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LEACHABILITY OF HEAVY METALS (Fe, Zn and Ni) FROM COAL MINE ROCKS

WYPŁUKIWANIE METALI CIĘŻKICH (Fe, Zn i Ni) ZE SKAŁ PRZYWĘGLOWYCH

Abstract: The majority of heat and energy delivered to Polish houses derive from coal combustion. The exploitation of underground resources is connected with excavation of huge quantities of metal-rich waste rocks. These metals may be released to the environment and contribute to the pollution of water and soil systems which is dangerous for biota and human health. The mobility and bioavailability of metals depend on their chemical form. In present work, we determined geochemical speciation of Fe, Ni and Zn in samples of waste rocks from five coal mines from both USCB and LCB. The most abundant metal in easily-extractable phases (water-soluble, exchangeable, acid-soluble) was Zn (MF_{Zn} = 24.4÷53.4) followed by Ni (MF_{Ni} = 5.1÷19.2) and Fe (MF_{Fe} = 0.2÷3.6). The mobility of Fe was similar in rocks originating from both coal basins (K-W, $p = 0.2253$), Ni was higher in LCB whereas Zn in USCB rocks (K-W, $p < 0.05$). It was also found that during first years of storage and exposure to natural weathering, only a small portion of metals was released to the environment as the total concentrations and fractionation of Fe, Ni and Zn were similar in fresh and weathered coal waste rocks from Wesola and Murcki coal mines, up to 3 and 15 years of weathering, respectively.

Keywords: waste rocks, heavy metal, geochemical speciation

In Poland, in spite of the changes in energy sector that took place during last decades, the majority of electricity and heat still derive from coal combustion (more than 90% in 2005) [1]. Almost all hard coal production in Poland is concentrated in the Upper Silesian Coal Basin (USCB) (Southern Poland). The only active coal mine (CM) outside USCB - Bogdanka CM is located in South-Eastern Poland and is the only CM exploiting resources of the Lublin Coal Basin (LCB). Coal mining activities is inevitably connected with the excavation of huge amounts of dump rocks [2, 3]. The disposal of waste rock originating from coal production is an important environmental issue due to the potential production of acidic and metal-rich drainage (AMD) [4]. Following transport of heavy metals to the soil and water system [5-10] results in growing hazard to living organisms, including people.

The threat posed by metals depends strongly on their mobility and bioavailability [11-13] which is different depending on metal geochemical form. Water-soluble and exchangeable forms are considered readily mobile and available to biota. Carbonate bound, occlusion in Fe and Mn oxides, or complexes with organic matter OM have been found to be released due to changes in pH and redox conditions and be responsible for long-term effects [14, 15] whereas metals incorporated in the crystalline lattices appear relatively stable.

The aim of the present study was to determine chemical portioning of Fe, Ni and Zn in coal waste rocks from both Polish coal basins and evaluate the amount of metals that may be released from the investigated material in short and long-term perspective. We also wanted to assess changes in chemical fractionation of Fe, Ni and Zn with the course of time.

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Material and method

The mine tailings used used for this work originated from Upper Silesian (USCB) and Lublin Coal Basins (LCB). USCB: samples were collected from currently exploited Murcki, Wesola and Wujek coal mines (M1, WU1, WU2, WE1) as well as the dumping areas (M2-M4, WE2, WE3). LCB: samples originated from Bogdanka (B1-B4), the only coal mine exploiting resources of the area. Fractionation of Fe, Zn and Ni was carried out following the sequential partial dissolution scheme proposed by Tessier [13] and following modifications proposed by Yu et al [16] the water soluble fraction step was added before the extraction of exchangeable fraction.

The relative index of metal mobility is calculated as a "mobility factor" [17-19] on the basis of the equation:

$$\mathrm{MF} = \frac{\mathrm{water-soluble + exchangeable + acid-soluble}}{\mathrm{water-soluble + exchangeable + acid-soluble + reducible + oxidizable + residual}}\, x100$$

Statistical analysis

Due to the non-parametrical character of the data, Kruskall-Wallis and U Mann--Whitney tests were applied and the significance level of $p < 0.05$ was accepted. Statistical tests were performed with Statistica 8 software.

