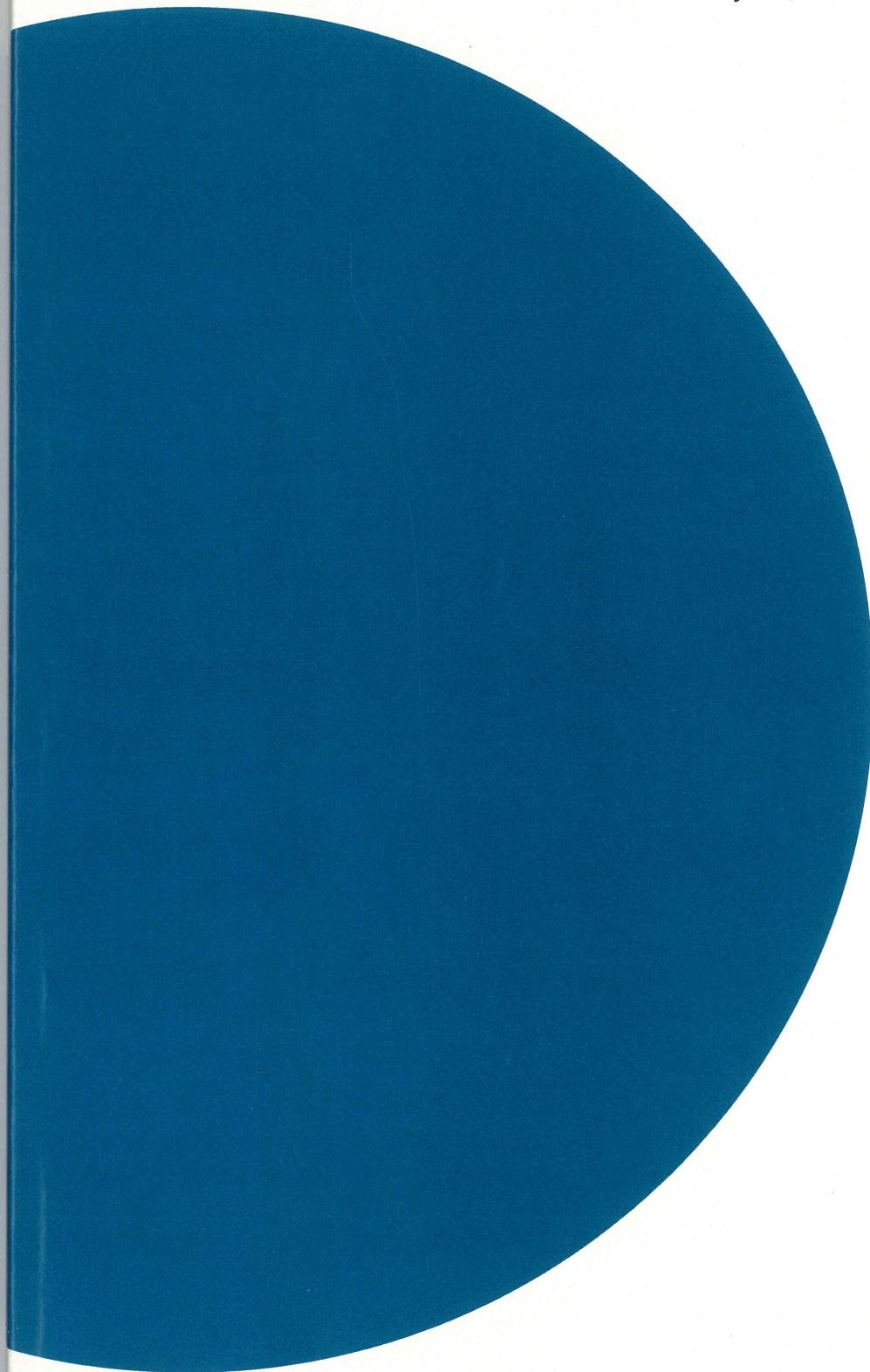


NEMLA

**Feasibility study on applicability of membrane interface probe
in limestone**

Claus Kjøller, Svenning Lyholm Jensen & Lykourgos Sigalas



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Summary

This report presents the outcome of a feasibility study of the applicability of the MIP technology in limestone. The study was initiated as a result of a number of innovation workshops – the NEMLA workshops - hosted by Capital Region of Denmark (CRD) with the overall aim to initiate the development of new emplacement methods in limestone for measurement of contamination with chlorinated solvents.

The present study was carried out as an experimental study in collaboration between COWI/Probing.dk and GEUS, and was funded by CRD. The study was executed in two phases:

- Phase 1 with the aim to evaluate the feasibility of measuring field relevant PCE concentrations in limestone with a standard MIP probe in a controlled set-up mimicking the situation where a standard MIP probe is placed in an open borehole. In this phase of the project, also simple numerical calculations were carried out with the purpose to better understand the results obtained in Phase 1 as well as to provide input for the experiments in Phase 2.
- Phase 2 where supplementary experiments were carried out with the purpose to point at possible options for development of the MIP technology to improve the measurement of chlorinated solvents in open boreholes in limestone.

The main finding of the study is that the MIP technology is generally only capable of measuring PCE contamination in limestone up to >1,000 ppb if close contact between limestone and MIP probe is ensured. Even at small gaps (2 mm) between limestone and MIP probe, the heating from the heater block of the MIP probe will cause convection in the gap, and as a consequence the contamination is carried away from the MIP membrane. Efforts to improve the measurements by confining the gap between MIP probe and limestone showed that contamination of the limestone with 500 ppb PCE could be detected with the MIP probe at a gap distance of up to 4 mm. At higher gap distances, the MIP probe could not detect the contamination.

Combining these findings with the fact that the caliper of an open borehole in limestone often may vary by several centimeters over tens of centimeter distances, it is not likely that a simple modification of the current MIP probe design can enable the development of new emplacement methods in limestone for measurement of contamination with chlorinated solvents. More radical changes to the current design should apply if the MIP membrane technology must be utilized.

A secondary finding of the study is that porosity and grain density of Copenhagen Limestone may vary considerably over very short distances (tens of cm). Thus, measured porosities varied between c. 15-45% and grain densities varied between c. 2.66-2.71 g/cm³. The exact reason for this variation is yet unexplained.

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Req. no.: 09201-714

1. Introduction

In 2013, the Capital Region of Denmark (CRD) hosted a number of workshops in an innovation project titled “New Emplacement Methods in Limestone Aquifers (NEMLA)” with the overall aim to initiate the development of new emplacement methods in limestone for measurement of contamination with chlorinated solvents. The methods shall ideally provide the same data quality and density as in the overburden with similar (or at least comparable) costs as in the overburden. The innovation process and results of the series of workshops are documented in the *NEMLA summary report* of Dec. 2013.

During the innovation process, four concepts were considered particularly promising and were chosen for possible further development. Several of these concepts build on the membrane interface probe (MIP) technology, which is already commonly used in overburden contamination studies. Therefore, a feasibility study of the applicability of the MIP technology in limestone was considered necessary prior to any decisions regarding further development of emplacement concepts in limestone.

This report presents the outcome of such a feasibility study carried out in collaboration between COWI/Probing.dk and GEUS. The study was funded by the CRD. The background for the project as well as the planned experimental work were described in detail in a memo from CRD dated 21.07.2015 with the title “Feasibility study on applicability of membrane interface probe (MIP) in limestone - Minutes from preliminary meeting Dec 8th 2014 and outline for proposal for the study”. This memo has served as the reference document for the work performed during the feasibility study.

The feasibility study has been carried out as an experimental study in two phases:

- Phase 1 where the scope of the planned experimental work was to evaluate the feasibility of measuring field relevant PCE concentrations in limestone with a standard MIP probe in a controlled set-up mimicking the situation where a standard MIP probe is placed in an open borehole. In this phase of the project, also simple numerical calculations were carried out with the purpose to better understand the results obtained in Phase 1 as well as to provide input for the experiments in Phase 2.
- Phase 2 where supplementary experiments were carried out with the purpose to point at possible options for development of the MIP technology to improve the measurement of chlorinated solvents in open boreholes in limestone.

Limestone specimens used in the experiments were supplied by Geo, and planning of the experiments as well as interpretation of experimental data has evolved from discussions with the project technical advisory committee (TAC) during the project. Members of the TAC where:

Niels Døssing Overheu – Project Manager – Capital Region of Denmark

Mads Therkelsen – Capital Region of Denmark – participant only in Phase 1

Henriette Kern Jespersen – Capital Region of Denmark – participant only in Phase 2

Thomas Hauerberg Larsen – Orbicon A/S

Mette Martina Broholm – DTU Environment, Technical University of Denmark

John Bastrup – Geo

Christian Buck – COWI/Probing.dk

Svenning Lyholm Jensen – COWI/Probing.dk

Claus Kjøller – Geological Survey of Denmark and Greenland (GEUS)

2. Phase 1 – Simulation of MIP in open limestone hole

2.1. Background

Prior to the experiments in Phase 1 of the project, meetings were held in the TAC in order to enable the most appropriate experimental programme to simulate the conditions in an open hole in the Danish limestone. The meetings resulted in the production of a preliminary experimental programme which was subsequently commented by Tom Christy from Geoprobe, who are manufacturing the MIP probing system. After adjustments according to the comments from Geoprobe, an experimental programme was decided upon by the TAC.

2.2. Experimental programme

As a consequence of the results obtained from the first part of the experiments, the experiments in Phase 1 were terminated before all suggested experiments had been carried out. The revised experimental programme is presented below.

2.2.1. *Acquisition and preparation of limestone cores*

Specimens with dimensions 10x10x13cm were cut from large Copenhagen Limestone blocks collected in one of the building sites for the Copenhagen Metro. Copenhagen Limestone was chosen because it was easily accessible and represents a large part of the Limestone that is contaminated with chlorinated solvents in the area around Copenhagen. Cutting was performed by Geo using tap water as cooling agent during the cutting. A total of 15 limestone pieces were prepared.

In addition to the prismatic specimens, a 1½” diameter plug sample was drilled from each of the limestone blocks where limestone pieces were cut from. In all, eight (8) of these 1½” diameter plugs were prepared, and were later used to determine the porosity and grain density variation by He-porosimetry (cf. Section 2.2.2). In addition, nine (9) 1” diameter plugs were sampled from three of the limestone blocks (Blocks 1, 3, and 5) in order to better understand variations in porosity at sub-block scale (cf. Section 2.3.1).

2.2.2. *Preparation for spiking*

At reception at GEUS Core Laboratory, each prismatic specimen was photographed on the slabbed side that during measurements with the MIP was facing the heater block (cf. Appendix 1).

Subsequently, specimens and plugs were oven dried at 110°C for up to 96 hours until no further weight loss in order to evaporate any fluid present in the cores. After oven drying, the prismatic specimens were weighed and the bulk volume was measured by ruler. Plugs were used for determination of porosity and grain density by He-porosimetry.

The He-porosity was determined by subtraction of the measured grain volume and the measured bulk volume. The Helium technique, employing Boyle's Law, is used for grain volume determination, applying a double chambered Helium porosimeter with digital readout. The sample bulk volume is measured by submersion of the plug in a mercury bath using Archimedes principle. Grain density is calculated from the grain volume measurement and the weight of the dry sample.

The Helium porosimeter was calibrated using a set of steel plugs (Core Laboratories™ volume reference plug set) before the measurement of plug specimens was initiated.

2.2.3. Spiking of limestone cores and saturation check

Following cooling to room temperature, the prismatic limestone specimens were spiked with PCE. The spiking was carried out by first placing the specimens in empty containers (10 L PVC buckets). Subsequently, the buckets were filled from bottom up with a 1,000 ppb PCE solution. The bottom-up filling was performed in order to minimize the amount of air trapped in the cores during filling. Filling was carried out at a reasonably slow pace in order to ensure the best possible saturation of the specimens by capillary force imbibition, but in the same time at a sufficiently high pace to minimize the evaporation of PCE from the solution. The resulting duration for filling of the buckets with PCE solution was between 120 s and 140 s. This saturation procedure was chosen over standard vacuum saturation (cf. Section 2.2.6) in order to avoid stripping of PCE during saturation.

Initially, the specimens were erroneously submerged in a solution of PCE with much higher concentration than 1,000 ppb. This was discovered prior to the remaining part of the experiments. As a consequence, the specimens were oven dried in order to evaporate the high concentration of PCE and subsequently re-saturated in a 1,000 ppb PCE solution. As will be discussed in Section 2.3.11, this procedure did apparently not remove all PCE from the specimens before re-saturation.

Immediately after the buckets were filled with PCE solution, a water sample was taken from each of the containers used, and the buckets were sealed and left until the MIP experiments for at least 2 days in a fume hood to ensure the best possible saturation of the prismatic specimens. In order to check if evaporation occurred from the buckets during saturation, a water sample was taken from the buckets immediately before MIP experiments with each prismatic specimen. Water samples were analyzed for content of chlorinated solvents by ALS Laboratory.

2.2.4. MIP measurement set-up and general sampling procedure

The actual feasibility test was carried out in a test set-up, where each of the spiked limestone specimens was measured while submerged in a vat with clean water (Figures 1 and 2).

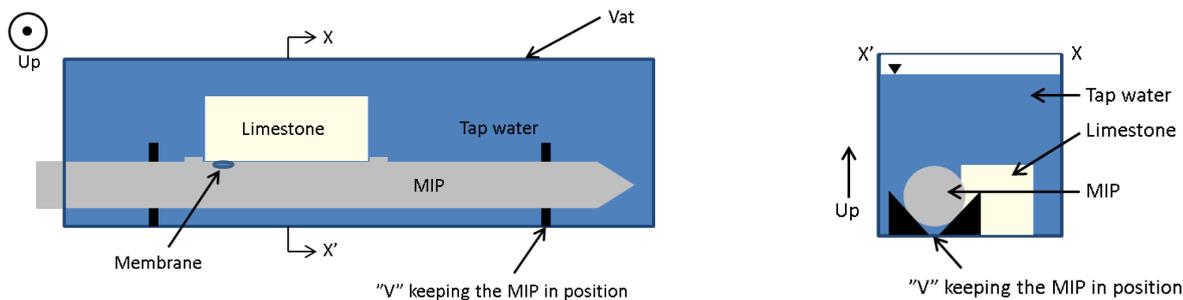


Figure 1: Schematic illustration of the test set-up.



Figure 2: Photography showing the test set-up.

Prior to placement of the spiked limestone specimens in the vat, the MIP was placed in the vat with the heater assembly facing sideways. Subsequently, 42 L of tap water was poured into the vat.

Prior to submersion of the limestone specimens in the vat, the limestone specimen was taken directly from the bucket where it was saturated, wiped with tissue on the surface, photographed on one side, and a small chip (about 50 g) was broken off the limestone specimen by use of a chisel. Subsequently, the broken off chip was transferred to a bottle in order to analyze the pre-experimental PCE content of the limestone. Immediately hereafter, the large limestone specimen was placed in the water-filled vat as shown in Figure 2 but at variable distance from the MIP. In general, the MIP heater block was pre-heated prior to placement of the limestone specimen, except for the experiment with specimen UCS-1 (Table 1).

As fast as possible after placement of the limestone specimen in the vat, i.e. within 30 s, the measurement with the MIP probe was initiated. The duration of each measurement was between 120 s and 150 s. General conditions for all measurements for all specimens included in this phase of the project are provided in Table 1.

Table 1: Test matrix for the NEMLA Feasibility study experiments carried out at GEUS in the period 08.09.2015 to 10.09.2015.

Sample ID	PCE concentration (ppb)	Size of gap (mm)	Pre-heat before submersion of specimen	Temperature of water in vat (°C)	Carrier gas flowrate (mL/min)	Time of exp
UCS-1	1000	0	no	18	55	08-09-2015 15:00
5a	1000	0	yes	18	55	09-09-2015 11:30
3	1000	0	yes	18	40	09-09-2015 13:20
4	1000	0	yes	15.5	40/55	09-09-2015 14:20
5	1000	2	yes	18	55	10-09-2015 10:35
5c	1000	0	yes	31	55	10-09-2015 13:20
7	1000	2	yes	21	55	10-09-2015 14:10
1b	1000	0	yes	11	55	10-09-2015 15:20

Immediately after removal from the vat, the surface of the limestone specimen was wiped with tissue and another chip was broken off the limestone specimen for analysis of the post-experimental PCE content. Furthermore, a sample of the water in the vat was taken in order to determine any content of PCE in the vat water. The water sample was taken after the water in the vat had been stirred by hand. All chemical analyses were carried out by ALS Laboratory.

In addition, and in a few cases, the background concentration in the water in the vat was measured with the MIP-probe after the prismatic specimen had been removed. In all, eight (8) limestone pieces were tested according to the experimental matrix shown in Table 1. In experiments where a specific distance to the MIP was tested, the distance was ensured by placement of small metal pieces with the desired thickness between the limestone and the heater assembly of the MIP probe.

A response test was performed at the beginning of each day; to ensure that the equipment was working properly, and to acquire a baseline for the following experiments. The procedure was as follows:

- A 500ml c. 1,000 ppb solution of PCE was produced and poured into a tube in a test stand.
- The preheated probe (120°C) was submerged into the PCE solution and left for 45 seconds, and then removed promptly.
- The ECD response and the temperature were logged in the Geoprobe software.

The response test was performed in a feature of the software which was separated from the normal acquisition. Normally, in the field, the response test is made with a 5 ppm solution, but to create an appropriate reference in our experiments, a c. 1,000 ppb solution was used. Furthermore, it was decided to use the response feature for the experiments as well. The response tests does not compensate for the trip time through the trunkline, as the normal results presented from this software do. The triptime was between 25 and 30 seconds.

Based on discussions with Fabian de Weirdt of Geoprobe, Belgium and on results from two response tests in c. 100 ppb PCE solutions an attempt was made to optimize the flow of the carrier gas in the trunkline to the MIP probe (cf. Table 1; Specimens 3 and 4). However, as this did not

improve the detection of contaminant in the limestone specimen, the remaining experiments were performed at the standard flowrate of 55 mL/min.

Due to suspected failure of the MIP probe, it was decided to replace the probe between 09.09.2015 and 10.09.2015. The “new” probe contained a membrane which was worn more down than the probe initially applied. This resulted in considerably higher ECD response from the second probe in response tests.

2.2.5. *MIP configuration*

The following MIP configuration was used for all experiments:

- Geoprobe Field instrument FI6000
- Geoprobe MIP controller box MP6500
- Geoprobe MiHpt trunkline with stainless steel liner. The trunkline was equipped with foam insulation and a heating thread that was keeping the trunkline at c. 50°C
- Geoprobe DI acquisition software v1.7
- ECD detector with a 512 attenuation setting in the DI acq software
- Geoprobe MiHpt Probe 6532

2.2.6. *Saturation test*

As a result of the basic petrophysical investigation where description of the porosity variation in the large limestone blocks was estimated, it was concluded that check of the saturation method for the prismatic limestone specimens through standard procedure Archimedes tests was not possible. This was specifically due to large variations in porosity and grain density at cm-scale. Therefore, an alternative and qualitative method was applied in order to investigate if saturation of the prismatic specimens by imbibition saturation in the PVC buckets was comparable to standard vacuum saturation in a vacuum chamber.

For the saturation test, four (4) prismatic specimens were subsequent to MIP experiments left to evaporate the PCE solution and then washed four times in deionized water before they were oven dried @ 110°C for at least 48 h until no further weight loss could be determined. Three (3) of these prismatic specimens were subsequently saturated with a 10% (w/w) Fluorescein solution. Fluorescein is a fluorescent tracer that is visible under UV illumination. Two of the prismatic specimens were saturated using imbibition saturation only – i.e. the general method used for saturating specimens in this study. The third specimen was saturated using vacuum saturation which is a commonly used method in core analysis.

When using vacuum saturation, the specimen is placed in a vacuum chamber and subsequently vacuum is applied to the chamber for at least 2 hours before the liquid is introduced to the chamber from the bottom and up. After leaving the specimen in the vacuum chamber for another hour the

specimen is transferred to a pressure chamber and pressure saturation is carried out at a pressure of 110 bar.

The fourth prismatic specimen used for the saturation tests was saturated with deionized water by vacuum saturation. This specimen was later used as a “blind” sample when the specimens were investigated by photography in UV-light.

Following saturation, the four specimens were cut in half and photographed under UV-light in order to investigate the distribution of Fluorescein as a function of saturation method.

2.3. Results

The results of Phase 1 of the NEMLA feasibility experiments are presented below. Initially in Sections 2.3.1-2.3.2, some general results are presented. Subsequently in Sections 2.3.3-2.3.12, the results from measurements on contaminated limestone specimens are presented, and finally the results from conceptual numerical models are presented.

2.3.1. Porosity distributions

Initially, plug samples were drilled from each of the eight large limestone blocks that were used for the feasibility tests in the laboratory. The purpose with these plug samples was to measure porosity and grain density in order for mass balance calculations to be performed. The results from the initial porosity measurements showed a large variation in porosity between 18.2% and 40.0% and grain density variations between 2.667 g/cm³ and 2.704 g/cm³ (cf. Figure 3).

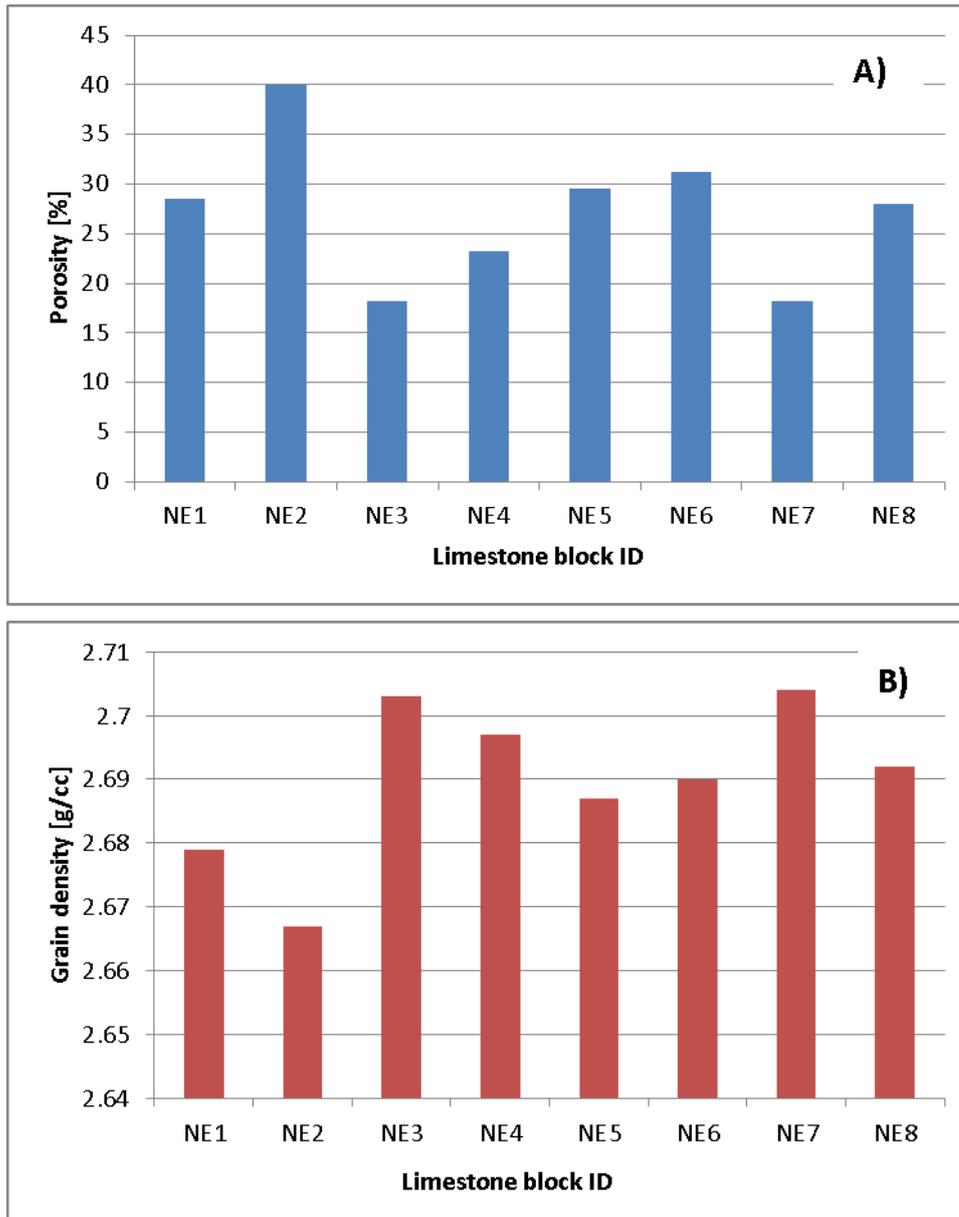


Figure 3: A) Porosity and B) grain density of eight 1½” limestone plugs sampled from each of the eight large limestone blocks where prismatic specimens were cut for the NEMLA feasibility study.

Apparently, the grain density is lower, the higher the porosity of the plug specimen. Since the density of pure calcite (CaCO_3) is 2.71 g/cm^3 , it seems that the lower the porosity, the more “clean” is the limestone. Impurities in the limestone may consist of quartz which has a density of 2.65 g/cm^3 or various clay minerals with lower grain density than calcite.

The large variation in porosity observed in Figure 3, raised the question whether this variation occurred at the 10 cm specimen scale or at a smaller scale. This was especially relevant with regard to the intention to be able to perform mass balance calculations for the feasibility experiments. However, since the limestone seemed to be very heterogeneous with distinct areas with darker grey colour and other areas with more white limestone (Figure 4), the small scale heterogeneity seemed most likely. In

order to better understand the scale of the porosity variation, a number of 1" plugs were sampled from three of the large limestone blocks used for preparation of prismatic specimens. Although it was not possible to sample completely homogeneous plugs, an attempt was made to take plug samples specifically from dark grey and white areas with the purpose to describe if the variation in porosity could be related to the colour variation of the limestone (Figure 4).

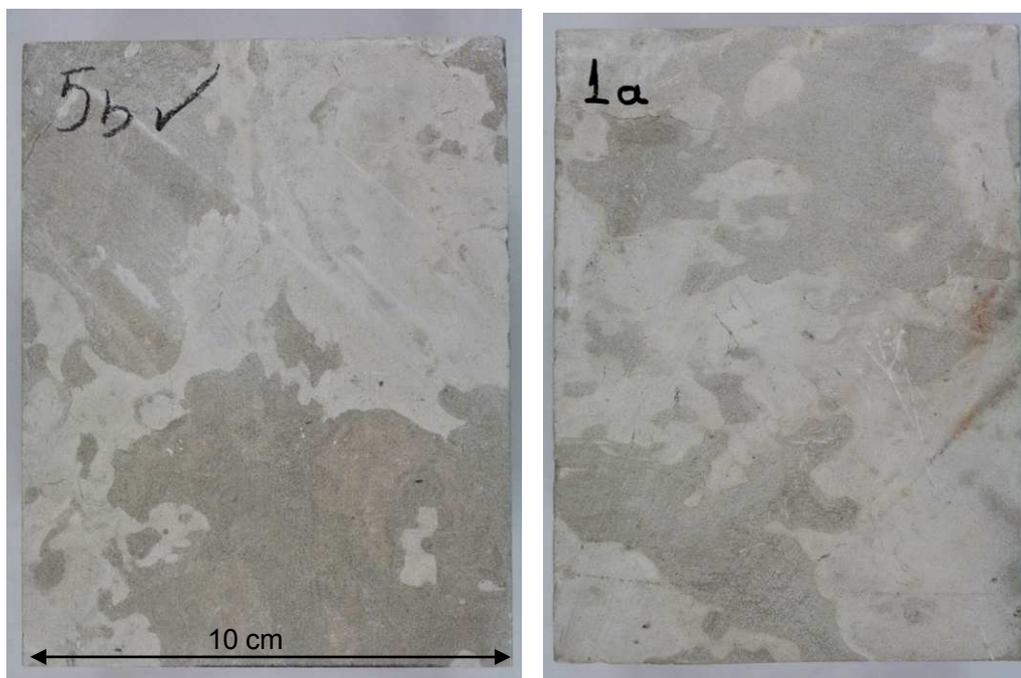


Figure 4: Prismatic specimens 5b and 1a used in the feasibility experiments. Pictures show that the specimens are very heterogeneous with distinct greyish and whiter areas.

