# **CHEMWEAK – JCR-7 project**

Report A1: Homogeneous dissolution of outcrop chalk samples

Claus Kjøller & Lykourgos Sigalas

GEOLOGICAL SURVEY OF DENMARK AND GREENLAND DANISH MINISTRY OF CLIMATE, ENERGY AND BUILDING



# **CHEMWEAK – JCR-7 project**

## Report A1: Homogeneous dissolution of outcrop chalk samples

Claus Kjøller & Lykourgos Sigalas GEUS Core Laboratory

Released 01.02.2020



GEOLOGICAL SURVEY OF DENMARK AND GREENLAND DANISH MINISTRY OF CLIMATE, ENERGY AND BUILDING

# Abstract

The CHEMWEAK project is part of phase 7 of the Joint Chalk Research (JCR) program. The project is carried out as a collaborative project between Geo, University of Stavanger (UiS), and GEUS with the overall objective to determine and quantify the effect on the rock mechanics parameters of various degrees of dissolution of chalk. In order to be able to reach this eventual goal, it has been necessary to first develop a method for homogeneous dissolution and preparation of chalk plug specimens for subsequent rock mechanical testing.

Initially, 98 plug specimens of Maastrichtian, Stevns outcrop chalk were used to establish a correlation between average CT-number and the porosity of the specimens. This enabled CT-imaging as a method for describing variations in porosity, and thereby also the homogeneity of samples prior to and after treatment according to the developed method.

A subset of 30 plug specimens were used for subsequent dissolution tests with either of two acid generating solutions: 1) The commercially available well stimulation product, Acidgen FG, that is a so-called retarded acid developing acid upon dilution in water and/or heating; or 2) acetic acid. In both cases, various dilutions were tested, and the homogeneity of the chalk dissolution was investigated by image analysis of CT-scanning images.

The application of Acidgen FG seemingly provides reproducible results and the possibility for creating homogeneous porosity changes of the tested outcrop chalk specimens. The original porosity distribution seems to be honored when solutions of 2% or 5% Acidgen FG are used in the experimental protocol, while application of 15% Acidgen FG solutions creates sample failure during dissolution. The experiments with 2% and 5% Acidgen FG have shown that it is possible to create homogeneous dissolution in the outcrop chalk specimens with a resulting porosity change of up to at least 3.5 p.u. in these highly porous carbonates. For comparison, the application of acetic acid in similar experiments apparently mostly creates fast dissolution of chalk specimens from the outside of the specimens. As a consequence there is little or no associated change in porosity, and if any change in porosity is obtained by the treatment, it is much more random and less reproducible than is the case by treatment with Acidgen FG solution.

Based on the results obtained in the present study, it can be concluded that dissolution of outcrop chalk specimens can be performed in a homogeneous way with up to 5% Acidgen FG by application of the method described and designed in the present report. On the other hand, homogeneous dissolution of outcrop chalk specimens with acetic acid seems not possible. In addition, it has been shown that image analysis of CT-images is a strong tool for evaluation of the homogeneity of chalk plug specimens.

# Contents

1.		Introduction	4
2.		Previous studies and rationale for experimental plan	5
	2.1	Previous studies and rationale for experimental plan	5
3.		Analytical procedure	7
	3.1 3.2	Sampling and overall workflow General treatment procedure	7 8
4.		Flow diagram of analytical procedure	11
5.		Analytical methods	12
	5.1 5.1.1 5.1.2 5.1.3 5.2 5.3	Conventional core analysis Gas permeability, uncorrected (GEUS steady state instrument) He-porosity and grain density Precision of CCAL data X-ray CT scanning Water sampling and chemical analyses.	12 12 12 12 12 13 14
6.		Results and discussion	15
	$\begin{array}{c} 6.1 \\ 6.1.1 \\ 6.2 \\ 6.2.1 \\ 6.2.2 \\ 6.2.3 \\ 6.3.1 \\ 6.3.2 \\ 6.3.3 \\ 6.4 \end{array}$	Initial state of specimens Porosity, permeability and grain density CT-imaging and homogeneity Dissolution with Acidgen FG Initial experiments Mass balances, porosity and permeability changes CT-imaging and homogeneity Dissolution with acetic acid Initial experiments Mass balances, porosity and permeability changes Mass balances, porosity and permeability changes CT-imaging and homogeneity Comparison and evaluation of method tested	15 17 21 22 24 24 30 33 34 35 40 41
7.		Conclusions	43
8.		References	44

# 1. Introduction

The CHEMWEAK project is part of phase 7 of the Joint Chalk Research (JCR) program. The JCR program was originally initiated in 1982 and has been extended in several phases since then. In JCR 7, the Norwegian Petroleum Directorate, the Danish Energy Agency and nine oil companies cooperate on research and development and share experience in order to improve recovery from chalk fields on the Norwegian and Danish sectors. The oil companies participating are:

- BP Norge AS
- ConocoPhillips Skandinavia AS
- Danish North Sea Fund
- DONG E&P A/S
- Hess Norge AS
- Mærsk Olie og Gas A/S
- Statoil Petroleum AS
- Shell Olie- og Gasudvinding Danmark B.V. (Holland)
- Total E&P Norge AS

The CHEMWEAK project is carried out as a collaborative project between Geo, University of Stavanger (UiS), and GEUS. Geo is the overall project manager of the CHEMWEAK project that has the overall objective to determine and quantify the effect on the rock mechanics parameters of various degrees of dissolution of chalk.

In order to obtain the overall objective of the CHEMWEAK project, it has been necessary to first develop a method for homogeneous dissolution of chalk, i.e. if test specimens cannot be dissolved homogeneously, it can be difficult to investigate the rock mechanics effects of various degrees of dissolution of the chalk. The aim of the developed method is to enable dissolution of chalk specimens in a controlled way so that various degrees of porosity change can be obtained.

This report describes the work that has been performed in order to develop and document the method for homogeneous dissolution and preparation of chalk plug specimens for subsequent rock mechanical testing. Preliminarily rock mechanics tests were carried out on three of the samples treated as part of the method development. A separate report describes the results of these tests /1/.

# 2. Previous studies and rationale for experimental plan

## 2.1 Previous studies and rationale for experimental plan

Laboratory studies dealing with dissolution of carbonate rocks are often related to either  $CO_2$  flooding or well stimulation experiments /2-7/. In these cases, flooding of plug specimens is carried out with the purpose of investigating various petrophysical or chemical aspects of the flooding, e.g. enhanced oil recovery due to  $CO_2$  flooding, chemical reactions as a consequence of the flooding, or even the formation of wormholes in the flooded specimens. Application of such specimens in subsequent rock mechanical tests may, however, provide rock mechanical results that are difficult to interpret in the context of the dissolution that has taken place in the tested specimen as the dissolution in such cases has most often occurred in an inhomogeneous way - either by formation of wormholes (e.g. /3/,/8/) or as compact dissolution at the inlet end of the specimen (e.g. /2/,/6/).

In order to control and optimize the acidizing stimulation treatment of production wells, wormholing has previously been studied in detail /6/,/9-10/. From these studies we know that the dissolution regime can be described as a function of two dimensionless numbers, the Peclet and Damköhler numbers, respectively, in a  $P_{e'}(P_e*D_a)$  plot as shown in Figure 1 /11-13/.



Figure 1: Dissolution regime as a function of the Peclet and the Damköhler numbers (from /5/).

The Peclet,  $P_e$ , and Damköhler,  $D_a$ , numbers are defined as shown in Equation 1 below /11-13/:

$$P_e = \frac{v_o * l}{D} \qquad ; \qquad D_a = \frac{\kappa}{v_o} \tag{1}$$

where  $v_o$  is the fluid velocity, l a characteristic length of a pore, D the molecular diffusion coefficient, and  $\kappa$  the chemical reaction rate for dissolution.

In studies where it is important to gain knowledge about the rock mechanical effects of carbonate dissolution on well or reservoir integrity, it is important that specimens undergoing rock mechanical tests are dissolved homogeneously if the effect of dissolution on rock mechanical properties is to be studied properly. As described in detail by Egermann et al. (2010) /5/, it is therefore important that experiments are carried out at conditions representing the upper left part of the diagram in Figure 1, if carbonate dissolution in rock specimens is performed with the purpose of studying possible rock mechanical effects as, e.g., a function of the change in porosity due to dissolution.

For the purpose of establishing experimental conditions favouring homogeneous dissolution, previous studies /4-5/,/7/ have applied so-called retarded acids or heat activated acids, which are organic acid pre-cursors that increase the rate of acid formation upon heat activation or in the presence of certain enzymes (see further in Chapter 6). Thereby, the Damköhler number is kept low initially by a low reaction rate,  $\kappa$ . Thus, both Egermann et al. (2010) /5/ and Ott et al. (2013) /4/ showed that dissolution of various limestone samples could be carried out in a reasonably homogeneous way. In addition, the specimens dissolved were subsequently used for rock mechanical tests that showed that rock mechanical parameters in general decreased as a function of the porosity increase (Figure 2).



**Figure 2:** Left: Young's modulus as a function of porosity change for both heterogeneous (wormholing due to CO<sub>2</sub>saturated brine injection) and homogeneous (RAT/retarded acid) dissolution patterns. Right: Failure envelope of samples treated with retarded acid and untreated samples (reference data). From /4/.

In light of the previous good results with homogeneous dissolution of limestone using retarded acids, it was decided to adapt this concept and adjust the experimental procedure of these previous studies in the present phase of the CHEMWEAK project. In addition, it was decided to follow the same experimental procedure, where the only exception was that the retarded acid was replaced with acetic acid. This was to be able to compare the performance of the retarded acid concept with a weak organic acid, which is well known as descaling agent in both industry and households.

# 3. Analytical procedure

#### 3.1 Sampling and overall workflow

A batch of 98 specimens of Stevns outcrop chalk of Maastrichtian age was plugged by Geo as described in a previous report /14/. Following plugging, the samples were marked as shown in Figure 3 and subsequently X-ray CT scanned along the two marked cross-sections. This marking was carried out in order to be able to scan the specimens along the same cross-sections at later stages of the projects. X-ray CT scanning was carried out at DTU Chemical Engineering.



