



## Contents of Rare Earth Elements in Acidic Waters Linked to Mining of Coal and Lignite (Upper Silesia and Muskau Bend, Southern Poland)

*Arkadiusz Bauerek<sup>1\*</sup>, Małgorzata Bebek<sup>1</sup>,  
Barbara Bialecka<sup>1</sup>, Krzysztof Mitko<sup>1</sup>, Maciej Thomas<sup>2</sup>*

<sup>1</sup>Central Mining Institute, Katowice, Poland

<sup>2</sup>F.P.H.U. Chemiqua, Kraków, Poland

\*corresponding author's e-mail: a.bauerek@gig.eu

### 1. Introduction

A group of 15 elements of the periodic table with atomic numbers 57-71 (lanthanum La, cerium Ce, praseodymium Pr, neodymium Nd, promethium Pm, samarium Sm, europium Eu, gadolinium Gd, terbium Tb, dysprosium Dy, holmium Ho, erbium Er, thulium Tm, ytterbium Yb, lutetium Lu) is defined as Rare Earth Elements (REEs). Due to similar properties and ionic radii, which are close to those of Yb and Lu, also scandium Sc and yttrium Y (with atomic numbers 21 and 39, respectively) are included in REEs (International Union Of Pure And Applied Chemistry 1970). Except for Pm, which does not have stable isotopes and, practically, does not occur in natural environment, the remaining elements quoted above form a group with relatively similar characteristics (Henderson 1984, Kabata-Pendias & Szteke 2012). In the surface environment fourteen from among the above mentioned elements are in an oxidation state of +3, whereas Ce<sup>3+</sup> redox can be oxidized to Ce<sup>4+</sup>, and Eu<sup>3+</sup> can be reduced to Eu<sup>2+</sup>.

A characteristic feature of lanthanides is their ionic radius decrease with an increase of atomic number from 103 pm for La<sup>3+</sup> to 86 pm for Lu<sup>3+</sup> („lanthanide contraction”). This phenomenon manifests itself in a change of properties - from more to less alkaline, as well as in solubility decrease with the rise of atomic weight as the ionic radius increases. The differentiation of properties leads to the formation of light REEs (LREEs), containing elements from La to Eu, and heavy REEs (HREEs), containing elements from Gd to Lu, including yttrium. In some works also a third group is distinguished – medium REEs (MREEs) – including elements from Sm to Dy.

Despite considerable scattering of REEs, their average contents in Earth's crust is significant – 0.018% (Kabata-Pendias & Szteke 2012), being on a par with the contents of non-ferrous metals (Cu, Zn, Ga, Ge, As, Cd, In, Sn, Sb, Hg, Tl Pb, Bi) (Polański & Smulikowski 1969). In igneous rocks most REEs occur in granitoids and rhyolites, though REE ore deposits are related to alkaline or ultra-alkaline rocks (Ryka & Maliszewska 1991). In a hypergenic environment REEs can form resistant to weathering primary minerals and can be built in new amorphous or crystalline mineral phases (Minarik et al. 1998, Kokowska-Popławska 2016, Migaszewski et al. 2019, Migaszewski & Gałuszka 2019).

One of the processes leading to secondary activation of REEs is natural or anthropogenic acidification of their environment. Relatively high concentrations of REEs can be found in waters influenced by the acidic mine drainage (AMD) process, where a lowered pH of waters and their increased aggressiveness leads to a release of REEs from the REE-bearing minerals contained in the rock matrix or mining waste (Bozau et al. 2004, Migaszewski et al. 2014, Sun et al. 2007, Varekamp et al. 2009, Zhao et al. 2007).

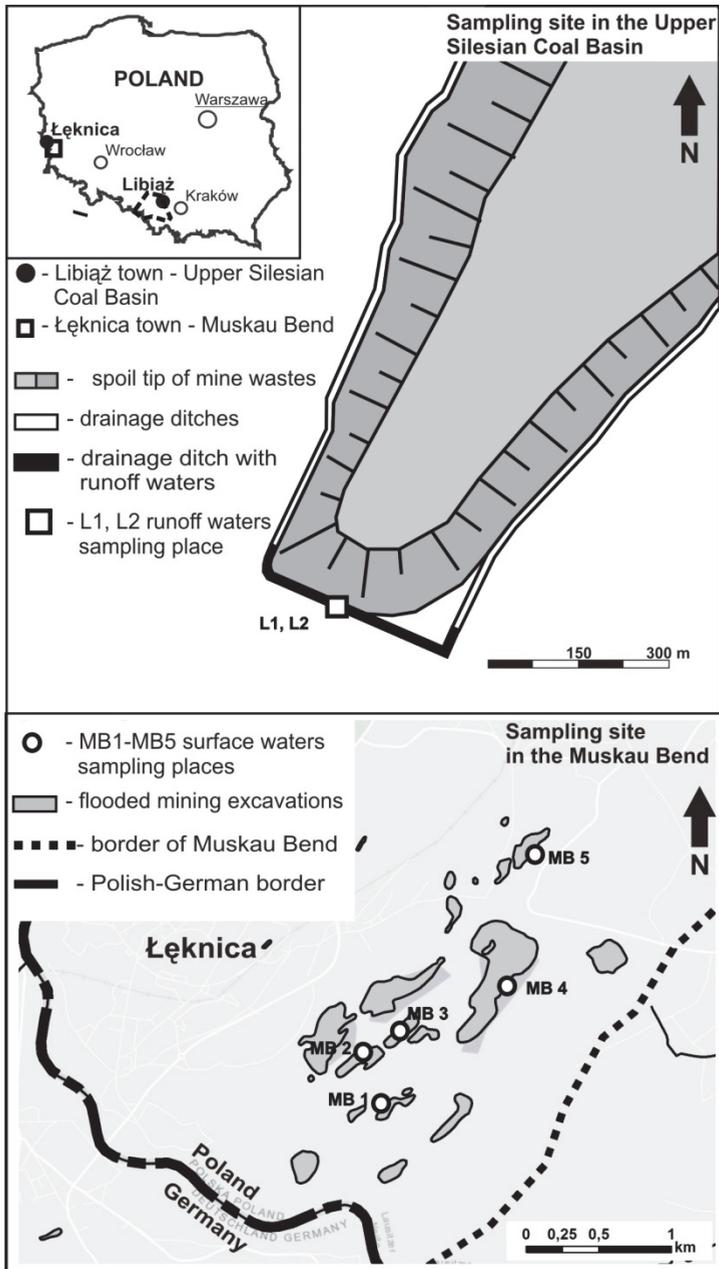
The article presents the first results of initial investigations showing the contents of REEs in AMD waters from the south of Poland, related to coal mining and old lignite mining. No studies on REEs content in acidic mine waters from this region of Poland have been conducted so far, therefore the Upper Silesia Coal Basin and the Muskau Bend were identified as prospective sites for further investigations into factors differentiating the contents of REEs in acidic waters.

