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MOBILITY OF SHALE DRILL CUTTINGS CONSTITUENTS

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Abstract: This study focuses on the abundance and mobility of metals and trace elements from shale drill cuttings into water, being the main component of the hydraulic fracturing fluid. The relationship between composition of the shale rock and the potential element release during standard water-based leaching tests was characterized by means of X-Ray Fluorescence spectroscopy (XRF). The XRF analysis confirmed the assumption of shales constituents mobility due to the water-rocks interaction. The mobility of studied constituents was expressed by means of variations in content of individual elements. Increased pH of leachates obtained as a result of water based leaching medium indicated releasing of alkaline origin components such as Ca, Rb, Mo, Sr. Measurements of TOC of the leachates indicated low levels of dissolved organic carbon.

Keywords: *shale, gas, flowback fluid, liquid residue, leaching, fracturing*

Introduction

Production of large amounts of flowback fluid is an important issue in Poland as a potential region for shale gas production. Treatment and recycling of the flowback may pose additional concerns due to leachability of chemicals deposited from the geological formations, which may pose risks to aquatic biota if directly discharged to the environment, and create problems in re-using of the fluid (Fakhru'l-Razi et al. 2009). Leaching is a process by which constituents soluble in liquid migrate from a solid material into an interacting fluid. As a consequence, this phenomenon may lead to formation of liquid waste with characteristics depending on the chemical and physical composition of the shale formation, the operational conditions of fracturing, along with pH, redox potential and composition of the contacting fluid (Heasman et al. 1997). The release of constituents is determined by a confluence of mass transfer mechanisms and chemical processes (Klein 1989).

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The longer the hydraulic fluid remains in the reservoir, the more significant the change in composition is. Therefore, the flowback in first few weeks after fracturing is characterized by a high flow rate and composition similar to the liquid introduced into the bed. After this period, the flow rate steadily decrease and the output stream is referred to as liquid residues. These include the remaining part of the fracturing fluid and the reservoir water. Consequently, the liquid composition changes significantly (Tessier et al. 1979). Along with the chemicals introduced with the HFF, the flowback fluid may contain a wide variety of dissolved constituents such as dissolved minerals, dissolved and dispersed oil compounds, salts, metal ions, naturally occurring radioactive materials (NORM), and dissolved gases (Johnson et al. 2008). Therefore, the chemical and physical characteristics of the shale formations and these waters are needed, and the constituents of concern should be identified. These components can make wastewater disposal difficult, and expensive and in addition may impair gas production (Fakhru'l-Razi et al. 2009). Consequently, the flowback may be considered hazardous and require treatment by using suitable technology giving harmless and valuable product to meet environmental regulations and be able to be reused (Calmano et al. 1993).

The elemental and mineralogical characteristics of the shale rocks and flowback fluids has been carried out by various research groups using different analytical methods. Falk and coworkers (2006) used Inductively Coupled Plasma Mass Spectrometry (ICP-MS) and Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) techniques to observe metals release and changes in pH during leaching test performed with water adjusted to pH 4.0. It was revealed that the concentration of heavy metals in leachate significantly increase in time along with pH decrease (Falk et al. 2006). The release by weathering of selected heavy metals and traces elements was investigated by Peng and co-authors by means of the ICP-MS analytical technique. It was concluded that weathering may be one of the most important sources of environmental contamination with heavy metals and traces elements in areas where black shales are collected and distributed (Peng et al. 2004). Chemical and mineralogical analysis of serpentinite rock samples to characterize the effect of weathering of toxic Cr and Ni metals was examined by Baneschi et al. (2013) by scanning electron microscopy (SEM), electron microprobe (EMP), X-Ray Fluorescence (XRF). To obtain quantitative information about the distribution of trace metals in different mineralogical phases (clay minerals, carbonates, amorphous Fe, Mn oxides, organic matter and other silicates and oxides) a seven-steps sequential extraction analysis was performed. The results suggest that Cr and Ni could be adsorbed by amorphous Mn and Fe hydroxides after the weathering of serpentinites and may be released at different redox conditions, increasing in this way their mobility in the environment (Baneschi et al. 2013). Chapman et al. (2012) tested samples of both hydraulic fracturing fluids and flowback produced during drilling process at Middle Devonian Marcellus Shale wellheads. Investigation was carried out to determine the utility of Sr isotopes in identifying and quantifying the interaction of produced waters with other waters in the region in the event of an accidental release. The Sr isotope was found out to constitute an extremely sensitive tracer with strong potential as a tool for verification the safety of water disposal, and to determine the origin of total dissolved solids (TDS) in surface and ground waters. Major elements and Sr isotope geochemistry were analyzed by ICP-MS and ICP-AES (Chapman et al. 2012).

