A FAST METHOD FOR HOMOGENEOUS DISSOLUTION OF CHALK SPECIMENS FOR LABORATORY EXPERIMENTS – DOCUMENTATION BY X-RAY CT-SCANNING AND SCANNING ELECTRON MICROSCOPY

Claus Kjøller,[1] Lykourgos Sigalas,[1] Helle F. Christensen,[2] and Mona Minde[3,4,5]
(1) Geological Survey of Denmark and Greenland
(2) Geo, Denmark
(3) University of Stavanger, Norway
(4) The National IOR Centre of Norway
(5) IRIS AS, The International Research Institute of Stavanger, Norway

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ABSTRACT

In chalk reservoirs, acid injection for well stimulation purposes as well as certain EOR methods, such as CO_2 injection, causes dissolution of the chalk matrix due to the acidic nature of fluid injected. The effects of the chalk dissolution e.g. on rock mechanical properties are currently not well understood. This is partly due to challenges with interpretation of results from laboratory experiments in the context of *in situ* reservoir conditions as laboratory experiments most often result in inhomogeneous dissolution of chalk specimens. To facilitate this challenge, we present a method for fast homogeneous dissolution of chalk specimens by a so-called retarded or heat activated acid (Acidgen™ FG) – and subsequent documentation by X-ray CT-scanning and Field Emission Gun Scanning Electron Microscopy (FEG-SEM) imaging.

The method was validated through dissolution tests using a large number of Stevns outcrop chalk specimens. Dissolution of the chalk was performed with either of two acidic or acid generating solutions: 1) Acidgen™ FG or 2) acetic acid. In both cases, the homogeneity of the chalk dissolution was investigated by image analysis of X-ray CT-scanning images, and for the Acidgen™ FG case also of FEG-SEM images.

By application of Acidgen™ FG it is possible to create homogeneous dissolution in the outcrop chalk specimens with a resulting absolute porosity change of up to at least 3.5% Likewise, the retarded acid creates homogeneous dissolution of reservoir chalk specimens. For comparison, the application of acetic acid mostly creates fast inhomogeneous dissolution from the outside of the chalk specimens. Combined image analysis of X-ray CT images and SEM images has proven a strong tool for evaluation of the homogeneity of the chalk plug specimens.

INTRODUCTION

Rock mechanical laboratory tests most often explore the rock mechanics of bulk plug specimens. As a consequence, it is important to obtain homogeneous dissolution when rock mechanical effects caused by dissolution of rocks are studied. For the purpose of establishing experimental conditions favouring homogeneous dissolution, previous studies [1-3] 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. Thereby, the Damköhler number [4-6] is kept low initially by a low reaction rate when the retarded acid is introduced into the core specimen. Both Egermann et al. (2010) [2] and Ott et al. (2013) [1] showed that dissolution of various limestone samples could be carried out in a reasonably homogeneous way. In both cases, the specimens dissolved were subsequently used for rock mechanical tests showing that rock mechanical properties, such as Young's modulus, in general decreased as a function of the reasonably homogeneous porosity increase. When the porosity was increased by wormhole formation i.e. inhomogeneous channel-like dissolution Ott et al. (2013) [1] found that the mechanical parameters were practically unaltered in similar rock specimens.

The goal of this paper is to pave the ground for understanding relations between chalk dissolution and rock mechanical changes. We do this by modifying the retarded acid method and comparing the results with dissolution of chalk with acetic acid. This paper presents the modified method for homogeneous dissolution of chalk specimens and documentation hereof using X-ray CT-scanning and FEG-SEM imaging.

PROCEDURE

Specimen preparation

During the first stage of the project, 98 specimens of Stevns outcrop chalk of Maastrichtian age were plugged, marked and delivered for CT-scanning. Initial state conventional core analysis (CCAL) then followed, including determination of porosity, single point N_2-gas permeability, and grain density. CT-scanning images were analysed for average Hounsfield Units (also 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, the 30 most homogeneous specimens were selected for experiments with Acidgen™ FG and acetic acid. Each test specimen was treated with Acidgen™ FG or acetic acid until up to six (6) acid solution treatment cycles were performed (the treatment cycle is described in detail below). Acidgen™ FG solutions of 2% (v/v), 5% (v/v), and 15% (v/v) were tested and compared with results from dissolution of specimens with 0.5% (v/v), 2% (v/v), and 5% (v/v) acetic acid.