**Figure 3:** Illustration showing the marking of samples for CT-scanning. The marking ensured that CT-scanning was always carried out along the same cross-section of the specimen at any subsequent CT-scanning.

After the initial CT-scanning, the plug specimens were retrieved at GEUS and initial state conventional core analyses (CCAL) were carried out. The CCAL include determination of porosity, single point  $N_2$ -gas permeability, and grain density. CT-scanning images were analyzed for average Hounsfield units (often referred to as CT-number) and standard deviation, and an initial subdivision of samples into homogeneous and less homogeneous samples was carried out qualitatively.

Subsequently, a set of 30 samples from the pool of most homogeneous samples were selected for experiments with Acidgen FG and acetic acid, while trims from the same quarry blocks as the plugs were taken from were crushed and sieved through a <1 mm sieve.

The crushed and sieved samples were used to carry out a part of the initial experiments, which were done in order to determine what concentrations of Acidgen FG and acetic acid as well as temperatures, reaction periods, etc. that were to be used in the cyclic treatment procedure that was followed in the experiments were plug specimens were applied (cf. Section 3.2). Thus, the preliminary experiments included some dissolution kinetics experiments as well as experiments where the acid formation kinetics from diluted solutions of Acidgen FG was tested. Eventually, the results of the preliminary experiments were used to design the final general treatment procedure (Section 3.2).

As a result of the preliminary experiments, it was chosen to split the set of 30 samples into groups of specimens that were treated according to the procedure in Section 3.2 with either 2%, 5%, or 15% Acidgen FG – or 0.5%, 2%, or 5% acetic acid solution. Tables and figures showing which specimens were selected for what type of solution are presented in Chapter 6 (Results).

Treatment of the specimens was done according to the general treatment procedure described in Section 3.2. In order to be able to compare the dissolution effect of different acid solutions as well as of different concentrations each solution, the same general procedure was followed irrespective of the solution used to dissolve chalk from the specimens.

In general, each test specimen was treated with acid solution (Acidgen FG or acetic acid) until the specimen was broken or until six (6) acid solution treatments were performed according to the general treatment procedure described in Section 3.2. However, two treated plug specimens (plug #17 and plug #82) were selected for preliminary rock mechanics tests at Geo together with the untreated plug specimen #48. As mentioned, the results of the rock mechanics tests are presented in a separate report /1/.

X-ray CT scanning was generally performed after 2, 4, and 6 treatments. However, for a subset of specimens (plugs #9, #20, #21, #22, #74 and #86) X-ray CT scanning was carried out after 4 and 6 treatments only.

## 3.2 General treatment procedure

Treatments were performed using either Acidgen FG (2%, 5%, or 15%) or acetic acid (0.5%, 2%, or 5%). The general treatment procedure is illustrated in Figure 4.



Figure 4: Illustration showing schematically the general procedure followed during treatment of the chalk specimens with acid solutions (Acidgen FG or acetic acid). See also text for further explanation.

The principle of the treatment is five treatment steps which all together results in dissolution of the treated plug specimen and a set of CCAL data for each treatment and CT-scan images every two treatments. The five steps are:

- 1. Vacuum saturation
- 2. Heating
- 3. Distilled water flooding
- 4. Drying
- 5. CCAL

Each of the five treatment steps are described in more detail below.

#### Vacuum saturation

As shown in Figure 5, the plug specimens were saturated with acid solutions in a bottom-up way. Cores and solutions were vacuumed before saturation. This method prevented air from jamming pore space and also speeded up the process.



Figure 5: Illustration showing schematically the vacuum saturation process used to saturate specimens with acid solution. The vacuum saturation process is described in further detail in the text. V1, V2, and V3 are valves.

The plug specimens were put in beakers and placed in the vacuum chamber. A hose connected to a vacuum adapter ended into the beaker. A separatory funnel contained the saturating solution which was sealed with a vacuum valve on top of it (Figure 5).

First, V1 and V2 were closed and the air was extracted from V3 for two hours. Then the separatory funnel was filled with the saturating solution and was vacuumed from V1, while V2 and V3 remained closed, until no air bubbles occurred. Finally, V1 was closed and V2 was opened in order for the solution to move into the plug specimen with a very small flow

rate. Thus, full saturation of the plug specimens was in most cases obtained after approximately five minutes.

After saturation, a 4 mL sample of the solution was collected from the beaker for Ca analysis.

During the initial phase of the experiments, it was observed to be important that Acidgen FG solutions were prepared from the stock solution with cold water (2-4 <sup>o</sup>C), and subsequently vacuumed immediately, so that formic acid formation was minimized before the solution had saturated the plug specimens (cf. also Section 6.2).

#### Heating

The saturated plug specimens were placed in air-tight vials and covered with the acid solution. Subsequently, specimens were placed in an oven at 50<sup>o</sup>C for a period that generally lasted 48 hr. However occasionally, the plugs stayed in the oven for 72 hr during weekends, which in some cases might have caused additional dissolution than in treatment steps where the plug specimens were placed in the oven for 48 hr (cf. Chapter 6).

After heating, a 4 mL sample of the solution was collected from the vials for Ca analysis.

#### Distilled water flooding

The plug specimens were flushed with distilled water in order to remove the acidic solution from their pore space and prepare them for the following treatment.

The waterflooding was carried out at room conditions. A sleeve pressure of 5 barg was applied to the specimens, and flooding was carried out at a water injection rate of 50 mL/hr. Sleeve pressure and flow rate were chosen to avoid sample failure and creation of wormholes. The flooding was stopped after five (5) pore volumes (PV) of water injection. At this stage, the specimens were considered acid-free. However, in order to test this assumption, samples of the effluent (4 mL) were collected on breakthrough and at the end of flooding for Ca analysis.

#### Drying

After flooding, plug specimens were placed in an oven at 75 <sup>o</sup>C for at least 24 hr, until all water was evaporated and no further weight loss could be registered from the specimens. Subsequently, the plug specimens were placed in a dehumidifying chamber until conventional core analyses were carried out.

#### Conventional Core Analysis (CCAL)

After each treatment, porosity, single point  $N_2$ -gas permeability, and grain density were measured in order to observe the effects of the treatment with acid solutions on the plug specimens.

Mass balance calculations were used to determine weight losses from the specimens caused by the acid solution treatments. Thus, wet weights were measured before and after the specimens were placed in the oven, as well as dry weights before and after each treatment cycle.

# 4. Flow diagram of analytical procedure



# 5. Analytical methods

The general experimental procedure has been described in chapter 2. In this chapter a more extensive description of the analytical methods is provided. The conventional core analysis methods used by GEUS Core Laboratory follow API recommended practice for core-analysis procedure /15/.

## 5.1 Conventional core analysis

#### 5.1.1 Gas permeability, uncorrected (GEUS steady state instrument)

The plug is mounted in a Hassler core holder, and a confining pressure of 400 psi (27.6 bar) is applied to the sleeve. The uncorrected permeability to gas is measured by flowing nitrogen gas ( $N_2$ ) through a plug of known dimensions at differential pressures between 0 and 1 bar. No back pressure is applied. In the present study, the gas permeability measurements were carried out at a differential pressure close to 1 bar corresponding to a mean pressure of 1.50 ± 0.05 bar.

The readings of the digital gas permeameter are checked regularly by routine measurement of permeable steel reference plugs (Core Laboratories<sup>™</sup> gas permeability reference plug set).

#### 5.1.2 He-porosity and grain density

The porosity is determined by subtraction of the measured grain volume from 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 cleaned and dried sample.

The Helium porosimeter is calibrated using a set of steel plugs (Core Laboratories<sup>™</sup> volume reference plug set) before the measurement of plug samples is initiated. The bulk volume apparatus is checked using a steel plug with known volume.

#### 5.1.3 Precision of CCAL data

The table below (Table 1) gives the precision (= reproducibility) at the 68% level of confidence (+/- 1 standard deviation) for the CCAL measurements performed at the GEUS Core Laboratory.

Measurement	Range, mD	Precision
Grain density		0.003 g/cc
Porosity		0.1 porosity-%
Permeability: (Klinkenberg)	0.01-0.1 0.1-1 > 1	15% 10% 4%
Permeability: (Conventional)	0.001-0.01 0.01-0.1 > 0.1	25% 15% 4%

 Table 1: Precision of CCAL measurements performed at GEUS Core Laboratory

## 5.2 X-ray CT scanning

The plug specimens were scanned with X-ray computerised tomography (CT-scanning) at DTU Chemical Engineering using the scanning parameters listed in Table 2.

**Table 2**: Scanning parameters used for

 X-ray CT scanning of plug specimens

X-ray or scanning of plug specimens.				
Sellar-ear	Ultra High			
120 kV	340 mAs			
Time=	2 s			
Slice=	4 mm			

For each plug specimen, two (2) longitudinal slices perpendicular to each other through the plug sample were imaged together with one (1) cross section. The longitudinal slices were recorded along the marked lines on the plug specimen so that imaging could be carried out at the same location when repeating the CT-scanning after 2, 4, and 6 treatments with acid solution, respectively.

The thickness of each recorded slice was 4 mm and the centre of each slice was placed along the marker on the plug specimen (cf. Figure 3).

The images received were in grey-scale and the image format used for further analysis was a Dicom raw image format. In the images, lighter shades (white=0% porosity) represent denser areas and darker shades (black=100% porosity) represent pore space. The grey scale in the image is numerically represented by the Hounsfield scale /16/ and post processing includes registration of the average Hounsfield units in selected areas of the image. Hounsfield units are often also referred to as CT-numbers. Typical average CT-numbers for North Sea chalk are in the range of 1200-2500 (pers. comm. Niels Springer). Image post-processing was done using the freeware ImageJ /17/.