Background

Sedimentary shale formations, and as a consequence drill cuttings, are composed mainly of inorganic materials such as clay minerals (illite, smectite, kaolinite, chlorite, biotite, mica), and siliciclastic minerals (quartz, sandstone, feldspar, orthoclase, plagioclase, biotite etc.), though carbonates (dolomite, calcite, limestone ect.) also occur. Shale rocks are enriched in kerogen, a mixture of organic substances, which brake down to form hydrocarbons (Durand 1980). The relative proportions of inorganic and organic materials in generated waste material depend on geology of shale formations varied with organic phase from the drilling fluid used in the vertical and horizontal drilling procedure. The composition of shale rocks as well as some geological properties of selected shale formations in USA, Canada, and Poland were collected and compared in Table 1. The brittle minerals content represented by siliciclastic and carbonate fractions is an important criterion to assess the shales potential for proper respond to hydraulic stimulation and formation of the tree-shaped network of fractures, favorable for gas extraction. Shales with a high percentage of quartz and carbonate as well as presence of illite provide more easily fracturing and breaking to a wide range of small-scale fractures providing numerous flow paths from the matrix to the wellbore. On the contrary, the high amount of ductile clays will result in the deformation of the bed instead of fracturing providing only few induces fractures (Zou et al. 2010). Therefore, shale formations with high quartz and low clay content typically have high Young’s modulus and low Poisson’s ratio making them more brittle, more prone to natural fractures, and good candidates for proper respond to hydraulic stimulation (Jaeger et al. 2009). The relation between siliciclastic, carbonate minerals and clays content is related with a depositional environment of the shale. It was observed that marine-deposited shales tend to have lower clay content along with higher amount of brittle minerals in comparison to non-marine shales being lacustrine, fluvial deposits as shown in Table 1 (Alexander et al. 2011).

For commercial development deposits with fragile mineral content over 40%, and clay content less than 30% are usually chosen. The average quartz content of shale gas formations in USA is 28–50%, with carbonate content of 4–16%, and total fragile mineral content is on average 46–60% (Zou et al. 2010). In classical example of shale formations Barnett shale in Fort Worth Basin (Texas, USA), being the non-marine deposits, the clay contend is assessed to be 20–50%, siliclastic minerals 35-50%, and carbonate fractions 0–30%. In comparison, in marine deposited Marcellus shale in

Appalachian Basin (eastern North America, USA) may contain from 20 to even 60% siliclastic minerals, 3–50 carbonate fractions, and lower clay content 10–35% (Bruner et al. 2011). Shale rocks in Poland are mainly marine-deposited formations, however the local structural geology is still poorly understood. Some early shale exploration revealed that quartz content in selected areas can be favorably high (40–80%), however along with high conducive to effective fracture stimulation clay content (30-40%). Further exploration drilling and seismic surveys are still needed to define potential sweet spots in Poland (EIA 2013).

To define the prospective area for development of shale gas, the parameters as total organic content (TOC) as well as thermal maturity are also used. High enough TOC content is required to generate and hold satisfactory gas level for commercial production. General grouping of shales based on TOC content (in wt% of rock) starts from non-source (<0.5), fair (0.5-1.0), good (1.0-2.0), and excellent gas source (>2) (Zhu et al. 2011). The TOC values for shale formations presented in Tab.1 are in the range of 0.5 to even 14 (wt%). For example in Barnett shale gas formation the TOC content was determined to be on average 2–6%, in Marcellus shale 2–10% (Jarvie et al. 2007), and the average TOC value in USA appears to be from 1,3% to 4% wt (Poprawa 2010). The TOC range of Polish samples was recognized to be quite high (1–14%) (EIA 2013). The main stratigraphic targets for shale gas exploration in Poland is approximately 500 m of high resistivity, and the high-TOC. According to the available data, the TOC values are in the range of 2–4% and 6% in Llandovery Baltic Basin section, and Podlasie Basin, respectively. The Upper Cambrian to Tremadocian shale, present only in the northern part of the Baltic Basin, contains high average TOC of 3–12% (EIA 2013).

Thermal maturity of the mineral formation can be indicated by vitrinite reflectance (VR expressed as $\%R_o$) as a measure of degree to which organic metamorphism has progressed. The higher thermal maturity, the lower TOC content of the formation and for hydrocarbon generation VR seems to be more than 0.5%.