In the second stage of the project, 71 reservoir chalk core specimens from undisclosed offshore chalk were cleaned using toluene-methanol interchangeable flushing at room conditions. After cleaning, the samples were CT-scanned and CCAL was carried out.

Subsequently, a set of 28 specimens from the pool of most homogeneous samples were selected for experiments with 5% (v/v) Acidgen™ FG.

General treatment procedure

The principle of the treatment is five treatment steps:

1) Vacuum saturate specimens at 5-10°C and at a duration that will ensure 100% occupation of the pore volume by the acid precursor solution.
2) Heat the specimens at 50°C for 48h, while remaining saturated with the acid solution. In case of Acidgen™ FG, heating increases the kinetics related to formation of formic acid from the acid precursor solution.
3) Flush the specimens with at least 4 pore volumes (PV) of tap water or demineralized water (DW) in order to remove the acidic solution from the pore space of the plug specimens. Complete removal of acid solution and dissolution products are documented by pH and Ca concentration measurements.
4) Dry the specimens at 75°C for at least 24h until all water is evaporated from the pore space.
5) CCAL in order to observe the effects of the treatment.

Initially, and after completion of every two (2) treatment cycles, specimens are X-ray CT-scanned for comparison.

RESULTS AND DISCUSSION

Initial CT-Scanning

We have used image analysis of X-ray CT-images to show that porosity increases homogeneously in our chalk specimens as a result of the treatment with Acidgen™ FG. However, 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. In theory, this relationship should be linear [7]. Figure 1 shows that for the set of Stevns outcrop chalk specimens, the average CT-number correlates linearly to porosity. Especially for the set of 30 most homogeneous specimens this is the case (Figure 1B).

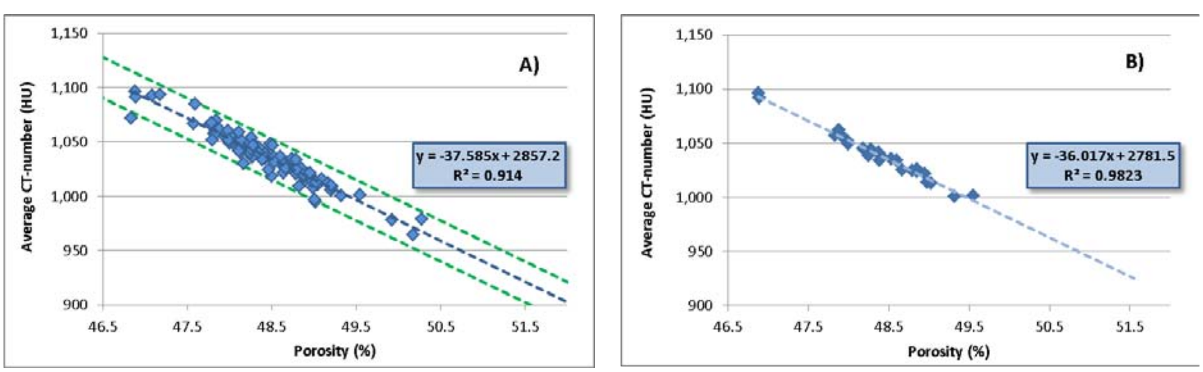

Figure 1: Average CT-number of Stevns outcrop chalk plug specimens vs. measured He-porosity A) all 98 and B) 30 selected specimens for dissolution tests.