Total REE contents in the examined acidic waters as well as normalized contents using North American Shale Composite (NASC) (Haskin et al. 1968, Gromet et al. 1984) were compared with data from other sites, where the water environment acidification was found as processes related to coal, ore and hard rock mining.

It should be noted that the phenomenon of environment contamination in mining areas due to the AMD process is one of the major environmental problems, which needs to be investigated further also in the context of REEs fractionation depending on local geochemical conditions.

## **2. Site description**

Investigations of the acidic runoff waters were conducted in the vicinity of an active coal mining wastes pile, located in the town of Libiąż, in the eastern part of the Upper Silesian Coal Basin (USCB) in the southern part of Poland (Fig. 1).



**Fig. 1.** Localization sampling sites in the eastern part of the Upper Silesia Coal Basin and post-mining lakes in the Muskau Bend

The pile, which has been functioning since the 1980s, contains mainly Carboniferous waste claystones as well as mudstones and sandstones, containing pieces of coal and pyrite ( $\text{FeS}_2$ ), which were produced in the process of coal mining from the Łaziska and Libiąż beds (Westphalian C and D) of the Cracow Sandstone Series (Gabzdyl & Gorol 2008). Currently this facility takes an area of 33.5 hectares, at a relative elevation of 35 m. Acidic waters are retained in a surrounding drainage ditch having a length of 300 m, a width of 5 m and a depth of maximum 1.0 m. This ditch is an element of the acidic water neutralisation system and does not contact underground waters.

Detailed characteristics of the geochemical environment and the variability of AMD waters in Libiąż have been presented in the paper by Bauerek et al (2017). Acidic waters related to the influence of former lignite mining on the environment have been sampled from 5 flooded excavations in the former coal mine “Babina”, located in Łęknica, on the territory of the Muscau Bend. Lignite deposits exploitation in this area was conducted during 1921-1974 and resulted in massive transformations of the landscape as well as the formation of several dozen deep (ranging from 5 to 22 m) anthropogenic reservoirs. Samples were taken from reservoirs characterized by the lowest pH of water, located in the area where mining works were finished at the latest (Jędrszak 1997, Lutyńska & Labus 2015, Skoczyńska-Gajda & Labus 2011).

The occurrence of Miocene lignite deposits directly near the surface is related to glaciotectionic deformations (slices, diapirs) of silty and sandy sediments of the Pliocene, Miocene and older Pleistocene Epoch in the area of terminal moraine of the glacier tongue of the Riss Glaciation (Haracz et al. 2012).

### **3. Materials and methods**

#### **3.1. Sampling and field measurements**

In the summer of 2018 field measurements were done and samples were taken from acidic waters in anthropogenic reservoirs, related to active coal mining (the area of Libiąż, Upper Silesian Coal Basin) and abandoned lignite mining (the area of Łęknica, Muscau Bend). These works resulted in obtaining 2 samples of acidic runoff waters (L1 and L2) and 5 samples of waters filling the lignite mining excavations (MB1, MB2, MB3, MB4 and MB5).

Field measurements of such parameters as: pH, specific electrolytic conductivity, redox potential, dissolved oxygen and temperature were taken using a multifunctional WTW MultiLine 350i meter. Water samples for laboratory tests were taken in glass or plastic bottles, depending on the examined parameter (groups of chemical parameters), and delivered cooled to the laboratory. Except field

measurements and acidity, the remaining parameters were determined in samples filtered in the field through a filter having a pore diameter of 0.45  $\mu\text{m}$ .

### 3.2. Laboratory tests

Total and mineral acidity in the examined water was determined using the potentiometric titration method (hot, with hydrogen peroxide) according to the methodology of American Public Health Association (1998) with expanded uncertainty  $U$  (for coverage factor  $k = 2$  and statistical significance 95%) reaching 20%. The concentration of chlorides ( $U = 8\%$ ) and sulphates ( $U = 10\%$ ) was determined by the ion chromatography method using a DIONEX ICS-5000 ion chromatograph. The concentrations of Ca, Mg, Na, K, Al,  $\text{Fe}_{\text{tot}}$  ( $U = 10\%$ ) were determined by inductively coupled plasma atomic emission spectrometry (ICP-AES) using a Perkin-Elmer Optima 5300DV spectrometer. The dissolved substances were determined by the weighing method ( $U = 10\%$ ). Iron  $\text{Fe}^{2+}$  was determined by the spectrophotometric method using a SPEKOL 1200 spectrophotometer ( $U = 10\%$ ). The concentration of  $\text{Fe}^{3+}$  was calculated as a difference between total iron ( $\text{Fe}_{\text{og}}$ ) and  $\text{Fe}^{2+}$ .

Rare earth elements were determined by the method of inductively coupled plasma atomic emission spectrometry (ICP-MS, Nexion 300S, produced by Perkin Elmer, USA), in accordance with methodology described in the work of Cykowska et al. (2017). Determination of rare earth elements' contents in acidic waters was conducted with expanded uncertainty  $U = 15\%$  (for Sc) and  $U = 10\%$  (for the remaining REEs).

The ICP-MS instrument was optimized with a standard daily procedure. A set of solutions prepared from the Multielement Calibration Standard (CCS-1, Inorganic Ventures, USA) was applied. Influence of physical interferences was minimized with the use of Re (ICP-45W-1, AccuStandard, USA) as an internal standard. The Certified Reference Materials (CRM) used for measuring REE concentrations were NCS DC 70314 and NCS DC 73324. Standard addition tests for selected acid water samples were also carried out.

All chemical analyses were conducted (according to ISO/IEC 17025:2005) in the accredited Laboratory of Water and Wastewater Analysis (Central Mining Institute, Katowice, Poland).

