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TNO report

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Salt project: the effect of salt precipitation on the transport properties of a rock matrix

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Summary

Salt and especially halite precipitation is occurring regularly in producing gas wells in the Dutch and English sector of the North-Sea. To mitigate this problem several production strategies are applied although with limited knowledge of the salt precipitation phenomena. The goal of the TKI Salt Precipitation projects is to examine the effect of salt precipitation on the transport properties of a rock matrix, as input for a model that mimics the effect of salt precipitation/water washes on gas production at full scale (gas field) conditions. Currently this kind of quantitative information is missing. The salt precipitation projects cover the development of a salt precipitation model, the execution of measurements to support the development and validation of the model, and performing a parameter study using the model. The model, based on the simulator Dumu^X is reported separately. The results of the parameter study will be reported separately as well. The setup of the experiments and the experimental results, all performed at ambient conditions, are described in this report. The routine- and special core analysis (RCAL and SCAL) were conducted by Panterra Geoconsultants B.V. and are reported separately.

For this study a model rock sample is taken (Obernkirchener outcrop sandstone), with uniform and interchangeable properties (same permeability and porosity), and with an effective permeability which reflects the average of a typical North Sea gas production field, that is roughly 10 mD. A mixture of salts was considered, but this was rejected at this stage as overcomplicating the analysis. Halite (NaCl) salt is selected, as being the most abundant salt component present in practice.

After a salting procedure was devised, a series of “virgin” (unsalted) and salted samples was produced. The properties of virgin and salted samples where then measured through RCAL and SCAL, salt dissolution rate experiments, and liquid uptake (by capillary action) rate experiments. The RCAL and SCAL includes porosity, density, absolute gas/liquid permeability and relative permeability, capillary pressure curves, for drainage and imbibition.

The results of the study are:

- Oberkirchener outcrop sandstone is suitable for the experiments
- The newly developed “gentle flood” flow-through method was considered the best method for salting the samples, as it gave the most acceptable results.
- The IC and ICP-OES methods were considered the best option to quantify the amount of salt in a salted sample within a reasonable amount of time.
- The results showed that salt was found throughout the sample, however in the center less salt is found.
- The time to reduce the salt content in a 50 mm sample by 60% by exposing it one sided to fresh water is about 20 days. For 150 $^{\circ}$C reservoir conditions it is estimated to be 2.5 to 5 days. The time constant is in principle a quadratic function of sample thickness.
- For a virgin sample it takes roughly 5 hours for water to travel a distance of 5 cm (travel distance scales roughly with the square root of time, so 10 cm takes 20 hours). From this it can be concluded that penetration depth of a typical water wash is rather limited, which would indicate that the precipitated salt that clogs the system is present rather superficial.

- For the samples salted with under-saturated brine, a permeability reduction is found throughout the sample. For the samples saturated with saturated brine the permeability reduction is mainly an effect of salt precipitation at the end face. The results of the latter samples should therefore be interpreted with care.
- It seems that pure water (also possibly brine), has an effect of damage rock liquid permeability. This effect complicates the effect of salt precipitation on the liquid permeability.
- The salt precipitation, obtained under the current experimental conditions has minor effects on the capillary pressure and relative permeability of the samples.

Contents

1 Introduction

Salt and especially halite precipitation is occurring regularly in producing gas wells in the Dutch and English sector of the North-Sea. To mitigate this problem several production strategies are applied although with limited knowledge of the salt precipitation phenomena. The goal of the TKI Salt Precipitation projects is to examine the effect of salt precipitation on the transport properties of a rock matrix, as input for a $Dumu^x$ model that mimics the effect of salt precipitation/water washes on gas production at full scale (gas field) conditions. Currently this kind of quantitative information is missing. The salt precipitation and dissolution modelling is reported separately, see amongst others [1].

For this a model rock sample is taken (Obernkirchener outcrop sandstone), with uniform and interchangeable properties, and with an effective permeability which reflects the average of a typical North Sea gas production field, that is roughly 10 mD. A mixture of salts was considered, but this was rejected at this stage as overcomplicating the analysis. Halite (NaCl) salt is selected, as being the most abundant salt component present in practice.

After a salting procedure was devised, a series of virgin and salted samples was produced. The properties of virgin and salted samples where then measured, that is salt dissolution rate experiments, liquid uptake rate by capillary action, routine- and special core analysis (RCAL and SCAL). The RCAL and SCAL includes porosity, density, absolute gas/liquid permeability and relative permeability, capillary pressure curves, for drainage and imbibition. These tests were all conducted at ambient conditions.

In the original project scope also experiments where planned at reservoir conditions, to be conducted in a dedicated high pressure (150 bara), high temperature (150 °C) test-setup. Though this test-setup was largely realized, the activity was halted because of budget considerations, and priority was given to the previously discussed property determination tests. The high pressure setup is described briefly, for documentation purposes.

In this report the ambient test results are reported. The model rock sample selection and its characteristics are described in Chapter 2. The procedure of salting the rock samples as well as the properties of the salted samples are described in Chapter 3. The dissolution and liquid uptake experiments have been performed at TNO and the set up and results of the experiments are described in respectively Chapter 4 and 5. The RCAL and SCAL tests were conducted by Panterra Geoconsultants B.V. and reported separately, see [2]. A few results of these tests are repeated in Chapter 6. The (unused) setup for the experiments at reservoir conditions is summarised in Chapter 7.

2 Model rock selection

2.1 Introduction

The goal of this study is to examine the effect of salt precipitation on the transport properties of a rock matrix. For this a model rock sample is taken (Obernkirchener outcrop sandstone), with uniform and interchangeable properties, and with an effective permeability which reflects the average of a typical North Sea gas production field, that is roughly 10 mD.

In the selection process alternative samples were considered and measured (permeability and porosity) before the final selection took place. These are not reported here. Also it was considered to use Lower Slochteren F16 core samples, but the variation between (adjacent) samples was so large that these samples were rejected.

Before the final selection of Obernkirchener sandstone, some preliminary tests were performed, and the effect of exposing the sandstone to test fluids (water and brine) was investigated on porosity and (gas/liquid) permeability. From the preliminary tests it was concluded that the exposure to liquid did not significantly alter the transport properties. This is important as otherwise the effect of salt precipitation on sample transport properties cannot be studied independently.

More details about the items in this introduction are discussed in the following sections.

2.2 Permeability from F16 field production data and F16 core samples

This section gives indicative properties of a F16 gas field, used to guide the selection of the model sample.

Table 2-1: Permeability from F16 gas production figures assuming steady state radial symmetric gas inflow

	Value
Gas production	$3.24 \cdot 10^5$ mn^3/day
Pressure at boundary (external radius 20m)	110 bar
Well pressure	73 bar
Producing height	24 m
Porosity	11%
Temperature	145 °C
Composition	PVT of pure CH4
Effective Permeability	9 mD

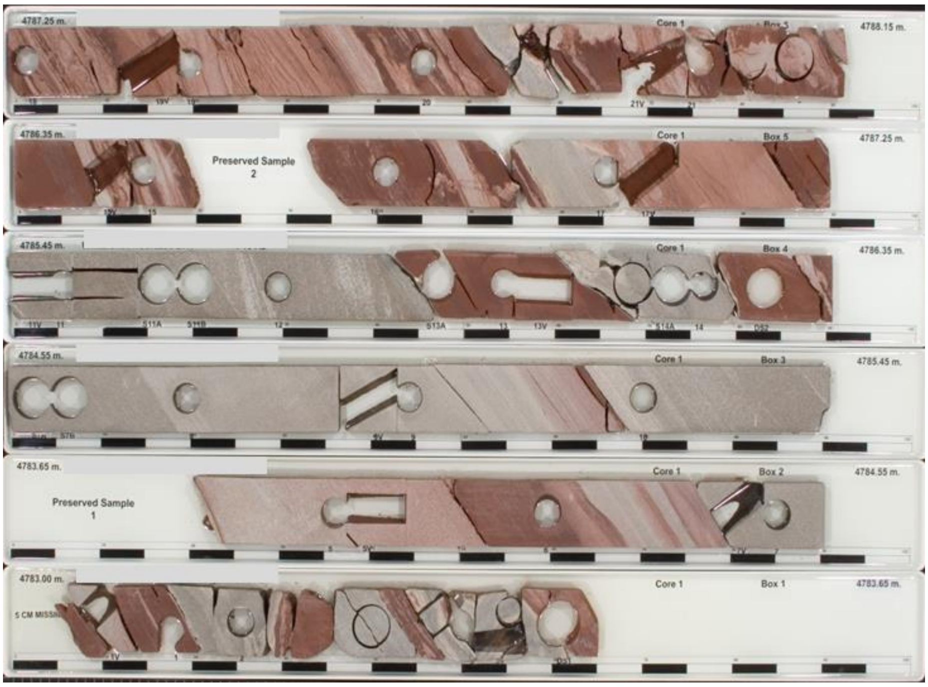


Figure 2-1: F16 Lower Slochteren core samples (producing interval)

Table 2-2: Permeability from F16 Lower Slochteren core samples (producing interval)

	Ambient He Porosity	Gas Horizontal Permeability	Emp. Klink. Hor. Perm.	Grain Density
	(% of Vb)	(mD)	(mD)	(g/ml)
Mean	7.7	8.3	7.2	2.7
Min	0.5	<0.01	<0.01	2.7
Max	16.9	114.0	104.2	2.8
1x stdev	4.6	20.9	18.8	0.0
2.6 x stdev	12	54	49	0

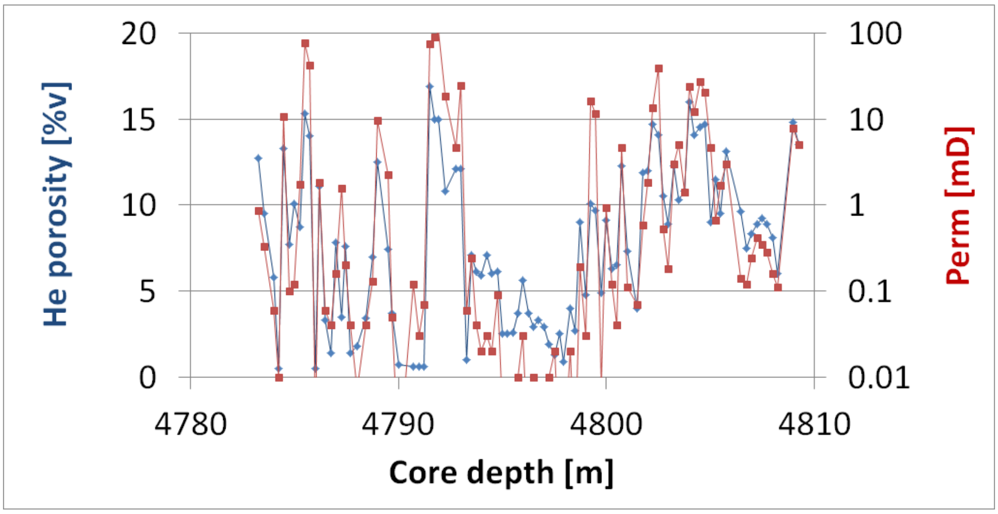


Figure 2-2: Permeability and porosity of F16 Lower Slochteren core samples, 94 in total (producing interval)

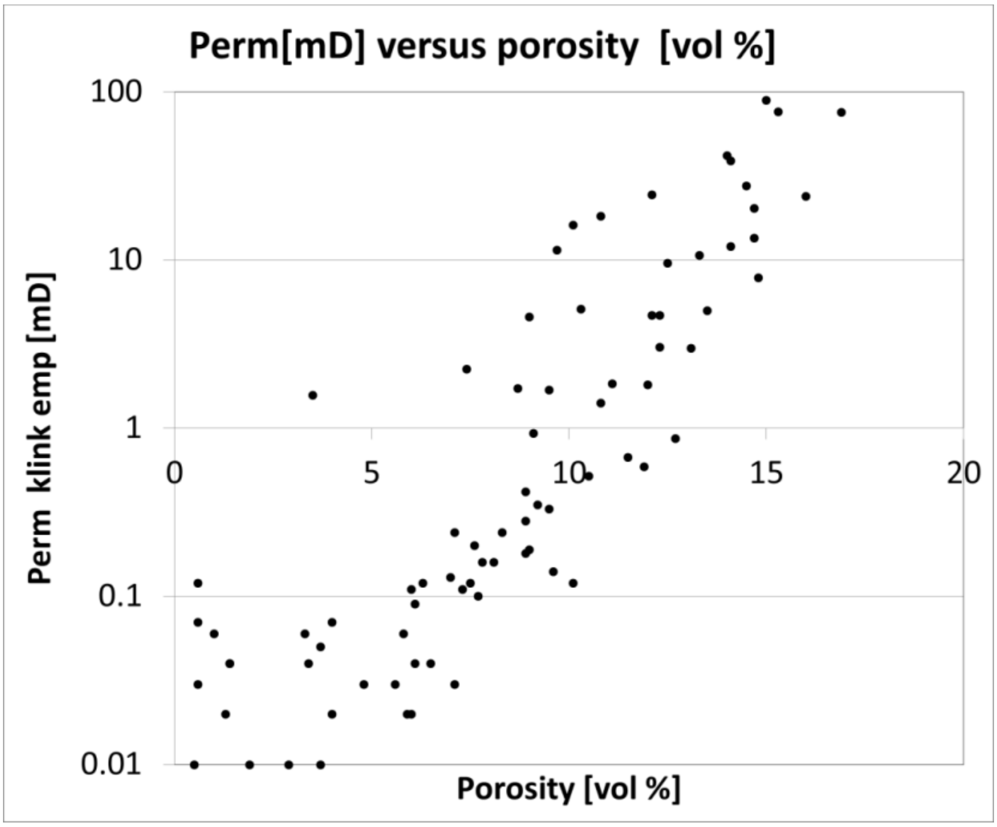


Figure 2-3: Horizontal He permeability versus porosity, F16 Lower Slochteren core samples

2.3 Pre-tests Obernkirchener sandstone samples

2.3.1 Composition

The typical XRD composition of the Obernkirchener sandstone sample is given in the table below. This particular sample was once soaked in undersatured halite solution with density 1140 kg/m^3 and dried, prior to the analysis (note the density of a saturated halite solution reads 1200 kg/m^3 at ambient conditions).

Table 2-3: Typical XRD composition of Obernkirchener sandstone

Quartz	Kaolinite	Plagioclase	Halite
94.8	3.7	1.3	0.2
94.5	3.5	1.6	0.4
95.1	4.1	0.5	0.2
95.9	3.3	0.6	0.1
95.9	3.3	0.7	0.2

2.3.2 *Mercury injection*

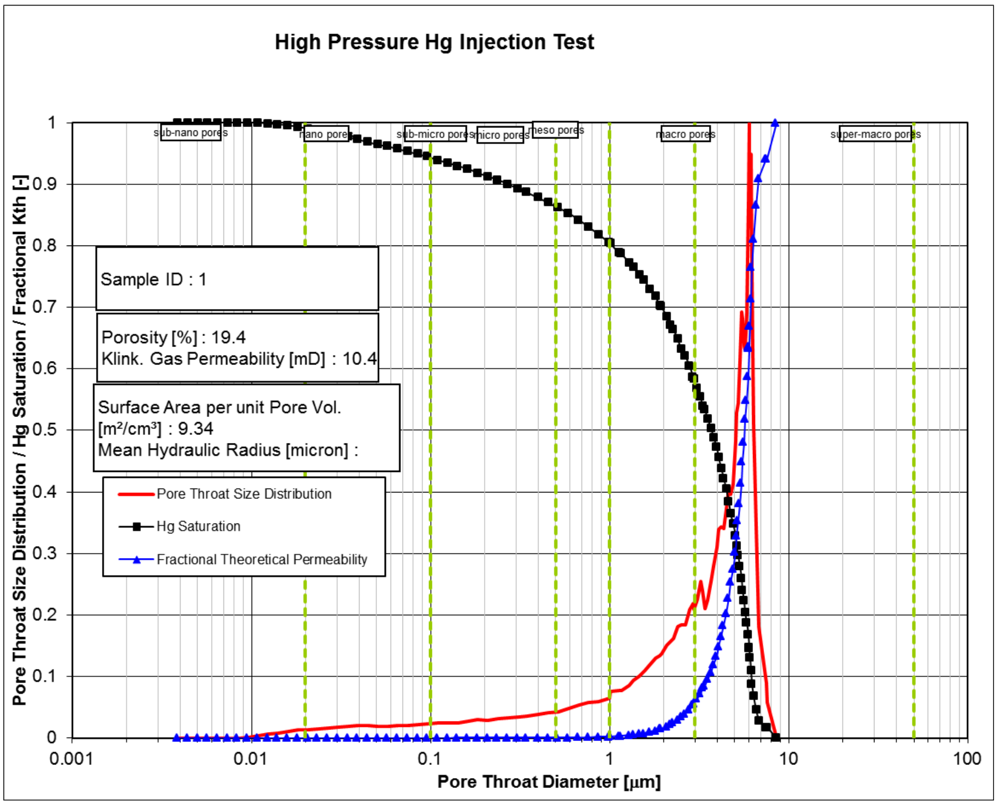


Figure 2-4: Measured Hg capillary pressure curve Obernkirchener sandstone.

2.3.3 *Permeability*

Prior to measuring permeability of the samples, the samples are fired at 500 °C, to remove any organic components that otherwise could interact with water/brine in later on experiments. This is done to avoid difficulties to discriminate in experiments between this effect on sample transport properties and that caused by the presence of salt. Before the actual permeability measurement, the samples are hot oven dried at 95 °C. Below the results are given. Typical cylindrical samples are used, 1.5 inch in diameter and 5 cm long. For one sample, the flow direction was reversed, to get an impression about accuracy and repeatability (in this case resulting in 1% variation in permeability).

