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Foreword

PÔVODNÉ ČLÁNKY – ORIGINAL PAPERS

COVER: Waste represents the ore of the 21th century. Compilation of photographs from the Internet.

OBÁLKA: Odpady predstavujú suroviny 21. storočia. Kompilácia fototografií z internetu.

Foreword

The presented issue of the geoscientific journal Mineralia Slovaca is atypical by its content. While the journal in its standard scope presents the information about the new findings in the geological setting of the Slovak territory, about natural raw material and its use, or the environmental topics, the submitted issue reminds that due to the time restriction of the raw material exploitation, the exhaustibility of reserves and the environmental risks of the exploitation and dressing, the recent modern society must pay much greater attention on the recovery of useful components from the already manufactured and used products, i.e. from the recent waste. The waste recycling is therefore necessary to be considered as an important task of the highly developed society of the 21st century and the waste obtains the importance of the source of the secondary raw material.

The presented review of the research trends in the raw material recycling and the recent obtained positive results encompasses the availability of the repeated obtaining of several useful elements (Cu, Zn, Ni, Ag, a.o.) and compounds (e.g. $MgCO_3$*) from the polluted water, settling pits, by the land reclamation in the industrial areas, or the processing of alkaline and Ni-Cd batteries. Several papers point to the toxicity and health risks accompanied with the presence of elements As, Sb, Cd, Pb, or the Ag nanoparticles in the living environment, and the inevitability of solving this problem. The journal presents various methodologies of the pollutants removing, including the environmentally friendly biological methods – biosorption, biological leaching, or bacterial reduction. The waste recycling by this way becomes, besides the secondary raw material source, also a task of the high environmental priority.*

Predkladané číslo geovedného časopisu Mineralia Slovaca je svojím obsahom netypické. Kým štandardne časopis poskytuje informácie o nových zisteniach v problematike geologickej stavby územia Slovenska, o nerastných surovinách a ich využívaní, či o problematike environmentálnej, predkladané číslo upozorňuje, že pre časové obmedzenie získavania nerastných surovín z prírodného prostredia, z dôvodu vyčerpateľnosti zásob a environmentálnych rizík ťažby a úpravníctva, musí byť v súčasnej modernej spoločnosti kladený podstatne väčší dôraz na znovuzískavanie úžitkových zložiek z už vyrobených a upotrebených produktov, t. j. zo súčasných odpadov. Preto je potrebné za dôležitú úlohu vyspelej spoločnosti 21. storočia považovať recykláciu odpadov, ktoré sa dostávajú do pozície zdroja druhotných surovín.

V prehľade o trendoch výskumu v problematike recyklácie surovín a doterajších, v mnohých smeroch pozitívnych, výsledkoch referujeme na stránkach predkladaného čísla časopisu o možnosti opätovného získavania viacerých kovov (Cu, Zn, Ni, Ag a ďalších) a úžitkových minerálov (napr. $MgCO_3$*) zo znečistených vôd, odkalísk, rekultiváciou pôdy z priemyselných oblastí či spracovaním alkalických a Ni-Cd batérií. Viacero príspevkov poukazuje na toxicitu a zdravotné riziká spojené s prítomnosťou As, Sb, Cd, Pb či nanočastíc Ag v životnom prostredí, a na ekologickú naliehavosť riešenia tohto problému. V predkladanom čísle časopisu prezentujeme rôzne metodiky odstraňovania polutantov vrátane ekologicky šetrných biologických metód – biosorpcie, biologického lúhovania či bakteriálnej redukcie. Recyklácia odpadov sa takto stáva popri zdroji surovín aj prioritnou environmentálnou úlohou.*

Zoltán Németh
Scientific editor

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Toxicity of arsenic and antimony in the area of Cu-Ag deposit Ľubietová

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Abstract

In the surroundings of the Ľubietová deposit the As and Sb contamination of the landscape components, i.e. sediments (both technogenous sediments and soils) and as well groundwater and surface water was described. As(V) and Sb(V) species are predominant species in the sediments while in the water As(III) and Sb(III) are dominant. The utilization of Eh-pH stability diagrams is complemented by the classic determination of As and Sb species by means of HG AAS method.

The presence of very toxic As(III) and Sb(III) species encourages the increased aspect during the estimation of the environmental risk within the studied area.

Key words: arsenic, antimony, speciation, toxicity, technogenous sediments, groundwater, surface water

Introduction

The decrease of pH and changes of oxidation–reduction potential (Eh) in sediments of the dump fields at the Ľubietová Cu-Ag deposit induces the release of toxic metal elements (mainly Cu, Fe, Cd, As, Sb, Pb, Zn, Mn, Ni, Co) from the solid phase where they are presented in the form of the less soluble minerals or in sorption complex into the groundwater and surface water. Concernig the environmental risk, toxic metals As and Sb represent the highest risk at the studied locality (according to Andráš et al., 2008).

Arsenic belongs among nerve poisons with cumulative character (Pitter, 1990). Elementary As^0 is insoluble in the water and is not considered as toxic. In a matter of fact, after its consummation its transition to various toxic compounds occurs. Arsenic begins to be toxic (arsenious oxide – As_2O_3) in the dose above 10 mg (1 to 2 mg per 1 kg of weight). Average fatal dose is 180 mg for grown-up man. Generally, 99 % of As is imported into the human organism by the water and food consummation. The as compounds have mutagenic, cancerous and teratogenic effects. Arsenic penetrates through the placenta into the breast milk. It binds on erythrocytes, deposits in the liver, kidney, skin, hair, nails, and cerebrum. It acts as capillary and cytostatic poison (Kafka and Punčochářová, 2002). It inhibits or blocks SH-group in enzymes by biochemical effect on human organism. It causes change of their effects, disconnects oxidation phosphorylations running in mitochondria whereby causing the destruction of respiration function of tissues. Arsenic replaces very often phosphorus and inhibits corresponding enzymes. It has an impact on capillary epithelium, causes destruction of blood vessels and increases their fragility. It accumulates in liver, bones, nails and hairs where it is mainly bound to S-S bridging of keratin (Benbrahim-Talla and Waalkes, 2008).

As toxicity increases in the order: organic compounds As(V) – arsenate, inorganic compounds containing As(V), organic compounds As(III) – arsenate, inorganic compounds As(III) – arsan. As(III) compounds are about 5 or 10 times more toxic than As(V) compounds (Lin and Puls, 2000) but As(V) has stronger cancerous effects. As(III) and As(V) can create methyl compounds (mono – di – trimethylarsenic) whereby causing the transition to less toxic forms (Matschullat, 2000). Majority of mammals methyl inorganic arsenic to dimethylarsenic acid. This substance is causing organ-specified toxicity and is promoting the formation of tumors in many organs (Benbrahim-Talla and Waalkes, 2008).

Acute poisoning by As is evident as gastro-intestinal disease accompanied by vomiting and diarrhea. As(III) inorganic compounds cause cancer of prostate, skin, blood vessels and kidney (Benbrahim-Talla and Waalkes, 2008). Chronic poisoning causes neurological difficulties, faint paralysis of hands and legs whereas gastro-intestinal symptoms are weaker. There can be observed formation of stains on the skin, decrease of potency, salivation, weight loss, central damage of visual and acoustic analyzer, painful peripheral polyneuritis, anemia, damage of bone

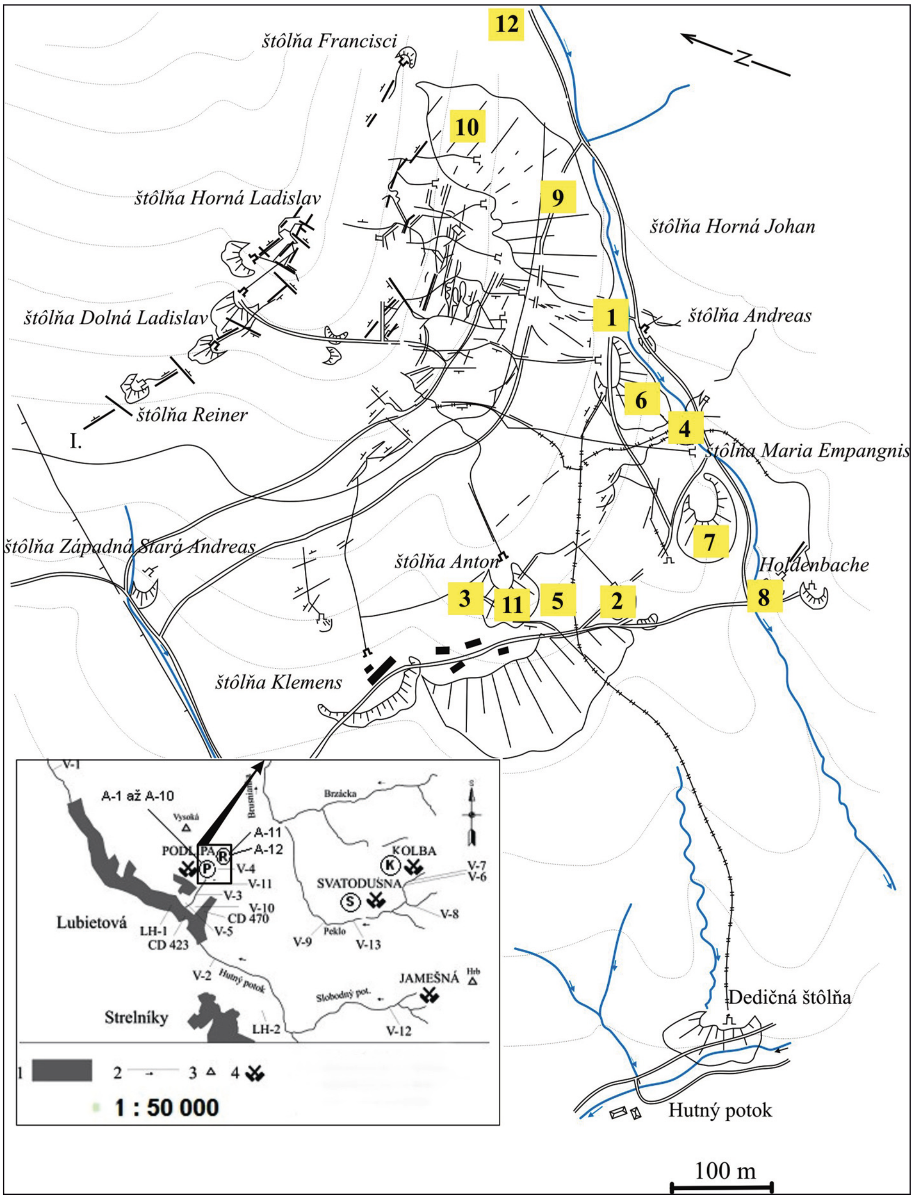


Fig. 1. Localization of the sampling points. a – samples of technogenous sediments; b – water samples.

marrow and spleen and neurological and hematological changes (Melicherčík and Melicherčíková, 1997). The most serious chronic effect is cancer of skin and lungs. Poisoning by As can be identified by horny skin with characteristical glaucous chromatosis, white stripes on nails and garlic--smelling breath (Kafka and Punčochářová, 2002).

In the fields treated by pesticides, arsenic is built into the soil and causes drop in productivity of arable crops and damage of trees (Kafka and Punčochářová, 2002).

The main source of As at the locality of Ľubietová is tetrahedrite, less important and more rare is arsenopyrite. During weathering, arsenic ore minerals are easy oxidized and As is transformed from forms with lower oxidation number to As(V) creating compounds of arsenic acid (Lin and Puls, 2000). It is soluble in the water but rarely can migrate to greater distances due to the fast reaction with metal cations and As and is bounded in the form of various arsenates.

Antimony compounds are less toxic than arsenic compounds. It is similar to arsenic with its impacts but poisoning by antimony is easier due to slower adsorption of its compounds. Soluble compounds in digestive tract hydrolyze, insoluble are less toxic. The most toxic compound of Sb is antimony potassium tartrate which is equally toxic as arsenious oxide and has similar disease effects.

Antimony causes temporary state reminding heart--attack. It inhibits some enzymes, influences metabolism of proteins and sugars, prevents the formation of glycogen in liver, and raises hypoglycemic states (Cejpek, 2000). Acute poisoning is evident as irritation of digestive tract, capillary dilatation, bloody diarrhea, persistent vomiting causing dehydration. There is observed the blood pressure drop causing collapse. There can be also observed bronchial spasma and persistent cough. Blood sugar level is decreasing and acute poisoning can be followed by symptoms of the liver damage.

During the long-term exposition the formation of stains on the skin on uncovered parts of the body can be observed as well as the degenerative changes on nails, formation of abscesses on nose septum, early loss teeth, chronic bagassosis, dyspepsia, vertigo, weight loss, cardiac-vessel diseases, failure of menstruation cycle and a retardation of the children´s growth up to 1 year. Sb can enter into the human organism by inhalation or by direct skin contact. Toxic dose is 150 mg (Marhold, 1980).

Elementary Sb is more toxic than its salts. Sb(III) compounds are 10 times more toxic than Sb(V) compounds (Smichowskia, 2008) and methyl forms of Sb are less toxic than its inorganic salts. Sb(III) is markedly carcinogenic. Antimony in waters is usually presented as Sb(III), Sb(V), $CH_3SbO(OH)_2$ and $(CH_3)_2Sb(OH)$.

Antimony is presented in nature mainly in the form of sulphides or oxides of Sb(III) and Sb(V), most frequently as antimonious oxide Sb_2O_3, antimonic sulphide Sb_2S_5 and antimony chloride $SbCl_3$ (Bencko et al., 1995). Oxidation mechanism of Sb(III) to Sb(V) is controlled by pH. This process is slower than by oxidation of many other metals (for instance Mn, Fe, etc.). Sb(III) can be stabilized by the formation of complex compounds (Leus and Johnson, 2005). It can bind very strongly on particles containing Fe, Mn or Al in the soils. From soils it gets into the food web (Smichowskia, 2008).

Knowledge on various levels of toxic effects and on quality of different impacts of individual compounds of toxic metals on living organisms led to the efforts to specify the forms of toxic metals. From the point of environment, As and Sb present serious danger due to highly toxic character of their compounds.

Methodology

For characterization of contamination of the landscape components there were collected samples of technogenous sediments (dump material, Fig. 1) and samples of the groundwater and surface water (water from wells, mine water and mineral water from the Linhart Spring). Reference site A-12 (Fig. 1) is situated outside of geochemical anomalies of heavy metals to represent similar rock environment (Permian greywacke) as on dump field. It enables the comparison with territories polluted with toxic metals due to the mine activities.

pH of sediments was determined in the water and 1 M KCL leachate according to guidelines described by Lintnerová and Majerčík (2005). Samples of the groundwater and surface water were collected 3 times: in December (drought period), on 31 March 2008 (rain period) and on 27 May 2008 (drought period).

Samples of technogenous sediments were analyzed in the ACME Analytical Laboratories in Vancouver (Canada) by the ICP/MS analysis. Fe content was in the water samples determined by AAS and As and Sb contents by means of hydride method (HG AAS) at the Water Research Institute in Bratislava. Determination of As speciation in the water was realized by the connection of hydride generator Labtech HG-2 and electrothermic automizer Perkin-Elmer HGA-500 with the aim to overconcentrate arsenic volatile compounds on modified surface of graphite cuvette (analysed by Ing. Adriana Shearman, CSc.).

Results

As and Sb distribution in the landscape components in the surroundings of the Ľubietová deposit

Distribution of toxic metals on the dump field is unequal and reflects their primary concentration in individual parts of dump field and geochemical relations of which migration capabilities are very important (Andráš et al., 2009).

Maximum concentrations of theoretical extractable As (7 – 289 ppm) and Sb (7.1 – 61.6 ppm) can be considered as relatively high (Tab. 1).

It is possible to divide samples of the groundwater (Tab. 2) into 2 classes: a) crude waters, b) drinking waters. It is possible to assign samples T-1, LH-8 and LH-9 to crude waters and water samples from the wells of the houses No. 423 and No. 470 (under the dump field Podlipa) to drinking waters where as well sample LH-1 of the mineral water from the Linhart Spring belongs. First group of samples was compared with the Regulation of the Ministry of Environment of the Slovak Republic No. 636/2004 Coll. – The public water-supply systems – where individual categories of standard methods of crude water treatment to drinking water are established. Second group of samples was compared with the Resolution of the Government of the Slovak Republic No. 354/2006 Coll., establishing requirements on water intended for human consumption (drinking water) and on monitoring of drinking water.

Crude water: Except As content in the samples LH-8 and LH-9 (limit value established by the Regulation No. 636/2004 Coll. is < 0.05 mg · l^{-1}) all samples were in accordance with requirements of the Regulation No. 636/2004 Coll.

Drinking water: Water samples from the wells of the houses No. 423 and No. 470 did not exceed limit values for indicators of heavy metals established by the Resolution

Tab. 1
pH and Eh values, Fe, As and Sb content in technogenous sediments from the Reiner and Podlipa dump fields

Sample	H_2O		1M KCl		%	mg · kg^{-1} (ppm)	
	pH	Eh (mV)	pH	Eh (mV)	Fe	As	Sb
A-1	5.14	77	4.61	109	1.31	162	62
A-2	5.89	34	5.40	63	1.42	10	7
A-3	4.87	94	4.21	131	1.94	71	22
A-4	5.46	59	5.33	66	2.64	169	59
A-5	5.77	42	5.37	64	1.71	60	17
A-6	5.17	74	5.06	83	2.06	134	49
A-7	7.93	–84	7.34	–58	1.32	16	12
A-8	5.42	36	5.22	42	0.91	61	18
A-9	5.03	83	5.01	85	1.84	130	28
A-10	5.25	71	5.14	78	1.12	32	17
A-11	6.11	22	5.95	30	2.37	206	36
A-12	4.21	133	3.47	173	1.38	7	10

Tab. 2
ICP-MS analyses of groundwater

Sample	pH	Eh (mV)	μg · l^{-1}		
			Fe	As	Sb
T-1	6.55	–4	11	< 1	< 1
T-1c	6.63	–10	17	< 1	< 1
LH-8	6.40	+1	200	58	< 1
LH-9	6.95	–27	120	61	< 1
ČD 423	6.72	–14	366	< 1	< 1
ČD 423c	6.71	–14	210	< 1	< 1
ČD 470	6.85	–21	146	5	1.42
ČD 470c	6.84	–20	120	1.52	1.21
LH-1a	6.40	+4	380		< 1
LH-1	6.51	–3	381		< 1
LH-1b	6.48	–2	2 260	2.52	< 1

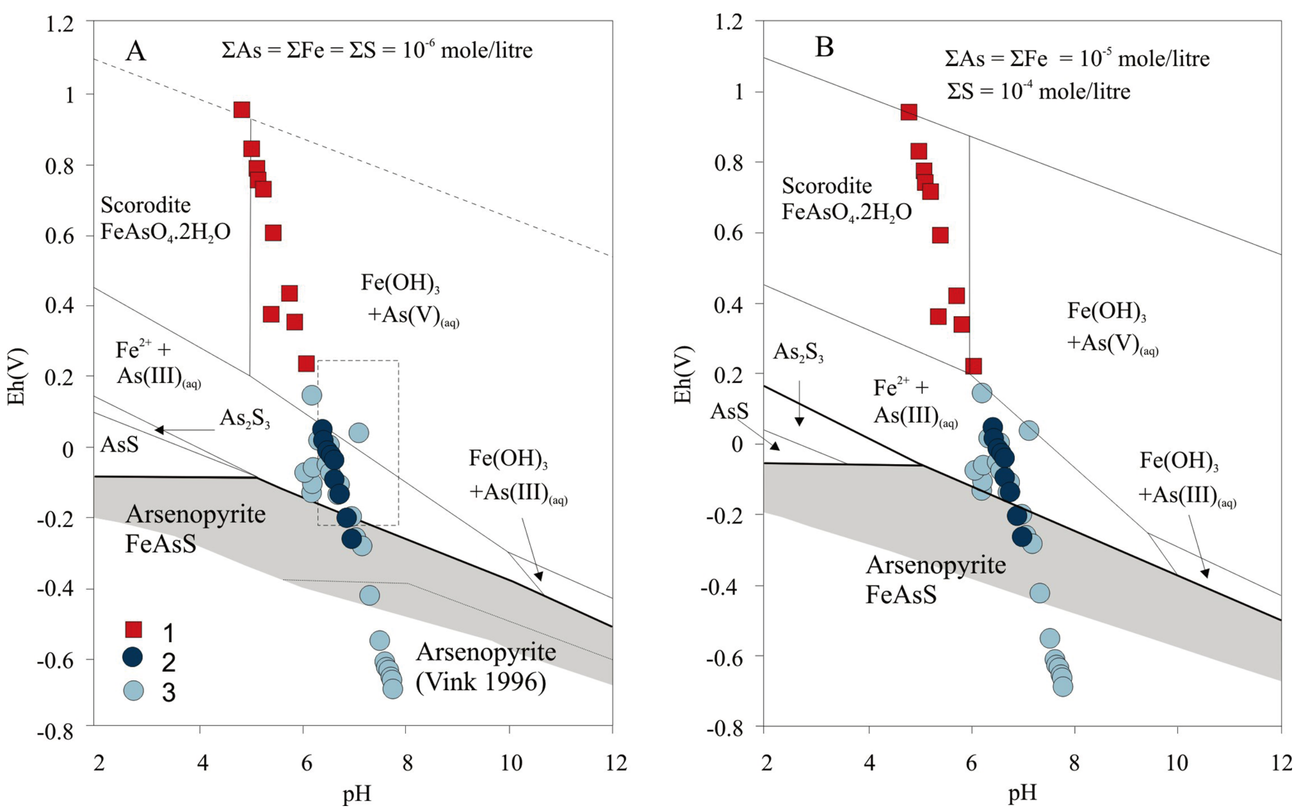
Explanatory notes to tables 2 and 3:
Sampling: a) December 2007, b) March 31, 2008, c) May 27, 2008

No. 354/2006 Coll., only water sample from the well of the house No. 470 exceeded limit values for Zn (3 mg · l^{-1}) and has high content of Cu (41.1 mg · l^{-1}, limit value is 30 mg · l^{-1}). The most polluted was the water sample from the mineral spring Linhart. It exceeded limit values for Mn (55 μg · l^{-1}, limit value is 0.05 mg · l^{-1}) and Cd (6 μg · l^{-1}, limit value is 0.003 mg · l^{-1}).

Surface water (including drainage water) had generally moderately acid character at the Podlipa Locality (pH 6.1

Tab. 3
ICP-MS analyses of surface water

Sample	pH	Eh (mV)	μg · l^{-1}		
			Fe	Sb	As
V-1a	7.7	–69	390	2.10	7.05
V-1c	7.7	–66	215	< 1.00	< 1.00
V-2a	7.6	–62	270	2.00	6.02
V-3a	6.7	–12	86	1.12	< 1.00
V-3b	6.2	14	101	1.88	3.41
V-3c	6.5	0	45	2.35	1.14
V-4a	6.5	–6	26	0.74	< 1.0
V-4b	7.5	–58	73	< 1.00	< 1.0
V-4c	6.54	–8	94	1.03	< 1.0
V-5*	6.2	–7	160	2.00	1.08
V-5a	6.2	–11	170	1.66	2.79
V5b	6.1	–8	210	2.21	3.21
V-6a	6.4	1	200	3.38	58.5
V-6d	7.1	3	57	3.25	37.9
V-7a	7.0	–27	120	3.44	61.5
V-7b	7.1	–29	8	4.38	38.5
V-8a	7.7	–66	540	1.13	5.03
V-8b	7.3	–43	466	1.20	38.5
V-9a	7.6	–64	260	5.10	52.0
V-9a	7.7	–67	250	4.98	48.4
V-10a	6.7	–14	263	1.72	< 1.0
V-10b	6.2	14	274	1.57	1.21
V-11b	6.7	–14	584	< 1.00	1.69
V-11c	6.9	–21			
V-12a	7.6	–63	140	1.10	5.0
V-13a	7.6	–64	260	5.10	49.0



Figs. 2 – 3. Eh-pH stability diagrams of the As-Fe-O-S system. A – Vink (1996); B – Pokrovski et al. (1996, 2000).

to 7.5) whereas water from the areas Kolba and Svätodušná had neutral or moderately alkalic character with pH values within the range of 7.0 (only in one case 6.4) to 7.7 (Tab. 3). Water pH was not influenced by the seasonal changer (summer vs. winter) at any from the studied localities.

