Application of a Peat-Humic Agent for AMD Remediation and Element Removal

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Abstract

The given work focused on solving the fundamental problem of environmental geochemistry and material science related to developing a new environmentally safe technology for AMD remediation and extraction of strategically important metals. A new peat-humic agent (PHA) using mechanical, chemical, and thermobaric treatment of peat from the Krugloe deposit (Novosibirsk Region, Russia). The PHA effectively removed potential pollutants (e.g., Zn, Cu, Cd, Pb, Ni, Co, Hg, Al, Fe, etc.) forming metal–organic residues, and neutralized moderately acidic acid mine drainage (AMD). The amount of the PHA to be added depended on the AMD composition. For instance, an AMD/PHA ratio of 500-1000 was effective for the Karabashmed tailings AMD, while an AMD/PHA ratio of 100-500 was effective for the Belovo sludge pond water. The metal concentrations of these treated AMDs met water quality standards. From 1 to 10 L of PHA would be needed to treat 1,000 L of moderately acidic and contaminated AMDs. Moreover, PHA would be a low cost material for contaminant removal considering the production cost and the anticipated price. The PHA can be used to modify kaolinite clay in order to create an organic-mineral complex and to intensify sorption properties of clay. The modified materials (PHA and organic-mineral complex) can be considered for developing an artificial complex organic-mineral barrier in sludge pond base. The PHA can be used to prevent sulfide tailings dusting. A novel, alternative method for AMD remediation and element removal using a PHA with subsequent thermal treatment of the metal–organic residue to minimize waste sludge production was proposed.

Key words: Acid mine drainage, peat-humic agent, AMD remediation, clay and peat modification, element recovery from waste, sulfide tailings dusting

Introduction

The waste products of the ore mining and processing industry 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, and other contaminants (GARD/INAP; Hudson-Edwards et al. 2011; Lottermoser 2007; Nordstrom 2011; Nordstrom and Alpers 1999; Nordstrom et al. 2000; Wolkersdorfer 2008; Younger 2002). AMD can also acidify and pollute soils located near mining areas and in floodplains downstream of them (Blair et al. 1980; Jambor et al. 2003; Lottermoser 2007; Thornton 1996; Williams 1975). The total global cost for remediation of AMD has been estimated at around US$10 (Tremblay and Hogan 2001). Various agents such as limestone, lime, caustic soda, ammonia, clay, activated carbon, zeolite, cellulose, fly ash, peat and waste green sends have been applied for AMD treatment (Bogush et al. 2015; Gaikwad and Gupta 2008; GARD/INAP; Johnson and Hallberg 2005; Skousen and Ziemkiewicz 1995).

In this work, we would like to discuss a potential application of the peat-humic agent as an alternative material for AMD remediation and element removal. Humic substances contained in peat play a significant role in element accumulation (Stevenson 1994; Varshal et al. 1993). Humic substances are complex mixtures of natural, high molecular weight, dark-colored, organic products of chemical-

microbiological synthesis occurring during decomposition of mortal remains of living organisms (Orlov 1990; Perminova et al. 2006; White 2013). They can be found almost everywhere in nature, with the highest content (up to 85%) observed in biogenic rock, such as peat, coals, sapropel and black shales (Perminova 2000 and 2008). Humic substances have an irregular and heterogeneous structure with a high surface area (Kleinhempel 1970). They consists of an aromatic core with numerous functional groups (carboxyls, hydroxyls, carbonyls, and others) and of peripheral aliphatic units composed mostly of polysaccharidic and polypeptidic chains, terpenoids, etc. (Stevenson 1994; Perminova et al. 2006). Therefore, humic substances can bind potential pollutants such as heavy metals, polar and hydrophobic organic compounds (e.g., pesticides and polychlorinated compounds) (Perminova et al. 2006).

Material and Methods

The liquid peat-humic agent (PHA) was developed by chemical (alkaline hydrolysis), mechanical, and thermobaric treatment using hydrodynamic cavitation of peat from the Krugloe deposit (Novosibirsk region, Russia) which contained about 60% of organic substances including humic and fulvic acids (43.5 and 26.8% of the total organic content, respectively).

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 used for AMD treatment experiments.