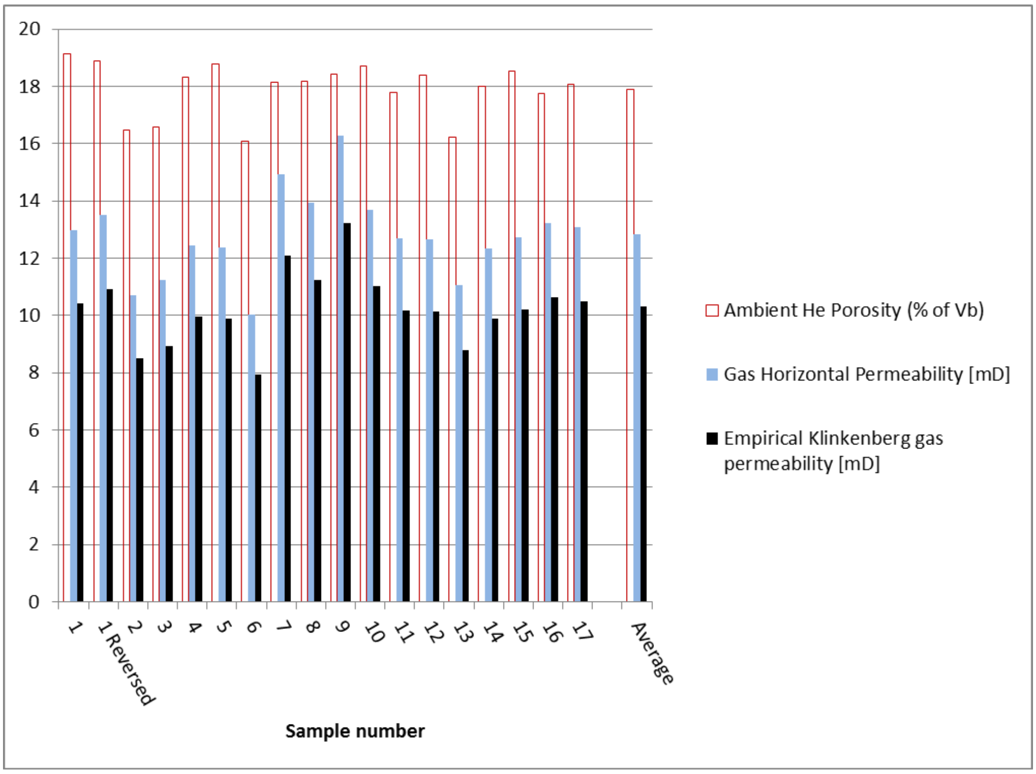


Figure 2-5: Gas horizontal permeability and porosity of Obernkirchener sandstone samples (pre-fired at 500 °C to reduce organic components)

Table 2-4: Gas horizontal permeability and porosity of Obernkirchener sandstone samples (pre-fired at 500 °C to reduce organic components)

Sample number	Ambient He Porosity (% of Vb)	Gas Horizontal Permeability (mD)	Emp. Klink. Hor. Perm. (mD)	Grain Density (g/ml)
1	19.1	13.0	10.4	2.66
1 flow reversed	18.9	13.5	10.9	2.65
2	16.5	10.7	8.5	2.66
3	16.6	11.2	8.9	2.65
4	18.3	12.5	10.0	2.65
5	18.8	12.4	9.9	2.65
6	16.1	10.0	7.9	2.65
7	18.1	14.9	12.1	2.65
8	18.2	13.9	11.2	2.66
9	18.4	16.3	13.2	2.66
10	18.7	13.7	11.0	2.64
11	17.8	12.7	10.2	2.65
12	18.4	12.7	10.1	2.64

13	16.2	11.1	8.8	2.65
14	18.0	12.3	9.9	2.64
15	18.5	12.7	10.2	2.65
16	17.7	13.2	10.6	2.65
Mean	17.9	12.7	10.2	2.65
σ	1.1	1.7	1.4	0.01
σ / mean [%]	6	13	14	0
2.6 x σ	2.8	4.4	3.7	0.01
2.6 x σ / mean [%]	15	34	36	1

The measured gas permeability is 12.7 mD ± 34% (99% confidence interval, that is ±2.6 x σ/mean). This permeability has the desired value (≈10 mD). Also the samples are quite uniform and interchangeable. Samples significantly deviating from average were rejected.

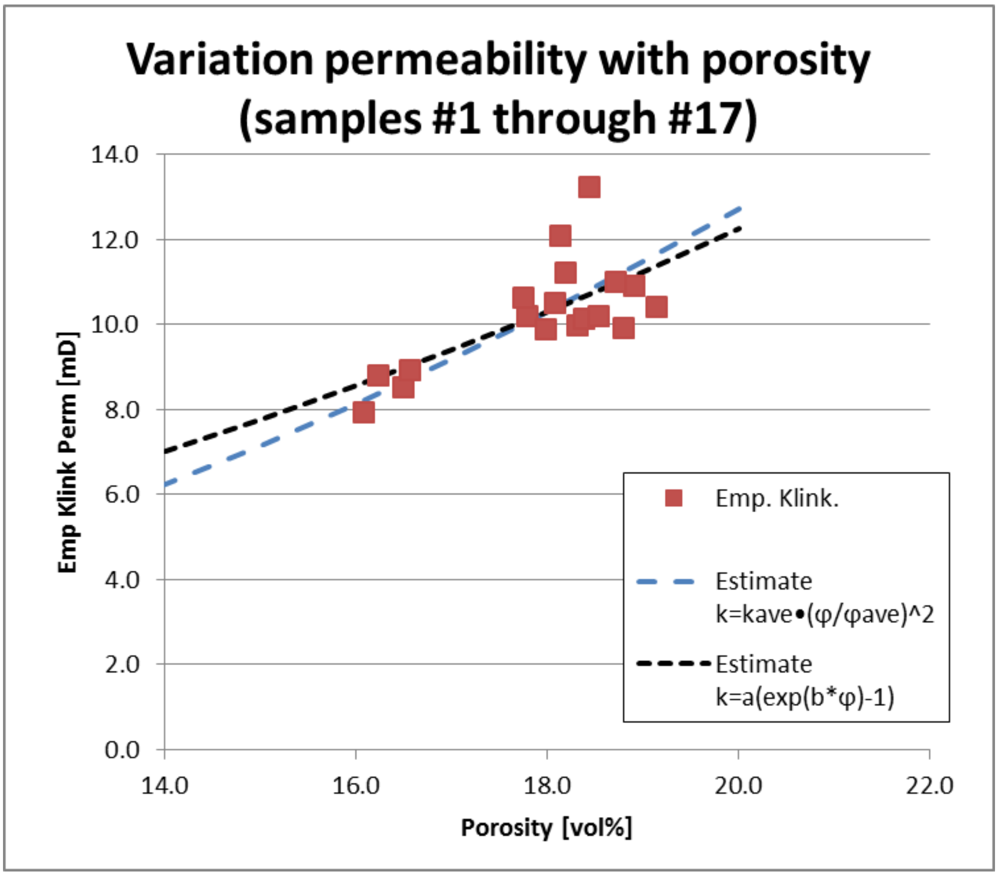


Figure 2-6: Obernkirchener sandstone. Permeability versus pororsity.

2.3.4 Exposure to liquid

As a last test, the candidate Obernkirchener sandstone test samples were subjected to demi-water and brine for a certain period of time. Exposure to liquid water or brine may for example result of dissolution of components, fine migration, etcetera, which may alter transport properties of the samples. Preferably its effect on transport properties is small, as otherwise it cannot be discriminated later on from the presence of precipitated salt. To quantify this, sandstone samples were exposed to liquid demi-water and brine (for a duration of 72 hours) and its effect on gas and water permeability (and porosity) was measured.

The results are given hereafter. From the preliminary tests it was concluded that the exposure to liquid did not significantly alter the transport properties.

2.3.4.1 *Exposure to demi water for 72 hr*

Three Obernkirchener sandstone samples (numbers #7, -#8 and -#9) where exposed to liquid demi-water for 72 hours, and its effect on gas and demi water permeability and porosity was measured.

Table 2-5: Effect of exposure to water on properties Obernkirchener sandstone

Phase 1A Demi-Water Permeability

		Initial Poroperm Data							Post Test Poroperm Data					
Sample Number	Core Depth (m)	Dry Weight (g)	Ambient He Porosity (% of Vb)	Gas Horizontal Permeability (mD)	Emp. Klink. Hor. Perm. (mD)	Grain Density (g/ml)	Initial Demi-Water Permeability (mD)	Demi-Water Permeability (72 hours lock in) (mD)	Dry Weight (g)	Ambient He Porosity (% of Vb)	Gas Horizontal Permeability (mD)	Emp. Klink. Hor. Perm. (mD)	Grain Density (g/ml)	Remarks npp=no plug possible
7	outcrop	116.64	18.1	14.9	12.1	2.65	11.1	10.3	116.63	17.9	14.9	12.0	2.65	
8	outcrop	116.72	18.2	13.9	11.2	2.66	10.5	9.7	116.70	18.0	15.2	12.3	2.65	
9	outcrop	115.66	18.4	16.3	13.2	2.66	12.1	11.7	115.64	18.1	16.6	13.5	2.65	

Phase 1B Repeatability

		Initial Poroperm Data					Reverse Direction Poroperm					
Sample Number	Core Depth (m)	Dry Weight (g)	Ambient He Porosity (% of Vb)	Gas Horizontal Permeability (mD)	Emp. Klink. Hor. Perm. (mD)	Grain Density (g/ml)	Dry Weight (g)	Ambient He Porosity (% of Vb)	Gas Horizontal Permeability (mD)	Emp. Klink. Hor. Perm. (mD)	Grain Density (g/ml)	Remarks npp=no plug possible
1	outcrop	115.45	19.1	13.0	10.4	2.66	115.44	18.9	13.5	10.9	2.65	

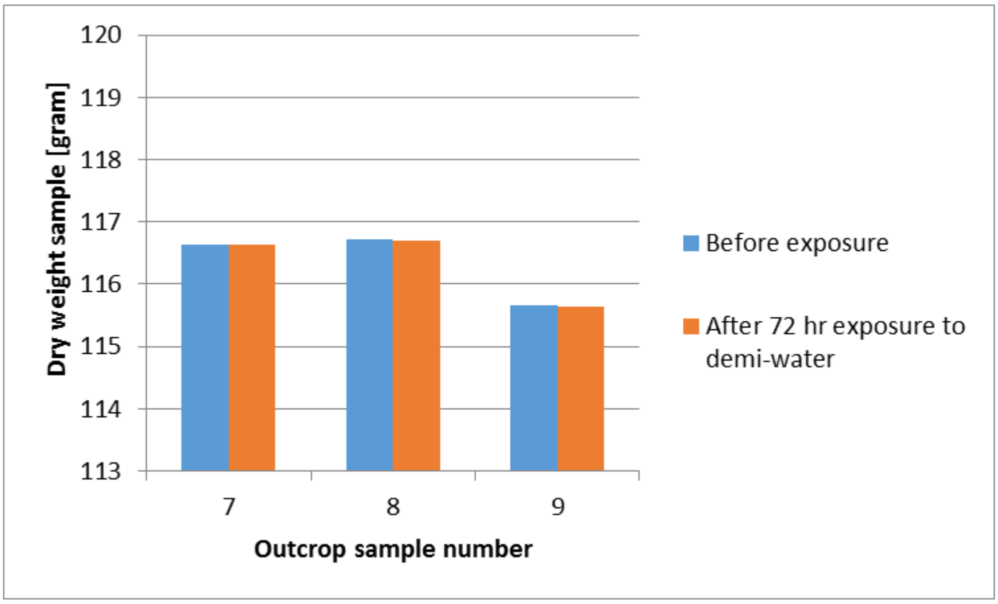


Figure 2-7: Effect of exposure to water on dry sample weight Obernkirchener sandstone

A marginal decrease in He gas porosity is detected after exposure to demi-water (despite negligible weight change), but this is within measurement accuracy.

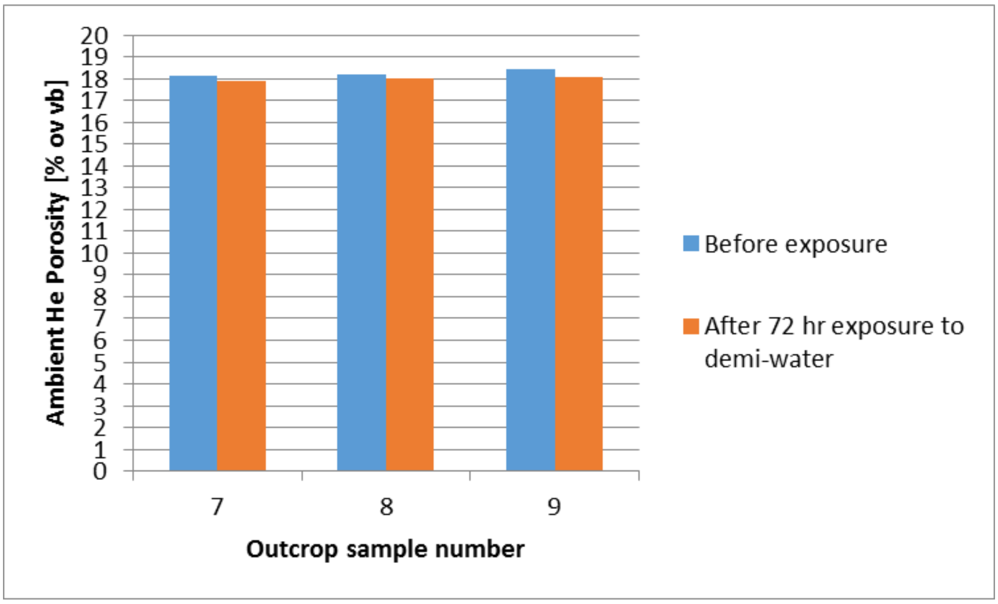


Figure 2-8: Effect of exposure to water on porosity Obernkirchener sandstone

The gas permeability is somewhat (roughly 20%) higher than the liquid permeability. This is most probably due to the fact that not the Klinkenberg permeability is determined, and assumed medium properties (density and viscosity) may deviate from actual medium properties. As at this point we are only interested in delta's (change before/after), this was not researched any further.

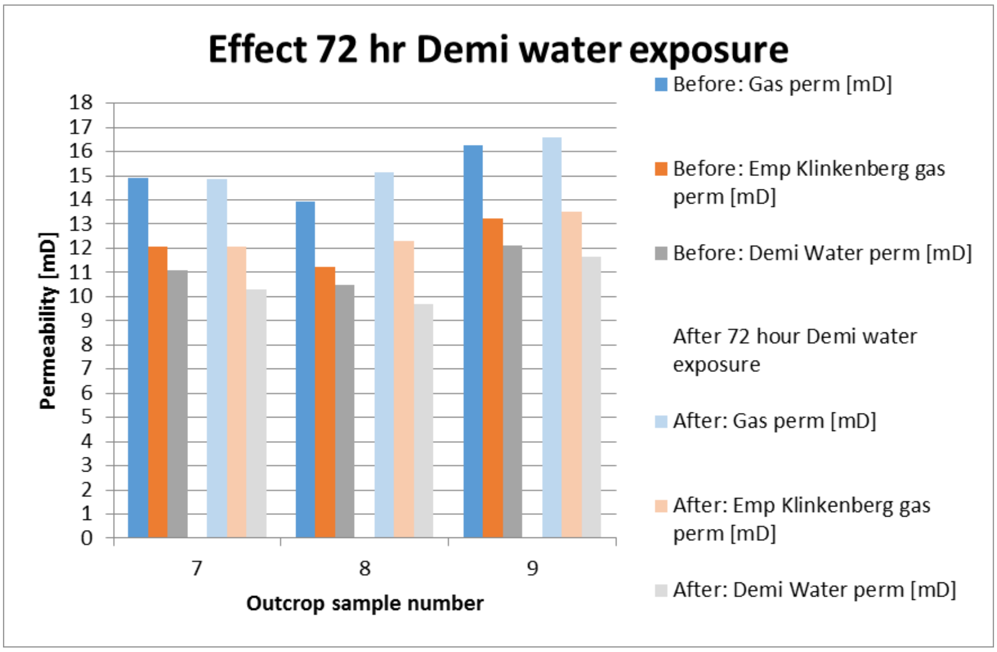


Figure 2-9: Effect of exposure to water on permeability Obernkirchener sandstone

The variation in gas permeability is assumed to be within the measurement error. To get a rough idea of the accuracy/reproducibility, the poroperm (gas permeability and gas porosity) of a particular sample was measured, after which the sample in the sample holder was reverted in direction and the poroperm remeasured, see next figure (the sample was not subjected to water). This results in a +5 to 10%

change in permeability. A more extensive investigation regarding accuracy/reproducibility was skipped at this point in time as being too costly.

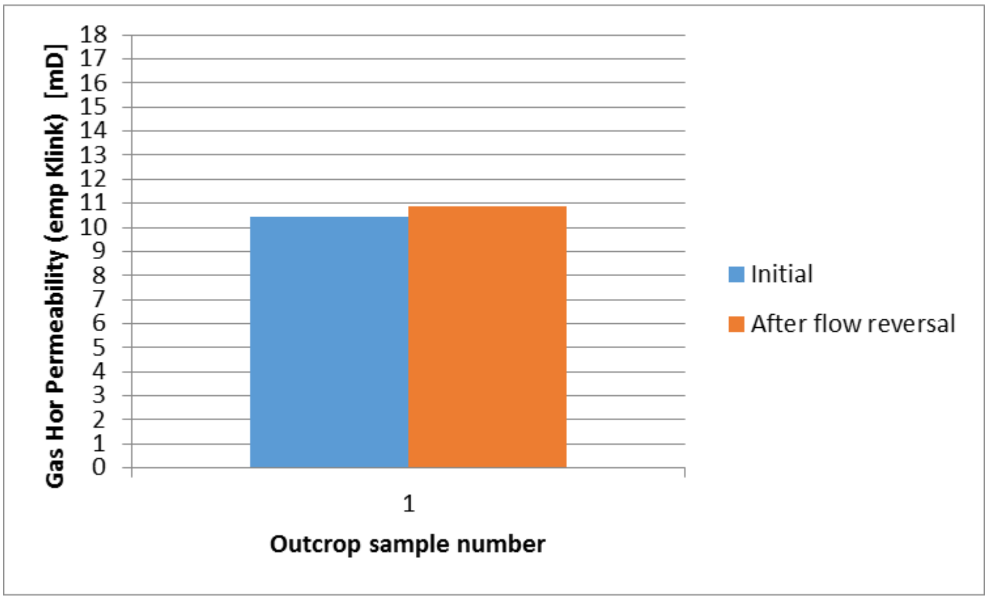


Figure 2-10: Effect of sample orientation on (gas) permeability of the Obernkirchener sandstone

Assuming that the measurement error of permeability is of the order ±5 to 10%, this means that any effect of outcrop sandstone exposure to demi-water lies within the measurement error.

2.3.4.2 *Exposure to brine for 72 hr*

Obernkirchener sandstone (numbers #4,- #12 and-#15) where exposed to under saturated NaCl brine (ρ=1140 kg/m^3) for 72 hours, and its effect on gas and brine permeability and porosity was measured:

- No significant change in weight was measured.
- No significant change in porosity was measured.
- No significant change in gas permeability was measured.
- A small decrease in brine permeability is detected, which is not supported from gas permeability.

