

Report

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Gas phase composition during the unsaturated period

Initial tests

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Abstract

The bentonite buffer in a considerable fraction of the deposition holes of a KBS-3 repository at the Forsmark site in Sweden is expected to remain water unsaturated for a long time period. It is therefore important to have information about the evolution of the chemical composition of the gases in the unsaturated bentonite, especially regarding oxygen and hydrogen sulphide.

This evolution can be investigated in laboratory scale tests by heating bentonite in isolated containers and by analysing the gas composition at regular intervals. Equipment has been developed at SKB in which the bentonite is heated by a centrally placed heater, made of either copper or stainless steel. Moreover, a gas analysis system has been designed to measure the concentration of oxygen (O₂), carbon dioxide (CO₂), hydrogen (H₂), hydrogen sulphide (H₂S) and sulphur dioxide (SO₂).

This report presents results from initial tests in which heating was performed for up to three months. The results indicate that the rate of oxygen consumption was approximately the same in the two tests, regardless if the heater was made of copper or of stainless steel. This suggests that the oxygen consumption was caused by processes in the bentonite rather than by oxidation of the metal.

Sammanfattning

Bentonitbufferten i en stor andel av deponeringshålen i ett KBS-3 förvar i Forsmark förväntas förbli vattenomättad under en lång tidsperiod. Det är därför viktigt att ha information om utvecklingen av den kemiska sammansättningen hos gasen i den omättade bentoniten, i synnerhet beträffande syrgas och vätesulfid.

Denna utveckling kan undersökas i laboratorieskaleförsök genom att värma bentonit i isolerade behållare och genom att analysera gassammansättningen med jämna mellanrum. Vid SKB har en testutrustning utvecklats där bentonit värms upp av en centralt placerad värmare, som består av antingen koppar eller rostfritt stål. Utöver detta har ett gasanalyssystem designats för att mäta koncentrationen av syrgas (O_2), koldioxid (CO_2), vätgas (H_2), vätesulfid (H_2S) och svaveldioxid (SO_2).

Den här rapporten presenterar resultat från inledande tester med uppvärmning under upp till tre månader. Resultaten indikerar att syreförbrukningshastigheten var ungefär den samma i de två testerna, oavsett om värmaren bestod av koppar eller av rostfritt stål. Detta antyder att syreförbrukningen orsakades av processer i bentoniten snarare än av metalloxidation.

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1 Introduction

In the rock at Forsmark, the saturation time for the buffer around the canister is expected to vary between a few tens of years to several thousand years depending on the position of the deposition hole in the rock. In most positions, the saturation time is expected to be more than 1 000 years. This means that the canister surface may be exposed to an unsaturated state for a relatively long time. A possible issue with respect to canister corrosion is the chemical composition of the gas in the unsaturated bentonite. The oxygen content (O_2) and the hydrogen sulphide (H_2S) are of particular significance.

Questions of interest include (SKB 2019):

- Will oxygen be consumed by the repository components during unsaturated conditions? If yes, at what rate?
- Will hydrogen sulphide be generated from minerals in the buffer?
- Can hydrogen sulphide be generated microbially in an unsaturated buffer?
- Can other gases form?

These questions are of particular interest for the Spent Fuel Repository since the gas composition will primarily affect the copper canister. It is not impossible, however, that the composition of the gas phase during the unsaturated period may also be of interest for BHA (i.e. the vault for legacy waste) in the repository for long-lived waste (SFL).

These processes have previously been investigated in laboratory tests performed by Birgersson and Goudarzi (2018), and the importance of the issue has motivated further studies at SKB. This report describes the experiences and findings from the initial tests which were performed during the winter of 2018/2019. The objective of these tests was primarily to try out the gas analysis system and the test procedure.

A description of the test equipment, the bentonite material and the gas analysis system is presented in Chapter 2. The initial tests and the measured evolution of different gas compositions are presented in Chapter 3. The test results are discussed in Chapter 4, especially regarding the consumption of oxygen and the generation of hydrogen gas. Finally, a number of modifications on the test equipment which are planned to be used in the next phase of this program is outlined in Chapter 5.

2 Materials and methods

2.1 Test equipment

The test equipment consisted of a heater surrounded by bentonite, which in turn was installed in a container made of stainless steel (SS2348 / EN1.4404 / ASTM 316L). Two sets of equipment have been used; one with a heater made of stainless steel, and one with a heater made of copper (purity 99.5 %). Each container consisted of a cylindrical tube with an inner diameter of 400 mm, a height of 500 mm and a thickness of 4 mm, and with a bottom plate and a top sheet, both with a thickness of 6 mm (Figure 2-1 and Figure 2-2). Each heater had an outer diameter of 80 mm and a height of 280 mm. The heating was achieved by circulating oil heated in a cylindrical vessel with an electrical heating coil, in turn controlled with a temperature sensor in the vessel and a PID regulator. The lateral surface of the heaters can be covered with a copper sheet, which means that these sheets can be easily dismantled and analysed separately. For the initial tests described here, only the copper heater and not the one made of stainless steel was covered with a copper sheet. The heaters/sheet was washed with ethanol prior to the test. Sensors for measurement of temperature (PT1000) and relative humidity (Vaisala sensors), were installed at four and three vertical positions, respectively, at the lateral surface of each container. The data from these sensors were however not retrieved due to inadequate data storage. Finally, each container was equipped with tubes for gas sampling with both inlet and outlet positioned close to the heater (in the inner slot, see below), approximately 200 mm above the bottom.