The results of the more specific sampling are shown in Figure 5. As shown, it seems that the greyish areas (plugs 3.1-3.3) of the limestone has lower porosity and higher grain density than the more white areas. Furthermore, the results show that the porosity of plug samples with a diameter of 1" taken from the same large limestone block, and with apparently similar color (e.g. plugs 1.1, 1.2, and 1.3) may vary much. Thus, plug 1.1 has a porosity of 30% and a grain density of 2.689 g/cm^3 while for comparison plug 1.3 has a porosity of 45% and a grain density of 2.660 g/cm^3 .

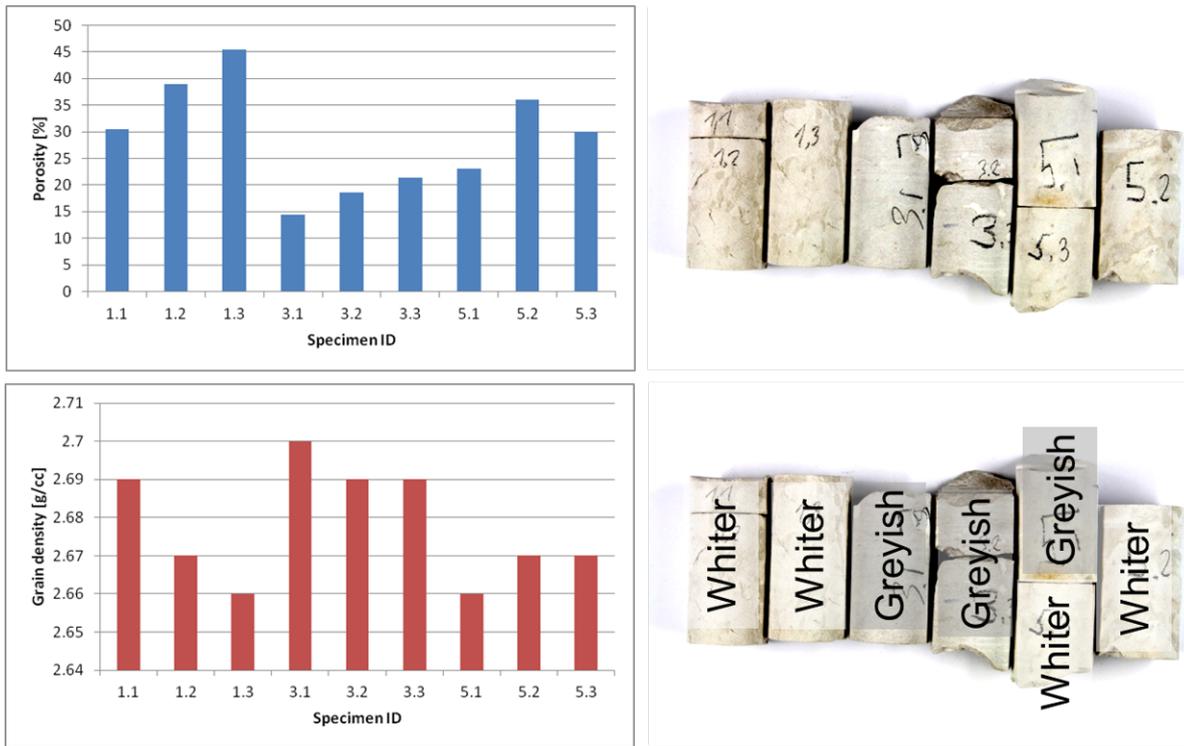


Figure 5: Porosity and grain density of 1" specimens specifically sampled from white and greyish areas in the large limestone blocks.

The large variation observed in porosity and grain density of the plugs shown in Figure 5 suggests that porosity variations are large in all prismatic samples used in the feasibility tests and that even within areas with similar visual expression, the porosity may vary much. Based on this finding, it was decided not to carry out mass balance calculations for the feasibility experiments, since these will depend on knowledge about the average porosity of each prismatic limestone specimen. The average porosity of the prismatic specimens was not measured directly and not possible to estimate with a reasonable uncertainty based on the available data.

2.3.2. Saturation tests

The purpose with the saturation tests with Fluorescein was to qualitatively assess whether the imbibition saturation method used in the present study provided as homogeneous a saturation of the prismatic specimens as a more conventional saturation method using vacuum saturation would do.

In order to first check the applicability of Fluorescein as a tracer for saturation in the specimens, photographs of the specimen saturated with Fluorescein by vacuum saturation (Figure 6, Specimen 5c) were compared to photographs of the specimen saturated with de-mineralized water (Figure 6, Specimen 5).

As shown in Figure 6 there is a clear fluorescent signal when exposed to UV light from the specimen that was saturated with Fluorescein (Specimen 5c) while the specimen saturated with de-mineralized

water (Specimen 5) is almost invisible when photographed under UV-light. Based on this observation, it was decided to use Fluorescein in the qualitative saturation studies.

It should be noted that areas with greyish limestone in Specimen 5c show less fluorescence than areas with whiter limestone. We have not investigated this phenomenon further in the current study since the purpose of the saturation test was only to investigate whether the imbibition method would be appropriate to saturate specimens sufficiently such that the saturation method would not be limiting for the capability of the MIP probe to determine the PCE contamination of the limestone specimens.

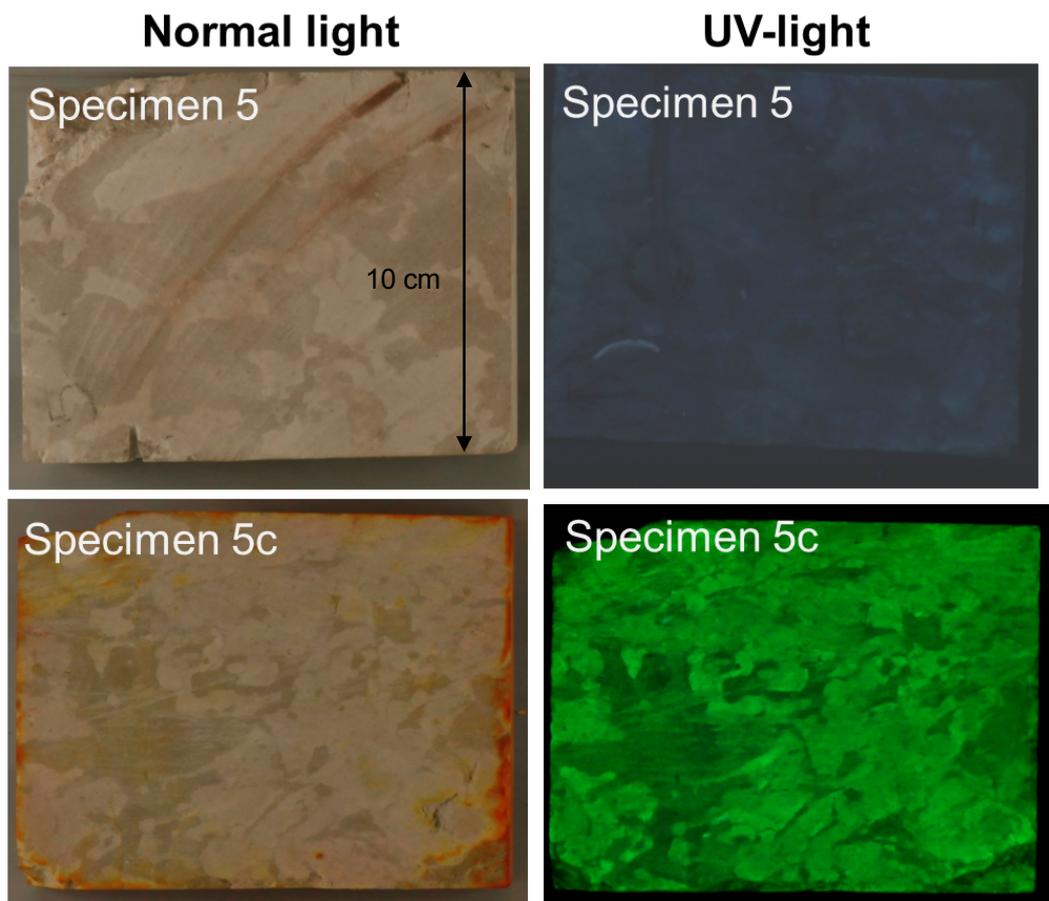


Figure 6: Photographs in normal light and ultra violet (UV) light of prismatic specimens after saturation with de-mineralized water (Specimen 5) and a 10% Fluorescein solution (Specimen 5c); both saturated by vacuum saturation. Just before photography, the specimens were cut/slabbled into two pieces. The photography shows the slabbled side of one half of the original specimen..

Figure 7 shows photographs of the two prismatic specimens that were saturated using the imbibition saturation method. Comparison of the photographs under UV light in Figure 7 with the photography of the vacuum saturated specimen under UV light (Figure 6, Specimen 5c) indicates that the samples saturated by the imbibition saturation method are as evenly saturated as the sample saturated by the traditional vacuum saturation method. Again, less fluorescence appears in areas with grey limestone (Figure 7) but fluorescence is observed from the entire slabbled surface, suggesting that imbibition occurs in the entire specimen during imbibition saturation.

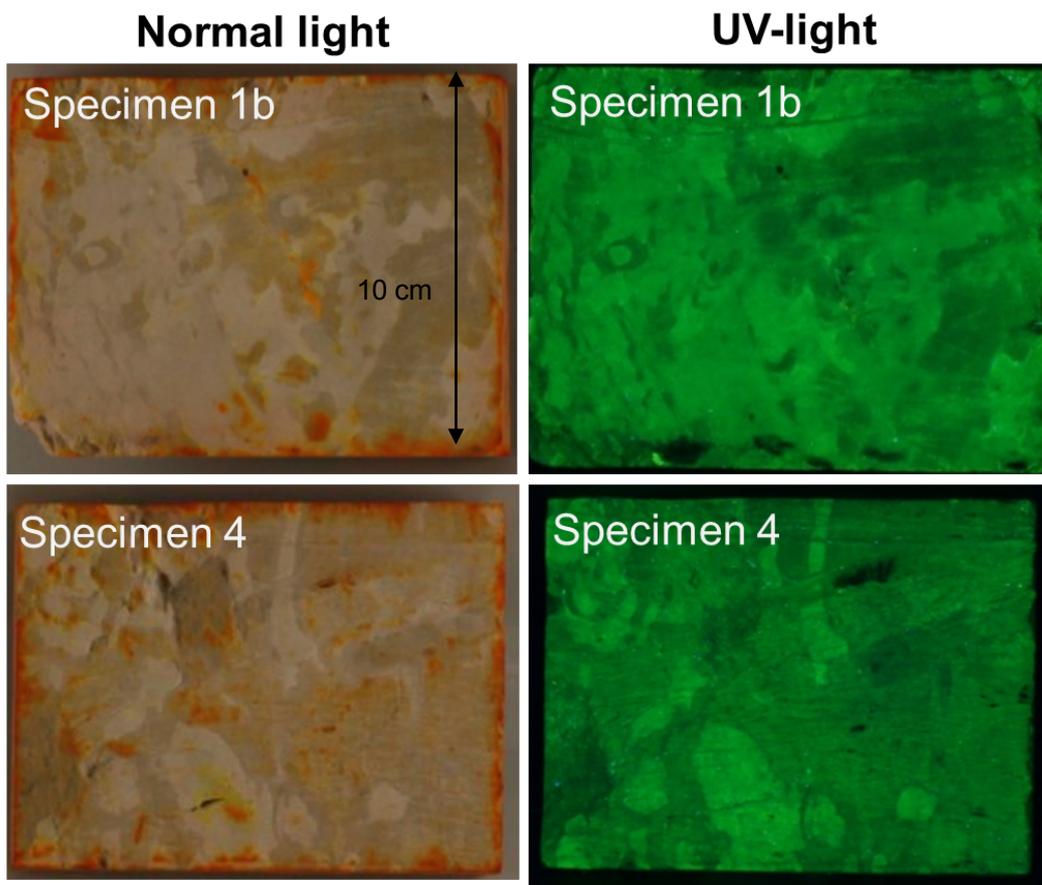
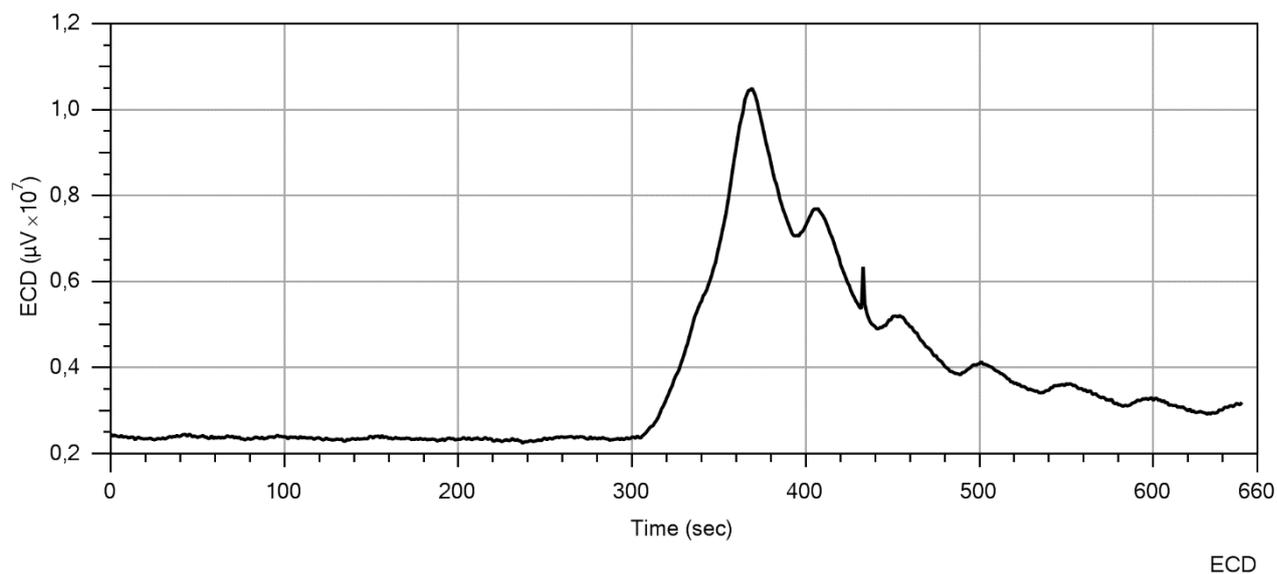


Figure 7: Photographs in normal light and ultra violet (UV) light of prismatic specimens after saturation with a 10% Fluorescein solution using the imbibition saturation method. Just before photography, the specimens were cut/slabbbed into two pieces. The photography shows the slabbbed side of one half of the original specimen.

2.3.3. Response in pure PCE solutions

The response of the MIP probe in c. 1,000 ppb PCE solutions was tested at the response test every morning. Furthermore, a response test with comparison of the response in c. 100 and 1,000 ppb PCE solution was carried out in order to check if the MIP probe could detect contamination down to 100 ppb. The results of the comparative response tests are shown in Figure 8.

A): Peak response c. 10,000 mV (1,000 ppb solution)



B): Peak response c. 3,600 mV (100 ppb solution)

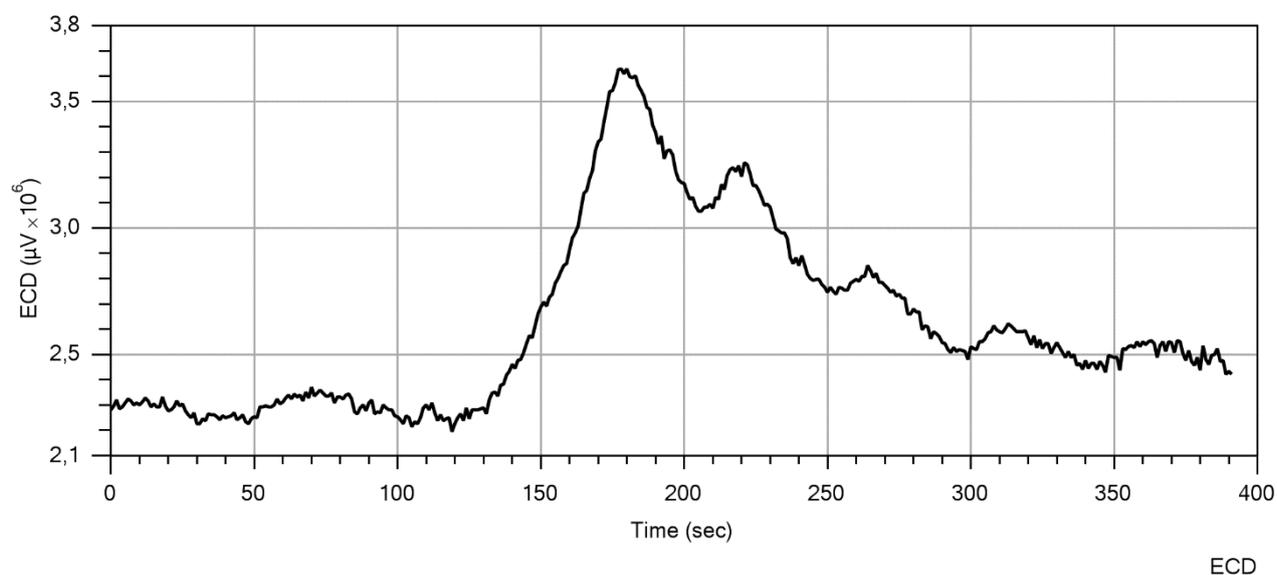


Figure 8: Response tests in A) c. 1,000 ppb PCE; B) c. 100 ppb PCE.

As shown in Figure 8, the response tests indicate that concentrations of PCE down to 100 ppb can be detected by the MIP probe as the signal obtained from the 100 ppb response test is clearly higher than the background signal corresponding to a response of c. 2,200 mV.

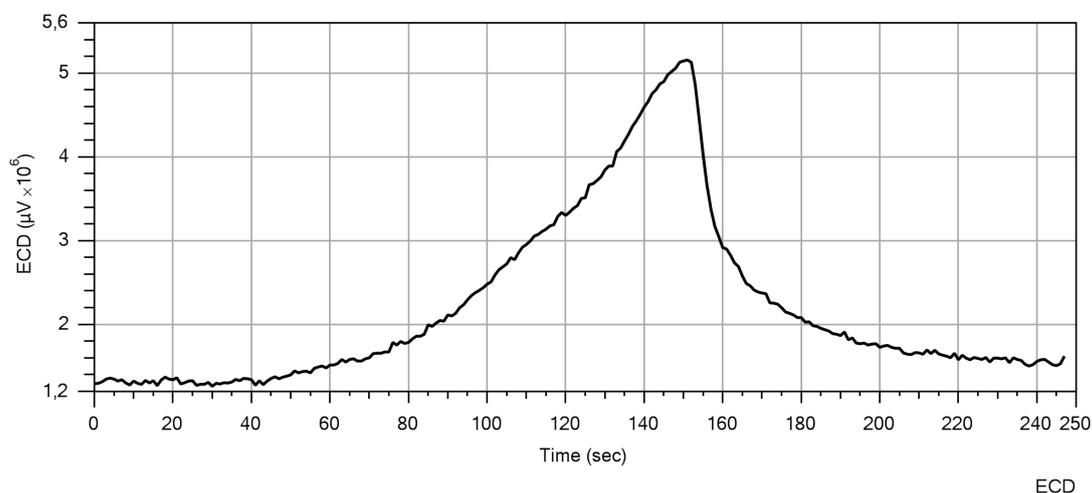
However, it should be noted that the responses obtained by the response test is the maximum obtainable response from the specific probe used on the specific day of the experiment. Thus, the response from limestone samples saturated with 1,000 ppb PCE solution was generally lower than the

response measured directly by submersion of the probe in a PCE solution with an identical PCE concentration. In addition, during the experiment it turned out that the response was much dependent on the specific MIP probe applied in the experiment (see below).

2.3.4. Dependence on MIP probe membrane

Due to problems with detecting the contamination in the limestone specimens by the end of 09.09.2015, it was decided to exchange the MIP probe with a different probe for the experiments starting 10.09.2015 and onwards. The “new” probe was equipped with a membrane that was worn more down than the MIP probe used during the preceding days. As a result of the different condition of the membrane, the ECD signal obtained in the c. 1,000 ppb response test (Figure 9B) was higher than for the probe with a newer membrane (Figure 9A). This indicates that the feasibility of the MIP technology may be a function of the membrane in the MIP probe.

A): Peak response c. 5,000 mV (File: KS-UCS1-pre-ECD.jpg)



B): Peak response c. 40,000 mV (File:KS-Specimen-5-pre-ECD.jpg)

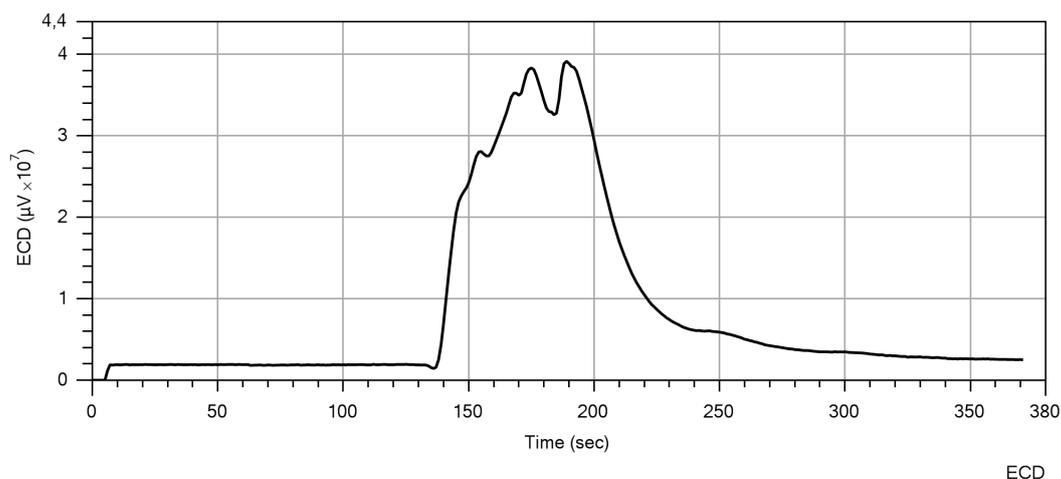


Figure 9: Response tests in c. 1,000 ppb PCE; A) with MIP probe #1 on 08.09.2015, B) with MIP probe #2 on 10.09.2015.

2.3.5. Effect of pre-heating

In the first two experiments, the test was to investigate the effect of pre-heating the heater block of the MIP probe outside the vat before commencement of measurements (cf. Table 1). Thus, for Specimen UCS-1 pre-heating outside the vat was not carried out, while for Specimen 5a pre-heating was performed before placing the MIP in the vat and before submersion of the limestone specimen in the vat. As shown by the results in Figures 10 and 11, the best ECD response was obtained in the test where pre-heating was carried out. As a consequence, pre-heating was performed in the remaining part of the experiments.

A further observation from these first experiments was that there is an amount of remaining contamination in the MIP probe system (probably mainly in the trunkline) that will disturb the following measurement if not removed first (cf. Figures 10 and 11).

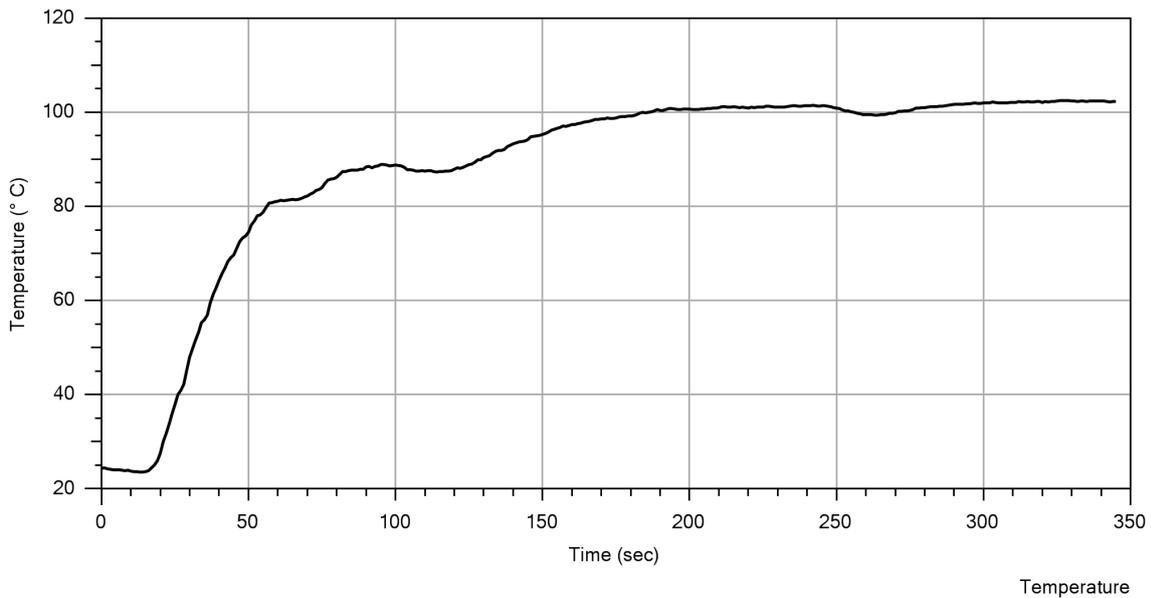
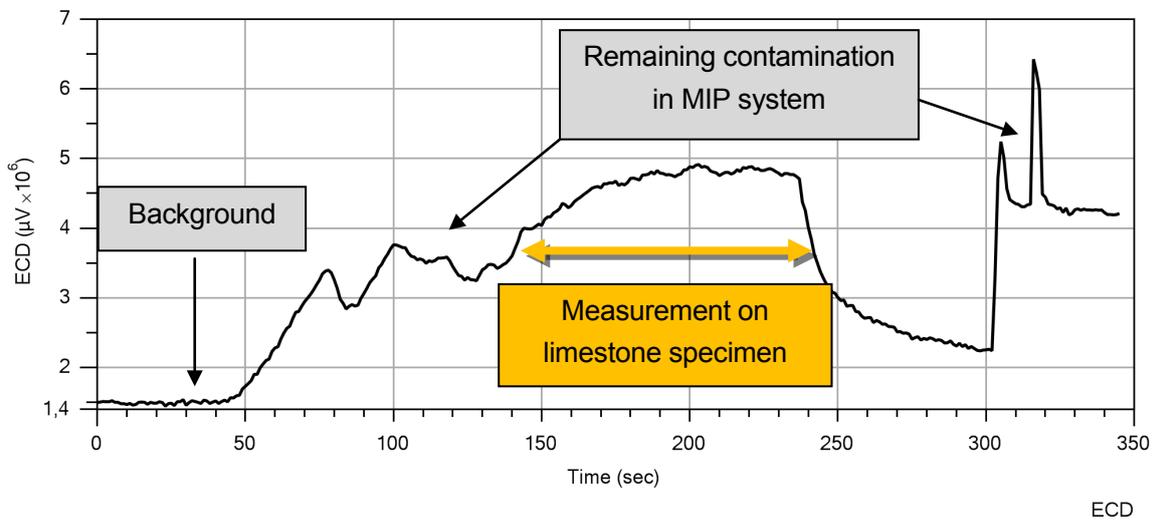


Figure 10: Results of test with Specimen UCS-1 (no pre-heating). ECD response and temperature recorded by MIP probe are shown. For other experimental details, see text and Table 1. (Files: KS-UCS1-post-ECD.jpg; KS-UCS1-post-temp.jpg)