Table 2-6: Effect of exposure to brine on properties Obernkirchener sandstone

		Initial Poroperm Data							Post Test Poroperm Data				
Sample Number	Core Depth (m)	Dry Weight (g)	Ambient He Porosity (% of Vb)	Gas Horizontal Permeability (mD)	Emp. Klink. Hor. Perm. (mD)	Grain Density (g/ml)	Initial Brine Permeability (mD)	Brine Permeability (72 hours lock in) (mD)	Dry Weight (g)	Ambient He Porosity (% of Vb)	Gas Horizontal Permeability (mD)	Emp. Klink. Hor. Perm. (mD)	Grain Density (g/ml)
4	outcrop	117.04	18.3	12.5	10.0	2.65	7.68	6.16	117.03	18.1	12.5	10.0	2.64
12	outcrop	116.86	18.4	12.7	10.1	2.64	7.00	6.51	116.85	18.4	12.4	9.9	2.64
15	outcrop	116.16	18.5	12.7	10.2	2.65	10.1	9.53	116.13	18.7	12.5	10.0	2.65

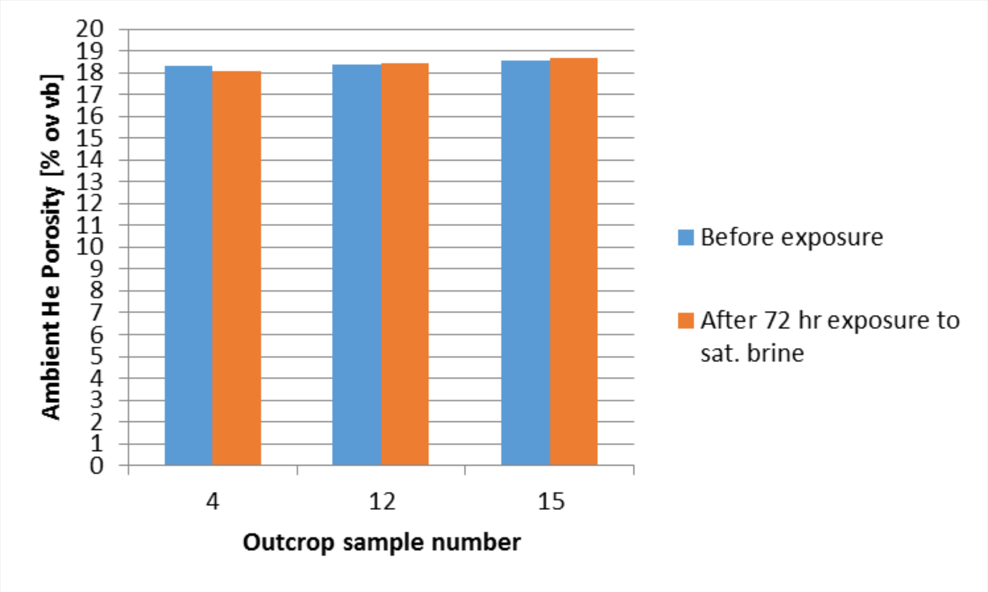


Figure 2-11: Effect of exposure to brine on porosity of the Obernkirchener sandstone

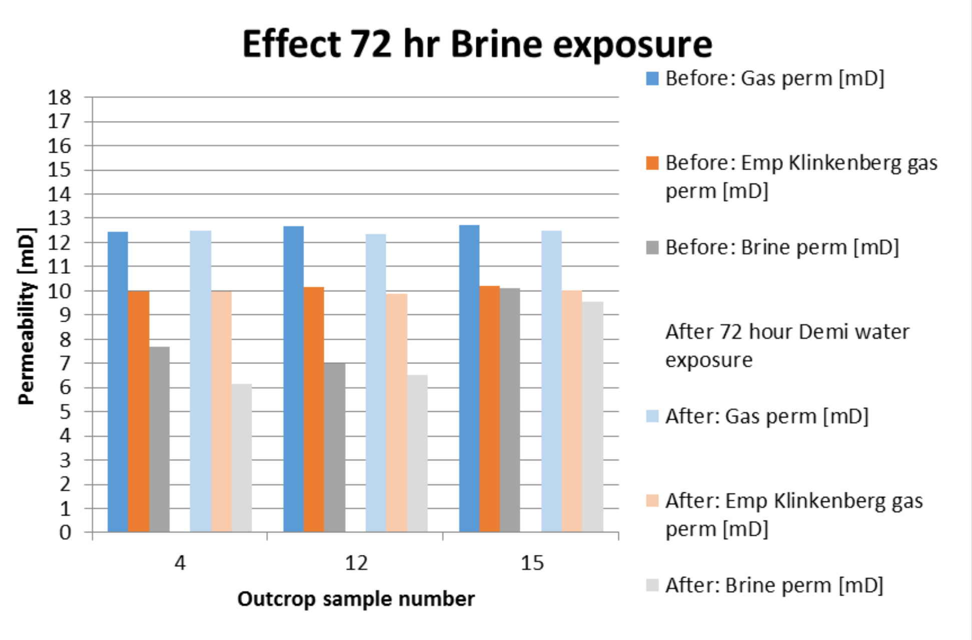


Figure 2-12: Effect of exposure to brine on the permeability of the Obernkirchener sandstone

3 Salting procedure

3.1 Introduction

To determine the effect of salt precipitation on sample transport properties a salting method is required that precipitates discrete amounts of salt uniformly distributed over the sample. The following three salting methods where investigated:

1. Freeze drying
2. External drying in a climate room
3. Flow-through drying

The methods are briefly discussed in this chapter. The flow-through drying method was considered to give the most acceptable results. All samples where finally produced by this flow-through drying, see also [2].

Next to this multiple methods where investigated to determine the salt content of the samples.

3.2 Method 1) Freeze drying

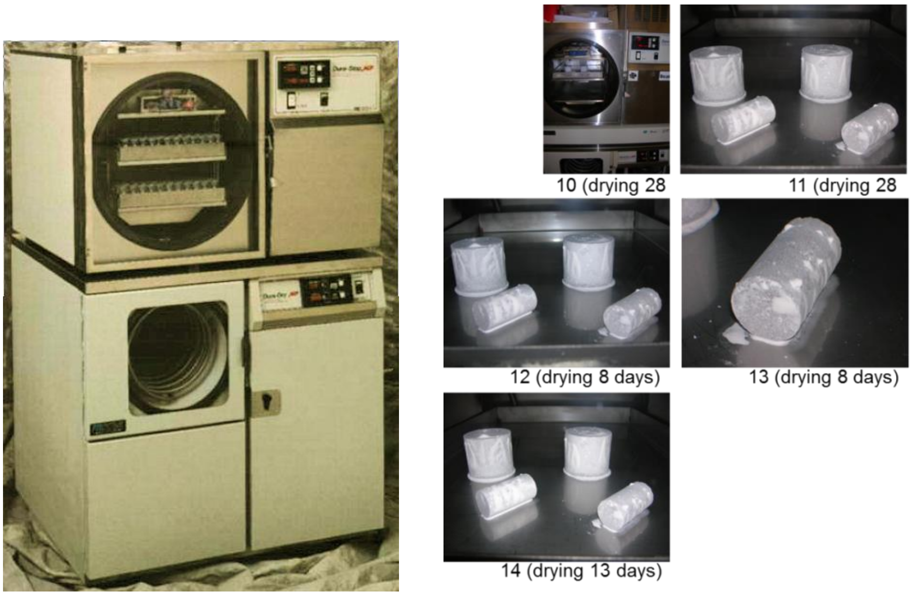
The freeze drying method was considered first, based on a procedure described in [3]. The method consists of flooding the sample with brine, instant freezing of the brine by submerging the sample in liquid nitrogen, followed by freeze drying the water out the sample, leaving the salt behind.

Multiple samples, of different sizes where prepared and freeze dried in this manner. The freeze dryer and some indicative results and SEM images are shown in the figures.

The salt distribution was measured by splitting the sample in parts, and per part measuring the weight increase when subjecting it to a constant humidity atmosphere, making use of the fact that salt is hygroscopic. This is a common and reliable techniques used in the building physics, though it is rather slow (typical requiring 3-4 weeks of processing time).

After running a couple of test, it was decided to abandon freeze drying as a viable option, because of a variety of reasons:

- Fear of damaging the sample when freezing the brine (thermal shock when sample is submerged in liquid N_2 & volumetric expansion of the brine during the phase change from liquid-solid)
- The form of the salt crystals/interaction with the matrix will be different than when drying from the liquid phase.
- The freeze drying process takes very prohibitive long time for the water to sublimate.



10 (drying 28

11 (drying 28

12 (drying 8 days)

13 (drying 8 days)

14 (drying 13 days)

Figure 3-1 Freeze dryer and samples in freeze dryer.

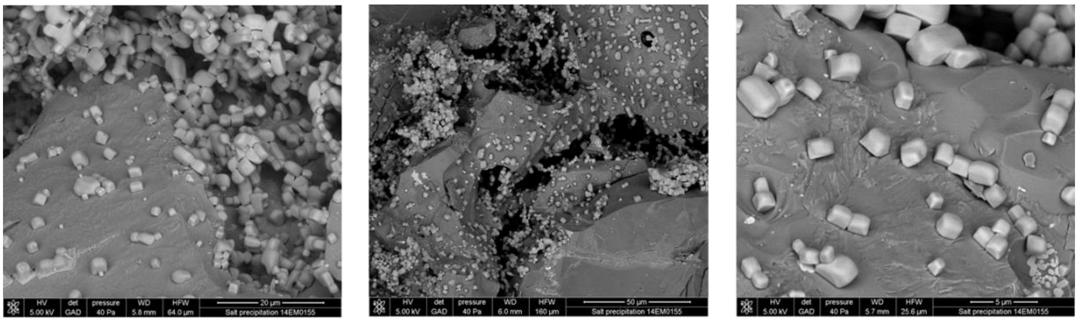
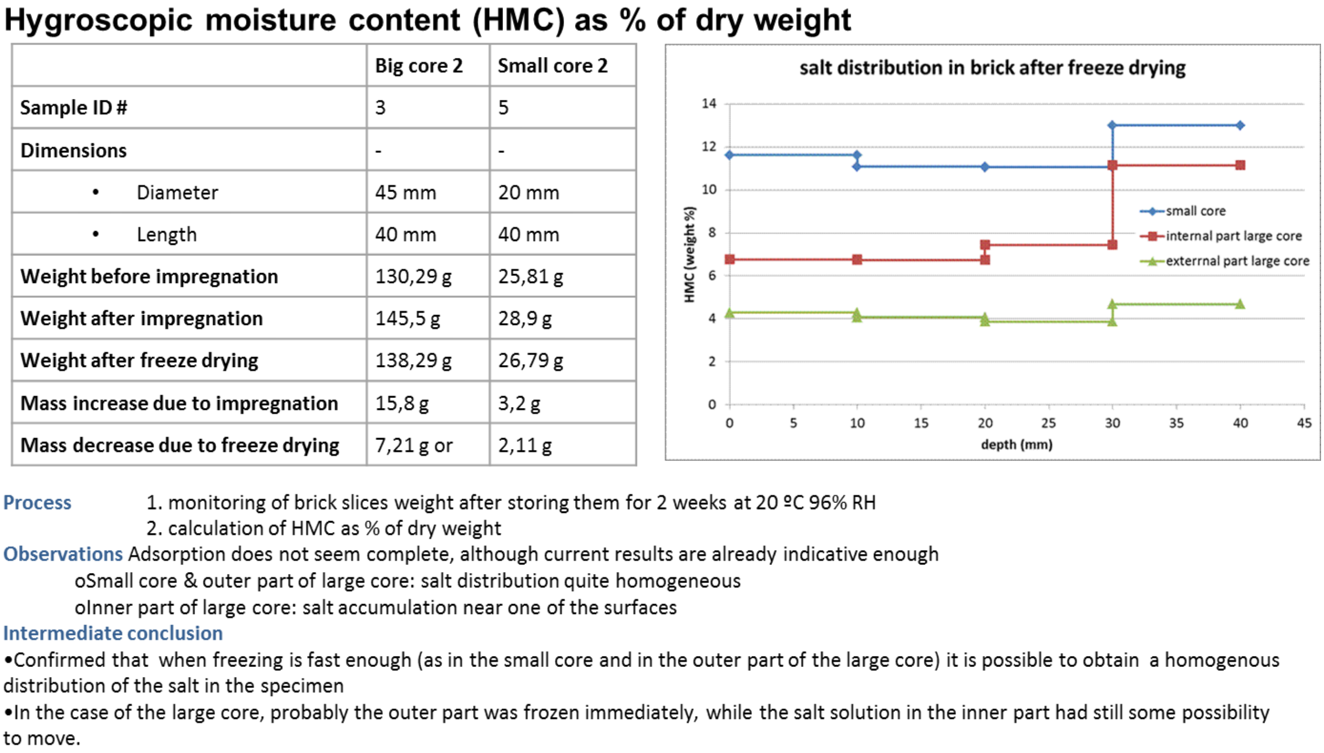


Figure 3-2: SEM images of freeze dried samples (split) with salt precipitated.



Hygroscopic moisture content (HMC) as % of dry weight

	Big core 2	Small core 2
Sample ID #	3	5
Dimensions	-	-
• Diameter	45 mm	20 mm
• Length	40 mm	40 mm
Weight before impregnation	130,29 g	25,81 g
Weight after impregnation	145,5 g	28,9 g
Weight after freeze drying	138,29 g	26,79 g
Mass increase due to impregnation	15,8 g	3,2 g
Mass decrease due to freeze drying	7,21 g or	2,11 g

Process 1. monitoring of brick slices weight after storing them for 2 weeks at 20 ºC 96% RH
2. calculation of HMC as % of dry weight

Observations Adsorption does not seem complete, although current results are already indicative enough
oSmall core & outer part of large core: salt distribution quite homogeneous
oInner part of large core: salt accumulation near one of the surfaces

Intermediate conclusion

•Confirmed that when freezing is fast enough (as in the small core and in the outer part of the large core) it is possible to obtain a homogenous distribution of the salt in the specimen

•In the case of the large core, probably the outer part was frozen immediately, while the salt solution in the inner part had still some possibility to move.

Figure 3-3: Salt distribution of freeze dried samples measured via the hygroscopic moisture content measurement method.

3.3 Method 2) External drying in a climate room

The method consists of flooding of a cylindrical sample with brine, followed by external drying of the water in a climate room (suppressing drying of the sample via the mantle). Various samples were prepared and dried according to this method, but soon this method was abandoned, as salt migrated to the surface, indicating that no uniform salted samples could be obtained in this way.

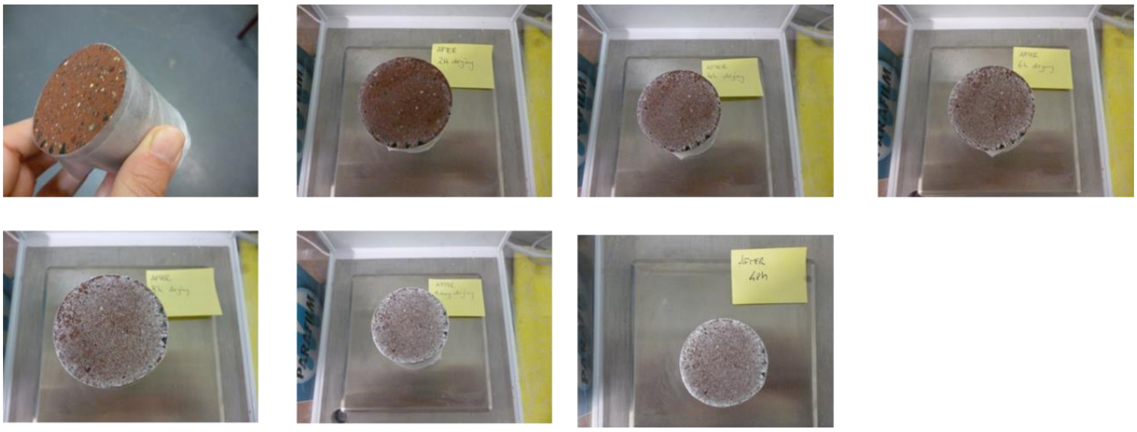


Figure 3-4: External air drying of a brine soaked sample in a climate room.

3.4 Method 3) Flow-through drying

The method consists of flooding the sample (typical dimensions 1.5 inch diameter, 5 cm long) with brine, followed by flow drying of the sample with nitrogen gas.

Two variations where tested:
1. “Brute force flood” with dry N_2
2. “Gentle flood” with humidified N_2 followed by flood with dry N_2
   - Mechanical expel part (typical 50%) of the (mobile) brine with humidified N_2 to prevent premature drying.
   - Flow-through drying of the remaining (rather immobile brine) with dry N_2
   - Reversing the flow direction one or more times, to prevent brine accumulation to the end of the sample.

With a Dumu^x simulation it was experimented with flooding times N_2 and resting times, before the final N_2 flood, see the following figure. NMR was used to non-intrusively determine intermediate brine/liquid contents.

The gentle flow-through drying method was considered to give the most acceptable results. All samples where finally produced by this method, see also [2].

