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APPENDIX A: GLOSSARY

ARD: Anaerobic reductive dechlorination, an in-situ mass transformation remedial technique for chlorinated ethenes involving the sequential replacement of chlorine atoms in the chlorinated ethene with hydrogen atoms (Jørgensen et al., 2005), described in detail in *Appendix G: Coupled remediation technologies*.

Asperities: irregularities along the inside of a fracture wall.

Basal till: A subglacial till, relatively homogeneous. A till carried at or deposited from under the bottom of a glacier (American Geological Institute, 1984).

Blast fracturing: refers to the use of explosives to create fractures in rock (Schuring, 2002).

Blow-up: fracture venting at ground surface, usually considered undesirable in a remedial context. Blow-up may occur due to: 1) too shallow fracturing depth; 2) too high injection pressures; 3) too high an injection flow rate; 4) induced fracture interception of a building foundation, natural fracture, sand lens that diverts the direction of fracture propagation, also referred to as **daylighting** (Suthersan, 1999).

Breaker: also called chemical breaker is an enzyme added to the guar slurry to ensure that it breaks down to a water-like consistency and thus does not clog the fracture. The breaker is usually designed to start breaking 2 to 8 hours after injection (Bures, 1998).

Clay-till: Till with significant clay-fraction, in Denmark 12 to > 30% clay (Larsen et al., 1995). See also **Till**.

Cohesion: the strength of a soil related to ability of the particles to adhere to each other. Values of cohesion can range from zero in a clean cohesionless sand to approximately 30 kPa in clays (Marshall and Holmes, 1988). Cohesive soils include clayey silt, sandy clay, silty clay, clay and organic clay, also referred to as formation **toughness** (US Dept of Labour, 2005).

Cross-linker: A chemical added to the guar gel to further increases its viscosity so the gel can hold a propping agent.

Daylighting: see **Blow-up**.

Dead-ice landscape: a complex pro-glacial landscape consisting of outwash deposits, flow and/or melt out tills and kettle lakes.

Deformability: the tendency of a material to change shape due to folding, faulting, shearing, compression, or extension as a result of various Earth forces (Hacettepe Univ., 2005). The degree of deformability ranges from *brittle* (where gradually increasing compressive pressure applied to a specimen causes no deformation until it ruptures abruptly into subunits or fragments) to *deformable* (where a specimen can be compressed to half its original thickness without rupture). Radial cracks may appear and extend inward (US Dept of Agr., 2005).

Dip: The angle that a (planar/linear) feature makes with the horizontal, measured perpendicular to the strike and in the vertical plane (American Geological Institute, 1984).

Dip-direction: Direction taken by a line as it intersects the horizontal (American Geological Institute, 1984).

Direct push: method of installing a drivepoint, or well casing by pushing it directly into the underground with a hydraulic force: geoprobe sampling is an example of direct push.

Driven casing: A common method of installing a casing in Canada and US adopted from cable-tool drilling of water wells in unconsolidated geologic material. A casing with welded joints, referred to as a casing sting, is driven down (hydraulically pushed) to the required depth using a cable tool or driven casing hammer. The borehole in which the casing is installed is *smaller* or *equal* to the exterior diameter of the casing. (BC MOE, 2005). A driven casing is often assumed to be sealed by the lateral pressure of the surrounding sediments (EPA, 1994). In recent years, however, the so-called 'micro-annulus' between the casing and the borehole is typically sealed with dry grout (bentonite, general purpose cement, etc.) to prevent cross contamination (Ohio Dept of Nat. Resources, 2005).

Effective unit weight (δ'): represents the effective pressure due to the weight of the overburden. Effective unit weight is determined by multiplying the density (unit weight) of a soil by the height of the overlying column of soil (Hacettepe Univ., 2005).

End Moraine: an accumulation of till in a ridge that marks the position of a stagnant glacier (American Geological Institute, 1984).

Environmental fracturing: the application of fluid injection fracturing (hydraulic, pneumatic) and blast fracturing in a remedial context.

Flow till/melt-out till: also called ablation till, an uneven layer or pile of till either overlying the ice or resting on a ground moraine formed from the same glacier (American Geological Institute, 1984).

Fracture density: the number of (natural) fractures per meter, the reciprocal of spacing (Klint, 2001a).

Fracture interval: an isolated zone of the borehole where environmental fracturing is undertaken.

Fracture interval spacing: the spacing between fractured zones. At some sites the spacing is constant over depth, at other sites certain depths are targeted and spacing between fractured zones is irregular.

Fracture radius: the lateral extent of an induced fracture, typically measured from the fracturing borehole to the most distant point of uplift, also referred to as **fracture length** or **maximum axis**.

Fracture trace frequency: number of (natural) fractures at a given depth divided by the length of profile examined. Gives the number of fractures/m. For horizontal fractures the fracture trace frequency equals fracture spacing. On vertical profiles, the 'scanline' necessarily is not perpendicular to the fractures so the fracture trace frequency is not equal to the fracture spacing (i.e. must be corrected for the angle discrepancy).

Hydraulic fracturing: refers to the injection of a liquid into cohesive soil or rock to induce fractures (EPA, 1994).

Hydrostatic pressure (P_0): in a groundwater context, the pressure exerted by water at higher levels in the saturated zone (Hacettepe Univ., 2005).

Initiation pressure: the pressure required to create/start/initiate a fracture.

In situ: remediation treatment of contaminants in the underground.

Leak-off: refers to the movement of fracture fluid into pores and natural fractures along the fracture plane. When the rate of injection equals the rate of leak-off into the formation, propagation ceases (EPA, 1994).

K_0 : coefficient of earth pressure at rest, a measure of the dominant principle stresses (vertical or horizontal) in the overburden. In overconsolidated sediments the ratio of stresses, $K_0 = (\sigma_h / \sigma_v) > 1$ (Blem et al., 2004).

Liquid limit: the water content at the change between the liquid and the plastic states. It is measured on thoroughly puddled soil material that has passed a number 40 sieve (0.43 mm) and is expressed on a dry weight basis (ASTM, 1984, US Dept of Agr. 2005).

Lodgement till: a type of basal till with a fissile structure. Elongated stones in lodgement tills are oriented with their long axes generally parallel to the direction of ice movement (American Geological Institute, 1984).

Mass reduction/destruction: refer to in situ remedial techniques where the mass of contaminant is reduced or destroyed in the underground for example, mass destruction of PCE via chemical oxidation of PCE with potassium permanganate, or chemical reduction with zero valent iron or ARD (Tuxen, 2002).

Mass transfer: in situ/on site remediation technique where contaminant is transferred from the underground to the surface, where some type of treatment is undertaken (either on-site or off-site).

Mass transformation: refers to an in situ remedial technology where the contaminant is transformed via a reaction to another hopefully less harmful product (Tuxen, 2002). ARD is an example of a mass transformation reaction where complete anaerobic reductive dechlorination of PCE results in ethane and ethane. Incomplete reactions, for example PCE to TCE, are also mass transformation reactions, although undesirable.

Orientation: the direction of a fracture trend relative to the points of a compass.

Overconsolidation: When sediments are initially deposited, the three principal stresses (σ_x , σ_y , and σ_z) are in equilibrium and equal to the overburden pressure. External forces for example glaciation, excavation, erosion, desiccation, etc. can change the stress fields (Suthersan, 1999). In the case of glacial sediments the weight of the glacier imposed a stress and consolidated the sediments. Glacial retreat decreased the vertical stress, while the horizontal stress remained unchanged. Most glacial sediments in Denmark are overconsolidated (Blem et al., 2004).

Overconsolidation ratio (OCR): is the ratio of the previous in situ stress to the present in situ stress.

$$OCR = \frac{\sigma_{pc}}{\sigma_0} \quad \sigma_{pc} = \text{Previous in situ stress; } \sigma_0 = \text{in situ stress.}$$

The value for σ_{pc} is determined using an empirical formula, which should be used with caution. The in situ stress term σ_0 is a function of the sediment density, depth and saturation. Tills in Denmark are generally overconsolidated i.e. $OCR > 1$ (Nilsson et al., 2000).

Plastic limit: The water content of a soil corresponding to an arbitrarily defined boundary between a plastic and a semisolid state (Hacettepe Univ., 2005). The measurement of the plastic limit is described in ASTM method D 4318-83.

Plasticity index: This is the range in water content over which soil material is plastic. The value is the difference between the liquid limit and the plastic limit of a (Hacettepe Univ., 2005).

Pneumatic fracturing: refers to the injection of a gas, typically highly pressurised air into cohesive soil or rock to induce fractures (EPA, 1994).

Propping agent: solid granular material injected with the guar (hydraulic fracturing) or gas (pneumatic fracturing) to hold fractures open after the injection process is completed. Medium- to coarse-grained sand to guar in a ratio of 1.2 to 1.8 kg sand per litre gel is typically used (EPA, 1994). Although other fine-grained or powered material, for example zero valent iron may be used depending upon the coupled remedial technique. The latter propping agent may be injected pneumatically.

psi: pounds per square inch, imperial pressure units where 1 psi = 6.895 kPa (Metric equipment manufacturers, 2005).

Radius of influence: the radius in which effects of fracturing can be measured (for example via hydraulic conductivity testing, pump tests, etc.) but where physical evidence of induced fractures may not be observable.

scfm: standard cubic feet per minute, imperial units of gas flow measurement where 1 scfm = 28.32 L/minute (Metric equipment manufactures, 2005)

Shelby tube: A thin-walled sampling tube used to take undisturbed soil samples in cohesive soils (silts and clays). The tube (steel, stainless steel, galvanised steel or brass) is pressed (with hydraulic force if necessary) into undisturbed soil. The thin tube containing the samples is removed from the sampling head capped and/or sealed and used to safely transport the sample (Global drilling supplies, 2005).

Strike: Direction taken by a structural surface as it intersects the horizontal (American Geological Institute, 1984).

Tensile strength (t_a): ability of a material to resist a stress tending to stretch it or pull it apart (American Geological Institute, 1984), expressed in units of force (ie newtons), also referred to as **cohesive strength**.

Till: Poorly sorted (diamict) sediment deposited directly by or in close connection to the activities of a glacier, there are 4 sub-classifications defined by the grain size distribution and degree of sorting of the till: clay-, silt-, sand-, and gravel-till (Larsen et al., 1995).

Tiltmeter: an electronic instrument which measures the movement/tilt of buildings, slopes, excavations etc. The instrument works like carpenter's level with a chamber of conductive fluid and a bubble which moves. Two electrodes attached to the fluid record the movement of the bubble and this correlates to the amount of movement (DGSI, 2005).

Toughness is related to plasticity. The classes are based on the relative force necessary to form with the fingers a roll 3 mm in diameter of < 2 mm soil material at a water content near the plastic limit (test D 2488 in ASTM, 1984) (US Dept of Agr. 2005).

Uplift: the vertical displacement of ground surface during fracturing due to injection of fluid into the underground, also referred to as surface **heave**.

APPENDIX B: DESCRIPTION OF HYDRAULIC FRACTURING TECHNOLOGY

B.1 Introduction

Hydraulic fracturing refers to the injection of a liquid under high pressure to induce a fracture at a desired depth in the underground (EPA, 1994). Hydraulic fracturing is generally described as producing a few discrete, large-aperture fractures (5-20 mm apertures) at selected depths with radii extending from 3 to about 16 m from the fracture well (EPA, 1994; US DOE, 1998; see also Table B.1; *Appendix C: Experiences with environmental fracturing*; and *Appendix Y: Electronic data, Table C.1*: US and Canadian experiences with environmental fracturing*).

B.2 Steps in hydraulic fracturing

Fracturing may be undertaken in the vadous, saturated and perched groundwater zones (Schuring, 2002). Hydraulic fracturing involves a number of steps which are depicted in Figure B.1 and described below.

B.2.1 The fracturing borehole

The first step in hydraulic fracturing consists of drilling a borehole so the fracturing equipment can be positioned in the formation at the desired depth. The borehole may be drilled using an auger drill, direct push, or other method. The radius of the borehole will depend upon the size of the fracturing equipment, as well as the number of completed wells planned for a particular borehole. The borehole may be open, cased or specially screened (no sand/gravel pack) (Schuring, 2002). If the formation is sufficiently cohesive, an open hole is possible, and then the fracture interval is isolated using 2 packers (US DOE, 1998). However, it may be difficult to adequately seal the borehole with packers in clays and silts, especially if they are saturated (EPA, 1994). In a North American remedial context, the borehole is typically cut by a temporary *driven casing* with an inner, pointed rod (drivepoint). Lateral pressure from the surrounding formation is assumed to seal the casing, thus preventing backventing of contaminated injection fluid up into the borehole (Schuring, 2002; US DOE, 1998). In some cases it may be deemed necessary to seal the annulus between the borehole and the casing with concrete or bentonite to ensure a complete seal (Blem et al., 2004; Ohio Dept. of Natural Resources, 2005).

B.2.2 Cutting a notch

A notch is cut to start the fracture. A drivepoint (or *Shelby tube*) is advanced beyond the bottom of the casing into the undisturbed sediments and then withdrawn. A specially designed nozzle is then

inserted into the bottom of the hole, below the depth of casing and rotated while fluid is injected at high pressure, for example water at about 24 MPa (3500 psi; US DOE, 1998) to about 70 MPa (10,000 psi; Strong et al., 2004) thereby cutting a notch or disc-shaped opening into the undisturbed matrix. The fluid and cuttings are collected at the surface. The notch typically extends 10-15 cm from the borehole (US DOE, 1998). Previously, it was believed that this notch could be used to force fracture propagation in a preferred horizontal orientation (Suthersan, 1999), however, experience has shown that it is extremely difficult to control fracture orientation. Nonetheless, this notch reduces the injection pressure required to initiate a fracture.

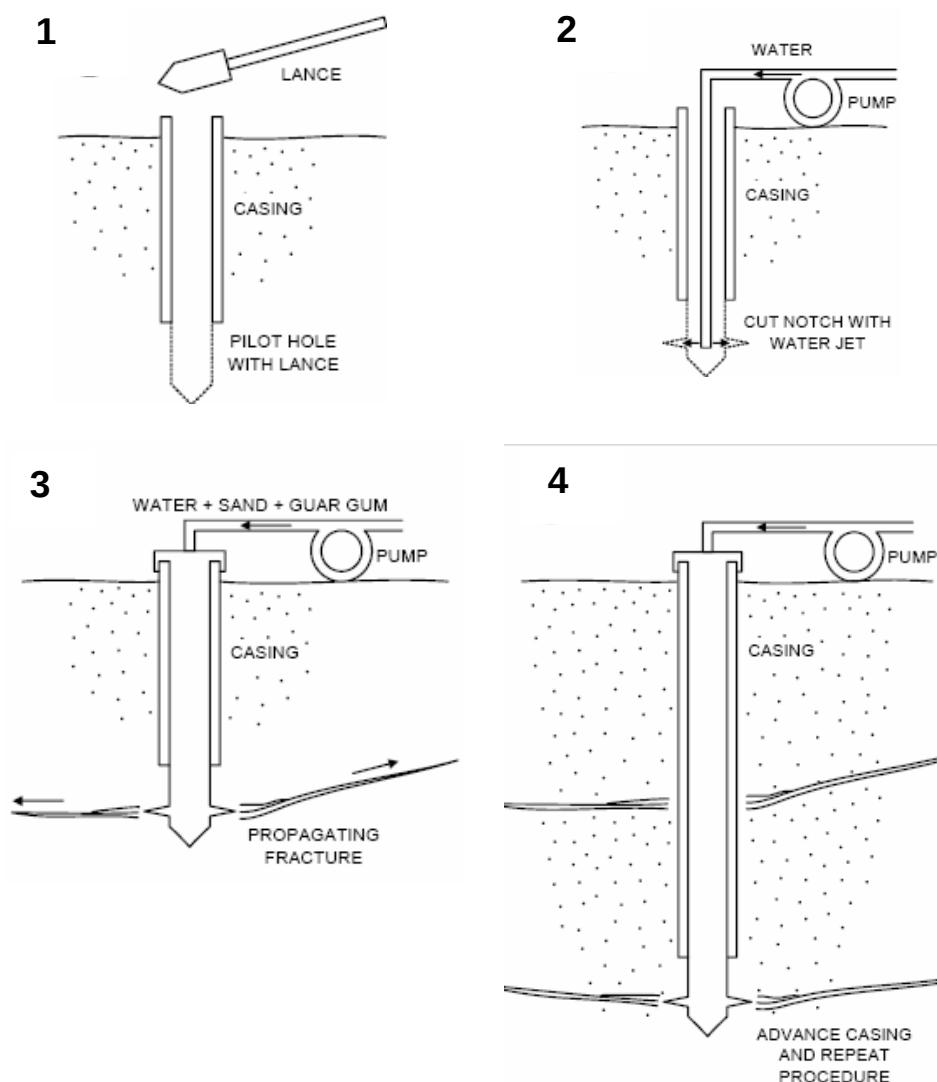


Figure B.1: The principles of hydraulic fracturing. (1) Typically a temporary casing is driven to the desired depth and a drivepoint (lance) is inserted into the undisturbed sediments. (2) A notch is cut immediately under the casing to start the fracture and reduce the initiation pressure required. (3) A slurry of sand and guar gel is injected under high pressure and flow rate to initiate and propagate a fracture. (4) After a fracture is completed the casing may be advanced (lowered deeper into the formation) and a new fracture created.

B.2.3 Initiation and propagation pressures

Creation and propagation of hydraulically induced fractures depend upon two operator-controlled

parameters: the injection pressure and the flow rate. The injection pressure must exceed a site-specific critical value which is a function of the natural strength of the formation and the in situ stresses at the fracture point, and thus depends upon a number of factors including *the degree of overconsolidation, formation cohesion (toughness of the formation)*, depth, degree of water saturation, etc. (Suthersan, 1999; Nilsson et al., 2000; Schuring, 2002). The initiation pressure required is generally less than 700 kPa (<100 psi) (Suthersan, 1999). Pressures of about 9000 kPa were applied at a site in Denmark and caused surface venting (Walsted et al, 2002). In addition to site-specific parameters, the required injection pressure increases with increasing depth, injection rate and fluid viscosity (EPA, 1994; US DOE, 1998).

After the fracture is initiated, the pressure required for fracture propagation drops to between 60 to 85 kPa plus about 20 kPa per m depth to 'lift the overburden' (EPA, 1994). The actual propagation pressure will depend upon the characteristics of the injection fluid and the site, and thus is based on past experience and trial and error at the site and depth in question (US DOE, 1998).

Although the pressure drops, the fluid injection must be maintained at a rate that exceeds the ability of the formation to receive the fluid so a fracture propagates (Suthersan, 1999; Schuring, 2002). Additional pressure will also be required to overcome friction losses in the equipment, delivery lines and geologic formation (Schuring, 2002). The pressure vs. time is monitored as an indication of whether the fracturing process has proceeded typically (Figure B.2).

The maximum radius and aperture of a hydraulic fracture is a function of the volume of fluid injected into it and the rate of *leak-off*: when the rate of injection equals the rate of leak-off into the formation, propagation ceases (EPA, 1994; Suthersan, 1999). Fracture propagation also ceases for the following reasons: if the fracture vents at ground surface; the fluid intersects a utility line, improperly sealed borehole, etc. and the pressure is 'bled off'; or the fluid meets a solid structure (Suthersan, 1999). On-site trial and error is the only method to determine optimal injection pressure and flow rate (Kidd, 2001).

The most commonly injected fluid in hydraulic fracturing appears to be a slurry based on 'continuous mix grade' biodegradable guar gum (EPA, 1994; Suthersan, 1999; Shuring, 2002). Guar is a food-based thickener and when mixed with water, it forms a short-chain polymer that rapidly attains a consistency of mineral oil (EPA, 1994). A *cross-linker* is added which further increases the guar gel viscosity so that it can hold a *propping agent*. A propping agent is solid granular material injected with the guar to hold fractures open after the injection process is completed.

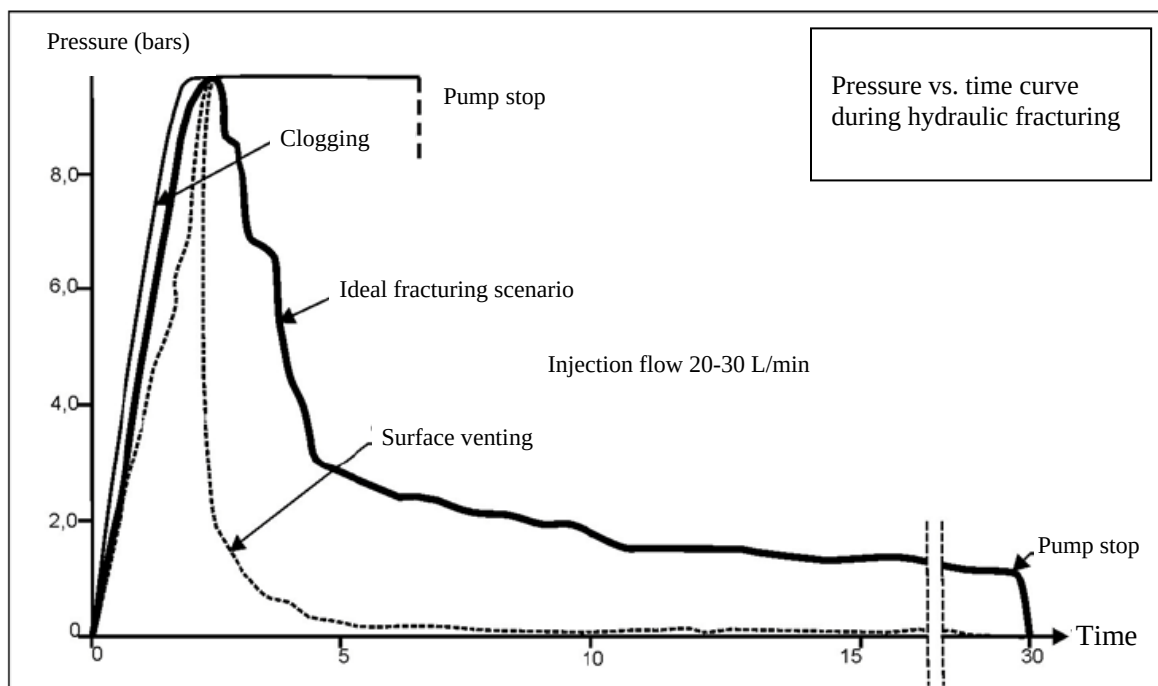


Figure B.2: Pressure vs. time curves during hydraulic fracturing. The figure depicts an ideal fracturing scenario (bold line) with a high initiation pressure (10 bars) followed by a lower propagation pressure which remains relatively constant (2-4 bars) until pump stop (1 bar = 100,000 Pa). The thin line represents clogging. The pressure remains high, until the pump is stopped because the slurry cannot force its way into the formation. The dashed line represents a case of surface venting, where a high pressure in the borehole cannot be maintained: there is no back pressure because the slurry is escaping to the surface. (Modified from Walsted et al., 2002)

Medium to coarse-grained sand to guar in a ratio of 1.2 to 1.8 kg sand per litre gel is typically used (EPA, 1994). An enzyme also referred to as a chemical "*breaker*" is added to the slurry to ensure that it breaks down to a water-like consistency and thus does not clog the fracture. Typically, the breaker is designed to activate about 2 to 8 hours after injection (Bures, 1998). Compared to water, guar gel has less leak-off and is able to carry more propping agent. The guar to sand ratio is adjusted for each fracture depending upon the depth and specific soil conditions (US DOE, 1998). Again, a test fracturing in an uncontaminated area of the proposed hydraulic fracturing site is recommended to adjust the slurry to site-specific conditions and design (pressure and flow rate) requirements (Suthersan, 1999).

Mixers capable of handling the required volumes of slurry components will be required on site. Pumps should be heavy-duty, capable of pumping the high-viscosity, high-sediment slurry. Monitoring equipment such as flow meters, pressure gauges, and uplift measurement equipment are also required.

B.3 Characteristics of hydraulic fractures

The literature study of US and Canadian experiences with fracturing revealed a wide range in quantitative results indicating that the applicability and results of fracturing are highly site dependent

(Schuring, 2002). Consequently, the values presented in Table B.1 should be considered as guideline values, rather than absolute parameter definitions.

Table B.1: Hydraulic fracturing requirements and results, obtained primarily from summary reports. Specific results from case studies are presented in *Appendix Y: Electronic Data, Table C.1*: US and Canadian experiences with environmental fracturing* and *Table C.5*: Danish experiences with environmental fracturing*, where some of the values may deviate from typical values quoted in the summary literature.

Characteristic	Hydraulic Fracturing
Aperture	1-2 cm ^A ; 0.5-1 cm; decreases with distance from injection point ^B ; very difficult to accurately determine at depth ^C
Uplift	Fracture aperture correlates with amount of uplift ^A ; decreases with fracturing depth due to ability of overlying formation to absorb the strain deformation; use of propping agent causes greatest permanent heave ^D
Fracture fluid	Guar gel slurry with sand. Back pressure can cause pressure venting leading to a spill at surface or in the fracture well ^A
Initiation pressure	<700 KPa (100 psi) ^B
Propagation pressure	<700 KPa (100 psi) ^B ; 60 to 85 kPa plus about 20 kPa per m depth ^C
Duration of Fracturing	5 to 10 minutes ^A ; 10-30 minutes ^D
Orientation	Fractures often are angular and intersect the surface ^A ; affected by heterogeneities in soil, existing fractures and to a lesser degree bedding planes; follows the path of least resistance ^B ; very difficult to determine dip in deep fractures; sand-filled induced fractures often intersect natural fractures and permeable lenses ^{C,E} .
Radius of fracture zone	4.6- 15m (15 to 50 ft) outward ^A ; 6-11, max 17 m (20 –35 ft, max 55 ft) ^B ; at depths between 1.5 to 5 m the max dimension (diameter) is approximately 3 times its depth ^C
Minimum depth possible	Generally > 3 m otherwise surface venting (daylighting) tends to occur, but in dense, stratified deposits shallower may be possible, i.e. min depth reported in literature is 1.2 m ^D
Maximum depth possible	About 9 m ^B ; 22.9m ^D
Injection interval	1.5 – 6 m (5 to 20 ft) ^A ; 0.5 to 1.0 m vertical intervals until the base of the contaminant zone is reached ^{E,G}
Minimum spacing between fractured intervals*	Fracturing intervals less than 0.5 ft tends to cause fractures to merge short distances from the borehold ^B
Longevity	Unknown, lack of longterm monitoring at least > 1 yr. ^A
Factors controlling max. dimensions	Volume of liquid injected (and rate of leak-off) ^B
Fracture density	Typically 1 to 2 major fractures per injection interval ^A

*The minimum distance between fractured intervals is poorly defined/described in the literature. In some studies the packer and fracturing equipment form a single unit and thus, while there is actually some spacing between the fractured zones, it is possible to have nearly continuous fracture intervals. In other studies only selected depths or geological units are fractured and the spacing between fracture intervals may be long and/or irregular. A: US DOE, 1998; B: Suthersan, 1999; C: EPA, 1994; D: Schuring, 2002; E: Bures, 1998; F: EPA, 1995; G: Siegrist et al. 1999.

B.4 Evaluation of remediation enhancement with hydraulic fracturing technology

All case studies in the literature report at least some degree of success in achieving their particular

goals, and often the degree of enhancement is substantial as indicated by Table B.2. However, the applicability of hydraulic fracturing at a particular site will depend upon a number of factors including: type of formation, depth of contamination, sensitivity of surface structures, proximity to a vendor, etc.

Table B.2: Summary of fracturing results as reported by other authors and based on literature search of 33 hydraulic fracturing case studies.

Enhancement	Results from 86 case studies ^A		Results of literature search (33 case studies)	Hydraulic Fracturing Consultant ^B
	Range of reported results	Average of reported results		
Increase in permeability / conductivity	5 to 153 times	34 times	1-2 orders of magnitude	Up to 3 orders of magnitude
Increase in mass removal rates	5 to 10 times	8 times	36-100% ^C	Up to 20 times
Increase in radius of well influence	1.0 to 7.6 m	4.9 m	5 to > 22 ft	-
Increase in radius of well influence	1.3 to 9 times	5 times	33 to 695%	Up to 5 times
A: from Schuring, 2002. Some of the 86 case studies may or may not be the same as those reported in Appendix Y: <i>Electronic data: Table of US, Canadian, and Danish Experiences with fracturing</i> . None of these 86 studies are blast-fracturing studies. B: Bures, 1989, all results based on a comparison to in-situ mass transfer remedial technologies in low-permeability soils. C: percent reduction in contaminant concentration				

B.5 Other aspects of environmental fracturing

There are many considerations or practices associated with environmental fracturing that are common for both hydraulic and pneumatic fracturing. The most important of these, for example site selection characteristics and possible risks associated with environmental fracturing, are discussed in Chapter 2. The following section presents aspects that are common to both types of fracturing, but which are considered of secondary importance/interest to the reader.

B.5.1 Creating fractures from horizontal boreholes

It is possible to create multiple fractures from a single horizontal borehole. The technique is similar to that described employed in vertical boreholes, except the fracturing and packer equipment is dragged through a horizontal borehole having a surface entry and exit point. Fractures are induced in packer-isolated intervals, generally 2 to 3 meters in length. The well casing and screen are pulled behind the fracturing equipment and left in the borehole after the fracturing is completed (Bures, 1998; Walsted et al., 2002).

There are several advantages associated with fracturing from a horizontal borehole. First, it is possible to drill the hole and create fractures under buildings and other structures (Bures, 1998). This is particularly useful at sites where contamination is located under floors. Secondly, the horizontal borehole is generally drilled through the area of contamination and thus, depending upon the con-

figuration of the contamination, this single borehole may have contact with a larger area of contamination compared to a conventional vertical borehole (Bures, 1998). Third, installation of a few horizontal wells compared to a number of vertical wells at a remedial site may be less expensive. Finally, creation of an upward gradient to the horizontal well may promote hydraulic containment of contamination at the site (Walsted et al., 2002). However, fracturing from a horizontal borehole has been undertaken in Denmark (Walsted et al., 2002) and the conclusion of that pilot-scale project was that the technology (as applied in Denmark) requires further development.

B.5.2 Well completion

Since fracturing is not a stand-alone technique, fracturing borehole(s) will likely be completed and used as monitoring and/or injection/withdrawal well(s) after fracturing activities are completed. Discrete screened intervals coinciding with the fracture intervals is a more expensive solution than a single long screen, but permits a more flexible use of the well for future remedial activities and monitoring, for example depth-specific monitoring. An alternative is installation of an appropriate number of small-diameter wells within the single borehole, each screened at a single depth coinciding with a fracture interval. Types of completed wells are illustrated in Figure B.3. The most appropriate type of well completion depends upon the budget available and the planned use of the wells.

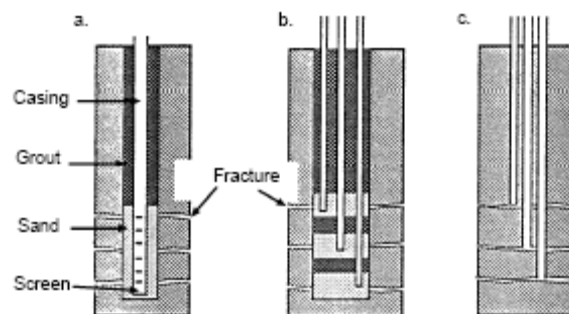


Figure B.3: Methods for completing wells with induced fractures a) screen across all fractures; b) casing each fracture; c) driven casing to each fracture (EPA, 1994).

APPENDIX C: EXPERIENCES WITH ENVIRONMENTAL FRACTURING

C.1 Introduction

Environmental fracturing, as described in Chapter 2, was developed in the United States and Canada. Its application in other parts of the world appears extremely limited, as only one application in Belgium and 2 in Denmark (Nilsson et al., 2000; Roote, 2000; Walsted et al., 2002; Blem et al., 2004)* were found in the literature. The following chapter provides an overview of the extensive American and Canadian experience with environmental fracturing, as well as the more recent Danish experiences.

C.2 US & Canadian experiences with environmental fracturing

The following overview of US and Canadian (and Belgium) experiences with environmental fracturing in low-permeability soils is based on a comprehensive literature study. The goal of the study was to provide documentation/evidence to evaluate the potential for application of environmental fracturing in Denmark. In particular the literature search focused on addressing the following questions:

- 1) Are relevant data for a given case published and thus accessible for comparison?
- 2) Has one type of environmental fracturing been favoured and, if so, why?
- 3) To what types of contamination has environmental fracturing been applied?
- 4) Which remediation techniques have been enhanced by environmental fracturing to date?
- 5) Have surface structures been affected by fracturing?
- 6) At what depths is fracturing possible?
- 7) How large an area may be expected affected by a fractured well?
- 8) Will fracturing stimulate advective flow (as well as shorten diffusion pathways)?
- 9) What degree of remediation enhancement may be expected by use of environmental fracturing?

The results of the literature search are discussed in the following sections.

C.2.1 Relevant case studies

Seventy-one relevant case studies from Canada and the US were found in the literature, as well as a single study from Belgium. Although data from the latter study was limited, the Belgium results are included in the following discussion of North American results, and all 72 sites are referred to as Canadian and US sites. The two Danish sites are discussed in a separate section.

* Based on personal communication with Knud-Erik Klint, GEUS, it is known that a hydraulic fracturing project is also currently ongoing (no published findings as of yet) – in Poland.

The case studies were selected based on the type of geologic media fractured: primarily till-type sites were selected. Case studies in which geology was not specified have also been included (only 5 of the 72 case studies). If these five studies are, in fact bedrock sites, the depth of fracturing and radius of fracturing may be larger than what would be typical in a low-permeability soil. Cases involving blast fracturing have been excluded, as this type of environmental fracturing is only conducted in bedrock.

The case study data have been assembled in an excel spreadsheet found in *Appendix Y:Electronic data, Table C.1*: US and Canadian experiences with environmental fracturing*, which will hereafter be referred to as Table C.1*. The data table represents a condensed summary of all the site information considered relevant to compare fracture sites and fracture results. Thus, it is a valuable resource for environmental consultants and researchers of environmental fracturing. The electronic form has been designed to permit sorting and searching of the data so statistics may be generated. Furthermore, the geographic location of each case study is included so users may identify sites and quickly find references to the original investigation(s).

Knowledge of site-specific conditions and results of previous case studies similar to a current project are valuable. While past experiences and rules-of-thumb are not guaranteed transferable to new sites, this type of information may reduce the amount of trial and error required with a new fracturing project. In addition, experiences from other sites provide a rough idea of what may be achievable at a proposed site. Environmental consultants can use this information as a first screening tool to weigh the likelihood of whether environmental fracturing is capable of producing the desired results at a specific site.

C.2.2 Status of selected case studies

Most of the case studies investigated (78%) were completed prior to 2000. Only 15% were still in progress, while the status of the remaining is unknown (Roote, 2000).

C.2.3 Hydraulic vs. pneumatic fracturing

Based on the literature search, application of the two types of environmental fracturing is evenly balanced: 54% of environmental fracturing is pneumatic, while the remaining 46% is hydraulic. The slight surplus of cases employing pneumatic fracturing could be taken to reflect the trend of its increasing use in recent years due to its claimed propensity for creating dense fracture networks rather than few distinct fractures (see Chapter 2). Roote (2000), however, states that the choice of fracturing type is governed by the proximity of a site to a research institute or vendor of either technology. This statement is partially supported by the literature search (Figure C.1), as both types of fracturing are used across the US and Canada, but with clear state-bound preferences. The state preferences are more likely to reflect state-proximity to a particular commercial supplier or state-experience with that supplier, than consideration of geology or contamination type of the state sites, as significant variation in geology and contaminants must be expected across a state. This is an

interesting finding as it suggests that neither technique has yet been proven superior in certain types of sediment/deposits.

From the literature, it is apparent that the two major hydraulic fracturing contractors are FRx, Inc. and FracRite, Ltd. in the US and Canada respectively, while Accutech Remedial Systems (ARS) Technologies, Inc. is the prominent pneumatic fracturing supplier. These vendors are specialised in environmental fracturing and have developed and patented several remedial systems to be coupled with fracturing at low-permeability, contaminated sites (ARS, 2005; FRx, 2005; NFEC, 2003; EPA, 2003; Blem et al., 2004; FracRite, 2005).

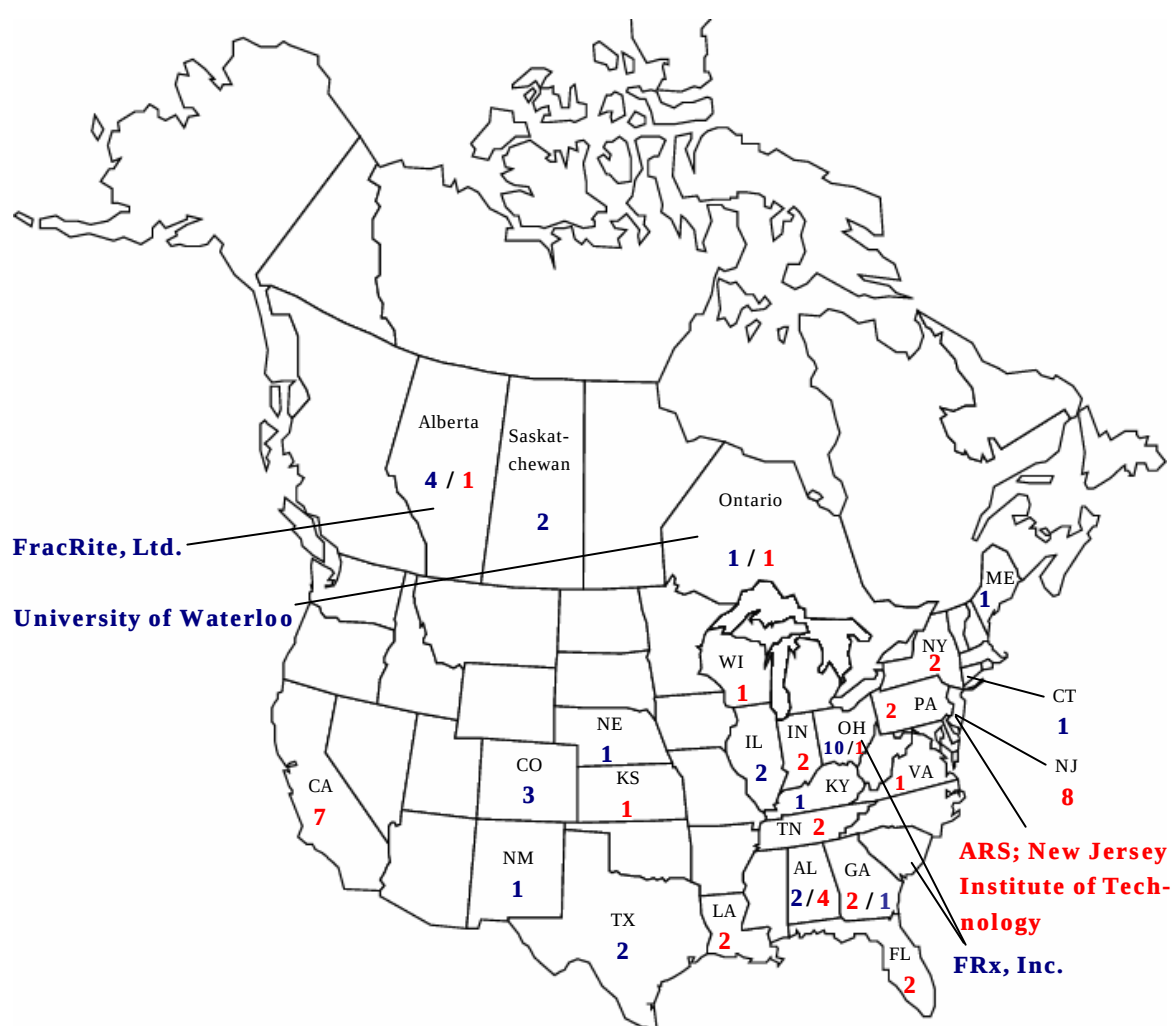


Figure C.1: Geographic distribution of cases (71 total) based on fracturing type employed and locations of major vendors/research facilities (patent holders). The blue numbers refer to hydraulic fracturing and the red numbers refer to pneumatic fracturing.

C.2.4 Types of contamination to which coupled remediation with fracturing has been applied

Figure C.2 shows that environmental fracturing has been employed primarily at sites contaminated with chlorinated solvents and secondly at sites contaminated with BTEX compounds and other

petroleum hydrocarbons. The dominance of solvents-remediation efforts coupled with fracturing stems from:

- the abundance of sites contaminated with these compounds due to their widespread usage and spillage especially at dry-cleaning facilities (see *Appendix N: Theory of chlorinated solvents*), and
- the serious threat to human health posed by these compounds if found in groundwater used as drinking water (*Appendix N: Theory of chlorinated solvents*; AVJ, 2001; Kjeldsen and Christensen, 1996).

Figure C.2 might prompt the erroneous conclusion that sites contaminated with solvents and BTEX compounds are particularly well-suited to undergo environmental fracturing. On the contrary, geology is the primary factor controlling the effectiveness of all in situ remediation technologies (Bures, 1998; Roote, 2000; Bures et al., 2003) and hence the choice of coupled remediation type.

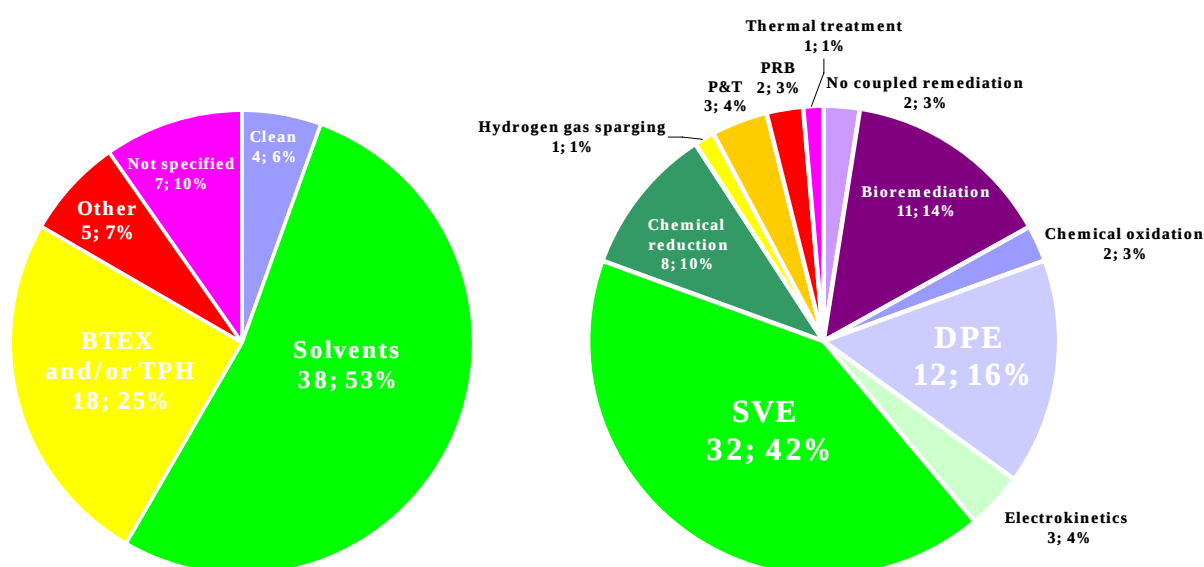


Figure C.2: Distribution of contaminants to which remediation with environmental fracturing has been applied.