2.2 Bentonite

In order to investigate the methodology and the equipment the initial tests were performed with spare blocks from the ABM project, mostly with IBECO Seal (with water content 14.7 % and dry density 1 844 kg/m³, see Sandén et al. 2018) and from the Concrete and Clay project, mostly with MX-80 (with water content 19.2 % and dry density 1 360 kg/m³, see Mårtensson 2015) and extruded pellets made from Milos bentonite. The installation of these materials is shown in Figure 2-3 to Figure 2-5. Geometrical specifications of container, heater and bentonite are given in Table 2-1.

Sulphur in bentonite is usually found in the form of gypsum or pyrite (Karlund et al. 2006). The total sulphur content of the bentonites used for the blocks (IBECO Seal and MX-80) was quantified to 0.24 % in the ABM-project (Svensson et al. 2011). This is significantly lower than the sulphur content of a Milos bentonite, e.g. Deponit CA-N which has been quantified to 0.7 % (Svensson et al. 2011) and larger than 1 % (Birgersson and Goudarzi 2018).

Table 2-1. Specifications of the components used in the tests.

	Stainless steel	Copper
Container height (m)	0.5	0.5
Container diameter (m)	0.4	0.4
Heater height (m)	0.28	0.28
Heater diameter (m)	0.08	0.08
Block diameter (m)	0.277	0.277
Ring diameter (m)	0.277/0.11	0.277/0.11
Water content rings (%)	15 ^a	19 ^b
Water content blocks (%)	15 ^a	19 ^b
Water content pellets (%)	17 ^c	17 ^c
Dry density block (kg/m ³)	1840 ^a	1580 ^b
Dry density rings (kg/m ³)	1840 ^a	1580 ^b
Dry density pellets (kg/m ³)	1000 ^c	1000 ^c
Dry mass block/rings (kg)	50	43
Dry mass pellets (kg)	33	33
Average degree of saturation (%)	41	40
Total gas volume (L)	19	20

a) IBECO Seal M-90 – old batch (SKB P-18-20).

b) Wyoming MX-80 (SKB P-15-01).

c) Assumptions.

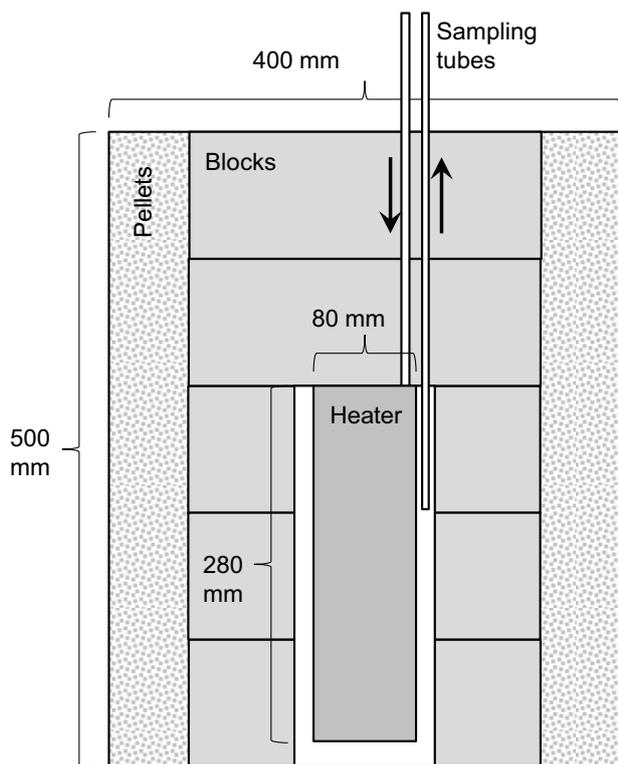


Figure 2-1. Schematic section drawing of container with heater and gas sampling tubes. A copper sheet was wrapped around the heater in the Cu-heater case.



Figure 2-2. Two stainless steel containers equipped with sensors for temperature and relative humidity (RH) and connections for online analysis of gas composition.