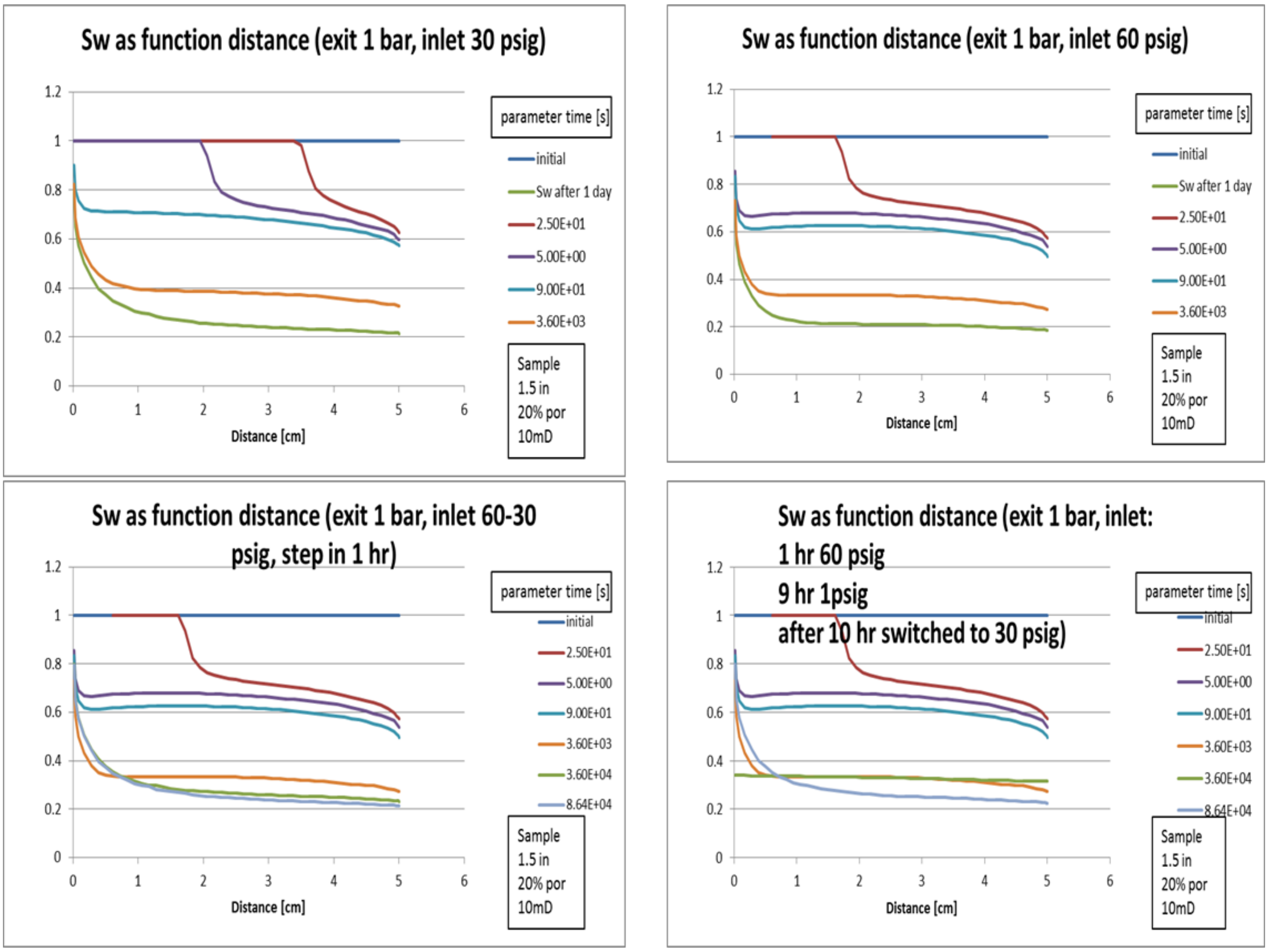
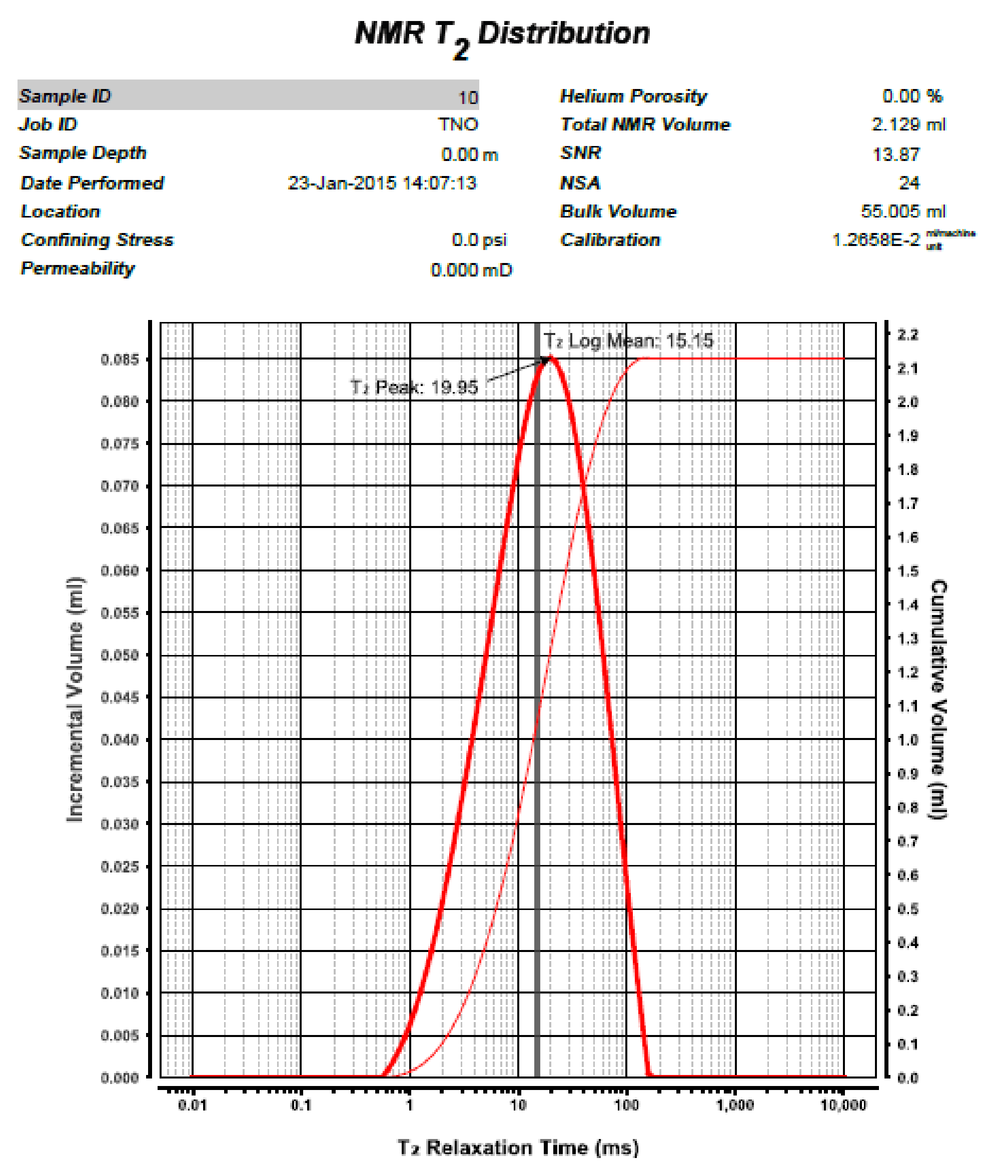


Figure 3-5: Dumu^x simulation of flooding the sample with N_2.



NMR T_2 Distribution

Sample ID	10	**Helium Porosity**	0.00 %
Job ID	TNO	**Total NMR Volume**	2.129 ml
Sample Depth	0.00 m	**SNR**	13.87
Date Performed	23-Jan-2015 14:07:13	**NSA**	24
Location		**Bulk Volume**	55.005 ml
Confining Stress	0.0 psi	**Calibration**	1.2658E-2 ml/machine unit
Permeability	0.000 mD		

Figure 3-6: Typical NMR measurement of residual water content (expressed as cumulative volume on the y-axis). The incremental volume versus relaxation time, gives an indication which pore sizes are occupied with brine.

3.5 Measurement of salt distribution over the sample

3.5.1 Methods

Next to measuring the (dry) weight increase of a sample before and after salting, a method was looked for, that (preferably quantitatively) gives the salt distribution over the sample.

Various methods where considered to determine the salt distribution in the samples.

- XRF (X-ray Fluorescence spectrometers)
- Hygroscopy
- XRD (X-ray Diffraction)
- IC (Ion exchange chromatography
- ICP-OES (Inductively coupled plasma optical emission spectrometry)

In [2] also an indirect comparative method of the salt distribution is presented, where the salted sample is split in parts, and per part the Klinkenberg gas permeability is determined. This is compared with the Klinkenberg gas permeability of the unsalted (virgin) sample, for more details see [2].

3.5.2 *Sample preparation*

For most methods, the sample is to be split in parts, and the parts (or fractions of it) are crushed into powder, prior to analysis. Hence typical an average over the crushed sample is obtained.

3.5.3 *Resolution/accuracy*

The method should be able to resolve small amounts of salt, that is resolve 1% in salt content by weight: In the situation where we soak a sample for 50% of the pore space with (almost saturated) brine, and subsequently dry it, typical 0.7% NaCl salt is added to the samples weight. Assuming that this amount of salt leads already to a significant reduction in permeability of the sample, the measurement method should be able to resolve a fraction of 1% in salt content by weight.

3.5.4 *Example*

Below, typical results of an analysis of three salted samples are shown, where a sample is split in 5 parts (in direction of flow-through drying when preparing the samples), where each part was again split into even smaller sub fractions.

For sample #14, a set of fractions (associated with parts 1 through 5) where measured with XRD, and another set of fractions (also associated with parts 1 through 5) where measured with ICP-OES. For comparison, the average weight increase of the sample due to salt is ≈0.7wt%. ICP-OES quantitatively performs well. The XRD performs poor, and in a separate analysis, using powders to which known amounts of salt where added, this was confirmed.

Below also a result of an IC (Ion exchange chromatography) is given for two samples #11 and #15. Sample #11 shows an increased salt content to the end of the sample, which is not desirable. The measured salt content by IC corresponds rather well with the measured increase in salt content by weighing.

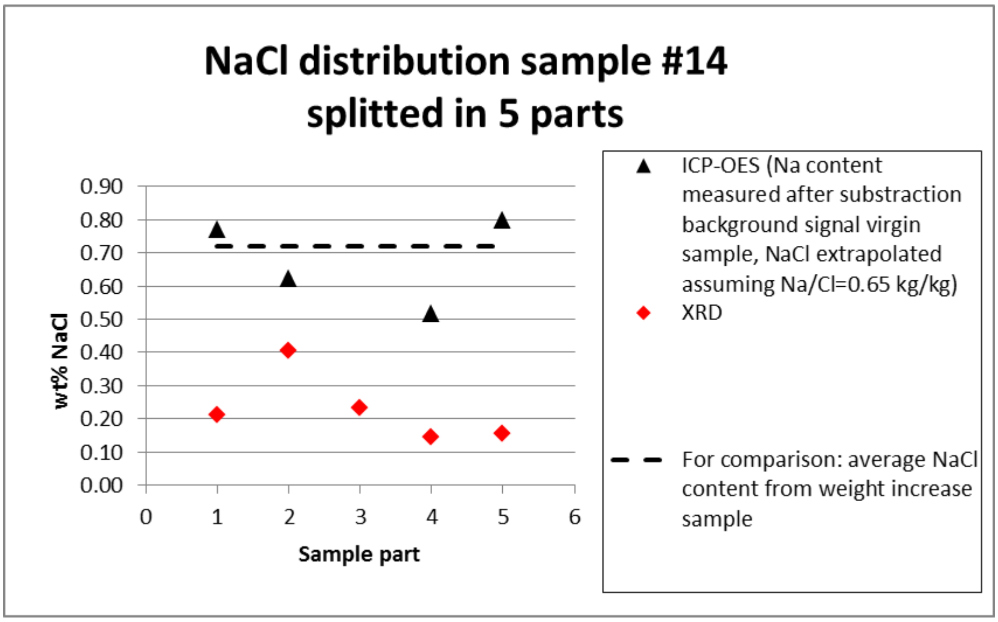


Figure 3-7: Measured salt concentration in a salted sample with XRD and ICP-OES.

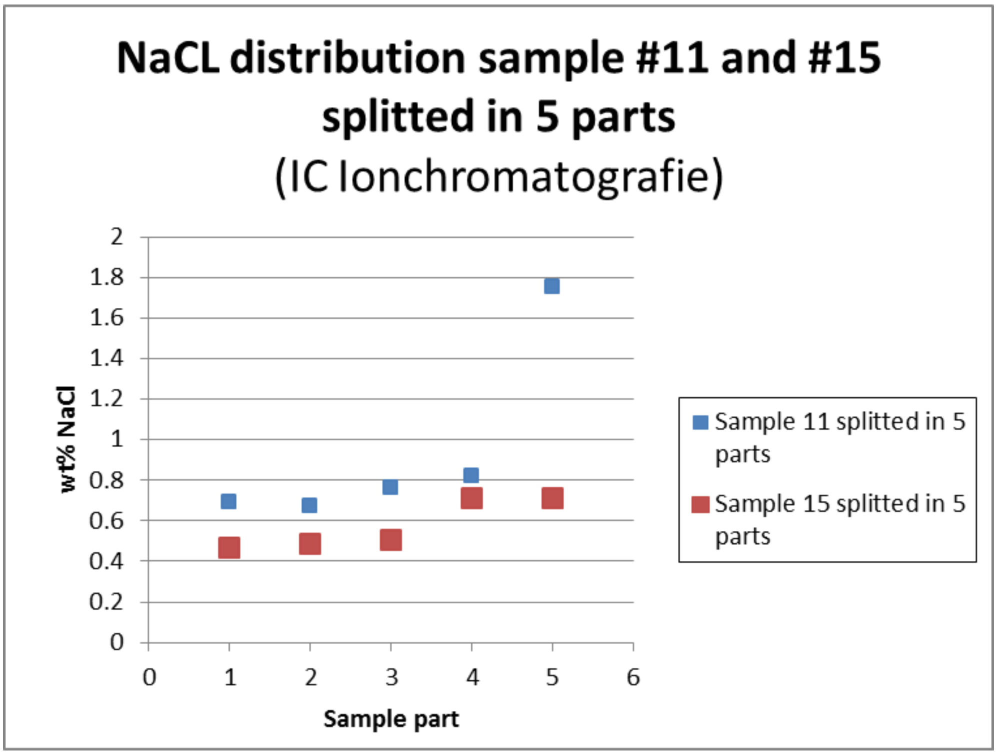


Figure 3-8: Measured salt concentration in two salted sample with IC. For comparison the average NaCl content of sample #11 from the weight increase of the sample was 1.02 wt%. Sample part 5 is towards the flow exit.

3.5.5 Discussion measurement method

- The (comparative) hygroscopic method (previously described discussing the freeze drying method) was considered to be too slow to be practical for our purpose.

- The (quantitative) XRF method is fast and able to resolve the amount of salt (ions and anions), but unfortunately is discontinued at Panterra and TNO. The XRF option is available at Philips Myplaza, but requires prior expensive calibration (for large number of samples cost roughly euro 260-360 per test, excluding calibration costs).
- XRD which measures salt (crystals) is fast and is available at Panterra (euro 450 per test), but it appeared not to be able to resolve the salt content to the required accuracy.
- IC (TNO-Rijswijk) and ICP-OES (University Utrecht, incidental basis) is a quantitative technique and can resolve the required amount of salt, and takes typical one week to process (cost typical euro 400 per test)

3.5.6 Discussion salting method

The results show that salt is found throughout the samples, and not only at the end faces, which was feared of. However this was considered as to be the best achievable.

3.6 Produced samples

3.6.1 Virgin, unsalted samples

The following table gives a list of samples, the majority of which is used to determine the sample properties, unsalted (virgin) or after salting [2]. The brine type that is used to salt the sample is mentioned in the last column (‘Super’ should be read as saturated brine, as it refers to supersaturated brine that is filtered to remove all fines before being used). Based on the virgin sample properties (permeability and porosity), the samples were grouped, such that a certain type of test is performed on samples that show small variation. As a result, some of the samples were rejected, see next Figure.

Table 3-1: Obernkirchner samples used for the analysis of sample properties, unsalted (virgin).

Sample ID	Ambient He Porosity (% of Vb)	4 point Klink. Perm. (mD)	Grain Density (g/cm^3)	Sample Length (cm)	Sample Dia. (cm)	Dry weight (g)	Analysis	Brine Type*
V#0	17.6	12.7	2.64	5.00	3.78	120.59	S1#0 - THS, SEM, Petrography	2/3 Brine
V#1	15.6	6.3	2.66	4.98	3.77	124.37		
V#2	18.8	11.6	2.65	4.99	3.78	118.58	V#2 - Brine Permeability	
V#3	16.5	9.9	2.65	4.92	3.75	119.82		
V#4	18.5	14.2	2.65	5.00	3.78	119.90	V#4 - Water Permeability	
V#5	18.2	12.8	2.66	4.98	3.76	119.12	V#5 - Krel by Centrifuge Imbibition	
V#6	18.8	11.4	2.65	5.00	3.78	119.48	S1#6 - Pc by Centrifuge Drainage	5/6 Brine
V#7	18.1	13.9	2.65	4.92	3.77	115.65	S1#7 - Pc by Centrifuge Imbibition	5/6 Brine
V#8	17.9	12.3	2.65	4.94	3.75	116.72	S1#8 - Water Uptake	2/3 Brine
V#9	16.1	9.6	2.65	4.93	3.76	119.11	V#9 – MICP	
V#10	17.9	11.5	2.65	4.92	3.75	117.45	S2#10 - Brine Permeability	Super
V#11	17.4	14.0	2.65	5.01	3.78	121.39	S2#11 - Water Permeability	Super
V#12	17.9	13.1	2.65	4.91	3.74	116.63		
V#13	16.2	9.7	2.65	4.91	3.76	119.81	S1#13 – MICP	5/6 Brine
V#14	16.1	8.4	2.65	4.91	3.76	119.03		
V#15	18.0	13.0	2.66	4.98	3.78	119.14	S1#15 - Water Uptake	2/3 Brine
V#16	16.8	9.6	2.65	5.01	3.77	122.66	S2#16 – MICP	Super
V#17	18.2	13.8	2.65	5.01	3.78	120.28	V#17 - Oil Permeability	
V#18	15.6	8.1	2.64	5.00	3.77	123.60		
V#19	17.3	11.0	2.65	4.78	3.76	113.94	V#19 - THS, SEM, Petrography	
V#20	19.1	12.2	2.65	4.98	3.77	118.67	V#20 - Water Uptake	
V#21	18.9	12.7	2.65	4.99	3.77	118.77	V#21 - Water Uptake	
V#22	19.0	12.3	2.65	4.99	3.77	118.87	V#22 - Water Uptake	
V#23	18.9	13.7	2.65	5.00	3.77	119.02	V#23 - Pc by Centrifuge Drainage	
V#24	17.6	12.1	2.65	5.00	3.75	120.40	S1#24 - Krel by Centrifuge Drainage	5/6 Brine
V#25	17.6	14.7	2.65	5.00	3.76	121.09	S1#25 - Oil Permeability	2/3 Brine
V#26	18.9	12.8	2.65	5.00	3.77	118.74	S1#26 - Krel by Centrifuge Imbibition	5/6 Brine
V#27	19.1	12.3	2.65	4.98	3.77	118.28	S2#27 - Water Uptake	Super
V#28	18.2	14.1	2.65	4.99	3.78	119.90	S1#28 - Brine Permeability	2/3 Brine
V#29	17.9	15.0	2.65	5.00	3.78	120.57		
V#30	17.7	13.0	2.65	5.02	3.77	120.30	V#30 - Salt Dissolution	
V#31	18.5	14.3	2.65	5.01	3.77	119.25	V#31 - Pc by Centrifuge Imbibition	
V#32	18.4	16.0	2.65	5.00	3.77	120.03		
V#33	19.3	13.9	2.65	4.99	3.76	118.19	S2#33 - Oil Permeability	Super
V#34	19.0	11.8	2.65	4.98	3.77	118.94	S1#34 - Salt Dissolution	5/6 Brine
V#35	18.8	12.5	2.65	5.00	3.77	118.39	V#35 Krel by Centrifuge Drainage	
V#36	19.2	14.6	2.65	5.05	3.77	119.21	S1#36 - Water Permeability	2/3 Brine
V#37	18.8	12.3	2.65	5.00	3.77	118.93	S2#37 - Salt Dissolution	Super
V#38	18.5	13.7	2.65	5.00	3.77	119.63		
V#39	19.0	11.2	2.65	4.99	3.78	119.03	S2#39 - THS, SEM, Petrography	Super
V#40	17.9	15.9	2.65	5.00	3.78	121.11		

**Types of brines used for salted sample preparation*

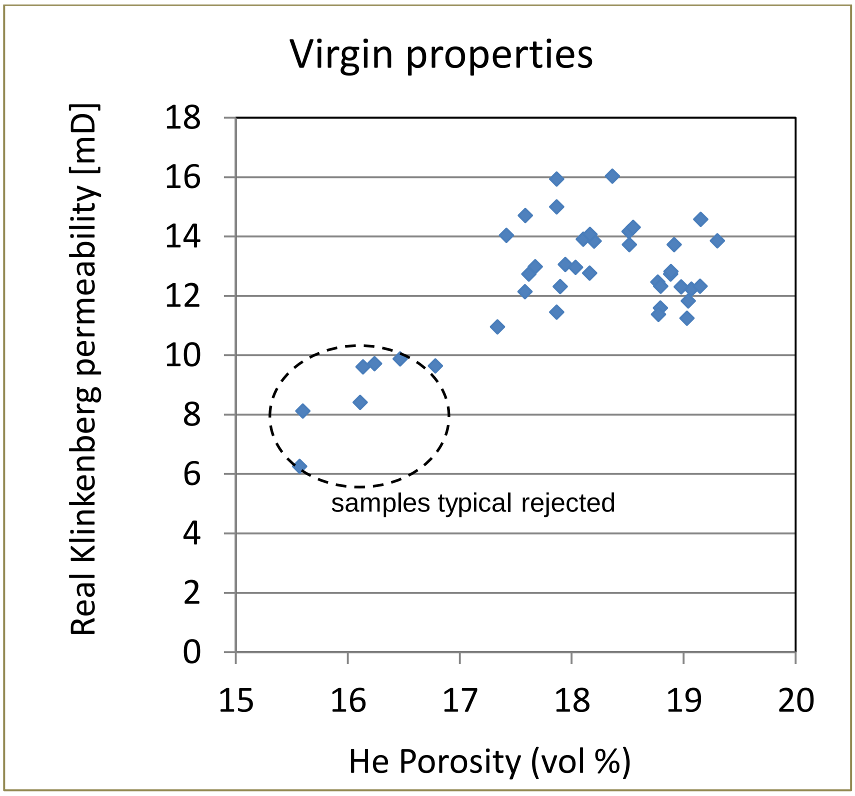


Figure 3-9: Klinkenberg permeability versus porosity of the virgin Obernkirchener sandstone samples

3.6.2 *Nomenclature samples*

Take for example, sample #99. It can appear in the Virgin state 'V' (that is not salted) or Salted state 'S'. For the salting procedure undersaturated brine ('S1') and saturated brine ('S2') is used.

