A Counter-Current Heat-Exchange Reactor for the Thermal Stimulation of Gas Hydrate and Petroleum Reservoirs

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Abstract

At the GFZ German Research Centre for Geosciences we have developed a safe and efficient method which allows for the decomposition of gas hydrates by the supply of heat inside the reservoir. The heat is generated *in situ* by a catalytic combustion of methane in a counter-current heat-exchange reactor. The reactor that Rudy Rogers, Professor Emeritus in Chemical Engineering at Mississippi State University, referred to as the "Schicks Combustor" is placed in a borehole in such way that the hot reaction zone is situated in the area of the hydrate layer.

The counter-current heat-exchange reactor developed at GFZ generates heat via a flameless catalytic oxidation of methane at a noble metal catalyst. The system is closed i.e. there is no contact of the reactants, catalyst and environment. For safety reasons, methane and air are fed separately through a tube-in-tube arrangement into the mixing chamber. Due to its cooling effect and for safety reasons air instead of pure oxygen is used. From the mixing chamber the gas mixture arrives in defined quantities on the catalyst bed, where methane and oxygen are converted into carbon dioxide and water. The hot product gases release their heat via an aluminum foam to the outer wall of the reactor and then to the environment. Simultaneously, the incoming gases are preheated. The reaction runs stable and autonomous between 673 and 823 K.

The counter-current heat-exchange reactor was designed as a lab reactor and a borehole tool. The lab reactor was tested in a reservoir simulator to investigate the heat transfer into gas hydrate bearing sediments. Therefore methane hydrate was generated in the **LA**rge **R**eservoir **S**imulator (**LARS**), an autoclave with a volume of 425 L. In a test with 80% hydrate saturation, the reservoir simulator warmed up within 12 hours after the ignition of the catalyst to such an extent that the temperature of the complete sample was above the dissociation temperature of the previously formed methane hydrate which dissociated completely and methane could therefore be produced. During this test, only 15% of the produced CH_4 was consumed to generate the energy needed for the thermal dissociation of the hydrates. The experience with the laboratory reactor served as basis for the design of a borehole tool which is suitable for the application in natural gas hydrate reservoirs. The borehole tool has a total length of 5120 mm, an outer diameter of 90 mm and weighs

ca. 100 kg. First results from field tests at the continental deep drilling site KTB in Windischeschenbach, Germany, confirm that the borehole tool reliably produces heat at depth.

Introduction

Clathrate hydrates of natural gases are crystalline solids composed of water and gas molecules. The water molecules form a three-dimensional hydrogen-bonded network with well-defined cavities which are stabilized due to the inclusion of guest molecules (von Stackelberg et al., 1947).

Natural occurring gas hydrates predominantly contain CH_4 and form in presence of sufficient amounts of water and gas at low temperature and elevated pressure conditions (Sloan and Koh, 2008). These conditions are fulfilled at all active and passive continental margins as well as permafrost regions where natural gas hydrate deposits were found in the past (Kvenvolden and Lorenson, 2001). Since natural gas hydrate deposits were detected worldwide it is assumed that huge amounts of CH_4 are stored in these unconventional fossil fuel reservoirs making them more and more attractive as a potential future energy resource. Different approaches such as depressurization, thermal stimulation and the injection of CO_2 or N_2-CO_2 gas mixtures have been tested in lab studies and field trials (e.g. Dallimore and Collett, 2005, Zhao et al., 2012, and literature within, Yamamoto et al., 2014, Boswell et al., 2017, Schicks et al., 2018). Nevertheless, up to know no convincing method was found for the efficient and environmental friendly production of CH_4 from hydrate-bearing sediments.

The first method which was tested in a field trial during the winter of 2001/2002 in the framework of the Mallik Scientific Drilling Project was the thermal stimulation and in the following we will focus on this method. In the framework of this field trial the thermal stimulation was achieved via pumping a hot fluid through the permafrost into depths of 900-1100 m where the hydrate-bearing sediment layer was detected. This field trial was successful insofar that it proved the possibility of producing CH_4 from natural gas hydrate deposits using thermal stimulation via the injection of a hot fluid. However, only about 470 m^3 (surface conditions) of CH_4 were produced from dissociated hydrates within about 123.4 h indicating that this method is probably not efficient enough to be economic feasible (Yasuda and Dallimore, 2007). This is due to the loss of heat during the transport of the hot fluid through hundreds of meters of permafrost resulting in a gentle heating effect at depth and thus a minor radial heat transfer into the hydrate deposit.