With utilization of comparison of the concentration values of toxic metals in the surface water from the studied localities with the recommended limit values pursuant to the Resolution of the Government of the Slovak Republic No. 296/2005 Coll. it is possible to state that recommended limit values were exceeded in the case of Cu (recommended limit value is 20 $\mu g \cdot l^{-1}$) and As (recommended limit value is 30 $\mu g \cdot l^{-1}$). Concentrations of individual studied metals were in the drought period generally about 3 times higher than in the rain period (Tabs. 2 and 3).

As and Sb speciation

Application of results of thermodynamic studies of various authors enabled to determine Fe, As and Sb speciation in the samples.

The Eh-pH stability diagrams of the As-Fe-O-S system (Figs. 2 and 3) displaying stability fields of arsenic calculated according to thermodynamic data published by Vink (1996) and Pokrovski et al. (1996, 2000) were adjusted by Lalínska (2009). Arsenic data of analysed samples of the technogenous sediments from Ľubietová falling within these diagrams mainly into the stability fields of complexes $Fe(OH)_3$ and As(V)(aq) or to mineral scorodite ($FeAsO_4 \cdot 2H_2O$). Probably, most of As occurs in solution in the less toxic oxidation level as As(V).

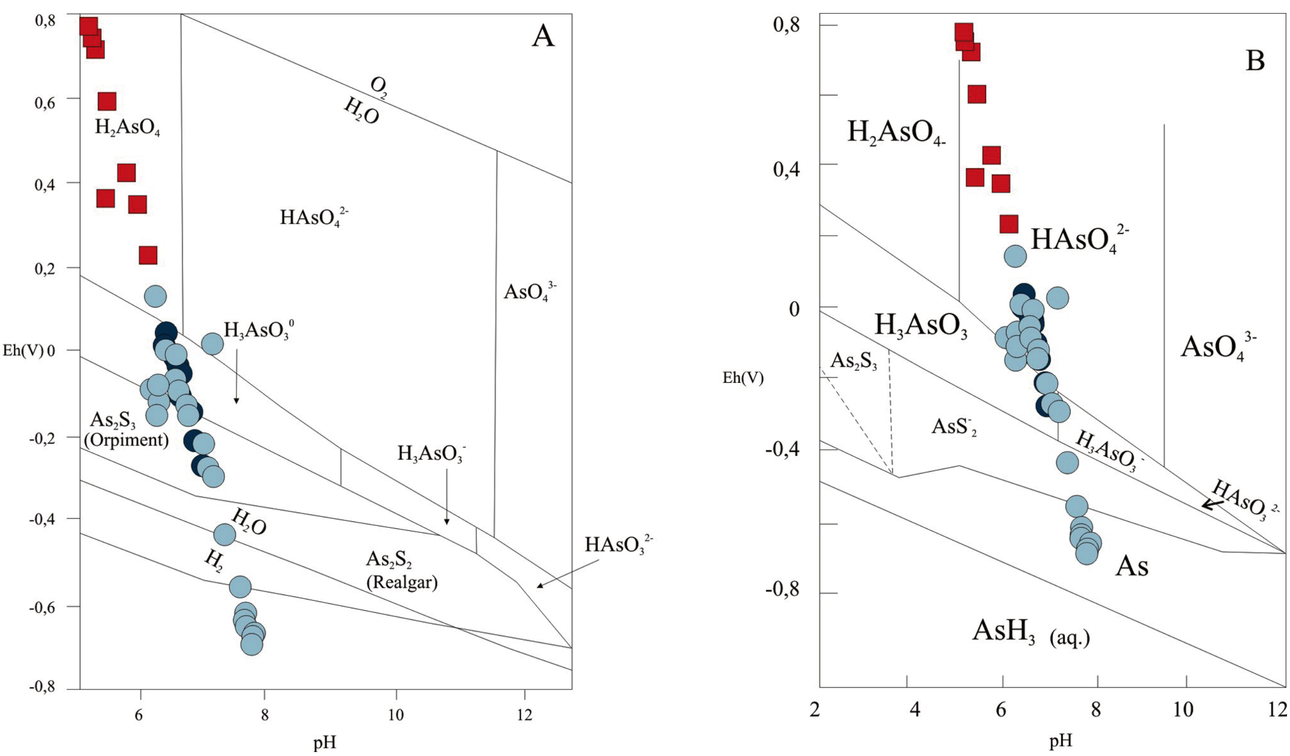
Similarly as in the previous paragraph, Eh-pH stability diagrams of the As-H_2O-S system (Figs. 4 and 5) published by Ryu et al. (2002) and Ferguson and Gavis (1972) point at As occurrence in the oxidation level (V) in the technogeneous sediments of the dump field and soil. Most of As occurs mobile in the solution in the form of complex H_2AsO_4.

The study of As speciation in the groundwater with utilization of Eh-pH stability diagrams points out that within the stability diagrams by Vink (1996) and Pokrovski et al. (1996, 2000) most of samples fall within the stability fields of As(III) (Figs. 2 and 3). According to stability diagrams of Ryu et al. (2002) and Ferguson and Gavis (1972) As occurs in the form of complex H_3AsO_3 (Figs. 4 and 5) or in the form of mineral orpiment As_2S_3 (Fig. 4) and complex $HAsO_4^{2-}$ (Fig. 5).

Arsenic in the surface water is presented as $As(III)_{(aq)}$ (Figs. 2 – 5), in the form of finely dispersed arsenopyrite (FeAsS; Figs. 2 and 3) or in the form of H_3AsO_3, As_2S_3, $HAsO_4^{2-}$, AsS^2 or in the elementary form (Figs. 4 and 5).

Antimony is according to Vink (1996) in the supergene oxidation conditions mobile and behaves as arsenic. Eh-pH stability diagram by Brookins (1988) and Vink (1996) enables to specify Sb speciation (Fig. 6). Samples of technogenous sediments from Ľubietová are falling within the stability field of complex SbO_3^-. Similar Sb form in the water with nearly neutral pH was described as well by Ashley et al. (2003).

In the groundwater antimony occurs mainly in the form of oxides Sb_4O_6. In one sample antimony occurs in the elementary form and in the other sample occurs on the



Figs. 4 – 5. Eh-pH stability diagrams of the As-H_2O-S system. A – Ryu et al. (2002); B – Ferguson and Gavis (1972).

boundary line of the stability fields of solution and stibnite Sb_2S_3 (Fig. 6).

In the surface water the predominant forms of antimony occurrence are oxides Sb_4O_6. The occurrence of antimony in the form of complex SbO_3^- and elementary Sb is marginal (Fig. 6).

Determination of As speciation by the method described by Hagarová et al. (2004) pointed at predominant the occurrence of As(V) in the surface water in the hypergenic conditions of the dump fields. About one third of samples showed certain portion of As(III) not exceeding 30 % and the remaining part should have been As(V). The highest portion of As(III) was determined in the samples of the mine water V-7 (30 %), in the samples of water from the mountain stream by the mine water inflow V-8 (45 %), in the samples of surface water from the Peklo valley V-9 (20 %) and in the sample of water from the stream of the reference site V-12 (15 %) where total contents of As and Sb were very low.

Discussion

Arsenic occurs in the water mostly in the following forms: $H_2AsO_4^-$, $HAsO_4^{2-}$ and $HAsO_2^0$ (Greenwood and Earnshaw, 1990) whereby As(III) is in the oxidation weathering zone more mobile than As(V) (Manning and Goldberg, 1997). The high As content in the water is connected with the decomposition of tetrahedrite (and arsenopyrite). It is controlled by the As sorption on amorphous Fe oxides and oxyhydroxides, clay minerals and hydro-goethite and by the decomposition of these secondary phases during changes of conditions (Andráš et al., 2009).

It is generally stated that in the reductive conditions As mobility is intended by bond of arsenates and arsenites on the surface of minerals, mainly on Fe oxyhydroxides. In the sulphide waters and in the systems containing sulphides, great part of dissolved As occurs in the form of As-S compounds playing important part during the dissolving of As sulphide minerals in alkalic conditions (Wallschläger and Stadey, 2004).

Sorption capacity of clay minerals, hydro-goethite and Fe oxyhydroxides against As is very high (up to 76 mg · l^{-1} of As in Fe oxyhydroxides under pH 5). As sorption depends on pH, time, As concentration in solution and temperature (Mohapatra et al., 2007). The most intense sorption is under pH 4 (García-Sanchez et al., 2002; Lombi et al., 2000). According to Mohapatra et al. (2007) the kaolinite

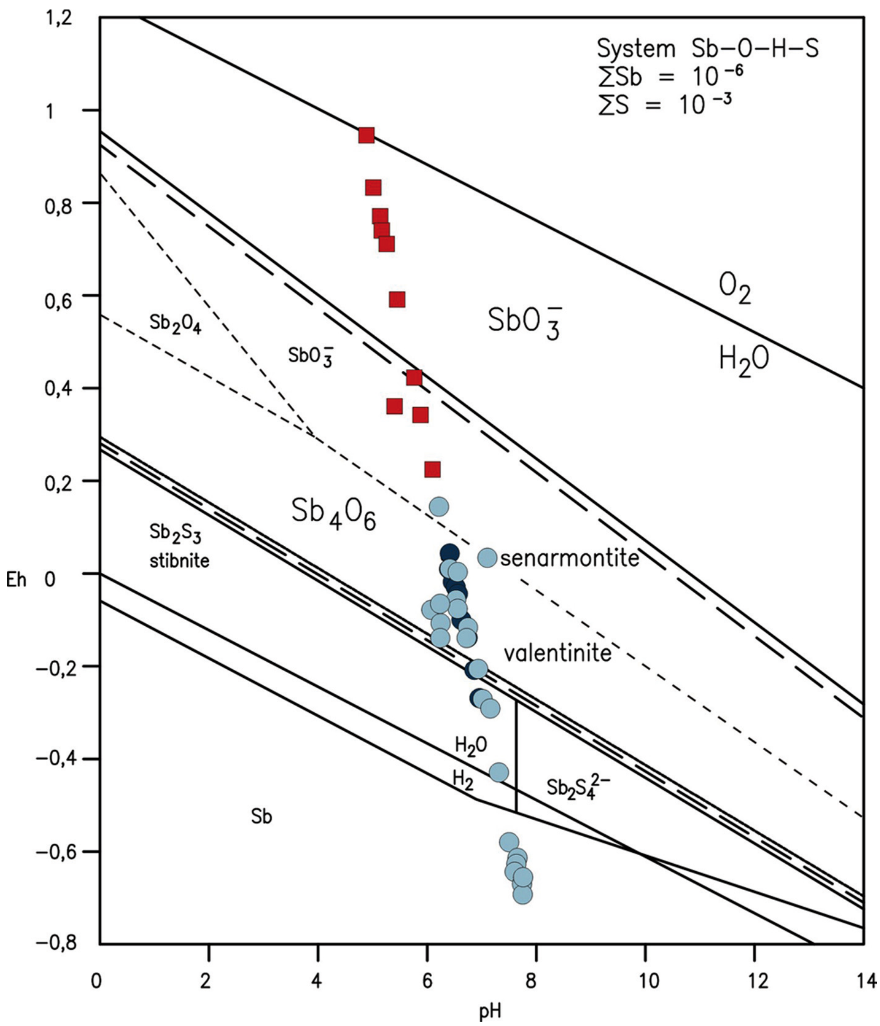


Fig. 6. Eh-pH stability diagram of Sb species (Brookins, 1988; Vink, 1996).

is the best sorbent of As(V) from clay minerals presented in the dump field Ľubietová-Podlipa. Less toxic As(V) sorbs on clay minerals more easier and quantitative than more toxic As(III). During this process As(III) is oxidized on As(V) (Lin and Puls, 2000). Low oxidation–reduction potential causes arsenic precipitation and therefore clay shale with content of organic matter or sulphides are richer in arsenic.

The greatest portion of As(III) was determined in the samples of the groundwater and the surface water with high negative values of Eh. Sb speciation was not verified by the hydride method HG AAS. Sb(III) and Sb(V) exist in natural conditions in soluble forms: Sb(V) as $Sb(OH)_6^-$ and Sb(III) in the form of $Sb(OH)_3$ (Filella et al., 2002). Hydrogoethite and Fe oxyhydroxides are important sorbents of Sb. Sb(III) and Sb(V) create on the surface of hydrogoethite and Fe oxyhydroxides complex compounds. Sb(III) can best sorb under pH 3 – 12 while maximum sorption of Sb(V) occurs under pH < 7. On the surface of hydrogoethite and Fe oxyhydroxides can occur during several days Sb(III) oxidation mainly under pH 3 – 5.9. Under pH ~ 9 its mobilization and release into the solution occurs while under pH < 7 it remains bounded on the surface of Fe oxides (Leus et al., 2006).

As Sb sorbs relative well on the surface of Fe oxides and oxyhydroxides it is possible to assume that part of Sb occurs in the water solution in the form of Sb_4O_6 and SbO_3^- particles < 0.4 μm (Lalínska, 2009). It is suggested from relatively high level of Fe : Sb correlation (Tabs. 1 – 3).

Andráš et al. (2008) found out that cementation process known at the Špania Dolina deposit occurs as well as at the Ľubietová deposit. It would be possible to use this process for construction of the Fe^0 – barrier to remove heavy metals (mostly Cu, As, Sb and Cd) from the drainage water.

Conclusions

Technogenous sediments and water at the locality of Ľubietová are contaminated by arsenic and antimony. In the sediments (and soils) there is predominant arsenic in the less toxic oxidation level as As(V) and occurs in the form of $FeAsO_4 \cdot 2H_2O$ or in the forms of H_2AsO_4 and $HAsO_4^{2-}$. The study of antimony speciation pointed out at the occurrence of SbO^{3-} species corresponding to minerals senarmontite and tripuhyite.

In the groundwater there is predominant As(III) in various forms as $H_3AsO_3^0$, $HAsO_4^{2-}$ and As_2S_3. Antimony is predominant as Sb_4O_6 which is identical with the valentinite. In the surface water As was determined in both oxidation levels as As(III) and As (V). There are predominant forms of $H_3AsO_3^0$ and As_2S_2.

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Minerals pretreatment for arsenic and cadmium removal from water solutions by mechanical activation

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Abstract

In this work, the sorption of As(III) and Cd(II) on mechanically activated minerals, such as magnetite Fe_3O_4 (Kiruna, Sweden), olivine $(Mg, Fe)_2SiO_4$ (Åheim, Norway) and talc $Mg_3[Si_4O_{10}](OH)_2$ (Hnúšťa, Slovakia), has been studied. Removal of heavy metals based on sorption on mineral surfaces has been suggested as an alternative approach. Activation processes based on the high-energy milling (mechanical activation) are used to modify the properties of materials and to enhance their reactivity. Sorption activity of mentioned minerals can be enhanced by the mechanical activation in high-energy mill Pulverisette 6 (Fritsch, Germany), where specific surface area (S_A) of mechanically activated magnetite increased. The increasing values of S_A of minerals relate with enhanced sorption ability to removal heavy metals from the water solution. The experimental results show that mechanically activated minerals are effective sorbents for low concentrations of heavy metals in the waste waters.

Key words: arsenic, cadmium, sorption, magnetite, olivine, talc, mechanical activation

Introduction

Arsenic and cadmium are chemical elements of significant ecological risk. Therefore a great attention is paid to them in environmental studies (Madhal and Suzuki, 2002). They are highly bioactive and toxic elements. Their presence at elevated levels in the drinking water and soils is threatening (Kang and Jin, 2004). Human beings and animals are exposed to a risk of intoxication by these elements through all components of the environment: water, air, soil, and food (Zakharova et al., 2002; Alam et al., 2003). They adversely affect biological activities as a teratogen, carcinogen or mutagen as well as having detrimental effects on the digestive system, respiratory system and immune system (Liao et al., 2005). Industrial and agricultural development has been largely responsible for the pollution of the environment with these toxic metals, although some contamination is derived from natural geological sources. Several methods have been proposed for the heavy metal removal, e.g. precipitation, membrane filtration, ion exchange and adsorption (Habashi, 1993). Many scientific works present the sorption of arsenic and cadmium onto different sorbents (Mohan et al., 2007; Yadanaparthi et al., 2009; Carrillo et al., 2006; Bhadoria et al., 2010) including magnetite (Gimenéz et al., 2007; Jönsson et al., 2009). Sorption activity can be enhanced by a pretreatment method where the solid state properties of a mineral could be changed. Mechanochemical pretreatment belongs among such methods (Baláž, 2008). Changes in the surface area as a consequence of milling can play an important role by intensification of the sorption process.

The aim of this work is to study the influence of the high-energy milling on sorption behaviour of As(III) and Cd(II) on magnetite, olivine and talc.

Experimental

Material

The investigation was carried out with the samples of magnetite (Kiruna, Sweden), olivine (Åheim, Norway) and talc (Hnúšťa, Slovakia). XRD patterns of minerals, which have been used in the sorption experiments, are shown in Fig. 1. Concentrate of olivine contains approximately 93 % of forsterite (Mg_2SiO_4) and 7 % of fayalite (Fe_2SiO_4) (Osland, 1998).

Mechanical activation

The mechanical activation of magnetite, olivine and talc was performed in a planetary mill Pulverisette 6 (Fritsch, Germany) at the following conditions: 50 balls of 10 mm diameter; material of the milling vial (V = 250 ml) and balls: tungsten carbide, ball charge: 360 g, sample charge: 10 g (magnetite), 18 g (olivine, talc); rotation speed: 500 rpm (magnetite), 450 rpm (olivine, talc), milling time in the range 1 – 120 min (magnetite), 2 – 30 min (olivine, talc).

Sorption tests

The sorption of As(III) and Cd(II) was running at various conditions (Tab. 1) in:

Tab. 1
Sorption conditions

Mineral	Amount of sample (g/L)	Sorption time and type of apparatus	
		As(III)	Cd(II)
Magnetite	8 in As(III)	0.25 – 6 hours, A	–
Olivine	8 in As(III) 5 in Cd(II)	0.25 – 6 hours, A	0.5 – 30 min, B
Talc	5 in Cd(II)	–	0.5 – 30 min, B

A. Erlenmayer´s banks placed on laboratory shaker constructed at the Institute of Geotechnics, Slovak Academy of Sciences. Initial arsenic concentration prepared from $NaAsO_2$ was 5 mg/L. During sorption tests the sorbent concentration was 8 g/L of arsenic water solution. The sorption was performed at 298 – 300 K. The sampling was made after 0.25, 0.5, 1, 2, 3, 4, 5 and 6 hours. Initial pH was 7.9. Final pH was 7.5.

B. Glass reactor (500 mL) with mechanical stirrer. Initial cadmium concentration prepared from $Cd(NO_3)_2 \cdot 4H_2O$ was 25 mg/L. The amount of cadmium solution was 200 mL. The sorption was performed at 298 – 300 K. Stirring rate of mechanical stirrer was 500 rpm. Initial pH was 5.5 and final pH was 9.5. The sampling was made after 0.5, 1, 2, 3, 5, 7, 10, 15, 20, 25 and 30 min. All 11 samples were taken from 200 mL cadmium solution (the volume of one sample was 3 mL) and this volume (3 mL) was replanished with the initial cadmium solution.

The values of As(III) and Cd(II) in the solution after sorption on non-activated and activated samples were determined by atomic absorption spectrometry using a SPECTRAA 240FS/240Z (Varian, Australia).

Specific surface area

The specific surface area S_A was determined by the low-temperature nitrogen adsorption method. The Gemini 2360 sorption apparatus (Micromeritics, USA) has been applied.

X-ray diffractometry

The X-ray diffraction measurements were carried out using a diffractometer X´Pert (Philips, Netherlands) working in the 2Θ geometry with CuKα radiation. The XRD lines were identified by comparing the measured patterns to the JCPDS data cards. The effect of mechanical activation was evaluated by the decrease of crystalline phase *X* of magnetite, olivine and talc according to formula (1):

$$X = \frac{U_0}{I_0} \cdot \frac{I_x}{U_x} \cdot 100\,(\%) \qquad (1)$$

where U_0 and U_x denote the background of the reference and activated sample, while I_0 and I_x are integral intensities of selected diffraction lines of reference sample and activated sample, respectively (Ohlherg and Strickler, 1962).

Results and discussion

Mechanical activation

There was estimated an increase of the surface area of all above mentioned minerals with the time of mechanical activation in a planetary mill. The dependence of the specific surface area on the time of milling is shown in Fig. 2. As can be seen, the specific surface area of mechanically activated magnetite increased from the value 0.1 m^2/g to 11.9 m^2/g (t_M = 90 min), olivine from value 0.3 m^2/g to 5.2 m^2/g (t_M = 30 min) and talc from the value 4.0 m^2/g to 70.7 m^2/g (t_M = 15 min). The values of surface area of magnetite and talc achieved its maximum after 90 and 15 min of milling, and then this value rapidly decreased. Formation of the new surface area during mechanical activation of olivine consists of two stages. In the first stage the increase in the surface area is almost proportional to the milling time, the second stage is steady. Process of the new surface formation was accompanied by the effect of particle enlargement (aggregation and/or agglomeration).

The lattice defects deformation in the bulk of minerals can be characterized by several physico-chemical methods (Baláž, 2000; Baláž, 2008). One of them is the X-ray diffractometry method (XRD), which allows the study of the disordering of minerals crystal structure. The changes induced by mechanical activation can be observed by looking at minerals lines broadening, shift and the reduction of line intensity. The noticeable decrease of crystallinine phase *X*, calculated to the formula (1), is determined at mechanically activated

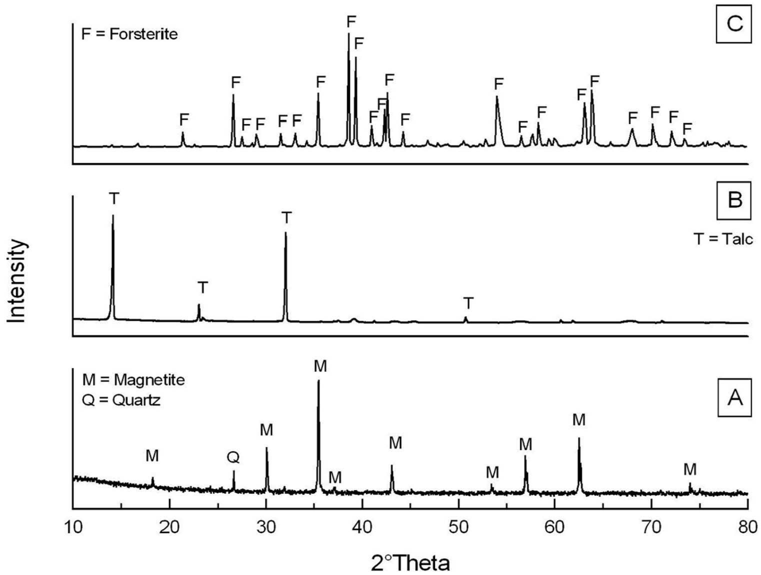

Fig. 1. XRD patterns of (A) magnetite, (B) talc and (C) olivine.

minerals (Fig. 2) and would provide complementary information about the amorphization of the process.

Sorption of As(III) and Cd(II)

Sorption experiments were done by 90 min mechanically activated magnetite, 30 min mechanically activated olivine and by 15 min mechanically activated talc, where the highest specific surface area was performed. In Fig. 3 there is a removal efficiency of arsenic E (%) from the water solutions in dependence with the sorption time for mechanically activated magnetite and olivine. As can be seen, sorption of As(III) on mechanically activated magnetite is immediate, while on mechanically activated olivine is phased. At magnetite, the equilibrium state of sorption occurs at the beginning of sorption times and than the removal efficiency of arsenic on magnetite increases very slowly. At olivine, this state occurs later and the curve becomes sigmoid. The highest removal efficiency of arsenic was detected after 6 hours of sorption, in the case of magnetite it was 96 % and of olivine 99 %.

