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Thermal Impact on Heavy Metal Bioavailability in Burnt Rocks of Waste Heap of Chervonohradska Coal-preparation Plant (Lviv Region, Ukraine)

Abstract: For effective waste management of mining industries is important to investigate their physical and mineralogical changes. For this purpose, X-ray-diffraction (XRD), thermogravimetry (TG), derivative thermogravimetry (DTG), and differential thermal analysis (DTA) methods were used. Changes in the contents of mobile forms of heavy metals in rocks were investigated using an acetate-ammonium buffer solution with a pH of 4.8 after burning rocks at a temperature of 800–850°C. The obtained data indicated the significant role of the mineral composition in the thermal behavior of the rock samples and the subsequent influence of the thermal processes on the changes in the bioavailability of heavy metals.

Keywords: environmental safety, coal mining, slagheap, waste rock, heavy metals, thermogravimetry, XRD

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1. Introduction

Mining complexes are areas where technogenesis processes are directly localized, so they are largely exposed to their negative impact. Basically, this happens due to the storage of waste rock that accumulates during coal mining and coal preparation [1–3]. Intensive coal mining and coal preparation change natural landscapes, the composition and structure of biocenoses [4], and groundwater levels; these cause pollution in all components of the natural environment [5–7] and, due to groundwater changes, cause the flooding of large areas [8].

The combustion of waste heaps within coal-mining areas is particularly harmful, as tailings have a high content of combustible components (mainly carbon and pyrite). The content of the main combustible components in mine waste may reach up to 30% carbon and up to 8% pyrite. These components undergo a natural oxidation process upon contact with oxygen, followed by the generation of heat [9, 10]. Various processes of anthropogenic pyrometamorphism take place inside waste heaps, and the spontaneous ignition of the heaps or their smoldering for long periods of time can often be observed; these result in radical changes in the phase compositions of the waste masses [11]. A peculiar zoning is formed around the burning areas due to the redistribution of the initial mineral composition. Small areas are formed in different parts of the slagheaps that preserve primary dump rocks – argillites, siltstones, and occasionally sandstones; these can be identified by the black color of a rock mass. In the burning areas, the mineral composition and petrographic characteristics of the waste change; they impregnate the rock mass, forming various deposits, crusts, veins, and inclusions [12, 13].

Burning waste heaps pose a threat to the environment in their impact zone; this is mainly due to the release of a high volume of pollutants into the atmosphere (mostly toxic – some carcinogenic), directly affecting human health and safety [14, 15]. The oxidation and combustion of the rocks are followed by emissions of a wide range of volatile components that are released from the rock mass. Water vapor is the main component of the emissions, which is formed by the evaporation and sublimation of the precipitation that has fallen into the combustion zone as well as by the release of free and bound water from the minerals and rocks. Water is a mineral-forming medium for most of the newly formed minerals: sulfates, bicarbonates, carbonates, phosphates, arsenates, etc. The lack of oxygen in the combustion centers of steam and gas emissions results in the retention of hydrogen sulfide, hydrocarbons, ammonia, and carbon monoxide. In the upper zones of waste heaps that have been penetrated by oxygen-enriched infiltration water, combustion takes place under conditions of excess oxygen. In the deeper burning zones, there is a lack of oxygen; here, the oxidation processes occur under anaerobic conditions [13].

Thermal processes in waste heaps also promote the formation of new minerals, which can be formed either inside a heap as a result of high-temperature mineral transformation or on its surface [12]. In [16], the mineral composition of mining waste in a rock mixture was investigated. Many scientific papers [17–20] have focused on the gross content of heavy metals in the rock mixtures of coal-mining and coal-preparation facilities. The results of the conducted research provided a scientific basis for understanding the main directions of the transformations of coal-preparation-dump substances during the process of the thermal transformations. However, this data is quite averaged, as it was based on a mixture of rocks. Coal-preparation waste heaps are typically composed of argillites, siltstones, and sandstones, but the proportion within each of these rocks varies greatly from one waste heap to another. These rocks also differ in their mineralogical and, consequently, their geochemical aspects; therefore, information on the chemical composition of a particular waste heap is difficult to extend to other waste heaps. Another problem with the research results that we reviewed is their focus on the gross chemical content. Information on the gross chemical content is applicable for mining operations but is insufficient for environmental-safety and disaster-risk assessment, since bioavailable forms of chemical elements are the main sources of ecosystem damage.

