Removal of metals from technogenic waters from abandoned coal mines using geochemical barriers

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Abstract

A study was made of the possibility of using natural materials (vermiculites, zeolite) and wastes (ash from the Partizansk Coal-Burning Power Plant) as sorbents in geochemical barriers to manage discharges (technogenic waters) from abandoned coal mines and reduce metal concentrations to established, acceptable standards. Vermiculite from the Kovdor deposit was shown to reduce the concentrations of Fe, Co, Ni, Cu, and Zn cations, in both direct and inverse soil column models, by between two and five times.

Key words: abandoned coal mines, geochemical barrier, metals, natural materials, sorbents, technogenic waters

INTRODUCTION

The abandonment of coal mines often leads to mine water discharge (technogenic waters) to the surface. Sometimes there is also frontal 'seepage' of water through the soil. Technogenic waters often contain toxic materials, including heavy metals, leading to contamination of soils, nearby water bodies and associated groundwater. China's coal mine drainage, for example, can be broadly characterized as: slightly contaminated, acidic, and highly saline, and containing elevated iron and manganese, and high sulfate and fluoride concentrations (Feng *et al.* 2014).

Different groundwaters in coal mining areas contain different heavy metal concentrations, because, for instance, of the forms of heavy metals present (e.g. Pb, Cd, Cu and Cr adsorbed by iron hydroxides) and varying water-rock interactions (e.g. Mn and Zn originating from carbonate rocks) (Sun *et al.* 2014). The chemical properties of soils – e.g., the concentrations of Ca, Mg, Pb, Fe, Cu, Zn, etc – can be changed significantly by coal mine water discharges, with negative impacts on them. Heavy metal contamination may limit the floral and faunal diversity in an area (Hossain *et al.* 2015). Open-cast coal mining is responsible for widespread degradation of water resources and aquatic ecosystems in the Appalachian Region, USA. The overburden tends to contribute high salinity loads to downstream aquatic systems (Sena *et al.* 2014).

In recent years, the idea of using the protective potential of the natural environment combined with artificial geochemical barriers has become widespread for protecting the environment from pollution (Perelman 1989; Banks 2003; Bayurova & Makarov 2013). There have been numerous studies of methods for protecting ground- and surface-waters from pollution using geochemical barriers (Banks *et al.* 1997; Benner *et al.* 1999; Bortnikova *et al.* 2006; Izotov *et al.* 2006; Makarov *et al.* 2012; Maksimovich & Hajrulina 2013). To create sorption (clay, loams, peat, etc.), alkaline (carbonates) and other barriers, natural materials are commonly used. The advantage is that they are relatively easily obtained and inexpensive. Using waste materials is also a

promising direction because, as well as being low cost, this solves another ecological problem (Perelman 1989).

Thus, artificial geochemical barriers make it possible to find efficient ways, in both ecological and economic terms, to treat industrial waters discharged to the surface.

Before implementing technogenic-scale water treatment schemes, the most effective natural materials must be chosen. Several geochemical barrier models have been developed and studied in relation to treating waters from industrial areas of the abandoned coal mines at 'Avangard' (Partizansk Coal Basin, Primorsky Krai, Russia).

METHODS

Research objectives

The laboratory experiment was carried out by the tube method (Vadyunina & Korchagina 1973) using a radial model of the geochemical sorption barrier. In addition to natural sorbents, soil samples selected in the industrial zone of the abandoned Avangard mine, in the Partizansk Coal Basin, were used. The Partizansk Coal Basin is in the southern part of Primorsky Krai, Russia. It operated from 1918 to 1998. In 1996–1998 water drainage from the mines ceased and they flooded. At present, mine water discharges onto the surface and penetrates to the groundwater. Soils, as surface formations, take much of the load of water-soluble components in the discharges. They are quite good sorbents and consequently accumulate polluting compounds, leading to natural water pollution. Soil samples for the experiment were selected layer by layer, from the humus-accumulative (0–8 cm) and middle (8–70 cm) horizons. Industrial water samples were taken from a mine water stream leaking onto the surface.

Geochemical barrier models

Both direct and inverse soil column models were constructed. In the direct column, the sequence of soil material installation corresponds to natural soil formation. In the inverse column, the middle soil horizon sample is placed on the top, because the technogenic water can come to the surface, seeping through the soil's genetic horizons from the bottom to the top (the inverse method). Technogenic water also can flow top-down through soil capillaries (direct method), and then, via intra-soil runoff, into water bodies.

In the experiment, two glass tubes of 5 cm diameter and height 20 to 30 cm were mounted on sieves, below which were filter papers. The tubes were loaded in 5 cm layers with humic and middle horizon soils, which had been sieved to 1 mm grain-size. Sorbents were added at the same time. The soil and sorbent density was uniform throughout the tubes' filled volumes. Technogenic water was passed through at constant 5 cm head so that it seeped through the soil and sorbent. Measuring cylinders were used to collect and record the filtered water. Once the water head was established above the soil, the times of first appearance of filtrate were recorded, indicating the end of absorption and start of filtration.

