



Project Acronym and Title:
**M4ShaleGas - Measuring, monitoring, mitigating and managing the
environmental impact of shale gas**

**Simulating the potential composition and mobility of compounds in flowback
water**

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Public introduction

M4ShaleGas stands for *Measuring, monitoring, mitigating and managing the environmental impact of shale gas* and is funded by the *European Union's Horizon 2020 Research and Innovation Programme*. The main goal of the M4ShaleGas project is to study and evaluate potential risks and impacts of shale gas exploration and exploitation. The focus lies on four main areas of potential impact: the subsurface, the surface, the atmosphere, and social impacts.

The European Commission's Energy Roadmap 2050 identifies gas as a critical fuel for the transformation of the energy system in the direction of lower CO₂ emissions and more renewable energy. Shale gas may contribute to this transformation.

Shale gas is – by definition – a natural gas found trapped in shale, a fine grained sedimentary rock composed of mud. There are several concerns related to shale gas exploration and production, many of them being associated with hydraulic fracking operations that are performed to stimulate gas flow in the shales. Potential risks and concerns include for example the fate of chemical compounds in the used hydraulic fracking and drilling fluids and their potential impact on shallow ground water. The fracking process may also induce small magnitude earthquakes. There is also an ongoing debate on greenhouse gas emissions of shale gas (CO₂ and methane) and its energy efficiency compared to other energy sources. There is a strong need for a better European knowledge base on shale gas operations and their environmental impacts particularly, if shale gas shall play a role in Europe's energy mix in the coming decennia. M4ShaleGas' main goal is to build such a knowledge base, including an inventory of best practices that minimise risks and impacts of shale gas exploration and production in Europe, as well as best practices for public engagement.

The M4ShaleGas project is carried out by 18 European research institutions and is coordinated by TNO-Netherlands Organization for Applied Scientific Research.

Executive Report Summary

This final report summarizes the work done in WP 11 on simulating the potential composition and mobility of compounds in flowback water. The full spectrum of work is presented, starting from reviewing compositions of fracking fluids, flowback and produced water from literature and real hydraulic fracking activities compared to laboratory experiments simulating flowback composition and related development of process modelling. This report starts with summarizing chemical composition of fracking fluids as well as flowback and produced waters. It becomes obvious that selection of chemical additives in fracking fluids is highly variable and not only dependent on the reservoir conditions. Also analytical results of the flowback samples from Wysin-2H well are summarized. To evaluate the effect of individual shales on the composition of flowback waters, samples from Posidonia, Alum, Mikulov and Marcellus formations were selected for lab experiments. In the lab, these shales were extracted with distilled water and an artificial fracking fluid under different pressure and temperature conditions. The artificial fracking fluid contained choline chloride (clay stabilizer) and butyldiglycol (friction reducer). These lab experiments showed clearly that fluid-rock interactions change the chemical composition of the fluid and this demonstrates that simulation/ modelling of flowback water composition in shale gas systems is not possible without consideration of the fractured shale geochemistry. Geochemical process models are supposed to support the risk assessment of potential shale gas exploitation with predictive simulations. Challenge is so far, that the processes underlying the reactions leading to mobilization of organic and inorganic compounds from shales by water-rock-interaction with fracking fluids are unclear. We have tested the hypothesis that kinetically governed dissolution of phyllosilicates, as dominating parts of the investigated shale systems, can be the basis for quantification. Further mineral phases relevant for the inorganic anions in the flowback like sulphate, phosphate and fluoride have been included into the system assuming thermodynamic equilibrium depended on the reaction progress of the shale. Shales and data from the lab experiments have been used for calibration of the system. However, the approach could not be evaluated. Further research and development is needed to provide a tool to quantify shale system behavior and mobilization of organic and inorganic compounds into flowback. At the end, scientific recommendations are presented about mitigating the environmental impact of flowback waters.



TABLE OF CONTENTS

	Page
1 INTRODUCTION	2
1.1 Context of M4ShaleGas	2
1.2 Study objectives for this report.....	2
1.3 Aims of this report.....	3
2 COMPOSITION OF FRACKING FLUIDS AND FLOWBACK	4
2.1 Summary of literature.....	4
2.2 Field study – Wysin.....	6
3 SIMULATION OF FLOWBACK COMPOSITION IN LAB EXPERIMENTS.....	9
3.1 Introduction – state of the art.....	9
3.2 Summary of results from lab experiments.....	10
4 MODELLING OF FLOWBACK COMPOSITION	13
4.1 Introduction	13
4.2 Simulation results	13
4.3 Comparison of results from lab and modeling studies with field data	14
5 RECOMMENDATIONS FOR RISK MITIGATION	17
6 REFERENCES	19



1 INTRODUCTION

1.1 Context of M4ShaleGas

Shale gas source rocks are widely distributed around the world and many countries have now started to investigate their shale gas potential. Some argue that shale gas has already proved to be a game changer in the U.S. energy market (EIA 2015¹). The European Commission's Energy Roadmap 2050 identifies gas as a critical energy source for the transformation of the energy system to a system with lower CO₂ emissions that combines gas with increasing contributions of renewable energy and increasing energy efficiency. It may be argued that in Europe, natural gas replacing coal and oil will contribute to emissions reduction on the short and medium terms.

There are, however, several concerns related to shale gas exploration and production, many of them being associated with the process of hydraulic fracking. There is also a debate on the greenhouse gas emissions of shale gas (CO₂ and methane) and its energy return on investment compared to other energy sources. Questions are raised about the specific environmental footprint of shale gas in Europe as a whole as well as in individual Member States. Shale gas basins are unevenly distributed among the European Member States and are not restricted within national borders, which makes close cooperation between the involved Member States essential. There is relatively little knowledge on the footprint in regions with a variety of geological and geopolitical settings as are present in Europe. Concerns and risks are clustered in the following four areas: subsurface, surface, atmosphere and society. As the European continent is densely populated, it is most certainly of vital importance to understand public perceptions of shale gas and for European publics to be fully engaged in the debate about its potential development.