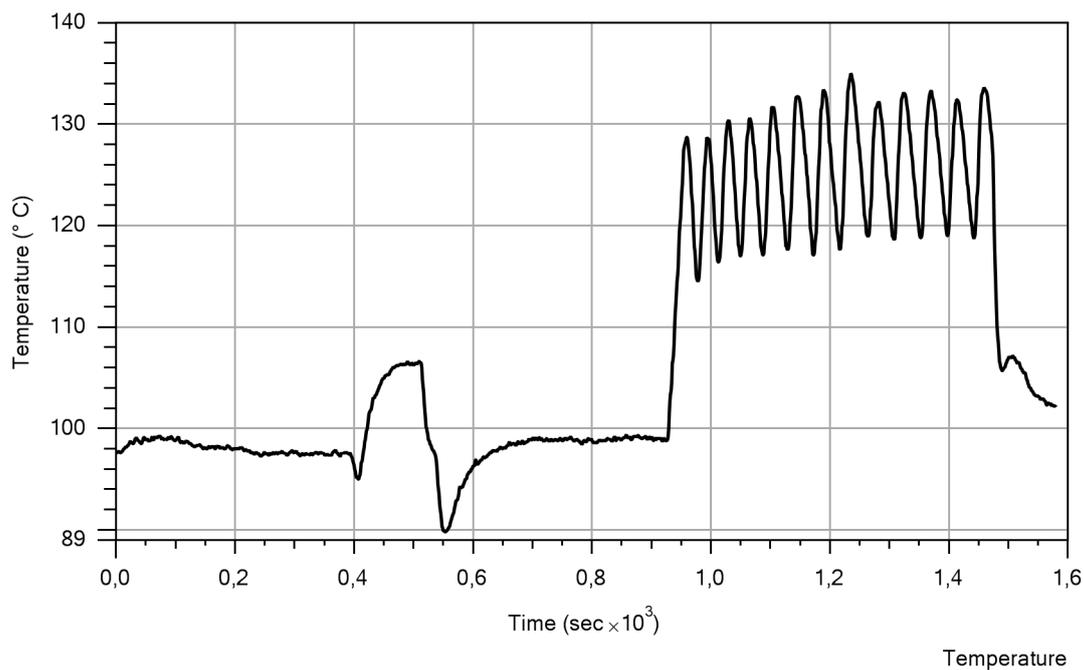
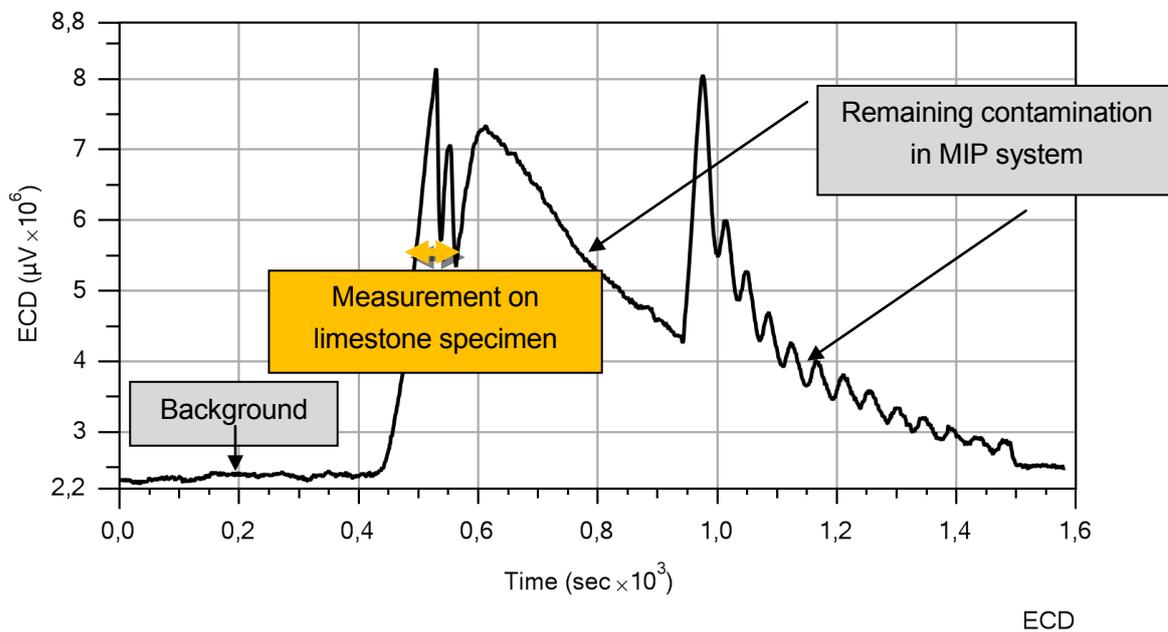


Figure 11: Results of test with Specimen 5a (with pre-heating). ECD response and temperature recorded by MIP probe are shown. For other experimental details, see text and Table 1. (Files: KS-Specimen-5a-ECD.jpg; KS-Specimen-5a-temp.jpg)

2.3.6. Reproducibility of contaminant detection

The experiment with Specimen 5a and the second half of the experiment with Specimen 4 were carried out at almost identical conditions though the temperature of the water in the vat was slightly

lower in the experiment with Specimen 4 (cf. Table 1). Furthermore, the measurement using Specimen 4 was carried out subsequent to a test with the specimen where measurements had first been attempted with a lower carrier gas flowrate. Since this resulted in a low response from the MIP probe, the measurement was performed again with the default flowrate after the specimen had been re-saturated with c. 1,000 ppb PCE solution in one of the plastic buckets where saturation was occurring.

As can be seen from a comparison of Figures 11 and 12, the responses from the two tests are reasonably comparable, suggesting that the detection of contaminant in the limestone is possible if contact between limestone and MIP probe is ensured.

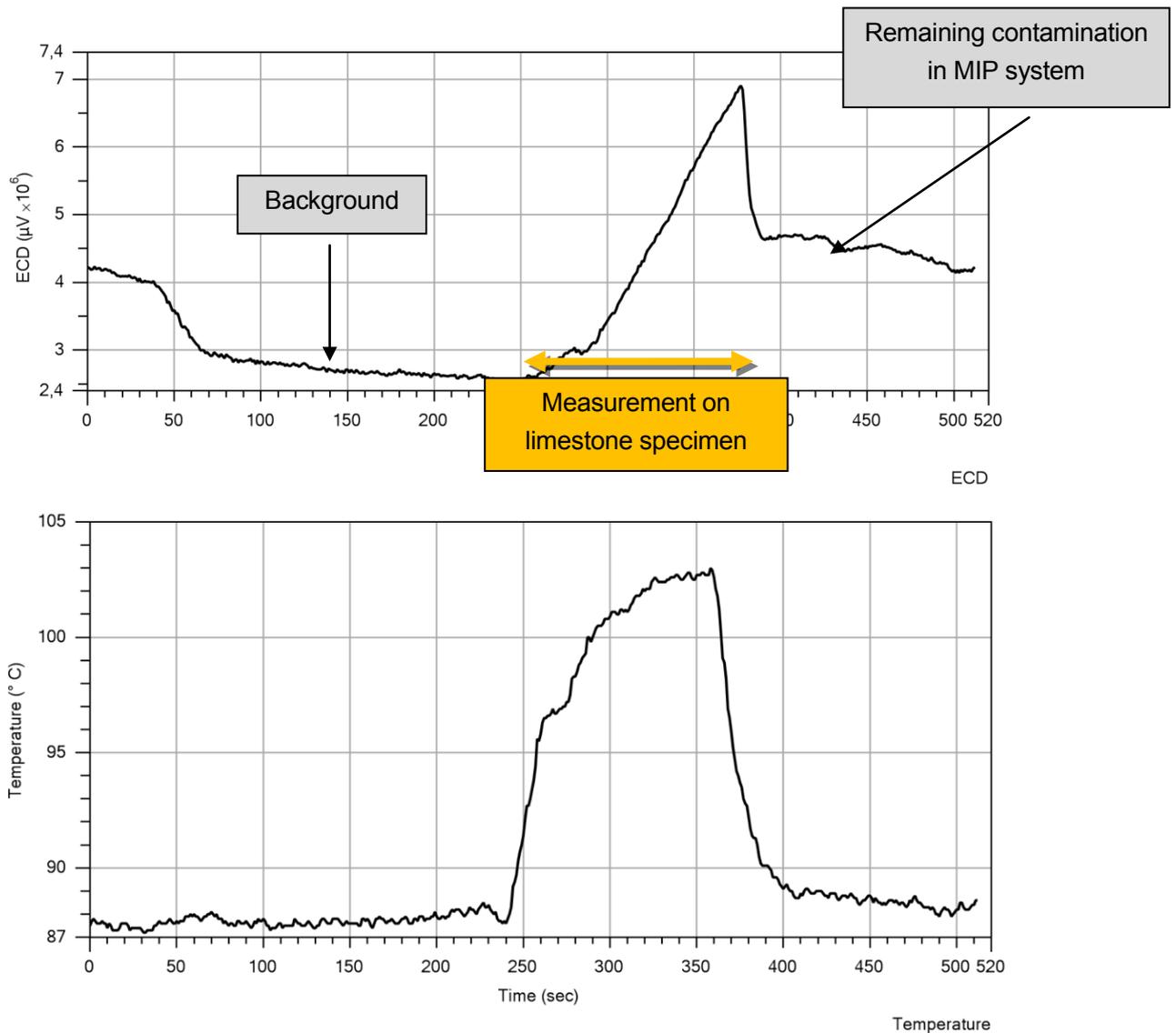


Figure 12: Results of test with Specimen 4. ECD response and temperature recorded by MIP probe are shown. For other experimental details, see text and Table 1. (Files: KS-Specimen-4-post-ECD.jpg; KS-Specimen-4-post-temp.jpg)

2.3.7. Effect of carrier gas flowrate

As mentioned above, it was speculated whether a change in the carrier gas flowrate could possibly improve the ECD signal from the MIP set-up. Therefore, two response tests in c. 1,000 ppb PCE solution and with different carrier gas flowrates were carried out. The flowrates tested were 40 mL/min and 65 mL/min. As shown by the increased response at 40 mL/min (Figure 13) compared to the response at 65 mL/min (Figure 14), this preliminary test suggested that the response of the probe could be improved by decreasing the carrier gas flowrate from the default 55 mL/min to 40 mL/min. However, when the flowrate of 40 mL/min was tested in the experimental set-up with a limestone specimen, the response was apparently lower at the flowrate of 40 mL/min (Figure 15) than at 55 mL/min (Figures 11 and 12). As a consequence, and because a detailed investigation of the signal-to-flowrate interdependency was outside the scope of this study, the remaining part of the experiments were carried out at the default flowrate of 55 mL/min.

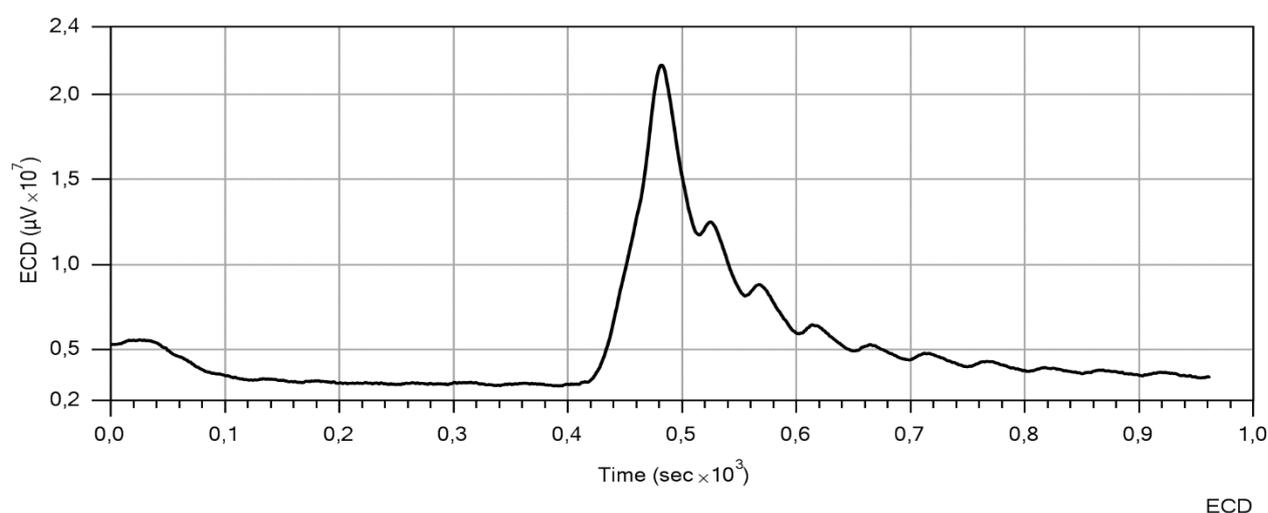


Figure 13: Response tests in c. 1,000 ppb PCE at a carrier gas flow rate of 40 mL/min.

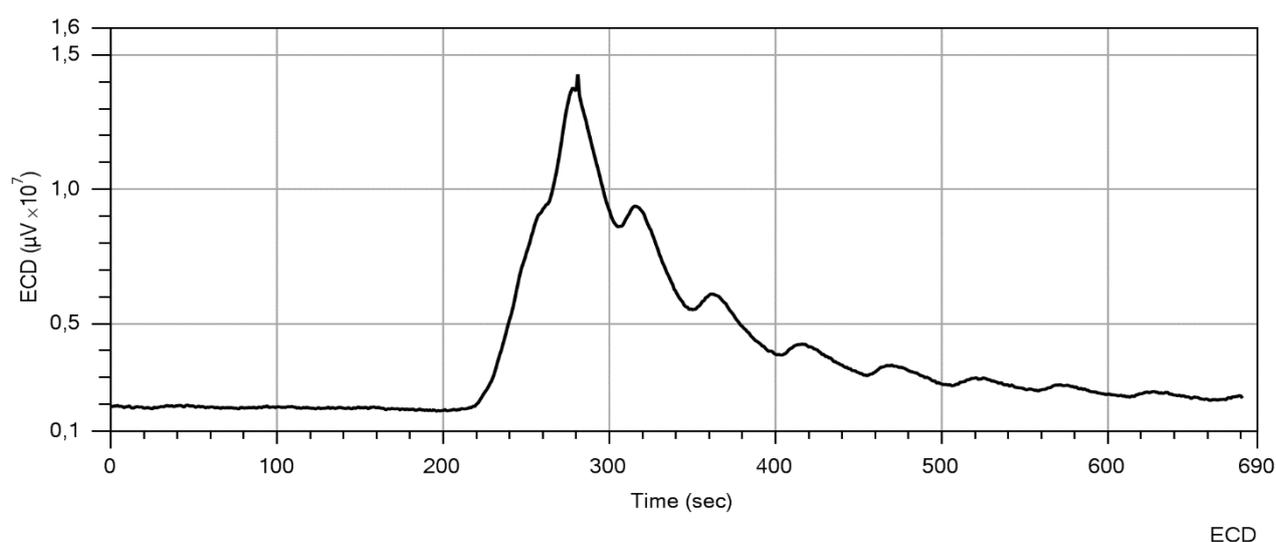


Figure 14: Response tests in c. 1,000 ppb PCE at a carrier gas flow rate of 65 mL/min.

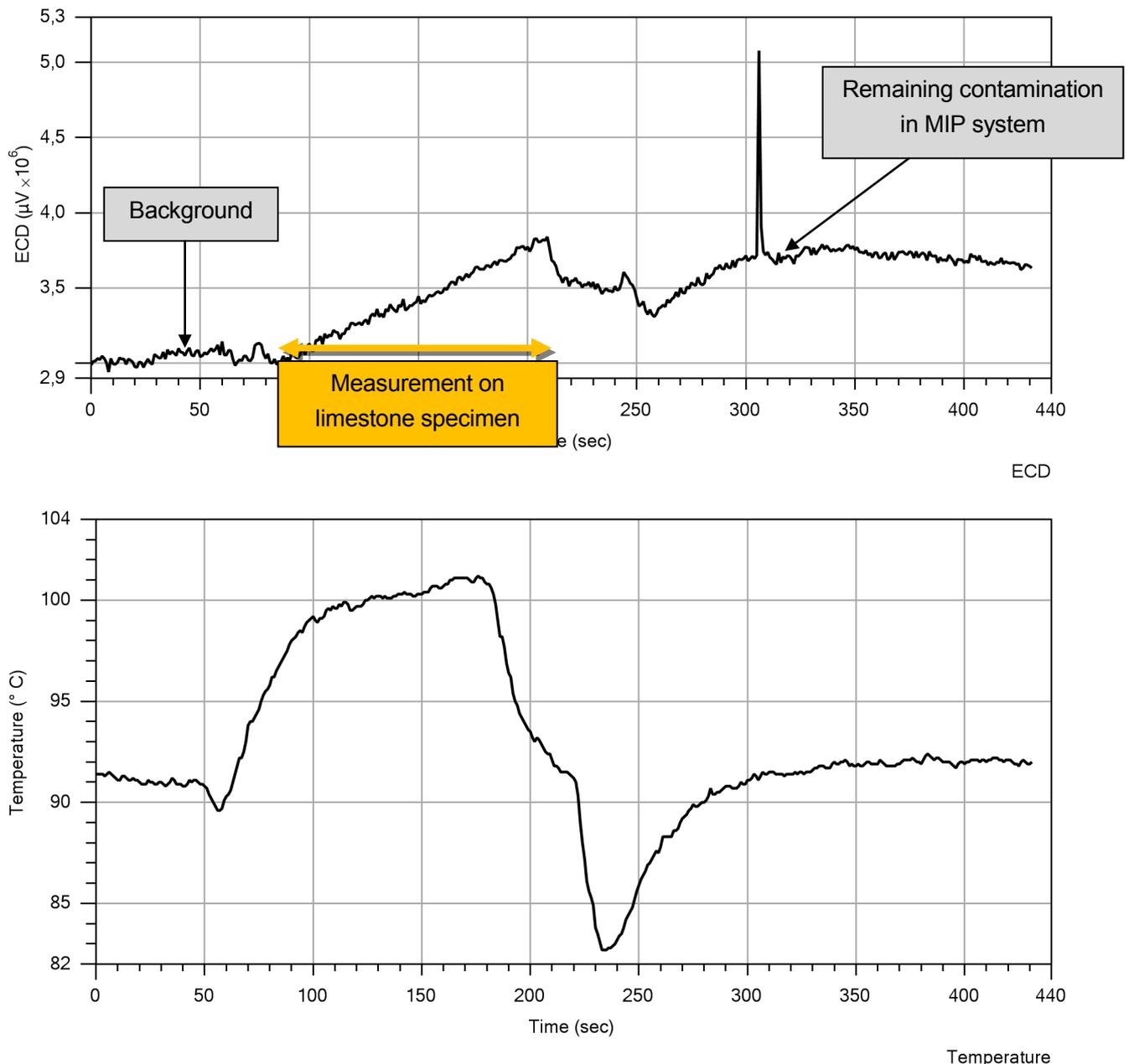


Figure 15: Results of test with Specimen 3. ECD response and temperature recorded by MIP probe are shown. For other experimental details, see text and Table 1. (Files: KS-Specimen-3-pre-ECD.jpg; KS-Specimen-3-pre-temp.jpg)

2.3.8. Effect of occurrence of gap between limestone and MIP probe

Experiments with Specimens 5 and 7 were carried out in order to investigate the capability of the MIP probe to detect contaminant in the limestone with a gap between limestone and MIP probe of 2 mm (cf. Table 1). As the MIP probe did not detect the contaminant in the first experiment with Specimen 5 (Figure 16), it was decided to increase the temperature of the water in the vat slightly from 18°C to 21°C for the experiment with Specimen 7. This was done, because the experiment with Specimen 5c

that was carried out at a vat water temperature of 31°C suggested that increasing the temperature of the water in the vat would significantly improve the response of the MIP probe (see also results below). However, though the temperature in the vat was increased for the experiment with Specimen 7, the MIP probe still showed a very low response to the contamination present in the limestone (Figure 17). Thus, the results indicate that the current construction of the MIP probe is inadequate for detection of contaminant in limestone as soon as direct contact between limestone and MIP probe is lost. The possible reason for this is elaborated upon below in Section 2.3.13 (Heat transport modelling).

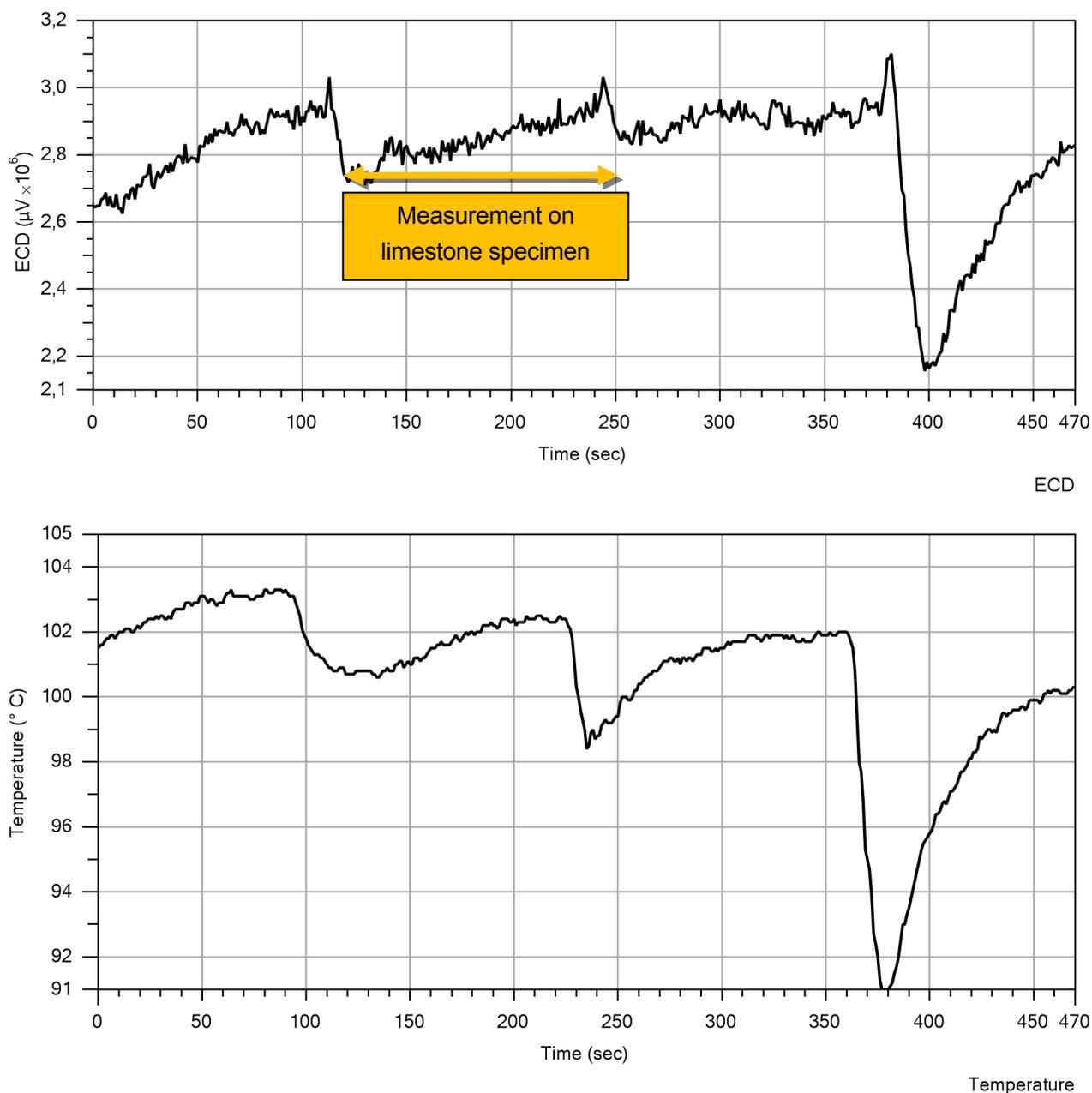


Figure 16: Results of test with Specimen 5. ECD response and temperature recorded by MIP probe are shown. For other experimental details, see text and Table 1. (Files: KS-Specimen-5-post-ECD.jpg; KS-Specimen-5-post-temp.jpg)

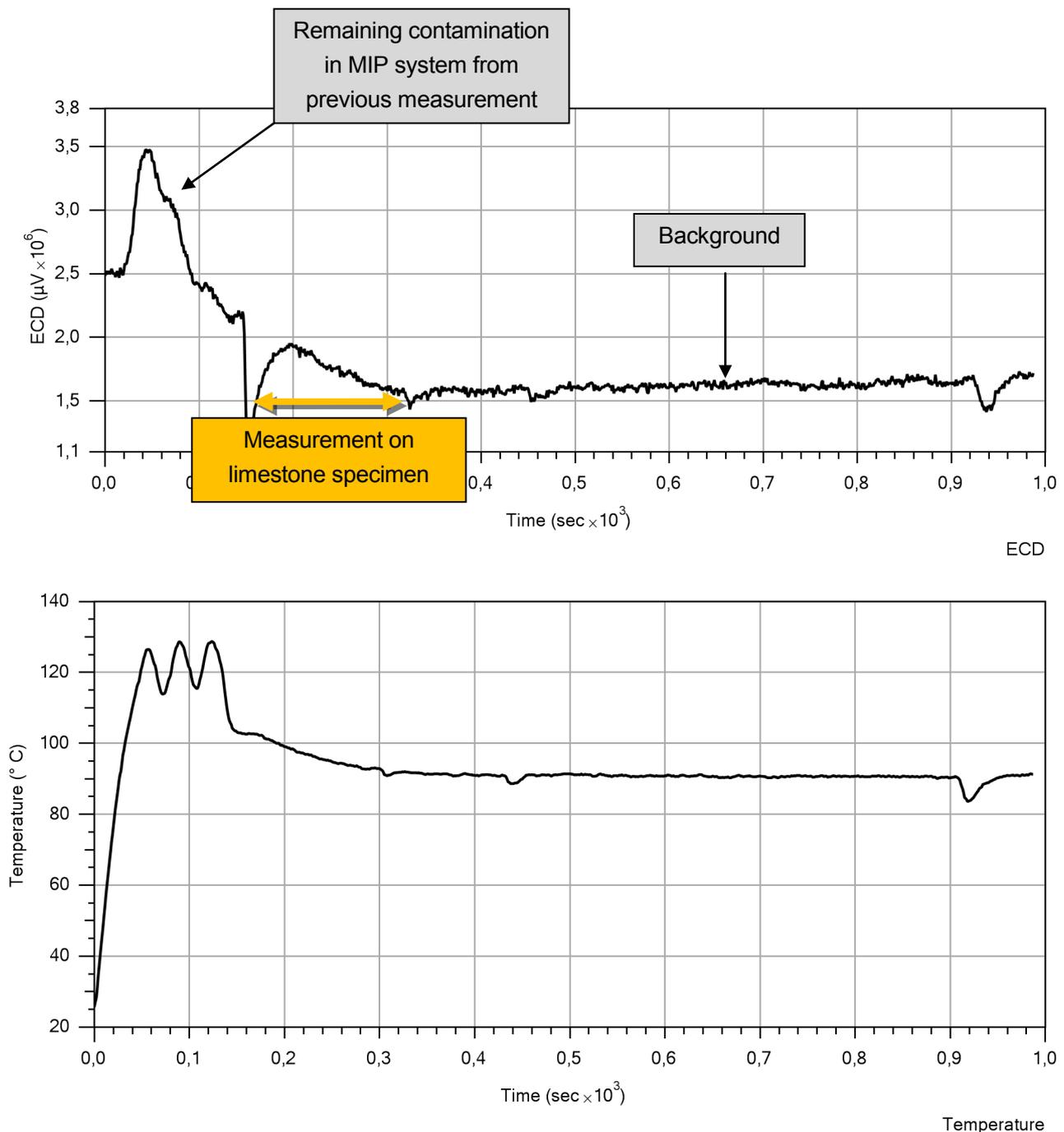


Figure 17: Results of test with Specimen 7. ECD response and temperature recorded by MIP probe are shown. For other experimental details, see text and Table 1. (Files: KS-Specimen-7-ECD.jpg; KS-Specimen-7-temp.jpg)

2.3.9. Effect of water temperature in vat

Experiments with Specimens 5c and 1b were performed in order to test the influence of the temperature of the water in the vat on the peak signal obtained by the MIP probe. This was done because it was suspected that the lack of detection of contaminant in the experiments with a gap between limestone and probe was due to cooling by convection in the gap.

As shown in Figures 18 and 19, the increase in vat water temperature improves the response of the MIP probe significantly, suggesting that improvement of the method could include development of the

set-up in a way that ensures the entrapment of the water between probe and limestone. This is further discussed below in Section 2.3.13 (Heat transport modelling) and was tested experimentally in Phase 2 of the project (cf. Chapter 3).