### 3.3. REEs enrichments and ratios

Concentrations of particular REEs in the examined acidic waters, their total concentrations ( $\Sigma\text{REEs}$  La-Lu), concentrations of LREEs (La-Eu), HREEs (Gd-Lu) and MREEs (Sm-Dy) as well as LREE/HREE ratios have been presented in Table 2.

The results obtained from REE measurements were normalized to North American Shale Composite (NASC) (Haskin et al. 1968; Gromet et al. 1984). Calculations allowed to compare REE concentrations collected from different anthropogenic reservoirs and identify any individual REE anomalies.

In addition, the  $La_{NASC}/Yb_{NASC}$  and  $Sm_{NASC}/Yb_{NASC}$  ratios were computed to assess depletion or enrichment of REE subgroups: LREE (La), MREE (Sm), and HREE (Yb).

Ratios values below 0.8 are indicative of negative anomalies whereas those above 1.2 point to positive anomalies (Grawunder et al. 2014).

The depletion or enrichment of individual REE elements:  $Ce/Ce_{NASC}$ ,  $Eu/Eu_{NASC}$ ,  $Gd/Gd_{NASC}$ ,  $Tb/Tb_{NASC}$  ratios in the USCB acidic waters were calculated from the Eq. (1) (Bau and Dulski 1996) and reported in Table 3:

$$Ce/Ce_{NASC} = Ce_{NASC} / (0.5La_{NASC} + 0.5Pr_{NASC}) \tag{1}$$

where:

$Ce_{NASC}$  – a background concentration whereas  $La_{NASC}$  and  $Pr_{NASC}$  are the NASC-normalized La and Pr concentrations, respectively.

For the calculations of  $Eu/Eu_{NASC}$ ,  $Gd/Gd_{NASC}$ ,  $Tb/Tb_{NASC}$  ratios, the following modified equations were applied:

$$Eu/Eu_{NASC} = Eu_{NASC} / (0.5Sm_{NASC} + 0.5Dy_{NASC}) \tag{2}$$

$$Gd/Gd_{NASC} = Gd_{NASC} / (0.5Sm_{NASC} + 0.5Dy_{NASC}) \tag{3}$$

$$Tb/Tb_{NASC} = Tb_{NASC} / (0.5Sm_{NASC} + 0.5Dy_{NASC}) \tag{4}$$

where:

$Eu_{NASC}/Gd_{NASC}/Tb_{NASC}$  – background concentrations whereas  $Sm_{NASC}$  and  $Dy_{NASC}$  are the NASC-normalized Sm and Dy concentrations, respectively.

Modification of equation (1) was needed because distinct enrichment of acidic waters from USCB in Eu, Gd and Tb excludes use of these elements in the calculation of the anomaly.

## 4. Results and discussion

### 4.1. Geochemistry of waters

The results of investigations of selected physicochemical parameters of AMD waters samples collected from the eastern part of the Upper Silesian Coal Basin and from selected reservoirs in the area of the Muscau Bend have been presented in Table 1.

Surface runoff waters which have been found in the vicinity of the waste pile containing coal waste belong to AMD waters. The pH values of waters represented by samples L1 and L2 are low, reaching 3.0 and 2.4, respectively. The hydrogeochemical character of the examined waters presented in Piper's rhomb diagram in Monition's modification (Bagińska & Macioszczyk 1986) indicates that water L1 belongs to the chloride-sulphate-sodium type (Cl-SO<sub>4</sub>-Na), whereas water L2 – to the sulphate-chloride-sodium type (SO<sub>4</sub>-Cl-Na) (Fig. 2).

The sum of dominant anions (SO<sub>4</sub><sup>2-</sup> + Cl<sup>-</sup>) expressed in milligram equivalent percentage is 99.4% mval and 98.7% mval, with the concentrations of sulphates reaching 41.8% mval and 67.2% mval, and the concentrations of chlorides – 57.6% mval and 31.4% mval in waters L1 and L2, respectively. The contents of sodium as the main cation are smaller, reaching 61.9% mval and 47.5% mval. The cation composition is complemented by magnesium, calcium and iron ions.

A very high acidity of water represented by sample L2 (3820 mg/l CaCO<sub>3</sub>) and a high concentration of sulphates (5630 mg/l), iron Fe<sup>3+</sup> (485 mg/l) and aluminium (227 mg/l) indicates that it is a stagnant water, which affected the silty sediments filling the surrounding drainage ditch over a long period of time (Bauerek et al. 2017). The acidic water represented by sample L1 is characterized by a distinctly higher pH (3.0) and lower concentrations of most ions: SO<sub>4</sub> – 3270 mg/l, Fe<sup>3+</sup> – 174 mg/l, Al – 53.3 mg/l. An exception is the concentration of chlorides, which reaches 3330 mg/l and is higher than the concentration of sulphates.

The characteristics of acidic mine waters from this location, presented in the work of Bauerek et al. (2017) demonstrate that water L1 should be classified as transitional water – between shortly retained and stagnant water in the ditch over a long period of time (a few weeks to 1-2 months). Due to a higher pH and lower acidity, such waters are characterized by lower aggressiveness towards silty sediments filling the ditch, and, in consequence, a lower ability to decompose mineral phases and leach metals.

Waters sampled from anthropogenic reservoirs in the area of the former lignite mine in the Muscau Bend are characterized by a pH ranging from 2.6 to 3.5; a dominance of sulphates (from 148 mg/l to 1150 mg/l) in the water ionic composition and higher concentrations of iron, reaching 101 mg/l. The above

mentioned features confirm that the chemical composition of these waters is shaped as a result of the AMD process. A much higher concentration of  $\text{Ca}^{2+}$  ion among cations, with very small contents of chlorides, causes that the examined AMD waters from Muscau Bend belong to the hydrogeochemical sulphate-calcium type (Fig. 2).

