

# Release of selected chemical elements from shale drill cuttings to aqueous solutions of different pH



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## ABSTRACT

The effect of pH changes on leachability of light and heavy metals from shale drill cuttings generated from unconventional shale gas production was investigated. Cuttings, being the primary byproduct generated from drilling operations, belong to the potentially hazardous type of wastes due to presence of heavy and radioactive elements and remains of drilling fluid. In this regard, assessment of potentially dangerous components (PDCs) from rock waste materials was performed by application of batch leaching tests, which has provided information on the sensitivity of leaching under externally imposed changes in pH (natural or caused by treatment) in specific scenarios. The description of shale rocks mineralogical and chemical properties was performed by means of X-ray fluorescence spectroscopy, diffractometry as well as scintillation spectrometry. The concentrations of released constituents due to the leaching tests were measured by atomic absorption spectrophotometry. Results were compared and discussed accordingly with the waste acceptable criteria of elution limits.

Analysis of the substrate revealed that the elemental composition was dominated by light elements, whereas heavy metals were present in trace amounts. However, noticeable release of barium (2.0–4.6%) was also recorded, which has originated from not only rock material but also drill mud. Minor mobility was observed for transition elements such as Cr, Co, Fe, Mn, Ni, Zn, Cu and Pb. Results revealed that drill cuttings follow the requirements for other than hazardous and municipal type of deposition, with exception for barium. Moreover, content of radioactive isotopes fulfill the requirements range of acceptable concentrations.

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## 1. Introduction

Drilling procedure during the unconventional hydrocarbon exploration and extraction generates various types of waste including drilling mud containing fine-grained rock fragments (cuttings). Drill cuttings are then separated from mud using vibrating screens, hydrocyclones and/or centrifuges. However, separation step does not remove drilling fluid entirely (Ifeadi, 2004). Diversity of produced wastes is related to the variable chemical composition of the rock reservoir, as well as drilling fluid, which has got significant effect on the determination of the potential environmental impacts. Drill cuttings from aquatic sedimentary shale formations are composed mainly of inorganic minerals, mainly clays interspersed with organic matter. Most commonly used drilling muds, in turn, may be based on water, oil or

glycol enriched with additives such as bentonite, inorganic salts (barium/calcium sulfates, sodium/potassium/calcium chlorides, potassium hydroxide etc.), polysaccharides and certain specialized chemicals. According to the European waste catalogue and hazardous waste list drilling cuttings are classified as group no. 01 05 – drilling muds and other drilling wastes (Commission Decision, 2011).

Release of the chemicals from rock waste materials is one of the main problems needed to be considered when designing storage, utilization and new management procedures of cuttings. To assess the range of release of the potentially dangerous components (PDCs) to the environment, leaching tests are commonly performed. Leaching is a process by which constituents migrate from a solid material into an interacting fluid under condition applied (Lavergren et al., 2009). As a consequence, this phenomenon may lead to formation of the liquids with properties depending on the chemical and physical composition of given wastes and the leaching operational conditions (pH, redox potential, composition of the

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interacting fluid, contact time, pressure or temperature) (Heasman et al., 1997). Moreover, the release of the constituents arises from a confluence of mass transfer mechanisms and chemical reactions (Klein, 1989).

The leaching experiments provide information on the factors that determine the release of variety of elements from secondary materials, in accordance to environmental concerns, rare/valuable metals recovery as well as specific field scenarios. Although this procedure is often used for characterisation and prediction of metal mobility from fly ash (Izquierdo and Querol, 2012) (Ugurlu, 2004) (Querol et al., 2001), contaminated soils (Dijkstra et al., 2004) (Sun et al., 2001) (Sahuquillo et al., 2003), sludges (Kazi et al., 2005) (Mantis et al., 2005) (Vijay and Sihorwala, 2003) or mining residues (Cappuyns and Swennen, 2008) (Concas et al., 2006) (Fällman and Hartlén, 1994), shale drill cuttings are poorly studied. For example, Lavergren et al. presented abundance and mobility of main and trace elements in black shales (Sweden) determined by water-based leaching and sequential chemical extraction to describe behavior of selected constituents in the mineral matrix. It was observed that shale is rich in many PDCs such as As, Cd, Mo, U, V, Zn, Ni and Cd. Water leaching experiments resulted in a considerable leaching of Mo from the unoxidized sample and Cd, Zn and Ni from acidic samples. Based on the pH-controlled experiments with addition of hydrogen peroxide it was concluded that Cd, Mo, Zn, Ni and U can be leached in considerable amounts from the shale material (Lavergren et al., 2009). Continuing research, the same group investigated leaching behavior of As, U and Ni from black shales in order to define mechanism of trace metals release and their behavior in pyritic acidic environment by means of a long-term humidity cell test combined with sequential chemical extraction. It was found that the degree of pyrite oxidation is a major factor controlling Ni release, being highly elevated in acidic conditions, as well as also related to the chalcophilic character of nickel. Leaching of the uranium was observed to be dependent on the redox potential of the system and controlled by the solubilization of carbonate U phases, whereas arsenic was removed by adsorption into the surface or coprecipitation with iron compounds (Yu et al., 2014). Möller and Giese determined the metal/element migration in metamorphic rocks under batch leaching test at different pH (3, 6 and 8.5). Mobility patterns in pH relation of Mn, Zn, Mg, Sr and Na were observed to be analogous, whereas Ca, K and Ba at pH = 3 was significantly higher, probably due to calcite dissolution and enhanced ion exchange in biotite. Moreover, the dissolution behavior of various minerals due to the contact time was also presented. For Al-bearing minerals, calcite and fluorite, the leached fractions of Al or Ca revealed minor percentage levels of dissolved material after 28 h of leaching. Chlorite and biotite, in turn, released nearly 60% Al content within 28 h. This behavior may explain strong influence of silicates on metals-based minerals (Möller and Giese, 1997). Li and co-workers applied leaching procedure in acidic conditions and under pressure (1.2 MPa) to extract V<sub>2</sub>O<sub>5</sub> from black shale (China) (Li et al., 2009). Leaching efficiency was investigated under different processing conditions (reaction time, temperature, concentration of sulfuric acid and iron (II) sulfate and liquid to solid ratio). Conditions for effective vanadium separation (90%) from black shales was proposed. Shale rock leaching tendency was also evaluated by our group as changes of given elements concentration in four samples of rock material before and after leaching procedure measured by XRF without pH dependence of the leaching fluid (Piszcz-Karaś et al., 2014).

Possibility of shale gas production in Poland (accompanied by drill cuttings formation), growing environmental and health awareness, concerns about effects of heavy metals exposure (even at trace levels) as well as insufficient data on cuttings leaching, lead us to undertake studies on the dissolution of elements from shale

drill cuttings. Leaching tests at various pH conditions were performed because changes in pH are one of the main factors that control the leaching process. Moreover, these experiments provide information on pH conditions imposed by external influences, both natural as well as caused by treatment, and of acid/base neutralization capacity. The leaching results stand also basis for geochemical speciation modelling. In this regard, the effect of pH on leachability of light and heavy metals from shale drill cuttings generated from unconventional shale gas production was investigated. To establish migration levels as a function of pH changes in a range of 3–12 in static parallel batch testing mode was applied. Atomic absorption spectrometry, elemental analysis, conductometry and potentiometry techniques were used to analyse drill cuttings and determine the amount of released constituents and characterize physicochemical properties of the leachates.