Hence

- 'V#99' refers to sample #99 in the 'Virgin' state (that is not-salted)
- 'S1#99' refers to sample #99 in the salted state (using undersaturated brine)
- 'S2#99' refers to sample #99 in the salted state (using saturated brine)

3.6.3 *Salted samples*

The Real Klinkenberg and He porosity before and after the salting procedure is listed in the following table, including sample weights.

Table 3-2: Obernkirchner samples, unsalted (virgin) and salted poroperm properties

Sample ID	Brine Type	Ambient He Porosity (% of Vb) *Virgin*	Ambient He Porosity (% of Vb) *Salted*	4 Point Klink. Perm. (mD) *Virgin*	4 point Klink. Perm. (mD) *Salted*	Grain Density (g/cm^3) *Virgin*	Grain Density (g/cm^3) *Salted*	Dry Weight (g) *Virgin*	Dry Weight (g) *Salted*
V#0 - S1#0	2/3 Brine	17.6	16.9	12.7	5.53	2.64	2.63	120.59	121.30
V#8 - S1#8	2/3 Brine	17.9	17.3	12.3	9.37	2.65	2.64	116.72	117.20
V#15 - S1#15	2/3 Brine	18.0	17.4	13.0	6.56	2.66	2.65	119.14	119.58
V#25 - S1#25	2/3 Brine	17.6	16.6	14.7	7.58	2.65	2.63	121.09	121.66
V#28 - S1#28	2/3 Brine	18.2	17.3	14.1	7.37	2.65	2.64	119.90	120.45
V#36 - S1#36	2/3 Brine	19.2	18.1	14.6	7.92	2.65	2.63	119.21	119.82
V#6 - S1#6	5/6 Brine	18.8	17.8	11.4	5.82	2.65	2.63	119.48	120.22
V#7 - S1#7	5/6 Brine	18.1	17.2	13.9	8.57	2.65	2.64	115.65	116.29
V#13 - S1#13	5/6 Brine	16.2	15.4	9.72	3.17	2.65	2.64	119.81	120.38
V#24 - S1#24	5/6 Brine	17.6	16.5	12.1	4.80	2.65	2.63	120.40	121.06
V#26 - S1#26	5/6 Brine	18.9	17.7	12.8	5.68	2.65	2.63	118.74	119.46
V#34 - S1#34	5/6 Brine	19.0	17.9	11.8	1.34	2.65	2.63	118.94	119.67
V#10 - S2#10	Super Brine	17.9	16.9	11.5	0.53	2.65	2.64	117.45	118.26
V#11 - S2#11	Super Brine	17.4	16.4	14.0	1.43	2.65	2.63	121.39	121.96
V#16 - S2#16	Super Brine	16.8	15.9	9.65	0.64	2.65	2.65	122.66	123.23
V#27 - S2#27	Super Brine	19.1	18.3	12.3	0.84	2.65	2.64	118.28	119.05
V#33 - S2#33	Super Brine	19.3	18.0	13.9	0.59	2.65	2.63	118.19	119.02
V#37 - S2#37	Super Brine	18.8	17.8	12.3	0.81	2.65	2.64	118.93	119.74
V#39 - S2#39	Super Brine	19.0	18.1	11.2	0.89	2.65	2.64	119.03	119.80

4 Salt dissolution by sweet water

4.1 Introduction

The goal of the dissolution measurement is to determine how fast halite (NaCl) salt can be removed from a rock sample, e.g. by a water wash (‘external’, that is from outside via the sample surface).

To model the salt transport, the effective diffusion coefficient of NaCl in water in the rock matrix must be known, which is measured in a dedicated salt dissolution setup. With the effective diffusion coefficient, the dissolution rate of samples with different properties and dimensions can be estimated at other conditions.

The model rock consists of virgin and salted Obernkirchener sandstone samples. In this chapter the results of the dissolution tests are reported.

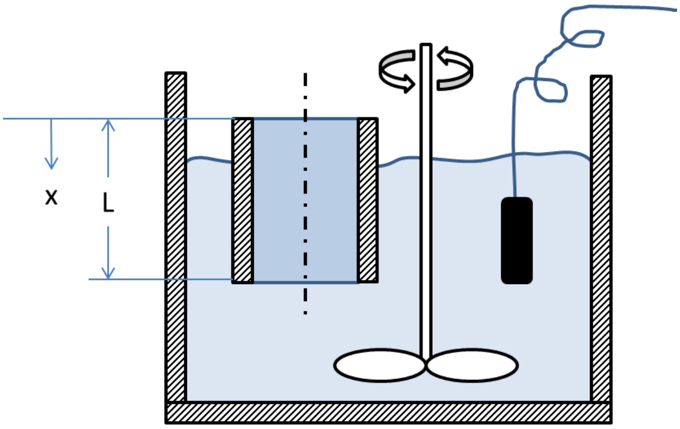


Figure 4-1: Salt dissolution test-setup: a salted cylindrical sample (length ‘L’) is exposed at one surface to (initially) ultra pure water (UPW). A salinity sensor measures the increase of salt content of the water in time (=dissolution rate from the sample).

4.2 Test method

The dissolution rate of NaCl salt is monitored in time from three Obernkirchener sandstone samples (separately) when exposed to a large but finite volume of (initial) pure water, at ambient conditions. One sample is not salted, and is only present for reference purposes. Two other samples are salted.

Per definition the salt dissolution rate from a sample at a certain instant in time equals the rate of salt increase of the water, which is recorded with a salinity sensor. Assuming that salt transport in the rock matrix occurs by diffusion, an analytical expression for the dissolution rate can be derived, which is an exponential relation in time. This expression contains a characteristic time constant, which contains the effective diffusion coefficient of NaCl in water in the porous matrix and the sample length ‘L’. When the measured time constant is compared to this theoretical time constant the effective diffusion coefficient (the only unknown) can be extracted.

4.3 Theory

4.3.1 Theoretical expression for the dissolution rate

Assume a cylindrical sample with homogeneous properties, with uniform initial salt concentration ‘c_0’ (at time t=0). Assume the cylinder mantle is sealed. At time t>0 one end of the sample (x=L) is subjected to a stepwise drop in concentration, by exposing it to a large (but finite) amount of water with salt concentration (effectively) zero $c_L \approx 0$. In principle a 1-dimensional salt concentration gradient will build-up in the sample, which slowly will decrease in time, as more salt is washed out from the sample. Assuming diffusion as predominant means of salt transport in the sample, an analytical expression for the salt concentration profile can be derived in time, which is given by the following series expansion, see also [4]:

$$c_{sample}(t,x) = c_0 \cdot \sum_{n=0}^{\infty} \frac{(-1)^n}{2n+1} \cdot \frac{4}{\pi} \cdot e^{-\left[\frac{(2n+1)\cdot\pi}{2\cdot L}\right]^2 \cdot D_{eff} \cdot t} \cdot \cos\left(\frac{(2n+1)\cdot\pi}{2\cdot L} \cdot x\right)$$

where ‘c’ is the salt concentration, ‘c_0’ the initial salt concentration, ‘L’ the sample length, ‘x’ position, ‘t’ time, ’D_{eff}’ the effective diffusion coefficient of salt in water in the rock matrix.

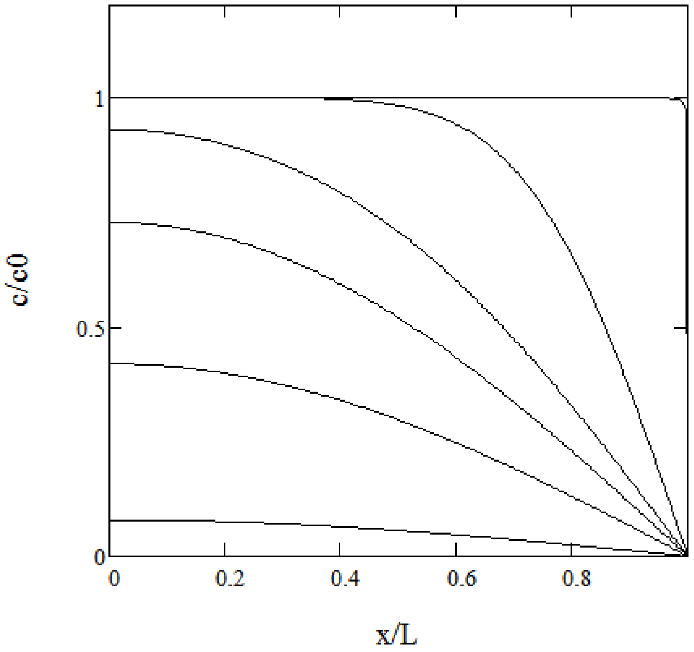


Figure 4-2: Impression of the 1-dimensional salt concentration profile in the sample at various instants in time, when exposed at x=L to water with zero salt concentration. The initial salt concentration is uniform with value c_0.

After a relatively short time already, this series can be approximated sufficient accurately by the first term (n=0):

$$c_{sample}(t,x) \approx c_0 \cdot \frac{4}{\pi} \cdot e^{-\frac{t}{a_0}} \cdot \cos\left(\frac{\pi}{2} \cdot \frac{x}{L}\right)$$

where the time constant (n=0) is given by:

$$a_0 = \left(\frac{2 \cdot L}{\pi}\right)^2 \cdot \frac{1}{D_{eff}}$$

The dissolution rate is the amount of salt travelling over the contact interface between sample and water, and is obtained by taking the spatial derivative of the sample salt concentration at the interface position (x = L). This also results in an exponential response function of time, with the same time constant a_0. Given the dissolution rate, the increase in salt concentration of the initial pure water is obtained, which again is an exponential relationship, with same time constant a_0 (where Δc refers to the final steady state concentration of salt in water compared to the initial salt concentration, zero in our case).:

$$c_{water}(t) \approx \Delta c \cdot \left(1 - e^{-\frac{t}{a_0}}\right)$$

Hence when fitting the measured salt concentration in water in time, with the theoretical expression, the characteristic time constant 'a_0' is obtained, which then gives the effective diffusion coefficient:

$$D_{eff} = \left(\frac{2 \cdot L}{\pi}\right)^2 \frac{1}{a_0}$$

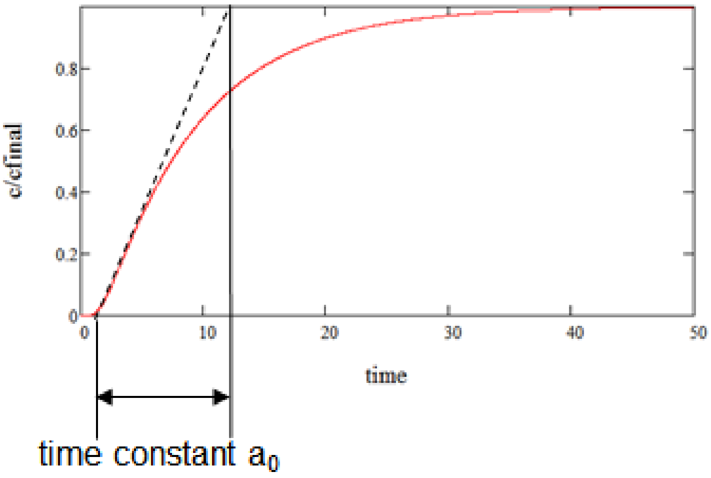


Figure 4-3: Impression of salt concentration response water, and extraction of the characteristic time constant.

The effective diffusion coefficient of salt in water in a porous matrix can be approximated by (assuming a bundle of pores, not necessarily straight bundles):

$$D_{eff} = \frac{D}{\tau}$$

Where 'D' the diffusion coefficient of salt in water, 'τ' the tortuosity factor.

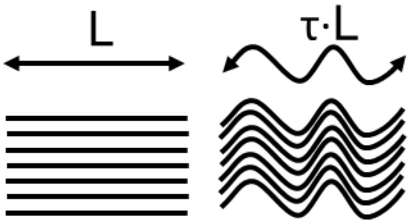


Figure 4-4: Tortuosity factor

The tortuosity factor can be interpreted as an elongation of the diffusion path. Hence the diffusion path between two points is not a straight line, but a curved path, which is a feature of the porous structure of the particular sample. The tortuosity factor in principle is always larger than unity. Note that in some literature the tortuosity factor refers to the inverse value. Note also that the tortuosity factor for ion diffusion can be different from e.g. gas traveling through the matrix. After inserting the appropriate value for the diffusion coefficient and porosity, an estimate of the tortuosity factor can be extracted, according to:

$$\tau = \frac{D}{D_{eff}}$$

4.3.2 *The diffusion coefficient of NaCl in water at ambient conditions*

The diffusion coefficient of various electrolyte solutions at 25 °C at various solute concentrations is given in the following Table [5]. In this table the diffusion coefficient slightly decreases with NaCl concentration. For NaCl the diffusion coefficient is given by D≈$1.484 \cdot 10^{-9}$ m^2/s, based on the highest 1.0M concentration listed (1 mole solute in 1 liter of solution). Note that the molarity of a saturated NaCl solution is roughly 6 M.

Table 4-1 Diffusion coefficient of electrolyte solutions at 25 °C [5]

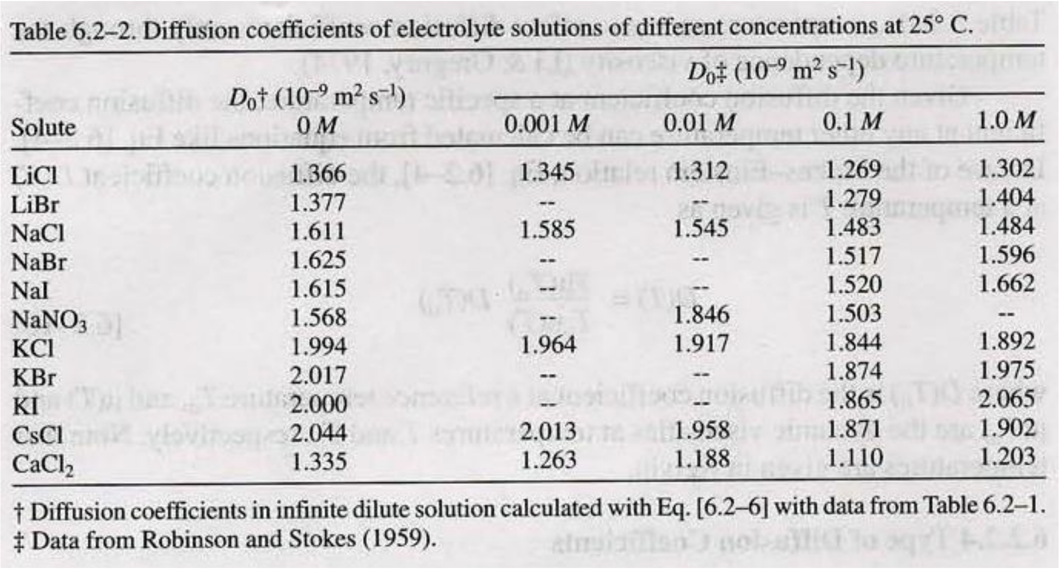


Table 6.2–2. Diffusion coefficients of electrolyte solutions of different concentrations at 25° C.

Solute	D_0† (10^{-9} m^2 s^{-1}) 0 *M*	D_0‡ (10^{-9} m^2 s^{-1}) 0.001 *M*	0.01 *M*	0.1 *M*	1.0 *M*
LiCl	1.366	1.345	1.312	1.269	1.302
LiBr	1.377	--	--	1.279	1.404
NaCl	1.611	1.585	1.545	1.483	1.484
NaBr	1.625	--	--	1.517	1.596
NaI	1.615	--	--	1.520	1.662
$NaNO_3$	1.568	--	1.846	1.503	--
KCl	1.994	1.964	1.917	1.844	1.892
KBr	2.017	--	--	1.874	1.975
KI	2.000	--	--	1.865	2.065
CsCl	2.044	2.013	1.958	1.871	1.902
$CaCl_2$	1.335	1.263	1.188	1.110	1.203

† Diffusion coefficients in infinite dilute solution calculated with Eq. [6.2–6] with data from Table 6.2–1.
‡ Data from Robinson and Stokes (1959).

It is not known whether the determination of these diffusion coefficients presume knowledge of the viscosity of the liquid, and take into account the effect of salt on the viscosity of water. Note that the viscosity of a saturated brine solution at 20 °C is almost twice the viscosity of pure water at 20 °C.

There are some other sources of diffusion coefficients of NaCl in water, which suggest a slight increase in diffusion coefficient with concentration, see next table [6] and next figure [7]. We however will use values from [5].