The thermal maturity of the oil prone prospective area has a $\%R_o$ greater than 0.7, but less than 1.0%, the wet gas and condensate are between 1.0% and 1.3%, whereas dry gas areas typically have an R_o greater than 1.3% (EIA 2013). For presented in Tab.1 shale formations VR varied between 0.3 and below 4 (Jarvie et al. 2005). The Barnett shale VR, reflecting the beginning of dry gas ($\%R_o = 1.2$), is considerably lower than for Marcellus shale ($\% R_o = 1.6$), and attributed to chemical interactions between petroleum, kerogen, and clay minerals in the shale or to a slow geological heating rate (Bruner et al. 2011).

In Poland $\%R_o$ was observed to be in between 0.85 for Lower Silurian to 1.8 for Upper Cambrian formations in all regions (Lis et al. 2000). The Upper Jurassic and Lower Cretaceous in the Baltic Basin locally have TOC >1.5%, but are thermally immature (R_o 0.5% to 0.7%), therefore were not assessed as potential area for gas exploration. For comparison, the Carboniferous shale in the Fore-Sudetic Monocline contains 1% to 5% TOC, is located in the dry gas thermal maturity window (R_o of 1.3% to 2.0%), and contains 20% to 60% silica with 2% to 8% total porosity.

As it was mentioned above some bed of shales are known to contain also trace metals (including heavy metals) or even are enriched in metals (Vine and Tourtelot, 1970). Systematic research on metal content in rocks, sediments, waters and biological substances revealed, that organic carbon-rich sediments are often enriched in metals, like Mo, V, Cu, Zn, or U probably due to their abundance in seawater (Goldschmidt 1954; Brumsack 2006). Trace elements can interact both with inorganic and organic compounds of shale formations. According to the Vine and Tourtelot (1970) the trace elements can be divided into connected with detrital minerals (Al, Ti, Ga, Zr, Sc), carbonate formations (Ca, Mg, Mn, Sr), and organic associations (Ag, Mo, Zn, Ni, Cu, Cr, V) (Brumsack 2006).

Tab. 1. Comparison of shale formation components

Shale Formation	TOC (%)	R_o (%)	Component (wt.%)	Chemical Elements
Barnett (USA); Non–marine–deposited shales (1)	2.0–7.0	1.10–2.00	Clay minerals (20–25/50): Illite, Smectite, Kaolinite, Siliciclastic fraction (35–50%): Quartz (40), Feldspar (7), Plagioclase (5) Carbonate minerals (0–30): Calcite, Dolomite, Siderite Other: Pyrite (2–6)	Sr, F, Ba, As, B, Br, U, Ag, Co, Cr, Cu, Mo, Ni, U, V, Zn, Th, Ra^{226}, Ra^{228}
Fayetteville (USA) Non–marine–deposited shales (2)	2.0–9.8	1.20–>4.00	Clay minerals: Chlorite (<5), Illite (20–25) Siliciclastic fraction: Quartz (40–50) Carbonate minerals: Calcite (5–10), Dolomite (5–10)	Fe, Mg, Al, K, Fe, Cr, Th, Zr, Co, Ti
Haynesville (USA) marine–deposited shale (3)	0.5–4.0	2.20–3.20	Clay minerals (25–35%): Illite, Kaolinite, Chlorite (25–35) Siliciclastic fraction (34%): Quartz, Potassium Feldspar, Dolomite, Plagioclase Carbonate minerals: Calcite (5–30%), Dolomite, Fe–Dolomite	Fe, Mg, Al, K, Cr, Zr, V, Co, Ni, U, S
Marcellus (USA) marine–deposited shales (4)	3.0–12.0	1.50–3.00	Clay minerals (10–35%): Illite, Smectite, Biotite, Montmorillonite Siliciclastic fraction (20–60%): Quartz, Muscovite, Feldspar (0–4), Mica (5–13) Carbonate minerals (3–50): Trona Other: Todorokite, Pyrite (5–13)	Ti, Na, Li, Ba Sr, Cs Cr, Mn, Mg, Al, Fe, ^{238}U,
Woodford (USA) marine–deposited shales (5)	1.0–14.0	1.10–3.00	Clay minerals: Illite (13–40%), Kaolinite (1–5%), Chlorite (0–5%) Siliciclastic fraction: Quartz (30–60), Mica, Feldspar (2–10%), Glauconite, Plagioclase (1–4%) Carbonate minerals (6–28%): Calcite (5–11%), Dolomite (0–9%) Other: Pyrite (0–20%), Apatite	Fe, Mg, Al, K, Cr, Pb, Bi, Ti, Cu, Zn, Co, V, Mo, U, S