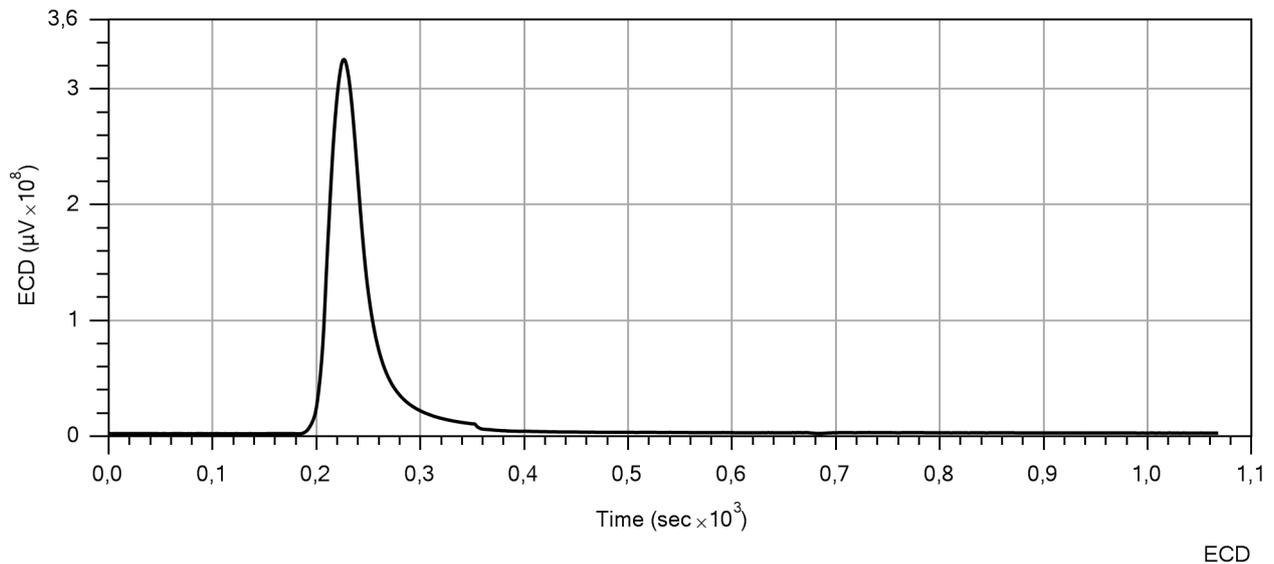


Figure 18: Results of test with Specimen 5c at 31°C. ECD response recorded by MIP probe are shown. For other experimental details, see text and Table 1. (Files: KS-Specimen-5c-ECD.jpg)

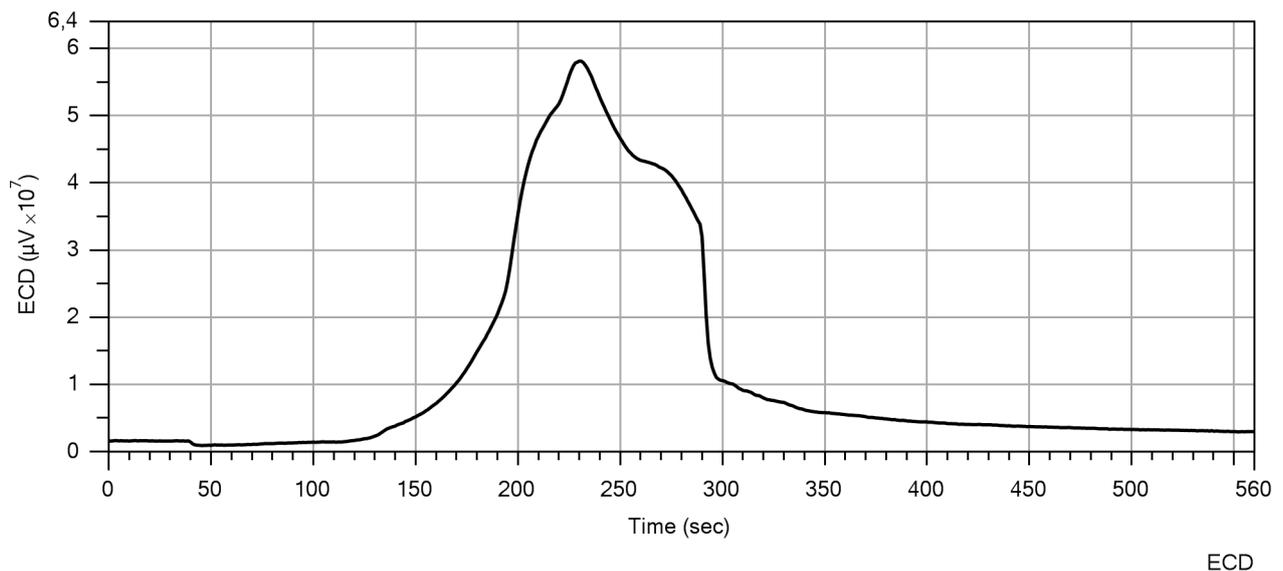


Figure 19: Results of test with Specimen 1b at 11°C. ECD response recorded by MIP probe are shown. For other experimental details, see text and Table 1. (Files: KS-Specimen-1b-ECD.jpg)

2.3.10. Considerations regarding temperature measurements with the probe

The limestone specimens did not reach temperatures sufficiently high to mobilize the PCE when the limestone was not in direct contact with the limestone. If the probe started from the same temperature as the water, the heating element stabilized at approximately 80°C, and from that point on the

temperature only rose very slowly. The probe temperature rose only as the water in the tank slowly became warmer.

When the temperature set point (120°C) is not achieved quickly, the temperature readings are not very informative. When the heating element reaches 120°C and the water was 18-20°C, then the readings were 80°C, so the temperature is measured somewhere in between the heating element and the water, and thus it does not provide the temperature of neither the outside of the probe nor the heating element. The temperature curves are to be studied keeping this in mind.

2.3.11. Sources of error - True concentrations in limestone specimens

Prior to the experiments with MIP measurements on prismatic specimens in the vat, it was discovered that the majority of prismatic specimens had initially been erroneously saturated in a 10,000 ppb PCE solution instead of the intended 1,000 ppb solution. As a consequence, it was decided to do an effort to re-saturate the specimens with a 1,000 ppb PCE solution before carrying out the experiments described above (cf. Section 2.2.3).

Chemical analyses of water samples taken before bringing the water in contact with the specimens show that the initial concentration of the saturation water was between 650 ppb and 930 ppb (Figure 20, "prior" samples). However, the majority of water samples from the PVC buckets after experiments contained considerably higher concentrations of PCE (Figure 20, "post" samples). This was the case for Specimens UCS-1, 1b, 5, 5a, 5c, and 7 where concentrations in the bulk water in the buckets were between 2,900 ppb and 6,800 ppb (Figure 20). The exception is Specimens 3 and 4 where concentrations of PCE in the bulk water were similar and c. 1,000 ppb prior to and after experiments.

The reason for the generally higher PCE concentrations observed in the bulk water in the PVC buckets after experiments compared to the PCE concentrations prior to experiments is most likely that the PCE contamination from the initial erroneous saturation with too high PCE content was not removed by the oven drying process applied. As a consequence, adsorbed PCE was dissolved in the bulk water of the buckets during the saturation process and caused higher PCE concentrations of the pore water in the prismatic specimens than intended. This is also partly reflected by the results from the analyses of rock chips taken prior to and after experiments in the vat, where chips taken from Specimens 3 and 4 show considerably lower sediment concentrations than the remaining Specimens (Figure 21).

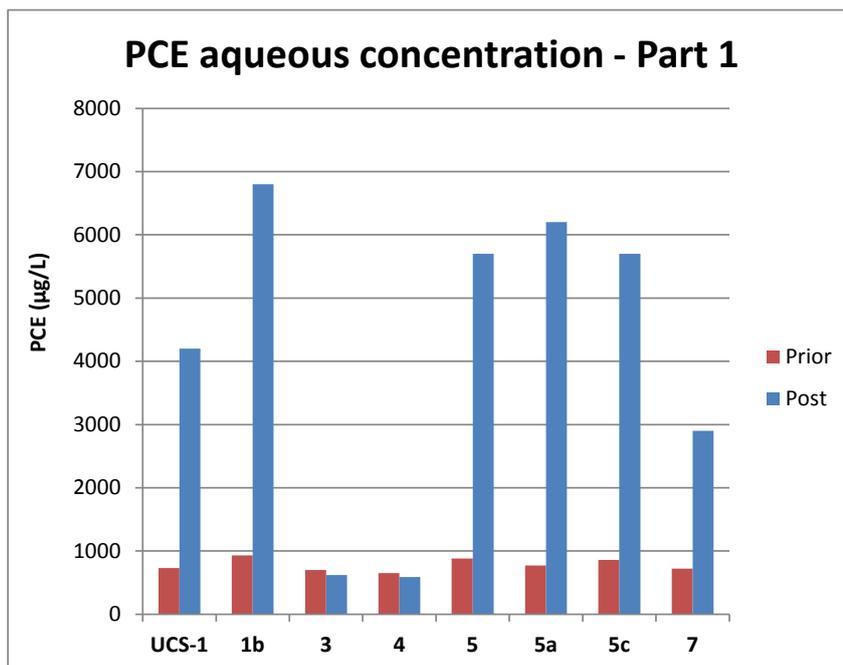


Figure 20: Aqueous concentration of PCE in bulk water used to saturate prismatic specimens in the NEMLA feasibility study – Phase 1. “Prior” refers to water samples taken from the freshly mixed PCE solution prior to contact with prismatic specimens. “Post” refers to water samples taken from the bulk water in the PVC buckets after the MIP experiment with the specific prismatic specimen was carried out.

If we assume no sorption, a porosity of 20-25%, and an average grain density of 2.67 g/cm³, an aqueous concentration of 1,000 ppb would give reason to a sediment concentration of c. 0.1 mg/kg dry matter. Comparing this with the data in Figure 21 partly confirms that the sediment concentration in Specimens UCS-1, 1b, 5, 5a, 5c, and 7 were higher than expected.

However, in general, i.e. also for Specimens 3 and 4, the measured sediment concentrations are 3-8 times lower than can be estimated from the aqueous concentrations after experiments (Figure 21) and with an assumption of no sorption. The reason for this discrepancy is most likely due to the fact that the external laboratory for this specific set of samples had chosen to measure the dry weight of the limestone chips prior to extraction of PCE from the sampled chips. Thus, the lid was removed from the sample container prior to extraction and analysis. As a consequence, it is likely that a large part of the PCE evaporated from the sediment sample container prior to analysis. The procedure was subsequently discussed with the external laboratory and changed for the Phase 2 experiments in order to avoid evaporation of contaminant during analysis.

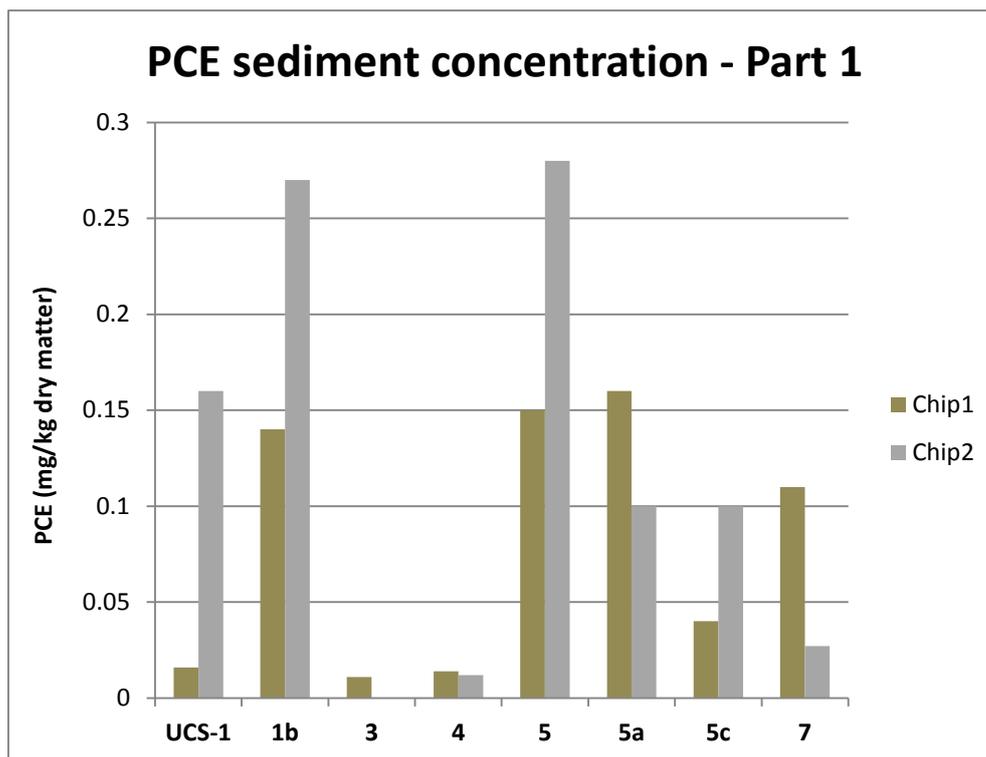


Figure 21: Measured content of PCE in limestone chips taken from the prismatic specimens used for MIP feasibility experiments. “Chip 1” refers to limestone chip sampled prior to test in the vat. “Chip 2” refers to limestone chip sampled after the test in the vat.

In general, it is assumed that the erroneous contamination of several of the prismatic limestone specimens has had an influence on the results of the MIP measurements in the experiments described above. Thus, the capability of the MIP method to measure PCE contamination is most likely overestimated somewhat in the experiments described above compared to field conditions where aqueous concentrations of 1,000 ppb and below are more likely than up to 10,000 ppb. However, the MIP probe was capable of measuring the contamination in Specimens 3 and 4 (cf. Figures 12 and 15), where the PCE concentration in the porewater was below 1,000 ppb and the solid PCE concentration was also low (Figures 20 and 21).

In summary, it is assumed that the erroneous contamination of the prismatic limestone specimens has had limited influence on the general conclusion that can be drawn from the experiments; namely that the current construction of the MIP probe is inadequate for detection of PCE contamination in limestone as soon as direct contact between limestone and MIP probe is lost.

2.3.12. PCE concentrations in vat

Figure 22 shows the PCE concentration in the water in the vat after the prismatic specimen was removed from the vat. As shown, PCE could be detected in the water in various concentrations. The concentration level is in general five orders of magnitude lower than in the porewater of the limestone specimens, suggesting that loss of contaminant to the water in the vat during experiments is limited. A rough mass balance calculation suggests that the mass loss of PCE to the water in the vat is c. 1%,

assuming an average concentration in the vat water of 0.5 ppb, a porosity of the limestone specimen of 25%, and an initial porewater concentration of 5,000 ppb.

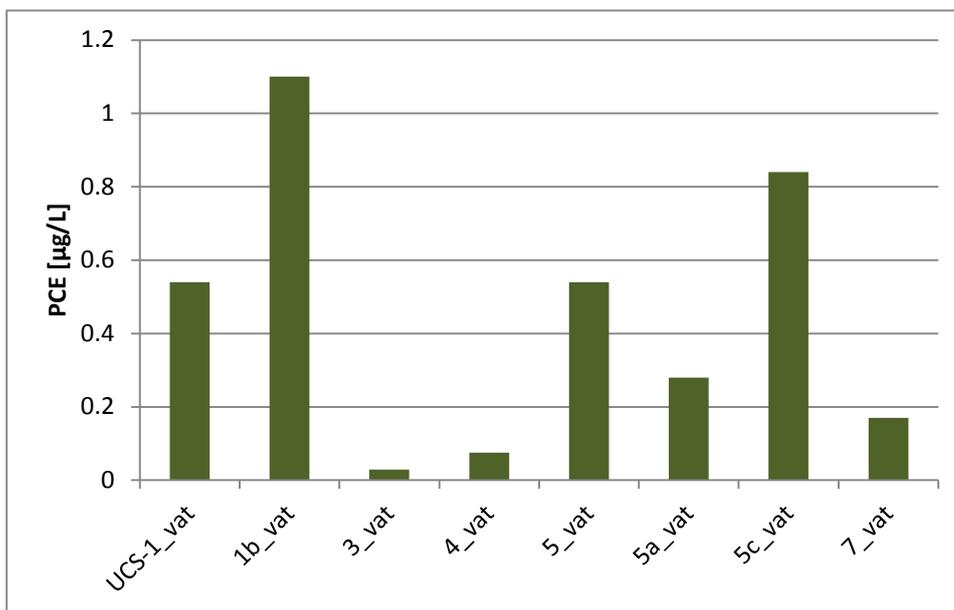


Figure 22: Measured concentration of PCE in vat water after experiments.

2.3.13. Heat transport modelling

As a consequence of the results obtained above, COWI/Probing.dk carried out some simple thermodynamic modelling in an effort to explain why the contaminant is not detected when a gap between limestone and probe is present. The results of the modelling are provided below.

To visualize the heat transfer processes taking place, the simulations were produced using the freeware Energy2D. All simulations are 2D simulations made from the same crude sketch and as such not exact simulations of the experiments carried out but rather conceptual models aimed at contributing to a better understanding of the obtained experimental results.

All figures shown are snap-shots taken at 1:45 min after the heater was turned on in the 2D model, and the background temperature was set to 18°C. Water, limestone and heater have all been defined through textbook parameters. The heating element has a thermostat in the center with a simulated temperature of 120°C. The applied effect of the heating element is reverse engineered to match the temperature measurements from our first experiment.

From the results in Figures 23-25 it is evident that convection takes place and causes low temperatures in the limestone specimen as soon as a gap between limestone and heater block is present.

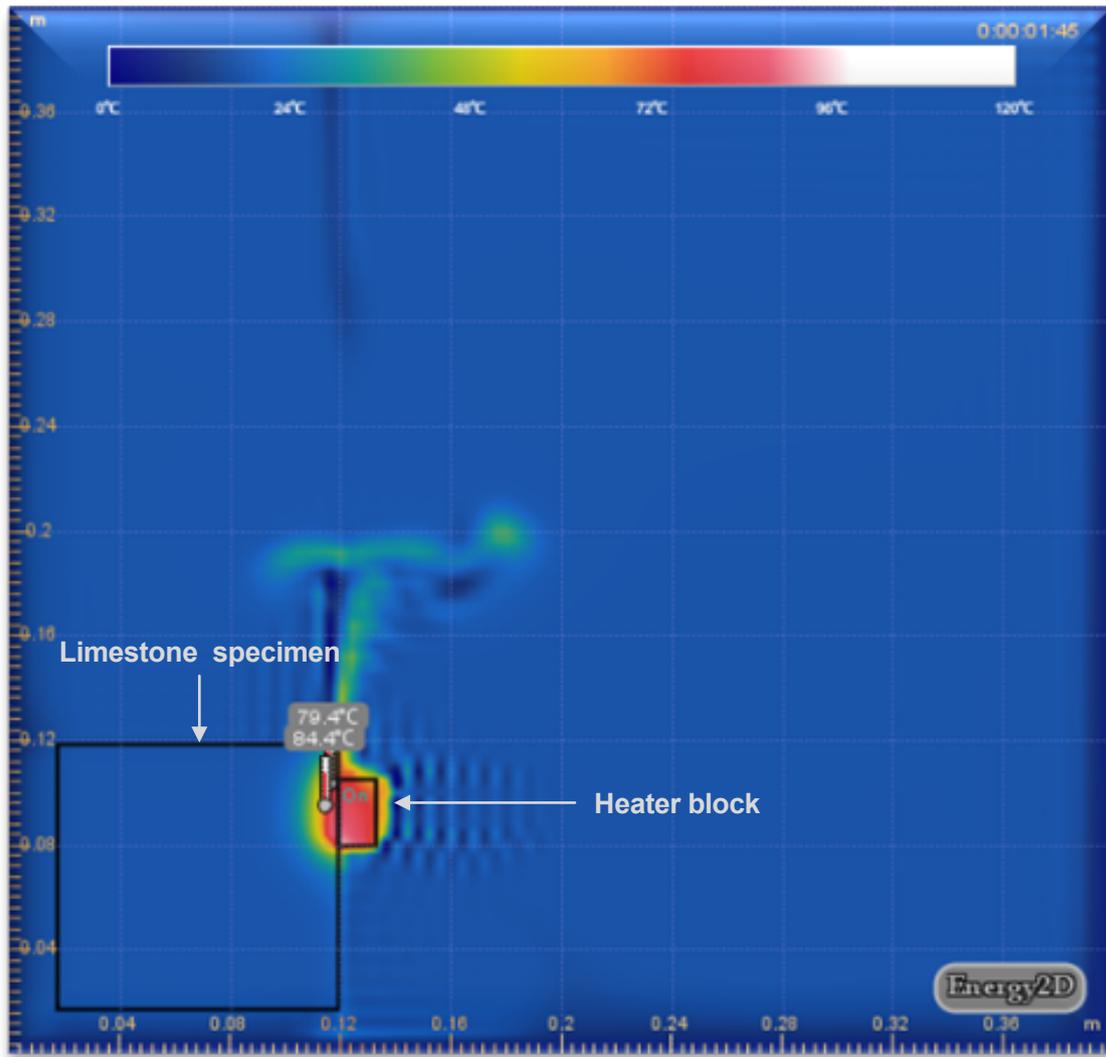


Figure 23: Results of heat transport simulation. Distance = 0 mm. Temp in specimen = 80-85 °C.

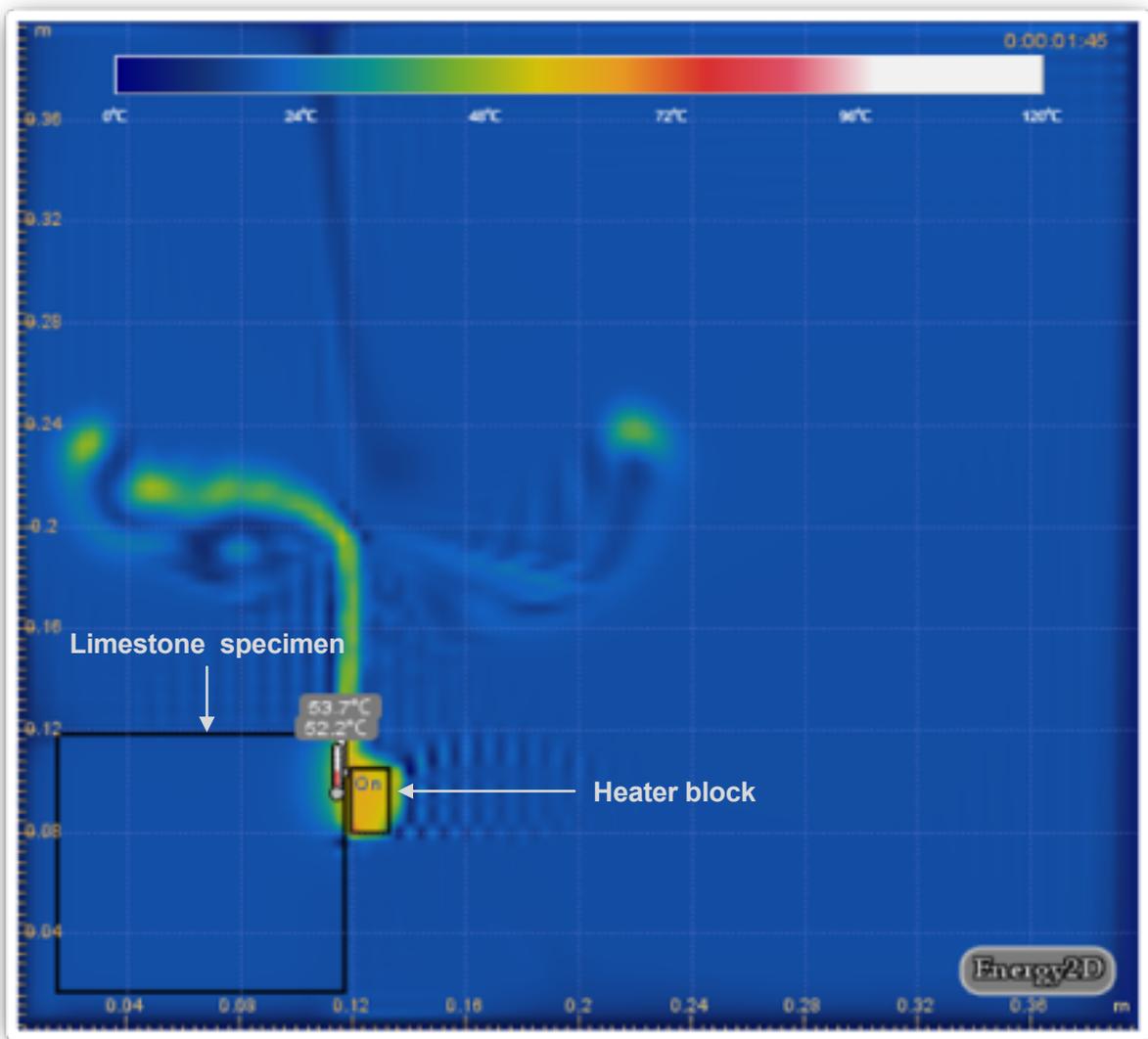


Figure 24: Results of heat transport simulation. Distance = 2 mm. Temp in specimen = 50-52 °C.

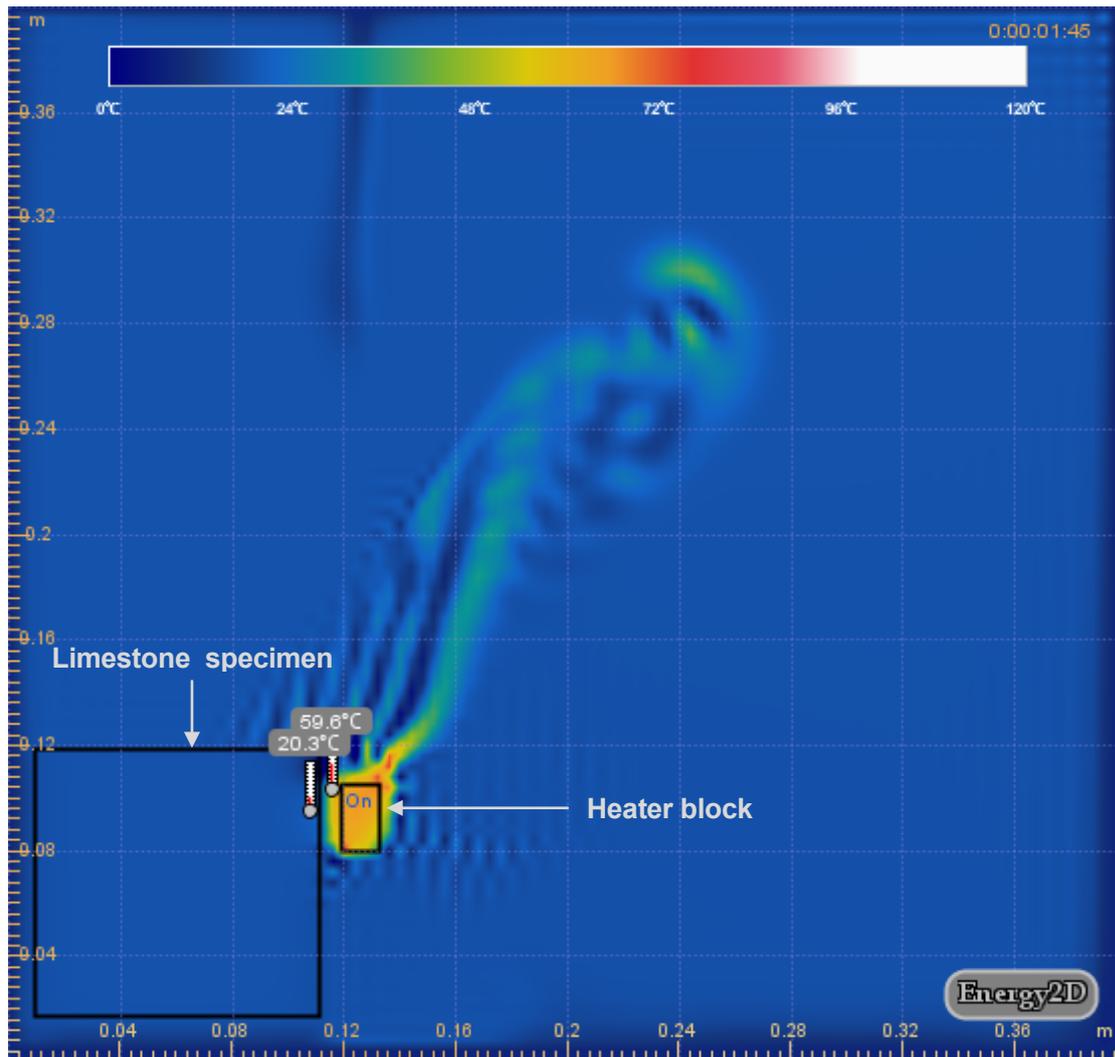


Figure 25: Results of heat transport simulation. Distance = 8 mm. Temp in specimen = 20 °C.