Accordingly, Europe has a strong need for a comprehensive knowledge base on potential environmental, societal and economic consequences of shale gas exploration and exploitation. Knowledge needs to be science-based, needs to be developed by research institutes with a strong track record in shale gas studies, and needs to cover the different attitudes and approaches to shale gas exploration and exploitation in Europe. The M4ShaleGas project is seeking to provide such a scientific knowledge base, integrating the scientific outcome of 18 research institutes across Europe. It addresses the issues raised in the Horizon 2020 call LCE 16 – 2014 on *Understanding, preventing and mitigating the potential environmental risks and impacts of shale gas exploration and exploitation*.

1.2 Study objectives for this report

Composition of flowback is related to the composition of the initial fracking fluid, the composition of the natural formation water of the shale and the possible interactions

¹ EIA (2015). Annual Energy Outlook 2015 with projections to 2040. U.S. Energy Information Administration (www.eia.gov).



between fracking fluid and shale system over time at the in-situ conditions. The interactions between shale formation and flowback water at in-reservoir conditions are an extremely important aspect to understand the controls on flowback water composition. In the ideal case composition of flowback should be quantifiable with geochemical process simulations.

This final report summarizes the work done in WP11. The main objective was to get quantitative estimates on real flowback water composition based on experimental data and modelling results as well as an assessment of the influence of flowback water on surface and shallow groundwater systems. In addition, scientific recommendations are provided about how to mitigate risks of environmental pollution with flowback water and how to treat the waste water properly.

1.3 Aims of this report

The first aim of this report is to provide an overview about the work done in WP11 about simulating the potential composition and mobility of compounds in flowback water. This comprises information on the current status in chemical composition of fracking fluids as well as flowback and produced waters from hydraulic fracking (HF) of shales. Here literature review was performed but also composition of fracking fluid and flowback samples from the HF of the Wysin-2H well were analysed and presented. The second aim was to provide information about the controls on flowback water composition due to interaction with the corresponding gas shale. Results of lab experiments with four different samples (Posidonia, Alum, Mikulov, Marcellus shales) are presented and fluid-rock interactions as well as possible effects of chemical additives are deciphered. The third aim was to provide information about the potential to quantify geochemical flowback water composition by numerical process simulations. Taking into account the system consisting of the fracking fluid, formation water and the shale system it would be beneficial to give valid prognoses for the fracking operations with regard to the treatment and/or disposal of the flowback water. We apply chemical process simulations to characterize the mobility of organic and inorganic compounds and assess the feasibility to predict flowback water compositions for selected shale systems. The models are set-up and calibrated using as many available field and lab data as possible, for example from various shale plays from around the world containing a variety of organic matter types and mineral assemblages. Geochemical process simulations are supposed to be part of an improved ability to predict the potential impact of HF on shallow and deeper hydrosphere at a regional scale. Scientific recommendations will be provided about mitigating risks of environmental pollution with flowback water as well as input to proper waste water treatment procedures.



2 COMPOSITION OF FRACKING FLUIDS AND FLOWBACK

2.1 Summary of literature

The growing importance of exploring gas and oil from unconventional reservoirs by HF also raises public concerns about the potential impacts on human health and the environment. Beside others, concerns are related to the enormous water demand for this technique as well as the application of tons of chemicals in the applied fracking fluids and the composition of the resulting flowback and produced waters. On the one hand, provision of these huge amounts of water may provide problems to the natural environment and drinking water supplies but on the other hand fracking fluid and flowback waters with unknown composition are feared to contain hazardous substances. The intermediate handling of these fluids as well as proper treatment are evaluated as still unsolved problems.

The applied fracking fluids generally consist of three parts: 1) the base fluid (i.e. water), 2) the additives and 3) the proppant. Each additive is a mixture of various chemicals with the main ingredient serving a specific purpose during HF (e.g. friction reducer, gelling agent, crosslinker, breakers, biocide, iron and clay stabilizer) (Spellman, 2012; Carter et al., 2013). The particular composition of the fracking fluid is selected by a design engineer based on the geological setting, reservoir geochemistry, economics, availability of chemicals, preference of the service company or operator and by empirical experience (Montgomery 2013a; US-EPA 2015b). The largest constituent of a typical fracturing fluid is water (>90%), followed by proppants (<10%) and additives (0.5 – 2%).

Chemical additives for fracking fluids are quite often described based on their function during HF and their structures that are used for the specific purposes (e.g. Waxman et al., 2011, Montgomery, 2013b, Stringfellow et al., 2014, US-EPA 2015b, Elsner & Hoelzer, 2016).

US-EPA published a detailed evaluation of the FracFocus database with respect to HF activities reported for well locations in 406 counties in 20 states from January 2011 to February 2013 (US-EPA 2015a). The database contains 692 unique chemical ingredients for additives, base fluids and proppants. Per gas disclosure, the median number of additive ingredients was 12. One or more ingredients were claimed confidential in more than 70% of the evaluated disclosures and operators designated 11% of all ingredient records as confidential business information. The most commonly reported additive ingredients for gas disclosures were hydrochloric acid, methanol and hydrotreated light petroleum distillates (Table 1). But a valid CAS-number for identification of the compounds was only assigned to about 65% of the over 1.2 million ingredients recorded in the database (US-EPA 2015a).

Due to reduced or lacking HF activities in most countries of the European Union, only few data sets exist about fracking fluid composition (e.g. check ngsfacts.org). There also seems to be the tendency to reduce the possible number of chemicals used for HF, as it is announced by ExxonMobil for future HF activities in Germany (ExxonMobil, 2017).



Table 1: Twenty most frequently reported additive ingredients in HF of gas wells, ranked by their frequency of occurrence (US-EPA 2015a).