Table 4-2: Diffusion coefficients of NaCl in water at 18.5 °C [6]

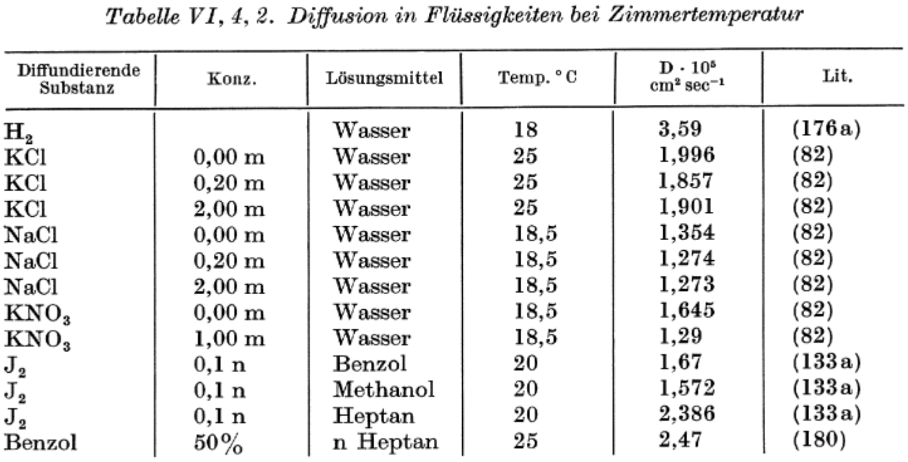


Tabelle VI, 4, 2. Diffusion in Flüssigkeiten bei Zimmertemperatur

Diffundierende Substanz	Konz.	Lösungsmittel	Temp. °C	$D \cdot 10^5$ $cm^2\,sec^{-1}$	Lit.
H_2		Wasser	18	3,59	(176a)
KCl	0,00 m	Wasser	25	1,996	(82)
KCl	0,20 m	Wasser	25	1,857	(82)
KCl	2,00 m	Wasser	25	1,901	(82)
NaCl	0,00 m	Wasser	18,5	1,354	(82)
NaCl	0,20 m	Wasser	18,5	1,274	(82)
NaCl	2,00 m	Wasser	18,5	1,273	(82)
KNO_3	0,00 m	Wasser	18,5	1,645	(82)
KNO_3	1,00 m	Wasser	18,5	1,29	(82)
J_2	0,1 n	Benzol	20	1,67	(133a)
J_2	0,1 n	Methanol	20	1,572	(133a)
J_2	0,1 n	Heptan	20	2,386	(133a)
Benzol	50%	n Heptan	25	2,47	(180)

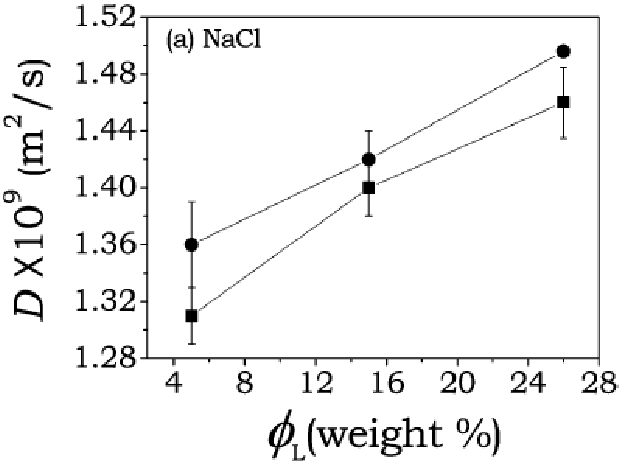


Figure 4-5: Plot of mass diffusion coefficient NaCl in water at 25 °C as function of NaCl concentration (wt salt per wt water+salt) [7]

4.4 Sample preparation

The samples are cylindrical in shape (∅38mm x 50 mm) . The samples are salted according to the procedure described before, and after salting are dry (dry weight ≈120 gram). The following three samples are prepared:

1. A virgin sample (containing no salt) for reference purposes
2. A sample prepared from 5/6 saturated brine
3. A sample prepared from saturated brine

The salted samples contain roughly ≈0.7 á 0.8 gram of salt. The pore volume of the samples is roughly 10 ml. When the samples are subjected to water, they will take up roughly 6.6 ml of water by capillary action. From capillary liquid uptake experiments (reported in the next chapter) this is known to take roughly 1 day, which is relatively short compared to the time constant for salt dissolution. The mantle of the cylinder is sealed with parafilm, such that they will not become in contact with water.

4.5 Test at ambient conditions

4.5.1 Test setup

The test setup consists of a glass jar with lid filled with ultra pure water (UPW), containing the sample, a salinity sensor, and magnetic stirrer, see next two figures.

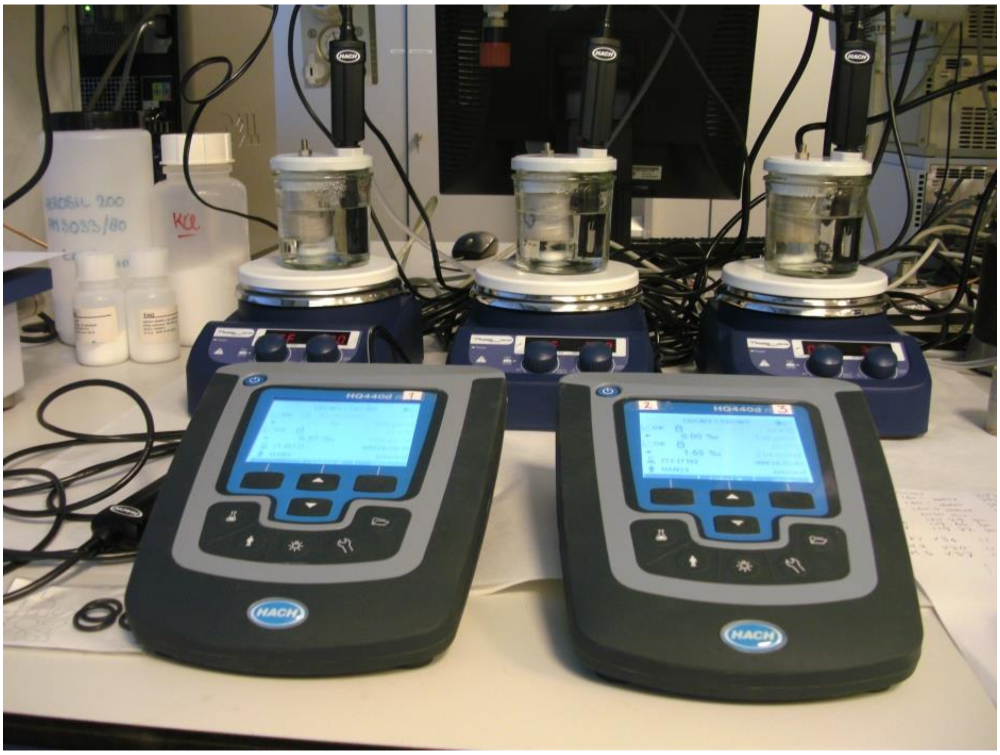


Figure 4-6: Setup to measure the salt dissolution rate of up to 4 samples in parallel (shown are three samples).

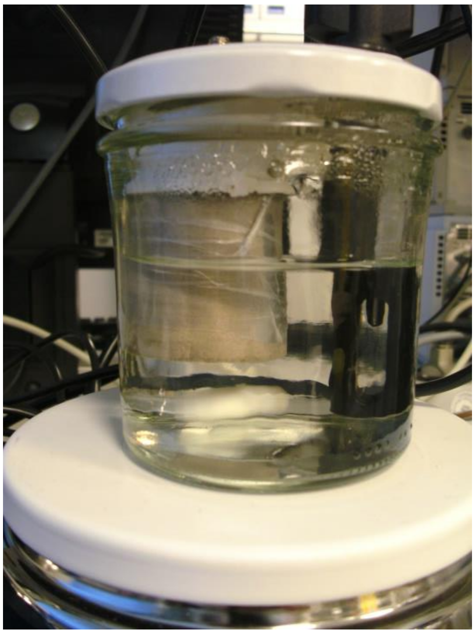


Figure 4-7: Glass jar with lid, containing sample, salinity sensor, and magnetic stirrer.

For the salted sample to be exposed to water with (almost) zero salt concentration, a glass jar containing a large volume of water is preferred. However in order to still be able to resolve the amount of salt in the water, the water volume cannot be too large. As compromise a glass jar is filled with 140±0.1 ml ultra pure water. With the sample containing roughly 0.75 gram of salt, and the (initial dry) sample absorbing roughly 6.6 ml water by capillary action, the average initial salt concentration in the sample is roughly 114 mg salt/gm water (1.94 M). If all salt is dissolved in the available water, the salt concentration will become roughly 5.4 mg/gm water (=5.4 $^{o}/_{oo}$ wt = 5.4 ppt wt = 0.09 M). Hence during a large part of the salt dissolution process, the sample can be considered to be exposed to water with relatively small salt concentration.

The glass jar is placed on a magnetic stirrer, continuously stirring the water (300 rpm), such that no salt concentration gradient can build up in the liquid, which could present a bottleneck for mass transfer.

The test are conducted at ambient conditions. The temperature during the test roughly ranges between 21 and 23°C.

4.5.2 *Salinity sensor*

The salt concentration of the water in the jar is measured at a 1 hr interval with a Hach-Lange HQ440D Benchtop Meter with a CDC401 series electrical conductivity probe. This is a graphite, 4-pole conductivity probe, which is capable to measure salinity between 0 to 42 ppt wt (= ‰ wt), with two digits resolution (reported accuracy 1 ppt). The unit of salinity is weight salt per weight of pure water. The associated electrical conductivity range is 0.01 μS/cm to 200.0 mS/cm. The probe also contains a temperature sensor (reported accuracy ±0.3 °C).

4.5.3 *Preparatory tests*

First the salt content of ultra pure water (UPW) was measured, which indeed was below the lower detection limit of the sensors (0.01 μS/cm). Also it was tested whether the virgin sample already contains natural salt, which could interfere with the measurement, by running the virgin sample in parallel to the salted samples. No detectable amount of salt was found.

4.6 Results

The following figure shows the salinity of the water in the jar in time. By fitting this curve to the expected theoretical exponential curve, the characteristic time constant is obtained. Though there are indications that the extrapolated asymptotic value for salinity somewhat larger than would be derived from a mass balance, this in principle does not affect the time constant. This can be due to e.g. the sensor or the measurement of salt content. The extracted time constants are given in the next table together with the effective diffusion coefficient and derived tortuosity factor, which indeed is larger than unity. For comparison, typical tortuosity factors for e.g. building bricks range from 2.7 to 4.3 [9].

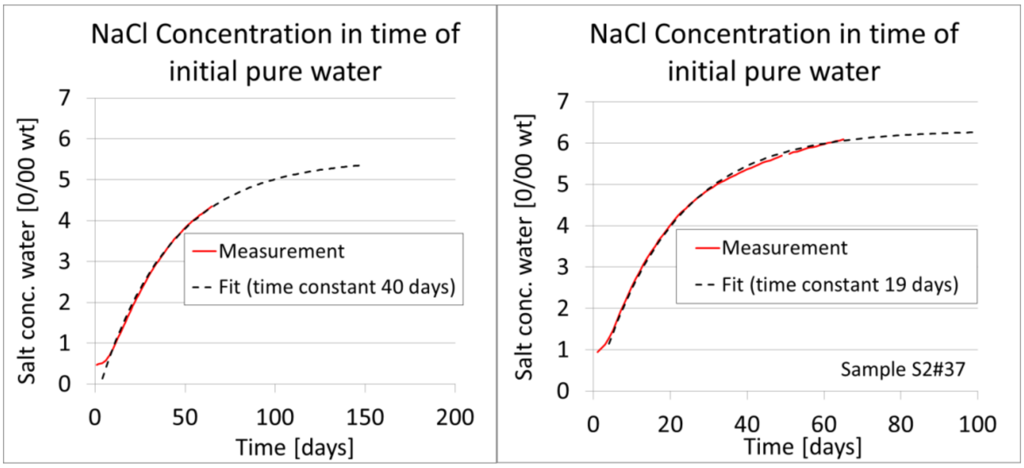


Figure 4-8: Salt concentration of water in time for sample a) S1#34 and b) S2#37

Table 4-3: Results dissolution test at ambient conditions

Sample Number	Virgin state				Amount salt due to salting procedure (g)	Brine type used for salting	Water in glass jar (gm)	Asymptotic salinity based on mass balance (°/₀₀ wt)	Measured time constant (days)	Measured D_{eff} (m^2/s)	Extracted tortuosity factor τ [2]
	Ambient He porosity (% of pore volume)	4 point Klink. Hor. Perm. (mD) [1]	Grain Density (g/ml)	Dry weight (g)							
V30	17.67	12.98	2.65	120.30	-	-	140.1	-	-		-
V34	19.04	11.83	2.65	118.94	0.73	5/6 sat brine	140.1	5.21	40	$2.9 \cdot 10^{-10}$	5.1
V37	18.80	12.32	2.65	118.93	0.81	sat brine	140	5.79	19	$6.2 \cdot 10^{-10}$	2.4

1) mD=milli Darcy, 2) Based on $D=1.484 \cdot 10^{-9}$ m^2/s

4.7 Extrapolation to elevated temperatures

4.7.1 *The diffusion coefficient of NaCl in water at elevated temperatures*

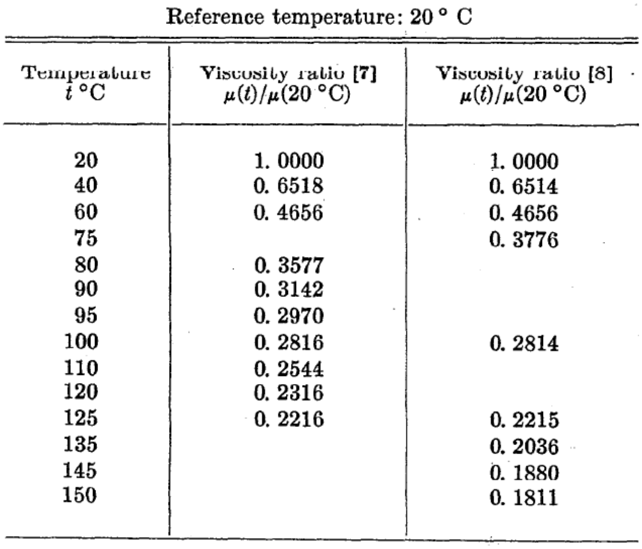
[5] gives an extrapolation expression for the diffusion coefficient of electrolyte solutions, relative to the value at reference conditions, involving temperature [K] and

dynamic viscosity of the liquid. The reference conditions are indicated by the index ‘0’:

$$D(T) \approx \frac{T \cdot \mu_0(T_0)}{T_0 \cdot \mu(T)} \cdot D_0(T_0)$$

For dilute species in water, we need the water viscosity as function of temperature, which is given in the following table.

Table 4-4: Viscosity of water as function of temperature [8]



Reference temperature: 20 ° C

Temperature t °C	Viscosity ratio [7] $\mu(t)/\mu(20\ °C)$	Viscosity ratio [8] $\mu(t)/\mu(20\ °C)$
20	1.0000	1.0000
40	0.6518	0.6514
60	0.4656	0.4656
75		0.3776
80	0.3577	
90	0.3142	
95	0.2970	
100	0.2816	0.2814
110	0.2544	
120	0.2316	
125	0.2216	0.2215
135		0.2036
145		0.1880
150		0.1811

For example we need the diffusion coefficient at 150 °C of a certain (dilute) species in water, where we know the diffusion coefficient at 20 °C. Then the 150 °C diffusion coefficients would be roughly 8 (=423K/293K x 1/0.1811) times larger than the ambient value.

4.7.2 *Response time at elevated temperatures*

Based on the extrapolated diffusion coefficient, we can say that the salt dissolution rate at 150 °C is estimated to be 8x faster than at ambient conditions.

4.8 Effect of water flow (in pores) on internal salt dissolution

In the test, the salt transport is via diffusion in water. Now what water speed (in the pores) would be required ‘U_{pore}’, to overcome the speed of diffusion of salt ? The diffusive speed of salt can be approximated by D_{eff}/L. In that case the speed of water should be larger than the salt diffusive speed, that is the Peclet number should be larger than unity:

$$Pe = \frac{U_{pore} \cdot L}{D_{eff}}$$

Hence at ambient conditions for the 50 mm sample under test this means that a very low flow velocity, less than 1 μm/s, in principle is already sufficient to overcome diffusion, which already can be realized by a fraction (hundredth) of a bar pressure difference. At elevated temperature (150 °C) the diffusion speed is roughly 8 times larger, requiring an 8 time larger water speed to overcome diffusion. The required pressure difference stays almost the same, as the viscosity is lower at elevated temperatures. Assuming this is at rather high water saturation levels, the capillary pressure is rather flat and low in this region, and the pressure difference to overcome capillary pressure rather low.

4.9 Conclusion

- The characteristic time constant to wash salt from a 50 mm Obernkirchener sandstone sample, by exposing it to fresh water at one side, is roughly 20 to 40 days at ambient conditions. This is the time to reduce the salt content by roughly 60%. The tortuosity factor of the samples was 2.4 to 5.1.
- The characteristic time constant at elevated temperatures, for example 150 °C, is estimated to be eight times faster (2.5 to 5 days), based on extrapolation of the diffusion coefficient.
- The time constant in principle is a quadratic function of sample thickness.

5 Capillary liquid uptake of samples

5.1 Introduction

The goal of the capillary liquid uptake measurement is to determine how far water or brine can penetrate an unsalted or salted rock sample in time by exposing its surface to the liquid under investigation.

This gives an indication of the required duration of a water wash, based on the suspected location of the precipitated salt in the rock, or vice versa, it can give an idea of the location of the salt, based on how long a water wash does take to restore the permeability of the sample. In case of a well with significant evaporation in the near well bore region (that can result in precipitation) capillary flow is considered as an important transport mechanism that transports water from the surrounding to the site of evaporation. In that case the capillary uptake rate gives an indication of amounts of water in time that can be transported to the site of evaporation as function of distance.

The model rock consists of virgin and salted Obernkirchener sandstone samples. In this chapter the results of the capillary liquid uptake tests are reported (at this point not taking into account cracks etc that might be present in the rock, as the investigated samples showed no cracks or fractures).

As the experiment is quite well defined, the results can be used to verify or tune the material properties in a simulation model like Dumu^x, which then can be used to study the e.g. the physical phenomena in the near well bore region.

5.2 Test method

The capillary liquid uptake is determined according to norm NEN-EN-1925 “Water Absorption Coefficient”, which determines the mass increase (per m^2) in time of a cylindrical sample with the end-surface exposed to water. The mass increase in time is written as $m(t) = A \cdot t^{1/2}$, where ‘A’ is referred to as water absorption coefficient. In our case we will also determine the uptake for other liquids.

5.3 Theory

Imagine a straight capillary of circular cross section (radius ‘r’). The liquid level in the capillary rises by capillary suction (surface tension ‘σ’). The flow in the capillary is laminar and the Haagen-Poseuille expression describes the viscous force, counteracting the capillary suction (viscosity). Gravity is neglected ($\rho \cdot g \cdot h < 2 \cdot \sigma / r$), as are inertia forces and evaporation.

