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# Mobility of Metals from Drill Cuttings

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**Abstract**

Forecasting threats resulting from the presence of heavy metals in various elements of the environment plays an important role in environmental studies. Metals in solid environmental samples are found in many forms and phases that differ in respect of mobility, bioavailability and toxicity. Pollution from deposited drilling wastes can penetrate into the environment, particularly the heavy metals may be released to the environment through rainfalls. Rainfalls may alter the $p^H$, redox conditions and may lead to migration of metals in surface and ground waters. The aim of the study was to determine whether drill cuttings contain metal forms capable of migration in aquatic and soil environment, which would increase their availability for flora and fauna.

**Keywords:** Drill cuttings; Heavy metals; Mobility

## Introduction

Recent developments in Poland have led to a growing interest in exploration of gases from alternative sources. The exploration and exploitation of these resources is inseparably connected with producing certain extraction wastes, e.g. drill cuttings and spent drilling fluid. According to the waste catalogue, these wastes are classified as group 0105 [1]. The composition of drilling wastes is diversified and mainly depends on the type of drilling fluids applied. Wastes in Poland are presently predominantly stored or used in road engineering [2]. Unfortunately, the available data on the impact of the stored wastes on the environment is limited. Presence of hydrocarbons and heavy metals in drilling wastes constitutes a problem for the natural environment, as heavy metals do not undergo biological processes and are retained by the environment. Deposited metals may percolate to water or soil and exert a negative impact on the development of organisms in contaminated habitats. Apart from the environmental factors, the intensity of the process in question is determined by the forms of metals and the types of bonds with solid phase components [3]. Chemical fractionation consists in consecutive extractions with solutions, conducted at an increasing leaching rate, and is a commonly applied solution for determining the share of forms and fractions constituting the total content of a given metal in solid samples. Sequential extraction analysis is frequently employed in the assessment of mobility and potential impact of substances on the environment. BCR is a commonly utilized method of sequential extraction for distinguishing the following fractions: exchangeable, reducible, oxidizable (bound to organic matter), and residual. In line with the BCR method procedure, heavy metals mobility is connected with the solubility of their forms and decreases with the consecutive steps of sequential extraction; ion exchange is the most mobile form of metals, whereas the residual form – the least [4]. Metals released from the ion-exchange fraction are highly-available for uptake. The reducing fraction comprises elements absorbed or co-precipitated with Fe and Mn oxides, is characterized by medium mobility and activates under reducing conditions. The oxidizable fraction includes the organic fraction metals and exhibits medium mobility; however, it is also characterized by long-lasting bioavailability, which activates under oxidizing conditions. The residual fraction includes metals strongly bound to the solid phase, is very stable, and metals of this fraction are not available to plants [5].While a vast body of literature describes the procedure of sequential extraction of sludge and soils, the application of extraction in drilling waste can seldom be found. The aim of the study was to determine whether the drill cuttings contain forms of metals capable of migration in aquatic and soil environment, which thus could become easily available to flora and fauna.

## Research Methodology

The tests were conducted on drill cuttings sample material obtained from the Maćkowice well, where potassium/polymer drilling fluid was utilized. Sequential extraction: Sequential extraction of trace elements was carried out as per Tessier et al. [5]. Drill cuttings in the amount of 1 g were extracted in the following order:

- **Fraction 1**: Exchangeable fraction: 0.11 M acetic acid, shaking by microwaves for 7 minutes (power 20 W) at 22°C.
- **Fraction 2**: Fe-Mn oxide bound fraction (reducible): 0.5 M hydroxylamine hydrochloride, pH=1.5 shaking by microwaves for 7 minutes (power 20 W) at 22°C.
- **Fraction 3**: Organic bound fraction (oxidizable): 30% hydrogen peroxide shaking by microwaves for 2 minutes (power 20 W) at 22°C, additional 1M ml, $p^H = 2$ shaking by microwaves for 6 minutes (power 20 W) at 22°C.
- **Fraction 4**: Residual fraction (bound to silicates and detritus materials): Total digestion with concentrated mixture of nitric acid and perchloric acid (3:1 v/v).

Centrifugation at 200 rpm for 15 min was performed for the sake of separation after each extraction, and supernatant was taken with a pipette for analysis [6]. The content of metals in particular forms was determined through inductively coupled plasma mass spectrometry by means of ICP-OES JY 238 Ultrace (Jobin Yvon-Horriba France).

