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Utilization of Sorbents for Heavy Metals Removal from Acid Mine Drainage

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The elimination of the consequences of mining activities belongs to the most serious environmental problems nowadays. Abandoned sulphide ore mines are serious source of acid mine drainage (AMD) enriched with SO_4^{2-}, Fe, Cu and other heavy metals, which contaminate surface water, sediments and soils. Smolnik deposit is a typical example of AMD source. This AMD with pH 3-4 contains high metal concentrations that vary in dependence on rainfall intensity (e.g. Fe 500-400 mg/L; Cu 3-1 mg/L; Zn 13-5 mg/L and Al 110-70 mg/L).
The main aim of this paper is to compare and to interpret some physical-chemical methods for the heavy metals removal from AMD out-flowing from the shaft Pech of the deposit Smolnik (Slovakia). For the study of metal recovery from AMD was used adsorption. The study shows the possibility of Cu, Fe, Al, Mn and Zn recovery from AMD.

1. Introduction

More than a century of mining has left many areas around the world filled with highly-toxic materials and known carcinogens. The issue is so widespread across the globe, and has been going on for so long, that the exact extent of the contamination is unknown and a complete list of affected sites remains unavailable. Studies of various geographic locations and anecdotal evidence, however, provide a robust understanding of the contamination and public health problem. The abandoned mine Smolnik is regarded as an environmental load in the Central Europe region, where AMD is generated and discharged from abandoned mine and contaminates the Smolnik creek catchment.
AMD is formed when sulphide minerals in rock are exposed to oxidizing conditions in coal and metal mining. There are many types of sulfide minerals, but iron sulphides common in coal regions, such as pyrite and marcasite, are the predominant AMD producers. Upon exposure to water and oxygen, pyretic minerals oxidize to form acidic, iron and sulfate–rich drainage. In general, sulphide-rich and carbonate-poor materials are expected to produce acidic drainage. In contrast, alkaline-rich materials, even with significant sulphide concentrations, often produce alkaline conditions in water

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(Kleinmann, 1990). The genesis of AMD is conditioned by the existence of autochthonous chemolithotrophic iron and sulphur oxidising bacteria of Acidithiobacillus genus. During exploitation, but mainly after the closure of mine, sulphide mineral deposits may become potential “natural biogeoreactors” producing AMD and functioning on the principle of biogenous catalysis of chemical oxidation of both primary and secondary sulphide minerals by the above-mentioned species of bacteria that live in symbiosis with other species of aerobic and anaerobic bacteria (Kušnierová and Fečko, 2001; Johnson, 1998; Harbuľáková et al., 2009). Due to this sulphide-weathering process, the water-insoluble sulphide is transformed into water-soluble sulphate.

In the Slovak Republic there are some localities with existing AMD generation conditions. The most critical values were observed in the abandoned deposit Smolnik. The stratiform deposit Smolnik belongs to the historically best-known and richest Cu – Fe ore deposits in Slovakia. In 1990 the mining activity in this locality was stopped. The mine was flooded till 1994. In 1994 an ecological collapse occurred, which caused the fish-kill and the global negative impact on the environment. The mine-system represents partly opened geochemical system into which rain and surface water drain. The continuation of AMD generation in the locality of Smolnik is not possible to stop and there is no chance for situation self-improvement (Šlesárová et al., 2008; Luptáková and Kušnierová, 2005; Luptáková et al., 2008; Špaldon et al., 2006).

There are various physical-chemical methods of such polluted water treatment e.g. neutralisation, ion exchange, precipitation, sorption, membrane processes, filtration. The choice of the suitable methods is based not only on concentration of heavy metals in surface water but on economical factors, too. Sorption belongs to effective and economically acceptable methods for heavy metals removal. Deorkar and Tavlarides (1998) developed an adsorption process of inorganic chemically active adsorbents (ICAAs) to selectively recover Fe^{3+}, Cu^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+} from AMD solutions without neutralization. More than 75% of copper was removed from solutions by active carbon and biosorbents prepared from mosses, the highest sorption capacity have active carbon (Garcia and Alvarey, 1990; Riveros, 2004; Deorkar et al., 2005). Among the most often tested sorbents of heavy metals belong: zeolite, carbonate, clays, turf, oxide and hydroxide of iron (Xinchao et al., 2005; Kumar et al., 2007) as well as unconventional materials like spent tea leaves (Lavecchia et al., 2010).

The paper deals with the utilization of five types of sorbents for Fe, Cu, Al, Mn and Zn removal from AMD (shaft Pech, locality Smolnik, Slovakia). The study was aimed on the sorption of metals from real AMD with pH 4.2, because pH plays a very important role in the sorption/removal of the contaminants. The novelty of proposed work lies in the study of using of natural and synthetic sorbents (produced in Slovak Republic) in acidic environment.