## 2. Experimental

### 2.1. Material

The studied raw material was derived from shale gas exploratory well located in the province of Pomerania Region of Baltic Basin, Poland. To ensure a good representativeness, the samples were collected from five sampling points of the shale deposit from the depth of 3120 m (sample no. 1), 3860 m (sample no. 2), 4030 m (sample no. 3), 4120 m (sample no. 4), and 4225 m (sample no. 5). The given sampling points are related to the length of the horizontal section of the borehole in shale formation. After careful homogenization, drying, grinding and sieving (0.063 mm) samples were used for mineralogical and elemental characterisation. Based on the chemical analysis one sample of rock material with the highest content of heavy metals was selected for further experiments.

### 2.2. Analytical methodology

Mineralogical characterisation of shale rock material was performed by X-ray diffraction using MinFlex 600 (Rigaku) with the indicative parameters of the excitation voltage (40 kV) and anode current intensity (15 mA) in the measuring range  $2\theta = 5-90$ . The quantitative mineral composition was calculated using Rietveld method, suitable for analysis of rocks containing clay minerals.

Elemental analysis was made by X-Ray fluorescence spectrometer (Bruker S8 TIGER Wavelength Dispersive X-Ray Fluorescence WDXRF). Compositions of the leachates were measured by atomic absorption spectrophotometry (AAS) (Thermo Scientific iCE 3000 Series) and UV/Vis spectroscopy (HachLange DR 6000™ with RFID Technology). Cation exchange capacity (CEC) was determined by compulsive exchange method with BaCl<sub>2</sub> (Gillman and Sumpter, 1986).

Organic matter was determined by ignition of the sample at 550 °C in the muffle furnace, whereas loss of ignition at 815 °C. Total carbon and total organic carbon was analyzed using CHNS elemental analyzer (Flash, 2000; Thermo).

Radioactivity evaluation of shale rock sample was based on calculation of the exposure rates ( $f_1$  and  $f_2$ ) by means of activity concentration of naturally radioactive isotopes (Ra<sub>226</sub>, Th<sub>232</sub>, K<sub>40</sub>) using spectrophotometer (Mazar-92). Analysis was conducted after 5 days of material storage in the Marinelli cylinder placed into the shielding chamber according to the guidelines for the non-modified materials (Institute of Building Technology, Instruction 455/2010: Natural radioactivity in raw and building materials). Exposure rates were calculated following equations (1) and (2), where  $f_1$  referred to internal exposure of organisms to gamma radiation of natural radioactive whereas  $f_2$  to radiation emitted by

radium decay products.

$$f_1 = \sum_i \frac{S_{ij}}{a_i} = \frac{S_K}{3000} + \frac{S_{Ra}}{300} + \frac{S_{Th}}{200} \quad (1)$$

$$f_2 = S_{Ra} \quad (2)$$

$S_K$ ,  $S_{Ra}$ ,  $S_{Th}$  – concentration of  $K_{40}$ ,  $Ra_{226}$ ,  $Th_{228}$  [Bq/kg];  $a_i$  – experimental equation equivalents [Bq/kg]

### 2.3. Leaching test

The leaching test of drill cuttings were performed in accordance with EN 12457-2 “Characterisation of waste – Leaching – Compliance test for leaching of granular waste materials and sludges – Part 2: One stage batch test at a liquid to solid ratio of 10 l/kg for materials with particle size below 4 mm (without or with size reduction)” (EN12457-2:2006) and Environmental Protection Agency Method 1313 test “Liquid-solid partitioning as a function of extract pH in solid materials using a parallel batch procedure” (EPA, 2009). To achieve the target pH values of leaching systems (3–12), in respect to the natural alkaline pH and buffering capacity of the investigated material, titration pre-tests were conducted. Material-specific pH curve was obtained by titration of the material by 0.2 N  $HNO_3$  or 0.1 N  $KOH$  solutions. Titration procedure protocol was hold, separately for the acidic and basic conditions, at constant liquid/solid ratio of 10 l/kg of dry matter (Kosson et al., 2002). A set of parallel extractions experiments in dilute acid, base and deionized water (DI) at fixed pH, constant LS ratio and at  $20 \pm 2$  °C were performed. High-density polyethylene wide-mouth containers were used as extraction vessels, in which the rock/fluid systems were continuously contacted for 24 h in order to reach equilibrium conditions. Liquid/solid phase separation was performed via centrifugation at 4000 rpm, vacuum filtration and final separation with 0.45- $\mu$ m pore size polypropylene membranes.

## 3. Results and discussion

### 3.1. Material characterisation

To view microstructure of shales used in this study SEM technique was applied. SEM images revealed characteristics of low permeable grey shales with lithified structure and clay flakes within the rock matrix. SEM pictures of the selected sample (no. 5) are presented in Fig. 1. Shales contain organic matter, inorganic minerals interspersed with some pores. Organic matter content (determined as solids volatile at 550 °C) in shale samples was found to be in range of 7.7–10.0%, with total organic carbon of 1.8–2.5%. Ash residues, being related with inorganic matter content, was determined to be 89.1–85.3% as shown in Table 1.

Mineralogical composition of the selected shale rock sample (no 5), evaluated by X-ray diffraction method, is shown in Fig. 2 along with the corresponding quantitative concentrations presented in Table 2. Shale rocks cover a wide range of mineralogical species including siliciclastic minerals and clays, though carbonates also occur. The dominant phase is represented by siliciclastic and clay minerals, constituting over 60% by mass. Quartz as free silica ranges from 19.0 to 27.5 w/w of the investigated materials, whereas the amount of the total bonded silica in a form of aluminosilicates, mainly illite and mica etc., were detected to be higher (51.6–63.7 w/w).

Among other minerals from aluminosilicates group plagioclase (2.0–9.5 w/w), potassium feldspar (2.4–4.3 w/w), chlorite (0.5–8.8 w/w) and illite-smectite (0.1–5.8 w/w) were detected in noticeably

large amounts. Presence of barite (more than 3% w/w) could originate from drilling operation since that chemical is commonly used as a weighting material in drilling mud. Moreover, presence of calcite (2.9–4.1 w/w) and dolomite (1.0–8.8 w/w) with noticeable pyrite content (2.1–4.1 w/w) was also revealed.