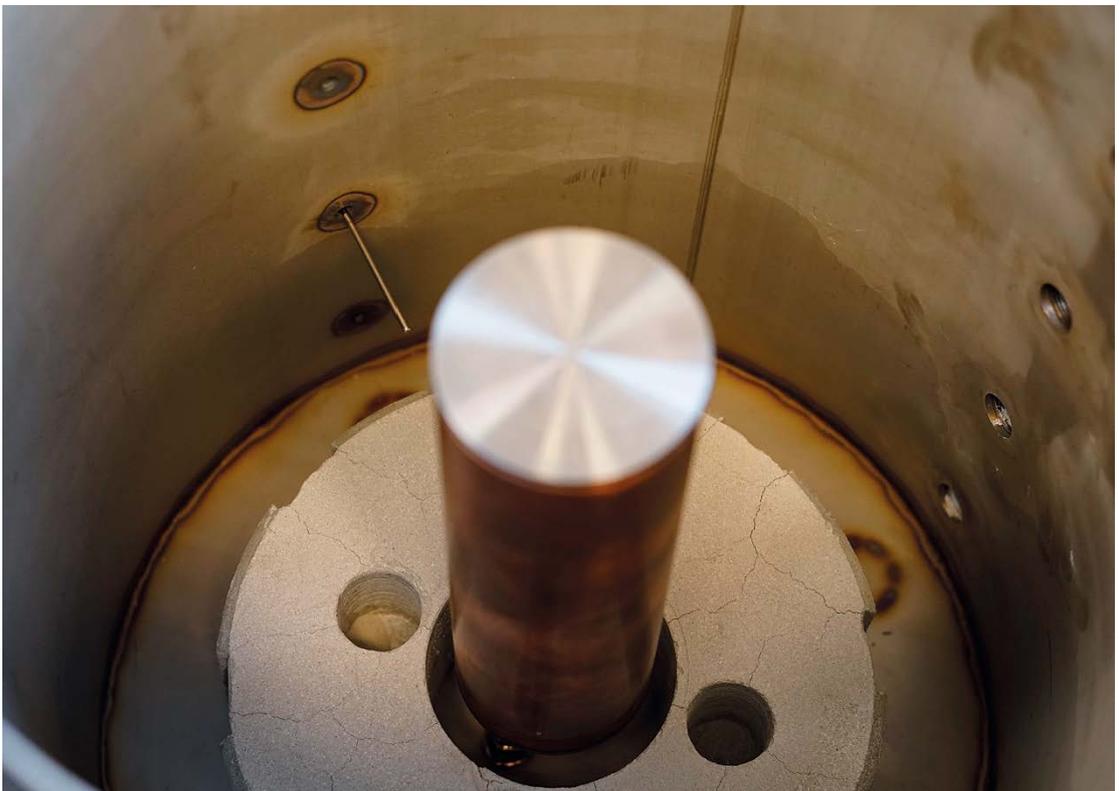


Figure 2-3. The copper heater with one surrounding bentonite block.

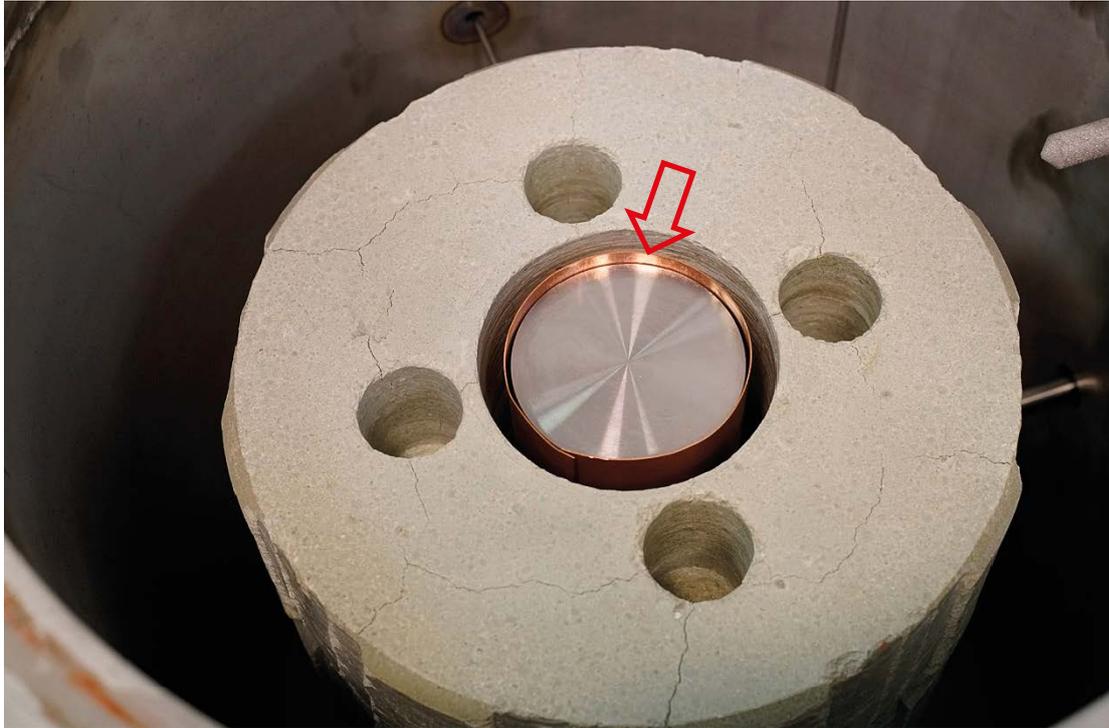


Figure 2-4. Copper heater with covering copper sheet (marked with arrow) and bentonite blocks. RH sensors in top right corner and temperature sensor at the top of the picture.



