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Investigations of gas evolution in an unsaturated KBS-3 repository

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Investigations of gas evolution in an unsaturated KBS-3 repository

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Abstract

Two tests have been designed and conducted in order to investigate the possible evolution of gases in the buffer of an unsaturated KBS-3 repository. One of the tests included a central heater in form of a copper tube as well as IBECO RWC bentonite blocks and pellets, configured to form a scaled model of an isolated unsaturated KBS-3 buffer (10 cm copper tube, approximately 30 cm bentonite block diameter). The other test was conducted in isothermal (room temperature or 50 °C), isolated conditions, and involved only bentonite pellets. The evolution of the oxygen concentration in the tests was monitored by occasional measurements using an in-situ system. At the end of the tests, gas was sampled and analysed in a dedicated accredited laboratory. The tests were conducted over the course of approximately one year.

Although the bentonite used was chosen due to its rather high sulfur content, no sulphide gas was detected in any of the samples. This result is a strong indication that such gas is not to be expected under semi-dry repository conditions. Furthermore, a pronounced oxygen consumption was noted in the test involving a copper tube – after approximately 50–60 days, the oxygen concentration was about 1 %. In contrast, the test which did not include a copper component showed no noticeable oxygen consumption at room temperature. From this difference in behaviour it can be concluded that oxygen is mainly consumed as a consequence of aerobic copper corrosion. This conclusion is also strengthen by visual proof of copper (I) and copper (II) oxides on the heater after test termination.

The gas samples were also analysed for carbon monoxide, methane, and other light hydrocarbons. None of these compounds were detected.

A noticeable carbon dioxide level was detected in both tests (above 1 %). A tentative explanation for this is carbonate dissolution as a consequence of pyrite oxidation and associated acidification.

Sammanfattning

Två försök har utformats och genomförts för att undersöka utvecklingen av gassamansättningen i bufferten i ett omättat KBS-3-förvar. Ett av försöken inkluderade en central värmare i form av ett kopparrör, samt IBECO RWC-bentonitblock och pelletar, konfigurerade som en skalmodell av en isolerad omättad KBS-3-buffert (10 cm kopparrör, ca 30 cm bentonitblockdiameter). Det andra försöket utfördes under isotermiska och isolerade förhållanden (rumstemperatur eller 50 °C) och innefattade endast bentonitpelletar. Utvecklingen av syrekoncentrationen i försöken mättes återkommande med hjälp av ett in situ-system. Innan försöken avslutades, samplades gas för analys i ett dedikerat laboratorium. Försöken pågick under ungefär ett år.

Trots att den använda bentoniten valdes på grund av dess ganska höga svavelhalt, detekterades ingen sulfidgas i något av proven. Detta resultat är en stark indikation på att sådan gas inte förväntas i ett omättat KBS-3-förvar. Vidare noterades en kraftig syreförbrukning i försöket som innehöll ett kopparrör – efter ungefär 50–60 dagar var syrehalten ca 1 procent i detta försök. Däremot visade försöket utan kopparkomponent ingen märkbar syreförbrukning vid rumstemperatur. Från denna skillnad i beteende mellan försöken kan man dra slutsatsen att syret huvudsakligen konsumeras som en följd av aerob kopparkorrosion. Denna slutsats stärks också genom att koppar (I) och koppar (II) oxider noterades på kopparvärmaren efter avslutat test.

Gasproverna analyserades också för kolmonoxid, metan och andra lätta kolväten. Ingen av dessa föreningar detekterades.

En förhöjd koldioxidnivå detekterades i båda testen (över 1 procent). En trolig förklaring till denna är karbonatupplösning som en följd av pyritoxidation och associerad försurning.

Contents

1 Introduction

If the host rock in a KBS-3 repository has relatively few fractures, saturation times of up to several thousand years can be anticipated (Malmborg et al. 2013). Since several buffer safety functions assumes saturation (SKB 2011), it becomes necessary in such scenarios to consider processes related to the presence of a gas phase within the buffer and the backfill during longer periods of time. This has been done e.g. with respect to the so called “sauna” effect (Birgersson and Goudarzi 2017). An additional aspect to consider in saturation scenarios of long time scales is the evolution of the composition of the gas within the repository. In particular, it is relevant to assess if significant canister corrosion due to gases, e.g, H_2S, is conceivable. This issue has also been raised by the Swedish regulator (Szakálos and Seetharaman 2012).

Here is reported an initial step made in investigating issues regarding the repository gas composition evolution. Laboratory scale tests have been conducted with the aim of capturing some features of a partly saturated KBS-3 buffer, and to gain insight regarding the evolution of the gas composition in such a system.

2 Test set-up

Two tests have been designed and conducted. The main goal was to create isolated systems which in various aspects resemble unsaturated buffer conditions. Consequently, efforts have been made create a reasonably gas tight confinement of bentonite (and possible other buffer materials), without access to external water, but with the possibility to sample the gas during various stages of the tests. A short specification of the main features of the tests is given in Table 2-1.

