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TECHNICAL ARTICLE

Acid Rock Drainage Remediation and Element Removal Using a Peat-Humic Agent with Subsequent Thermal Treatment of the Metal–Organic Residue

Anna A. Bogush[1] · **Vladimir G. Voronin**[2] · **Vera D. Tikhova**[3] · **Gennadiy N. Anoshin**[1]

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Abstract A novel, alternative method for acid rock drainage (ARD) remediation and metal recovery has been developed that uses a peat-humic agent (PHA) created by mechanical, chemical, and thermobaric treatment of peat from the Krugloe deposit (Novosibirsk region, Russia). The PHA effectively neutralised moderately acidic ARD and removed potential pollutants (e.g. Fe, Al, Zn, Cu, Pb, Cd, Ni, Co, and Hg), forming metal–organic residues. The organic matter can be removed completely from the metal–organic residues by heating them at 450–500 °C. After this treatment, the metal concentrate residues generally contained aggregates (20–350 µm in size), mainly composed of metal oxides and sulphates. Thermal decomposition of the organic matter in the PHA and metal–organic residues is an exothermic process with significant calorific value (9–15 kJ/g).

Keywords Pollution · Wastewater treatment · Acid mine drainage · Metal recovery

Introduction

Vast amount of waste has been generated globally during the last century as a result of mining and mineral processing (Alekseenko 2000; Jambor et al. 2003; Lottermoser 2007; Nordstrom 2011; Panin 2002). About 95 % of the materials mined or removed for extraction of Cu, Pb, Zn, Au, and Ag become waste (Da Rosa et al. 1997). Mine tailings are some of the most hazardous mine waste products because the produced acidity mobilizes potentially harmful elements (Blair et al. 1980; Hudson-Edwards et al. 2011; Jambor et al. 2003; Lottermoser 2007; Nordstrom 2000; Williams 1975; Zipper et al. 2011). Solid mine wastes (e.g. waste rocks, tailings, slags, and sludges) are usually disposed off in landfills, tailing ponds, and dumps (Tchobanoglaus and Kreith 2002), where sulphide minerals, if present, can be oxidized by atmospheric oxygen and microbial activity in the presence of water, forming acid rock drainage (ARD) with potentially high concentrations of SO_4^{2-}, Fe, Al, Zn, Cu, Cd, Pb, Ni, Co, Cr, and other contaminants (Bogush et al. 2012; Lottermoser 2007; Nordstrom et al. 2000; Nordstrom 2011; Nordstrom and Alpers 1999). ARD can seriously degrade water quality, and can kill or damage plants and aquatic organisms (Nordstrom 2011). Additionally, ARD can corrode metal pipes and structures, and break down concrete and metallic compounds (Gaikwad and Gupta 2008).

Active and passive treatment systems are widely implemented for ARD remediation (Coulton et al. 2003; Gaikwad and Gupta 2008; Johnson 2000; Johnson and Hallberg 2002; Kleinmann et al. 1998; Lottermoser 2007; Nordstrom 2011; Younger 2000; Younger et al. 2002, 2003). Supplemental Table 1 compares the main advantages and disadvantages of the most widely used ARD treatment technology. The optimal ARD treatment choice

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✉ Anna A. Bogush
annakhol@gmail.com

[1] Institute of Geology and Mineralogy SB RAS, Koptyuga Pr. 3, Novosibirsk, Russia 630090

[2] Planeta-Ra Ltd, Lazurnaya Str 4/3, Novosibirsk, Russia 630133

[3] Institute of Organic Chemistry SB RAS, Lavrenteva Pr. 9, Novosibirsk, Russia 630090

depends on technical (ARD composition, acidity, amount, flow rate, the desired final water quality, etc.) and economic (installation costs—materials, equipments, and labor; variable costs—reagents, annual labor, and maintenance; risk factors, etc.) factors (GARD/INAP; Zinck and Griffith 2013).

In this work, a novel and alternative method for ARD remediation and recovery of strategically important metals using a new humic agent derived from peat are considered. Humic substances contained in peat, lignite, sapropel, and other organogenic matter can play a significant role in element concentration (Aleksandrova 1980; Orlov and Osipova 1988; Orlov 1990; Stevenson 1994; Varshal et al. 1993). Humic substances are complex mixtures of natural, high molecular weight (>500 μm), dark-colored, organic compounds formed by decomposition of vegetation and animal residue by microorganisms and abiotic factors (Orlov 1990; White 2013). Humic substances occur naturally, with the highest content (up to 85 %) observed in biogenic lithologies, such as coal, peat, sapropel, and black shale (Perminova 2000, 2008). Humic substances have a complex, variable, and irregular structure and high surface area, and contain numerous functional groups (hydroxyl, carboxyl, phenolate, carbonyl, amide and others), all of which lead to unique chemical and biological properties. Humic substances have long been known to form stable complexes with metal ions (Buffle et al. 1980; Livens 1991; Tipping and Hurley 1992; Varshal et al. 1993). Additionally, humic substances are usually strong chelators with stability constants in excess of 10^{10} (White 2013). Peat is a common natural material widely used in ARD passive treatment systems and plays an important role in ARD remediation (GARD/INAP). Sobolewski et al. (1995) investigated copper removal from mine drainage in an experimental wetland and determined that the Cu was predominantly retained in the wetland peat in organic and exchangeable fractions. Similarly, Zn, Pb, Cu, As, and Au from Ursk sulphide tailings were found to be concentrated in an organic-mineral complex barrier consisting of peat, humic substances, clay minerals, and iron oxyhydroxides (Bogush et al. 2012). Recently, it was proposed to use a peat-humic agent (PHA) as a sorbent for ARD remediation in two stages: (1) metal complexation and removal during ARD treatment; (2) separation of the purified solution and the flaky sediment by filtering through activated carbon or expanded clay aggregates (Bogush and Voronin 2011). This approach is cost-effective and would reduce the environmental hazards of mine waste. The main disadvantage of this ARD treatment is that it produces a sludge that must be disposed of. Here, we propose thermal treatment of the metal–organic residue (MOR) after treatment with the PHA in order to produce a metal-concentrate residue and avoid sludge disposal.