Figure C.3: Distribution of remediation techniques coupled with fracturing at the 72 case study sites. Permeable reactive barriers (PRBs) are usually associated with chemical reduction via zero valent iron (ZVI). In the figure, however, PRBs and chemical reduction are given as separate remediation techniques, as the first includes more than just ZVI-barriers, and the second refers specifically to chemical reduction via ARS' FeroxSM technology

C.2.5 Coupled in situ remediation techniques

Figure C.3 illustrates that the mass transfer remediation techniques SVE (Soil Vapour Enhancement) and DPE (Dual Phase Extraction) are the remediation techniques most frequently coupled to fracturing. This correlates well the high proportion of fracturing sites contaminated with lighter VOCs being remediated (Roote, 2000; see also Figure C.2). Coupling to in situ mass destruction remedial techniques is also significant. In fact, Figure C.3 is based on case studies dating from the

early 1990s to the present day. Thus, the figure does not entirely reflect the current trend in remediation that is moving away from fracturing coupled with in situ mass transfer remediation techniques to fracturing coupled with chemical and biological remediation, e.g. anaerobic reductive dechlorination, chemical oxidation and chemical reduction of solvents (Bures et al., 2003; NFEC, 2003; EPA, 2003; Siegrist et al., 1999; US DOE, 2000). Selected in situ remedial techniques, where enhancement via application of environmental fracturing has been undertaken and show promise are discussed in *Appendix G: Coupled remediation technologies*.

C.2.6 Surface structures

Only 4 of the case studies included Table C.1* specifically mention fracturing directly under, or in close proximity to buildings (Roote, 2000; NFEC, 2003; ARS, 2005a). In all 4 cases, however, it is stated that fracturing was carried out without significant impact to these buildings. Residual heaves are thus assumed to have been approximately 2 cm or less, as Nilsson et al. (2000) states that residual heaves exceeding this height may impact structure integrity. It is recommended that the surface heave to horizontal distance ratio not exceed 1:300 (Schuring 2002). At the Hunter's Point Shipyard site, a residual heave of 2.5 cm (1 inch; NFEC, 2003) was observed, but only in 1 of the 4 fracturing boreholes at the site (NFEC, 2003), and without significant impact to on-site buildings.

C.2.7 Targeted depths

According to Roote (2000), most environmental fracturing projects (both hydraulic and pneumatic) have targeted depths of 3-8 m (10-25 ft; Roote, 2000), while fracturing at depths of less than 3 m b.s. (10 ft) and until 15m b.s. (50 ft) are also quite common. The statement is supported by the 36 cases (out of the 72 included in the summary Table C.1*) for which such data is available, see Figure C.4. The most common fracturing depth here is approximately 2.5 m b.s. (8 ft b.s.) or 64% (23) of the case studies. Approximately 50% of all cases involved fracturing at depths between 1.8 – 4.6 m b.s. (6-15 ft b.s.), while only approximately 10% of cases involved fracturing at depths greater than 15 m b.s. (50 ft b.s.).

Thus, the common range of fracturing depths overlaps with the depths at which spilled or leaked contamination is typically found as well the depths at which low-permeability glacial deposits are found in Denmark (greater than 1 m b.s. to generally about 8-25 m b.s.; Klint, 2005 personal communication).

Roote (2000) states that the maximum documented pneumatic fracturing depth is about 14 m b.s. (45 ft b.s.). While ARS Consultants (2005) claim that there is no theoretical depth limit for initiating a fracture in a geologic formation as long as sufficient pressure and flow can be delivered to the fracture zone, the maximum depth to which ARS has been able to achieve horizontal pneumatic fractures is as yet 23 m b.s. (75 ft b.s.); no mention was made concerning the geology (ARS 2005a). At some depth the vertical and horizontal stresses in the overburden will become similar and fracture propagation may become more vertical. Klint (2005, personal communication) states

that hydraulic fracturing at depths exceeding 10 m b.s. is not practical, when its purpose is to induce horizontally orientated fractures. Thus the literature search and Figure C.4 indicate that hydraulic and pneumatic fracturing technologies appear to be capable of creating induced fractures to the depths that would be required in a remedial context in Denmark.

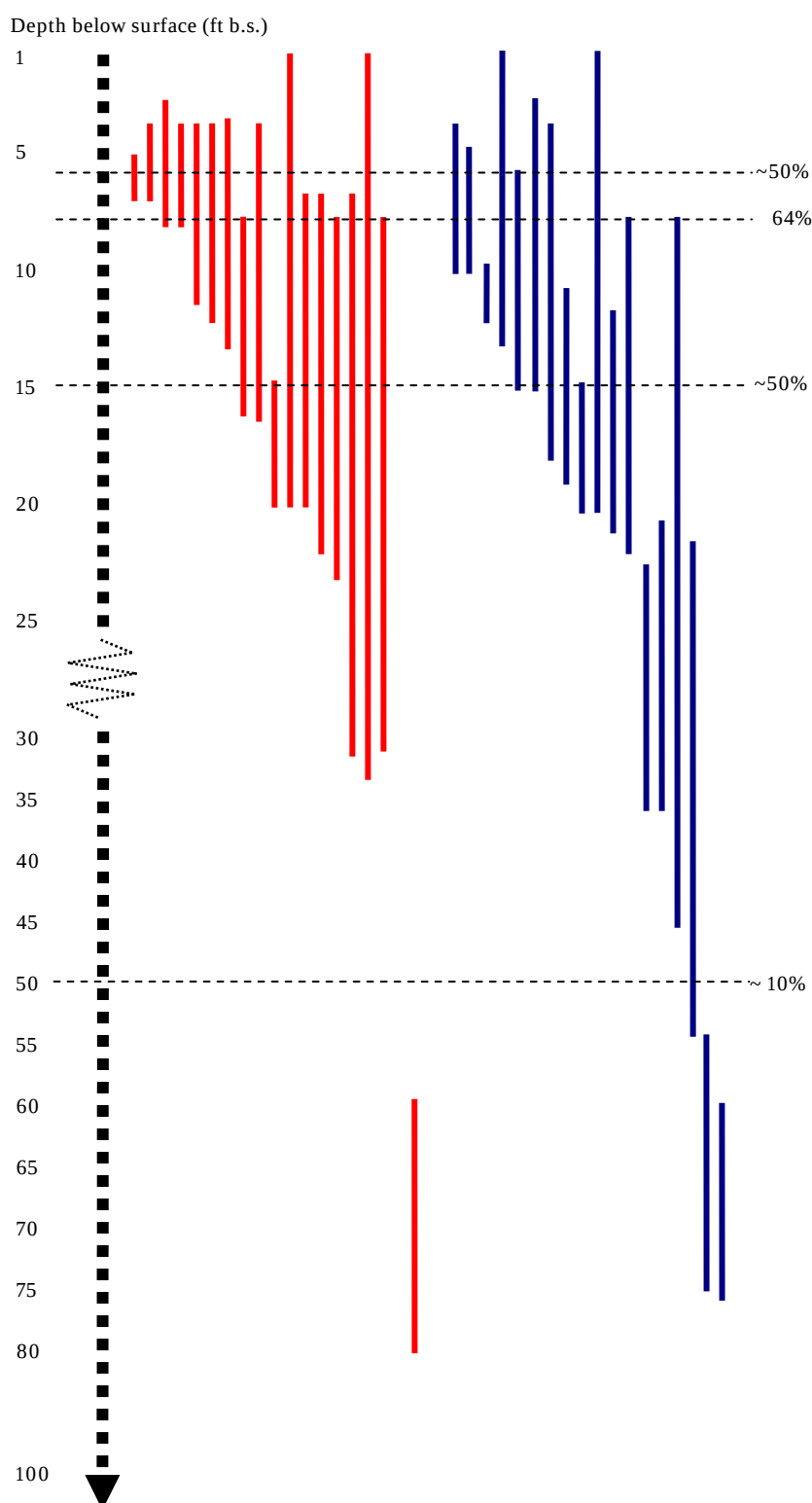


Figure C.4: Distribution of targeted and achieved depth of fracturing in 36 case studies where such data was specified. Hydraulic fractures are depicted in blue, while pneumatic fractures are red. The depth interval where 50% of the studies conducted fracturing ranges from 6 to 15 ft b.s. Only 10% of the studies reported fracturing at depths greater than 50 ft.

C.2.8 Fracture radius and radius of influence

Thirty-five of the 72 selected cases studies give figures for fracture radius and/or radius of influence achieved in the fractured wells at the given sites. The span of achieved radii is large, see Figure C.5. The radii have been measured in a variety of ways, and radius of influence may refer to a radius where hydraulic and/or vapour effects were observed. It is thus reasonable to expect a fracture radius of at least 3 m (10 ft) using either environmental fracturing method. The actual fracture radii and radii of influence at a specific site will be a function of the operator-defined parameters and site geology.

Blem et al. (2004) and Nilsson et al. (2000) state that the radius of influence of hydraulically induced fractures is often three times larger than the actual fracture radius. This statement is not, however, clearly supported by the data presented in Figure C.5.

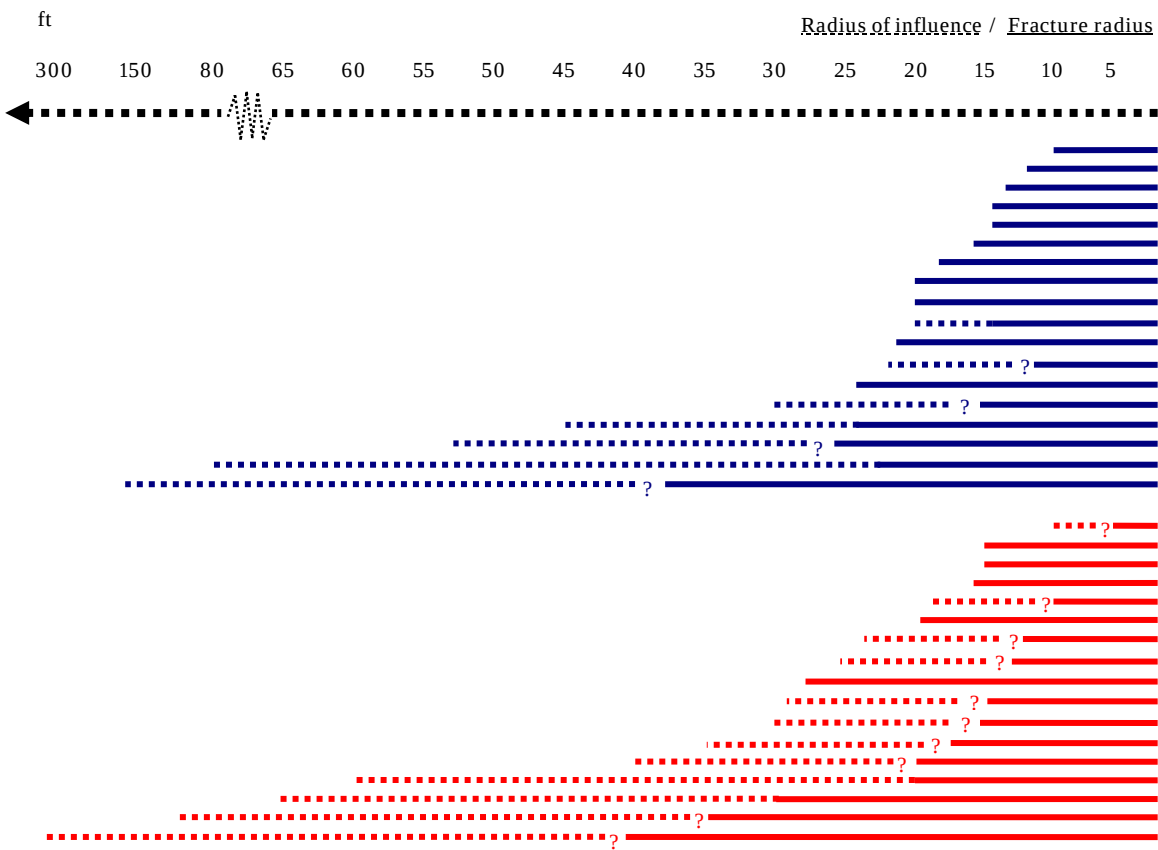


Figure C.5: Observed fracture radii and radii of influence at 35 of the 72 sites included in literature search. Full lines indicate fracture radii, while dashed lines indicate radii of influence. Question-marks indicate that only a radius of influence (not a fracture radius) has been stated, i.e. the fracture radius is unknown. Hydraulic fractures are depicted in blue and pneumatic fractures in red.

C.2.9 Fracture aperture

Only 17 of the 72 selected case studies give values for induced fracture aperture and/or surface heave.

Pneumatic fractures

Of the 17, 4 are pneumatic cases, see Table C.2 below. Based on this data, it is not possible to establish a typical range of apertures to be expected with pneumatic fracturing. Nilsson et al. (2000) state, however, that an aperture of 0.02-0.04 in (0.5-1 mm) is common.

Table C.2: Reported pneumatic fracture apertures.

Apertures/Heaves	Comments	Case and source
0.13 in (0,33 cm)	Aperture correlated with average residual heave.	Gasoline refinery, Marcus Hook, Pennsylvania (Roote, 2000; EPA, 1995; Venkatraman et al., 1998)
1 in (2,54 cm)	Aperture inferred from observed ground heave of 1 in. Not specified, however, whether heave in question is initial / maximal or net / residual.	Manufacturing facility, Shreveport, Louisiana (Roote, 2000; ARS, 2005a, LA001)
1.93 in (4,90 cm)	Aperture inferred from observed ground heave during injection. Thus likely representative of maximal heave and not necessarily aperture.	Industrial site, Roseland, New Jersey (Roote, 2000; ARS, 2005a, NJ006)
0.01 in (0.02 cm)	Aperture stated to be negligible and in the range of several hundred microns.	Navy Marine Corps Logistics Base, Albany, Georgia (ARS, 2005a, GA001; Palaia and Sprinkle, 2004; Strong et al., 2004)

Hydraulic fractures

The apertures were given in 13 hydraulic fracturing case studies and are shown in Table C.3. An average hydraulic fracture aperture of 0.69 in (1.75 cm) may be computed from the data. This correlates well with the average aperture of 0.4-0.8 in (1-2 cm) stated by Nilsson et al. (2000).

Table C.3: Reported hydraulic fracture apertures.

Apertures/Heaves		Comments	Case and source
Reported	Inferred average		
0.5 in	0.5 in	Figure stated as average aperture.	Former gas plant and compressor station, Alberta, Canada (Roote, 2000; Bures, 1998)
0.5 in / 1-1.5 cm	0.5 in	-	Linemaster Switch Superfund site, Woodstock, Connecticut (Roote, 2000; FRx, 2005; Nilsson et al., 2000)
0.6 in	0.6 in	Figure stated as average aperture.	Former sour gas plant site, Alberta, Canada (Roote, 2000; Bures, 1998)
0.6-1 in	0.8 in	-	Storage tank site, Beaumont, Texas (Roote, 2000)
0.7 cm	0.28 in	Figure stated as maximum aperture.	Navy Marine Corps Logistics Base, Albany, Georgia (Strong et al., 2004)
1 in / 3-30 mm	0.65 in	Aperture correlated with measurement of maximum uplift of ground surface.	Xerox Corporation site, Oak Brook, Illinois (Frank and Barkley, 1994)
1.5-2.5 cm	0.79 in	-	EPA Center Hill Testing Facility, Cincinnati, Ohio (Nilsson et al., 2000)
1.2-2.3 cm	0.69 in	-	LUST site, Dayton, Ohio (Nilsson et al., 2000)
11-21 mm	0.63 in	Aperture correlated with measurement of maximum uplift of ground surface over fracture zone.	Mobil Gas Station, Addison (Frank and Barkley, 1994)
1-4.65 cm	1.11 in	Aperture correlated with measurement of minimum surface uplift.	Laidlaw site, Ontario, Canada (Roote, 2000; USDOE, 1996?; Nilsson et al., 2000)
2-10 mm	0.24 in	Aperture determined by core sampling in test cell.	US DOE Portsmouth gaseous diffusion plant, Piketon, Ohio (Siegrist et al., 1999)
2-3 cm	0.98 in	-	Ohio (Roote, 2000)
23-35 mm	1.18 in	-	Dristler Brickyard site, Louisville, Kentucky (Bures et al., 2003)

C.2.10 Evaluation of remediation enhancement

Sections of the following table have been presented elsewhere in the report. The complete table is presented here to facilitate comparison of results achieved using the two technologies. Both types of environmental fracturing appear to provide a significant degree of remediation enhancement.

Table C.4: Summary of fracturing results as reported by other authors and based on literature search of case studies (see Table C.1* for details).

Enhancement	Results from 86 case studies ^A		Results of literature search	Hydraulic Fracturing Consultant ^B
	Range of reported results	Average of reported results		
Pneumatic fracturing				
Increase in permeability/conductivity	1.5 to 175 times	28 times	1 to > 1 order of magnitude	
Increase in mass removal rates	3 to 25 times	10 times	50-99.9% ^C	
Fracture radius	1.4 to 10.7 m	4.9 m	8 to > 30 ft	
Increase in radius of well influence	1.4 to 30 times	8 times	50 to 200%	
Hydraulic fracturing				
Increase in permeability/conductivity	5 to 153 times	34 times	1-2 orders of magnitude	Up to 3 orders of magnitude
Increase in mass removal rates	5 to 10 times	8 times	36-100% ^D	Up to 20 times
Increase in radius of well influence	1.0 to 7.6 m	4.9 m	5 to > 22 ft	-
Increase in radius of well influence	1.3 to 9 times	5 times	33 to 695%	Up to 5 times
A: from Schuring, 2002. Some of the 86 case studies may or may not be the same as those reported in Table C.1*. None of these 86 studies are blast-fracturing studies. B: Bures, 1989, all results based on a comparison to in-situ mass transfer remedial technologies in low-permeability soils. C: percent reduction in contaminant concentration				

In the early days of environmental fracturing it was expected that a general increase in extraction rate of 10-50 times, similar to that observed with fracturing in the oil and water well industries, could readily be transferred to the environmental remediation field (EPA, 1994). In most cases, initial results of environmental fracturing supported this thesis through dramatic increases in flow rates to extraction wells (see Table C.4) and orders of magnitude increases in concentrations of contaminants removed (EPA, 1995).

Long-term measurements of mass removal rates often display an initial spike, and then falling concentrations (EPA, 1995; Martin et al., 2002). This is often attributed to diffusion limitations (as discussed in Chapter 2). However, removal rates typically remain elevated at least several times above pre-fracture rates (Schuring, 2002).

Eighteen of the case studies included in Table C.1* give figures for relative contaminant reduction (in %) achieved by means of environmental fracturing. Ten of the 18 also state the residual contamination concentrations. For pneumatic and hydraulic fracturing combined the reduction percentages vary from 36-100%. In 14 of 18 cases a 90% reduction or greater in at least part of the remediation area was reported. In absolute figures this translates to residual concentrations varying

from the non-detectable to 200 ppm (mg/L). For most of the sites 7 (or 70%), however, the range was less than 1 ppm (mg/L) concentrations.

These apparently encouraging figures must be considered in the light of clean-up goals/remediation targets, which have not, in most of these cases, been identified, and even if they are met, residual concentrations may remain significantly above Danish drinking water criteria (0.1 µg/L for the total content of chlorinated solvents). Documentation of residual concentrations nearing Danish drinking water guidelines were not found in the case study literature search.

C.3 Experiences with environmental fracturing in Denmark

Only hydraulic fracturing has been conducted in Denmark: first in 2000 with a horizontal borehole (Walsted et al., 2002); second in 2001 with vertical boreholes (Blem et al., 2004). Both were financed by the Technology Development Programme for Soil and Groundwater Pollution under the Danish Environmental Protection Agency (DK-EPA). The details of these studies are summarized in *Appendix Y: Electronic data, Table C.5*: Danish experiences with environmental fracturing*. Both of the Danish hydraulic fracturing projects were conducted as preliminary tests of the technology on Danish soil – at clayey till sites on the island of Zealand. Pneumatic fracturing has not yet been attempted in Denmark (Ramsay, 1999).

The fracturing test utilizing vertical boreholes was considered successful (Nilsson et al., 2003, Blem et al., 2004), giving rise to recommendations for use of this method in full-scale remediation enhancement in the clayey soils/sediments covering a considerable part of Denmark, i.e. large parts of Zealand, Funen and Eastern Jutland. Especially till sediments (and Tertiary clays) are expected to have great potential for successful creation of horizontal hydraulic fractures, as these sediments are often overconsolidated. The actual employment of hydraulic fracturing in full-scale remediation context in Denmark has yet to be tested.

The initial results of the fracturing test using horizontal boreholes (drains) were inconclusive, as a significant increase in hydraulic radius of influence was seen, but no increase in water extraction was achieved (Walsted et al., 2002). Furthermore, several instances of surface venting were experienced during fracturing via the horizontal boreholes (Walsted et al., 2002). Nilsson et al. (2003) conclude that the method is not yet suited for commercial (full-scale) use in Denmark.

Pneumatic fracturing has to date not been conducted outside North America. The pneumatic fracturing test linked to this project, conducted in December 2005, is thus the first of its kind in Denmark. The results of the test and a discussion of its potential in a remedial context in Denmark are given in Chapters 6 and 7.

C.4 Costs of environmental fracturing

The cost of environmental fracturing is not discussed as it is difficult to 1) correlate costs from pilot projects to full-scale site remediation; 2) to estimate potential costs in Denmark relative to Canada and the US where a number of fracturing contractors are established. However, if fracturing is able to create a more homogeneous/uniform geologic deposit and thereby reduce remedial times, then it may 'pay for itself' (Schuring 2002).

C.5 Conclusions

Tables C.1* and C.5* represent a review and summary of 72 US and Canadian case studies and 2 Danish studies, respectively, presented in accessible 'searchable tables'. This is a valuable resource for environmental consultants and researchers of environmental fracturing.

The application of hydraulic or pneumatic fracturing thus far appears to depend on state preference/experience with a certain contractor or research institute rather than technical and/or geological considerations.

Environmental fracturing is applied predominately to solvents and BTEX/hydrocarbon contaminated sites and has consequently often been coupled with vapour extraction remediation techniques. However, fracturing is increasingly applied to enhance mass destruction remedial methods.

Although remedial enhancement via environmental fracturing appears successful, much of the post-fracturing testing is short-term and 'black-box' meaning that improvements in mass removal rates are typically measured soon after fracturing and where or how the permeability of a deposit is improved is seldom investigated. Decreasing removal rates are often attributed to diffusion limitations. While mass reduction rates are high (36-100% decreases in contaminant concentrations, residual concentrations nearing Danish drinking water guidelines have not been documented.

The achievable depths, fracture radii and radii of influence attributable to environmental fracturing are suitable in a Danish remedial context. Only two trials of (hydraulic) fracturing have been reported in the literature. Fracturing from vertical boreholes appears most promising.

APPENDIX D: DISCUSSION OF DIRECTIONS OF STRESS AND OVERCONSOLIDATION

D.1 Stress and orientation of induced fractures

Fractures tend to form in the direction normal to the least stress (EPA, 1994; Suthersan, 1999; see Figure D.1). When sediments are initially deposited, the three principal stresses (σ_x , σ_y , and σ_z or σ_v and $2 \times \sigma_n$, as depicted in the figure) are in equilibrium and equal to the overburden pressure. External forces, for example glaciation, excavation, erosion, desiccation, etc. can change the stress fields (Suthersan, 1999). Glacial sediments in Denmark are referred to as overconsolidated ($K_o = (\sigma_h/\sigma_v) > 1$) (Blem et al., 2004). This means that the compaction of the sedimentary materials is greater than the present day stress. I.e. glacial retreat decreased the vertical stress, while the horizontal stress remained unchanged. Since most sediments in Denmark are overconsolidated, and since the principal stress is thus least in the vertical direction, horizontal fractures will tend to form.

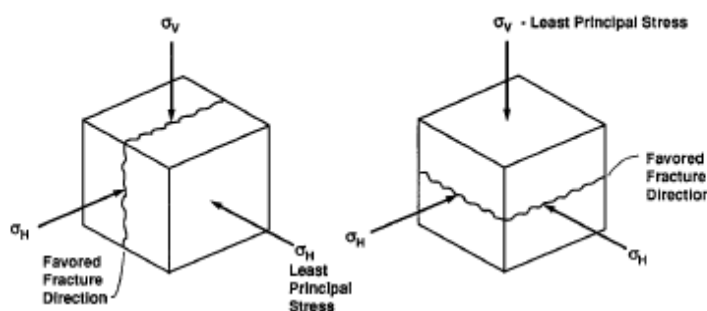


Figure D.1: Relationship between direction of least principal stress and direction of fracture propagation (from Suthersan, 1999).

The ratio of horizontal to vertical stress is referred to as a K_o value (coefficient of earth pressure at rest). When K_o values are greater than 1.0, flat-lying fractures tend to form, and the larger the K_o value, the more flat-lying the fractures will tend to be (Suthersan, 1999).

D.2 Overconsolidation and directions of stress

An overconsolidation ratio may also be used to determine the likelihood of horizontal fractures (Blem et al., 2004):

$$OCR = \frac{\sigma_{pc}}{\sigma_0}$$

where: OCR = the overconsolidation factor
 σ_{pc} = previous in situ stress
 σ_0 = present in situ stress.

The value for σ_{pc} is determined using an empirical formula, which should be used with caution (Nilsson et al., 2000). The in situ stress term σ_0 is a function of the sediment density, depth and saturation (Nilsson et al., 2000). Values from two Danish sites are listed in Table D.1

Table D.1: Values for previous in situ stress, present in situ stress and calculated OCR values for 2 Danish sites, Næstved (Slagelsevej 190) (Walsted et al., 2002) and Haslev (Blem et al., 2004). σ_0 values for the Haslev site are calculated assuming a water table at 6 m b.s. Although the OCR values are greater than 1, and horizontal fractures would be expected, a number of the induced fractures were steeply climbing towards ground surface at the Næstved site. At the Haslev site fractures were subhorizontal and trending downwards.

	Soil Type	Depth below surface [m]	σ_{pc} [kPa]	σ_0 [kPa]	OCR
Næstved	Moraine clay	2.5	400	28	14
	Sand	3.53	500	40	12
	Moraine clay	4.53	400	52	7
	Moraine clay	2.5	180	28	6
	Moraine clay	3.55	400	40	10
	Moraine clay	4.55	300	52	6
Haslev	Moraine clay	2.4	200	48	2
	Moraine clay	4.3	400	86	4
	Moraine clay	6.3	700	124	4
	Moraine clay	8.2	500	146	3

A number of assumed values are used in both the K_0 and OCR calculations, and since there are examples where vertical fractures have formed even though the K_0 and OCR values were greater than one, as in the case of the Næstved site, it is likely sufficient to assume that all sediments in Denmark are overconsolidated and that generally fracture propagation will be *initially* horizontal. Weakness, existing fractures and other ‘paths of least resistance’ in the matrix will likely affect the direction of fracture propagation. For example, induced fractures may be horizontal near the injection well and then climb towards the surface, following existing fractures.

APPENDIX E: METHOD TO ESTIMATE REQUIRED INITIATION PRESSURE FOR PNEUMATIC FRACTURING

The pressure required to initiate a pneumatic fracture depends upon the *cohesive (tensile)* strength of the formation and the overburden pressure (a function of the density and depth). A method to calculate a rough estimate of the required initiation pressure may be obtained using the expression in Box E.1 which assumes that the geologic material is brittle, elastic and *overconsolidated* (Suthersan, 1999):

Box E.1: Method to estimate the required initiation pressure for pneumatic fracturing. Modified from Suthersan (1999).

$$P_i = C\delta' Z + t_a + P_0 ,$$

where:

P_i is the required initiation pressure (Pa);

C is a coefficient (ranging from 2.0 to 2.5) $(s^2)^{-1}$;

δ' is the effective unit weight defined as the soil density (kg/m^3) multiplied by the height of the overlying soil column (m);

Z is the overburden depth (m)

t_a is apparent tensile strength (N per unit area), which is a measure of the ability of a material to resist a stress tending to stretch it or pull it apart. Determined from laboratory investigations;

P_0 is hydrostatic pressure (Pa or N/m^2), the pressure exerted by water at higher levels in the saturated zone.

Substituting in typical values for a clay at about 6 m (20 ft) depth gives a required initiation pressure of about 700 kPa (100 psi; Suthersan, 1999). Considering the uncertainty in determining some of these parameters, and their variability across a site and over depth, it will likely be more practical and just as appropriate to adopt a reasonable initiation pressure used at a similar site and test it at the fracture site.

APPENDIX F: DIRECT AND INDIRECT METHODS TO EVALUATE ENVIRONMENTAL FRACTURING RESULTS

F.1 Introduction

Most of the literature regarding environmental fracturing stems from remedial pilot projects or full-scale commercial remedial projects rather than scientific field studies. Consequently, the majority of the fracture evaluation results are presented in terms of easily measured physical parameters or improved fluid extraction or mass removal rates, etc. Indirect methods of measurement are typical because they are simple and inexpensive. This appendix provides the reader with a short discussion of some of the monitoring and evaluation methods used to evaluate fracturing results and some of the shortcomings inherent in these methods. Knowledge of these monitoring and evaluation methods allows the environmental consultant or other researchers to critically assess the results reported in case studies.

F.2 Direct and indirect methods to determine fracture aperture

Determination of fracture aperture is an example of a parameter which is seldom measured directly, although the accuracy of this term is important in advection and diffusion calculations.

F.2.1 Aperture estimation from uplift data from fractures induced to about 5 m depth

The amount of residual uplift (after fracturing has ceased) is assumed to be directly proportional to the aperture of the fracture (EPA, 1994; Suthersan, 1999) at depths until about 5 m b.s. (i.e. when the fracture length to depth ratio is roughly 3 (EPA, 1994). Below about 5 m b.s. the aperture becomes difficult to determine: they become smaller due to the ability of the overlying formation to absorb the strain of deformation (Schuring, 2002). The assumption of a direct correlation between uplift and aperture is problematic for a number of reasons:

- 1) The amount of uplift is also a function of site-specific characteristics such as overburden depth and *deformability*. Consequently assuming a 1:1 ratio for amount of vertical uplift to fracture aperture must be considered a rough estimate at best.
- 2) Using uplift measurements as a surrogate measurement of fracture aperture may be inappropriate at a number of sites. At a site in Denmark, hydraulically fractured at 4.5 m b.s., no measureable uplift (< 1 mm) was observed although visual inspection of cores revealed fractures with apertures of 0 to 20 mm (Walsted et al., 2002). Similar results were observed at a second Danish site (Blem et al., 2004). At a number of sites, hydraulic and other testing conducted after fracturing indicate that the radius of influence extends beyond the zone

of uplift (Schuring, 2002; Blem et al., 2004), suggesting that open fractures may be created although not detected by uplift monitoring equipment.

- 3) This method attributes all uplift to the creation of a single fracture: forking or multiple fractures are not considered. Although the fracture interval is typically large (> 0.5 m), cores are rarely investigated to confirm whether only a single fracture was created.

F.2.2 Aperture estimation from uplift data from fractures induced at depths greater than 5 m

At fracturing depths greater than 5 m, the hydraulic fracture aperture is estimated from the radial extent of uplift and the volume of fluid pumped into the formation. However, this method may be problematic for the following reasons:

- 1) The aperture may be overestimated as this method does not consider fluid losses into the pores and existing fractures (leak-off).
- 2) Since the amount of uplift decreases with depth (Schuring, 2002) it may be difficult to accurately determine the radial extent of uplift associated with fracturing below 5 m.

Apertures of pneumatic fractures below about 5 m are difficult to estimate from uplift data for the above reasons and also because pneumatic apertures are so small, that accurate measurement of uplift is difficult.

At the Vasby field site (discussed in Chapter 6), observations of change in elevation rather than just residual uplift (final elevation minus start elevation) revealed that there was further collapse of the formation between fracturing events, i.e. after measurement of residual uplift at a particular elevation. Strong et al. (2004) mention that groundwater and pressure effects, etc. may take time to dissipate. This suggests that the observations of formation collapse at Vasby could have been due to slow tracer dissipation. This raises the question of whether uplift measurements, taken immediately after injection has ceased, overestimate apertures.

F.3 Estimation of fracture radius

Similarly, fracture radius (the lateral extent of fractures) may affect hydraulic conductivity by orders of magnitude, but is typically measured indirectly. Some direct and indirect measurement methods and their shortcomings are listed below:

- 1) The maximum radial extent of uplift is often assumed to be the fracture radius (EPA, 1994) but as discussed above, the amount of uplift is difficult to determine at depth.
- 2) The fracture radius is also assumed to be related to the fracturing depth. According to EPA (1994) the size of fractures increases with depth, with typical ratios of maximum length to depth of 3:1 at depths between 1.5 to 5 m b.s. and 4:1 at depths > 5 m b.s.
- 3) The radius of influence (the radius in which some hydraulic, permeability, etc. effect can be measured) is often used as a surrogate for the fracture radius. However, Blem et al. (2004) and Nilsson et al. (2000) state that the radius of influence of hydraulically induced

fractures is often three times larger than the actual fracture radius. This latter statement was not confirmed by the literature search, thus, it is uncertain what the relationship between these 2 radii is.

- 4) Cores provide a direct method to document the fracture radius, but it may be difficult to 'capture' the fractures as observed by Markesic (2000) and at the Vasby site.
- 5) A tracer test may provide good documentation of the fracture radius, but requires very small injection and sampling intervals to be precise, consequently this method is time consuming and expensive.

F.4 Estimation of fracture form and orientation

The lack of detailed field information of fracture radii in 3 dimensions has given rise to persistent conceptual models in the literature that may not adequately describe induced fractures. For example, fractures are often described as 'steeply dipping elongated features to flat-lying circular disks or bowl-shaped features' (EPA, 1994) or having a 'predominately radial pattern' (US DOE, 1998).

The orientation, dip and radius of fractures are typically estimated indirectly from the few levelling fix points or tiltmeter readings taken during the fracturing activities. The area of uplift is assumed to be circular or elliptical, although this assumption may arise from expectations and the sparse number of instruments rather than actual observations. In fact, the form depends upon type of fluid, rate or pressure of injection, configuration of borehole plus loading at ground surface, permeability, formation heterogeneity and subsurface borings (EPA, 1994). More recent observations from field work, especially visual inspection of cores/excavations (Markesic, 2000; Blem et al., 2004) suggest that fracture propagation is strongly affected by local heterogeneities and that fractures follow the path of least resistance (US DOE, 1998; Suthersan, 1999). Environmental fractures may in fact be 'spoke-shaped' (Markesic, 2000), highly asymmetric (Blem et al., 2004), or 'irregularly lobe-shaped' (Strong et al., 2004). Consequently, fracture form and orientation is perhaps best described as being site-specific.

F.5 Evaluation of soil permeability improvements

Soil permeability improvements due to fracturing are estimated indirectly by monitoring pressure changes in monitoring wells using pressure transducers, water level measurements or simply plastic bags sealed to the well tops, during and perhaps after fracturing. The time until response is observed and the magnitude of response is a measure of the degree of connectivity created by the fracturing. It may be difficult to determine the extent of fracture propagation in multiple-fracture wells if the groundwater displacement or pressure change does not dissipate before the next fracture is created (Strong et al., 2004). Fluid extraction, pumping tests, or mass removal tests are often conducted as part of remedial activities, for example SVE, DPE, pump and treat etc., where pre- and post-fracturing results provide evidence of the permeability enhancement (Schuring, 2002). All

these techniques are, however, ‘black box’ techniques, meaning that they provide no understanding of how or where permeability has been improved. Furthermore, extraction, pumping, or mass removal tests are seldom conducted for more than one year, thus long-term enhancements associated with environmental fracturing are uncertain.

Slug tests performed on the fractured wells and monitoring wells (if the latter appear to be within the radius of influence) will provide concrete information regarding the degree of enhancement of hydraulic conductivity caused by fracturing. But these methods only sample a small volume of geologic material immediately around the well (Freeze and Cherry, 1979).

F.6 Visual inspection of induced fractures

Visual inspection of cores/excavations and tracer tests provide some of the most valuable information regarding the effect of fracturing, because this type of data is specific in the x, y and z directions, and thus provides a degree of detail regarding fracture characteristics which is not possible to obtain with the other techniques. While there is some concern that coring may disturb samples and actually create new stress fractures (McKay et al., 1993a) new techniques of injecting coloured sand or dye tracers are addressing this problem (Blem et al., 2004). An excavation provides a unique opportunity to investigate induced fractures in 3D and in the context of the site geology. However this method is expensive and unsuited to small and/or contaminated sites.

F.7 Summary

The above discussion illustrates that effects of environmental fracturing are typically evaluated indirectly, and over short time frames. The most common parameters evaluated: changes in permeability, removal rates, radius, and radius of influence, are often estimated using ‘black box’ techniques that do not illuminate fracture characteristics. The lack of precise, directly-measured field data makes it difficult for environmental consultants to anticipate the fracture characteristics that will be induced at a particular type of site. Better documentation of 1) operator-defined fracturing parameters and subsequent fracturing results, and 2) observed fracturing results compared to anticipated results, are required to further the state of knowledge regarding environmental fracturing, and to further its use in a remedial context.

APPENDIX G: COUPLED REMEDIATION TECHNOLOGIES

Over the years, a number of techniques have been developed and tested in the context of remediating soil and groundwater contaminated with chlorinated solvents. However, no single technique has been shown to achieve adequate remediation when applied alone in low-permeability soils (AVJ, 2003; Christ et al., 2005; Jørgensen et al., 2005).

Remediation results in these settings have been more promising, when coupled with environmental fracturing (Riser-Roberts, 1998; Roote, 2000; US DOE, 2000; Schuring, 2002). Focus was earlier on *mass transfer* techniques, such as soil vapour extraction (SVE) and dual phase extraction (DPE), while it is now on *mass transformation* or *reduction* techniques, because these have the distinct advantage of being less disruptive. Based on the literature study of environmental fracturing experiences, the mass reduction techniques most favoured and/or showing most coupling potential at present are chemical oxidation with potassium permanganate, and chemical reduction with nano-scale zero valent iron (ZVI). The most promising transformation technique is enhanced anaerobic reductive dechlorination (ARD).

The following chapter gives a short description of each of the above-mentioned mass transformation/reduction techniques, which have been, or are likely to be coupled with environmental fracturing in remediation efforts undertaken at low-permeability sites. As the specifics of the techniques are not a focus area of this project, the references given are primarily newer research papers and summary reports.

G.1 Chemical oxidation

The following section is, unless another source is specifically stated, based on T. Jørgensen et al. (2003) and Christensen (2004).

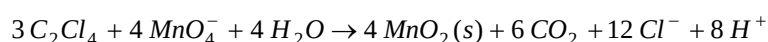
In situ chemical oxidation is a method for direct oxidation of contaminants that has proven especially effective on chlorinated solvents. The method has been applied at field scale since the 1990s, and involves injection of an oxidising agent, which, in the case of chlorinated solvents, breaks the double bond between the compounds' central carbon atoms, thereby ultimately producing carbon dioxide, water, and chloride ions. Thus, the process has no harmful by-products.

The technique is well-suited for source but not plume control/remediation, as the oxidising agents not only oxidise the contaminants but also the organic content of the soil, and reduced inorganic compounds. Thus, large amounts of oxidising agent would be required for plume remediation. In cases where both source and plume require remedial action, chemical oxidation of the source may thus be coupled with another technique suited for plume remediation.

In aquifers with reducing conditions, the oxidising agent will also serve to oxidise reduced inorganic compounds, when the reducing conditions are altered to oxidising conditions. This can entail oxidation of (heavy) metals from stable to more mobile compounds. Any oxidised metals are, however, expected to return to their normal oxidation levels, when the natural and more reducing conditions are re-established after remediation efforts are completed or upon transport to more reducing areas downstream. Nonetheless, the risk of metal mobilisation should be considered at every proposed chemical oxidation remediation site.

At present, the four most commonly used oxidants are ozone, hydrogen peroxide (Fenton's Reagent), (sodium) persulphate, and (sodium or potassium) permanganate. Ozone, due to its gaseous form, is only applicable to the unsaturated zone, while the reactivity of Fenton's Reagent and persulphate are affected by aquifer carbonate content and pH. Permanganate, on the other hand, is a chemically stable oxidant unaffected by these geochemical conditions. For example, it is effective over a large pH-range of 3.5 to 12 (Siegrist et al., 2000). The fact that it works well in the saturated zone further adds to the advantages of its use. Its use can, due to MnO_2 -precipitation, result in clogging of injection-equipment and the (porous) media into which it is injected, but this problem is typically only experienced when larger amounts of free phase contamination are present. Potassium permanganate is usually preferred over sodium permanganate, as it is less expensive: it costs 25 DKR/kg. In Jørgensen et al. (2003) a requirement of 4-5 kg permanganate/kg sediment was estimated, and hence the compound was mixed with water to form 60 m³ of 5% solution, i.e. a total use of 3000 kg at a total price of 75000 DKR.

Field and laboratory investigations conducted by Broholm et al. (2005) of chemical oxidation of PCE by potassium permanganate have revealed a first order degradation rate of $\lambda = 0.2-4 \text{ h}^{-1}$ (= 4.8-96 d⁻¹). The reaction scheme is as follows:



Another advantage of permanganate is its ability to diffuse into the clay matrix upon injection into fractures (Siegrist et al., 1999; Broholm et al., 2005; Broholm et al., 2006), thus extending the remediation zone. Hedeselskabet (2005) use an effective diffusion coefficient (D_e) of $3.05 \cdot 10^{-6} \text{ cm}^2/\text{s}$ for permanganate in till (no retardation expected, i.e. $D_e = D_e^*$). This rate is approximately one order of magnitude larger than the diffusion rate of PCE in till also given in Hedeselskabet (2005): $D_e = 1.54 \cdot 10^{-6} \text{ cm}^2/\text{s}$, i.e. $D_e^* = 3.54 \cdot 10^{-7} \text{ cm}^2/\text{s}$, when accounting for its retardation due to sorption ($R = 4.36$). Thus, if remediation at a contaminated, low-permeability till site is limited by the slow diffusion of the contaminants out of the clay matrix and into (induced) fractures, the injection of permanganate into the fractures could counter these remediation limitations by diffusing into the matrix, cutting remediation time significantly, see Figure G.1 for illustration.