Table 2-1. Specification of the performed tests. Deponit Can indicate calcium dominated bentonite from Milos island, Greece, RH indicate the relative humidity, T indicate temperature

	Thermal gradient test	Isothermal test
Temperature	Spatially varying, max 80 °C	Isothermal, room-T or 50 °C
Metals	Stainless steel, copper, titanium	Stainless steel
Bentonite	Deponit-Can, blocks and pellets	Dep-Can, pellets
Main measurements	O_2 evolution, RH, T, gas sampling	O_2 evolution, gas sampling

2.1 Thermal gradient test

One of the tests includes a heater made of copper, and its schematic design is shown in Figure 2-1. With a copper heater at the center, while the set-up is placed in room temperature, this test is expected to develop gradients in moisture and temperature. It is therefore referred to as the *thermal gradient test.*

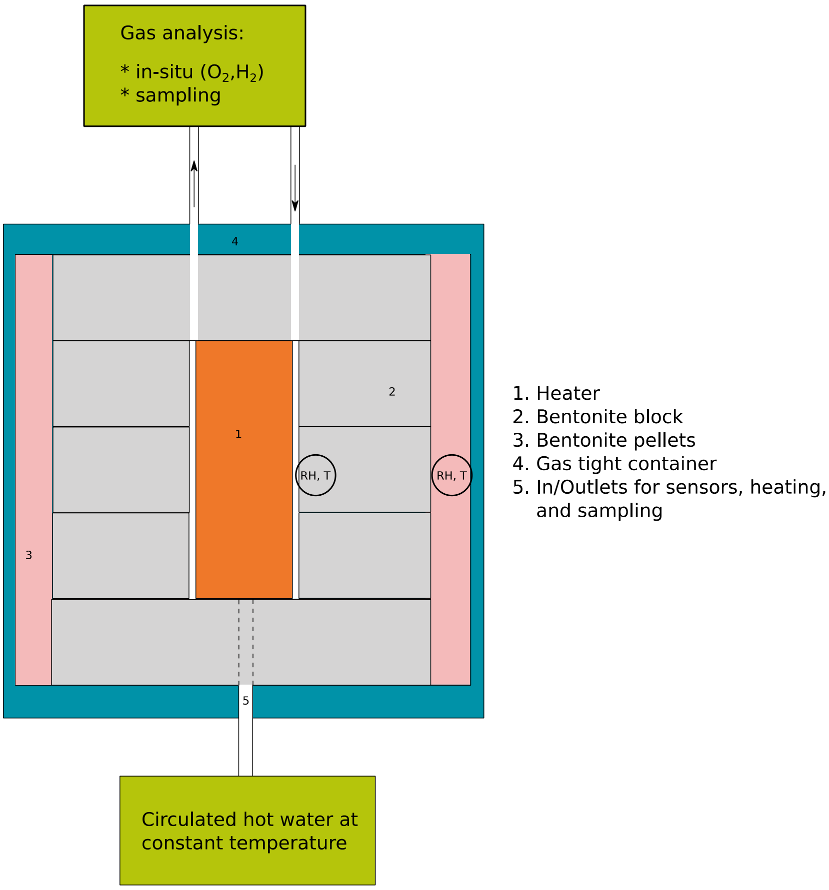

Figure 2-1. Schematics of the set-up for the thermal gradient test.

In addition, as the test includes copper metal, it is expected to consume oxygen due to aerobic corrosion of the copper. Some minerals, especially pyrite, in the bentonite may react with oxygen especially at the thermal gradient test. Other included materials, like stainless steel, titanium and plastics were expected to have insignificant reactions with oxygen. In-situ testing of the gas is made via tubes in the inner slot between heater and bentonite.

2.1.1 Container

The container is made of stainless steel and consists of a "barrel" and a lid, shown in Figure 2-2. The container has inlet and outlet holes for supporting a water based heating system, as also used in lab tests for investigating the "sauna" effect (Birgersson and Goudarzi 2016). The lid has openings for in situ gas analysis (oxygen) and gas sampling, RH-sensor cables, and a total pressure gauge. The lid is attached to the "barrel" by 20 screws and is sealed with a large o-ring (Figure 2-2).

Geometrical specifications of container, heater and bentonite is given in Table 2-2.

Table 2-2. Specifications of the components of the thermal gradient test.

Container height	50 cm
Container diameter	35 cm
Heater height	33 cm
Heater diameter	10.8 cm
Block diameter	28 cm
Ring diameter	28 cm/11 cm
Water-to-solid mass ratio rings	0.28
Water-to-solid mass ratio blocks	0.24
Water-to-solid mass ratio pellets	0.23
Dry density block	1540 kg/m^3
Dry density rings	1464 kg/m^3
Dry density pellets	900 kg/m^3
Dry mass blocks/rings	42 kg
Dry mass pellets	15 kg
Average degree of saturation	0.6
Total gas volume	ca 10 L

Figure 2-2. The container of the thermal gradient test. Left: the "barrel" seen from the top. The holes for inlet and outlet of heating water are visible. Right: The lid with the RH sensors and the total pressure gauge attached.