Treatments with Acidgen™ FG

From the subset of the 30 most homogenous specimens, 18 were treated with various concentrations of Acidgen™ FG: Eight (8) specimens with 2% (v/v), six (6) specimens with 5% (v/v), and four (4) specimens with 15% (v/v). In all cases, there was a nearly linear porosity increase as a function of the number of treatments (Figure 2). In addition, the magnitude of the porosity increase was proportional to the concentration of Acidgen™ FG (Figure 2). Treatment of chalk specimens with 15% (v/v) Acidgen™ FG solution resulted in specimen failure after 2 treatments along healed hairline fractures in the specimens. This was most likely because of local pressure increase in the specimens due to CO_2 formation caused by the dissolution of the chalk. Therefore, a concentration of 5% (v/v) Acidgen™ FG was considered the upper limit for subsequent treatments according to the present method.

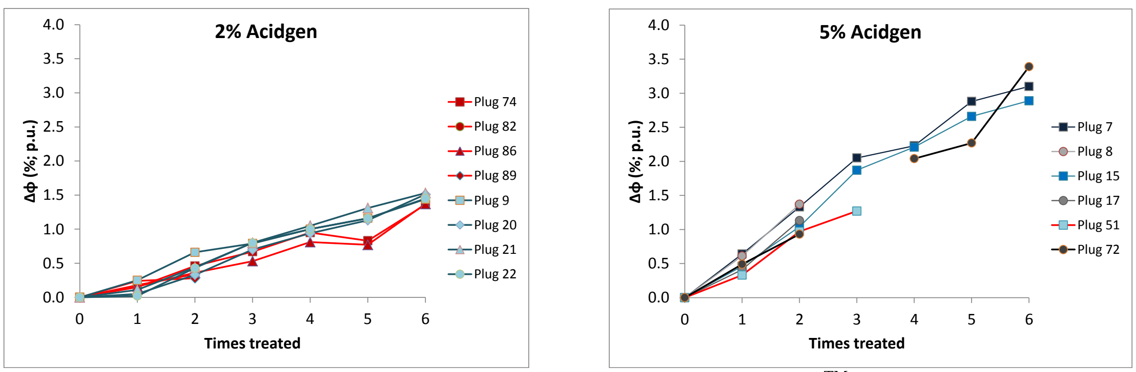

Figure 2: Absolute change in porosity as a function of number of Acidgen™ FG treatments for outcrop chalk specimens treated with Acidgen™ FG solution

The homogeneity of the dissolution is verified by X-ray CT-image analysis (Figure 3). Histogram plotting particularly helps obtaining the level of homogeneity of a specimen.

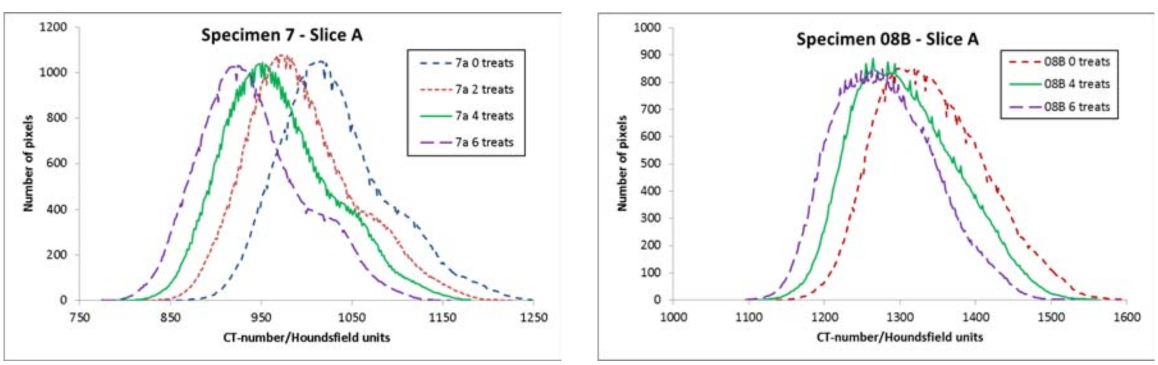

Figure 3: Histograms representing image analysis of CT-images after treatments of outcrop plug specimen # 7 and reservoir plug specimen # 08B, both treated with 5% Acidgen™ FG solution.