The following materials were also used in the experimental work: 1) kaolinite clay (Dorogino deposit, Novosibirsk region); 2) peat ("Krugloe" deposit, Kochenevski area, Novosibirsk region); 3) limestone (Chernorechensk deposit, Iskitim area, Novosibirsk region); 4) haydite sand (particle size ≈ 1-3 mm); 5) activated carbon (State Standard 6217-74).
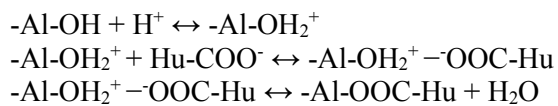
Laboratory researches were carried out in the analytical center of the Institute of geology and mineralogy SB RAS. The combination of field, experimental, mineralogical, physical and chemical research has been applied. Various methods, such as sieve analysis, AAS, ICP-OES, ICP-MS, XRF, IC, FTIR, XRD, STA and SEM/EDS were used for our investigation.

Results and Discussion

Clay Modified by the PHA (organic-mineral complex)

The micro addition of the peat-humic agent was used to modify kaolinite clay in order to create an organic-mineral complex. Element adsorption (Zn, Cd, Pb, and Cu) onto peat, kaolinite clay, PHA, and organic-mineral complex was investigated.

Formation of the organic-mineral complex mainly depends on electrostatic interaction, hydrogen bonding (-OH…H) and interaction between carboxyl group of the PHA ($Hu\text{-}COO^-$) and hydroxyl group of kaolinite (HO-Al-):

$-Al\text{-}OH + H^+ \leftrightarrow -Al\text{-}OH_2^+$
$-Al\text{-}OH_2^+ + Hu\text{-}COO^- \leftrightarrow -Al\text{-}OH_2^+\ {}^-OOC\text{-}Hu$
$-Al\text{-}OH_2^+\ {}^-OOC\text{-}Hu \leftrightarrow -Al\text{-}OOC\text{-}Hu + H_2O$

Ion exchange and cation bridging also play significant role in the organic-mineral complex formation:

$2Hu\text{-}COOH + Me^{2+} \leftrightarrow Hu\text{-}COO\text{-}Me\text{-}OOC\text{-}Hu + 2H^+$

During this process solid particles are getting bigger, easily settling out from solution (fig. 1).

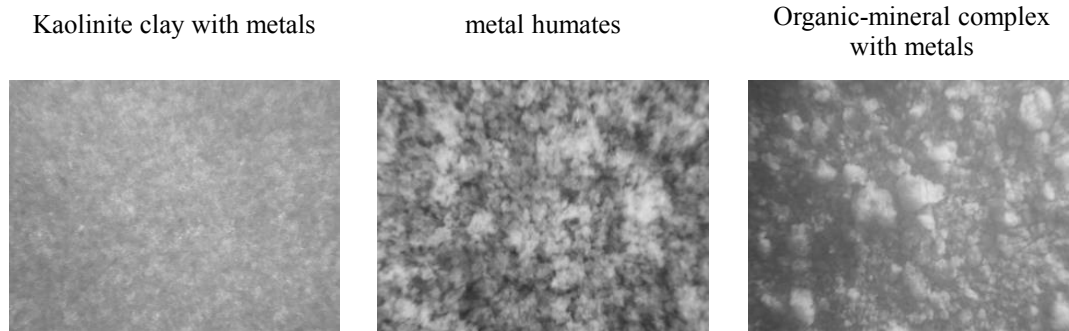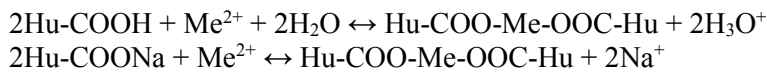Kaolinite clay with metals　　　metal humates　　　Organic-mineral complex with metals

Figure 1 *Light microscopy images of kaolinite clay, PHA, and organic mineral complex with adsorbed metals in solution.*

Binding of potentially toxic elements with the PHA usually goes via the exchange mechanism with formation of poorly soluble humates. Carboxyl groups in the PHA play an extremely important role for element sorption (Bogush et al. 2007; Bogush and Voronin 2011). Humic acid (Hu-COOH) and sodium humate (Hu-COONa) dissociate to form a humate ion, a hydroxonium ion, and a sodium ion. The humate ion reacts with a metal ion and forms a humate complex:

$$2Hu\text{-}COOH + Me^{2+} + 2H_2O \leftrightarrow Hu\text{-}COO\text{-}Me\text{-}OOC\text{-}Hu + 2H_3O^+$$
$$2Hu\text{-}COONa + Me^{2+} \leftrightarrow Hu\text{-}COO\text{-}Me\text{-}OOC\text{-}Hu + 2Na^+$$

Additionally, humic substances are usually strong chelators with stability constants in excess of 10^{10} (White 2013).