2.1.2 Heater

The heater consists of a copper tube of diameter 10.8 cm. This tube was washed in hydrochloric acid and flushed with large amount of water and finally airdried before the start of the experiment in order to – as far as possible – get rid of corrosion products initially present on the surface.

The copper tube was connected to the system for circulating and heating water (Figure 2-3). The heater was regulated as to keep the temperature in the copper tube at 80 °C.

2.1.3 Bentonite

The bentonite used for both blocks and pellets is IBECO RWC/Deponit CAN (Svensson et al. 2011). This material was mainly chosen because of its sulfur content (Karnland 2010), in order to investigate the possibility of development of sulphide gas. An elemental analysis (performed by an external accredited laboratory) of the actual material used for producing blocks and rings is presented in Table 2-3. Analysis was made on two different samples of the material. Except for sulfur and organic carbon, the substances show minor variation. The sulfur content in both samples were larger than 1 %.

The blocks and rings were manufactured exclusively for the present test, with pre-wetted bentonite in order to achieve a saturation level somewhere in between the expected initial state of a KBS-3 repository and a fully water saturated system. For the same reason the bentonite pellets were preconditioned by increasing their water content. The average overall degree of saturation in the test is 60 %. The specification of the involved bentonite components is listed in Table 2-2.

Figure 2-4 shows pictures from the assembly of the bentonite blocks in the experimental set-up.

Figure 2-3. *The copper heater assembled in the thermal gradient test. The photograph to the right shows the connection at the bottom of the "barrel" for flowing heated water. The water heater is seen in Figure 2-6. The green cable seen in the right picture is for the thermocouple controlling the heat regulation.*

Table 2-3. Elemental analysis of two samples of the bentonite used for blocks, rings and pellets (Deponit CAN).

Substance	Amount (of total solids) Sample #1	 Sample #2
SiO_2	54 %	53.4 %
Al2O$_3$	17.9 %	17.8 %
CaO	2.1 %	2.12 %
Fe_2O_2	6.32 %	6.24 %
K_2O	0.506 %	0.53 %
MgO	2.38 %	2.35 %
MnO	0.0325 %	0.0308 %
Na_2O	1.07 %	1.05 %
P_2O_2	0.199 %	0.184 %
TiO_2	0.710 %	0.686 %
As	15.4 ppm	12.3 ppm
Ba	1 360 ppm	1 150 ppm
Be	4.20 ppm	4.43 ppm
Cd	0.0959 ppm	0.0502 ppm
Co	4.35 ppm	4.50 ppm
Cr	11.3 ppm	<10 ppm
Cu	27.1 ppm	23.2 ppm
Hg	0.509 ppm	0.464 ppm
Nb	9.81 ppm	9.63 ppm
Ni	3.64 ppm	3.34 ppm
Pb	16.6 ppm	15.3 ppm
S	16 300 ppm	12 100 ppm
Sc	13.5 ppm	13.1 ppm
Sr	148 ppm	143 ppm
V	136 ppm	130 ppm
W	1.91 ppm	1.79 ppm
Y	19.1 ppm	18.9 ppm
Zn	70.7 ppm	58.6 ppm
Zr	178 ppm	184 ppm
C-tot	0.202 %	0.442 %
Total organic carbon	<0.05 %	0.226 %

Figure 2-4. *Left: Assembly of the blocks and rings. In this picture is also seen the titanium tubing for the RH-sensor located close to the heater. Right: Bottom side of the top block in the thermal gradient test. This block has a milled hole for fitting the top of the heater.*

2.1.4 Instrumentation

In order to monitor the processes towards steady-state, the thermal gradient test was equipped with two relative humidity (RH) sensors, which also measured temperature. These sensors were automatically sampled using the computerized data collection system at the Clay Technology lab. Approximate sensor locations are indicated in Figure 2-1. The sensor values here reported relates directly to the fabrication calibration (i.e. no additional calibration was performed).

The test was also equipped with a pressure gauge in order to give an indication of overpressure in the vessel due to temperature elevation (see Figure 2-6).

2.2 Isothermal test

The second test has no heater and contains only bentonite pellets (apart from a stainless steel container). It was maintained at constant temperature (room temperature or at 50 °C). It is be referred to as the *isothermal test.* Also this test is equipped with in- and outlets for in-situ gas testing (similar to what is pictured in Figure 2-1). The specifications for the test is given in Table 2-4.

2.2.1 Container

The container is made of stainless steel in the same manner as for the thermal gradient test. Similarly it consists of a "barrel" and a lid, sealed with an o-ring. The lid have openings for in-situ oxygen measurements and gas sampling. The isothermal test was designed to contain approximately 20 L gas and 20 kg of solid bentonite mass. A photograph of the test under operation is shown in Figure 2-6.