## Results and Discussion

Table 1 presents total content of metals in the examined

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drill cuttings sample. Among the presented analytes, the highest concentration was observed for Ba – 1911.33 ppm, whereas the lowest for Cd – 30 ppb. Our results indicate a similar tendency reported in the study of samples from drill cuttings piles in the United States, where barium concentration exceeded 2000 ppm. In addition, the examined samples were characterized by a high content of zinc (over 500 ppm) and lead (approximately 300 ppm) [7]. The waste tests were expanded by inclusion of iron and manganese, whose content in drill cuttings is of certain significance, due to their abundance in Earth's crust [8]. Manganese accumulates in coal beds, therefore, its content in certain types of coal ash amounts to 2000 ppm [9]. Comparative analysis of drill cuttings composition is a difficult task, since it mainly depends on the employed drilling technology and the composition of utilized fluids. The concentrations of metals obtained from the study remain within permissible concentration levels in particular groups, according to the Polish Regulation of Minister of Environment on the assessment of Earth surface contamination (Journal of Laws 2016, item 1395) [10]. Barium constitutes an exception, with the concentration slightly exceeding 1500 ppm, i.e., the permissible value for category IV soil (mining areas). Barium is commonly employed in drilling, both in Poland and the USA, where it is used as a thickening agent. In drilling waste, barium is found in the form of barium sulphate, which is hardly-soluble and thus does not threaten the environment. The remaining heavy metals in drill cuttings are found in trace amounts, which therefore renders them harmless to the environment.

Table 2 presents total content of examined fractions and juxtaposed against the maximum permissible values for leached pollutants, specified in the Polish Regulation of the Minister of Environment of 18th November 2014 on the conditions of waste disposal into water or ground and on substances particularly harmful to the aquatic environment [11]. Particular attention should be drawn to the measured concentration of barium, which exceeds the permissible value for pollutants in wastewater discharged into waters or soil by the factor of four. The remaining metals are within the standards determined by Polish legal regulations. Figures 1-4 present the concentrations of metals in particular fractions 1-4. Zero emission means shift from "cradle to grave" (LCA) to "cradle to cradle".

The greatest share of exchangeable fraction was observed for Mn and Ni (42%), as well as for Co (36%). Among the considered metals, the highest share of F2 fraction is found in cadmium (67%), iron (99%), manganese (47%), and zinc (46%). The share of F2 fraction in such metals as nickel, chromium, and cobalt amounts to 20%. Lead and copper were the metals which were fully released in fraction 3, barium and chromium in fraction 3 constituted 70%, while, cobalt reached 50% and zinc – 40%. The highest amount of metals was released in this fraction, which is characterized by medium mobility. However, bioavailability of metals in this fraction changes over time. Barium was the metal with the highest share in the residual fraction, and yet was only released in 14%.

| Metal | Concentration [ppm] ± SD |
|---|---|
| Ba | 1911.33 ± 16.6 |
| Cd | <n.o |
| Cr | 65.76 ± 4.40 |
| Cu | 104.29 ± 0.32 |
| Ni | 21.75 ± 0.46 |
| Pb | 41.92 ± 0.18 |
| Zn | 62.1 ± 0.45 |
| Co | 0.2 ± 0.01 |
| Fe | 14369.8 ± 137.2 |
| Mn | 469.13 ±20.1 |

**Table 1:** Concentration of metals in drilling cuttings [8].

| Metals[ppm] | Total concentrations of metals from four considered fractions | Permissible values of pollutants in wastewater introduced to waters or soil [11] |
|---|---|---|
| Ba | 8.24 | 2 |
| Cd | 0.01 | 0.4 |
| Cr | 0.08 | 0.5 |
| Cu | 0.31 | 0.5 |
| Pb | 0.11 | 0.5 |
| Ni | 0.18 | 0.5 |
| Zn | 1.66 | 2.0 |
| Co | 0.03 | 1.0 |
| Fe | 17.68 | n.o |
| Mn | 4.41 | n.o |

**Table 2**: Total (I+II+III+IV) concentration of metals in drilling cuttings.

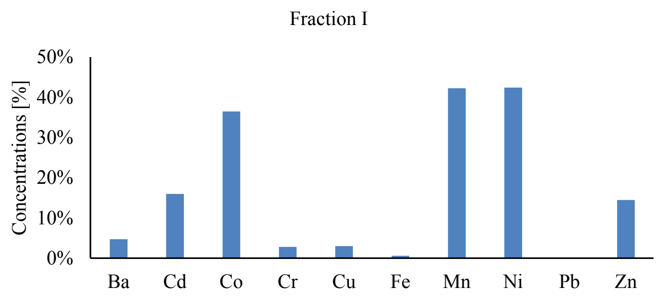


**Figure 1:** Percentage of metals removed from drill cuttings in BCR procedure (F1 – exchangeable), F2 – reducible, F3 – organic, F4 – residual).