Figure 2-5. Test container filled with bentonite blocks and surrounding pellets.

2.3 Gas analyses

The gas analysis system was supplied by OmniProcess AB and was designed to measure the concentration of the following gases: oxygen (O₂), carbon dioxide (CO₂), hydrogen (H₂), hydrogen sulphide (H₂S) and sulphur dioxide (SO₂). A compilation of manufacturers, names, methods, measuring intervals, detection limits and required flow rates is shown in Table 2-2. The system was designed with different pumps and valves with which the flow rate through the different instrument could be set. A flow scheme for the different gas analysers is shown in Figure 2-6. The total flow rate through the system was 2.7 l/min. The carbon dioxide sensor was not equipped with any display and could therefore not be used in these tests.

The gas analysis system was initially filled with air. The volume of this system can be estimated to approximately 0.02 litres, which corresponds to 0.1 % of the gas volume in one of the tests containers. The successive mixing of gas in the two containers is therefore marginal as long as the total number of sampling events is limited.

Table 2-2. Compilation of instruments and their characteristics.

Gas	Manufacturer	Instrument	Method	Measuring interval	Detection limit	Flow rate (l/min)
O ₂	Servomex	Multiexact 4100	Paramagnetic cell	0 – 25 %	0.01 %	0.1
CO ₂	Vaisala	GMP343	NDIR infrared cell	0 – 1000 ppm	3 ppm	0.1
H ₂	Compur	Statox 501	Electrochemical cell	0 – 150 ppm	10 ppm	0.1
H ₂ S	Servomex	SERVOTOUGH Laserexact	Laser	0 – 10 ppm	1 ppb	2
SO ₂	ThermoFisher SCIENTIFIC	iQ Series 43	Pulsated UV fluorescence	0 – 1 ppm	1 ppb	0.5

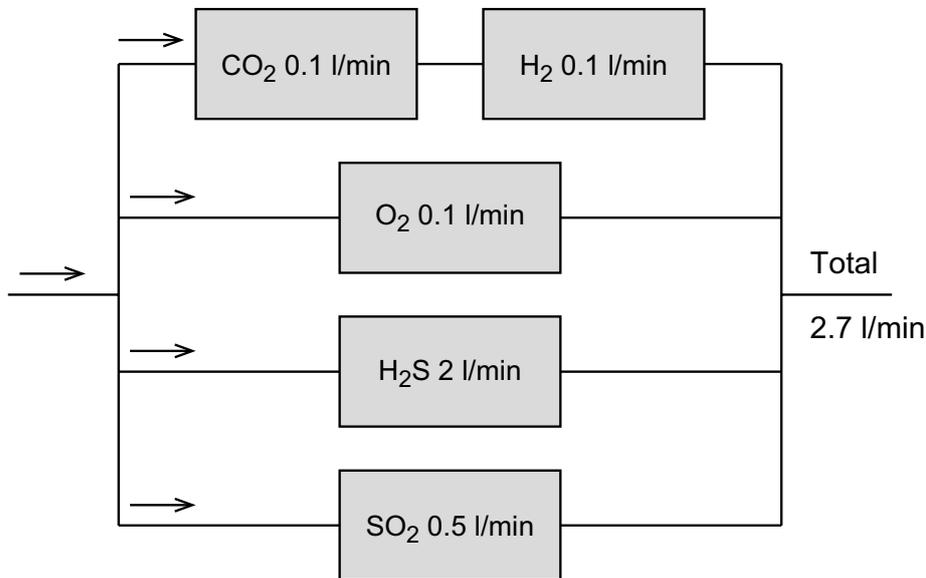


Figure 2-6. Flow scheme for different gas analysers.

3 Results

3.1 Evolution of gases

The composition of gases in the copper heater test case was monitored during approximately 3 months (from 2018-11-21 to 2019-02-25). The corresponding period for the test case with stainless steel was approximately three weeks shorter (2018-12-12 to 2019-02-25). The temperature of the copper heater was set to 58 °C during the first 16 days after which the temperature was increased to and maintained at 80 °C. This higher temperature level was previously used in the thermal gradient tests reported by Birgersson and Goudarzi (2018), and also for the test case with the stainless-steel heater in this study.

The evolution of oxygen concentration is shown in Figure 3-1. It can be noted that the decrease in the O₂ concentration occurred at a lower rate during the initial period with 58 °C in the test with the copper heater. A steady reduction in the concentration was found for both test cases after this, with a rate in the order of 2 % per month. These trends were interrupted in the beginning of February 2019 and this coincided with the flushing of the measuring system with nitrogen gas. The latter was motivated by the accumulation of water in the gas analysis system, which was caused by condensation of vapour from the bentonite. Moreover, a minimum flow rate is required for the used O₂-sensor which is based on a paramagnetic cell. The increasing O₂-trends may therefore be caused by a reduced flow rate through this O₂-sensor.