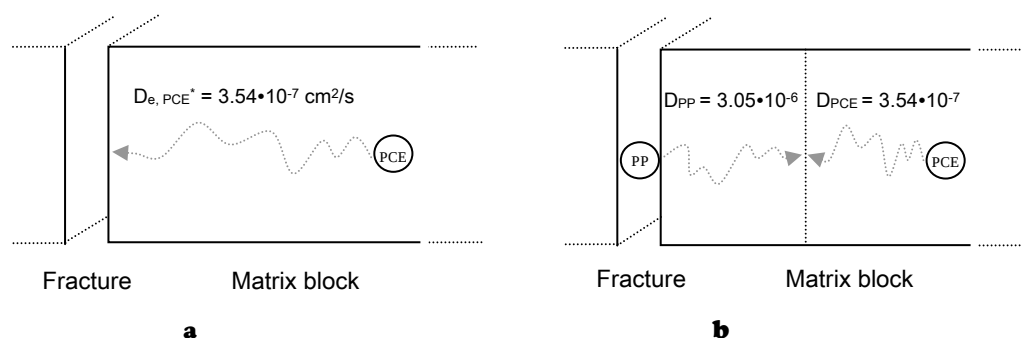


Figure G.1: Illustration of the dependency of remediation time on the distance over which contaminant in the middle of the matrix must diffuse to come into contact with remedial agent: in (b) remediation time is significantly reduced compared to (a).

However, the modelling studies conducted by Hedeselskabet (2005) show that injection of large amounts of permanganate will be necessary to ensure complete remediation at contaminated sites, as will a long timeframe, due to restriction of the above described permanganate diffusion into the clay matrix upon its encounter with contaminants, organic material and minerals (Broholm et al., 2005).

Use of the compound has further disadvantages:

- 1) It may cause naturally occurring *Dehalococcoides* bacteria (discussed below) to become inactive or die. This is a problem if chemical oxidation is to be coupled with ARD.
- 2) It should not, by Danish standards, be used in the vicinity of drinking water extraction wells, as the Danish EPA has set its MCL in drinking water to 1 $\mu\text{g/L}$.*
- 3) Very strict health and safety guidelines must be followed during handling of the compound, as the Danish EPA has categorised it as a dangerous substance.

Since the use of the technology is fairly new in low-permeability media, the long-term environmental effects from its use are still unknown. It has, however, had widespread success in high-permeability media, where distribution of the oxidant is less problematic. Furthermore, the above-mentioned diffusion rates suggest that it could be a successful remedial method at low-permeability sites when coupled with fracturing, even considering the requirements of injection of large amounts of permanganate over a long time period.

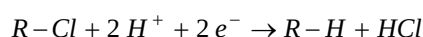
G.2 Anaerobic reductive dechlorination

The following section is, unless another source is specifically stated, based on Jørgensen et al. (2005) and Cox and Durant (2005).

* Such considerations are not weighted in the US, where the oxidant is used indiscriminately.

Complete biodegradation of chlorinated ethenes to the innocuous compounds ethene or ethane can be achieved by reductive dechlorination under anaerobic conditions by the bacterial strain *Dehalococcoides Ethenogens* via the microbiological process dehalorespiration.

The anaerobic reductive dechlorination (ARD) consists of a stepwise substitution of the compounds' chlorine-atoms from the original molecule with a hydrogen atom:



The complete sequential degradation path is as follows in Figure G.2.

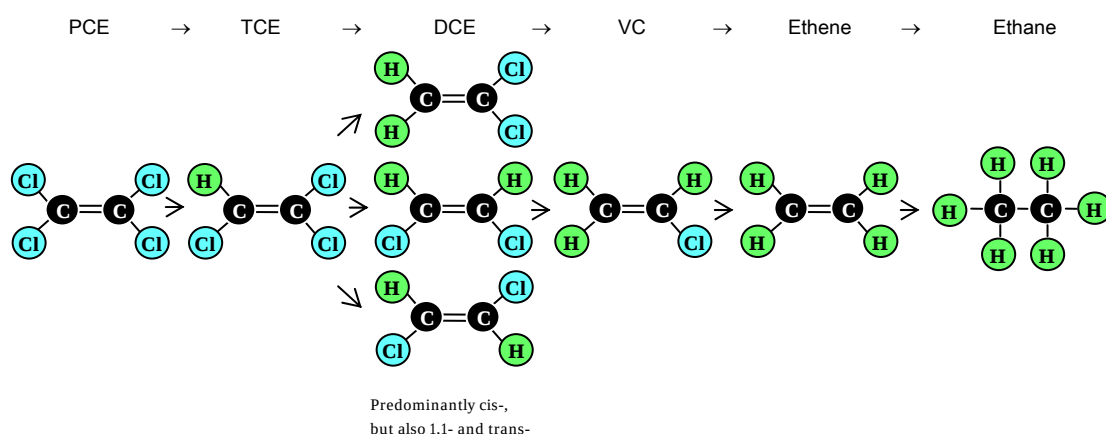


Figure G.2: Sequential dechlorination of chlorinated ethenes.

Soils that lack the *Dehalococcoides* bacteria require bioaugmentation to achieve harmless degradation products from the higher chlorinated contaminants. Several stable enrichment cultures that contain organisms phylogenetically closely related to *Dehalococcoides* are capable of mediating complete dechlorination of TCE to ethene (Major et al., 2002).

When the right bacteria are present (naturally or augmented), the limiting factor in dechlorination (via dehalorespiration) becomes the lack of electron donors to facilitate the process. I.e., presence of suitable donors of hydrogen is required. Rates of natural attenuation via ARD are on the order of 0.18-0.30 yr⁻¹ when enough hydrogen is present (> 1nM), while they drop to 0.003-0.015 yr⁻¹ when the hydrogen supply is limited (< 1nM) (Gonsoulin et al., 2004).

Enhanced ARD may thus involve stimulation of indigenous bacteria via injection of donor (bio-stimulation) and perhaps of addition of dehalorespiring organisms if none are present indigenously (bioaugmentation). The enhancement can result in degradation rates of 0.6-2.5 d⁻¹ (Major et al., 2002), i.e. an improvement of 4-6 orders of magnitude.

In situ injection of donors which release hydrogen during fermentation is a promising method. Donors include methanol, ethanol lactate, propionate, and butyrate, or more complex organic materials

such as sugar cane, corncobs, and wood chips (Jianzhong et al., 2002). The natural biopolymer chitin was also recently tested (Martin et al., 2002) and shows promise[†].

ARD is primarily a method for plume control, but has recently been proven applicable in source zone environments.

The process has been thoroughly investigated in laboratory studies as well as pilot field studies, all in homogenous aquifer materials consisting of both sandy and clayey-silt soils. In fact, Jørgensen et al. (2005) have compiled a screening model for site suitability for ARD. This is discussed in *Appendix I: Assessment of site suitability for ARD*.

Enhanced ARD must be applied more widely before realistic cost-estimates can be calculated. However, use of the technique seems to be a feasible full-scale remediation strategy in low-permeability media when coupled with fracturing.

G.3 Chemical reduction with zero valent iron

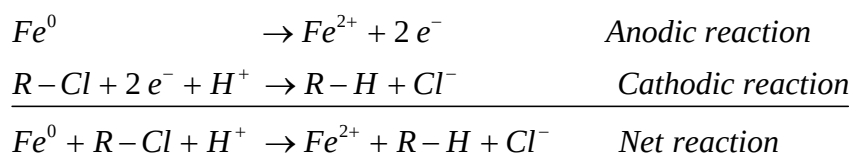
Reductive dechlorination of chlorinated solvents can also be achieved abiotically with zero valent iron (ZVI), instead of biologically by means of naturally present bacterial populations.

The use of granular ZVI to create permeable reactive barriers (PRBs) was initially applied in the early 1990s and is now a maturing technology, having found application and success in a number of full-scale remediation efforts (EPA, 1998; Kjelsen, 2004). Here, anaerobic reduction of chlorinated solvents takes place via corrosion of the ZVI, i.e. the solvents act as electron acceptors (oxidants) and serve to oxidise ZVI to ferrous iron:

[†] Research has shown that the hydrogen concentration in an aquifer determines which bacterial population will dominate. Substrates with slow and steady hydrogen yield favour the dechlorinating bacteria, whereas high hydrogen levels favour other competing species, e.g. methanogenic bacteria. Propionate, which is the dominant volatile fatty acid produced via chitin, has proven to be one of the best substrates for the dehalogenators, as it releases hydrogen during fermentation at a slow and steady rate and at adequately low concentrations (below methanogenesis threshold) to meet their specific needs and minimise potential for competition issues between dechlorination and methanogenesis (Martin et al., 2002; Jianzhong et al., 2002). Thus, advantages of chitin are:

- Once emplaced in a formation, it is degraded slowly, becoming a relatively long-lived source of nitrogen and electron donor in the form of VFAs for ARD.
- It is effective under variably saturated conditions: considerable concentrations of VFA are only released when chitin is saturated, the same conditions under which chlorinated aliphatic hydrocarbons are mobilized and must be degraded. VFA production slows under saturated conditions making the electron donor available only when necessary and longevity of chitin in the subsurface is thus maximised.
- It is the most plentiful natural biopolymer (next to cellulose) in the world, and is thus available at low cost.

(Martin et al., 2002)



The reaction occurs at the iron metal surface, under anaerobic conditions[‡] (EPA, 1998). Positive side effects of the reaction (which consists of oxidising the iron and reducing the chlorinated solvent) are:

- 1) production of H_2 , and thus perhaps stimulation biological degradation of the solvents via the *Dehalococcoides* bacteria (Jørgensen, 2004), see Section X.2 above; and
- 2) immobilisation of (heavy) metals (Zhang, 2003).

The application of ZVI-PRBs has a practical depth-limit, however, as they require some excavation to install. While the injection of ZVI to the subsurface via fracturing was not earlier considered a feasible approach to overcoming this excavation requirement/depth limitation, due to the size of the ZVI-granules employed, the emergence of nanoscale ZVI is expanding its possibilities (Vance, 2005). These small particles (< 100 nm) have a specific surface area on the order of $30 \text{ m}^2/\text{g}$, which, compared to that of granular ZVI ($1 \text{ m}^2/\text{g}$), induces a degradation rate 10-100 times faster. Furthermore, they can be dissolved in water for injection as a simple fluid into groundwater aquifers, where their small particle size allows them to spread in the aquifer. As reaction rates deduced from laboratory studies for both chemical oxidation (with permanganate) and chemical reduction with ZVI are on the same order of magnitude (Siegrist et al., 1999), field reaction rates are also expected to be on the same order of magnitude, i.e. 4.8 d^{-1} , see Section G.1 above.

The technique is suited for both source and plume remediation when using nanoscale ZVI, while only plume remediation is possible with granular ZVI PRBs, see Figure G.3.

[‡] Under aerobic conditions, dissolved oxygen is the preferred electron acceptor although several chlorinated hydrocarbons, e.g. PCE, have oxidation potentials similar to it.

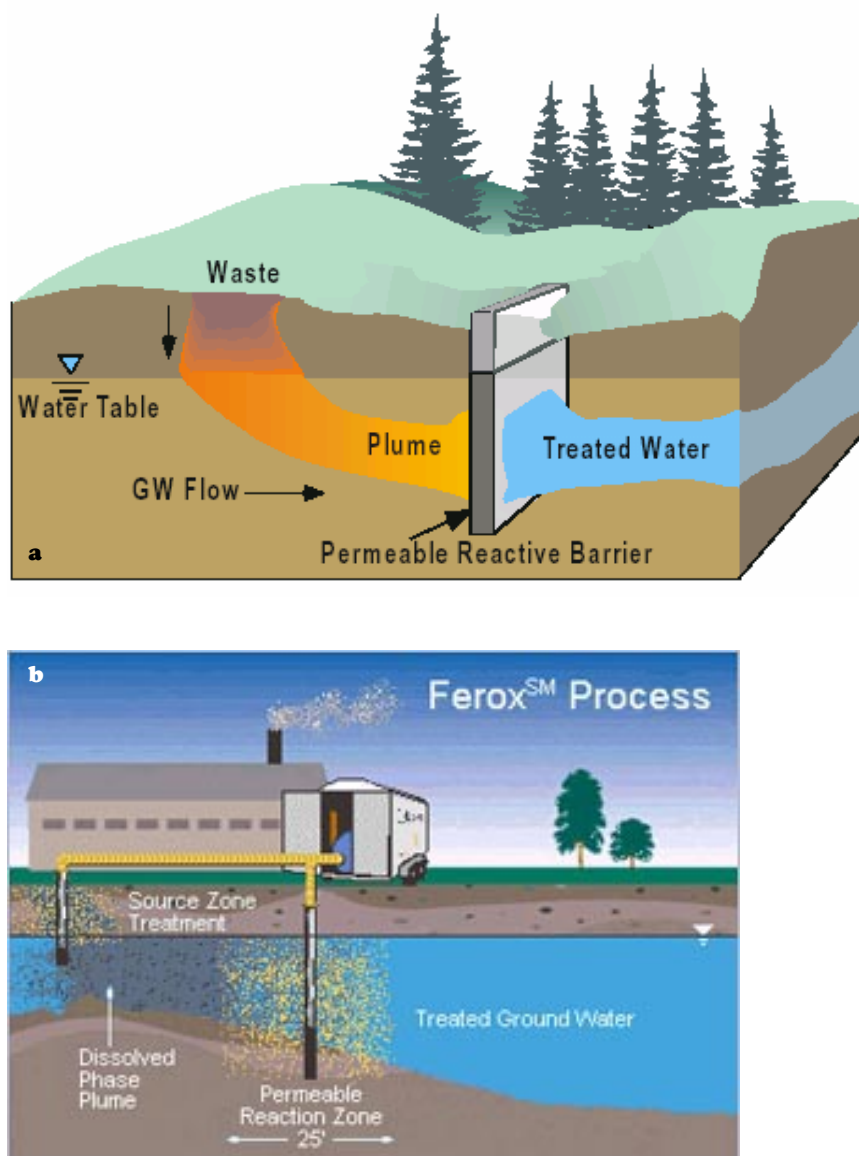


Figure G.3: (a) Plume remediation via permeable reactive barrier filled with granular ZVI (EPA, 1998); (b) Source and plume remediation via (fracturing) injection of nanoscale ZVI (ARS, 2005a).

Figure G.3b illustrates the FeroxSM method developed and patented by ARS. It is a method for nanoscale ZVI-injection into the subsurface, which has been applied at both pilot and full scale with success (contaminant concentration reductions from 52-99%) in the US, see *Appendix Y: Electronic data, Table C.1: US and Canadian experiences with environmental fracturing*. The method is a coupling of pneumatic fracturing and the chemical reduction remediation technique.

The cost of nanoscale ZVI is 13-22 DKR/kg (1-1.70 USD/lb; ARS, 2005a). Sources do not agree on the contaminant to ZVI ratio required to ensure satisfactory remediation with chemical reduction: in connection with the Marshall SFC site (see *Appendix Y, Table C.1*), the EPA (2003) states that a 1:200 ratio is necessary, when the contaminant in question is TCE, while the NFEC (2003) for the Hunter's Point Shipyard site state that a ratio of at least 1:500 is required, both referring to and claiming agreement with completed bench-mark tests. The disagreement could stem from dif-

ferent clean-up targets at the mentioned sites, although no specific clean-up goals were set in either case (FRTR, 2005). Only NFEC (2003) gives a rule-of-thumb independent of specific contaminant concentrations: “In general, an iron-to-soil ratio of 0.004 is necessary to achieve a sufficiently reductive environment for the degradation of TCE to occur, regardless of the mass of TCE...” (NFEC, 2003).

While FeroxSM is a commercial technique, available for full scale remediation efforts, the above shows that further research and development is necessary.

G.4 Pros and cons of the outlined mass reduction/transformation technologies

Table G.1 summarises the pros and cons, as discussed in the above, for the three mass transformation/reduction techniques presently favoured in remediation efforts at sites contaminated with chlorinated solvents.

It is difficult to compare the prices of implementing the three remediation techniques, as they will be highly site dependent, i.e. depend on the extent of contamination, required substance:contaminant/sediment mass ratio, etc. However, it seems that chemical oxidation is the most expensive technique, as the amounts required and its price (4-5 kg/kg sediment; 25 DKR/kg) both exceed those stated for ZVI (0.004 kg/kg soil; 13-22 DKR/kg). The costs of ARD are presumed very low if e.g. chitin is chosen as donor.

G.5 Advantages of coupling with environmental fracturing

Each of the above-mentioned techniques has been shown to have the potential to adequately remediate chlorinated solvent contaminations in permeable media. Coupling with environmental fracturing may well be the answer to achieving similar remediation levels in low-permeability soils, as more fractures represent:

- 1) more emplacement zones (for donor, permanganate, and/or ZVI);
- 2) shorter diffusion pathways to fractures, where degradation or mass removal activities occur; and
- 3) potential to create a wider reaction zone at least in the case of permanganate (Broholm et al., 2006).

Table G.1: Some pros and cons of the three most favoured mass transformation/reduction remediation techniques.

Technique	<i>Chemical oxidation w/ potassium permanganate</i>	<i>Anaerobic reductive dechlorination</i>	<i>Chemical reduction w/ nanoscale ZVI</i>
Substance to inject	Potassium permanganate	Hydrogen donor (and bacteria)	Nanoscale ZVI
Pros	Fast degradation rate of 4.8-96 d⁻¹ Well-suited for source remediation Destroys chlorinated ethenes without production of harmful daughter products Is able to diffuse into low-permeable clay matrix and thus reduce remediation time	Fast degradation rate of 0.6-2.5 d⁻¹ Well-suited for plume remediation; also applicable to source zones Many effective donors available, some at very low cost	Fast degradation rate on the order of 4.8 d⁻¹ Well-suited for source and plume remediation Immobilises (heavy) metals Reaction produces hydrogen, which may then be used by bacteria in (natural or enhanced) ARD
Cons	Can cause (heavy) metal mobilisation Can cause clogging of injection equipment and contaminated media Not suited for plume remediation (and inhibits bacteria, thus disabling potential for coupling with ARD) Necessitates strict health and safety measures		
Tested at low-permeability sites with fracturing?	Several pilot studies (Navy MCLB, GA, USA; US DOE Gaseous Diffusion Plant, OH, USA)	1 pilot study (Dristler Brickyard Site, KY, USA)	Several pilot and full scale studies (primarily ARS sites)
Remediation efficiency at these sites	Contaminant concentration reduction 36-99.9%	No quantitative figures given, but stated as successful	52-99.9%

APPENDIX H: PLANNING FIELD WORK AT A PROPOSED FRACTURING SITE

H.1 Introduction

This appendix provides the environmental consultant with suggestions regarding useful background information, tests that ought to be completed, and other considerations that should be addressed prior to application of environmental fracturing at a site. The success of fracturing activities is strongly correlated to the degree of knowledge the environmental consultant has about the site geology, and the location and type of contamination (Kidd, 2001; Blem et al., 2004; Klint, 2005, personal communication). Final decisions regarding operator-determined parameters, location of fracturing and monitoring wells, fracture interval spacing, etc. should be made in consultation with the fracturing consultant(s).

H.2 Geology

At least one continuous exploratory core from an uncontaminated area of the site is recommended (Kidd, 2001). A detailed visual examination of cores/soil material, grain size analysis, natural moisture content, evaluation of consistency/relative density, plasticity testing, location of water table, and in situ permeability testing is recommended to obtain a thorough understanding of the formation characteristics (Schuring, 2002). The state of knowledge regarding environmental fracturing will be furthered when fracture results may be set in the context of the site characteristics and when fracturing of results may be compared among sites.

A detailed geological profile depicting layering (Kidd, 2001) is necessary to evaluate the location of fracturing intervals if a number of wells are to be fractured, as well as to evaluate potential interference of sand lenses, previous excavations, etc.

The geology of the site should be compared to that of previously fractured sites with similar geology to obtain initial estimates of suitable initiation pressures and propagation pressures, flow rate, etc. An estimate of the required initiation pressure for pneumatic fracturing may be calculated (*Appendix E: Method to estimate required initiation pressure for pneumatic fracturing*).

H.3 Natural fractures

The presence of natural fractures must be considered. The ability of induced fractures to improve the connectivity /permeability at a site appears to be strongly related to the presence of naturally occurring fractures at depth (EPA, 1994; Klint, 2005 personal communication). Furthermore, natu-

ral fractures will likely have some influence on the orientation and form of induced fractures (EPA, 1994; Suthersan, 1999). Fracturing at depths above the redox boundary is associated with a high risk of surface venting due to the density of natural fractures and biopores. Also, fracturing in or near a DNAPL source zone at sites with potential for extensive vertical fractures is not recommended due to the risk for DNAPL mobilization and groundwater contamination (US DOE, 1998; Schuring, 2002).

A geomorphological map, as illustrated in Figure H.1, gives a quick overview of the type of till found at a certain site, and thus the types of glacial-tectonic fractures to be expected at the site. Subsequently, a geological basis-data map (not illustrated) or borehole logs (for example from the Jupiter borehole data base; GEUS, 2005b) will be useful in evaluating the extent of glacial-tectonic and contraction fracturing at the site, as these illustrate what lies beneath the till layers – high- or low-permeability layers – as well as the approximate location of the redox boundary (marked by transition from oxidised, reddish clay-sediment to reduced, blue-gray clay-sediment). Thus, the map gives an idea of

- whether or not the till at the site is well- or poorly drained, permitting an educated guess as to the extent of natural glacial-tectonic fracturing found at the site, and
- the probable penetration depth of naturally occurring contraction fractures (Klint et al., 2001).

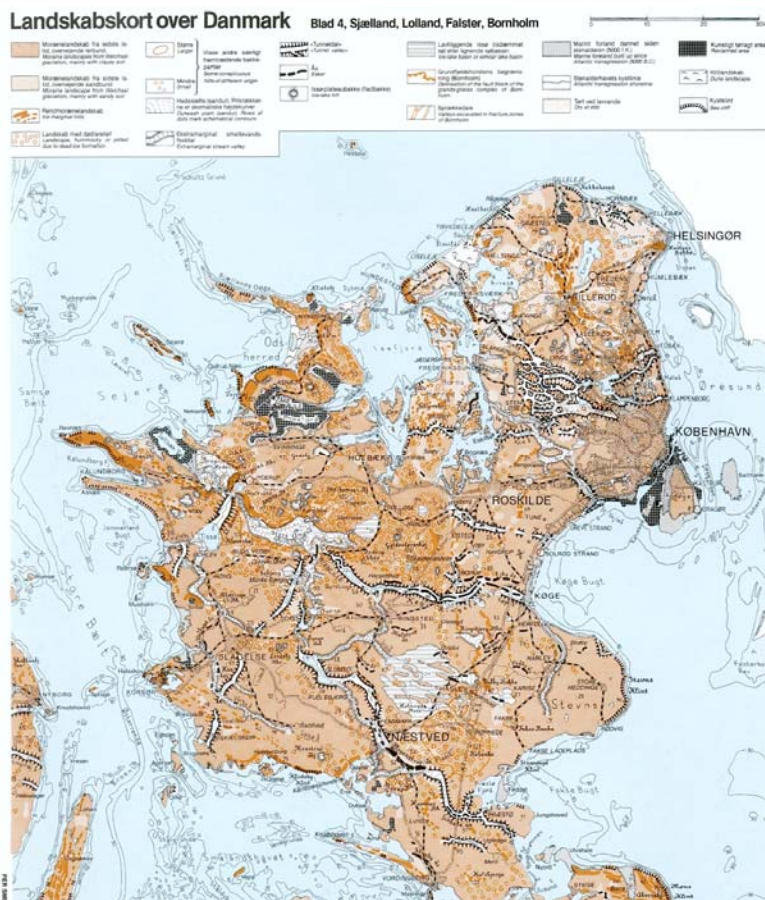


Figure H.1: Geomorphological map showing most of the Danish island Zealand (Smed, 1987).

H.4 Test fracturing

A test fracture in an uncontaminated area of the site is strongly recommended as both the initiation pressure, propagation pressure, flow rate, and suitable sand to guar gel ratio (in the case of hydraulic fracturing) are site-specific (Kidd, 2001). Furthermore, a test fracturing will also reveal bedding effects (EPA, 1994). At sites with sensitive structures, or utility lines, a test fracturing is particularly important to obtain an indication of expected uplift.

H.5 Location of fracturing well(s)

The fracture wells should be located so that their expected radii of influence will overlap in plan view (Suthersan, 1999). Such a design will increase the likelihood of enhancing the permeability throughout the contaminated zone and improve delivery to reactive substances in coupled remediation. Fracturing wells should be located as far as possible from structures, utility lines, etc.

H.6 Grouting

Induced fractures have a tendency to ‘find’ abandoned boreholes, monitoring wells, utility lines, etc. if these are not properly grouted (US DOE 1998; Schuring, 2002; ARS, 2005, personal communication). ARS recommends cement grout over bentonite, as the latter can be jetted out during fracturing (ARS, 2005, personal communication). It may not be possible to grout utility lines, in which case the fracturing should be planned so that utility lines are outside the anticipated radius of fracture influence.

H.7 Monitoring of the fracturing results and phased fracturing

Ideally the fracturing program would be implemented in phases (Suthersan, 1999). During the fracturing process, uplift and pressure changes in monitoring wells would be measured. A detailed evaluation of the radius of influence of the fracture well(s) measured using suction head or draw-down tests before and after fracturing will indicate the extent of fracture influence. Ideally a tracer test would be conducted (Schuring, 2002). New fracture wells would be installed, or new intervals fractured depending upon the results of the testing of the first phase of fracturing. Ideally testing would be conducted after one year to investigate the longevity of the induced fractures.

Such a program will provide solid background and field information which will increase the likelihood of successful fracturing activities, as well as further the state of knowledge regarding environmental fracturing.

APPENDIX I: ASSESSMENT OF SITE SUITABILITY FOR ARD

In Jørgensen et al. (2005), knowledge on *in situ* ARD has been assembled and used to compile a screening model for assessment of site suitability for ARD.

The model is to function as a tool for assessment of the suitability of a given site contaminated with chlorinated solvents for remediation via *in situ* ARD. The assessment criteria are divided into 4 main groups:

- 1) Preliminary studies and hydrogeological profile
- 2) Contamination profile
- 3) Geochemical profile
- 4) Logistical factors

The higher the point score, the more suited a site is in relation to a certain assessment category. However, the degree of certainty associated with values assigned to point-scoring parameters within each category also influences the final point score of a site. Thus, a parameter value that might warrant a high score will nonetheless receive a low/negative score if the value is not associated with some level of certainty.

I.1 Assessment Category 1

Under the first category, points are given in relation to hydrogeological conditions and contaminant distribution. See Table I.1.

Table I.1: Factors influencing point score in the first assessment category of site-suitability for ARD developed by Jørgensen et al. (2005).

Parameter	High point score if	Low point score if	Reason for inclusion in evaluation
Hydraulic conductivity and heterogeneity	high	low	indicate how easily injected donors/substrates will be able to disperse and thus come into contact with the contamination present at the site
Content of organic material	low	high	indicates to what extent the contamination present at the site will be sorbed and thus inaccessible to aqueous biological degradation
Contamination distribution	surficial	deep	indicates the magnitude of start-up and operation costs that are to be expected in connection with a remediation effort at the site
	and/or narrow plume	and/or wide plume	

I.2 Assessment Category 2

Under the second category, points are given in relation to presence of various chemical and organic compounds. See Table I.2.

Table I.2: Factors influencing point score in the second assessment category of site-suitability for ARD developed by Jørgensen et al. (2005).

Compound	High score if	Low score if	Reason for inclusion in evaluation
Degradation products - ethene - VC - cis-DCE	present	absent	indicate natural presence of <i>Dehalococcoides</i> and how favourable its living conditions are
Small amounts of dissolved petroleum (TPH) compounds	present	absent	function as electron donors and thus contribute to achieving/sustaining reduced redox conditions
Tetrachloromethane and/or chloroform	absent	present	known to limit degradation rates of ARD
Free-phase chlorinated solvents	absent	present	will complicate evaluation of results from short-term pilot studies due to continued dissolution of contamination
Free-phase hydrocarbons	absent	Present	medium for dissolution of chlorinated solvents, facilitating slow and continuous release to the aqueous phase, i.e. ground water

I.3 Assessment Category 3

Under the third category, points are given in relation to (geo)chemical conditions. See Table I.3.

Table I.3: Factors influencing point score in the third assessment category of site-suitability for ARD developed by Jørgensen et al. (2005).

Parameter	High score if	Low score if	Reason for inclusion in evaluation
Redox conditions	reduced	oxidised	indicate how favourable the living conditions of <i>Dehalococcoides</i> are
pH	neutral	extreme (low or high)	
Ionic strength (salt content)	low	high	
Sulphate concentrations	low	high	Indicate level of competition between ARD and sulphate reduction reaction for organic matter

I.4 Assessment Category 4

Under the fourth category, points are given in relation to logistics, i.e. accessibility of

- 1) the site itself, i.e.
 - a. extent of nearby or directly overlying buildings
 - b. existing containment/monitoring infrastructure
- 2) electricity
- 3) water
- 4) local technician to administer maintenance and ongoing sampling

Naturally, good accessibility will result in a high score, as remediation efforts are thus enabled/eased physically and economically.

Proximity of the site to recipient water bodies and/or drinking water extraction areas is the final assessment parameter within the category. Close proximity will result in a low/negative score.

I.5 Trial of screening model

Based on the screening of 13 sites (all on Funen) with varying hydrogeological, contamination, geochemical, and logistics profiles, Jørgensen et al. (2005) conclude that the quantitative evaluations of the model correlate well with what would qualitatively be expected in relation to the suitability of the sites for remediation via in situ ARD. The model is thus thought to be representative and generally applicable for assessment of site suitability for ARD.

I.6 Till sites

One of the screened sites – Sortebrovej 26, Tommerup, Funen (site no. 11) – is a till site and is evaluated as follows by the screening model:

Box I.1: Jørgensen et al. (2005) evaluation of a typical Danish contaminated till site via the screening model for suitability for remediation via in situ ARD.

Site: Sortebrovej 26, Tommerup – typical Danish till site of contamination

- Category 1:** With regard to preliminary investigations and hydrogeological profile, the site is deemed unsuited for in situ ARD due to
- geological heterogeneity – the subsurface of the site consists of till (interlaced with sand lenses/stringers), resulting in low hydraulic conductivity, and
 - deep contamination.
 - Thus, the site score for Category 1 is 2 (highest score given in the category is 34).
- Category 2:** With regard to contamination profile, the site is deemed potentially suited for in situ ARD as
- presence of cis-DCE and VC have been detected.
 - Thus, the site score for Category 2 is 20 (highest score given in the Category is 40).
- Category 3:** With regard to geochemical profile, the site is deemed well-suited for in situ ARD as
- anaerobic conditions, i.e. reduced redox conditions are present.
 - Thus, the site score for Category 3 is 20 (highest point score given in the category).
- Category 4:** With regard to logistics, the site is deemed well-suited for in situ ARD as
- it is easily accessible.
 - Thus, the site score for Category 4 is 10 (highest point score given in the category).

The total score of the site (52) gives it a ranking of 5 out of the 13 screened sites. However, the qualitative assessment of the site states that it is, on the face of it, not very suited for in situ ARD. The overall conclusion with regard to the suitability of the site for ARD is:

“Sortebrovej 26 represents a site of low hydraulic conductivity (till), and has received a relatively high score for its accessibility, favourable geochemical conditions, and presence of degradation products. The main drawback of the site is the relatively large vertical distribution of contamination.” (Jørgensen et al., 2003)

The Tommerup site is thought to be representative of (contaminated) Danish till sites within Categories 1 and 3, while its good accessibility (Category 4) is not a common characteristic: as stated in Chapter 1, many sites contaminated with chlorinated solvents are found in urban areas, thus having poor accessibility.

As the use of fracturing may serve to minimise the influence of factors detracting from till site suit-

ability for *in situ* ARD (low hydraulic conductivity and poor accessibility), its potential for remediation enhancement is clear in this context. Thus, *in situ* ARD can – with few exceptions – be viewed as a promising method for remediation of this type of site.

I.7 Preliminary investigations to maximise certainty of screening model evaluation

To minimise the uncertainty surrounding parameter values critical to point scoring in the screening model and thus maximise the certainty of the model's evaluation of site suitability for ARD, the investigations outlined in the table below should be carried out.

Table I.4: Investigations required to provide a reliable hydrogeological profile, contamination profile and geochemical profile of a site for use in evaluation of the site's suitability for remediation by *in situ* ARD.

Requirement	Necessary preliminary investigations
<i>Hydrogeological profile</i>	1. Review of existing geological literature/profiling for the site
	2. Sediment sampling and analysis via auger drilling in order to construct geological profiles, and evaluate organic content and hydraulic conductivity of the subsurface
<i>Contamination profile</i>	3. Water sampling and analysis via geoprobe drilling in order to evaluate
	a. extent of contamination distribution horizontally and vertically
<i>Geochemical profile</i>	b. presence of degradation products
	c. concentrations of redox compounds (nitrate, iron, sulphate, methane)
	d. pH
	e. salt content (NaCl)

APPENDIX J: COMPLETE VERSION OF TABLE 3.2* - COMPARISON OF TILL CHARACTERISTICS AT 21 DANISH SITES AND 1 CANADIAN SITE

See following pages

Table 3.2*: Comparison of till characteristics at 21 Danish sites and 1 Canadian site.

Site (main reference)	Landscape	Till description	% clay	f_{sc}	tortuosity	Dry bulk density (g/cm ³)	Porosity	OCR	Hydraulic conductivity (m/s)	Depth to redox boundary (m b.s.)	Fracture Aperture (μ m)	Number fracture systems (Klint, 2004a)	Fracture spacing	Max. fracture depth (Klint, 2004a)
<i>Avedøre</i> (McKay et al., 1999)	Ground moraine over limestone bedrock (Klint et al., 2001); lodgement till	Basal till (Klint, 2001); Clay till 7.5-8 m thick with at least 1 thin sand layer overlying Danien limestone aquifer	1-3 m b.s.: 6-16						2 m b.s.: $8.5 \cdot 10^{-7}$ to $1.1 \cdot 10^{-6}$ 4 m b.s.: 10^{-9} to 10^{-7}	~3 (Houmark and Nielsen, 2005)	Surface: 3 cm 0.4 m b.s.: 2-3 mm	5	Vertical/subvertical: System 1(contraction fractures): 70 cm extending to 3 m b.s., System 2 (glacial tectonic shear or neotectonic fractures): 3 -35 cm, extending > 5 m b.s., System 3 (glacial tectonic extension fractures): 30 cm, extending > 5 m b.s., System 4 (contraction fractures): random Horizontal: closely spaced especially between 1.3 and 1.7 m b.s.: 3 cm > 2 m b.s.: shear fractures	>5.5 m
<i>Dalumvej</i> (Hedesel- skabet, 2005)		Clayey-till with large sand lense		0.0033 (till); 0 (sand lens)	0.275 (till)); 0.33 (sand lens)	1.96 (till); 1.81 (sand lens)	0.275 (till); 0.33 (sand lens)							
<i>Englandsvej</i>	Ground moraine over limestone bedrock (Klint, 2004a)											5	At least one system is glacialtectonic (Klint et al., 2001)	> 6 m
<i>Estrup</i>	Ground moraine (Klint, 2004a)	Little Belt clay till from late Saalian Paleobaltic advance. Very complex geology. Predominately clay till, but also meltwater clay, peat, meltwater sand etc. (Lindhardt et al., 2001); Not covered by Weichselian glaciation, but exposed to extensive freeze- thaw processes (Jørgensen et al., 2003); Well-drained (Klint, 2001)		0.0015 – 0.0078 (Lindhardt et al., 2001)		1.55 – 1.78 (Lindhardt et al., 2001) (grain density 0.2675 g/cm ³)	4 m b.s.: 0.32 (Lindhardt et al., 2001)		1 to 4 m b.s.: 10^{-9} - 10^{-7} (Lindhardt et al., 2001)	~5.5 (Klint et al, 2001)		3	Vertical: 2 to 3.5 m b.s.: 4-16 fractures per 10 horizontal cm 3.5 to 5 m b.s.: 1-7 fractures per 10 horizontal cm Horizontal: 2 to 3.5 m b.s.: 5-35 fractures per 10 vertical cm 3.5 to 5 m b.s.: 1-7 fractures per 10 vertical cm (Lindhardt et al., 2001) Extensively fractured to a depth of 5 m (Jørgensen et al., 2003)	> 5 m
<i>Fårdrup</i> (Lindhardt et al., 2001)	Undulating ground moraine (Klint, 2004a); Belt Sea till deposited during Weichselian advance, underlain by Mid Danish till clayey till	Dominantly clay till with a few stringers < 100 cm wide of sand till, glacialfluvial sand/clay/silt till; Basal till (Klint, 2001)	19- 23 % till	2.5 to 5 m b.s.: 0.0008 – 0.0023 till		1.78 – 1.84 till (grain density 2.679, 2.686)	3.5 m b.s.: 0.23 5 m b.s.: 0.22 till		10^{-9}	~4.5 (Klint et al, 2001); 4 to 6 m b.s. till		3 (Klint, 2004b); 4	Vertical: System 1: 2 to 3.5 m b.s.: 35-40 cm, visible from 1 to 5.5 m b.s. System 2: visible from 1 to 3.3 m b.s. System 4: 35-40 cm Horizontal (shear & freeze-thaw) 1 to 2.5 m b.s.: 4-20 fractures per vertical 10 cm 2.5 to 5 m b.s.: 1-5 fractures per vertical 10 cm most intensive at 1.8 to 2.3 m b.s. (Lindhardt et al., 2001)	> 5 m
<i>Flakkebjerg</i> (Klint and Gravesen, 1999)	Ground moraine over outwash plain (Klint, 2004a); Weichselian lodgement clayey till	Sandy clayey till with meltwater sediments 10 m thick, overlying meltwater sand aquifer, overlying clay till overlying regional aquifer; Basal till (Klint, 2001)	10 -15 %				0 to 2 m b.s.: 0.3 - 0.4; 2 to 4 m b.s.: 0.25 - 0.30				3.5 to 4 m b.s.		4 Vertical: (shear) 2 to 5 m b.s.: 14-77 cm Horizontal: (shear) 1.5 to 5.5 m b.s.: 9-50 cm Conjunction: (shear) 1 to 4.5 m: 53-667 cm Contraction: (vertical) 0 to 1.5 m b.s.: 5-8 cm (Klint and Gravesen, 1999)	> 6 m

Site	Landscape	Till description	% clay	f_{ec}	tortuosity	Dry bulk density (g/cm ³)	Porosity	OCR	Hydraulic conductivity (m/s)	Depth to redox boundary (m b.s.)	Fracture Aperture (μm)	Number fracture systems (Klint, 2004a)	Fracture spacing	Max. fracture depth (Klint, 2004a)
<i>Gedser Odde</i>	End or recessional moraine (Klint, 2004a)	Basal till (Klint, 2001)								~4.5 (Klint et al., 2001)		3		> 6 m
<i>Gjorslev</i>	Ground moraine over limestone bedrock (Klint, 2004a and b)	Varying degrees of sandy, silty, gravely moraine clay (Klint, 2004a); 7 to 15 m thick overlying fractured limestone (Klint, 2004b)				3.6 m b.s.: 1.87 4.75 m b.s.: 1.87 (Iversen and Jacobsen, 2004)			4.65 to 4.85 m b.s.: $5.8 \cdot 10^{-7}$ – $1.3 \cdot 10^{-4}$ (Iversen and Jacobsen, 2004)	~4.2 to 4.8 m b.s. (Klint, 2004a)		3	~ Vertical : 2 m b.s.: 10 cm; 4 m b.s.: 50 cm; 5 m b.s.: 150 cm ~ Horizontal : 1.8 to 3.5 m b.s.: 1-4 cm 3.5 to 4 m b.s.: 4 -10 cm > 4 m b.s.: massive Contraction : n.a. (Klint, 2004b)	> 5 m
<i>Grundfjor</i>	Undulating ground moraine (Klint, 2004a)	Thin layer (~ 5 to 15 m) Weichsel till over a layer of meltwater sand and gravel (Ernsten and Thorling, 1997); clay till (sandy, very silty, with gravel) 1.8 m thick overlying sand till (very clayey, observed at 3 m b.s. (Klint, 2004b)		Meltwater clay: 0.004; meltwater silt: 0.006 (Ernsten and Thorling, 1997)		2.3 m b.s.: 1.71 3.6 m b.s.: 1.55 (Iversen and Jacobsen, 2004)	0.20 -0.30 (Jørgensen et al., 1994)		3.5 to 3.7 m b.s.: $2.3 \cdot 10^{-7}$ - $1.2 \cdot 10^{-6}$ (Iversen and Jacobsen, 2004)	~ 2 m b.s. (Klint, 2004b)		2	Subhorizontal (shear): 2 to 3 m b.s.: ~6-30 cm gently dipping : 2 to 3 m b.s.: ~ 13-165 cm (Klint, 2004b) Contraction : 0 to 2 m b.s.: intensely fractured, predominately vertical. (Klint, 2004b)	> 3 m
<i>Haslev (Hydraulic fracturing site)</i> (Blem et al., 2004)	Ground morain over limestone bedrock (Klint, 2004a); Lodgement till (Jakobsen and Klint, 1999)	Clayey till (with streaks of sand or silt) 15-17 m thick overlying 1-2 m glaciofluvial deposits overlying Palaeocene limestone (Jakobsen and Klint, 1999); clay till varying from heavy clay with sand and gravel to sandy and slightly gravely clay till; well-drained (Klint, 2001)	~ 16 - 20% (Jakobsen and Klint, 1999); 14- 22%			1.81 - 1.95 estimated from ϕ	0.271 - 0.326	2-5	2 m b.s.: $1.7 \cdot 10^{-6}$ 4.5 m b.s.: $6.7 \cdot 10^{-9}$; 8 m b.s.: $2.07 \cdot 10^{-9}$	~4 to 5.5 (Klint et al, 2001); ~ 4.5 m b.s.	Horizontal: ~ 1000 (Jakobsen and Klint, 1999)	3	~ Vertical (glacialtectonic extension fractures): 1.5 to 9 m b.s.: 50-60 cm ~ Horizontal (glacial tectonic shear fractures): 1.5 to 9m b.s.: 80 cm Contraction : (vert/horiz) 0 to 4.5 m b.s.: 1-4 cm (Jakobsen and Klint, 1999)	> 9 m
<i>Havdrup</i>	Ground moraine (Klint, 2004a); probably Weichselian (Jørgensen and Fredericia, 1992)	Basal till (Klint, 2001); 0-5 m b.s.: sandy clay till; 5-6 m b.s.: sand; 6-10 m b.s.: interbedded sand and till; 10-16 m b.s.: till; > 16m b.s.: limestone (Jørgensen and Fredericia, 1992)	18 -22% (Jørgensen and Fredericia, 1992)				0.25 -0.32 (Jørgensen et al., 2003)		Weathered : 10^{-5} to 10^{-7} (Jørgensen and Spliid, 1994) Unweathered: $5 \cdot 10^{-10}$ (Jørgensen et al., 2003)	~3.2 (Klint et al., 2001)	All types 1-1.5 m b.s.: 82 2-2.5 m b.s.: 71 4-4.5 m b.s.: 31 (calculated from K data, Jørgensen and Spliid, 1994)	3	Vertical & horizontal : (visual inspection at 3 excavations) 1 m b.s.: 21, 60, 30 cm 2 to 2.5 m b.s.: 35, 70, 600 cm 3 m b.s.: 80 cm, 200 cm, none < 4.5 m b.s.: 300 cm, 500 cm, none Contraction : (~ vertical) 0.75 to 1.6 m b.s.: 20 – 35 cm, random orientation (Jørgensen and Spliid, 1998)	> 5 m
<i>Højstrup</i>	Ground moraine over limestone bedrock (Klint, 2004a)	Clay till (somewhat sandy, silty, little gravel) with occasional sand lenses. Basal till deposited during the late Baltic advance (<i>ungbaltiske advance</i>) (Klint, 2004b)	~ 14 – 17% (Klint, 2004b)	1.5 to 1.55 m b.s.: 0.019 (Jakobsen et al., 2004)		3.5 m b.s.: 1.88 (Iversen and Jacobsen, 2004)			3.4 to 3.6 m b.s.: 10^{-10} – $5 \cdot 10^{-7}$ (Iversen and Jacobsen, 2004)	~3.8 m b.s. (Klint, 2004b).		3	Sub vertical : 2 m b.s.: 12 cm 4 m b.s.: 50 cm 5 m b.s.: ~ 200 cm Subhorizontal : 1.8 to 2.3 m b.s.: 1-4 cm ~ 3 m b.s.: 2-8 cm > 3.7 m b.s.: massive (Klint, 2004b)	> 5 m
<i>Kamstrup</i>	Basal lodgement till (Klint et al., 2001)	Clayey till (5-7 m thick) overlying well-drained, thick, sand layer (Jørgensen et al., 2003)								~5.5 (Klint et al., 2001)		3		> 7 m