2.2.2 Bentonite

The isothermal test is filled only with IBECO RWC bentonite pellets, of the same type as used in the thermal gradient test, pre-conditioned to a water-to-solid mass ratio of 0.23.

Table 2-4. Specifications of the components of the isothermal test.

Container height	34 cm
Container diameter	35 cm
Dry mass pellets	20 kg
Water ratio pellets	0.23
Average degree of saturation	0.18
Total gas volume	ca 20 L

2.2.3 Instrumentation

The isothermal test was not instrumented. The test is exposed to isothermal conditions, either room temperature, or placed in an oven at 50 °C. Figure 2-5 shows a photograph of the test placed in the oven.

Figure 2-5. The isothermal test placed in the oven.

2.3 Oxygen measurement

Oxygen levels were occasionally measured in-situ in the two tests by connecting an industrial gas analyser XGA 301 (Mitchell instruments) equipped with a Zirconia oxygen sensor, with measurement range 1 ppm – 30 %. In the measuring procedure, the sensor is connected via the connection tubing on the test containers and pumped for 30–180 s before reading off the oxygen level. This way of performing the measurements may introduce a small amount of fresh air into the systems at each measurement.

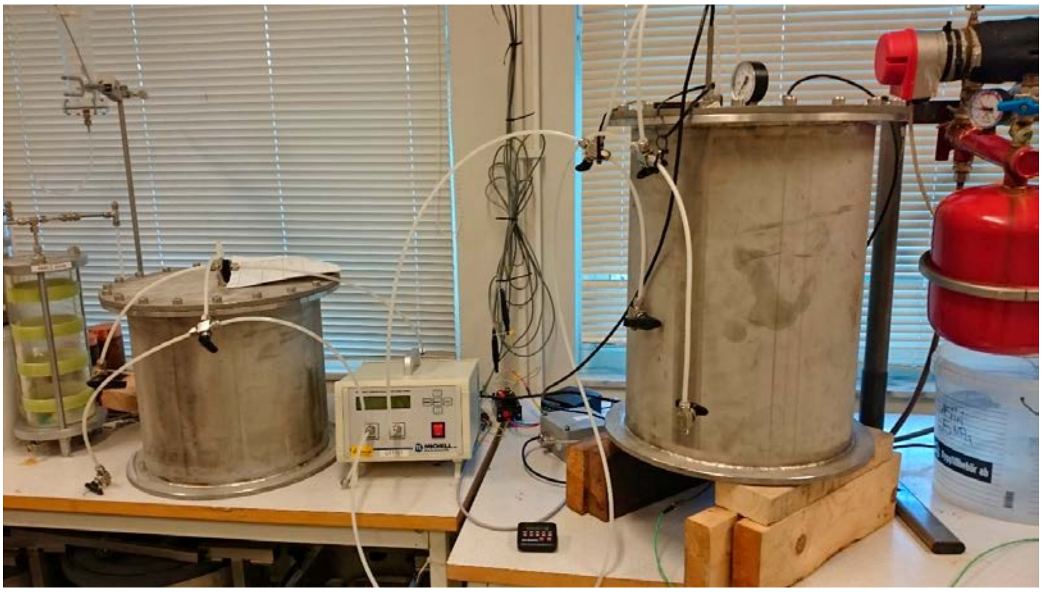

Figure 2-6. *The isothermal (left) and thermal gradient (right) tests under operation in the lab. In the middle of the picture is seen the oxygen analyser (at the time of the photograph, connected to the thermal gradient test). To the far right is also seen the water heating system.*

3 Results

The thermal gradient test was started May 8, 2017, and the heating system was switched on May 15. The isothermal test was initiated on May 18, 2017. The first 111 days, this test was placed in room temperature in the laboratory. At day 111, the test was placed in an oven at 50 °C, where it was kept until termination. Both tests were terminated on May 3, 2018, the temperature gradient test had then been running for 361 days (353 days with the heater on), and the isothermal test had been running for 350 days (239 days in 50 °C).

3.1 Temperature and RH-evolution in the thermal gradient test

Figure 3-1 shows the evolution of the measured RH and temperature in the thermal gradient test (approximate location of the sensors are indicated in Figure 2-1). It can be noted that although the temperature of the heater is 80 °C, the temperature in the bentonite block near the heater is only approximately 50 °C. There is apparently a huge drop in temperature over inner slot region. In the outer pellets slot, the temperature was about 40 °C throughout the test. Thus, at this position in the set-up, the temperature drops approximately 10 degrees over the bentonite (block and pellets). Note that these measurements only give a rough estimate of the temperature distribution in the full test – there is certainly heat transport also in the axial direction.