Materials and Methods

A liquid PHA was developed by chemical (alkaline hydrolysis), mechanical, and thermobaric treatment using hydrodynamic cavitation of peat from the Krugloe deposit (Novosibirsk region, Russia) (Bogush and Voronin 2011). Drainage water from the tailings produced by the Belovo zinc processing plant (Belovo, Kemerovo region), the gold concentration plant (Ursk, Kemerovo region), the Altay polimetal Ltd. plant (Gornyk, Altay region), and the Karabashmed plant (Karabash, Chelybinsk region) were sampled and filtered on site through 0.45 μm membrane filters. Then, some of the filtered samples were divided into two sub-samples: one was acidified to $pH < 2$ with ultra-pure HNO_3 and retained in amber-plastic containers with minimal headspace for element analysis; the second was used for analysis of ion composition. The Eh and pH were analysed on site. Total dissolved solids (TDS) was measured using a Hanna conductivity/TDS tester. The laboratory work was carried out at the analytical centre of the Institute of Geology and Mineralogy of the Siberian Branch of the Russian Academy of Sciences. The sampled ARD were used for the treatment experiments (Fig. 1). 100 mL of each ARD was placed in a 150 mL glass beaker. The PHA was then added to the drainage water samples (DWS), with agitation, in three DWS/PHA volumetric ratios: 100, 500, and 1000. The solution pH was measured before and after PHA addition using an Ionomer-4151 (TD-ANION, Russia). DWS were filtered after treatment through 0.45 μm membrane filters and acidified to $pH < 2$. Concentrations of Al, Fe, Zn, Cd, Cu, Pb, Co, and Ni in the DWS and treated DWS were analysed using ICP-AES (IRIS, Intertech Corporation; PGS-2, Carl Zeiss) and AAS (Solaar M6, Thermo Scientific; Perkin Elmer 3030 Z; Pye-Unicam SP-9). Hg was analysed by cold-vapor AA spectrometry. Each experiment was conducted in triplicate and the results were averaged. The range of variation did not exceed 8 % for any of the analysed elements.

Equilibrium calculations were performed using the WATERQ4F computer program (Ball and Nordstrom 1991) and applying the thermodynamic database from that software to calculate the saturation index (SI) for minerals that might be precipitated and be controlling element concentrations. The temperature, pH, Eh, major anion and cation concentrations, and trace element concentrations measured in the DWS were used for equilibrium modelling. The SI gives information about whether the water is saturated ($SI = 0$), undersaturated ($SI < 0$), or supersaturated ($SI > 0$) with respect to a given mineral. Minerals with SIs from -1 to $+1$ were considered to be the potential solubility controlling minerals.

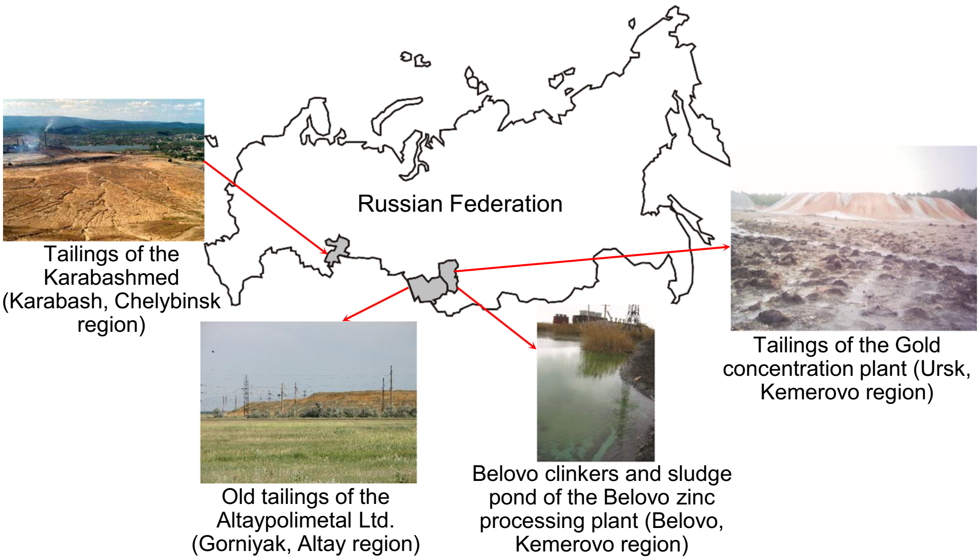

Fig. 1 Sketch map showing the locations of the sites described, with photos of the wastes from the mining and processing industry

The PHA and MORs from element removal experiments from the Belovo clinkers and Ursk tailings DWS were thermally treated. Simultaneous thermal analysis (STA) with simultaneous application of thermogravimetry (TG), differential thermogravimetry (DTG), and differential scanning calorimetry (DSC) were used to investigate temperature conditions, caloric effects, and mass changes. The STA was performed using a NETZSCH STA 409 PC Luxx analyzer and 5–10 mg of organic bearing materials within a temperature range of 25–600 °C with a heating rate of 10 °C per min. An 85 µL sampler of Pt-crucible with a lid, and an identical empty crucible as a reference, were used for this analysis. A furnace atmosphere consisting of synthetic air (80 % He and 20 % O_2) flowing at 30 mL/min and He protective gas flowing at 10 mL/min was applied. Weight losses were calculated from the TG curves.

The morphology and microstructure of the MORs and the residue after thermal treatment (500 °C) were investigated using a TESCAN MIRA 3 LMU and LEO 1430VP high-performance, variable pressure, analytical scanning electron microscope (SEM). Energy-dispersive x-ray spectroscopy (EDS; Oxford Instrument X-Max 80 EDS-system) was used for microanalysis of the solid phases viewed by SEM.