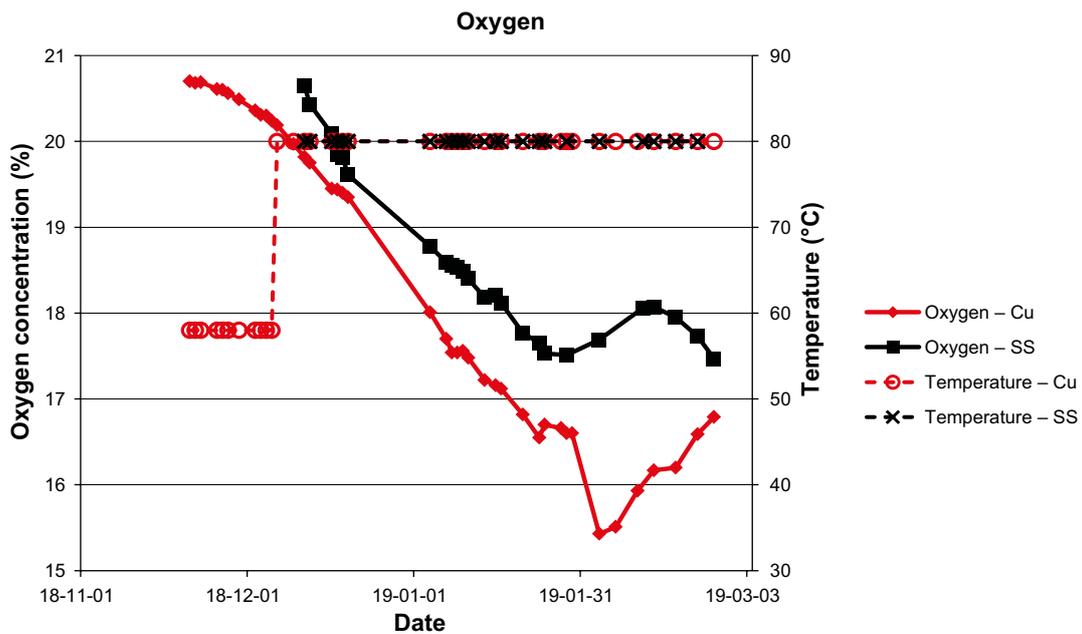


Figure 3-1. Evolution of oxygen concentration and temperature.

The evolution of hydrogen gas concentration is shown in Figure 3-2. A rapid increase in the concentration up to a level of 37 ppm was found for the copper heater test case during the first three weeks. A slightly lower rate was found during the initial period with 58 °C. The hydrogen concentration exceeded the measuring interval (0 – 150 ppm) after this. In contrast, no detectable hydrogen concentrations were found for the test case with stainless steel.

The registered concentrations of hydrogen sulphide in both test cases were found to be lower than 0.4 ppm and displayed quite irregular trends, see Figure 3-3. The corresponding concentrations of sulphur dioxide in both test cases were found in the interval 0.047 to 0.055 ppm, see Figure 3-4. It is difficult to interpret these results and to assess whether they represent actual concentrations or if they reflect the precision and the lower limit of measurement for the sensors.

