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Activity concentrations of ^{238}U and ^{226}Ra in two European black shales and their experimentally-derived leachates

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ABSTRACT

The production of gas from unconventional resources became an important position in the world energy economics. In 2012, the European Commission's Joint Research Centre estimate 16 trillion cubic meters (Tcm) of technically recoverable shale gas in Europe. Taking into account that the exploitation of unconventional gas can be accompanied by serious health risks due to the release of toxic chemical components and natural occurring radionuclides into the return flow water and their near-surface accumulation in secondary precipitates, we investigated the release of U, Th and Ra from black shales by interaction with drilling fluids containing additives that are commonly employed for shale gas exploitation.

We performed leaching tests at elevated temperatures and pressures with an Alum black shale from Bornholm, Denmark and a Posidonia black shale from Lower Saxony, Germany. The Alum shale is a carbonate free black shale with pyrite and barite, containing 74.4 µg/g U. The Posidonia shales is a calcareous shale with pyrite but without detectable amounts of barite containing 3.6 µg/g U.

Pyrite oxidized during the tests forming sulfuric acid which lowered the pH on values between 2 and 3 of the extraction fluid from the Alum shale favoring a release of U from the Alum shale to the fluid during the short-term and in the beginning of the long-term experiments. The activity concentration of ^{238}U is as high as 23.9 mBq/ml in the fluid for those experiments. The release of U and Th into the fluid is almost independent of pressure. The amount of uranium in the European shales is similar to that of the Marcellus Shale in the United States but the daughter product of ^{238}U, the ^{226}Ra activity concentrations in the experimentally derived leachates from the European shales are quite low in comparison to that found in industrially derived flowback fluids from the Marcellus shale. This difference could mainly be due to missing Cl in the reaction fluid used in our experiments and a lower fluid to solid ratio in the industrial plays than in the experiments due to subsequent fracking and minute cracks from which Ra can easily be released.

1. Introduction

Increasing gas production from unconventional shale gas plays in the United States (U.S.) and the related engineering improvements for shale gas production in terms of drilling and hydraulic fracturing took also exploitation of European shale gas under consideration. The U.S. Energy Information Administration (U.S. EIA, 2013) estimated that Europe could hold 13.4 Tcm (trillion cubic meters) technically recoverable shale gas. A similar value of 15.9 Tcm was estimated by the European Commission's Joint Research Centre (JRC, 2012). 132 shale gas exploitation and appraisal wells have been drilled in Europe so far, most of them in Poland, Sweden and the UK (AAPG, 2016). Due to commercial viability, political barriers and public concerns, roughly 2/3 of all companies relinquished their concessions or let them expire (AAPG, 2016). In Germany, eight wells were drilled since 2008 in the Wealden or in the Posidonia formation (both Lower Saxony) but no details about the gas flow were published. One well was drilled in the Alum shale in Denmark and the drilling of 17 shallow wells into the Alum shale of Ostergötland is reported for Sweden from which only some showed a gas flow (AAPG, 2016).

The production of unconventional gas is linked with a high-pressure injection of several thousand cubic meters of water for each well (Gregory et al., 2011; SEAB, 2011) to create minute cracks in which hydrocarbons can flow to the wellbore. The formation and the operator determine the composition of the suspension for injection that is generally made of 90% water, 9–9.5% sand or ceramics and 1–0.5%

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chemical additives (e.g. Arthur et al., 2008; King, 2012; Wood et al., 2011). Additives could include small volumes of mainly hydrochloric acid (< 10 m^3) injected during the initial stage of the gas exploitation to clean perforation tunnels and dissolve carbonate precipitates that seal veins. Chelating agents (e.g. citric, acetic acid) are added to the fracturing fluid to prevent the precipitation of iron and manganese compounds. Additional ingredients of the fracturing fluid could be corrosion inhibitors, friction reducers, surfactants, clay stabilizers, biocides and cross-linkers tailored for the specific lithological conditions (e.g. Arthur et al., 2008; Stringfellow et al., 2014). In practice, 10–80% of the injected suspension returns to the surface: the so called flowback (Arthur et al., 2008; Wood et al., 2011). The amount of flowback depends on formation characteristics, well design and operating parameters.

To date, much of the research on the environmental impacts of unconventional gas production is related to the origin of gas leakages during drilling, exploitation and production (e.g. Molofsky et al., 2013), the chemical composition of the flowback (e.g. Barbot et al., 2013; Chermak and Schreiber, 2014; Dieterich et al., 2016; Gregory et al., 2011; Gordalla et al., 2013; Renock et al., 2016), the release of microbiota and organic molecules from the shales (e.g. Hölzer et al., 2016; Strong et al., 2013; Zhu et al., 2015) and the enrichment of toxic trace elements like As, Cd, Co, Cr, Hg, Ni, Zn, U, V in the flowback (e.g. Marcon et al., 2017; Wilke et al., 2015; Chermak and Schreiber, 2014 and references therein). Some studies deal with the release of naturally occurring radionuclides (NORs) of oil- and gas-field produced waters, scales or drill cuttings but these studies cover only very specific areas such as the Marcellus shale in the Appalachian Basin (U.S.) (e.g. Chen and Sharma, 2016; Phan et al., 2015; Nelson et al., 2015, 2014; Haluszczak et al., 2012; Rowan et al., 2011; NYSDEC, 2009), the Bowland shale in the UK (Environment Agency, 2011) or one shale in Pomerania, Poland (Mykowska et al., 2015; Mykowska and Hupka, 2014). Therein, the focus is on alpha particle emitter of the ^{238}U -, ^{235}U - and ^{232}Th - decay series e.g. ^{226}Ra (Fig. 1).