**Table 1.** Physico-chemical characteristics acidic waters

Parameter	Eastern part of the Upper Silesia Coal Basin		Southern part of the Muscau Bend				
	L1	L2	MB1	MB 2	MB 3	MB 4	MB5
pH	3.0	2.4	2.8	2.9	2.8	2.6	3.5
EC ( $\mu\text{S}/\text{cm}$ )	12 400	11 300	1 800	1 770	1 880	1 840	396
TDS (mg/l)	10 800	12100	1620	1690	1780	1480	218
Eh (mV)	510	547	496	546	544	567	396
Alkalinity (mg/l $\text{CaCO}_3$ )	< 5	< 5	< 5	< 5	< 5	< 5	< 5
Acidity tot. (mg/l $\text{CaCO}_3$ )	1020	3820	650	483	578	750	103
Major ions (mg/l)							
$\text{Ca}^{2+}$	467	323	163	217	200	103	27.7
$\text{Mg}^{2+}$	340	417	29.6	35.7	33.8	21.2	5.71
$\text{Na}^+$	2250	1430	6.67	7.01	6.71	6.53	5.01
$\text{K}^+$	52.4	5.47	6.37	8.02	7.23	5.47	4.50
$\text{Cl}^-$	3330	1940	6.2	4.8	4.8	4.3	6.9
$\text{SO}_4^{2-}$	3270	5630	1040	1120	1150	1000	148
$\text{Fe}^{2+}$	23	15	39	1.2	3	2.4	1
$\text{Fe}^{3+}$	174	485	101	51.3	94.6	125.6	0.58
Al	63.3	227	3.96	28.0	18.4	24.8	4.85

Despite the features which are typical of AMD waters, the examined waters from the former lignite mine „Babina” are characterized by a relatively low concentration of total dissolved solids (from 218 mg/l to 1780 mg/l) and low acidity (from 103 mg/l  $\text{CaCO}_3$  to 750 mg/l  $\text{CaCO}_3$ ) compared to the acidic waters from the USCB.

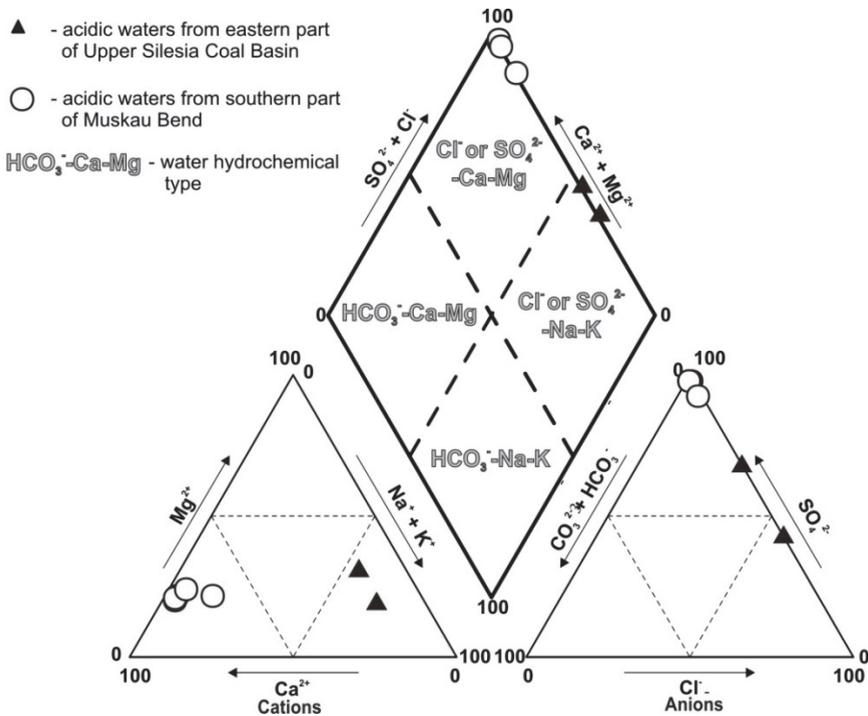
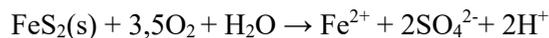


Fig. 2. Chemical composition of analyzed acidic waters from the eastern part of the Upper Silesia Coal Basin and the Muskau Bend

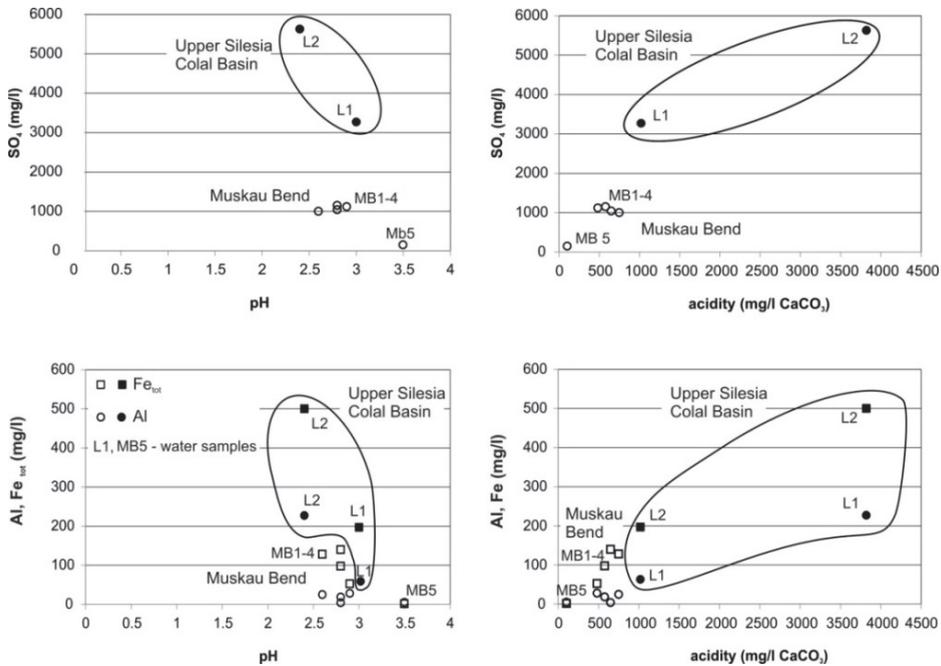
Low pH values of the waters subjected to investigations are related to the oxidation of pyrite contained in the waste shale of the Carboniferous in the coal mining waste pile in Libiąż as well as in Miocene loams, sands and pieces of lignite in the vicinity of water reservoirs of the Muskau Bend (Bozau et al. 2004, Bauerek et al. 2017). The first stage of water acidity occurs due to pyrite decomposition in the presence of atmospheric oxygen and water according to the following reaction (Lattermoser 2010):



However, the major stage of water acidity takes place as a result of the bacterial oxidation of iron  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  with the participation of chemautotrophic acidophilic microorganisms, e.g. *Acidithiobacillus ferrooxidans* bacteria (Lattermoser 2010).