Site	Landscape	Till description	% clay	f_{oc}	tortuosity	Dry bulk density (g/cm ³)	Porosity	OCR	Hydraulic conductivity (m/s)	Depth to redox boundary (m b.s.)	Fracture Aperture (μm)	Number fracture systems (Klint, 2004a)	Fracture spacing	Max. fracture depth (Klint, 2004a)
Lillebæk (Styczen et al., 2004)	Undulating ground moraine (Klint, 2004a)	1-26 m clayey till overlying 0-10 m thick sand lense overlying clayey till; Basal till (Klint, 2001)	4.9-30.5, avg: 18.6	0-0.0087, avg: 0.0018		1.61- 1.82	31.5- 42.5, avg: 36.5		Vertical: $4.37 \cdot 10^{-7}$ Horizontal: $4.37 \cdot 10^{-6}$	~4 (Klint et al., 2001)		3		> 4 m
Mammen	Undulating ground moraine over meltwater sand (plateau) (Klint, 2004b)	1.5 m clay till (very sandy and silty) underlain by 3 m clayey sand till underlain by 0.5 m meltwater sand. Likely a lodgement till. Contains sand and clay stringers (Klint, 2004b)				3.5 m b.s.: 1.73 5.5 m b.s.: 1.53 (Iversen and Jacobsen, 2004)			5.4 m b.s.: $3.5 \cdot 10^{-5}$ - $1.3 \cdot 10^{-4}$ (Iversen and Jacobsen, 2004)	> 6 m b.s. (Klint, 2004b)		2	Contraction: random orientation 0.5 to ~1.8 m b.s.: 20 cm 2 m b.s.: 200 cm (Klint, 2004b)	< 2 m
Rantzausgade	Ground moraine over limestone bedrock (Klint, 2004a)	1-1.5 m b.s. sandy till; 1.5 –3.8 m b.s. very sandy, silty, strongly consolidated clay till with gravel. At 3 m depth, a 2-cm thick sand layer with wide extent (Nygaard, 1999); Basal till (Klint, 2001)								~3 (Klint et al, 2001)		3	Vertical: (glacial tectonic) 3m b.s.: 70 cm Horizontal: (glacial tectonic-shear and/or freeze-thaw) 1.6m b.s.: 0.4 cm 3.5 m b.s.: 3cm Contraction: unsystematic (Nygaard, 1999)	>3.5 m
Ringe (Nilsson et al., 2001b)	Subglacial lodgement till	Clayey till, (5 to 7 m thick) overlying well-drained thick sand layer (Jørgensen et al., 2003); fractured clay till (sandy loam) 13 m thick with 2 m thick sand-silt lens, overlying 14-17 m thick sand layer	9.5 (Sidle et al., 1998); 7- 10 %				0 to 2.5 m b.s.: 0.353; 3.5 to 4 m b.s.: 0.337 (Sidle et al., 1998); 11.5 m b.s.:0.23		2.5 m b.s.: $5.81 \cdot 10^{-5}$; 4m b.s.: $8 \cdot 10^{-6}$ (Sidle et al., 1998); 1' 10^{-9} - $3 \cdot 10^{-11}$ m/s	~5 m; ~6.5 (Klint et al, 2001)	2.5 m b.s.:101-158; 4 m b.s.: 65-127 (Sidle et al, 1998) calculated from tracer test & cubic law	3 to 4	Vertical (Conjunctive shear : 3.3 to 4.7 m b.s.: 17 cm Horizontal (shear): only developed below 4 m 3.3 to 4.7 m b.s.: 23 cm Contraction (~vertical): 3.3-4.7 m b.s.: 18 cm (Klint and Fredericia 1995) decreasing rapidly below 2.4 m. - 2 major and 1 to 2 minor fracture systems which vary in density and inclination with depth (Sidle et al., 1998)	>5 m
Slagelsevej 190 (Hydraulic fracturing site) (Walsted et al., 2002)	2-23 m b.s., glacial till overlying Danien limestone aquifer	Silty, sandy to very sandy clay till	< 20%			1.86 - 1.97 estimated from ϕ and ρ_s	0.265 - 0.307 avg of 4 depths = 0.281	6-14	2 to 3.5 m b.s.: $1.5 \cdot 10^{-7}$ 4.3 m b.s.: $3.5 \cdot 10^{-8}$	2.3 m b.s.				
Slæggerup (Lindhardt et al., 2001)	Ground moraine over limestone bedrock (Klint, 2004a)	Complex interbedded clay till sand till, glaciofluvial sand glacialfluvial clay; basal till (Klint, 2001)	0 to 2.5 m b.s.: 40 – 50 % 3.5 to 6 m b.s.: 13- 26% 5 to 13.7 m b.s.: 13-19 %	0.0006 – 0.0021		1.2 m b.s.: 1.70 2.1 m b.s.: 2.01 (grain density at 4 m b.s.: 2.667g /cm ³)	0 to 2.5 m b.s.: 0.46 3.5 to 6 m b.s.: 0.28		0 to 2.5 m b.s.: $7.3 \cdot 10^{-7}$ 3.5 to 6 m b.s.: $7.3 \cdot 10^{-9}$, $3.9 \cdot 10^{-8}$	~3.5 (Klint et al, 2001)		3	Vertical: 1 to 2 m b.s.: 0-20 fractures per horizontal 10 cm 2 to 3 m b.s.: 0-20 fractures per horizontal 10 cm 3 to 5 m b.s.: 2-14 fractures per horizontal 10 cm Horizontal: 1 to 2 m b.s.: 0-20 fractures per vertical 10 cm 2 to 3 m b.s.: 3-20 fractures per vertical 10 cm 3 to 5 m b.s.: 0-5 fractures per vertical 10 cm (Lindhardt et al., 2001)	>5 m

Site	Landscape	Till description	% clay	f_{oc}	tortuosity	Dry bulk density (g/cm ³)	Porosity	OCR	Hydraulic conductivity (m/s)	Depth to redox boundary (m b.s.)	Fracture Aperture (μm)	Number fracture systems (Klint, 2004a)	Fracture spacing	Max. fracture depth (Klint, 2004a)
<i>Silstrup</i> (Lindhardt et al., 2001)	End, recessional or interlobate moraine (Klint, 2004a)	Thick clay basal till overlying heavy marine clay (Klint 2001); Weichselian glacial till with isolated thin layers and lenses of glacialfluvial sand as well as silt and clay stringers; poorly drained	20-30%	0.0016 – 0.0033		1.73-1.77	0.33 -0.35		1.3 to 3.5 m b.s.: 10^{-7} - 10^{-5}	~3.5 m (Klint et al, 2001)		2 (Klint, 2004a); 1	Vertical: 1.8 to 3.1 m b.s.: 8-20 fractures per horizontal 10 cm, disappear between 3.1 and 4.5 m b.s. (Lindhardt et al., 2001) Horizontal/sub horizontal: 0.7 to 1.8 m b.s.: intensely fractured 1.8 to 3.1 m b.s.: 0 fractures 3.1 to 4.5 m b.s.: 5-20 fractures per vertical 10 cm	< 4 m
<i>Vasby</i> (<i>Pneumatic Fracturing site</i>) (Christianse n and Wood, 2006)	Basal till over meltwater sand landscape (Houmark-Nielsen et al., 2005)	Sandy-clay flow/melt-out till (~ 2 m thick overlying sandy-clayey basal till ~10-17 m thick							8 m b.s.: $3.5 \cdot 10^{-7}$ 12 m b.s.: $2.1 \cdot 10^{-8}$ (København's Amt, 2005b)	3.5-4 m	Tenths of mm to ~ 2 cm.	3	Vertical/ (sub) vertical: 1 to 2.8 m b.s.:12-14 cm 4.3 m b.s.: 50 cm 4 to 6 m b.s.: ~1 to 1.5 m Horizontal: 1 m b.s.: 20 fractures/ 20 vertical cm. 2-4 m b.s.: 1 fracture/20 vertical cm > 4 m b.s : ~20 cm	
<i>Laidlaw Sarnia, Canada</i> (<i>Pneumatic. Fractured</i>)	clayey till plain 30-50 m thick overlying bedrock (Cherry, 1989); perhaps glacial lacustrian (Klint, 1996)	silty clay with large contents of stones, gravel, sand stringers and lenses (Klint, 1996)	40 % (Myrand et al 1992); 55 - 60% (D'Astous et al., 1988)	0.005 - 0.008 (Myrand et al 1992); 0.007 - 0.013, avg: 0.011 (Johnson, 1989)	0.20 - 0.33 (Johnson, 1989)	1.77 Myrand et al 1992); 1.6 (Johnson, 1989)			Weathered zone (4 to 6 m b.s.): 10^{-5} to 10^{-7} ; un-weathered zone: 2 to 3 orders of magnitude smaller (D'Astous et al., 1988); 10^{-10} (McKay et al., 1993a)	4-6 m b.s. (D'Astous et al., 1988) Canadian tills: to 40 (Sidle et al., 1989)	1-43 (McKay et al., 1993a) calculated from cubic law and K; 0.026 – 0.032 using Navier-Stokes equation (D'Astous et al., 1989)	3 (Klint, 1996)	Vertical &Horizontal: non-systematic, spacing varies between 60 to 170 cm between profiles, orientations and depths (Cherry, 1989) Contraction: (horizontal/sub horizontal) 0 to 3 m b.s.: 1- 2 cm 1.8 to 3 m b.s. irregular spacing, yet zoned (Klint 1996); Fractures mostly vertical 1 m b.s.: 1 fracture per 2 cm horizontal distance 2 m b.s.: 1 fracture per 5 cm 5 m b.s.: 1 fracture per m (D'Astous et al., 1989)	10 m (Cherry, 1989)

APPENDIX K: NATURAL FRACTURES AND DEPOSITIONAL ENVIRONMENTS OF TILLS

This appendix gives a brief discussion of glacial landscapes, associated deposits and till types for the reader who is unfamiliar with this subject. Furthermore, a more thorough discussion of hydrofractures and contraction fractures than given in Chapter 3 is provided.

K.1 Glacial-tectonic fractures and depositional landscapes

Erosional and depositional forces acting in, under, on, and in-front-of glaciers give rise to distinct glacial environments; subglacial, supraglacial, proglacial and glacial margin, in which distinct types of deposits/landforms are created (Marsh and Dozier, 1981). These landforms have characteristic grain sizes, degrees of sorting, types of geologic features (faults, folds, fractures) etc. (Klint, 2001). Figures K.1a and b illustrate subglacial, supraglacial, proglacial and glacial margin environments and the landforms created during and after glacial advance over the area.

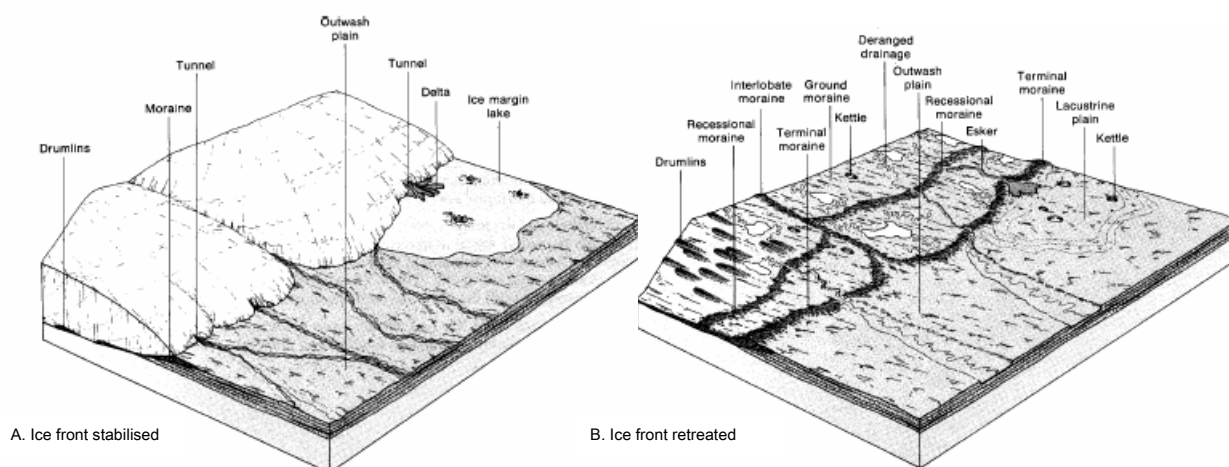


Figure K.1: a) subglacial, supraglacial, proglacial, and glacial margin environments and some of the associated landforms; b) some the landforms created by the glacial and glacial-fluvial process are visible after the ice has retreated (from Nelson Eby, 2005)

The subglacial basal till, carried at or deposited under a glacier (American Geological Institute, 1984) is the most common till type in Denmark (Houmark-Nielsen et al., 2005). Lodgement till is a type of basal till in which elongated stones are oriented with their long axis generally parallel to the direction of ice movement and with a compact fissile structure (American Geological Institute, 1984). Typical tills associated with supraglacial, proglacial and glacial margin environment are flow tills and melt-out tills. The characteristics of these environments, the types of glacial deposits and their geological characteristics are listed in Box K.1.

Box K.1: Summary over glacial depositional environments, types of fractures and associated sediment types (from Klint, 2001).

Land systems and depositional environment	Deformation processes and associated fractures and other structures.	Associated sediment types
The Sub-glacial land system: Include all landforms related to sub-glacial deformation and deposition. The till plain is the most widespread sub-glacial land form, but it also include eskers, drumlins, tunnel valleys etc. The sub-glacial land system often overprints older land systems and deformations may penetrate into the underlying older sediments.	Fracture types and other structures: Conjugating shear-fractures perpendicular to the ice-movement direction. Extensional fractures parallel to the ice-movement direction. Low-angle sheared sand-lenses and sediment-filled shear-fractures with a dominating "up-ice dip", Glacitectonites. Hydro-fractures (sediment sills and dykes) Drag-folds, reverse and normal faults. Deformation processes: Sub-glacial loading and shear. Drainage and melt-water recharge from the glacier are influencing the deformation style in a sense of ductile/plastic deformation during saturated conditions, or brittle deformation during well-drained conditions.	Sub glacial sediments: A and B-type Basal-till (ductile and brittle deformation) Sub-glacial melt-out till. Glacitectonites. Deformed older sediments.
The glacier-marginal land system: Consist of marginal push-ridge systems, with elongated ice marginal hills, cross-cut by melt-water valleys.	Fracture types and other structures: Large-scale thrust faulting, reverse, normal faulting and folding striking perpendicular to the ice-movement direction. Soft sediment intrusions (diapirism). All types of fractures. Deformation processes: Pro-glacial push (gravity spreading) results in a high variability of deformations.	Mixed sediments Dislocated slabs of glacial or older primary low-permeable sediments are often mixed with glacio-fluvial sediments, flow-till, and melt-out till.
The supra-glacial land system: Is dominated by hummocky moraine plain with a dead-ice relief. Numerous small hills and depressions are typical in this land system. The supra-glacial sediments often cover marginal or sub-glacial land systems.	Fracture types and other structures: Random oriented folds, faults and fractures. Collapse structures (normal faults). Deformation processes: In front of an advancing glaciers stacked sequences of supra-glacial sediment with a general up-ice dip are frequent, but once the ice stagnates, down and back-wasting processes results in generally random distributed structures, mixed with glacio-lacustrine and glacio-fluvial structures.	Supra-glacial sediments Supra glacial melt-out till. Flow-till. Glacio-lacustrine clay/silt /sand. Glacio-fluvial clay/silt/sand and gravel/boulders.
Pro-glacial land system: Is dominated by primarily fluvial and lacustrine sediments deposited in front of the glacier. Areas that were not overridden by glaciers during the last glaciation were perma-frozen, and were smoothed by periglacial processes. Finally silt/clay and drop material were deposited in lakes and in the sea.	Fracture types and other structures: Random oriented contraction orthogonal or polygonal fractures in fine-grained sediments. Ice and sand wedges in sandy sediments, sub-horizontal highly fractured zones. Kettle structures. Normal faults and vertical fractures. Deformation processes: Periglacial processes primarily freeze/thaw, but also desiccation processes create various cryogenic structures. Melting of ground ice may create subsidence or soil-creep resulting in various deformations. Neo-tectonic faults/fractures are formed above old fault-zones due to glacial rebound. Grounding icebergs may deform lake or marine sediments.	Pro-glacial sediments: Glacio-fluvial Clay/silt/sand and gravel. Debris flows. Aeolian sand. Glacio-lacustrine clay/silt/sand sometimes with scattered stones (drop-till in ice-marginal lakes). Marine sediments from flooded areas sometimes with drop material from icebergs.
The post glacial landscape: Large areas has risen from the sea. As a result of sea-level changes caused by eu-stasi after melting of the ice-shields and subsequent iso-stasi. All the above landscapes are furthermore influenced by human activity.	Fracture types and other structures: Desiccation fractures and freeze/thaw fractures, local stress release fractures along coastal cliffs. Neo-tectonic fractures above salt structures, and along major fault-zones. Deformation processes: Desiccation and freeze thaw processes still prevail in most areas on a small scale, along with occasional minor earthquakes. Chemical weathering processes are affecting the sediment properties everywhere, and erosion along the coast may create stress release fractures on steep cliff sections,	Interglacial sediments: Ongoing sedimentation of fluvial clay/silt/sand and gravel in rivers Lacustrine clay/silt/sand, peat and bogs in lakes. Marine sandy and clayey sediments in some risen and dammed areas. Aeolian sand.

Surface loading conditions are thought to have great influence on the types of till and hence formation of fractures and other features (folding, faulting, etc.). The characteristics of the types of fractures formed in the depositional environments listed above are summarised in Box K.2.

Box K.2: Fracture types and characteristics in tills (diamictic deposits) (from Klint, 2001).

Fracture types and characteristics in diamict deposits				
Fracture types	Typical fracture orientation		Size trace-length.	Fracture Characteristics Shape (m scale), Surface character and roughness (cm scale)
	Locally	Regional		
Glaciotectonic fractures				
<u>Glacitectonites</u>	Horizontal brecciated shear zones	Horizontal zone	0.1-1 m thick zones	Small irregular peds (>1-4 cm)
<u>Shearzones/shearplanes</u>	Horizontal sub-horizontal. Systematic	Horizontal sub-horizontal. Systematic	2- >20 meters long	<i>Shape:</i> Straight- Random <i>Character:</i> Planar-undulating <i>Roughness:</i> Slickensides, rough Often silt/sand filled
<u>Low-angle shear-fractures.</u>	Oblique, down-ice dip, strike perpendicular to ice-movement direction Systematic	Oblique, dipping down-ice, strike perpendicular to ice-movement direction Systematic	1- >12 meters	<i>Shape:</i> Listric- sigmoidal. <i>Character:</i> Planar-undulating <i>Roughness:</i> Slickensides, rough often thin silt or sand fill.
<u>Conjugating shear-fractures.</u> Acute angle between conjugating sets <30°	Oblique to vertical perpendicular to ice-movement direction Systematic	Oblique to vertical perpendicular to ice-movement direction Systematic	1->12 meters	<i>Shape:</i> Straight, listric, sigmoidal <i>Character:</i> Planar-undulating <i>Roughness:</i> Slickensides, smooth, rough
<u>Extension fractures</u>	Vertical, Sub-vertical Parallel to ice-movement direction. Systematic	Vertical, Sub-vertical Parallel to ice-movement direction. Systematic	0.1- >10 m	<i>Shape:</i> Random-straight <i>Character:</i> Irregular-undulating <i>Roughness:</i> Rough
<u>Hydro fractures.</u> 1. Downward infilled 2. Upward infilled 3. Large clastic dykes (burst out plumes)	Horizontal to vertical, perpendicular to ice-movement direction, dipping, down-ice 1-2: Systematic	Variable distribution Depends on local drainage conditions. 1-2: Systematic-non-systematic	0.1- >2 m long. Several cm thick	<i>Shape:</i> Random <i>Character:</i> Irregular Undulating. Massive or laminated filling of clay/silt/sand gravel.
Contraction fractures				
<u>Desiccation fractures</u> Orthogonal, oriented Orthogonal, random Polygonal non-sorted	Sub-vertical Systematic Non-systematic Non-systematic	Sub-vertical Non-systematic Non-systematic Non-systematic	Polygons 5-40 cm wide	<i>Shape:</i> Straight-random <i>Character:</i> Irregular columns <i>Roughness:</i> rough. Sedimentfilled near surface. Primarily in clayey sediments
<u>Ice wedges</u> Orthogonal, oriented Orthogonal, random Polygonal non-sorted	Sub-vertical Systematic Non-systematic Non-systematic	Sub-vertical Non-systematic Non-systematic Non-systematic	Polygons 1- >10 m wide	Open, sediment filled fractures, often wedge-shaped irregular fractures. Primarily in sandy sediments
<u>Tensile fracturing</u> due to frost heave.	Sub-vertical Non-systematic	Sub-vertical Non-systematic	< 1 m deep fractures	Random Irregular fractures wedge shaped fractures in water saturated sediments.
<u>Frost cracks</u> Due to segregation ice.	Non-systematic Vertical and horizontal micro-fractures in sub-horizontal zones	Non-systematic Depends on topography, texture and grain-size distribution.	0.3-5 cm spacing. Increasing downwards	<i>Character:</i> Random <i>Shape:</i> irregular. "Brick pattern" <i>Roughness:</i> rough
Neo-tectonic fractures				
<u>Neo-tectonic fractures</u>	Systematic Vertical/sub-vertical	Systematic Vertical/sub-vertical	<10->100m	<i>Character:</i> Straight <i>Shape:</i> planar <i>Roughness:</i> Smooth, slickensides

When Boxes K.1 and K.2 are used together it becomes clear that basal till sites are most interesting as potential sites for environmental fracturing. These sediments are relatively homogeneous compared to supra, pro- or glacial margin sediments, and have relatively low-permeabilities. Furthermore, the natural fractures are typically systematic in basal tills. Thus, a certain increase in the natural connectivity of the deposit can be anticipated via the application of environmental fracturing.

Glaciotectonic shear (vertical and horizontal) and extension fractures are described in detail in Chapter 3. Below, contraction fractures are described in greater detail than in Chapter 3. Hydrofractures, which were only named in Chapter 3 are briefly discussed.

K.1.1 Contraction fractures

Contraction fractures are formed due to climactic changes that result in desiccation (drying-out) and/or freeze-thaw processes in the subsurface (Klint, 2004a). Thus, they may be expected in all cohesive deposits.

Climactic changes large enough to induce desiccation and freeze-thaw processes are typically associated with the alternating periods of glacial advance and retreat within a given ice age, and the transition periods between ice ages and interglacial periods. Thus, contraction features are common in deposits that have been affected by periglacial processes, i.e. have not been in direct contact with a given glacier¹ but been affected by climactic changes related to it and have been influenced by frost heaves and desiccation (Klint, 2004a). Thus, all cohesive deposits in the Prequaternary strata that were surficial until being overlain by Quaternary deposits, as well as all cohesive Quaternary deposits, are likely to contain contraction fractures (Klint, 2004a).

The presence of contraction fractures in the subsurface tends to decrease with depth. This observation correlates well with the fact that effects of freeze-thaw and desiccation processes decreases with distance from surface.

Usually, the depth of the redox boundary coincides with the maximum penetration depth of contraction fractures at a given (low-permeability) locality. The redox boundary is typically representative of the lowest groundwater table occurring in summer (Klint et al., 2001). This water table, and thus the redox boundary and fracture penetration depth, is, according to Klint et al. (2001), typically found at depths of 4-6 m b.s. in Danish till plains, and deeper in elevated (hilly) areas.

Freeze-thaw fractures

Freeze-thaw fractures, a sub-division of contraction fractures, are usually found from 1-3 m b.s. and make up a dense network of small, irregular fractures. The fractures are typically sub-horizontal with fracture spacing of less than 0.5 cm, so that the fracture density sometimes exceeds 100 fractures per vertical meter (Klint, 2004a). This gives rise to a fissile structure in near-surface tills.

Desiccation fractures

In general, desiccation (and freeze-thaw) fractures, on account of being common in all cohesive deposits, are found almost everywhere in Denmark. However, one condition that prohibits forma-

¹ I.e. covered or deposited by it

tion of desiccation fracture, even in what was the shallow subsurface in Quaternary times, is constant saturation. This is often the case in low-lying areas, see Figure K.2. Thus, present local topography can (as it in most cases reflects earlier topography variation) have great influence on the penetration depth of desiccation fractures: low-lying areas are more prone to constant saturation and thus have considerably shallower penetration of desiccation fractures compared to elevated areas (Klint et al., 2001). Contrary to freeze-thaw fractures, desiccation fractures are usually vertical and form irregularly shaped polygons of varying sizes (Klint et al., 2001), see Figure K.3 below.

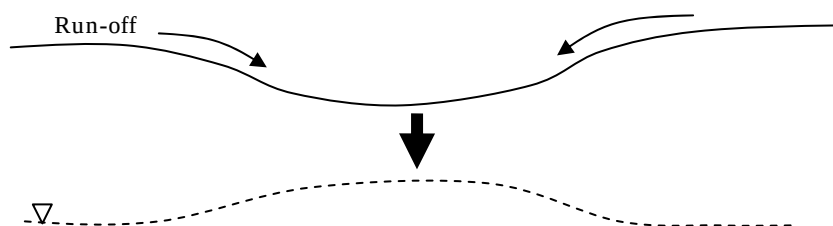


Figure K.2: Topography influences the depth of the groundwater table below ground surface, and thus also the maximum penetration depth of desiccation fractures.



Figure K.3: Example of (vertical) desiccation fractures forming irregularly shaped polygons of varying sizes (compliments of K.E.S. Klint).

K.1.2 Hydrofractures

Hydrofractures are unique in that they are formed due to poor subglacial drainage conditions, where high porewater pressure results in intrusion of water or water-saturated sediment to neighbouring sediments (Klint, 2001; Klint et al., 2001). They are not common, probably due to the fact that they are typically found near the bottom of till deposits, possibly on the border to an underlying sand layer (Klint et al., 2001).

APPENDIX L: TRANSPORT IN FRACTURED LOW-PERMEABILITY DEPOSITS

Since the late 1980s and the rising awareness of the potential for transport of free and aqueous phase DNAPLs in fractured low-permeability geologic media, there has been interest in understanding the complex relationships between fractured media characteristics, contaminant characteristics and the relative importance of advection and diffusion at a particular site and at a particular location in the porous medium. In the following discussion, diffusion is considered from a late-time remedial scenario, i.e. the process of interest is reverse diffusion from the matrix to the fracture.

Transport of dissolved solutes in fractured low-permeability geologic material is controlled by 1) advection in the fractures, 2) diffusion in the matrix and 3) attenuation processes including sorption, precipitation, and degradation in both the fractures and matrix (McKay et al., 1993a). The general advection-dispersion equation accounts for all of these processes, and can be adapted to describe transport in a particular domain of interest (Equation L.1).

$$\frac{\partial C}{\partial t} = \frac{D}{R} \cdot \frac{\partial^2 C}{\partial x^2} - v \cdot \frac{\partial C}{\partial x} - \lambda \cdot C \quad (\text{L.1})$$

where $\partial C / \partial t$ is the change in solute concentration over time; D is the hydrodynamic dispersion coefficient [L^2/T]*; R is a retardation factor [dimensionless]; v is the average linear groundwater velocity [L/T] (discussed later), λ is a reaction/degradation† term [T^{-1}]; C is the solute concentration [M/L^3]; and x is the distance along the flow-line [L].

The components of Equation L.1 may be broken down into many interrelated sub-parameters, and are discussed in the following.

L.1 Solute transport in fractures

In a remedial context and at a site-wide scale, the transport of soluble contaminants in fractures is an important process.

At the scale of a single fracture solute transport is primarily advective. Darcy's law is adapted so that the advection term (v) in Equation L.1 is calculated using the hydraulic conductivity of the fracture (K_f). According to the *Cubic Law* (see Box L.1) the hydraulic conductivity of the fracture (K_f) is a function of the square of the fracture aperture ($2b$).

* Dimensions are given in a general form where L represents a length unit, T represents a time unit, etc.

† The chosen degradation term represents 1st order degradation, but could generally have been any type of reaction, $r(C)$.

Box L.1: Explanation of the Cubic Law, describing advective flow through a single fracture.

The Cubic Law:

$$Q = K_f (2b) \frac{dh}{dx} \quad (\text{L.2})$$

where:

$$K_f = \frac{(\rho g)}{12\mu} (2b)^2 \quad (\text{L.3})$$

and where Q is the volumetric flow rate [L^3/T]; $2b$ is the fracture aperture [L]; dh/dx is the head gradient along the fracture; ρ is the fluid density [M/L^3]; g is the gravitational acceleration [L/T^2]; and μ is the viscosity [$\text{Pa}\cdot\text{T}$].

Fractures are idealised by a ‘parallel plate model’ which assumes the following fracture characteristics: flat, smooth surfaces of uniform aperture, and infinite length. Flow is assumed to be laminar and the fluid is assumed to be viscous and incompressible. The expression for flow in a parallel plate fracture is referred to as the ‘cubic law’ because the volumetric flow is a function of the fracture aperture cubed (Schwartz and Zhang, 2003).

Thus, the equation for advective transport component of a solute in a fracture is given in Equation L.4:

$$\frac{\partial C}{\partial t} = -v \cdot \frac{\partial C}{\partial x} \Rightarrow \text{where } v = \left(-K_f \cdot \frac{\partial h}{\partial x} \right) \quad (\text{L.4})$$

where v is the average linear velocity of the solute [L/T]; K_f is the hydraulic conductivity of the fracture (M/T) as described in Box L.1; C is the solute concentration [M/L^3]; and x is the distance along the flow-line [L].

Since g and μ in Equation L.4 are constants and ρ may be considered constant for a particular solute in groundwater, it becomes apparent that the fracture aperture ($2b$) is a crucial parameter in rates of advective transport in fractured, low-permeability deposits.

When the scale of interest is increased to include a fracture network, then the advective term is expressed by the following equation:

$$v = \frac{-K_f}{\phi_f} \cdot \frac{dh}{dx} \quad (\text{L.5})$$

where K_f refers to the hydraulic conductivity of the fractures and ϕ_f refers to the fracture porosity ($\phi_f = (2b)/(2B)$ where $(2b)$ is the fracture aperture and $(2B)$ is the fracture spacing).

Retardation in fractures is described by the following equation (from Jørgensen and Spliid, 1998):

$$R_f = 1 + \frac{2K_d}{(2b)} \quad (\text{L.6})$$

Where K_d in this context refers to the fracture-surface distribution coefficient. In most cases the retardation will be determined empirically from the equation:

$$R_f = \frac{v_{\text{water}}}{v_{\text{solute}}} \quad (\text{L.7})$$

as estimation of $K_{d \text{ fracture-surface}}$ is difficult in practice.

Similarly, longitudinal dispersion in fractures is generally ignored as no (field) values exist (Jørgensen and Spliid, 1998).

Other attenuation processes which may affect contaminant concentrations in a fracture are discussed in Section L.3.

L.2 Diffusion in the matrix

L.2.1 Fick's second law

In the so-called *matrix blocks* (the low-permeability porous geologic material between the fractures) transport will be almost exclusively diffusive. Jørgensen and Spliid (1998) estimate that 0.1 to 0.01% of the bulk flow occurs in the unfractured matrix. This is a reasonable assumption considering that the hydraulic conductivities of unfractured low-permeability deposits (K_m) are typically many orders of magnitude less than the bulk hydraulic conductivities (K_b) or the fracture hydraulic conductivities (K_f) (Cherry, 1989; McKay et al., 1999a and 1999b).

Fick's Second Law[‡] which may be used to describe the diffusion of a sorbing solute, in a homogeneous porous medium, in one dimension, is expressed in Equation L.8 (Broholm et al., 1999; Ball et al., 1997):

$$\frac{\partial C}{\partial t} = D_e^* \frac{\partial^2 C}{\partial x^2} \quad (\text{L.8})$$

where C is the concentration of the solute in the aqueous phase in the matrix [M/L³]; t is time [T]; D_e^* is the apparent effective diffusion coefficient [L²/T] for a sorbing compound, and will be re-

[‡] When Fick's First Law, describing diffusion due to a concentration gradient is combined with the Equation of Continuity, an equation is obtained describing the concentration of a diffusing solute in space and time.

ferred to as the apparent diffusion coefficient in the remainder of the text; and x is the distance from the source along the flow-line [L].

The resemblance of this equation to the second term in the advection-dispersion equation (Equation L.1) is obvious: in the matrix the advection term is negligible, and dispersivity is insignificant at low velocities thus, any dispersion is due to diffusion. Consequently, the dispersion coefficient (D) in Equation L.1 is replaced with an apparent diffusion coefficient for a sorbing species (D_e^*) in Equation L.8.

The driving force of the diffusion equation is the concentration gradient. If equal concentrations of the same solute are assumed in two matrix blocks, then the block with the smaller x value, i.e. the shorter diffusion pathway will, in effect, have the higher concentration gradient, and thus a more rapid flux from the matrix. This demonstrates that the fracture spacing ($2B$) in a formation will play a crucial role in diffusive flux from the matrix blocks, and thus, a crucial role in remediation times.

L.2.2 The apparent diffusion coefficient (D_e^*)

The apparent diffusion coefficient for a sorbing compound is defined by the following relationship (Broholm et al., 1999):

$$D_e^* = \frac{\tau D}{R} \quad (\text{L.9})$$

where D_e^* is the apparent diffusion coefficient for a sorbing species [L^2/T]; D is the free-solute diffusion coefficient in water [L^2/T]; R is the retardation factor for reactive compounds [dimensionless]; and τ is the ‘apparent tortuosity’ factor [-].

The tortuosity factor (τ)

The tortuosity factor attempts to quantify the increased length of diffusion pathways resulting from solutes being forced to diffuse around particles in the porous matrix (Freeze and Cherry, 1979). Consequently, the apparent diffusion coefficient is smaller than the diffusion coefficient in water. The more tortuous the pathway, the smaller the apparent diffusion coefficient will be. Mathematically, tortuosity is described by the relationship below:

$$\tau = \phi^p \quad (\text{L.10})$$

where τ is the tortuosity factor [-]; ϕ is the matrix porosity [-]; and p is an exponent. In a literature review performed by Ball et al. (1997) tortuosity values of 1.3 to 1.5 for organic chemical diffusion in a soil-bentonite system were noted, while a range of 0.8 to 2.4 with an average of 1.5 was observed for solutes in clay till. Based on laboratory and field values p has been found to vary between 1.3 and 5.4, although in silty and clayey deposits p generally falls within the range of 0.4 to 2.0 with an average of 1.1 (Parker et al., 2004).

Retardation factor (R)

The effect of sorption on the apparent diffusion coefficient is expressed through a retardation factor (R) described below (Freeze and Cherry, 1979):

$$R = 1 + \frac{\rho_b}{\phi} K_d \quad (\text{L.11})$$

Where R is the retardation factor [-]; ρ_b is the porous media dry bulk density [M/L^3]; ϕ is the porosity [-]; and K_d is the linear sorption coefficient also called a partitioning coefficient [$\text{L}^3/\text{M}_{\text{dry soil}}$].

The partitioning coefficient (K_d)

The partitioning coefficient may be estimated from sorption isotherms, according to Equation L.12 (Freeze and Cherry, 1979):

$$K_d = \frac{C_s}{C_w} \quad (\text{L.12})$$

Where K_d is the distribution coefficient [$\text{L}^3/\text{M}_{\text{dry soil}}$]; C_s is the mass of solute per unit mass dry soil [$\text{M}_{\text{solute}}/\text{M}_{\text{dry soil}}$]; and C_w is the concentration of the solute in solution in equilibrium with the mass of solute sorbed [$\text{M}_{\text{solute}}/\text{L}^3$] (Freeze and Cherry, 1979). For chlorinated solvents, which are hydrophobic, the distribution coefficient may also be estimated using Equation L.13: this is the so-called f_{oc} -derived K_d value.

$$K_d = K_{oc} \cdot f_{oc} \quad (\text{L.13})$$

where K_{oc} represents the partitioning coefficient with respect to organic carbon [L^3/M]; and f_{oc} is the fraction of organic carbon present in the sediment (Kjeldsen and Christensen, 1996).

Selecting an appropriate apparent diffusion coefficient is less straight-forward than may appear from the above equations. A diffusion coefficient may be determined directly from diffusion profiles measured in the field or in the laboratory, but this is time consuming and cumbersome for a single solute, let alone a multi-component mixture. Thus D_e^* values are typically estimated from K_d values (Equations L.9 and L.11-L.13). D_e^* values estimated from K_d values should be used with care. Discrepancies of an order of magnitude between field D_e^* values versus batch- K_d or f_{oc} -derived K_d values have been observed (Myrand et al., 1992).

L.3 The reaction term (λ)

As a conservative assumption, biologically mediated reactions are assumed to occur in fractures only since it is unknown whether bacteria would be present in the matrix.

The reaction term (λ) represents a reaction and/or degradation term. In the case of chlorinated solvents the reaction term could represent e.g. anaerobic reductive dechlorination (ARD), chemical oxidation with permanganate or chemical reduction with zero valent iron (ZVI), see *Appendix G: Coupled remediation technologies*.

Anaerobic reductive dechlorination is assumed to be a sequential degradation process described as a first order kinetic process, while the other two are straightforward single-step first order degradation. The degradation rate is proportional to the concentration of the degrading compound (C) [M/L^3] and a degradation constant (k_1) [T^{-1}]. Thus the reaction term (λ) in Equation L.1 is replaced with the expression below (Schwartz and Zhang, 2003):

$$\frac{\partial C}{\partial t} = -k_1 C \quad (L.14)$$

This differential equation can be solved given an initial situation, expressed mathematically in Equation L.15 (Schwartz and Zhang, 2003):

$$C = C_0 e^{-k_1 t} \quad (L.15)$$

Equation L.15 indicates that the initial concentration will be reduced exponentially as a function of time and the degradation rate constant (k_1).

When the degradation process is assumed sequential the complete reaction for the compound of interest may be expressed as:

$$\frac{\partial C_1}{\partial t} = -k_1 C_1 \quad (L.16)$$

$$\frac{\partial C_2}{\partial t} = y_1 k_1 C_1 - k_2 C_2 \quad (L.17)$$

$$\frac{\partial C_3}{\partial t} = y_2 k_2 C_2 - k_3 C_3 \quad (L.18)$$

etc.

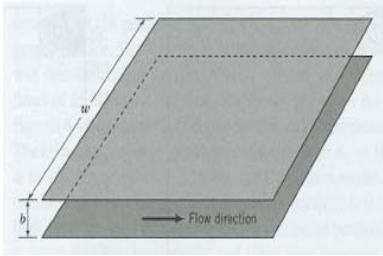
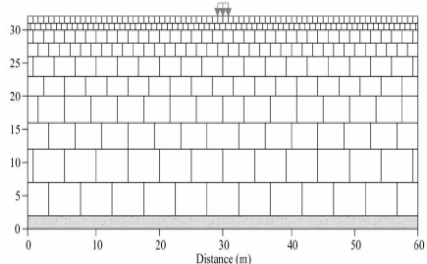
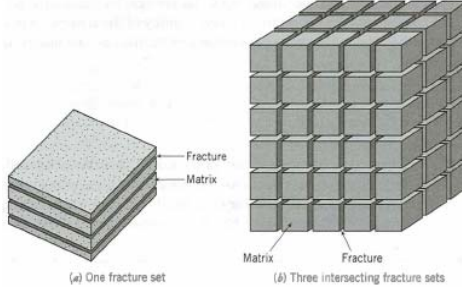
In the case of PCE degradation via anaerobic reductive dechlorination, C_1 represents the concentration of PCE, while C_2 to C_4 represent concentrations of its daughter products, TCE, DCE and VC respectively; k_1 to k_4 represent the degradation rate constants for PCE, TCE, DCE, and VC, respectively; and y_1 to y_3 represent the relationship between molar weights of the parent and daughter products. In the case of the above compounds y_1 to y_3 are equal to 1.