## 5.3 Water sampling and chemical analyses

Water samples for chemical analyses (Ca-concentration) were sampled in a sterile syringe and filtered through 0.2  $\mu$ m Satorius cellulose acetate (CA) before preservation using 1% suprapur 7M HNO<sub>3</sub>. Chemical analyses were carried out at GEUS using ICP-MS. The ICP-MS apparatus used was of the type PerkinElmer Elan 6100DRC ICP-MS.

Measurement of pH was carried out at room conditions with a Mettler-Toledo InLab Micro-Pro electrode connected to a Mettler-Toledo SevenEasy pH-meter with automatic temperature compensation.

## 6. Results and discussion

In this chapter the results of the experimental work are presented and discussed. First, in Section 6.1, the initial characterization of the 98 plug specimens from the Sigerslev quarry is presented together with a discussion of the rationale for using processed X-ray CT scanning results as a proxy for describing the homogeneity of the chalk specimens. The subsequent sections (Sections 6.2 and 6.3) describe the results obtained by treating selected specimens with Acidgen FG and acetic acid, respectively.

## 6.1 Initial state of specimens

The best possible foundation for evaluating whether chalk specimens are homogeneously dissolved by the treatment procedures applied in the current study is a thorough characterization of the initial state of the samples. Since the main variable of interest for the subsequent parts of the CHEMWEAK project is the sample porosity, the major focus has been on describing the initial porosity variation in the set of specimens as well as to establish a method for evaluating the spatial distribution of porosity in a specific specimen.

#### 6.1.1 Porosity, permeability and grain density

In general, it appears from the dataset representing the initial porosity and permeability of the test specimen set that both the porosity and permeability of the set with 98 plug specimens is normally distributed (Figures 6 and 7). The porosity ranges from 46.84 p.u. to 50.28 p.u. with an average porosity of 48.43 p.u. and a standard deviation of 0.61 p.u.. The N<sub>2</sub>-gas permeability ranges from 5.173 mD to 7.488 mD with an average single point N<sub>2</sub>-gas permeability of 6.392 mD and a standard deviation of 0.904 mD. Grain densities (not shown) vary between 2.698 g/cc and 2.748 g/cc with an average grain density of 2.710 g/cc and a standard deviation of 0.006 g/cc.

The very small variation in grain density suggests that most of the specimens are relatively "clean" and composed of close to 100 % calcium carbonate (grain density of 2.71 g/cc). Furthermore, the petrophysical data correspond well with data obtained by Frykman (2001) /23/ in a geostatistical study of 365 outcrop specimens from the Sigerslev quarry. This suggests that the specimens are representative to the Maastrichtian outcrop chalk from the Stevns area.

The correlation between porosity and permeability is not excellent (Figure 8). However, overall the highest permeabilities are observed at the highest porosities and the trend obtained is somewhat similar to the trend observed by Frykman (2001) /23/.



**Figure 6:** Porosity distribution of the 98 plug specimens from Stevns outcrop chalk. The normal distribution shown in the diagram is a normal distribution function with average of 48.34 p.u. and standard deviation of 0.61 p.u.



**Figure 7:** Permeability distribution of the 98 plug specimens from Stevns outcrop chalk. The normal distribution shown in the diagram is a normal distribution function with average of 6.392 mD. and standard deviation of 0.904 mD.



Figure 8: Permeability vs. porosity of the 98 plug specimens from Stevns outcrop chalk. Note that the permeability scale is linear. The dotted lines correspond to the standard deviations derived from the dataset while full lines indicate average porosity and permeability, respectively.

#### 6.1.2 CT-imaging and homogeneity

A prerequisite for using the CT-number as a measure for the porosity distribution in a plug specimen is that it is possible to establish a correlation between the measured CT-number and the porosity. The average CT-number (or Hounsfield units, HU) that can be obtained from any part of a CT-image, can be expressed as /16/

$$HU = 1000 * \frac{(\mu - \mu_{water})}{(\mu_{water} - \mu_{air})}$$
(2)

where  $\mu$  is the linear absorption coefficient of the bulk material and  $\mu_{water}$  and  $\mu_{air}$  are the linear absorption coefficients of water and air, respectively. Thus, according to Equation 2, the CT-number for pure air is -1000 HU, while pure water has a CT-number of 0 HU. Dense matter has a CT-number of *c*. 3000 HU.

If the CT-scanned plug specimen under consideration consists of a dry material with porosity  $\varphi$ , and linear absorption coefficient  $\mu_{matrix}$  for the grain matrix we have for a selected part of a CT-image that /18/:

$$\mu \cong (1 - \varphi) * \mu_{matrix} \tag{3}$$

Equation 3 is derived from the fact that the linear absorption coefficient of air is orders of magnitude lower than that of the solid matrix /19/.

In combination, Equations 2 and 3 suggest that the CT-number is a linear function of porosity, and that we may use the CT-number distribution in an X-ray CT image to represent the distribution of porosity within the plug specimen that the X-ray CT image depicts. However, as will be shown later, the straight forward relationship between porosity and CT-number derived above may be subject to some limitations due to experimentally introduced uncertainties.

Ideally, if the resolution of the CT-image was high enough, we would be able to distinguish single pores from solid matrix in a CT-image. However, the resolution of the CT-images recorded at DTU gives a pixel size of 156x156 µm and averages the density in a slice of 4 mm in thickness, while the typical size of pores in chalk is at the µm-scale. Therefore, we need to rely on average considerations. However, this is already implicitly given in Equation 2 which forms the basis for the methodology used in the project.

CT-imaging has in several previous studies proven useful for identification of wormhole formation (e.g. /4-5/, /8/), and therefore we suggest that the CT-images as well can be used to elaborate whether preferential dissolution takes place in one end of the sample rather than in another end.

We have chosen to represent the results of the image analysis of CT-images in two ways:

- As an average CT-number and associated standard deviation of the entire CT-image. This is done both in order to investigate the possible correlation between porosity and average CT-number, and in order to provide an estimate on the standard deviation that represents the minimum change in CT-number which statistically gives a significant change in CT-number.
- 2. As a histogram showing the distribution of pixels in the entire CT-image. Essentially, the same information is obtained in the histogram as in the average CT-number. However, the histogram also provides a visual indication of the distribution type of CT-numbers in each sample and as such an indication on the homogeneity of the sample.

Figure 9 shows a plot of the average CT-number vs. plug specimen porosity for all 98 plug specimens that were initially CT-scanned before any treatments were started.



**Figure 9:** Average CT-number of whole plug specimens vs. measured He-porosity of the 98 plug specimens of Stevns outcrop chalk. The blue dotted line shows a linear fit to the dataset while the green dotted lines show a +/- 0.5 p.u. deviation from the best linear fit.

As shown, the general trend is a decreasing average CT-number with decreasing porosity, and a linear fit provides a reasonable correlation ( $R^2 = 0.914$ ). According to the obtained linear relationship, the average CT-number is close to -1000 HU at 100% porosity and close to 3000 HU in the case of zero porosity. This is in very good agreement with the theory (cf. Equations 2 and 3). Thus for the purpose of our study, this simple analysis suggests that changes in average CT-numbers between two different treatments of the same plug specimen represent changes in the porosity of the plug specimen.

Figure 9 shows some scatter of the data around the linear fit causing a general precision of the porosity estimate from the CT-number of +/- 0.5 p.u. The variations have not been studied in detail, but are most probably due to various inhomogeneities, such as healed hair-lines, shell or pyrite fragments, and occurrence of highly porous subareas in some samples (Figure 10).



**Figure 10:** Examples of plug specimens with various inhomogeneities that may affect the relationship between average CT-number and porosity. A) Shell or pyrite fragments – plug #50. B) Healed hairline – plug #78. C) Higher porosity in the left part of the plug specimen (darker area) than in the right part of the image – plug #88.

The even better fit and precision between average CT-number and porosity for the 30 assumed homogeneous plug specimens selected for dissolution tests ( $R^2$ =0.9823; Figure 11) further suggests that the scatter in Figure 9 is due to various inhomogeneities in the plugs. X-ray CT-images for all 30 specimens selected for dissolution tests are shown in Appendix A.



Figure 11: Average CT-number of whole plug specimens vs. measured He-porosity of the 30 plug specimens of Stevns outcrop chalk selected for dissolution tests. The dotted line shows a linear fit to the.

To illustrate the application of the histograms, Figure 12 shows CT-images with corresponding histograms for an inhomogeneous plug specimen (plug #94) and a homogeneous plug specimen (plug #15), respectively. As shown, there is a clearly darker area present in the upper left part of plug #94 compared to the remaining part of the plug specimen. The darker area most probably represents an area with higher porosity and results in a bi-modal distribution of the CT-numbers in the CT-image as illustrated by the histogram in Figure 12A. For comparison, the histogram from the CT-image of a seemingly homogeneous plug specimen results in a uni-modal distribution of CT-numbers (Figure 12B). In addition and as a result of the two distinct different distributions, the calculated standard deviation of CT-numbers is much lower for the homogeneous plug specimen (standard deviation of 86; Figure 12A).

A similar analysis of the CT-images recorded after 2, 4, and 6 acid treatments, respectively, is expected to provide a good indication on whether plug specimens have been dissolved homogeneously. I.e., if the distribution of CT-numbers is the same type and the standard deviation is of equal size after treatment as before treatments were performed, a decrease in mean CT-number is expected to represent a homogeneous increase in porosity of a plug specimen.



Figure 12: CT.images and histograms of A) inhomogeneous sample with bi-modal CT-number distribution and B) homogeneous sample with uni-modal distribution.