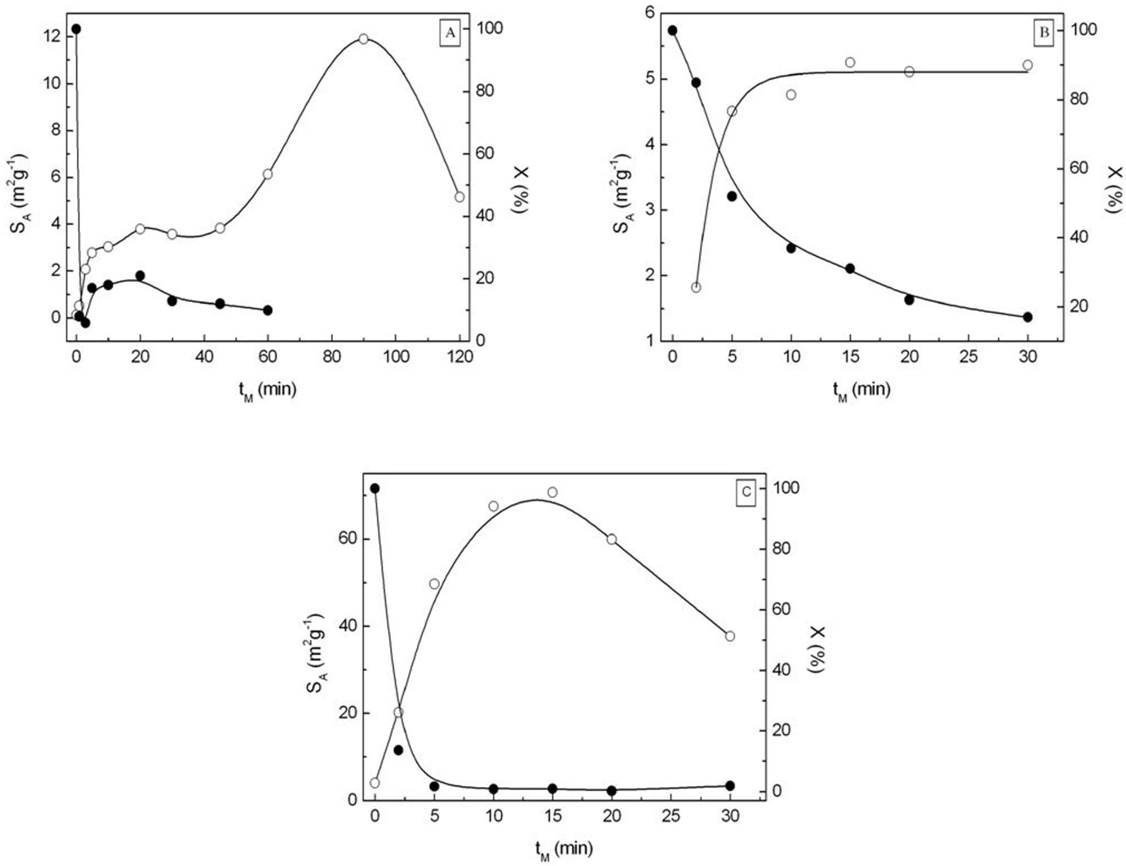

Fig. 2. Specific surface area, S_A, and content of crystalline phase, *X* of (A) magnetite, (B) olivine and (C) talc as a function of milling time, t_M.

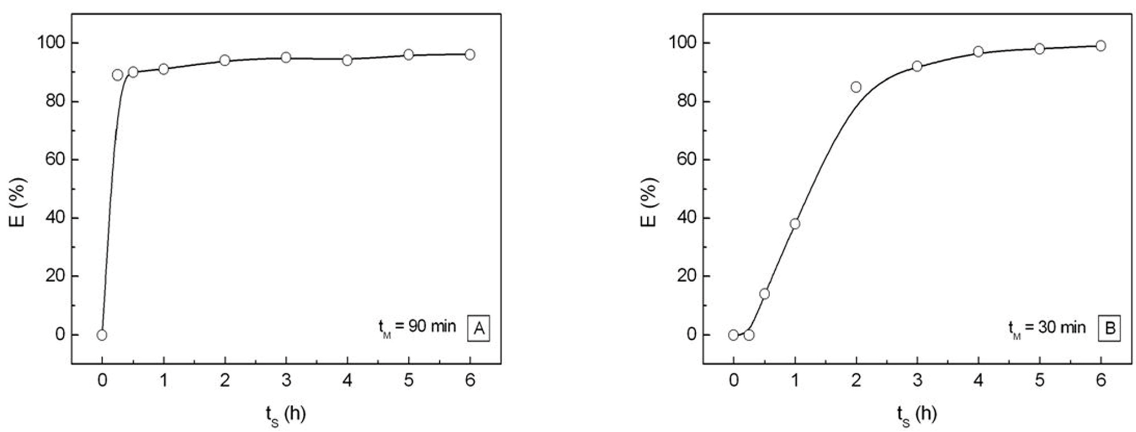

Fig. 3. Removal efficiency of arsenic, *E*, vs. sorption time, t_S, for (A) magnetite (t_M = 90 min) and (B) olivine (t_M = 30 min).

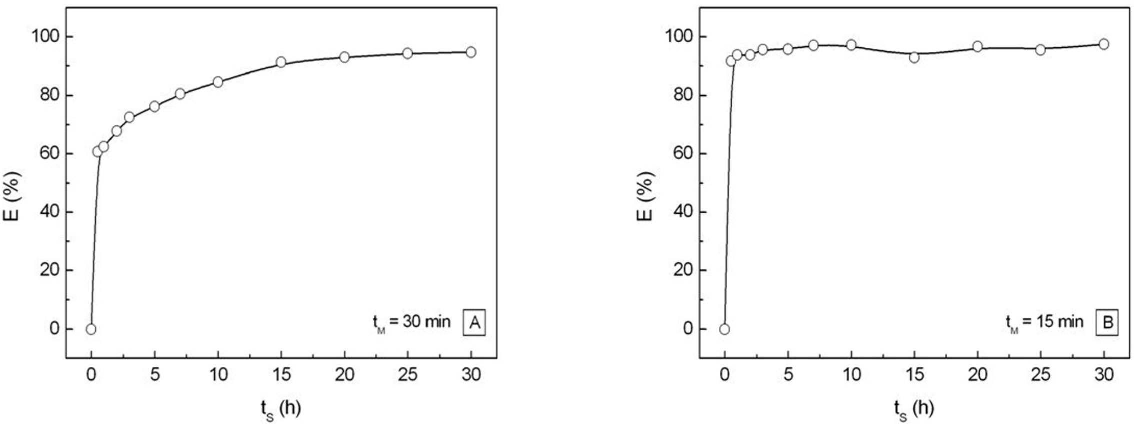

Fig. 4. Removal efficiency of cadmium, *E*, vs. sorption time, t_S, for (A) olivine (t_M = 30 min) and (B) talc (t_M = 15 min).

In Fig. 4 there is a removal efficiency of cadmium E (%) from the water solutions in dependence with the sorption time for mechanically activated olivine and talc.

As can be seen, sorption of Cd(II) on mechanically activated olivine is again phased, while on mechanically activated talc is immediate. The highest removal efficiency of cadmium was detected after 30 min of sorption, in the case of olivine it was 95 % and of talc 97 %.

We can conclude that mechanically activated magnetite, olivine and talc are effective minerals for removal of low concentrations of heavy metals, such as cadmium and arsenic from the waste waters. Sorption ability is in all activated samples more than 90 %, while sorption ability of non-activated samples was not detected.

Conclusion

We investigated that mechanical activation of minerals in a planetary mill causes the increase of its specific surface area with the milling time. The increasing values of S_A of minerals relate with the enhanced sorption ability to remove heavy metals from the water solution. The experimental results show that mechanically activated minerals are effective materials for removal of low heavy metal concentrations in the waste waters.

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Biosorption of Cu^{2+} and Zn^{2+} by immobilized biosorbents: Study of the biosorbent stability and capacity

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Abstract

The utilization of biosorbent immobilized in polymer matrix is studied to widen the biosorption application in the recent practice. These biosorbents have the right size, mechanical strength, rigidity and porosity. In this work the algae immobilized in calcium alginate were used as biosorbent. The stability of immobilized biosorbents in acidic solutions (pH 1; 2.5 and 5) was observed. Three differently prepared groups of immobilized beads (gel, dry and dry dipped in water for 12 hours before the experiment) were used. All groups of beads were stabile in the weak pH solutions but low pH (pH = 1) caused disintegration of beads. Apparently low pH is not suitable for application of biosorbents immobilized in calcium alginate. Biosorption of copper and zinc from the single and binary metals was also studied. Higher capacity of biosorption (36.7 mg · g^{-1}) was found for copper ions in comparison with the zinc ions where the maximum observed biosorption capacity was 27 mg · g^{-1}. The presence of another ion decreased the biosorption capacity of both studied metals. The maximum biosorption capacity from two-ion solution was 32.6 and 10.5 mg · g^{-1} for Cu and Zn, respectively.

Key words: immobilization, pH, stability, swelling, biosorption, *Chlorella kessleri*

Introduction

The removal of toxic metals from wastewater is a matter of great interest in the field of water pollution (Fiol et al., 2006). In the past decades, one has been looking for inexpensive technologies to control metal pollution. As a cost-effective mean, biosorption has been extensively studied for removing a wide variety of soluble heavy metals (Liu and Liu, 2008). Biosorption can be defined as a passive sequestering of metal ions by metabolically inactive biomass (Kaduková and Štofko, 2006; Wang and Chen, 2009). Biomass immobilization is an essential step for an industrial scale-up of biosorption. Unlike biomass in its native state, immobilization provides biosorbent particles with the adequate size, density and mechanical strength required by continuous systems (Volesky, 2003). Besides, immobilization can save the cost of separating the biomass from the treated solution which can represent up to 60 % of the total cost. This process also enables biomass regeneration in various adsorption-desorption cycles. Natural polysaccharide gel matrixes, such as alginate, are widely used and represent a cost effective alternative to synthetic polymers (Lagoa and Rodrigues, 2007). Alginate is a component of the outer cell wall of the brown algae and it is responsible for the high metal uptakes of algae. Additionally, alginate itself has biosorption capacity, favouring a possible synergic effect with the immobilized biomass (Mata et al., 2009). The knowledge of biosorbents stability in various environments is one of the main requirements for their usage in the columns. It was found that calcium alginate is very little stabile in alkalic conditions and the presence of Na^+ and K^+ ions (Ivánová et al., 2009).

The aim of this study was to investigate the swelling behaviour and stability of algae immobilized in the calcium alginate in acidic solutions. Additionaly the capacity of immobilized biosorbents to remove copper and zinc ions from the single and binary metal aqueous solutions was studied.

Materials and methods

Biosorbent

Chlorella kessleri, an unicellular green alga, obtained from the Institute of Botany of Slovak Academy of Science was used in this study. It was grown at 25 °C in aerated and lighted liquid medium Milieu Bristol (Kaduková and Virčíková, 2003). In the Log phase of growth, *Ch. kessleri* cells were cooled, centrifuged at 3 000 rpm for 5 min, washed twice with distilled water and then dried at 100 °C for 3 h. Dried powdered biomass was used for immobilization.

Preparation of immobilized algae in calcium alginate beads

Powder prepared from dried algae *Chlorella kessleri* was mixed with 3 % sodium alginate solution in the ratio

1 : 9. The solution was then dropped from a height of 20 cm into gelling medium of 0.2 M calcium chloride solution using a syringe with a needle. On the principle of simple ion exchange water soluble sodium alginate was converted to water insoluble and stable calcium alginate salt. The formed beads were cured in the gelling medium for 2 hours. Prepared beads were consequently divided into three groups:

A. Gel immobilized beads (stored in distilled water). The average size of the bead was found to be 2.6 mm.

B. Dry immobilized beads dipped in distilled water for 12 hours before using. The average size of the bead was (after dipping) 1.7 mm.

C. Dry immobilized beads, with the size 1.3 mm.

Swelling and stability study

The pH values of sulphuric acid solutions used in experiments were 1, 2.5 and 5. Exactly 10 beads from each fraction were immersed in the tubs with 10 ml of acidic solutions and stored at laboratory temperature. Changes of weight and diameter of beads were observed.

The % weight change of the beads with respect to time was calculated according to the formula

$$m_c = \frac{m_f - m_i}{m_i} . 100 \tag{1}$$

where m_c – weight change [%]
m_f – weight of the beads in the swollen state [g]
m_i – initial weight of the beads [g]

Biosorption study

Immobilized algae were used for biosorption of copper and zinc ions from the single and binary metal solutions with initial concentration 135 mg · dm^{-3} and 150 mg · dm^{-3} for Cu^{2+} and Zn^{2+}, respectively. pH value of used solutions was 4.5. This pH value was chosen according to previous experimental studies (Horváthová et al., 2008). Fraction A (gel beads) were used for biosorption study. Concentration of dry biosorbent added into the solutions was 2 g · dm^{-3} (it represents 250 beads). These solutions were stirred during 24 hours. At selected time intervals, solution samples were withdrawn for metal analysis. The concentration of Cu^{2+} and Zn^{2+} ions was measured by atomic absorption spectroscopy (Varian AA20+).

The metal uptake q_t at the time t was calculated from the mass balance equation as follows:

$$q_t = \frac{V(C_0 - C_t)}{m} \tag{2}$$

where q_t – the quantity of metal uptake by biomass [mg · g^{-1}] at time t
C_0 – the initial metal concentration [mg · dm^{-3}]
C_t – metal concentration at time t [mg · dm^{-3}]
V – the volume of solution [dm^3]
m – dry weight of the biomass added [g]

Results and discussion

Swelling studies

Wastewater is the heterogeneous mixture of different ions with various pH values so knowing the behaviour of biosorbents in various environments before their application is crucial. Three different pH values (1; 2.5; 5) were chosen for the study of the influence of acidic conditions to the stability of calcium alginate beads. The beads were exposed to the influence of sulphuric acid until their degradation was so large that there was no possibility to handle them. The effect of sulphuric acid to three studied fractions of calcium alginate beads is visible in the Fig. 1.

Fraction A (gel beads) swelled during the first day irrespectively on the pH value of solutions. At pH 1 the beads weight increased only by 3 % but then started to decrease, at day 4 beads had original weight and then the weight of beads was lowering but they kept their shape. The beads at pH 2.5 and 5 have swelled greatly during the first day. The weight of them has grown by 50 %. During next day the weight of these beads did not change significantly. After 29 days beads in solution with pH 1 and 2.5 were degraded in such great extent that they were not able to keep their shape and have disintegrated.

Beads from fraction B (dry beads immersed in water before usage) swelled by 20 % at pH 1 and 5 and by 100 % at pH 2.5 during the first day. After the first day the weight of beads at pH 2.5 and 5 did not change considerably until the end of the experiment. In contrary, the beads from solution with pH 1 started to shrink after first day and continuously loosed their weight. Beads from all studied pH values softened till the end of the experiment but still kept their shape.

Dry beads from the fraction C changed their weight in the greatest extent in comparison with previous two fractions. They swelled by 100 % during the first day. Beads from solution with pH 1 loosed about 25 % of their weight between day 4 and 8 but later their weight did not change significantly. At pH 2.5 the weight of beads started to change after 29 days but then beads shrunken fast and loosed majority of their weight but still did not fall under their original weight. They disintegrated after 44 days of the experiment. The changes in weight of beads in pH 5 were not significant during the experiment. Beads from solutions with pH 1 and 5 kept their shape but after 44 days were difficult for handling.

Changes in bead diameters were also measured but they corresponded with weight changes.

All beads swelled during the first day. It was probably caused because of acid solution penetration into the bead and filling of free space among polymer chains. According to Hoffman (2002) the main reason of hydrogel swelling is the hydration of hydrophilic groups of alginate. Shrinking was observed only at pH 1 at all fractions and at pH 2.5 at fraction C. It was not observed at solutions with pH 5. At low pH probably carboxylic groups of alginate were protonated and hence electrostatic repulsion among these groups lessened and shrinkage was favoured (Hoffman, 2002). Shrinking of beads from fraction C (dry beads) could be caused by a little content of water in their bodies so higher amount of acid solution could enter inside in comparison with bead from fraction A and B which all contained some amount of water before the experiment. Penetration of weak acidic solution caused probably mostly swelling while penetration of strong acidic solution (because of protonation and consequent chain repulsion) caused shrinking.

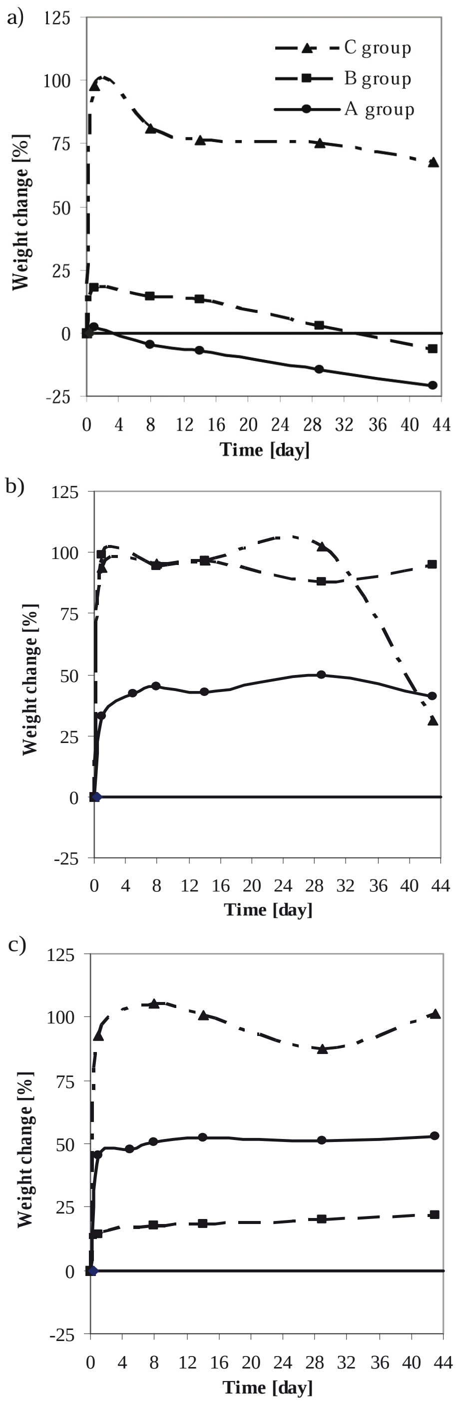

Fig. 1. Swelling profiles of gel (A) and dry (B, C) immobilized beads in solutions of sulphuric acid with: a) pH = 1; b) pH = 2.5 and c) pH = 5.

Application of immobilized algae for the removal of Cu^{2+} and Zn^{2+} ions from the single and binary metal aqueous solutions

Biosorption of Cu^{2+} ion from the single and binary solutions is visible from the Figs. 2A and 2C. Previous experiments (Horváthová, 2008) confirmed that optimal pH for the copper biosorption is in the range 4 – 5 so values from this interval were used for experiments. During the first 30 minutes the biosorption was fast and later continued slowly until equilibrium was reached. Six and four hours were necessary to reach the equilibrium in the single and binary solutions, respectively. The two-step-process of biosorption can be connected with the nature of used biosorbent. During the first fast step metal ions were probably adsorbed onto the surface of beads and then in the second step they diffused inside the beads. Maximum biosorption capacity of immobilized biosorbent for Cu^{2+} ions was 36.7 and 32.6 mg · g^{-1} from the single and binary solutions, respectively.

Biosorption of Zn^{2+} ions from the single and binary solutions is shown in the Figs. 2B and 2C. The two step behaviour was observed also in the case of Zn biosorption by immobilized biosorbent. Maximum values of biosorption capacity for Zn were 27 and 10.5 mg · g^{-1} of biosorbent from the single and binary metal solutions, respectively. Time necessary for equilibrium was 6 hours in the case of single metal solution. But in the case of two-ion solutions the concentration of Cu^{2+} ions did not change after 4 hours but concentration of Zn^{2+} ion slightly changed during the whole experiment. Although, changes in Zn^{2+} concentration did not exceed 6 %.

Presence of Cu^{2+} ions in solution significantly decreased the Zn^{2+} biosorption. Zn^{2+} ions did not have so significant influence on Cu^{2+} biosorption although also in this case very slight decrease of biosorption capacity was observed.

For both studied metal ions visible decrease of the biosorption capacity after its steep increase was observed (although the decrease of Cu^{2+} biosorption capacity in two-ion solution was neglectable). Kaduková and Virčíková (2005) found similar phenomenon during the study of Cu bioaccumulation by living cells of *Ch. kessleri*. Authors proposed that cell wall damage followed by the cell death could be responsible for it. But they did not observe it when non-living cells (biosorption) were used. But Melčáková and Horváthová (2010), studying biosorption of Zn with plant debris *(Reynoutria japonica),* and Štofko et al. (2007), studying biosorption of Cu and Zn by saw dust, observed similarly the decrease of biosorption capacity after its initial steep increase. In both cases authors suggested that water content in used materials could cause the behaviour. As in our experiment biosorbent was used in the form of gel beads presence of water inside the beads could influence the biosorption capacity and caused the release of ions previously adsorbed on the biosorbent surface. Further studies are necessary to explain this behaviour.

Conclusions

Knowledge of the behaviour of biosorbents immobilized in polymer matrix is one of the key factors for their application in practice.

Weakly acidic pH value of solutions caused significant increase of weight of calcium alginate beads. Probably higher volume of water had to enter into the bead to protonate all available sites in the calcium alginate chains. But in spite of bead weight increase beads were usable. The protonation was probably not enough strong to cause the disintegration of beads. To eliminate the weight increase is better to use gel beads (they already contain specific amount of the water) or to dip dry beads into water before the use. The utilization of alginate immobilized biosorbents in solution with low pH values (around 1) is not suitable because of strong damage of their structure which results in beads disintegration.

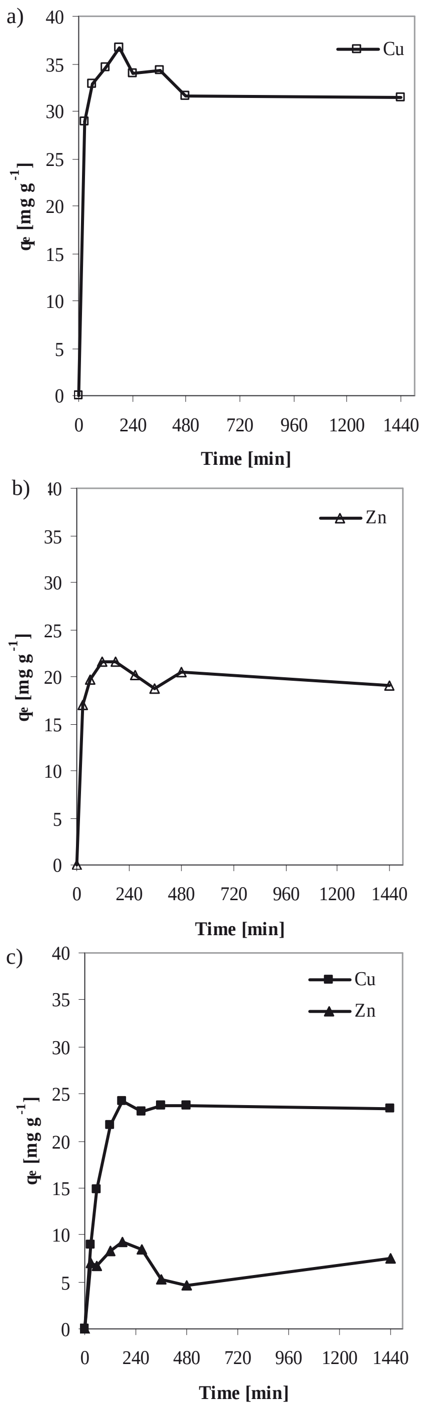

Fig. 2. Changes in metal concentrations in solutions after addition of biosorbents a) in single solution of Cu^{2+} ($pH_{initial}$ = 5; $C_{Cu,\ initial}$ = 135 mg · l^{-1}) or b) Zn^{2+} ($pH_{initial}$ = 4.15; $C_{Zu,\ initial}$ = 150 mg · l^{-1}) and c) in binary solution of Cu^{2+} and Zn^{2+} ($pH_{initial}$ = 5; $C_{Cu,\ initial}$ = 135 mg · l^{-1}; $C_{Zu,\ initial}$ = 150 mg · l^{-1}).

Immobilized biosorbents show satisfactory copper and zinc biosorption capacity but in the process kinetics there is possible to observe phenomena similar with metal ion biosorption by plant debris (saw-dust, dry leaves …) which are probably connected with the water content in biosorbent particles. Further study is necessary to elucidate this behaviour.

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Mineral characteristics of dust outlets from rotary furnaces of iron ore works Siderite, Ltd., Nižná Slaná

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Abstract

The paper deals with the mineral and chemical composition of the dust outlets from the rotary furnaces of the iron ore works Siderite, Ltd., Nižná Slaná. The products of dry and wet high gradient magnetic separation were studied with the aim to determine the distribution of mineral phases and chemical components using XRD, AAS and Mössbauer spectroscopy. Maghemite accompanied by siderite was found as a dominant mineral in magnetic products. An occurrence of siderite, quartz, ankerite, sericite and chlorite in non-magnetic products was detected.