The CT-image histograms shift towards lower average CT-numbers as a result of the dissolution of carbonate in the specimens. In the same time, the modal distribution of CT-numbers is maintained and the standard deviation does not change considerably due to the treatment with Acidgen™ FG. Thus, the initial porosity distribution is maintained during the Acidgen™ FG treatment, even for specimens with an initially slightly less homogeneous porosity distribution as illustrated for plug #7. Furthermore, the methodology is valid for homogeneous dissolution of both outcrop chalk specimens (plug #7, Figure 3) and reservoir chalk specimens (plug #08B, Figure 3).

Thorough analysis of 850 FEG-SEM images of treated as well as untreated outcrop chalk specimens further suggests that dissolution of the chalk specimens following the method presented herein creates a homogeneous porosity change. Thus, the main feature resulting from the dissolution is an increase in the number of partly dissolved and dismantled coccolith rings as well as the amount of smaller grains <1 μm (Figure 4).

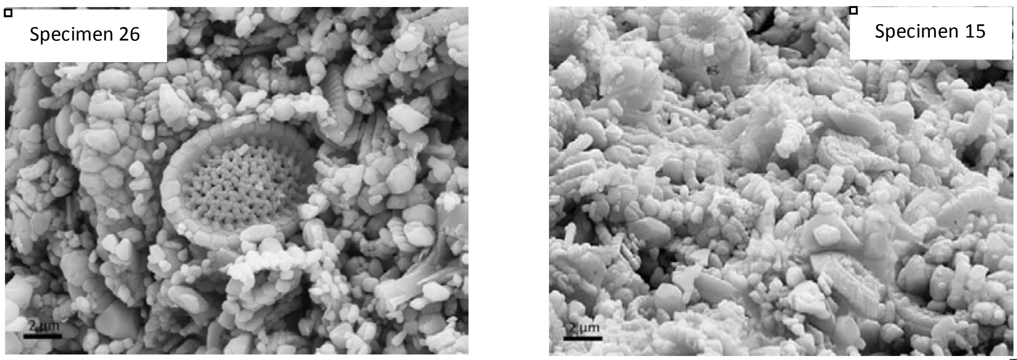

Figure 4: FEG-SEM micrographs of plug #26 (untreated) and plug #15 (treated with 5% Acidgen™ FG) showing a considerably larger number of grains in the fraction <1μm in the treated specimen.

Treatments with acetic acid

From the set of homogenous specimens, 12 were treated with various concentrations of acetic acid between 0.2% (v/v) and 5% (v/v). In all cases, chalk dissolution was observed but there was little or no porosity change due to the treatment. However, a notable change to the specimens' dimensions occurred, where length and diameter of the plug specimens were reduced (Figure 5), indicating that dissolution of the chalk occurred instantly when the specimens were exposed to acetic acid. Ca concentrations and pH levels were similar to the levels in the Acidgen™ FG experiments, indicating that comparable amounts of chalk dissolved in the two types of experiments.

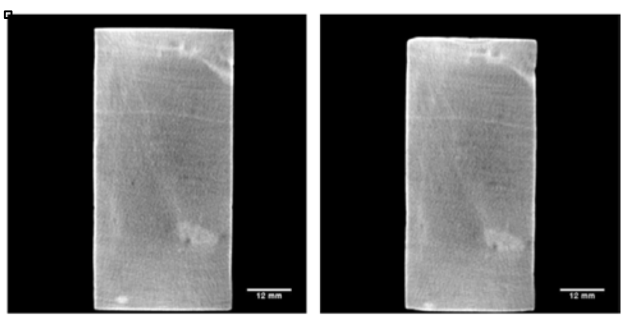

Figure 5: CT-images of plug specimen #57. A) Before treatment with 2% acetic acid. B) After 6 treatments with 2% acetic acid. Note that the specimen has become considerably smaller due to the treatment.

CONCLUSIONS

- Image analysis of CT-images of plug specimens is a powerful tool to evaluate and document homogeneity and dissolution of chalk specimens.
- Dissolution of outcrop chalk specimens can be performed in a homogeneous way with up to 5% Acidgen™ FG by application of the method presented here.
- Homogeneous dissolution of outcrop chalk specimens with acetic acid is not possible.

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