## 6.2 Dissolution with Acidgen FG

Acidgen FG is a commercial formic acid precursor, available from Cleansorb Limited and used for acidizing treatments of oil and gas wells. Acidgen FG has in a few cases previously been used to create homogeneous dissolution of carbonate samples as is also the objective of the present study /4-5/,/7/. It hydrolyses to produce formic acid in-situ as a result of heating, or as a result of enzyme action, if a suitable enzyme is included in the formulation. In oilfield applications it is typically used at concentrations of 5-15% w/v. The product dissolves readily in water and most oilfield brines. Solutions of Acidgen FG in water will generate formic acid at a low but measurable rate at room temperature. The generation of formic acid takes place according to the following reaction:

Acidgen FG + 
$$H_2O \rightarrow$$
 Formic acid + alcohol (4)

In the case of the Acidgen FG stock solution, there is only a very low concentration of free organic acid present, i.e. typically there is a maximum of 0.5% free acid (formic acid) in the

concentrate. However, as indicated by Reaction 4 the organic acid formation starts as soon as the stock solution is diluted in water. According to Cleansorb (Ralph Harris, pers. comm.), the rate of acid generation is a function of Acidgen FG dilution, pH, temperature, and concentration of any catalyst, e.g. enzymes. In the present case, Acidgen FG was used without catalysts in order to avoid possible contamination of sample surfaces with enzymes. Therefore in our experiments, the rate of Reaction 4 is expected to depend only on pH and temperature; i.e. the rate increases with increasing pH as well as with increasing temperature. As the reaction taking place in our experiments is taking place in a calcium carbonate buffered system that is open to the atmosphere, the only way to control the rate of Reaction 4 in the experiments is really to control the temperature at which the reaction takes place.

Following the formation of formic acid in a chalk sample, the main reaction taking place will be dissolution of calcium carbonate according to Reaction 5:

 $\begin{array}{rcl} 2\mathsf{HCOOH} & + & \mathsf{CaCO}_3 & \leftrightarrow & \mathsf{Ca}(\mathsf{HCOO})_2 & + & \mathsf{CO}_2 + \mathsf{H}_2\mathsf{O} & (5) \\ \\ \mathsf{Formic} \ \mathsf{acid} & + & \mathsf{calcium} \ \mathsf{carbonate} & \leftrightarrow & \mathsf{calcium} \ \mathsf{formate} & + & \mathsf{CO}_2 + \mathsf{water} \end{array}$ 

Since there is excess of carbonate in a chalk sample and since the dissolution kinetics of calcium carbonate are generally fast, the rate of reaction will mainly be a function of acid concentration and temperature. In general, as suggested from a variety of studies of dissolution of carbonate with organic acids (e.g. /8/,/20/), it is expected that the rate of Reaction 5 will increase with increasing acid concentration and temperature.

Since the objective of the present project is to perform homogeneous dissolution of chalk plug specimens in a controlled and reproducible way, the procedure with dissolution by Acidgen FG was split in two steps:

Step 1 – where the reaction rate of Reaction 4 was kept as low as possible while introducing the solution into the porespace of the plug specimens

Step 2 – where the reaction rates of Reactions 4 and 5 were increased in order to keep the shut-in period for dissolution as short as possible. This was done by increasing the temperature.

The following sections describe the results obtained from the experiments with Acidgen FG.

#### 6.2.1 Initial experiments

Since there are no general guidelines available as regard the optimal Acidgen FG concentration, temperatures, and shut-in periods to use for creation of homogeneous dissolution in chalk specimens, initial experiments were performed in order to provide the basis for the design of the experimental procedure in the remaining part of the project.

Acidgen FG solutions of 2% (w/v) and 5% (w/v) where prepared, and the pH of the solutions was measured at various intervals in order to provide information regarding the rate of

Reaction 4. For both solutions, the rate of acid generation was measured as a function of temperature (Figure 13).



**Figure 13:** Measured pH in diluted Acidgen FG solutions as a function of time after the diluted solution was made from the stock Acidgen FG solution. The large jump in pH of the 2% Acidgen FG solution between 6 and 8 days may be due to a calibration error of the pH electrode.

The increase of the reaction rate of Reaction 4 with increasing temperature is shown as a faster pH drop at high temperature compared to low temperature (Figure 13). Thus, at 50°C, the pH is almost constant at pH 2.3 one day after the dilutions of Acidgen FG were made, while at a temperature of  $4^{\circ}$ C and below, the pH continues to decrease during a period of 12 days after the diluted solution was made. Figure 13 also shows that the acid generation at 50°C is only slightly faster than at 25°C.

In Figure 14, the pH of the diluted solutions of Acidgen FG is shown for the first day of the experiment. As shown, the acid production is relatively low during the first two hours after preparation in both of the tested solutions at a temperature of 4°C and below, and even at room temperature (25°C, Figure 14), acid production is relatively slow during the first one hour after preparation.



**Figure 14:** Measured pH in diluted Acidgen FG solutions during the first day after the diluted solution was made from the stock Acidgen FG solution. The figure represents the initial part of Figure 13.

Based on the obtained results, it was decided to keep all solutions in the refrigerator (at 5°C) prior to saturation of chalk specimens with the Acidgen FG solution, and to prepare the Acidgen FG solutions immediately before introduction into the plug specimens. The following vacuum saturation, which was carried out at room temperature, was generally

performed during a period of less than one hour. Furthermore, based on the pH measurements shown in Figures 13 and 14, it was decided to have a general oven shut-in period of 48 hours at 50°C.

#### 6.2.2 Mass balances, porosity and permeability changes

The specimens selected for Acidgen FG experiments are listed in table 3.

Treatment	Specimen ID	Porosity (%)	N <sub>2</sub> -gas perm. (mD)
	Q	/8.00	6 90/
	20	48.00	5.546
	20	40.30	5.340 E 921
	21	40.42	5.651
2% Acidgen	22	47.94	5.625
	74	47.83	5.862
	82	48.26	7.141
	86	47.99	5.879
	89	47.80	6.035
	7	48.28	6.871
	8	48.85	6.968
E% Asidaan	15	48.25	6.270
5% Actugen	17	48.18	6.694
	51	46.88	5.877
	72	46.89	5.683
	24	48.88	6.563
15% Asidaan	27	48.44	6.159
15% Actugen	28	48.08	6.008
	32	48.10	6.226

 Table 3: List of initial petrophysical properties of plug specimens selected for Acidgen FG experiments.

As indicated in the table, subsets of samples were treated with 2%, 5%, and 15% Acidgen FG, respectively. This was done in order to determine the optimal concentration of Acidgen FG solution for the homogeneous dissolution of the chalk as well as to identify possible limitations caused by the acid precursor concentration. Treatments were performed as described in detail in Chapter 3 and the treatment procedure was repeated up to six times per specimen.

In some cases, the treatments stopped before reaching six treatments. For two plug specimens (plug #17 and plug #82) this was because of the selection for rock mechanics experiments after 2-3 treatments /1/, while for the remaining samples (plug #89 - 2% Acidgen FG; plugs #8 and #51 – 5% Acidgen FG; plugs #24, #27, #28, and #32 – 15% Acidgen FG), the stop in treatments was due to sample failure.

Specifically for samples treated by 15% Acidgen FG, sample failure occurred during heating in the oven at the second treatment. The samples broke in several parts as exemplified in Figure 15. Comparison of the broken samples with the initial state X-ray CT images, suggests that the fractures in the 15% Acidgen treated specimens occur along healed hairlines in the samples. The most probable reason for the failure in these specimens is that  $CO_2$  generated as part of the dissolution process (Reaction 5) is generated faster than the permeability of the specimen allows it to escape from the specimens. Thus, an overpressure is built up in the specimens, eventually causing failure. The failure occurs along the healed hairlines as these are probably the parts of the specimens with lowest rock mechanical strength.



**Figure 15:** Pictures of outcrop chalk specimens after the second treatment with 15% Acidgen FG solution. The pictures clearly show the sample failure occurring along healed hairlines in the samples. Specimens are *c*. 38 mm in diameter.

Figure 16 shows the mass loss from each individual specimen after each treatment with Acidgen FG solution. The general trend is that for each Acidgen FG solution, the mass loss per treatment is relatively constant. Thus, for 2% Acidgen FG, the general trend is that approximately 1.3-1.4 g of sample is dissolved per treatment, while for 5% Acidgen FG the average mass loss is around 3.0 g per treatment. Deviations such as the increased mass loss for samples #9, #20, #21, #22 at the 2<sup>nd</sup> treatment remain currently unexplained but may be due to experimental errors such as dilution errors during preparation of Acidgen FG solution or similar.

In general, the results shown in Figure 16 indicate that the experimental procedure followed creates reproducible results, and further that, with some uncertainty, it is possible to predict the mass of sample dissolved per treatment. The latter is especially the case for specimens treated with 2% Acidgen FG solution (cf. Figure 16). Altogether, this suggests that for future experiments, it is possible to estimate the number of treatments needed to dissolve a certain percentage of carbonate in a sample, provided the Acidgen FG concentration.



Figure 16: Mass loss per treatment from chalk specimens treated with Acidgen FG solutions.

The general good reproducibility of the dissolution of specimens as illustrated by the mass loss plot in Figure 16 is further illustrated by the Ca concentrations measured during the experiment (Figure 17). Thus, during the treatment with Acidgen FG, dissolution of the chalk specimen takes place only after the specimen has been placed in the oven (sampling stage 2, Figure 17), while initially after saturation with Acidgen FG, the Ca concentration in the beaker with chalk specimen and Acidgen FG solution is low (sampling stage 1, Figure 17). For most of the Acidgen FG treatments, the Ca analyses show similar concentrations in the effluent water during water flooding after treatment (sampling stage 3, Figure 17) as was obtained in the water in the beaker during the reaction time in the oven. This suggests that the system with Acidgen FG and chalk specimen was in equilibrium before water flooding was initiated. Finally, the close to zero concentration at sampling stage 4 (Figure 17) indicates that all reactants were removed from the specimens before drying and CCAL were carried out.



**Figure 17:** Ca-concentrations in solutions in contact with plug specimen # 74 during treatment with 2% Acidgen FG solution. Stage 1: Concentration in solution just after vacuum saturation. Stage 2: Concentration in solution after 48 h shut-in period in the oven. Stage 3: Concentration of effluent during the initial part of the water flooding of the specimen. Stage 4: Concentration at the end of the water flooding before preparation for CCAL.