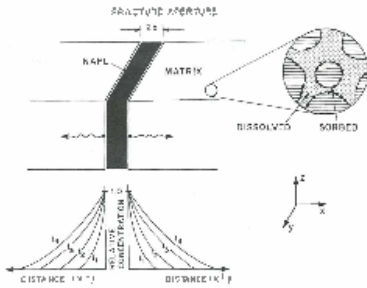
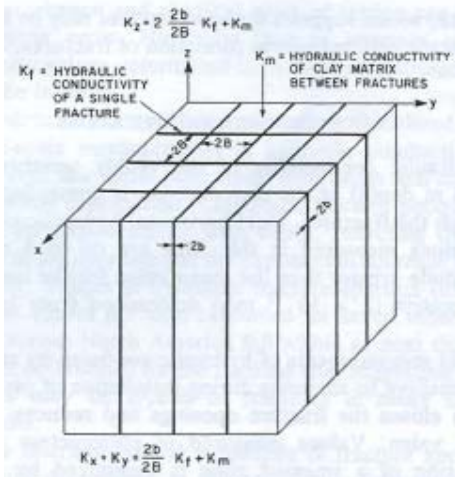
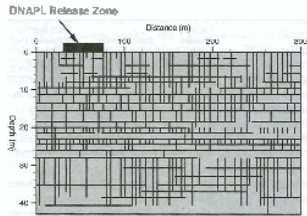
APPENDIX M: FRACTURE NETWORK MODELS

A number of conceptual models exist to simulate transport in fractured, low-permeability deposits: Box M.1 describes some of these. The suitability of a particular model depends upon the goal of the modelling exercise, the scale and timeframe of interest.

All the modelling approaches described in Box M.1 are extremely sensitive to fracture aperture and fracture spacing values, as these parameters control the hydraulic conductivity of the domain as a whole. In a remedial context, fracture spacing is perhaps the dominant parameter controlling transport as spacing (and to a lesser degree aperture, porosity, and tortuosity) determines the length of the diffusion pathway, and consequently long-term remediation times.

Box M.1: Commonly used models to simulate transport in fractured low-permeability media.

Description of conceptual models	Illustration of conceptual models	Uses of the models
Parallel Plate Models This type of model considers flow in a parallel plate fracture, slot fracture or intersecting fracture sets. Diffusion into the matrix is ignored. Here the permeability of a network of fractures is the product of the permeability in a single fracture and the fracture porosity. The hydraulic conductivity term becomes: $K_f = \left(\frac{\rho g}{12\mu} (2b)^2 \right) \cdot \phi_f$ where $\phi_f = (2b)/(2B)$ and where $(2b)$ is the fracture aperture and $(2B)$ is the fracture spacing (Schwartz and Zhang, 2003).	 'b' in the figure is (2b) elsewhere in the text. (from Schwartz and Zhang, 2003)	This type of model is relatively disused since it is only applicable where 1) fracture frequency is so high that advective transport completely dominates in the deposit or 2) the matrix porosity is so small that matrix diffusion is negligible.
Discrete Fracture Network Models These models couple a solution for flow and advective transport along individual, discrete, evenly-spaced parallel fractures with diffusion perpendicular to the fracture wall into a porous matrix (McKay et al., 1993c p 3886). Flow velocity is generally calculated based on the cubic law (see Box L.1, Appendix L). The scale of interest may be a single fracture, but more typically a fracture network.	 (from Reynolds and Kueper, 2001)	This approach has been used by McKay et al. (1993c); Sonnenborg et al. (1996) (using FRACTRAN); Ding et al. (2000); Reynolds and Kueper (2001) (using the Queen's University Multi-Phase Flow Simulator); and Kueper and Reynolds (2002) (using the previously mentioned model).
Dual or Double Porosity Models A complex fracture system is simplified into 2 homogeneous overlapping porous systems. The matrix is conceptualised as disjointed blocks of (conventional) porous media where transport is diffusive. The fracture domain, through which flow occurs, is also conceptualised as a porous medium. Each domain is described by its own set of hydraulic characteristics. A transfer function describes flow/transport between the two systems (Schwartz and Zhang, 2003; Karimi-Fard et al., 2004).	 (from Schwartz and Zhang, 2003)	This type model may be applicable at large scales and at sites with highly interconnected fractures. Dual porosity models are poorly suited to scenarios where only a few, large-scale fractures are present. Furthermore, it is difficult to evaluate the transfer function between domains accurately, especially in complex, heterogeneous domains (Karimi-Fard et al., 2004).

Fickian Diffusion Models This type of model is appropriate for scenarios where 1) the low-permeability material is intact, 2) the fracture spacing is very wide, 3) rates of advective transport are insignificant, and/or 4) where the scale of interest is small.	 (from Parker et al., 1994)	Researchers who have successfully used this type of model to match field profiles are Ball et al. (1997) to model diffusion in a 2-layer aquitard and Johnson et al. (1989) who used a Fickian diffusion model to simulate profiles in intact glaciolacustrine clay in Sarnia (Canada). Parker et al. (1994) and Parker et al. (1997) used a Fickian diffusion-based model to investigate dissolution of DNAPLs in a parallel-plate fractures and subsequent ‘disappearance’ (diffusion) into porous matrices.
Equivalent Porous Medium (EPM) Models (Also referred to as the Equivalent Continuum Approach.) EPM models assume that the geologic material is sufficiently densely fractured and/or the scale is large enough that the fractured low-permeability deposit behaves like a porous media with large grains (the grains being the matrix blocks). The equivalent permeability of the equivalent porous media is a function of the permeability of the fracture network and the matrix network. In this type of model the permeability is given by (Schwartz and Zhang, 2003): $k = \frac{k_m + \frac{A_f}{A_m} k_f}{1 + \frac{A_f}{A_m}}$ Where k_m is the matrix permeability, k_f is the permeability of the fracture network, and A_m and A_f are the cross-sectional contact areas of the matrix and fractures. The EPM conceptual model assumes that flow occurs through the fractures and diffusion occurs in the matrix. There is one set of hydraulic characteristics and a single flow equation for the entire domain.	 (from McKay et al., 1993c)	This type of approach has been used with varying degrees of success by a number of researchers including McKay et al. (1993c) and Sidle et al. (1998). This type of model may be applicable where the scale of interest is greater than the representative equivalent volume of the fractured media and where the fractures are highly interconnected.
Geostatistical Fracture Models These models are similar to discrete fracture models, but here statistical information regarding fracture characteristics (aperture, length, spacing, etc.) is used to generate fracture domains (either statistically matching field observations or hypothetical scenarios). A numerical model simulates advection and diffusion through the domain.	 (from Slough et al., 1999)	Researchers who have used this method include Parker et al. (1996); Markesic (2000) (using FRAC3DVS); Kueper and Reynolds (2002); and Hedeselskabet (2005) (using MODFLOW with the RT3D reaction module).

APPENDIX N: THEORY OF CHLORINATED SOLVENTS

N.1 Introduction

The term chlorinated solvents refers to the halogenated aliphatics chemical group (Kjeldsen and Christensen, 1996; *Amternes Videnscenter for Jordforurening*, hereafter AVJ, 2001). These chemicals are effective de-greasing agents and have thus been widely used for this purpose in metal and electronic industries, as solvents in paints and varnishes, as well as in the textile industry, (particularly in dry cleaning). In addition these compounds have been used as coolants and some have been components in leaded gasoline (Kjeldsen and Christensen, 1996).

The chlorinated solvents used in Denmark are primarily trichloroethylene (TCE), tetrachloroethylene (PCE), 1,1,1-trichloroethane (TCA), and dichloromethane (DCM) (Kjeldsen and Christensen, 1996). TCE has been imported to Denmark since the 1940s, while PCE first arrived on the Danish market in about 1960. Consumption of these compounds peaked in the 1960s and 1970s. By 2001, consumption dropped to approximately one-tenth of the maximum consumption, or approximately 1,200 tons/yr. (AVJ, 2001). Table N.1 lists chemical, common, and trade names of the compounds. Table N.2 lists typical uses of the compounds. In addition to the compounds most commonly used in Denmark, the tables also include dichloroethylene (DCE), vinyl chloride (VC), and 1,2-dichloroethane (DCA), as these are known and frequently found degradation products of PCE (and TCE) and TCA, respectively. Furthermore, DCA and VC are of particular interest, as they have been documented as carcinogenic (Kjeldsen and Christensen, 1996; AVJ, 2001). DCE is typically in the form *c*-1,2-DCE (AVJ, 2001).

Awareness of the toxicity of these compounds is relatively recent. The lack of awareness combined with their extensive use has resulted in soil and groundwater contamination, particularly with PCE and TCE, in Denmark. Contaminated sites are typically found in urban areas as a result of spills and leakage from storage containers, pipes, and sewers, although contamination may also arise from seepage from disposal sites and underground gasoline tanks (Kjeldsen and Christensen, 1996; AVJ, 2001).

In the case of a spill or other uncontrolled release of chlorinated solvents to the environment, the majority of the solvent mass will quickly volatilise (discussed later). The few percent mass remaining in the soil and, with time, the groundwater will in many cases result in aqueous solvent concentrations in excess of the Danish drinking water quality guideline of 1 µg/L* for the total

* There is a specific Danish drinking water quality criteria of 0.2 µg/L for VC (Kjeldsen and Christensen, 1996; AVJ, 2001).

content of chlorinated organic compounds (excluding thihalomethanes and pesticides) (Kjeldsen and Christensen, 1996; AVJ, 2001).

Table N.1: Common and trade names for the most commonly used chlorinated aliphatics (Merek, 1996; AVJ 2001).

Compound	Common name(s)	Trade name(s)
Tetrachloroethylene	Tetrachloroethene, PCE, Perchloroethylene PER, carbon bichloride, carbon dichloride, ethylene tetrachloride	Ankilostin, Blacosolve No. 2 DeeSolv, Didakene, DowPer, Isoform, Midsolv, Nema, Perclene, Perclene TG, Percosolv, Per-Ex, Perklone, Perm-A-Kleen, Per Sec, Phillsolv, Tetracap, Tetravec, Tetrophil, Wecosolv
Trichloroethylene	Trichloroethene, TCE, TRI, Ethylene trichloride, ethinyl trichloride, aceylene trichloride	Algylen, Alka-Tri, Aramenth, Blacosolv, Ethyl Trichloroethylene, Ex-Tri, Gemalgene, Germalgene, Hi-Tri, Narcogen, Tri, Trilene, Trimar, Triclene, Trichloren, Trichloen, Tri-Clene, Trethylene, Westrosol, Chlorylen
1,1,1-Trichloroethane	TCA, methylchloroform, MCF, methyltrichlormethane, α -trichlorethan, α -trichlormethane	Axothen No. 3, Barcothene Nu, Blake-solv 421, CF2 Film Clean, Chloroethene VG, Chloromane, Insolv VG, Methyl Chloroform Tech, KwickSolv, Penolene 643, Tri-Ethane, Triple One
Dichloromethane	DCM, Methylene chloride, methylene dichloride, methylene bichloride	No particular trade name
Dichloroethylene (trans-, 1,2- cis- 1,2- and 1,1-)	DCE, 1,1 dichloroethene Ethylene dichloride, acetylenchloride	No particular trade name
Vinyl chloride	VC, chloroethylene	No particular trade name
1,2-Dichloroethane	1,2-dichloroethane, 1,2-DCE, 1,2-ethylen dichloride, 1,2-ethyliden dichloride, 2-dichloroethane, α -, β -dichloroethane, dichloremulsion, dichloroethane, borer sol, Brocide, Destruxol borsersol, Dutch liquid, Dutch oil, EDC, >ethane dichloride, Ethylene dichloride, ethylene chloride, Freon 150, glycol dichloride, symdichlorethane	Not found

Table N.2: Typical uses of chlorinated solvents in Denmark and other countries. Table translated directly from AVJ (2001) with additional information from Kjeldsen and Christensen (1996) and www.atsdr.cdc.gov/toxfaq (2005).

Compound	Uses in Denmark	Uses in US and other countries
PCE	Dry cleaning, degreasing skins prior to tanning, production of medicines, production of 'flexoplader', de-greasing of light metals, cleaning agent, water-proofing agent	Dry cleaning, metal degreasing, solvent, production of CFC-compounds
TCE	Degreasing of skins prior to tanning, metal-degreasing, dry cleaning, extraction processes in food industry, cleaning and gluing processes in plastics and rubber industries, glue, varnish and cleaning agent.	Metal degreasing, cleaning liquid, solvent, coolant, extractions agent, production of ink, paint, varnish, glue, pesticides, PVC, hydrofluorocarbons, anaesthetics
TCA	Degreasing of skins prior to tanning, metal-degreasing	Metal degreasing, aerosols, dry cleaning (leather), lubricant, solvent in glue, paint, ink, cutting oils, etc, production of pesticides, aerosols, electronics, hydrofluorocarbons
DCM	Cleaning of tools/machines in plastics, and graphics industries, removal of rubber mouldings, extractions in pharmaceutical industry and analytical laboratories, paint remover, glue, cleaning agent	Aerosols, paint remover, urethane foam, solvent in chemical and plastics industries, degreasing agent
1,2 DCE	None found, though a typical degradation product of PCE	Solvent for rubber and wax
1,1-DCE	None found, though a typical degradation product of PCE	Production of 1,1,1-trichloroethane, acrylic fibres, co-polymers with other alkylates, previously an anaesthetic
VC	None found, but a typical degradation product of PCE	Production of PVC and mixed polymers
1,2-DCA	None found, though a typical degradation product of PCE and TCA	Production of VC and production of plastic and vinyl products (PVC pipes, furniture, car seats etc), solvent, additive to leaded gasoline

N.2 Physical-Chemical Data

In the following discussion, the term chlorinated solvents refers to all of the compounds listed in Tables N.1 and N.2 unless otherwise stated. Table N.3 summarises various physical-chemical data for selected chlorinated solvents.

Table N.3: Physical-chemical data for selected chlorinated solvents (modified from Kjeldsen and Christensen, 1996).

Compound	Molar weight (MV) [g/mol]	Viscosity (μ) [cP]	Density (ρ) [kg/L]	Vaporisation pressure (p) [Pa]	Solubility (C_w) [mg/L]	Distribution coefficient in	
						air vs. water (K_H) [-]	octonal vs. water ($\log K_{ow}$) [-]
PCE	165.83	1.932	1.6311	2415	240	0.72	2.88
TCE	131.39	0.566	1.4679	9900	1400	0.39	2.53
1,1,1-TCA	133.41	0.903	1.3492	16500	1250	0.7	2.49
DCM	84.94	0.449	1.3348	48300	13200	0.09	1.25
1,1-DCE	96.94	0.36	1.22	80500	3344	1.1	2.13
c-1,2-DCE	96.94	0.444	1.2736	27000	3500	0.17	1.86
t-1,2-DCE	96.94	0.404	1.2546	44400	6260	0.38	1.93
VC	62.5	-	0.92	354600	2763	1.1	1.38
DCA	98.96	0.887	1.26	105.40	8606	-	1.48

N.2.1 Volatility

The chlorinated solvents used in Denmark and their degradation products are all volatile (Henry's Law constants $K_H > 0$). Thus, in the case of a spill, most of the solvent mass will volatilise.

N.2.2 Sorption

Sorption of aqueous solvents to soil and aquifer material is assumed to be described by an equation relating an octonal-water partitioning coefficient (K_{ow}) to the amount of organic material present in the soil/aquifer. The resulting term is called a sorption coefficient (K_{oc}). The greater the K_{oc} value the greater the sorption: compounds for which $K_{oc} < 100$ are considered mobile (Baun and Kusk, 2004). From the calculated values for K_{oc} it is evident that only PCE sorbs to a significant degree to soil or aquifer material.

Table N.4: Sorption coefficients for selected chlorinated solvents calculated using the following formula: $\log K_{oc} = 1.04 \cdot \log K_{ow} - 0.84$ (from Kjeldsen and Christensen, 1996). The $\log K_{ow}$ values are taken from Table N.3. The formula is valid for soils where the fraction of organic matter $f_{oc} > 0.001$ (Baun and Kusk, 2004).

Compound	K_{oc}
PCE	143
TCE	61.8
TCA	56.2
DCM	2.9
DCE (1,1- / c-1,2- / tr-1,2-)	23.7 / n 12.4 / 14.7
VC	3.9
DCA	5.0

N.2.3 Bioaccumulation

The bioaccumulation or bioconcentration factor (BCF) for selected chlorinated solvents was calculated using the formula presented in the Table N.5 caption. All the compounds listed in the table have a $BCF < 100$ indicating that these compounds do not bioaccumulate to a significant degree (Baun and Kusk, 2003).

Table N.5: Bioaccumulation factors for selected chlorinated solvents calculated using the following formula: $\log BCF = 0.85 \cdot \log K_{ow} - 0.70$ (valid for neutral and non-polar compounds, formula from Baun and Kusk, 2004). The $\log K_{ow}$ values are taken from Table N.3. A $BCF < 100$ indicates little bioaccumulation.

Compound	BCF
PCE	56
TCE	28
TCA	26
DCM	2.3
DCE (1,1-/ c-1,2- / tr-1,2-)	13 / 7.6 / 8.7
VC	3.0
DCA	3.6

N.2.4 Human Toxicity

All the chlorinated solvents discussed have a narcotic effect. Long-term exposure may lead to memory loss. VC and DCA are proven carcinogens while TCE and PCE are suspected carcinogens (Kjeldsen and Christensen, 1996; Baun and Kusk, 2004).

N.2.5 Phase distribution and fugacity

If free phase is present, the majority of the solvent mass (about 98%) will tend to be in the gas phase (Kjeldsen and Christensen, 1996). The remaining fraction will become distributed between the porewater and the aquifer material. Transport and phase transfer processes are discussed in the following sections.

N.3 Transport and spreading processes in soil

Due to their chemical-physical characteristics, chlorinated solvents are affected by a number of transport and spreading processes. The following discussion considers a typical spill situation where a large quantity of chlorinated solvent is spilled on the surface of the ground or in the unsaturated zone. Figure N.1 depicts the transport and spreading that may take place in the subsurface. The numbers on the figure correspond to the text sections below. The physical-chemical characteristics of VC differ significantly from the other compounds and consequently, transport and spreading of VC is described in a later section.

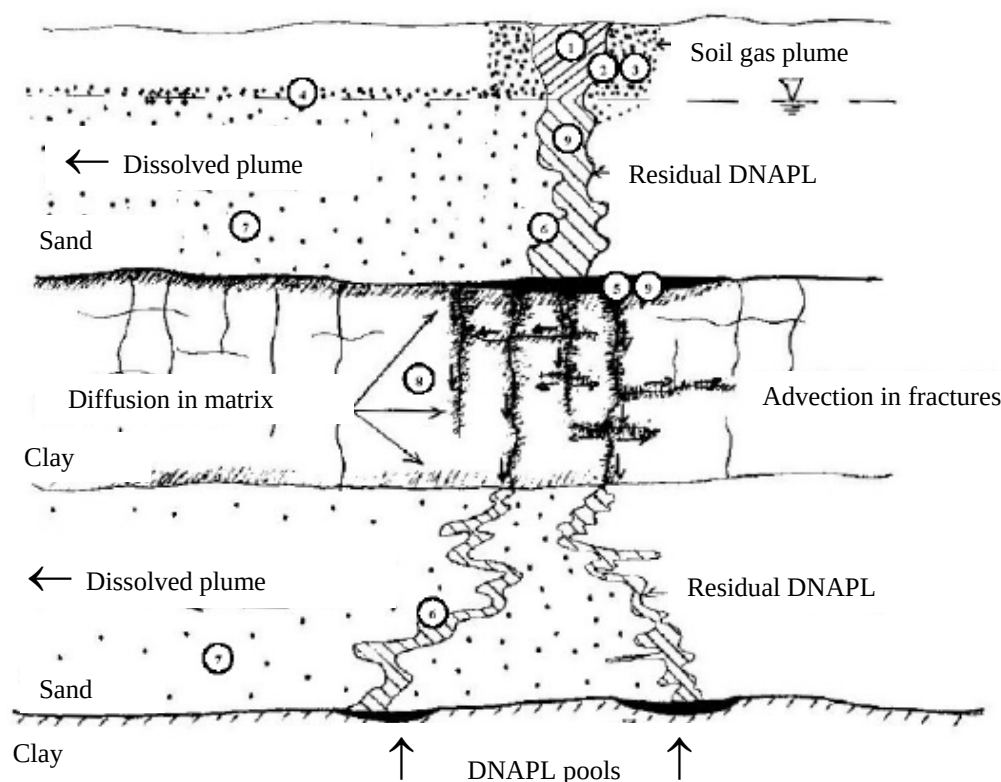


Figure N.1: Transport and spreading processes for selected chlorinated solvents in the sub-surface (modified from Kjeldsen and Christensen, 1996; AVJ 2001).

1. Downward transport of free phase in the unsaturated zone

Chlorinated solvents (with the exception of VC) are heavier than water, less viscous than water, and weakly soluble, thus the name DNAPL (dense, non-aqueous phase liquids). The spreading of free phase is controlled by gravity and local geology. In the case of a surface/near-surface spill, the compound will move downwards through the unsaturated zone as a connected 'blob' through the locally more permeable layers.

2. Diffusion of free phase to gas phase in the unsaturated zone

Chlorinated solvents are, as mentioned previously, volatile. Thus there is a transfer process whereby the compounds diffuse from the free phase to the gas phase.

3. Spreading of the gas phase in the unsaturated zone

Chlorinated solvents in the gas phase are spread via diffusion, which is controlled by concentration gradients, and convection in the soil gas of the unsaturated zone pore volume. Thus, solvent contamination can also be found 'up gradient' of the groundwater flow direction in a soil gas plume. If the gas-phase solvent diffuses to ground surface it may give rise to air quality problems both in- and outdoors. In Denmark, the air quality guidelines for TCE and PCE are 0.001 and 0.006 mg/m³, respectively for so-called sensitive areas, for example a residence with children. The air quality guideline for businesses which handle these compounds is 55 mg/m³ (NIRAS, 2004).

4. Partitioning between aqueous and gas phase in the unsaturated zone and between the saturated and unsaturated zones

Gas-phase contamination may result in partitioning of the solvent from the soil gas in the unsaturated zone to porewater in the unsaturated and saturated zones. Partitioning may occur directly from the unsaturated to saturated zones or via infiltrating water passing through the contaminated soil gas plume in the unsaturated zone. This process may result in groundwater contamination up-gradient of the source (spill). The extent of up-gradient contamination depends upon the following: 1) the permeability and thickness of the geologic material of which the unsaturated zone is composed and 2) the age and composition of the contamination. The significance of transport via infiltrating groundwater is also dependent upon the percolation rate.

Similarly, down-gradient of the contaminant source, a partitioning between the aqueous contaminant plume and the soil gas in the overlying unsaturated zone may occur. Partitioning occurs where relatively high concentrations in the aqueous plume are found at the contact between the saturated and unsaturated zones.

Sorption to / desorption from soil particles in the unsaturated zone

The fraction of the aqueous solvent that will sorb to soil and aquifer material is dependent upon the sorption coefficient K_{oc} of the particular compound and the fraction of organic carbon present in the soil/aquifer material. The distribution of a compound between soil and porewater is described by a partitioning coefficient (K_d) for the individual compound. Generally, the chlorinated solvents discussed here have low K_{ow} values (see Table N.3) and thus sorb weakly to soil/aquifer material. An exception is PCE where, if there is no free phase present, will partition so that about 60 % is in the gas phase and about 40 % is sorbed to the soil particles (AVJ, 2001). Sorption processes are not illustrated in Figure N.1. A surface or near-surface spill could result in soil concentrations above Danish guidelines.

5. Downward transport of free phase in the saturated zone

Because chlorinated solvents are heavier than water, the direction of groundwater flow has no effect on free phase transport. As in the unsaturated zone, transport is controlled by gravity and geology. In the capillary and saturated zones, capillary forces are also significant. The free phase must attain a certain height (and thus infiltration pressure) to overcome the capillary pressure (and thus resistance) of the pore water before the DNAPL is able to infiltrate into the soil pores and replace the pore water. In low permeability deposits or narrow fractures, the downward transport may cease until the free phase attains adequate height to displace the pore water. Hindrance of downward transport may result in accumulation of free phase, and in some cases horizontal spreading at the top of the capillary zone as illustrated in Figure N.1 Low permeability units may also hinder downward transport until adequate pressure is built up, see process 9.

6. Dissolution of free phase to pore water

Although chlorinated solvents are referred to as non-aqueous, they are more accurately characterised as weakly soluble. Calculations show that 1 litre of TCE must be diluted with 1.46 million m³ groundwater in order to meet the Danish drinking water guideline of 1 µg/L (Kjeldsen

and Christensen, 1996). Thus, due to their weak solubility and consequently slow rates of dissolution, spills of chlorinated solvents may act as contaminant sources for decades or centuries.

7. Advective transport of dissolved compounds in (sand) aquifers

In aquifers, aqueous chlorinated solvents are transported advectively in the direction of groundwater flow. Local inhomogenities increase the degree of spreading both horizontally and vertically. The zone of dissolved solvents is referred to as the contaminant plume.

8. Coupled transport processes in fractured clay till, interbedded sand and clay deposits etc.

In the case of a spill where the geology is heterogeneous, for example fractured clay till or chalk deposits or interbedded high and low permeability layers, complex 'coupled' transport processes may arise.

In fractures and permeable layers, aqueous solvents will be rapidly transported via advection. The direction(s) of transport is a function of the orientation and hydraulic gradients of the layers relative to one another. Consequently, aqueous solvents may be transported locally in a direction which differs from the dominant/large-scale groundwater flow direction.

In conjunction with the advective transport, a slow diffusion process may occur whereby aqueous solvents diffuse from fractures and/or sand lenses into the soil matrix and/or low permeability layers. The diffusion process is controlled by concentration gradients. If the concentration in the fractures/sand lenses falls, there may be a slow diffusion of compounds from the matrix (if concentrations are relatively higher) out into the fractures/lenses. This process is referred to as reverse diffusion. Slow reverse diffusion from low-permeability deposits represents a long-term source of low-concentration contamination.

Sorption to /desorption from soil particles in the saturated zone

If no free phase is present, the compounds will have a tendency to be present in the aqueous phase. Although as mentioned previously, PCE sorbs more than the other compounds: about 30 to 40% of PCE will be sorbed to soil or aquifer material (AVJ, 2001).

9. Residuals and DNAPL pools

During the downward transport of free phase, blobs or ganglia of free phase may become trapped in small pores, narrow fractures and/or low permeability layers becoming unconnected from the larger mass of free phase. These small, unconnected blobs are called residual free phase. In some cases the downward transport may be hindered by low permeability geological layers. The free phase may accumulate on top of such units forming so-called DNAPL pools. Residuals and pools are sources of contamination which are extremely difficult to find and remove.

Spreading and transport of VC

Since VC is not produced in Denmark, it is never present as free phase in the Danish environment. VC is a degradation product. It is more soluble than the solvents described previously and VC has a lower sorption capacity, making it the most mobile of the solvents discussed in this appendix. The

spread and transport of VC is governed by the following processes which have been described in detail above: spreading of gas-phase VC in the unsaturated zone; partitioning between aqueous and gas phases; advective transport of aqueous VC in (sand) aquifers; as well as coupled transport processes in fractured till, interbedded sands and clays, etc. Due to VC's low sorption capacity, sorption/desorption processes are less significant than is the case for the chlorinated solvents discussed previously.

N.4 Degradation

Degradation of chlorinated solvents is often incomplete and typically slow. Under natural conditions, the most significant degradation is biologically mediated: Table N.6 provides an overview of which biological degradation processes are effective for which compounds. While abiotic degradation is extremely slow, it may nevertheless become a significant process considering that chlorinated solvents may be present in the underground for decades. Furthermore, in a remedial situation, abiotic degradation may be accelerated/enhanced by stimulating selected conditions (Kjeldsen and Christensen, 1996). Whether or not a particular process occurs and at what rate it proceeds depends to a large degree on the redox conditions in at the site of interest (AVJ, 2001).

Table N.6: Summary of the biological degradation processes which have been documented effective for selected chlorinated solvents (AVJ, 2001).

Compound	Anaerobic reductive dechlorination (ARD)	Anaerobic oxidation	Aerobic oxidation	Aerobic co-metabolism
PCE	+			
TCE	+			+
TCA	+			+
DCM		+	+	+
DCE	+	+	+	+
VC	+	+	+	+
DCA	+	+		+

Degradation reactions are described below for the sake of completeness. Anaerobic reductive dechlorination (ARD) and abiotic degradation reactions with zero valent iron and potassium permanganate are described in more detail in *Appendix G: Coupled remediation technologies*.

N.4.1 Anaerobic biological degradation reactions

In anaerobic biological degradation processes, chlorinated solvents are typically secondary substrate for the bacteria. Thus, the presence of a suitable primary substrate is a prerequisite for the process to occur (Kjeldsen and Christensen, 1996).

Anaerobic reductive dechlorination

ARD is the most commonly observed degradation process for chlorinated solvents. It refers to the process whereby a chlorine atom on the chlorinated solvent compound splits off and is replaced by a hydrogen atom, thus reducing the compound (Kjeldsen and Christensen, 1996). The process is sequential meaning that only one compound is reduced at a time, and only one atom is removed per step. An electron donor is required, usually hydrogen (AVJ, 2001). The degradation rate for a specific chlorinated solvent depends upon the number of chlorine atoms that must be substituted and the redox conditions in the subsurface.). Typical rates for anaerobic reductive chlorination for selected solvents are mentioned in *Appendix G: Coupled remediation technologies*.

Dechlorination generally proceeds best under methanogenic conditions, although the reactions will proceed under sulphate reducing and denitrifying conditions. An exception is TCA which has not been observed to degrade under denitrifying conditions (Kjeldsen and Christensen, 1996). The sequential nature of the reductive dechlorination process may lead to an accumulation of degradation products (Kjeldsen and Christensen, 1996; AVJ, 2001). VC in particular is often observed to accumulate because its degradation rate is slower than that of the other chlorinate solvents, and it requires strongly reducing conditions for the degradation reaction to proceed (AVJ, 2001).

N.4.1 Anaerobic oxidation

Under reducing conditions, DCE and VC can function as electron donors (instead of as electron acceptors in the reductive dechlorination process, described above) and become oxidised. Carbon dioxide, sulphate, iron (III) or manganese (IV) will, depending upon the redox conditions function as electron acceptors. Under manganese-reducing conditions, DCE can be oxidised directly to carbon dioxide. Otherwise, it must first be reduced to VC and thereafter oxidised (AVJ, 2001).

N.4.2 Aerobic biological degradation reactions

PCE is persistent under aerobic conditions, while degradation of TCE is limited (AVJ, 2001).

Aerobic oxidation

In aerobic degradation reactions, DCE and VC function as primary substrate (electron donors) for the micro-organisms. Oxygen is used as an electron acceptor. DCE and VC can be oxidised directly to carbon dioxide. The VC oxidation reaction occurs more rapidly than the DCE reaction. Since DCE and VC are produced under reducing conditions (from the reductive dechlorination of PCE/TCE.) oxidising conditions are seldom present simultaneously with the presence of DCE or VC. However, at the periphery of the contaminant plume or in zones where contaminated and aerobic groundwater meet, there may be a possibility for the aerobic oxidation reactions to proceed (AVJ, 2001).

Aerobic co-metabolic oxidation

Co-metabolic oxidation is a process by which enzymes metabolise a primary substrate (compounds such as methane, propane, phenols, ethylene and toluene) and simultaneously co-metabolise (oxidise) compounds such as TCE, DCE-isomers and VC to carbon dioxide, chloride and other non-volatile substances. As with aerobic oxidation, degradation of chlorinated solvents via aerobic co-metabolic oxidation only occurs to a limited extent under natural conditions as oxygen, the primary substrates and chlorinated solvent contamination are rarely found together in the same environment.

Abiotic degradation reactions

Under natural conditions, abiotic degradation of chlorinated solvents, particularly PCE and TCE in soil and groundwater, is limited. Abiotic degradation may be stimulated by means of some of the following techniques: increasing the pH (by stimulating hydrolysis and/or dehydrohalogenesis); addition of hydrogen sulphide (by stimulating SH-substitutions); addition of iron[†] as a catalyst; addition of potassium permanganate (an oxidant). Iron and potassium permanganate augmentations are effective in accelerating abiotic degradation of PCE and TCE. DCE degradation is not catalysed by addition of iron (Kjeldsen and Christensen, 1996).

N.5 Methods of remediation

The following section is based on AVJ (2003) unless otherwise stated. A number of more and less well-proven methods and techniques to remediate soil contaminated with chlorinated solvents are listed below:

- 1) Excavation
- 2) Vacuum ventilation
- 3) Air-sparging
- 4) Steam stripping
- 5) Thermal conduction
- 6) Environmental fracturing combined with other techniques
- 7) Chemical oxidation
- 8) Stimulated natural degradation, typically anaerobic reductive dechlorination (ARD)
- 9) Passive ventilation
- 10) Pump-and-treat
- 11) Reactive permeable iron barriers

Common to the first seven methods in the list is that they all produce a reduction in the contaminant mass at a given site (i.e. address the source and in some cases also the plume of

[†] Both zinc and iron are well suited catalysts of abiotic degradation reactions. Iron is the least expensive and thus, is most often chosen (Kjeldsen and Christensen, 1996).

contamination). The remaining four methods are typically used to contain a plume of contamination. Over time the amount of contaminant mass at the source will be reduced, but initially the goal of these techniques is reduction in the contaminant concentrations in the plume.

Generally, soil, air and/or water removed in connection with remedial activities must itself undergo treatment to remove gas-phase, aqueous-phase and/or sorbed contaminants. Table N.7 lists which methods are most suitable where, technical considerations, degree of remediation and costs associated with the individual methods.

Table N.7: Remediation methods for sites contaminated with chlorinated solvents and required site characteristics for implementation of these methods. 1) The technique can be used in a range of situations and typically in combination with other remediation techniques. Thus, the 'answer' depends upon the coupled technique. 2) The parenthesis signifies that that are special conditions must be met for the particular soil type. 3) Refers the size site where the technique is both technically and economically feasible. 4) The assessment is based on information from the literature and field experience in Denmark. 5) Excavation of clay and silt (saturated and unsaturated) to a level under the head level in the underlying groundwater aquifer requires measures to prevent washout in the excavation (i.e. sinking the local groundwater level) (AVJ, 2003).

Technique ¹	Use (in situ, on site, ex situ)	Geology ² (Peat, gytje, clay, silt, sand, gravel, chalk, fractured)	Hydrogeology (Unsaturated zone saturated zone (confined, unconfined))	Design Considerations (Investigations, tests)	Site Size ³ (relative) large medium small)	Effect (remediation/ containment High > 90 % Medium 50-90% Low < 10%)	Timeframe for Remediation (Short > ¼ yr Medium ¾ - 3 yrs Long > 3 yrs)	Construction Costs (relative) High Medium Low)	Operating Costs (relative) High Medium Low)
Excavation	On/Ex site	all	Saturated and unsaturated (clay)	Geotechnics, consolidation test near structures	Small- large	High	Short	Medium-high	None
Vacuum ventilation	In situ	Sand –gravel (chalk)	Unsaturated zone	Effective air permeability, water content and grain size analysis	Small- large	Medium	Medium	Medium	Medium
Air-sparging	In situ	Sand –gravel	Saturated zone (unconfined)	Injection test, grain size analysis	Small- large	Medium	Medium	Medium-high	Medium
Steam stripping	In situ	Sand –gravel (chalk), interbedded clay stingers < 3 mm	Saturated and unsaturated	Effective air permeability, water content, grain size analysis, hydraulic conductivity	Small- large	High	Short	Medium-high	High
Thermal conduction	In situ	Clay, silt, sand	Saturated and unsaturated zone (clay)	Water content, grain size analysis, hydraulic conductivity	Small	High ⁴	Short	High	High
Fracturing coupled with other technique	In situ	Clay, silt, chalk, rock	Saturated and unsaturated		Medium- large	1	1	High	High
Chemical oxidation	In situ	Fractured clay, silt, sand (chalk)	Saturated zone	Hydraulic conductivity, sediment's natural oxidant consumption, pilot test	Small- large	Medium-high	Medium	Medium-high	Low-medium
Stimulated ARD	In situ	Fractured clay, silt, sand	Saturated zone	Hydraulic conductivity, sediment's natural organic matter consumption, biological characterisation	Small- large	Medium	Long	Low-medium	Low-medium
Passive ventilation	In situ	Sand, chalk	Unsaturated zone	Effective air permeability, water content, grain size analysis, pilot test	Small- large	Some effect locally	Long	Low	Low
Pump-and-treat	On/Ex site	Sand, chalk	Saturated zone	Hydraulic conductivity, gradient, groundwater chemistry	Small- large	High	Long	Medium	Medium
Reactive iron wall	In situ	Sand, gravel	Saturated zone	Hydraulic conductivity, gradient, groundwater chemistry	Small- medium	Medium-high	Long	High	Low

APPENDIX O: IMPLEMENTING THE CONCEPTUAL MODEL IN MATLAB

The following appendix first describes the work carried out in MATLAB to implement the conceptual model described in Chapter 4 and subsequently gives an overview of all simulations run in MATLAB with the model. An spreadsheet containing all modelling results is given on electronic form in *Appendix Y: Electronic data, Modelling results*.

O.1 Handling of the advection-dispersion equation in MATLAB

The general advection-dispersion equation given in the beginning of Chapter 4 (Equation 4.1) is restated with sorption, diffusion, advective, and degradation terms below:

$$R \cdot \frac{\partial C}{\partial t} = D \cdot \frac{\partial^2 C}{\partial x^2} - v \cdot \frac{\partial C}{\partial x} - \lambda \cdot C \quad (\text{O.1})$$

The equation (X.1) is a partial differential equation (PDE), which may be solved to yield a concentration profile in space for a specific time. The numerical modelling program MATLAB solves such equations using a built-in function *pdepe*. For *pdepe* to recognize a PDE, it must be given in the form:

$$c \left(x, t, C, \frac{\partial C}{\partial x} \right) \frac{\partial C}{\partial t} = x^{-m} \frac{\partial}{\partial x} \left(x^m f \left(x, t, C, \frac{\partial C}{\partial x} \right) \right) + s \left(x, t, C, \frac{\partial C}{\partial x} \right) \quad (\text{O.2})$$

I.e. expressions for the variables m , c , f , and s must be given. When working with slab symmetry*, m is 0 (MATLAB, 2005). Expressions for the remaining variables for sorption (c), diffusion-advection (f), and degradation (s) are obtained by comparing the two equations (O.1 and O.2):

$$c = c \left(x, t, C, \frac{\partial C}{\partial x} \right) = R \quad (\text{O.3})$$

$$f = f \left(x, t, C, \frac{\partial C}{\partial x} \right) = D \cdot \frac{\partial C}{\partial x} - v \cdot C \quad \left(D \cdot \frac{\partial^2 C}{\partial x^2} - v \cdot \frac{\partial C}{\partial x} = \frac{\partial}{\partial x} \left(D \cdot \frac{\partial C}{\partial x} - v \cdot C \right) \right) \quad (\text{O.4})$$

$$s = s \left(x, t, C, \frac{\partial C}{\partial x} \right) = -\lambda \cdot C \quad (\text{O.5})$$

For MATLAB to solve Equation O.2, the program furthermore requires a set of initial and boundary conditions. In the context of our modelling exercise, the initial conditions refer to the initial contaminant concentrations (in matrix and fracture). The boundary conditions are given by:

* With circular/radial symmetry m would be 1 or 2.

$$p(x, t, C) + q(x, t) f\left(x, t, C, \frac{\partial C}{\partial x}\right) = 0 \quad (\text{O.6})$$

I.e. values for p and q must at the model's left and right boundaries (p_l , q_l , p_r , and q_r [†]) must be specified, if MATLAB is to solve the differential equation.

Box O.1: Explanation of MATLAB's p and q syntax for boundary conditions.

Below, two simple contamination scenarios and their corresponding boundary conditions are stated to clarify MATLAB's syntax.

Scenario	1	2
	A contaminant source is present and continually replenishes the matrix, as diffusion from matrix into fracture(s) progresses. No flux over symmetry line in fracture (left boundary).	An initial and uniform concentration of contaminant is present throughout the matrix, but depletes as diffusion into fracture progresses. I.e. no flux over either boundary (constituted by symmetry line in fracture and symmetry line in matrix).
Boundary conditions	$C(0, t) = 0 = \text{const.}$ $\Leftrightarrow$ no flux boundary $\Rightarrow \begin{cases} q_l = 1 \\ p_l = 0 \end{cases}$ $C(x_m, t) = C_i = \text{const.}$ $\Leftrightarrow$ fixed concentration boundary $\Rightarrow \begin{cases} q_r = 0 \\ p_r = C(x_m, t) - C_i \end{cases}$	$C(0, t) = 0 = \text{const.}$ $C(x_m, t) \neq \text{const.}$ $\Leftrightarrow$ no flux boundaries $\Rightarrow \begin{cases} q_l = 1 \\ p_l = 0 \\ q_r = 1 \\ p_r = 0 \end{cases}$

A **no flux boundary** is given by $q = 1$ and $p = 0$:

- Setting q to 1 at a given boundary signifies that concentration depletion will take place at that boundary via diffusion/advection (see Equation O.6).
- As p represents replenishment of concentration C across a given model boundary (see Equation O.6), setting it to zero means that no concentration replenishment will take place at the given boundary.

A **fixed concentration boundary** is given by $q = 0$ and $p = C(x_{\text{boundary}}, t) - C_i$:

- Setting q to 0 at a given boundary signifies that concentration depletion (via diffusion/advection) will not take place at that boundary.
- Setting p to $C(x_{\text{boundary}}, t) - C_i$, means that $C(x_{\text{boundary}}, t) - C_i = 0$, as p must equal 0 to satisfy Equation 6.6, when q is also 0. I.e. $C(x_{\text{boundary}}, t) = C_i$, signifying constant concentration replenishment to maintain C_i at the given boundary.

The initial conditions are the same for both scenarios, namely:

$$C(x, 0) = 0 \quad \text{for} \quad 0 \leq x \leq x_b$$

$$C(x, 0) = C_i \quad \text{for} \quad x_b < x \leq x_m$$

[†] MATLAB syntax: l = left boundary, r = right boundary.

In summary, MATLAB requires specification of m , $c(R)$, D and $f(v)$, $s(\lambda)$, p_l , p_r , q_l , q_r , and initial conditions to solve Equation O.2.

O.1.1 Implementing the conceptual model in MATLAB

The conceptual model described in Chapter 4 was thus implemented in a MATLAB script specifying a core function (expressions for c , f , and s), initial conditions, boundary conditions, and all parameters contained within the three expressions.

Core function

The core function states expressions for the MATLAB variables c , f , and s , described in the previous section.

Box O.2: Core function implemented in MATLAB script to solve Equation O.2.

```
function [c,f,s] = core(xmesh,tspan,ccc,dcccdx,R,Db,Dm,Ci,Cr,lambdab,lambdam,xb);
c = R;
if xmesh < xb
f = Db*dcccdx; %expression for diffusion in fracture
s = -lambdab*ccc; %expression for degradation in fracture
else
f = Dm*dcccdx; %expression for diffusion in matrix
s = -lambdam*ccc; %expression for degradation in matrix (no degradation if lambdam = 0)
end
end;
```

As may be seen from Box O.2 and Equation O.3, the sorption term c is given simply by the retardation coefficient R . According to Equation O.4, the transport term f represents diffusion/dispersion, and advection. In the model it is given by diffusion alone (no advection term $v \cdot C$) in both fracture and matrix, as advection is considered negligible within the low-permeability matrix and, as stated previously, impracticable to model in the fracture (would require 2D). Instead, advection in the fracture is represented/simulated by implementing high degradation rates in the s term.