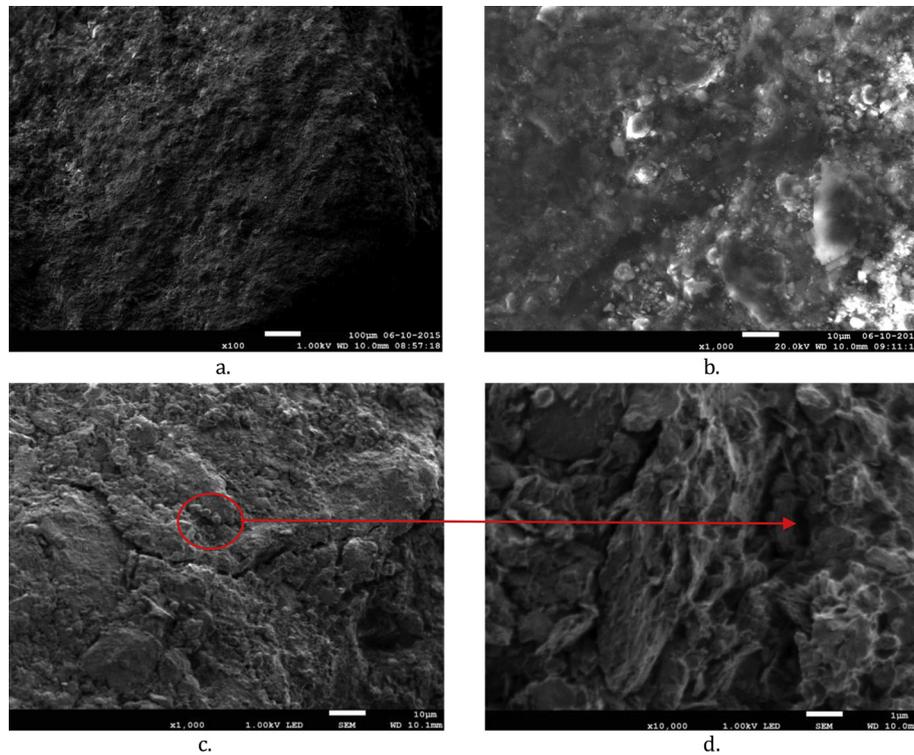
More detailed elemental composition analysis of the samples, expressed as a percentage of mass content of the element in a form of oxide (w/w), was performed by X-ray fluorescence spectroscopy and given in Table 3. Results indicated the major concentration of  $SiO_2$  and  $Al_2O_3$ , that was 7.87–18.1 and 50.7–66.4% w/w respectively. Obtained data confirmed that materials are composed mainly of aluminosilicate minerals. This assumption was also visualized by presence of characteristics accessory elements as  $CaO$  (4.37–6.83% w/w),  $MgO$  (1.32–4.09% w/w),  $Fe_2O_3$  (4.90–5.43% w/w),  $K_2O$  (3.22–4.35% w/w),  $Na_2O$  (0.29–2.29% w/w) forming feldspars, plagioclases or micas. High content of  $BaO$  (4.00–6.88 w/w) and  $Cl$  (0.77–1.36 w/w) may indicate presence of drilling fluid residue. The cuttings were also enriched with some potentially hazardous elements such as  $SrO$  (0.07–0.17% w/w),  $CuO$  (0.02–0.04% w/w),  $ZnO$  (0.02–0.04% w/w)  $Cr_2O_3$  0.02% w/w and other as  $MnO$  (0.07–0.08% w/w),  $Ni$  (0.03% w/w) as well as  $P_2O_5$  (0.07–0.13% w/w). Abundance of  $Cr$  and  $Ni$  could be related with the presence of clay minerals such as kaolinite and mixed layer of the materials (Patterson et al., 1986), (Sonibare et al., 2011). Comparing to the average geochemistry of the earth crust, the studied samples are enriched in  $Cu$ ,  $Zn$ ,  $Ba$  and  $Cr$  (Kabata-Pendias, 2011) (Krauskopf and Bird, 1967).

The potential of the clays and other minerals of shales to ion exchange depend on both mineral crystalline structure and contact fluid chemical composition. Susceptibility of the specific material to replace some of the cations with other positively charged species, through interlayer bonds strength, is reflected by cation exchange capacity (CEC) (Rogala et al., 2014). The CEC value is defined as the total sum of exchangeable cations in the sample that is available at a specific pH. Cations which are retained by electrostatic forces may be readily exchanged within the solid-liquid interactions.

Shales as rocks with claystone origin have the ability to attract and hold certain ions which maintain their specific exchangeable capacities that are directly related to the reactivity of the shale. The well-known tendency is also that the higher CEC of the material, the stronger electrical interactions, and thus the more reactive is the shale. The CEC values of the shales were found to be relatively in the range of 0.6–1.5 meq/100 g of solid which is below the moderately reactive shales (10–20 meq/100 g) and similar to non-reactive limestone or sandstone (<1 meq/100 g) (Okoro and Adewale, 2014), (Guo et al., 2012). However, CEC values in a range of 1–10 meq/100 g should be a scope of interest in terms of environmental concerns (Okoro and Adewale, 2014), (Stephens et al., 2009).

### 3.2. Leaching test

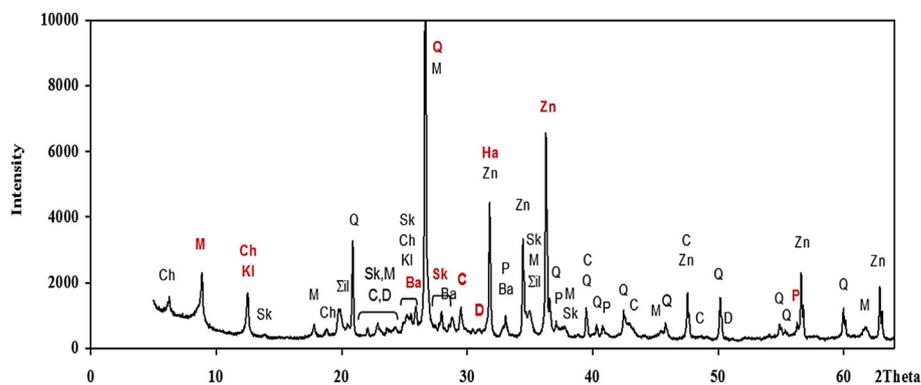
To understand the leaching properties, it is essential to remember that shale drill cuttings are heterogeneous materials and its elements may be not evenly distributed throughout. In accordance to the leaching tests assumptions, first of all it was required to prepare solid-liquid systems at specified pH. In this regard an acid-base titration of the selected shale sample was performed (Kosson et al., 2002). The amount of titrant ( $HNO_3$  or  $KOH$  solutions) required to be added to the shale-water systems was recalculated basing on the titration curve. The output pH of the investigated rock material was alkaline (pH = 8.85), therefore it was easier to prepare leaching systems with pH > 7, in turn to reach acidic pH values up to 3 it was more time and titrant-consuming. The cause of this phenomenon could be explained by a buffering



**Fig. 1.** SEM images of shale cuttings: a. magnification  $\times 100$ , excitation voltage 1 kV, b. magnification  $\times 2,000$ , excitation voltage 20 kV, c-d. magnification  $\times 10,000$ , excitation voltage 1 kV.

**Table 1**  
Physicochemical analysis of shale cuttings.

Parameter	Content [%]				
	1	2	3	4	5
Organic matter	$7.7 \pm 0.3$	$9.1 \pm 0.4$	$10.0 \pm 0.7$	$7.7 \pm 0.3$	$7.7 \pm 0.2$
Loss of ignition	$10.9 \pm 0.4$	$13.9 \pm 0.7$	$14.7 \pm 0.1$	$11.1 \pm 0.1$	$11.4 \pm 0.2$
Total carbon	$4.3 \pm 0.2$	$2.8 \pm 0.4$	$3.4 \pm 0.2$	$3.7 \pm 0.4$	$4.3 \pm 0.6$
Total organic carbon	$2.4 \pm 0.4$	$1.8 \pm 0.2$	$2.4 \pm 0.5$	$2.5 \pm 0.3$	$2.0 \pm 0.4$



**Fig. 2.** Diffraction pattern of the shale samples main mineral phases, (Q – Quartz, Sk – K – feldspar, M – mica and illite group minerals, m – mica, l – illite, C – calcite, D – dolomite, P – pyrite, Ba – barite, Pl – plagioclase, I/S – illite-smectite mixed layer, Ch – chlorite, Kl – kaolinite, Zn – internal standard).

ability of the alkaline cuttings constituents. The results of the leaching experiments at various pH values and as a function of the element content in the leachate are shown in Fig. 3. The elements investigated in this study may be divided into two groups: major (Ca, Mg, Na, K) and trace elements (Zn, Cu, Cr, Ni, Fe, Pb, Mn, Co). As

it was expected, it has been shown that chemical behavior of shale depends on the pH of the leaching agent.

Calcium was observed to be the major cation in the greatest quantity irrespective of the leaching conditions. This element may be present in the shale rock in a form

**Table 2**  
Mineralogical composition of shale rock samples performed by XRD, standard measurement uncertainty  $\pm 5\%$ .