The RH close to the heater reached 100 % as the heater was switched on, only to drop to approximately 63 % as the system evolved. The RH in the pellets stayed approximately constant at 85 %–80 %. This evolution in relative humidity indicates that water has been transported away from the bentonite closest to the heater, while the water content in the pellets slot has basically remained constant. However, the measurements of water content at the termination of the tests confirmed that the bentonite had dried quite extensively in regions near the heater, while water had accumulated near the walls of the container, as further discussed in Section 3.5.

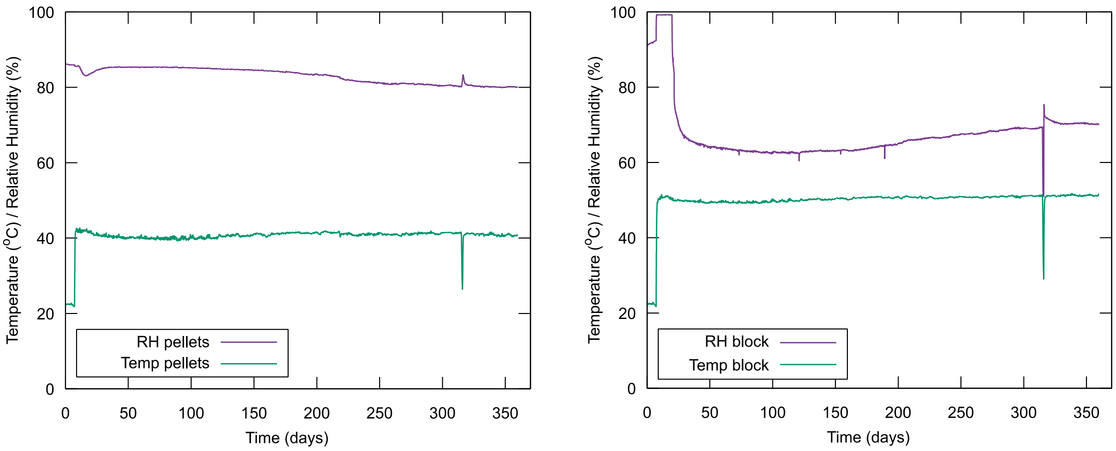

Figure 3-1. *Evolution of temperature and relative humidity in the thermal gradient test. Approximate positions of the sensors are indicated in Figure 2-1. The spikes seen in all the curves at day 315 are due to an unintentional shut-off of the heating system for a few hours in connection with gas sampling.*

3.2 Oxygen consumption

3.2.1 Thermal gradient test

The evolution of the oxygen level in the thermal gradient test is shown in Figure 3-2. An immediate drop in oxygen is seen, and the rate of oxygen consumption is increased as the heating system was switched on (day 7). This oxygen consumption is reasonably ascribed to aerobic corrosion of the copper (Section 3.5). After approximately 60 days, the oxygen level reached a near steady value of approximately 1 %. After about 150 days, a very slow increase of the oxygen level was noted. During the end of the test, gas was sampled and analysed externally (Section 3.4). In connection with this sampling, the in-situ measurement showed an increased oxygen level. This is probably due to a certain leakage of the tests, as further discussed in sections 3.4 and 4.

3.2.2 Isothermal test

The evolution of the oxygen level in the isothermal test is displayed in Figure 3-3. The first 111 days, the test was placed in room temperature in the laboratory and no significant oxygen consumption was recorded. At day 111, the test was placed in an oven at 50 °C in order to observe possible changes in oxygen content as found in the thermal gradient test. A slight continuous drop in oxygen levels was observed as a consequence. After an additional 150 days, this drop in oxygen level reached a steady value. During the end of the test, gas was sampled and analysed externally (see Section 3.4).

3.3 Total pressure

The total pressure gauge gave a small response during the course of the thermal gradient test, indicating a certain overpressure (i.e. above atmospheric pressure). This was, however, most probably an artefact caused by bentonite swelling; at the termination of the test it was revealed that the top part was considerably wet (Section 3.5), and the pressure gauge was therefore probably isolated from the rest of the gas volume of the test. Therefore, no further consideration of the recorded total pressure is made.

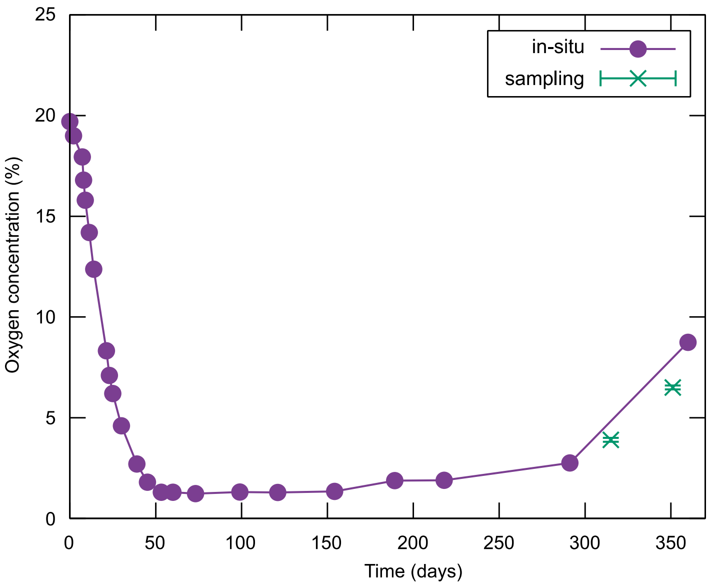

Figure 3-2. *Oxygen evolution in the thermal gradient test. The heater was switched on after 7 days. Sampling was performed at day 315 and day 351 (see Section 3.4).*