To illustrate a possible way forward to achieve higher temperatures in the limestone, a simulation was performed with 8 mm distance between limestone specimen and heater block. In the same time the space between heater block and limestone was confined by a simulated cover of rubber. In the simple 2D model set-up, this results in a limestone temperature of 47°C compared to 20°C without cover (compare Figures 25 and 26).

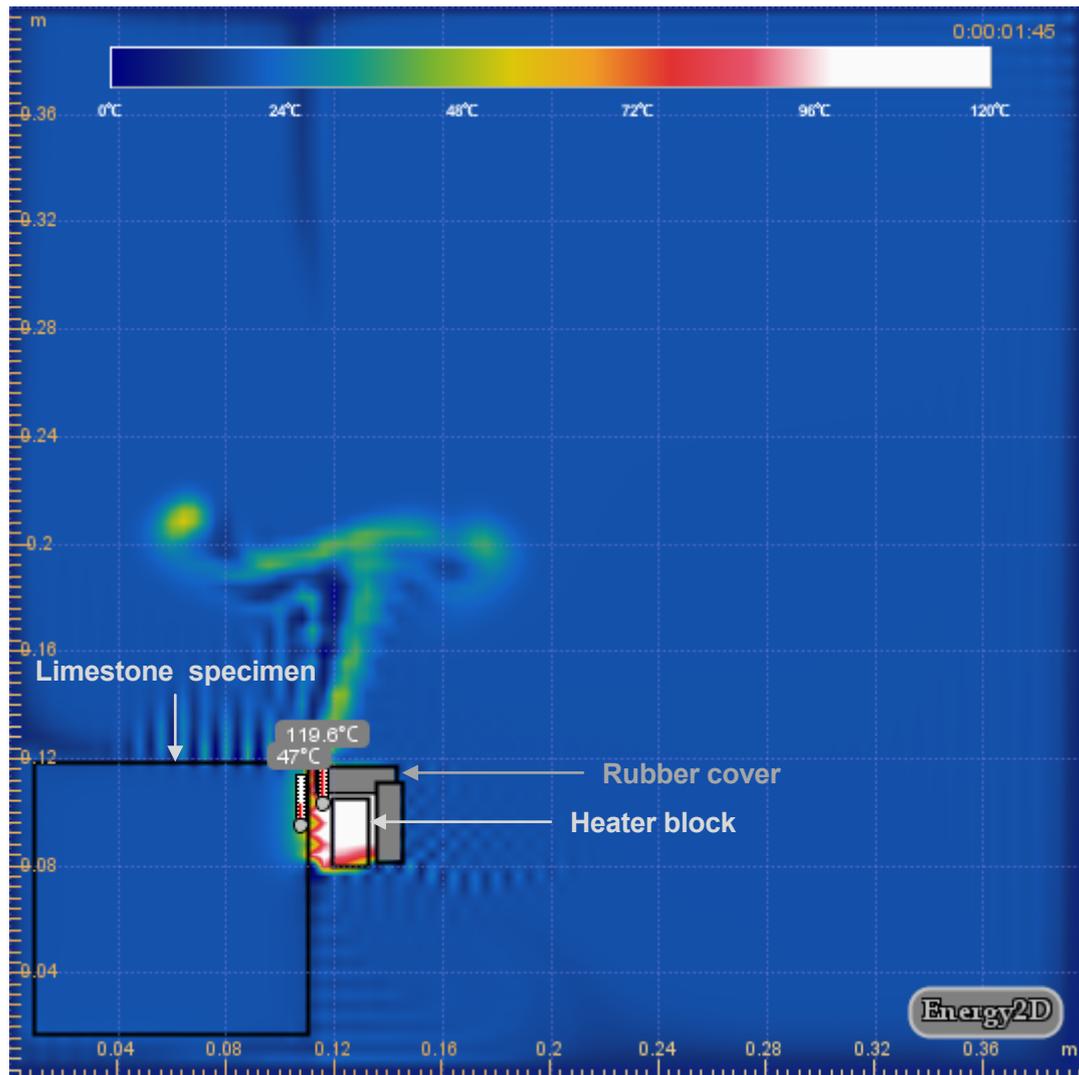


Figure 26: Results of heat transport simulation with rubber cover. Distance = 8 mm. Temp in specimen = 47°C.

2.4. Preliminary conclusions and considerations

In conclusion, it is suggested that the inadequate detection of contaminant by the MIP probe even at very small distances between probe and limestone was mainly caused by convection in the space between limestone and MIP. Thus, when conducting the experiments with a 2mm gap between limestone and probe, the heat from the heater block of the MIP probe must pass through liquid water. As the water apparently conducts energy flow away from the gap at a higher rate than energy is transferred in the direction of the limestone, convection sets in and results in low temperatures in the limestone and little or no transfer of contaminant to carrier gas of the MIP set-up. The latter conclusion is supported by simple numerical calculations performed by COWI/Probing.dk.

Based on these conclusions a number of ways forward in the project were discussed at a meeting on 23.09.2015. With 7 limestone specimens left for further tests, it was decided to continue the feasibility study in a second phase with a modified set-up of the MIP probe system such that convection in the gap between limestone and MIP probe was limited as much as possible.

3. Phase 2 – Testing alternative solutions

3.1. Background

Based on the findings from Phase 1 of the project, possible ways forward were discussed at the TAC-meeting on 23.09.2015. Based on the discussion, it was decided to continue the project with Phase 2, where specific focus should be on testing the feasibility of the MIP probing technology under the assumption that gaps between limestone and MIP probe can be confined.

Thus, the aim of Phase 2 of the NEMLA feasibility study was to set up laboratory experiments in a way such that heat transfer from the heating block of the MIP probe to the limestone specimen was facilitated and convection between heater and limestone could be avoided. Thereby, the aim was to provide an experimental basis for decisions regarding the future direction of the NEMLA project.

3.2. Methodology

Basically, the same methodology was used in Phase 2 of the project as in Phase 1. Thus, tests were carried out using the standard MIP probe to measure contaminant concentration in prismatic limestone specimens that were submerged in a water filled vat. Specimens had prior to tests been saturated with water with a specific contaminant concentration by imbibition saturation in plastic buckets. Furthermore, water and limestone samples were taken prior to and after experiments in order to understand possible variations occurring as a consequence of the experimental procedure.

The detailed description of this methodology is provided in Sections 2.2.3 to 2.2.5. However, the following changes were applied in Phase 2.

3.2.1. *Orientation of MIP probe and limestone in vat*

In order to better simulate the conditions in an open borehole, it was decided to change the placement of the MIP probe in the vat from a horizontal position to a vertical – or upright – position (Figure 27). In addition to the better simulation of true borehole conditions, the vertical orientation ensured that convection caused by the heat from the heater block, if occurring, would transport contaminated water in a vertical direction to the MIP membrane, thereby possibly increasing the sensitivity of the MIP measurement.

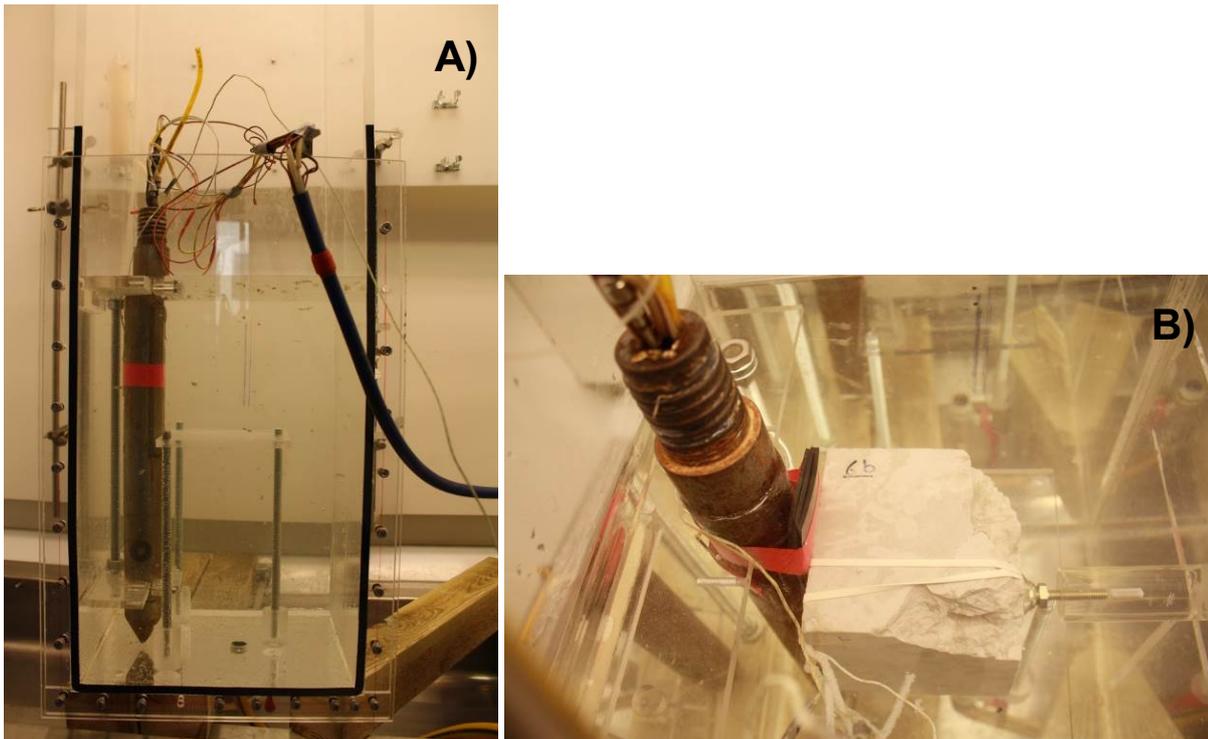


Figure 27: Photographs showing the experimental set up for the Phase 2 experiments in the NEMLA feasibility study. A) Position of MIP probe in the vat. B) Placement of limestone specimen during MIP measurements.

3.2.2. Temperature measurements

Since the data obtained in Phase 1 were limited with regard to temperature development during the experiments, it was decided to include detailed temperature measurements in the Phase 2 experiments. Thus, a number of temperature sensors (thermocouples) were placed at the surface of the limestone as well as in the vat and on the backside of the MIP probe. The placement of thermocouples is illustrated in Figure 28.

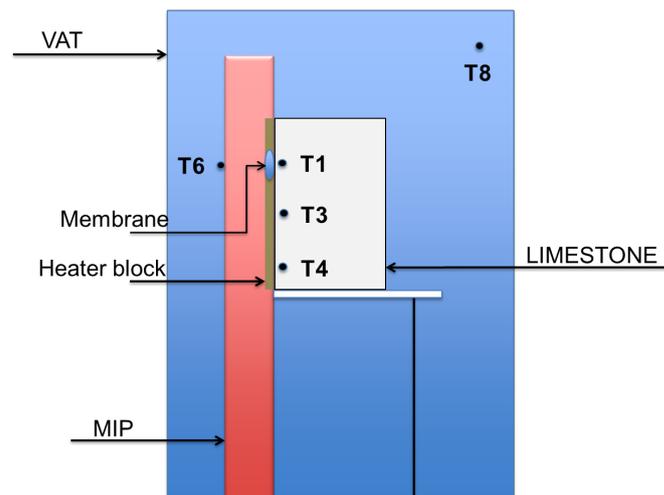


Figure 28: Schematic illustration of experimental set up for the Phase 2 experiments in the NEMLA feasibility study, including placement of thermocouples used to continuously measure the temperature during experiments. T1, T3, T4, T6, and T8 refer to individual thermistors.

A pico® TC-08 Thermo Couple Data Logger was used to collect data from the thermocouples with a sampling rate of one measurement per second, and the PicoLog software was used to export data to excel spreadsheet format for further analysis.

Thermocouples measuring the temperature at the limestone surface were placed in cuts made in the limestone surface (Figure 29).

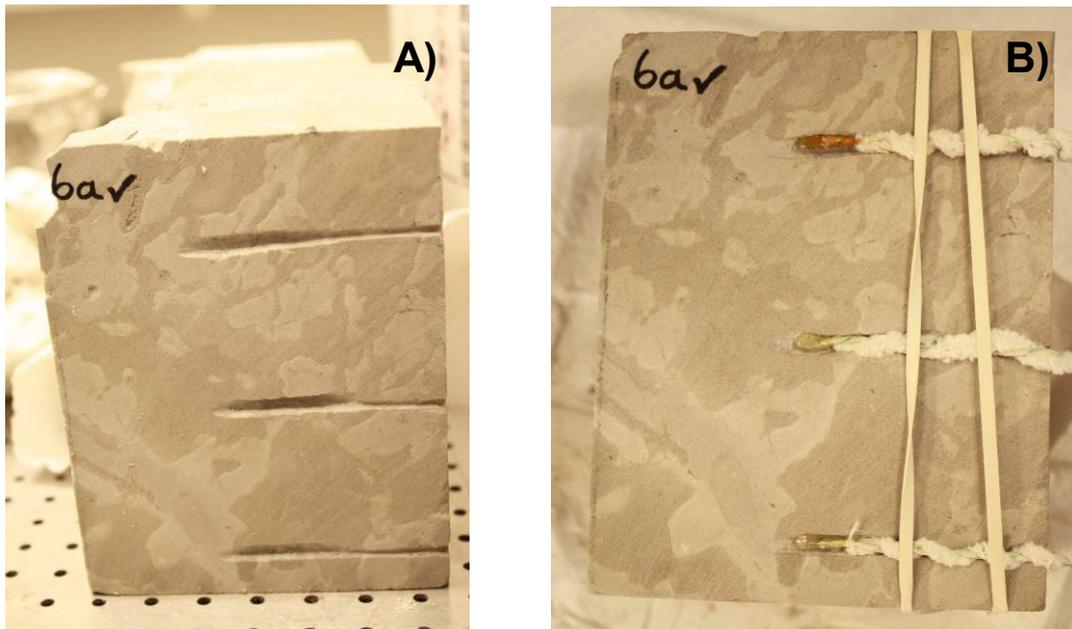


Figure 29: Photograph showing placement of thermocouples at the limestone surface for the Phase 2 experiments. A) cuts made for thermocouples. B) Placement of thermocouples.

3.2.3. *Confinement of gap between heater block and limestone*

In order to confine the gap between MIP probe and limestone specimen and to ensure better transmission of heat from the heater block to the limestone specimens, a number of special cut and 2 mm thick pieces of Viton rubber were placed between limestone specimens and MIP probe (Figure 30). The exact number of Viton rubber pieces depended on the desired distance between MIP probe and limestone specimen in the specific experiment. The experimental plan is presented in Table 2 (cf. Section 2.4.4).

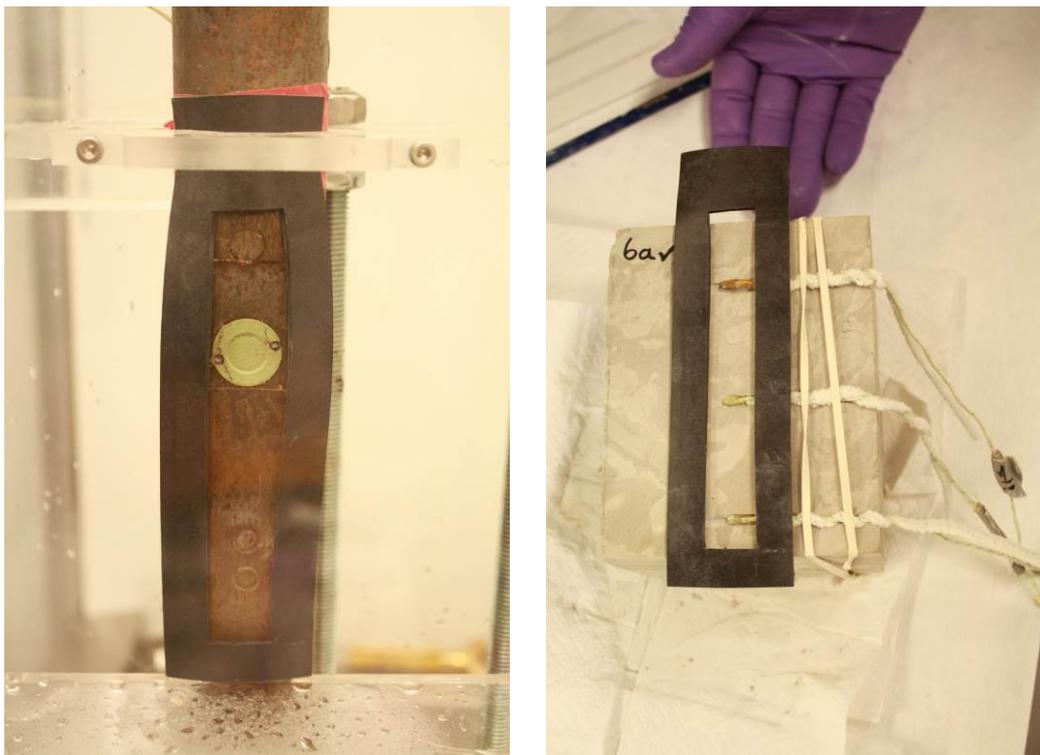


Figure 30: Photographs showing the placement of special cut Viton rubber pieces. A) Placement against MIP probe. B) Placement against limestone specimen.

3.2.4. *Aqueous concentrations and experimental plan*

For the experiments in Phase 2 it was decided to saturate the prismatic limestone specimens with a 500 ppb PCE solution. However, chemical analyses obtained after the experiments were finalized, revealed that for three of the tested specimens, the concentration of the contaminant solution was only 75 ppb (cf. Section 3.3.1). The error in preparation of the contaminant solution has most likely occurred due to inadequate mixing of the solution or erroneous solution preparation.

Specific implications for the experimental results are discussed in Section 3.3.

3.2.5. *Experimental plan*

With inclusion of the above mentioned modifications of the experimental set-up, the overall plan for the experiments in Phase 2 was to carry out a number of experiments similar to the experiments in Phase 1 and with an increasing gap between limestone specimens and MIP probe. The main purpose of these experiments was to investigate the maximum gap distance at which PCE contamination of the limestone could be measured under ideal laboratory conditions.

In all, six (6) MIP measurements were carried out, including five (5) measurements on limestone specimens and one (1) blank measurement where the limestone specimen was replaced by a Viton rubber plate in the experimental set-up.

Experimental details are provided in Table 2.

Table 2: Experimental plan for the NEMLA feasibility study Phase 2 experiments.

Blok ID	PCE conc ($\mu\text{g/L}$)	Gap size
1a	~75	0 mm
6a	~500	2 mm
8a	~500	4 mm
6b	~75	6 mm
6c	~75	10 mm
none/blank	-	10 mm

3.3. Results

The experiments in Phase 2 were all carried out on 01.03.2016 starting with a response test followed by experiments with prismatic limestone specimens where increasing distances between MIP probe and limestone specimens were tested. The final test comprised a blank test (cf. Section 3.2.3). Results are presented below.

3.3.1. PCE concentrations in water and sediment

Figure 31 shows the aqueous concentration of PCE in the plastic buckets used for the saturation of the prismatic specimens. As shown, the concentration of PCE prior to experiments is generally comparable to the concentration measured after experiments. This indicates that no or very little loss of PCE by evaporation has occurred during the period where saturation was allowed to take place.

In contrast to the Phase 1 experiments, the similar concentrations prior to and after experiments indicate that the prismatic limestone specimens were clean and free of PCE prior to the experiments.

Furthermore, Figure 31 shows the fact that Specimens 1a, 6b, and 6c were saturated in a 75 ppb PCE solution while Specimens 6a and 8a were saturated in a 500 ppb PCE solution.

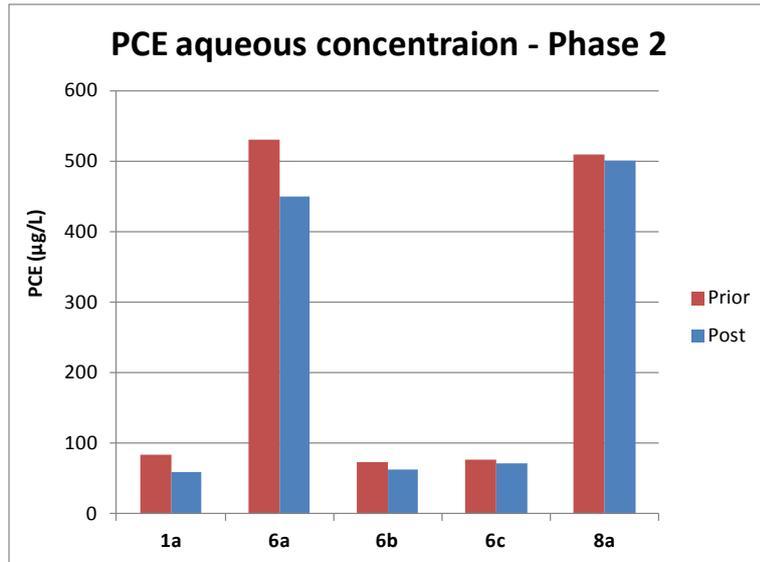


Figure 31: Aqueous concentration of PCE in bulk water used to saturate prismatic specimens in the NEMLA feasibility study – Phase 2. “Prior” refers to water samples taken from the freshly mixed PCE solution prior to contact with prismatic specimens. “Post” refers to water samples taken from the bulk water in the plastic buckets after the MIP experiment with the specific prismatic specimen was carried out.

The measured sediment concentrations also show similar content of PCE prior to and after experiments (Figure 32). The exception is Specimen 6a where the solid concentration of PCE is somewhat lower after the experiment than prior to the experiment. This may indicate that some loss of PCE to the atmosphere occurred during the experiment. However, the difference may also be due to local porosity variations in Specimen 6a giving reason to different measured concentrations in the two chips. Specimens 1a, 6b, and 6c have higher sediment content of PCE after experiments than prior to experiments, which is interpreted as due to such local porosity variations.

In Figure 32, also an estimate on the expected sediment concentration is included which is based on the measured aqueous PCE concentration in Figure 31. The estimate is based on an assumption of no sorption together with a porosity of 25% and a grain density of 2.67 g/cm³. As shown, the estimated sediment concentration is considerably lower than the measured concentrations, indicating that PCE sorbs to the limestone surface.

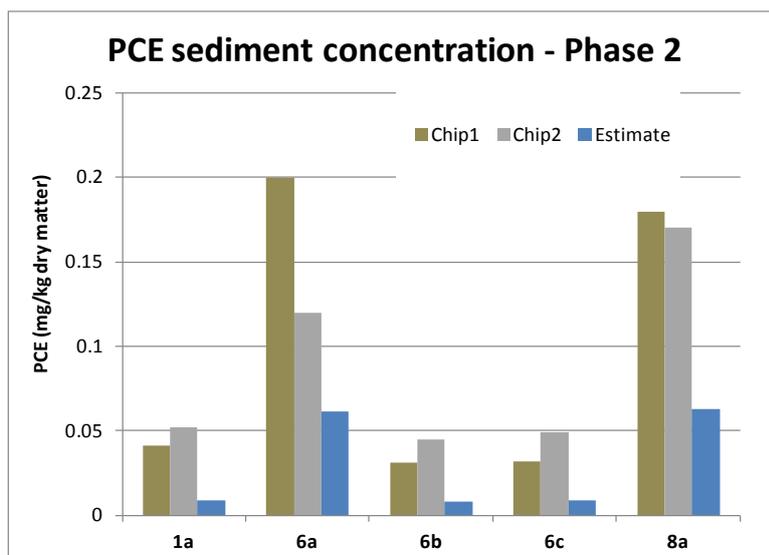
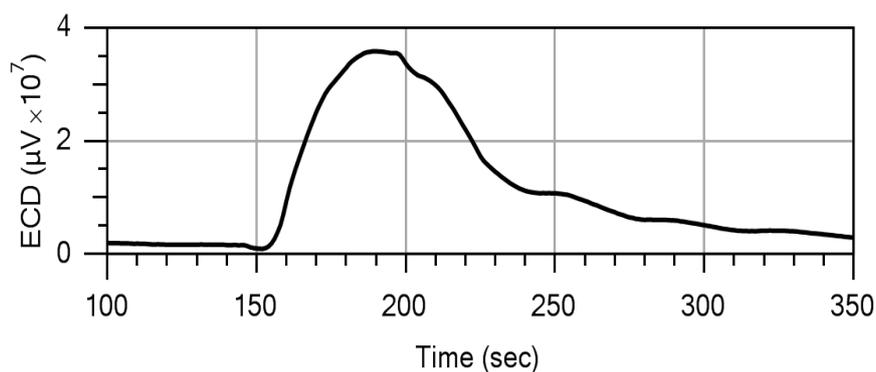


Figure 32: Measured content of PCE in limestone chips taken from the prismatic specimens used for MIP feasibility experiments. “Chip 1” refers to limestone chip sampled prior to test in the vat. “Chip 2” refers to limestone chip sampled after the test in the vat. “Estimate” refers to estimated sediment concentration based on an average of the aqueous concentrations (Figure 31) and assuming a porosity of 25% and a grain density of 2.67 g/cm³.

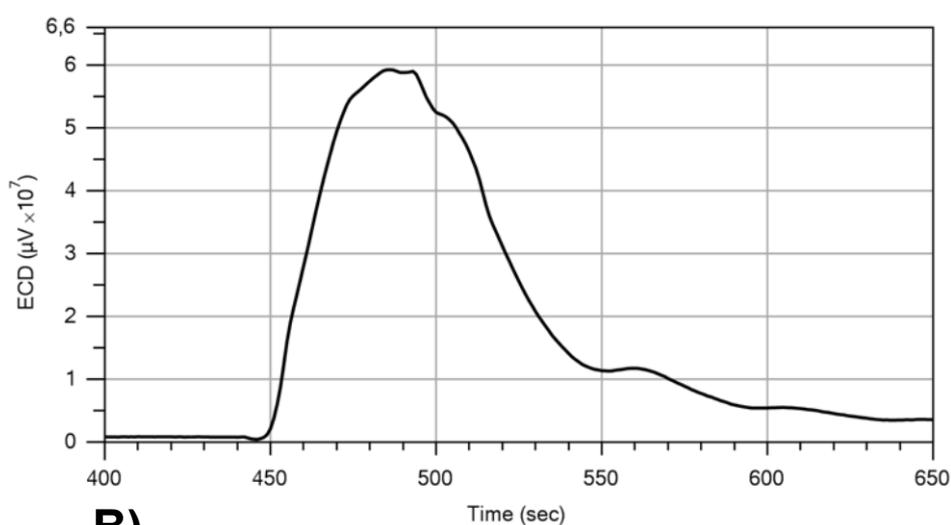
3.3.2. Response test

The response test in a 500 ppb TCE solution showed a response of c. 35,000 mV (Figure 33A) while a response test in a 1,000 ppb PCE solution showed a response of c. 60,000 mV (Figure 33B). Based on this observation, we assume proportionality between contaminant concentration and the ECD signal measured by the specific MIP probe used for the Phase 2 experiments. Bearing this in mind, it should be expected that the ECD signal from Specimens 1a, 6b, 6c would be c. 7 times lower than the signal obtained from Specimens 6a and 8a if all other conditions are similar.



A)

ECD



B)

ECD

Figure 33: Response tests on 01.03.2016 with MIP probe in pure solutions of A) 500 ppb TCE; B) 1,000 ppb PCE.

3.3.3. MIP and temperature results

0 mm gap

The results from the experiment with 0 mm gap between MIP probe and limestone specimen showed an ECD peak response of 3,300 mV for a specimen saturated with a 75 ppb solution (Figure 34). For comparison, the results from Phase 1 of the project showed ECD peak responses generally between 3,000 mV and 10,000 mV for specimens saturated in solutions with a much higher content of PCE. The reason for the improved sensitivity of the probe to identify PCE contamination in limestone in the Phase 2 experiment is most likely due to the different orientation of the experimental set up. Thus, the vertical set up used in Phase 2 enables both convection and gravity flow of contaminated water to pass the by the MIP membrane. However, the different response in Phase 2 may also be due to other facts such as a specifically well performing membrane, etc.