On the plots of dependencies between the concentrations of major parameters ( $\text{SO}_4$ , Al, Fe) and pH and acidity one can clearly see the separation of surface runoff waters from the eastern part of the USCBA (Fig. 3). It is noteworthy that the

use of acidity for differentiating the results allows us to more clearly separate waters from different locations than by using the pH parameter as a differentiating indicator. On charts showing the correlation between the concentrations of  $\text{SO}_4$ , Al,  $\text{Fe}_{\text{tot}}$  and acidity, points that represent samples of water from the Muscau Bend are grouped in a small area of relatively low contents of the parameters above mentioned. On the other hand, points representing acidic waters of the surface runoff from the area of the USBS confirm the results of previous investigations, indicating a high variability of water chemistry (Bauerek et al. 2017).



**Fig. 3.** Plots of  $\text{SO}_4$ , Al,  $\text{Fe}_{\text{tot}}$  concentrations versus pH and acidity of AMD waters

Concentrations of  $\text{SO}_4$ , Al, and  $\text{Fe}_{\text{tot}}$  grouped according to pH indicate that six out of seven water samples show a similar pH range, i.e. from 2.4 to 3.0, whereas sample MB5, which is characterized by the highest pH (3.5), clearly stands out from the remaining samples of waters collected from the Muscau Bend as it has the lowest concentration of  $\text{SO}_4$  (103 mg/l) and  $\text{Fe}_{\text{tot}}$  (1.58 mg/l).

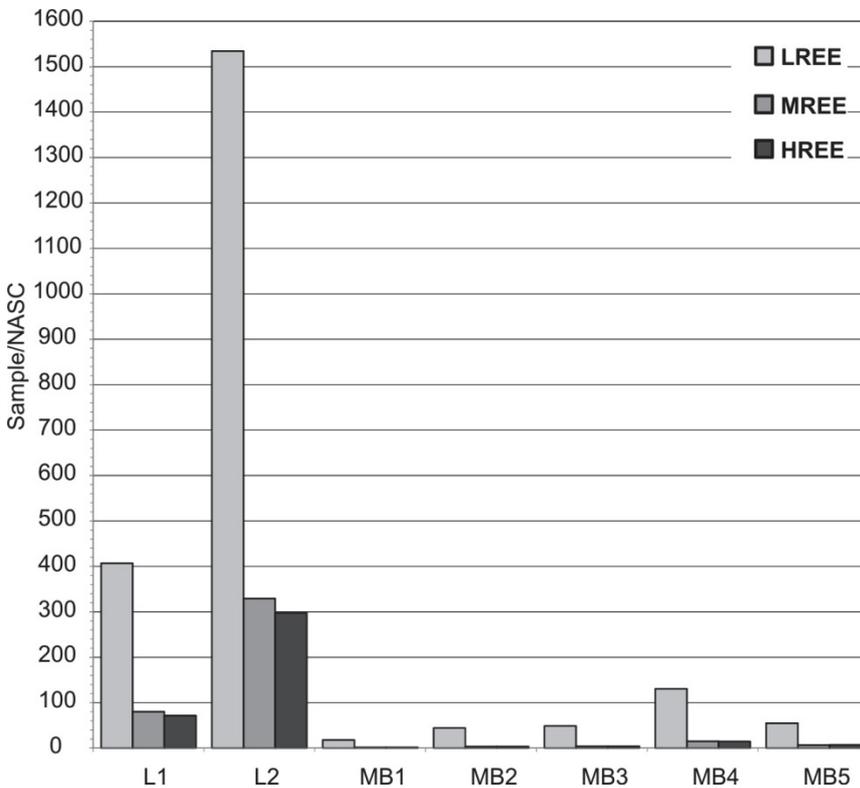
#### 4.2. Measured concentration of REEs

Acidic runoff waters from the eastern part of USCB contain 3.3 to 93 times more REEs (contents of  $\Sigma$ REE for L1 is 478.53  $\mu\text{g/l}$  and 1831.97  $\mu\text{g/l}$  for L2) compared to waters filling the former lignite mining excavations (the contents of  $\Sigma$ REE ranges from 19.7  $\mu\text{g/l}$  to 145.30  $\mu\text{g/l}$ ) (Table 2).

**Table 2.** Measured concentrations of REEs and ratios in the AMD waters of the Upper Silesia Coal Basin and the Muskau Bend

Parameter	Eastern part of the Upper Silesia Coal Basin		Southern part of the Muskau Bend				
	L1	L2	MB 1	MB 2	MB 3	MB 4	MB 5
Light REE (La-Eu)			$\mu\text{g/l}$				
La	65.0	209.1	5.10	14.10	15.20	31.00	15.00
Ce	181.0	687.7	8.60	22.00	24.00	64.00	26.00
Pr	24	95	0.80	1.70	2.00	6.40	2.50
Nd	107	416	2.80	5.50	6.50	24.00	9.20
Sm	25	103	0.50	0.80	0.90	4.30	1.60
Eu	5.3	23.6	0.10	0.20	0.20	0.90	0.40
Heavy REE (Gd-Lu)							
Gd	26.9	102.4	0.60	1.2	1.40	4.80	2.20
Tb	3.4	15.6	0.10	0.20	0.20	0.70	0.40
Dy	19.6	84.6	0.50	1.00	1.30	4.10	2.10
Ho	3.3	14.7	0.10	0.20	0.20	0.80	0.40
Er	9.1	39.8	0.20	0.50	0.60	2.20	1.20
Tm	1.2	5.0	0.05	0.10	0.10	0.30	0.10
Yb	7.2	31.0	0.20	0.30	0.30	1.60	0.80
Lu	1.0	4.2	0.05	0.05	0.05	0.20	0.10
$\Sigma$ REE	478.53	1831.97	19.70	47.85	52.95	145.30	62.00
LREE	406.92	1534.68	17.90	44.30	48.80	130.60	54.70
MREE (Sm-Dy)	79.98	329.43	1.80	3.40	4.00	14.80	6.70
HREE	71.61	297.30	1.80	3.55	4.15	14.70	7.30
LREE/ HREE	5.68	5.16	9.94	12.48	11.76	8.88	7.49

In the examined waters the content of HREEs is much lower compared to LREEs, but in the waters from the USBC it is two times higher (the average value of LREE/HREE is 5.4) compared to the waters from the Muskau Bend (the average value of LREE/HREE is 10.1) (Table 2, Fig. 4). In terms of contents of individual REEs, the examined waters are similar. In the acidic waters from the USBC and the Muskau Bend the dominant element is Ce, the contents of which reach 181.0  $\mu\text{g/l}$  and 687.7  $\mu\text{g/l}$  and from 8.6  $\mu\text{g/l}$  to 64  $\mu\text{g/l}$ , respectively. Nd (the contents 107  $\mu\text{g/l}$  and 416  $\mu\text{g/l}$ ) and La (the contents 65  $\mu\text{g/l}$  and 209.1  $\mu\text{g/l}$ ) have the second and third place in the USBC waters, while in the acidic waters from the Muskau Bend these elements occur in a reverse order: La (5.1-31  $\mu\text{g/l}$ ) prevails over Nd (2.8-24  $\mu\text{g/l}$ ).