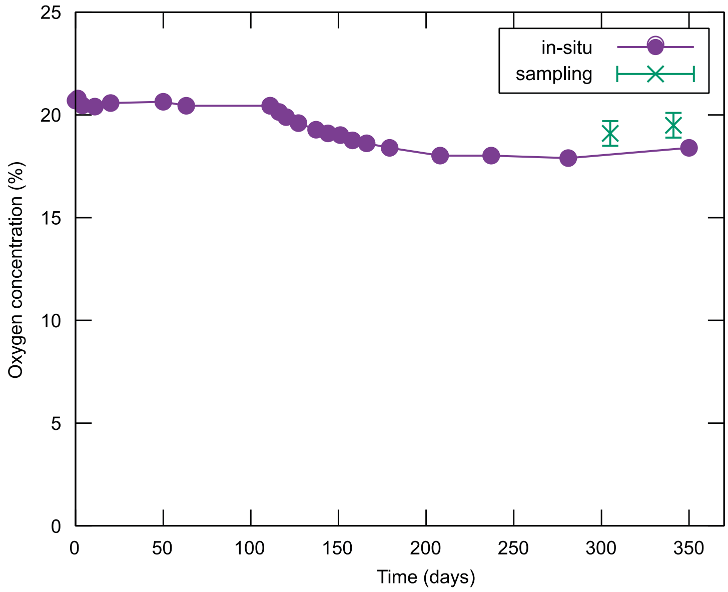

Figure 3-3. Oxygen evolution in the isothermal test. From day 0 to day 111, the test was kept at room temperature (21 °C–22 °C). From day 111 the test was put in an oven at 50 °C. Sampling was performed on day 305 and day 341 (Section 3.4).

3.4 Gas sampling

Gas was sampled for external analysis with the following procedure. One of the tubes used for the in-situ oxygen measurements (see e.g. Figure 2-6) was connected to a vacuum pump, which in turn was connected to the sample bag, as shown in Figure 3-4. In order to minimize contamination from atmospheric oxygen, all external tubing was flushed with nitrogen before conducting the sampling.

Two samples were taken from each of the tests within an approximately 5 weeks interval (i.e. 4 samples in total). The samples were analysed (by an accredited external laboratory) using gas chromatography, as well as an optical feedback cavity enhanced absorption spectrometer (for sulphide). The main result from the analysis is presented in Table 3-1.

The analysed oxygen levels broadly confirmed the on-line measurements (Section 3.2); in the temperature gradient test the oxygen levels was considerably lower as compared to the isothermal test. The analysed oxygen levels in the temperature gradient test was however somewhat higher as compared to the in-situ measurements. Furthermore, the oxygen level – at least in the temperature gradient test – was larger in the second sample as compared to the first. This indicates a certain leakage of the test set-up. As the sampling procedure causes a certain pressure drop in the test, a certain inflow of air from the outside is induced. Part of the oxygen thus introduced was still detectable at the second sampling. This interpretation is also supported by the final in-situ oxygen measurement, which was performed just before termination and only a few days after the second sampling (Section 3.2). Also in case of the isothermal test was a slightly larger oxygen level measured during the second test (it is, however, within error margins). It is however reasonable to assume that this set-up had less leakage problems.

Table 3-1. Gas composition of the analysed samples. Unit is vol-% except for H_2S.

Sample	TGT01	TGT02	IT01	IT02
O_2	3.9	5.9	19.1	19.5
N_2	94.6	91.0	79.7	77.8
H_2	0.1	0.1	0.1	0.1
CO_2	1.5	1.3	1.2	0.9
CO	< 0.1	< 0.1	< 0.1	< 0.1
CH_4	< 0.1	< 0.1	< 0.1	< 0.1
H_2S	< 0.1 ppm	< 0.1 ppm	< 0.1 ppm	< 0.1 ppm

Figure 3-4. *Gas sampling of the temperature gradient test. A vacuum pump was connected to one of the outlets of the tests and to the sample bag.*

In all tests, a substantial amount of CO_2 was detected, in the range 0.9–1.5 %, which may be compared to the content in air of 0.04 %. A small – but detectable – amount of H_2. The samples taken at the first sampling (TGT01 and IT01) were additionally analysed for light hydrocarbons, of which none were detected (detection limit 5 ppm). No sulphide was detected in any of the samples.