The seepage coefficients were calculated from the data using Equation (1) (Vadyunina & Korchagina 1973):

$$K_t = \frac{Q}{S \cdot T \cdot I} \tag{1}$$

where K_t – seepage coefficient, cm·min^{-1};

Q – water consumption, cm^3;

S – tube section area, cm^2;

T – time, min;

I – hydraulic gradient.

The contents of chromium(VI), iron (total), cobalt, nickel, copper, and zinc in filtrate were determined with a portable spectrophotometer Hach DR2700-01B1 (Germany), and the pH with a FiveEasyPlus 20 pH meter (Mettler Toledo).

Sorbent and soil characteristics

Details of the sorbent and soil characteristics used in the models are given in: Table 1 (fraction size), Table 2 (chemical composition), Table 3 (X-ray phase composition and cation exchange capacity), Table 4 (filterability), and Figure 1 (IR absorption spectra).

Table 1 | Sorbent fraction sizes

Sorbent	Fraction size, mm
Vermiculite – Koksharovka deposit	3–4
Vermiculite – Kovdor deposit	0.25–0.50
Ash[a] from Partizansk CBPP	0.1–0.2
Zeolite – Chuguevka deposit	2–3
Soils (humus and medial horizons)	≤1 mm

NOTE – [a]The ash was calcined and the iron compounds removed by magnetic separation.

Table 2 | Proportional compositions of sorbents and soils (%)

Sorbent	pH	SiO_2	Al_2O_3	MgO	CaO	Fe_2O_3	K_2O	Na_2O
Koksharovka vermiculite[a]	9.02	42.72	11.81	24.52	5.75	8.74	0.14	n/d
Kovdor vermiculite	6.95	37.57	12.42	12.40	2.80	14.27	4.55	1.10
Chuguevka zeolite[b]	7.30	72.30	17.10	0.20	3.61	1.60	3.79	1.14
CBPP ash	9.75	51.79	27.04	3.65	2.74	10.03	3.10	0.40
Soil humus horizon	6.50	55.08	25.61	0.96	2.70	8.69	4.09	n/d
Soil medial horizon	6.31	59.91	23.97	0.75	0.95	8.83	5.57	n/d

n/d, not detected.
[a]Source Shapkin et al. (2014b).
[b]Source Shapkin et al. (2014a).

Table 3 | Physico-chemical characteristics of sorbents and soils

Sorbent	Cation exchange capacity, mmol-eq/100 g	XPA results
Kovdor vermiculite	216.03	C[a] (73% - vermiculite; 27% - clinochlore)
Koksharovka vermiculite	62.87	C (43% - vermiculite; 57% - biotite)
Chuguevka zeolite	44.65	C (68% - mullite; 32% - quartz)
CBPP ash	55.68	К (66% - geylandite; 34% - mordenite)
Soil humus horizon	71.04	C (quartz, kaolinite, illite, montmorillonite, muscovite)
Soil medial horizon	39.38	C (quartz, kaolinite, illite, montmorillonite, muscovite)

Note [a]Crystal phase.

Table 4 | Water permeability characteristics of soil and sorption barriers

Study objects	Direct method			Inverse method		
	$T_{seep.}$, min	Q, ml	K_t, cm·min^{-1}	$T_{seep.}$, min	Q, ml	K_t
Filtration through soil						
Distilled water	34	160	0.48	64	170	0.27
Technogenic discharge water	31	160	0.53	56	170	0.31
Filtering technogenic water through soil with sorbents						
Koksharovka vermiculite	87	180	0.32	145	190	0.20
Kovdor vermiculite	64	210	0.51	83	210	0.39
CBPP ash	48	190	0.61	75	220	0.45
Chuguevka zeolite	38	190	0.77	61	200	0.51

Sorbent chemical composition was determined by energy dispersive X-ray fluorescence spectroscopy (EDRF) using a Shimadzu EDX 800 HS spectrometer (Japan).

The sorbents' IR absorption spectra were recorded in the range 400 to 4,000 cm^{-1} in potassium bromide (KBr) on a Bruker Vertex 70 Fourier spectrometer (Germany). X-ray phase analysis (XPA) of the sorbents and clay soil fraction in the geochemical barriers was done by the Bragg-Brentano method (Kheiker & Zevin 1963) in Cu Kα-radiation on a Bruker D8 Advance diffractometer (Germany). Phase identification in the experimental X-ray patterns was done using EVA Software's powder diffraction pattern database PDF-2 (The Powder Diffraction File) (Kovba & Trunov 1976).