The planned investigation of variations in the bioavailable forms of heavy metals in argillites separately from argillites that have been affected by thermal effects will provide deeper insight into the processes of the geochemical transformations of such rocks and extend the results to other coal-mining dumps by making appropriate recalculations based on the ratios between the main dump rocks. The exploration of changes in heavy metal contents and bioavailability before and after rock combustion will create a scientific basis for utilizing waste heap rocks, recultivating disturbed areas [21–23], and optimizing coal mining and coal preparation [24–27].

The object of our research is the rocks (argillites and siltstones) of a waste heap at the Chervonohradska Processing Plant.

The subject of the research is the processes that can be observed during the heating of experimental samples of argillite and siltstone and the variability of the contents of mobile forms of heavy metals (Mn, Cu, Pb, Co, Fe, Cd, Cr, Ni, and Zn) in different temperature regions.

The aim of the research is to investigate the effect of the temperature regime of rocks on their heavy metal bioavailability.

2. Material and Methods

Rocks from different parts of the Chervonohradska Processing Plant waste heap were taken from ten samples at depths of 0.2–0.3 m. The average lithological compositions of the investigated dumps reflected the composition of the coal bed; namely, argillite (70–97%), siltstone (8–28%), sandstone (1–20%), coal (1–7%), pyrite (1%), etc. The ash content of the rocks was 54–94%, and the chemical composition of the rocks (the average of four types) was as follows: SiO_2 – 56.2%; Al_2O_3 – 23.71%; Fe_2SO_4 – 10.18%; K_2O – 2.44%; TiO_2 – 1.09%; CaO – 0.99%; MgO – 0.73%; Na_2O – 0.5% [28].

For the research, the samples were separated by their lithological compositions; then, they were dried, crushed, and sieved using laboratory sieves with a diameter of 1.25 mm (since the argillite and siltstone contents constituted the bulk of the dump rock, their characterizations were of the greatest interest).

X-ray phase analysis was performed on an Aeris Research benchtop X-ray powder diffractometer (Malvern PANalytical) using CuKα radiation. The anode voltage and amperage were 40 kV and 15 mA, respectively. The 2θ diffractogram angles ranged from 7 to 100 degrees, with a scan step of 0.01°. The phases were identified by comparing the experimental diffractograms with the theoretical ones from the COD database. If the peaks matched, the phase was considered to be present in the sample.

The thermal analysis was carried out on a Paulik-Paulik-Erdey Q-1500D derivatograph that was connected to a personal computer; the analysis was performed within a temperature range of 20–1000°C (with free air access to the furnace). The heating rate of the samples was 10°C per minute. The samples weighed 500 mg, and the reference substance was aluminum oxide. Thermogravimetry (TG), derivative thermogravimetry (DTG), and differential thermal analysis (DTA) were used in the investigation.

The mobile forms of the heavy metals were determined after burning the rocks in a muffle furnace at a temperature of 800–850°C for 3 hours using an acetate-ammonium buffer solution (AABS) with a pH of 4.8 in accordance with DSTU 4729:2007, DSTU 4770.1:2007, DSTU 4770.2:2007, DSTU 4770.3:2007, DSTU 4770.4:2007, DSTU 4770.5:2007, DSTU 4770.7:2007, DSTU 4770.8:2007, and DSTU 4770.9:2007. The concentrations of the heavy metals in the extracts were determined by the atomic-absorption method using an AAS-115-M-1 spectrometer.

3. Results and Discussions

3.1. XRD

Due to the often-high temperatures in waste heaps during their smoldering and spontaneous combustion (up to 800°C and above), rocks are destroyed, and their structures change; this may lead to soil and water pollution. Combustion sites are sources of hot mineralized chemically aggressive trace element-rich water liquids. The combustion process and the produced chemically aggressive liquids completely transform the mineral and chemical composition of the primary rock mass – not only in the burning areas, but also beyond their peripheries [13]. Therefore, it is necessary to determine the structure and phase composition of the rocks under investigation. According to the X-ray diffraction (XRD) analyses (Figs. 1, 2), the studied argillite and siltstone from the Chervonohradska Processing Plant waste heap were identified by clay minerals (kaolinite and muscovite), while the non-clay part was represented by quartz and iron carbonate (Table 1).