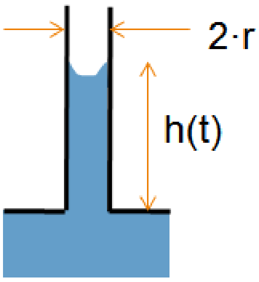


Figure 5-1: Straight capillary with uniform cylindrical cross section

The capillary suction pressure is given by:

$$\Delta p = \frac{2 \cdot \sigma \cdot \cos(\theta)}{r}$$

The viscous friction force is a function of flow velocity and height of the liquid: column (‘h’):

$$\mathrm{v} = \frac{r^2}{8\mu} \frac{\Delta p}{h}$$

The change in column height in time is the flow velocity:

$$\mathrm{v} = \frac{dh}{dt}$$

Combining the expression gives the differential equation:

$$\frac{\mathrm{d}h}{dt} = \frac{r}{8\mu} \frac{2\sigma \cos(\theta)}{h}$$

With general solution:

$$h = \sqrt{\frac{r \cdot \sigma \cdot \cos(\theta)}{2 \cdot \mu}} \cdot \sqrt{t}$$

Hence the liquid level (and mass increase) according to this simplification scales with the square root of time. Gravity plays a role for relatively large column heights, in which case the pressure differential over the column reads (the plus signs applies for gravity assisting surface tension, minus for gravity opposing surface tension):

$$\Delta p = \frac{2 \cdot \sigma \cdot \cos(\theta)}{r} \pm \rho \cdot g \cdot h$$

Now the solution reads (select minus sign in case gravity is counteracting capillary action, and plus sign in case gravity is helping capillary action), where the column height is an implicit function of time:

$$h_0 \cdot \ln\left(\frac{h_0}{h_0 \pm h}\right) \pm h = C \cdot t$$

Where

$$h_0 = \frac{2 \cdot \sigma \cdot \cos(\theta)}{\rho \cdot g \cdot r} \quad C = \frac{\rho \cdot g \cdot r^2}{8 \cdot \mu}$$

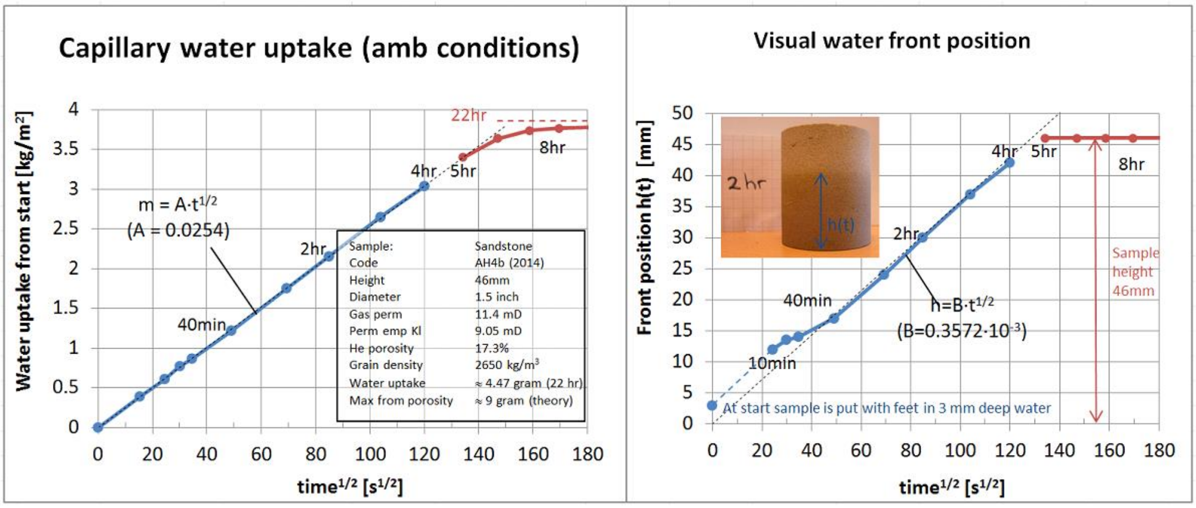
For example. In case r=1 μm and water at ambient conditions (σ=72 mN/m, μ=0.001 Pa·s, ρ=1000 kg/m^3, θ=0^o), the equilibrium water column height (capillary suction balancing gravity) reads $h_0 \approx 14$ m.

In reality, for a real pore system the situation is more complex, and deviations from ideal may occur. In general the mass uptake [kg/m^2/s] and front position [m] is abbreviated to:

$$\dot{m} = B \cdot \sqrt{t}$$
$$h = A \cdot \sqrt{t}$$

5.4 Example capillary water uptake

The following figure shows the capillary water uptake in time at ambient conditions, when a Kircherner sandstone sample (1.5 inch diameter, height 46 mm) is put with its feet in roughly 3 mm water (glass jar). The liquid position 'h' is determined via visual inspection (discoloration, see insert in right hand side of Figure 5-2) and therefore contains an arbitrary element. The cylinder mantle is not sealed for water. In between the weight measurement (by removing the sample from the jar and placing it on a weighing scale), the glass jar is closed by a glass lid, to prevent premature evaporation.



Sample:	Sandstone
Code	AH4b (2014)
Height	46mm
Diameter	1.5 inch
Gas perm	11.4 mD
Perm emp Kl	9.05 mD
He porosity	17.3%
Grain density	2650 kg/m^3
Water uptake	≈ 4.47 gram (22 hr)
Max from porosity	≈ 9 gram (theory)

Figure 5-2: Capillary water uptake of Obernkirchener sandstone in time

In this case the capillary water uptake and liquid front position clearly scales with the square root of time, until the front arrives at the other end of the sample.

The capillary uptake coefficient (‘A’) and front position are roughly related to each other, by making a mass balance, assuming that the sample is infiltrated with water only to a certain fraction (in general smaller than one):

$$A \approx \rho \cdot \Psi \cdot S_w \cdot B$$

This volumetric saturation ‘Sw’ is estimated from the pore volume ‘Ψ’ that is infiltrated with water after relatively a long time. For the Obernkirchener sample under investigation roughly 50% of the pore volume is filled with water ($S_w \approx 0.5$) after 24 hr. For the Obernkirchener sandstone the conversion of ‘B’ to ‘A’ then would give: $A \approx 1000 \cdot 0.173 \cdot (4.47/9) \cdot 0.3572 \cdot 10^{-3} = 0.031$ kg/m^2/s$^{0.5}$ where the measured value is 0.0254 kg/m^2/s$^{0.5}$, which is quite consistent.

5.5 Results

For the reported samples, the cylinders mantle was sealed with resin, such that it becomes impenetrable for the liquid under investigation. The (bottom) surface exposed to the liquid is not sealed (nor is the opposite top surface, such that entrapped air can escape).

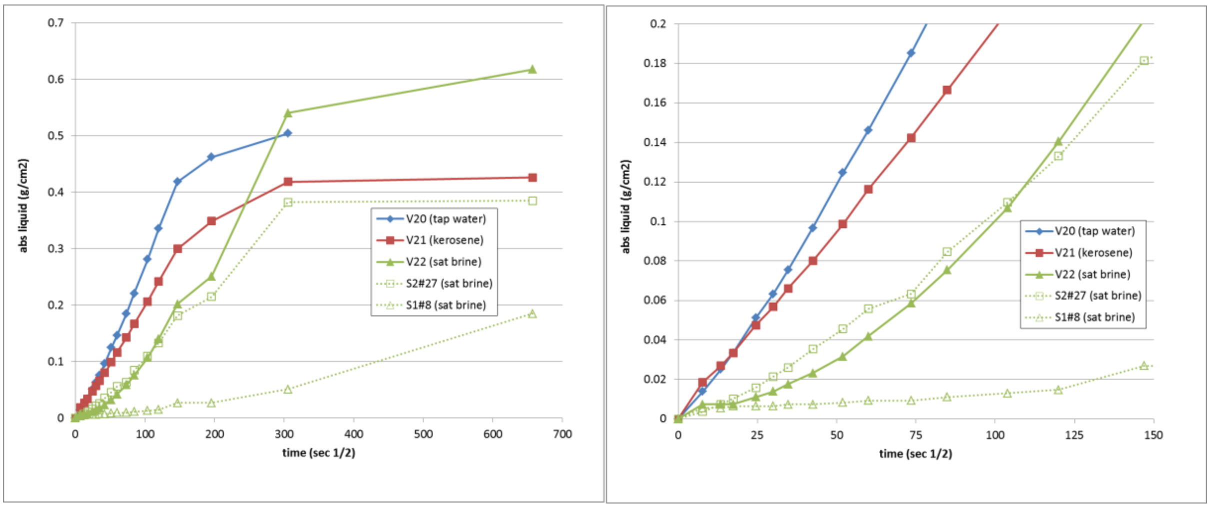


Figure 5-3: Capillary water uptake of Obernkirchener sandstone in time. Depicted along the x-axis is the square root of time [s$^{0.5}$], and along the y-axis the cumulative amount of liquid absorbed [gram/cm^2]

The slope ‘A’ for (tap) water uptake is similar for the virgin sample V20, and the virgin sample as presented in the previous section. It takes roughly 5 hours for the liquid to travel a distance of 4 á 5 cm (uncracked sample) or even slower for a virgin sample in combination of kerosene or saturated brine. The travel time in a salted sample is even more slower. It cannot be explained why the absorption of saturated brine takes much longer for the S1 sample than the S2 sample. There is no clue that the S1 sample surfaces might be clocked with salt (from the permeability measurement of the samples before and after salting, see [2]).

5.6 Conclusions

For the virgin sandstone sample it takes roughly 5 hours for water to travel a distance of 5 cm, starting with a dry sample. Note that the sample is not fractured or cracked. The travel distance scales roughly with the square root of time. Hence it will take approximately 20 hours to travel twice the distance, that is 10 cm. For the other fluids investigated (kerosene or brine) or salted samples, the travel time is even longer for the same distance. For comparison, the shut-in time for a (batch) water wash in a production well is typical a few hours (less than one day). From this it is concluded that the penetration depth of a typical water wash is rather limited. Hence when it is possible to restart gas production after a water wash, this would indicate that the precipitated salt that clogs the system is present rather superficial.

6 Sample transport properties (RCAL and SCAL)

6.1 Transport properties

The transport properties of virgin and salted Obernkirchener sandstone were determined (routine- and special core analysis RCAL and SCAL). Transport properties measured are:

- Capillary pressure curves (drainage and imbibition)
    - Centrifuge & mercury injection
- Absolute permeability
    - Klinkenberg gas & liquid
- Relative permeability (drainage and imbibition)
    - Centrifuge
- Porosity
    - Gas porosity (sample not lost)

6.2 Test liquids

Test liquids used are

- Water
- Brine
- Kerosene

Table 6-1: Test liquids and selected properties at 20 °C

Fluid Type	Density (g/cm³)	Viscosity (cP)
Demi Water	0.998	0.987
2/3 Brine	1.138	1.538
5/6 Brine	1.167	1.745
Super Brine	1.203	2.031
Kerosene Oil	0.802	1.973

Tests were conducted to investigate the interaction of the selected fluids with the (salted) samples.

Complicating aspect is that the test liquids ideally should not interact with the precipitated salt being present, e.g. by prematurely dissolving the salt (unless intentionally). Otherwise the transport properties of the salted sample cannot be determined anymore (for the given salt content and state of the salt). On the other hand, favourably the liquids should have properties close to that of a watery system, as in the real situation. For this purpose saturated brine and kerosene where selected in the end, still being practical to handle.

Kerosene replaces gas in .e.g. relperm centrifuge tests as non-wetting phase, as this otherwise leads to problems due to the high mobility of gas compared to water/brine.

6.3 Permeability reduction and other results

The RCAL and SCAL tests were conducted by Panterra Geoconsultants B.V. and the results are reported separately, see [2].

The typical reduction in permeability as function of reduction in porosity for Obernkirchener sandstone due to NaCl salt is repeated below. The blue and red markers refer to salted samples prepared with under saturated brine (‘S1’). The green markers refer to salted samples prepared with saturated brine (‘S2’), where salt may have been collected preferentially on the outer surface, and which therefore should be discarded.

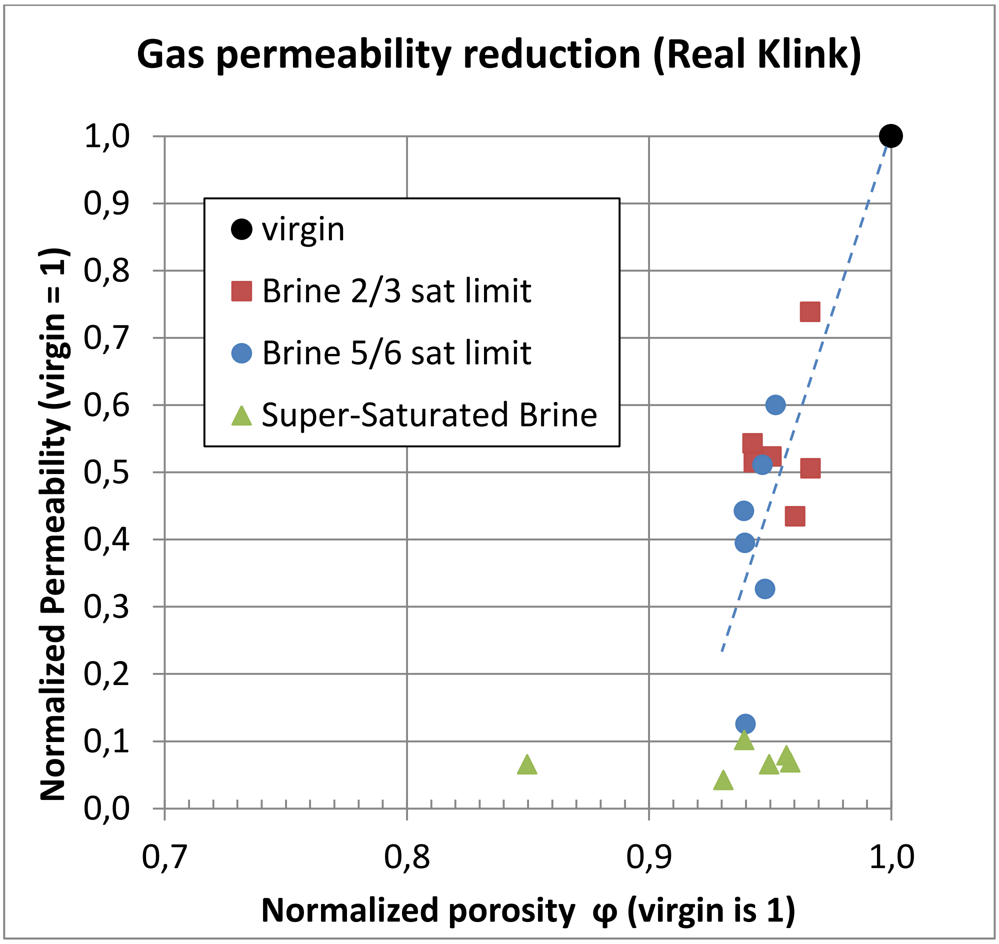


Figure 6-1: The typical reduction in permeability as function of reduction in porosity, for Obernkirchener sandstone, due to NaCl salt precipitation.

7 High pressure high temperature test setup

7.1 Introduction

In the original project scope also salt precipitation experiments where planned at reservoir conditions (elevated pressures and temperatures), to be conducted in a dedicated high pressure, high temperature test-setup. Though this test-setup was largely realized, the activity was halted because of budget considerations, and priority was given to the ambient tests.

The high pressure setup is described briefly, for documentation purposes.
The main pressure vessel of the setup is shown with the pressure dome assembled in Figure 7-1 and removed in Figure 7-2.

Figure 7-1: Assembled reactor

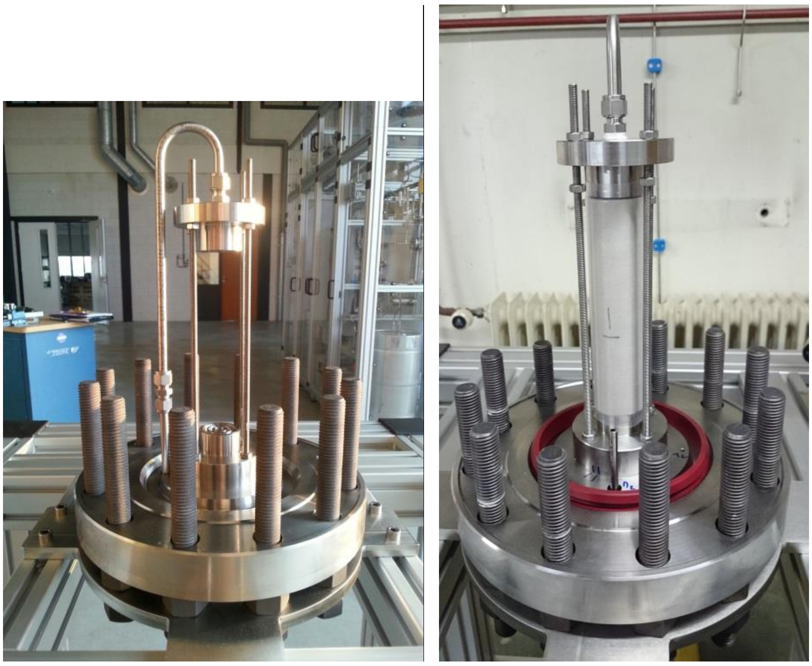


Figure 7-2: Reactor with pressure dome removed to see the sample position (sample typical 16 cm long, 1.5 inch diameter)

7.2 Requirements

The following basic set of requirements where used, for the reactor design:

- Core sample
  - Typical dimension Ø41mm, L165mm (varying)
  - Typical initial permeability sample 10mD
- The conditions of this experiment should reflect the reality of wells;
  - Temperature on sample: up to 150 °C
  - Pressure to sample: up to 150bar
  - Source of NaCl, via brine
- Fluids
  - Gas: For practicality and safety it was decided to use nitrogen as a gas.
  - Brine: Via injection or capillary suction
  - Available flow of nitrogen to the sample: up to 100ln/min
  - Available flow of brine to the sample: up to 10ml/min
- Measurement of permeability change sample;
  - Measure the pressure drop over the sample
  - Measure the flow through the sample
  - Measure the temperature of the sample

7.3 Mounting of sample in reactor

The samples could be of various lengths, even within a small tolerance. For accurate measurements, the sample had to be clamped into the setup. See next figure for a rendered image of the design of the reactor. Several parts are annotated for clarity.

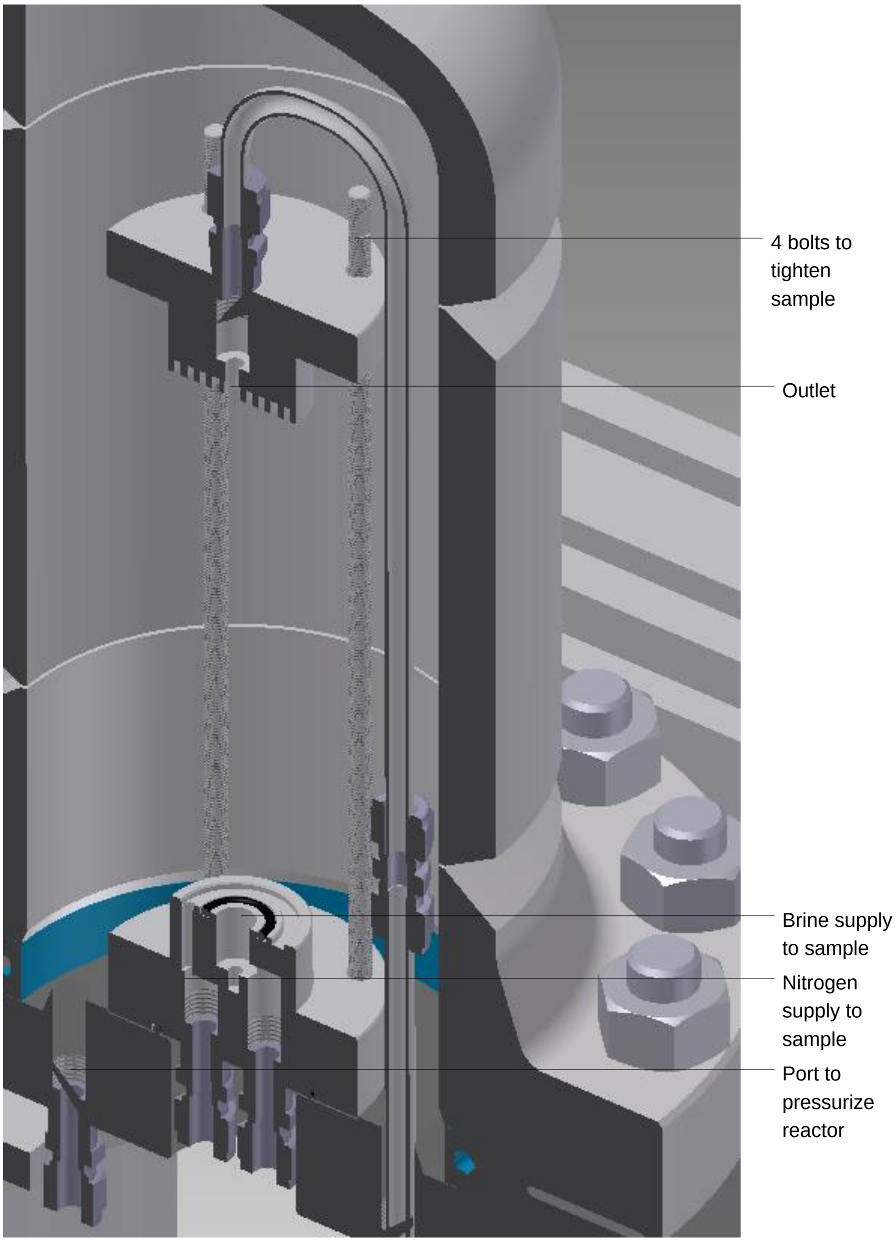


Figure 7-3: Section face reactor design

This design allows the sample to be exposed to a set flow of nitrogen and brine.