Results and discussion

In fresh rock samples Fe was the most abundant metal of all investigated (av. 2468.22 mg/kg) (Fig. 1), which was present mostly in residual phase (60.8% [WU2] - 82.1% [B2]) (Fig. 2). Fe was followed by Zn (552.92 mg/kg) and Ni (356.04 mg/kg) (Fig. 1). Similarly to Fe, the majority of Ni in the investigated fresh rocks was bound with residual fraction (60.7% [B4] - 77.5% [M1]) (Fig. 2).

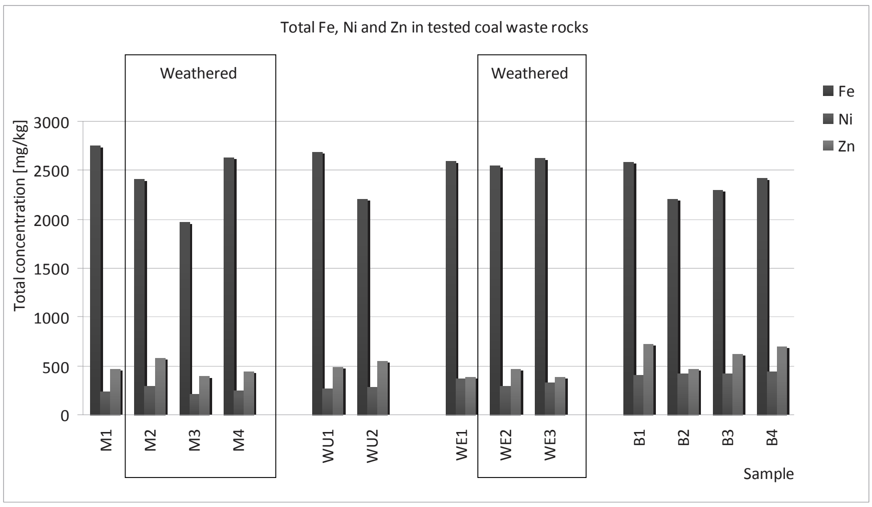

Fig. 1. Total concentrations of Fe, Ni and Zn in waste rocks originating from different Polish coal mines