For the limitation of heat loss and most efficient use of heat for the decomposition of natural gas hydrates, *in situ* combustion (ISC) could be an alternative method. Here, the heat source (e.g. an authothermal heater) is placed and generates heat straight within the gas hydrate deposit. For the exploitation of unconventional oil deposits such as heavy oil and bitumen reservoirs, ISC and steam- assisted gravity drainage (SAGD) are already established methods (Yang and Gates, 2009). The SAGD process is similar to the thermal stimulation used during the Mallik Scientific Drilling Project: the steam is generated at the surface and injected into the formation and is therefor accompanied with heat loss. In contrast, when using ISC, the heat is generated in the reservoir via injection of oxygen to initiate the combustion of the fuel (e.g. bitumen) (Yang and Gates, 2009). A direct contact between the reservoir and the steam or the combustions front is given. This is porbably a disadvantage when using in situ combustion for the thermal stimulation of natural gas hydrate depsosits. Therefore, the approach of *in situ* combustion developed at GFZ is a closed system in terms of a flameless, catalytic oxidation of CH_4 within a counter-current heat-exchange reactor. There is no direct contact between the catalytic reaction zone or the reaction products and the reservoir (Schicks et al., 2013). The basis of the idea is to use the exothermal heat of the catalytic total oxidation of CH_4 given in the following reaction equation (Lee and Trimm, 1995):

$$CH_4 + 2\,O_2 \leftrightarrow CO_2 + 2\,H_2O \qquad \Delta H = -\,802.7\text{ kJ/mol} \qquad (1)$$

A catalyst permits the conversion of CH_4 with air into CO_2 and H_2O below the auto-ignition temperature of CH_4 in air at 868 K and outside the flammability limits (Air Liquid, 1966). This leads to a double secured

application of the heater with safe operation. In addition, the relatively low reaction temperature allows the use of cost-effective standard materials for the reactor and prevents the formation of NO_x. Since the decomposition of CH_4 hydrates requires about +52 kJ/mol (Rydzy et al., 2007) whereas the total oxidation of CH_4 releases about -803 kJ/mol, only a small amount of the released CH_4 has to be consumed for this thermal stimulation method.

For the production of gas from gas hydrates, other groups have also adapted the ISC method, although there are some significant differences compared to the counter-current heat-exchange reactor developed at GFZ, which has been referred to as "Schicks combustor" in literature (Rogers, 2015).

In 2007 Castaldi and co-workers proposed a process in which the heat is generated by combusting a liquid hydrocarbon fuel with oxygen (optionally catalytic). The warm combustion products, carbon dioxide and water, are fed into the formation and decompose the gas hydrates. In order to enhance control of the combustion process and at the same time promote the decomposition of the hydrate, additional carbon dioxide is added to the oxygen stream. In this way, thermal stimulation and carbon dioxide sequestering are combined to achieve higher gas production from hydrates (Castaldi et al., 2007). In contrast, the exhaust gases do not enter the formation in the process developed at GFZ.

Cranganu has developed a similar process in which a gaseous fuel and air are led together from the surface of the earth into a combustion chamber, where they are ignited by a spark. This is the main difference to the heat-exchange reactor, which generates the required heat by a flameless catalytic combustion. After the fuel has been completely converted, the exhaust gases are transported back to the earth's surface and a new fuel/air mixture is fed into the combustion chamber so that a circulation process is created. The gas released from the hydrates is led to the earth's surface in a tube separate from the exhaust gases (Cranganu, 2009).

Both methods have been described theoretically in a scientific publication, but to us there are no publications on the construction of a prototype and corresponding tests with gas hydrates in the laboratory or in the field known.

On behalf of the US Department of Energy (DOE, National Energy Technology Laboratory NETL), the American company Precision Combustion Inc. (PCI) 2010, developed a prototype based on *in situ* combustion as part of the Gas Hydrate R&D Program. PCI had various variants of the process patented in previous years (Pfefferle, 2005, Pfefferle, 2008, Pfefferle 2009), which also had to be taken into account in the patenting of the counter-current heat-exchange reactor due to similarities. In a report by the US Department of Energy on the completion of the project and on the company's website, the process is described in such a way that natural gas and oxygen are fed separately into a combustion chamber where they are catalytically converted. The combustion products are fed into the formation, which then heats up. In order to better control the reaction temperature and improve process safety, water is added to the oxygen stream. This water evaporates in the combustion chamber. The water vapor is then led into the formation, leading to the decomposition of the hydrates. This process is related to the steam injection described above, with the difference that the steam is produced on site and gets directly into the formation without transport losses. As an alternative to steam, the use of carbon dioxide, which is added to the oxygen stream, is also proposed. The "on-site heat production" could thus be combined with carbon dioxide sequestration in order to additionally promote the decomposition of the hydrate. According to PCI, the energy requirement for the process is about 12% to 15% of the methane produced. This is comparable to the counter-current heat-exchange reactor developed at GFZ. The catalytic burner developed by PCI was tested on a laboratory scale. (NETL 2011, PCI Combustion, Inc. 2017).

The main differences to the counter-current heat-exchange reactor developed at GFZ are that no pure methane is used as fuel gas. In addition, the fuel gas is converted in the oxyfuel process, i.e. with pure oxygen. This allows higher temperatures to be achieved. The provision of oxygen in the field, however, is accompanied by a high technical effort. Furthermore, in the process proposed by PCI, water or carbon dioxide is added to the oxygen stream in order to better control the combustion process and the temperature

of the exhaust gases. The hot exhaust gases are fed into the formation to heat it up. This is not the case with the counter-current heat-exchange reactor developed at GFZ.