No.	Mineral	Concentration [% w/w]						
		1	2	3	4	5	Range	
1	Q	Quartz	33.3	19.0	27.3	27.5	23.4	19.0–27.5
2	C	Calcite	2.7	8.4	5.9	5.7	2.9	2.7–8.4
3	D	Dolomite	1.2	8.8	7.7	1.0	1.1	1.0–8.8
4	P	Pyrite	0.4	2.4	0.5	3.8	4.1	0.4–4.1
5	Ba	Barite	0.6	8.2	7.0	2.9	4.8	0.6–8.2
6	Ch	Chlorite	0.5	6.1	5.8	7.1	8.8	0.5–8.8
7	Pl	Plagioclase	2.0	9.5	8.1	2.8	3.8	2.0–9.5
8	Sk-K	Feldspar	2.5	4.3	4.2	3.8	2.4	2.4–4.3
9	m + I	Mica + Illite	53.7	23.3	21.7	35.4	42.1	21.7–53.7
10	I/S	Illite-Smectite mixed layer	1.7	0.1	0.2	0.7	5.8	0.1–5.8
11	KI	Kaolinite	1.5	9.9	11.6	9.4	0.8	0.8–11.6
12	$\Sigma$ Al + Si	Aluminosilicates	61.9	53.2	51.6	59.3	63.7	51.6–63.7

**Table 3**  
Elemental composition of shale rock samples performed by XRF, standard measurement uncertainty  $\pm 5\%$ .

No.	Element	Concentration [% w/w]					Range
		1	2	3	4	5	
1	SiO <sub>2</sub>	67.10	55.85	56.27	66.40	50.70	50.7–67.1
2	Al <sub>2</sub> O <sub>3</sub>	8.69	11.55	11.66	7.87	18.08	7.87–18.08
3	CaO	4.37	6.83	6.72	4.72	4.78	4.37–6.83
4	BaO	4.00	6.88	6.02	4.82	4.07	4.00–6.88
5	Fe <sub>2</sub> O <sub>3</sub>	5.27	4.77	4.80	5.34	5.43	4.90–5.43
6	SO <sub>3</sub>	3.55	3.87	3.92	4.12	4.63	4.12–4.63
7	K <sub>2</sub> O	3.32	4.15	4.35	3.22	3.54	3.22–4.35
8	MgO	1.43	3.25	3.15	1.32	4.09	1.32–4.09
9	Na <sub>2</sub> O	0.35	1.16	1.23	0.29	2.29	0.29–2.29
10	Cl	0.91	0.77	0.89	1.00	1.36	0.77–1.36
11	TiO <sub>2</sub>	0.68	0.56	0.58	0.61	0.69	0.56–0.69
12	SrO	0.08	0.17	0.15	0.09	0.07	0.07–0.17
13	P <sub>2</sub> O <sub>5</sub>	0.08	0.11	0.13	0.08	0.09	0.08–0.13
14	CuO	0.03	0.04	0.02	0.02	0.07	0.02–0.07
15	ZnO	0.02	0.03	0.02	0.02	0.04	0.02–0.04
16	MnO	0.07	0.04	0.05	0.08	0.06	0.04–0.08
17	NiO	0.01	0.01	0.01	< LLD	0.01	up to 0.01
18	CoO	0.01	< LLD	< LLD	< LLD	< LLD	up to 0.01
19	Cr <sub>2</sub> O <sub>3</sub>	< LLD	< LLD	0.01	0.02	< LLD	0.01–0.02
20	PbO	0.01	0.02	0.02	0.02	< LLD	0.01–0.02

LLD – lower limit of detection.

of various minerals, primarily as carbonate (calcite, dolomite) and sulphate minerals (gypsum), that are susceptible to acidic media (Salminen, 2005). Therefore, the highest leaching ability of calcium to aqueous solution was observed for the lowest pH values (1400 mg/kg), that was about 3%. Due to the contact with acidic solutions, carbon dioxide is generated, releasing Ca or/and Mg. The elution gradually decreased with increasing alkalinity to about 145 mg/kg at pH 12.

Sodium and potassium are likely to be associated with abundance in feldspars and clays (illite, mica). Interaction with aqueous solution may result mainly in dissolution of surface salts, nevertheless liquid may also, to some extent, interact with elements of the rock matrix. Sodium, reveal similar tendency such as Ca, being the most leachable in acidic conditions (830 mg/kg), with release reaching 3% of a content in raw material. The release significantly drops in pH 4–8 to around 250 mg/kg, and further to about 150 mg/kg under alkaline conditions. Potassium species seem to be almost equally dissolved across the pH range (163–54 mg/kg). The maximum release was seen in both acidic and basic pH, reaching about 3% of the raw material and was respectively, 137 and 163 mg/kg. Relative mobility of potassium toward sodium is lower as a result of potassium being stronger adsorbed on the surface of clay minerals and organic matter as well as larger atomic size.

Magnesium in carbonate rocks is an easily exchangeable element (eg. with Fe), however it may also occur in a form of a thin layer in sedimentary deposits (chlorite, biotite) with limited mobility (Magiure and Cowan, 2002). Moreover, Mg accompanied by Ca (Na, K as well), belongs to lithophilic elements that stay on or close the rock surface (Goldschmidt, 1954). As a consequence, during leaching, the behavior of Mg resembles that of Ca. However, maximal concentration of Mg released from the sample is lower (closed to 700 mg/kg at pH 3) and decreased to below 7 mg/kg at pH 11. The generally lower concentration of Mg in the leachates in comparison to Ca results from the presence of Mg mainly in a form of a difficultly available sedimentary deposits as well as the lower total content in the shale cuttings.

It was also observed that approximately 0.7% of copper (~5 mg/kg) was leached at pH 3–6. With increasing pH amount of copper displaced to the liquid phase is gradually reduced from about 5 to 1.5 mg/kg. Copper is strongly associated with sulphur and is potentially present as insoluble sulfides. Therefore, relatively low Cu leachability in alkaline conditions may be explain by its chalcophilic affinity.

Chromium is present in the shale rocks in a form of the most common oxidation form (Cr<sup>3+</sup>), often bounded with organic substances, but primarily occurring as accessory element in hydro-micas (Salminen, 2005). Chromium belongs generally to a low mobility elements especially near-neutral pH values as it was confirmed (1.2–1.4 mg/kg). Otherwise like many trace metals, Cr is eluting under extreme pH conditions, where above pH 9 maintained at a constant level approximately 2.3 mg/kg.

Cobalt is potentially leachable due to aluminosilicates fraction affinity. Moreover, as a one of the chalcophilic and siderophilic elements, can occur in a form of covalent bonded sulfides. It is mostly present as accessory element in mica and may be associated with iron sulfides such as pyrite concentrated within the fine-grained fraction (Salminen, 2005). Geochemical association of Co with Fe-bearing species could explain poor Co leaching susceptibility under neutral and alkaline conditions. The leaching diagram presents the maximum concentration of leachates at acidic pH (1.34 mg/kg), decline to about 0.1 mg/kg dissolution under neutral conditions, and subsequently decreases toward in higher pH values (0.05–0.12 mg/kg). That means that cobalt, accompanied by Fe, are rapidly removed from shale under acidic conditions.