2. Material and methods

For study of Fe, Cu, Al, Mn and Zn cations removal from AMD by adsorption, Inorganic composite sorbent SLOVAKITE (IPRES inžiniering s.r.o.), Active carbon (granularity ≤ 1 mm), Turf brush PEATSORB, Universal crushed sorbent ECO-DRY

(REO AMOS Slovakia) and Zeolite (granularity 0.5 - 1 mm, 2.5 - 5 mm, 4 - 8 mm) (Zeocem, a.s., Bystré, Slovakia) were used. The experiments were carried out using untreated AMD with pH 4.2. Concentrations of dissolved ions are presented in Table 1.

Table 1: Chemical composition of AMD

Raw AMD	Fe	Cu	Al	Mn	Zn
mg/L	338	1.16	44.4	26	5.81

The ion removal efficiency by sorptive materials was tested at laboratory temperature under static conditions. 5 g, 3 g and 1 g of sorbents: inorganic composite sorbent SLOVAKITE, active carbon and turf brush PEATSORB, and 5 g of sorbents: universal crushed sorbent ECO-DRY, and zeolites with granularity 0.5 - 1 mm, 2,5 - 5 mm, 4 - 8 mm, were mixed with 100 mL of raw AMD for 24h, then they were filtrated. In filtrates were determined pH (pHmeter METTLER TOLEDO) and concentrations of Fe, Cu, Al Mn and Zn by colorimeter DR 890 (HACH LANGE).

3. Experimental results

The efficiency of sorbents on Fe, Cu, Al, Mn and Zn removal from AMD are presented in Figures 1-5.

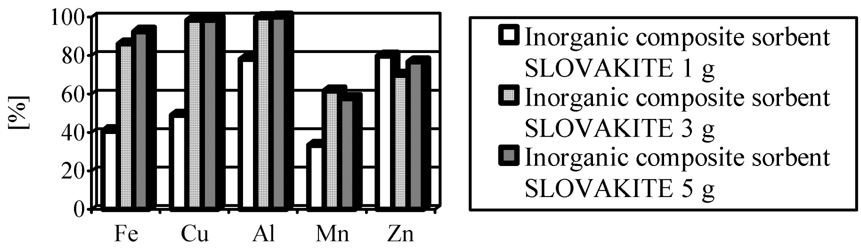

Figure 1: The efficiency of Inorganic composite sorbent SLOVAKITE on Fe, Cu, Al, Mn and Zn removal from AMD

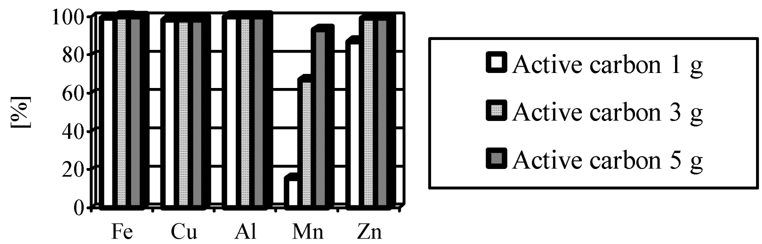

Figure 2: The efficiency of Active carbon on Fe, Cu, Al, Mn and Zn removal from AMD

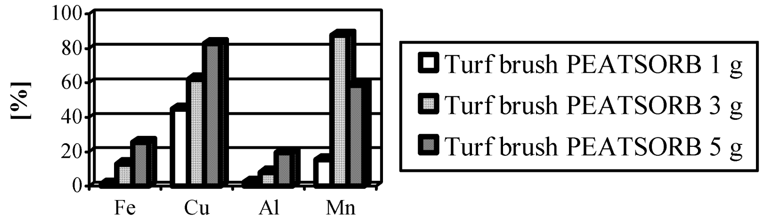

Figure 3: The efficiency of Turf brush PEATSORB on Fe, Cu, Al, Mn and Zn removal from AMD

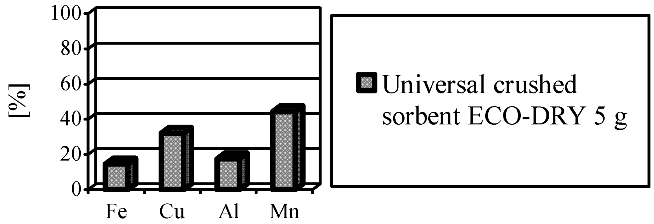

Figure 4: The efficiency of Universal crushed sorbent ECO-DRY on Fe, Cu, Al, and Mn removal from AMD

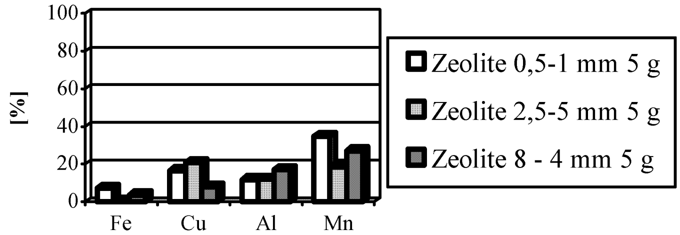

Figure 5: The efficiency of Zeolite on Fe, Cu, Al, and Mn removal from AMD

The results of the pH measurements in filtrates are presented in Table 2. The solubility of Fe, Al, Cu and Zn in raw AMD is a function of pH. Iron (III) is precipitated at pH about 4, Cu at pH > 4, Zn at pH 5.5 - 7.0 and most of the aluminium is precipitated when pH is above 5. However, aluminium resolubilized at pH above 10 (Xinchao et al., 2005). As resulted from Table 2, the decrease of metal cations concentration cannot be assigned exclusively to the sorption efficiency of active carbon and Slovakite because of the precipitation of studied cations if pH > 4.

