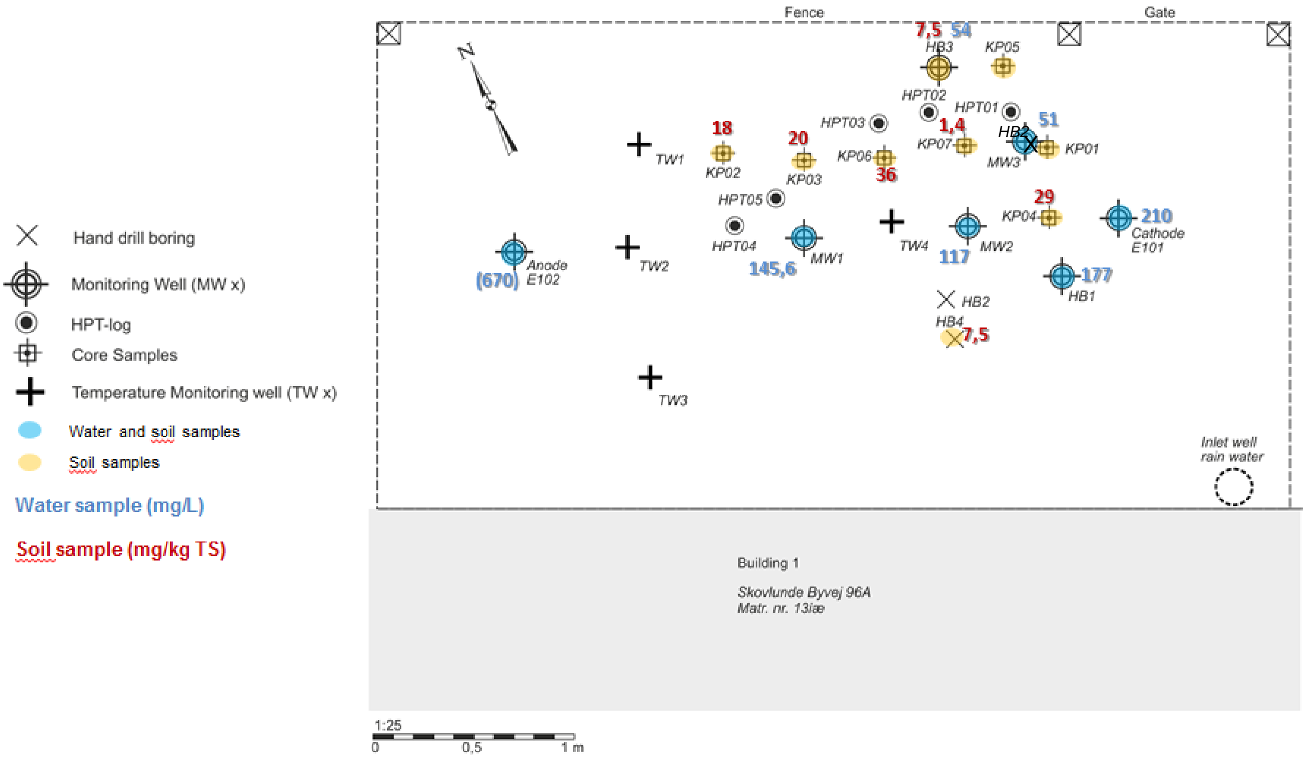

Figure 10.7: Maximum concentrations of chloride measured over time and depth in both water and soil samples. Concentration in parenthesis is considered unreliable.

Although only a few data points exist, the same trend could be seen for chloride in ground water with approximately 50 mg/l to the north and above 100 mg/l in the middle of the test field. Unfortunately chloride was not analyzed at the Anode Well during the heating stage, and the concentration measured at the end of the migration stage (670 mg/l) seem unrealistically high and is thus considered unreliable. Based on the rest of the chloride data, the highest concentrations are found in the cathode well and elevated concentrations are found between the cathode well and MW1.

10.2 Soil samples

The following chapter presents and discusses the results of soil sample analyses for sulfate, PCE and chloride. Data are presented in the figures below and in appendix 8, and analytical reports are attached in appendix 10.

10.2.1 Sulfate

During each soil sampling event, multiple samples were taken from within the target treatment interval. The average sulfate concentrations in these soil core samples are presented in Figure 10.8. In general, an increasing trend in sulfate concentrations in soil samples during the pilot test can be observed. Baseline concentrations were 65.5 mg/kg and increased to greater than 490.0 mg/kg during the migration stage. Average sulfate concentrations measured during the cooling stage were approximately an order and a half of magnitude higher than baseline (between 3680 – 6550 mg/kg).