Soil samples for XPA were prepared according to the method proposed by Gorbunov (1971). In this, a fraction of sub-0.001 mm (clay-size) material was isolated from the soil sample by repeated soaking. The clay fraction includes the smallest soil particles – e.g., colloids, etc – which are the most active components and provide its sorption properties. The humus and amorphous minerals – e.g., non-silicate sesquioxides and silica – were then removed as it is thought that their presence affects the clarity of radiographs. The humus was removed with 30% hydrogen peroxide heated in a water bath. The non-silicate forms of sesquioxides were removed by the Mehra-Jackson method (Mehra & Jackson 1960), and amorphous silica by boiling with sodium hydroxide solution (0.5 mol·L^{-1}) and subsequent centrifugation.

The pH of the aqueous extract was determined by placing 5 g of sample in a flask, adding 50 cm^3 of water, and boiling for three minutes in a flask with a reflux condenser. The flask's contents were filtered, and the filtrate was cooled and its pH measured.

The cation exchange capacity of the sorbents and soils was determined by the Bobko-Askinazi-Aleshin method (Vorob'eva 2006).

RESULTS AND DISCUSSION

Properties of sorbents and soils

The physico-chemical characteristics of the sorbents are presented in Table 2. As can be seen, the Kovdor vermiculite contains twice as much magnesium and calcium as that from Koksharovka. The latter, however, is characterized by high contents of potassium and iron, and the presence of sodium. The zeolite from Chuguevka deposit and ash from the Partizansk Coal-Burning Power Plant (CBPP) consist mainly of silicon and aluminium. Water extracted from the Kovdor vermiculite and ash is alkaline, and from the Koksharovka vermiculite and Chuguevka zeolite deposit broadly neutral, similar to the soils.

The phase identification in the XRD patterns revealed the presence of highly dispersed kaolinite, montmorillonite and illite group minerals in the soils (Table 3).
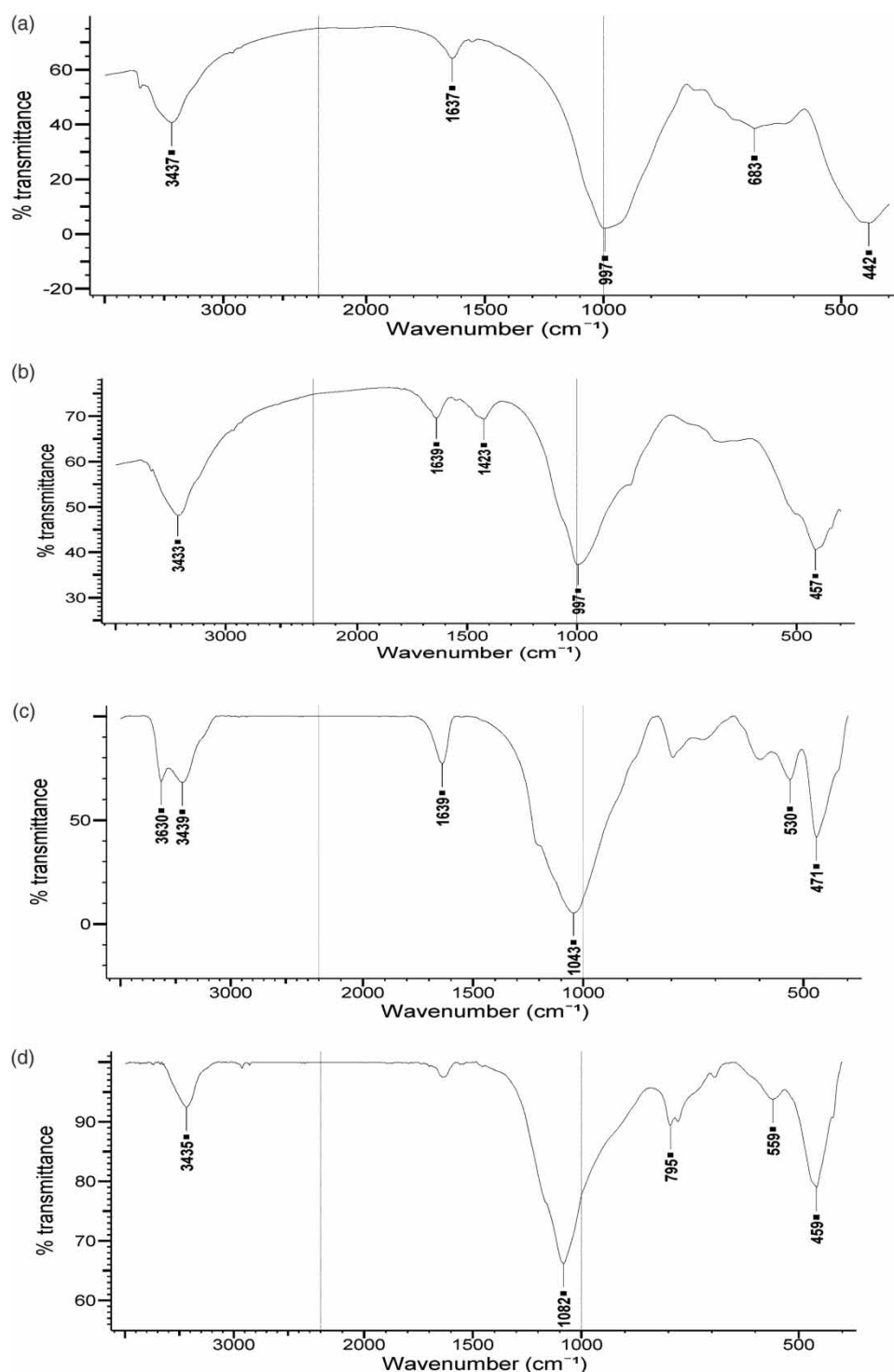
Figure 1 | FT-IR sorbent spectra: (a) Kovdor vermiculite; (b) Koksharovka vermiculite; (c) Chuguevka zeolite; (d) Partizansk CBPP ash.