The mass loss caused by the Acidgen FG treatments is followed by a corresponding increase in porosity as a result of each Acidgen FG treatment (Figure 18). As the case was for the mass loss, the porosity change caused per treatment with Acidgen FG seems easiest to reproduce for the specimens treated with 2% Acidgen FG solution. The observed close-to-linear relationship between porosity and number of Acidgen FG treatments suggests that the experimental procedure followed causes dissolution of the chalk specimens not only on the outside of the plug specimens but also in the interior pore space. However, though it is likely, the results shown in Figure 18 do not indicate whether the increase in porosity obtained by the Acidgen FG treatment causes a homogeneous dissolution of the samples or not.

Figure 18 also suggests that the final porosity after a specific number of treatments with a specific concentration of Acidgen FG may be predicted with a precision of 0.5-0.7 p.u. independently on the initial porosity of the sample. However, there is a slight tendency that the samples with initially lowest porosity also show the lowest change in porosity with the number of acid treatments. This makes reasonable sense as the amount of acid available for dissolution per unit of chalk surface area is slightly higher in samples with high porosity than samples with low porosity.



Figure 18: Absolute change in porosity as a function of number of Acidgen FG treatments for chalk specimens treated with Acidgen FG solution.

As for the porosity, the permeability also increases with the number of Acidgen FG treatments. However, as illustrated by Figure 19, the trend is not as clear and linear as the trend for the porosity. Comparison of Figures 18 and 19 further suggests that the permeability is affected to a higher degree as soon as the change in porosity is higher than 2.0 p.u. from





Figure 19: Permeability as a function of number of Acidgen FG treatments for chalk specimens treated with Acidgen FG solution.

Overall, the CCAL data obtained after each Acidgen FG treatment suggest that the experimental procedure applied using Acidgen FG to dissolve carbonate in the tested outcrop chalk samples creates reproducible results and the possibility to dissolve carbonate from the samples with an approximate uncertainty on the predicted change in porosity per Acidgen FG treatment of 0.5-0.7% p.u.. Apparently, the best reproducibility and the lowest number of specimen failures take place by application of a 2% Acidgen FG solution, but by choosing this solution, the number of Acidgen FG treatments needed for dissolving a certain percentage of a specimen also increases considerably. Thus, for future treatments, the Acidgen FG solution applied will need to depend on a trade-of between the time available and the precision wanted.

#### 6.2.3 CT-imaging and homogeneity

Even though great care was taken during the treatment of plug specimens with Acidgen FG, chips and pieces broke off several of the specimens due to the treatment. As a result and as already mentioned, the treatment of some plugs needed to stop completely before all six treatment cycles were completed. For other specimens, the treatment could continue after trimming.

Figure 20 shows the average CT-number vs. porosity of specimens that were treated with Acidgen FG solution. The plot also shows the trend line obtained from the initial state measurements on all 30 plugs selected for the dissolution study before any treatment was commenced (cf. Figure 13). Apparently, the initial correlation obtained from all 30 specimens is close to being maintained after treating the plug specimens with Acidgen FG as long as samples that were trimmed during the treatment process are excluded from the analysis. Thus, the dissolution of calcium carbonate with Acidgen FG causes the data in Figure 20 to shift towards the lower right corner of the diagram along the linear trend line as a result of an increase in porosity and corresponding decrease in average CT-number. This definitely indicates that changes in average CT-numbers as a result of the treatments with Acidgen FG can be assumed to represent changes in the porosity distribution in the plug specimens.



Figure 20: Average CT-number of whole plug specimens vs. measured He-porosity of the plug specimens of Stevns outcrop chalk that were treated with Acidgen FG solution and not broken during treatment. The blue dotted line shows a linear regression fit to all data points from specimens not trimmed during the six treatments. The red dotted line shows the linear regression fit originally obtained by fitting to the pre-treatment dataset (cf. Figure 11).Yellow symbols show post-treatment data from specimens that were trimmed at some point during the six treatments with Acidgen FG solution.

As illustrated by the data points in Figure 20, representing specimens that were trimmed at some point during the six treatment cycles with Acidgen FG, the linear trend between average CT-number and porosity is dependent on the size of the specimen. Thus, as the specimens become smaller, the average CT-numbers tend to increase and deviate from the original linear trend. The reason for this is apparently that X-ray beam hardening is influencing the entire CT-image and not only the rim of the CT-image as illustrated by the seemingly thin white frame around all specimens in the CT-images (e.g. Figure 10). The influence from beam hardening on the entire image also becomes obvious from a simple cross-sectional analysis of Hounsfield units along the length axis of a seemingly homogeneous specimen (Figure 21). As shown, there is a clear trend that the CT-number becomes higher towards the ends of the specimen and reaches a minimum in the center of the specimen. Thus, the only specimens included in the following analysis are specimens where CT-images have been recorded on approximately equal size plug specimens.



**Figure 21:** CT-image of plug specimen #20. The result of the image analysis along the white dotted line, as shown to the right in the figure, illustrates that beam hardening affects the entire CT-image.

As an example of the histogram analysis, Figure 22A) shows histograms of CT-images of plug #22. The histograms shown represent images of the plug specimen recorded before treatment and after 2, 4, and 6 treatments, respectively. As shown, the average CT-number decreases as a result of the increased porosity due to dissolution of carbonate in the specimen. In the same time, the uni-modal distribution of CT-numbers is maintained and the standard deviation does not change considerably due to the treatment with Acidgen FG. Apparently, the initial porosity distribution is maintained during the Acidgen FG treatment procedure, even for specimens with an initially slightly less homogeneous porosity distribution as illustrated for plug #7 in Figure 22B). Similar image analyses are available for all non-shortened specimens in Appendix B. All together, these results suggest that the specimens are dissolved homogeneously by the treatment with Acidgen FG.



**Figure 22:** Histograms representing image analysis of CT-images after 0, 2, 4, and 6 treatments with Acidgen FG, respectively. A) Plug specimen # 22 treated with 2% Acidgen FG. B) Plug specimen # 7 treated with 5% Acidgen FG.

## 6.3 Dissolution with acetic acid

Acetic acid is the second simplest carboxylic acid after formic acid, and as such a weak organic acid. Acetic acid was introduced in the experimental protocol for two reasons:

- 1. First, acetic acid is well known in the household as a descaling agent that increases it's reaction rate with carbonate when the temperature is increased; e.g. in coffee boilers, etc.
- 2. Compared to the Acidgen FG experiments, where the organic acid (formic acid) is produced mainly after the introduction of Acidgen FG solution into the plugs, the acetic acid is present initially at saturation. Therefore, the use of acetic acid makes a good case for comparing with the performance of the Acidgen FG solution.

The dissolution of calcium carbonate with acetic acid can be described by the following reaction:

$$\begin{array}{rcl} 2CH_{3}COOH & + & CaCO_{3} & \leftrightarrow & Ca(CH_{3}COO)_{2} & + & CO_{2} + H_{2}O & (6) \\ acetic acid & + & calcium carbonate & \leftrightarrow & calcium acetate & + & CO_{2} + water \end{array}$$

The dissolution rate of calcite (the most common calcium carbonate mineral) with acetic acid has been shown to be much slower than dissolution of calcite with the stronger inorganic acid HCl /21-22/. In the same time, the dissolution rate of calcite with acetic acid is dependent on the temperature (Figure 23), and therefore the application of acetic acid with the general experimental procedure described in Section 3.2 seemed straight forward as a comparative study to the Acidgen FG experiments.



Figure 23: Effects of temperature on the rate of calcite dissolution with 0.5 M acetic acid (from Fredd and Fogler, 1998).

#### 6.3.1 Initial experiments

As the experimental procedure followed with the acetic acid experiments was identical to the procedure followed during the experiments with Acidgen FG (cf. Section 3.2), only a single initial experiment was performed with acetic acid before plug specimens were dissolved. The initial experiment was performed to provide an estimate on the reaction rate of acetic acid with the chalk compared to the dissolution rate in the experiments with Acidgen FG. In the experiment, crushed chalk was submerged in either 2% acetic acid or 15% Acidgen FG and placed in an oven @ 50°C. Filtered water samples were taken at regular intervals and subsequently analysed for Ca content. The results (Figure 24) show that chalk dissolution with acetic acid is very fast compared to the dissolution taking place in the container with Acidgen FG. Furthermore, dissolution seems to reach equilibrium already during the initial part of the experiment in the case of acetic acid.



Figure 24: Ca concentration vs. time in experiments where crushed chalk was dissolved with 2% acetic acid or 15% Acidgen FG, respectively.

Based on these initial experiments as well as on previous studies of calcite dissolution kinetics with acetic acid /8/, the acetic acid experiments were performed with solutions of 0.5%, 2%, and 5% acetic acid, respectively.

#### 6.3.2 Mass balances, porosity and permeability changes

The specimens selected for acetic acid experiments are listed in table 4.

Treatment	Specimen ID	Porosity (%)	N <sub>2</sub> -gas perm. (mD)
	34	48.6	6.758
	36	49.32	6.778
0.5% ACON	37	49.55	6.758
	43	48.85	6.588
	54	48.98	6.543
	57	48.39	6.289
2% ACON	61	49.03	6.276
	65	48.95	6.271
	64	48.53	6.308
	66	48.67	6.143
5% ACUH	68	47.88	5.173
	73	48.8	6.107

 Table 4: List of initial petrophysical properties of plug specimens selected for acetic acid experiments.
Treatments with acetic acid were performed as described in detail in Chapter 3, and the treatment procedure was repeated up to six times per specimen. However, in most cases the treatments stopped before reaching six treatments, either because of specimen failure or because treatments showed to have no or negative effect on the porosity of the specimens.

Figure 25 shows the mass loss from each individual specimen after each treatment with acetic acid. In general, the mass loss from each specimen per treatment is higher with increasing strength of the acetic acid. Thus, for the specimens treated with 5% acetic acid the mass loss per treatment is more than 4 g, while for the specimens treated with 0.5% acetic acid, the mass loss is less than 2 g. However, compared to the Acidgen FG experiments (Figure 16), the mass loss obtained by acetic acid treatments seems less reproducible. This is a first indication that acetic acid is not as good a reactant as the Acidgen FG in the case where homogeneous dissolution in the whole plug specimen is wanted.