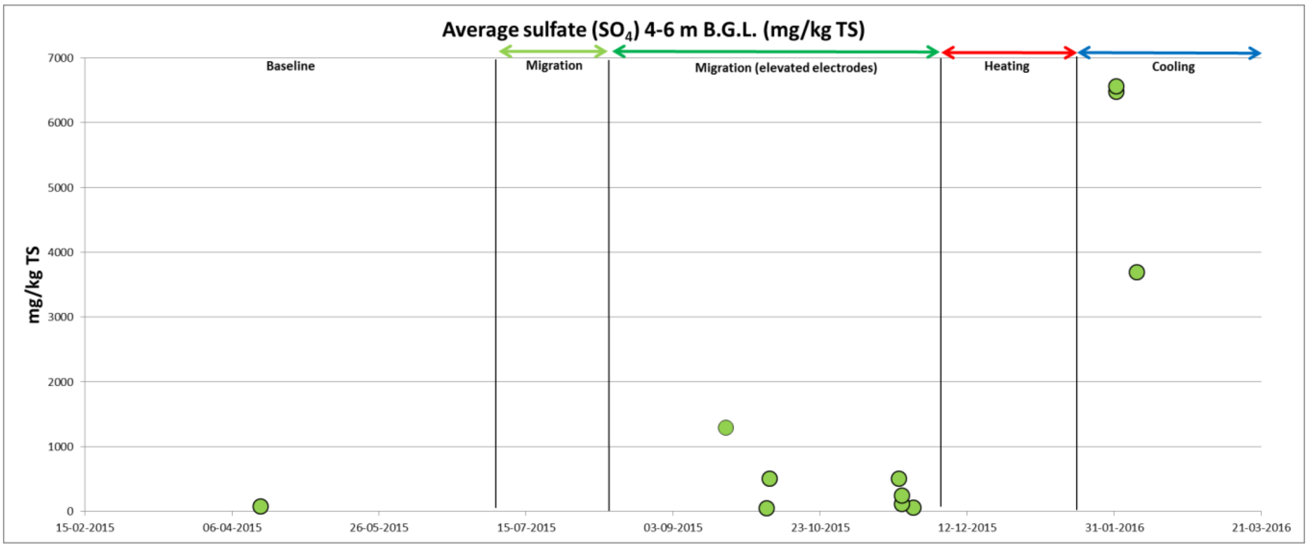

Figure 10.8: Average sulfate concentrations measured in soil samples 4-6 m bgl.during pilot test.

In addition to the increase in sulfate concentration following heating, it appears that in general sulfate concentrations are also seen to increase with depth within the target treatment area (Figure 10.9).

It should be noted that the potential exists for the sulfate analytical results from soil to be comprised of a mixture of sulfate and persulfate. The analytical techniques used for soil samples cannot differentiate the two and will report persulfate as sulfate.

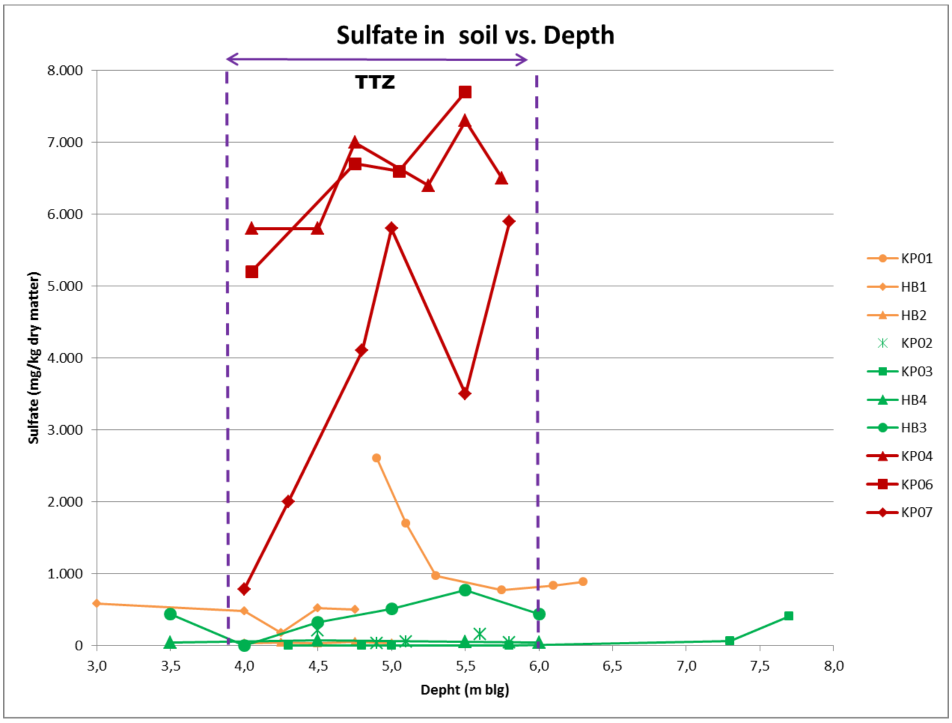

Figure 10.9: Sulfate concentration in soil vs depth. Yellow represents early in the migration stage, green late in the migration stage and red the end of the heating stage.

10.2.2 *PCE*

Average PCE concentrations in soil core samples for each borehole/core are presented in Figure 10.10. No clear trends are observed in average PCE soil concentrations. Baseline concentrations were measured between 121.6 and 179.0 mg/kg. Measured PCE concentrations ranged between 102 and 214 mg/kg during the DC migration stage and ranged between 113.8 and 175.5 mg/kg during the cooling stage (Figure 10.10).

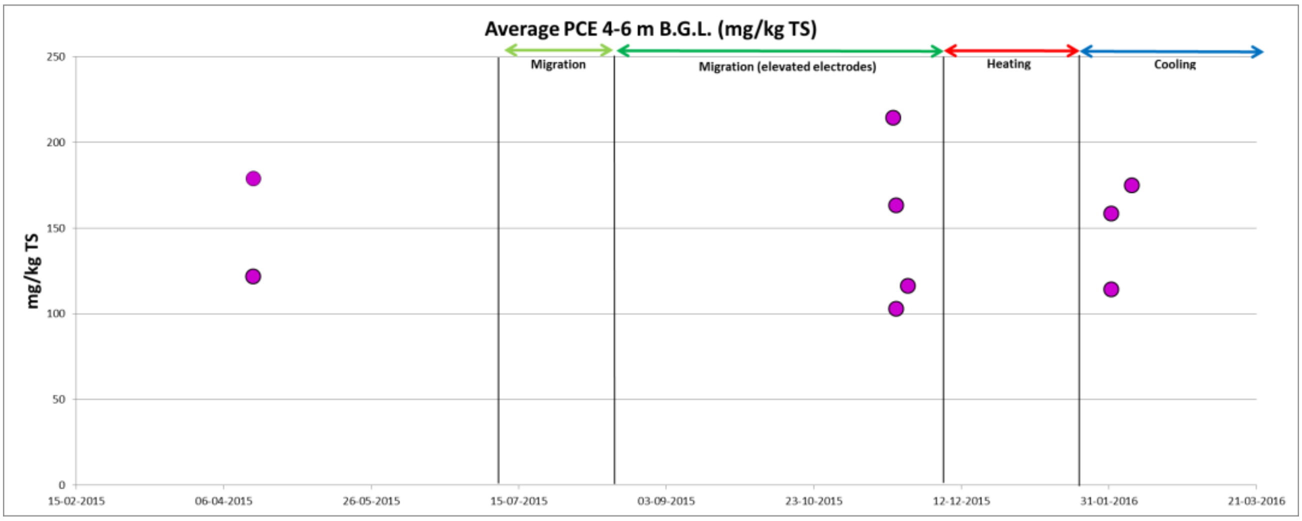

Figure 10.10: Average PCE concentrations measured in soil samples 4-6 m bgl during pilot test.