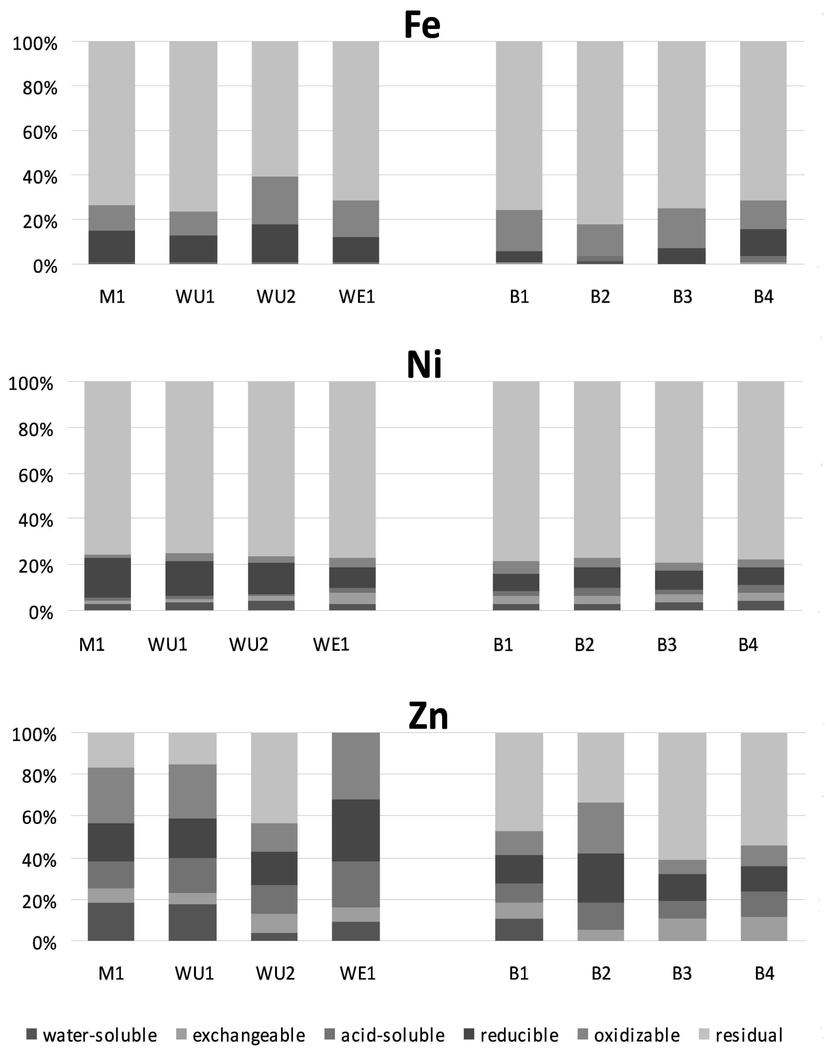

Fig. 2. Proportional distribution of Fe, Ni and Zn between fractions in fresh rock samples

The distribution of Zn between fractions in fresh rock samples differed from reported for Fe and Ni. The results show that the pool of labile metal (water-soluble+exchangeable+acid-soluble) does not depend on its total concentration. In spite of the fact that the total highest concentrations between investigated metals were found for Fe, the most abundant metal in labile phase was Zn (high MF values) (Tab. 1). Statistical analyses showed that the mobility of Fe was similar in rocks originating from both coal basins (K-W, $p = 0.2253$), Ni was higher in LCB whereas Zn in USCB rocks (K-W, $p < 0.05$). However, the pool of easily leachable Fe and Ni was higher in rocks collected from LCB (K-W; $p < 0.05$) whereas the Zn was comparable in rocks from both coal basins.

Table 1

Mobility factors and selected properties of the investigated coal waste rocks

Sample	**MF_{Fe}**	**MF_{Ni}**	**MF_{Zn}**
M1	0.8	5.1	43.7
M2	2.8	7.1	46.5
M3	0.5	6.4	41.4
M4	1.2	6.4	53.4
WU1	0.6	6.5	45.0
WU2	0.5	8.0	41.3
WE1	0.6	14.3	38.5
WE2	1.1	8.6	43.2
WE3	2.8	10.3	48.1
B1	0.7	13.4	46.3
B2	3.6	16.0	24.4
B3	0.2	14.9	37.3
B4	3.6	19.2	43.3

In the weathered rocks [M2-M4, WU2-WU3] total concentrations of the metals investigated were similar to those reported for fresh rock originating from an appropriate coal mine. The sequential extraction of samples subjected to natural weathering revealed that there were only minor changes in proportional distribution of those metals between geochemical forms including the increase of water-soluble (Fe and Ni) and exchangeable (Ni and Zn) metals (Fig. 3). Similar phenomena have recently been described for waste material from surface coal mine sites in Southern Wales [6]. It can be therefore assumed that in short-terme perspective the environmental hazard due to Fe, Ni and Zn leaching from it is of minor importance. However, with the course of time the decrease in rock pH may appear and following mobilization of metals bound to other geochemical fractions, especially carbonates. Additionally, waste rocks from both coal basins contain substantial amounts of metals, especially Fe and Zn, bound to phases susceptible to oxidation (Figs 2 and 3). Waste rocks are often used for civil engineering purposes which causes an increase in the exposed area of waste rock subjected to weathering and may contribute to the intensification of heavy metals elution and transport to water and soil system.