Chemical Compound	CAS-No.	Number of Disclosures (%)
Hydrochloric acid	7647-01-0	12,351 (73%)
Methanol	67-56-1	12,269 (72%)
Distillates, petroleum, hydrotreated light	64742-47-8	11,897 (70%)
Isopropanol	67-63-0	8,008 (47%)
Water	7732-18-5	7,998 (47%)
Ethanol	64-17-5	6,325 (37%)
Propargyl alcohol	107-19-7	5,811 (34%)
Glutaraldehyde	111-30-8	5,635 (33%)
Ethylene glycol	107-21-1	5,493 (32%)
Citric acid	77-92-9	4,832 (28%)
Sodium hydroxide	1310-73-2	4,656 (27%)
Peroxydisulfuric acid, diammonium salt	7727-54-0	4,618 (27%)
Quartz	14808-60-7	3,758 (22%)
2,2-Dibromo-3-nitrilpropionamide	10222-01-2	3,668 (22%)
Sodium chloride	7647-14-5	3,608 (21%)
Guar gum	9000-30-0	3,586 (21%)
Acetic acid	64-19-7	3,563 (21%)
2-Butoxyethanol	111-76-2	3,325 (20%)
Naphthalene	91-20-3	3,294 (19%)
Solvent naphtha, petroleum, heavy arom.	64742-94-5	3,287 (19%)

After HF is completed, the pressure will be reduced and the water will flow back from the well. Initially this water, called flowback, is mostly fracking fluid, but with time, it becomes more similar to the natural formation water, e.g. increase in salinity, and decrease in DOC (Cluff et al., 2014). This late stage water is also called produced water. Composition of flowback is related to the composition of the initial fracking fluid, the composition of the natural formation water of the shale and the possible interactions between fracking fluid and shale system over time at the in-situ conditions. Concerning composition of flowback water, inorganic constituents (metals, salts), organic compounds (hydrocarbons, organic acids) and naturally occurring radioactive material (NORM) have to be considered.

Chemical characterization of flowback addresses mostly inorganic chemicals including salts, scalants and heavy metals. With respect to organic components, flowback is usually characterized using general parameters, such as total and dissolved organic carbon (TOC and DOC), oil and grease and the sum of concentrations of benzene, toluene, ethylbenzene, and xylenes (BTEX). For example, the U.S. Geological Survey National Produced Water Database contains data on TOC, DOC, biological oxygen demand (BOD), chemical oxygen demand (COD) and several individual organic compounds (methane, acetone, acetate, BTEX, phenols, ethylene glycol) but only for limited number of shale gas producing wells (Butkovskiy et al., 2017). Data on the exact composition of flowback with respect to organic compounds are still scarce, mostly because the complex nature of these liquids remains an analytical challenge (for review see Oetjen et al., 2017 and Luek and Gonsior, 2017).



Besides quality of flowback water composition, also the amount of flowback is interesting. Here, several statements on the recovery of injected fracking fluid exist. Jia declared that industry data revealed that about one third of the injected water is typically recovered (Jia et al., 2013). Stringfellow stated that the volumetric recovery of injected water in the initial or flowback period varies widely and is strongly influenced by formation characteristics; while values as low as 5% and as high as 85% have been reported, recoveries between 30% and 50% appear representative (Stringfellow et al., 2014).

In general, full disclosure of the applied HF chemicals is important to reduce the possible risks and hazards related to HF. Only when it is known which compounds are injected into the reservoir, it will be feasible to assess the possibility of subsurface reactions in the shale formation which may potentially generate new, as yet unidentified transformation products which reach the surface with the flowback. To be able to apply optimized wastewater treatment, the composition of flowback and produced water needs to be known. Knowledge of the most frequently used HF chemicals is further essential for risk assessment (environmental behavior, toxicity) (Gordalla et al., 2013).

2.2 Field study – Wysin

Within the project it was possible to get access to base water (natural water with biocide), slickwater (natural water with chemical additives but without proppant) and flowback samples from the HF activities taking place at well Wysin-2H in Poland. This horizontal borehole is drilled into Silurian shales in a depth of about 3800 m. Here, the lower part of the succession (Wenlock Formation) was drilled which is almost 2 km in thickness (Porebski et al., 2013; Montcoudiol et al., 2017).

Base water and slick water were sampled in June 2016, flowback samples were taken on different days from 1st July 2016 to 17th July 2016 and from different places like e.g. well head, gas buster, manifold or separator. The samples were analysed for inorganic constituents at GFZ, PGI and INIG, a comparison of the analytical results is given in report D10.3 (Kukulska-Zajac et al., 2017). During data reduction and interpretation it became obvious that the application of analytical routines developed for natural drinking or groundwater analysis is neither feasible for flowback waters due to their high concentrations of salts nor for the slickwater due to the high viscosity. Thus, in all labs dilution of samples was done using Millipore water or hydrochlorid acid from 1:10 up to 1:100000. For the major elements, namely Na, Ca, Sr, K, mg, Ba, Fe, Li and Mn, ranges and trends are mostly similar for all three analytical routines used. Nonetheless, given values are not similar within their uncertainties. Cl and Br were analysed as well and their concentrations are similar in range and trend and within their uncertainties. Due to sample dilution and different sensitivities for different analytical instruments, the detection limits for minor and trace elements such as Sb, As, Cr, Cu, Co, Ni, Cd and V were often higher than the concentrations in the samples. Here, the application of a High-Resolution Induced-Coupled-Plasma Mass-Spectrometer (HR-ICP-MS) with detection limit at 1ppb ($\sim\mu\text{g/l}$) for almost all elements provided exact concentrations for



all formerly mentioned minor and trace elements. For further details see Kukulska-Zajac et al., 2017.