10.2.3 *Chloride*

The maximum chloride concentrations over time and depth from soil core samples are presented in Figure 10.7. All chloride data from soil samples are presented in appendix 8.

The highest maximum chloride concentrations measured over time and depth in soil samples were measured in KP02, KP03, KP04 and KP06 (Figure 10.7) ranging between 18 – 36 mg/kg. These soil samples were collected on an overall approximately SE-NW axis almost parallel to the axis between the cathode and the anode wells. Within the periphery of the pilot test area, concentrations of chloride in soil cores from HB3 and HB4 (Figure 10.7) were measured at 7.5 mg/kg within both soil core samples.

The vertical distribution of chloride in the soil profile is almost uniform with no significant trend of increasing or decreasing values with depth.

10.3 Temperature

Temperature data are presented in Appendix 5.

10.3.1 *Heating phase & cooling phase*

The AC powered heating phase was conducted between 1 Dec. 2015 – 19 Jan. 2016. Previous laboratory testing prior to the pilot test indicated that persulfate activation and degradation of PCE was achieved at temperatures greater than 30 °C, and that the degradation rate of PCE for the site soils increased with increasing temperature. Laboratory testing indicated that for higher persulfate doses (10 g/L, 20 g/L) and the highest temperature tested (40 °C), PCE degradation was essentially complete within 3 days. For lower persulfate doses (5 g/L) and lower temperatures (30 °C) PCE degradation was mostly complete within 7 days, however low concentrations of PCE remained in the test vials following 7 days of treatment.

The spatial distribution of temperature within the pilot test area for the period is presented in Figure 10.11. During the initial start-up of the heating phase, temperatures within the pilot test area were measured at approximately 15 °C and were gradually increasing during the heating stage, reaching the target activation temperature of 30 °C at all measuring points within 30 days of the beginning of the heating cycle. The target temperature was maintained across the treatment area for a minimum of 10 days. Temperatures within the treatment area increased to between 40 and 60 °C before the end of the heating cycle, however temperatures did not exceed 60 °C, and remained thus well below the boiling point of water and PCE. Temperatures were monitored during the cooling phase, and returned to ambient levels within 70 days.

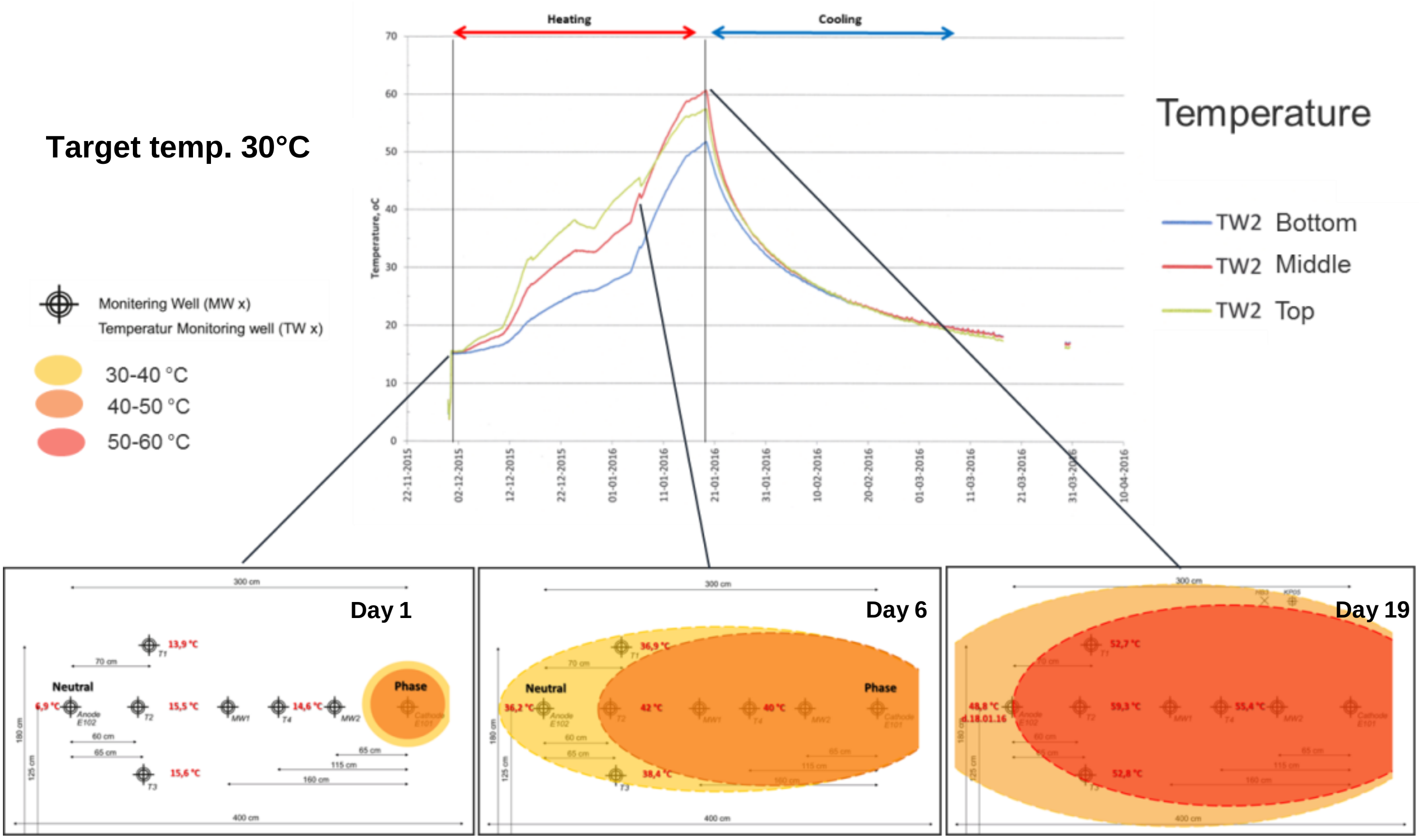

Figure 10.11: Spatial distribution of temperature within the pilot test area. Bottom figures show the lateral distribution of the maximum temperature at days 1, 6 and 19 of the heating stage.