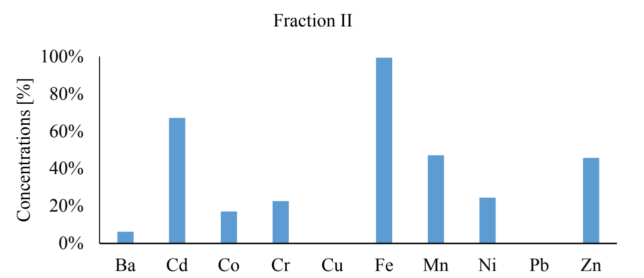


**Figure 2:** Percentage of metals removed from drill cuttings in BCR procedure (F2 – reducible).

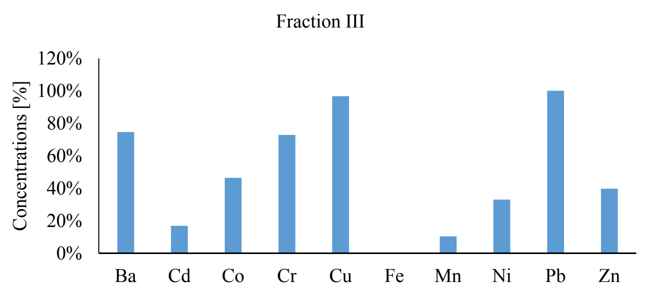


**Figure 3:** Percentage of metals removed from drill cuttings in BCR procedure (F3 – organic).

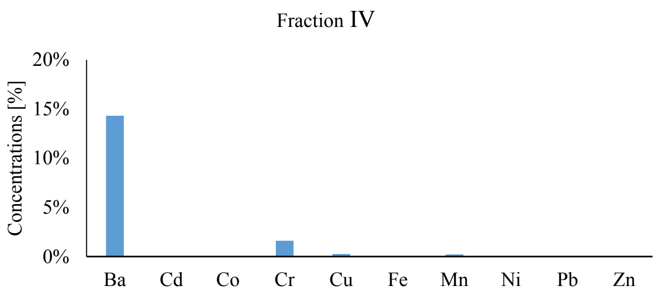


**Figure 4:** Percentage of metals removed from drill cuttings in BCR procedure (F4 – residual).

| Metals [ppm] | Fraction I | Fraction II | Fraction III | Fraction IV |
|---|---|---|---|---|
| Ba | 0.39 | 0.52 | 6.15 | 1.18 |
| Cd | 0.0008 | 0.004 | 0.0009 | 0 |
| Co | 0.017 | 0.005 | 0.014 | 0 |
| Cr | 0.002 | 0.019 | 0.059 | 0.001 |
| Cu | 0.009 | 0 | 0.296 | 0.0008 |
| Fe | 0.105 | 17.56 | 0.01 | 0 |
| Mn | 1.86 | 2.01 | 0.46 | 0.01 |
| Ni | 0.077 | 0.04 | 0.059 | 0 |
| Pb | 0 | 0 | 0.11 | 0 |
| Zn | 0.24 | 0.76 | 0.66 | 0 |

**Table 3:** Concentration of various forms of the metals (mgkg$^{-1}$).

Studies showed that manganese and iron, which are components of polymer/potassium drilling fluids, are hazardous to the environment. Iron and manganese are found in abundance in the Earth's crust and constitute the most mobile elements. Their mobility changes with the weather conditions. Moreover, the impact of manganese on the environment depends on the amount of iron and loamy minerals. Drilling wastes are characterized by high content of loamy minerals (approximately 45.5%), which may inhibit migration of manganese into the environment. Moreover, pollution of the environment by manganese is form-dependent [9]. Table 3 presents the concentration of metals in particular fractions.

Similar results of drilling waste fractionation were obtained by Stuckman. In his studies, Cu, Ni, Zn, Cd, and Co were mainly related with the oxidizable fraction. These metals exhibited the tendency for a long-term release [12].

The research conducted by Ghode showed the highest concentration of Ba and Cr in the organic fraction. However, according to the author, their activation in environmental conditions is unlikely.

Our results show certain discrepancy from the results obtained by Duel and Holliday. The studies, carried out on 31 drilling fluids, showed that such metals as As, Ba, Cd, and Cr were found in the residual fraction, while Pb was found in the reducible fraction, and Zn in oxidizable forms [13].

The published results of research carried out by Westerlund proved that Zn, Cu, Cd, and Pb have the highest share in the leachable fraction [14].

Results from our research and the review of literature indicate that the impact of wastes on the environment is diverse, with a broad range of impact. Simultaneously, this impact differs for each drilled well, and may result from the particular composition of drilling fluids and the geological structure in the well site.

## Conclusion

The conducted study on the assessment of the content of particular heavy metal fractions in drilling wastes showed that metals are mainly bound in the organic fraction. Furthermore, metals of the organic fraction are characterized by long-term long mobility, which indicates the need for constant monitoring of deposits containing this type of wastes. However, taking into account low heavy metal concentrations in frilling wastes, it appears that they do not pollute surface waters or the soil and water environment.

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