**Fig. 4.** Measured concentrations of LREEs, MREEs and HREEs in acidic waters

Concentrations of REEs in acidic waters sampled from the vicinity of coal waste pile are characterized by high variability, which probably results from different time of acidic water retention in the vicinity of silty sediments, being

the carriers of REEs (Kokowska-Popławska 2012, Zhao et al. 2007). A comparison of shortly retained water, represented by sample L1, with stagnant waters, represented by sample L2, revealed that the acidic runoff waters were 4 times (from 3.2 to 4.5 times) richer in REEs, which was accompanied by a 3.7-fold increase in acidity, lowered pH – from 3.0 to 2.4, and an increased content of soluble components (Table 1).

A comparison of REEs contents in acidic waters L1 and L2 with the results of tests for AMD waters from other locations indicates that the waters from the eastern part of USCB have a relatively higher content of REEs. For example, water L1 has a higher total concentration of  $\Sigma$ REEs than in the natural standard reference water sample PPREE 1 (Animas River, Colorado, USA), where the value of  $\Sigma$ REEs reaches 457.73  $\mu\text{g/l}$  (Verplanck et al. 2001). On the other hand, the acidic water represented by sample L2 is characterized by  $\Sigma$ REE concentration of 1831,9  $\mu\text{g/l}$ , which is 4 times higher than that in the reference water. The total concentration of  $\Sigma$ REEs in the acidic runoff waters from the mining waste pile in the eastern part of USCB is higher than the values quoted for AMD waters pumped from Sitai coal mine (north China), where the average total value of  $\Sigma$ REEs is 61.2  $\mu\text{g/l}$  (Zhao et al. 2007). The recorded total concentrations of  $\Sigma$ REEs in samples L1 and L2 are on a comparable level or higher than the total concentration of REEs in waters flowing from the former Zn-Pb mine ( $\Sigma$ REEs 1940  $\mu\text{g/l}$ ) in Montevecchio/Sardinia/Italy (Cidu et al. 2011) and in waters from lignite open pit mines in Lusatia/Germany ( $\Sigma$ REEs = 770  $\mu\text{g/l}$ ) (Bozau 2004). Whereas REEs concentrations in acidic runoff waters are much lower than in the waters from the former uranium mine in Thuringia/Germany ( $\Sigma$ REEs = 8150  $\mu\text{g/l}$ ) (Grawunder & Merten 2012), Osamu Utsumi uranium mine in Brazil ( $\Sigma$ REEs = 29 000  $\mu\text{g/l}$ ) (Miekeley et al. 1992).

REEs concentrations in acidic runoff waters from USCB are much lower comparing to the REEs concentrations in some shallow water bodies in Wiśniówka quarries in south-central Poland (pools:  $\Sigma$ REEs = 17 916  $\mu\text{g/l}$ , de-watering ditch  $\Sigma$ REEs = 8519  $\mu\text{g/l}$ ). However periodically (depending on the residence time), the sum of REEs recorded in the ditches in vicinity of the coal waste pile (USCB) is higher than in waters from mine pit lakes (Podwiśniówka pit lake  $\Sigma$ REEs = 684  $\mu\text{g/l}$ , Wiśniówka Duża pit lake  $\Sigma$ REEs = 219  $\mu\text{g/l}$ ) (Migaszewski et al. 2019). This may suggest that the two mentioned shallow water reservoirs contain more aggressive waters with greater leaching ability of REE-containing minerals.

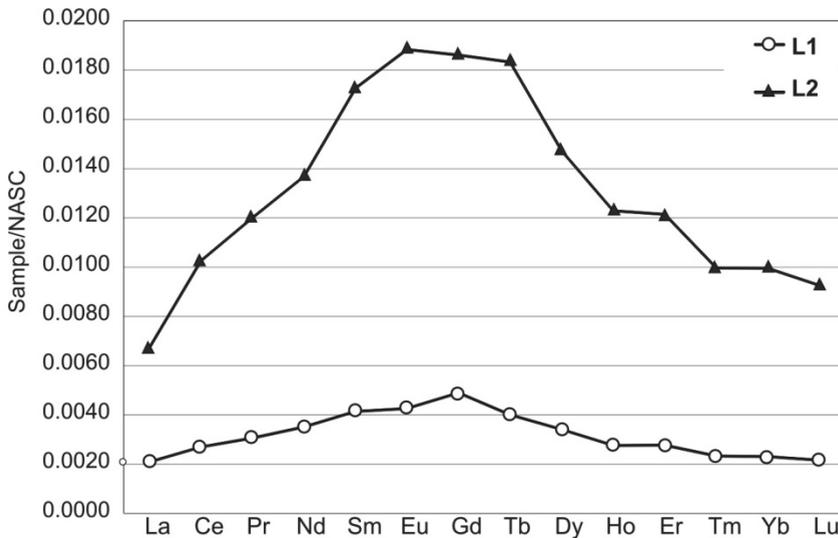
AMD waters form the southern part of the Muskau Bend area affected by former mining of lignite – they are less rich in REEs due to dilution by ground waters. Concentrations of  $\Sigma$ REEs in waters from abandoned open pit mining excavations and depressions caused by mining subsidence varied from 19.7 to

145.3 µg/l. Such results are similar to REEs contents in streams and aquifers affected by AMD reported from Spain and USA (Olias et al. 2008, Verplanck et al. 2004).