The sorbents' chemical compositions and properties (Tables 2 and 3) suggest that the high exchange/sorption capacity of the Kovdor vermiculite arises from the presence of hydrated (exchange) Mg^{2+} ions between packets of a three-ply packet-layer lattice. The Koksharovka vermiculite, however, has a collapsed type of crystal lattice with fixed (non-exchangeable) potassium cations. This is confirmed by the high contents of MgO and K_2O in the Kovdor vermiculite, twice and four times those found in the Koksharovka vermiculite. In addition, according to XPA, the Kovdor vermiculite contains about twice as much vermiculite material.

The IR spectra of the Kovdor and Koksharovka vermiculites are similar (Figure 1(a) and 1(b)). They include an intense absorption band of valence non-bridge Si-O aluminosilicate group bonds with a maximum at 998 cm^{-1}. The absorption bands at 457 and 670 cm^{-1} can be attributed to Si-O-Si group deformation vibrations. The band at 3,434 cm^{-1} is caused by the presence of absorbed and capillary water. The deformation vibrations of these groups are in the region of 1,639 cm^{-1}. The Kovdor vermiculite is distinguished by a band at 1,423 cm^{-1}, corresponding to OH group deformation vibrations at the vertices of silica-oxygen tetrahedrons, and an inflection at $\sim$ 940 cm^{-1} indicating the presence of aluminium hydroxide OH group octahedrons (Figure 1(b)). It is possible that these cause the Kovdor vermiculite medium's alkaline reaction.

In the Chuguevka zeolite IR spectrum an absorption band at 1,044 cm^{-1} corresponds to the stretch vibrations of Si-O-Si (Al) bridge bonds (Figure 1(c)). The CBPP ash spectrum includes a band at 1,083 cm^{-1} indicating the presence of Si-O-Si frame groupings (Figure 1(d)). The absorption bands in the range 400 to 800 cm^{-1} in both spectra can be attributed to various vibrations of Si-O, Al-O, and Si-O-Si bonds. The sorbent spectra include absorption bands of stretch vibrations of various types of OH groups, with a maximum in the 3,400 to 3,600 cm^{-1} region, as well as deformation vibrations in the range of about 1,600 cm^{-1}.

As shown in Table 4, the soil seepage coefficients of distilled and technogenic discharge waters do not differ materially (less than 9.4%). The technogenic discharge water seepage coefficients in the geochemical barrier model using Kovdor vermiculite are the closest to those of the soil. The Chuguevka zeolite and CBPP ash contribute to an increase in the seepage coefficient, which speeds the technogenic discharge water's filtration through the soil. The vermiculite from Koksharovka, however, reduces the seepage rate.

Studying filtration capacity

The different chemical species observed in the technogenic water behaved differently in passage through the various sorbents (Figures 2–6).

Chromium

In practice, chromates are not accumulated in the soil, and their concentration before and after soil filtration is the same. Kovdor vermiculite has no effect on chromate ions, in either direct or inverse methods. The Koksharovka vermiculite, in contrast, has the best sorption abilities and adsorbs chromates almost completely from a direct industrial water feed (Figure 2).

Iron

With respect to iron, the Koksharovka vermiculite and Chuguevka zeolite behaved identically in the direct method, with almost no change in iron concentration, whereas the Kovdor vermiculite and CBPP ash both reduced the concentration, in both the direct and inverse methods. It is possible that iron loses its mobility due to the increased alkalinity after passing through the alkaline sorbents layers (Figure 3).