At GFZ, organic constituents of the flowback were characterized. It is obvious that the content of dissolved organic carbon (DOC) in the flowback samples is decreasing over time from 436 mg C/l (sample taken after HF but prior to N₂ lift) to 250 mg C/l (sample taken 17 days after HF). DOC in the injected slickwater used for HF was much higher, reaching 1300 mg C/l. These samples were also analysed for the content of low molecular weight organic acid anions like formate, acetate and propionate, that have been described to be part of the flowback earlier (Akob et al., 2015). The slickwater sample contained medium amounts of formate and acetate with 14.4 and 13.1 mg/l, respectively. Concentrations of formate are in a similar range in the flowback water samples, starting from 37.7 mg/l in the first flowback and decreasing to 12.6 mg/l in the flowback taken 17 days after HF. Acetate concentration in the first flowback is about 46.2 mg/l and is increasing over time to a maximum value of 92.2 mg/l (after 7 days) and then decreasing to 47.3 mg/l in flowback taken after 17 days. Propionate was not detectable in the slickwater but is present in quite variable concentrations (from 2 to 134 mg/l) in the different flowback samples (Vieth-Hillebrand et al., in preparation).

High resolution mass spectrometry with FT-ICR-MS was done for selected flowback water samples and the slickwater to determine elemental formulas for individual dissolved organic molecules. The total number identified compounds (monoisotopic peaks) is quite low in the slickwater sample (468 peaks), but is much lower in the flowback water sampled after 6 days (229 peaks) and is higher in the flowback sampled after 13 days (982 peaks). It is interesting to note that 60 % of these compounds are unique in the slickwater and not present in the early or late flowback water samples. In contrast, in the early flowback only 1.7 % of the compounds are unique and in the late flowback 66.8 % of the compounds are unique. This indicates that on the one hand only 40 % of the injected compounds in the flowback are coming back to the surface in the investigated flowback within the first 2 weeks and on the other hand about 2/3 of the compounds in the late flowback are not present in the slickwater but seem to be derived from the shale system, formation water or transformation of the injected HF compounds.

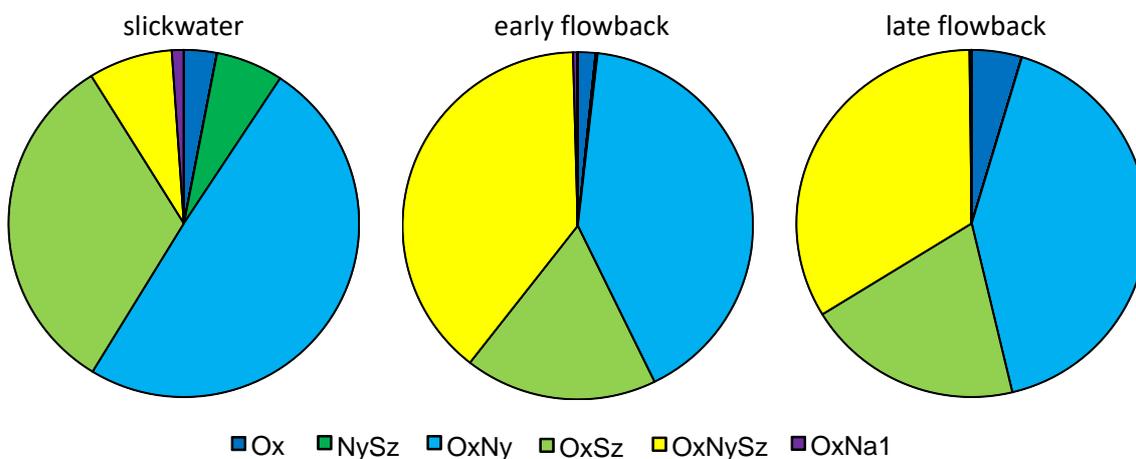


Figure 1: Pie charts displaying elemental class distribution (as percentage of total monoisotopic ion abundance) in slickwater, early and late flowback water samples from Wysin-2H as detected by ESI(-)-FT-ICR-MS.

With FT-ICR-MS, polar organic compounds containing heteroelements (like N, S, and O) in the molecular mass range between m/z 200 and 1000 are detectable. Based on the high-resolution, very precise molecular masses of individual compounds can be detected enabling calculation of individual elemental formulas. These elemental formulas are then summarized into elemental classes, as shown in Figure 1. The pie charts show relative intensities of the assigned peaks belonging to different elemental classes. Here, the elemental formulas indicate organic molecules consisting of different numbers of C, H, O, N, S and Na; however, numbers of C and H are not taken into consideration in this first step of data evaluation. FT-ICR-MS detectable compounds in the slickwater sample are dominated by organic molecules containing O and N (O_xN_y) as well as O and S (O_xS_z). In the early flowback samples, percentages of these O_xN_y and O_xS_z compounds are lower but percentage of O, N and S containing compounds ($O_xN_yS_z$) is strongly increased. Over time, only minor changes are observable in the distribution of the relative intensities of the different elemental classes, the late flowback is dominated by O_xN_y , $O_xN_yS_z$ and O_xS_z compounds (Vieth-Hillebrand et al., in preparation).



3 SIMULATION OF FLOWBACK COMPOSITION IN LAB EXPERIMENTS

3.1 Introduction – state of the art

Composition of flowback is mainly related to the composition and fate of the initial fracking fluid, the composition of the natural formation water of the shale and the interactions between fracking fluid and shale system over time at the in-situ conditions. The interactions between shale formation and the fracking fluid at in-reservoir conditions are an extremely important aspect to understand the controls on flowback water composition. Therefore, to understand those controls, the composition of the fracked shale, the initial fracking fluids, and the natural formation waters need to be analysed so that processes relevant in the reservoir can be clarified. To date, only few studies are dealing with investigation of fluid-rock interactions in shale systems under controlled lab conditions (Wilke et al., 2015; Marcon et al., 2017; Labus et al., 2017; Kahrilas et al., 2016; Paukert Vankeuren et al 2017; Vieth-Hillebrand et al., 2017).