X-ray diffraction analysis (XRD; DRON-3 M powder diffractometer using filtered CuKα-radiation) was used to characterize the crystalline phases in the residue from the element extraction experiment after thermal treatment. The software includes search-match access to the International Centre for Diffraction Data (ICDD) database for phase identification.

Results and Discussion

Composition of the Acid Rock Drainages

The total dissolved solids (TDS), pH, Eh, ion compositions, concentrations of Fe, Al, Zn, Cu, Pb, Cd, Ni, Co, and Hg in the water samples are given in Table 1, along with national maximum permissible concentrations (MPCs) for drinking water (SanPiN 2.1.4.1074-01, 2002) and general standards for discharge of environmental pollutants (GSDEP 1993). The lowest pH (2.7) was in the ARD from the old Altay polimetal Ltd. waste deposit (Gornyak), and the highest pH (4.8) was in the Belovo zinc processing plant sludge pond (Table 1). The TDS of the ARDs are quite high, with the ARD from the Ursk tailings being SO_4–Fe–Al type, and the ARDs from the Belovo clinkers and sludge pond being SO_4–Cl–Ca–Zn–Cu–Na type. All these ARDs can be considered brackish (Table 2, Masters and Ela 2007). Table 1 shows that the concentrations of potential pollutants were significantly enriched in the ARD exceeding maximum permissible GSDEP concentrations.

Acidity of investigated ARDs can be estimated using following equation (Hedin et al. 1994):

$$\begin{aligned} \mathrm{A} &= 50\cdot\left[2\times\left(\mathrm{Fe}^{2+}/56\right)+3\cdot\left(\mathrm{Fe}^{3+}/55.8\right)\right.\\ &\quad\left.+2\cdot(\mathrm{Mn}/54.9)+3\cdot(\mathrm{Al}/27.0)+1000\cdot\left(10^{-\mathrm{pH}}\right)\right] \end{aligned}$$

where A is acidity, expressed as mg/L $CaCO_3$ equivalent (50 is the initial multiplication factor because 50 mg of $CaCO_3$ can neutralize 1 mg of H^+); Fe^{2+}, Fe^{3+}, Mn, and Al are concentrations in solution (mg/L). Hedin et al. (1994) explained that this equation is appropriate for

Table 1 TDS, pH, Eh, acidity, ionic and element composition in mg/L of acid mine drainages [modified from Bogush and Voronin (2011)]

Sample	TDS (g/L)	pH	Eh	A*	SO_4^{2-}	Cl^-	Ca	Mg	Na	K
ARD from the Ursk tailings	10	2.97	610	6480	7300	–	310	75	15	0.3
ARD from the Belovo clinkers	6.6	4.1	480	2660	3900	250	420	43	280	60
ARD from the old waste deposit (Gornyak)	–	2.7	–	2720	–	–	–	–	–	–
ARD from the Belovo sludge pond	6.7	4.8	390	710	1600	190	320	20	180	40
ARD from the Karabashmed tailings	–	3.6	–	320	–	–	–	–	–	–
General standards for discharge of environmental pollutants (GSDEP)	–	5.5–9	–	–	–	–	–	–	–	–
MPC drink water (SanPiN 2.1.4.1074-01, 2002)	1–1.5	6–9	–	–	500	350	–	–	200	–

Sample	Fe	Al	Zn	Cu	Pb	Cd	Ni	Co	Hg
ARD from the Ursk tailings	1700	600	23	5.0	–	0.03	–		0.01
ARD from the Belovo clinkers	0.18	21	910	730	–	6.0	5.9	5.1	–
ARD from the old waste deposit (Gornyak)	210	350	160	37	0.4	0.86	0.56	0.81	–
ARD from the Belovo sludge pond	0.22	18	120	270	–	1.2	0.68	0.6	–
ARD from the Karabashmed tailings	8.8	31	18	59	–	0.06	0.18	0.13	–
General standards for discharge of environmental pollutants (GSDEP)	3.0	–	5.0	3.0	0.1	2.0	3.0	–	0.01
MPC drink water (SanPiN 2.1.4.1074-01, 2002)	0.3	0.5	5.0	1.0	0.03	0.001	0.1	0.1	0.0005

* A—calculated acidity as mg/L $CaCO_3$

waters with $pH < 4.5$ (no alkalinity), but it is also commonly used for higher pH waters that contain alkalinity. Kirby and Cravotta (2005a) noticed that this equation underestimates contributions from HSO_4^- and H^+, but overestimates the acidity due to Fe^{3+} and Al^{3+}; however, these errors tend to approximately cancel each other. When other acid-soluble metals are present in known concentrations (Zn, Cu, etc.), they should also be considered for acidity estimation (Zipper et al. 2011). There is a good agreement between measured hot acidity and calculated acidity for the pH range of 1.6–8.5 and acidity up to 15,000 mg/L as $CaCO_3$ (Hedin et al. 1994; Kirby and Cravotta 2005b). Also Fe(III) will not contribute much to acidity in the pH range from 2.5 to 8.3 because of the low solubility of Fe(III) solid phases and the tendency to hydrolyze at low pH (Kirby and Cravotta 2005b). Therefore, the following equation can be applied for acidity estimation in this work (Kirby and Cravotta 2005b):

$$A = 50 \times \left(10^{3-pH} + 2C_{Fe}/55.8 + 2C_{Mn}/54.9 + 3C_{Al}/27.0\right)$$

where C_{Fe}, C_{Mn}, and C_{Al} are analytical concentrations in solution (mg/L). Calculated acidity of investigated ARDs ranged from 320 to 6480 mg/L $CaCO_3$ (Table 1).