Complete temperature sequences for TW1, TW2, TW3, TW4, CW and AW during the AC heating stage are presented in Figure 10.12 and Appendix 5.

During the first week, fine-tuning and adjustments performed in order to optimize the system in response to AC power, is reflected within the temperature graphs Figure 10.12.

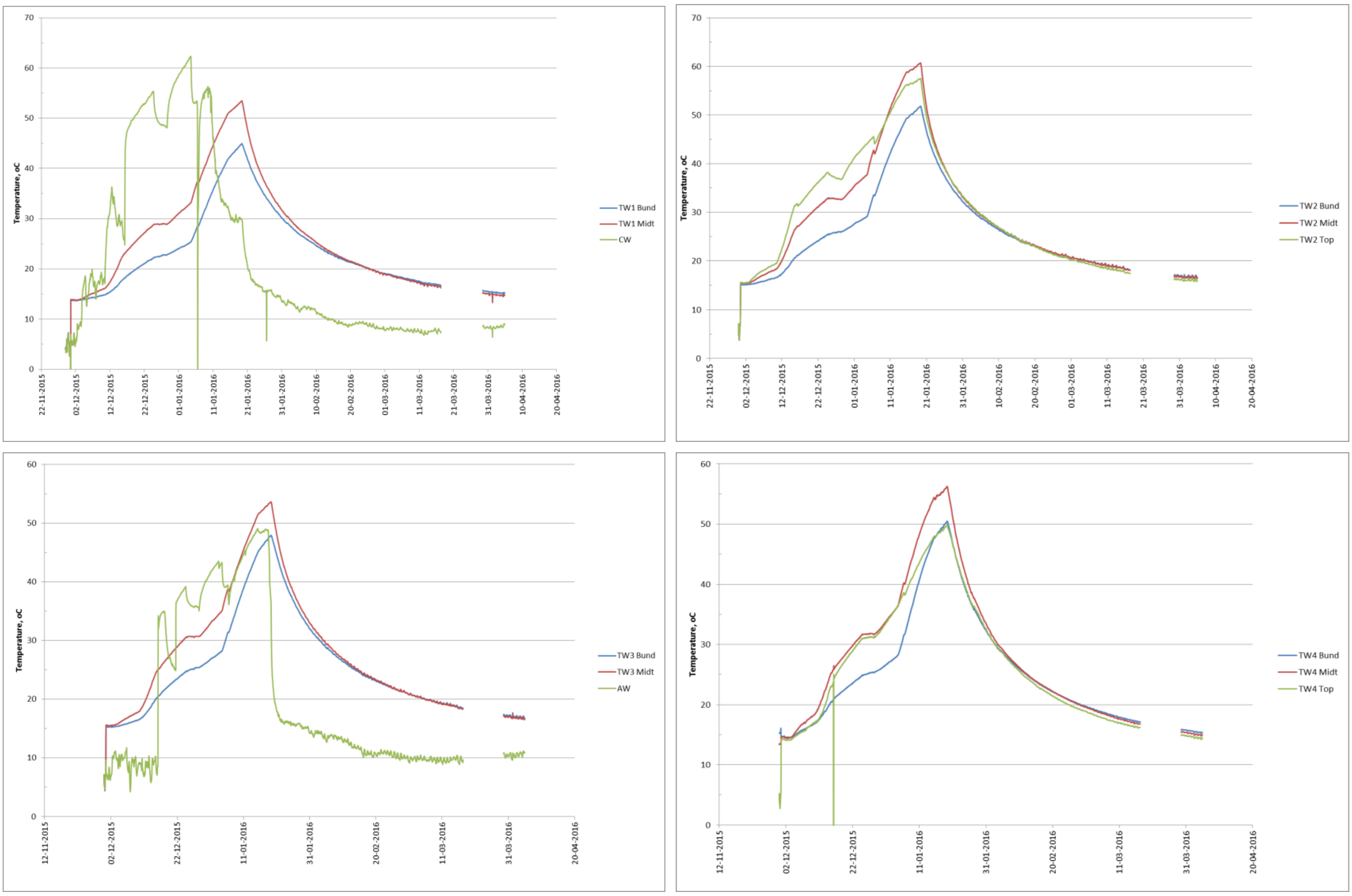

Figure 10.12: Temperature sequence for TW1, TW2, TW3, TW4, CW and AW during pilot test. For higher resolution see Appendix 5.

11 EVALUATION

11.1 Operation

The EK-TAP™ pilot test was operated for approximately 6 months. The following sections outline the overall monitoring and operation of the system during the operational period.

11.1.1 Hardware.

Materials used in the construction of the system were designed to be chemically resistant and durable where possible. Piping and tubing consisted of PE or PVC, and connections and wetted pump areas were steel or brass. Despite this approach, within a few weeks of operation leaks began to occur and given the nature of the chemicals used in the pilot test some deterioration of infrastructure occurred (Figure 11.1).

Figure 11.1: Operation leaks during the test period.

The electrodes were made of titanium tube coated with a MMO (mixed metal oxide) coating designed for operation in harsh conditions. Electrodes were not significantly corroded during the operation period, but at the top and tip signs of minor corrosion could be seen following the test (Figure 11.2). The same electrodes were used for the entire test period, and spares were available at the site in the event of electrode failure.