Key words: High Gradient Magnetic Separation, siderite roasting, dust outlet, maghemite

Introduction

The iron ore works Siderite, Ltd., Nižná Slaná was the only producer of iron ore in Slovakia. Due to the economic problems its operation was shutdown in August 2008. The run-off-mine ore was subjected to crushing and classifying. The coarser classes were pre-treated using a dry high intensity magnetic separation. Only class with a grain size of 0 – 4 mm was led through bypass and directly added to magnetic product obtained by separation of coarser classes. In such way obtained material has been roasted in the rotary furnaces with the aim to improve the magnetic properties of the main utility Fe-bearing mineral, i.e. siderite. Thus, during magnetizing roasting, siderite was changed into magnetite and/or maghemite with much higher magnetic susceptibility. After cooling the roasted ore was wet ground to a grain size 90 % bellow 63 µm and subjected to wet low intensity magnetic separation. Magnetic product was filtered and led to pelletizing plant. Final product – blast furnace pellets usually contained 55.4 % of Fe, 3.4 % of Mn and 5 % of SiO_2 (Mihók, 1997; Lukáč, 2002; Hredzák et al., 2008a).

A one of the first reports about magnetic separation and mineral composition of dust outlets from the rotary furnaces studied an influence of low intensity magnetic separator drum revolution on products quality. Thus, from the feed of dust outlet with 35 – 38 % Fe and 13 – 16 % SiO_2 a magnetic product with 41 – 46 % Fe and 8 – 12 % SiO_2 at a mass yield of 59 – 67 % was obtained. Recovery of Fe and SiO_2 into magnetic product attained 72 – 78 % and 36 – 53 %, respectively (Zaťko et al., 1979).

Latterly, a detailed research on the application of dry and wet ways of the high gradient magnetic separation was performed. A dependence of products quality on applied magnetic induction at separation has been studied. The cleaner products were obtained by the wet way. So, from the feed with 26 – 28 % Fe and 16 – 18 % SiO_2 the magnetic products with 44.21 – 45.71 % Fe and 1.20 – 2.55 % SiO_2 at the mass yield of 31.86 – 37.03 % were attained. The recovery of iron and SiO_2 into magnetic products achieved 52.35 – 59.54 % and 2.24 – 5.26 %, respectively (Hredzák et al., 2008b, c).

Methods of experimental work and assessment

The High Gradient Magnetic Separation (HGMS) has been carried out using universal laboratory magnetic separator JONES in a cassette located between its poles. The cassette was lined by two grooved plates made of magnetically soft iron. In such way required induction and gradient of magnetic field were achieved (Hredzák et al., 2008b, c).

The assessment of separation products was performed using classical material balance method. After determination of mass yields the products of magnetic separation were subjected to chemical analyses and volume magnetic susceptibility measuring. Loss on ignition (LOI) at 900 °C and SiO_2 content was assayed gravimetrically. Other elements have been analysed by the atomic absorption spectroscopy using the device VARIAN with accessories: Fast Sequential AAS AA240FS, Zeeman AAS AA240Z with Programmable Sample Dispenser PSD120, Graphite Tube Atomizer GTA120 and Vapor Generation Accessory VGA-77.

The volume magnetic susceptibility was measured using the Kappabridge KLY-2, Geofyzika Brno, at following

Tab. 1
Products quality of dry magnetic separation at the induction of 0.09T

Product	Mass yield [%]	κ	Fe [%]	SiO_2 [%]	Mn [%]	LOI [%]	As [%]	Al [%]	Mg [%]	Ca [%]	Zn [ppm]	Cu [ppm]
M	38.94	288,921	37.12	12.13	1.95	6.88	0.299	3.67	3.24	1.38	360	150
N	61.06	38,012	21.85	19.89	1.15	18.48	0.219	4.30	2.18	1.81	310	75
feed	100.00	135,711	27.80	16.87	1.46	13.96	0.250	4.05	2.59	1.64	329	104

Tab. 2
Products quality of dry magnetic separation at the induction of 0.30T

Product	Mass yield [%]	κ	Fe [%]	SiO_2 [%]	Mn [%]	LOI [%]	As [%]	Al [%]	Mg [%]	Ca [%]	Zn [ppm]	Cu [ppm]
M	61.61	214,466	31.04	14.29	1.66	10.74	0.303	4.12	2.84	1.46	360	245
N	38.39	13,146	19.64	25.44	1.07	18.80	0.204	4.71	2.14	1.81	335	85
feed	100.00	137,184	26.66	18.57	1.43	13.83	0.265	4.34	2.57	1.60	350	184

Tab. 3
Products quality of wet magnetic separation at the induction of 0.10T

Product	Mass yield [%]	κ	Fe [%]	SiO_2 [%]	Mn [%]	LOI [%]	As [%]	Al [%]	Mg [%]	Ca [%]	Zn [ppm]	Cu [ppm]
M	24.97	368,285	48.78	1.85	2.93	1.70	0.220	1.67	3.50	1.47	343	155
N	75.03	37,368	21.52	19.40	1.19	18.43	0.160	4.25	2.12	1.99	377	145
feed	100.00	119,990	28.33	15.02	1.62	14.25	0.175	3.61	2.46	1.86	369	147

Tab. 4
Products quality of wet magnetic separation at the induction of 0.30T

Product	Mass yield [%]	κ	Fe [%]	SiO_2 [%]	Mn [%]	LOI [%]	As [%]	Al [%]	Mg [%]	Ca [%]	Zn [ppm]	Cu [ppm]
M	36.71	304,699	41.76	4.10	2.64	7.05	0.270	1.97	3.20	1.54	295	157
N	63.29	3,620	18.47	21.86	0.95	18.46	0.215	5.69	1.62	2.10	370	143
feed	100.00	114,152	27.02	15.34	1.57	14.27	0.235	4.32	2.20	1.89	342	148

Tab. 5
Recoveries of components into products of dry magnetic separation at the induction of 0.09T [%]

Product	Fe	SiO_2	Mn	LOI	As	Al	Mg	Ca	Zn	Cu
M	52.00	28.00	51.97	19.19	46.50	35.21	48.72	32.67	42.55	56.05
N	48.00	72.00	48.03	80.81	53.50	64.79	51.28	67.33	57.45	43.95
feed	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

Tab. 6
Recoveries of components into products of dry magnetic separation at the induction of 0.30T [%]

Product	Fe	SiO_2	Mn	LOI	As	Al	Mg	Ca	Zn	Cu
M	71.72	47.41	71.42	47.83	70.47	58.38	68.02	56.55	63.30	82.23
N	28.28	52.59	28.58	52.17	29.53	41.62	31.98	43.45	36.70	17.77
feed	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

Tab. 7
Recoveries of components into products of wet magnetic separation at the induction of 0.1T [%]

Product	Fe	SiO_2	Mn	LOI	As	Al	Mg	Ca	Zn	Cu
M	43.00	3.08	45.03	2.98	31.39	11.56	35.46	19.73	23.24	26.24
N	57.00	96.92	54.97	97.02	68.61	88.44	64.54	80.27	76.76	73.76
feed	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

Tab. 8
Recoveries of components into products of wet magnetic separation at the induction of 0.3T [%]

Product	Fe	SiO_2	Mn	LOI	As	Al	Mg	Ca	Zn	Cu
M	56.74	9.81	61.72	18.14	42.15	16.72	53.40	29.84	31.62	38.91
N	43.26	90.19	38.28	81.86	57.85	83.28	46.60	70.16	68.38	61.09
feed	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

Tab. 9
Evaluation of Mössbauer spectrum of magnetic product obtained at 0.09T by dry way

iron	δ [mm/s]	ΔE_Q (ε) [mm/s]	H [T]	σ_B [T]	I [%]
Fe^{2+}	1.22	1.77		0	18.00
Fe^{3+} in γ-Fe_2O_3	0.31		48.62	1.19	57.93
Fe^{3+} in γ-Fe_2O_3	0.48		45.34	3.46	24.07
Sum of iron		100.00			

Tab. 10
Evaluation of Mössbauer spectrum of magnetic product obtained at 0.1T by wet way

iron	δ [mm/s]	ΔE_Q (ε) [mm/s]	H [T]	σ_B [T]	I [%]
Fe^{2+}	1.21	1.74		0	7.87
Fe^{3+} in γ-Fe_2O_3	0.31		48.69	1.31	59.59
Fe^{3+} in γ-Fe_2O_3	0.47		45.10	3.51	32.54
Sum of iron		100.00			

conditions: the magnetic field intensity of 300 $A \cdot m^{-1}$, the field homogeneity of 0.2 %, the operating frequency of 920 Hz, the range of $-1{,}999 \cdot 10^{-6} \div +650{,}000 \cdot 10^{-6}$ SI unit.

The XRD study of magnetic separation products was performed using the device DRON-UM1 with goniometer GUR-8 at following conditions: radiation CuKα, Cu-filter, voltage 30 kV, current 20 mA, step of goniometer 2°/min. The device id equipped by evaluating program developed by PETRA-ARTEP, Ltd., Košice, which operates on the application interface Control WEB2000. A d-spacing was performed using available published data (Beran and Zemann, 1977; Davies and Evans, 1956; Graf, 1961; Gualtieri, 2000; Hamer et al., 2003; Hazen et al., 1989; Parra et al., 2005; Proust et al., 1986; Reeder and Dollase, 1989; Smith, 1992; Tomita and Sudo, 1971).

The room-temperature Mössbauer spectroscopy measurements were made in transmission geometry using a conventional spectrometer in a constant acceleration mode. A ^{57}Co/Rh gamma-ray source was used. The velocity scale was calibrated relative to ^{57}Fe in Rh. A proportional counter was used to detect the transmitted gamma-rays. Mössbauer spectral analysis software RECOIL (Lagarec and Rancourt, 1998) was used for the quantitative evaluation of the spectra. The spectra were fitted using the Voigt-based fitting method providing distributions of hyperfine parameters.

Results and discussion

The products of magnetic separation obtained at the lowest and the highest values of magnetic induction were subjected to mineralogical study. The qualities of studied products and recoveries of observed components into separation products are introduced in Tables 1 – 4 and 5 to 8, respectively (where κ – volume magnetic susceptibility in 10^{-6} SI units, LOI – lost on ignition, M – magnetic product, N – non-magnetic product). The XRD patterns are shown in Figs. 1 – 8, where used abbreviations mean (Hovorka and Spišiak, 1984): Magh – maghemite γ(gamma)-Fe_2O_3, Sdr – siderite $FeCO_3$, Qtz – quartz α(alpha)-SiO_2, Ank – ankerite Ca(Fe^{++}, Mg, Mn)$(CO_3)_2$, Ser – sericite and Chl – chlorite.

The Mössbauer spectra of magnetic products obtained at the lowest magnetic induction are illustrated in Figs. 9 to 10. An interpretation of Mössbauer spectra is given in Tables 9 – 10.

As it is shown in Tables 1 – 4 the cleaner magnetic products were obtained using wet way magnetic separation. Generally, the iron content is higher by 10 %, the SiO_2 content and LOI values are lower by 10 % and 3 – 5 %, respectively. A relatively high iron content in non-magnetic product and a low iron recovery into magnetic product advert to the iron loss in non-magnetic product.

These losses explain the results of mineralogical analyses. In all magnetic products, especially in those, which were obtained using the induction of 0.3T. The maghemite is accompanied by siderite. Thus, siderite not only lowers the Fe content in magnetic products as a carrier CO_2 in its lattice (as a LOI in chemical analysis), but also it is the cause of Fe losses in non-magnetic products due to its low magnetic susceptibility.

Firstly, with regards to low iron content in magnetic products, as it implies from the Table 9 in the case of the cleanest magnetic product obtained by dry way at 0.09T an 82 % of the total iron is bonded in the structure of maghemite. The rest of iron as a bivalent one is fixed in other minerals, above all in siderite, which was approved by XRD analyses. Similarly, as to magnetic product achieved using the wet way of separation, a share of iron in maghemite attains of 92.13 % (Tab. 10).

Secondly, with respect to iron losses siderite in all non-magnetic products was determined as a dominant mineral accompanied by quartz, sericite and ankerite.

Conclusion

The research on mineral composition of magnetic separation products at dust outlets upgrading was carried out with the purpose to determine the mineral phase distribution and to verify the conversion of siderite to

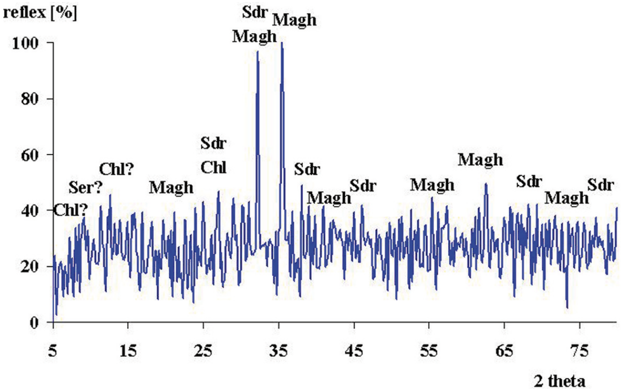

Fig. 1. XRD pattern of magnetic product obtained at 0.09T by dry way.

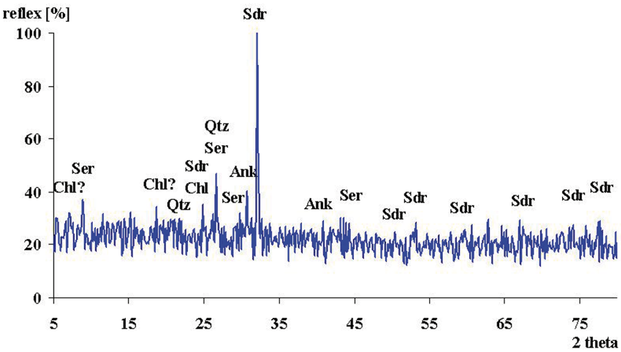

Fig. 2. XRD pattern of non-magnetic product obtained at 0.09T by dry way.

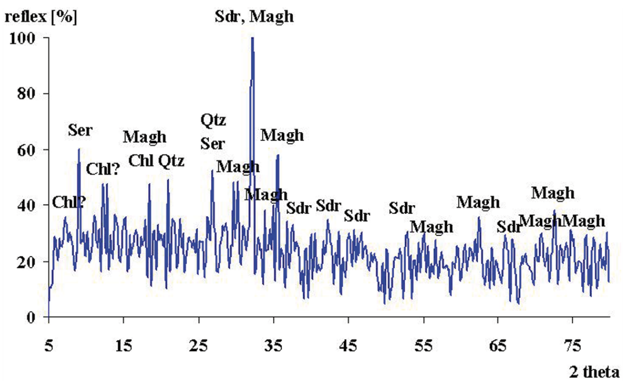

Fig. 3. XRD pattern of magnetic product obtained at 0.3T by dry way.

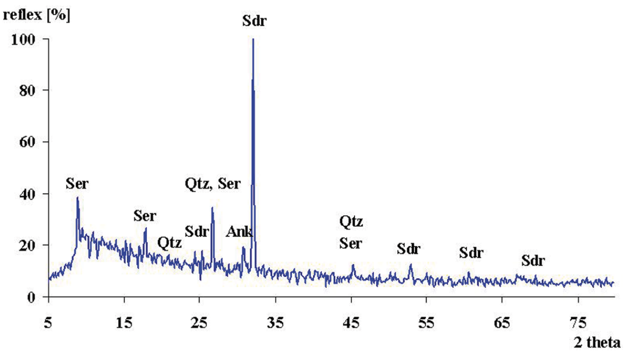

Fig. 4. XRD pattern of non-magnetic product obtained at 0.3T by dry way.

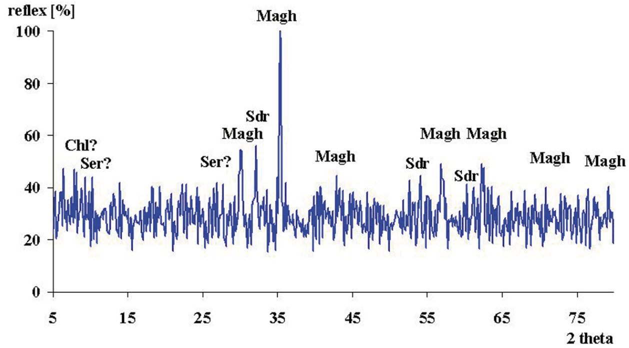

Fig. 5. XRD pattern of magnetic product obtained at 0.1T by wet way.

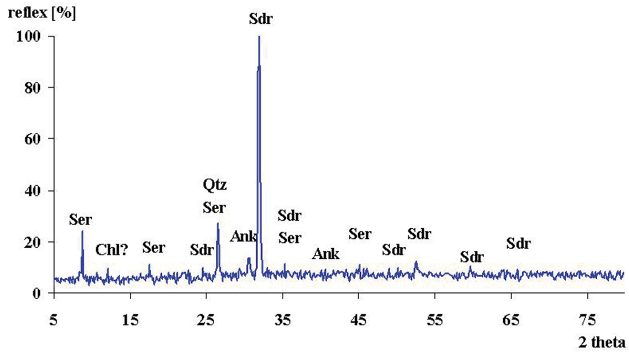

Fig. 6. XRD pattern of non-magnetic product obtained at 0.1T by wet way.

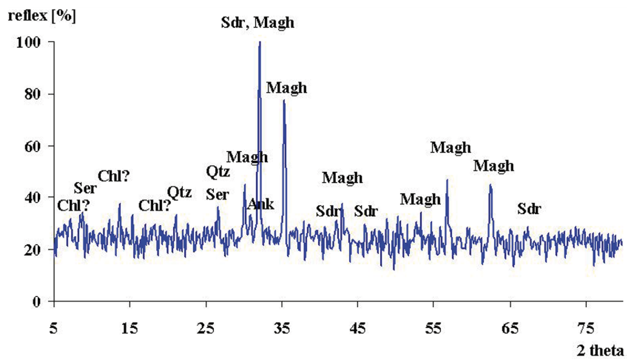

Fig. 7. XRD pattern of magnetic product obtained at 0.3T by wet way.

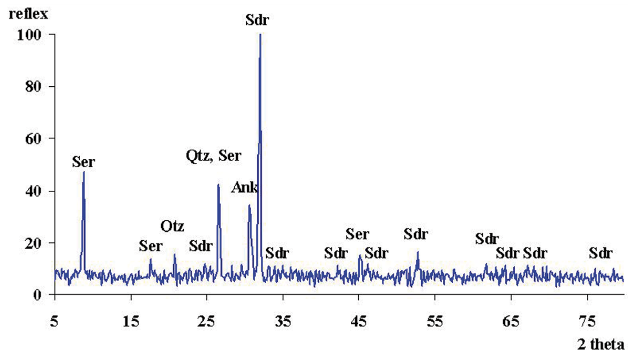

Fig. 8. XRD pattern of non-magnetic product obtained at 0.3T by wet way.

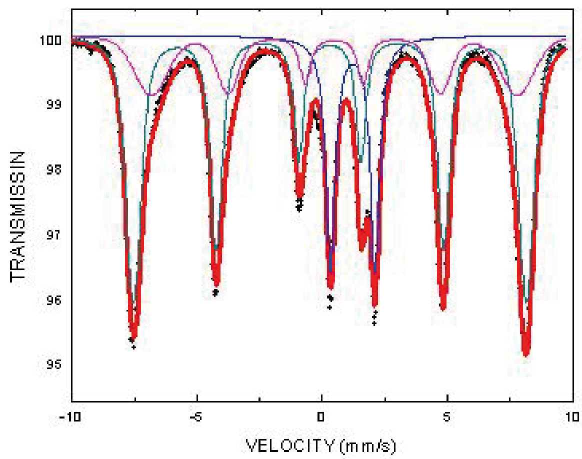

Fig. 9. Mössbauer spectrum of magnetic product obtained at 0.09T by dry way.

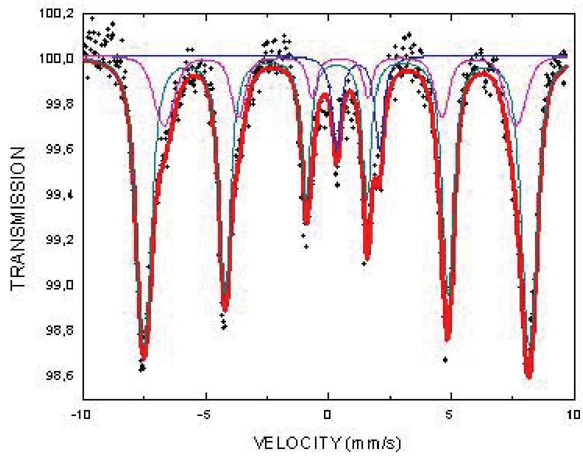

Fig. 10. Mössbauer spectrum of magnetic product obtained at 0.1T by wet way.

magnetic phases. Thus, chemical analyses, XRD study and Mössbauer spectroscopy were performed.

From viewpoint of Fe-concentrate quality it was proven that wet way of separation is preferable to dry one. In this way prepared magnetic products has higher iron content by 10 % and SiO_2 content was lower by 10 %.

The XRD study and Mössbauer spectroscopy confirmed the occurrence of siderite, which causes the unfavourable parameters of separation process. So, to prepare an iron concentrate of commercial quality and to prevent the iron losses in tailings it is needed the thermal pre-treatment of dust outlet aimed at the dead roasting of CO_2, i.e. the total conversion of siderite to magnetic phase such as maghemite and/or magnetite.

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Bioleaching of Ni from contaminated sediments of the water reservoir Ružín I using autochthonous bacteria and *Bacillus megaterium*

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Abstract

Water reservoir Ružín I on the territory of Eastern Slovakia is rich in sediments being contaminated with several heavy metals. They come from the mining and metallurgical industrial activities carried out near the water reservoir. This work is dealing with the study of the mobility of Ni between the liquid phase and sediment matrix. During the bioleaching processes carried out in the laboratory the conditions given by the environment of the dam were imitated and preserved also in the flasks. Bacterial species *Bacillus megaterium* were used to increase the efficiency of Ni bioleaching. The obtained results were compared with the activation of autochthonous microflora. Kinetics of bioleaching was measured for 40 days. The bioleaching of Ni in the presence of autochthonous microflora achieved higher intensity and effectivity as in the case of the application of *Bacillus megaterium*. Because of the known mobility of Ni in the sedimentary environment there is important to assess the risk of its inadvertent release into the aqueous solution. Bacterial dissolution of Fe was simultaneously monitored during the bioleaching processes, because the most of the Ni was present in the Fe oxides and hydroxides.

Key words: heavy metals, nickel, iron, bioleaching, heterotrophic bacteria, *Bacillus megaterium*

Introduction

Water reservoir Ružín I in the inlet of the Hornád river is one of the most affected localities in the Eastern Slovakia by the contamination by heavy metals (Hg, Pb, Cu, Ni, Co, Zn, As, Sb, Cd) because of the intensive mining and metallurgical activities in this area (Brehuv et al., 2005). Bottom sediments of this water reservoir even after the attenuation of the industrial activity present the important receptors of the pollution. The amount of the contaminated sediment deposited annually onto the bottom of the tank moreover brings about a risk in term of its functions´ restrictions. The issue of its work out and the next use means a poser also for experts. Contaminated sediments could be considered as a special waste classified into the 832 02 category by EWC (European Waste Catalogue and Hazardous Waste List). This category includes wastes inadvisable for disposal by thermal and physical-chemical processes. Treatment of these sediments is possible after their relocation to the dumping site, where the leaching and removal of undesirable metals could be ensured with biological processes. After the application of bioremediation technologies sediments are reusable for example in agriculture and building industry. Bioleaching of heavy metals from the contaminated sediments is affected by several physical-chemical and biological factors: character of contaminated particles, temperature, O_2 and CO_2 concentrations, pH, redoxpotential, composition of the medium, bacterial genus involved in the bioleaching process and its concentration (Chen et al., 2001). Depending on the character of the sediment particles, metals can be bound with them in various chemical forms, which in term of their mutual chemical interactions, mobility, bioavailability and potential toxicity, exhibit different properties (Singh et al., 2005). For the evaluation of the mobility of elements in water-sedimentary system usually the fractionation analysis of sediments called sequential extraction procedures is used (Vojteková et al., 2006). Sequential extraction method was proposed by Tessier et al. It allows to determine the fractionation of metals and to control their deposition into the environment and therefore to assess their potential impact on the aquatic biota and also to propose appropriate remediation techniques for their elimination (Korfali et al., 2004). This sequential extraction method includes the distribution of heavy metals into the following fractions: ionic exchange fraction, carbonate fraction, fraction of iron and manganese oxides, fraction of organic matter and sulphides and residual fraction containing alumosilicate components of the sediment (Tessier et al., 1979). Most of the metals presented in the sediment usually occur in the residual fraction. Under the normal experimental conditions, metals presented in this fraction are insoluble and with solid bindings. Therefore their presence in this form is considered as an indicator of the rivers´ system contamination (Singh et al., 2005). Oxides of iron and manganese, which usually occur in the form of films and

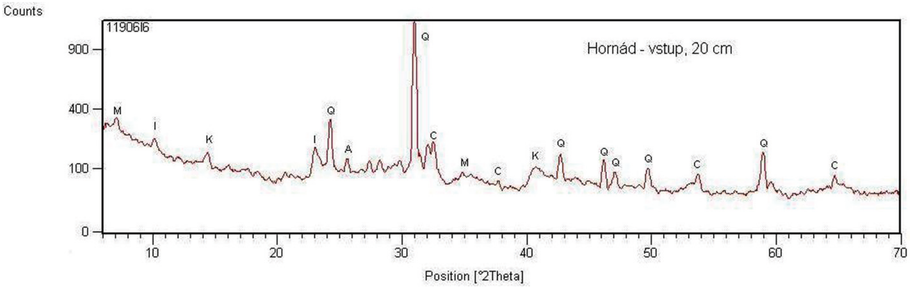

Fig. 1. Mineralogical composition of the sediment sample, depth 20 cm, X-ray analysis. Legend: C – chlorite, I – illite, K – kaolinite, A – albite, M 15 – montmorillonite 15A, M 22 – montmorillonite 22A, Q – quartz.

new-precipitated secondary minerals together with organic matter and clays, represent also an important component. Stated oxides preferentially adsorb or co-precipitate heavy metals occurring in the water column. From this point of view, they suppose to be the most effective surface-active phase of sediments (Hartley et al., 2004; Lombi et al., 2004).