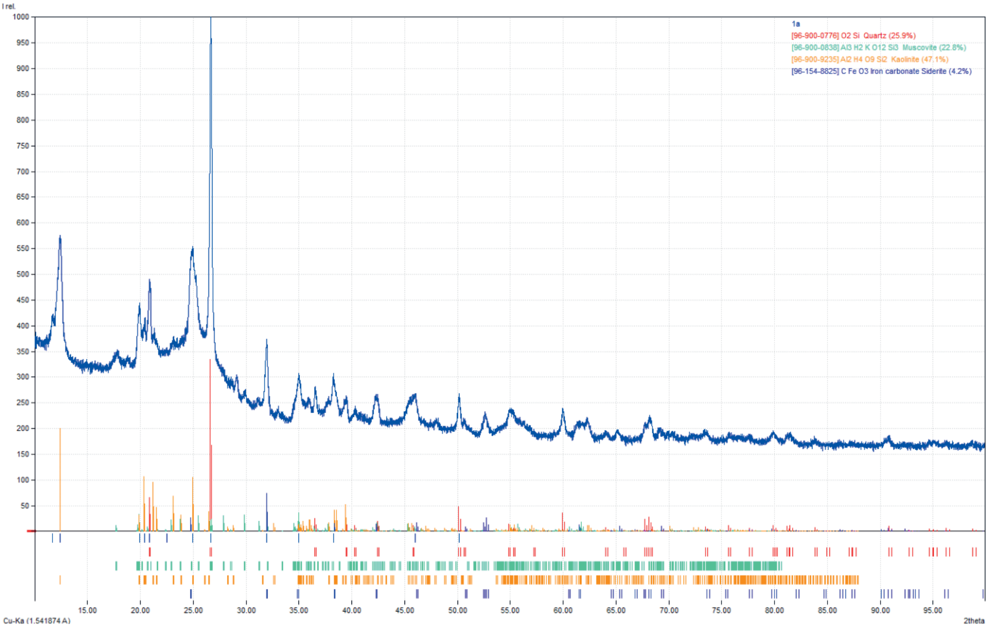

Fig. 1. XRD pattern of coal-processing waste – argillite

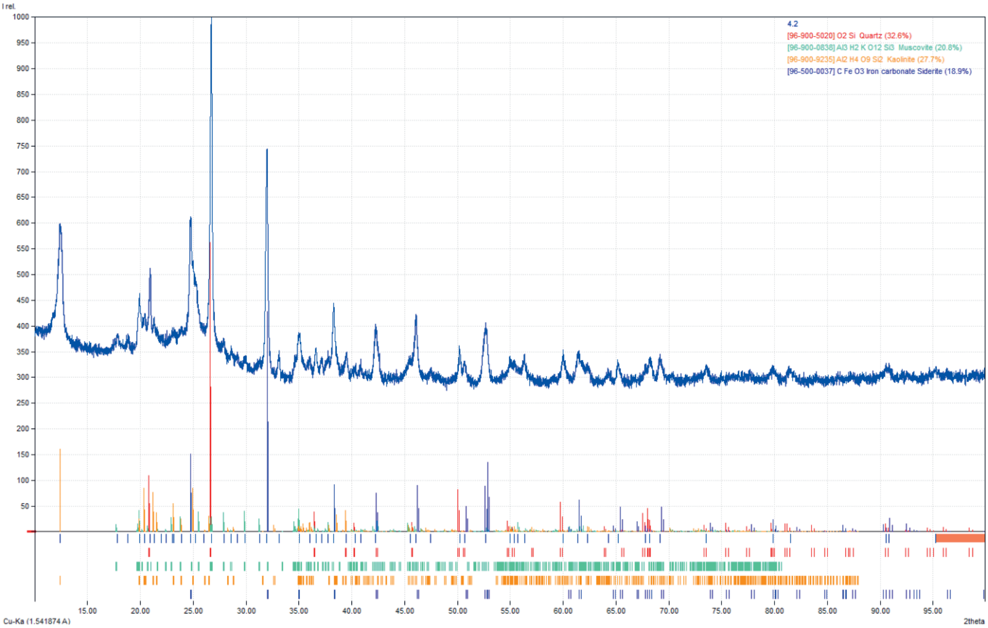

Fig. 2. XRD pattern of coal-processing waste – siltstone

Table 1. Calculation of mineral composition of coal-preparation waste

Mineral	Mineral contents [wt.%]	
	argillite*	siltstone*
SiO_2 (quartz)	25.9	32.6
$Al_2Si_2O_5[OH]_4$ (kaolinite 1A)	47.1	27.7
$KAl_3Si_3O_{10}[OH]_2$ (muscovite)	22.8	20.8
$FeCO_3$ (iron(II) carbonate, siderite)	4.2	18.9

* Identifying and calculating the content of the main element of the coal (carbon) was not possible from the obtained diffractogram of the sample. One reason is that the carbon was in an amorphous state in the sample (without a long-range atomic order); hence, its lines were absent from the diffraction pattern. Accordingly, the true percentage of the phase content of the total carbon content will be much lower than that which is calculated above.

It should be noted that the presence of poisonous substances (and possibly amorphous silica) in the samples reduced the sensitivity of the XRD method for determining the lower syngonium minerals (feldspars in particular).

3.2. Thermogravimetric Analysis