Zinc in shale rocks is presented mainly as ferromagnesian silicates, detrital oxides and clay minerals due to substitution of Fe<sup>2+</sup> and Mg<sup>2+</sup>, since both elements have similar ionic radii to Zn<sup>2+</sup> (74 p.m.) (Salminen, 2005). Zinc has also a greater affinity to organic matter than Cd (Tipping and Hurley, 1992). The solubility of Zn as a function of the pH dependence presents a U-shaped relation with a minimum near pH 7. Zinc mobility was found to be greater under

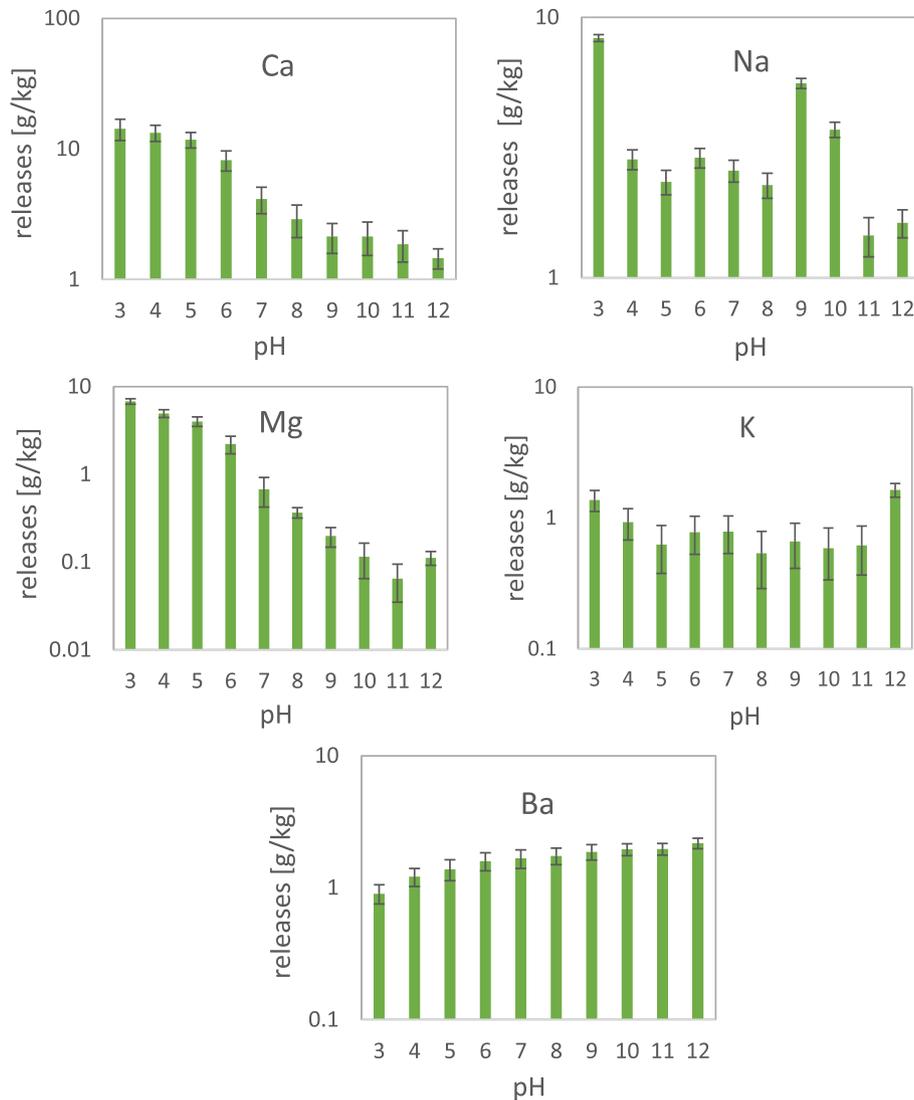


Fig. 3. Trends in leaching behavior of selected elements as a function the various pH.

acidic conditions (about 8.5 mg/dm<sup>3</sup>) where it occurs mainly in a form of Zn<sup>2+</sup>. At higher pH values, Zn may form complexes with carbonate and hydroxyl anions (Mohamed and Antia, 1998), therefore we observed lower solubility. Leaching of Zn reveals a slight increase at higher pH due to its amphoteric nature.

Similar to Zn, iron reveals chalcophile behavior accompanied by affinity to oxygen. Due to its strong bonding to sulphur, Fe is leached mainly under aggressive acidic conditions, thus the highest leaching ability was observed for the solution with the lowest pH values (129 mg/kg), that was about 0.25% of Fe in the raw material. At higher pH leaching level sharply dropped and was maintained at the constant level of 0.2–0.4 mg/kg. Relatively low mobility of iron under most common environmental conditions results from limited solubility of iron (III) hydroxide.

Distribution of Pb may be controlled by presence in a form of sulphide minerals, detrital minerals such as feldspar, mica, clay (Heinrichs et al., 1980) as well as its affinity towards organic matter. It was observed that acidic environment enhances leaching of lead to aqueous solution, especially from sulphide minerals. Minimum solubility was observed at pH 6, followed by increase in Pb mobility under alkaline conditions. Nevertheless, the leachable concentrations remain at lower levels (below 1 mg/kg of Pb) in the 4–12 pH

range. Low mobility of lead may result from low distribution in the sedimentary rocks and release being restricted by sorption on clay, organic matter, secondary iron and manganese oxides, as well as ability to form poorly soluble secondary minerals with sulphate, carbonate, hydroxy carbonate or phosphate anions.

Manganese is a lithophile element that in sedimentary rocks, such as shales, may be distributed in a form of oxides as an accessory element in calcite and in carbonate rocks. Abundance of Mn in shale rocks during diagenesis is also associated with presence of low mobile Fe-hydroxides (Schieber, 1995), moreover manganese may occur as hydrous oxides of Mn<sup>3+</sup> and Mn<sup>4+</sup> forming hardly soluble surface concretions (Mohamed and Antia, 1998). In our study, this behavior was confirmed by the increased concentration of Mn being leached in acidic solution (164 mg/kg), due to the solubility of Mn<sup>2+</sup> ions. However, similarly to other metals manganese was barely soluble by water (6.8 mg/kg) as well as alkaline extractants (<0.1 mg/mg), indicating Mn being not susceptible to the influence of alkaline environment.

Nickel is a siderophilic metallic element with chalcophilic and lithophilic affinities. It is present primarily in the form of oxides in minerals such as illite or spinel (Ruppert et al., 1996), although the Ni sulphide minerals may also appear (Finkelman, 1995). The highest