The reactions of metals, which are important from an environmental point of view, take place in anoxic environment natural for the activity of dissimilatory chemoauthotrophic and heterotrophic microorganisms using metals as an analogue of O_2. The process of the reduction of iron and manganese by microorganisms, through reduction solubility of solid Fe (III) and Mn (IV) oxides, affects the conversion of the mineralogical composition of sediments and provides energy necessary for the growth of microorganisms (Lloyd, 2003). As a result of the release of Fe (III) as electron acceptors come to the influence of the mobility of toxic metals which are bonded with the stated minerals (Lovley et al., 2000). The changes of the mobility of metals remit to a certain degree of instability in an aquatic environment caused by the influence of microflora and the possibility of their entry and accumulation in the food chain links.

The purpose of this work is to promote understanding of the process of nickel mobility as one of the contaminants of sedimentary environments of the dam Ružín, depending on the mineralogical composition of sediment and activities of autochthonous microflora, or selected bacterial species in the laboratory conditions. Understanding, exploitation and regulation of this process in in-situ conditions provides a purposeful remediation method of sediments contaminated with heavy metals.

Material and methods

The samples of the sediment were collected from the sediments´ surface layer, depth 20 cm, in the coastal zone Ružín I Hornád – entry. Obtained samples were stabilized by deep-freezing (–15 °C) with an allowance to preserve the integrity of samples in accordance with ISO 5667-12.

The mineralogical composition of the samples was determined by X-ray diffraction analysis (Xpert Philips – Germany) and the content of Ni and Fe in the sediment matrix by atomic absorption spectrometry (AAS OPTION – spectrometer, AA – 30, Australia).

Effect of bacterial cultures and observed leaching medium for the extraction of heavy metals from the sediment was monitored during the bioleaching processes carried out in Erlenmeyer flask with the volume 1 000 ml at 25 °C for 40 days partially aerobically in the static conditions. Erlenmeyer flasks´ content consisted of 30 g sediment, 600 ml of sterile nutrient medium and bacterial inoculum with a concentration of 10^{10} cfu/ml. Gradual changes in the metal concentrations observed in the nutrient media were monitored in four day intervals by the atomic absorption spectrometry (AAS Varian AA-Z 240 with GTA-120 and AA 240-FS, Australia). The monitoring of the bioleaching processes revealed the kinetics of Fe and Ni extraction and also the activity of bacterial strains and as demonstrated below it allows the precise timing of the subsequent repeated exchanges of bioleaching medium. The purpose of this procedure was to achieve the highest removable metal leaching from the matrix sediment with bacterial activity.

Bacterial species *Bacillus megaterium* used in the bioleaching process has been isolated from the samples of sediments and identified by BBL identification system (Becton – Dickinson, USA). Bacterial cells were cultivated on nutrient agar No. 2 (Imuna Šarišské Michaľany) at 28 °C for 18 hours and centrifuged at 5 000 rpm for 15 minutes. Consequently the cell suspension was washed by physiological solution and added at concentration 10^{10} into the Ashby´s solution (glucose 2g/100 ml $(NH_4)_2SO_4$, K_2HPO_4, $MgSO_4 \cdot 7\,H_2O$, NaCl). The changes in pH during the bioleaching process were measured by potentiometry at PHM 210 METERLAB (France).

The sequential extraction of metals from sediments was performed according to Tessier et al. (1975). Homogenized sediment samples of the quantity of 1 g were dried at 105 °C for 5 hours. They were subsequently agitated with the extractant and centrifuged at 5 000 rpm for 10 min. Supernatant was purified by decantation. Aroused pellet was purified with the distilled water. This process was repeated for using different extraction reagents. The essential characteristic of each extraction solution presents

Tab. 1
Extraction agent used by sequential extraction method according to Tessier (Tessier et al., 1979; Lake, 1987; Pickering, 1986)

Fraction	Extraction solution
Exchangeable	1M $MgCl_2$
Carbonates	1M NaOAc, HOAc
Iron and manganese oxides	0.04 M $NH_2OH \cdot HCl$ in 25 % HOAc
Organic matter	0.02 M HNO_3 in 30 % H_2O_2
Residual	mixture 5 : 1 HF and $HClO_4$

Tab. 2
Physical – chemical characteristics of the sediment sample

Sample	TOC (%)	pH	Eh (mV)	Dry weight (%)
Ružín I	4.05	7.13	341.4	57.02

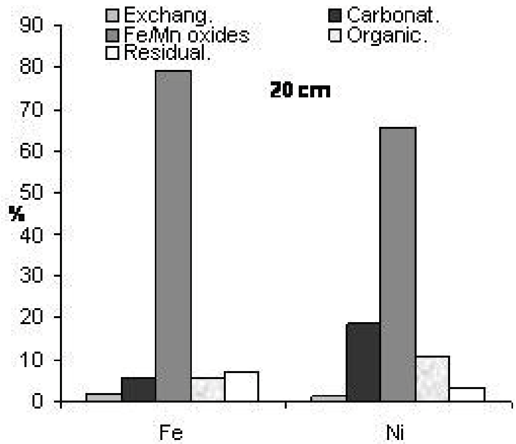

Fig. 2. The effectivity of Fe and Ni extraction by using a sequential extraction by Tessier.

its ability to minimize the dissolution of other fraction, than it is intended. Extraction reagents used during the sequential extraction of metals from sediments are listed in Tab. 1.

Results and discussions

The mineralogical composition of sediment shown in Fig. 1 confirms its alumosilicate character with a dominance of quartz and amorphous phases indicating the presence of Fe oxides and hydroxides. From the mineralogical point of view there was found, that the composition of the sediment represents an environment offering optimal conditions for the growth of so–called “silicate bacteria” including *Bacillus megaterium*.

The top layer of the sediment represents the contact zone between the liquid and solid phases of the sedimentary environment. It reflects the current load of sediments with occurring contaminants. Depending on changes of the physical-chemical properties of the environment, the top layer of the sediment represents a risk metal release into the liquid phase and their subsequent incorporation into the food chain links. The total content of the organic matter, representing 4.05 % (Tab. 2) is able to adsorb a certain amount of Ni that is reversibly releasable from this phase back into the environment. Humic substances enter by the activity of indigenous species of heterotrophic bacteria into the biochemical reactions with an indirect mechanism of the reduction of insoluble Fe (III) to Fe (II). Anaerobic conditions, pH values close to the neutral and the presence of a sufficient amount of organic material could admit the activity of bacterial species supporting the mobility of Ni in the sedimentary environment.

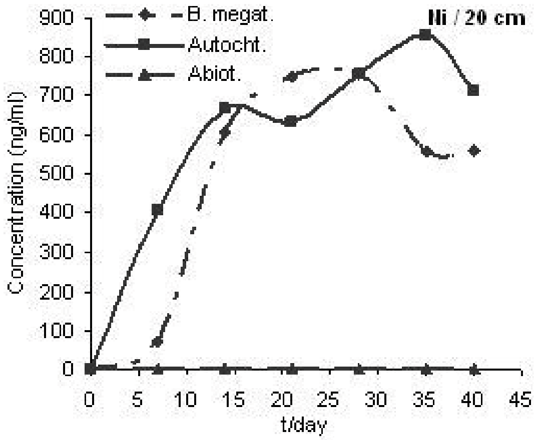

Fig. 3. The kinetics of the bioleaching of Ni.

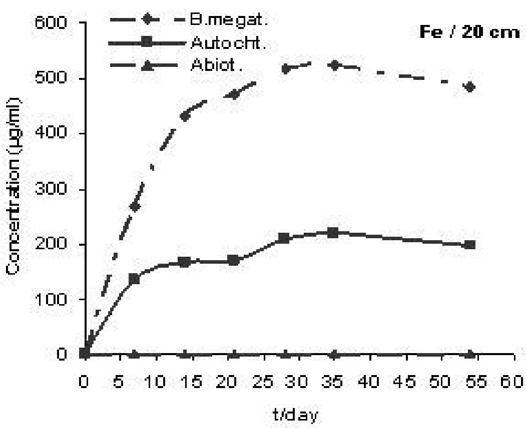

Fig. 4. The kinetics of the bioleaching of Fe.

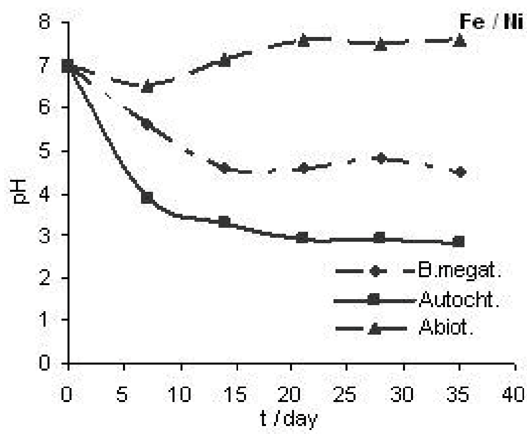

Fig. 5. The kinetics of pH in the bioleaching system.

Fig. 2 describes the binding options of Ni in particular fractions of the sediment and demonstrates its dominant presence (66.36 %) in the fraction of Fe and Mn oxides and hydroxides. These oxides are found in the sediment between particles of other minerals, either as a thin film or as individual particles. In anoxic conditions they are characterized by thermodynamic instability. They have an excellent ability to bind several heavy metals preferentially in their structure. The activity of Fe (III) reducing microorganisms causes changes in the structure of alumosilicate components and also in the structure of amorphous Fe oxides, which is leading to the release of Ni into the liquid phase. Understanding the process of mobilization of Ni and the possibility of its regulation permits the utilization of indigenous or inoculated bacterial species for the bioleaching processes of Ni. The task of the experiment was to determine the effectivity of the bacterial species *Bacillus megaterium* in the releasing of Ni and Fe from the sediment matrix in comparison with using the autochthonous microflora. The maximum concentration of Ni in solution was recorded in 27th day at bioleaching by bacterial species *Bacillus megaterium*, and 35th day at bioleaching by autochthonous microflora. Kinetics of Ni and Fe bioleaching processes in term of the time did not correspond to each other. For the Fe in both cases the maximum concentration was reached in 27th day of bioleaching. Comparing the overall extraction efficiency, the maximum efficiency was achieved by using bacterial species *Bacillus megaterium* by bioleaching of Ni and activation of autochthonous microflora was efficient by bioleaching of Ni (Figs. 3 and 4). The decrease of Ni and Fe concentration in the bioleaching medium was related to the accumulation of metabolites of heterotrophic bacterial species (fatty acids), which reduced the pH of the bioleaching system. It causes a decrease in activity of presented microflora and also the extraction of metals into the solution. The decrease in pH, as shown in Fig. 5 refers to the production of fatty acids in to bioleaching process.

Conclusions

The determination of bioleaching kinetics in a 45--day interval is important for the finding of the time of the maximum activity of the presented microflora in the process of metal leaching in specified conditions and also in the term of time for the bioleaching medium exchange at the subsequent discontinuous bioleaching before the decrease of the extraction.

Bioleaching system without bioaugmentation (Control) and without addition of bioleaching medium showed at absence of Ni and Fe in the liquid phase (Figs. 3 and 4). Control in Fig. 5 showed the buffering capacity of sediment during the monitoring of metals mobility. Ashby´s mineral medium with the addition of glucose as organic carbon source led to an increasing mobility of Ni and Fe in bioleaching system caused by the activity of indigenous heterotrophic bacterial species. The inoculation of bacterial species *Bacillus megaterium* in symbiosis with the autochthonous microflora in stated conditions showed the highest efficiency in bioleaching of Fe from the sediment. The bioleaching of Ni was efficiently by using of autochthonous microflora. According to these results, bioleaching of the sediments could be still an actual issue for the next studies.

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Possibilities of processing and utilization of tailings from the settling pit nearby the Rudňany village (Eastern Slovakia)

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Abstract

The contribution deals with the mineral and chemical composition of the sandy tailings in the settling pit nearby the Rudňany village. The distribution of the mineral components in the pit body and their zonation in the dependence on beneficiation technologies change during the siderite, tetrahedrite and barite concentrates production are described. The results of magnetic separation and flotation of sands from the pit and the flowsheet proposal of wasteless processing technology are also presented.

Key words: settling pit, tailings, magnetic separation, flotation, flowsheet

Introduction

The tailings coming from the mining and mineral processing technologies are considered to be the secondary raw materials. They often contain utility components of interesting grade being a result of application of obsolete technologies in the past. Their complex utilization is significant for national economics not only from the economic point of view but also from the ecological one. The tailings represent already disintegrated material of the various grain sizes, i.e. lumpy, coarse, fine-grained, often flotation fineness, which are deposited on the surface as refuse piles and settling pits. Thus, as to their further use the operations of crushing and grinding will be reduced or they may be totally excluded from the technological flowsheet. Moreover, an excavating of these materials on the surface is less expensive than the underground mining of the ores. For these reasons the processing of such secondary materials may bring a profit despite of lower content of utility components in comparison with the crude ores. Taking it all, a removal of dumping areas results in the reduction of harmful loading, unfavourably influencing the environment.

Characteristics of the Rudňany settling pit

The settling pit nearby the Rudňany village was managed by the so-called New industrial plant (mineral processing plant) of the former Rudňany branch of closed Iron Ore Works, Inc., later ŽELBA, Inc., Spišská Nová Ves. It was formed by the silting-up of the tailings coming from the processing of complex siderite-sulphidic and barite-sulphidic ores exploited in the Rudňany and Poráč-Zlatník deposits in 1963 – 2003. The ore processing consisted of crushing, grinding, classifying, gravity concentration, magnetic separation, flotation and also roasting.

The settling pit is located in the cadastral districts of the Markušovce and the Závadka villages in the bottom part of the Markušovce valley. Its area is of 35.1 hectares, the length attains of 1,085 meters and the width ranges from 165 to 345 metres. The thickness of deposited materials varies in the dependence on initial ground levels and it may achieve maximally about 38 metres. The settling pit is bounded by the natural ground level of the valley and also by three earthen dams. There is no water stream there. Recently, the settling pit is in operation. The tailings from the flotation of the barite ore exploited in the Rudňany deposit are silting-up on the back part of settling pit opposite the key dam.

Altogether 9,800,000 tons of the tailings of so-called flotation sands at a density of 1.59 $t \cdot m^{-3}$ and a total volume of 6,200,000 m^3 are deposited in the settling pit. The presented data has been calculated on the basis of statistical observation of deposited tailings amount, i.e. the increases by silting-up and the decreases caused by the excavation of sands from the settling pit (Karoli et al., 2008).

Naturally, the deposited tailings come from lodestuff and accompanying rocks of exploited deposits. Firstly, as to minerals from the lodestuff, the quartz, siderite, barite, dolomite, ankerite, tetrahedrite, chalcopyrite and pyrite are present as dominant minerals. Moreover, albite, specularite and fuchsite also occur. Secondly, as to accompanying rocks, basalts, basalt tuffites and pelitic metasediments, namely graphite phyllites prevail. Paragneisses, chlorite phyllites, sandstones, conglomerates and hydrothermally

Tab. 1
Model material balance recalculation of the Rudňany settling pit

layer / years	weight of layer [t] / part by weight in settling pit [%]	volume density of layer [$t.m^{-3}$]	$BaSO_4$	Fe	Cu
			content of component in layer [%] / weight of component in layer [t] / part by weight in layer [%]		
upper layer	2,789,409	1.42	13.01	17.23	0.054
1985 - till now	28.34		353,525	480,588	1,509
			20.17	23.61	24.76
middle layer	3,835,823	1.40	17.39	21.77	0.071
1975 - 1984	38.98		666,905	835,083	2,723
			38.04	41.04	44.68
bottom layer	3,215,768	1.89	22.78	22.37	0.058
1963 - 1974	32.68		732,621	719,496	1,862
			41.79	35.35	30.56
sum / average	9,841,000	1.54	17.81	20.68	0.060
	100.00		1,753,051	2,035,167	6,094
			100.00	100.00	100.00

Tab. 2
Grain size and chemical analysis of the material from settling pit

grain size [mm]	mass yield [g]	mass yield [%]	content [%] Fe	content [%] SiO_2	content [%] $BaSO_4$	content [%] Cu	recovery [%] Fe	recovery [%] SiO_2	recovery [%] $BaSO_4$	recovery [%] Cu
+1.000	90.0	0.86	13.65	31.49	6.69	0.089	0.77	0.72	0.71	1.74
0.500 – 1.000	190.0	1.81	8.22	49.85	0.64	0.033	0.98	2.40	0.14	1.35
0.160 – 0.500	2,930.0	27.92	10.68	48.48	2.74	0.035	19.55	36.01	9.43	22.16
0.090 – 0.160	2,458.0	23.42	15.92	34.37	8.24	0.030	24.45	21.42	23.79	15.93
0.071 – 0.090	566.0	5.39	19.52	31.21	12.10	0.052	6.90	4.48	8.04	6.36
0.020 – 0.071	2,022.0	19.26	17.82	36.03	9.98	0.047	22.50	18.46	23.70	20.53
– 0.020	2,240.0	21.34	17.76	29.07	12.99	0.066	24.85	16.51	34.18	31.94
feed	10,496.0	100.00	15.40	38.12	8.11	0.046	100.00	100.00	100.00	100.00

altered varieties of these rocks are also often present. An average chemical composition may be characterized by the results of the semiquantitative analysis as follows:

$10^2 – 10^1$ Fe, Si
$10^1 – 10^0$ Al, Ba, Ca, Mg, Mn
$10^0 – 10^{-1}$ Cu, K, Na, Ti
$10^{-1} – 10^{-2}$ Hg, Sb, Sr, Zn
$10^{-2} – 10^{-3}$ B, Co, Cr, Ni, Pb, V, Ag, Be, Ga, Sn

Thus, the major elements represent: Fe, Si, Al, Ba, Ca, Mg and Mn. All these elements are bonded in the above mentioned dominant utility and the gangue minerals of exploited deposits. The content of the non-ferrous heavy metals in order may attain about $10^{-0} – 10^{-3}$ %. These metals are bonded in the insoluble form, namely in sulphides.

On the basis of data about the amounts and quality of deposited tailings a study on material balance and composition of individual layers of the settling pit has been carried out. So a performance of the settling pit was divided to two periods (Jančura and Čechová, 2001):

– 1st period – from 1963 to 1974, so called "old settling pit",

– 2nd period – from 1975 to present time, after realization of the project on the capacity increase of the settling pit in 1974.

Naturally, as time goes on a material of various qualities in the dependence on the changes in the level of treatment techniques as well as on the feed quality to mineral processing plant was gradually deposited. Thus, from a viewpoint of barite content, the settling pit may be divided into three layers (Jančura and Čechová, 2001):

1) Bottom layer, so called "old settling pit", formed during the first stage of silting-up in the border of original dams (1963 – 1974);

2) Middle layer, which was formed by the silting-up the "old settling pit" after capacity increase (1975 – 1984);

3) Upper layer, so called "low grade cover" characteristic by the decreased content of utility components as a result of an improvement of technological parameters of the magnetic separation and flotation (1985 – recent).

A total amount of material, its volume density, content of components and their part by weight and percentage in individual layers were determined. The results are introduced in Tab. 1.

Statistical average annual values of barite content monitored during the years of 1963 – 2000 show significant differences, which result in various content of barite in individual layers. For instance the difference between the bottom and middle layer is of 5.39 %, and between the bottom and upper layer it attains 9.77 %. Similarly, the distribution of iron and copper in the settling pit is very variable, too. So from the viewpoints of the content and spatial distribution of the utility components in the settling pit it can be regarded as a non-uniform body. Further detailed prospecting, using suitable wells density will enable the cost-effective utilization of the material from the settling pit.

The reserves of the barite ore in the Rudňany deposit will be mined out during several years (Karoli et al., 2008). But the production of the barite concentrate can continuously carry on after solving and designing technology for the processing of the flotation sands from the settling pit. Owing to verification, the behaviour of flotation sands during their processing, the laboratory analyses and experiments on their upgrading were performed (Kovaničová et al., 2001).

Mineralogical and chemical analyses of flotation sands

Microscopic study was carried out with the aim to determine a grade of the mineral liberation. Thus, 95 – 100 % of barite, siderite, quartz and slates in the grain size class under 0.5 mm are liberated. The liberation grade of sulphides was investigated in more details. So in a grain size class of 0.16 – 0.50 mm the liberation is of 80 – 90 %, in a class of 0.09 – 0.16 mm it runs of 95 – 100 % and finally in a class of 0 – 0.09 mm it attains almost 100 %. The obtained results point to the fact that mineral components of the flotation sands are sufficiently liberated and therefore no further grinding is needed.

The chemical composition of sands as a dependence on a grain size was studied. The results of the grain size and chemical analyses as well as the recoveries of observed components into the grain size classes are presented in Tab. 2.

An upgrading of sands using classifying techniques is impossible because no significant concentration of any component in a grain size class was observed. On the other side a portion of grain size classes under 0.5 mm, i.e. the classes with sufficiently liberated minerals attains of 97.33 %. On the basis of this fact a successful application of separation method may be expected.

Results of separation and discussion

Owing to the chemical and mineral composition of sands, the physical and physical-chemical properties of dominant minerals an obtaining of siderite and barite concentrates as well as tailings, containing quartz and slates applicable as building material may be considered. Firstly, the magnetic separation was applied with the aim to prepare the siderite concentrate in a magnetic product. Secondly, a non-magnetic product was subjected to flotation to obtain the barite concentrate in a floating product and quartz-bearing tailings in a cell one. The results of laboratory experiments on magnetic separation and flotation are introduced in Tabs. 3 and 4, respectively.

The application of the magnetic separation resulted in almost twofold enhancement of the iron content in the magnetic product in comparison with the feed quality. Similarly, the recovery of iron into magnetic product and on the other side the recoveries of SiO_2 and $BaSO_4$ into a non-magnetic product achieved appropriate values.

Tab. 3
Average parameters of magnetic separation – laboratory experiment

product	mass yield	content [%]			recovery [%]		
	[%]	Fe	SiO_2	$BaSO_4$	Fe	SiO_2	$BaSO_4$
magnetic	44.40	27.90	18.28	1.59	83.47	20.48	8.68
non-magnetic	55.60	4.41	56.68	13.35	16.53	79.52	91.32
feed	100.00	14.84	39.63	8.13	100.00	100.00	100.00

Tab. 4
Average parameters of flotation – laboratory experiment

product	mass yield	content [%]			recovery [%]		
	[%]	Fe	SiO_2	$BaSO_4$	Fe	SiO_2	$BaSO_4$
concentrate	12.04	0.76	1.57	91.30	2.07	0.34	82.34
tailings	87.96	4.91	64.22	2.68	97.93	99.66	17.66
feed	100.00	4.41	56.68	13.35	100.00	100.00	100.00

Tab. 5
Average parameters of flotation – full-scale experiment

product	mass yield	content [%]			recovery [%]		
	[%]	Fe	SiO_2	$BaSO_4$	Fe	SiO_2	$BaSO_4$
concentrate	25.52	0.64	0.71	96.99	4.66	0.36	91.61
tailings	74.48	3.73	67.02	3.05	95.34	99.64	8.39
feed	100.00	3.50	50.10	27.02	100.00	100.00	100.00

As to flotation test a relatively high-grade barite concentrate has been obtained. The content of $BaSO_4$ in floating product was almost by sevenfold higher compared to feed. A high recovery of barite into floating product at small mass yield was also attained.