Shale Formation	TOC (%)	R_o (%)	Component (wt.%)	Chemical Elements
Pierre (Canada) marine–deposited shales (6)	1.0–6.0		Clay minerals (60–70): Smectite (20), Illite (6), Kaolinite (11) Siliciclastic fraction: Quartz (20–43), Orthoclase (2), Plagioclase (7), Feldspar Carbonate minerals (5): Calcite (2), Siderite (2) Other: Pyrite (1)	Fe, Mg, Al, K, Cr, Ti, V, Co, Cu, Pb, Zn, As,
New Albany (USA) (7)	>1.0–13.00	0.5–1.0	Clay minerals: Siliciclastic fraction: Quartz, Feldspar, Glauconite Carbonate minerals: Dolomite Other: Pyrite, Phosphorite	Fe, P, F, U, Cu, Pb, Zn, Ni, Cd, Co, Mn, Mo, V, Sb, Se
Baltic Basin (8) Poland average	1–6 3.9	1–2.6 0.85–1.8	Clay minerals (30–48/80%) Siliciclastic fraction (25–63%)Clay minerals (30–40%) Siliciclastic fraction: quartz (40–80%)	Ca, K, Na, Mg, Zr, Ti, Fe, Mn, Cr,, Al, V, B, F

[*] Apatite $Ca_5(PO_4)_3(F,Cl,OH)$
Calcite $CaCO_3$
Dolomite $(CaMg)(CO_3)_2$
Glauconite $(K,Na)(Fe^{3+},Al,Mg)_2(Si,Al)_4O_{10}(OH)$
Kaolinite $Al_2Si_2O_5(OH)_4$
Pyrite Fe_2S
Plagioclase $NaAlSi_3O_8 – CaAl_2Si_2O_8$
Todorokite $(Na,Ca,K,Ba,Sr)_{1-x}(Mn,Mg,Al)_6O_{12}\cdot 3\text{-}4H_2$
Biotite $K(Mg,Fe)_3(AlSi_3O_{10})(OH,F)_2$
Chlorite $(Mg,Fe)_3(Si,Al)_4O_{10}(OH)_2\cdot(Mg,Fe)_3(OH)_6$
Feldspar $(KAlSi_3O_8 – NaAlSi_3O_8 – CaAl_2Si_2O_8)$
Illite $(K,H_3O)(Al,Mg,Fe)_2(Si,Al)_4O_{10}[(OH)_2,(H_2O)]$
Montmorillonite $(Al_2O_3\cdot SiO_2\cdot nH_2O)$
Phosphorite $Ca_5(PO_4)_3F$
Siderite $FeCO_3$

1. (Aydemir 2011), (Orth et al. 1986); 2. (Bai et al. 2012) (Kidder et al. 2003); 3. (Hammes et al. 2012) (Dix et al. 2010); 4. (Harrell et al. 1991) (Onuoha et al. 2011); 5. (Comer 1991) (Harris 2013); 6. (Metwally et al. 2012) (Rader et al. 1961) (Kennedy et al. 2002); 7. (Ettensohn et al. 1981) (Ripley et al. 1990) (Tuttle et al. 2009) 8.(EIA 2013) (Marcinkowski et al. 2013)

Leaching test

The leaching test of rock samples was performed in accordance to the European Standard EN 12457-2 1313, 2002. The tests were conducted in compliance with leaching test for crushed material. One-stage batch test with distilled water at constant liquid to solid ratio (L/S) of 10 and temperature 25 ºC was performed. The rock-water mixture was continuously agitated for 24 hours at 300 rpm/min with the aim of reaching equilibrium conditions. Liquid/solid phase separation was preformed via centrifugation at average RCF = 1456×g for 10 min, followed by pressure filtration in order to obtain the solid material as well as leachate meant for further chemical analysis.

Analytical methodology

Organic matter content in rock samples was determined by ignition at 550 ^{o}C of samples in the muffle furnace. Content of total organic carbon was conducted by Shimadzu TOC-Vcsh Total Organic Carbon Analyzer. Mineralogical characterization was performed by X-ray diffraction using Xpert PRO-MPD, Philips. Elemental analysis of shale rocks before and after leaching was made by a X-Ray Fluorescence Spectrometer (Bruker S8 TIGER Wavelength dispersive X-Ray Fluorescence

WDXRF). Leachates were characterized taking into account total organic carbon content (LiquiTOC Elementar AnalysenSysteme GmbH) and pH (glass electrode ERH-111 and Multifunction Computer Meter, Elmetron).