Figure 25: Mass loss per treatment from chalk specimens treated with acetic acid.

A further indication on the less suitability of acetic acid for homogeneous dissolution of the chalk specimens is the fact that equilibrium Ca-concentrations seem to be obtained already during saturation of the specimens as indicated by the similar Ca concentrations in the solutions after Stage 1, 2, and 3 (Figure 26). Figure 26 further shows that water flooding of the acetic acid treated specimens seems to remove all reactants from the pore space before CCAL analysis.



**Figure 26:** Ca-concentrations in solutions in contact with plug specimen # 36 during treatment with 0.5% acetic acid. Stage 1: Concentration in solution just after vacuum saturation. Stage 2: Concentration in solution after 48 h shut-in period in the oven. Stage 3: Concentration of effluent during the initial part of the water flooding of the specimen. Stage 4: Concentration at the end of the water flooding before preparation for CCAL.

In Figure 27, the porosity changes caused by the acetic acid treatments are illustrated. As shown, the porosity change is only to a limited extend reproducible when comparing different plug specimens. Furthermore, while dissolution is apparently taking place during the treatments with acetic acid as indicated by both weight loss (Figure 25) and Ca concentrations (Figure 26), the dissolution does not cause any significant change in porosity for specimens treated with either 0.5% or 2% acetic acid, and in some cases even a decrease in porosity is observed after a treatment step with acetic acid. This indicates that most dissolution probably takes place from the outside of the specimen, as was already indicated by the high Ca concentrations obtained during saturation of the specimens.

![](_page_38_Figure_0.jpeg)

Figure 27: Absolute change in porosity as a function of number of acetic acid treatments for chalk specimens treated with acetic acid.

Interestingly, the permeability of specimens treated with either 2% or 5% acetic acid seems to increase in a reproducible way and following a somewhat linear function of the number of treatments. Thus, suggesting that some dissolution takes place in the interior of the plug specimens during the acetic acid treatment as well, though this dissolution does not cause any change in porosity whatsoever. The specific reason for this could be subject to further study in future projects.

![](_page_39_Figure_0.jpeg)

Figure 28: Permeability as a function of number of acetic acid treatments for chalk specimens treated with acetic acid.

#### 6.3.3 CT-imaging and homogeneity

The lack of any porosity change as a result of the acetic acid treatments is further illustrated by the cross-plot between average CT-numbers and porosity (Figure 29). As shown, even after five and six treatments with acetic acid, the specimens plot in the same area of the diagram as prior to treatment with acetic acid.

![](_page_40_Figure_2.jpeg)

Figure 29: Average CT-number of whole plug specimens vs. measured He-porosity of the plug specimens of Stevns outcrop chalk treated with acetic acid. The blue dotted line shows a linear regression fit to all data points in the figure.

The most obvious effect of the treatments to the relationship between average CT-number and porosity is the negative effect on the correlation coefficient changing from  $R^2 = 0.9823$ for the initial dataset (Figure 11) to  $R^2 = 0.7626$  in the dataset representing the acetic acid treated samples. The most probable reason for this is that the specimens treated with acetic acid apparently dissolves mainly from the outside of the specimen as illustrated for plug specimen #57 in Figure 30. This will eventually cause a larger scatter in the CT-number at similar porosities, as the comparison will be based on plug specimens of different size, and therefore on CT-images with different beam hardening influences as discussed previously.

![](_page_40_Figure_5.jpeg)

**Figure 30:** CT-images of plug specimen #57. A) Before treatment with 2% acetic acid. B) After 6 treatments with 2% acetic acid. Note that the specimen has become considerably smaller due to the treatment with acetic acid.

The preferential dissolution of the specimens from the outside during treatment with acetic acid is further illustrated by the histogram analysis showing no shift of the histogram along the x-axis even after up to six treatments with acetic acid (Figure 31). However, the dissolution apparently maintains the porosity distribution of the specimens as illustrated by the histograms with similar shape after 0, 2, 4, and 6 treatments, respectively.

![](_page_41_Figure_1.jpeg)

Figure 31: Histograms representing image analysis of CT-images after 0, 2, 4, and 6 treatments with 2% acetic acid, respectively - Plug specimen # 57.

#### 6.4 Comparison and evaluation of method tested

As already discussed in the previous sections, there is a large difference in the results obtained by application of Acidgen FG and acetic acid, respectively, for dissolution of calcium carbonate in outcrop chalk specimens.

The application of Acidgen FG seemingly provides reproducible results and the possibility for creating homogeneous porosity changes of the tested outcrop chalk specimens. The original porosity distribution seems to be honored when solutions of 2% or 5% Acidgen FG are used in the experimental protocol, while application of 15% Acidgen FG solutions in an unconfined set-up, as used in the present study, creates a too fast dissolution and associated production of  $CO_2$  compared to the outcrop chalk permeability. Therefore, sample failure is experienced at the high Acidgen FG concentration. However, the experiments with 2% and 5% Acidgen FG have shown that it is possible to create homogeneous dissolution in the outcrop chalk specimens, thereby changing the porosity at least 3.5 p.u. in these highly porous carbonates.

For comparison, the application of acetic acid in similar experiments apparently mostly creates fast dissolution of chalk specimens from the outside of the specimens. As a consequence, there is little or no associated change in porosity, and if any change in porosity is obtained by the treatment, it is much more random and less reproducible than is the case by treatment with Acidgen FG solution.

Overall, the results obtained in the present study suggest that application of 2% or 5% Acidgen FG solutions for homogeneous dissolution of chalk is preferable in future studies that have the purpose of preparing chalk specimens with homogeneous porosity changes for, e.g., rock mechanical studies.

# 7. Conclusions

Based on the results obtained in the present study, it can be concluded that:

- Image analysis of CT-images of plug specimens is a powerful tool to evaluate and document homogeneity and dissolution of chalk specimens. However, CT-images are highly influenced by beam hardening, and therefore great care should be taken during image analysis if the dimensions of specimens under investigation are changed, e.g. as a result of treatment during experiments.
- Dissolution of outcrop chalk specimens can be performed in a homogeneous way with up to 5% Acidgen FG by application of the method described and designed as part of the CHEMWEAK project.
- Homogeneous dissolution of outcrop chalk specimens with acetic acid is not possible.

### 8. References

/1/ Geo, 2014. Stevns Chalk treated Acidgen<sup>™</sup>, preliminary assessment. Triaxial compression tests. Geo project no.: 36983, report C2, 7pp.

/2/ Kjøller, C. & Zuta, J., 2012. CO<sub>2</sub>-brine-rock interactions in reservoir chalk rock – a coupled experimental and numerical approach for obtaining hydrochemical results at reservoir conditions. Paper SCA 2012-04, Proceedings of the International Symposium of the Society of Core Analysts. Aberdeen, Scotland, UK, 27-30 August, 2012. 12 pp.

/3/ Svec, R.K. & Grigg, R.B., 2001. Physical effects of WAG fluids on carbonate core plugs, Paper SPE 71496, SPE Annual Technical Conference Proceedings.

/4/ Ott, H., Oedai, S., Pentland, C.H., Eide-Engdahl, K., van der Linden, A.J., Gharbi, O., Bauer, A. & Makurat, A., 2013. CO<sub>2</sub> reactive transport in limestone: Flow regimes, fluid flow, and mechanical rock properties. Paper SCA 2013-029, Proceedings of the International Symposium of the Society of Core Analysts. Napa Valley, California, USA, 16-19 September, 2013. 12 pp.

/5/ Egermann, P., Bekri, S. & Vizika, O., 2010. An integrated approach to assess the petrophysical properties of rocks altered by rock-fluid interactions (CO<sub>2</sub> injection). Petrophysics, 51, 32-40.

/6/ Grigg, R.B. & Svec, R.K., 2003. Co-injected  $CO_2$ -brine interactions with Indiana Limestone. Paper SCA 2003-019, Proceedings of the International Symposium of the Society of Core Analysts. Pau, France, 21-24 September, 2003. 13 pp.

/7/ Egermann, P., Bemer, E. & Binzner, E., 2006. An experimental investigation of the rock properties evolution associated to different levels of CO<sub>2</sub> injection like alteration processes. Paper SCA 2006-034, Proceedings of the International Symposium of the Society of Core Analysts. Trondheim, Norway, 12-16 September, 2006. 15 pp.

/8/ Fredd, C.N. & Fogler, H.S., 1998. Influence of transport and reaction on wormhole formation in porous media. Fluid mechanics and transport phenomena, AIChE Journal, 44, 1933-1949.

/9/ Daccord, G. Toubol, E. & Lenormand, R., 1989. Carbonate acidizing: toward a quantitative model of the wormholing phenomenon. SPE Production Engineering, 4, 63-68.

/10/ Bazin, B., 2001. From matrix acidizing to acid fracturing: a laboratory evaluation of acid/rock interactions. SPE Production & Facilities, 16, 22-29.

/11/ Schechter, R.S. & Gidley, J.L., 1969. The change in pore size distribution from surface reaction in porous media. AIChE Journal, 15, 339-350.

/12/ Daccord, G., Lenormand, R. & Lietard, O., 1993. Chemical dissolution of a porous medium by a reactive – I model for the wormholing phenomenon. Chemical Engineering Science, 48, 169-178.

/13/ Békri, S., Thovert, J.F. & Adler, P.M., 1995. Dissolution of porous media. Chemical Engineering Science, 50, 2765-2791.

/14/ Geo, 2014. CHEMWEAK, Stevns Chalk, Specimen preparation, GEO project no 36983, Report C1. 5 pp.

/15/ American Petroleum Institute, 1998. Recommended Practices for Core Analysis. Recommended Practice 40. Second Edition, February 1998. API, Washington D.C.