Supplemental Table 2 presents the calculated element species (%) and the saturation index (SI) for ARDs from the Ursk tailings, the Belovo clinkers, and the Belovo sludge pond. Iron is mainly present as dissolved ions and a neutral Fe(II) sulphate complex. A small portion of the Fe is present as cationic (6.13 %) and anionic (1.46 %) sulphate complexes, with < 1 % present in other forms (Fe^{3+}, bisulphates, hydroxides, etc.) in the ARD from the Ursk tailings. Al prevails as a cationic sulphate complex (62–65 %), aquatic ion (16–20 %), and an anionic sulphate complex (10–21 %), with <4.5 % present as cationic hydroxide complexes. Zn, Cu, Cd, and Ni are mainly present as aquatic ions (42–69 %), which are the most accessible for live organisms, and neutral sulphate complexes (>30–42 %). A small portion of the Zn and Cd occurs as anionic sulphate complexes. Cd occurs as a cationic chloride complex (10–12 %) in the ARDs from the Belovo clinkers and sludge pond, but only <0.5 % of the Zn, Cu, and Ni are present in this form.

The following solid phases can form in ARDs: (1) jurbanite, K-jarosite, and goethite in the ARD from the Ursk tailings; (2) alunite, diaspore, jurbanite, and goethite in the ARD from the Belovo clinkers; (3) alunite, diaspore, basaluminite, gibbsite, jurbanite, and goethite in the ARD from the Belovo sludge pond.

ARD Treatment and Metal Removal by the Peat-Humic Agent

The element concentrations in treated DWS (mg/L), the removal efficiency (%), pH, and calculated acidity of treated drainage waters at different DWS/PHA ratios are shown in Table 2. A flaky deep-brown sediment was formed by mixing the alkaline PHA with the DWSs. Increases in pH were observed in all static experiments. At the 1000 DWS/PHA ratio, the pH changed slightly, with the exception of the treated ARD and sludge pond water

Table 2 Element concentrations in treated DWS (mg/L)/the removal efficiency (%), pH, and acidity of treated drainage waters at different DWS/PHA ratios [modified from Bogush and Voronin (2011)]

Sample	pH	A	Fe	Al	Zn	Cu	Pb	Cd	Ni	Co	Hg
DWS/PHA = 100											
DWS from the Ursk tailings	4.0	1850	310/81.8	230/61.7	5.5/76.1	1.0/80.0	–	0.0039/87.0	–	–	0.00001/99.9
DWS from the Belovo clinkers	6.2	790	0.0089/95.1	0.021/99.9	300/67	210/71.2	–	1.2/80.0	1.5/74.6	1.2/76.5	–
DWS from the old waste deposit (Gornyak)	3.7	860	54/74.3	120/65.7	67/58.1	1.8/95.1	0.008/98	0.0086/99.0	0.028/95.0	0.12/85.2	–
DWS from the Belovo sludge pond	8.2	0.68	0.013/94.1	0.017/99.9	0.11/99.9	0.25/99.9	–	0.001/99.9	0.075/89.0	0.036/94.0	–
DWS from the Karabashmed tailings	5.0	0.79	0.005/99.9	0.03/99.9	0.017/99.9	0.056/99.9	–	0.0001/99.8	–	–	–
DWS/PHA = 500											
DWS from the Ursk tailings	3.6	3900	950/44.1	390/35.0	14/39.1	2.4/52.0	–	0.015/50.0	–	–	0.0002/98
DWS from the Belovo clinkers	5.3	1980	0.009/95	0.2/99.0	720/20.8	560/23.3	–	4.6/23.3	5.0/15.3	4.2/17.6	–
DWS from the old waste deposit (Gornyak)	3.1	1950	130/38.1	260/25.7	130/18.8	24/35.1	0.0081/98.0	0.49/43.0	0.33/41.1	0.64/21.0	–
DWS from the Belovo sludge pond	7.1	11	0.012/94.5	0.019/99.9	4.8/96.0	2.5/99.1	–	0.29/75.8	0.27/60.3	0.26/56.7	–
DWS from the Karabashmed tailings	4.5	2.2	0.0057/99.9	0.045/99.9	0.34/98.1	0.074/99.9	–	0.0001/99.9	–	–	–
DWS/PHA = 1000											
DWS from the Ursk tailings	3.1	4890	1200/29.4	480/20.0	18/21.7	3.8/24.0	–	0.023/23.3	–	–	0.0056/44.0
DWS from the Belovo clinkers	5.1	2310	0.009/95	8.4/60	810/11.0	650/11.0	–	5.2/13.3	5.7/3.4	4.7/7.8	–
DWS from the old waste deposit (Gornyak)	2.9	2160	160/23.8	290/17.1	140/12.5	34/8.1	0.0083/97.9	0.77/10.5	0.46/17.9	0.77/4.9	–
DWS from the Belovo sludge pond	6.4	310	0.015/93.2	6.1/66.1	47/60.8	130/51.9	–	1.1/8.3	0.52/23.5	0.47/21.7	–
DWS from the Karabashmed tailings	3.9	41	0.085/99	4.9/84.1	2.0/88.9	3.1/94.7	–	0.0001/99.9	–	–	–

from the Belovo zinc processing plant (Belovo, Kemerovo region) where the pH reached slightly acidic and near-neutral values, respectively. A decrease of the DWS/PHA ratio to 500 and 100 led to the pH of the Belovo sludge pond DWS increasing up to 7.1 and 8.2, respectively. The pH increased up to 5.3 and 6.2 for DWS/PHA ratios of 500 and 100, respectively. The treated DWS from the Karabashmed tailings became slightly acidic (4.5–5.0) at the 100 and 500 ARD/PHA ratios. The pH of the highly acidic drainage of the old Gornyak waste deposit and Ursk deposits reached 3.7 and 4.0, respectively, by PHA at 100 DWS/PHA ratios.