Initial and boundary conditions

Initial and boundary conditions are implemented in the script according to contaminant scenario 2 given in Box O.1 above (see also Equation O.5 and Chapter 4, Section 4.3.1: Conceptual model, *Contamination scenario*), see Box O.3 and O.4.

Box O.3: Initial conditions implemented in MATLAB script to solve Equation O.2.

```
function ccc0 = ic(xmesh,R,Db,Dm,Ci,Cl,Cr,lambdab,lambdam,xb);
if xmesh < xb
    ccc0 = 0; %no initial concentration in fracture
else
    ccc0 = Ci; %initial uniform concentration in matrix
end
end;
```

Box O.4: Boundary conditions implemented in MATLAB script to solve Equation O.2.

```
function [pl,ql,pr,qr] =
bc(xmeshl,cccl,xmeshr,cccr,tspan,R,Db,Dm,Ci,Cl,Cr,lambdab,lambdam,xb);
qr=1;
pr=0; % no-flux boundary ⇔ initial uniform concentration in matrix depleting over time
(w diffusion), i.e. no replenishment from a source
ql=1;
pl=0; % no-flux boundary ⇔ no input/output over symmetry line in fracture (rates of
degradation and diffusion interdependent)
```

Linking the functions and statement of parameters

The core function and initial and boundary conditions are linked via an overall function at the beginning of the script, see Box O.5 below.

Box O.5: Function linking core, and initial and boundary conditions.

```
function [problem2deg,xmesh] =
problem2deg(R,Db,Dm,Ci,Cl,Cr,xl,xb,xr,xstepsb,xstepsm,t0,tend,tsteps,lambdab,lambdam)

xmeshb=linspace(xl,3*xb,xstepsb);
xmeshm=linspace(3*xb+0.01,xr,xstepsm);
xmesh=[xmeshb xmeshm];

tspan=linspace(t0,tend,tsteps);

m=0;

problem2deg=pdepe(m,@core,@ic,@bc,xmesh,tspan,[],R,Db,Dm,Ci,Cl,Cr,lambdab,lambdam,xb);
```

The last line given in Box O.5 tells MATLAB that the stipulated functions are to be viewed as parts of a differential equation.

As can be seen from Boxes O.2-O.4 a set of parameters are stated for each of the implemented functions. These are the parameters necessary for MATLAB to utilise each function. A summary list of all parameters utilised in the script is given in the linking-function, see Box O.5.

To run the script, i.e. make MATLAB solve the specified differential equation, it is called upon in the MATLAB command window, as shown in Box O.6. In this call function, chosen values for the previously mentioned parameters are given (in the same order as in the script's linking-function). To plot the concentration values returned by MATLAB, a simple script was employed, see the following section, O.1.2: *Sub-routines*.

Pinpointing the time at which the maximum contaminant concentration in the matrix is 10 µg/L would require a lot of trial and error via the script described above. Two extra scripts localising this time have thus also been employed (*tendopt.m* and *cmin.m*), again see the following section, O.1.2: *Sub-routines*.

Box O.6: Example of function call in MATLAB's control window.

```
>> [concddeg, xmesh] = problem2deg(4.358, 5.61e-6, 1.54e-6, 240, 0, 240, 0, 0.025,
25.025, 100, 500, 0, 2.5264e9, 100, 1.67e-4, 0)
```

The command above returns concentration values for the specified points – in this case 100 in the fracture and 500 in the matrix – when

- retardation, $R = 4.358$,
- diffusion in the fracture, $D_b = 5.61 \cdot 10^{-6} \text{ cm}^2/\text{s}$,
- diffusion in the matrix, $D_m = 1.54 \cdot 10^{-6} \text{ cm}^2/\text{s}$,
- initial contaminant concentration (in the matrix), $C_i = 240 \text{ mg/L}$,
- initial contaminant concentration on the left boundary of the model (i.e. in the middle of the fracture), $C_l = 0$,
- initial contaminant concentration on the right boundary of the model (i.e. in the middle of the matrix block), $C_r = 0$,
- leftmost x-coordinate, $x_l = 0$,
- half-aperture of fracture, $x_b = 0.25 \text{ mm}$ (i.e. full aperture $2b = 0.5 \text{ mm}$),
- distance from fracture middle to matrix middle, $x_m = 25.025 \text{ cm}$ (i.e. full matrix block width $2B = 2 \cdot (25.025 - 0.025) \text{ cm} = 50 \text{ cm}$)
- number of calculation points in the fracture, $x_{stepsb} = 100$,
- number of calculation points in the matrix, $x_{stepsm} = 500$,
- initial time step, $t_0 = 0$
- final time step, $t_{end} = 2.5264 \cdot 10^9 \text{ s}$, or approximately 80 years (where $C \leq 10 \text{ µg/L}$),
- number of time steps, $t_{steps} = 100$ (i.e. each time step = $2.5264 \cdot 10^7 \text{ s}$, or 0.8 years),
- degradation rate in the fracture, $\lambda_b = \lambda_{bda_b} = 1.67 \cdot 10^{-4} \text{ s}^{-1}$ ($= 14.43 \text{ d}^{-1}$) and
- degradation rate in the matrix, $\lambda_m = \lambda_{mda_m} = 0$.

O.1.2 Sub-routines

The main script of the model is given in its entirety in Box O.7 below (fragments were shown in Boxes O.2-O.5). Boxes O.8 and O.9 show the supporting scripts used to pinpoint the time at which

the maximum contaminant concentration in the matrix is 10 $\mu\text{g/L}$ for a given set of input parameters, and plot the concentration values returned by MATLAB.

Box O.7: Primary MATLAB script utilised in modelling.

```
% Modelling: Sensitivity analysis of physical & fracturing parameters

function [problem2deg, xmesh] =
problem2deg(R,Db,Dm,Ci,Cl,Cr,xl,xb,xr,xstepsb,xstepsm,t0,tend,tsteps,lambdab,lambdam)

xmeshb=linspace(xl,3*xb,xstepsb);
xmeshm=linspace(3*xb+0.01,xr,xstepsm);
xmesh=[xmeshb xmeshm];

tspan=linspace(t0,tend,tsteps);

m=0;

problem2deg=pdepe(m,@core,@ic,@bc,xmesh,tspan,[],R,Db,Dm,Ci,Cl,Cr,lambdab,lambdam,xb);

%core:
function [c,f,s] = core(xmesh,tspan,ccc,dcccdx,R,Db,Dm,Ci,Cl,Cr,lambdab,lambdam,xb);
c = R;
if xmesh < xb
    f = Db*dcccdx; % diff in fracture
    s = -lambdab*ccc; % deg in fracture
else
    f = Dm*dcccdx; % diff in matrix
    s = -lambdam*ccc; % deg in matrix (no deg if lambdam is set to 0)
end
end;

%initial conditions:

function ccc0 = ic(xmesh,R,Db,Dm,Ci,Cl,Cr,lambdab,lambdam,xb);
if xmesh < xb
    ccc0 = 0; % no initial conc in fracture
else
    ccc0 = Ci; % initial uniform conc in matrix
end
end;

%boundary conditions:

function [pl,ql,pr,qr] = bc(xmeshl,cccl,xmeshr,cccr,tspan,R,Db,Dm,Ci,Cl,Cr,lambdab,lambdam,xb);

qr=1;
pr=0; %no flux boundary <=> initial uniform conc in matrix depleting over time (w diffusion)
ql=1;
pl=0; %no flux boundary <=> no input/output over symmetry line in fracture (rates of deg and diff
interdependent)

end
```


Box O.8: Supporting scripts used to pinpoint the time at which the maximum contaminant concentration in the matrix is 10 µg/L for a given set of input parameters.

tendopt.m:

```
% tend optimization

function tendopt = tendopt(R,Db,Dm,Ci,Cl,Cr,xl,xl,xr,xstepsb,xstepsm,t0,tend,tsteps,lambdab,lambdam)

imax = size(tend);
imax=imax(2);

for i = 1:1:imax
    concdeg =
    problem2deg(R,Db,Dm,Ci,Cl,Cr,xl,xl,xr,xstepsb,xstepsm,t0,tend(i),tsteps,lambdab,lambdam);
    tendopt(i) = concdeg(end,end);
end
```

cmin.m:

```
function cmin=cmin(tend,R,Db,Dm,Ci,Cl,Cr,xl,xl,xr,xstepsb,xstepsm,t0,tsteps,lambdab,lambdam,c0)
% c0 = target remediation concentration
tend
cmod=problem2deg(R,Db,Dm,Ci,Cl,Cr,xl,xl,xr,xstepsb,xstepsm,t0,tend,tsteps,lambdab,lambdam);
cmod=cmod(end,end);

cmin=(c0-cmod)^2 % absolute difference between target concentration and modelled concentration -
squared to prevent negative values
```

Box O.9: Supporting script used to plot concentration values returned by MATLAB.

grafdeg.m:

```
plot(xmesh,concdeg(91,:), 'k')

hold on

plot(xmesh,concdeg(92,:), 'b')
plot(xmesh,concdeg(93,:), 'c')
plot(xmesh,concdeg(94,:), 'g')
plot(xmesh,concdeg(95,:), 'r')
plot(xmesh,concdeg(96,:), 'm')
plot(xmesh,concdeg(97,:), 'y')
plot(xmesh,concdeg(98,:), 'k:')
plot(xmesh,concdeg(99,:), 'b:')
plot(xmesh,concdeg(100,:), 'c:')
title('Diffusion profile')
xlabel('Distance from fracture midpoint [cm]')
ylabel('Contaminant concentration [ug/L]')
%legend('Timestep 91','Timestep 92','Timestep 93','Timestep 94','Timestep 95','Timestep
96','Timestep 97','Timestep 98','Timestep 99','Timestep 100')
```

O.2 Overview of MATLAB simulations

The following pages provide an overview of all MATLAB simulations carried out for the modelling study discussed in Chapter 4. In each simulation, concentration profile data for 100 time-

steps (each one hundredth of the calculated remediation time t_r) were calculated. Illustration of diffusion- or degradation-limitation is thus provided via plots of concentration variation throughout the simulated matrix for the last 10 time-steps of each simulation.

Sim. #	Matlab command call	Timesteps	Plot
1	<pre>>> [concddeg,xmesh] = problem2deg(4.358,5.61e-6,1.54e-6,240000,0,240000,0,0.025,25.025,100,500,0,7.5373e9,100,2.78e-4,0)</pre>	91-100	
2	<pre>>> [concddeg,xmesh] = problem2deg(4.358,5.61e-6,1.54e-6,240000,0,240000,0,0.05,5.05,100,500,0,3.0997e8,100,2.78e-4,0)</pre>	91-100	
3	<pre>>> [concddeg,xmesh] = problem2deg(2.452,6.23e-6,1.71e-6,1400000,0,1400000,0,0.025,25.025,100,500,0,4.4243e9,100,6.94e-4,0)</pre>	91-100	

Sim. #	Matlab command call	Timesteps	Plot
4	<pre>>> [concddeg,xmesh] = problem2deg(2.452,6.23e-6,1.71e-6,1400000,0,1400000,0,0.05,5.05,100,500,0,1.7951e8,100,6.94e-4,0)</pre>	91-100	
5	<pre>>> [concddeg,xmesh] = problem2deg(1.292,7.08e-6,1.95e-6,3500000,0,3500000,0,0.025,25.025,100,500,0,2.2664e9,100,1.67e-4,0)</pre>	91-100	
6	<pre>>> [concddeg,xmesh] = problem2deg(1.292,7.08e-6,1.95e-6,3500000,0,3500000,0,0.05,5.05,100,500,0,9.5743e7,100,1.67e-4,0)</pre>	91-100	

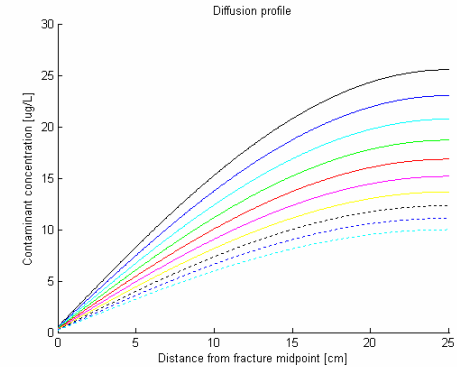
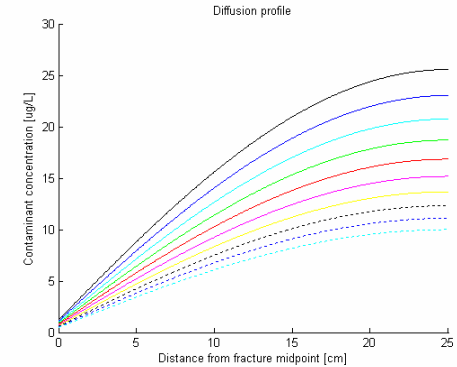
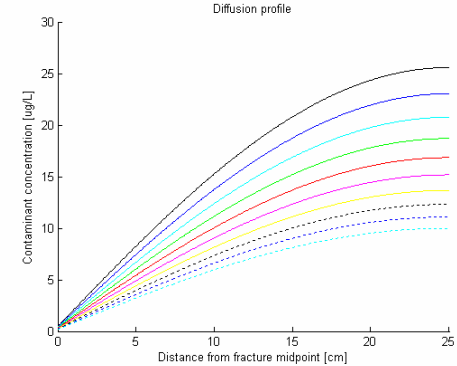
Sim. #	Matlab command call	Timesteps	Plot
7	<pre>>> [concddeg,xmesh] = problem2deg(1.092,8.34e-6,2.29e-6,2763000,0,2763000,0,0.025,25.025,100,500,0,1.5873e9,100,2.50e-4,0)</pre>	91-100	
8	<pre>>> [concddeg,xmesh] = problem2deg(1.092,8.34e-6,2.29e-6,2763000,0,2763000,0,0.05,5.05,100,500,0,6.6368e7,100,2.50e-4,0)</pre>	91-100	
9	<pre>>> [concddeg,xmesh] = problem2deg(4.358,5.61e-6,1.54e-6,240000,0,240000,0,0.025,25.025,100,500,0,7.5092e9,100,3.54e-4,0)</pre>	91-100	

Sim. #	Matlab command call	Timesteps	Plot
10	<pre>>> [concddeg,xmesh] = problem2deg(4.358,5.61e-6,1.54e-6,240000,0,240000,0,0.025,25.025,100,500,0,8.4650e9,100,3.54e-5,0)</pre>	91-100	
11	<pre>>> [concddeg,xmesh] = problem2deg(4.358,5.61e-6,1.54e-6,240000,0,240000,0,0.025,25.025,100,500,0,1.9050e10,100,3.54e-6,0)</pre>	91-100	
12	<pre>>> [concddeg,xmesh] = problem2deg(4.358,5.61e-6,1.54e-6,240000,0,240000,0,0.025,25.025,100,500,0,1.3060e11,100,3.54e-7,0)</pre>	91-100	

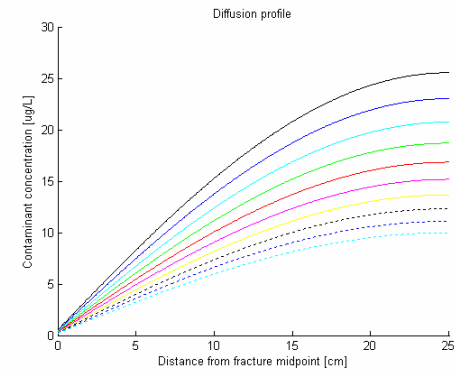
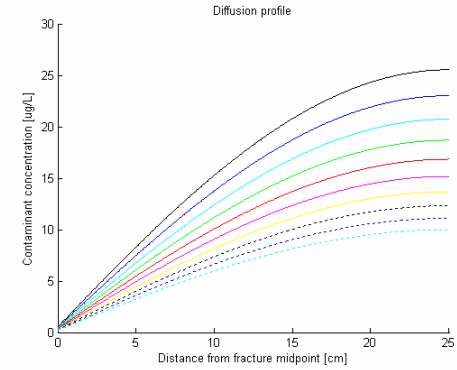
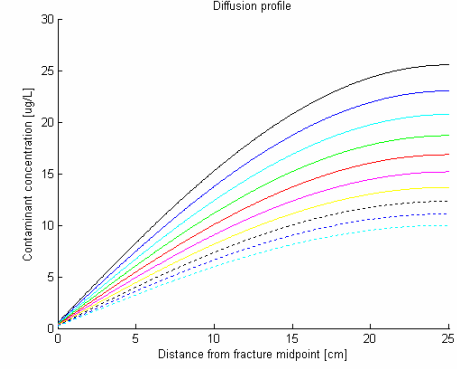
Sim. #	Matlab command call	Timesteps	Plot
13	<pre>>> [concddeg,xmesh] = problem2deg(4.358,5.61e-6,1.54e-6,240000,0,240000,0,0.025,25.025,100,500,0,1.2511e12,100,3.54e-8,0)</pre>	91-100	
14	<pre>>> [concddeg,xmesh] = problem2deg(4.358,5.61e-6,1.54e-6,240000,0,240000,0,10,35,100,500,0,7.4278e9,100,2.78e-4,0)</pre>	91-100	
15	<pre>>> [concddeg,xmesh] = problem2deg(4.358,5.61e-6,1.54e-6,240000,0,240000,0,0.05,0.175,100,500,0,6.7912e5,100,2.78e-4,0)</pre>	91-100	

Sim. #	Matlab command call	Timesteps	Plot
16	<pre>>> [concddeg,xmesh] = problem2deg(4.358,5.61e-6,1.54e-6,240000,0,240000,0,10,35,100,500,0,1.2014e10,100,2.78e-8,0)</pre>	91-100	
17	<pre>>> [concddeg,xmesh] = problem2deg(4.358,5.61e-6,1.54e-6,240000,0,240000,0,0.05,0.175,100,500,0,5.3533e9,100,2.78e-8,0)</pre>	91-100	
18	<pre>>> [concddeg,xmesh] = problem2deg(4.358,5.61e-6,1.54e- 6,240000,0,240000,0,0.05,5.05,100,500,0,3.0997e8,100,2.78e-4,0)</pre>	91-100	

Sim. #	Matlab command call	Timesteps	Plot
19	<pre>>> [concddeg,xmesh] = problem2deg(4.358,5.61e-6,1.54e-6,240000,0,240000,0,0.05,5.05,100,500,0,1.5963e11,100,2.78e-8,0)</pre>	91-100	
20	<pre>>> [concddeg,xmesh] = problem2deg(4.358,5.61e-9,1.54e-9,240000,0,240000,0,0.025,25.025,100,500,0,8.4650e12,100,3.54e-8,0)</pre>	91-100	
21	<pre>>> [concddeg,xmesh] = problem2deg(12.464,5.61e-6,1.54e-6,240000,0,240000,0,0.025,25.025,100,500,0,2.1809e10,100,1.67e-4,0)</pre>	91-100	

Sim. #	Matlab command call	Timesteps	Plot
22	<pre>>> [concddeg,xmesh] = problem2deg(2.911,5.61e-6,1.54e-6,240000,0,240000,0,0.025,25.025,100,500,0,5.0936e9,100,1.67e-4,0)</pre>	91-100	 Diffusion profile Contaminant concentration [µg/L] Distance from fracture midpoint [cm]
23	<pre>>> [concddeg,xmesh] = problem2deg(4.358,5.61e-6,3.35e-6,240000,0,240000,0,0.025,25.025,100,500,0,3.6265e9,100,1.67e-4,0)</pre>	91-100	 Diffusion profile Contaminant concentration [µg/L] Distance from fracture midpoint [cm]
24	<pre>>> [concddeg,xmesh] = problem2deg(4.358,5.61e-6,1.36e-6,240000,0,240000,0,0.025,25.025,100,500,0,8.5997e9,100,1.67e-4,0)</pre>	91-100	 Diffusion profile Contaminant concentration [µg/L] Distance from fracture midpoint [cm]

Sim. #	Matlab command call	Timesteps	Plot
25	<pre>>> [concddeg,xmesh] = problem2deg(4.358,5.61e-6,4.24e-7,240000,0,240000,0,0.025,25.025,100,500,0,2.7094e10,100,1.67e-4,0)</pre>	91-100	
26	<pre>>> [concddeg,xmesh] = problem2deg(4.234,5.61e-6,1.54e-6,240000,0,240000,0,0.025,25.025,100,500,0,7.4086e9,100,1.67e-4,0)</pre>	91-100	
27	<pre>>> [concddeg,xmesh] = problem2deg(4.420,5.61e-6,1.54e-6,240000,0,240000,0,0.025,25.025,100,500,0,7.7341e9,100,1.67e-4,0)</pre>	91-100	

Sim. #	Matlab command call	Timesteps	Plot
28	<pre>>> [concddeg,xmesh] = problem2deg(2.018,5.61e-6,1.54e-6,240000,0,240000,0,0.025,25.025,100,500,0,3.5311e9,100,1.67e-4,0)</pre>	91-100	 Diffusion profile Contaminant concentration [ug/L] Distance from fracture midpoint [cm]
29	<pre>>> [concddeg,xmesh] = problem2deg(11.176,5.61e-6,1.54e-6,240000,0,240000,0,0.025,25.025,100,500,0,1.9556e10,100,1.67e-4,0)</pre>	91-100	 Diffusion profile Contaminant concentration [ug/L] Distance from fracture midpoint [cm]
30	<pre>>> [concddeg,xmesh] = problem2deg(1,5.61e-6,1.54e-6,240000,0,240000,0,0.025,25.025,100,500,0,1.7498e9,100,1.67e-4,0)</pre>	91-100	 Diffusion profile Contaminant concentration [ug/L] Distance from fracture midpoint [cm]

Sim. #	Matlab command call	Timesteps	Plot
31	<pre>>> [concdeg,xmesh] = problem2deg(4.358,5.61e-6,1.54e-6,240000,0,240000,0,0.025,100.025,100,500,0,1.1935e11,100,1.67e-4,0)</pre>	91-100	
32	<pre>>> [concdeg,xmesh] = problem2deg(4.358,5.61e-6,1.54e-6,240000,0,240000,0,0.025,50.025,100,500,0,3.0038e10,100,1.67e-4,0)</pre>	91-100	
33	<pre>>> [concdeg,xmesh] = problem2deg(4.358,5.61e-6,1.54e-6,240000,0,240000,0,0.025,10.025,100,500,0,1.2740e9,100,1.67e-4,0)</pre>	91-100	

Sim. #	Matlab command call	Timesteps	Plot
34	<pre>>> [concdeg,xmesh] = problem2deg(4.358,5.61e-6,1.54e-6,240000,0,240000,0,0.025,5.025,100,500,0,3.4144e8,100,1.67e-4,0)</pre>	91-100	
35	<pre>>> [concdeg,xmesh] = problem2deg(4.358,5.61e-6,1.54e-6,240000,0,240000,0,0.025,2.525,100,500,0,9.7219e7,100,1.67e-4,0)</pre>	91-100	
36	<pre>>> [concdeg,xmesh] = problem2deg(4.358,5.61e-6,1.54e-6,240000,0,240000,0,0.005,25.005,100,500,0,8.5284e9,100,1.67e-4,0)</pre>	91-100	

Sim. #	Matlab command call	Timesteps	Plot
37	<pre>>> [concddeg,xmesh] = problem2deg(4.358,5.61e-6,1.54e-6,240000,0,240000,0,0.1,25.1,100,500,0,7.4643e9,100,1.67e-4,0)</pre>	91-100	
38	<pre>>> [concddeg,xmesh] = problem2deg(4.358,5.61e-6,1.54e-6,240000,0,240000,0,0.035,25.035,100,500,0,7.5579e9,100,1.67e-4,0)</pre>	91-100	
39	<pre>>> [concddeg,xmesh] = problem2deg(4.358,5.61e-6,1.54e-6,240000,0,240000,0,0.05,5.05,100,500,0,3.1892e8,100,1.67e-4,0)</pre>	91-100	

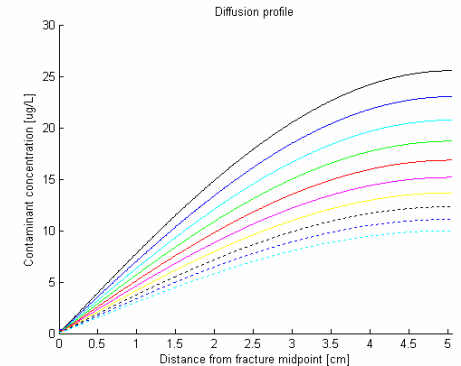
Sim. #	Matlab command call	Timesteps	Plot
40	<pre>>> [concddeg,xmesh] = problem2deg(2.452,6.23e-6,1.71e-6,1400000,0,1400000,0,0.025,25.025,100,500,0,4.5386e9,100,1.67e-4,0)</pre>	91-100	
41	<pre>>> [concddeg,xmesh] = problem2deg(2.452,6.23e-6,1.71e-6,1400000,0,1400000,0,0.05,5.05,100,500,0,1.9070e8,100,1.67e-4,0)</pre>	91-100	
42	<pre>>> [concddeg,xmesh] = problem2deg(1.292,7.08e-6,1.95e-6,3500000,0,3500000,0,0.025,25.025,100,500,0,2.2664e9,100,1.67e-4,0)</pre>	91-100	

Sim. #	Matlab command call	Timesteps	Plot
43	<pre>>> [concddeg, xmesh] = problem2deg(1.292, 7.08e-6, 1.95e-6, 3500000, 0, 3500000, 0, 0.05, 5.05, 100, 500, 0, 9.5743e7, 100, 1.67e-4, 0)</pre>	91-100	
44	<pre>>> [concddeg, xmesh] = problem2deg(1.092, 8.34e-6, 2.29e-6, 2763000, 0, 2763000, 0, 0.025, 25.025, 100, 500, 0, 1.6104e9, 100, 1.67e-4, 0)</pre>	91-100	
45	<pre>>> [concddeg, xmesh] = problem2deg(1.092, 8.34e-6, 2.29e-6, 2763000, 0, 2763000, 0, 0.05, 5.05, 100, 500, 0, 6.8773e7, 100, 1.67e-4, 0)</pre>	91-100	

Sim. #	Matlab command call	Timesteps	Plot
46	<pre>>> [concddeg,xmesh] = problem2deg(4.358,5.61e-6,1.54e-6,240000,0,240000,0,0.05,5.05,100,500,0,4.0589e8,100,3.54e-5,0)</pre>	91-100	
47	<pre>>> [concddeg,xmesh] = problem2deg(4.358,5.61e-6,1.54e-6,240000,0,240000,0,0.05,5.05,100,500,0,1.5087e9,100,3.54e-6,0)</pre>	91-100	
48	<pre>[concddeg,xmesh] = problem2deg(4.358,5.61e-6,1.54e-6,240000,0,240000,0,0.05,5.05,100,500,0,1.2769e10,100,3.54e-7,0)</pre>	91-100	

Sim. #	Matlab command call	Timesteps	Plot
49	<pre>>> [concddeg,xmesh] = problem2deg(4.358,5.61e-6,1.54e-6,240000,0,240000,0,0.05,5.05,100,500,0,1.2556e11,100,3.54e-8,0)</pre>	91-100	
50	<pre>>> [concddeg,xmesh] = problem2deg(1.092,8.34e-6,2.29e-6,2763000,0,2763000,0,0.025,25.025,100,500,0,1.5976e9,100,2.1e-4,0)</pre>	91-100	
51	<pre>>> [concddeg,xmesh] = problem2deg(1.092,8.34e-6,2.29e-6,2763000,0,2763000,0,0.025,25.025,100,500,0,2.1123e9,100,2.1e-5,0)</pre>	91-100	

Sim. #	Matlab command call	Timesteps	Plot
52	<pre>[concddeg,xmesh] = problem2deg(1.092,8.34e-6,2.29e-6,2763000,0,2763000,0,0.025,25.025,100,500,0,7.8469e9,100,2.1e-6,0)</pre>	91-100	Diffusion profile
53	<pre>>> [concddeg,xmesh] = problem2deg(1.092,8.34e-6,2.29e-6,2763000,0,2763000,0,0.025,25.025,100,500,0,6.6441e10,100,2.1e-7,0)</pre>	91-100	Diffusion profile
54	<pre>>> [concddeg,xmesh] = problem2deg(4.358,5.61e-6,1.54e-6,240000,0,240000,0,0.05,5.05,100,500,0,3.1892e8,100,1.67e-4,0)</pre>	91-100	Diffusion profile

Sim. #	Matlab command call	Timesteps	Plot
55	<pre>>> [concddeg,xmesh] = problem2deg(4.358,5.61e-6,4.24e-7,240000,0,240000,0,0.05,5.05,100,500,0,1.0982e9,100,1.67e-4,0)</pre>	91-100	 The plot, titled 'Diffusion profile', shows the contaminant concentration in $\mu\text{g/L}$ on the y-axis (ranging from 0 to 30) against the distance from the fracture midpoint in cm on the x-axis (ranging from 0 to 5). Multiple curves are plotted, representing different time steps. The curves start at (0,0) and increase as distance increases, with higher time steps resulting in higher concentrations. The curves are color-coded and include both solid and dashed lines for each time step.

APPENDIX P: MAP OF THE VASBY SITE

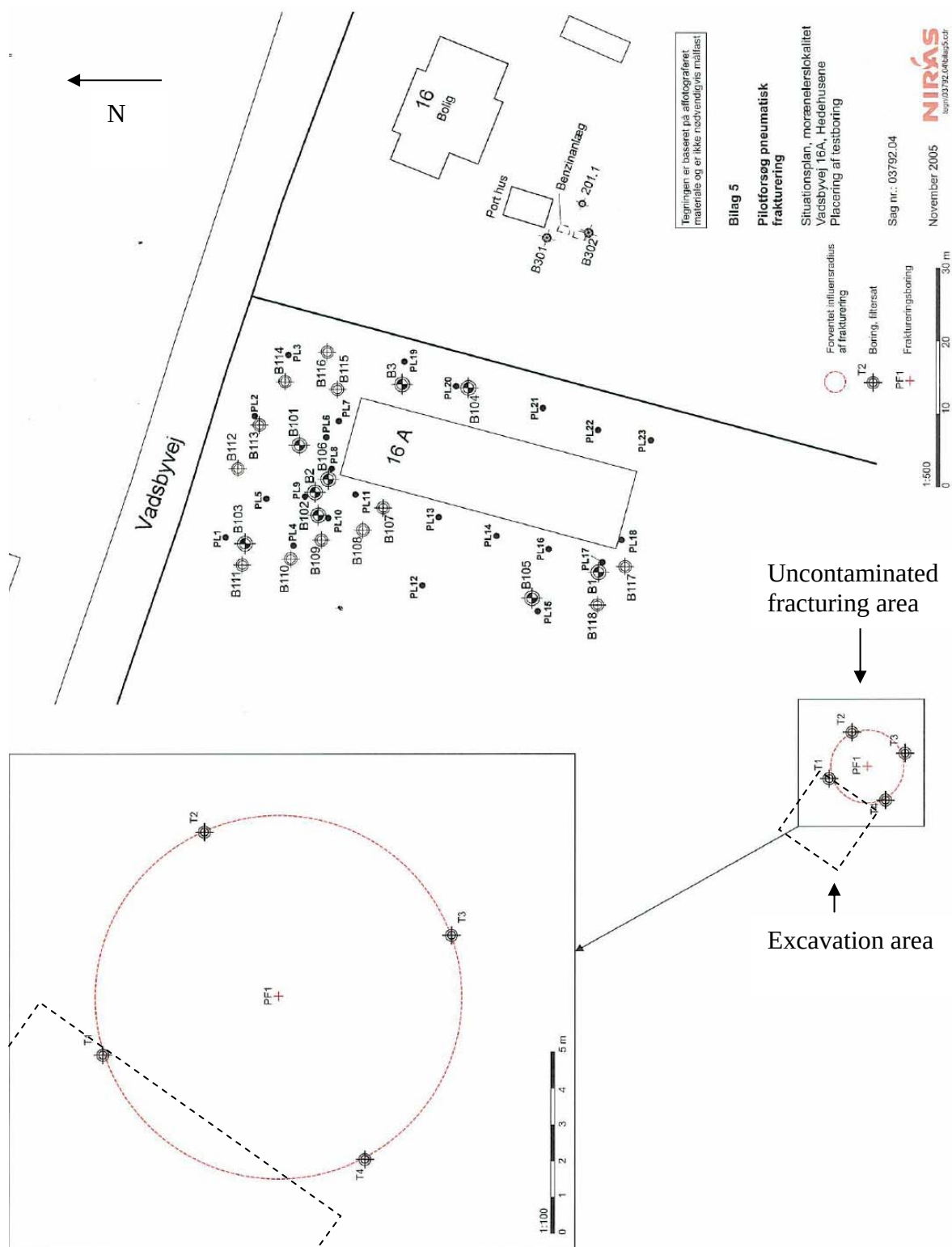


Figure P.1: Vasby site map. Compliments of NIRAS. Approximate location of excavation superimposed.

APPENDIX Q: SOIL SURVEY METHOD AND DESCRIPTION OF CORES KF0-KF3

Q.1 Method

Q.1.1 Introduction to the methods used to investigate the soil cores

Four cores were obtained in clear plastic tubes using a geoprobe. KF0 was retrieved prior to fracturing, while KF1, KF2 and KF3 were retrieved after fracturing was completed. The cores were picked up from the Vasby site and immediately stored in a dark room at 10 °C, until they were inspected and/or photographed.

The investigation of the cores for the present project involved a visual inspection of the cores for the presence of natural fractures and brilliant blue tracer under daylight conditions as well as analysis of the soil texture. These investigations were undertaken after the cores were photographed.

Q.1.2 Visual inspection of the cores and hand texture analysis

The total length of each core was recorded. For each vertical meter, approximately 1.16 m of core was retrieved. Unfortunately, determining a conversion factor between the core length and actual depth below surface is complicated by the fact that a number of cores were incomplete. In these cases, the depth was determined based on an 'educated guess' based on 1) geoprobe coring method; 2) what portion of the core would most likely be lost; 3) and the appearance of the actual core. Thus, the some depths mentioned in the text have an uncertainty of about ± 10 cm.

The following information was recorded: soil colour, texture, stoniness, presence of natural fractures, and presence of induced fractures. The soil texture was determined using the finger assessment of soil texture field test described in the Soil Survey Field Manual produced by the Canadian Ministry of Natural Resources (undated). Figure Q.1 depicts the method.

Q.1.3 Notes from the visual inspection and texture analysis

The notes from the visual inspection and hand texture analysis are given below.

Based on the finger analysis the overburden at the Vasby site is classified (according to the system in Figure X.1) as a sandy clay. Note that the worm/root holes (noted in the core descriptions) are more likely natural fractures containing reduced organic matter and/or finer clayey material.

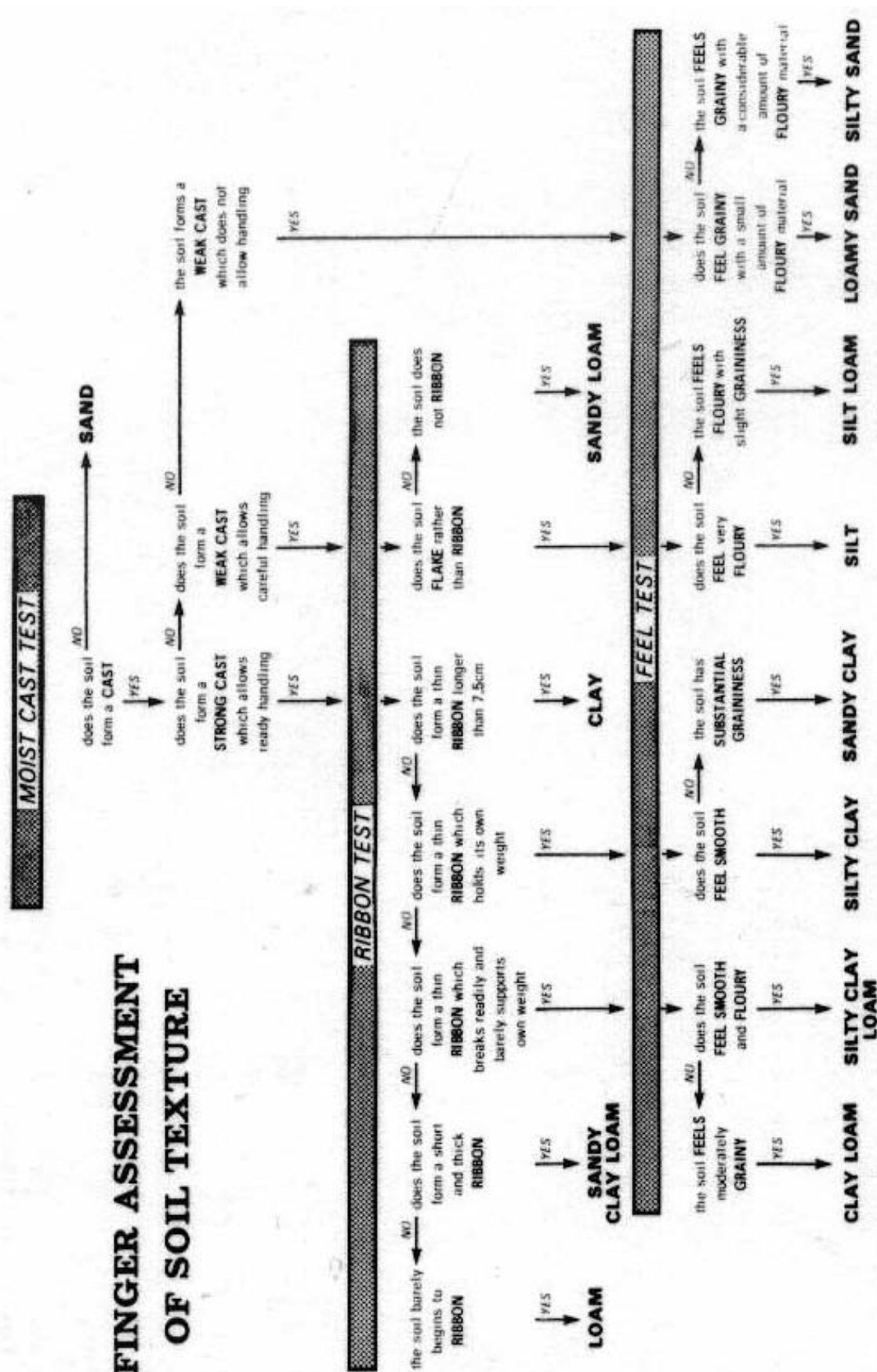


Figure Q.1 Finger assessment of soil texture field test method from Canadian Ministry of Natural Resources (undated).

