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Flow-through extraction of oil and gas shales under controlled stress using organic solvents: Implications for organic matter-related porosity and permeability changes with thermal maturity

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ABSTRACT

Four core plugs from the Lower Jurassic Posidonia Shale of the Hils Syncline in northern Germany have been subjected to flow-through extraction tests with dichloromethane (DCM) under controlled stress conditions in a tri-axial flow cell. The samples represent a maturity sequence from 0.53 to 1.45% VRr. The bitumen sequentially extracted from the natural pore space of the shale plugs was analyzed for its geochemical composition. Changes in rock matrix density, porosity and permeability resulting from the removal of soluble organic matter were determined. The relative porosity increase of the plugs after extraction ranged from 6 to 13% and correlated with the extract yield. Klinkenberg-corrected permeability coefficients measured with helium increased by a factor of 17.0 for the immature/early mature sample and 26.6 for the overmature sample. Petrographical investigations after extraction indicate that fluid flow occurred predominantly parallel to bedding as evidenced by open fractures and fractures bearing residues that apparently precipitated from the DCM solution. Compositional variations of the extracts over time are interpreted in terms of the organic geochemical inventory of bitumen associated with the natural pore system and its accessibility at different maturity levels. These patterns deviate strongly from the bulk rock extracts of the powdered samples.

1. Introduction

Increased production from unconventional hydrocarbon resources in the US has led to a scientific and industrial focus on oil and gas shales in Europe. In several European countries, geological surveys and petroleum companies have started to evaluate and characterize abundant black shale formations for their prospectivity and gas shale properties such as organic richness, thermal maturity, porosity and matrix permeability (Horsfield and Schulz, 2010). In Germany, three formations are regarded as the most important targets for gas shale exploration: the Lower Carboniferous Upper Alum Shale (Uffmann et al., 2012), the Lower Jurassic Posidonia Shale (Bruns et al., 2013) and the Lower Cretaceous Wealden Shale (Berner, 2011; Rippen et al., 2013). Among these promising black shale formations, the Posidonia Shale of the Lower Saxony Basin is the most well-known and investigated one. Core material from the Hils Syncline, representing a complete maturity range of the Posidonia Shale from immature to overmature samples has been studied intensively in the past (e.g. Leythaeuser et al., 1988; Littke et al., 1988; Rullkötter et al., 1988; Littke et al., 1991a, 1991b, 1991c; Sundararaman et al., 1993; Bernard et al., 2012). While most of these studies dealt with the organic petrological, organic geochemical and sedimentological properties, recent publications by the GASH (Gas Shales in Europe) Consortium research framework focused also on the petrophysical characterization of these fine grained sedimentary rocks. These investigations included measurements of permeability with different permeating fluids (Ghanizadeh et al., 2014) and determination of porosity and gas sorption capacity (Gasparik et al., 2014).

Systematic and significant changes in porosity and permeability of black shales due to thermal maturation have been documented. Ghanizadeh et al. (2014) report a decrease in porosity by up to 70% from the immature to mature stage of the Posidonia Shale. Similar observations have been made for other gas shales such as the New Albany Shale (Mastalerz et al., 2013). This development has been attributed to pore throat or pore plugging by hydrocarbons generated in the "oil window". With ongoing maturation and upon entering the gas window, porosities are reported to increase again. In overmature samples, secondary cracking of primary petroleum (mostly solid bitumen) creates secondary porosity (Bernard et al., 2012). Due to the interconnectivity of this secondary pore system, a significant increase of permeability can be observed over the same maturity range (Ghanizadeh et al., 2014). Nevertheless, isolated pores that do not contribute to permeability can still exist

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within organic matter as known from coal research (Giffin et al., 2013). Furthermore, recent studies on the Woodford shale suggest more complex dependencies of intra-organic porosity evolution during thermal maturation on organic matter composition and the mineral matrix (Curtis et al., 2012). Estimating the accessible porosity and permeability in the oil and gas mature stage of black shales is crucial for the successful production from oil and gas shales. Porosity not only influences the maximum amount of free gas/oil that can be stored in carbonaceous shales butalso controls the accessibility of sorption surfaces of organic matter and clay minerals. In addition, rock matrix permeability directly influences the production performance of shales.

This study was undertaken to investigate how soluble organic matter (bitumen) is distributed in the pore space of carbonaceous shales of different maturity levels and how it influences porosity and permeability with progressing thermal maturation. In particular it aimed for estimating the portion of transport porosity occupied by bitumen (in the immature stage) and residual bitumen (e.g. solid bitumen, in a petrographical sense) in mature to overmature stages.

Flow-through extraction experiments were performed in tri-axial flow cells under in-situ stress conditions using the organic solvent dichloromethane (DCM) as permeate.