Cobalt and nickel

These two cations behave similarly (Figure 4). Nickel ions, unlike cobalt, however, are fixed during passage through the soil and their concentration in the filtrate decreases. The Koksharovka vermiculite retains neither nickel nor cobalt in either the direct or inverse methods. In the inverse method, they are actively washed out of the humus horizon, and their concentrations in the filtrate are two
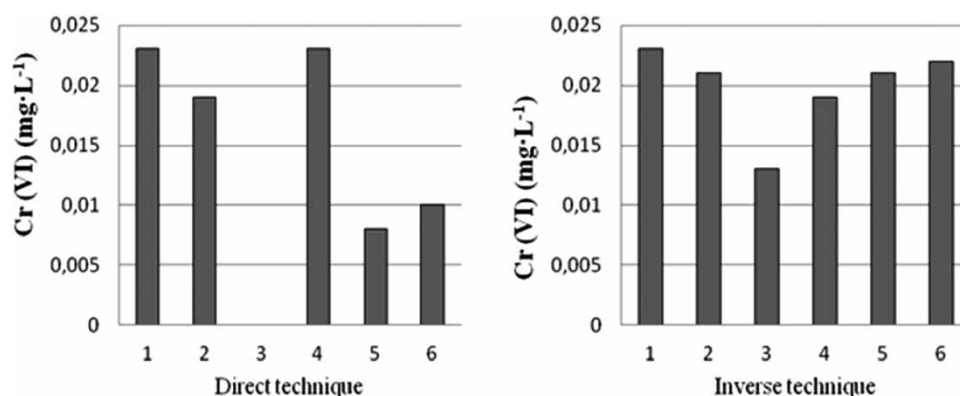
Figure 2 | Chromium content in waters filtered through geochemical sorption barriers: 1 – technogenic water; 2 – technogenic water-soil; 3 – technogenic water-soil-Koksharovka vermiculite; 4 – technogenic water-soil-Kovdor vermiculite; 5 – technogenic water-soil-CBPP ash; 6 – technogenic water-soil-Chuguevka zeolite.
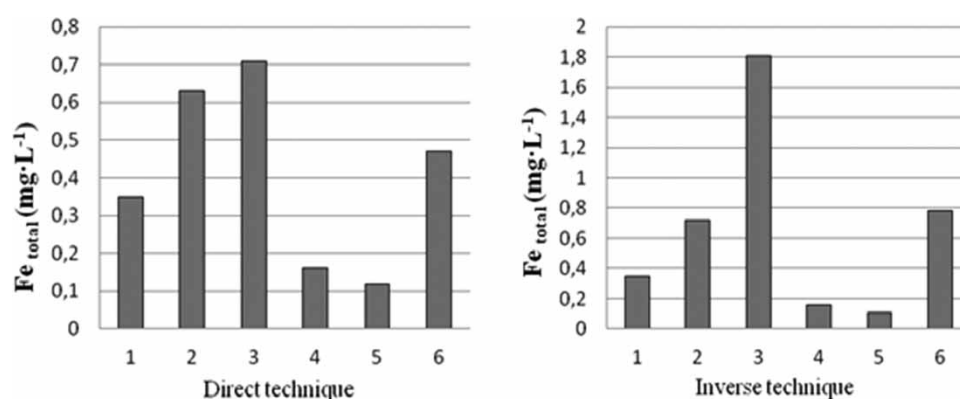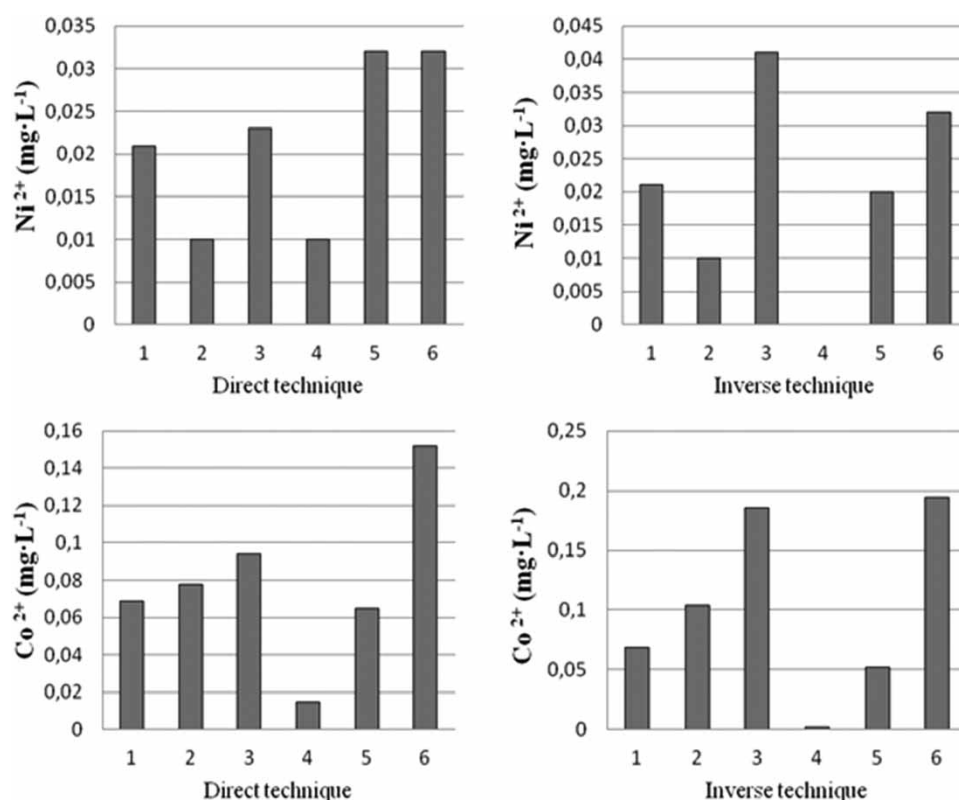