Results and discussion

The shales used in this study, shown in Fig. 1, were extracted from marine deposits in Baltic Basin formed in Lower Silurian Llandrovery age (Franus et al. 2009). Organic matter content (determined as solids volatile in 550^{o}C) in shale samples was 3.22% ± 0.22, with total organic carbon 0.85% ± 0.03. Total organic carbon content is much lower than average value for Baltic Basin (4%) mentioned in the report "Technically Recoverable Shale Oil and Shale Gas Resources" published in 2013 by U.S. Energy Information Administration, grouping this bed into fair gas source in terms of its organic richness. According to the period of shale formation, average TOC values for individual sections of the Llandovery Baltic Basin are usually within the range from 1 to 2.5%, whereas Wenlock sections in central, western, and eastern parts of the Baltic Basin usually was determined to be 0.5-1.3%, and 1–1.7% TOC, respectively (Ehlers 1958).

Fig. 1. Picture of studied shale rock material

X-ray diffraction analysis was performed to evaluate the samples detailed mineralogy. The results revealed that the samples cover a wide range of mineralogical composition including mainly clay, siliclastic, and carbonate minerals, as well as other phases. The dominant mineral phase in shale samples was quartz, constituting approximately half of their weight.

X-ray pattern of the powdered shale samples were recorded with Cu target Kα-ray (λ = 1.5406 Å) in the range 2Θ = 10–60 with a 0.02 step interval and 2.0 scan step size for better resolution of the mineral phases as shown in Fig. 2.

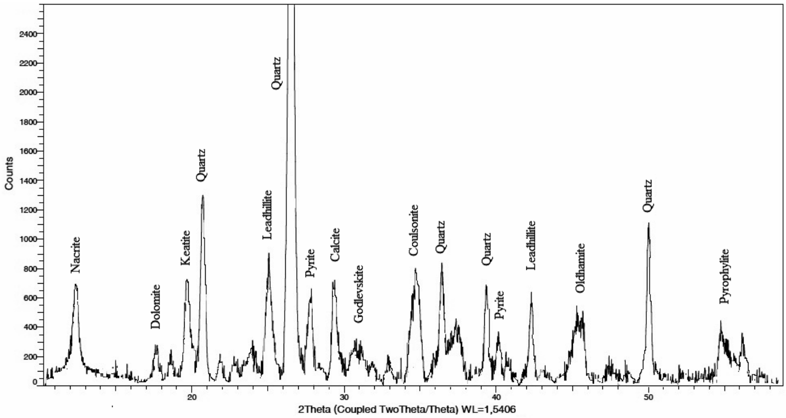

Fig. 2. Diffraction pattern of the shale samples main mineral phases

Furthermore, the X-ray diffraction pattern of the clay components were recorded in the range $2\Theta = 2–30$ with a 0.02 step interval and 2.0 scan step size indicating presence of illite, chlorite and kaolinite or nacrite $Al_2Si_2O_5(OH)_4$ (Fig. 3).

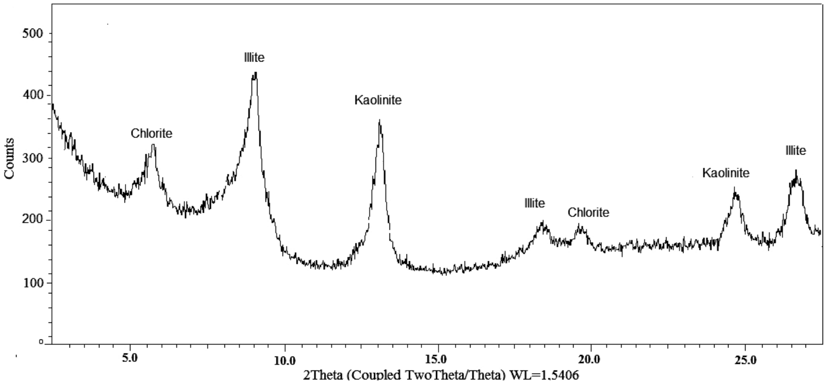

Fig. 3. Diffraction pattern of the clay components

Small proportions of siliciclastic minerals mainly in a form of quartz but also feldspar and micas as muscovite and biotite as well as pyrophyllite ($Al_2Si_4O_{10}(OH)_2$) were observed.

The carbonate-bearing minerals are present mostly in a form of calcite, dolomite and leadhilite ($Pb_4(SO_4)(CO_3)_2(OH)_2$). Moreover pyrite and other minerals like godlevskite $(Ni,Fe)_9S_8$, coulsonite (FeV_2O_4), oldhamite (CaS) were observed in minority. The high quartz and low clay content in our samples indicate that the shale may respond favorably to hydraulic stimulation. The XRD mineral analysis results are summarized in Table 2.