The PHA has a highest q_{max} value comparing to other investigated materials (tab. 1). It was shown that peat adsorbed elements better than kaolinite clay. Elements were well adsorbed onto kaolinite clay at pH from 6.5 to 8.5, but onto peat at pH from 4.5 to 6.8. The organic-mineral complex has adsorption capacity in about 2 times higher than natural clay and can adsorb metals in extended interval of pH from 5 to 8.5. Also the element desorption is less than 3% for all investigated elements.

Table 1 *Element adsorption on natural and modified materials.*

aterial	Kaolinite clay	peat	PHA	Organic-mineral complex (kaolinite clay + PHA)
	$q_{max,}$ mg/g			
Zn	14±0.6	39±0.4	155±5	22±0.8
Cd	10±0.7	44±1.1	170±9	17±1.2
Cu	11±0.9	38±0.6	150±6	21±1.1
Pb	23±1.2	109±0.3	390±12	46±3

q_{max} is the amount of sorbate necessary to complete a monolayer

Prevention of Sulfide Tailings Dusting

The big issues concerning with sulfide tailings are prevention of acid mine drainage generation and aeolian transportation of fine tailings particles on surrounding territories (forest, reservoirs, cropland, and local residential lands). We have already known some solutions of this problem, for example, tailings could be covered by break stone, clay or cement. We propose alternative solution that is covering sulfide tailings by peat-humic agent. Sulfide tailings mainly consist of fine particles (less than 0.25 mm), approximately 70-80%.

The unoxidized waste from the gold concentration plant (Ursk, Kemerovo region) and the oxidized waste from the Altay polimetal Ltd. plant (Gornyk, Altay region) were used. Two fine particle size fractions of solid waste (SW) of sulfide tailings (0.16-0.25 mm and <0.16 mm) which gave the greatest contribution to the particle size distribution of investigated wastes (approximately 65-85%), were used for lab experiments. The PHA was added to solid waste at the different liquid to solid ratio (L/S: 1, 0.5, and 0.2). The particle size distribution was determined by sieve analysis.

Table 2 shows particle size distribution after addition of PHA to the fine particle fractions of sulfide wastes. The fraction of >2 mm particles was considerable and formation of aggregates were observed. The percentage of >2 mm particles was higher for oxidized waste because it contained iron oxides/hydroxides which may easily interact with the PHA forming organic-mineral complex.

Table 2 Particle size distribution in the experiment with PHA addition to the fine particle fractions of sulfide tailings.

Particle fraction, mm	> 2	1-2	1-0.25	0.25-0.16	< 0.16
Experiment	Particle size distribution, %				
Ursk SW (<0.16 mm); L/S=1	51.89	5.72	2.21	0.9	39.3
Ursk SW (<0.16 mm); L/S=0.5	50.58	5.89	2.82	1.11	39.6
Ursk SW (<0.16 mm); L/S=0.2	43.83	6.32	4.56	2.18	43.1
Ursk SW (0.25-0.16 mm); L/S=1	36.33	3.89	3.99	55.78	-
Ursk SW (0.25-0.16 mm); L/S=0.5	38.89	3.76	5.32	53.99	-
Ursk SW (0.25-0.16 mm); L/S=0.2	38.22	4.25	10.91	46.62	-
Oxidized waste from Gornyk					
Gornyk SW (<0.16 mm); L/S=1	82.78	3.14	1.86	2.16	12.78
Gornyk SW (<0.16 mm); L/S=0.5	77.71	5.52	3.71	1.1	11.95
Gornyk SW (<0.16 mm); L/S=0.2	56.23	10.56	2.62	1.6	28.98
Gornyk SW (0.25-0.16 mm); L/S=1	71.41	5.15	6.16	17.27	-
Gornyk SW (0.25-0.16 mm); L/S=0.5	42.89	7.11	10.62	39.38	-
Gornyk SW (0.25-0.16 mm); L/S=0.2	48.39	1.91	5.93	43.76	-