Figure 3 | Iron content in waters filtered through geochemical sorption barriers: 1 – technogenic water; 2 – technogenic water-soil; 3 – technogenic water-soil-Koksharovka vermiculite; 4 – technogenic water-soil-Kovdor vermiculite; 5 – technogenic water-soil-CBPP ash; 6 – technogenic water-soil-Chuguevka zeolite.

and four times higher, respectively, than in the influent, and this is also related to the low seepage coefficient. When the influent passes through Kovdor vermiculite, the migration of nickel and cobalt ions decreases apparently because they can be adsorbed by the sorbent's aluminosilicate component – viz. its high ion exchange capacity (Table 3). In the humus horizon these ions, when alkalinized, can be fixed, leading to a significant concentration decrease in the filtrate. The CBPP ash has almost no effect on the ionic concentration in the direct method but reduces cobalt ion mobility slightly. Zeolites promote the release of nickel and cobalt from the humus horizon.

Copper

In the direct method, copper is retained in the column by Koksharovka vermiculite – i.e., it is adsorbed – whereas, in the columns with both Kovdor vermiculite and CBPP ash, the copper concentration is increased in the effluent. (The Kovdor vermiculite column increased the copper concentration four-fold, in transit, and that with CBPP ash threefold.) In the inverse method columns, the copper concentration increases in the waters passing through the column with Koksharovka vermiculite, but decreases in transit through columns with Kovdor vermiculite and CBPP ash (Figure 5). The increased copper content is most likely to have originated in copper-contaminated soil horizons, which carry different forms of copper compound. In the humus horizon, organo-mineral copper compounds with large molecules predominate, whereas, in the middle horizon, ionic (cationic) exchange

Figure 4 | Nickel and cobalt contents, separately, in waters filtered through geochemical sorption barriers: 1 – technogenic water; 2 – technogenic water-soil; 3 – technogenic water-soil-Koksharovka vermiculite; 4 – technogenic water-soil-Kovdor vermiculite; 5 – technogenic water-soil-CBPP ash; 6 – technogenic water-soil-Chuguevka zeolite.

forms are predominant and associated with the montmorillonite clays, according to the XPA data. The unequal effluent copper content between the direct and inverse methods also arises because of the different column filtration capacities – for example, the seepage coefficients for the direct and inverse method columns with Koksharovka vermiculite were 0.32 and 0.20 cm·min^{-1}, respectively. Consequently, the transit water/solid phase interaction (soil and sorbent) times differ, the slower times increasing the probability of copper ion release to the infiltration waters. It is also possible that changes occurred in the media reactions because of interaction between the technogenic water and sorbents.

The Kovdor vermiculite and CBPP ash release copper ions, but, when water passes through these sorbents, the pH rises to 9, which may help dissolve the silicate constituent of the medial horizon to which the copper ions are bound. In the inverse method, an increase in copper concentration in the Koksharovka vermiculite column, compared with a column containing soils, is apparently due to a lower seepage coefficient. Kovdor vermiculite and CBPP ash both reduce the rate of copper migration from the humus horizon because the water becomes more alkaline, leading to the formation of immobile copper compounds. Zeolite, ionic sieve, retains small amounts of copper, in both the direct and inverse methods (Figure 5).
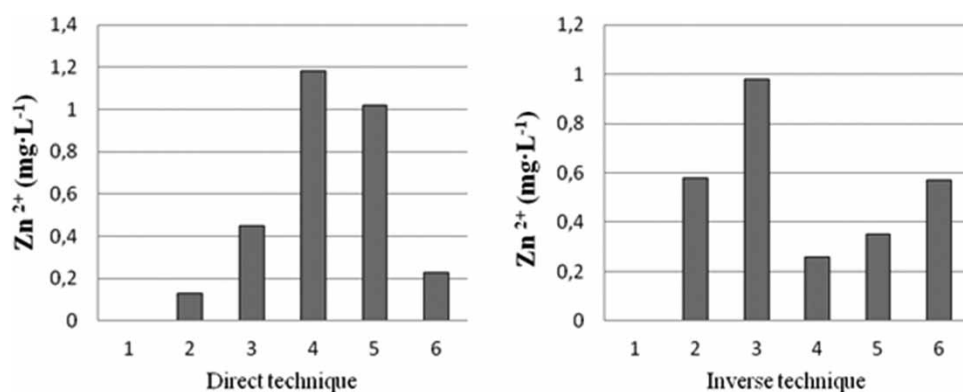
Zinc