Construction and functional principles of the counter-current heat-exchange reactor

The first concept of the counter-current heat-exchange reactor for the thermal stimulation of hydrate bearing sediments via *in situ* combustion was presented in 2011 (Schicks et al., 2011). This first prototype was a laboratory scale reactor with a total length of 457 mm and an outer diameter of 40 mm. The outer shell consisted of a Ni-based-alloy (ThyssenKrupp VDM) with a thickness of 4 mm. This material was chosen because of its seawater resistance and mechanical stability under high pressure (25 MPa) even at temperatures up to 873 K. With this high mechanical stability, the reactor can be applied in an environment with high external pressure comparable to conditions in natural gas hydrate reservoirs. Au-tothermal recuperators use the heat exchange of the hot product flow with the cold educts inlet flow. With such an arrangement, the reaction runs autonomous without any additional heating devices. In the first prototype of the reactor at laboratory scale, the cold educts CH_4 (fuel) and air (oxidant) flowed separately through ceramic pipes which were implemented in the catalyst bed where the exothermal reaction is running. The educt tube consisted of Al_2O_3 ceramics with an outer diameter of 8 mm containing two inner tubes with 1 mm diameter each. The pre-heated educts are mixed in the mixing chamber in front of the catalyst bed and flow finally through the perforated plate into the catalyst bed. However, it turned out that the flow of the educts through the parallel inner tubes of the Al_2O_3 ceramic tube resulted in an insufficient mixing of the educts in front of the catalyst bed and thus, in a low combustion rate. Therefore, the ceramic tube was replaced in the second prototype of the reactor at laboratory scale with a tube-in-tube arrangement. Both of these tubes end in a nozzle which permits a complete mixing of the educts before entering the catalyst bed. This better mixing of the educt gases resulted in a significant higher combustion rate. The heat released from the combustion process warmed up the educt pipes and the reactor shell and subsequently the environment (Schicks et al., 2013).

Based on the results and experiences with the counter-current heat-exchange reactor at laboratory scale a borehole tool was developed and realized. The borehole tool has a total length of 5120 mm and an outer diameter of 90 mm. It is made of stainless steel. The thickness of the outer casing is 7 mm and assures an operational area up to 2000 m depth. The borehole tool is relatively lightweight with about 100 kg. Figure 1 shows exterior view of the counter-current heat-exchange reactor as a borehole tool.
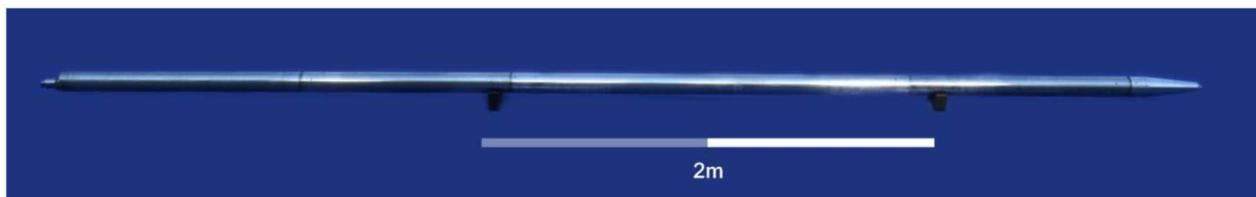

Figure 1—Exterior view of the counter-current heat exchange reactor as a borehole tool.

The up-scaling of the laboratory scale counter-current heat-exchange reactor to the borehole tool required certain adaptations and new solutions presented in detail in the following chapters.

Catalyst

The identification of a catalyst with a high conversion rate of CH_4 into CO_2 and H_2O operating over a long time without significant changes is crucial for the application of this concept of catalytic *in situ* combustion for the production of gas from hydrate-bearing sediments. Chauki et al. (1994) already reported

that palladium (Pd) is suitable as a catalytic active material for the total oxidation of CH_4. They observed a conversion rate of CH_4 of up to 100% at temperatures about 745 K. Therefore, Pd was selected as one element for the catalytic active material. For the first tests we used a catalyst which consisted of 10wt% Pd supported on ZrO_2 prepared by simple impregnation techniques. For this, the required amount of metal salt $Pd(NO_3)_2 \cdot H_2O$ (99.9%, Alfa Aesar GmbH & Co KG) was dissolved in deionized water and stirred until a clear solution containing 1% Pd in H_2O resulted. Then ZrO_2 (99%, ABCR Dr. Braunagel GmbH & Co. KG) in powder form was added to the solution and constantly stirred under external heat supply at about 360 K. After 6 h a slurry and later a powder formed, which was subsequent dried in air at 573 K for 5 h. The catalyst was then pressed to a pellet and broken on a sieve (Ø 1.2 - 1.4 mm). The particles (Pd/ZrO_2) were interspersed into pores of aluminum foam (10 ppi) that acted as a carrier for the catalyst and enlarged the dimensions of the catalyst bed (Figure 2a).