Core KF0

Retrieved 01-12-2005 (prior to pneumatic fracturing, 05-12-2005). Inspected: 07-12-2005

Distance from top of tube (cm)	Estimated depth (m b.s.)	Geological material	Colour	Other * Note: worm/root holes are likely natural fractures.
2-3 m b.s. (core = 114 cm long)				
0-2	2.00-2.02	Empty tube		
2-39	2.02-2.34	CLAY, sandy, silty ~ 10% gravel + small stones, slightly rounded, mostly flint and limestone	Yellow-brown with ochre	~ vertical worm/root hole with ochre halo and grey silty-clayey infill. Very broken, rough appearance
38-88	2.34-2.76	CLAY, silty, sandy. ~ 10% gravel + small stones	Yellow-brown	Ochre and black (manganese?) mottles, broken appearance
88-116	2.76-3.00	CLAY, silty, sandy. ~ 10% gravel + small stones	Grey-brown	Ochre stripes, Perhaps a natural fracture, at 109 cm from top, ~ horizontal. After 109 cm appears more massive/uniform
3-4 m b.s. (core = 114 cm long)				
0-2	3.00-3.02	Empty tube		
2-6 to 8.5	3.02-3.05 to 3.07	CLAY, silty, slightly sandy (fine) Very uniform texture	Yellow-brown	Perhaps hydraulically conductive . Perhaps a fracture face or more sandy lens
6 to 8.5-21	3.05 to 3.07-3.18	CLAY, sandy, silty ~ 10% gravel + small stones, slightly rounded, mostly flint and limestone	Medium grey	
21-33	3.18-3.28			Natural fracture. Ochre ppts. very tortuous form. Abort 1-2 mm wide
33-116	3.28-4.00	CLAY, sandy, silty ~ 10% gravel + small stones, slightly rounded, mostly flint and limestone	Medium grey	
4-5 m b.s (core = 31 cm long)				
0-31	4.00-4.27	CLAY, sandy, silty ~ 10% gravel + small stones, slightly rounded, mostly flint and limestone		
	4.27-5.00	Empty tube		
5-6 m b.s (core = 103 cm long, missing from bottom of tube)				
0	5.00			Perhaps fracture plane, ochre colouring
0-3	5.00-5.03	CLAY, v. sandy, silty, ~ 10 % gravel, small stones, somewhat rounded, mostly flint and limestone	Grey-yellow	Perhaps an oxidised halo around a vertical fracture
3-103	5.03-5.89	CLAY, v. sandy, silty, ~ 10 % gravel, small stones, somewhat rounded, mostly flint and limestone		
	5.89-6.00	Empty tube		
6-7 m b.s (core = 116 cm long)				
0-10	6.00 – 6.09	CLAY, very sandy Hydraulically conductive	Yellow-brown	
10-20	6.09-6.17	SAND (fine) clayey Hydraulically conductive	Yellow-brown	Most of the sample is washed away
20-31	6.17-6.27	SAND, very clayey, very silty wet	Yellow-brown	
30-116	6.27-7.00	CLAY, v. sandy, silty, ~ 10 % gravel, small stones, mostly flint and limestone	Medium grey	Ochre mottles
7-8 m b.s (core = 116 cm long)				
0-116	7.00-8.00	CLAY, v. sandy, silty, ~ 10 % gravel, small stones, somewhat rounded, mostly flint and limestone	Medium grey	No visible fractures

Core KF1

Retrieved 06-12-2005 (same day as site was pneumatically fractured). Inspected: 07-12-2005

Distance from top of tube (cm)	Estimated depth (m b.s.)	Geological material	Colour	Other * Note: worm/root holes are likely natural fractures.
2-3 m b.s. (core = 112 cm long, geoprobe tip in end of tube)				
0-58	2.00-2.50	CLAY, sandy, silty ~ 10% gravel + small stones, slightly rounded, mostly flint and limestone	Grey-brown	Ochre mottles
16	2.14			Natural fracture. About 0.5 mm wide, horizontal, ochre ppt.
26	2.22			Natural fracture. Open, horizontal, ochre ppt.
30	2.26			Natural fracture. Horizontal, ochre ppt.
42-67	2.36-2.58			Worm/root hole* ~ vertical, ochre halo surrounding grey-coloured silty-clayey infill. About 1.5 to 2.3 cm wide
58-112	2.50-2.97	CLAY, sandy, silty ~ 10% gravel + small stones, slightly rounded, mostly flint and limestone		Ochre discolouration diffuse light-grey vertical stripe – perhaps a worm hole? About 0.7 – 1.3 cm wide
	2.97-3.00	Empty tube		
3-4 m b.s. (core = 116 cm long)				
0-4	3.00-3.03	Empty tube		
4-73	3.03-3.63	CLAY, sandy, silty. ~ 3 % gravel, mostly flint and limestone	Yellow-brown	Worm holes, dendritic pattern, 0.1 – 1 cm wide, > 16 cm long, Ochre mottles
18.5	3.16			Natural fracture. No precipitates, ~ 1 mm wide
68	3.59			Induced fracture: dark green interior with magenta edge and bright green in the matrix. ~ horizontal. No natural ppts visible
73-116	3.63-4.00	CLAY, sandy, silty. ~ 10 % gravel, mostly flint and limestone	Medium grey	
4-5 m b.s (core = 110 cm long, missing from bottom of tube)				
0-9 to 12	4.00-4.08/4.10	SAND, very clayey, silty,	Yellow-brown	Wet and appears somewhat washed out /away
9 to 12 - 110	4.08/4.10-4.95	CLAY, sandy, silty. ~ 10 % gravel, small stones, mostly flint and limestone	Medium grey	
20-24	4.17-4.21			Induced fracture. Magenta interior, blue edge, 'S'-shaped. Magenta area from 1 to 6 mm wide. Open in places, No natural ppts visible.
	4.95-5.00	Empty tube		
5-6 m b.s (core = 109 cm long, 7 cm missing from bottom of tube)				
0-109	5.00-5.94	CLAY, v. sandy, silty, ~ 10 % gravel, small stones, somewhat rounded, mostly flint and limestone	Medium grey	
29	5.25			Induced fracture. Magenta interior, blue edge, ~horizontal. Magenta area about 1-2 mm wide, not open. No natural ppts. visible.
101-104	5.87-5.90			Induced fracture. Magenta interior, blue edge, cutting diagonally down through the core. Open. No natural ppts. visible.
	5.90-6.00	Empty tube		

6-7 m b.s (core = 113 cm long, 3 cm missing from top of tube)				
0-3	6.00- 6.03	Empty tube		
3- 116	6.03-7.00	CLAY, silty, slightly sandy, ~ 10 % gravel, small stones, somewhat rounded, mostly flint and limestone	Medium grey	No visible natural fractures
7-8 m b.s (core = 116 cm long)				
0-6	7.00-7.05	SAND, clayey, silty Small amount of gravel	Grey-brown	Most of the sample is washed away
6- 116	7.05-8.00	CLAY, silty, slightly sandy, ~ 10 % gravel, small stones, somewhat rounded, mostly flint and limestone	Medium grey	No visible natural fractures

Core KF2

Retrieved 07-12-2005 (day after pneumatic fracturing). Inspected: 08-12-2005, cores 6-7 and 7-8 inspected 09-12-2005

Distance from top of tube (cm)	Estimated depth (m b.s.)	Geological material	Colour	Other * Note: worm/root holes are likely natural fractures.
2-3 m b.s. (core = 79 cm long, missing core in top of tube)				
0-79	2.00-2.68	CLAY, sandy, silty ~ 10% gravel + small stones, slightly rounded, mostly flint and limestone	Yellow-brown	Ochre mottles Diffuse light-grey worm/root holes with sandy-clay fill, about 1-3 cm wide
60-61	2.52-2.53			Induced fracture. Magenta interior, blue edge, ~horizontal. Magenta area about 0.5 cm wide. Location coincides with area with ochre ppts.
77-79	2.66-2.68			Natural fracture. Open, upside-down 'L'-shape, ochre ppt.
	2.68-3.00	Guess: geoprobe hit stone ∴ sample not pushed to top of tube ∴ bottom of sample missing.		
3-4 m b.s. (core = 116 cm long, but missing 23 cm in middle of core)				
0-5	3.00-3.04	CLAY, sandy, silty.	Yellow-brown	
5-10	3.04-3.09	CLAY, sandy, silty.	Grey-brown	
10-32	3.09-3.28	CLAY, sandy, silty ~ 10% gravel + small stones, mostly flint and limestone	Medium grey	Natural fracture. Torturous nearly vertical shape, ochre ppts., open
32-57	3.28-3.49	Empty tube		
57-116	3.49-4.00	CLAY, sandy, silty. ~ 10 % gravel, small stones	Medium grey	Ochre ppt. around a small stone
4-5 m b.s (core = 113.5 cm long)				
0-2.5	4.00-4.02	Empty tube		
2.5-116	4.02-5.00	CLAY, sandy, silty. ~ 10 % gravel, small stones, mostly flint and limestone	Medium grey	
33.5	4.29			Induced fracture. Magenta interior, blue edge, ~horizontal. Magenta area 1 mm wide.
35	4.30			Induced fracture. Magenta interior, blue edge, ~horizontal. About 1- 2 cm wide. Open
37	4.32			Induced fracture. Magenta interior, blue edge, ~horizontal. Magenta area about 1 cm wide.
5-6 m b.s (core <91 cm long, missing sample from both ends)				
0-3	5.00-5.03	Empty tube		
3-3.5	5.03-5.03	SAND (fine) clayey, silty	Yellow-brown	Wet. Maybe contamination from another sample?
3.5-91	5.03-5.78	CLAY, v. sandy, silty ~ 10 % gravel, small stones, somewhat rounded, mostly flint and limestone	Yellow-brown	
	5.78-6.00	Empty tube		
6-7 m b.s (core = 116 cm long)				
0-116	6.00-7.00	CLAY, sandy, silty, ~ 10 % gravel, small stones, somewhat rounded, mostly flint and limestone	Medium grey	
7-8 m b.s (core = 116 cm long)				
0-7	7.00-7.06	CLAY, sandy, silty	Medium grey + yellow-brown +	Area with natural fractures?

			chocolate brown	
7- 116	7.06-8.00	CLAY, sandy, silty, ~ 10 % gravel, small stones, flint and limestone	Medium grey	

Core KF3

Retrieved 08-12-2005. Photographed 09-12-2005. Geology and fractures inspected and described: 12-12-2005.

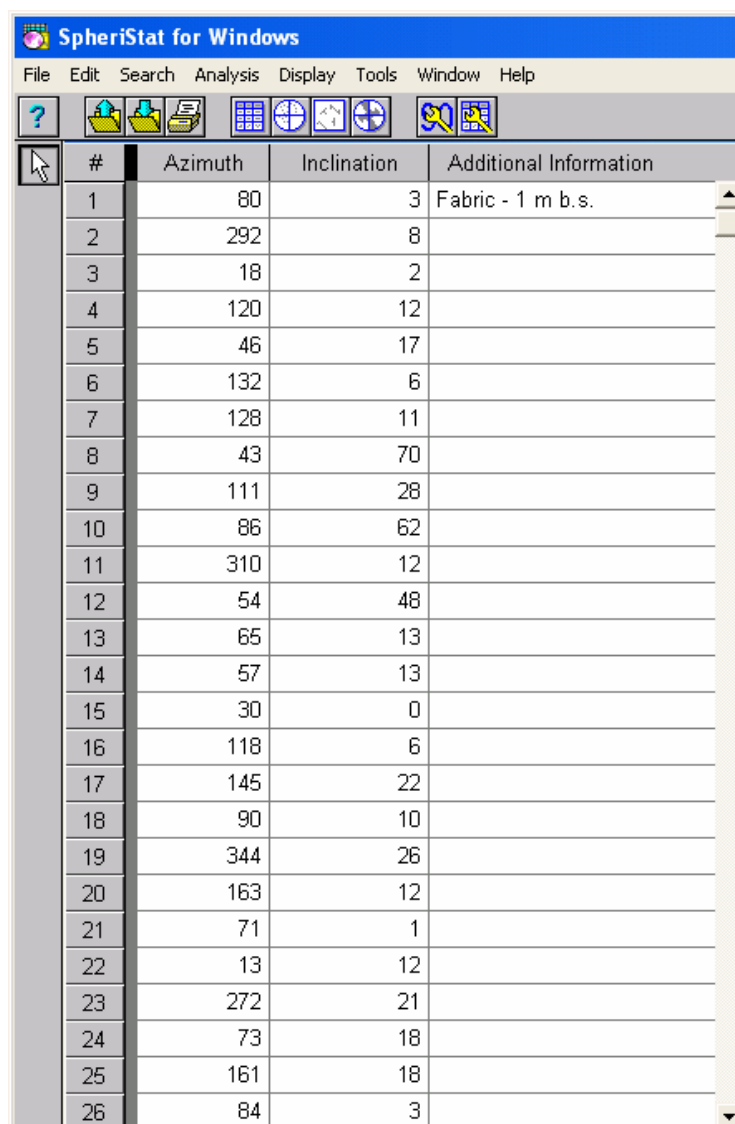
Distance from top of tube (cm)	Estimated depth (m b.s.)	Geological material	Colour	Other * Note: worm/root holes are likely natural fractures.
3-4 m b.s. (core = 95 cm long, but missing from top of tube)				
0-21	3.00-3.18	Empty tube		
21-53	3.18-3.46	CLAY, sandy, silty ~ 10% gravel + small stones, mostly limestone	Grey-brown	
53-116	3.46-4.00	CLAY, sandy, silty ~ 10% gravel + small stones, mostly flint and limestone	Medium grey	
58-59	3.50-3.51			Induced fracture Magenta interior, blue edge, upside-down bowl shape. No ochre ppts.
61	3.53			Induced fracture Magenta interior, blue edge, ~ horizontal ~ 0.7 mm wide, open. No ochre ppts.
4-5 m b.s. (core = 110 cm long)				
0-6	4.00-4.05	Empty tube		
6-7 to 9	4.05-4.08	CLAY, very sandy, silty. No gravel	Yellow-brown	Wet. Very uneven transition between layers.
7 to 9-116	4.08-5.00	CLAY, sandy, silty ~ 10% gravel + small stones, slightly rounded, mostly flint and limestone	Medium grey	
5-6 m b.s. (core = 102 cm long)				
0-15	5.00-5.13	Empty tube		
15-16	5.13-5.14	CLAY, sandy	grey	
16-21	5.14-5.18	CLAY, sandy, silty	Yellow-brown	Moist
21-116	5.18-6.00	CLAY, sandy, silty ~ 10% gravel + small stones, mostly flint and limestone	Medium grey	
57-66	5.49-5.57			Induced fracture Magenta interior, blue edge, diagonal downwards, open, no ochre ppts.
91	5.78			Induced fracture Magenta interior, blue edge, ~ horizontal, ~0.1 mm wide, open, no ochre ppts.
95-116	5.81-6.00			Induced fracture zone Tortuous, ~ vertical Magenta interior, blue edge, near a small stone, no ochre ppt.
6-6.6 m b.s. (core = 44 cm long)				
0-4	6.00-6.04	Empty tube		
4-6	6.04-6.06	CLAY, very sandy (fine), silty Almost no gravel	Medium grey	
6-24	6.06-6.24	CLAY, very sandy (fine), silty	Yellow + medium grey	Transition zone or strongly bioturbated zone
24-29	6.24-6.29	SAND (medium to coarse), clayey, silty	Yellow-brown	
30-48	6.30-6.48	CLAY, sandy, silty, ~ 10 % gravel, small stones, mostly limestone	Medium grey	
	6.48-6.60	Guess: sample lost from bottom of tube		
6.6-8 m b.s. (core = 116 cm long)				
0-2.5	6.60-6.63	Geoprobe tip		
2.5- 116	6.63-8.00	CLAY, sandy, silty, ~ 10 % gravel, small stones, mostly limestone	Medium grey	

8-9 m b.s. (core = 116 cm long)				
0-2	8.00 -8.02	Empty tube		
2-9	8.02-8.0.8	CLAY, sandy, silty Almost no gravel Yellow clay perhaps more sandy	Yellow + grey	Transition zone or strongly bioturbated zone
9-116	8.08-9.00	CLAY, sandy, silty ~ 10% gravel + small stones, mostly flint and limestone	Medium grey	
9-10 m b.s. (core = 116 cm long)				
0-2	9.00-9.02	Empty tube		
2-116	9.02-10.00	CLAY, sandy (fine), silty ~ 10% gravel + small stones, mostly flint and limestone	Medium grey	

APPENDIX R: FABRIC DATA AND STRIKE AND DIP MEASUREMENTS OF NATURAL FRACTURES AT THE VASBY SITE

The following tables R.1-R.3 display fabric data consisting of dip and dip direction measurements of small elongated stones exposed in the Vasby excavation on 3 horizontal surfaces. Strike and dip measurements of the large natural fractures observed on the vertical profiles of the excavation are given in Tables R.4-R.5. Dip direction and strike measurements are listed in columns headed *Azimuth*^{*}, while dip measurements are listed in columns headed *Inclination*[†].

Table R.1: Fabric data - 1 m b.s.

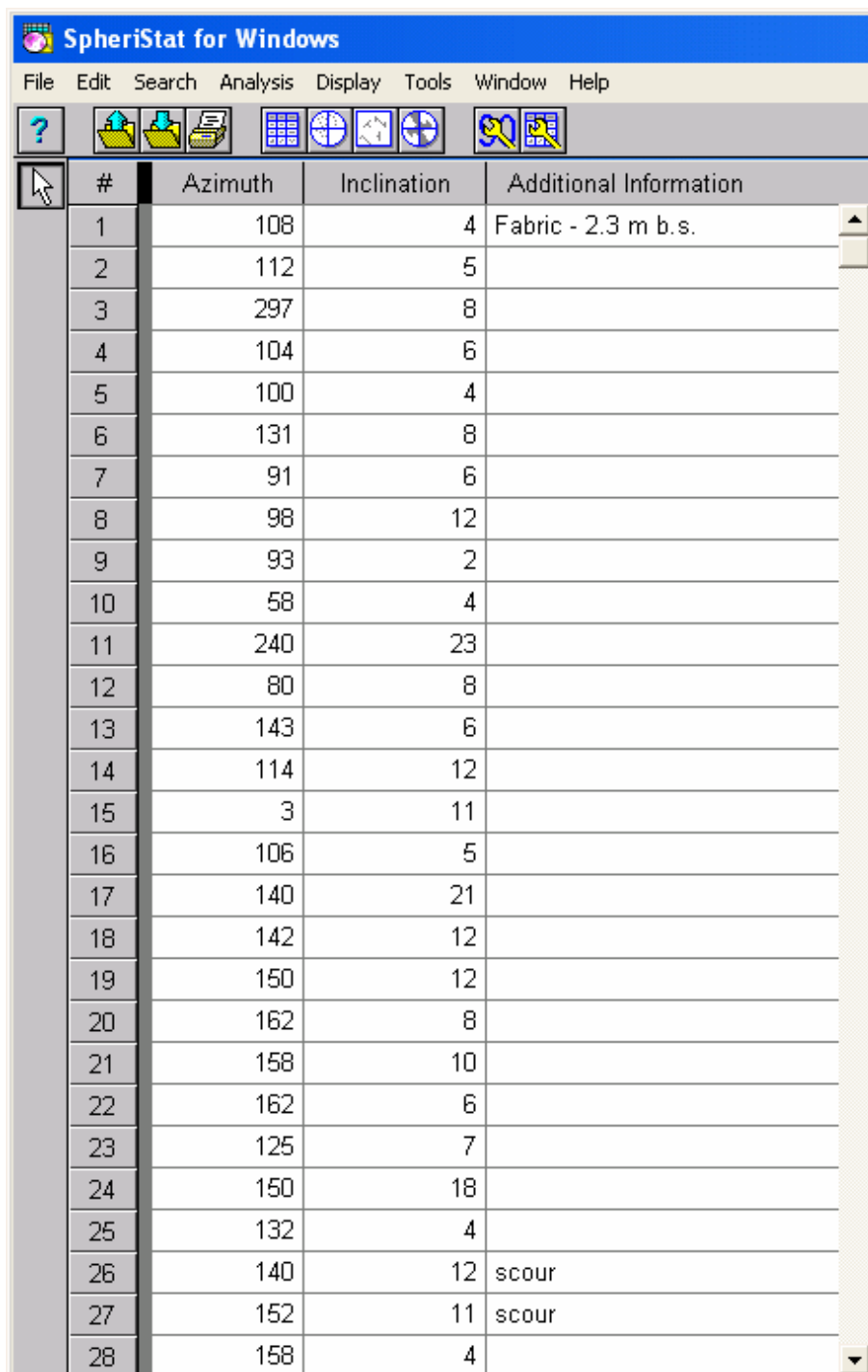


#	Azimuth	Inclination	Additional Information
1	80	3	Fabric - 1 m b.s.
2	292	8	
3	18	2	
4	120	12	
5	46	17	
6	132	6	
7	128	11	
8	43	70	
9	111	28	
10	86	62	
11	310	12	
12	54	48	
13	65	13	
14	57	13	
15	30	0	
16	118	6	
17	145	22	
18	90	10	
19	344	26	
20	163	12	
21	71	1	
22	13	12	
23	272	21	
24	73	18	
25	161	18	
26	84	3	

^{*} Azimuth is the direction of a horizontal line as measured on an imaginary horizontal circle (American Geological Institute, 1984).

[†] Inclination = deviation from vertical or horizontal (American Geological Institute, 1984).

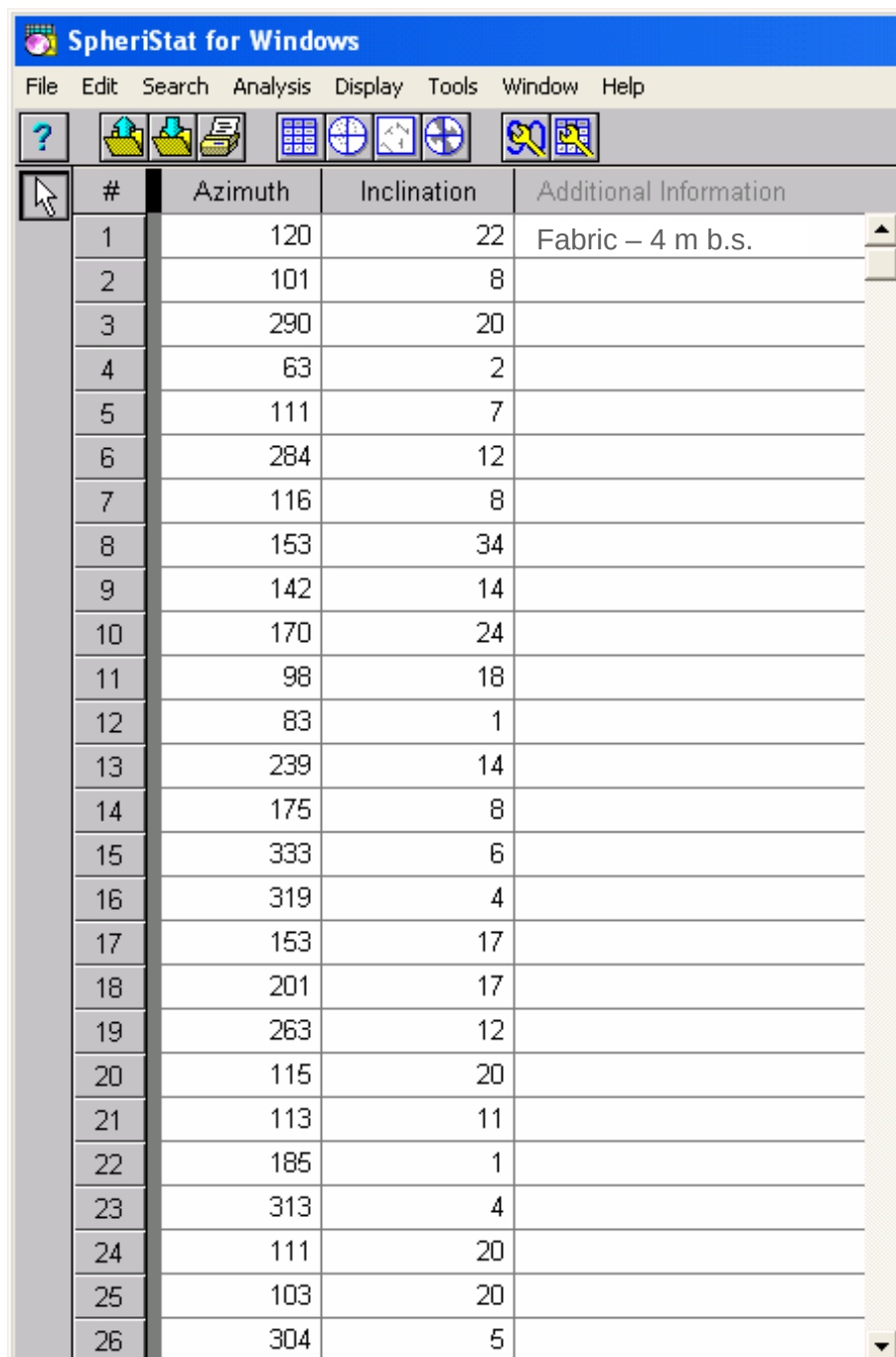
Table R.2: Fabric data - 2.3 m b.s. Scour marks from a few stones included.



The image shows a screenshot of the SpheriStat for Windows software interface. The window title is "SpheriStat for Windows". The menu bar includes File, Edit, Search, Analysis, Display, Tools, Window, and Help. Below the menu bar is a toolbar with various icons for file operations and data analysis. The main data area is a table with the following columns: #, Azimuth, Inclination, and Additional Information. The table contains 28 rows of data. The first row (1) has an Azimuth of 108, Inclination of 4, and Additional Information of "Fabric - 2.3 m b.s.". The last two rows (26 and 27) have "scour" in the Additional Information column.

#	Azimuth	Inclination	Additional Information
1	108	4	Fabric - 2.3 m b.s.
2	112	5	
3	297	8	
4	104	6	
5	100	4	
6	131	8	
7	91	6	
8	98	12	
9	93	2	
10	58	4	
11	240	23	
12	80	8	
13	143	6	
14	114	12	
15	3	11	
16	106	5	
17	140	21	
18	142	12	
19	150	12	
20	162	8	
21	158	10	
22	162	6	
23	125	7	
24	150	18	
25	132	4	
26	140	12	scour
27	152	11	scour
28	158	4	

Table R.3: Fabric data - 4 m b.s.



The screenshot shows the SpheriStat for Windows application window. The title bar reads "SpheriStat for Windows". The menu bar includes "File", "Edit", "Search", "Analysis", "Display", "Tools", "Window", and "Help". The toolbar contains icons for help, file operations, and data visualization. The main data table has four columns: "#", "Azimuth", "Inclination", and "Additional Information". The table contains 26 rows of data. The first row's "Additional Information" cell contains the text "Fabric - 4 m b.s.", which is also reflected in the table caption.

#	Azimuth	Inclination	Additional Information
1	120	22	Fabric - 4 m b.s.
2	101	8	
3	290	20	
4	63	2	
5	111	7	
6	284	12	
7	116	8	
8	153	34	
9	142	14	
10	170	24	
11	98	18	
12	83	1	
13	239	14	
14	175	8	
15	333	6	
16	319	4	
17	153	17	
18	201	17	
19	263	12	
20	115	20	
21	113	11	
22	185	1	
23	313	4	
24	111	20	
25	103	20	
26	304	5	

Table R.4: Strike and dip measurements of natural fractures – Profiles 1 (#1-28) and 3 (#29-38), 1 m b.s.

SpheriStat for Windows				
File Edit Search Analysis Display Tools Window Help				
?				
#	Azimuth	Inclination	Additional Information	
1	188	90W	Profile 1 and 3 - 1 m b.s.	
2	190	85W		
3	63	80SE		
4	159	90W		
5	183	90W		
6	130	90SW		
7	352	70E		
8	218	84NW		
9	6	88E		
10	196	74W		
11	191	70W		
12	2	80E		
13	200	88W		
14	356	72E		
15	209	77NW		
16	195	90W		
17	56	82SE		
18	348	82E		
19	270	83N		
20	163	88W		
21	346	78E		
22	231	88NW		
23	219	82NW		
24	347	86E		
25	210	73NW		
26	10	79E		
27	209	67NW		
28	261	87N		
29	0	83E		
30	254	88N		
31	50	72SE		
32	338	74E		
33	358	88E		
34	166	70W		
35	36	82SE		
36	57	83SE		
37	210	72NW		
38	359	88E		

Table R.5: Strike and dip measurements of natural fractures – Profile 2 (#1-29) and 4 (#30-40), 2.8 m b.s. The numbers given in the 'additional information' column represent the observed colours of the fractures: 1) grey (reduced), 2) ochre (iron precipitates), 3) black (manganese precipitates), and 4) grey-blue (CaCO_3 precipitate).

SpheriStat for Windows				
File Edit Search Analysis Display Tools Window Help				
#	Azimuth	Inclination	Additional Information	
1	122	58SW	Profile 2 and 4 - 2.8 m b.s. (1+4)	
2	163	80W	1+4	
3	227	86NW	2	
4	303	85NE	1+4	
5	98	14S	1+4	
6	71	71S	1+4	
7	342	70E	1+4	
8	53	66SE	1+4	
9	336	86NE	1+4	
10	110	8S	1+4	
11	328	81NE	1+4	
12	48	71SE	2	
13	324	70NE	1+4	
14	118	44SW	1+4	
15	105	90S	1+4	
16	343	83E	2	
17	68	69S	2	
18	235	11NW	1+4	
19	167	84W	1+4	
20	338	80E	1+4	
21	3	90E	1+4	
22	19	85E	2	
23	128	12SW	2	
24	345	81E	2	
25	346	80E	2	
26	85	75S	2	
27	354	77E	1+4	
28	352	77E	2	
29	223	90NW	1+4	
30	184	70W	1	
31	230	76NW	1	
32	212	90NW	1	
33	350	4E	1	
34	178	70W	1	
35	192	90W	1	
36	124	16SW	horizontal	
37	69	70S		
38	225	83NW		
39	184	80W		
40	342	82E		

APPENDIX S: THE EXCAVATION PROFILES

Figure S.1 depicts the main features observed from the profiles of the Vasby excavation. The survey rods are positioned with a distance of approximately 2 m. Each stripe (alternating red and white) on the rods is 20 cm.

Figure S.1: Photo of the main excavation profiles (Profile 1 & 2). Major fractures, CaCO_3 boundary, redox boundary, sand lenses, and large stones superimposed.



APPENDIX T: CONVERTING VERTICAL FRACTURE TRACE FREQUENCY TO SPACING

PROFILE 1 - 1 m b.s.

Fracture system*	Strike of profile	Avg. strike of fractures	Angle between strike of profile and fractures, a	Length of profile, l	# of 1 st order fractures, N_1	# of 2 nd order fractures, N_2	Total #, N_{tot}	Spacing of 1 st order fractures	Spacing of 2 nd order fractures	Total spacing	Frequency of 1 st order fractures	Frequency of 2 nd order fractures	Total frequency
2	126	74	52	6.5	9	2	10	0.58	6.8	0.52	1.7	0.1	1.9
3	126	89	37	6.5	19	2	21	0.21	2.6	0.19	4.8	0.4	5.4
										Cumulative spacing			
										0.14 m			
													7.3 per m

PROFILE 2 - 2.8 m b.s.

Fracture system*	Strike of profile	Avg. strike of fractures	Angle between strike of profile and fractures, a	Length of profile, l	# of 1 st order fractures, N_1	# of 2 nd order fractures, N_2	Total #, N_{tot}	Spacing of 1 st order fractures	Spacing of 2 nd order fractures	Total spacing	Frequency of 1 st order fractures	Frequency of 2 nd order fractures	Total frequency
2	120	64	56	4	6	3	9	0.57	1.2	0.37	1.8	0.0	2.7
3	120	165	45	4	15	2	16	0.19	3.8	0.18	5.3	0.3	5.6
										Cumulative spacing			
										0.12 m			
													8.3 per m

*System 2: Vertical shear fractures (perpendicular to ice movement direction, blue squares in figure)

*System 3: Vertical extension fractures (parallel to ice movement direction, green circles in figure)

(System 1: Horizontal shear fractures)

The formula used to calculate the spacings of the individual fracture systems is:

$$spacing = \sin\left(\frac{a \cdot \pi}{180}\right) \cdot \left(\frac{l}{N-1} + \frac{l}{2(N+1)}\right) \quad (T.1)$$

Frequency is subsequently calculated by: $frequency = \frac{1}{spacing}$

Finally, the cumulative spacing for both fracture systems is calculated via:

$$cumulative\ spacing = \frac{1}{cumulative\ frequency} = \frac{1}{freq2 + freq3}$$

In Profile 1, only a single 2nd order System 2 fracture was observed. Similarly, a single 2nd order System 3 fracture was observed in Profile 2. As EquationT.1 cannot calculate the spacing of 1 fracture, the spacing for 2 fractures was calculated instead and multiplied by 2 to obtain the correct spacing.

APPENDIX U: TRACER INVESTIGATIONS

U.1 Purpose

A qualitative investigation of tracer 'disappearance' rates and 'interference' was undertaken to evaluate which tracer(s) would be most persistent/visible, and thus most suitable for injection at the pneumatic fracturing site (Vasby), as they were to assist in verification of the pneumatic fracturing extent and induced fracture apertures via core sampling, water sampling, and excavation.

U.2 Introduction

Investigators from DTU (Technical University of Denmark) and NIRAS (an environmental consulting firm) involved with other aspects of the pneumatic fracturing project at the field site selected the fluorescent dye tracers uranine and rhodamine WT (here after referred to as rhodamine) to be injected immediately after the pneumatic fracturing of PF1. The purpose of the tracer injection was to mark the induced fractures, thereby facilitating visual identification in cores to be taken immediately after fracturing.

In an initial trial of the visibility of the two tracers, uranine and rhodamine were sparingly painted onto the surface of a fresh fracture and then observed immediately after with the naked eye and with UV lamps in a dark room. At concentrations of 100 mg/L and 1000 mg/L uranine was visible and clearly visible, respectively, as a bright green trace under a UV-lamp in a dark room. Uranine was not visible to the naked eye at these concentrations. Rhodamine at concentrations of 100 mg/L and 1000 mg/L respectively, was visible as a dark-orange trace under UV-lamps in a dark room. At concentrations of 1000 mg/L rhodamine was visible with the naked eye as a pale magenta-pink trace. When the samples were investigated a week later, no tracer was visible with the naked eye or UV lamps. It was uncertain whether this was due to light-sensitive degradation of the tracers, other degradation processes or diffusion into the soil matrix.

The results of tracer trials raised a number of concerns regarding the tracer visibility in the proposed excavation. Firstly, it was uncertain whether the tracer concentrations would be high enough at the excavation location (about 5 m from PF1) to be visible. Secondly, the use of a UV-lamp in the field was deemed cumbersome, especially if darkroom conditions would be required to see the fractures. Thirdly, there was a concern that the induced fractures might not be 'captured' during the fracture characterisation process if the rate of light-sensitive degradation was rapid relative to the timelag between excavation and completion of the laboratory fracture characterisation. Finally, the excavation was planned to take place about a week after the fracturing was completed. This raised concerns regarding how quickly the tracers would degrade and/or diffuse into the clay till matrix

resulting in visually undetectable tracer concentrations along the fractures. Therefore, a qualitative investigation of the 'disappearance' rates of the previously tested tracers and two others was undertaken. 'Interference' among the tracers resulting in lack of visual detection was also investigated.

U.3 Method

Four tracers were investigated, uranine, rhodamine, optical white, and brilliant blue (a food colouring, E-133). The latter was selected because the authors learned it has been used successfully as a tracer at till (Markesic, 2000) and other sites (predominately loam and sand) (Forrer et al., 1999; Germán-Heins and Flury, 1999; Ketelsen and Meyer-Windel, 1999; Forrer et al., 2000; Kasteel et al., 2002) and has been reported visible to the naked eye (except in extremely dark soil) after 90 days (Kasteel et al., 2005).

U.3.1 Investigation of tracer visibility and potential interference in water samples

Investigation of visibility in water

The following standard solutions were observed visually under 1) daylight conditions, and 2) under an UV-lamp, and photographed to investigate the visibility of the tracer in water samples:

- 1) Uranine, 1000 mg/L
- 2) Rhodamine WT, 1000 mg/L
- 3) Optical white, 1000 mg/L
- 4) Mixture of uranine and rhodamine in which both have resulting concentrations of 1000 mg/L (U+R)
- 5) Mixture of uranine, rhodamine WT, and optical white, all at resulting concentrations of 1000 mg/L (U+R+W)
- 6) Mixture of uranine, rhodamine WT, optical white, and brilliant blue, all at resulting concentrations of 1000 mg/L (U+R+W+B).
- 7) Brilliant blue, 1000 mg/L.

Investigation of potential interference in water via fluorometer measurements

An investigation of potential interference by brilliant blue on uranine and rhodamine detection in a GGUN-FL Fluorometer was investigated. Since the fluorometer is sensitive to solution turbidity (fine suspended matter), there was concern that the brilliant blue at high concentrations could cause interference in the tracer detection.

The following solutions (all 100 ppb (0.1 mg/L)) were tested in the fluorometer, and the concentration of uranine and rhodamine was observed: uranine; rhodamine; U+R; U+R+W; U+R+W+B. If brilliant blue has no effect, measured concentrations of uranine and rhodamine would be expected to be similar to the concentrations measured in the pure solutions. A previous test of U+R and

U+R+W indicated little interference between these tracers. At the time of the experiment, the tracer injection concentration (to be applied at the fracturing site) was yet unknown, but the concentration of 0.1 mg/L was selected as it is within the detection range of the fluorometer.

U.3.2 Investigation of tracer visibility and potential interference on soil

Investigation of potential interference on soil

The investigation was performed on four, 20-cm core samples from Havdrup from unknown depths. The cores had been stored for about 3 years at 10° C in stainless steel tubes which were capped and sealed with tape. Some of the cores had a crumbly texture, perhaps due to moisture loss.

The core material is described as a clay till (*moræneler*). Based on a hand analysis of the soil (also called field texture analysis, see *Appendix Q: Soil survey method and description of cores KF0-KF3*) the soil is described as a very fine sandy, silty clay with occasional small stones.

Each core cylinder was cut into approximately 5 slices, creating 5 cylinders with a thickness of about 2 cm. Each cylinder was then cut in half (Figure U.1a) and a ‘fracture’ was created by gently breaking each half-cylinder in two. A total of 30 fracture samples were made. The required number of samples is determined by the number of tracers/tracer mixtures to be tested (6, see below) multiplied by the selected number of hours elapsed (1, 6, 26, 48 and 72 hours) between each test.



Figure U.1: (a) cutting the 2-cm thick cylinders in half; (b) painting rhodamine tracer on one fracture-face of the induced fracture.

One face of each fracture was painted with a single tracer or one tracer mixture (Figure U.1b). The tracer was applied (using a dedicated paint brush) until the entire fracture surface was coloured by the tracer (or, in the case of optical white, the fracture-face appeared moist). Attempts were made to apply a similar amount of tracer to each fracture. The fracture was then closed by gently pressing the adjoining fracture sides together.

Each of the following tracers or mixtures was applied to 5 fracture samples each:

- 1) Uranine, 1000 mg/L

- 2) Rhodamine WT, 1000 mg/L
- 3) Optical white, 1000 mg/L
- 4) Mixture of uranine and rhodamine in which both have resulting concentrations of 1000 mg/L (U+R)
- 5) Mixture of uranine, rhodamine WT, and optical white, all at resulting concentrations of 1000 mg/L (U+R+W)
- 6) Mixture of uranine, rhodamine WT, optical white, and brilliant blue, all at concentrations of 1000 mg/L (U+R+W+B).

The fracture samples were wrapped in aluminium foil and stored in sealed plastic bags. The samples were divided into five groups so that one of each tracer/tracer mixture was represented in each group to be inspected: 1, 6, 24, 48 and 72 hours after painting. The six samples for each time were stored in designated plastic bag at room temperature.

After the designated amount of time had elapsed, the plastic bag and aluminium foil was removed from the sample. A hobby knife was used to cut a slice perpendicular to the fracture-face (the dashed line in Figure U.2), thereby exposing the tracer-painted fracture on both halves of the sample.

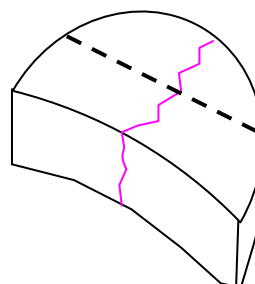


Figure U.2: The induced fracture has been painted with rhodamine and closed by pressing adjacent sides of the fracture together. For visual inspection the sample was cut open (along the dashed line) to expose the fracture. The 'inside' faces of the cut were examined visually under daylight and UV conditions.

The knife was wiped clean on paper towel, rinsed with water, and dried with paper towel between each sample to prevent cross-contamination. There was no evidence of fluorescent tracer on the knife under the UV-lamp after this cleaning procedure. The visibility of the tracer/tracer mixture was assessed visually under daylight conditions and using a UV-lamp. The samples were photographed under a UV-lamp alone (camera setting: 30 sec., *fstop* 10), and under an UV-lamp and photographer's lamp which is referred to as daylight conditions (camera setting: 0.5 sec., *fstop* 29).

Investigation of visible brilliant blue concentrations

Standard solutions of brilliant blue at concentrations of 10,000 mg/L, 5000 mg/L and 1000 mg/L were painted on core samples to determine qualitatively which concentrations would be suitable for

brilliant blue tracer injection.

Investigation of high brilliant blue concentration influence on uranine & rhodamine visibility

Brilliant blue (10,000 mg/L) was painted onto a fracture face followed by a uranine and rhodamine mixture (both compounds present at concentrations of 1000 mg/L). The fracture was pressed closed, opened, and observed under UV and daylight conditions.

U.4 Results

U.4.1 Results of tracer visibility and potential interference in water samples

Visibility in water

Figure U.3 depicts the tracers/tracer mixtures under daylight conditions. With the exception of optical white, all the tracers are visible in water samples under daylight conditions. The mixture U+R+W+B is so dark in colour that it appears opaque.

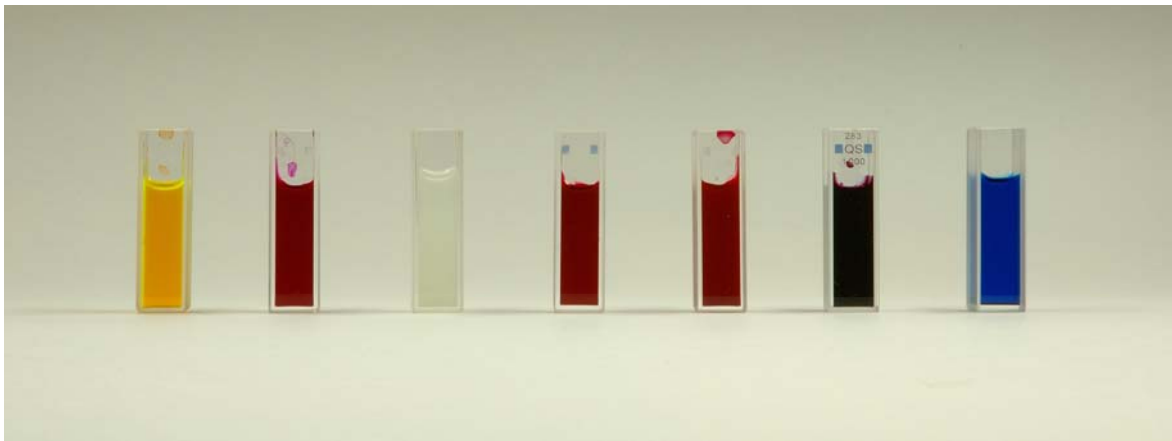


Figure U.3: Tracers under daylight conditions. Concentrations of all tracers are 1000 mg/L. From left to right the tracers are uranine; rhodamine; optical white; uranine+rhodamine; uranine+rhodamine+optical white; uranine+rhodamine+optical white+brilliant blue; brilliant blue.

Figure U.4 depicts the tracers under UV conditions. The fluorescence of the tracers in their pure form is satisfactory. The fluorescence of the U+R and U+R+W mixtures is visible, although not as strong as when the tracers are in their pure solutions (unmixed). The fluorescence of U+R+W+B is poor. The mixture is a muddy dark-green colour under the UV-lamp. Brilliant blue is not fluorescent and thus appears dark under the UV-lamp.

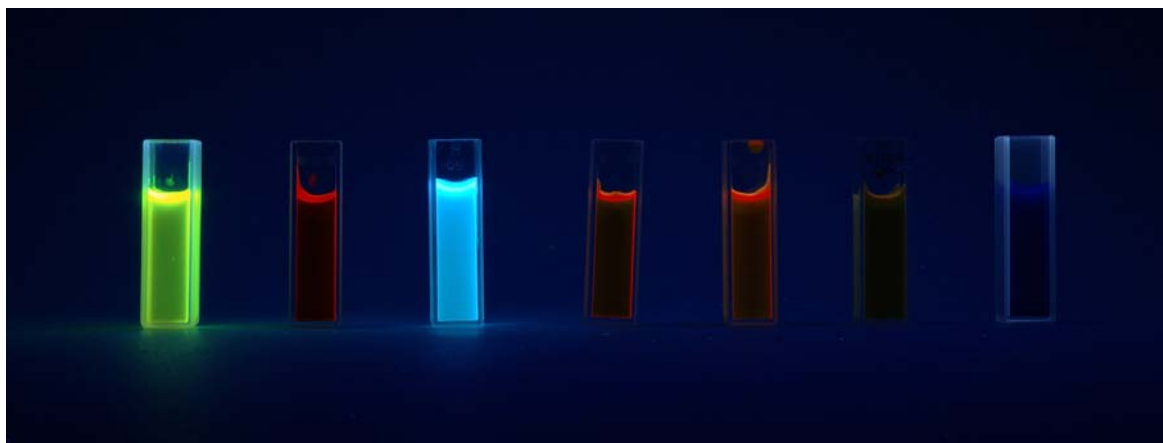


Figure U.4: depicts the tracers under UV conditions. Concentrations of all tracers are 1000 mg/L. From left to right the tracers are uranine; rhodamine; optical white; uranine+rhodamine; uranine+rhodamine+optical white; uranine+rhodamine+optical white+brilliant blue; brilliant blue.

Interference in water determined via fluorometer measurements

Results from the fluorometer tests may be seen in *Appendix Y: Electronic data, Fluorometer tests*. The methods used to calculate uranine and rhodamine concentrations in the tested water samples may be seen at the end of the document. No significant interference was seen between the tracers when mixed, except perhaps in the U+R+W sample. As no interference was seen in the U+R+W+B sample, however, the lower concentrations of uranine and rhodamine measured in the U+R+W sample are assumed to reflect poor precision in the manufacture of the sample.