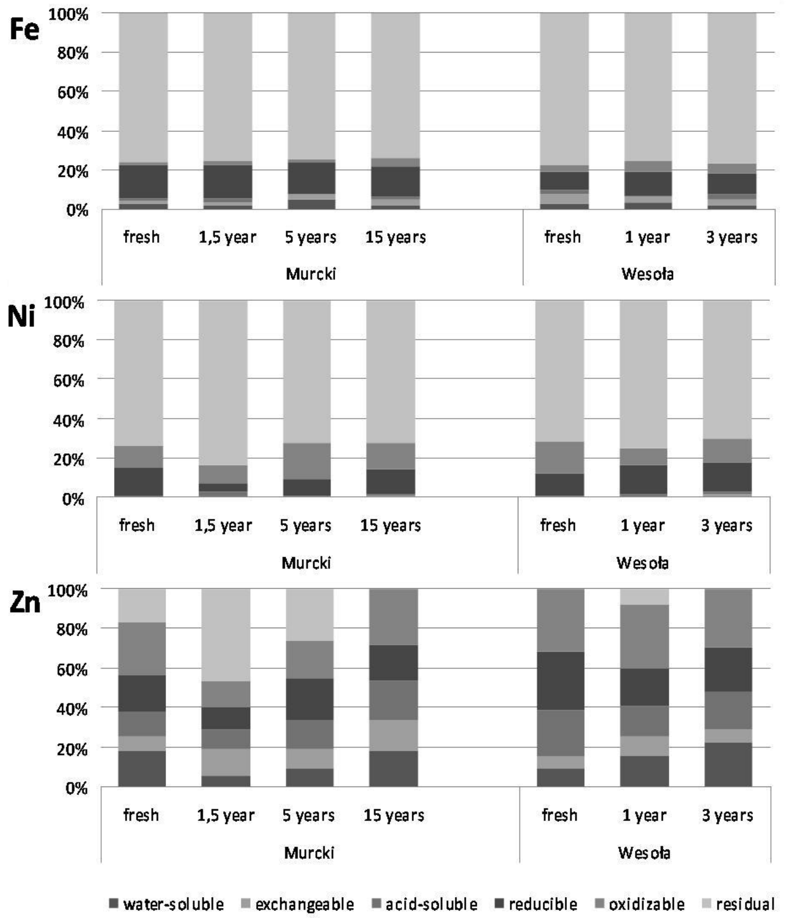

Fig. 3. Proportional distribution of Fe, Ni and Zn between fractions in fresh rock samples

Abbreviations

LCB - Lublin Coal basin, USCB - Upper Silesian Coal Basin, capacity, MF - mobility factor, AMD - acid mine drainage, CM - coal mine, W-S - water soluble, EX - exchangeable, A-S - acid-soluble, RD - reducible, OX - oxidizable, RS - residual.

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WYPŁUKIWANIE METALI CIĘŻKICH (Fe, Zn i Ni) ZE SKAŁ PRZYWĘGLOWYCH

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Abstrakt: Większość ciepła i energii dostarczanej do polskich domostw pochodzi ze spalania węgla kamiennego. Podziemna eksploatacja tego surowca związana jest z wydobyciem na powierzchnię dużych ilości bogatych w metale skał przywęglowych. Metale te mogą zostać uwolnione do środowiska, przyczyniając się tym samym do zanieczyszczenia gleby i wody, które jest niebezpieczne dla organizmów żywych i zdrowia ludzi. Mobilność i biodostępność metali zależy od ich chemicznej postaci. W bieżącej pracy przedstawiono wyniki geochemicznej specjacji Fe, Ni oraz Zn w próbkach odpadowych skał przywęglowych z pięciu kopalni GZW i LZW. Wykazano, że w łatwo wypłukiwanej formie (wodno-rozpuszczalnej, wymiennej, kwaso-rozpuszczalnej) największe stężenia osiągał Zn (MF_{Zn} = 24,4÷53,4), następnie Ni (MF_{Ni} = 5,1÷19,2) i Fe (MF_{Fe} = 0,2÷3,6). Mobilność Fe była porównywalna w skałach pochodzących z obu Zagłębi (K-W, p = 0,2253), Ni większa z LCB, natomiast Zn z USCB (K-W, $p < 0,05$). Przeprowadzone badania wskazują, że przez pierwsze lata składowania jedynie niewielka część metali zostaje uwolniona do środowiska, ponieważ zarówno stężenia całkowite, jak i specjacja Fe, Ni i Zn były podobne w świeżych i zwietrzałych skałach kopalni Wesoła i Murcki (odpowiednio do 3 i 15 lat wietrzenia).

Słowa kluczowe: skały odpadowe, metale ciężkie, geochemiczna specjacja