Based on the results of thermogravimetric analyses, the temperatures of the phase transformations and chemical reactions of the analyzed materials were found. The nature of the thermogravimetric and differential thermogravimetric curves (Fig. 3) that were obtained as a result of the derivative thermogravimetry studies were similar to those that were described in [29] for siltstones, but no thermogravimetric studies of siltstone could be found in our literature review.

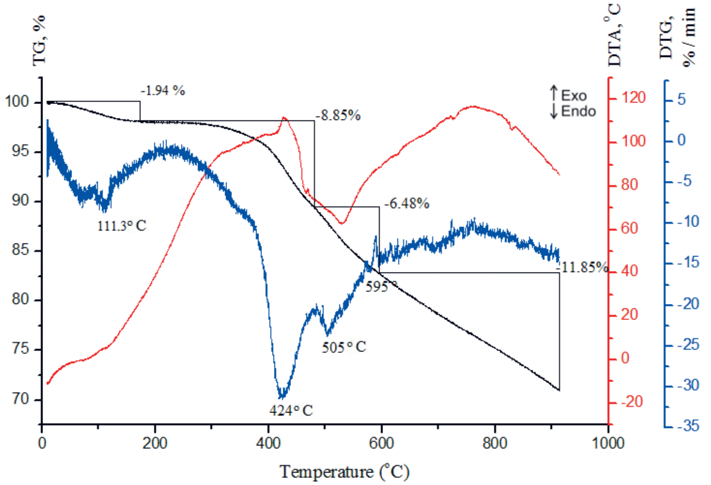

Fig. 3. TG, DTG, and DTA curves of argillite

As seen in Figure 3, the onset of mass loss occurs at temperatures of 70–190°C; this process is characteristic of the free and adsorbed water release. Within a temperature range of 280–490°C, a rapid mass loss could be observed in the siltstone, which can be explained by the decomposition of the siderite (1) and the burnout of the volatile compounds (specifically, the hydrocarbons). Within a temperature range of 500–600°C, the dehydration of kaolinite $Al_2Si_2O_5[OH]_4$ (a clay material from the group of aluminum aqueous silicates) occurred. The muscovite ($KAl_3Si_3O_{10}[OH]_2$) lost water within a temperature range of 600–900°C; its total mass loss after heating to 912°C was 29.12%:

$$3FeCO_3 \xrightarrow{280\text{–}490°C} Fe_3O_4 + CO + CO_2\uparrow \qquad (1)$$