Overall, the response measured from Specimen 1a suggests that if good contact between specimen and MIP probe is obtained, there is reason to believe that the MIP technology can be used to identify realistic *in situ* concentrations of PCE in limestone.

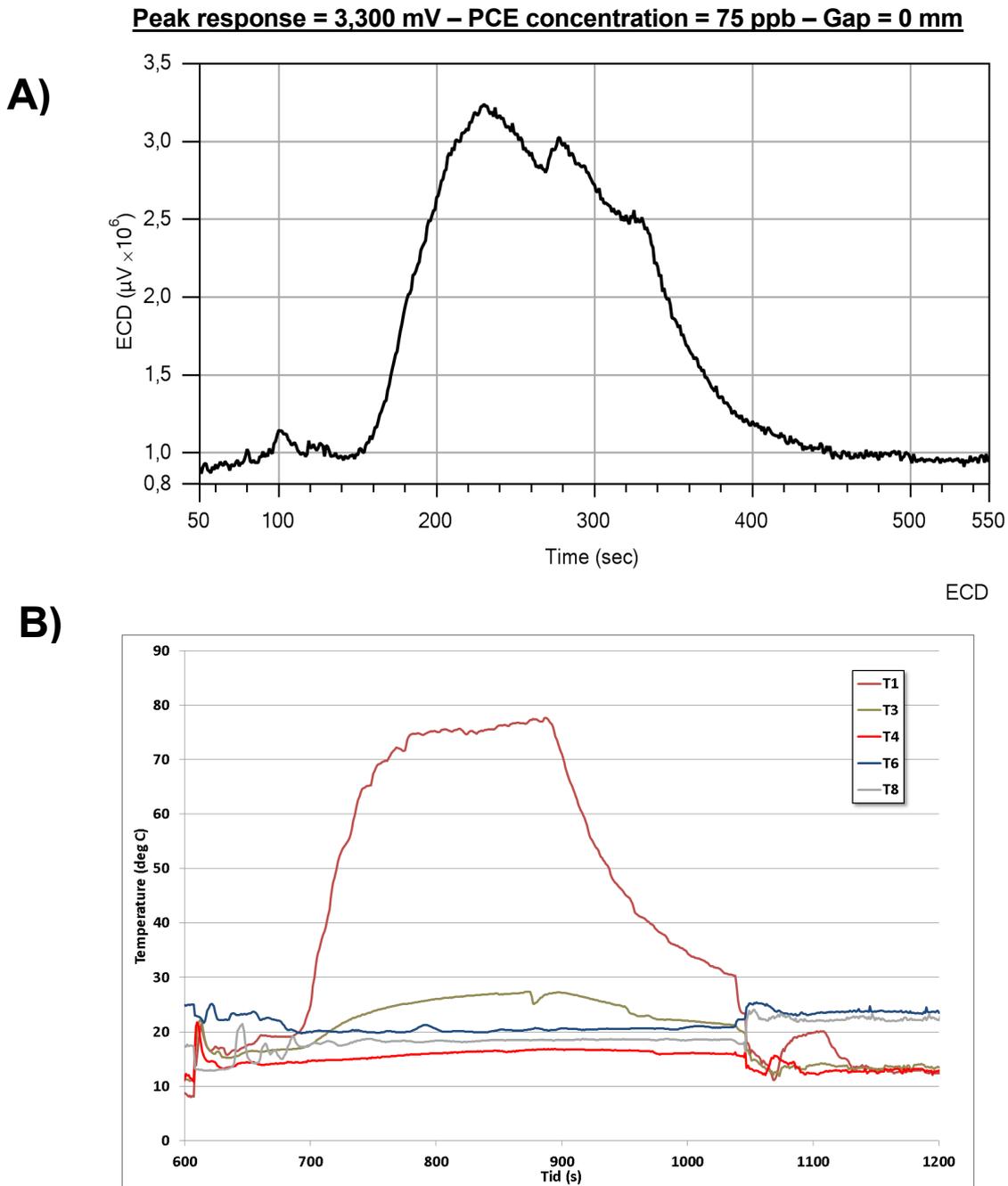


Figure 34: Results of test with Specimen 1a. A) ECD response recorded by MIP probe. B) Thermocouple temperature measurements. For experimental details, see text and Table 2. Note that the x-axis is not identical in the two different plots.

The temperature measurements show that heating occurs only in the uppermost third of the part of limestone in contact with the MIP probe (Figure 34B). Thus, thermocouple T1 shows a good response

to the heating and a maximum temperature of 78°C which is sufficient to allow evaporation of PCE from the limestone. However, all other thermocouples show little or no response to the heating. This indicates that only the upper part of the heater block is heated during measurements, and that the measurements with the MIP probe could probably be improved by extending the area where heating takes place.

2 mm gap

The experiment with 2 mm gap between limestone specimen and MIP probe also shows a clear response to the contamination with an ECD response of 2,200 mV. However, taking into consideration that the limestone specimen in this case was saturated with a 500 ppb PCE solution, the gap between limestone and MIP probe apparently gives reason to a considerable loss of signal. The confinement of the gap, however, seems to provide much better results than in Phase 1, where a gap of 2 mm gave reason to an almost complete loss of signal.

Comparison of Figures 35A and 35B shows a couple of incidents where the temperature and the ECD signal drop concomitantly. The reason for these incidences was difficulties with keeping a tight contact between limestone, Viton rubber, and MIP probe during the heating period. Therefore, at the incidents small amounts of cold water was allowed to slip into the otherwise confined space between probe and limestone specimen. From the results, it is obvious that it is of utmost importance for the MIP probe to measure the contamination that such incidences are avoided.

Compared to the experiment with zero distance between probe and limestone, the temperature on the backside of the MIP probe increased as a consequence of the experiment. The reason for this difference remains unexplained.

Peak response = 2,200 mV – PCE concentration = 500 ppb – Gap = 2 mm

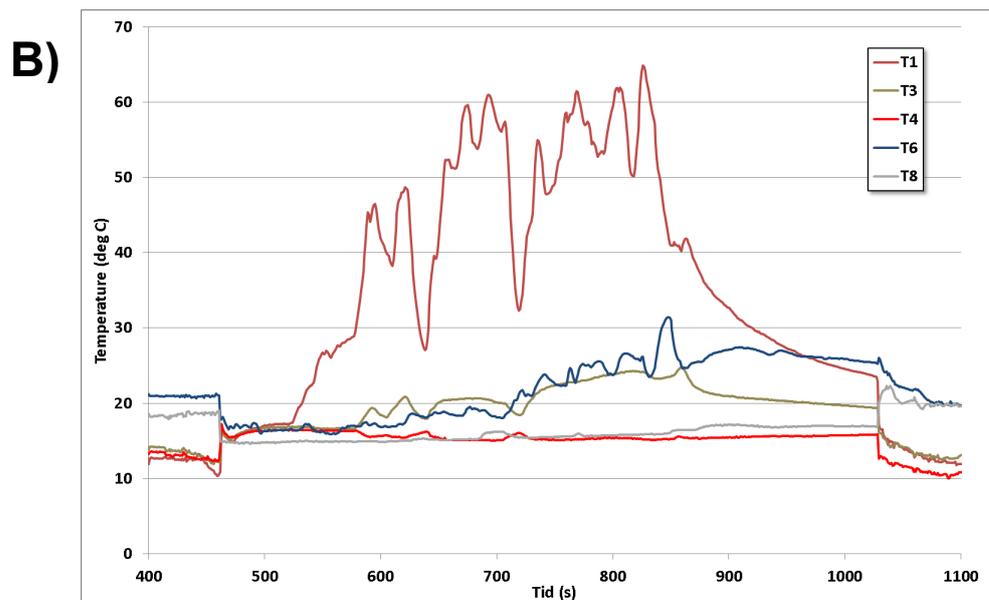
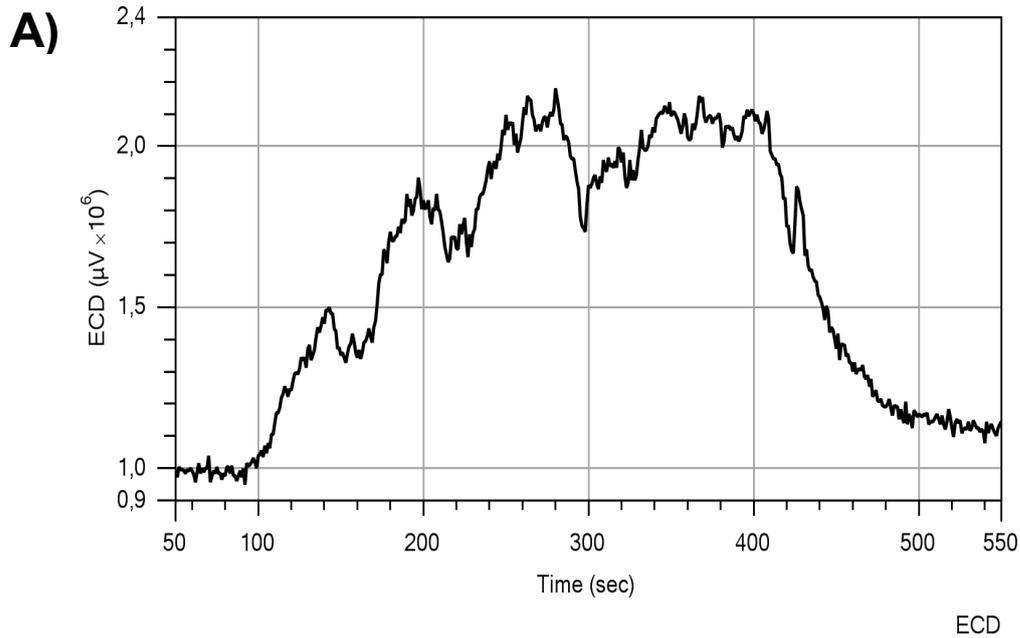


Figure 35: Results of test with Specimen 6a. A) ECD response recorded by MIP probe. B) Thermocouple temperature measurements. For experimental details, see text and Table 2. Note that the x-axis is not identical in the two different plots.

4 mm gap

Figure 36 shows that apparently the contamination of Specimen 8a with a 500 ppb PCE solution can be detected by the MIP probe even if there is a 4 mm confined gap between limestone and MIP probe. In correspondence with the increased distance, the peak response of 1,250 mV is lower than for the

measurement with a 2 mm gap (cf. Figure 35). It should be noted that the peak response is close to the peak response of c. 900 mV in the blank experiment (cf. Figure 39).

As indicated by the temperature measurements as well as the ECD curve, this experiment was carried out without any unintended leaks of cold water being introduced into the confined space between limestone and MIP probe. However, the temperature maximum at the limestone surface of 48°C suggested that the heat transfer from probe to limestone during the experiment was not optimal.

Peak response = 1,250 mV – PCE concentration = 500 ppb – Gap = 4 mm

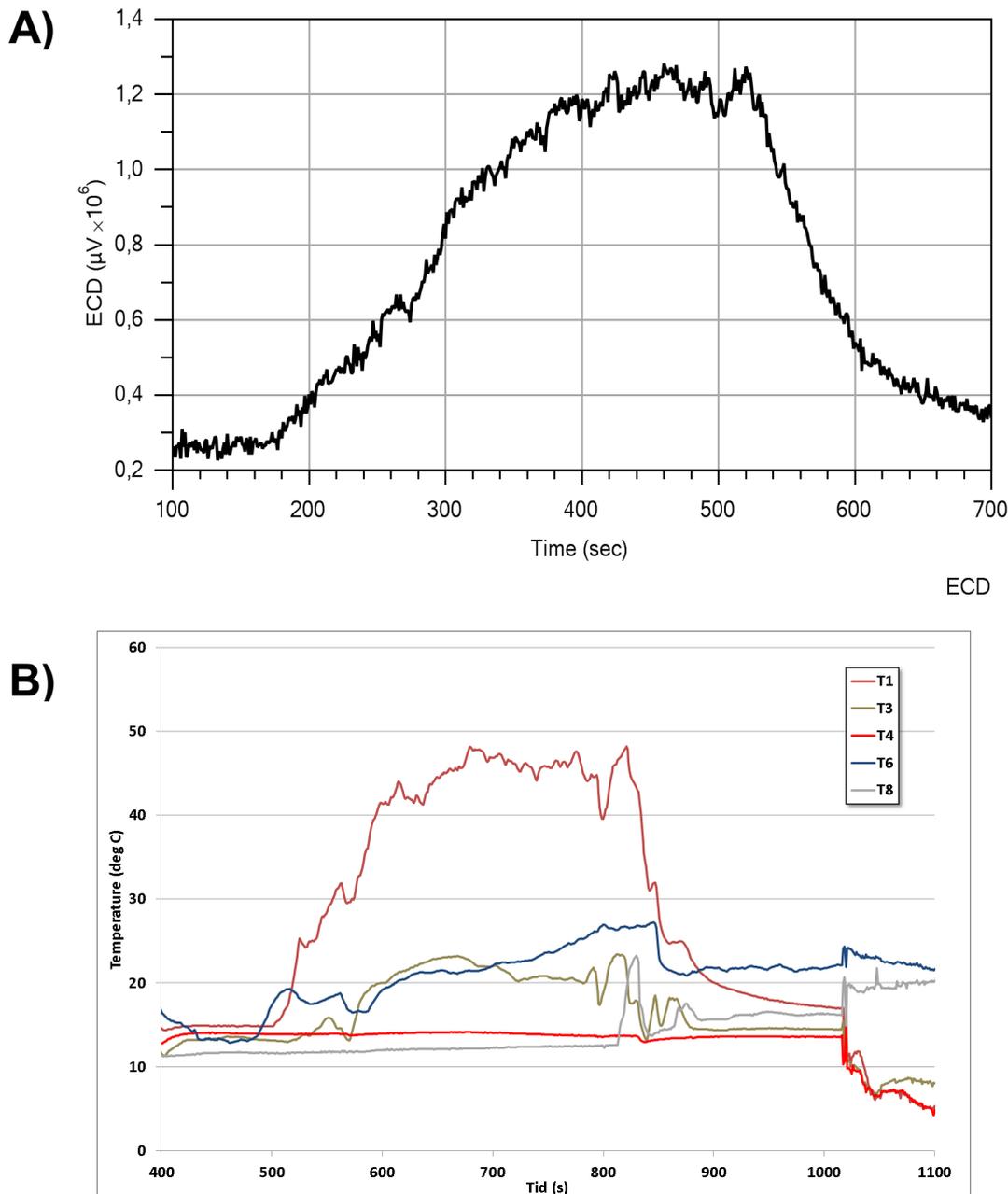


Figure 36: Results of test with Specimen 8a. A) ECD response recorded by MIP probe. B) Thermocouple temperature measurements. For experimental details, see text and Table 2. Note that the x-axis is not identical in the two different plots.

6 mm gap

At a gap distance of 6 mm the ECD response curve is not as good as in the previous experiments, although an elevated ECD response can be observed when the heater of the MIP probe is turned on (Figure 37). One explanation for the less distinct response curve could be that the PCE concentration in the limestone specimen in this experiment was only 75 ppb compared to 500 ppb in the experiments with 2 mm and 4 mm gap distance. The ECD response of 1,100 mV is very close to the peak response of 900 mV in the blank experiment, indicating that the response measured in this experiment is mainly caused by the background contribution coming from Viton rubber, and possible other temperature effects.

Compared to the previous experiments, a higher temperature is obtained at the limestone surface in this experiment. The reason is most likely that the Viton rubber packing was modified for this experiment such that the confined volume making up the space between limestone and MIP probe was smaller than in the previous experiments.

Peak response = 1,100 mV – PCE concentration = 75 ppb – Gap = 6 mm

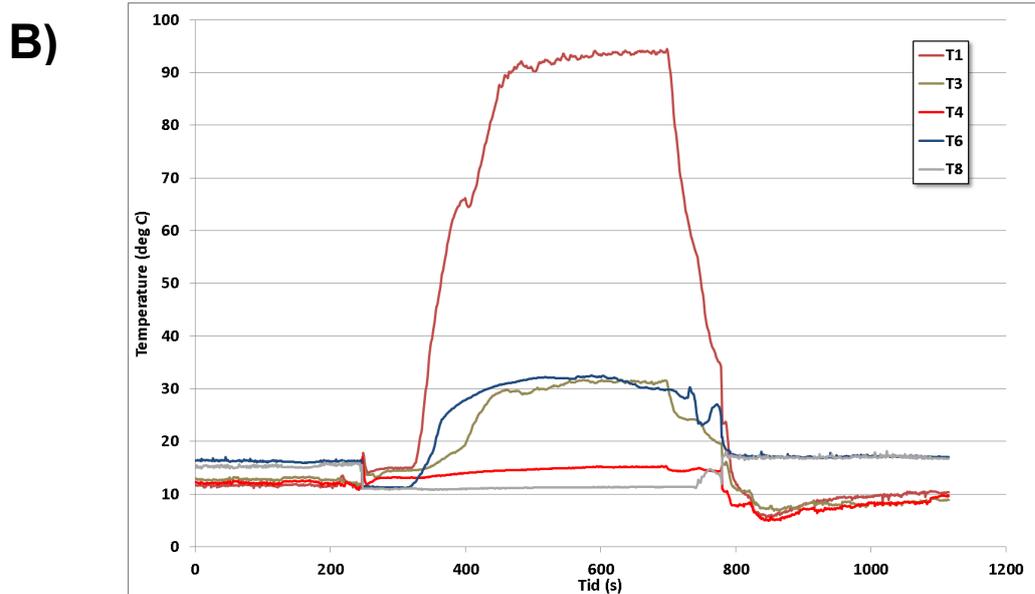
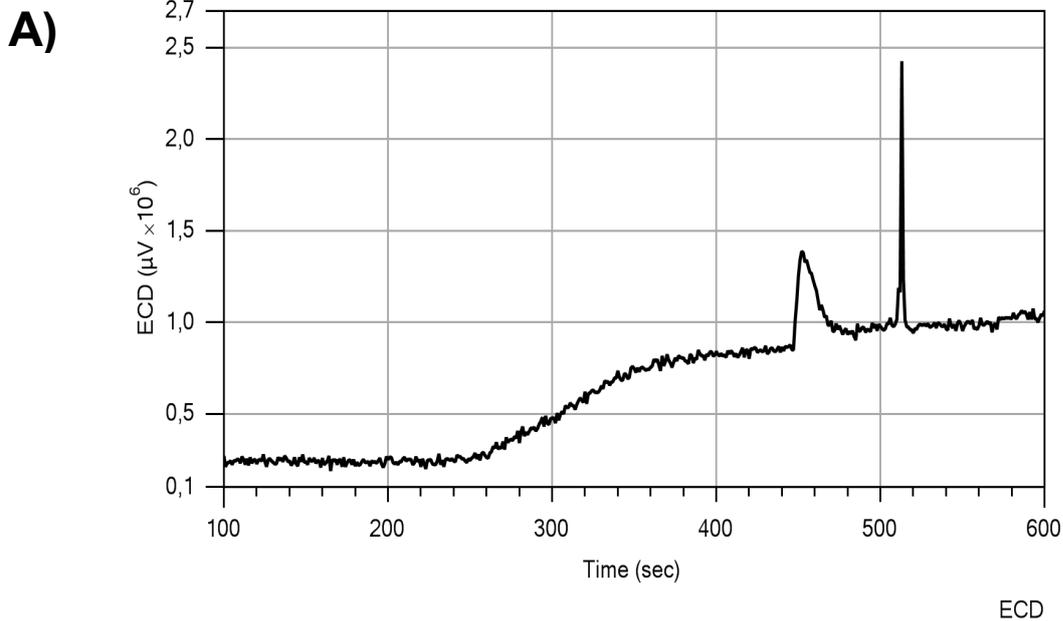


Figure 37: Results of test with Specimen 6b. A) ECD response recorded by MIP probe. B) Thermocouple temperature measurements. For experimental details, see text and Table 2. Note that the x-axis is not identical in the two different plots.

10 mm gap

As shown by Figure 38, the peak response for a gap distance of 10 mm is almost equal to the peak response at 6 mm gap distance (cf. Figure 37). Furthermore, the peak response of 1,000 mV is very close to the response in the blank test of 900 mV. Therefore, it is most likely that the measured response is due to background contributions rather than a response from the contaminated limestone specimen.

As for the experiment with 6 mm gap, the modified Viton rubber packing provides reasonably high temperatures at the limestone surface (cf. Figure 38B).

Peak response = 1,000 mV – PCE concentration = 75 ppb – Gap = 10 mm

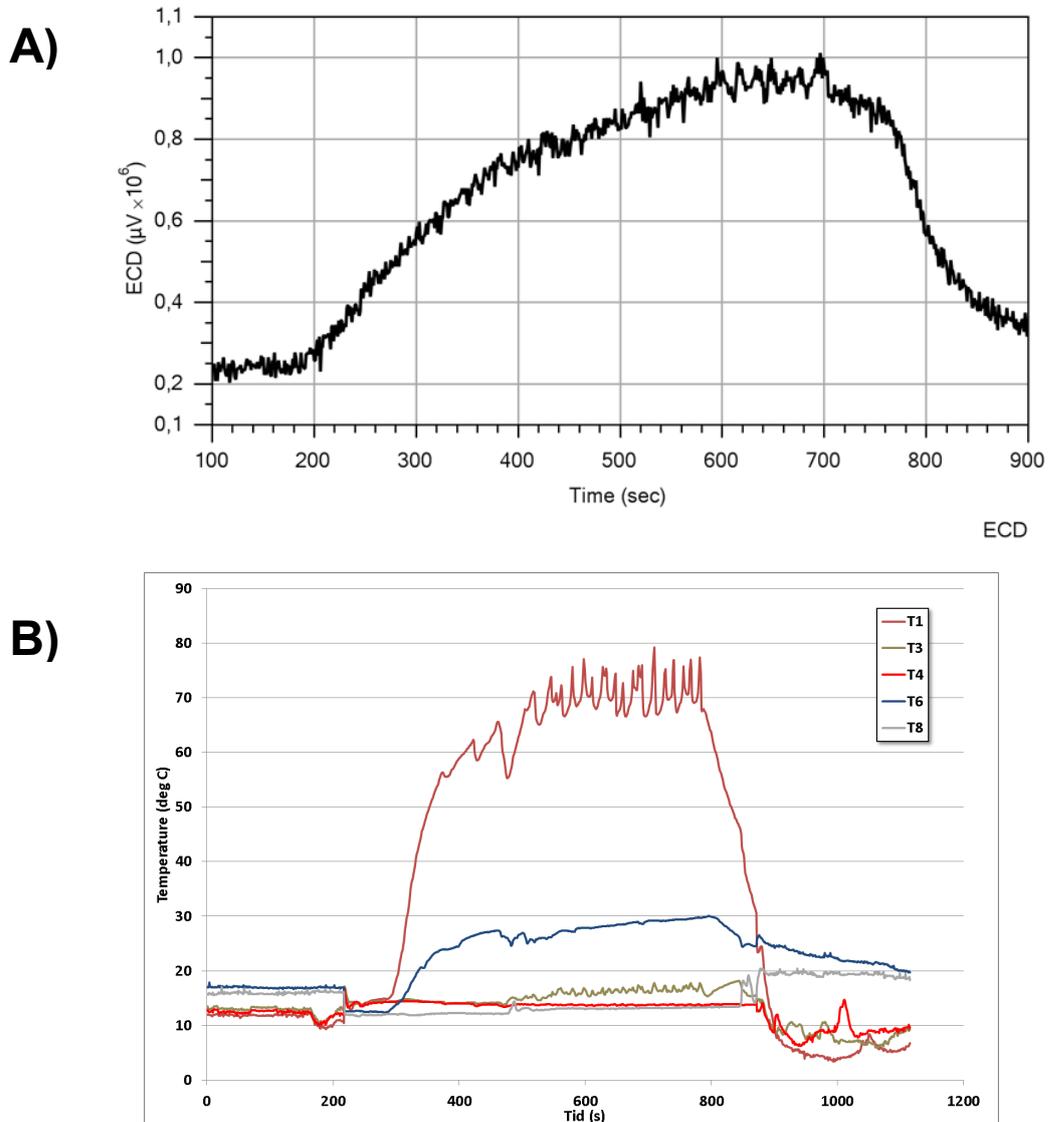


Figure 38: Results of test with Specimen 6c. A) ECD response recorded by MIP probe. B) Thermocouple temperature measurements. For experimental details, see text and Table 2. Note that the x-axis is not identical in the two different plots.

Blank experiment

In the blank experiment where the set up was tested with a 10 mm confined space without contaminated limestone present, the ECD response of the MIP probe was 900 mV (Figure 39) As shown by Figure 39B, it was difficult with the applied set up to keep the gap completely confined during the experiment. As a consequence, the temperature was unstable during the experiment and may have caused that the ECD response was less distinct than in previous experiments.

Based on this experiment, it is assessed that a reasonable background ECD value is between 700 mV and 1,100 mV with the applied MIP probe and set up.

Peak response = 900 mV – PCE concentration = 0 ppb – Gap = 10 mm

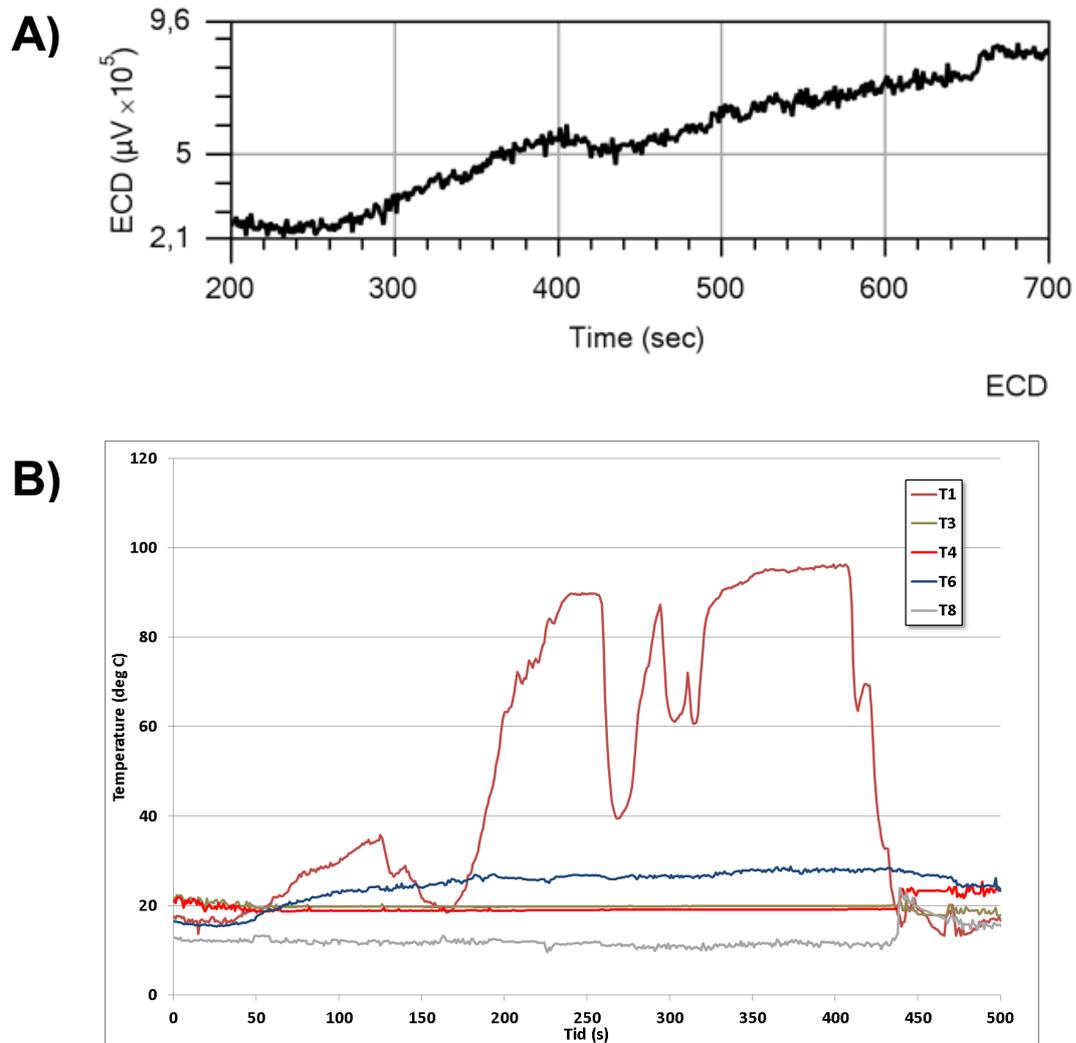


Figure 39: Results of blank test. A) ECD response recorded by MIP probe. B) Thermocouple temperature measurements. For experimental details, see text and Table 2. Note that the x-axis is not identical in the two different plots.