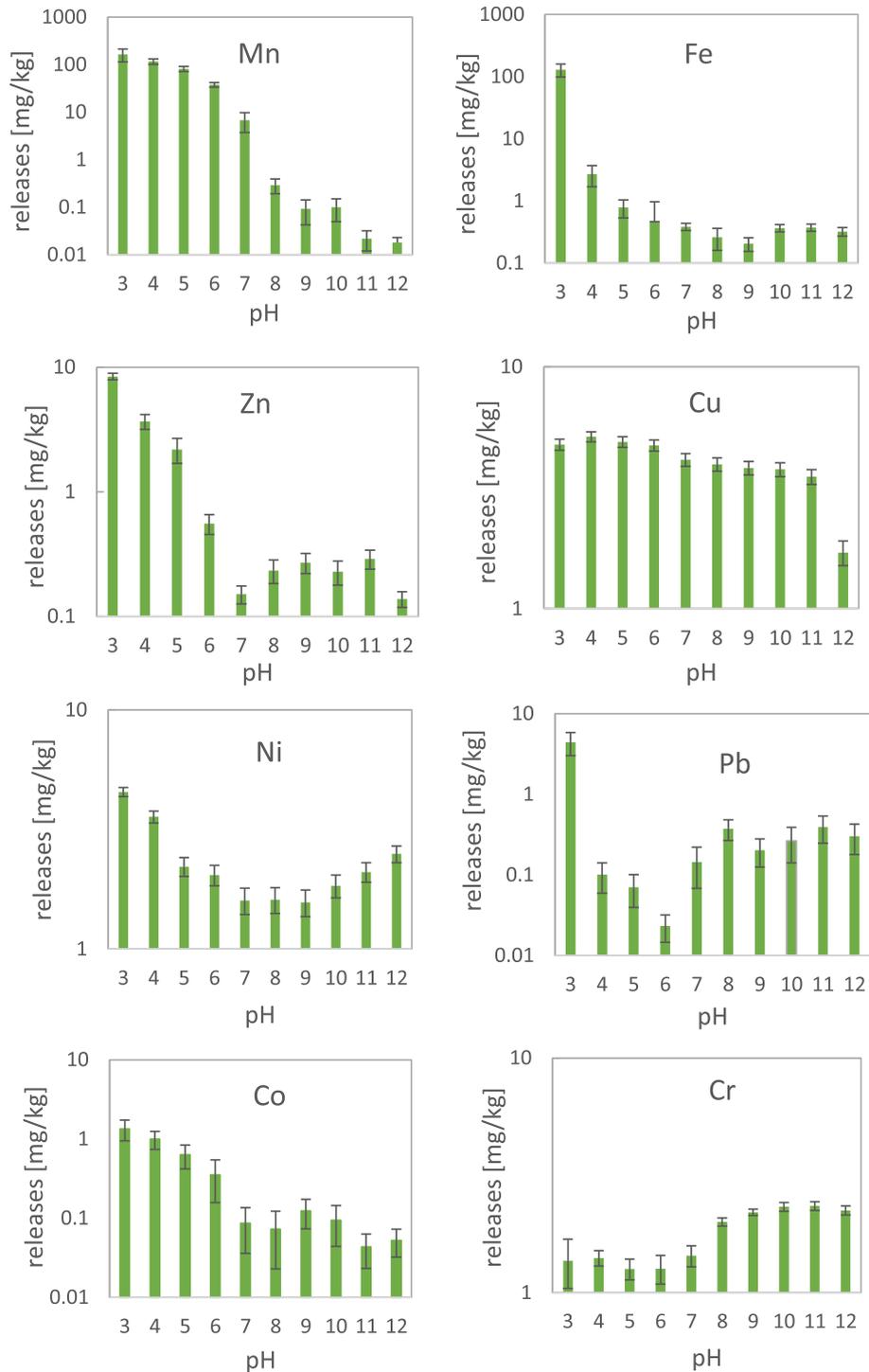


Fig. 3. (continued).

leaching ability of nickel to aqueous solution was observed for the acidic conditions possibly due to the availability of predominant  $\text{Ni}^{2+}$  charge cations. The lowest leachable levels, in turn, were obtained in the pH 8–10 region (1.6 mg/kg). At alkaline pH its releases rise up to above 2.5 mg/kg, providing evidence of Ni amphoteric behavior. Explanation of the above was oxide dissolution with hydroxylation followed by amphoteric dissociation of surface groups (Torrás et al., 2011).

Barium content in both raw material and leachates was higher

than expected - due to presence of residues of drilling mud in cuttings. Nevertheless, some contribution of Ba in aqueous solution, may be also related with its occurrence in sedimentary rocks minerals such as feldspars and phyllosilicates (illite, kaolinite) (Torrás et al., 2011). Moreover, in plagioclase so as in the non-silicate minerals (calcite)  $\text{Ba}^{2+}$  may exchange the  $\text{Ca}^{2+}$  ions (Sonibare et al., 2011). Barium release under different pH conditions was only slightly pH-dependent. Experiments revealed increase of barium release from 2.0% at pH 3 towards 4.6% at pH 12. The highest

achieved leaching rate (2174 mg/kg) is much greater than amount determined in shales 270–800 mg/kg (Chermak and Schreiber, 2014). In compare, the average concentration of barium in produced waters of Marcellus Shale in Pennsylvania reached 2224 mg/kg (Barbot et al., 2013).

Conductivity dependence of the systems before and after leaching in a function of pH is presented in Fig. 4. Under the acidic conditions the initial conductivity was relatively high, above 10 mS/cm (pH 3), due to the presence of a strong electrolyte - nitric acid being dissociated in the liquid phase. The high conductivity of these solutions may be also related with high diffusion coefficient of hydrogen cation (Acar and Alshawabkeh, 1993). Leaching experiments during which shale sample is dynamically contacted with acidic solution (pH 3 and 4) provided a drastic decrease of the conductivity in these systems. That behavior is related with composition of the shales providing high pH of the rock sample (8.9). With increasing pH both initial and final conductivity of the systems were significantly lower due to decreasing amount of acid needed for reaching proper pH as well as buffering properties. In comparison, conductivity of the systems with moderate and alkaline pH values before and after leaching experiments were similar.

Hydraulic fracturing fluids commonly used in shale gas production are characterized by pH close to 8–9. In this regard leaching profiles of shale cuttings were presented in Fig. 5. Release of the investigated constituents was observed to have similar trend under both pH conditions. Considering levels of elution, elements can be divided in three groups. The highly mobile group included sodium, calcium, barium and potassium since these elements were prevalent in various minerals in shale rock. However, the high level of barium elution, as mentioned above, was probably a result of mud residuals. The difference in leachability between two pH values was detected for potassium, where concentration of this element in leachate at pH 9 was almost ten times less than at pH 8. Inversely, sodium content at pH 9 was two-fold higher comparing mobility at pH 8. The subsequent group with lower mobility consisted of copper, chromium and nickel (concentration ranges below 4 mg/l). The least quantities of elution, below 0.5 mg/l, was indicated for magnesium, zinc, iron, manganese, cobalt and lead, irrespectively to pH conditions.

Leaching limitation values, considering the environmental conditions, applied for waste acceptable criteria for different types of landfills, were summarized in Table 4. The criteria refer to hazardous (A), inert (B) and other than hazardous and inert wastes (C) and consequently correspond to the prospective landfill deposition. The results presented here revealed that the leaching levels follow the requirements for other than hazardous and municipal type of

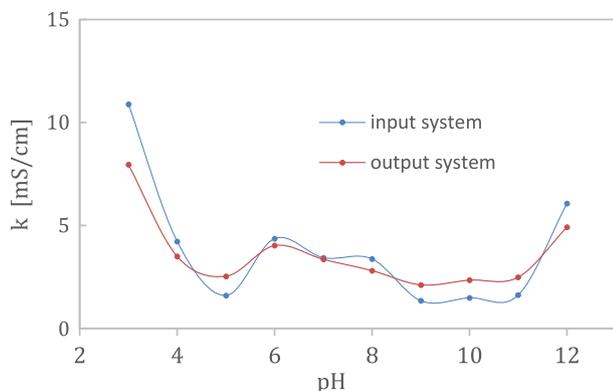


Fig. 4. Conductivity changes in the systems at different pH before and after leaching experiments.

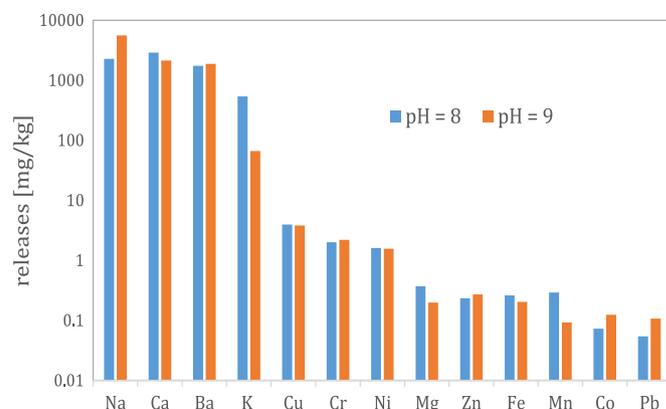


Fig. 5. Leaching behavior of selected elements under condition similar to pH of hydraulic fracturing fluids.

Table 4

Waste acceptable criteria for the leaching tests at a liquid-solid ratio of 10 l/kg (Council Decision, 2003).