^{238}U series nuclides are often enriched in TOC-rich shales when U was scavenged as U(IV) under reducing conditions (e.g. Chen and Sharma, 2016; Chermak and Schreiber, 2014; Schovsbo, 2002; Stetten et al., 2018; Raiswell and Berner, 1985). It can be assumed that the reservoir of leachable U-series nuclides initially relates dominantly to scavenging and/or chemical precipitation of uranium from weathering fluids whereas the proportion of U^{238}- and Th^{232}-series nuclides remobilized from weathering resistant minerals (e.g. zircon) is negligible. Uranium may be initially co-precipitated with Fe(Mn)OOH (Muller et al., 1995 and references therein) or hosting in biogenic calcite (Russell et al., 1994) and may be initially or post-depositional immobilized as U(IV) to form, e.g. secondary uraninite (UO_2), coffeinite ($U(SiO_4)_{1-x}(OH)_{4x}$) or autunite ($Ca[(UO_2)(PO_4)]_2 \cdot 10–12\ H_2O$), depending on the composition of the coexisting fluids during early stages of sediment burial (Duff et al., 2002; Fredrickson et al., 2000; Cumberland et al., 2016; Lecomte et al., 2017).

The release of U into the drilling fluid may depend on the amount of leachable U available from the shale deposits processed for gas exploitation but also from the carbonate and sulfide contents of the shale (e.g. Nelson et al., 2015; Wilke et al., 2015). Interaction of pyrite-rich shales with oxic fluids generates sulfuric acid that dissolves carbonates and can generate fluids with low pH when the buffering capacity of the carbonate gets exhausted (Chermak and Schreiber, 2014; Wilke et al., 2015). Decrease in pH favors the release of weakly bound cations from cation exchange sites and the solubility of minerals hosting uranium. If acids are present, either as ingredient in the fracturing fluid or formed by fluid-rock interactions during the course of shale gas production, U(IV) would be mobile even under reducing conditions (Garrels and Christ, 1965). Oxygen-containing fluids force the formation of easily soluble U(VI)-oxyanions. U(VI) or U(IV) release due to pH decrease during solid-fluid interactions may be associated with the formation of less soluble secondary U(VI) or U(IV) precipitates with CO_3^{2-} or PO_4^{3-} that may counteract uranium increase in the return fluids (Sanding & Bruno, 1992; Stetten et al., 2018).

^{226}Ra ($T_{1/2}$ = 1600 a; ^{238}U - series) and ^{228}Ra ($T_{1/2}$ = 5.76 a; ^{232}Th-series) behave less mobile in natural environments (e.g. Vengosh et al., 2014), though they frequently show slightly enhanced activities in groundwater compared to their activities in surface waters (Schettler et al., 2015 and references therein). ^{226}Ra and ^{228}Ra are preferentially sorbed to ion-exchange sites of particle surfaces (Ames et al., 1983), get co-precipitated with $BaSO_4$ or $BaCO_3$ (Langmuir and Riese, 1985) or may be taken up by plants (Bettencourt et al., 1988). Moreover, Ra is efficiently scavenged by Mn(IV)-hydroxides which finds analytical application as a pre-concentration step for Ra (Charette et al., 2015 and references therein). These reactions will lower the concentration of dissolved Ra in the drilling fluid and can yield substantial accumulative enrichments of Ra and its decay products (^{210}Pb, ^{210}Po) in coexisting solids at near-surface compartments (e.g. Nelson et al., 2015 and references therein).

In this study, we determine and assess the activity concentrations of ^{238}U, and ^{232}Th from one Alum and one Posidonian black shale and, furthermore, the activity concentration of ^{238}U and the radioactive decay product ^{226}Ra from the experimentally derived black shale leachates. We intend to increase the knowledge about the amount of radioactive elements that might be enclosed in the drill cutting waste and that may become mobilized from black shales into the fluids, the radioactivity they produce and how European shales prospected for gas production differ in this topic from shales used for unconventional gas production in the U.S. (e.g. the Marcellus shales).

2. Experimental settings

2.1. Black shales

A black shale sample from the Upper Cambrian Alum shale of Scandinavia (Skelbro-2, Bornholm, Denmark) and one from the lower Jurassic Posidonia shale of central Europe (Haddessen, NW-Germany) were chosen to simulate temporal changes in the composition of flow back water by solid/fluid interaction in lab experiments under defined conditions (Table 1; Fig. 2; see Wilke et al., 2015 for details). The

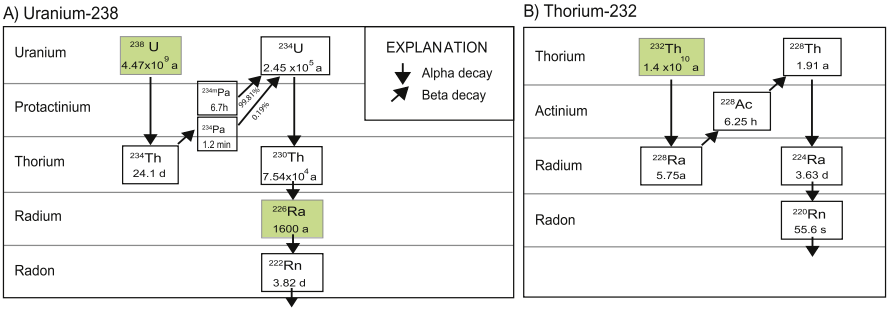

Fig. 1. Upper radioactive decay chains for A) ^{238}U and B) ^{232}Th. Half-lives are given: a = years, d = days, h = hours, m = minutes, s = seconds. Half-lives from the international nuclear structure and decay data network under the auspices of the IAEA. https://www-nds.iaea.org/relnsd/NdsEnsdf/QueryForm.html. Radionuclides marked by a green background were quantitatively determined for this study.

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