Table 2. Mineralogical composition of shale rock samples performed by XRD

Mineral	Component
Clay minerals	chlorite illite kaolinite (nacrite)
Siliciclastic	quartz (keatite) feldspar (plagioclase) mica (muscovite/biotite) pyrophyllite
Carbonate minerals	calcite dolomite leadhillite
Other	pyrite godlevskite coulsonite oldhamite

The detailed elemental characteristics of shale rock material was carried out by X-ray fluorescence spectroscopy. The results expressed as the percentage of mass content with experimental errors and lower limit detection are presented in Table 3. The XRF elemental analysis results confirmed that shale samples are composed mainly of aluminosilicate of Ca, Mg, Fe, K, Na forming feldspar, plagioclase, micas and pyrophyllite minerals. These main elements (excluding oxygen) form approximately 46.80 wt% of inorganic fraction. The residue 1.76 wt% is comprised of the elements like Ti, S, V, Mn, Zn, Sr, P, Zr, Cu, Rb, Ni, Cr and Mo, named in this work as trace elements. In comparison to the average geochemistry of earth crust, the studied samples are enriched in Mo, V, Zn, Cu, Ni.

Our results are in agreement with data obtained by Mainali (2012), who examined major and trace elements concentrations in the Hansville shale formation using a hand-held X-ray fluorescence spectroscopy. Cumulative average weight percent of major (Mg, Al, Si, P, S, K, Ca, Ti, Mn, Fe) and trace elements (V, Cr, Co, Ni, Cu, Zn, Th, Rb, U, Sr, Zr, Mo) was about 43% and 0.14% respectively (Mainali 2012). Multiple analysis of minor elements in Pierre Shale was followed by Rader and Grimaldi (1961), and revealed that all samples contained Ti from 0.05 to 0.5%, V, Zn, Cr, Mg in the range from 50 to 500 ppm, Co, Pb, Cu, Ni As from 5 to 50 ppm, and narrow range of 1.0 to 5.0 ppm Se, Mo, U, W.

Leachability of chemical elements from the shale formation to water was investigated by leaching test for crushed material. Constituents migration due to a leaching process of selected grain size fractions was based on determination of the changes in mass concentration of chemical elements against the content in original

Table 3. Elemental analysis of shale rock material by XRF

Element	Conc. [%m/m]	Stat. error [%]	LLD [PPM]
Si	21.99	0.45	64.40
Fe	8.44	0.28	37.20
Al	7.08	0.74	65.80
K	4.08	0.95	32.00
Ca	3.59	1.23	51.30
Mg	1.62	1.42	117.40
Ti	0.63	2.16	27.80
S	0.37	2.86	25.90
Na	0.35	5.16	188.30
Mn	0.14	2.84	23.90
Sr	0.06	3.31	10.40
P	0.05	10.6	41.80
Zr	0.03	3.09	13.90
V	0.03	9.26	42.50
Rb	0.03	3.33	11.30
Zn	0.02	6.33	14.30
Cr	0.02	11.20	34.50
Cu	0.02	11.70	15.90
Ni	0.01	16.70	18.00
Mo	0.01	12.30	11.00

shale samples, measured by XRF spectroscopy. The results of leaching test in respect to particle size fractions, presented in Figs 4-5 revealed that some elements may be released from the shale structure by deionized water. For most of the chemical elements it was shown that the highest weight loss appeared in fraction 1.When analysing main elements, it can be seen that calcium, present in parent rock in amount of 3.6 wt% mainly in siliciclastic and carbonate minerals is leached by water medium to concentration close or below 2 wt%. The Ca^{2+} ions collected in leachates may be identified as easily exchangeable ions located in interlayer sites in clays or as resulting from primary dissolved carbonates. Aluminium and silica compounds are also main elements and occur in variety of minerals (quartz, feldspars, clays) in the parent rock. Despite Al is strongly hydrolysing element, content remain relatively unchanged comparing the parent shale with the leached samples (decreased by 5–11% from an initial value for fraction 2–4), except the first fraction (4.0–2.362 mm), was a 50% decrease of calculated weight. Similar scenario was reported for silica element, were a reduction of 3–10% in weight loss percentage for fraction 2–4, was observed. Concentrations of sodium (0.35 wt%) and potassium (4.1 wt%), bounded in feldspars, clays and oldhamite, also decreased to 0.1–0.25, and 2.6–3.7 wt%, respectively.

Decrease of sodium element may suggest also mass loss of plagioclase. These observations indicated minor leachabilty of Al, Si, Na and K compounds from the sample to aqueous solution in applied leaching conditions. Magnesium content of 1.62 wt%, being present primarily in clays, only slightly declined. The compounds of iron were readily leached from the solids samples irrespective of granularity of the sample (decreased by 10–40% from an initial value). Iron is accumulated in the shales mainly as a sulphide fraction in pyrite, silicate association as chlorite, and to lower extend in godlevskite, oldhamite, coulsonite. The results stays in the contrary to data presented by Lavergren et al. (2009), who observed iron compounds associated mainly with sulphide, Fe-bearing silicates and to some extend with organic material, fractions highly insoluble in water (Lavergren et al. 2009).