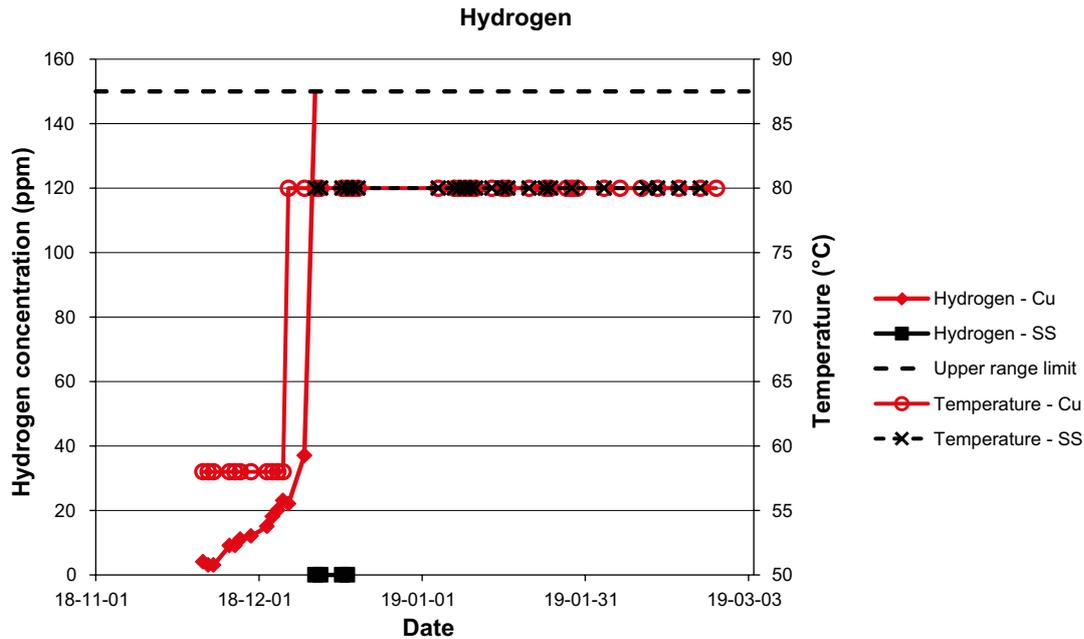


Figure 3-2. Evolution of hydrogen concentration and temperature. The dashed horizontal line is the upper limit of hydrogen concentration that can be measured.

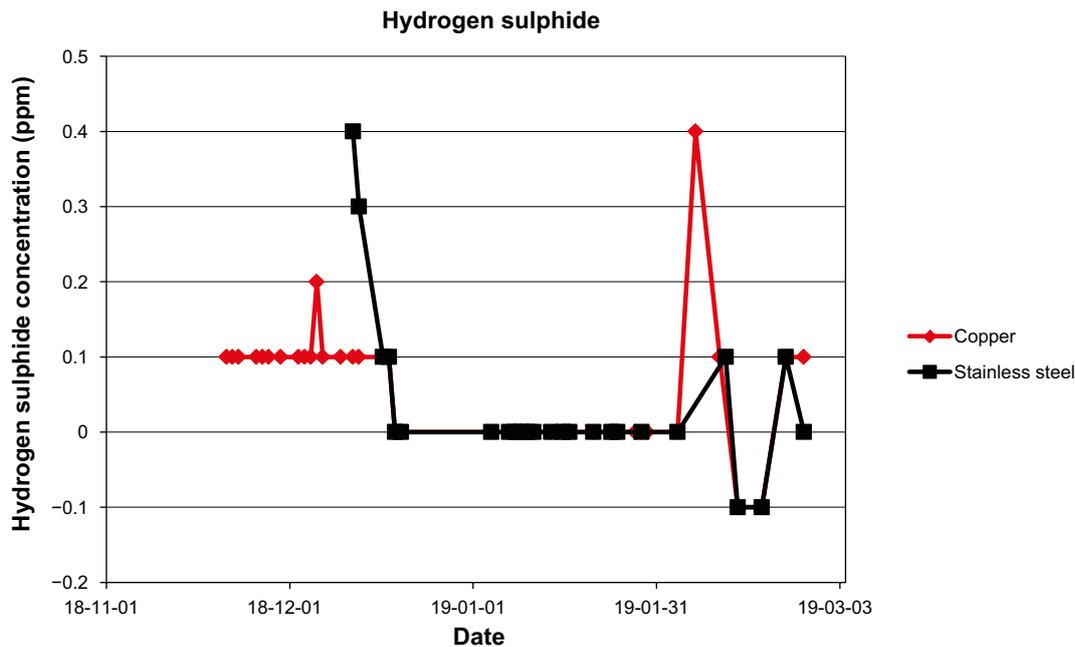


Figure 3-3. Evolution of hydrogen sulphide concentration. Negative values reflect the precision and the lower limit of measurement.

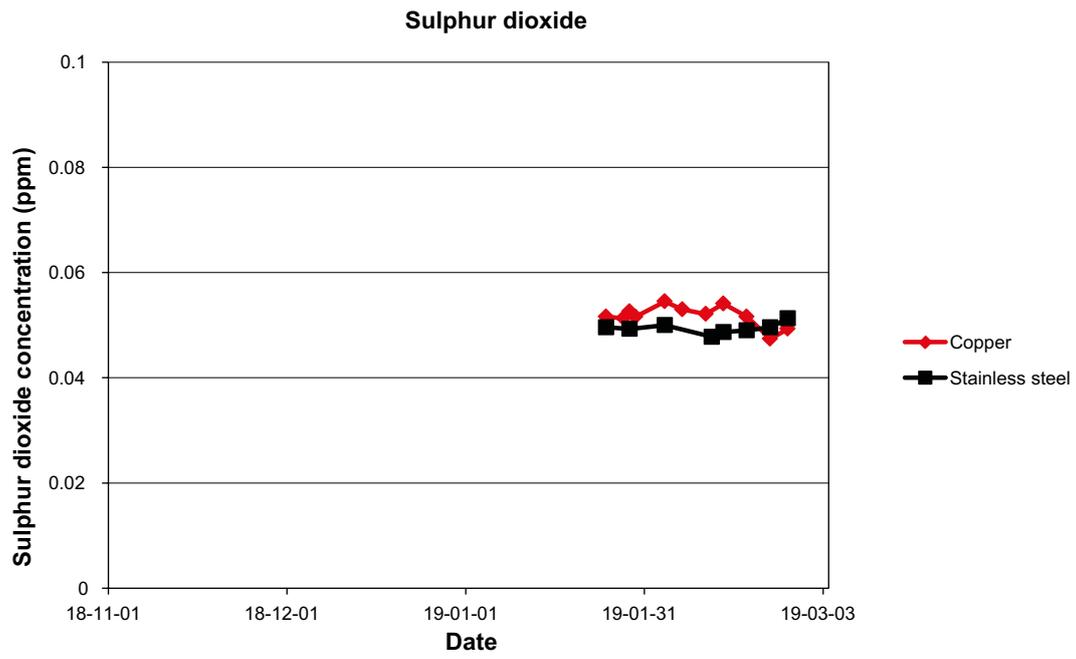


Figure 3-4. Evolution of sulphur dioxide concentration.