7.3.1 *Preventing bypass – core sleeve*

Bypass flow over the sample had to be prevented. When using a solid sample holder, the bypass would occur as seen in the next figure.

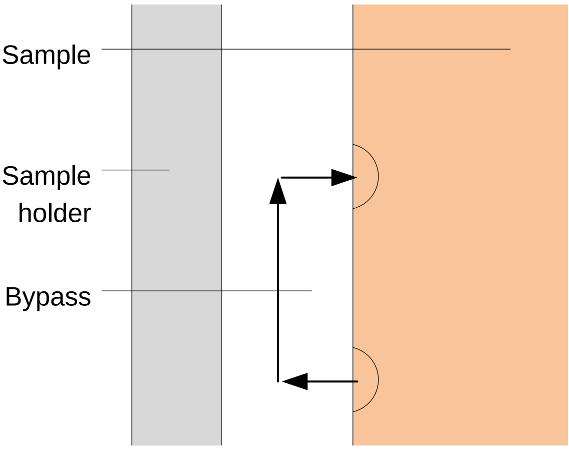


Figure 7-4: Bypass flow

Thus, the sample holder had to be flexible. It was decided to use a core sleeve for this purpose. The sample would be placed in the core sleeve, before this would be mounted in the setup. The core sleeve would then be exposed to a higher pressure than the supplied pressure to the sample, thus pushing the core sleeve against the sample and preventing bypass flow.

7.4 Complete experimental setup

The following figure shows the experimental setup. As it contains too many details for one page, the complete design will be described in parts.

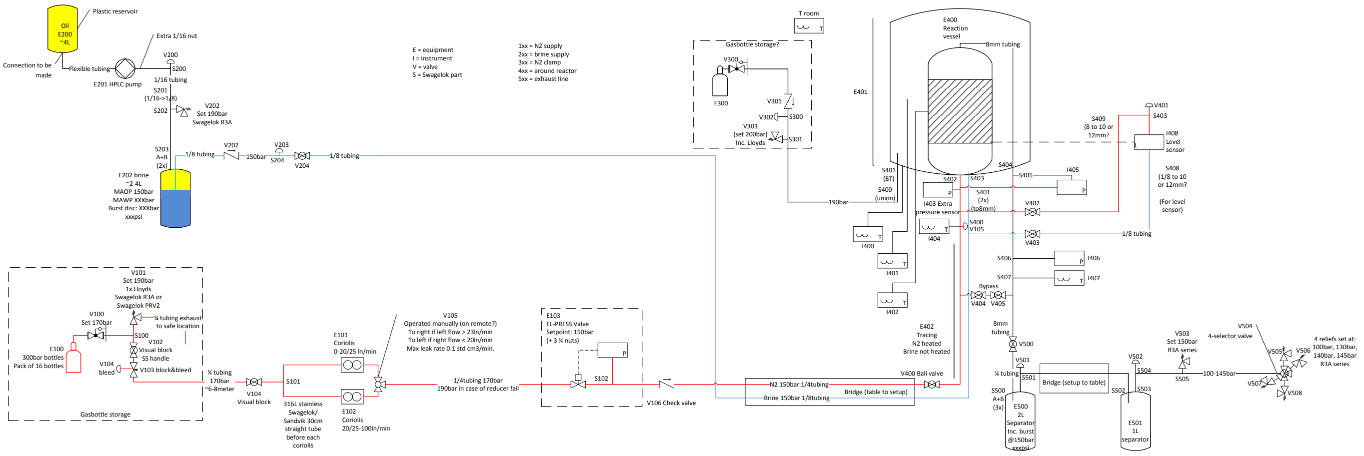


Figure 7-5: Design of complete setup
- top left: brine supply
- bottom left: nitrogen supply
- right: heating of supply, reactor and regulated outlet

7.4.1 *Brine supply*

The following figure shows a detailed drawing of the brine supply.

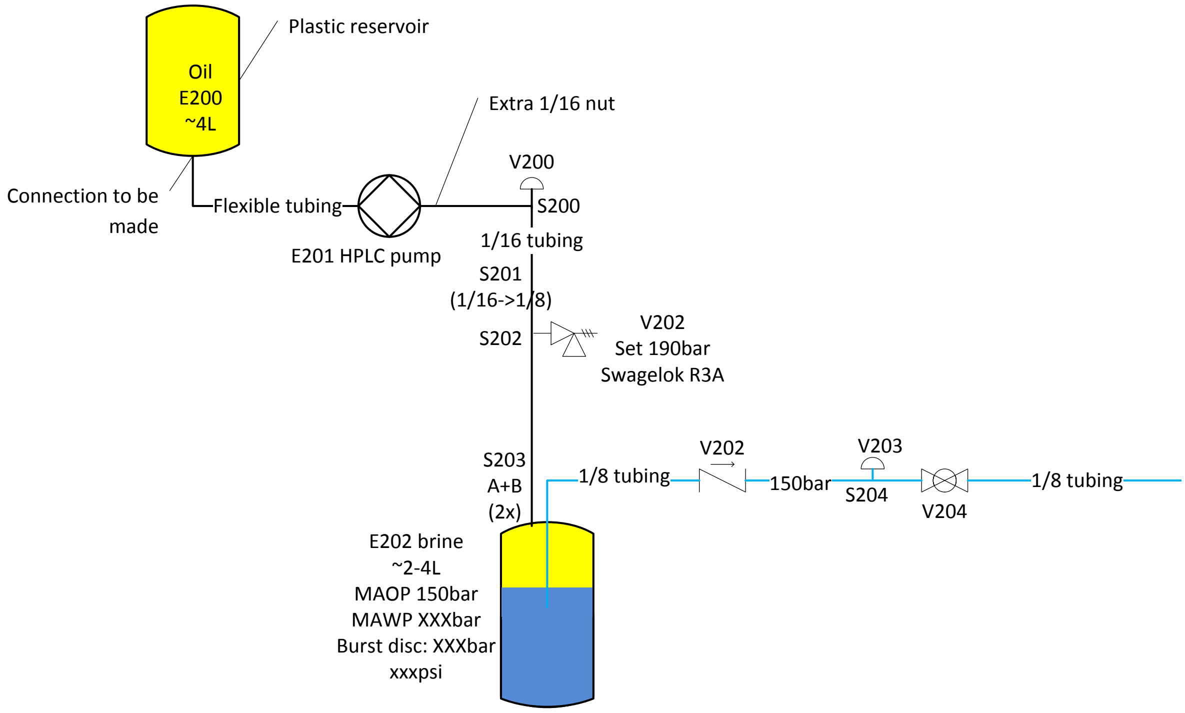


Figure 7-6: Brine supply

The brine had to be supplied at a precise and controlled flow under a high pressure. An HPLC pump is very suitable for this purpose. However, the risk would be that the HPLC pump would get clogged with salt crystals. It was therefore decided to use the HPLC to pump oil to a second reservoir containing the brine. The brine would then be pushed out by the oil through the 1/8 tubing, on its way to the reactor. This design would then prevent the HPLC pump from being exposed to brine directly.

7.4.2 *Nitrogen supply*

A high amount of nitrogen at a high pressure would be consumed by the experiments. The design therefor had to encompass a connection to a to be placed package of 16 300 bar nitrogen cylinders. Standard cylinders of nitrogen are supplied at 200 bar. It was decided to use 300 bar, as the cylinders at ~160 bar would be useless for a 150 bar experiment. See the following figure.

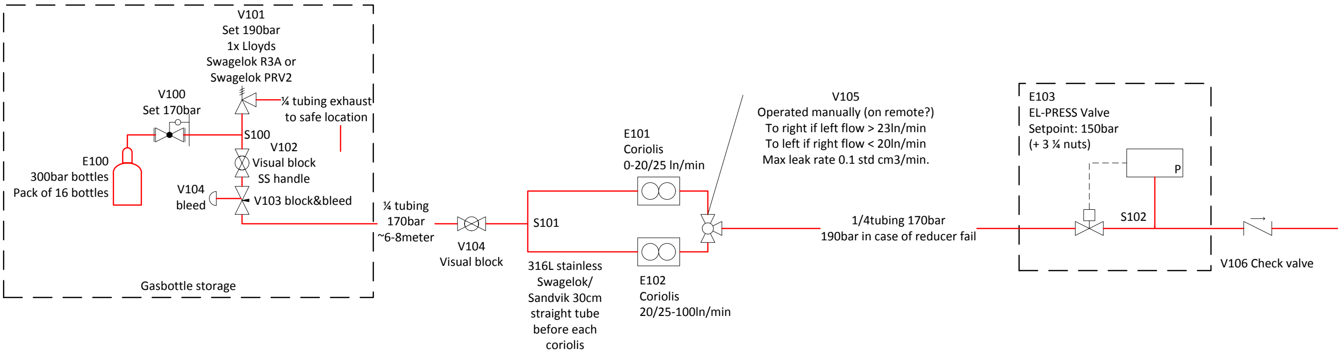


Figure 7-7: Nitrogen supply
- Left: nitrogen supply and pressure regulators
- Middle: Coriolis flow meters;
- Top: for the range of 0 to 20/25 ln/min
- Bottom: 20/25-100 ln/min
- Right: pressure controller

7.4.3 *Setup excluding supply*

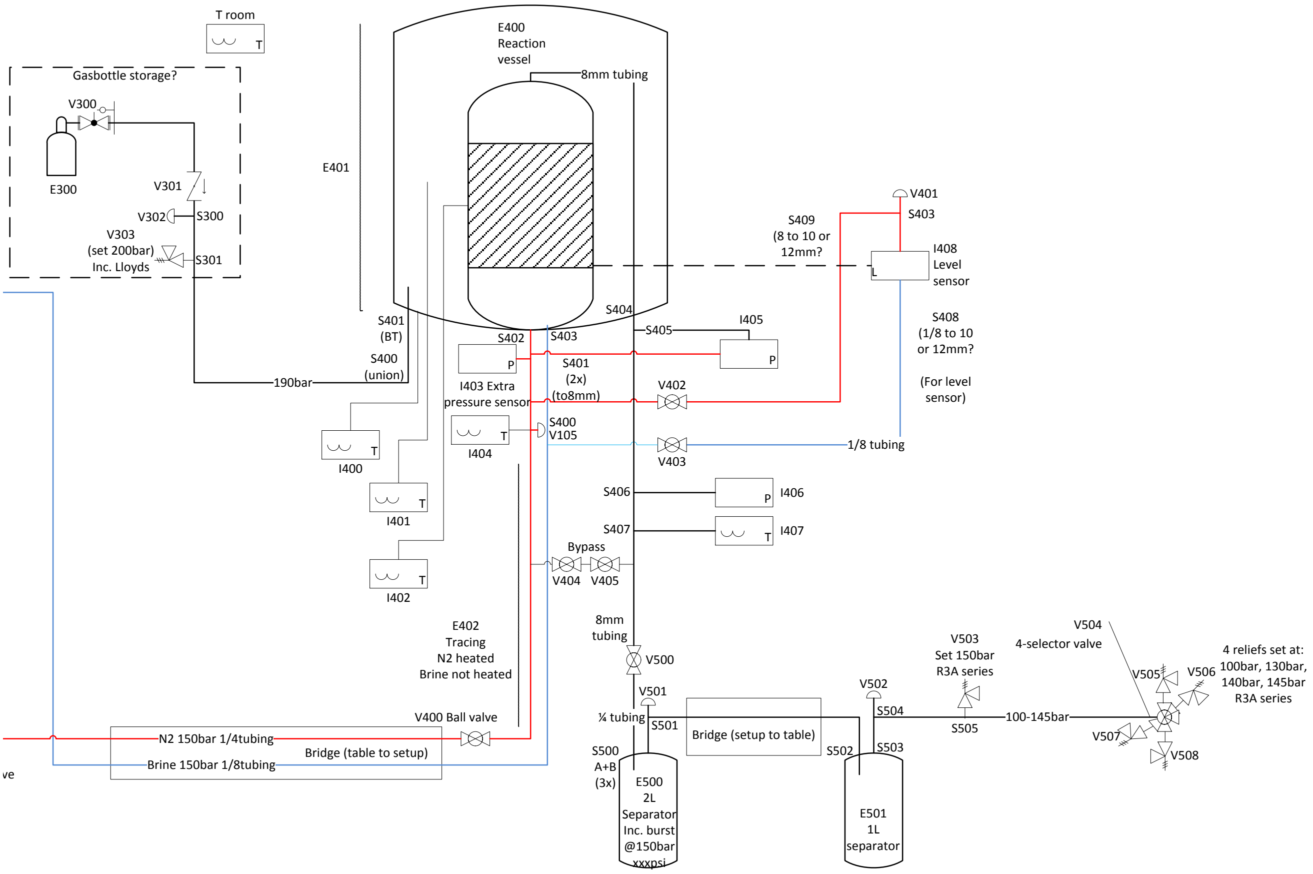


Figure 7-8: Setup excluding supply
- Top left: to pressurize reactor
- Bottom left: supply lines to heating (red: nitrogen, blue: brine)
- Top right: reactor
- Bottom right: outlet

7.4.4 *Pressurizing the reactor*

The reactor needs to be exposed to a slightly higher pressure than the nitrogen supply, in order to push the core sleeve against the core. The gas used for this would be nitrogen.

7.4.5 *Heated supply*

In order to keep the sample at its target temperature, both the reactor and the supply lines had to be heated. Several thermocouples were placed in the design to monitor this process.

7.4.6 *Reactor*

The main purpose of the reactor is to hold the sample. In order to monitor and control the brine level exposer, a level sensor (right of the reactor in the design) was mounted. If brine supply would be necessary, the level sensor would switch the HPLC pump on, and off if the brine would be at the required level.
One of the more important pieces of measuring equipment in the experimental setup is the pressure differential sensor, placed just under the reactor.

7.4.7 Regulated outlet

The pressure at the outlet had to be regulated at a set pressure as well. However, this flow would be contaminated with brine. Salt crystals in the brine would be detrimental to the more accurate regulating equipment. It was decided to place two separators before the pressure relief valves.

8 Conclusions

The Obernkirchener outcrop sandstone has been chosen to take samples of for examining the effect of salt precipitation on the transport of a rock matrix. This sandstone has quite uniform and interchangeable properties and has an effective permeability which reflects the average of a typical North Sea gas production field, that is roughly 10 mD. From preliminary tests it was concluded that the exposure to liquid did not significantly alter the transport properties (gas and brine permeability and porosity).

For a number of experiments the samples needed to be salted. Various methods were tested (freeze drying, external drying in a climate room, and flow through drying), and finally the “gentle flood” flow-through drying method (using humidified N_2 followed by dry N_2) was considered to give the most acceptable results. All samples where finally produced at Panterra by this method.

Several methods (hygroscopic, XRF, XRD, IC, and ICP-OES) have been considered to determine the salt content and spatial distribution of the salt in the salted samples. IC (TNO-Rijswijk) and ICP-OES (University Utrecht, incidental basis) were considered to be the best option as both are a quantitative technique and can resolve the required amount of salt, and take typical one week to process (cost typical euro 400 per test). The results showed that salt is found throughout the samples, and not only at the end faces, which was feared of. The distribution indicates that in the center less salt is found. However this was considered as to be the best achievable result.

From the dissolution experiment (conducted at TNO) it can be concluded that:

- The characteristic time constant to wash salt from a 50 mm Obernkirchener sandstone sample, by exposing it to fresh water at one side, is roughly 20 to 40 days at ambient conditions. This is the time to reduce the salt content by roughly 60%. The tortuosity factor of the samples was 2.4 to 5.1.
- The characteristic time constant at elevated temperatures, for example 150 $^{\circ}$C, is estimated to be eight times faster (2.5 to 5 days), based on extrapolation of the diffusion coefficient.
- The time constant in principle is a quadratic function of sample thickness.

The liquid uptake experiment (conducted at TNO) resulted in the following.
For the virgin sandstone sample it takes roughly 5 hours for water to travel a distance of 5 cm, starting with a dry sample. Note that the sample is not fractured or cracked. The travel distance scales roughly with the square root of time. Hence it will take approximately 20 hours to travel twice the distance, that is 10 cm. For the other fluids investigated (kerosene or brine) or salted samples, the travel time is even longer for the same distance. For comparison, the shut-in time for a (batch) water wash in a production well is typical a few hours (less than one day). From this it is concluded that the penetration depth of a typical water wash is rather limited (for uncracked stone). Hence when it is possible to restart gas production after a water wash, this would indicate that the precipitated salt that clogs the system is present rather superficial.

The RCAL and SCAL experiments on salted and non-salted (“virgin”) samples have been performed by Panterra. The results are described in a separate report [2]. Some conclusions of that report are repeated here:

- Salted samples have been prepared from virgin samples by soaking them in under-saturated brine (‘S1’ samples) and saturated brine (‘S2’ samples), followed by drainage and flow through drying.
- For the S1 samples, a permeability reduction is found throughout the sample. For the S2 samples the permeability reduction is mainly an effect of salt precipitation at the end face. The results of the S2 samples should therefore be interpreted with care.
- It seems that pure water (also possibly brine), has an effect of damage rock liquid permeability. This effect complicates the effect of salt precipitation on the liquid permeability.
- The salt precipitation, obtained under the current experimental conditions has minor effects on the capillary pressure and relative permeability of the samples. This is mainly due to the salted samples interact with even super saturated brine before these tests started. Or the sample selections in some of the tests do not represent or factor the localized salt precipitation.

9 Signature

Delft, 27 January 2016

TNO

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10 Literature

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