Table 2: Results of pH in AMD and filtrates after sorption

	pH
AMD	4.2
Inorganic composite sorbent SLOVAKITE 1g	4.52
Inorganic composite sorbent SLOVAKITE 3g	5.86
Inorganic composite sorbent SLOVAKITE 5g	5.73
Active carbon 1g	4.85
Active carbon 3g	5.72
Active carbon 5g	6.97
Turf brush PEATSORB 1g	3.21
Turf brush PEATSORB 3g	2.92
Turf brush PEATSORB 5g	2.92
Universal crushed sorbent ECO-DRY 5g	4.18
Zeolite 8 - 4 mm 5g	4.42
Zeolite 2.5 - 5 mm 5g	4.2
Zeolite 0.5 - 1 mm 5g	4.15

4. Conclusion

This study showed the possibility of the natural and synthetic adsorbents utilization for Cu, Fe, Al, Mn and Zn removal from AMD. Active carbon was the most efficient for Fe removal – decrease of Fe concentration in AMD is about 99.98 %. Decrease of Cu concentration in AMD using Active carbon and Inorganic composite sorbent SLOVAKITE was, in both cases, 98.3 %. For the removal of Al were the most efficient Active carbon and Inorganic composite sorbent SLOVAKITE (about 99.98 %). For the Mn is the most effective adsorbent Active carbon (93.08%) and Turf brush PEATSORB (87.69 %). Sorption of the studied metal cations is ambiguous because of the increase of pH in filtrates above to 4. These results will be used for study of the sorption capacity and the sorption kinetics of the most efficient sorbents with the aim of their using for acid mine drainage treatment.

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References

Deorkar N.V. and Tavlarides L.L., 1998, Adsorption processes for metal recovery from acid mine waste. The Berkley pit problem. Environ. Prog., 17, 2, 120-125.

Garcia S.A. and Alvarey A.E., 1999, Sorption of heavy metals from industrial waste water by low-cost mineral silicates. Clay minerals, 34, 3, 469-47.

Harbuľáková V., Eštoková A., Števulová N., Luptáková A. and Janák G., 2009, Acid mine drainage as the factor of microbial involved corrosion of concrete samples.

SGEM 2009: Modern management of mine producing, geology and environmental protection: 9th International Multidisciplinary Scientific Geoconference, Bulgaria, Albena Resort: Conference proceeding. Sofia: Bulgarian Academy of Sciences, 439-446.

Johnson B.D., 1998, Biodiversity and ecology of acidophilic microorganisms. FEMS Microbiol. Ecol. 27, 307-317.

Kleinmann R.L.P., 1990, Acid mine drainage in the United States. Proceedings, First Midwestern Region Reclamation Conference, Southern Illinois University, Carbondale, Illinois, USA, 1-8.

Kumar D., Sambi S.S., Sharma S.K. and Kumar V., 2007, Removal of Nickel ions from Aqueous Solutions on Packed bed of Zeolite NaX, Chemical Engineering Transactions, 11, 191-197.

Kušnierová M. and Fečko P., 2001, Mineral biotechnologies in mining and treatment of sulphidic deposits. Ostrava: VSB - Technical University, Ostrava, Czech Republic, 143 (in Slovak).

Lavecchia R., Pugliese A. and Zuorro A., 2010, Removal of lead from aqueous solutions by spent tea leaves, Chemical Engineering Transactions, 19, 73-78.

Luptáková A. and Kušnierová M., 2005, Bioremediation of Acid Mine Drainage by SRB. In: Hydrometallurgy, 77, 97 – 102.

Luptáková A., Mačingová E. and Apiariová K., 2008, The Selective Precipitation of Metals by Bacterially Produced Hydrogen Sulphide. Acta Metallurgica Slovaca, Special issue 1/2008, 149-154.

Riveros P.A., 2004, The extraction of Fe (III) using cation Exchange carboxylic resins. Hydrometallurgy, 72, 3-4, 279-290.

Šlesárová A., Zeman J. and Kušnierová M., 2007, Geochemical characteristics of acid mine drainage at the Smolník deposit (Slovakia). IMWA Symposium 2007: Water in Mining Environments, R. Cidu and F. Frau (Eds), Cagliari, Italy, 467-371.

Špaldon, T., Brehuv, J., Bobro, M., Hančuľák J., and Šestinová, O., 2006, Mining development the Spiš-Gemer ore-location. Acta Montanistica Slovaca, 11, 375-379 (in Slovak).

Xinchao W., Roger C., Viadero J. and Karen M., 2005, Recovery of iron and aluminium from acid mine drainage by selective precipitation. Environ. Eng. Sci., 22, 6, 745-755.