The acidity of the highly acidic DWSs from the Ursk tailings, the Belovo clinkers, and the old waste deposit (Gornyak) were reduced by 71.5, 70.5, and 68.4 %, respectively, for the 100 DWS/PHA ratio. DWS acidity for the Belovo sludge pond decreased from 710 to 310 mg/L of $CaCO_3$ at the 1000 DWS/PHA ratio. However, decreasing the DWS/PHA ratio to 100 led to almost complete neutralisation of the DWS from the Belovo sludge pond. A similar trend in decreasing acidity was observed for the DWS from the Karabashmed tailings; the acidity at a DWS/PHA ratio of 500 and 100 were reduced by 99.3 and 99.8 %, respectively (Table 2).

The contaminant concentrations in the treated DWSs decreased in all of the experiments, with the removal efficiency gradually improved by increasing PHA concentrations (Table 2). Contaminant concentrations were below the GSDEP for all of the investigated DWS/PHA ratios and below the MPC for drinking water for the 100 and 500 DWS/PHA ratio. Only Al and Cu concentrations slightly exceeded the MPC for drinking water at the 1000 DWS/PHA ratio. Almost all of the Fe, Al, Zn, Cu, Cd, Ni, and Co were removed from the Belovo sludge pond water with 100–500 DWS/PHA ratios, and the concentrations met GSDEP and MPC thresholds (Table 1). Almost all of the Fe, but only up to 60 % of the Al were removed from the Belovo clinker DWS at the 1000 DWS/PHA ratio. It was mentioned above that the ARD from the Belovo clinker had higher concentrations of Zn, Cu, Cd, Ni, and Co than the Belovo sludge pond water. Therefore, higher quantities of PHA had to be used for complete removal of these pollutants. For example, the removal percentages of Fe, Al, Zn, Cu, Cd, Ni, and Co from the Belovo clinker DWS ranged within 71–99.9 % at the 100 DWS/PHA ratio, and the Cd and Ni concentrations met GSDEP thresholds. However, Zn and Cu concentrations still exceeded water quality standards after the highly contaminated Belovo clinker DWS was treated at the tested PHA dosages.

It was possible to remove 98 % of the Pb from the highly contaminated Gornyak waste deposit ARD using the 1000 DWS/PHA ratio, but the removal percentages of other elements (Fe, Al, Zn, Cu, Cd, Ni and Co) were quite low (Table 2). Decreasing the DWS (Gornyak)/PHA ratio to 100 considerably increased contaminant removal, allowing the Cu, Pb, Cd, Ni, and Co concentrations to meet GSDEP thresholds.

The Ursk tailings ARD had the highest total concentration of potential contaminants among all of the investigated ARDs. It was possible to remove 98 % of the Hg, 52 % of the Cu, 49 % of the Cd and the 44 % of Fe from the Ursk tailings ARD using the 500 DWS/PHA ratio. Using the 100 Ursk DWS/PHA ratio gave high element removal percentages, but only Cd and Hg met GSDEP and MPC thresholds, respectively.

It was previously shown (Bogush et al. 2007; Bogush and Voronin 2011) that potentially toxic elements were sorbed by the PHA (physical adsorption and formation of metal humates). Carboxyl groups in the PHA play a major role in the formation of metal-humate complexes (Bogush et al. 2007). Moreover, hydrolysis, aggregation, inter- and intra-molecular bridging, co-precipitation of elements with secondary phases such as ferric hydroxide, and physical adsorption of contaminants on aggregated surfaces of secondary phases can take place simultaneously in a complex system such as a mixture of ARD and the alkaline PHA.

Thermal Treatment of the Peat-Humic Agent and Metal–Organic Residues

The heat flow, weight changes, and amount of heat released by the thermal treatment of the PHA and two metal–organic residues after the ARD contaminant removal experiments (Belovo and Ursk) were investigated. STA results for the PHA demonstrate three characteristic regions in the interval from 25 to 600 °C. The first temperature region, at around 100 °C, is mainly due to the loss of hygroscopic moisture and represented in the curve by a slight weight loss (3.1 wt%) and a slightly visible endothermic process. The second temperature region (200–300 °C) shows the mass loss (29.2 wt%) attributed to decomposition of organic matter, mainly low molecular weight organic compounds, polysaccharides, and peripheral humic acid components such as carboxylic and phenolic functional groups. The third thermal effects, around 489 °C, show the main mass loss (60.9 wt%), which corresponds to the decomposition of the more thermostable organic matter such as the humic acid core structures (mainly aromatic components). The total mass loss is very high (93 wt%), corresponding to removal of organic matter from the PHA. Organic matter decomposition is an exothermic process, as clearly seen on the DSC curve. The area under the DSC curve is proportional to the amount of heat released; about 20 kJ/g is released by thermal treatment of the PHA.

STA results of the MOR produced after mixing the alkaline PHA with the Belovo and Ursk ARD were investigated in detail. The first mass loss (4.1–6.4 wt%), around 100 °C, is mainly due to water volatilization. The second mass loss (19.8 wt% for the Belovo MOR and 16.1 wt% for the Ursk MOR) at about 220–320 °C is due to decomposition of less stable organic matter. For the Belovo MOR, the last two exothermic mass loss effects (40.1 and 3.7 wt%), at 380–480 °C, correspond to decomposition of the more thermostable organic matter. For the Ursk MOR, the degradation observed at 350–460 °C has significant mass loss (37.8 wt%) and an exothermic effect. It is interesting that the main mass loss of the thermostable organic matter occurs at a lower temperature (around 383–390 °C) for the Belovo and Ursk MOR than for the PHA (489 °C). This may be due to the metals in the MORs. The total mass losses are 70.4 and 58 wt% in the Belovo and Ursk MOR, respectively, which are less than for the PHA. The difference of the total mass loss of the PHA and MORs (22.6 wt% for the Belovo MOR and 35 wt% for the Ursk MOR) likely corresponds to the total metal-bearing content removed from the ARDs. The total heat releases were 15 and 9.6 kJ/g for the Belovo and Ursk MOR.