By reconstituting in-situ stress conditions it was attempted to close artificial pathways (fractures, cracks) resulting from stress relief and sample preparation. Permeability measurements were conducted before and after the extraction runs to estimate changes in pore interconnectivity and effective transport porosity.

In addition, the extracts collected in long-term flow tests were examined to assess the compositional differences of solid bitumen in larger and smaller pores. For this purpose the bulk and sequential extracts were screened by thin-layer chromatography combined with a flame ionization detector (TLC-FID).

2. Samples

The flow-through solvent extraction experiments described here were conducted on core plugs of the Lower Jurassic (Toarcian) Posidonia Shale collected from three shallow wells from the Hils Syncline in the Lower Saxony Basin (Littke et al., 1991a). The sample set represents a complete range of thermal maturity ranging from immature (Wickensen; 0.53% random vitrinite reflectance (VR_r)), oil-window maturity (Harderode; 0.88% VR_r) and overmature (Haddessen; 1.45% VR_r). The actual plugs and sample coding used in this work are the same as in the work of Ghanizadeh et al. (2014) (Table 1).

3. Experimental

3.1. Permeability and flow-through solvent extraction experiments

3.1.1. Experimental setup

Fig. 1 shows a flow-scheme of the experimental setup used for the flow-through extraction tests and the permeability measurements conducted in this study. The “triaxial” flow cell in this setup is used to apply stress on the sample during measurements and extraction. These cells were constructed to accommodate samples of 28.5 mm diameter and lengths of several millimeters to a few centimeters. Axial load is operated by cylindrical pistons, while confining pressure (P_{conf}) is applied via a high-pressure liquid chromatography (HPLC) pump using water as confining fluid. Axial load and confining pressure can be controlled and adjusted independently. Stainless steel metal filters are installed above and below the sample to divert and disperse the fluid flow.

This setup effectively creates two compartments of defined volumes depending on the lengths of the piston capillaries and the void volume of the metal filters, separated by the sample plug. Additionally, each compartment is connected to a pressure transducer (P_{up}, P_{down} in Fig. 1). Before each experiment run, the volumes of the compartments were determined by helium expansion from a calibrated volume.

Three valves are connected to the triaxial cell as shown in Fig. 1. Valve V1 is used for fluid selection and allows a rapid change from gas supplied from a pressure cylinder and solvent (DCM) provided by a HPLC pump operated in constant pressure mode. Valve V2 is used for opening and closing the upstream compartment. Valve V3 is used for pressure equilibration between the upstream and downstream compartments and as a fluid outlet through the graduated pipette. Extract sampling was then performed through valve V4, allowing gravity-driven flow of the fluid from the graduated pipette into the sampling vial.

3.2. Workflow

The workflow of the experimental procedure is shown in Fig. 2. The sample plugs were first dried in a vacuum oven at 105 °C and their dimensions and weights were recorded. Subsequently their grain density (skeletal density) and porosity was determined. After installing the samples in the triaxial flow cell their permeability coefficients were determined as a function of stress using helium as permeating fluid.

Table 1
Petrophysical and elemental geochemical characteristics of source rock samples before flow-through extraction.

Before extraction					
General information	Sample number	10/116	10/105	10/102	10/111
	Well	Wickensen	Harderode	Harderode	Haddessen
	Plug orientation relative to bedding	⊥	⊥	II	⊥
	Depth (m)	54.6	66.8	44.5	60.6
	Thermal maturity (% VRr)	0.53	0.88	0.88	1.45
Petrophysical properties	Plug height (mm)	6.0	17.1	15.5	13.3
	Plug diameter (mm)	28.3	28.1	28.3	28.0
	Plug weight (dry; g)	7.3872	25.7963	22.5935	18.8588
	Porosity (v.%)	17.8	4.9	5.2	13.4
	Skeletal density (g/cm^3)	2.35	2.54	2.48	2.65
	Klinkenberg corrected permeability (nD)	61.1	0.8	28.3	35.9
Elemental/bulk geochemistry	TOC (wt.%)	13.02	5.89	7.90	6.44
	TIC (wt.%)	5.70	3.98	6.06	6.62
	Tmax (°C)	427	443	445	463
	S1 (mg HC/g rock)	5.07	1.55	3.86	1.49
	S2 (mg HC/g rock)	83.20	24.23	32.03	5.16
	HI (mg/g TOC)	639	411	405	80
	OI (mg/g TOC)	21	24	17	23
	PI	0.06	0.06	0.11	0.22
	BI	0.39	0.26	0.49	0.23
	Bulk extraction yield (SE_i; g bitumen/g TOC)	0.0267	0.0388	0.0411	0.0289