The results of the studies show that the sorbents do not adsorb zinc cations. In the direct method, the zinc concentration increased in the infiltration waters, the greatest increase (five- or six-fold) occurring during filtration through Kovdor vermiculite and ash. Consequently, the zinc content, washed from the soil humus horizon and not retained by the sorbent, increases even more in transit through the medial horizon due to increased alkalinity of the waters in transit. In the inverse method, the zinc
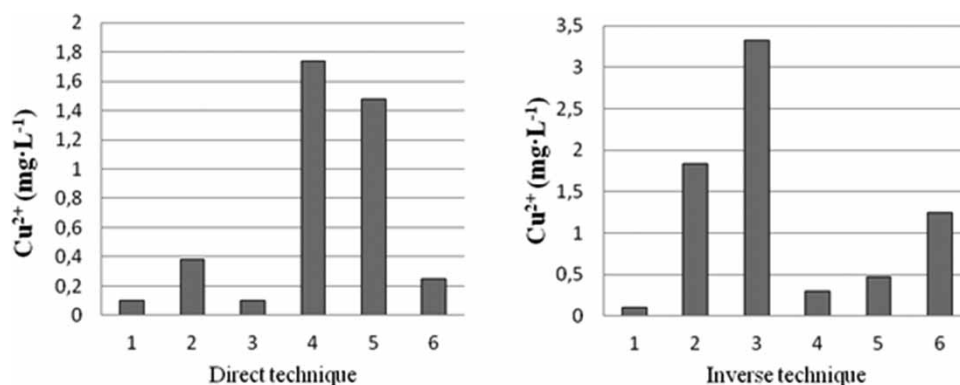
Figure 5 | Copper content in waters filtered through geochemical sorption barriers: 1 – technogenic water; 2 – technogenic water-soil; 3 – technogenic water-soil-Koksharovka vermiculite; 4 – technogenic water-soil-Kovdor vermiculite; 5 – technogenic water-soil-CBPP ash; 6 – technogenic water-soil-Chuguevka zeolite.

Figure 6 | Zinc content in waters filtered through geochemical sorption barriers: 1 – technogenic water; 2 – technogenic water-soil; 3 – technogenic water-soil-Koksharovka vermiculite; 4 – technogenic water-soil-Kovdor vermiculite; 5 – technogenic water-soil-CBPP ash; 6 – technogenic water-soil-Chuguevka zeolite.

concentration decreases with filtration through both CBPP ash and Kovdor vermiculite (Figure 6). This was also seen in the copper experiments and perhaps the reasons are the same.

In general, the study showed that the use of natural materials and industrial wastes as sorbents can help to deal with locally random industrial wastewater discharges, and reduce the metal concentrations in them. The Kovdor vermiculite deposit is the most suitable sorbent for the metal ions studied (Figures 2–6). Geochemical models of direct input using Kovdor vermiculite lower the Fe and Co concentrations by between four and five times, while inverse flow models lower Fe and Co concentrations five times, Cu – six times, and Zn – twice (Table 5).

Table 5 | Metal cation content in waters filtered through geochemical sorption barriers based on Kovdor vermiculite

| Metals | Concentration, mg·L^{-1} | | | | |
| | – Technogenic water | – Technogenic water-soil | | Kovdor vermiculite | |
		Direct method	Inverse method	Direct method	Inverse method
Chromium	0.023	0.019	0.021	0.023	0.019
Iron	0.35	0.63	0.72	0.16	0.16
Cobalt	0.069	0.078	0.104	0.015	0.02
Nickel	0.021	0.010	0.010	0.010	<0.007
Copper	0.10	0.38	1.83	1.74	0.30
Zinc	<0.01	0.13	0.58	1.18	0.26

CONCLUSIONS

Natural mineral and technogenic materials are proposed for metal cation removal from technogenic waters formed in industrial zones near abandoned coal mines. Vermiculites from the Koksharovka and Kovdor deposits, zeolite from Chuguevka, and ash from the Partizansk CBPP all reduce metal concentrations in industrial wastewaters, by creating alkalinity and sorption barriers. Kovdor vermiculite is the preferred material for a geochemical barrier. The cation removal efficiency at a seepage coefficient of 0.51 cm·min^{-1}, by the direct method is: Fe – 75%, Co – 81%. In the inverse method (seepage coefficient 0.39 cm·min^{-1}), removal efficiency was: Fe – 78%, Co – 81%, Cu – 84%, Zn – 55%,

REFERENCES

Banks, D., Younger, P. L., Arnesen, R. T., Iversen, E. R. & Banks, S. B. 1997 Mine-water chemistry: the good, the bad and the ugly. *Environmental Geology* **32**(3), 157–174.