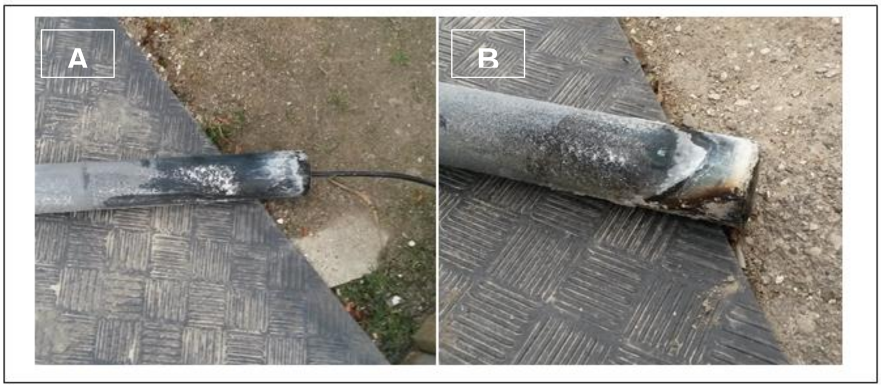

Figure 11.2: Top (A) and bottom (B) of electrode following the test period.

Peristaltic pumps were used throughout the system such that all solutions would not be in contact with pump parts, and replacement of the drive tubing would be an easy maintenance operation.

11.1.2 *Monitoring system*

pH stability of buffer solution

During the DC stage, one of the major challenges was to keep the injected solution at neutral, i.e. pH between 6 – 8. The pH level was continuously monitored via the PLC and the PLC was checked offsite at least twice a week. Experience from the first weeks of operation showed that pH could drop from about 7 to less than 5 within a week. However, pH was easily raised by adding buffer to the solution.

The pH probe was mounted in-line to provide continuous monitoring. pH was measured in the circulating liquid and taken as representative of an average pH of the liquid in the buffer tank and well. Measurements were done for a period of 15 minutes every second hour. Each well (Cathode well and Anode well) contained a total of approximately 50 liters of solution.

Heating during DC stage

Temperature monitoring of the cathode well was performed in the same manner as the pH monitoring. The purpose of the monitoring was to demonstrate that temperatures in the system did not approach the activation temperature of persulfate.

The buffer tanks were placed in a room with air-conditioning and the temperature was kept between 18 - 23 °C. The cycling of water from the buffer tanks through the electrode wells ensured that temperature increases were appropriately managed, and well temperatures did not exceed 25 °C over the course of the test.

Monitoring the distribution of persulfate

The initial monitoring program for documentation of the distribution of persulfate was based on the change in conductivity in groundwater (an increase in conductivity would indicate the arrival of the high EC persulfate solution). Persulfate solution and buffer solution has a high electrical conductivity, typically > 10.000 µS/cm, which is well above the electrical conductivity of ground water (400 – 1.000 µS/cm). Migration of high concentrations of persulfate through the treatment area would result in a measureable increase in the EC of the groundwater.

The target treatment zone on this site consists of partially saturated low permeable clay with a very low flow of water in the soil matrix. To make sure that the migration of persulfate occurs and to follow the migration over time it is important to monitor in more than one well. In this case continuous monitoring was conducted in only one well, and it was placed right between the cathode and anode well. Manual measurements has in this case shown, that the continuous monitoring should have taken place in at least two wells. Or if only one well was available, then the monitoring should take place in a well closer to the distribution well

(CW). Furthermore distribution of persulfate based only on data from conductivity measurements of ground water has shown not to be sufficient.

Recirculation

Recirculation of the fluid between the injection well (CW or AW) and the associated amendment tank seems to be necessary in this case, where there is no or a very low natural ground water movement. With recirculation it is possible to make sure that the solutions in the wells are changed over time and by that to keep the target concentrations of especially NaPS at the desired level. Recirculation showed also to be necessary to keep pH neutral in both the cathode well and the anode well.

11.2 Migration of NaPS

Input concentrations of NaPS (as measured at the cathode well) ranged from 44.3 g/L to 88 g/L during the migration phase, and decreased to 0.023 g/L during the cooling phase (where NaPS amendment had terminated). Generally, the target NaPS input concentration (54 g/L) was achieved during the test.

NaPS was detected in groundwater during operational sampling in MW-2, MW-3, and HB-1. The highest concentrations of NaPS measured during operational monitoring were found at MW-3 immediately after its installation. The concentration of NaPS in MW-3 decreased following early highs to an average of approximately 500 mg/L. Following the heating stage, NaPS concentrations in MW-3 were essentially ND indicating all NaPS present was converted to the sulfate radical during the heating phase. Measured concentrations of NaPS in MW-2 and HB-1 were orders of magnitude lower than in MW-3 and detections were highly variable during sampling. Based on the water samples during the operational period, NaPS migrated radially away from the cathode well, with a preferential migration in the direction of MW-3.

11.2.1 Groundwater: NaPS vs Sulfate

Following activation of NaPS and generation of the sulfate radical, reaction with organics or natural decomposition will transition the sulfate radical to sulfate. Increased sulfate concentrations can be indicative of transport of NaPS and subsequent decomposition, or activation of the NaPS followed by decomposition and transport of the resultant sulfate.

Sulfate concentrations in MW-3, HB-1, and HB-3 were above baseline conditions (56 mg/L) when they were installed, indicating migration to these locations within the first 2 – 3 months of system operation. The arrival of the sulfate migration front was captured in MW-2 in September, approximately 1 month in advance of the arrival of the NaPS front. The presence of sulfate at concentrations above background indicates that activation of persulfate and decomposition to sulfate is occurring in the system, even in the absence of heat. This is likely due to the presence of iron in the natural soils. Analysis performed following the pilot test on reduced zone soils remaining from the laboratory testing found 18,400 mg/kg of iron. Dissolved iron has the potential to activate NaPS, particularly ferrous (+2) iron. Dissolved iron concentration at the site were measured in MW-1 and MW-2 on August 12 and were 0.07 and 0.02 mg/L respectively. These are not considered high concentrations in groundwater. The dominant form of dissolved iron (ferric or ferrous) at the site is unknown, but is typically ferrous. When dissolved ferrous iron reacts with the oxidant, it will itself be oxidized and then rapidly precipitate from the dissolved phase. Thus activation by iron will not necessarily be reflected in increasing concentrations of dissolved iron.