Waste heaps and coal-preparation waste contain about 1% pyrite; the oxidation of this leads to the formation of sulfuric acid and easily soluble iron sulfates [10]. This process takes place in three stages [30, 31]:

- Stage I – oxidation of pyrite under catalytic action of Thiobacillus ferrooxidans bacteria (with heat release of 1440 kJ/mol):

$$2FeS_2 + 7O_2 + 2H_2O \rightarrow 2FeSO_4 + 2H_2SO_4 \qquad (2)$$

- Stage II – transformation of ferrous iron into ferric iron under action of same species of bacteria (with heat release of 102 kJ/mol):

$$4FeSO_4 + 2H_2SO_4 + O_2 = 2Fe_2(SO_4)_3 + 2H_2O \qquad (3)$$

- Stage III – decomposition of sulfide to sulfate and reduction of ferric iron to ferrous iron (with heat release of 11 kJ/mol):

$$Fe_2(SO_4)_3 + 6H_2O = 2Fe(OH)_3 + 3H_2SO_4 \qquad (4)$$

In the case of chalcopyrite $FeCuS_2$, the first stage of oxidation may occur according to the following scheme:

$$FeCuS_2 + 4O_2 = Fe^{2+} + Cu^{2+} + 2SO_4^{2-} \qquad (5)$$

The oxidation of the pyrite and the heat generation leads to temperature increases inside the dumps and the creation of optimal conditions for the development of mesophilic microorganisms and the activation of hypergenic processes. At temperatures of 248–261°C, gaseous sulfur is self-igniting (thus, causing the burning of waste heaps):

$$S_2 + 2O_2 = 2SO_2\uparrow \qquad (6)$$

At temperatures above 600°C, carbon oxidation occurs [31]; this can also explain the mass losses at 600°C and above in both of the studied samples:

$$C + O_2 = CO_2\uparrow \tag{7}$$

$$2C + O_2 = 2CO\uparrow \tag{8}$$

The main source of the formation of mobile Mn^{2+} may be the interaction of ferrous(II) sulfate and pyrolusite [32], which goes through the following stages:

- Stage I – pyrite oxidation follows Equation (2);
- Stage II – interaction of $FeSO_4$ at high temperatures with pyrolusite (primary manganese ore), which is associated ore of iron and copper deposits:

$$4MnO_2 + 4FeSO_4 \rightarrow 4MnSO_4 + 2Fe_2O_3 + O_2 \tag{9}$$

- Stage III – dissociation of $MnSO_4$ (salt is highly soluble, so it migrates from waste heaps to soils and water bodies):

$$MnSO_4 \rightarrow Mn^{2+} + SO_4^{2-} \tag{10}$$

The initial mass loss of the siltstone (Fig. 4) coincided with that of the argillite (likely due to the removal of the hygroscopic water and organic matter), while the rapid mass loss within a temperature range of 280–490°C was caused by the decomposition of the siderite and the burning of the volatile compounds (as well as the further dehydration of the kaolinite). It should be noted that SiO_2 as α quartz transforms into β quartz at a temperature of 573°C, and the muscovite's water loss occurs at around 850°C. The total mass loss after heating to 925°C was 44.26%. As an additional note on the thermal analysis, it should be noted that the common characteristics of the samples were the presence of two ranges of endothermic peaks (which were associated with the dehydroxylation of the kaolinite). The characteristics of the DTA curves for both of the wastes were similar in the first pronounced exothermic peaks but differed in the intensity and temperature maxima of the processes within a temperature range of 600–900°C.

It is notable that, when a rock is heated to 100–110°C, moisture is released. As the temperature rises to 200°C, the gases that are deposited in the coal are released (mainly carbon dioxide and hydrocarbons). At temperatures of 200–250°C, the significant decomposition of the combustible substance begins and the carbon dioxide emissions increase; resin products appear at around 300°C. The intensive decomposition of coal occurs between 350°C and 500°C. The volume of the emitted gases sharply increases; they become combustible during this period, as they contain high amounts of hydrocarbons, methane, and hydrogen (in addition to carbon dioxide). At temperatures of 550–1100°C, the gases are released at rates that are 4- to 5-times greater than they were within a temperature range of 200–500°C. These gases contain methane, hydrogen, and nitrogen. Sulfur in a rock mass that is present with pyrite releases sulfur dioxide at temperatures of 170–260°C (during the slow oxidation). The intensive decomposition of pyrite occurs at temperatures above 300°C and is finally completed at 600°C. The products of the oxidation zone at temperatures above 800°C are involved in secondary reactions [33].