When considering trace elements almost all of this elements were easily leached to liquid in the water-based leaching test. In all samples, the exception was sulphur, found to not migrate to aqueous phase probably due to abundance in the insoluble in water piryte form or godlevskite, and oldhamite. The concentration of Zr was unchanged except for a decrease in the fraction 1, which was found to be associated with the residual fractions, whereas abundance of Mn, Zn, Sr, Rb V, Cr, Mo and P compounds indicated limited relative leaching ability from the shale.

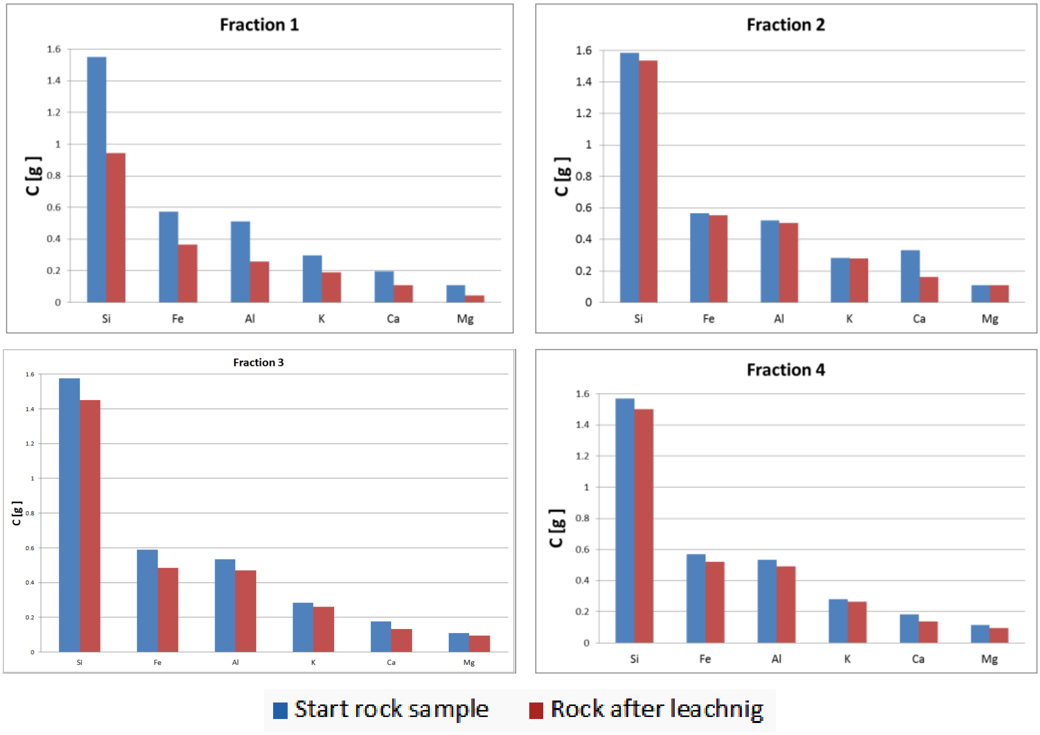

Fig. 4. Changes of shale rock main elements concentration after leaching procedure