These results were confirmed by the field experiment (fig. 2). It was shown that the particle size distribution of tailings material was changed after treatment by the PHA. Fraction of >2 mm particles was increased to approximately 50-80%. The complex geochemical barrier was formed at the top layer of sulfide tailings (pH increase, formation of organic-mineral complex). Thus, a complex geochemical barrier was formed at the top of sulfide tailings (pH increase, formation of organic-mineral complex).
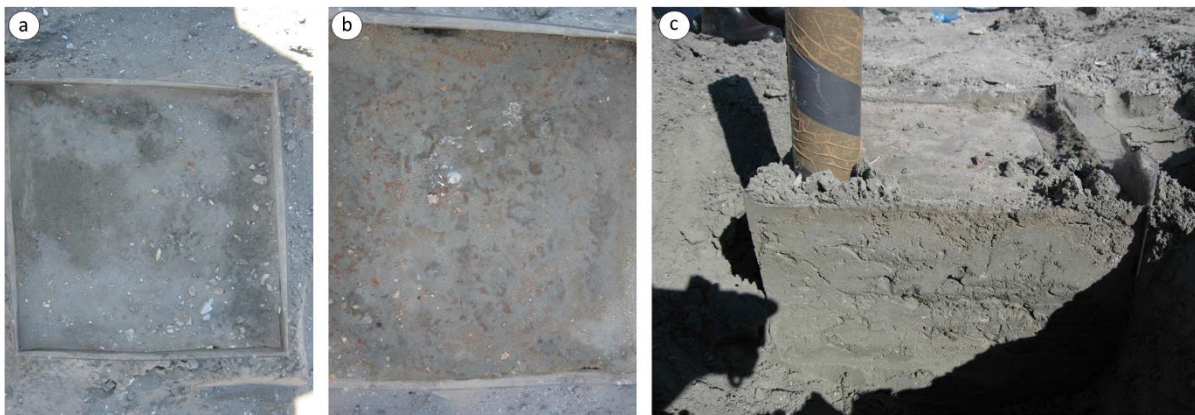

Figure 2 Images of the field experiment on prevention of aeolian transportation: a) blank experiment; b) addition of the PHA with limestone; c) visual changes in top layer after treatment.

AMDs treatment by the PHA

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 treated by the PHA (Bogush and Voronin 2011; Bogush et al. 2015).

The PHA effectively removed potentially toxic elements (Hg, Cd, Pb, Zn, Cu, etc.) and increased the pH of all treated AMDs. Complete neutralization was achieved for the AMDs from the Belovo sludge pond and Karabashmed tailings. The amount of the PHA to be added depended on the AMD composition. For instance, an AMD/PHA ratio of 500–1000 was effective for the Karabashmed

tailings AMD, while an AMD/PHA ratio of 100–500 was effective for the Belovo sludge pond water. The metal concentrations of these treated AMDs met water quality standards. Using tested AMD/PHA ratios, partial acidity and metal removal was obtained after treatment of the highly acidic and contaminated AMDs of the Ursk tailings, the Belovo clinkers, and the old waste deposit (Gornyak). An increased AMD/PHA ratio was required for the more highly acidic and contaminated AMDs (Bogush et al. 2015).

The flaky sediment (metal-organic residue (MOR)) that was formed after AMD treatment by the PHA can be removed by filtration through activated carbon or haydite sand. Activated carbon is best to use after treatment of highly contaminated solutions. However, it is cheaper to use haydite sand, especially for slightly acidic drainage (Bogush and Voronin 2011).

Element Removal from AMD Using the PHA with Subsequent Thermal Treatment of the Metal–Organic Residue

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.

The metal-concentrate residues generally contained aggregates with different size range (20–350 lm). 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 or as a raw material in cement clinker production, was detected as a main phase in the residue after thermal treatment of the PHA-Ursk AMD precipitate. Tenorite (CuO) was detected as a main phase in the residue after thermal treatment of the PHA-Belovo AMD precipitate. 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).The metal-concentrate residues can be used for metal production by the blast-furnace, pyroprocessing, and hydrometallurgical methods (Bogush et al. 2015).