Marcon and co-authors (2017) described lab experiments where they used a gold reactor cell filled with rock chips of Marcellus shale and compared changes in fluid chemistry when exposing rock chips with synthetic formation fluid or with synthetic formation fluid plus synthetic fracking fluid. Experiments run with temperature of 130°C, pressure of 28 MPa and a water:rock ratio of 20:1 over a time period of approx. 2 weeks. These experiments showed that clay and carbonate dissolution, secondary clay and anhydrite precipitation, and early-stage (24 to 48 h) fluid enrichment of certain elements followed by depletion in later stages (i.e. Al, Cd, Co, Cr, Cu, Ni, Sc, Zn) occurred for the Marcellus shale samples if in contact with synthetic brine and fracking fluid. Other elements such as As, Fe, Mn, Sr, and Y increased in concentration and remained elevated throughout the duration of the experiment with fracking fluid. The presence of fracking fluid resulted in release of organic compounds like formate, propionate and citrate as well as benzene, toluene and dimethylbenzene. Only in the experiment with fracking fluid, TOC of the rock chips increased by 7% during the runtime indicating sorption of fracking chemicals onto the shale.

Paukert Vankeuren and coauthors (2017) presented results of a flow-through cell experiment filled with Marcellus core material. Residence time of the different test fluids was about 100 minutes. It was the aim of this study to simulate shut-in period of HF as well as the effect of different HF fluid compositions. The focus was on re-use of produced water for HF activities. Significant mineral changes observed were calcite dissolution and barite precipitation. The effect of CO₂-based energized fracking fluid on rock samples was studied by Labus and co-authors (2017) by using an autoclave system filled with polish shale and set to temperature and pressure of 80°C and 250 bar, respectively.

The fate of the quite commonly applied biocide glutaraldehyde under the specific conditions of HF activities was investigated by Kahrilas and co-authors (2016). In their experiments stainless steel reactors were used at different temperatures and pressures and it was the aim of the work to simulate the downhole chemistry of this biocide. The



results show that glutaraldehyde rapidly autopolymerizes, forming water-soluble dimers and trimers, and eventually precipitates out at high temperatures (~ 140 °C) and/or alkaline pH. Interestingly, salinity was found to significantly inhibit transformation of glutaraldehyde. Pressure and shale did not affect the transformation and/or removal of the biocide from the bulk fluid. This study nicely demonstrates that knowledge about fate of individual chemicals under “normal” environmental conditions is not directly transferable to their behavior under downhole conditions during HF activities.

3.2 Summary of results from lab experiments

For lab experiments three potential European shale gas systems (Alum, Posidonia, Mikulov) were selected and the Marcellus shale from the Elimспорт quarry, in Pennsylvania (USA), was taken for comparison. Details about these samples were presented earlier (see Vieth-Hillebrand et al., 2016).

Water extraction was performed to evaluate the potential of the different shales to release organic and inorganic compounds when in contact with water. The effect of pressure and fracking chemicals was investigated in autoclave experiments, where the same samples were extracted with artificial fracking fluid, at the same temperature, but with higher pressure and longer run time of the experiment. The autoclave experiments lasted for about 6 days because previous results with autoclave systems using Alum and Posidonia shale samples clearly showed that extraction or mobilization occurred within the first few days of experimental run time (Wilke et al., 2015). The artificial fracking fluid contained choline chloride (clay stabilizer) and butyldiglycol (friction reducer). Aqueous samples from these experiments were analysed for their concentrations of different inorganic and organic compounds by HR-ICP-MS, IC, and LC-OCD. A special attention is given to the concentration of Th and U from European shale samples and to activities of ^{238}U and ^{226}Ra in the water extracts.

All samples show release of inorganic anions like low amounts of fluoride and nitrate. Phosphate concentrations are low in extracts from Mikulov and Posidonia shale samples but higher in Marcellus and Alum shale extracts. Release of sulfate is tremendously high in extracts of the Alum shale sample but still high in extracts of the Marcellus, Posidonia and Mikulov shale samples. The release of sulfate can be related to the presence of pyrite and pyrite oxidation. With pyrite oxidation, sulfuric acid will form and will decrease the pH of the artificial fracking fluids which itself enhances elemental extraction or mobilization. Carbonates, as present e.g. in the Posidonia shale, may buffer the pH and mitigate the elemental release (Wilke et al., 2015).

Previous results (Wilke et al., 2015) where Alum and Posidonia shale samples were extracted with an artificial fracking fluid in an autoclave system clearly showed mobilization of heavy elements like As, Cd, Co, Cr, Ni, Zn, V, Ba. This occurred preferentially within the first few days of experimental run time. In the autoclave experiments with the Marcellus outcrop sample from Elimспорт quarry, release of Sr, Mn, Ca, Li and Rb (in ppb) was detectable in the fluid samples. The sample from the Mikulov formation showed release of Ca (35 ppm), Ba (90 ppb), Sr (4.9 ppm) and Li (150 ppb) over the run-time of the autoclave experiment.



In addition, naturally occurring radioactive material (NORM) can be mobilized during shale extractions. ^{238}U series nucleides are often enriched in TOC-rich shales when U was scavenged as U(IV) under reducing conditions (Raiswell and Berner, 1985). If oxygen-containing water is injected into the shale during hydraulic fracking, it is likely that U(IV) may be oxidised to the soluble and hence readily mobile hexavalent U(VI)-oxyanions. A decrease in pH favours the release of weakly bound cations from cation exchange sites and the solubility of minerals hosting uranium. If acids form or are present in the fluids, U(IV) would be mobile even under reducing conditions (Garrels and Christ, 1965). The daughter isotope ^{226}Ra behave less mobile in natural environments and is preferentially sorbed on particle surfaces by ion exchange, such as clays, might be co-precipitated with BaSO_4 or BaCO_3 or is scavenged by Mn(IV)-hydroxides (Wilke et al., submitted).