/16/ Hounsfield, G.N., 1980. Computed Medical Imaging Nobel Lecture, 8 December 1979, J Radiology, 61, 459-68.

/17/ Schneider, C.A., Rasband, W.S. & Eliceiri, K.W., 2012. NIH Image to ImageJ: 25 years of image analysis. Nature Methods, 9, 671-675.

/18/ Maas, J.G. & Heebing, A., 2013. Quantitative X-ray CT for SCAL plug homogeneity assessment. Paper SCA 2013-004, Proceedings of the International Symposium of the Society of Core Analysts. Napa Valley, California, USA, 16-19 September, 2013. 12 pp.

/19/ Hubbell, J.H. & Seltzer, S.M., 2004. Tables of X-Ray Mass Attenuation Coefficients and Mass Energy-Absorption Coefficients (version 1.4). [Online] Available: http://physics.nist.gov/xaamdi [2014.12.19]. National Institute of Standards and Technology, Gaithersburg, MD.

/20/ Blinkova, E.V. & Eliseev, E.I., 2005. Dissolution of calcium carbonate in aqueous solutions of acetic acid. Russian Journal of Applied Chemistry, 78, 1064-1066.

/21/ Harris, F. N., 1961. Applications of acetic acid to well completion, stimulation and reconditioning. Journal of Petroleum Technology, 637-639.

/22/ Nierode, D. E. & Williams, B. B., 1971. Characteristics of acid reaction in limestone formations. SPE Journal. 406-418.

/23/ Frykman, P., 2001. Spatial variability in petrophysical properties in Upper Maastrichtian chalk outcrops at Stevns Klint, Denmark. Marine and Petroleum Geology, 18, 1041-1062.

## Appendix A

Initial state X-ray CT scanning images of the 30 selected plug specimens for further treatment and analysis

This appendix contains the initial state CT-scanning images of the 30 plug specimens selected for treatment with either Acidgen FG or acetic acid.

The appendix summarizes information from two longitudinal slices in the plug specimen. "Cross-section A" refers to the slice representing scanning along the 1->3 marker line (Figure A1) while "Cross section B" refers to scanning along the 2-> 4 marker line.

![](_page_47_Figure_4.jpeg)

Figure A1: Illustration showing the marking of samples for CT-scanning. The marking ensured that CT-scanning was always carried out along the same cross-section of the specimen at any subsequent CT-scanning.

Cross-section A Cross-section B Cross-section A Cross-section B   Average CT = 1030 Average CT = 1041 Average CT = 1014 Average CT = 1014 Average CT = 1015   Sdev = 66 Sdev = 77 Sdev = 61 Sdev = 65   Plug #9 Plug #15 Cross-section B Cross-section B   Cross-section A Cross-section B Cross-section A Cross-section B   Average CT = Average CT = 1027 Average CT = 1032 Sdev = 60   Average CT = Average CT = 1027 Sdev = 60 Sdev = 60   Plug #17 Plug #20 Cross-section B Cross-section A Cross-section B   Cross-section A Cross-section B Cross-section A Cross-section B Cross-section B   Average CT = Average CT = 1027 Average CT = 1032 Sdev = 60 Sdev = 60   Plug #17 Plug #20 Cross-section A Cross-section B Cross-section B Cross-section B   Average CT = 1039 Average CT = 1034 Average CT = 1041 Average CT = 1041 Sdev = 57   Average CT = 1039 Average CT = 1034 Average CT = 1041 Sdev = 57	Plug #7		Plug #8	
Average CT = 1030 Average CT = 1041 Average CT = 1014 Average CT = 1015   Sdev = 66 Sdev = 77 Sdev = 61 Average CT = 1015   Sdev = 66 Sdev = 77 Sdev = 61 Sdev = 65   Plug #9 Plug #15   Cross-section A Cross-section B Cross-section A Cross-section B   Average CT = Average CT = Average CT = 1027 Average CT = 1032   Average CT = Average CT = Sdev = 69 Sdev = 60   Plug #17 Plug #20   Cross-section A Cross-section B Cross-section A Cross-section B   Image CT = Nerage CT = 1034 Average CT = 1041 Average CT = 1041   Average CT = 1039 Average CT = 1034 Average CT = 1041 Average CT = 1041	Cross-section A	Cross-section B	Cross-section A	Cross-section B
Average CT = 1030 Sdev = 66Average CT = 1041 Sdev = 77Average CT = 1014 Sdev = 61Average CT = 1015 Sdev = 65Plug #9Plug #15Cross-section ACross-section BCross-section ACross-section BImage: Cross-section AImage: Cross-section BImage: Cross-section BImage: Cross-section BImage: Cross-section AImage: Cross-section BImage: Cross-section BImage: Cross-section BImage: Cross-section AImage: Cross-section BImage: Cross-section BImage: Cross-section BImage: Cross-section AImage: Cross-section BImage: Cross-section AImage: Cross-section BImage: Cross-section ACross-section BImage: Cross-section AImage: Cross-section BImage: Cross-section ACross-section BCross-section ACross-section BImage: Cross-section ACross-section BImage: Cross-section BImage: Cross-section BImage: Cross-section ACross-section BImage: Cross-section BImage: Cross-section BImage: Cross-section ACross-section BImage: Cross-section BImage: Cross-section BImage: Cross-section AImage: Cross-section BImage: Cross-section BImage: Cross-section BImage: Cross-section AIm				
Sdev = 66Sdev = 77Sdev = 61Sdev = 65Plug #9Plug #15Cross-section ACross-section BCross-section ACross-section BImage: Cross-section AImage: Cross-section AImage: Cross-section BImage: Cross-section BImage: Cross-section AImage: Cross-section BImage: Cross-section BImage: Cross-section BImage: Cross-section AImage: Cross-section BImage: Cross-section BImage: Cross-sect	Average CT = 1030	Average CT = 1041	Average CT = 1014	Average CT = 1015
Plug #9Plug #15Cross-section ACross-section BCross-section ACross-section BImage: Cross-section AImage: Cross-section AImage: Cross-section BImage: Cross-section AImage: Cross-section BAverage CT = Sdev =Average CT = Sdev = 59Average CT = 1027 Sdev = 59Average CT = 1032 Sdev = 60Average CT = 1032 Sdev = 60Plug #17Plug #20Cross-section ACross-section BCross-section ACross-section BImage: Cross-section BCross-section ACross-section BCross-section AImage: Cross-section BCross-section ACross-section BCross-section AImage: Cross-section ACross-section BCross-section ACross-section BImage: Cross-section ACross-section BCross-section ACross-section BImage: Cross-section ACross-section BCross-section ACross-section BImage: Cross-section BCross-section ACross-section BCross-section BImage: Cross-section BCross-section ACross-section BCross-section BImage: Cross-section BCross-section ACross-section BCross-section BImage: Cross-section BCross-section BCross-section BCross-section BImage:	Sdev = 66	Sdev = 77	Sdev = 61	Sdev = 65
Plug #9 Plug #15   Cross-section A Cross-section B Cross-section A Cross-section B   Image: CT = sector A   Average CT = sector A Average CT = sector B Average CT = 1027 Average CT = 1032   Sdev = Sdev = 59 Sdev = 60   Image: Cross-section A Cross-section B Cross-section A   Cross-section A Cross-section B Cross-section A   Image: CT = 1039 Average CT = 1034 Average CT = 1041   Average CT = 1039 Sdev = 62 Sdev = 51				
Closs-section ACloss-section BCloss-section ACloss-section BImage CT = Sdev =Average CT = Sdev =Average CT = 1027 Sdev = 59Average CT = 1032 Sdev = 60Image CT = Plug #17Average CT = 1027 Sdev = 59Average CT = 1032 Sdev = 60Image CT = Image CT = 1027 Sdev = 59Average CT = 1032 Sdev = 59Image CT = 1032 Sdev = 60Image CT = Image CT = 1034Image CT = 1041 Sdev = 51Average CT = 1041 Sdev = 57	Plug	g #9	Plug	#15 Cross section B
Average CT = Sdev =Average CT = Sdev = 59Average CT = 1027 Sdev = 59Average CT = 1032 	Cross-section A	Cross-section B	Cross-section A	Cross-section B
Average CT = Sdev =Average CT = Sdev = 59Average CT = 1027 Sdev = 59Average CT = 1032 Sdev = 60Plug #17Plug #20Cross-section ACross-section BCross-section ACross-section BImage: CT = 1030Image: CT = 1034 Sdev = 63Average CT = 1041 Sdev = 51Average CT = 1041 Sdev = 57				
Sdev = Sdev = 59 Sdev = 60   Plug #17 Plug #20   Cross-section A Cross-section B Cross-section A Cross-section B   Image: Cross-section A Image: Cross-section B Image: Cross-section B Image: Cross-section B   Image: Cross-section A Image: Cross-section B Image: Cross-section B Image: Cross-section B Image: Cross-section B   Image: Cross-section B Image: Cross-section B Image: Cross-section B Image: Cross-section B Image: Cross-section B   Image: Cross-section B Image: Cross-section B Image: Cross-section B Image: Cross-section B Image: Cross-section B   Image: Cross-section B Image: Cross-section B Image: Cross-section B Image: Cross-section B Image: Cross-section B Image: Cross-section B   Average CT = 1039 Average CT = 1034 Average CT = 1041 Average CT = 1041 Average CT = 1041   Sdev = 63 Sdev = 62 Sdev = 51 Sdev = 57	Average CT =	Average CT =	Average CT = 1027	Average CT = 1032
Plug #17 Plug #20   Cross-section A Cross-section B Cross-section A   Image: Cross-section A Image: Cross-section B Image: Cross-section B   Image: Cross-section A Image: Cross-section B Image: Cross-section B   Image: Cross-section B Image: Cross-section B Image: Cross-section B   Image: Cross-section B Image: Cross-section B Image: Cross-section B   Image: Cross-section B Image: Cross-section B Image: Cross-section B   Image: Cross-section B Image: Cross-section B Image: Cross-section B   Image: Cross-section B Image: Cross-section B Image: Cross-section B   Image: Cross-section B Image: Cross-section B Image: Cross-section B   Image: Cross-section B Image: Cross-section B Image: Cross-section B   Image: Cross-section B Image: Cross-section B Image: Cross-section B   Image: Cross-section B Image: Cross-section B Image: Cross-section B   Image: Cross-section B Image: Cross-section B Image: Cross-section B   Image: Cross-section B Image: Cross-section B Image: Cross-section B   Image: Cross-section B Image: Cross-section B Image: Cross-section B	Sdev =	Sdev =	Sdev = 59	Sdev = 60
Plug #17Plug #20Cross-section ACross-section BCross-section ACross-section BImage: Cross-section AImage: Cross-section AImage: Cross-section AImage: Cross-section BImage: Cross-section				
Cross-section A Cross-section B Cross-section A Cross-section B   Image: Cross-section A Image: Cross-section A Image: Cross-section B Image: Cross-section B   Image: Cross-section A Image: Cross-section B Image: Cross-section B Image: Cross-section B   Image: Cross-section A Image: Cross-section B Image: Cross-section B Image: Cross-section B   Average CT = 1039 Average CT = 1034 Average CT = 1041 Average CT = 1041   Sdev = 63 Sdev = 62 Sdev = 51 Sdev = 57	Plug	g #17	Plug	<b>#20</b>
Average CT = 1039Average CT = 1034Average CT = 1041Average CT = 1041Sdev = 63Sdev = 62Sdev = 51Sdev = 57	Cross-section A	Cross-section B	Cross-section A	Cross-section B
Average C1   = 1039   Average C1   = 1034   Average C1   = 1041   Average C1   = 1041     Sdev = 63   Sdev = 62   Sdev = 51   Sdev = 57   Sdev = 57				
	Sdev = $63$	Sdev = 62	Sdev = 51	Sdev = 57