A novel, alternative method for AMD remediation and element extraction using the PHA with subsequent thermal treatment of the MOR (fig. 3) to minimize waste sludge production was proposed (patent RU N2011139274; Bogush et al. 2015).
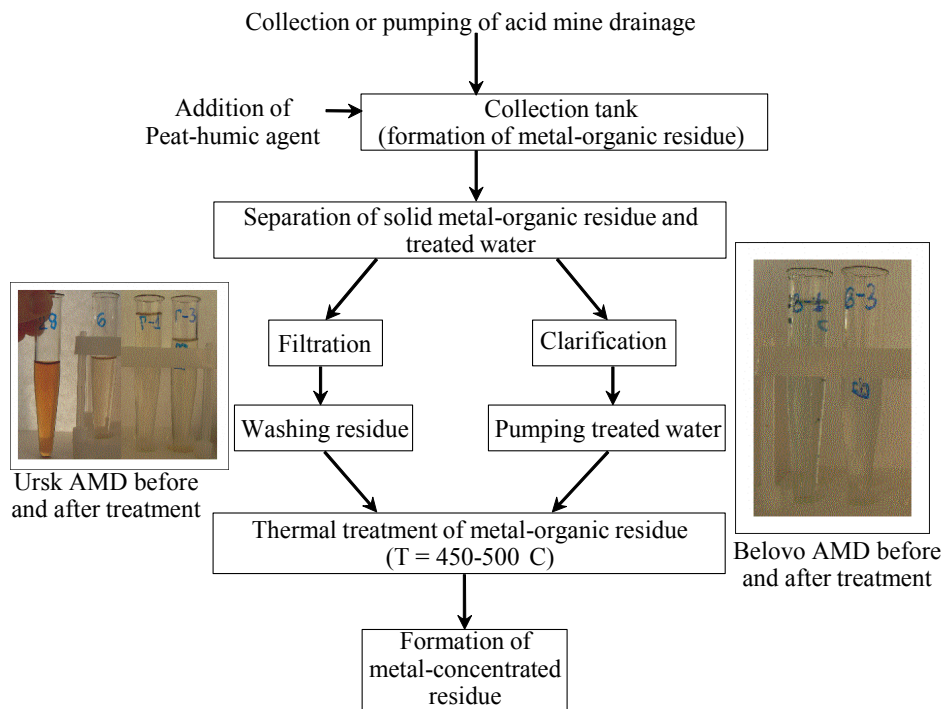

Figure 3 *The schematic technological process for metal extraction from AMD using the PHA with subsequent thermal treatment (modified from Bogush et al. 2015).*

Conclusions

Potential application of the new peat-humic agent as an alternative material for AMD remediation and element removal was discussed in this work. The PHA effectively removed potential pollutants from AMD and neutralized moderately acidic acid mine drainage. The amount of the PHA to be added depended on the AMD composition. The PHA would be a low cost material for contaminant removal. On average, 1.7 L of the PHA can be produced from 1 kg of this peat. The production and transportation cost of 1 m3 of peat in Russia is about $ 10 (US). On average, 1.7 L of PHA can be produced from 1 kg of peat, and up to 1,000 L/h can be produced in a single reactor. At this rate, the production cost of 1 L of PHA is about $ 0.5, and so the sale price would be about $1. Two litres of PHA would be needed to treat 1,000 L of slightly acidic mine drainage (Bogush and Voronin 2011).

The PHA can be used to modify kaolinite clay in order to create an organic-mineral complex and to intensify sorption properties of clay. The organic-mineral complex has adsorption capacity in about 2 times higher than natural clay and can adsorb metals in extended interval of pH from 5 to 8.5. The modified materials (PHA and organic-mineral complex) can be considered for developing an artificial complex organic-mineral barrier in sludge pond base. This barrier can consist of natural (clay, limestone, peat) and modified materials (PHA and organic-mineral complex) which may considerably reduce penetration of drainage solution into bottom layers and ground water, neutralize AMD and concentrate potentially toxic elements.

The PHA can be used to prevent effectively sulfide tailings dusting. The particle size distribution of tailings material was changed after treatment by the PHA. Fraction of >2 mm particles was increased to approximately 50-80%. The complex geochemical barrier was formed at the top layer of sulfide tailings.

A novel, alternative method for AMD remediation and element removal using a PHA with subsequent thermal treatment of the MOR was proposed. This new method can solve two problems: 1) effective treatment of AMD from potential pollutants and production of treated water which can be used in mining industry; 2) extraction of strategically important metals (Cu, Zn, Pb, Ni, Co, Ag, Au, etc.) from AMD.

Acknowledgements

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