ICP-MS data show a more than 20-times higher U content in the Alum shale (74.4 ppm) compared to the Posidonia shale (3.6 ppm). 11.1 ppm of ^{232}Th was obtained from the Alum shale and 6.6 ppm from the Posidonia shale. Under oxidizing but neutral experimental conditions about 0.2% of the uranium was mobilized from the carbonate-rich Posidonia shale. Under oxidizing and acidic experimental conditions up to 32% of the uranium from the pyrite-rich Alum shale was mobilized into the fluids. The activity of ^{238}U is as high as 23.7 mBq/ml in the fluids of the Alum shale experiments. For all Posidonia shale extracts the activity of ^{238}U is very low (≤ 0.0078 mBq/ml) or below detection limit. The activities for ^{226}Ra lie between 6.1-8.3 mBq/ml in Alum shale experiments whereas the activities of dissolved ^{226}Ra remained at about 5.2 mBq/ml for experiments with the Posidonia shale (Wilke et al., submitted). The enhanced ^{238}U and ^{226}Ra activities in the artificial fracking fluids from experiments with the Alum shale can be directly related to the much higher U-content of the Alum shales as well as to the differences in mineralogy. The Alum is characterized by high pyrite content and lack of carbonates whereas the Posidonia has similar content of pyrite but high content of carbonates. This can be related to the pH values between 2 and 3 in the artificial flowback fluids of the Alum shale experiments and pH between 7 and 8 in those experiments with the Posidonia shale. For comparison, the US Geological Survey analysed 14 production waters from Devonian Marcellus shale in Bradford County, PA and obtained ^{226}Ra activities as high as 201 mBq/ml (Rowen et al., 2011). One report from the Environmental Agency of the UK (2011) showed that the flowback from the Preese Hall well in the Bowland shale had ^{226}Ra activities between 14 and 90 mBq/ml.

All water extracts indicate release of organic acids from the shales if being in contact with hot water for 48 hours, but quality and quantity of dissolved organic acid composition are different from sample to sample (Vieth-Hillebrand et al., 2017). In previous experiments it became obvious that thermal maturity of the shale organic matter has a strong control on the organic acid composition and concentration (Zhu et al., 2015). The overmature Alum shale sample only releases low amount of acetate (water extract), but higher amounts of formate and acetate if in contact with artificial fracking fluid for 6 days. Also extracts from the mature Posidonia shale show higher concentrations of acetate and formate if being in contact with artificial fracking fluid. The immature Mikulov shale sample shows high concentrations of organic acids in the



water extract and slightly higher concentrations of acetate and formate in the autoclave samples after contact with artificial fracking fluid for 6 days.

To summarize, lab experiments showed clearly that fluid-rock interactions change the chemical composition of the fluid and this demonstrates that any simulation or modelling of flowback water composition in shale gas systems has to consider the interactions between the fracking fluid and the fractured gas shale system. This comprises e.g. organic and inorganic geochemistry of the shale, but also in-situ temperature and pressure conditions as well as the residence time of fracking chemicals (Vieth-Hillebrand et al., 2017).



4 MODELLING OF FLOWBACK COMPOSITION

4.1 Introduction

Simulation refers to using models of any physical, mathematical or otherwise logical representation of a system or process over time, very often to provide data as a basis for decision making. With regard to HF it is the final aim of model development to provide a tool which enables a risk assessment of potential shale systems to be exploited without the necessity for field experiments.

Within this project, a geochemical process model should be set-up based on studies about the chemical composition of fracking fluids (see D11.1) as well as the composition of flowback waters (see D11.2). In D11.1 the chemical composition of fracking fluids as well as flowback and produced waters from different shale gas plays in the USA, Canada and Europe was presented as highly variable. As far as possible these results are taken into account. To do that we compared various simulation codes and their underlying data sets to find the most appropriate modelling program. Within this project, samples from Posidonia (Germany), Alum (Denmark), Mikulov (Czech Republic) and Marcellus (USA) formations were investigated in lab experiments. In the lab, these shales were extracted with an artificial fracking fluid under different pressure and temperature conditions. The autoclave experiments lasted for about 6 days because extraction and/or mobilization of organic and inorganic compounds occur within the first few days of experimental run time (Wilke et al., 2015; Vieth-Hillebrand et al., 2017). The results showed clearly that flowback water compositions in shale gas systems highly depend on the fractured shale geochemistry. These experimental results were used for calibration and validation of the geochemical models.

4.2 Simulation results

Any geochemical model requires underlying datasets with thermodynamic and kinetic constants. For the simulations within this report we have used the “minteq.4v.dat” because it is the most comprehensive one and compatible with the chosen simulator PHREEQC. Nevertheless, it has to be confessed that most of the organic additives to fracking fluids are not available in the data sets, except for the organic acids. This makes clear that further work is needed to extend the existing data sets with thermodynamic and kinetic constants accordingly based on new and extensive laboratory work in the future.

The processes behind the reactions leading to mobilization of organic and inorganic compounds from the shales into the extract are unclear so far and additional research is needed (Wilke et al., 2015; Vieth-Hillebrand et al., 2017). The hypotheses we test here is the kinetically governed dissolution of parts of the shale. Beside quartz, which does not react on the investigated time scale, phyllosilicates dominate the shale samples. Our approach is to dissolve synthetic shales with varying amounts of organic acids. We have chosen kaolinite to represent the group of phyllosilicates. Compared to other components of the shales phyllosilicates react relatively slow. Therefore, the other mineral phases detected and additional ones relevant for the inorganic anions in the extract like sulphate, phosphate and fluoride were included into the system assuming



that thermodynamic equilibrium depended on the reaction progress of the synthetic shale.