3.5 Termination

In the temperature gradient test, after a short period (hours) of cooling after shutting of the heater, the bentonite was removed from the top down. Figure 3-5 shows the bentonite directly after the top lid had been removed. The darker colour of the bentonite reveals that the bentonite is rather moist. Evidently, water had accumulated in the top of test. In particular it can be noted that the pellets filling had swelled and homogenized quite extensively.

As the bentonite was removed from the container, samples were taken for water content determination at various places within the set-up. In general the bentonite blocks and rings were well preserved, i.e. there were no visible cracks; the cracks seen in the photographs were caused during the termination in order to be able to remove the blocks, and in order to take samples for water determination. Figure 3-6 shows the test when bentonite had been removed down to the mid-ring of the set-up. It may be noted that system was here considerably drier as compared to the top part (Figure 3-5) – the pellets at this level were not as much homogenized as in the top.

The recorded water-to-solid mass ratios and the approximate positions where sampling was made is shown in Figure 3-7. The measured water distribution confirms that the system dried significantly next to the heater during the course of the tests, while water accumulated in the pellets slot, particular in the upper part. Note that the initial water-to-solid mass ratio for blocks and rings was 0.28 and 0.24 respectively, and the initial water-to-solid mass ratio was 0.23 for the pellets. It should be noted that some of the bentonite samples taken for analysis of water content were quite heterogeneous (with respect to water content). The values here reported thus represent mean values of the particular samples taken, and the water distribution presented in Figure 3-7 only broadly represent the water distribution in the test (this is particularly significant for the pellets, which were very moist at the interface to the sample container, while they could be fairly dry at the interface to the blocks, see e.g. Figure 3-6).

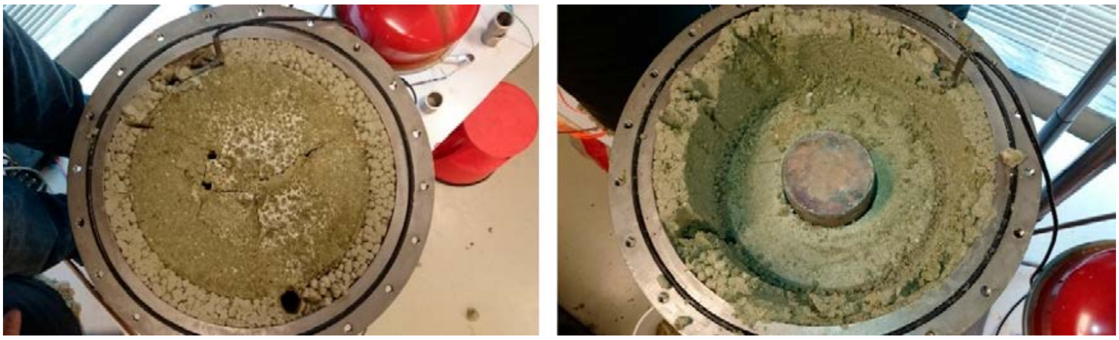

Figure 3-5. *Left: Temperature gradient test after removing the lid at termination. In the top is seen the cable and tubing for one of the RH-sensors, in the middle is seen the two holes where tubes where inserted for gas sampling in the slot region between heater and bentonite. At the bottom is seen a hole where the other RH sensor were located (it was pulled out during opening). Right: After removing the top block. The top of the copper heater is exposed, the homogenization of the top of the pellets slot is clearly seen.*

Figure 3-6. *Sampling at the level of the mid-ring. The pellets slot was considerably dryer and less homogenized at this level in comparison with the top part. In the top right of the photograph is seen the RH-sensor which was located in this particular bentonite block during operation.*

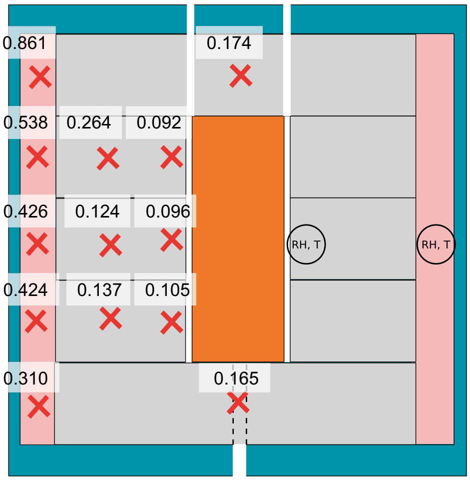

Figure 3-7. *Values of measured water-to-solid mass ratios at different positions in the temperature gradient test at termination. Red crosses indicate approximate positions of where samples were taken.*

Comparing with the measured RH-evolution (Section 3.1) it may be noted that the RH measured in the pellets slot at the end of the test (approximately 80 %) does not correspond to the measured water-to-solid mass ratio; such a value of the water-to-solid mass ratio (0.426) is expected to give an RH-value close to 100 % (Dueck 2004). This is, however, probably not a sign of malfunction of the RH-sensor, but rather reflects the very uneven water distribution within the pellets slot in this position in the test. Note, for instance, that the measured water-to-solid mass ratio in the adjacent block is 0.124, which corresponds to an RH considerably lower than 80 %.