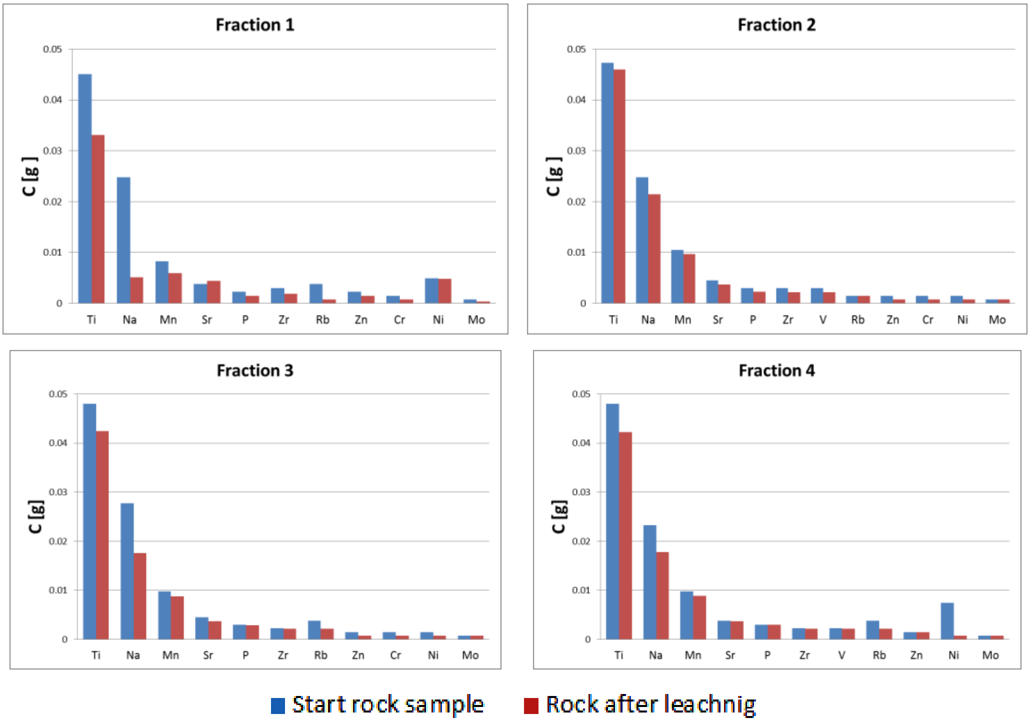

Fig. 5. Changes of shale rock trace elements concentration after leaching procedure

Leachates obtained after the water leaching tests were separated and characterized in respect to total organic carbon content. The relationship between TOC in received leachates and particles size distribution of rock fractions used in experiments is shown in Table 4. It was observed that organic compounds were released to aqueous phase in amount less than 20 ppm of TOC. Generally, the TOC content increase with increasing size distribution of the rock particles due to increasing surface area of the samples.

Table 4. TOC and pH of leachates after water leaching

	Blank	1	2	3	4
TOC [mg/dm^3]	0.02±0.07	8.28±0.12	12.06±0.20	16.06±0.140	16.58±0.17
pH	6.91±0.05	8.40±0.06	8.54±0.06	8.16±0.36	8.51±0.06

Leaching tests performed with deionized water (pH value of 6.91) results in increase of pH of the aqueous solutions to values near 8, comparable for all fraction, due to release of alkaline origin components. Changes in the pH of leaching medium may have high impact on the mobility of heavy metals, the lower pH, the greater solubility of metal ions. Solubility of individual metals may vary with the type of binding (Heasman et al. 1997). Lower pH values may lead also to carbonates and hydroxides dissolution, when metal ions are displaced by hydrogen ions. Elevated salinity level, on the other side, may shift toward higher pH and lead to competition between dissolved Ca2+ and/or Mg2+ cation. In addition, change redox potential leads to a change in metal binding forms in the solid phase and a decrease in pH-value, which increases the mobility of metal (Calmano et al. 1993).

Conclusions

The shale rock samples from marine deposits in Baltic Basin formed in Lower Silurian Llandrovery age have been characterized in terms of mineral composition as well as main and trace constituents present and transported to aqueous phase, by measurements of geochemically relevant chemical elements calculated weight loss. The X-ray diffraction analysis revealed that main mineral phases in shale are formed by quartz, clays, calcite, micas, pyrophyllite, and dolomite. Pyrite, leadhillite, oldhamite, godlevskite, coulsonite, and feldspar were observed in minority.

The concentration values of twenty elements of shale rock used in the experiments were determined by X-ray fluorescence spectroscopy technique before and after leaching tests. The main elements (mainly Si, Al, Ca, Mg, Fe, K, N) form approximately 46.80 wt% of inorganic fraction, whereas the 1.76 wt% is comprised of the trace elements. The results of water-based leaching test indicate decreasing content of Ca, Ti, Mg, P, V, Zn, Sr, Rb, Ni, Cr, Mo. Considering obtained results it can be expected that produced waste waters may contain mainly constituents as Fe, Al, K, Ca, Mg, Ti, Na and minor Mn, Sr, V, Rb, Cr, Ni and Mo. Determination of the total organic carbon content in leachates revealed a minor leachablity of organic matter from shales towards water. Low TOC in untreated water prevents difficulties with flowback water disposal. The increased pH values are in agreement with the XRF results in respect to alkaline compounds release in all fractions.

The results of this study indicate that many of the shale constituents are potentially leachable, and may create a disposal issue of the flowback water. On the other hand some may stay in drill cuttings, which also need to be properly disposed. Presented studies are a preliminary step for further research with other leaching agents giving wider understanding of a raised problem. Study of shales as a potential precursor of storage material for future possible high level waste disposal should be under investigation.

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