In general, all of the STA diagrams showed three main thermal degradation processes: (1) loss of hygroscopic moisture at around 100 °C; (2) decomposition of the more thermolabile components of organic matter at 200–320 °C; and (3) decomposition of the more thermostable components of the organic matter at 380–500 °C. Therefore, organic matter can be removed from MORs by heating them up to 500 °C. Additionally, significant heat was released during the thermal decomposition of the organic matter in the PHA and MORs.

Microstructure and Chemical Composition of Residues Before and after Thermal Treatment

SEM images of MORs after the Belovo and Ursk ARD treatment are presented in Fig. 2. MORs produced after mixing the alkaline PHA with the Belovo ARD contain dark-brown aggregates of different size (50–400 μm). These aggregates are homogeneous, composed of C, O, Fe, Al, and S, with Si and P impurities (Fig. 2a, spectrum 1). The MOR formed after mixing the alkaline PHA with the ARD from Ursk deposit contained aggregates (20–200 μm) that consist of C, O, Cu, Zn, Fe, Ca, and S as major elements, with Si and Al impurities (Fig. 2b, spectrum 2). Other mineral phases were not observed in MORs. These results confirm that the organic phase takes up elements that form metal–organic phases. Previous work (Bogush et al. 2007) showed that PHA forms stable complexes with metal ions. The element removal (Table 2) and the SEM data correlated well.

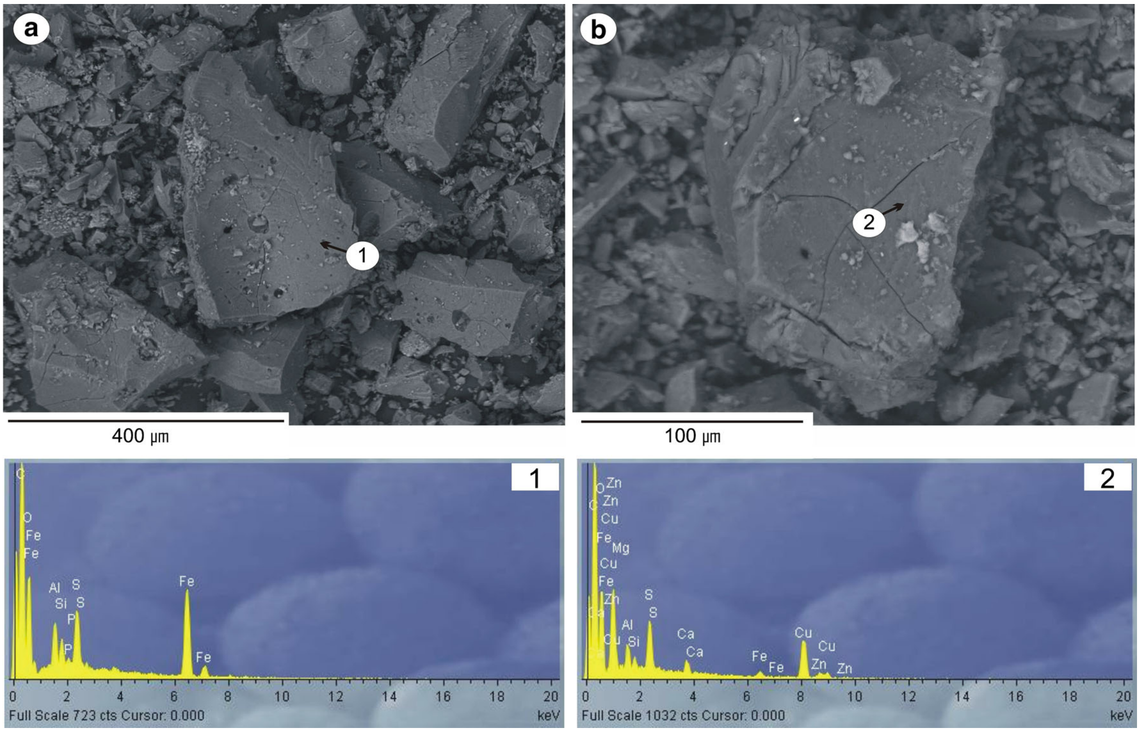

Fig. 2 Scanning electron microscopy images of metal-organic residues after Belovo (**a**) and Ursk (**b**) ARD treatment; 1 and 2—EDS spectra of points 1 and 2