Due to the lack of knowledge of the underlying processes occurring within the autoclave experiments as well as incomplete data sets, the only way to provide a process model is the data driven calibration of the four investigated shale systems. We have chosen a data driven calibration of the four investigated shale systems Posidonia (Germany), Alum (Denmark), Mikulov (Czech Republic) and Marcellus (USA) using the measured amounts of the organic acid anions (formate, acetate, oxalate and butyrate). Saline extraction fluids with sodium chloride background concentrations of 328 mg/l to 354 mg/l were defined. Calcite, pyrite, fluorapatite and anhydrite/barite are in contact with the synthetic fracking fluid (organic free due to the lack of data) available for water-rock-interactions depended on the reaction progress of the synthetic shale. The resulting concentrations of sulfate, phosphate and fluoride will be used to evaluate our hypotheses and approach to quantify mobilization of organic and inorganic compounds into the extract. The calibration works out successfully. The resulting simulated concentrations of sulfate, phosphate and fluoride as well as the pH reveal that the tested hypothesis does not meet the observations. The evaluation of our approach failed (for details see D11.3, Kühn et al., 2017). Next step could be a test if sorption processes govern the shale system behaviour.

Based on this simulation study, further research work can be deciphered: laboratory experiments are required to (1) extend the geochemical data sets with organic compounds for the simulation codes and (2) to improve the process understanding of geochemical mobilization from shales; (3) with accordingly improved models other hypotheses need to be tested.

4.3 Comparison of results from lab and modeling studies with field data

Mikulov Fm. was selected as a case study to compare the lab and modeling results with the field data. The Mikulov formation was deposited on the European passive margin in a continental slope setting with water depth of 1000-2000 m. The thickness of the Mikulov Fm. is up to 2500 m (Figure 2) and the marlstone lithology is very uniform with a few reservoir intervals where the formation water was earlier sampled. The formation extends from the Czech Republic to Austria and close to the Slovak border it is terminated by tectonics. During the Alpine and Carpathian mountain building events the SE Bohemian Massif was covered Carpathian overthrust sheets and buried to do depth of 1 to 11 km (Figures 2 and 3).

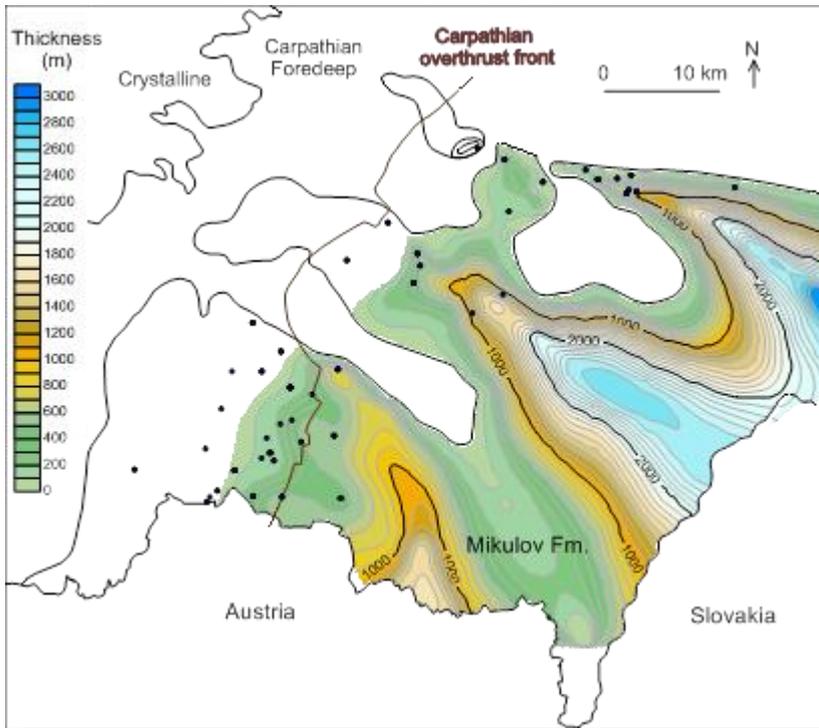


Figure 2: Regional extent and thickness of the Upper Jurassic Mikulov Formation.

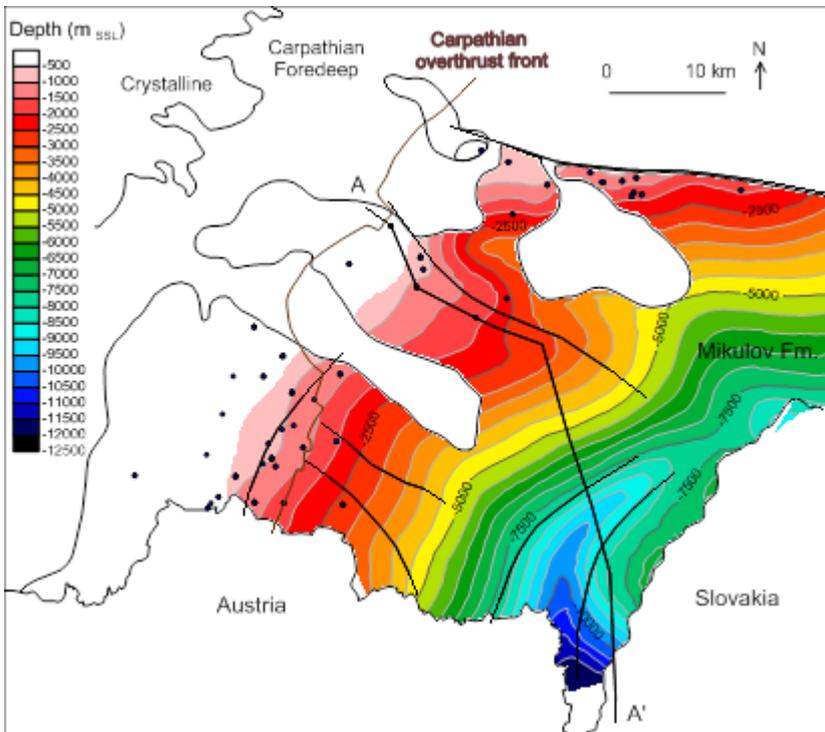


Figure 3: Depth below sea level of the top of the Upper Jurassic Mikulov Formation.



The Mikulov marls contain about 38% of carbonates and 2.3% TOC, planktonic algae form the dominant kerogen type II. Temperature gradient is 21-28 °C/km.