Plug #21		Plug #22	
Cross-section A	Cross-section B	Cross-section A	Cross-section B
			A Aller
Average CT = 1037	Average CT = 1038	Average CT = 1060	Average CT = 1051
Sdev = 55	Sdev = 61	Sdev = 52	Sdev = 61
	#24	Plug	#21
Cross-section A	Cross-section B	Cross-section A	Cross-section B
Average CT = 1005	Average CT = 1014	Average CT = 1029	Average CT = 1037
Sdev = 61	Sdev = 68	Sdev = 64	Sdev = 51
Plug	<b>j #28</b>	Plug	#32
Cross-section A	Cross-section B	Cross-section A	Cross-section B
Sdev = $65$	Sdev = $67$	Sdev = $62$	Sdev = $55$
0000 - 00		0000 - 02	0007 - 00

Plug #34		Plug #36	
Cross-section A	Cross-section B	Cross-section A	Cross-section B
Average CT = 1016	Average CT = 1031	Average CT = 995	Average CT = 988
Sdev = 62	Sdev = 71	Sdev = 66	Sdev = 63
Pluç	j #37	Plug	#43
Cross-section A	Cross-section B	Cross-section A	Cross-section B
Average CT = 991	Average $CT = 995$	Average CT = 1018	Average CT = 1012
Sdev = $58$	Sdev = 61	Sdev = $61$	Sdev = $62$
Plug #51		Plug #54	
Cross-section A	Cross-section B	Cross-section A	Cross-section B
Average $CT = 1096$	Average $CT = 1096$	Average CT = 1008	Average CT = 1006
Sdev = 64	Sdev = 62	Sdev = 59	Sdev = 57
0000 - 04		0uev - 33	00ev - 01

Plug #57		Plug #61	
Cross-section A	Cross-section B	Cross-section A	Cross-section B
Average CT = 1027	Average CT = 1041	Average CT = 1005	Average CT = 1006
Sdev = 61	Sdev = 72	Sdev = 59	Sdev = 57
Plug	<b>#64</b>	Plug	) #65
Cross-section A	Cross-section B	Cross-section A	Cross-section B
Average CT = 1026	Average CT = 1025	Average CT = 1012	Average CT = 1012
Sdev = 63	Sdev = $60$	Sdev = $65$	Sdev = $67$
Plug #66		Plug #68	
Cross-section A	Cross-section B	Cross-section A	Cross-section B
Average CT = 1015	Average CT = 1015	Average CT = 1059	Average CT = 1042
Sdev = 71	Sdev = 67	Sdev = 68	Sdev = 65

Plug #72		Plug #73	
Cross-section A	Cross-section B	Cross-section A	Cross-section B
Average CT = 1089	Average CT = 1095	Average CT = 1016	Average CT = 1015
Sdev = 53	Sdev = 63	Sdev = 64	Sdev = 63
Plug	j #74	Plug	#82
Cross-section A	Cross-section B	Cross-section A	Cross-section B
Average CT = 1048	Average CT = 1048	Average CT = 1042	Average CT = 1025
Sdev = 68	Sdev = 69	Sdev = 78	Sdev = 61
Dive	- #00	Dive #90	
Plug	Gross costion R	Plug	#89
Sdev = 62	Sdev = 61	Sdev = 77	Sdev = 84

## Appendix B

Histograms of CT-images of plug specimens

This appendix contains histograms of CT-images of plug specimens used for dissolution experiments.

For each plug specimen, a histogram per CT-scanning event is presented. Thus, in most cases, a histogram is shown representing the CT-images recorded initially, and after 2,4, and 6 treatments, respectively.

The appendix contains only CT-images of plug specimens that were not shortened as part of the dissolution process because it was observed that the influence on CT-numbers from beam hardening is different for samples with different sizes. Therefore, it is not possible to compare CT-images of specimens before and after shortening with the purpose of assessing whether dissolution has taken place homogeneously.

When analyzing CT-images with the use of ImageJ, the histogram of the CT-numbers present in each CT-image, is drawn based on a sub-division of CT-numbers in exactly 256 groups (or bins). This is default in ImageJ and not possible to change. Thus, the interval of CT-numbers represented in each group may vary from image to image.

In our case, the subdivision created by ImageJ in most cases results in "doubler histograms" as exemplified by the dots in Figure B1. The exact reason for this remains unexplained but is most probably due to a systematic technical variation introduced during the recording of the CT-image. In order to be able to compare histograms from two different treatments, we have chosen to level out the "doubler histograms" by plotting a moving average for 7 bins per point (solid line in Figure B1). However, for the initial state CT-image, the raw histogram provided by ImageJ is also shown.

![](_page_54_Figure_7.jpeg)

**Figure B1:** Example showing the "doubler histogram" obtained by the image analysis with ImageJ (dots) and the curve leveling the doubler effect out by averaging over 7 bins (solid line). The example is from plug #22, Cross-section A.

### PLUG #7 – Cross-section A

### Treated with 5% Acidgen FG

![](_page_55_Figure_4.jpeg)

![](_page_55_Figure_5.jpeg)

### PLUG #7 – Cross-section B

![](_page_56_Figure_3.jpeg)

![](_page_56_Figure_4.jpeg)

![](_page_56_Figure_5.jpeg)

### PLUG #15 - Cross-section A

### Treated with 5% Acidgen FG

![](_page_57_Figure_4.jpeg)

![](_page_57_Figure_5.jpeg)

### PLUG #15 – Cross-section B

### Treated with 5% Acidgen FG

![](_page_58_Figure_4.jpeg)

![](_page_58_Figure_5.jpeg)

### PLUG #21 – Cross-section A

![](_page_59_Figure_3.jpeg)

![](_page_59_Figure_4.jpeg)

![](_page_59_Figure_5.jpeg)

### PLUG #21 - Cross-section B

![](_page_60_Figure_3.jpeg)

![](_page_60_Figure_4.jpeg)

![](_page_60_Figure_5.jpeg)

### PLUG #22 - Cross-section A

### Treated with 2% Acidgen FG

![](_page_61_Figure_4.jpeg)

![](_page_61_Figure_5.jpeg)

### PLUG #22 - Cross-section B

### Treated with 2% Acidgen FG

![](_page_62_Figure_4.jpeg)

![](_page_62_Figure_5.jpeg)

### PLUG #36 - Cross-section A

### Treated with 0.5% acetic acid

![](_page_63_Figure_4.jpeg)

![](_page_63_Figure_5.jpeg)

### PLUG #36 - Cross-section B

### Treated with 0.5% acetic acid

![](_page_64_Figure_4.jpeg)

![](_page_64_Figure_5.jpeg)

### PLUG #43 - Cross-section A

![](_page_65_Figure_3.jpeg)

![](_page_65_Figure_4.jpeg)

![](_page_65_Figure_5.jpeg)

### PLUG #43 - Cross-section B

### Treated with 0.5% acetic acid

![](_page_66_Figure_4.jpeg)

![](_page_66_Figure_5.jpeg)

#### PLUG #57 - Cross-section A

![](_page_67_Figure_3.jpeg)

![](_page_67_Figure_4.jpeg)

![](_page_67_Figure_5.jpeg)

### PLUG #57 - Cross-section B

![](_page_68_Figure_3.jpeg)

![](_page_68_Figure_4.jpeg)

![](_page_68_Figure_5.jpeg)

### PLUG #61 – Cross-section A

![](_page_69_Figure_3.jpeg)

![](_page_69_Figure_4.jpeg)

![](_page_69_Figure_5.jpeg)

### PLUG #61 – Cross-section B

### Treated with 2% acetic acid

![](_page_70_Figure_4.jpeg)

![](_page_70_Figure_5.jpeg)

### PLUG #64 - Cross-section A

### Treated with 5% acetic acid

![](_page_71_Figure_4.jpeg)

![](_page_71_Figure_5.jpeg)
#### PLUG #64 - Cross-section B







### PLUG #66 - Cross-section A







#### PLUG #66 - Cross-section B







## PLUG #74 - Cross-section A

# Treated with 2% Acidgen FG





## PLUG #74 - Cross-section B

# Treated with 2% Acidgen FG