Banks, S. B. 2003 The Coal Authority Minewater Treatment Programme: an update on the performance of operational schemes. In *National Conference 'Mine Water Treatment: A Decade of Progress'*, Newcastle upon Tyne, UK.

Bayurova, L. Y. & Makarov, D. V. 2013 Artificial geochemical barriers for solving environmental and technological problems. *Scientific Bulletin of Moscow State Mining University* **2**, 11–19.

Benner, S. G., Blowes, D. W. & Gould, W. D. 1999 Geochemistry of a permeable reactive barrier for metal and acid mine drainage. *Environmental Science and Technology* **33**(16), 2793–2799.

Bortnikova, S. B., Gas'kova, O. L. & Bessonova, E. P. 2006 *Geochemistry of Technogenic Systems*. Academic Publishing House 'Geo', Novosibirsk (Russia).

Feng, Q., Li, T., Qian, B., Zhou, L., Gao, B. & Yuan, T. 2014 Chemical characteristics and utilization of coal mine drainage in China. *Mine Water and the Environment* **33**(3), 276–286.

Gorbunov, N. I. (ed.) 1971 *Methods of Mineralogical and Micromorphological Study of Soils*. Nauka, Moscow (Russia).

Hossain, M. N., Paul, S. K. & Hasan, M. M. 2015 Environmental impacts of coal mine and thermal power plant to the surroundings of Barapukuria, Dinajpur, Bangladesh. *Environmental Monitoring and Assessment* **187**, 202.

Izotov, A. A., Koverdyaev, O. N. & Vershinina, O. O. 2006 Ways of reducing the impact of drainage water on the environment in mining areas. *Mining Journal* **10**, 103–106.

Kheiker, D. M. & Zevin, L. S. 1963 *X-ray Diffraction*. Fizmatgiz, Moscow (Russia).

Kovba, L. M. & Trunov, V. K. 1976 *X-ray Analysis*. Publishing House of Moscow University, Moscow (Russia).

Makarov, D. V., Maslobaev, V. A., Nesterov, D. P., Svetlov, A. V., Men'shikov, Y. P., Korneva, E. A. & Bayurova, Y. L. 2012 The Use of geochemical barriers in waste water treatment and recovery of non-ferrous metals. *Ecology of Industrial Production* **2**, 43–46.

Maksimovich, N. G. & Hajrulina, E. A. 2013 Geochemical methods in the solution of problems of environmental protection. *Geographical Bulletin* **27**(4), 59–64.

Mehra, O. P. & Jackson, M. L. 1960 Iron oxide removal from soils and clays by a dithionite-citrate system buffered with sodium bicarbonate. *Clays and Clay Minerals* **7**, 317–327.

Perelman, A. I. 1989 *Geochemistry*. Vysshaya Shkola, Moscow (Russia).

Sena, K., Barton, C., Angel, P., Agouridis, C. & Warner, R. 2014 Influence of spoil type on chemistry and hydrology of interflow on a surface coal mine in the eastern US coalfield. *Water Air and Soil Pollution* **225**, 2171.

Shapkin, N. P., Razov, V. I., Hal'chenko, I. G., Shkuratov, A. L., Ermak, I. M. & Davydova, V. N. 2014a Preparation of organomodified aluminosilicates for purification of biological solutions. *Russian Journal of Inorganic Chemistry* **59**(6), 587–591.

Shapkin, N. P., Shkuratov, A. L., Khal'chenko, I. G., Maiorov, V. I., Leont'ev, L. B. & Shapkina, V. Y. 2014b A study of the adsorption properties of modified layered silicate. *Colloid Journal* **76**(6), 746–752.

Sun, L., Gui, H. & Peng, W. 2014 Heavy metals in groundwater from the Wolonghu coal mine, northern Anhui Province, China and their hydrological implications. *Water Practice & Technology* **9**(1), 79–87.

Vadyunina, A. F. & Korchagina, Z. A. 1973 *Methods of Investigation of Physical Properties of Soils*. Vysshaya Shkola, Moscow (Russia).

Vorob'eva, L. A. (ed.) 2006 *Theory and Practice of Chemical Analysis of Soils*. GEOS, Moscow (Russia).