**4.3. NASC-normalized concentration of REEs**

North American Shale composite (NASC), (Haskin et al. 1968, Gromet et al. 1984) was used for normalization of REEs concentrations in acidic waters. Plots of shale normalizing the REE patterns of AMD waters from the USCB and the Muskau Bend are presented in the Figures 5 and 6, respectively.

The REE NASC-normalized pattern of acidic runoff waters (L1 and L2) shows a positive anomaly of MREEs with Sm, Eu, Gd and Tb enrichment (Fig. 5), and depletion in LREEs. This is the reverse relationship when compared with measured REE concentration.



**Fig. 5.** NASC-normalized REE pattern in acidic runoff waters from the eastern part of the Upper Silesian Coal Basin

A similar roof-shaped NASC-normalized REE pattern was found in AMD pit waters located within Upper Cambrian quartzite in the Holy Cross Mountain and for acidic fresh water lake on Axel-Heiberg Island (northwest Canada) (Migaszewski et al. 2014, 2016, 2019), Johannesson & Lyons 1995).

Low values of  $La_{NASC}/Sm_{NASC}$  concentration ratios (0.39 and 0.5) in acidic runoff waters indicate LREEs depletion, while values of  $Sm_{NASC}/Yb_{NASC}$  ratios (1.73 and 1.80) point domination of MREEs group (Table 3).

The NASC normalized plots of waters L1 and L2 are very similar in shape but they are shifted relative to the axis of concentration. This suggests that processes which shape REEs concentrations are the same but at a different stage. Shortly retained water with a higher pH and lower acidity are less rich in REEs than aggressive, strong acidified waters, staying in a ditch for a relatively long time (weeks or even months).

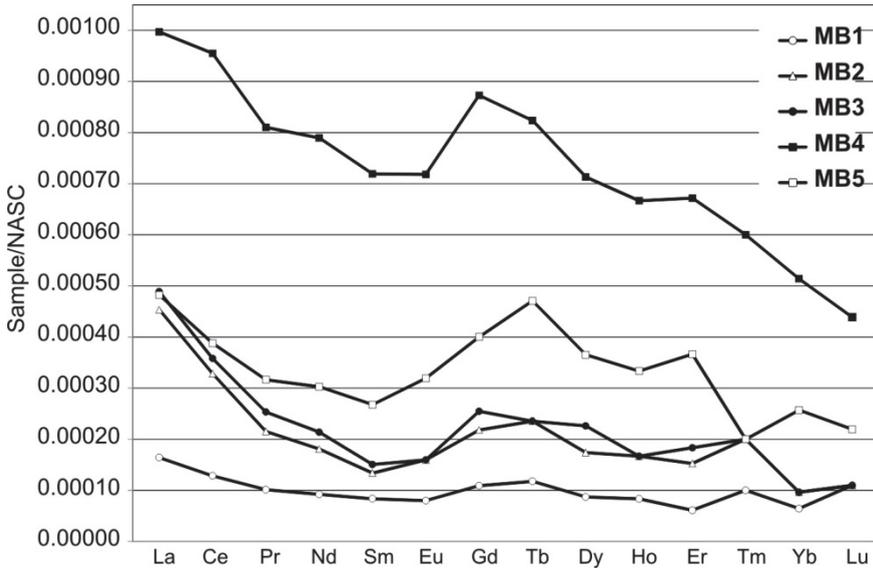
**Table 3.** NASC normalized REEs concentrations ratios in AMD waters of the Upper Silesia Coal Basin and the Muskau Bend

Parameter	Eastern part of the Upper Silesia Coal Basin		Southern part of the Muskau Bend				
	L1	L2	MB 1	MB 2	MB 3	MB 4	MB 5
$LREE_{NASC}/HREE_{NASC}$	0.80	0.75	0.89	1.09	1.10	0.94	0.79
$La_{NASC}/Yb_{NASC}$	0.91	0.68	2.55	4.71	5.07	1.94	1.88
$La_{NASC}/Sm_{NASC}$	0.50	0.39	1.96	3.39	3.25	1.39	1.80
$Sm_{NASC}/Yb_{NASC}$	1.80	1.73	1.30	1.39	1.56	1.40	1.04
$Ce/Ce_{NASC}$	1.05	1.10	0.97	0.98	0.97	1.06	0.97
$Eu/Eu_{NASC}$	1.13	1.18	0.94	1.04	0.85	1.00	1.01
$Gd/Gd_{NASC}$	1.30	1.16	1.28	1.42	1.35	1.22	1.26
$Tb/Tb_{NASC}$	1.06	1.15	1.38	1.53	1.25	1.15	1.49

The NASC-normalized REE concentration patterns of acidic waters in post-mining lakes from the southern part of the Muskau Bend differs significantly from that determined for the acidic runoff waters in the USCB. Samples MB1-MB5 were characterized by two visible positive anomalies of the contents of LREEs, especially La and Ce, and enrichment with Gd, Tb and Dy, included in MREEs (Fig. 6). A similar NASC-normalized pattern of REE contents was found in the waters from artificial post-mining lakes, resulting from lignite exploitation, in the eastern part of Germany (Bozau et al. 2004).

NASC-normalized concentration ratios computed for acidic waters from Muskau Bend point strong positive anomaly of LREE enrichment ( $La_{NASC}/Yb_{NASC}$  ratios from 1.88 to 5.07). MREEs positive anomaly is marked by  $Sm_{NASC}/Yb_{NASC}$  ratios varied from 1.30 to 1.56 (Table 3).

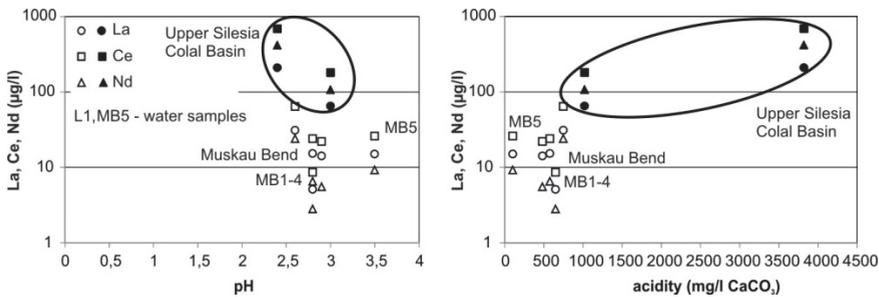
Of the individual MREEs elements, only Gd and Tb, in acidic waters collected from the Muskau Bend, are significantly enriched ( $> 1.2$ ), relative to NASC concentrations (Table 3). Gd/Gd<sub>NASC</sub> and Tb/Tb<sub>NASC</sub> ratios are from 1.22 to 1.42 and from 1.25 to 1.53, respectively.