After terminating the isothermal test, two determinations of the water-to-solid mass ratio of the pellets was made, both giving the value of 0.239, in good agreement with the design value.

Figure 3-8 shows the copper heater of the thermal gradient test after termination. Localized black corrosion spots are clearly seen. These are most probably copper(II)oxide, and thus explains the oxygen consumption in this test.

On the top side of the heater was also noted a red spot, which definitely had appeared during the course of the test (compare Figure 2-4 and Figure 3-5). This is most probably copper (I) oxide. A picture of the top of the heater after termination is shown in Figure 3-9.

0° 90° 180° 270°

Figure 3-8. *Overview of the copper heater in the thermal gradient test after termination. Black corrosion spots (CuO) are clearly seen. The gray/white stains are bentonite.*

Figure 3-9. *Top of the heater in the thermal gradient test after termination. A black corrosion product (CuO) is seen in the upper part, a red corrosion product (Cu_2O) is visible in the lower part.*

4 Discussion

A main result of the present study is that no sulphide gas was detected. In the case of the thermal gradient test, this may have been expected, since the copper heater would function as a sink for sulphide even if it was produced. That no sulphide gas was detected also in the isothermal test is, however, a good indication that significant amounts of such gases are not to be expected under semi-dry repository conditions. It should be noted that the bentonite used in this study was chosen due to its significant sulfur content (pyrite). But even with this condition, no sulphide gas could be detected (detection limit < 0.1 ppm).

Another main result is the observed oxygen consumption in the temperature gradient test. It is clear that the main reason for this consumption is due to corrosion processes on the copper heater, since a similar behaviour is missing in the isothermal test, which did not include a copper component. Further confirmation of this conclusion is given by direct observation of formed copper oxides on the heater after terminating the test.

The time scale for consuming the oxygen in the temperature gradient test was approximately 50–60 days. Furthermore, it was clearly demonstrated that the consumption rate increased with increasing temperature; during the first seven days of the test, the heater was not turned on and the oxygen level decreased considerably slower.

The LOT field test at Äspö hard rock laboratory (Karnland et al. 2009) consists of bentonite/copper heater parcels of very similar dimensions as the present set-up (except for being considerably longer in the axial direction). The present results thus strongly confirm the assumptions which has been made regarding the fate of the initially present oxygen in the LOT test, namely that the oxygen is consumed rather quickly due to aerobic copper corrosion, with a rate that is highest in the hottest regions. It is also interesting to note that the time scale for the oxygen depletion in the present test is rather similar to that recorded in the Field-scale emplacement test (FE) in the Mont Terri rock laboratory (Müller et al. 2017).

Looking at the oxygen consumption in the isothermal test, it is seen that there is a process which seems to be activated when the temperature is raised to 50 °C. Since the isothermal test did not contain copper, this behaviour must be ascribed to some other process. A suggestion is oxidation of pyrite. In a moist environment, pyrite present in the bentonite is expected to oxidize and form sulfuric acid as (Dos Santos et al. 2016)

FeS_2 (pyrite) + $7/2\ O_2 + H_2O \rightarrow Fe^{2+} + 2\ SO_4^{2-} + 2\ H^+$

This acidification will in turn promote the release of CO_2 due to carbonate dissolution (the bentonite contains e.g. calcite)

$CO_3^{2-} + 2\ H^+ \rightarrow CO_2 + H_2O$

Thus, pyrite oxidation does not only explain the oxygen consumption recorded in the isothermal test, but also gives a reasonable explanation for the observed elevated CO_2 concentrations. A pyrite oxidation process is expected also in the thermal gradient test, which also show an elevated CO_2 concentration.

There are reasons to believe that the temperature gradient test suffered from some problems with leakage. This is primarily concluded from the in-situ oxygen measurements before and after taking the gas samples (Figure 3-2). A plausible explanation is that the sampling procedure caused an under pressure in the container, which, in turn, induced an inflow of air (oxygen) as a consequence of leakage. On the other hand, during the main course of the test, no significant pressure drops are expected to occur, and any inflow of oxygen is reasonably diffusion controlled, leading to the steady-state level of oxygen of 1–2 % as detected by the in-situ measurements. It may consequently be so that the amount of aerobic corrosion occurring in the temperature gradient test is more extensive than what is suggested by the initial amount of oxygen. A mass balance check of the amount of copper oxides on the heater could possible give more information on the extent of leakage. Judging from the redistribution of water during the course of the test, it may be speculated that the leaking occurred in the bottom of the test, where the bentonite was relatively dry. In contrast, in the top of the test, the bentonite became basically water saturated (Figure 3-5), and thus functioned as a seal in itself. An enhanced leakage in the bottom due to drying may also explain the weak increase of the oxygen level observed during the second half of test.

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