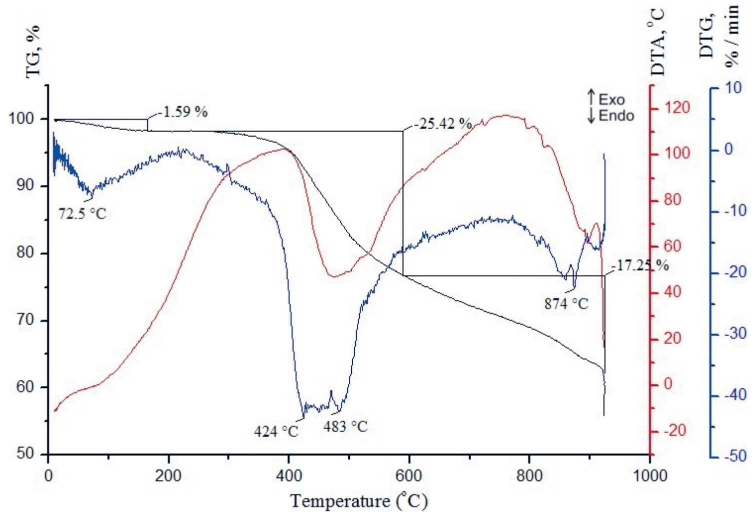

Fig. 4. TG, DTG, and DTA curves of siltstone

3.3. Changes in Contents of Mobile Forms of Heavy Metals

Another environmental risk is the possibility of increasing the bioavailability of certain toxic metals due to the thermal effects on waste heap rocks. However, the research on assessing the environmental state of the technogenically transformed mining areas in Ukraine has mainly focused on the concentrations of gross forms of heavy metals [5].

As mentioned above, waste heaps are prone to spontaneous combustion, which occurs mainly near the surface (on the side of the oxygen intake). According to the burning stage, spoil heaps are divided into burning, dying, extinguished, and unburnt materials [34]. Three zones with different stages of thermal transformation can be distinguished in spontaneously combusted coal-waste dumps; namely, macroscopically thermally untransformed, moderately thermally transformed, and intensively thermally transformed zones. The thermally untransformed zone is characterized by the presence of high amounts of organic matter (coal) and minerals that are typical for coal rocks. In the moderate thermal transformed zone, a small amount (or none at all) of organic matter and the oxidation of Fe-containing minerals can be detected, resulting in the characteristic brick-red color of the waste from this zone. In the zone of intense thermal transformation, organic matter and clay minerals are completely lost and replaced by the high-temperature minerals that are typical for contact metamorphism [12].

The heavy metal risk to living organisms depends on the mobile compound content; the gross metal content should be used to characterize the overall pollution status and potential risk. Research [35–37] has revealed an increased content of mobile forms of Mn, Fe, and Ni in the argillite and siltstone of the Chervonohradska Processing Plant waste heap; the most dangerous situation arises when the metals in the rocks are in mobile compounds that can be directly absorbed by the biota. A major area of interest is the study of changes in the contents of mobile forms of heavy metals in rocks after they have been burnt (Table 2). The increased contents of Mn, Fe, and Ni may reflect the mineral compositions of the studied rocks, as kaolinite and muscovite may contain impurities of Fe and Cr.

In general, the concentrations of most of the metals increase during a rock's combustion (Fig. 5). The most intensive changes occur with the Fe in argillite (21 times) and siltstone (33 times) as well as the Mn in argillite (14 times).