So, independently on laboratory tests a full-scale experiment on flotation of non-magnetic product was performed. It is needed to mention that a fed sample of non-magnetic product was of higher quality than one fed during the laboratory test. This fact resulted in better quality of floating product as it is presented in Tab. 5.

On the basis of laboratory and full-scale experiments a wasteless technology was proposed. The flowsheet of processing technology is introduced in Fig. 1. The flowsheet covers the obtaining of all utility components but it must be stated that at given time and prices some products are not marketable.

Conclusion

The laboratory magnetic separation and flotation tests and the full-scale flotation experiments applied in the processing of flotation sands from the Rudňany settling pit showed that it is possible to produce siderite and high--grade barite concentrate as well as the quartzy sands utilizable in the building industry.

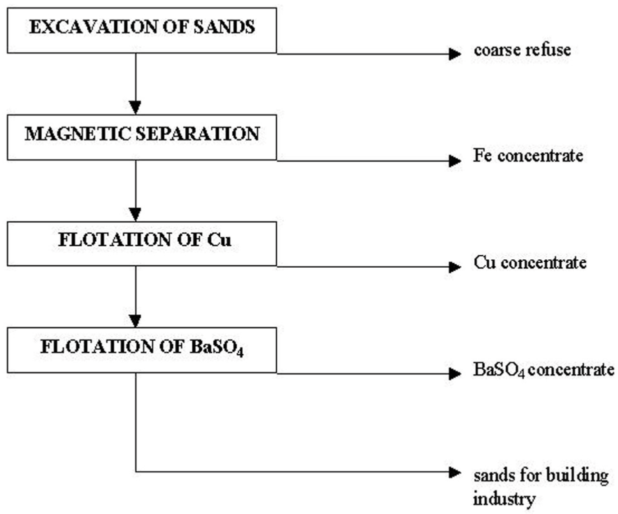

Fig. 1. Processing technology flowsheet.

Recently, the obtaining of high-grade barite concentrate and sands for building industry is a foreground task. The iron and copper-bearing sulphide concentrates are not saleable now. But a necessity of their winning arises from the requirements for commercial quality of barite concentrate and sands for building industry to avoid a contamination of the final products above all by sulphides.

The realization of flotation sands processing from the settling pit will results in:

– Upgrading onto industrially utilizable products;

– Improvement in utilization effectiveness of engineering facilities;

– Offering of job opportunities in the region by continuing of present productive activity;

– Reduction of ecological loading in the Rudňany village surrounding.

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Flotation of river-born sediment from the old ecological load of Černý příkop in Ostrava, Czech Republic

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Abstract

The paper deals with an evaluation of the flotation application suitability in the sludge decontamination from the Černý příkop situated in the city of Ostrava. We used Montanol 551 as a flotation collector, which are commonly used in coal mineral processing. The water quality in the Černý příkop is predominantly determined by the quality of the discharged water from the Ján Šverma Coking Plant, MCHZ (chemical industry) and the water from the Central Waste Water Treatment Plant for Ostrava, which participate in the course aquosity with two thirds. Application of the flotation is used as a new quick method of decontamination of organic pollutants as PAHs, PCBs and petroleum hydrocarbons C_{10} – C_{40}. Flotation of organic pollutants is very effective and more than 90 % of hydrocarbons C_{10} – C_{40}, 70 % of PCB and 70 % of PAH from the sediments was removed.

Key words: flotation, PAHs, PCBs, Petroleum hydrocarbons C_{10} – C_{40}

Introduction

Organic pollutants belong among the most ubiquitous in our environment. They have accumulated because of a variety of anthropogenic causes and because of their greater hydrophobicity (i.e., their lack of solubility in the water). The organic chemical industry, which manufactures the carbon-containing chemicals, produces an enormous number of materials that are essential to the economy and to the modern life. This industry obtains raw materials from the petroleum industry and converts them to the intermediate materials or basic finished chemicals. Organic chemical industries are among the largest producers of the toxic wastes (Mukesh et al., 2005). The high content of organic pollutants such as PAHs, PCBs and petroleum hydrocarbons C_{10} – C_{40} in the sediments is real problem in the city of Ostrava. These pollutants have entered into the sediments predominantly from the waste water from both the above mentioned sources, larger part being from the Ján Šverma Coking Plant and probably there is a seepage from the industrial premises of the Ján Šverma Coking Plant and the near-by petroleum oil lagoons Ostramo, which affect the content of hydrocarbons C_{10} – C_{40} and PCB in the sediment.

Organics, which include polycyclic aromatic hydrocarbons (PAHs), chlorinated aromatic hydrocarbons, chlorinated aliphatic hydrocarbons, halogenated hydrocarbons, biphenyls, phenols, aniline derivatives, phenol ethoxylates, and benzoic acid derivatives, are ubiquitous in our environment. Both anthropogenic and natural causes are known for their accumulation. They are found in the water, marine systems, soil, sewage, and air. These are the most common pollutants and are known to persist in the environment. Some of them, such as the PAHs, are potential carcinogens. All of them are reported to have adverse effects on the human and animal health. Some of these, like the polyhalogenated aromatics, are chemically inert and therefore can only be degraded by biological means. The degradation could be either by aerobic or anaerobic pathways. A brief outline of both these pathways is necessary to be able to design suitable degradation pathways for a given contaminant (Simpson et al., 1995). Hydrocarbons C_{10} – C_{40} represent a term used to describe a several hundred chemical compounds that originally come from the crude oil. Crude oil is used to make petroleum products, which can contaminate the environment. Because there are so many different chemicals in the crude oil and in other petroleum products, it is not practical to measure each one separately. However, it is useful to measure the total amount of hydrocarbons C_{10} – C_{40} at a site. Hydrocarbons C_{10} – C_{40} are a mixture of chemicals, but they are all made mainly from the hydrogen and carbon, called hydrocarbons. Scientists divide hydrocarbons C_{10} – C_{40} into groups of petroleum hydrocarbons that act alike in soil or water. These groups are called petroleum hydrocarbon fractions. Each fraction contains many individual chemicals. Some chemicals that may be found in hydrocarbons C_{10} – C_{40} are hexane, jet fuels, mineral oils, benzene, toluene, xylenes, naphthalene, and fluorene, as well as other petroleum products and gasoline components (Li et al., 2002).

Polychlorinated biphenyls (PCBs) are mixtures of up to 209 individual chlorinated compounds (known as congeners). There are no known natural sources of PCBs.

Tab. 1
Organic pollutant content in the sediment solids from the Černý příkop (mg · kg^{-1} solids)

Benzene	BTEX	EOX	$C_{10} – C_{40}$	Tetrachlorethene	Trichlorethene	PAH(15)	PCB(6)
3.58	8.722	14.4	2880	0.76	1.06	541	0.644

Notes: PCB (congeners 28, 52, 101, 138, 153, 180), BTEX (volatile organic compounds – benzene, toluene, ethylbenzene and xylenes), EOX – organic halides extractable by a specified organic solvent

PCBs are either oily liquids or solids that are colourless to light yellow. Some PCBs can exist as a vapor in air. Flotation has not been applied in the cleaning of organically contaminated soils and sediments in the Czech Republic so far. In the CR there are only references on the application of flotation predominantly in the cleaning of oiled water which can be found in the textbooks on the theory of flotation (Kmeť, 1986; Fečko et al., 2009).

Description of the Černý příkop locality

The Černý příkop rises in Ostrava, the municipality of Mariánské Hory, located approximately 230 m above sea level. It runs through the city district of Moravská Ostrava and Přívoz and near the confluence of the Odra and Ostravice rivers it flows into the Odra river. The course is about 5 km long and Q355 is 0.074 m^3 · s^{-1}. Waste water from the Ján Šverma Coking Plant and the Central Waste Water Treatment Plant for Ostrava (UCOV) is discharged into the Černý příkop. The average value of BSK5 in 2007 was 7.2 mg · l^{-1} (4th quality class) and CHSK 37.5 mg · l^{-1} (5th quality class). Also the parameter of ammoniated nitrogen of 3.28 mg/l places this water course into the 5th quality class. Out of the monitored parameters only total phosphorus (0.25 mg · l^{-1}) and electrolytic conductivity of 122 mS · m^{-1} are placed into the class 3. The water quality in the Černý příkop is predominantly determined by the quality of the discharged water from the Ján Šverma Coking Plant (0.014 m^3 · s^{-1}) and the water from the Central Waste Water Treatment Plant for Ostrava (0.038 m^3 · s^{-1}), which participate in the course aquosity with two thirds.

Within the construction of D 47 motorway a partial relocation of the water course into a new bed (2.47 km) had been planned below the waste water discharge from the Ján Šverma Coking Plant. The relocation of the water course also required a removal of the sediments. The sediment reached the thickness of 1.8 m, the average thickness of the sediment in the bed was 1.2 m and the minimum thickness of the sediment was 0.2 m (shipyard). The sediment comprised of organic pollutants in the concentrations (see Tab. 2), which prevented its dumping on a disposal site. Also the content of organic carbon in the sediment solids (30.82 %) was the second key parameter, which limited its dumping on a disposal site (5 % TOC). The content of heavy metals in the water extract meets the requirements of Regulation 294/2005 Coll. The problem sediment pollutants are mainly PAH, PCB and petroleum hydrocarbons $C_{10} – C_{40}$.

With regard to the fact that the content of the organic pollutants in the solids exceeded (see in Tab. 1) the limits for dumping this waste on disposal sites a suitable decontaminating technology had to be selected, which would permit a safe disposal of the waste on the disposal site or a new method of utilization of the decontaminated sediment (e.g. for land reclamation).

Materials and methods

Mineralogical composition of the Černý příkop sediment

Four samples of sediments from different sampling points were taken. The mineralogical composition analysis of the samples was carried out on an all-levels sample. An X-ray diffraction analysis was done in the laboratories of the Institute of Geological Engineering at VŠB-TU Ostrava. The measurements were carried out on a modernized, fully automated diffractometer URD-6 (Rich. Seifert-FPM, SRN). The following phases were identified on the samples in question: ankerite, chlorite, kaolinite, muscovite, orthoclase, plagioclase, amorphous, quartz (see Fig. 1).

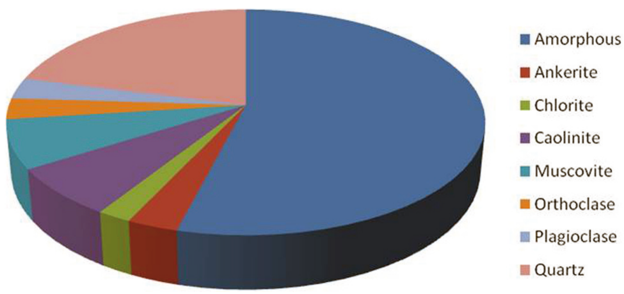

Fig. 1. Mineralogical composition of the Černý příkop sediments.

Flotation experiments

The flotation experiments were carried out in the laboratories of the Institute of Environmental Engineering at the VŠB-TU Ostrava on a flotation machine VRF-1, a product of RD Příbram with an active capacity of 1 litre, under the following conditions:

- Condensation: 150 g · l^{-1}
- Montanol 551 collector dose: 500 g · t^{-1}
- Pulp collector agitation: 2 min.
- Flotation time: 10 min.

Tab. 2
Flotation results – Sampling point 1

Product	Yield	Content			Recovery		
		PAH	Σ PCB	$C_4 - C_{10}$	PAH	Σ PCB	$C_4 - C_{10}$
	%	$mg \cdot kg^{-1}$	$mg \cdot kg^{-1}$	$mg \cdot kg^{-1}$	%	%	%
K1	67.23	6 293	0.458	4 636	74.49	87.72	95.99
O1	32.77	293	0.396	1 812	25.51	12.28	4.01
P	100	5 061	0.351	3 065.4	100.00	100	100

Notes: K – concentrate, O – tailings, P – feed

Tab. 3
Flotation results – Sampling point 2

Product	Yield	Content			Recovery		
		PAH	Σ PCB	$C_4 - C_{10}$	PAH	Σ PCB	$C_4 - C_{10}$
	%	$mg \cdot kg^{-1}$	$mg \cdot kg^{-1}$	$mg \cdot kg^{-1}$	%	%	%
K2	59.91	1 493	0.348	106	78.66	69.04	78.14
O2	40.09	934	0.206	50	21.34	30.96	21.86
P	100	1 276	0.302	85.15	100	100.00	100.00

Notes: K – concentrate, O – tailings, P – feed

Tab. 4
Flotation results – Sampling point 3

Product	Yield	Content			Recovery		
		PAH	Σ PCB	$C_4 - C_{10}$	PAH	Σ PCB	$C_4 - C_{10}$
	%	$mg \cdot kg^{-1}$	$mg \cdot kg^{-1}$	$mg \cdot kg^{-1}$	%	%	%
K3	57.12	1 082	0.330	4 607	68.75	69.56	78.647
O3	42.88	710	0.219	1 819	31.25	30.44	21.353
P	100	899	0.271	3 065.4	100.00	100.00	100

Notes: K – concentrate, O – tailings, P – feed

Tab. 5
Flotation results – Sampling point 4

Product	Yield	Content			Recovery		
		PAH	Σ PCB	$C_4 - C_{10}$	PAH	Σ PCB	$C_4 - C_{10}$
	%	$mg \cdot kg^{-1}$	$mg \cdot kg^{-1}$	$mg \cdot kg^{-1}$	%	%	%
K4	61.10	641	0.327	< 0.5	78.96	58.08	–
O4	38.90	222.7	0.367	< 0.5	21.04	41.92	–
P	100	496	0.344		100.00	100.00	–

Notes: K – concentrate, O – tailings, P – feed

Results and discussion

Having finished the flotation, the flotation products (both the concentrate and the tailings) were filtered, dried and underwent chemical analyses for PAHs, PCBs and hydrocarbons $C_{10} - C_{40}$, which were carried out in the laboratories of VÚHU, a. s. in Most. The flotation experiments were done on 4 samples from different sampling points. First sample was removed near from pollutant outlet water from the Ján Šverma Coking Plant and MCHZ Borsodcem. Another samples were removed in 200 m intervals. Fig. 2 shows first sampling point.

The results of flotation experiments (see Tabs. 2 and 5) imply that flotation applied on the samples in question is very effective and the obtained results are excellent. Applying flotation a high recovery of polluting material in the concentrates was succeeded in. The results confirm that the sediments drawn in closer sites to the industrial premises contain much larger proportions of pollutants than the sediments from more remote sites from the pollution sources. In the sample No. 1, in the case of which the highest pollutant concentrations were measured, the efficiency of flotation was 74 % for PAHs, 95 % for hydrocarbons $C_4 - C_{10}$ and 87 % for PCBs. In the sample No. 2, which was drawn from a site situated 200 m from the first sampling point, lower pollutant concentrations were measured. By means of flotation it was possible to remove 68 % of PAHs, 78 % of hydrocarbons $C_4 - C_{10}$ and 69 % of PCBs. The third sampling point was 400 m from the discharge. The efficiency of flotation was 78 % for PAHs, 78 % for hydrocarbons $C_4 - C_{10}$ and 69 % for PCBs. The fourth sampling point was situated 600 m from the discharge. The efficiency of flotation was 74 % for PAHs and 58 % for PCBs. The content of hydrocarbons $C_4 - C_{10}$ was below the detection level.

Fig. 2. First sampling point.

Conclusion

The objective of the work was to verify an application of separation by the flotation in the decontamination of sediment samples from Černý příkop situated in the city of Ostrava. The content of pollutants was over 80 %, which means that the given inexpensive technology would be able to treat the sediments which represent an immense ecological load for the city of Ostrava. It can be said that setting the conditions right, froth flotation is positively a very effective tool how to decontaminate sediments. Despite the fact the experiment was carried out using sediments, it can be expected that the application of flotation shall be efficient also with other materials that may be polluted with similar substances.

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Verification of flotation agents based on residues from pyrolysis of wood

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Abstract

The paper deals with the research in 2 newly prepared flotation agents based on residues from the pyrolysis of wood which are compared with commonly applied Montanol 551 collector. They are tested on the black-coal slurry samples from the Jankowice Mine in Poland, both in the laboratory as well as in pilot conditions. With respect to a significant financial demands of the commercial flotation agents, which are used in the Czech preparation plants, the newly prepared flotation agents are based on residues from the pyrolysis of wood, which are economically very interesting products. The research results imply that compared with the Belgian collector of Montanol 551, a collector labelled KOPD 11 is its very good substitute.

Key words: flotation agents, pyrolysis of wood, flotation

Introduction

Coal is a raw material mined for purposes of numerous industries, e.g. metallurgy, power-engineering, chemistry and many other branches. At the beginning of the 21st century, the global significance of coal for the civilization is universal.

Currently, mining of black coal is stagnating despite the fact that the consumption of industrial raw materials, the natural resources of which are not renewable and depletable by the human action, is increasing. The level of slump in the coal mining is dependent on the development of both international and national conditions. Another significant factor having an influence on this is the fulfilment of the international agreement on gradual reduction of the sulphur oxides released into the atmosphere. There is a question how to deal with the issues in connection with the slump in coal mining. One possibility is as perfect preparation of the mined coal as possible, as well as maximum utilization of its combustible component (Ralston et al., 2003).

This trend represents new objectives for mineral dressing – to prepare and comprehensively use the finest coal fractions that originate from the processes of black coal preparation. The created large share of slurry fractions cannot be processed applying classical dressing methods. Those fractions then leave the preparation plant unused, they get into the circuit water of waste water treatment plants, they deteriorate the processes of sedimentation, filtration, water courses get polluted and there are losses in the valuable raw materials as the coal slurries are dewatered in the sludge beds or lagoons and they remain unutilized.

Thanks to flotation as a technological method of dressing mineral resources and secondary raw materials it is possible to deal with an uneasy task of ensuring an effective, practical and complex utilization of the material sources. Flotation belongs among the methods which permit processing of the fine, non-homogeneous black--coal slurry (Kmeť, 1992).

Materials and methods

Flotation tests were implemented in the laboratory of the Institute of Environmental Engineering at VŠB-TU Ostrava, applying a laboratory flotation machine VRF-1, a product of RD Příbram. It is a pneumo-mechanical mixing flotation machine with an own air admission.

Flotation was carried out under the conditions below:

- feed density: 150 g · l^{-1}
- sample grain-size: < 0.5 mm
- flotation agent dose: 500 g · t^{-1}
- agitation time of pulp and flotation agent: 1 minute
- flotation time: 5 minutes

Pilot tests were carried out on a pilot flotation machine. It is a pneumo-mechanical mixing flotation machine with an own air admission.

Flotation was carried out under the conditions below:

- feed density: 1 800 g · l^{-1}
- sample grain-size: < 0.5 mm,
- flotation agent dose: 2 000 g · t^{-1}
- agitation time of pulp and flotation agent: 10 minute
- flotation time: 10 minutes

Fig. 1. Pilot flotation machine.

Fractional flotation was implemented. The laboratory flotation concentrates were sampled after the 1st, 2nd, 3rd and 5th minutes. The pilot flotation concentrates were sampled after the 2nd, 4th, 6th and 10th minutes. Having terminated flotation, the flotation concentrates and tailings were filtered in a pressure filter and dried in a drier at the temperature of 105 °C. The dried samples were weighed, quartered and an ash content analysis was carried out.

In total, 3 flotation agents based on residues from the pyrolysis of wood were tested (KOPD 3, KOPD 9, KOPD 11) and they were compared with a commonly applied collector of Montanol 551. All the flotation agents were tested on the black-coal slurry samples from Jankowice in Poland.

Characteristics of the applied flotation agents

Regarding the fact that producers do not state the chemical compositions of their flotation agents, the agents underwent IR spectroscopy which was implemented in the Central Analytical Laboratories of VŠB-TU Ostrava. The following flotation agents were used to test selectivity of the individual flotation collectors:

- **Montanol 551** – The IR spectra analysis implies the following composition of carboxylic compounds, aromatic and aliphatic hydrocarbons, alkenes, alcohols, phenols, glycols, esters, ethers and alkanes.
- **KOPDs** – These are flotation agents arising from the residues from the pyrolysis of wood during production of activated coal in SLZ CHÉMIA, a. s. (KOPD 9, KOPD 11). The producer declares the composition of carboxylic acids, alcohols, aliphatic hydrocarbons and water (Kušnierová et al., 2009).

Results and discussion

Both pilot and laboratory flotation tests of the lower rank black-coal slurries from the Jankowice Mine in Poland were carried out and compared. The coal from the Mine of Jankowice is of a lower quality and thus the ash contents are over 10 %, which is considered to be a limit for the quality coal. The flotation results are apparent from Tables below. First, the laboratory test results are presented, being followed by the pilot test results.

Fig. 2. Flotation froth in pilot flotation machine.

As apparent from Tab. 1 the collector of Montanol 551 shows very good selective properties. In the first two minutes of flotation, over 60 % floats out. The yield in the first flotation minute is about 19 %. The flotation time is optimal and the collector makes the coal easily treatable. See in Tab. 1.

In the case of the two following flotation tests using the KOPD 9 and KOPD 11 flotation agents (see Tabs. 2 and 3) an excellent ash content was obtained in the first concentrate, which was mere 18.48 % and a considerably high yield. The agent of KOPD 9 did not provide as high yield in the first minute, but in the second minute the total yield exceeded a 50 % level. It can be said that the newly prepared flotation agents are quality substitutes of Montanol 551.

Easy treatability of Montanol 551 on the Jankowice coal sample is clear from the Tab. 4. The ash content in the first two minutes ranges from 17 % to 36.4 % of the yield. Comparing with the ash content after four minutes, ash rises to 29.6 % and the yield drops to 45.8 %. It can be said that in the case of this agent the ideal flotation time is up to 2 minutes at the top yield.

Applying the agent of KOPD 11 (see Tab. 5) an easy treatability of the coal is apparent. A large yield in the first two minutes is obtained at prominent ash content and the following fast drop in the yield in the next minutes indicates the necessity to shorten the flotation time to 1 minute, which provides a higher quality flotation concentrate at a lower yield.