**Fig. 6.** NASC-normalized REE concentration patterns in acidic surface waters from the southern part of the Muskau Bend

Concentrations of three major REEs (La, Ce and Nd) in acidic waters from two coal mining sites, grouped according to pH and acidity, have been presented in Fig. 7. Acidic waters from the eastern part of the USCB on the plot of La, Ce and Nd versus acidity are a clearly separate group, located in the range of relatively high REE concentrations, accompanied by high acidity ( $> 1000 \text{ mg/l CaCO}_3$ ).

Presentation of the concentrations of REEs grouped according to pH indicates that in the vicinity of the coal mining waste pile the process of REEs release from rock matrix in contact with acidic waters occurs with greater intensity. Due to higher water aggressiveness (acidity 1020 and 3820  $\text{mg/l CaCO}_3$ ), the concentrations of all REEs ( $\Sigma\text{REE } 478.53 \text{ }\mu\text{g/l}$  and  $1831.97 \text{ }\mu\text{g/l}$ ) in acidic runoff waters from the USCB are several times higher than in the flooded lignite mining excavations ( $\Sigma\text{REE}$  from  $19.7 \text{ }\mu\text{g/l}$  to  $145.30 \text{ }\mu\text{g/l}$ ).



**Fig. 7.** Plots of La, Ce and Nd concentrations against pH and acidity in AMD waters from the USCB and the Muskau Bend

Considerable differentiation in REEs concentrations in the investigated acidic waters is probably also related to the local hydrodynamic system. Acidic water samples from the ditch surrounding the coal waste pile are slightly diluted with rainwaters, originating directly from precipitation. Most probably waters from the flooded lignite mining excavations are diluted with underground waters, as these reservoirs are not separated from the aquifer.

## 5. Conclusions

Acidic runoff waters from areas in the vicinity of coal waste piles (Upper Silesia Coal Basin-USCB) and flooded lignite mining excavations (Muskau Bend) are an example of AMD waters rich in rare earth elements (REEs). High concentrations of REEs in acidic waters from the USCB result mainly from the high aggressiveness of acidic waters in relation to loamy sediments filling the drainage ditch, which are the source of REEs, and increase as the water remains in the ditch.

A characteristic feature of acidic waters from the two sites is an evident dominance of the LRREs (La-Eu) over the fraction of the HREEs (Gd-Lu). In the USCB waters this disproportion is twice higher than in the waters from the Muskau Bend. NASC-normalized REE concentration pattern concentrations show that the waters from the USCB are rich in MREEs (Sm, Eu, Gd and Tb), while the waters from the Muskau Bend are characterized by a positive anomaly of LREEs (La and Ce) and a less marked anomaly of MREEs (Gd, Tb and Dy).

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## Abstract

The aim of the research was comparison rare earth elements contents in acidic waters related to coal mining in the eastern part of the Upper Silesian Coal Basin (USCB), southern Poland, and the former lignite mining in the Polish part of the Muskau Bend. Acidic runoff waters flowing down from mine waste piles in the USCB are enriched with REEs ( $\Sigma$ REEs 478.5 and 1831.9  $\mu\text{g/l}$ ) compared to waters filling old lignite mining excavations ( $\Sigma$ REEs 19.7-145.3  $\mu\text{g/l}$ ). High concentrations of REEs in acidic waters from the USCB result from their high aggressiveness (acidity 1020 mg/l  $\text{CaCO}_3$  and 3820 mg/l  $\text{CaCO}_3$ , pH 2.4 and 3.0) to loamy sediments being a source of REEs, and increase as the time of their contact increases. Concentrations of NASC-normalized REEs show that waters from the USCB are enriched in MREEs (Sm, Eu, Gd and Tb), while the waters from the Muskau Bend are characterized by a positive anomaly of LREEs (La and Ce) and a less marked anomaly of MREEs (Gd, Tb and Dy).

## Keywords:

acid mine drainage (AMD), rare earth elements (REE), coal, lignite, acidity, sulfates

## Zawartości pierwiastków ziem rzadkich w kwaśnych wodach związanych z górnictwem węgla kamiennego i węgla brunatnego (Górny Śląsk i Łuk Mużakowa, południowa Polska)

## Streszczenie

Celem badań było porównanie zawartości pierwiastków ziem rzadkich w kwaśnych wodach związanych z wydobyciem węgla kamiennego, we wschodniej części Górnośląskiego Zagłębia Węglowego (GZW) oraz związanych z dawnym wydobyciem węgla brunatnego w polskiej części Łuku Mużakowa. Kwaśne wody spływu powierzchniowego z hałd odpadów górniczych GZW są wzbogacone w pierwiastki ziem rzadkich (REE) ( $\Sigma$ REE 478,5 i 1831,9  $\mu\text{g/l}$ ) w porównaniu do wód wypełniających stare wyrobiska górnicze węgla brunatnego ( $\Sigma$ REE 19,7-145,3  $\mu\text{g/l}$ ). Wysokie stężenia REE w kwaśnych wodach z GZW wynikają z ich wysokiej agresywności (kwasowość 1020 mg/l  $\text{CaCO}_3$  i 3820 mg/l

CaCO<sub>3</sub>, pH 2,4 i 3,0) względem ilastych osadów będących źródłem REE i rosną wraz z upływem czasu ich kontaktu z osadami. Stężenia pierwiastków ziem rzadkich znormalizowane do północnoamerykańskiego łupku złożonego (NASC) pokazują, że kwaśne wody z GZW są wzbogacone w pośrednie pierwiastki ziem rzadkich (MREE) (Sm, Eu, Gd i Tb), podczas gdy wody z Łuku Mużakowa charakteryzują się dodatnią anomalią stężeń lekkich pierwiastków ziem rzadkich LREE (La i Ce) i mniej wyraźnymi anomaliami pierwiastków pośrednich MREE (Gd, Tb i Dy).

**Słowa kluczowe:**

kwaśny drenaż górniczy, pierwiastki ziem rzadkich, węgiel, węgiel brunatny, kwasowość, siarczany