Table 2. Contents of mobile forms of heavy metals in waste rock from Chervonohradska Processing Plant

Chemical element	Chemical content [mg/kg]				
	MAC for soils [38, 39]	unburnt argillite [35–37]	burnt argillite	unburnt siltstone [35–37]	burnt siltstone
Mn	60.0–140.0	681.73	48.2	197.9	180.0
Cu	3.0	0.59	2.2	1.69	0.5
Pb	6.0	4.49	1.0	2.69	0.52
Co	5.0	1.89	2.2	1.59	1.8
Fe	–	3048.78	142.1	1724.14	51.6
Cd	–	0.35	1.4	0.39	0.5
Cr	6.0	14.99	2.5	3.99	1.7
Ni	4.0	2.1	2.0	4.39	1.3
Zn	23.0	3.99	2.7	6.39	7.6

The concentration coefficients of the Pb, Cr, Cu, Ni in burnt rocks range from 2 to 10 as compared to those in unburnt rocks. According to the concentration coefficient decrease in burnt rocks as compared to unburnt rocks, they can be arranged in the following rows: for argillite – Fe (21), Mn (14), Cr (6), Pb (5), and Zn (1.5); for siltstone – Fe (33), Pb (5), Cu and Ni (3), and Cr (2). The accumulation of metal in burnt rocks is a typical process, since burning significantly reduces the masses of rocks and increases their metal contents; thermal treatment promotes the transitions of the metals from bound forms to those that are more bioavailable. A certain decrease in Cd and Cu concentrations in burnt siltstones is atypical. It is likely that a significant part of the Cd and Cu in unburnt siltstones is in those compounds that become volatile upon thermal exposure; thus, some Cd and Cu are released into the atmosphere during combustion. Additional gas-geochemical studies are required to verify this hypothesis.

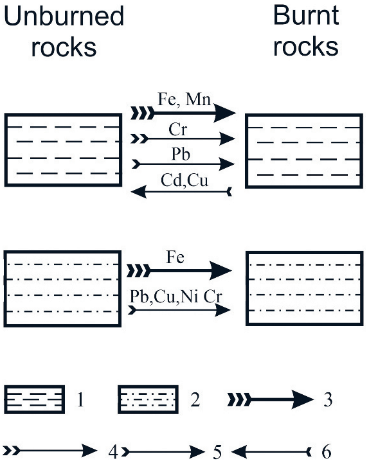

Fig. 5. Characteristics of variations in concentrations of mobile forms of chemical elements in rocks due to their thermal transformations: 1 – argillite, 2 – siltstone, 3 – more-than-10-fold change of chemical element concentration, 4 – change of chemical element concentration (6- to 10-times); 5, 6 – change of chemical element concentration (2- to 5-times)

Thus, there have been significant changes in the contents of the mobile forms of heavy metals in coal-mining waste due to thermal exposure, accompanied by changes in their leachability; anthropogenic geochemical processes can be active for a long time and eventually lead to significant geological transformations.

4. Conclusions

An X-ray diffraction (XRD) analysis of the mineral structures of argillite and siltstone revealed that the main mineral-forming components were clay minerals kaolinite 1A and muscovite (their shares in the rock reaching over 69.9 and 48.5%, respectively) as well as quartz and siderite (also present in the rocks). The physical and mineralogical changes in the heated rock samples were investigated for a better understanding of the thermal processes that occurred in each rock type using thermogravimetry (TG), derivative thermogravimetry (DTG), and differential thermal analysis (DTA). The obtained data indicated the important role of the mineral's composition in the thermal behaviors of the tested rocks. For each type of rock, significant changes in its mineral composition could observed at its threshold temperature. This behavior was confirmed by the TG/DSC/DTG analyses. The bioavailability of the studied heavy metals (Mn, Fe, Ni, Pb, and Cr) decreased in different ranges after thermal treatment, the Zn content increased in the siltstone, the Cu content increased in the argillite, and the Co and Cd contents increased in both of the studied samples.

Author Contributions

Iryna Kochmar: conceptualization, investigation, formal analysis, project administration, resources, supervision, visualization, writing – original draft.

Vasyl Karabyn: conceptualization, formal analysis, methodology, project administration, supervision, visualization, writing – review & editing.

Kateryna Stepova: methodology, formal analysis, writing – review & editing.

Vitalii Stadnik: investigation, resources.

Martyn Sozanskyi: investigation, resources.

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