In the case of the agent of KOPD 9 a difficult treatability was identified in the same coal sample, which results

Tab. 1
Results of the laboratory flotation – Montanol 511

Fraction	time	Yield	Ash cont.	Ash abundance	Σ ash abundance	Σ ash yield	Aver. ash content	Σ ash abundance	Σ ash yield	Aver. ash content
	min.	%	%	kg · 10 t^{-1}	kg · 10 t^{-1}	%	%	kg · 10 t^{-1}	%	%
KL1	1	35.23	35.68	19.64	700.68	700.68	35.68	19.64	3 733.29	100.00
KL2	2	34.78	35.22	27.78	978.42	1 679.10	70.90	23.68	3 032.61	64.32
KL3	3	5.24	5.31	39.23	208.17	1 887.27	76.20	24.77	2 054.19	29.10
KL4	5	2.08	2.11	43.71	92.07	1 979.34	78.31	25.28	1 846.02	23.80
OL1	5	21.42	21.69	80.86	1 753.95	3 733.29	100.00	37.33	1 753.95	21.69
P	98.75	100.00	37.33	3 733.00						

Notes: K – concentrate, O – tailings, P – feed

Tab. 2
Results of the laboratory flotation – KOPD 11

Fraction	time	Yield	Ash cont.	Ash abundance	Σ ash abundance	Σ ash yield	Aver. ash content	Σ ash abundance	Σ ash yield	Aver. ash content
	min.	%	%	kg · 10 t^{-1}	kg · 10 t^{-1}	%	%	kg · 10 t^{-1}	%	%
KL5	1	83.29	55.99	18.48	1 034.62	1 034.62	55.99	18.48	3 419.84	100.00
KL6	2	17.28	11.62	28.97	336.49	1 371.11	67.60	20.28	2 385.22	44.01
KL7	3	10.64	7.15	30.38	217.28	1 588.39	74.75	21.25	2 048.73	32.40
KL8	5	6.68	4.49	37.97	170.49	1 758.88	79.24	22.20	1 831.45	25.25
OL9	5	30.88	20.76	80.02	1 660.96	3 419.84	100.00	34.20	1 660.96	20.76
P	148.77	100.00	34.20	3 420.00						

Notes: K – concentrate, O – tailings, P – feed

Tab. 3
Results of the laboratory flotation – KOPD 9

Fraction	time	Yield	Ash cont.	Ash abundance	Σ ash abundance	Σ ash yield	Aver. ash content	Σ ash abundance	Σ ash yield	Aver. ash content
	min.	%	%	kg · 10 t^{-1}	kg · 10 t^{-1}	%	%	kg · 10 t^{-1}	%	%
KL9	1	52.10	36.03	21.22	764.51	764.51	36.03	21.22	3 798.67	100.00
KL10	2	31.53	21.80	21.59	470.74	1 235.25	57.83	21.36	3 034.16	63.97
KL11	3	11.46	7.92	26.95	213.57	1 448.82	65.76	22.03	2 563.42	42.17
KL12	5	7.12	4.92	36.71	180.74	1 629.56	70.68	23.06	2 349.85	34.24
OL3	5	42.40	29.32	73.98	2 169.11	3 798.67	100.00	37.99	2 169.11	29.32
P	144.61	100.00	37.99	3 799.00						

Notes: K – concentrate, O – tailings, P – feed

Tab. 4
Results of the pilot flotation – Montanol 511

Fraction	time	Yield	Ash cont.	Ash abundance	Σ ash abundance	Σ ash yield	Aver. ash content	Σ ash abundance	Σ ash yield	Aver. ash content
	min.	%	%	kg · 10 t^{-1}	kg · 10 t^{-1}	%	%	kg · 10 t^{-1}	%	%
KP1	< 2	36.4	17.0	617.3	617.3	36.4	17.0	3 343.1	100.0	33.4
KP2	2 – 4	45.8	29.6	1 357.1	1 974.4	82.2	24.0	2 725.7	63.6	42.9
KP3	4 – 6	3.7	66.2	244.9	2 219.3	85.9	25.8	1 368.7	17.8	76.9
KP4	6 – 10	1.6	74.6	119.3	2 338.6	87.6	26.7	1 123.8	14.1	79.7
OP1	> 10	12.4	81.0	1 004.5	3 343.1	100.0	33.4	1 004.5	12.4	81.0
P	100.0	3 343.1								

Notes: K – concentrate, O – tailings, P – feed

Tab. 5
Results of the pilot flotation – KOPD 11

Fraction	time	Yield	Ash cont.	Ash abundance	Σ ash abundance	Σ ash yield	Aver. ash content	Σ ash abundance	Σ ash yield	Aver. ash content
	min.	%	%	kg · 10 t^{-1}	kg · 10 t^{-1}	%	%	kg · 10 t^{-1}	%	%
KP5	< 2	51.0	20.8	1 060.8	1 060.8	51.0	20.8	3 763.3	100.0	37.6
KP6	2 – 4	18.5	33.1	612.4	1 673.2	69.5	24.1	2 702.5	49.0	55.2
KP7	4 – 6	5.5	41.1	226.1	1 899.3	75.0	25.3	2 090.1	30.5	68.5
KP8	6 – 10	3.0	59.6	178.8	2 078.1	78.0	26.6	1 864.0	25.0	74.6
OP2	> 10	22.0	76.6	1 685.2	3 763.3	100.0	376.3	1 685.2	22.0	76.6
P	100.0	3 763.3								

Notes: K – concentrate, O – tailings, P – feed

Tab. 6
Results of the pilot flotation – KOPD 9

Fraction	time	Yield	Ash cont.	Ash abundance	Σ ash abundance	Σ ash yield	Aver. ash content	Σ ash abundance	Σ ash yield	Aver. ash content
	min.	%	%	kg · 10 t^{-1}	kg · 10 t^{-1}	%	%	kg · 10 t^{-1}	%	%
KP9	< 2	28.9	14.9	430.6	430.6	28.9	14.9	3 941.7	100.0	39.4
KP10	2 – 4	13.0	20.7	269.1	699.7	41.9	16.7	3 511.1	71.1	49.4
KP11	4 – 6	7.3	29.6	216.1	915.8	49.2	18.6	3 242.0	58.1	55.8
KP12	6 – 10	7.3	39.1	285.4	1 201.2	56.5	21.3	3 025.9	50.8	59.6
OP3	> 10	43.5	63.0	2 740.5	3 941.7	100.0	39.4	2 740.5	43.5	63.0
P	100.0	3 941.7								

Notes: K – concentrate, O – tailings, P – feed

in a low recovery with a high ash content in all the sampling periods. See in Tab. 6.

Conclusion

It is apparent from the flotation experiments that all the examined agents may be used in the flotation of the black coal. The application of the flotation agents prior to their introduction into the preparation process requires further testing in the pilot flotation machines in the practice. The tests partially differ from those carried out in the laboratory conditions. Another argument to support further efforts to make use of KOPD flotation agents is a high price of the collector of Montanol 551, which may become one reason why the flotation agents of KOPD 9 and KOPD 11 could be used in the Czech preparation plants. Despite clearly higher costs when compared with other preparation methods, flotation still remains the highest quality option how to separate fine fractions.

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$MgCO_3$ obtaining from wastewaters generated during the acidic leaching of zinc concentrates

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Abstract

Leachates formed in the process of zinc concentrates leaching by means of HCl solutions were utilized for the magnesite obtaining. Earlier defined process parameters were adjusted to precipitation of magnesium carbonate. Leachate impurities, such as iron, calcium and other ions were removed by the precipitation, adjusting pH level. Optionally the ion exchange process was used to achieve a best quality of magnesium solution. Crystalline $MgCO_3$ was precipitated using Na_2CO_3 solution. The product contained 28.7 % of MgO with 98.5 % purity of the final product.

Key words: wastewaters, zinc contentrates, acidic leaching, $MgCO_3$

Introduction

Synthesis of required materials with controlled size and morphology is often driven by the industry requirements in the diverse areas. Magnesium carbonate is mainly used to produce magnesium metal and basic refractory materials. The other applications combine flooring, fireproofing, cosmetics (toothpastes, face powders, etc.), pharmaceuticals (antacids, laxatives, cardiac regulators), food additives, paints, pigments, rubbers, lithographing inks, and the use as precursors to prepare other magnesium-based chemicals. Although magnesium carbonate is well known in the form of the anhydrous salt called *magnesite* ($MgCO_3$), several hydrated and basic minerals also exist: di-, tri- and pentahydrates are known as *barringtonite* ($MgCO_3 \cdot 2H_2O$), *nesquehonite* ($MgCO_3 \cdot 3H_2O$) and *lansfordite* ($MgCO_3 \cdot 5H_2O$), respectively. Some basic forms such as *artinite* ($MgCO_3 \cdot Mg(OH)_2 \cdot 3H_2O$), *hydromagnesite* ($4\ MgCO_3 \cdot Mg(OH)_2 \cdot 4H_2O$) and *dypingite* ($4MgCO_3 \cdot Mg(OH)_2 \cdot 5H_2O$) also occur as minerals.

There are many possibilities of the magnesium carbonate obtaining, but the interesting one proposed below is based on the leachates generated during the processing of the Zn, Pb concentrates. Magnesium carbonates have been studied for both their preparation and properties (Kloprogge, 2003; Min, 2010; Deelman, 2003; Sheila, 1989), but many questions still remain opened concerning the formation of the magnesium carbonates in both natural and artificial systems, due to the presence of different forms of hydrated or basic carbonates (Wang, 2008).

Characterization of investigated problem

During processing of zinc concentrates the leachates are generated, containing magnesium, calcium and other metals depending on the raw ore content. Purification processes, adapted to the zinc concentrate quality improvement, use different kinds of mineral acids, in order to remove magnesium from the final product. Among these leaching agents the sulphuric, phosphoric and hydrochloric acids were tested, and the results were described (Jarosiński, 2009; Jarosiński, 2010).

In this study the solution formed during hydrochloric acid leaching is investigated, in order to precipitate magnesium carbonate by the reaction:

$$MgCl_2 \cdot Na_2CO_3 + nH_2O \Rightarrow MgCO_3 \cdot nH_2O + 2\ NaCl$$

The parameters of precipitation, as well as possibilities of different forms of magnesium carbonate obtaining were studied.

The aim of the present work is to select proper conditions and target precipitates with the adequate crystallographic characteristics for extracting magnesium from the brine, and prepare magnesium carbonate hydrates with the high purity.

Experimental part

Materials

Leachates were prepared in the laboratory as the model chlorine solution, containing the following concentrations [mg/dm^3]: 0.115 Mg; 0.235 Ca; 0.020 Fe; 0.030 Zn; 0.055 Pb. The above chemical content was adapted from the experiments with post flotation wastewaters, obtained during the zinc concentrates extraction with the hydrochloric acid (Jarosiński, 2009).

All chemical reagents used for leachate preparation (Na_2CO_3, KOH) had were analytical grade without further purification.

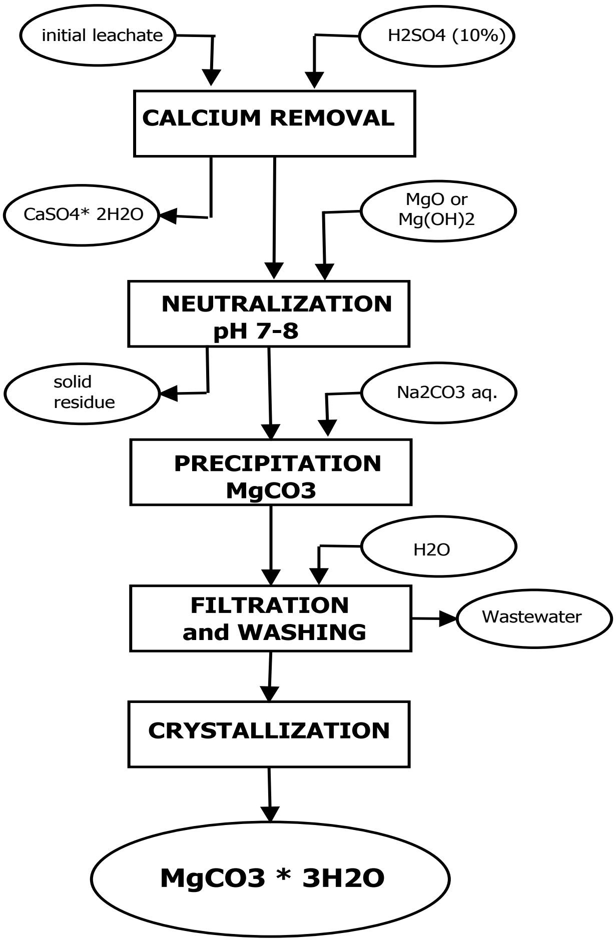

Fig. 1. Simplified flowsheet of the experimental procedure.

Experimental procedures

The experiments were performed in a 1-liter double--jacketed glass reactor, connected with a water circulator. Reaction mixture was agitated at a rate 300 r.p.m. and then filtered under vacuum in a Buchner-type filter. The experimental procedure is presented in Fig. 1 in the form of the simplified flowsheet.

Purification of $MgCl_2$ solution

Calcium ions, the major dissolved impurity of the leachate, were precipitated as sulphates, using sulphuric acid solution (Jarosiński, 2009). The other dissolved impurities like iron, zinc and lead were removed by the precipitation at pH 7 – 8 for 15 minutes at 45 °C by the addition of magnesium oxide or hydroxide.

$MgCO_3$ precipitation

Purified solution of magnesium chloride (0.5 mol/dm^3) was mixed with the sodium carbonate solution (0.5 mol/dm^3) in the glass reactor. The experiments were carried out within the temperature range 20 – 45 °C, using different time of reaction (up to 240 minutes). At the end of each experimental cycle, the slurry was settled till the next day and then washed with distilled water for 5 minutes, to remove any possible ionic remnants. Finally, each sample was dried in a drier at 50 °C for 10 hours.

Product characterization

The structure and morphology of the synthesized samples were examined using the X-ray powder diffraction and scanning electron microscopy. X-ray powder diffraction (XRD, Philips model with X´Pert system) patterns were recorded on a diffractometer (using CuKα radiation). A diffractometer scanning rate was applied to record the patterns in the 2Θ angle range from 10° to 60°. The morphology of the samples was examined by a scanning electron microscopy (FEI E-SEM XL30 with X EDAX GEMINI 4000 dispersion spectrometer).

The concentration of magnesium ions in the solution was determined by the titration method using standard EDTA solution. The concentration of the other ions was determined using ICP – MS spectrometer (Perkin Elmer model).

The density of the product was tested using standard procedure with the glass densitometer.

The results and discussion

XRD observations

It is generally recognized that the properties of crystals are profoundly influenced by the temperature during their preparation and the time of the reaction. Fig. 2 displays the typical XRD pattern of the $MgCO_3 \cdot 3H_2O$ sample. The diffraction peaks confirm a high purity of the carbonate sample.

SEM images

Fig. 3 provides a typical SEM image corresponding to the magnesium carbonate hydrates prepared at 40 °C. The presented sample exhibits good morphology and the surface is covered by many small grain-like crystals. The main particles are needle-like with different sizes, as shown in Fig. 3. The length of crystals is in the range 5 – 53 μm with the axis diameter in the range of 2 – 8 μm. The needle-like particles exhibit smooth surfaces.

The other precipitates (magnesium carbonate hydrates), which synthesized at lower temperatures and shorter reaction time (25 °C, several minutes), were poor crystalline or even amorphous products.

Purity of $MgCO_3 \cdot 3H_2O$

A certain amount of $MgCO_3 \cdot 3H_2O$ sample was dissolved in a slightly excessive hydrochloric acid of low concentration. The concentration of magnesium ions in the solution was determined by the titration method using standard EDTA solution. The Mg content in the tested

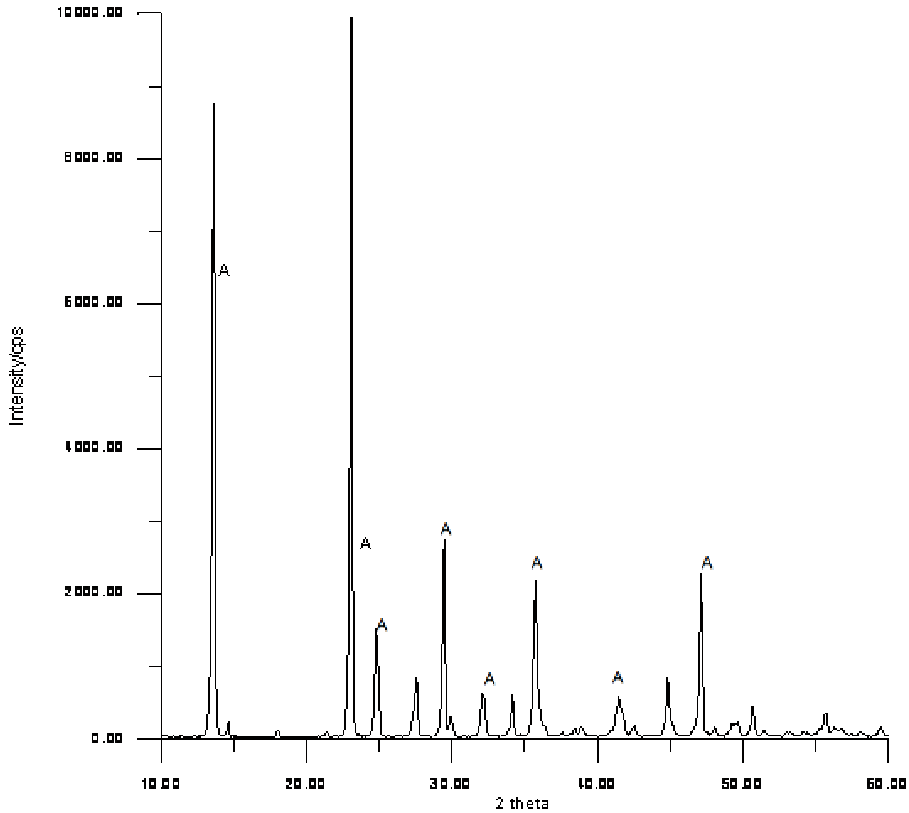

Fig. 2. XRD pattern of precipitated sample, A- $MgCO_3 \cdot 3H_2O$.

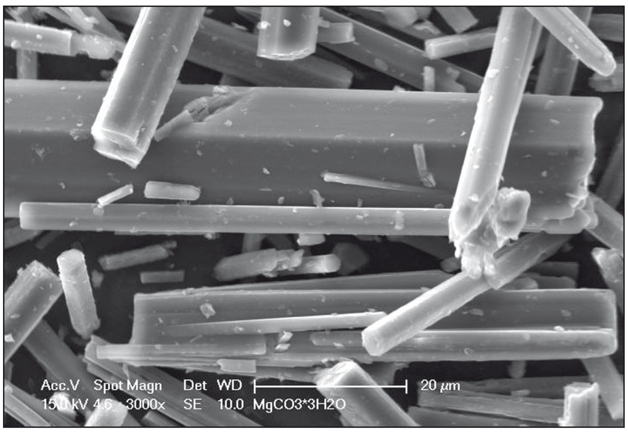

Fig. 3. SEM morphology for the particles of $MgCO_3 \cdot 3H_2O$.

samples was in the range 14.5 – 17.3 % that corresponded to 82.5 – 98.5 % purity of the products. The other impurities bounded into the structure of the magnesium carbonate hydrates did not exceed the level of 0.38 % that was determined by ICP analysis.

Conclusions

Purification process of the wastewaters, obtained during zinc concentrate processing, was examined in this study. As a result of purification the solution containing mainly magnesium ions was obtained. Magnesium carbonate trihydrate was prepared using homogeneous precipitation process at different reaction temperatures and times. In the temperature range 25 – 45 °C pure nesquehonite $MgCO_3 \cdot 3H_2O$ was obtained, but only at 40 °C needle-like crystals were identified. The morphology of the magnesium carbonate trihydrate changed from needle-like to amorphous, in dependence on the precipitation parameters. The uptake of the ionic impurities (Zn, Pb, Fe) in the magnesium carbonate hydrates could be neglected, because its amount does not exceed 0.38 %.

It seems that the purification method proposed for magnesium carbonate production from waste leachate is the appropriate way of its utilization. By the method applied in this study magnesium can be effectively separated from the leachate and using sodium carbonate (or the other water soluble carbonates) magnesium carbonate hydrates with the high purity can be produced.

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Elimination of chloride and fluoride from raw zinc oxides derived from steel dusts processing

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Abstract

On the account of diminished recourses of zinc ores and large requirement on metallic zinc as well as its compounds the recyclable materials are used in larger extent. For example the steel dust serves for obtaining raw dust of zinc oxide as a by-product. This dust contains undesirable components such as chlorine and fluorine. Presented work aims to eliminate these components from the raw zinc oxide obtained from the steel dust because in the case of its hydrometallurgical processing these impurities are liable for the corrosion of zinc and decreasing of technical and economical indexes. Removal of the chloride and fluoride ions was conducted in two stages: first – previous removal on the way of the water leaching, and the second – connected with the removal of above impurities by the soda solutions. Effect of the temperature on the degree of these impurities removal was determined. It was found that the degree of removal of chloride did not depend on the temperature of the process as well as on the amount of used soda on the contrary in the case of fluoride removal.

Key words: waste, receiving zinc, elimination

Introduction

The interest on the secondary sources of zinc is dictated by the large demand on zinc, resulting from the increase of the requirement on the protection by the zinc coating common use in the building engineering and car industry.

At beginning of this century in our country the consumption of zinc recyclable materials amounted to 3 % whereas in the highly industrialized countries as Germany or Great Britain it was totalled on level of 30 per cent. The zinc compounds such as sulphates, phosphates and other are produced practically from the secondary materials at present. The costs of these salts producing from the above materials are lower than the costs of salts obtaining from the natural raw materials. Further the technologies of their salts obtaining from the secondary materials are friendly for environment (Jarosiński, 2007; Jha et al., 2001).

The industrial experience indicates more and more application of the recyclable materials in technological processes. Such trends favour development of recycling technologies.

More than the mined ore and processed metallic zinc and its compounds, there is used the zinc waste deriving from steel industry, for example the dust from the electric arc furnaces, dust of blast-furnaces or rolling scales (Havlik et al., 2006; Zięba et al., 2007). The obtained zinc oxide from such materials contains halides. For example the presence of the chloride anions in electrolyte for obtaining of cathode zinc contributes to zinc corrosion as well as to decreasing of the current efficiency or of zinc quality. The presence of these impurities in the zinc compounds is also undesirable especially in products used as microelements in admixtures of feeds.

For the removal halides from the zinc oxides two ways are used. The first way is connected with the chlorides removal by washing. The second solution relies on the thermal treatment. In practice the first solution is preferred.

In this work the investigation on removal of some impurities contained in zinc oxide derived from the processing of the steel dust.

Experiments

In the laboratory experiments the zinc oxides derived from one of domestic plants were used. The process of the chloride and fluorides obtaining from the raw zinc oxide is operates in two stages. In the first stage of the preliminary removal of chlorides the washing of the soluble salts is done by the water as a washing agent. The mass ratio of the liquid to solid phases has amounted to 9 : 1. The reaction was performed in thermostatic flask at the temperature 60 ± 0.1 °C.

The purpose of the second stage was the removal of fluorides as well as the traces of chlorides remaining after first the step. The elimination of fluorides as well as chlorides succeeds by the washing of soluble salts. The agent was the water solution of the sodium carbonate. Quantity of the soda in relation to used samples derived after the first stage amounted to 5, 10 and 15 %. The mass ratio of liquid to solid phase amounted to 9 : 1, too. The washing was carried out at temperatures ranges 60 – 90 °C. Time of treatments was up to 2 hours.

Results and discussion

The chemical composition of tested zinc oxide is presented in Tab. 1. Results of the fluorides and chlorides elimination after two stages of washing are recapitulated in Tabs. 2 and 3.

On the basis of obtained results the degree of chlorides and fluorides elimination was calculated using following formula:

$$\alpha = \frac{x_i - \frac{x_{Znp} \cdot m_p}{x_{Znk}} \cdot c_i}{x_i} \cdot 100[\%]$$

where: x_i – content "i" component in initial samples [%], x_{Znp} – content of zinc in initial sample [%], x_{Znk} – content of zinc in sample after washing [%], c_i – concentration of "i" component after II stage of washing.

The dependence of the degree of chlorides elimination on the content of soda in washing agent and on temperature is shown in Tab. 4 together with the obtained results of the degree of fluoride elimination for various soda contents in the washing agent.

The presented data indicate that degree of elimination of chlorides was high and practically reached 100 %. It was found that degree of chlorides elimination does not depend in essential way on the temperature of the process. Degrees of fluorides elimination from tested material were lower than the degrees of chlorides and fitted into the range 45 – 73 %. Efficiency of fluorides elimination in two stage process of washing depends on the temperature as well as the amount of the soda addition. Increase of the temperature process was beneficial on the degree of fluoride elimination.

Tab. 1
The chemical composition of tested zinc oxide

Metal	Zn	Fe	Pb	Cl	F
Content [%]	59.5	3.15	6.42	5.9	0.12

Tab. 2
Test results after 2. stage of washing

Condition		Content of components in solution [%]		
Na_2CO_3 [g]	T [°C]	Zn	Cl	F
5	60	67.29	0.028	0.0745
	90	66.39	0.020	0.0510
10	60	66.52	0.023	0.0655
	90	66.25	0.012	0.0390
15	60	65.97	0.0195	0.0580
	90	65.88	0.0110	0.0360

Tab. 3
Chemical composition of 2. stage of washing

Condition		Content of component in solution [g/dm^3]		
Na_2CO_3 [g]	T [°C]	Zn	Cl	F
5	60	0.0090	0.74	0.045
	90	0.0027	0.96	0.068
10	60	0.0010	0.78	0.056
	90	0.0011	1.02	0.081
15	60	0.0022	0.92	0.068
	90	0.0037	1.06	0.088

Tab. 4
Dependence of the degree of chloride elimination on soda amount in the solution

Condition		Degree of elimination [%]	
Na_2CO_3 [g]	T [°C]	Cl	F
5	60	99.58	45.11
	90	99.70	61.91
10	60	99.65	51.17
	90	99.82	70.81
15	60	99.70	56.41
	90	99.83	72.91

Conclusions

The test results allowed to state that two stage process of washing of the zinc oxide in the purpose of halides elimination is effective. Degree of the chlorides elimination was very high reaching almost the value of 100 %. This degree does not depend on the temperature treatment.

Degree of fluoride elimination at the temperature 90 °C is high and amounts to 73 %. Efficiency of discussed treatment depends on temperature as well as soda content in the washing agent.