11.2.2 *Groundwater vs soil*

Soil samples were obtained from a number of locations within the target treatment area over the course of the pilot test (KP01-07, HB1-4). Sulfate analyses from these additional soil samples provide a better picture of the overall migration direction and extent achieved during the test. The preferential migration in the direction of MW3 (indicated in the water sample data) is seen very clearly in the soils data. Sulfate concentrations in soil at KP06, KP07, and HB3 to the north of the cathode well (6550 mg/kg, 3680 mg/kg, and 496 mg/kg respectively) are elevated as compared to baseline soil measurements (< 100 mg/kg). The distance from the cathode well to KP07 (north of the cathode-anode axis) is more than twice the distance from the cathode well to HB1 (south of the cathode-anode axis), however the sulfate concentration in HB1 averaged only 493 mg/kg. Sulfate concentrations in HB2 and HB4 (further from the cathode well than HB1 to the south of the cathode-anode axis) are equivalent to baseline measurements indicating that sulfate has been transported at least twice the distance on the north side of the cathode – anode axis than on the south. The non-uniform distribution might be explained by the unsaturated conditions in the soil profile, which could have caused the voltage field to have a preferential slightly curved direction towards the anode well. Moreover, the cathode well was screened across two strata; partly till – partly clay. It cannot be excluded that the conductivity in the clay layer is greater than in the till, and thus there has been a major transportation in the clay layer. Furthermore, the fact that surface (roof) water has seeped down and out in the voltage field may have affected the preferential flux to follow the dispersion like water inflow/infiltration had.

Soil data also indicates the potential for transport at depths below the target interval. Sulfate concentrations from a depth of 7.7 m in KP03 (407 mg/kg) may indicate preferential transport at depth, however there are limited other samples to support this possibility. This may be caused by tip effect, when the electrodes were located at the original, lower depth.

11.2.3 *Soil vs EC logs (HPT)*

As part of the additional investigations undertaken to collect data on the actual persulfate migration, direct push testing was performed to generate EC profiles with depth. Five locations were investigated (HPT01-05) to a depth of approximately 8 m (Figure 9.2). A region of increased EC at the target treatment depth is clearly seen at location HPT01, and possibly at HPT02 and HPT04 (Figure 9.3). Soil testing confirmed that the increased EC reading at HPT01 indicated the presence of increased sulfate and total sulfur (Figure 9.4).

11.2.4 *Interpretation*

Assessment of soil, water, and EC log data obtained during the pilot test indicates that persulfate migration occurred preferentially on the north side of the cathode-anode axis. Persulfate migration is confirmed as far as MW2 (0.7 m) and MW3 (0.6 m), however, persulfate likely migrated past these two locations. Sulfate migration (likely after activation with iron) has been demonstrated to have occurred as far as MW1 (1.5 m) along the cathode-anode axis and as far as HB3 (1 m) to the north of the cathode-anode axis. The confirmed distribution of persulfate and sulfate are shown in Figure 11.3. It should be noted that the potential exists for the sulfate analytical results from soil to be comprised of a mixture of sulfate and persulfate. The analytical techniques used for soil samples cannot differentiate the two and will report persulfate as sulfate.