Since Ohtsuka (2011) reported in his study that iridium (Ir) and platinum (Pt) are also suitable catalytic active materials for the oxidation of CH_4 over ZrO_2 supported materials, we tested these metals as well as rhodium (Rh) and nickel (Ni). In addition to ZrO_2 the simple impregnation technique was also applied on Al2O3 and ceramic mats as potential substrates (Figure 2b).
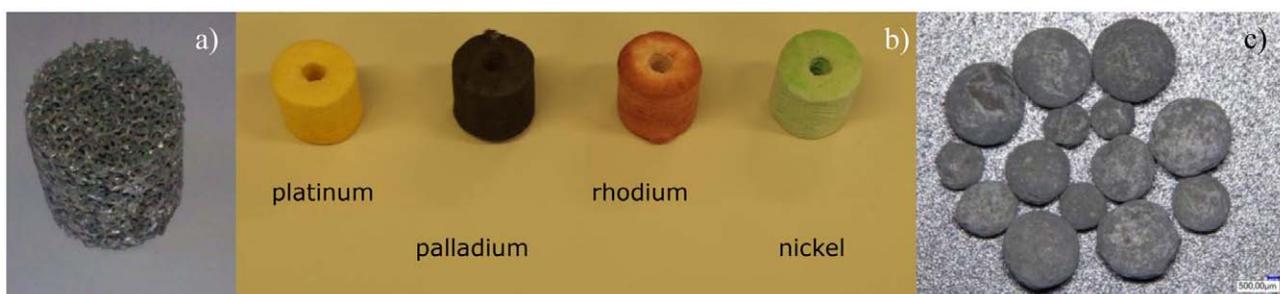

Figure 2—Different catalytic active metals on varying support material: a) Pd/ZrO_2 particles interspersed into pores of aluminum foam; b) ceramic mats impregnated with solutions of metal salts; c) "HeraPur®" catalyst (0,5% Pd on Al_2O_3).

To activate the catalysts inside the counter-current heat-exchange reactor, the catalysts were ignited using H_2. Each catalyst was exposed to temperatures >498 K using the exothermal conversion reaction of H_2 with air to H_2O to ensure a successful ignition of the CH_4 combustion after changeover of fuels from H_2 to CH_4. The reaction was run at about 773 K until conversion and selectivity reached a fairly stable state. For shutting down the reactor CH_4 was switched off, but the heater cooled down with a constant air flow of 2.5 L/min for 1 h to be ready for the next run. When tested in the counter-current heat- exchange reactor on laboratory scale ZrO_2-supported Ir and Pt catalyst particles showed the highest conversion rates for CH_4 (up to 99%) at stable reaction condition at 723 K over several hours whereas Pd showed good results with respect to the stability of the catalyst over several hours but only fair conversion rates of CH_4 ($\geq 60\%$) (Schicks et al., 2013). However, the preparation of several grams of catalyst required a significant amount of the expensive appropriate metal salts which might be a criterion of exclusion for the application in the borehole tool where larger amounts of catalyst are needed. To address this problem, commercial catalysts containing Pd, Ir or Pt where selected and tested in the countercurrent heat-exchange reactor at laboratory scale. As one reasonably priced alternative to the noble metal catalyst a universal metal catalyst from UNIFIT KATALYSATOREN GmbH (Engelsbrand, Germany) was tested, but the stabilization of the catalytic oxidation reaction of CH_4 at a certain temperature could not be realized, making the application of this catalyst in the borehole tool impossible. Apart from that we also tested a customized nanostructured catalyst manufactured by the company ODB-Tec. Originally the catalyst was developed for the oxidation of small amounts of H_2 in air at room temperature; however, it was also suitable for the combustion of hydrocarbons. On a titanium support grid a nanostructured layer of

TiO_2 was formed which was subsequently coated by a nanoscale Pt layer. Unfortunately, it was not possible to run the lab reactor at constant temperature conditions when using this catalyst.

It turned out that the commercial and economically priced catalyst "HeraPur®" (Figure 2c) from Heraeus GmbH & CoKG consisting of 0.5% of Pd on an alumina support with high surface area (250 m^2/g) showed stable reaction temperatures and reasonable conversion rates and was therefore selected for the application in the borehole tool.

Water trap
According to equation 1 the total oxidation of CH_4 generates water which affects the function of the catalyst. During the catalytic combustion of CH_4 the temperature of the catalyst is high enough for the evaporation of the water molecules. However, to avoid any reflux from colder areas in the vicinity of the catalyst bed, the water has to be removed. For this reason a water trap (Figure 3) and a custom-made water pump (Muschong, Figure 4) were installed in the borehole tool to allow for further removal of the water from the trap into the environment, even under pressure gradients up to 35 MPa. The dimensions of the pump were adjusted to enable an installation of the pump into the borehole tool (length: 167 mm, width: 58 mm).

Figure 3—Picture of the water trap.