4 Discussion

The presented tests were mainly performed with the objective to try out the gas analysis system and the test procedure. In general, the test duration was too short to draw any conclusions from the results. The main reason for terminating the test was the risks associated with the heating system with circulating heated oil. In addition, the occurrence of condensation of hot vapour from the test containers was found to be detrimental for the gas analysis system. Some overall observations can nevertheless be made from the recorded evolution of the gas composition.

The test results indicated that the rate of oxygen consumption was approximately the same in the two tests, regardless if the heater was made of copper or of stainless steel. These observations therefore suggest that the *oxygen consumption was caused by processes in the bentonite* rather than by oxidation of the metal, because it seems unlikely that the stainless steel would be oxidized with the same rate as the copper. In contrast, the hydrogen production was much more pronounced in the case with the copper heater than in the case with the stainless-steel heater. This result therefore suggests that the *hydrogen gas originates from the copper material* rather than being produced by some process in the bentonite.

If the *oxygen consumption* is caused by processes in the bentonite (e.g. through oxidation of pyrite) then it can be expected that the reaction rate will increase with an increasing content of pyrite or with an increasing ratio between the area and the volume of the gas-filled pores (Figure 4-1a). The consumption rate in these tests was found to be approximately 2 vol% per month. The corresponding consumption rate observed in the heater test presented by Birgersson and Goudarzi (2018) was approximately one order of magnitude higher. This difference may be explained with the higher pyrite content, a lower proportion of pellets, and possibly a higher water content, in the earlier test.

The alternative explanation that oxygen was consumed by the heaters, and that the rate of consumption would be transport limited and thereby giving rise to seemingly equal rates for the two metals, seems to be unlikely, since the time-scale of the experiment is much longer than the characteristic time to equilibrate the gas phase in the inner slot with the gas phase in the bentonite. The latter can be estimated as $L^2/D \approx 3$ hours, where L is a characteristic diffusion length in the bentonite (≈ 0.1 m) and D is the diffusivity of O_2 in the material ($\approx 10^{-6}$ m²/s which is a factor 20 lower than the diffusivity of O_2 in air). The thermal gradient test presented by Birgersson and Goudarzi (2018) display a much higher rate of oxygen consumption than in the current tests, and this does therefore not support to notion of a transport limited consumption rate.

The isothermal test presented by Birgersson and Goudarzi (2018) was performed at a temperature (50 °C) which was significantly lower than the heater temperature in the current tests. It is therefore not surprising that the rate of oxygen consumption was relatively low in the isothermal test, but it is difficult to explain why the oxygen concentration levelled off. It may be speculated that the water content is a limiting factor for the pyrite oxidation. This could then imply that the oxygen consumption would be more extensive in the tests with thermal gradients in which higher water contents occur in the cooler parts.

The amount of oxygen gas consumed in the experiment corresponds to a theoretical copper corrosion depth if all lost oxygen is assumed to have formed cuprous oxide (Cu_2O). With the data for the test in question such a depth would amount to approximately 20 μm . The copper oxide layer should be thicker than this and clearly observable, and the copper sheet did display some colour shift after the test. However, the thickness of this layer was significantly thinner than the theoretical corrosion depth, and this therefore supports the notion that the metals were not the major oxygen sinks in the experiments.

If the *hydrogen gas* is generated by outgassing from the copper material, then it can be expected that the rate of hydrogen evolution will increase with an increasing ratio between metal area and the gas-filled pore volume. For hydrogen it is however difficult to compare the results in the current study with those presented by Birgersson and Goudarzi (2018), which were obtained through gas chromatography. The highest measured hydrogen concentration was > 150 ppm in the current test, whereas the corresponding value in the earlier test was 1 000 ppm. These levels were however registered at very different times during the tests: after 20–70 and 300–350 days, for the current and the earlier test, respectively.