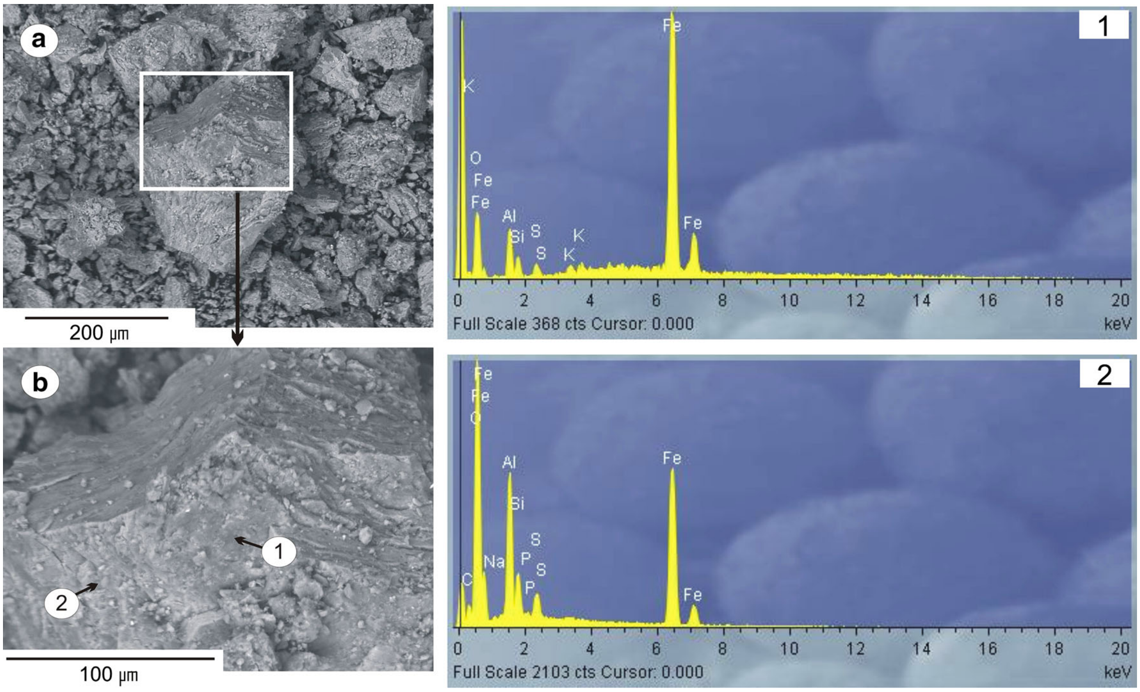

Fig. 3 Scanning electron microscopy images (**a** and **b**) of residue after thermal treatment of metal-organic residue produced after mixing the alkaline PHA with the Ursk ARD. 1 and 3—EDS spectra of points 1 and 2

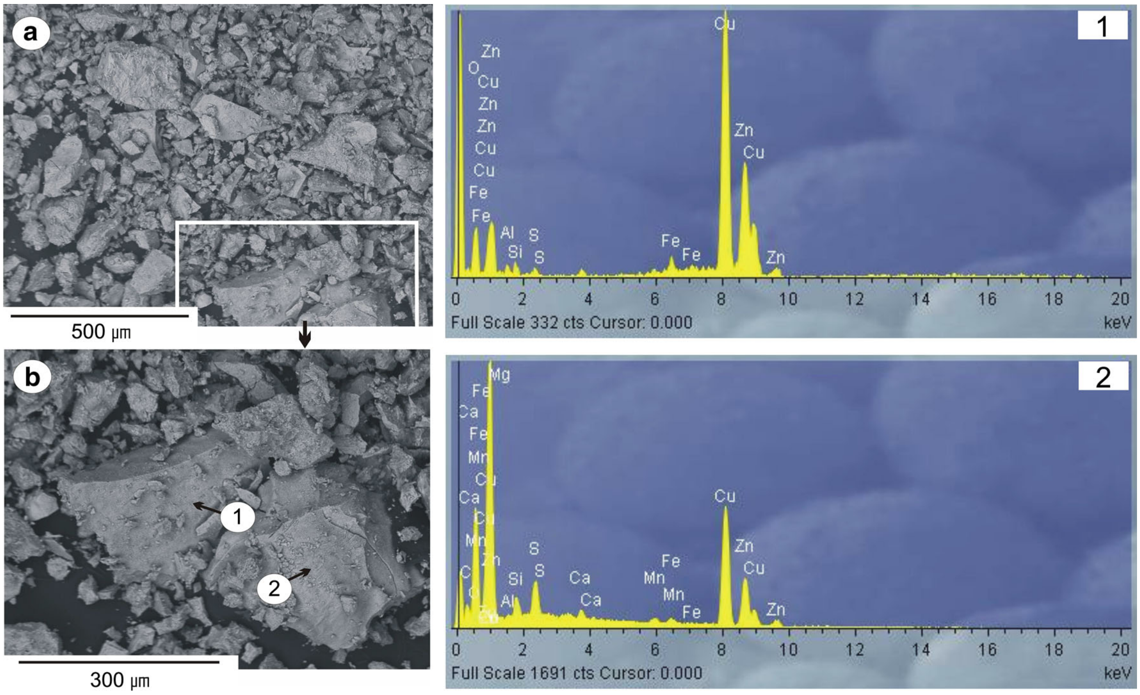

Fig. 4 Scanning electron microscopy images (**a** and **b**) of residues after thermal treatment of metal-organic residue produced after mixing the alkaline PHA with the Belovo ARD. 1 and 3—EDS spectra of points 1 and 2

Figures 3 and 4 show SEM images of the residues after thermal treatment. The PHA-Ursk ARD precipitate residues contained differently sized aggregates (20–250 µm, Fig. 4a), mainly consisting of O, Fe, and Al as major elements (probably Fe and Al oxides); hematite (Fe_2O_3) was detected as a major phase in this sample by XRD. These phases also contained S, P, Na, and K impurities (Fig. 3b, spectra 1 and 2). Aggregates (20–350 µm, Fig. 4a) in the residues of the PHA-Belovo DWS precipitate mainly consisted of Zn, Cu, and O (probably Cu and Zn oxides) with S, Ca, Al, Si, Fe, and Mn impurities (Fig. 4, spectra 1). For instance, tenorite (CuO) was detected as a major phase in this sample by XRD. Also some particles contained Zn, Cu, S, and O as major elements, most probably as Zn and Cu sulphates (Fig. 4, spectra 2). Residues of organic matter were not observed in these samples by SEM and C content was below the EDS detection limit.

Metal Removal from ARD using PHA

A novel, alternative method for ARD remediation and element removal using a PHA with subsequent thermal treatment of the MOR (Fig. 5) to minimize waste sludge production was proposed (patent N2011139274, RU). The process has four steps: (1) The ARD should be collected or pumped into a tank and an appropriate amount of PHA (based on the ARD composition) should be added with agitation; (2) Liquid to solid separation: (a) filtration with a filter press or (b) gravity thickening and pumping of the treated water; (3) dewatering and drying of the filter residue or sludge; 4) Thermal treatment of the metal–organic complex at 450–500 °C in order to remove the organic matter and produce a metal-concentrated residue that is mainly composed of metal oxides and sulphate. Using higher temperatures would increase costs, risk the loss of strategically important metals, and potentially cause volatile harmful impurities to contaminate the air. The metal-concentrated residues can be used for metal production by the blast-furnace method, pyro-processing, or hydrometallurgical methods. The significant heat (9–15 kJ/g) released by the thermal decomposition of the organic matter contained in the metal–organic residues can be used for domestic needs (heating, electricity, etc.). The calorific value of the MOR is comparable to the calorific value of fuels such as dry wood (14–22 kJ/g), lignite (5.5–15 kJ/g), and sub-bituminous coal (8.5–25 kJ/g). However, the CO_2 emissions from the thermal treatment stage could be an environmental issue.