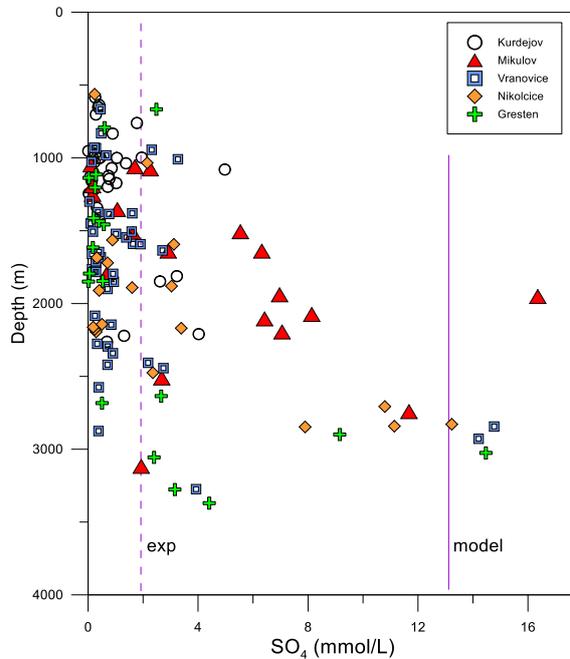


Figure 4: Amount of sulfate in relationship to depth in the Jurassic formation in the SE Bohemian Massif; the stratigraphic units are ordered from top to bottom as shown in the legend. The reference lines show the experimental (exp) and modeling results.

Even though the modelling prediction for sulfate concentration in the Mikulov Fm. is 7 times higher than the experimental data, the results of the most abundant compounds fit quite well to the field observations based on the CGS internal hydrogeochemical database. The Mikulov formation waters measured on the samples from deep wells contain between 2 and 17 mmol/L (400-1600 mg/L) sulfate (Figure 4). The modelled amounts of acetate, formate, oxalate and butyrate are in agreement with the experimental data.



5 RECOMMENDATIONS FOR RISK MITIGATION

The main objective of the work done in this work package was to get quantitative estimates on flowback water composition based on experimental data and modelling results as well as an assessment of the influence of flowback water on surface and shallow groundwater systems. This knowledge about flowback water composition should serve as base to develop scientific recommendations to mitigate risks of environmental pollution with flowback water and provide input to proper waste water treatment procedures.

To evaluate the composition of flowback water is related to extensive knowledge about composition of the applied fracking fluid, the shale composition and knowledge about possible interactions and reactions occurring in HF activities. Therefore, it is a necessary prerequisite to know the composition (quality and quantity) of the applied HF fluids. This is only possible with full disclosure of all chemical additives and their ingredients. Second, it is necessary to characterize the shale system, with its mineralogical as well as its organic composition. Also maturity of the organic matter is important, as it was observed that maturity influences the mobility of organic compounds in shale organic matter. In addition, in-situ temperature and pressure, or at least valid assumptions about them, are necessary. And third, analytical methods have to be established that are suitable for these complex samples with high salinities, various viscosities and high load of organic as well as inorganic compounds. Here, one also has to take into account that most monitoring efforts target on specific compounds, but also the unknown compounds – including unreported chemicals and transformation products – must be accounted for (Oetjen et al., 2017).

If it is known which compounds are present in HF activities, then evaluation of their fate and behavior can be done. For this, physico-chemical properties of the individual constituents as well as their transformations and degradability (abiotic and biotic) need to be known. To be able to evaluate the mobility of chemicals, the behavior of this compound under the individual/specific conditions during HF and in the shale system needs to be known. This approach is getting quite complicated if considering that routinely chemicals are tested with respect to their chemical behavior or environmental fate under “normal” environmental conditions (like temperatures of about 20 or 25°C and atmospheric pressure), but not under downhole conditions with elevated temperatures and pressures. It also has to be taken into account that in HF activities not only one chemical is applied dissolved in pure water, but a certain number of compounds is applied in base water that also contains e.g. salts and proppants. Here, the presence of a multitude of different compounds may lead to cosolvency effects, or high salt concentrations influence the load of organic compounds. In addition, the susceptibility of individual compounds to aerobic microbial degradation may become limited in the presence of high salt concentrations (>40 g/l) or may lead to longer lag periods of the microbial community (Kekacs et al., 2015).

Simulation or modelling of the flowback water composition will be very helpful prior to real HF activities. But simulation is restricted to the quality of the available chemical



data base and the knowledge about the relevant processes occurring in-situ. Here, it is obvious that available data is very limited for commonly applied organic compounds. The organic additives of fracking fluids are not available in the data sets, except for the low molecular weight organic acids. This makes clear that further work is needed to extend the existing data sets with thermodynamic and kinetic constants accordingly based on new and extensive laboratory work in the future. In addition, lab experiments are necessary to improve the process understanding of geochemical mobilization from shales. This needs to be improved to be able to provide realistic simulations about flowback water composition.

Fracking fluids, flowback and produced waters from HF activities with their critical and sometimes unknown chemical composition may provide impact on the environment in a variety of different pathways (for review see e.g. Vengosh et al., 2014). Subsurface pathways that may result in the release of fracking fluids to aquifers include failure of well integrity, improperly abandoned wells, and existing faults or fractures in geologic formations between the target formations and aquifers. The probability of groundwater contamination by these pathways is generally thought to be low. Surface pathways include spills from the transport, storage, and handling of fracking fluid additives as well as flowback water from the formation. Surface spills and releases are the more likely groundwater contamination pathway (Rogers et al., 2015). Recommendations about safe drilling techniques and fluid handling are out of the scope of this work, but environmental impact of these fluids may be reduced if the number of potentially harmful or toxic compounds is reduced and compounds with known potential to produce harmful metabolites or transformation products also should be avoided. But knowledge about the fate of applied chemicals under downhole conditions and in interaction with shales is restricted and needs to be increased with special lab and field studies dedicated to HF activities.



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