Degassing of hydrogen from Cu-OFP has been modelled by Hedin (2020), based on experimental observations of degassing of 2 mm thick Cu-OFP pieces in water at 70 °C. Both the model and the experiments suggest degassing rates of at most 10^{-13} mol $H_2/(cm^2 \cdot s)$ at 70 °C. It takes several years for such samples to degas, so the thickness of the sample is insignificant if it exceeds ~ 1 mm in an experiment that lasts a few months. With data from the experiment reported here, with an initial phase of 16 days and a lateral heater surface of 700 cm^2 , one gets a gas amount of approximately 10^{-4} mol, assuming the same outgassing flux as above. If the copper sheet would display the same flux, then this would yield an amount that is three times higher. This is approximately one order of magnitude higher than the gas amount that follows from the measured concentration (20 ppm) and the gas-filled pore volume (20 litres) at 58 °C, which yields 1.5×10^{-5} mol. If the hydrogen content in the heater and the copper sheet is similar to the amount in the Cu-OFP pieces mentioned above, and if this is bound in a similar way in the metal, then it may be concluded that it is not unreasonable that the observed H_2 in the gas phase is due to outgassing from the copper.

Hydrogen gas may also be formed as a result of pyrite oxidation. Since pyrite is a highly reduced mineral it can be expected that this will define the redox potential in the adjacent water phase, and this will in turn lead to a specific H_2 -pressure at equilibrium. It is however, difficult to explain why there was no detectable hydrogen gas in the test case with stainless steel.

The test results did not show any significant concentrations of *hydrogen sulphide*, although temporary values up to 0.4 ppm were observed in both test cases (Figure 3-3). The total sulphur content in the used bentonite blocks was significantly lower than what is generally found in a Milos bentonite (see Section 2.2) and this can therefore explain the low concentrations of H_2S in these tests. Hydrogen sulphide could potentially be formed in two ways: through dissolution of pyrite (King 2013) or, microbially, through sulphate reduction. The latter will not generally occur as long as oxic and dry conditions are maintained. This process could therefore potentially be enhanced by evacuating and replacing the initial pore space air with nitrogen gas and by increasing the water content. Such a procedure could also include a minor content of hydrogen gas in order to ensure the presence of a reducing agent.

The procedure of extracting and injecting gas with specific flow rates and durations implies that a certain gas volume is circulated during each measurement (e.g. $2.7 \text{ l/min} \times 30 \text{ min} \approx 80 \text{ l}$). In relation to the total gas volume of the test equipment (estimated to be $\sim 20 \text{ l}$), this may *potentially* imply a turnover rate of ~ 4 per sampling event. However, the close vicinity between the inlet and the outlet means that the actual turnover rate probably was significantly lower. In general, it can be expected that any major gas concentration gradient will be equilibrated due to diffusion (Figure 4-1b). Moreover, the extent of the gas circulation caused by the sampling is expected to be related to the distance between inlet and outlet, and the gas permeability of the bentonite.

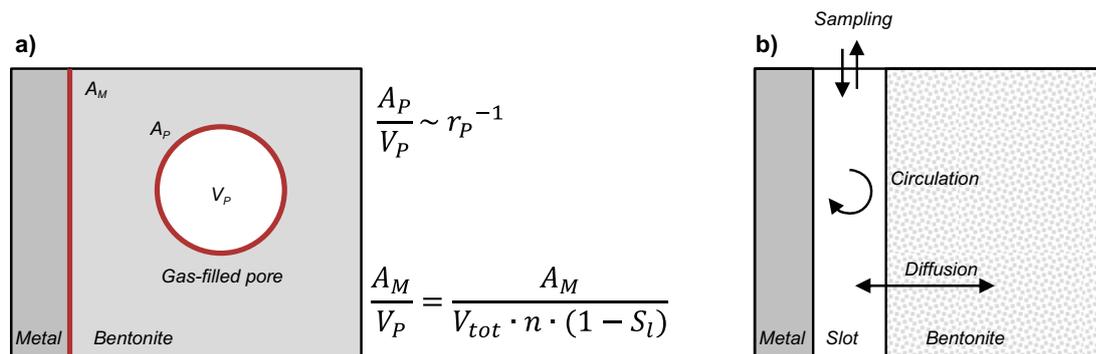


Figure 4-1. Schematic description of hypothetical governing area/volume ratios (a), and transport processes (b). Pore area: A_P ; pore volume: V_P ; pore radius: r_P ; metal area: A_M ; total volume: V_{tot} ; porosity: n ; liquid saturation: S_l .

5 Future work

The experiences and results from the initial tests have brought about a number of modifications on the test equipment which are planned to be used in the next phase of this program. One thing is to investigate the gas composition evolution in the absence of any metals and with isothermal conditions, and for this purpose a new test setup is planned in which the bentonite is placed inside a gastight glass container, equipped with tubes for gas sampling, which in turn is placed in a temperature chamber. This will provide a simpler and more well-defined test-condition which will enable more conclusive observations of the evolution of gases in the bentonite. Corresponding tests conditions with copper sheets in air, without bentonite, will also be provided. A second modification is the installation of condensation traps, which can prevent the hot vapour from entering the gas analysis system. A third modification is the expansion of the measuring ranges for some of the gas sensors, especially for the H₂-sensor which was found to be too narrow in the initial tests. Finally, the prospects of quantifying gases formed as a result of oxidation or dissolution of pyrite will be enhanced by using a bentonite with a higher content of sulphur.

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