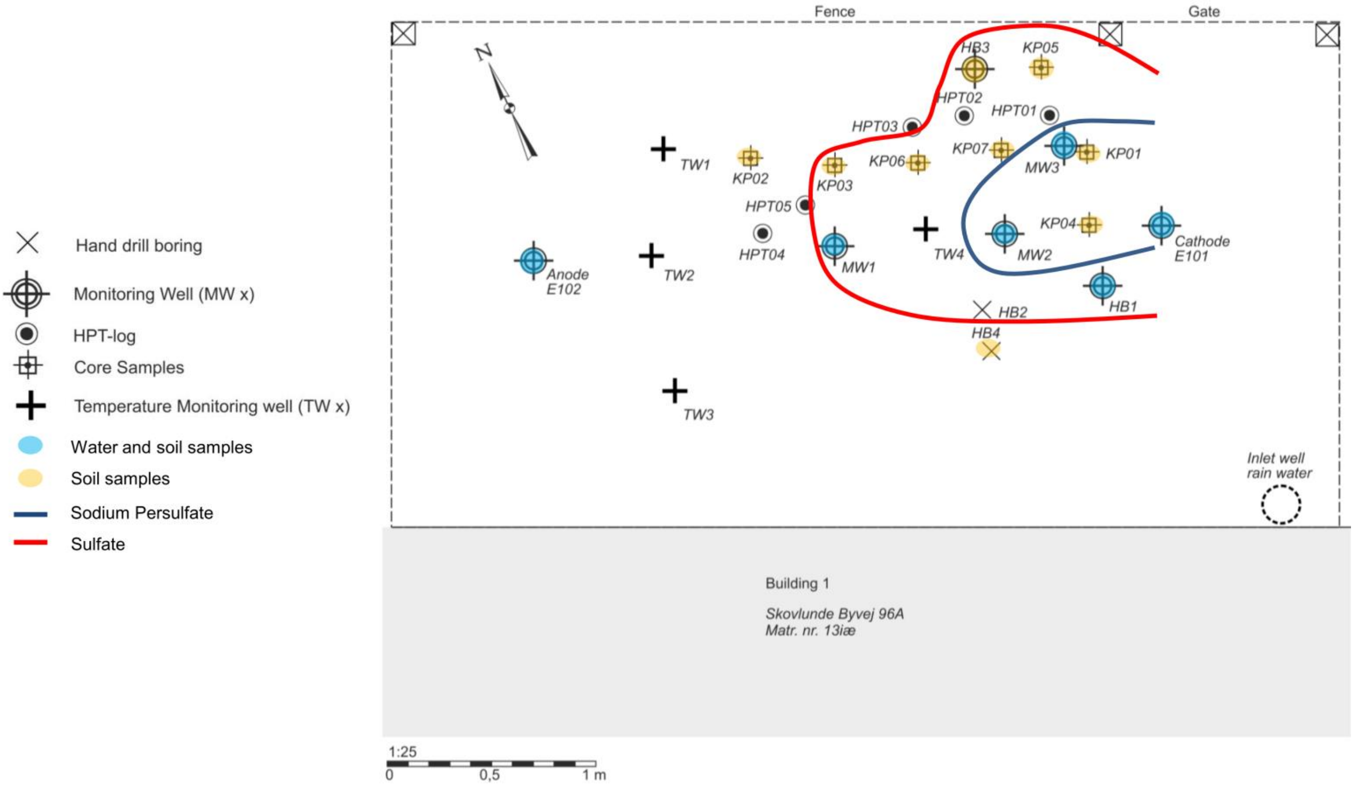

Figure 11.3: Confirmed spatial distribution of persulfate and sulfate within the pilot test site.

11.3 Heating

Assessment of temperature data obtained during the pilot test indicates that it was possible to use the same electrodes both during the AC and DC stages, which was one of the assessment metrics of the single dipole test. Temperatures exceeded target temperatures (30 °C) within the central part of the test site due to the time required to reach target temperatures across the entire test site for activation of the persulfate. It would potentially be easier to control heating temperatures with installation of a second pair of electrodes in order to reach target temperatures within the entire test field and reducing power consumption in response to temperatures above the target temperature.

Time duration for heat transfer from the phase at the cathode to reach neutral at the anode, amounted to approximately 30 days in response to reach target temperatures. Duration of cooling time after end of heating stage amounted to approximately 70 days in order to reach ambient temperature levels within the test site. Temperatures during the cooling phase were monitored to evaluate potentially further heating cycles for further degradation/oxidation of PCE. With installation of a second pair of electrodes it could potentially reduce the duration of a heating and a cooling stage, an advantage if several heating cycles were desired.

11.4 Activation and PCE oxidation

11.4.1 Activation by natural Fe

As discussed in 11.2.1, some degree of NaPS activation likely occurred at the site due to the presence of dissolved iron in the test area. The degree of activation due to the presence of dissolved iron (as compared to heating) is unknown. Generally, activation of persulfate by heat is more effective than through dissolved iron.

11.4.2 Activation by heating

Heat activation of NaPS at the site was demonstrated to be effective as NaPS concentrations were below detection limits in all monitoring wells at the site following the heating stage. Concentrations of NaPS in the cathode well dropped to near ND following the heating cycle, indicating essentially complete transition of NaPS to the persulfate radical and decomposition to sulfate. This is further supported by the increase in sulfate concentration in the cathode well (9.7 to 33 g/L) between the start and end of the heating stage.

Oxidation of PCE

Overall, oxidation of PCE over the course of the pilot test was demonstrated in water samples (figure 10.5). Baseline samples taken from MW-1 and MW-2 showed concentrations of PCE greater than 100 mg/L. Following the migration stage, concentrations of PCE in these monitoring wells were less than 50 mg/L. Concentrations of PCE remained constant or slightly increased during the heating stage, and are indicating rebound towards baseline levels following the cooling stage.

Rebound is likely occurring through recontamination of the groundwater from PCE contained in soil (either in the sorbed or DNAPL phases), as soil concentrations were only slightly reduced from baseline conditions by the end of the pilot test (10.2.3).

Chloride concentrations are expected to increase during oxidation of PCE, as chloride is released from the PCE molecule during its oxidation. An increase in chloride concentrations (from baseline to the end of the pilot test) was seen in the cathode well, MW-1, and HB-1. Only minimal increase in chloride concentration was seen in MW-2, despite the evidence of both NaPS migration to that well and increased sulfate indicating activation and decomposition of persulfate.

11.5 Future operation

11.5.1 Monitoring parameters

The monitoring program for the pilot test was comprehensive and effective for the intended performance. The data collected during the pilot test are useful and should be collected in future testing. Given the lower than anticipated migration rate of NaPS at the site, having the additional monitoring infrastructure (HB-1, MW-3) present at the beginning of the test would have provided additional information to refine the migration rate and spatial consistency of migration.

For future implementation of the technology, additional monitoring locations for voltage (both laterally and vertically) would allow for a better understanding of the overall electric field generated by the electrodes. In addition, measurements of dissolved iron and iron speciation would allow for a more complete understanding of the activation and decomposition process of NaPS. In addition, direct measurements of persulfate in soil would be beneficial. A technique for this has recently been developed by SiREM laboratories.

11.5.2 Unsaturated conditions

The variably saturated soil conditions at the site presented challenges to implementation of the technology. The electric field is sensitive to the degree of saturation of the soil, and as a result migration rates and directions in variably saturated soil are difficult to predict prior to testing. The variable nature of the saturation, in combination with the variability of the stratigraphy, resulted in lower migration rates than expected as well as preferential migration towards MW-3. Future implementation of the technology at the site would benefit from a presaturation phase using electroosmosis to decrease the variability and thus increase the uniformity of NaPS migration.

11.5.3 Cooling – time schedule for multiple cycles of operation

The site returned to ambient background temperature in approximately 70 days. Temperatures in the treatment area fell below 20 °C in approximately 40 days, indicating that the required cool-down period for the site prior to a second migration stage is a minimum of 40 days. The rate of cooling observed at the site is slightly faster than estimated from modeling performed prior to the pilot test.

12 CONCLUSIONS AND RECOMMENDATIONS

The EK-TAP™ single dipole field pilot test has successfully demonstrated the migration of persulfate through low permeability clayey till and subsequent activation through electrical resistance heating of the treatment area. The results indicated oxidation of PCE present in the groundwater within the test area.