The brilliant blue solution is seen to contain trace amounts of uranine and rhodamine, but these are considered negligible.

U.4.2 Results of tracer visibility on soil

The photographic results of the investigation are found at the end of the document. Note that it was difficult to ensure completely equal quantities tracer applied to the cores. Thus some of the variation in colour/fluorescence intensity may be due to variation in tracer mass applied. Also, aluminium foil was stuck to the end of some cores and appears as a sharply coloured area in some of the UV photographs.

Uranine

Uranine was not, at the applied concentration, visible under daylight conditions at any time. Under UV conditions, uranine was visible until the end of 72 hours. Between 0 and 24 hours the green colour became more diffuse. At 48 hours and 72 hours there was a noticeable decrease in the visibility of uranine in the fracture.

Rhodamine

Rhodamine was visible, as a pale magenta line, under daylight conditions until the end of the experiment. The visibility of rhodamine under UV conditions was similar to that observed for uranine. From 0 to 24 hours the orange colour became more diffuse. After 24 hours there was a noticeable decrease in the visibility of rhodamine in the fracture.

Optical White

The photographic documentation reveals that optical white is not visible under daylight or UV conditions at a concentration of 1000 mg/L. The apparent fluorescence of optical white at 72 hours under UV conditions was due to the presence of chalk in the sediment.

Uranine + Rhodamine

The uranine+rhodamine mixture was visible until the end of the experiment as a pale magenta line. Under UV conditions the green uranine colour dominated, although in the 24-hour photograph an orange rhodamine trace is visible at the edge of the green area. The effect of time on visibility was similar to that observed for the tracers alone: the colour becomes more diffuse and is clearly less intense after 24 hours. The intensity of the green colour at 72 hours may be due to more tracer being applied, as discussed previously.

Uranine + Rhodamine + optical white

Under daylight conditions the rhodamine colour dominated, and a pale magenta trace was visible over time. Under UV conditions uranine dominated the fluorescence. The intensity of the fluorescence with time is similar to that observed for uranine alone. Optical white appears to have no effect on uranine and rhodamine fluorescence.

Uranine + Rhodamine + optical white + brilliant blue

Under daylight conditions a weak purplish trace (a combination of rhodamine and brilliant blue colours) was visible until the end of the experiment. Although the trace was not always visible in the sample slices that were photographed, the colour was visible on the fracture face when the samples were gently opened along the fracture. Brilliant blue does not appear to have affected the fluorescence of uranine or rhodamine, as the U+R+W+B photographs for each time are similar to the corresponding U+R photographs.

Results of investigation of visibility of brilliant blue concentrations

The results of the investigation of brilliant blue visibility are found at the end of the document. Based on a visual inspection of the cores, quite high concentrations of brilliant blue are required for visibility. The aqueous sample of unknown concentration is a sample of brilliant blue in propylenglycol, a food colouring bought at Matas (*bolche farve*). The food colouring sample is readily soluble and available pre-mixed in large volumes.

Results of investigation of high brilliant blue concentrations on uranine and rhodamine

The results of the investigation of potential interference of high brilliant blue concentrations on uranine and rhodamine visibility fluorescence are found in the document BB evaluation. Under daylight conditions both brilliant blue (10,000 mg/L) and rhodamine (1000 mg/L) was clearly visible. Under UV conditions the brilliant blue had no apparent effect on uranine fluorescence.

U.5 Conclusions

Uranine and rhodamine either in pure solutions or mixtures diffused into the matrix and became less intense under UV-light over time. After 24 hours the intensity of the tracers was noticeably diminished. After 48 hours, the tracer becomes difficult to distinguish. Uranine's green colour dominated under UV conditions and thus was the most suitable tracer for UV applications.

Under daylight conditions, only rhodamine (and brilliant blue) was visible. The intensity of colour did not appear to change significantly over 72 hours.

Optical white was not visible under daylight or UV conditions at any time.

Brilliant blue did not appear to interfere with detection of uranine or rhodamine fluorescence, even at high concentrations.

For the proposed excavation, brilliant blue (injected at a concentration of >10,000 mg/L) appears to be the most visible and thus most suitable tracer.

For the proposed core sampling (to be viewed under UV-light), uranine (and rhodamine) appears to be the most visible and thus most suitable tracer.

Injecting a mixture of the tracers to ensure fracture visibility in both the excavation and core samples is not deemed problematic, as the results above indicate no significant tracer interference in either water or soil.

SEPARATION OF TWO TRACERS

The GGUN-FL Fluorometer contains two sets of optics that can be set to measure the presence of two different fluorescents in a solution. The fluorometer evaluates the amounts present via voltage measurements (measurements dubbed L1C1 for tracer 1 and L2C2 for tracer 2). In this case, the fluorescents of interest are uranine and rhodamine WT, and the fluorometer is programmed with their stats by first running a standard solution of uranine and a standard solution of rhodamine WT and storing the data obtained. Furthermore, data from a “standard” tap water sample are stored. The optics that measure the presence (voltage) of one fluorescent tracer are sensitive to the presence (voltage) of the other tracer. I.e. the optics that are set to measure uranine presence are sensitive to rhodamine WT presence and vice versa. The fluorometer therefore uses the formulas stated below to distinguish between the voltages given off by the two tracers in a solution.

$$C_{Uranine} = \frac{C_{22} \cdot X_1 - C_{12} \cdot X_2}{C_{11} \cdot C_{22} - C_{12} \cdot C_{21}} \text{ and } C_{RWT} = \frac{C_{11} \cdot X_2 - C_{21} \cdot X_1}{C_{11} \cdot C_{22} - C_{12} \cdot C_{21}} \text{ (Schnegg and Doerfliger, 1997)}$$

where

C11 = the L1C1 signal for a 0.1 mg/L uranine standard minus the L1C1 signal for tap water

C12 = the L1C1 signal for a 0.1 mg/L rhodamine WT standard minus the L1C1 signal for tap water

C21 = the L2C2 signal for a 0.1 mg/L uranine standard minus the L2C2 signal for tap water

C22 = the L2C2 signal for a 0.1 mg/L rhodamine WT standard minus the L2C2 signal for tap water

X1 = the L1C1 signal for the sample undergoing analysis minus the L1C1 signal for tap water

X2 = the L2C2 signal for the sample undergoing analysis minus the L2C2 signal for tap water

All signals are given in mV, and the resulting concentration is in 0.1 mg/L Uranine and 0.1 mg/L Rhodamine WT units respectively.

The formulas are only valid for the linear parts of the tracers' standard curves.

TRACER COLOURATION OF CORES IN DAYLIGHT

See following pages

**COMPOUND /
MIXTURE**

Daylight inspection –
0 HRS

Daylight inspection –
6 HRS

Daylight inspection –
24 HRS

Daylight inspection –
48 HRS

Daylight inspection –
72 HRS

Uranine



No picture taken: not
visible (see 0 hrs)

No picture taken: not
visible (see 0 hrs)

No picture taken: not
visible (see 0 hrs)

No picture taken: not visible
(see 0 hrs)

Rhodamine WT



Optical White



No picture taken: not
visible (see 0 hrs)

No picture taken: not
visible (see 0 hrs)



Not visible - iron discoloration

No picture taken: not visible
(see 0 hrs)

**COMPOUND /
MIXTURE**

Daylight inspection –
0 hrs

Daylight inspection –
6 hrs

Daylight inspection –
24 hrs

Daylight inspection –
48 hrs

Daylight inspection –
72 hrs

*Uranine +
Rhodamine WT*



Slightly visible: pinkish-purple line

No picture taken:
slightly visible (see 0
hrs)

No picture taken:
slightly visible (see 0
hrs)



Slightly visible - iron discoloration



*Uranine +
Rhodamine WT
+ Optical White*



Slightly visible: pinkish-purple line

No picture taken:
slightly visible (see 0
hrs)

No picture taken:
slightly visible (see 0
hrs)

No picture taken:
slightly visible (see 0
hrs)



*Uranine +
Rhodamine WT
+ Optical White
+ Brilliant Blue*



Slightly visible: bluish-purple line



TRACER FLUORESCENCE

See following pages

COMPOUND /
MIXTURE

0 HRS

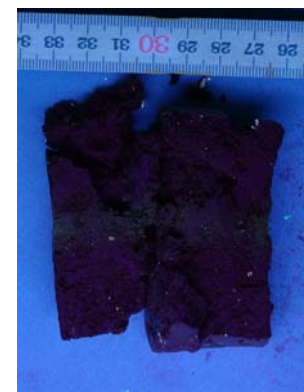
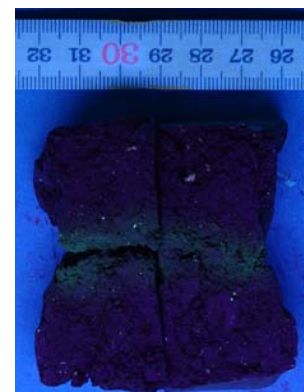
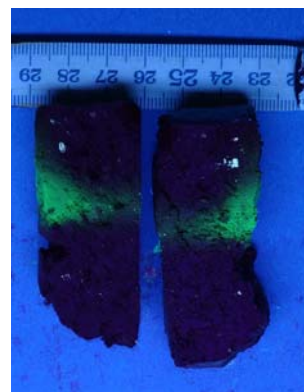
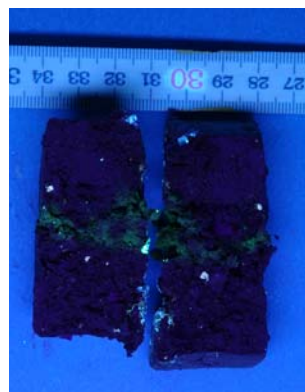
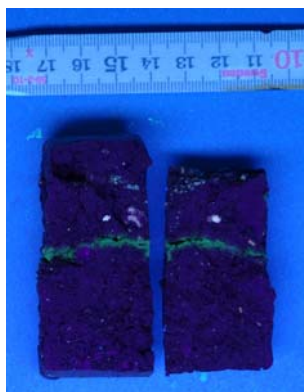
6 HRS

24 HRS

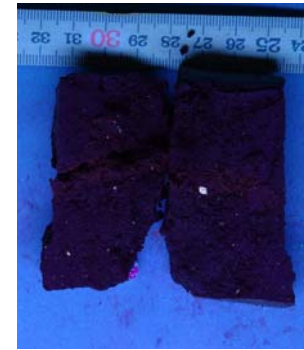
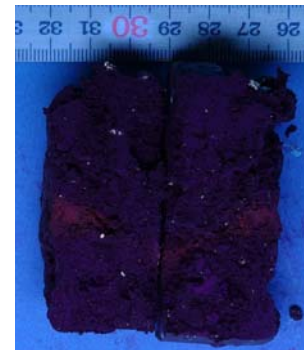
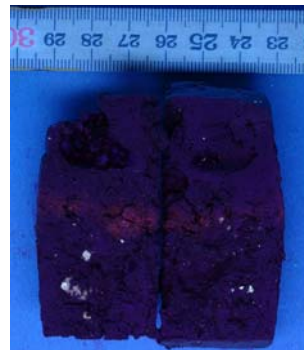
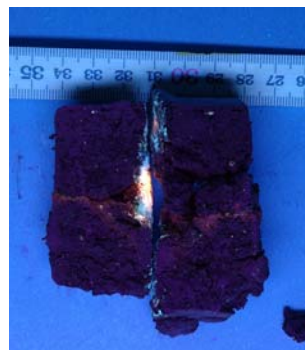
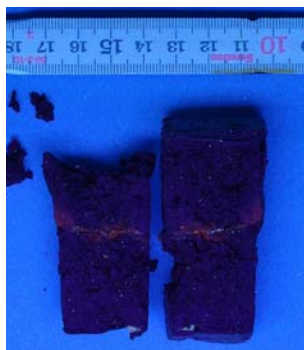
48 HRS

72 HRS

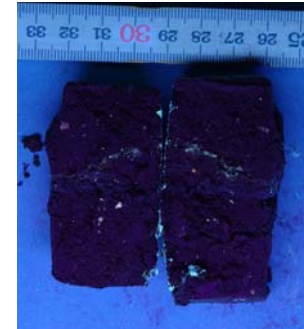
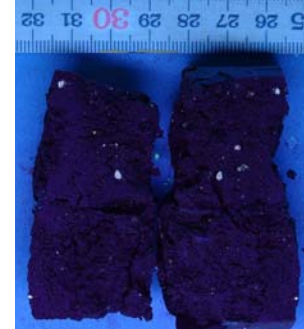
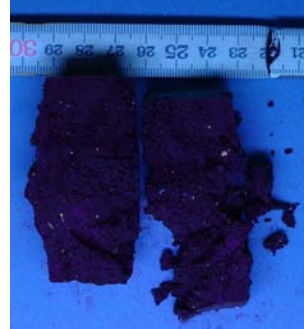
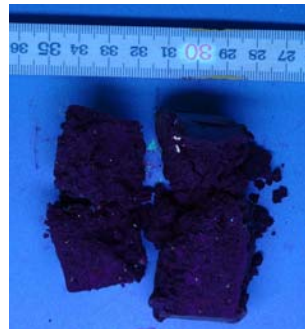
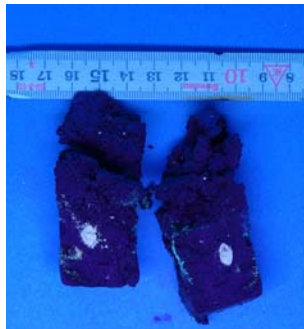
Uranine



Rhodamine WT



Optical White



**COMPOUND /
MIXTURE**

0 hrs

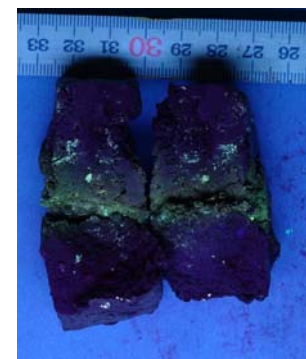
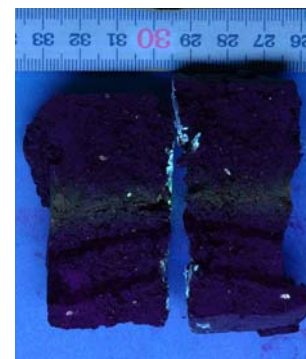
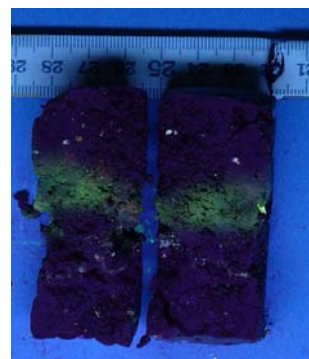
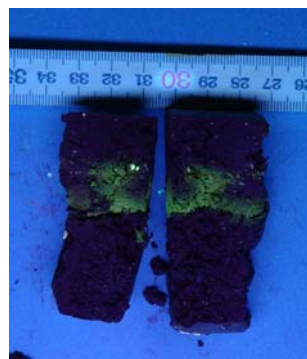
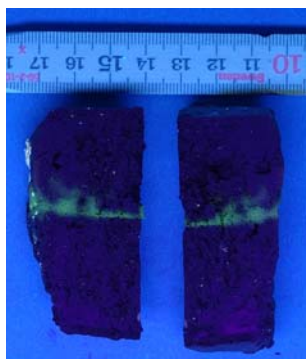
6 hrs

24 hrs

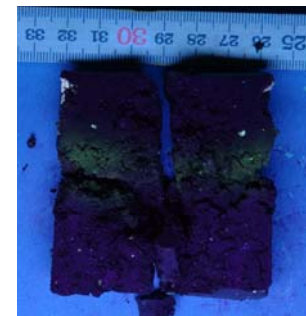
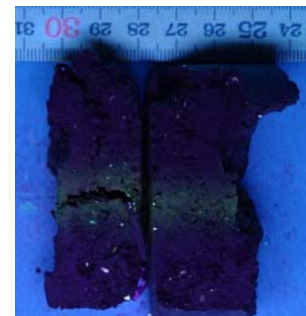
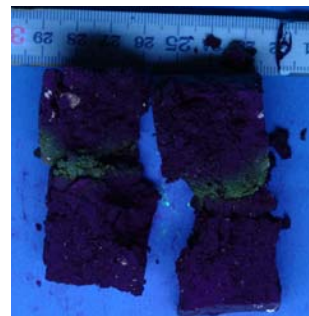
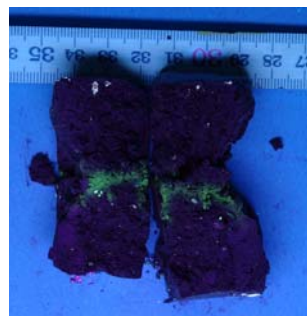
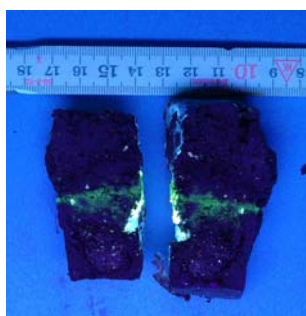
48 hrs

72 hrs

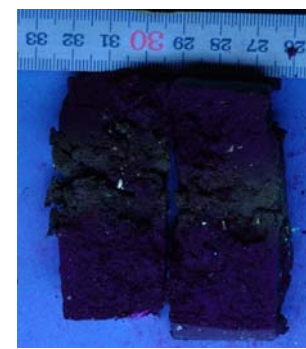
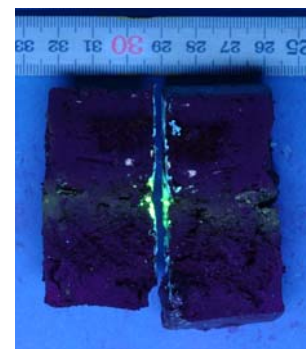
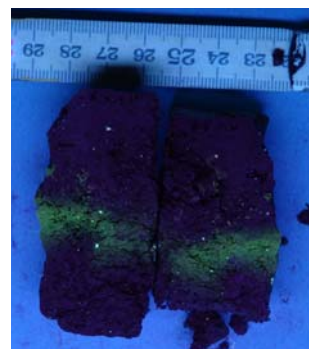
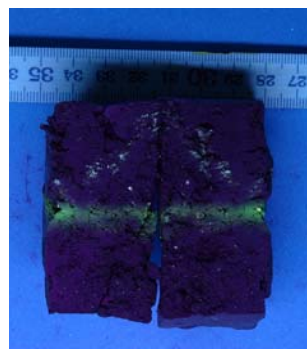
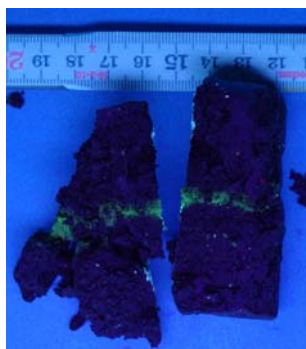
*Uranine +
Rhodamine WT*



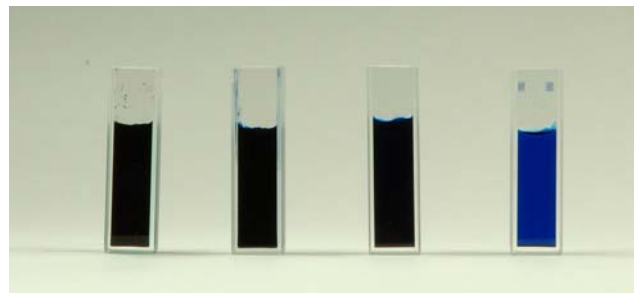
*Uranine +
Rhodamine WT
+ Optical White*



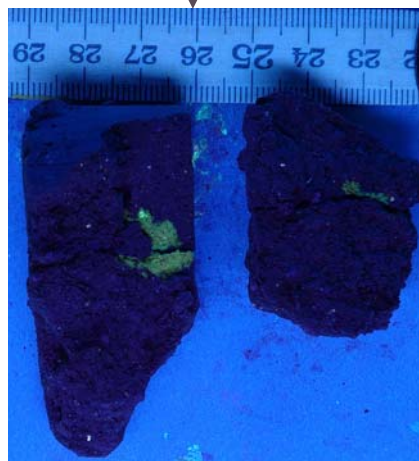
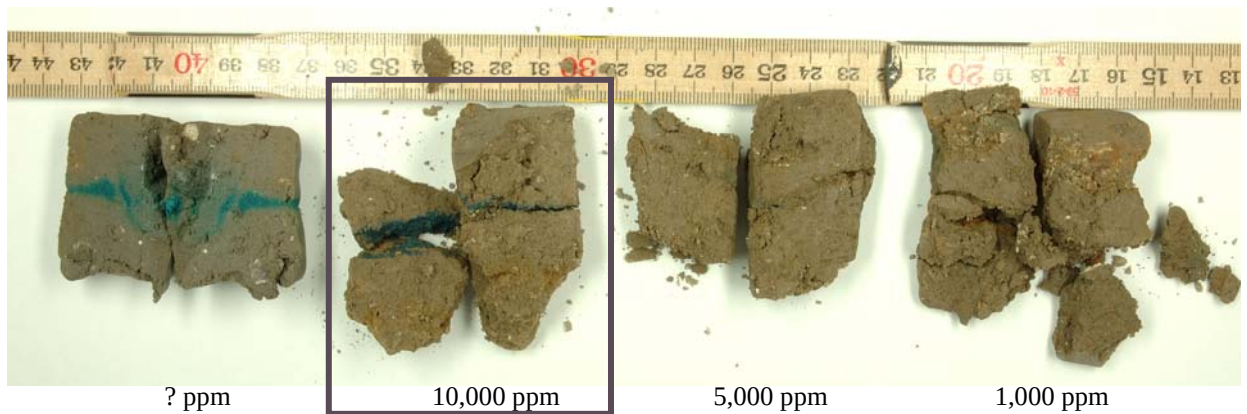
*Uranine +
Rhodamine WT
+ Optical White
+ Brilliant Blue*



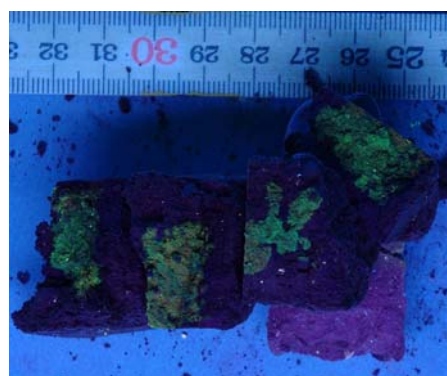
EVALUATION OF BRILLIANT BLUE INTERFERENCE WITH URANINE AND RHODAMINE FLUORESCENCE



BB: ? ppm 10,000 ppm 5,000 ppm 1,000 ppm



1,000 ppm Uranine &
Rhodamine WT mixture
added to 'fracture' already
brushed with 10,000 ppm
BB core



Core opened to reveal 'fracture' surface – no shading of uranine and rhodamine WT fluorescence by BB

APPENDIX V: LABORATORY INVESTIGATION OF FLUORESCENT TRACERS IN CORES KF0-KF3

Four cores were taken from the Vadsby site in December 2005, KF0 - KF3. The cores were taken with a geoprobe over the depth interval 2-8 m b.s. (KF3: 3-10 m b.s.) and thus consisted of 6 (or 7) ~1 m-sections, from which induced fractures were to be identified via the fluorescent tracers. Soil samples were to be taken from the cores to measure concentrations of the fluorescent dye tracers and bromide. Thus the lab work required to adequately describe and analyse the cores was comprehensive and time-consuming. The authors formed half of the 4-person team that worked with the first three cores, KF0 – KF2. The authors also characterised the fourth core, KF3, geologically.

Research Assistant Stine Brok Christensen was responsible for the lab work. Københavns Amt (2006) contains results obtained from all cores taken at the Vadsby site.

V.1 KF0

KF0 was a control core taken prior to the fracturing of the Vadsby site. The lab procedure for handling the core was thus:

1. The core (all 6 sections) was cut through, as shown in Figure V.1 below.



Figure V.1: Cutting the cores in half (lengthwise).

2. **Visual inspection.** One half of the core was then photographed under
 - a. simulated daylight conditions, and
 - b. UV-light. See Figure V.2.

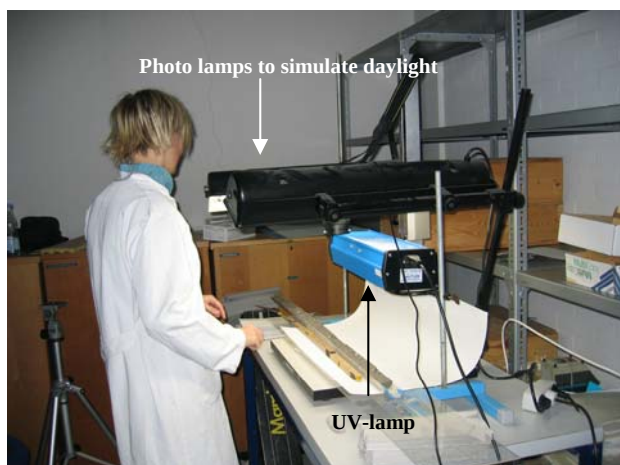


Figure V.2: The photography setup.



Figure V.3: Geological description of core.

3. **Geological description.** The same half of the core subsequently underwent geological description, see Figure V.3 and *Appendix Q: Soil survey method and description of cores KF0-KF3*.
4. **Sampling.** The other half of the core was (during (2) and (3)) covered with aluminum foil and stored in a dark room at 10°C until the team was ready to sample it. 2 x 5 samples of core sediment were taken per meter core.
 - a. *Fluorescence sampling.* 5 samples each weighing 0.1-0.5 g were taken per meter with the specially-made sampling apparatus shown in Figure V.4. The samples were transferred to medicine glasses containing 20 mL of BORAX, again see Figure V.4, which were weighed before and after sample addition (without resetting to zero between the first and second weighing) to ensure accurate weight notation of the samples. The sample glasses were then shaken until the samples were completely dissolved and thus ready to undergo filtration and analysis in the fluorometer* for presence of fluorescents (Uranine and Rhodamine WT).



Figure V.4: (a) Fluorescence sampling. (b) Transferring the sample to a medicine glass. (b) Weighing the sample.

* Also used in preparatory lab work discussed in *Appendix U: Tracer investigations*.

- b. *Bromide sampling.* At the same sampling positions, samples of approximately 2 cm³ were then taken and transferred to Pyrex tubes containing 5 mL of IC[†]-eluent, see Figure V.5. These were likewise shaken to ensure complete dissolution. Later, the samples were filtrated and analysed for bromide-content.



Figure V.5: Bromide sampling.

V.2 KF1 and KF2

The cores KF1 and KF2 were taken shortly after fracturing was completed at the Vasby site (the same day and the day after, respectively), while KF3 was retrieved 2 days after. Their locations are shown in Figure 6.1. Previous lab work conducted by the authors (see *Appendix U: Tracer investigations*) had shown that it was important to analyse the cores within 48 hours of the fracturing, as the fluorescence of a tracer mixture with resultant concentrations of 1000 mg/L of all (fluorescent) components faded markedly after this time period.

The lab procedure for the analysis of KF1, KF2, and KF3 was largely the same as for KF0. The authors participated in all aspects of analysis (Steps 1-4) of KF1, Steps 1-3 for KF2, and only Step 3 for KF3.

1. 1 section of core was cut through, as shown in Figure V.1 above.
2. *Visual inspection.* One half of the core section was then photographed alongside the corresponding section of KF0 under
 - a. simulated daylight conditions, and
 - b. UV-light. See Figure V.6.

[†] IC = ion chromatograph

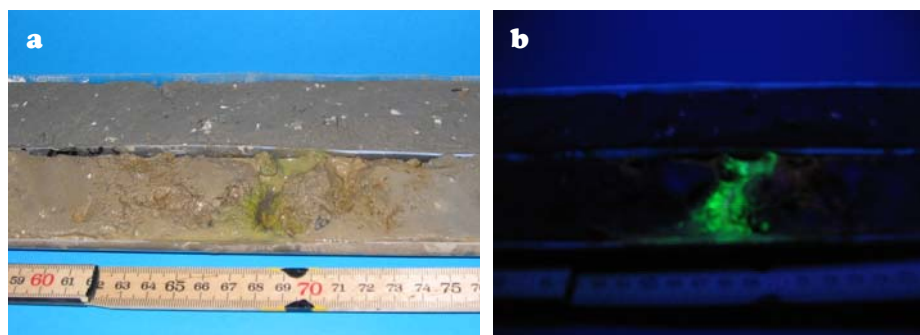


Figure V.6: (a) Photo of induced fracture under daylight conditions. (b) Photo of induced fracture under UV-light.

Special care was taken to centralise and focus the fractured/fluorescent areas during photography.

3. *Geological description.* The same half of the core section subsequently underwent geological description, see Figure V.3 and *Appendix Q: Soil survey method and description of cores KF0-KF3.*
4. (1)-(3) were repeated until all six sections of a core were visually inspected and geologically described.
5. *Sampling.* Three sampling areas were (based on the visual/geological inspection) chosen for KF1:
 - a. one area in the 4-5 m b.s. core section, and
 - b. two areas in 5-6 m b.s. core section (one near the top and one near the bottom).

Again, sampling was carried out in the other half of the core sections, which had (during (2) and (3)) been covered in aluminum foil and stored in a dark room at 10°C. In each sampling area, ~1 sample set per 0.5 cm of core sediment was taken in the directly fractured area and surrounding diffusion area, while ~1 sample set per 2 cm was taken in the apparently unaffected adjacent areas. Every sample set was again to be used in fluorescence and bromide analysis, as described above.

APPENDIX W: SELECTED OBSERVATIONS FROM THE PNEUMATIC FRACTURING PILOT STUDY AT VASBY

W.1 Uplift data

The following uplift data was recorded during the pneumatic fracturing. *Start* refers to start elevation prior to fracturing. *Max* refers to the max elevation observed during injection of gas. *Residual* refers to the elevation measured after gas injection ceased. *Tracer* refers to maximum elevation observed during injection of tracer. *Residual 2* refers to the residual after injection of tracer ceased. *After ½ hour* refers to elevation measurements taken a ½ hour after tracer injection at the 6-7 m b.s. fracturing interval.

Table W.1: Uplift data measured at PT2 (about 3 m from PF1 on a line towards T1)

Uplift	7-8m	6-7m	5-6m	4-5m	3-4m
start	34.55	34.90	34.80	34.80	34.80
max		35.20	34.85	34.90	34.90
residual	34.90	34.95	34.80	34.85	34.80
tracer	35.25	35.30	34.90		
Residual 2	34.95	35.10	34.85		
after ½ hr		35.00			

width of fractures 0,25

Table W.2: Uplift data measured at PT3 (about 3 m from PF1 on a line towards T4)

Uplift	7-8m	6-7m	5-6m	4-5m	3-4m
start	34.9	35.10	35.10	35.20	
max	35.3	35.35	35.30	35.30	
residual	35.00	35.10	35.10	35.20	
tracer	35.30	35.40	35.35		
Residual 2	35.10	35.20	35.20		
after ½ hr		35.15			

width of fracture: > 0,3

W.2 Rules-of-thumb

A number of rules-of-thumb or general practices were mentioned in the literature. These are presented in Table W.3 along with observations from the pneumatic fracturing as the Vasby site.

Table W.3: Comparison of rules-of-thumb and typical values mentioned in the literature vs. characteristics of fractures induced at the Vasby site, Hedehusene.

Characteristic	Rule-of-thumb	Typical literature values	Fracture 7-8 m b.s.	Fracture 6-7 m b.s.	Fracture 5-6 m b.s.	Fracture 4-5 m b.s.	Fracture 3-4 m b.s.
Aperture (2b)	Estimated from uplift: When depth < 5m, then 2b $\approx$ amount of residual uplift (EPA, 1994)	0.5 – 1 mm (Suthersan, 1999; Nilsson et al., 2000)	Assuming about 1 fracture per fracturing interval and a total uplift of about 7 mm gives an average fracture aperture of 1.4 mm. Based on visual observation of cores, open induced fractures with apertures of 0.1 to 0.7 mm were observed. Zones/strips of tracer ranged in width from a few mm to 10-20 mm wide. From the excavation aperture varied from tenths of mm to a few cm.				
Uplift (residual)	About 10-20% of initial uplift (Suthersan, 1999) Depth > 6 m then $\approx$ no uplift (Schuring, 2002) Dense soils = less uplift (Schuring, 2002)	Depth < 6 m uplift $\approx$ aperture values from literature Depth > 6 m $\approx$ no uplift	*Near T1: 1.0 cm (0.4 in) Near T4: 0.5 cm (0.2 in)	*Near T1: 0.3 cm (0.1 in) Near T4: 0.1 cm (0.05 in)	*Near T1: 0.1cm (0.05 in) Near T4: 0.3 cm (0.1 in)	*Near T1: 0.1 cm (0.05 in) Near T4: 0	*Near T1: 0 Near T4: n.a.
Fracture length (maximum) (also called max. diameter of fracture zone)	When depth = 1,5 - 5 m b.s., then depth to fracture length ratio = 1:3 to 1.4 (EPA, 1994; Walsted et al., 2002). Maximum diameter increases with depth (EPA, 1994) vs. depth > 5 m b.s., then depth to length ratio < 1:3 Nilsson et al., 2000)	5 to 12 m, avg = 8,5 m long (Nilsson et al., 2000) max length to depth= 1:3 to 1:4 (EPA, 1994)	Maximum fracture length (diameter) was about 9.5 m observed at about 5 m b.s. based on field observations and evidence of tracer. The field monitoring network may not have been extensive enough to adequately delineate the extent of fractures, but it appears that the rule of thumb does not hold at the field site.				
Minor axis (minimum fracture length)	minor axis length = depth * 1.2 (EPA, 1994) Longest axis typically 17% longer than shortest axis (Nilsson et al., 2000)	5-8 m	Inadequate monitoring network to determine a minimum fracture length.				
Radius of Influence	3 times the physical extent of the fracture (Blem et al., 2004)	15 to 36 m (based on typical lengths)	At least ~10 m (gas venting observed)	At least ~10 m (gas venting observed)	At least 5 m (tracer in monitoring wells T1, T4)	At least 5 m (tracer in monitoring wells T1, T4)	At least 5 m (tracer in monitoring wells T1, T4)
Orientation /form	Typically claimed: In low-permeability deposits gently dipping toward injection point, bowl-shaped and upwardly sub-horizontal (EPA, 1994; Suthersan, 1999; Nilsson et al., 2000) But also: Pneumatic fractures tend to propagate along existing fractures and propagate along path of least resistance (Suthersan, 1999; Kidd, 2001)	Field evidence: Orientation and dip strongly influenced by local conditions and 'path of least resistance' (Bures, 1998; Suthersan, 1999; Markesic, 2000; Kidd, 2001; Blem et al., 2004)	It is unknown which fractures were induced by which fracturing event, however if one fracture is assumed to be formed from each fracturing elevation, then the field observations suggest the fractures may be bowl-shaped, dipping towards the fracturing well. Figures depicting the extent of fracture influence suggest that the 'bowl shape' fractures are not continuous in all directions. In cores: relationship between location of natural fractures/ more permeable features and induced fractures inconclusive. In the excavation induced fractures coincided with location of natural fractures.				

*Uplift calculated from final residual elevation (after tracer injection) minus start elevation at each fracturing elevation. Due to start elevations that are lower than previous residual elevations, the sum of uplifts calculated in this way is greater than the total uplift determined by the final residual elevation (3-4 m) minus the initial start elevation (7-8 m). See text for a more complete explanation. na: not available.

Characteristic	Rule-of-thumb	Typical literature values	Fracture 7-8 m b.s.	Fracture 6-7 m b.s.	Fracture 6-5 m b.s.	Fracture 4-5 m b.s.	Fracture 3-4 m.b.s
Dip	Strongly dependent upon site conditions (EPA, 1994). Dips towards fracturing well.	5-25° (EPA, 1994) 10-50° (Walsted et al., 2002)	Based on observations from the excavation, the fractures dip towards SE, towards PF1				
Induced fracture spacing/intensity	Claim: dense fracture network (EPA, 1995; DOE, 1989)	Not found	Based on cores: spacing of induced fractures varied from 1 cm to > 2 m to apparently massive.				
Minmum fracturing depth	< 3 m typically results in surface venting (Schuring, 2002). The closer to the surface the greater that risk of surface venting (Walsted et al., 2002).	3 m	Likely deeper than about 4 m (due to number of biopores from 1-2 m and intensity of natural fractures from surface to redox boundary).				
Injection interval	Reversed proportionality between fracture depth and density, i.e. the deeper the fracture the larger the spacing to the previous fracture ought to be, as otherwise they tend to merge at short distances from the borehole (Suthersan, 1999). >0.5 ft spacing tends to cause fractures to merge a short distance from fracture well (Suthersan, 1999).	0.2 to 0.9 m intervals, but 0.6 m is typical (Schuring, 2002).	~ 0.9 m	~ 0.9 m	~ 0.9 m	~ 0.9 m	~ 0.9 m
Injection time	After about 20 seconds, fracture propagation ceases and continued pneumatic injection only holds the fracture open on a 'pillow' of air (Suthersan, 1999).	10-60 seconds (Kidd, 2001) ~20 seconds is typical (EPA, 1994; Kidd, 2001; Schuring, 2002)	12 seconds (total time unknown)	15 seconds (total time unknown)	15 seconds (total time unknown)	15 seconds (total time with tracer injection 175 seconds)	16 seconds 3 minutes total with tracer injection
Injection rate	Critical parameter as fracture propagation is hampered by leak-off after about 20 seconds. Therefore, injection rate = deciding factor in determining maximum aperture and fracture length (Suthersan, 1999; Nilsson et al., 2000).	25-50 m ³ /minute (EPA, 1994)	~26.6 m ³ /min. (940 scfm**)	~21.2 m ³ /min. (750 scfm)	~17.0 m ³ /min. (600 scfm)	~13.6 m ³ /min. (480 scfm) tracer: 8.2 m ³ /min. (290 scfm)	~6.8 m ³ /min. (240 scfm) tracer: 7.7 m ³ /min. (200 scfm)
Initiation pressure	Depends upon confining/in situ stress, toughness and tensile strength of formation; initial rate of injection; size of incipient fractures; pores/defects in borehole wall; overburden pressure (EPA, 1994; Suthersan, 1999). Pressure required to 'lift' overburden = 14 to 21kN/m ² per 0.3 m depth (2-3 psi/ft depth; Schuring, 2002).	~ 700 kPa at ~ 6 m depth (Suthersan, 1999; 500 to 2000 kPa see Chapter 2)	862 kPa (125 psi)	414 kPa (60 psi)	379 kPa (55 psi)	310 kPa (45 psi)	276 kPa (40 psi)
Propagation pressure	Propagation pressure decreases with time from an initially high initiation pressure until the end of the injection time.	Less than initiation pressure	586 kPa (85 psi)	276 kPa (40 psi)	138 kPa (20 psi)	138 kPa (20 psi)	138 kPa (20 psi)

**scfm = standard cubic feet per minute. na: not available.

Characteristic	Rule-of-thumb	Typical literature values	Fracture 7-8 m b.s.	Fracture 6-7 m b.s.	Fracture 6-5 m b.s.	Fracture 4-5 m b.s.	Fracture 3-4 m.b.b
OCR (over-consolidation ratio)	OCR> 1 then fractures tend to be horizontal OCR values tend to increase with depth	6-14 (Walsted et al., 2002)	na	na	na	na	na

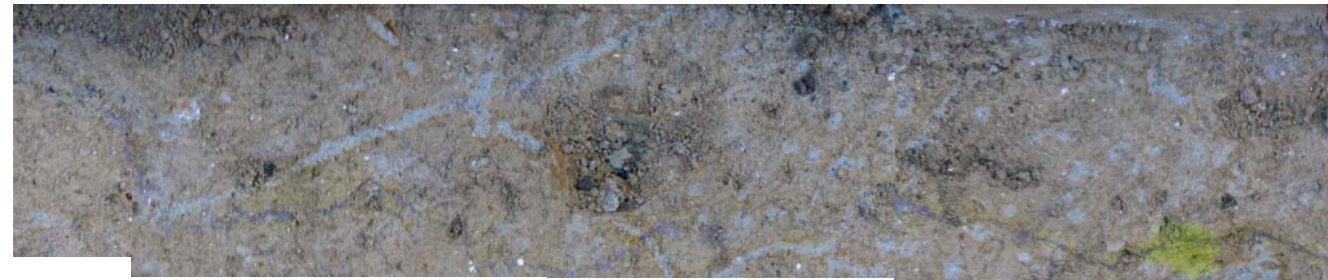
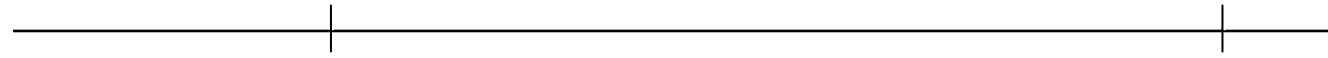
** na: not available.

APPENDIX X: INDUCED FRACTURES OBSERVED IN EXCAVATION

On the following fold-out page, photos have been composited to display the full visible lengths of the induced fractures observed in the excavation (Fractures 1 and 2).

4 m

5 m

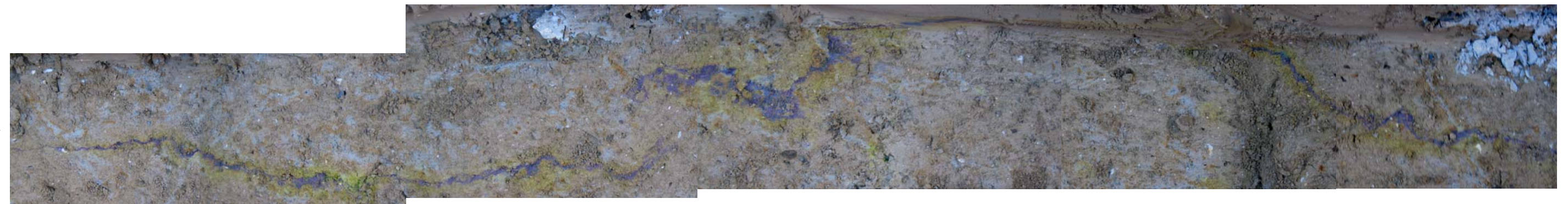
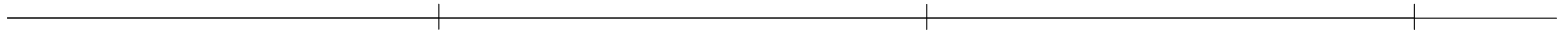


fracture 1

6 m

7 m

8 m



fracture 2



APPENDIX Y: ELECTRONIC DATA

The enclosed CD contains the following data:

- Table C.1*: US and Canadian experiences with environmental fracturing
- Table C.5*: Danish experiences with environmental fracturing
- MATLAB modelling results
- Fluorometer test results

The CD also contains a PDF version of this report in its entirety.