Figure 4—a) Muschong pump installed in the borehole tool for water removal, b) Custom made Muschong pump

Gas supply and reaction control
In the framework of the laboratory experiments all gases for the catalytic combustion were supplied by gas bottles. The continuous flow of the gases was controlled using mass flow controllers (MFC) for both gases, air and the fuel gas (Bronkhorst EL-Flow select, AK Ruurlo, the Netherlands). Usually 5 L/min of air were fed into the reactor during the ignition and combustion process. The amount of fuel gas was adjusted to the stoichiometric ratio until a constant temperature at the catalyst indicates a stable catalytic reaction. Mass flow of the gases were controlled manually or using the Bronkhorst FlowView software. For the ignition process and preheating of the catalyst H_2 and air were used. After the temperature at the catalyst reached $\geq$ 473 K the fuel gas was changed from H_2 to CH_4 by shifting the vent manually.

For the test of the borehole tool at depth in the KTB Deep Crustal lab of the GFZ at Windischeschenbach a similar set-up was realized. The fuel gases H_2 or CH_4 and synthetic air were provided via a flat-pack consisting of three hydraulic tubes with an inner diameter of 4.2 mm. The third tube was used for the flue gas. The gas flow of the fuel gas was controlled using a mass flow controller (model F-211AI-70K-AGD-22-V from Bronkhorst Mättig GmbH, Germany). The air flow was controlled using a combi-nation of a control valve (model BHM5824 from Samson AG, Germany) and a mass flow meter (model F-133MI-AGD-44-V from Bronkhorst Mättig GmbH, Germany). Figure 5 depicts the gas supply at the KTB.
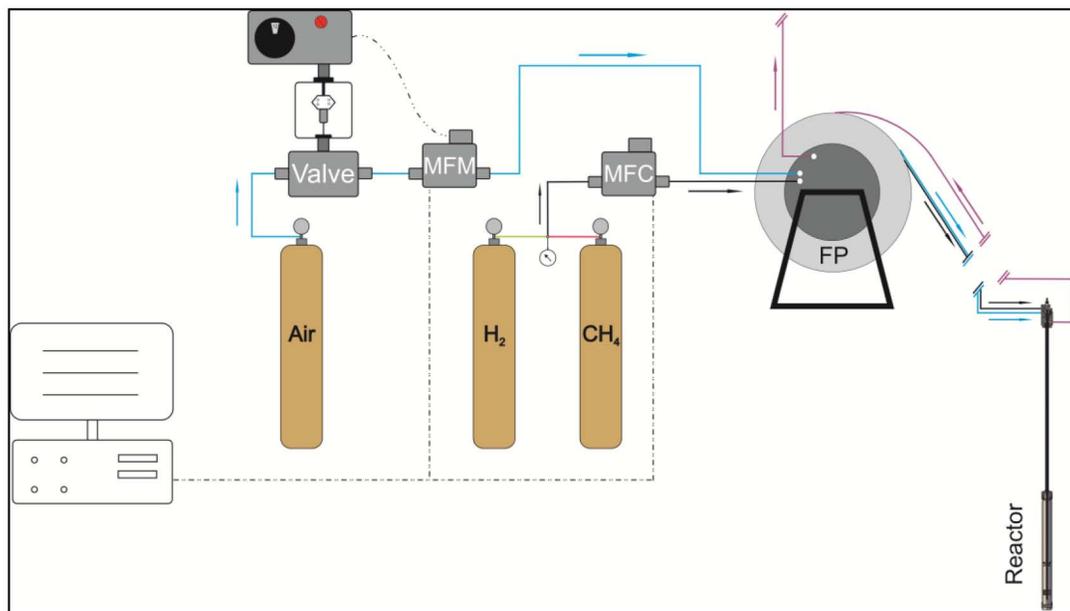

Figure 5—Gas supply at the KTB: MFM – mass flow meter, MFC – mass flow controller, FP – flat-pack (see text for details)

Within the borehole tool the fuel gas and air were transported separately until they reach the mixing chamber (see Figure 6) in front of the catalyst bed. Check valves at the end of the tubes avoided an un-controlled intrusion of air into the fuel gas tube and vice versa.
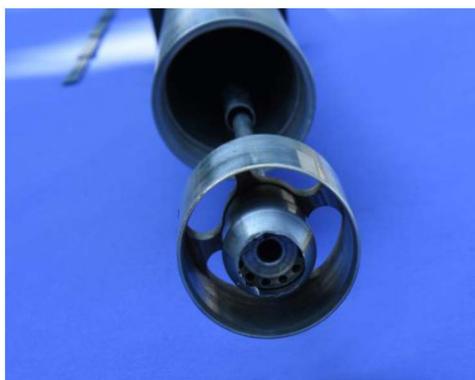

Figure 6—Gas mixing chamber inside the borehole tool. (catalyst bed is not shown.)