- The persulfate migration rate in the pilot test was lower than anticipated from the preceding lab testing and modeling. The distribution of persulfate in the treatment area was not uniform, and indicated a preferential migration to the north side of the cathode-anode axis. These deviations from the anticipated spatial distribution are mainly due to the variably saturated nature of the clayey till soils in the test area.

- Future implementations of the approach in variably saturated or partially saturated conditions would benefit from a preliminary saturation step using EK-Saturate.

- The electrode well spacing of 3 m chosen for the test was likely too great, given the variably saturated nature of the site. Future implementations in similar cases should use persulfate supply wells between the electrodes and potentially a reduced electrode spacing.

- The pilot test has demonstrated that the deployed MMO coated titanium electrodes as well as the installed electrode and monitoring wells were applicable for both the DC (migration) and the AC (heating) stages of the EK-TAP™ pilot test. A significant feature of the EK-TAP™ concept has thus been proven viable.

- During start-up and operation of the DC (migration) of the pilot test some adjustments were made to the original layout, mainly pertaining to functioning of the fluid amendment system with the variably saturated, low permeable soil.

- Equally due to the variably saturated conditions and the variability in stratigraphy of the test site soils, the monitoring infrastructure was expanded during the migration stage to include more laterally located monitoring wells. For future applications a more spatially extended monitoring network that includes voltage monitoring would be favorable to include in the initial design.

- PCE oxidation by activated persulfate has been demonstrated in the water phase in the test area. Concentrations have been reduced from above 100 mg/l to well below 50 mg/l during the migration and heating stages. During the cooling stage, the PCE water concentrations rebounded due to release from sorbed or DNAPL mass in the soil. Due to the high PCE loading of the soil at the test site, soil PCE concentrations have not been significantly reduced during the pilot test.

- Activation of the NaPS at the site has likely occurred both by naturally occurring iron and by heat activation. Data show that heat activation has played a vital role in completely activating the amended NaPS and in oxidizing the dissolved PCE (as documented by increase in chloride concentrations).

- By heating of the soil during the AC stage, complete activation of the amended NaPS was achieved. The target temperature of 30°C was reached in the entire treatment area within 30 days of the AC operation. Given the relatively small test volume and thus a high relative surface area, the temperatures in the middle of the treatment depth interval exceeded the target temperature before 30°C was reached at the test volume boundaries. It is thus not possible to point at an optimum field activation temperature based on the performed pilot test.

- Temperatures in the treatment area fell below 20 °C in approximately 40 days, indicating that the required cool-down period for the site prior to a second migration stage is a minimum of 40 days.

The current status of the EK-TAP™ technology is highly promising. In addition to the dipole pilot test at the Ballerup site, a dipole pilot test has recently been completed in Canada with strong evidence of amendment migration and contaminant degradation. Four additional EK-TAP™ pilot tests are either currently underway or in the planning and design stages. These pilot tests use a “5-spot” pattern with a central anode and cathodes position equally around the central anode on the corners of a square. The three currently operational pilot tests have been in operation for between 2 weeks and 6 months, and a large volume of performance data is expected to be available within the next 3-6 months. Geosyntec has also been awarded an ESTCP Dem/Val project for the EK-TAP technology. This Dem/Val project will begin in 2017.

Some perspectives for the EK-TAP™ technology can be drawn from the performed single dipole test

- The technology targets remediation in low-permeable or heterogeneous soils

- As compared to the more proven technology of EK-BIO, EK-TAP™ can treat contaminants that are not readily biodegradable, such as TCA and 1,4-dioxane.

- Given the challenges with achieving a uniform distribution in the variably saturated soils encountered in this single dipole test, future testing and use of the technology is recommended for fully saturated soils.

- When estimating dosing and total consumption of NaPS at future sites, the natural iron content should be taken into account

- Dipole applications of EK technologies are more challenging than other configurations. Future implementations should consider electrode configurations more similar to those used in the EK-BIO full-scale project at Skuldelev where space allows.

Prior to implementing the EK-TAP™ technology at full scale, further pilot testing should document

- The achievable persulfate migration rate

- The degradation rate for contaminants within the treatment area as a function of the persulfate concentrations migrated under the EK fields

- The number of cycles necessary to achieve target treatment goals (recognizing that the number of cycles will depend on the actual degree of contamination and DNAPL presence)

- The remedial effect on contaminants that are not readily biodegradable, such as TCA and 1,4-dioxane.

13 REFERENCES

/1/ Christiansen, C.M., 2010: Methods for enhanced delivery of in situ remediation amendments in contaminated clay till. PhD Thesis, Technical University of Denmark.

/2/ Region Hovedstaden 2012: Udviklingsgrund i Region Hovedstaden, baggrundsnotat, 2012

/3/ Region Hovestaden 2011: Skovlunde Byvej 96A Lokalitets nr. 151-00015 Fastlæggelse af indsatsområde til afværgeforanstaltninger, November 2011.

/4/ Region Hovedstaden. EK-ISCO. Elektrokinetisk stimuleret kemisk oxidation Laboratorieforsøg til proof-of-concept. NIRAS A/S & Geosyntec. September 2014

/5/ Technical Memorandum: Additional Laboratory Testing of Electrokinetically-Delivered Thermally-Activated Persulfate (EK-TAP^{TM}), Skovlunde Byvej 96a, Ballerup, Denmark. Geosyntec January 2015

/6/ Region Hovedstaden, Center for Regional Udvikling. Elektrokinetisk Termisk Aktiveret Persulfat. Udbudsmateriale NIRAS A/S. Februar 2015

/7/ Region Hovedstaden. EK-TAP. Oplæg til supplerende laboratorieforsøg og dipol felttest. Juli 2015. NIRAS A/S & Geosyntec

/8/ Wu, M.Z., Reynolds, D.A., Prommer, H., Fourie, A., and D.G. Thomas. 2012. Numerical Evaluation of Voltage Gradient Constraints on Electrokinetic Injection of Amendments, Advances in Water Resources, Vol. 38, pgs. 60-69.