4. Implications for feasibility of MIP in limestone

As discussed in Section 3.3.2, the response test prior to the Phase 2 experiments indicated proportionality between PCE concentration in solution and the ECD response if the same MIP probe was used.

Since the same MIP probe was used in all experiments in Phase 2 we have chosen to compare all Phase 2 measurements by “normalizing” measurements above the “detection limit” of 1,100 mV to a 500 ppb PCE solution. In practice this means that the ECD response of 3,300 mV at zero distance with 75 ppb PCE contamination is scaled to the “equivalent” value of 22,000 ppb for a corresponding hypothetical 500 ppb PCE contamination in order to compare with the measurements at 2 mm and 4 mm distance. Measurements at 6 mm and 10 mm distance are considered below detection limit and therefore not scaled.

Using the above described methodology, the Peak ECD response can be plotted as a function of gap distance in the Phase 2 experiments (Figure 40).

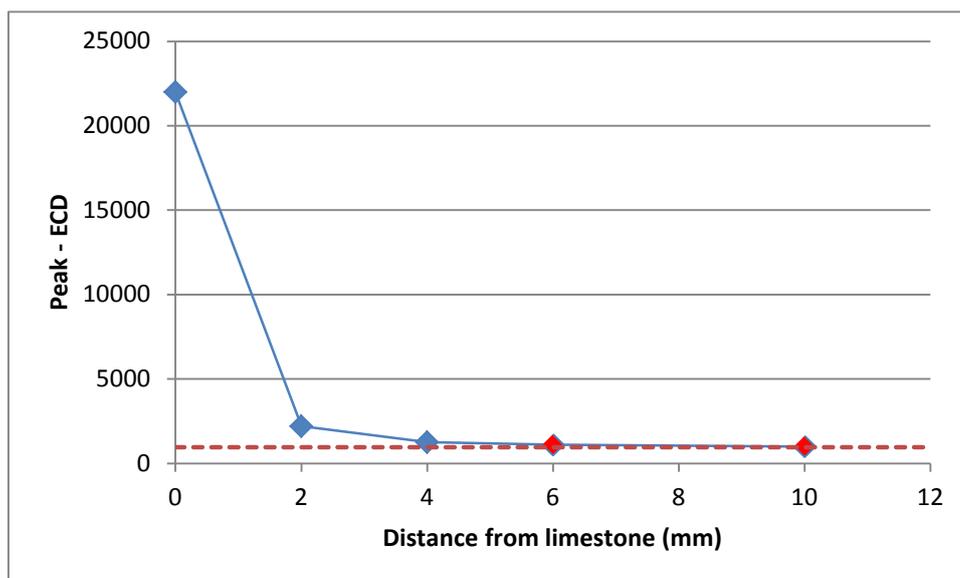


Figure 40: Peak ECD response (in mV) as a function of distance between MIP probe and limestone specimen in the NEMLA Feasibility Study Phase 2. Red dotted line indicates background measurements. Red squared symbols are considered below detection limit.

As shown by Figure 40, the addition of a Viton rubber packing between MIP probe and limestone enables measurement of contamination with 500 ppb PCE solutions in limestone up to a distance between limestone and MIP probe of 4 mm in the laboratory set up used in this study. At distances above 4 mm, detection of the PCE contamination seems not to be possible with the current set up.

Compared to the results of Phase 1, the addition of a Viton rubber packing is a clear improvement since it allows for small gaps to be present without losing the ability to detect the PCE contamination.

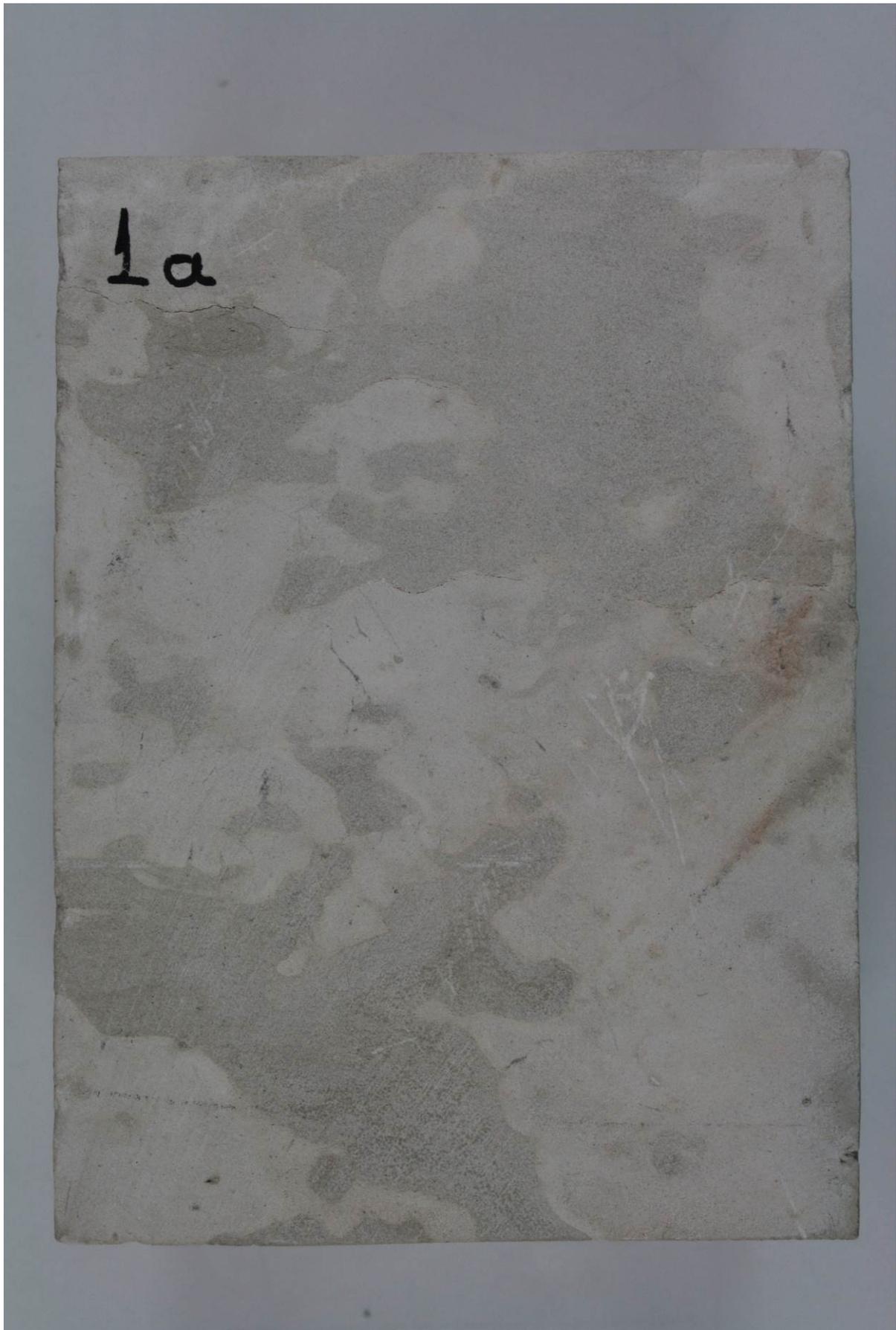
However, the measurement is extremely dependent on a completely tight seal between MIP probe and limestone since even small leaks causes temperature drops and potentially also convection and loss of ability to detect the contamination.

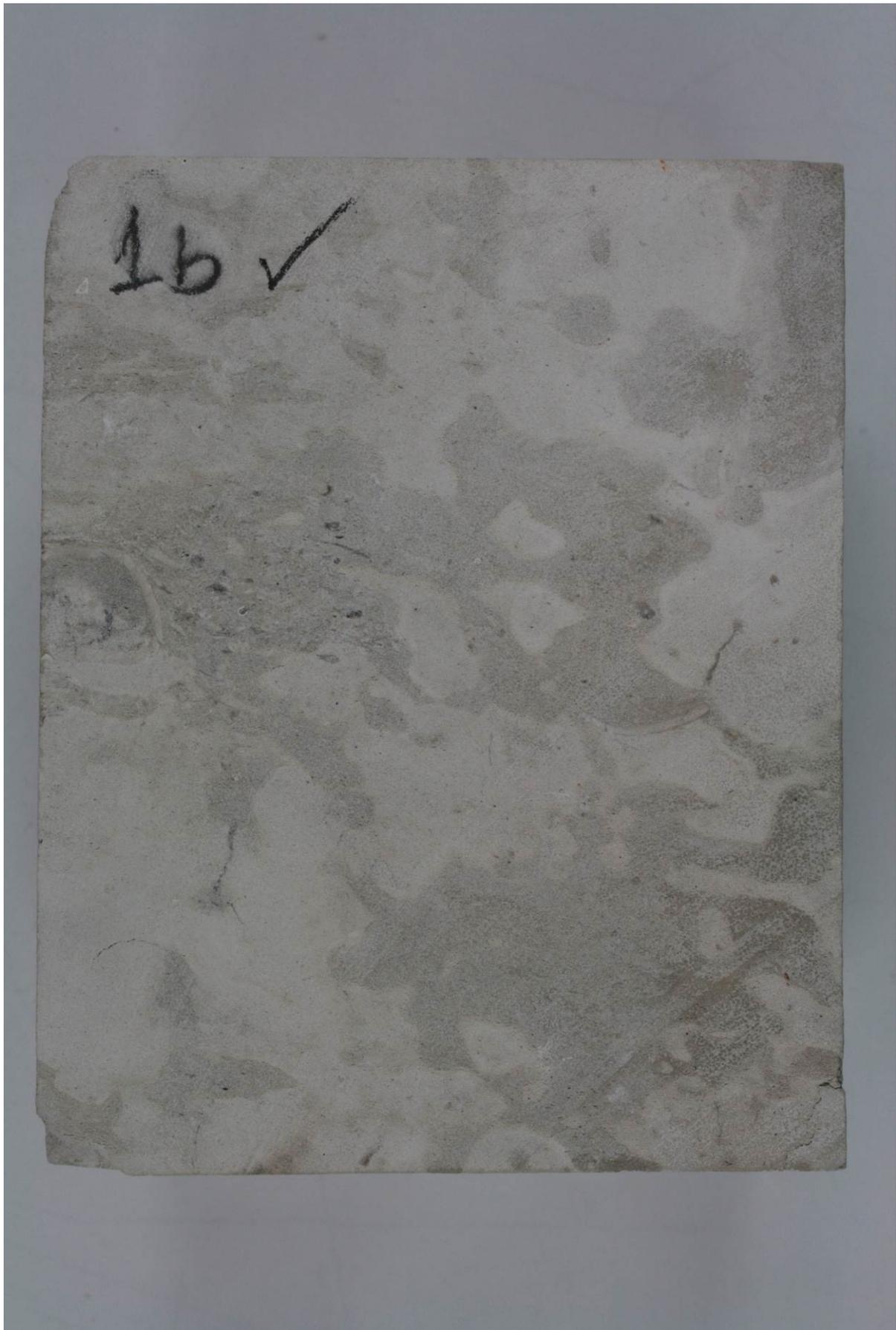
Taking the above general findings into account and further bearing in mind that the caliper of an open borehole in limestone often may vary by several centimeters over tens of centimeter distances, it is not likely that a simple modification of the current MIP probe design can enable the development of new emplacement methods in limestone for measurement of contamination with chlorinated solvents. More radical changes to the current design should apply if the MIP membrane technology must be utilized.

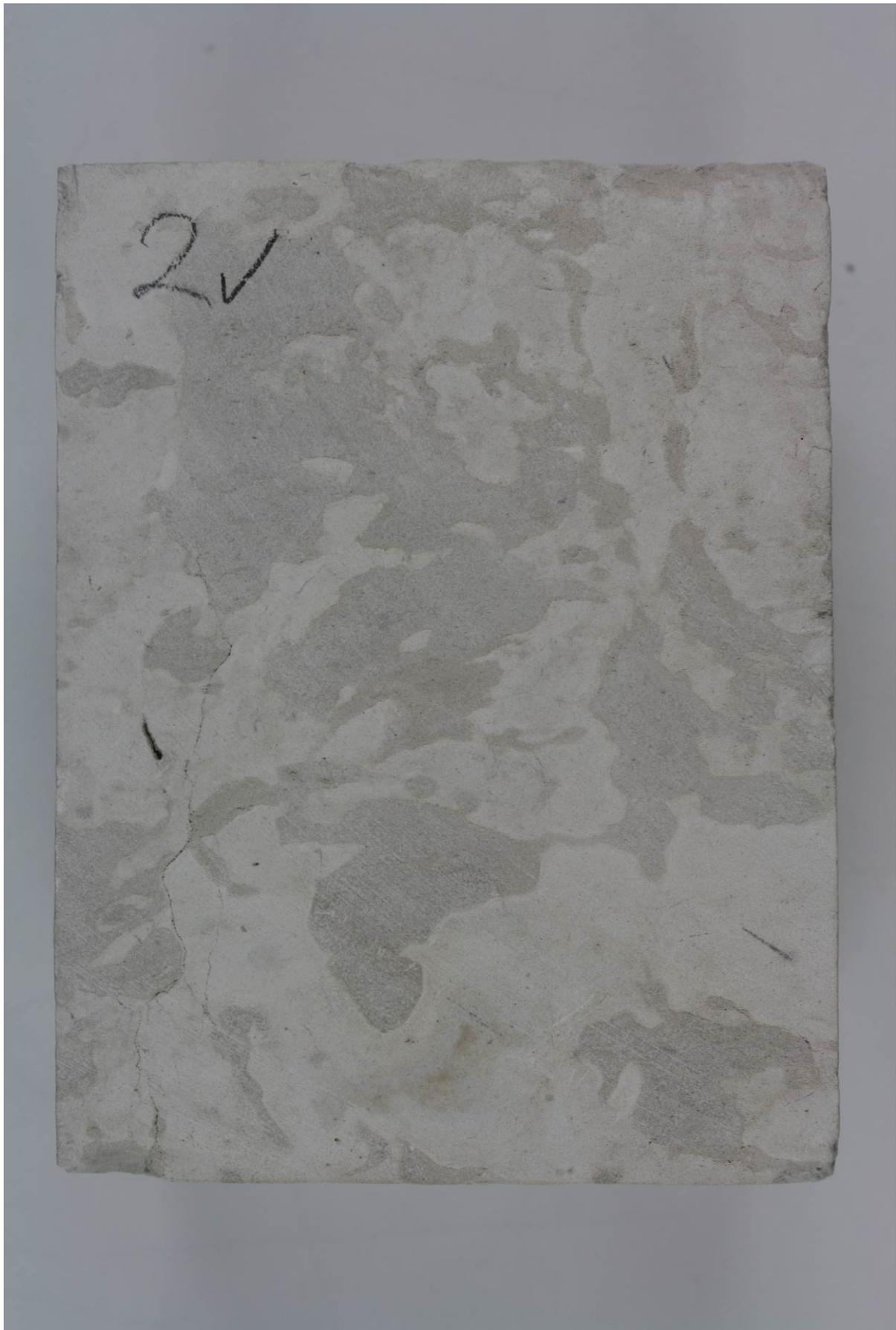
In conclusion, further innovative solutions are required before the desired new emplacement method is ready to use.

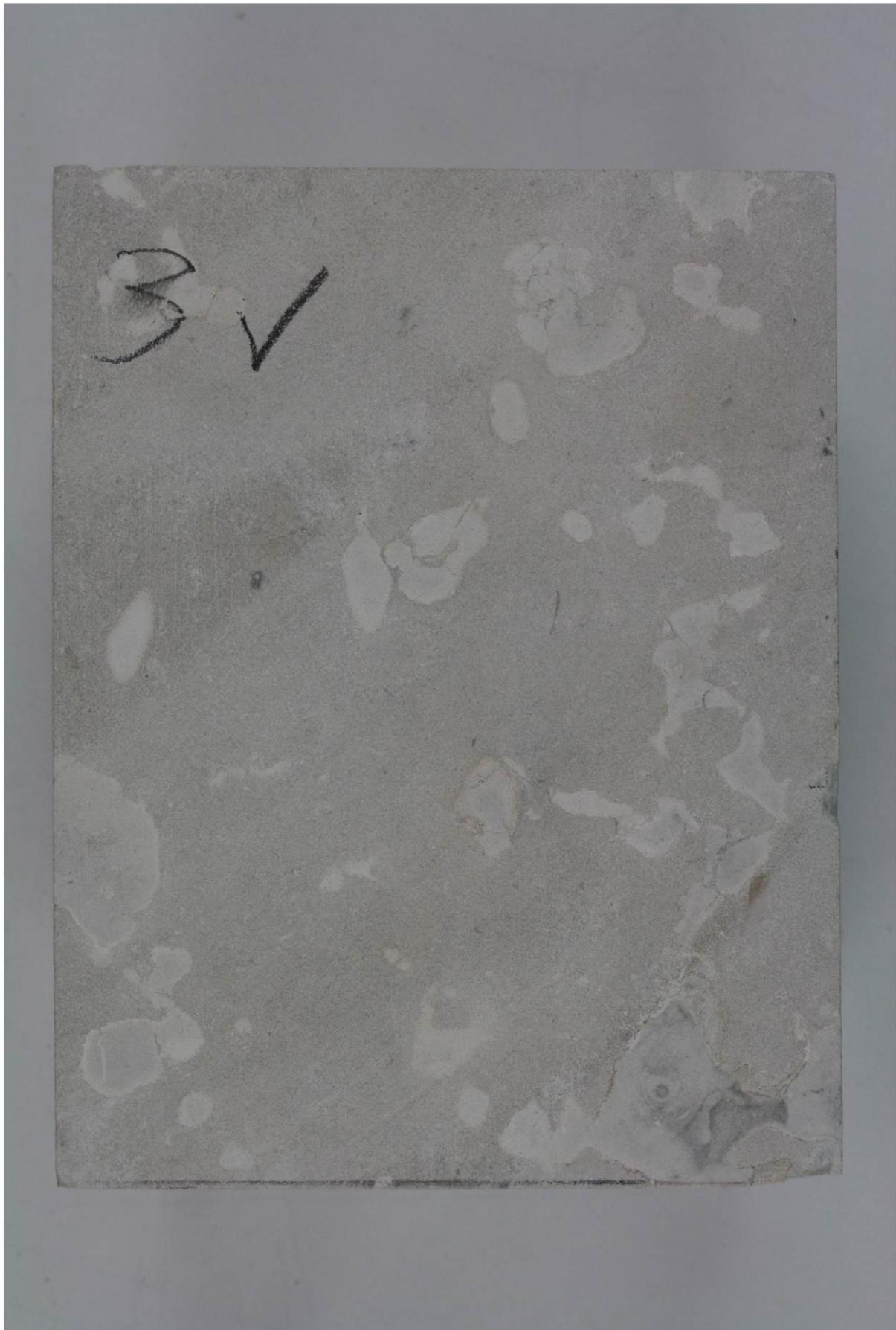
APPENDIX A

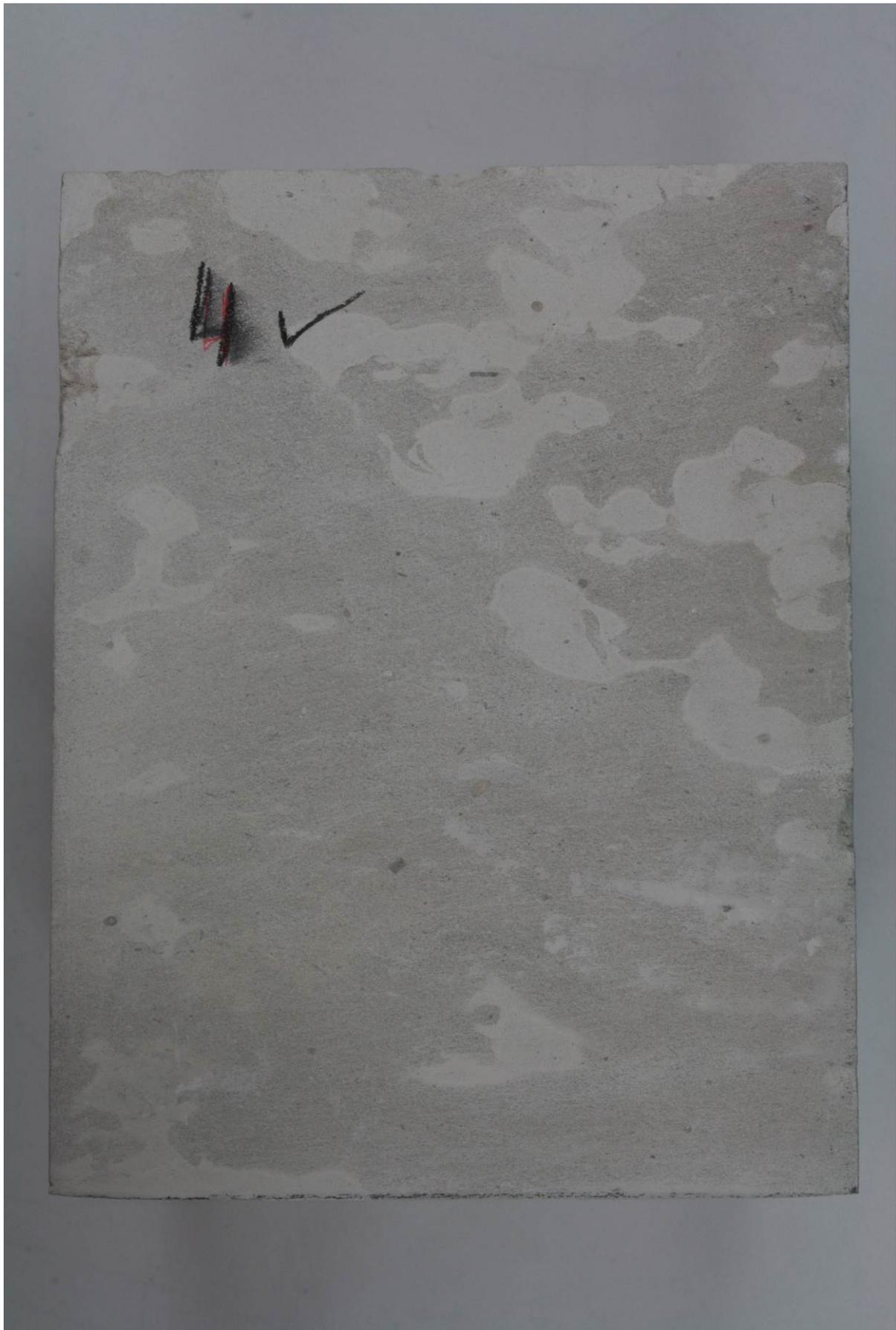
Photographs of prismatic limestone specimens