During the first functional test at the KTB Deep Crustal Laboratory of the GFZ (KTB-TL) in Windisch-eschenbach (Germany) we used a 7-wire Rochester cable which allowed for the measurement of the pressure in the reactor as well as the temperatures in the catalyst bed and the water trap (two Pt100 with two 4-20mA signal transformers Jumo dTrans T05B) and to run the water pump for the disposal of the reaction water into the borehole via a Vicor V300C24C150BL DC-DC converter. This first functionality test was successful

insofar, that we were able to ignite the catalyst with H_2 and air to preheat the catalyst and to switch the reaction from hydrogen-air to methane-air (see also chapter 3.2 "Experimental test of the borehole tool"). The change of the fuel gas is combined with a temperature increase from about 473 K to about 573 K in the catalyst bed. However, shortly after this temperature was reached the temperature sensor in the catalyst bed failed and we had to shot down the reaction for safety reasons. To improve the control of sensors we integrated a custom-made telemetry unit (Tele 1709, LogIn GmbH) (Figure 7) in the top of the reactor. The telemetry unit facilitates a digital data transfer and communication with the surface system over the cable and abolished the limitations provided by the 7-wire cable, with respect to the numbers of sensors and safety switches. It allowed the addition of another temperature sensor in the heat-exchange unit close to the catalyst bed as well as a level sensor, which automatically switched the water pump on and of, depending on the amount of produced reaction water and finally, a magnetic valve to interrupt the air supply directly in the reactor for a quick shot down of the reaction. The telemetry unit provides much more flexibility for further changes, addition and improvements.
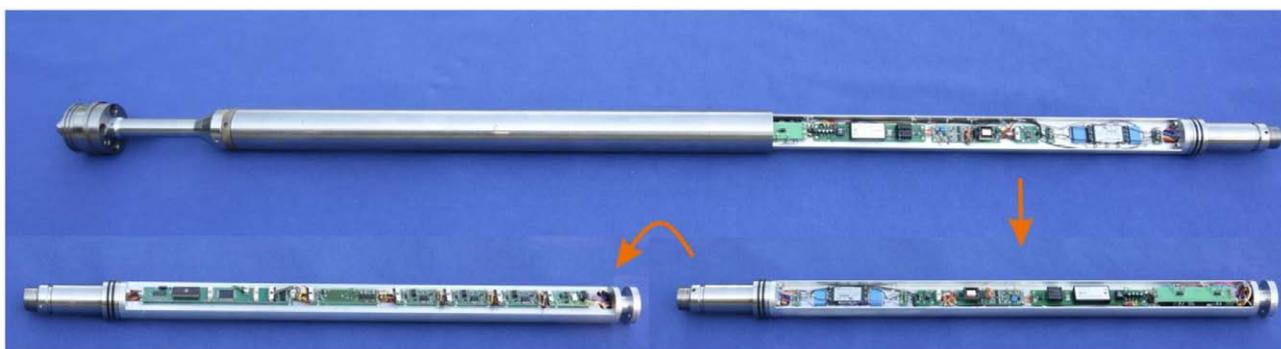

Figure 7—Picture of the telemetry unit in and outside the casing of the borehole tool.

Heat transport

The total oxidation of CH_4 is an endothermal reaction where heat is generated at the catalyst bed. The heat is transported via heat conduction and the flow of the hot flue gases. The generated heat has to be used twofold: 1.) for the preheating of the cold educts to ensure a continuous and stable reaction at the catalyst and 2.) the thermal stimulation of the environment inducing e.g. the decomposition of natural gas hydrates in the vicinity of the borehole tool. For the optimization of the heat transfer, in particular the heat transfer of the hot flue gases to the reactor wall, open-cell aluminum foams of different pore sizes were tested (Figure 8). Care was taken that the selected open-cell aluminum foam showed a maximum increase of heat transfer and only a minimum change in flow-resistance.

Figure 8—Open-cell aluminum foams with different pore sizes

For the tight fitting of the open-cell aluminum foam in the borehole tool with high contact to the reactor walls the aluminum foams were cooled in liquid nitrogen before their installation into the borehole tool (Figure 9). For the borehole tool an open-cell aluminum foam with 10 ppi manufactured by the Fraunhofer Institute for Manufacturing Technology and Advanced Materials IFAM was used.
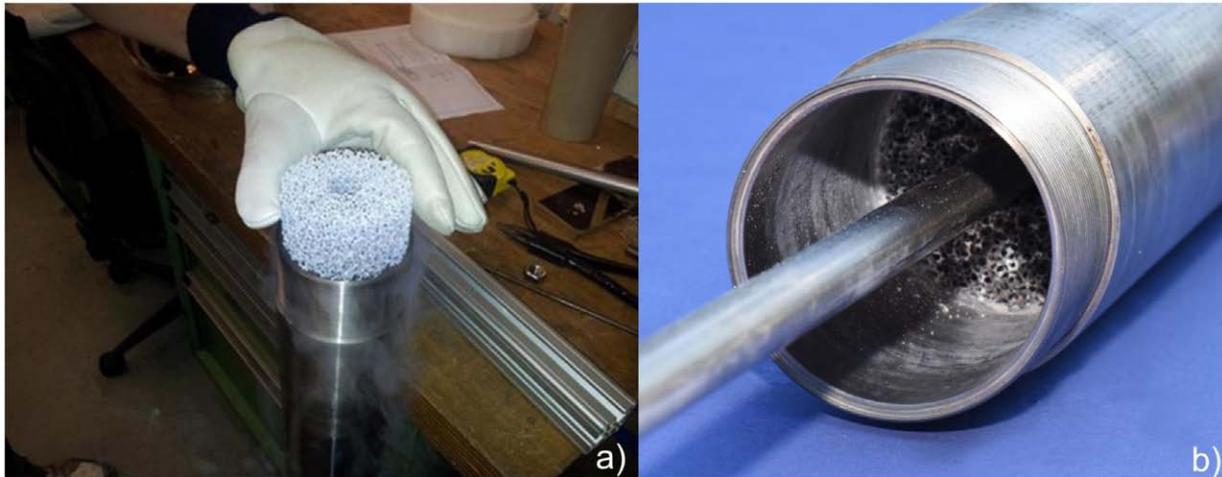