	Requirements [mg/kg] H <sup>A</sup> /I <sup>B</sup> /Other <sup>C</sup>	Maximum release		Landfill compliance
		[mg/kg]	pH	
Ni	40/0.4/10	4.5	3	<sup>C</sup> requirements
Zn	200/4/50	8.4	3	<sup>C</sup> requirements
Cu	100/2/50	5.1	4	<sup>C</sup> requirements
Cr	70/0.5/10	2.3	10	<sup>C</sup> requirements
Pb	50/0.5/10	1.2	3	<sup>C</sup> requirements
Ba	300/20/100	2.170	12	<sup>A</sup> requirements

deposition, with exception for barium. However, it should be pointed that other than barite drilling muds may be also implemented during drilling operations. In this regard, these results indicate a relatively minor environment impact of solid waste from shale gas extraction. Nonetheless, the ranges of given pollutants require adequate storage to prevent unrespectable tailings release.

### 3.3. Radioactivity measurements

It is well known that minerals and unprocessed raw materials contain radionuclides of natural origin, that was previously studied by the research group (Mykowska et al., 2015). Considering the environmental impact, the concentrations of radioactive isotopes (radium, thorium and potassium) were measured for sample 5 (Table 5). Based on Instruction 455/2010 of Natural Radioactivity in Raw and Building Materials, the exposure rates were calculated. Both rates  $f_1$  and  $f_2$  refer to exposure limitations to gamma radiation of natural radioactive and radiation emitted by radium decay products, respectively. Results indicated that both  $f_1$  and  $f_2$  fulfill the requirements range of acceptable concentrations given by  $f_1 \leq 1$  and  $f_2 \leq 240$  [Bq/kg]. The naturally radioactive isotopes concentration of  $^{226}\text{Ra}$ ,  $^{228}\text{Th}$  and  $^{40}\text{K}$  found for shales were up to  $85.2 \pm 5.7$ ,  $93.3 \pm 5.6$ ,  $303.1 \pm 15.2$  [Bq/kg] (Abbadly et al., 2005). Whereas, the corresponding values for clays were found to be up to

Table 5

Individual radioactive isotopes average concentrations determined for sample no. 5

Naturally radioactive isotopes [Bq/kg]			Exposure rate	
Radium $^{226}\text{Ra}$ [ $S_{\text{Ra}}$ ]	Thorium $^{228}\text{Th}$ [ $S_{\text{Th}}$ ]	Potassium $^{40}\text{K}$ [ $S_{\text{K}}$ ]	$f_1$	$f_2$ [Bq/kg]
$66.3 \pm 8.9$	$37.9 \pm 3.7$	$899.4 \pm 72.4$	$0.7 \pm 0.1$	$66.3 \pm 8.9$

70 ( $^{226}\text{Ra}$ ), 44 ( $^{232}\text{Th}$ ), 751 ( $^{40}\text{K}$ ) [Bq/kg] (Khater et al., 2013). Differences are derived from the changes in geological formations as well as geochemical behavior of the radionuclides according to the locations.

#### 4. Conclusions

Drill cuttings as a secondary material from extraction sites were investigated and discussed in order to assess the potential release of dangerous components under externally imposed changes in pH (natural or caused by treatment) in specific conditions. The rock-forming silicates such as plagioclase, micas and illite, chlorite, kaolinite and alkali feldspar were found to constitute to dominant mineral phases in drill cuttings. The overall analysis of the substrate indicated that the elemental composition was dominated by  $\text{Si} > \text{Al} > \text{Fe} > \text{Ba} > \text{Ca} > \text{K} > \text{Mg} > \text{S} > \text{Na}$  elements, whereas heavy metals were in trace amounts.

Leaching batch test as a quality control and compliance tool was used to describe solubility and release of selected chemical elements to aqueous solution at different pH (3–12). Despite low cation exchange capacity values, shale leachates were found to contain elements of potential concerns. Metals partitioning was strongly affected by pH value of leaching medium and controlled by the mineral forms as well as individual constituent properties (chalcophilic, lithophilic, siderophilic). Furthermore, the differences between mobility ranges depended on both type of sub-mineral connection and atomic size.

Cationic elements were more prone to migrate to the acidic eluent than to the alkali one. According to the mobility levels, the constituents can be divided into two main groups. The major release was recorded for Ca, Mg, Na, K under acidic conditions and reached about 3% comparing with the initial concentration. Moreover, noticeable release, in the range of 2.0–4.6% was also recorded for barium, however it does not only originate from rock material but also from drill mud. Minor mobility was observed for transition elements such as Cr, Co, Fe, Mn, Ni, Zn, Cu and Pb. Mobility of metals with the predominant charge  $^{2+}$  (Cu, Ni, Pb, Zn) was especially enhanced under acidic conditions. The highly mobile group in pH 8–9, being relevant for hydraulic fracturing fluids commonly used in shale gas production, included sodium, calcium, barium and potassium. The subsequent group with lower mobility consisted of copper, chromium and nickel (concentration ranges below 4 mg/l), followed by magnesium, zinc, iron, manganese, cobalt and lead with elution below 0.5 mg/l.

Systematic characteristics of sedimentary origin shale cuttings may be a background for designing of the storage facilities, utilization and new procedures for management of drilling solid wastes. Proposed methods, so far seem to be unattractive regarding both economic (reinjection, thermal desorption) and energy issues (incineration) or time consuming decomposition of organic residues (bioremediation, phytoremediation). Moreover, solution based on incompatible assumptions with rational waste management requirements (ground storage) should be avoided. Chemical characteristics of shale drill cuttings, as well as results of leaching test indicated applicability of this secondary material as possible substrate for manufacturing of building materials by thermal processes. The high-temperature modification would decrease the leaching levels.