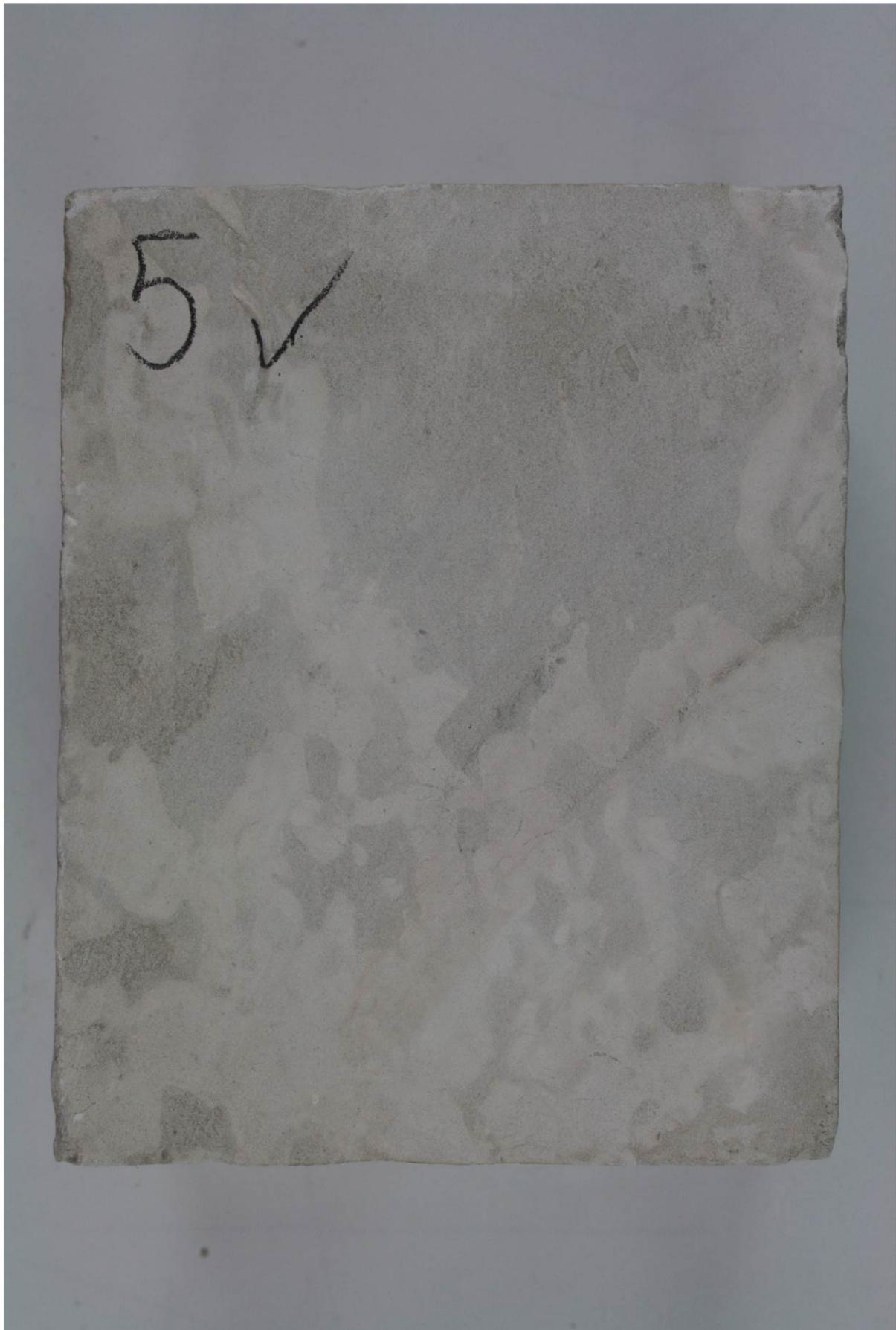


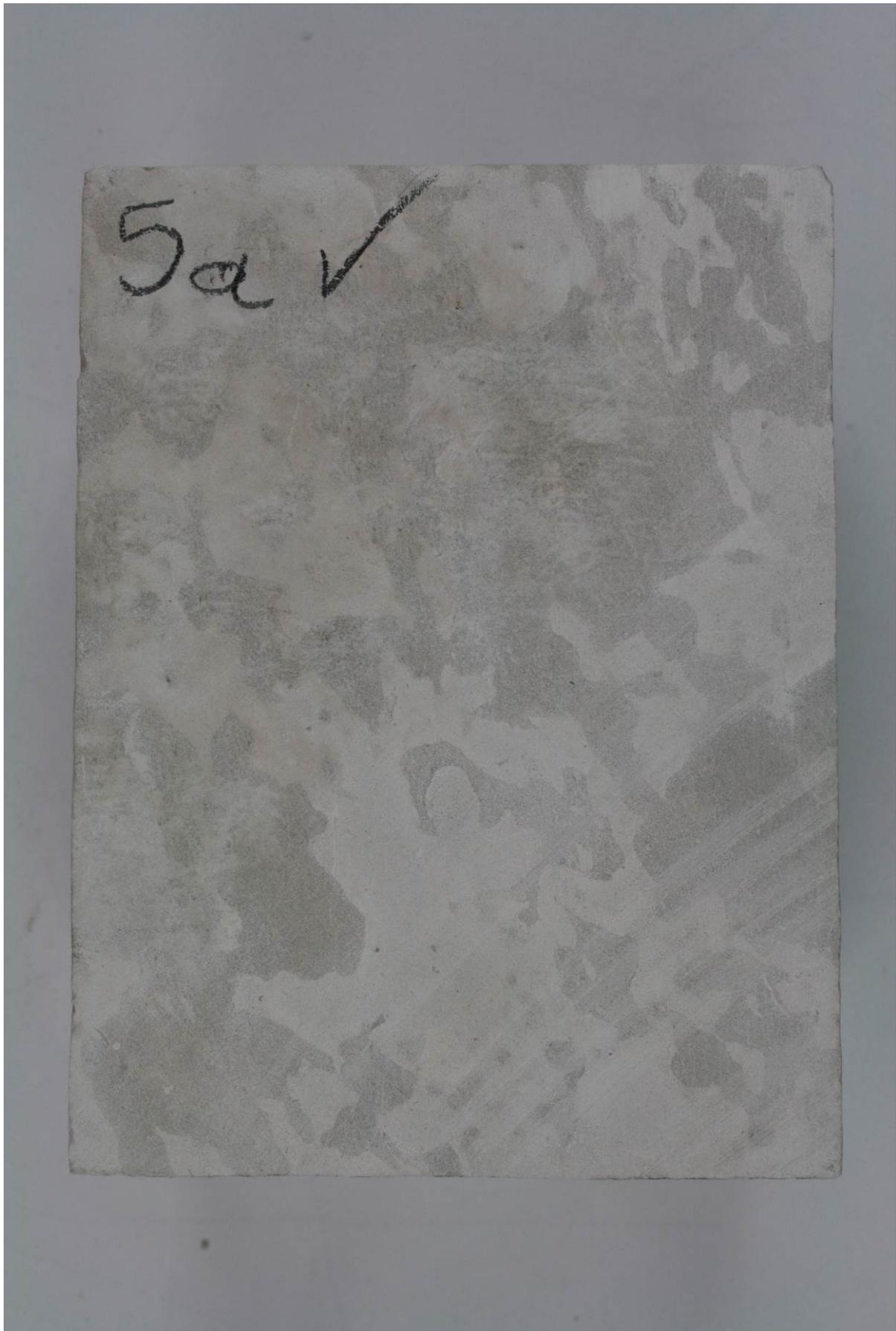


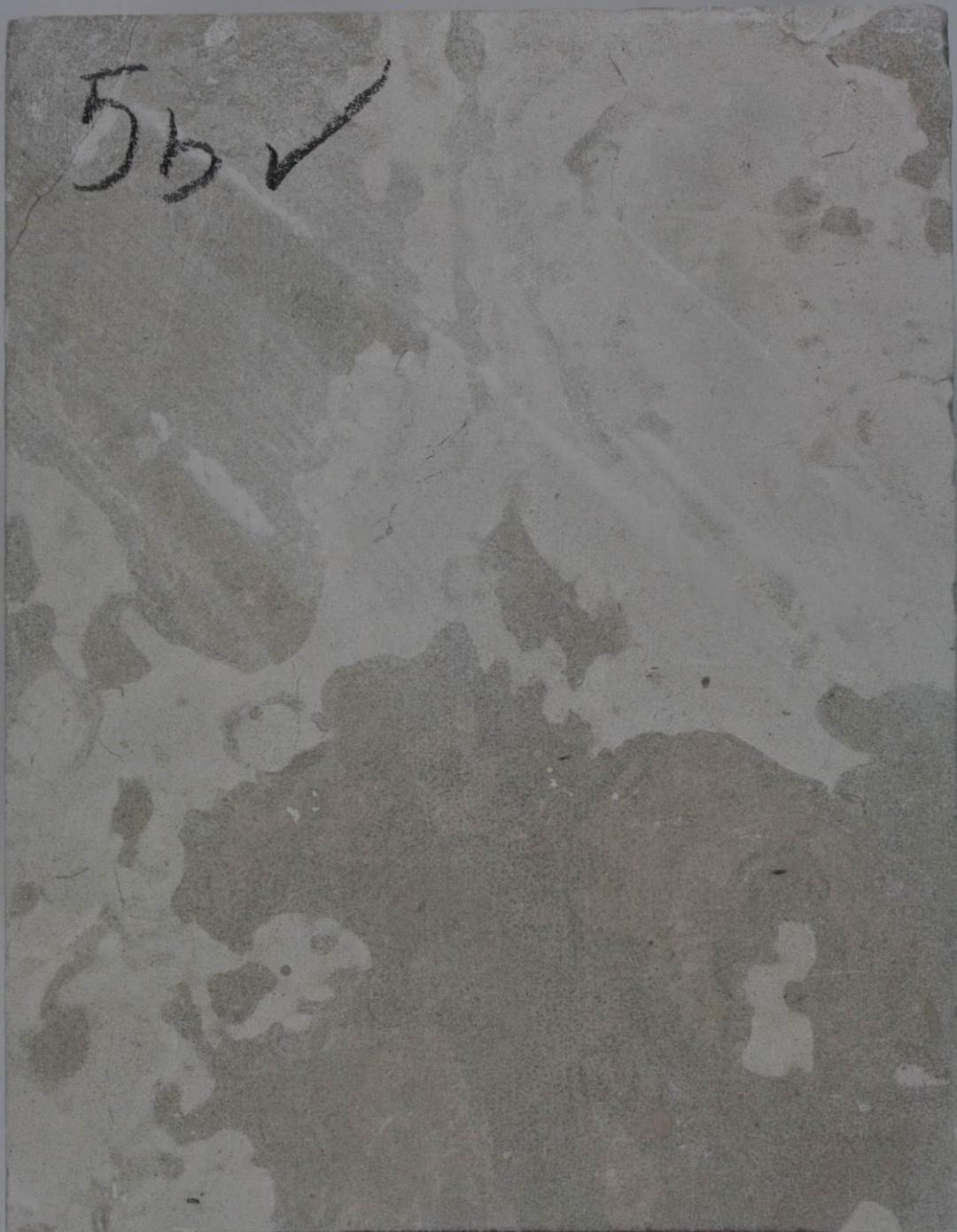




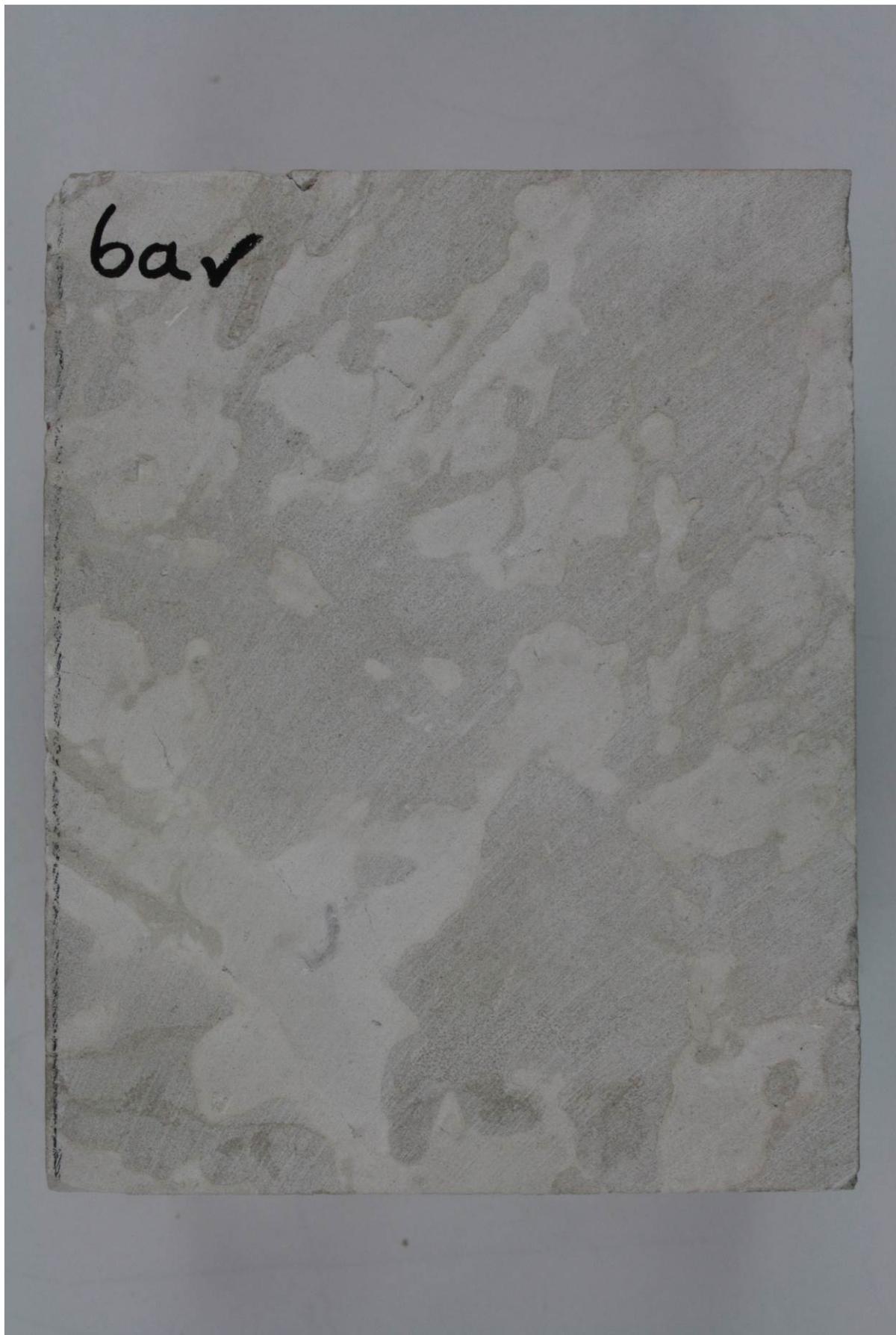


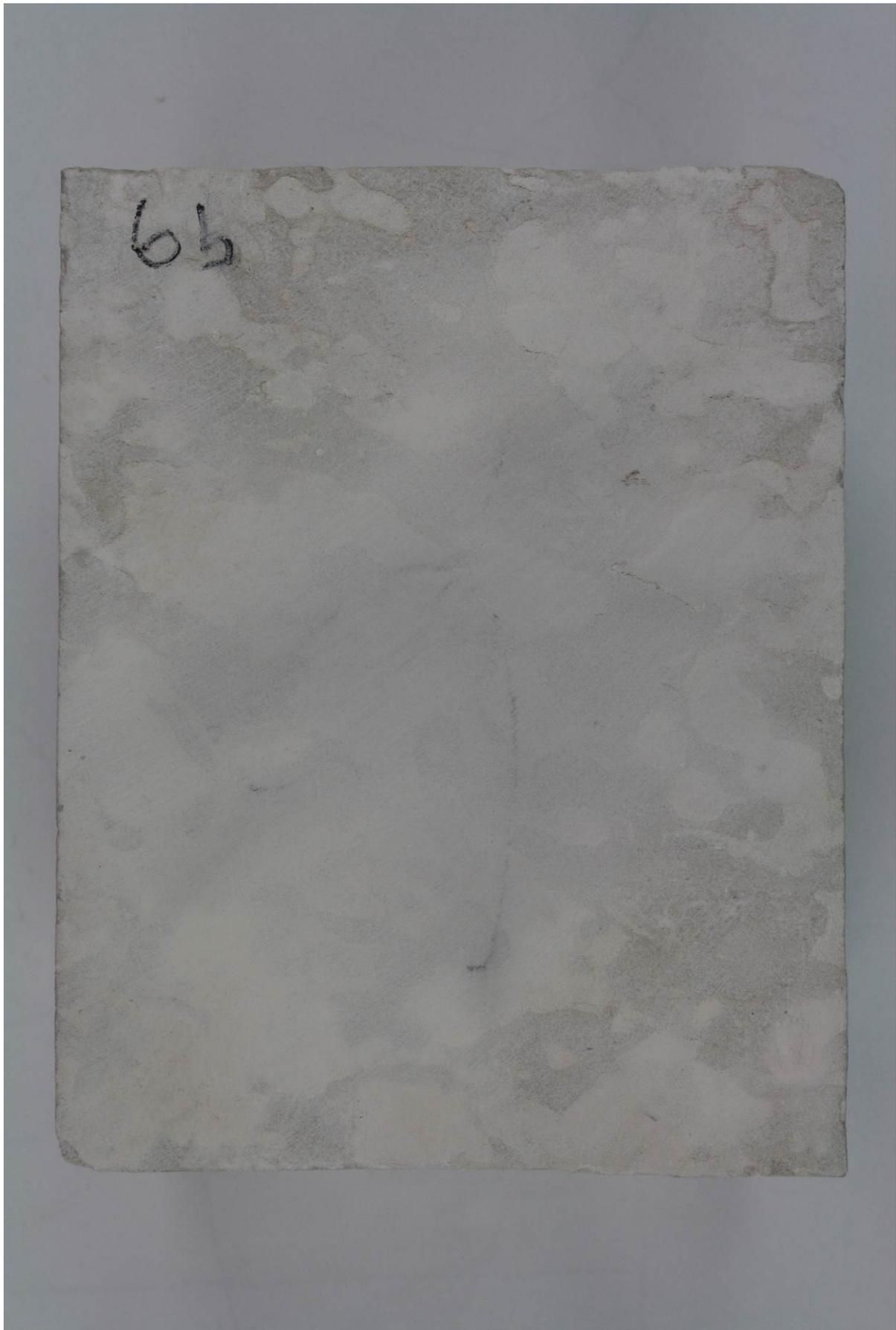


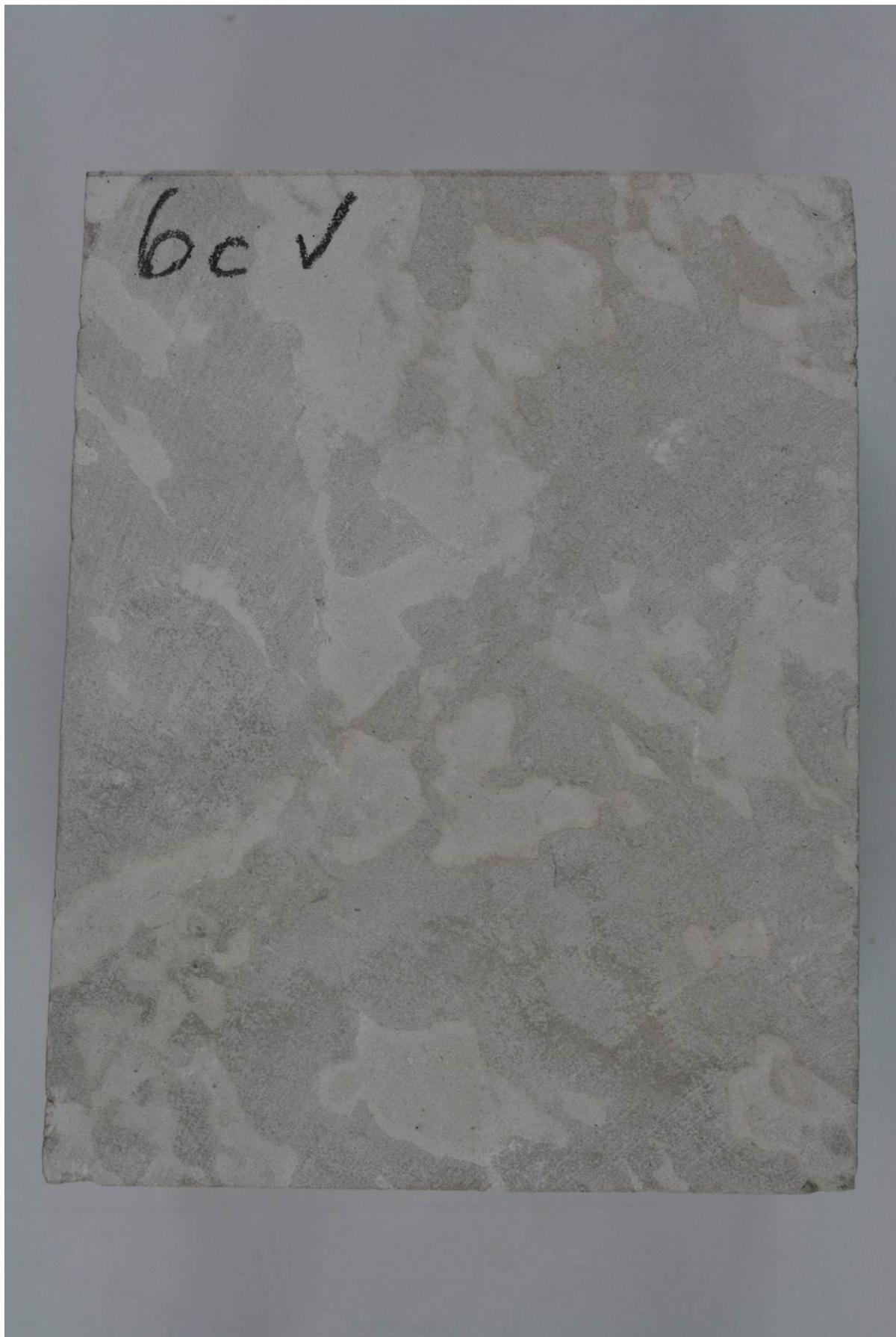


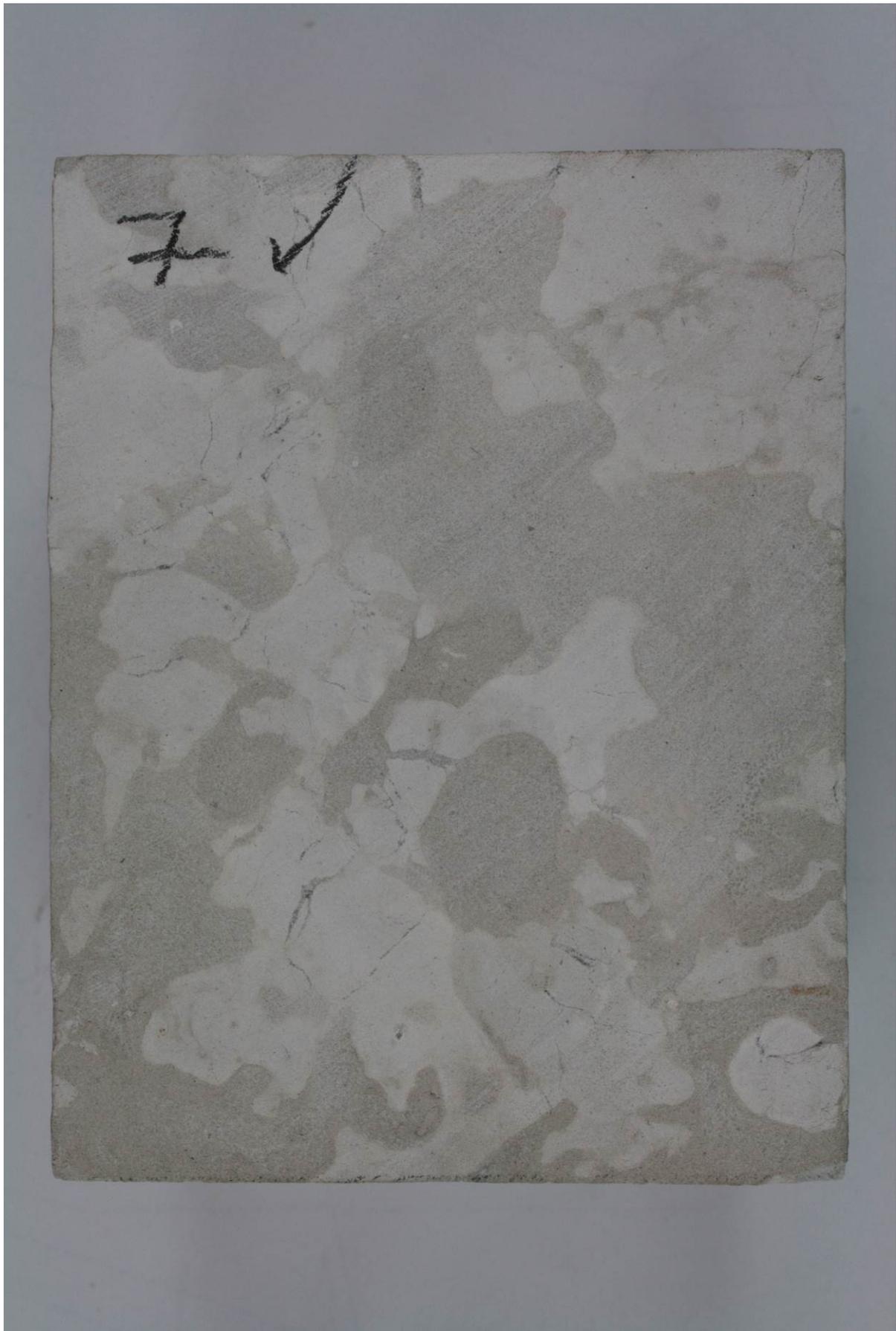


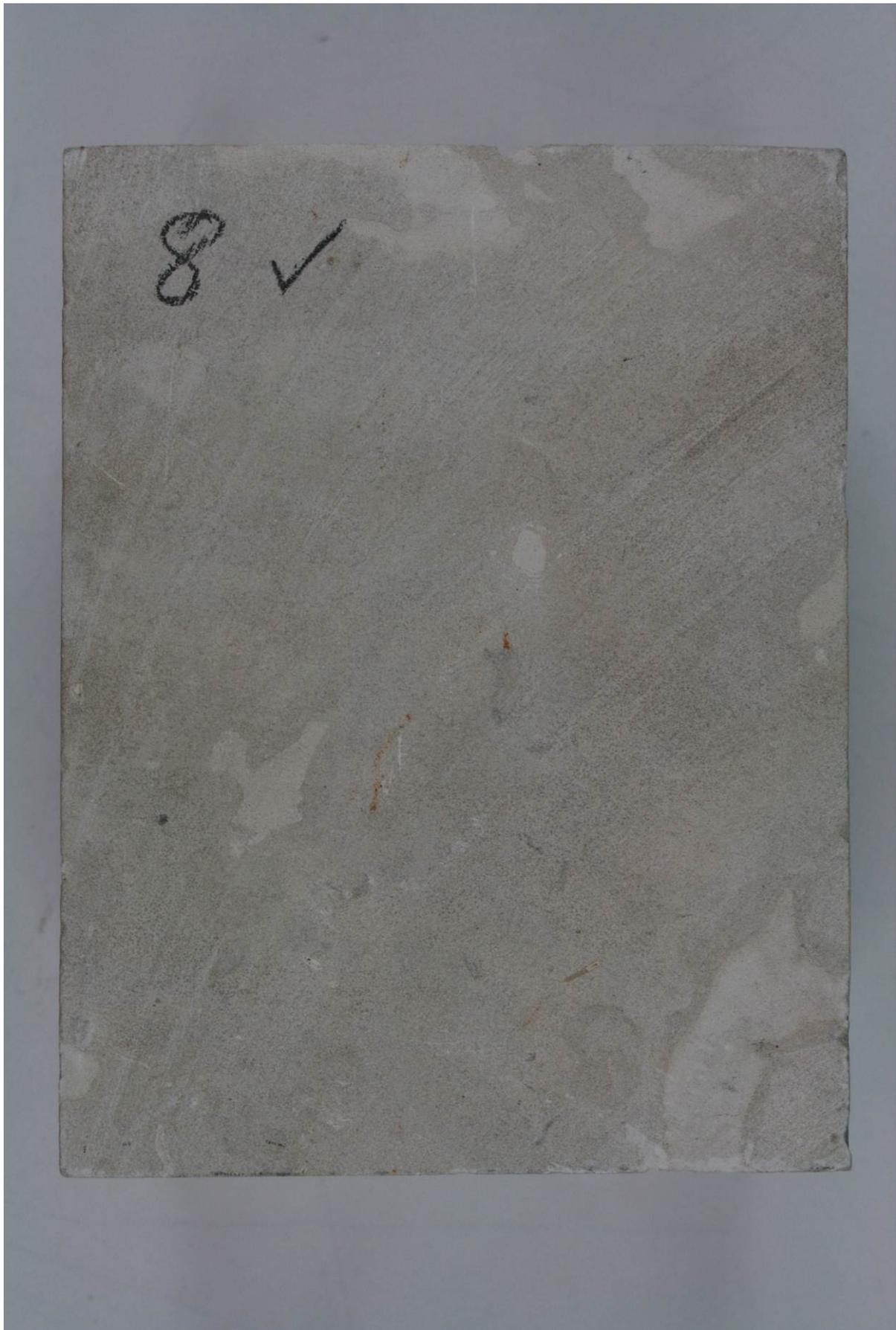


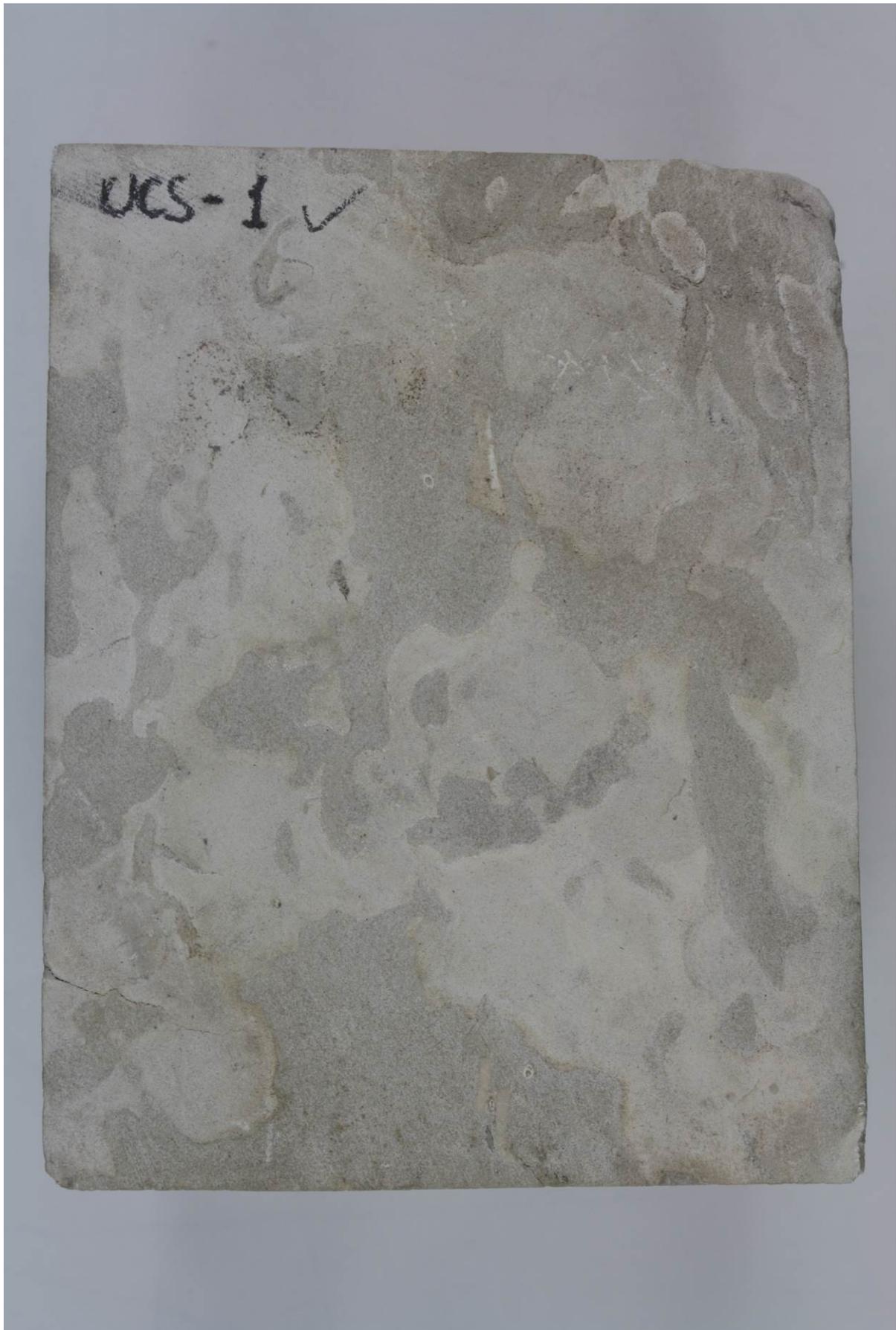












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