Figure 9—a) Open-cell aluminum foam was cooled in liquid nitrogen before it was installed into the borehole tool. This procedure ensures a tight fitting of the foam with a high contact between foam and reactor wall. b) Aluminum foam inside the borehole tool.

Results from laboratory and field tests

Both, the counter-current heat-exchange reactor at lab scale and the borehole tool have been tested. However, the performance of the different experiments varied depending on the intention and the challenges.

Experimental tests of the counter-current heat-exchange reactor at laboratory scale
The intention of the lab scale reactor test was to prove

- that the chosen catalyst supports the total oxidation of CH_4 in a stable and controlled reaction,

- that the generated heat of this reaction is efficiently transported into the environment, and

- that this method can be used efficiently for the dissociation of CH_4 hydrates in the vicinity of the reactor and thus for the production of CH_4 from hydrate bearing sediments.

The production test applying *in situ* combustion using the catalytic reactor was performed in the LArge Reservoir Simulator (LARS), which has been described in detail elsewhere (Spangenberg et al., 2014, 2015). The main component of LARS is the pressure vessel, which is made of steel and has an inner diameter of 600 mm and a depth of 1500 mm, the maximum size of the sediment sample is therefore limited to a size of a diameter of 460 mm and a length of 1300 mm. In preparation for the production test, the sediment sample was filled in a neoprene jacket that was closed with stainless steel plates at the bottom and top containing the ports for the pore fluid. The top closure also contains the lead-throughs for the catalytic reactor and the temperature sensors. Several temperature sensors were distributed within the sediment sample and allowed for monitoring the temperature development and distribution in the sample during the experiment. The complete system can be pressurized up to 25 MPa. A water-glycol mixture was used as cooling medium but also to provide the confining pressure. The sediment sample is saturated with brine and the hydrate was formed from CH_4 dissolved in this brine at 277 K representing hydrate reservoir conditions in nature. For the hydrate formation procedure the pore fluid circulated through the system. For the continuous enrichment of the brine with CH_4 the brine was transported out of the sample and injected it into the gas charging vessel

through a spray nozzle, where CH_4 was dissolved in the brine and the CH_4-rich brine was pumped back into the sample. For the production test a hydrate saturation of 80% in sandy sediment was achieved. The test was performed at a pore pressure of 8 MPa and a confining pressure of 12 MPa. The catalyst was ignited and preheated with H_2 and air until the temperature at the catalyst reached 473 K. Thereafter, the fuel was changed from H_2 to CH_4 and the catalytic total oxidation reaction of CH_4 was stable at about 773 K.

The high temperature at the catalyst bed and the good heat transport induced a dissociation of the gas hydrates in the vicinity of the reactor. The changes of the temperature in the sediments indicated a convection of a hot fluid phase through the sediments enhancing the heat transfer from the reactor into the environment. After approximately 12 h all temperature sensors detected temperatures equal to or higher than the equilibrium temperature of CH_4 hydrate at the chosen pressure conditions indicating that almost all hydrate within the sediments dissociated. It turned out that during the first 12 h of the production test 23.5 L H_2O but almost no gas was produced. One explanation for this observation could be that the re-leased gas did not migrate immediately to the production tube which was located in the top center of the pressure vessel. However, the 23.5 L can be interpretd as the the fluid expansion due to hydrate dissocia-tion at constant pressure. Therefore, the overall fluid expansion of 23.5 L at 8 MPa equates to 1880 L of CH_4 at 0.1 MPa. Taking into account that the heat was generated in the middle of the sediment sample, the released gas migrated into the cold region at the top of LARS where it may have formed hydrates again and stopped further gas migration. During the 12 h of the production test 288 L of CH_4 were cata-lytically converted to CO_2 and H_2O. In conclusion, an equivalent of 15% of the produced CH_4 was used for the generation of the needed heat to dissociate the hydrates in the sediments during the production test. The results of this production test are described in detail elsewhere (Schicks et al., 2013).