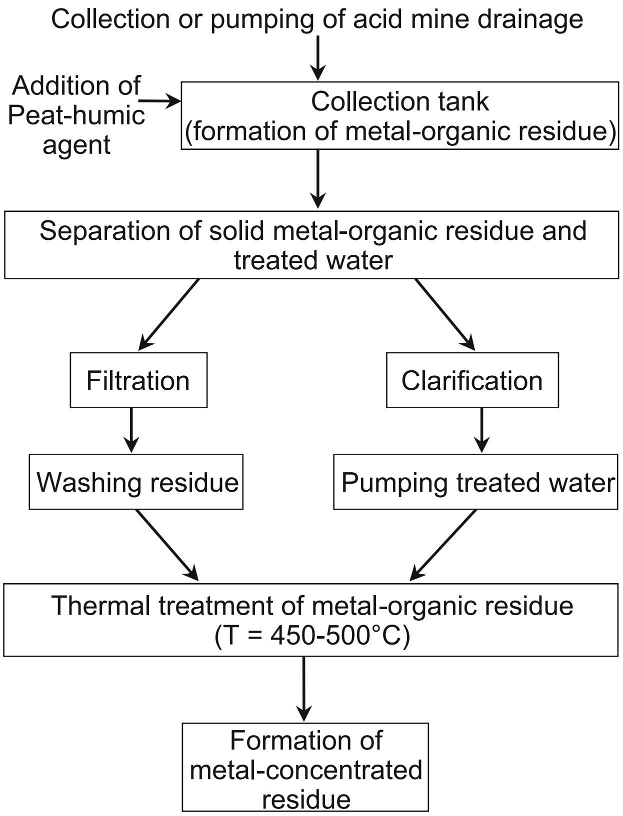

Fig. 5 The schematic technological process for metal extraction from acid rock drainage using the peat-humic agent with subsequent thermal treatment

It is quite difficult to estimate the feasibility of this treatment scheme based only on our laboratory experiments; a pilot-scale study is required. The feasibility of economic metal removal from ARD depends on numerous factors: the chemical composition, available volume, location, specifications, availability of a potential buyer for the recovered metals, economic factors, and regulatory and liability concerns (Smith et al. 2013).

Conclusion

ARD and sludge pond waters from the Belovo Zn processing plant may be potential targets for recovery of Zn and Cu. The PHA effectively removed potentially toxic elements (Hg, Cd, Pb, Zn, Cu, etc.) and increased the pH of all treated DWSs. Complete neutralization was achieved for the DWSs from the Belovo sludge pond and Karabashmed tailings. The amount of the PHA to be added depended on the ARD composition. For instance, an ARD/PHA ratio of 500–1000 was effective for the Karabashmed tailings ARD, while an ARD/PHA ratio of 100–500 was effective for the Belovo sludge pond water. The metal concentrations of these treated ARDs met water quality standards. Using tested DWS/PHA ratios, partial acidity and metal removal was obtained after treatment of the highly acidic and contaminated DWSs of the Ursk tailings, the Belovo clinkers, and the old waste deposit (Gornyak). An increased DWS/PHA ratio was required for the more highly acidic and contaminated ARDs. Therefore, from 1 to 10 L of PHA would be needed to treat 1000 L of moderately acidic and contaminated ARDs. This investigation showed that PHA could be used to improve ARD quality. Moreover, considering the production cost and the anticipated price of the PHA, it would be a low cost material for contaminant removal (Bogush and Voronin 2011).

Thermal treatment of MOR was proposed in order to produce a metal-concentrate residue and avoid waste sludge disposal to the environment. Organic matter can be removed completely from MORs by heating them at 450–500 °C. Using higher temperatures would increase costs, loss of strategically important metals, and secondary environmental pollution by volatile harmful impurities. However, a temperature range of 450–500 °C could still lead to emissions of Hg, As, and Cd if they are present. The metal-concentrate residues generally contained aggregates with different size range (20–350 μm). These aggregates were mainly composed of metal oxides and sulphates. Hematite (Fe_2O_3), which can be potentially applied as a pigment in colored concretes, was detected as a main phase in the residue after thermal treatment of the PHA-Ursk DWS precipitate. Tenorite (CuO) was detected as a main phase in the residue after thermal treatment of the PHA-Belovo DWS precipitate. Thermal decomposition of the organic matter in the PHA and the MORs was an exothermic process in which significant heat was released. The metal-concentrate residues can be used for metal production by the blast-furnace, pyroprocessing, and hydrometallurgical methods.

This procedure appears to be a novel, alternative ARD treatment with promising potential for metal recovery and reduced disposal costs. It is quite difficult to give a proper conclusion about operational costs because the proposed method was only tested at the laboratory scale. An industrial trial is needed to complete process economics.

Recommendations for further investigation include: additional tests to evaluate effective ARD/PHA ratios for highly acidic and contaminated ARDs; optimization of some steps in the process (i.e. liquid to solid separation; dewatering and drying of filter residue/sludge); determination of the mass balance of the process; evaluation of alternative sources or method for thermal treatment, and: trial industrial experiments using the proposed technological scheme with a detailed economical evaluation. As a suggestion, the metal–organic sludge could be directly used (co-processed) with metal concentrate from metal production in a roasting and sintering step (appropriate study is required).

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