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#### References

- Abbady, A.G., Uosif, M.A., El-taher, A., 2005. Natural radioactivity and dose assessment for phosphate rocks from Wadi El-Mashash and El-Mahamid Mines, Egypt. *J. Environ. Radioact.* 84 (1), 65–78.
- Acar, Y.B., Alshawabkeh, A.N., 1993. Principles of electrokinetic remediation. *Environ. Sci. Technol.* 27 (13), 2638–2647.
- Barbot, E., et al., 2013. Spatial and temporal correlation of water quality parameters of produced waters from devonian-age shale following hydraulic fracturing. *Environ. Sci. Technol.* 47 (6), 2562–2569.
- Cappuyens, V., Swennen, R., 2008. The application of  $\text{pH}_{\text{stat}}$  leaching tests to assess the pH-dependent release of trace metals from soils, sediments and waste materials. *J. Hazard. Mater.* 158 (1), 185–195.
- Chermak, J.A., Schreiber, M.E., 2014. Mineralogy and trace element geochemistry of gas shales in the United States: environmental implications. *Int. J. Coal Geol.* 126, 32–44.
- 2001/119/EC: Commission Decision of 22 January 2001 amending Decision 2000/532/EC replacing Decision 94/3/EC establishing a list of wastes pursuant to Article 1(a) of Council Directive 75/442/EEC on waste and Council Decision 94/904/EC establishing a list of hazardous waste pursuant to Article 1(4) of Council directive 91/689/EEC on hazardous waste.
- Concas, A., et al., 2006. Mobility of heavy metals from tailings to stream waters in a mining activity contaminated site. *Chemosphere* 63 (2), 244–253.
- 2003/33/EC: Council decision of 19 December 2002 establishing criteria and procedures for the acceptance of waste at landfills pursuant to Article 16 of and Annex II to Directive 1999/31/EC.
- Dijkstra, J.J., Meussen, J.C.L., Comans, R.N.J., 2004. Leaching of heavy metals from contaminated Soils: an experimental and modeling study. *Environ. Sci. Technol.* 38 (16), 4390–4395.
- EN 12457–2, 2006. Characterization of Waste – Leaching – Compliance Test for Leaching of Granular Waste Materials and Sludges – Part 2: One Stage Batch Test at a Liquid to Solid Ratio of 10 L/kg for Materials with particle Size below 4 Mm (Without or with Size Reduction).
- EPA Method 1313, 2009. Leaching Test (Liquid–solid Partitioning as a Function of Extract pH) of Inorganic Species in Solid Materials Using a Parallel Batch Extraction Test.
- Fällman, A.M., Hartlén, J., 1994. Leaching of Slags and Ashes - Controlling Factors in Field Experiments versus in Laboratory Tests. *Studies in Environmental Science*, vol. 60. Elsevier, pp. 39–54.
- Finkelmann, R.B., 1995. Modes of Occurrence of Environmentally-sensitive Trace Elements in Coal. *Environmental Aspects of Trace Elements in Coal*. Springer, pp. 24–50.
- Gillman, G., Sumpter, E., 1986. Modification to the compulsive exchange method for measuring exchange characteristics of soils. *Soil Res.* 24 (1), 61–66.
- Goldschmidt, V.M., 1954. *Geochemistry*. Soil Sci. 78 (2).
- Guo, Q., et al., 2012. Shale Gas Drilling Experience and Lessons Learned from Eagle Ford. SPE Americas Unconventional Resources Conference, Society of Petroleum Engineers.
- Heasman, L., van der Sloot, H., Quevauviller, P., 1997. Harmonization of Leaching/ extraction Tests. 70. Elsevier Science.
- Heinrichs, H., Schulz-Dobrick, B., Wedepohl, K.H., 1980. Terrestrial geochemistry of Cd, Bi, Ti, Pb, Zn and Rb. *Geochimica Cosmochimica Acta* 44 (10), 1519–1533.
- Ifeadi, C., 2004. The treatment of drill cuttings using dispersion by chemical reaction (DCR). In: A Paper Prepared for Presentation at the DPR Health, Safety & Environment (HSE) International Conference on Oil and Gas Industry in Port Harcourt, Nigeria.
- Institute of Building Technology, Instruction 455/2010: Natural radioactivity in raw and building materials.
- Izquierdo, M., Querol, X., 2012. Leaching behaviour of elements from coal combustion fly ash: an overview. *Int. J. Coal Geol.* 94, 54–66.
- Kabata-Pendias, A., 2011. *Trace Elements in Soils and Plants*, fourth ed., vol. 353. CRC Press Taylor & Francis Group, Boca Raton, USA.
- Kazi, T.G., et al., 2005. Evaluating the mobility of toxic metals in untreated industrial wastewater sludge using a BCR sequential extraction procedure and a leaching test. *Anal. Bioanal. Chem.* 383 (2), 297–304.
- Khater, A.E.M., et al., 2013. Natural radionuclides in clay deposits: concentration and dose assessment. *Radiat. Prot. Dosim.* 156 (3), 321–330.
- Klein, W., 1989. Mobility of environmental chemicals, including abiotic degradation. *Ecotoxicol. Clim.* 9 (5), 65–78.
- Kosson, D.S., et al., 2002. An integrated framework for evaluating leaching in waste management and utilization of secondary materials. *Environ. Eng. Sci.* 19 (3), 159–204.
- Krauskopf, K.B., Bird, D.K., 1967. *Introduction to Geochemistry*, vol. 721. McGraw-Hill, New York.
- Lavergren, U., et al., 2009. Mobility of trace elements in black shale assessed by leaching tests and sequential chemical extraction. *Geochem. Explor. Environ. Anal.* 9 (1), 71–79.
- Li, M., et al., 2009. Extraction of vanadium from black shale using pressure acid leaching. *Hydrometallurgy* 98 (3), 308–313.
- Magiure, M.E., Cowan, J.A., 2002. *Magnesium chemistry and biochemistry*.

- Biomaterials 15, 203–210.
- Mantis, I., Voutsas, D., Samara, 2005. Assessment of the environmental hazard from municipal and industrial wastewater treatment sludge by employing chemical and biological methods. *Ecotoxicol. Environ. Saf.* 62 (3), 397–407.
- Mohamed, A.-M.O., Antia, H.E., 1998. *Geoenvironmental Engineering*. Elsevier.
- Möller, P., Giese, U., 1997. Determination of easily accessible metal fractions in rocks by batch leaching with acid cation-exchange resin. *Chem. Geol.* 137 (1–2), 41–55.
- Mykowska, a., et al., 2015. Radioactivity of drilling cuttings from shale resources of the lower paleozoic baltic basin. *Physicochem. Problems Mineral Process.* 51 (2).
- Okoro, E.E., Adewale, D., 2014. Experimental analysis of shale for evaluating shale drilling fluid interaction in Agbada formation. *Br. J. Appl. Sci. Technol.* 4 (35), 4878.
- Patterson, J.H., et al., 1986. Geochemistry and mineralogical residences of trace elements in oil shales from Julia Creek, Queensland, Australia. *Chem. Geol.* 55 (1), 1–16.
- Piszcz-Karaś, K., Łuczak, J., Hupka, J., 2014. Mobility of shale drill cuttings constituents. *Physicochem. Probl. Min. Process* 50 (2), 795–810.
- Querol, X., et al., 2001. Extraction of soluble major and trace elements from fly ash in open and closed leaching systems. *Fuel* 80 (6), 801–813.
- Rogala, A., et al., 2014. Carbon dioxide sequestration during shale gas recovery. *Physicochem. Probl. Min. Process* 50 (2), 681–692.
- Ruppert, L., et al., 1996. Origin and significance of high nickel and chromium concentrations in Pliocene lignite of the Kosovo Basin, Serbia. *Int. J. coal Geol.* 29 (4), 235–258.
- Sahuquillo, A., Rigol, A., Rauret, G., 2003. Overview of the use of leaching/extraction tests for risk assessment of trace metals in contaminated soils and sediments. *TrAC Trends Anal. Chem.* 22 (3), 152–159.
- Salminen, R., 2005. *Geochemical Atlas of Europe Part 1: Background Information, Methodology and Maps*. Geological Survey of Finland, Finland.
- Schieber, J., 1995. Anomalous iron distribution in shales as a manifestation of “non-clastic iron” supply to sedimentary basins: relevance for pyritic shales, base-metal mineralization, and oolitic ironstone deposits. *Miner. Deposita* 30 (3–4), 294–302.
- Sonibare, O.O., et al., 2011. Mineral and trace element composition of the Lokpanta oil shales in the Lower Benue Trough, Nigeria. *Fuel* 90 (9), 2843–2849.
- Stephens, M., Gomez, S., Churan, M., 2009. Laboratory methods to assess shale reactivity with drilling fluids. In: *National Technical Conference & Exhibition (AADE)*, New Orleans, LA.
- Sun, B., et al., 2001. Leaching of heavy metals from contaminated soils using EDTA. *Environ. Pollut.* 113 (2), 111–120.
- Tipping, E., Hurley, M.A., 1992. A unifying model of cation binding by humic substances. *Geochimica Cosmochimica Acta* 56 (10), 3627–3641.
- Torras, J., et al., 2011. Semi-dynamic leaching tests of nickel containing wastes stabilized/solidified with magnesium potassium phosphate cements. *J. Hazard. Mater.* 186 (2–3), 1954–1960.
- Ugurlu, A., 2004. Leaching characteristics of fly ash. *Environ. Geol.* 46 (6), 890–895.
- Vijay, R., Sihorwala, T.A., 2003. Identification and leaching characteristics of sludge generated from metal pickling and electroplating industries by toxicity characteristics leaching procedure (TCLP). *Environ. Monit. Assess.* 84 (3), 193–202.
- Yu, C., et al., 2014. Retention and transport of arsenic, uranium and nickel in a black shale setting revealed by a long-term humidity cell test and sequential chemical extractions. *Chem. Geol.* 363 (0), 134–144.