Experimental test of the borehole tool
Since there was no opportunity to test the borehole tool in the framework of a gas hydrate production field trial, we decided to perform at least a functionality test at the KTB Deep Crustal Laboratory of the GFZ (KTB-TL), which is a worldwide unique research site for a wide variety of experiments, tests and measurements under *in situ* borehole conditions. The KTB-TL utilizes the two deep boreholes drilled during the KTB project (1987-1995), the so-called pilot hole (KTB-VB, 4 km) and the ultra-deep main hole (KTB-HB, 9.1 km). Both wells are nearly completely cased. The constellation of two very deep boreholes in crystalline rocks close to each other (200 m) with easy accessibility and full technical infra-structure allows deep borehole experiments at reasonable costs. The KTB site is located in Windisch- eschenbach in southeastern Germany. The drill site itself lies within the zone of Erbendorf-VohenstrauB, a smaller crustal segment of highly metamorphic rocks of a Variscian continental collision zone. The thermal gradient of 28 °C/km leads to high temperature and pressure conditions (T > 443 K, p > 65 MPa) in the deeper part of the well which offers ideal test beds for high-tech developments and testing of new scientific and technical methods. It should be noted that the water level lies in the KTB-VB close to the surface and in the KTB-HB at 70 m.

The idea behind the functionality test of the counter-current heat-exchange reactor as a borehole tool at the KTB was primarily to prove

- that the borehole tool resists pressure differences up to 20 MPa,

- that catalytic oxidation of CH_4 can be applied securely at depth, and

- the efficiency of the tool in terms of heat transfer into the environment.

For the pressure test the borehole tool was placed in the KTB-HB at 2000 m depth. After recovering the reactor there was no mechanical damage or water leakage.

For the functionality test the borehole tool was placed at 630 m depth. One feed gas pipe was flushed with CH_4, before H_2 was injected. The other feed gas pipe was fed with air. The flue gas pipe was con-nected to a gas chromatograph (Compact GC, Global Analyser Solutions) providing a continuous analysis of the flue gas. When air and H_2 reached the catalyst bed the temperature at the catalyst immediately increased indicating the catalytic oxidation of H_2 to H_2O had started. The increase in temperature at the catalyst bed proceeded moderately suggesting a controlled reaction. The amount of H_2 was calculated to increase the temperature at the catalyst bed to at least 473 K. Thereafter CH_4 was provided for the *in situ* combustion process. The abrupt rise in temperature at the catalyst to 573 K indicated that the conversion of CH_4 with air to CO_2 and H_2O had started. In addition, the analysis of the flue gas revealed an increase of CO_2 and a decrease of O_2 in the flue gas (Figure 10)
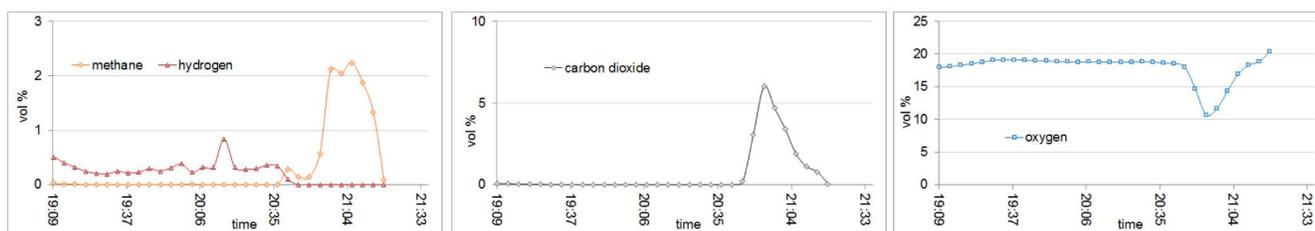
Figure 10—changes of flue gas composition over time measured with gas chromatography left: changes of H_2 and CH_4 (in vol%); middle: changes in CO_2 (in vol%); right: changes of O_2 (in vol%)

Summary and Outlook

Within the German national research initiative "SUGAR" (2008-2018) we were able to develop and to test a counter-current heat-exchange reactor for the catalytic combustion of CH_4 in a pilot plant scale. We were able to show that with our method, the heat can be generated in the borehole where it is needed in an efficient, safe and technically proven process. This distinguishes the counter-current heat-exchange reactor from other thermal processes for the thermal stimulation of gas hydrate-bearing sediments:

Our method is efficient because the heat is generated at depth and therefore no heat losses arise from transport. The production test using the reactor in the large reservoir simulator LARS for the thermal dissociation of hydrates in sediments showed promising results: about 15% of the produced CH_4 were needed for the generation of the sufficient heat to dissociate the hydrates in the sediments. Based on these promising results the reactor was scaled up to a borehole tool with a total length of 5120 mm and an outer diameter of 90 mm. This borehole tool was successfully tested in a functionality test at the KTB Deep Crustal Laboratory of the GFZ. In this first test we were able to show that the method of *in situ* combustion using a counter-current heat-exchange reactor for the catalytic conversion of CH_4 can be safely applied at depth for a secure and controlled downhole heat generation. The counter-current heat- exchange reactor can therefore be used for the generation of heat within hydrate bearing sediments but also for other applications e.g. enhanced oil recovery. Both, the laboratory reactor and borehole tool are ready for use and are available for application testing procedures.

Future developments will focus on the applicability of the borehole tool for additional applications and the improvement of its functionality. This could be among others the direct feed of CH_4 from the environment into the catalyst bed to avoid the supply of fuel from the surface. Further we aim a field test in natural gas hydrate deposits.

Acknowledgement

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