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Black coal fly ash as the Si-Al matrix for the heat proof materials preparation

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Abstract

Presented are the results of experiments focused on the study of thermal treatment influence of selected black coal fly ash from the heating plant in Košice. Study was realized with the original not pre-treated fly ash sample and sample with Al additive in different mixing rates. The obtained results confirmed that after the thermal treatment occurred the phase´s change of the material. By the 1 050 °C degree there was the decrease of amorphous phase remarked that was transformed on the mullite and corundum. This information allowed the possibility to use the examined fly ash sample as a matrix for the mullite composites preparation providing the stoichiometric change of thermally treated mixture.

Key words: black coal fly ash, refractory materials, mullite

Introduction

The black coal fly ash is the accessory waste product of the black coal combustion in the power plants and heating plants. All unburnable components contained in burned coal are concentrated in the fly ashes. Some of the accessory minerals occur in the original form without any qualitative changes, e.g. quartz and magnetite. Alumosilicates and the part of quartz is under the heating influence transformed on the new Si, Si-Al crystalline structures, e.g. cristobalite, feldspars, mullite, montmorillonite, etc. (Fečko et al., 2005; Kušnierová et al., 2005).The bulk of the unburnable components (over 80 %) is transformed on the amorphous vitric Si-Al phases in the combustion process.

Mullite ($3Al_2O_3 \cdot 2SiO_2$) is the only one stabile chemical compound in Al_2O_3 – SiO_2 system (Hankýř et al., 2008). Mullite in the nature originated by the contact of lava flows with the rocks of the high Al content (Berry et al., 1987). Mullite is characterized by specific facilities as well as the high heat proof to 1 850 °C, relatively high hardness 7.5° of the Mohs scale and the high resistance to acids (Berry et al., 1987; Kušnierová et al., 1976). Just these properties have determined the areas of the mullite, mullite and corundum substances industrial usage preferably in the heat proof and ceramic materials for metallurgy and glass industry (Treadwell et al., 1996; Valenta, 2007). Technological processes of mullite and mullite substances production are based on natural minerals from the aluminosilicates group. It is concerned on the group of three polymorphous minerals Al_2SiO_5 (andalusite, sillimanite and kyanite) as well as topaz $Al_2SiO_5(FOH)_2$ and in a large extent also the mixture of kaolinite $Al_4Si_4O_{10}(OH)_8$ and SiO_2 (Berry et al., 1987; Bűchner et al., 1991).

Many authors, e.g. Dana et al. (2004), Treadwell et al. (1996), Hankýř et al. (2008), Kušnierová et al. (1976), Karklit et al. (1974) and Gončarov et al. (1961) achieved results that have confirmed that the mullitization pass on the different materials basics containing the basic components Al_2O_3 – SiO_2 in its matrix, providing treatment of its stoichiometric ratio content in the mullite including waste materials as well as the energetic wastes (Dong et al., 2010; Suriyanarayanan et al., 2009; Jung et al., 2001; Kušnierová et al., 2010).

The high content of Si and Al in the fly ashes is a good precondition for its use as a secondary raw material for the heat proof materials and the mullite heat proof materials production. This is resulting from the consideration that the natural sources of mullite of industrial meaning were not discovered until now and it is not probable that will be discovered. The next factor for the fly ashes usage is the resemblance of its genesis in the nature to the processes running by the coal combustion and fly ashes generation. The melted not burned part of the fly ash is in touch with the isothermal components containing Al and mullite is produced in the process consequently what was confirmed by XRD analysis (Fečko et al., 2005).

Fečko et al. (2005) and Michalíková et al. (2005) write that the mullite content in the fly ashes depends on the composition and content of the accessory unburnable parts of coal as well as on the process and temperature of combustion. The fact is that from the point of Si and Al content are the brown coal fly ashes more perspective. These are nowadays in the high amounts used in the building industry for their qualitative parameters and they are free for the use in this industrial area in the whole produced capacity. On the other hand the black coal fly ashes are for their qualitative parameters hold to be waste in the whole scale in Slovakia and are dumped. That is why there was realized a research of the black coal fly ash from the heating plant Teko Košice for its usage as a matrix for the heat proof Si-Al materials of mullite type preparation.

Experimental procedures

Fly ash sample properties

The experiments were realized with the black coal fly ash sample from the heating plant Teko Košice of properties that are summarized in the Tab. 1. The ratio of the main building components Al : Si in the fly ash matrix is 0.44.

From the XRD analysis of fly ash sample it was find out that the dominant phase in the fly ash is an amorphous vitric phase. Identified were also following minerals: quartz, cristobalite, anhydrite, feldspar, corundum, magnetite, hematite and graphite.

From the morphological point of view there can be in the fly ash differentiated the spherical (Fig. 1A), idiomorphic and allotriomorphic vitric particles as well as the porous particles (Fig. 1B) of unburned coal (Fig. 1C) and particles of originally not transformed minerals. Physical properties of the fly ash as well as the specific surface, softening range, taw fusion point are summarized in Tab. 2.

The fly ash sample can be characterized as a very fine-grained ploy-component dispersion of 0 – 1 mm grain size. We can see from the results showed in the Tab. 3 that the content of particles under 40 μm is of 50 %. That is advantage for composite mixture from the point of its contact surface. Results in Tab. 3 offer also information about the main building elements as well as Al and Si distribution. The content of these elements is different in the different grain sizes and the most profitable it is in the finest grain size under 40 μm.

Tab. 1
Chemical properties of fly ash sample

Annealing lost (%)	SiO_2 (%)	Al_2O_3 (%)	Fe_2O_3 (%)	CaO (%)	TiO_2 (%)	MgO (%)	Na_2O_3 (%)	K_2O (%)	P_2O_5 (%)	S_{total} (%)	pH
15.5	47.10	20.86	8.83	23.80	0.76	1.21	0.78	2.14	0.35	0.15	12.4

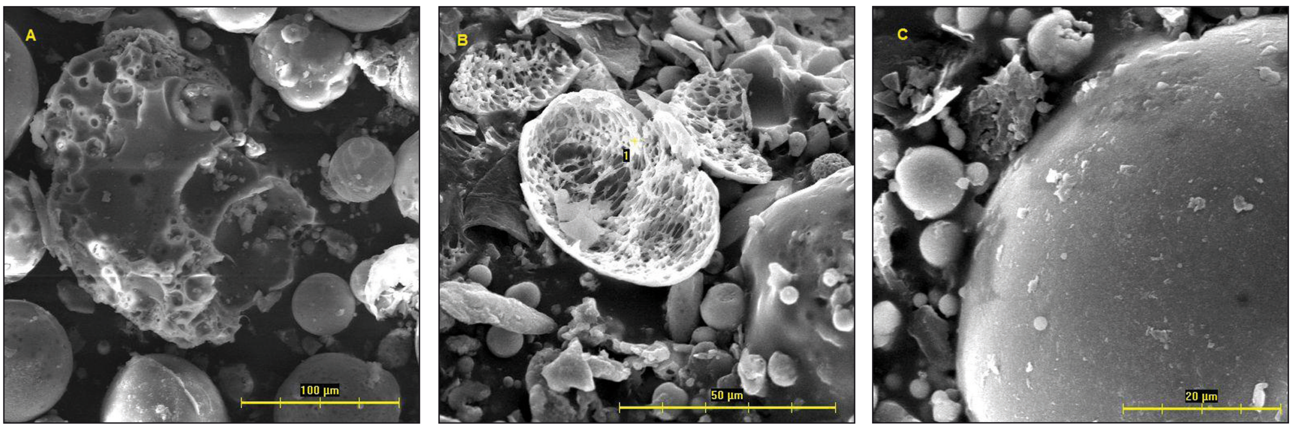

Fig. 1. Morphology of fly ash. A – spherical particles, B – porous particles, C – unburned coal particles.

Tab. 2
Physical properties of fly ash

Specific weight (kg/cm^3)	Softening range (°C)	Taw point (°C)	Fusion point (°C)
2.49	1 140 – 1 240	1 210 – 1 310	1 300 – 1 380

Tab. 3
Fly ash grain class composition and its main elements distribution

Grain class (mm)	Mass yield (%)	SiO_2 (%)	Al_2O_3 (%)
0.1 – 0.5	16.22	41.50	–
0.071 – 0.1	17.52	34.15	11.00
0.04 – 0.071	18.13	45.30	16.20
– 0.04	48.13	52.91	20.90

Composite mixtures

The composite mixtures were prepared using the Al additive ($Al(OH)_3$) form in three mixing rates. Prepared were mixtures with the stoichiometric ratio Al : Si similar to ratio of mullite that is 1.5. Each component was weighted in considered ratio of the fly ash and the additive as is shown in Tab. 4.

Afterwards the homogenization (10 minutes) and mechanical activation (10 minutes) in the planetary mill of prepared composite mixtures have followed.

Tab. 4
Mixing rates of prepared composites samples

Sample	Fly ash and Al additive mixture ratio	Al to Si mixture rate
P	1 : 0	0.44
T1	1 : 1	1.80
T2	2 : 1.5	1.48
T3	2 : 1	1.10
mullite standard	–	1.50

Mullitization

Prepared mixtures were thermally treated in the temperature range of 0 – 1 500 °C. The process of thermal transformation by 0, 850, 1 050 and 1 500 °C was evaluated by the XRD analysis.

There was added to the process of mullitization the inert standard-pure ZnO (ca 5 weight %) with the aim to quantify amorphous components and new-produced phases in the composite mixtures. The samples were homogenized with this standard by the micro-milling and consequently and boxed up to the glass cuvette.

Measurement was provided by the full automatic diffraction meter URD-6 (Rich Seifert-FPM, Germany) under the following conditions: emission of $CoK\alpha$/Ni rejecter, potential of 40kV, electric current 35 mA, step mode 0.05° 2Θ with the step time of 3 s with the digital processing of measured data. For the measuring and results evaluation there was used the software RayfleX (RayfleX ScanX and RayfleX Analyze, 2.289 version).

Results and discussion

The process of the thermal treatment of the original fly ash without occurring phases changes is documented in the Tab. 5 and Fig. 2.

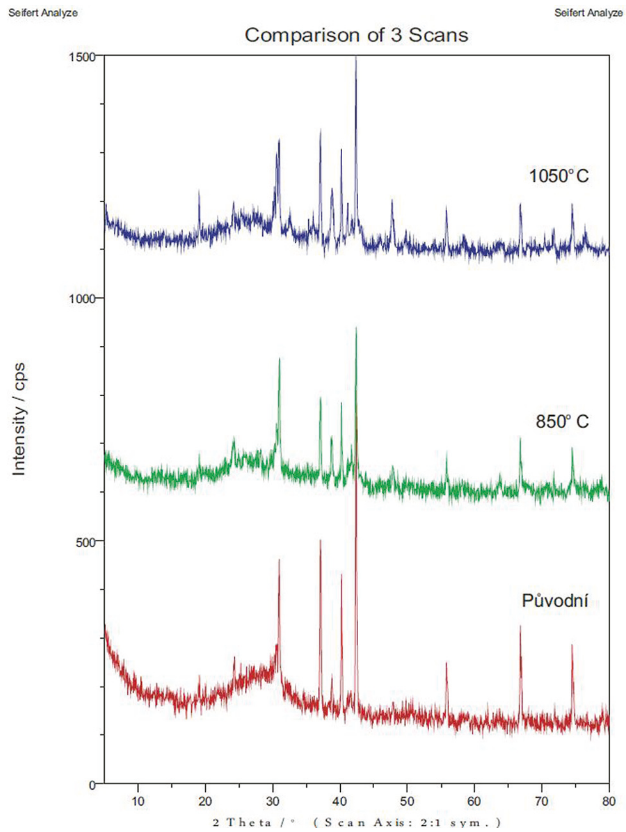

Fig. 2. The comparison of XRD analysis of original fly ash sample (P) and sample thermally treated by 850 and 1 050 °C.

Presented results inform that the increasing of temperature of the thermal transformation of original fly ash caused the decrease of the amorphous phase from 83.05 % to 64.30 %. There was detected also an increase of mullite composition from 10.55 to 22.70 % and by 850 °C the corundum production, that was by

Tab. 5
The thermal treatment of fly ash and its composite mixtures influence on its phases composition

Sample	Burning temperature (°C)	Amorphous phases (%)	Mullite (%)	Corundum (%)	Amount of mullite and corundum (%)
P	0	83.05	10.66	–	10.66
	850	72.30	9.29	2.96	12.25
	1 050	64.30	22.70	–	22.70
	1 500	melting	melting	melting	–

Tab. 6
The influence of thermal treatment on the composition of fly ash composites

Sample	Burning temperature (°C)	Amorphous phases (%)	Mullite (%)	Corundum (%)	Amount of mullite and corundum (%)
T1	0	30.00	5.40	–	5.40
	850	86.58	3.96	1.44	5.40
	1 050	54.00	12.70	23.90	36.60
	1 500	2.10	59.00	38.90	97.90
T2	0	37.40	4.61	–	4.61
	850	88.50	3.84	0.54	4.38
	1 050	63.00	14.30	13.30	27.6
	1 500	21.50	63.80	13.30	77.1
T3	0	50.50	6.79	–	6.79
	850	86.20	4.82	0.85	5.67
	1 050	69.20	14.54	7.45	21.99
	1 500	39.80	56.80	2.35	59.15

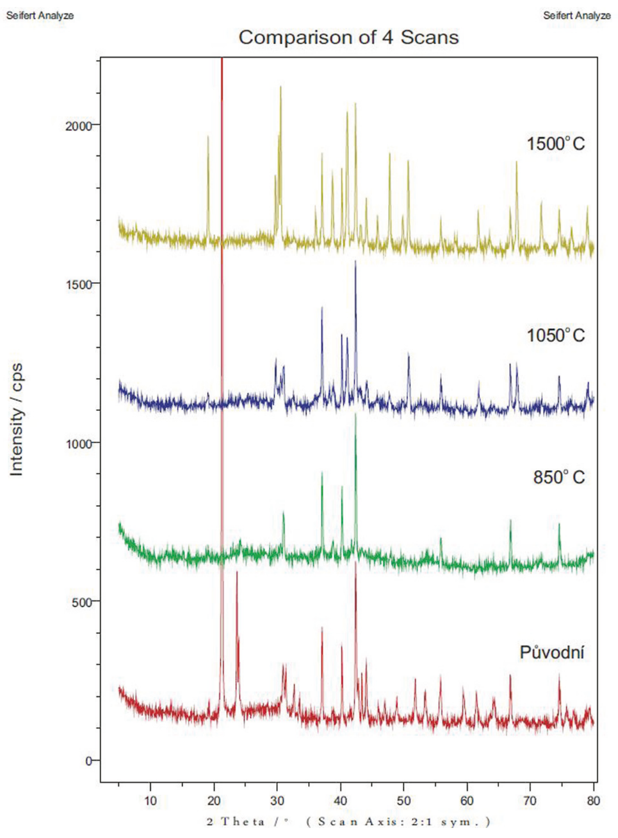

Fig. 3. The comparison of XRD analysis of fly ash mixture sample (T1) of 1 : 1 mixing rate thermally treated at 850, 1 050 and 1 500 °C.

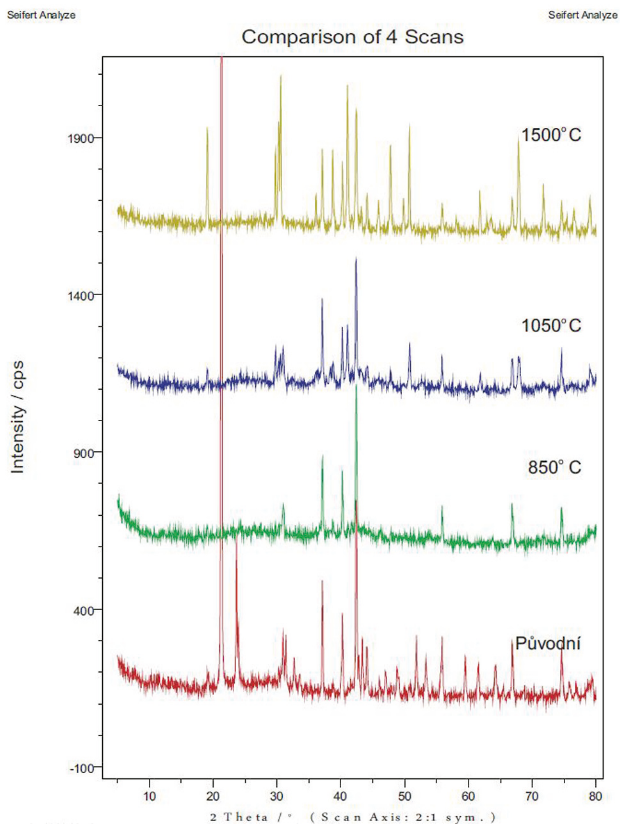

Fig. 4. The comparison of XRD analysis of fly ash mixture sample (T2) of 2 : 1.5 mixing rate thermally treated at 850, 1 050 and 1 500 °C.

1 050 °C transformed on mullite. With the next increase of temperature the pure fly ash sample without any additive was melted that disable analysis. Melting of the sample is related with its thermal properties as well as the taw and fusion points (1 300 – 1 380 °C).

The process of the thermal changes of fly ash and Al additive samples is documented in Tab. 6 and Figs. 3, 4 and 5. In all cases there was registered a high increase of the amorphous phase content by the 850 °C. By this temperature the majority of the sample fractions were

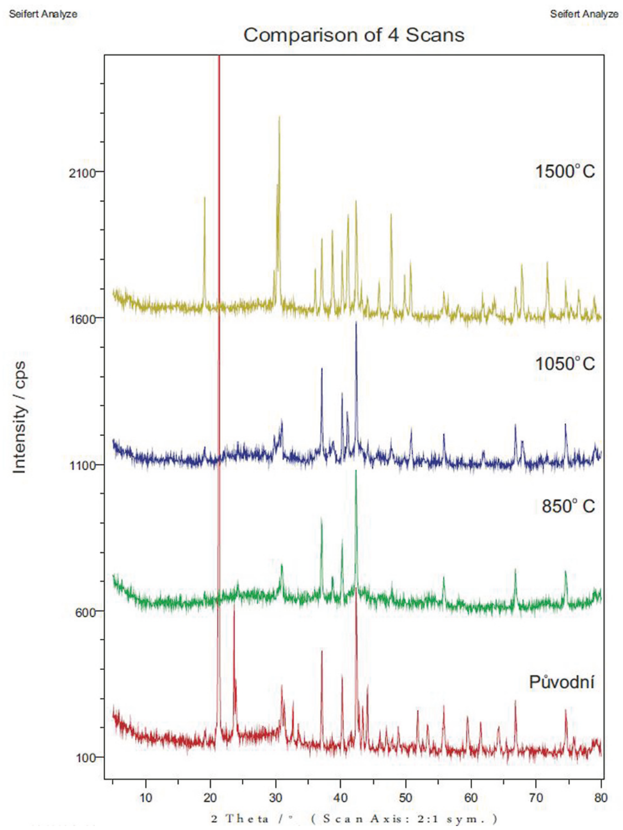

Fig. 5. The comparison of XRD analysis of fly ash mixture sample (T3) of 2 : 1 mixing rate thermally treated at 850, 1 050 and 1 500 °C.

changed and the sample changed to vitric. By the next temperature increasing the sample vas devitrified and the heat proof components as mullite and corundum were crystallized.

The comparison of achieved results of the thermal mullitization from the point of Al : Si ratio in prepared samples showed the important influence of this factor on the process of samples phases transformation. The highest content of mullite (63 %) was reached by the thermal transformation of the sample T2 (mixing rate 1.48) by the temperature 1 500 °C.

The highest content of the heat proof phases together (mullite and corundum) was in the sample T1 (mixing rate 1.8) by the temperature 1 500 °C. In this sample was the content of mullite 59 % and corundum 38.9 %.

In terms of qualitative changes of the composite mixtures and its dependence on temperature is apparent that by the 850 °C were original crystalline phases destroyed and the content of vitric amorphous phase increased. This case is related with the Al additive content, that´s taw point is at 300 °C. Near the temperatures over 1 050 °C was the melt devitrified and mullite and corundum originated. In this range over the 1 050 °C there can be anticipated as optimal conditions focused on the thermal transformation of the thermally treated composite dispersion on the mullite material.

Conclusion

Presented informative results showed that the Si-Al matrix of the black coal fly ashes can be used for the heat proof and abrasive industrially useful materials production by the optimal thermal conditions and mixing rates with the suitable Al additive. The fly ashes mullitization process belongs among the sophistic technologies of the waste black coal fly ashes usage as the secondary raw material. Fly ashes wastes economical appreciation will depend on the further study of this process and optimization of the conditions of thermal transformation. The wide field offers the modelling of the mullite composite mixtures from the fly ashes and additives as well as natural or waste products of high Al content.

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Biological transformation of alkaline earth metal sulphates

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Abstract

The aim of this paper is to verify experimentally the possibility of the biological transformation of the alkaline earth metal sulphates ($CaSO_4$ and $BaSO_4$) to carbonates by sulphate-reducing bacteria. These carbonates can be used in some industrial technologies (e.g. the energetic industry – the recycling of desulphurization agent (limestone) for the thermal power plant, the electrical industry – the production of colour display).

Key words: gypsum, barite, sulphate-reducing bacteria, biological transformation

Introduction

In nature the sulphur can be found as a pure element or in the form of sulphide and sulphate minerals. Common naturally occurring sulphur compounds include the sulphide minerals, such as pyrite (FeS_2), cinnabar (HgS), galena (PbS), sphalerite (ZnS) and stibnite (Sb_2S_3); and the sulphates, such as gypsum ($CaSO_4$), alunite ($KAl(SO_4)_2$), celestite ($SrSO_4$) and barite ($BaSO_4$). The biological circulation of sulphur and its compounds in the biosphere is considered as one of the basic biological systems on the Earth (Lide, 1998). The participating populations of different species of microorganisms (MO) are able to transform organic substances into inorganic ones and vice versa supporting the circulation of sulphur in the nature. The natural biological circulation of sulphur consists of assimilation and dissimilation parts. The microbial population of the dissimilation part is called sulphuretum (Postgate, 1984). In addition to other MO also the sulphate-reducing bacteria (SRB) take part in the sulphuretum. They realize the conversion of sulphate to hydrogen sulphide under anaerobic conditions (Odom and Singleton, 1993). Gaseous hydrogen or organic substrates (lactate, malate, etc.) are the electron donor and sulphate is the electron acceptor (equations 1 and 2). In this process produced gaseous hydrogen sulphide reacts easily in the water medium with heavy metal cations forming sparingly soluble sulphides of the given metals (equation 3):

$$4\,H_2 + SO_4^{2-} \xrightarrow{SRB} H_2S + 2\,H_2O + 2\,OH^- \qquad (1)$$

$$4\,CH_3COCOONa + 5\,MgSO_4 \xrightarrow{SRB} 5\,MgCO_3 + 2\,Na_2CO_3 + 5\,H_2S + 5\,CO_2 + H_2O \qquad (2)$$

$$Me^{2+} + H_2S \rightarrow MeS + 2H^+ \ (Me^{2+} \text{ – metal cation}) \qquad (3)$$

The above-listed equations show the possibility of using SRB for the removal of soluble heavy metals and sulphates from acid mine drainage (AMD) (Skousen et al., 1998; Luptáková et al., 2002; Kaksonen and Puhakka, 2007) or other industrial waste waters (Cork and Cusanovich, 1979). In addition, the equation 2 suggests the usage of bacterial sulphate reduction by SRB on the treatment process for sulphate-contained sludge (Cork, 1985; Baldi et al., 1996; Kennedy and Everett, 2001; Luptáková et al., 2003) being the basis of the biological transformation of sulphates to carbonates.

The objective of our study is to verify experimentally the possibility of the biological transformation of the alkaline earth of metals sulphates – $CaSO_4$ and $BaSO_4$ by SRB. Under the appropriate conditions the SRB are able to convert with a high efficiency the alkaline earth metal sulphates in corresponding carbonates. These can be utilized by some industrial technologies (e.g. in the energetic industry – the recycling of desulphurization agent (limestone) for the thermal power plant, in the electrical industry – the production of colour display).

Materials and methods

In the experiment a culture of SRB (genera *Desulfovibrio* and *Desulfotomaculum*) was used. It was obtained from drinking mineral water Gajdovka (locality Košice-north, Slovak Republic). Culture was grown in a Postgate lactate medium that was prepared sulphate-free. The pH was adjusted to 7.2 – 7.5 with 5 M NaOH solution. Culture medium contained gypsum or barite as the solid-phase electron acceptors. SRB were grown at 30 °C under static and anaerobic conditions. The inoculum of SRB was 10 % (v/v). For the series of anaerobic tests SRB adapted or non-adapted were used on the presence of gypsum or barite. At the adaptation procedure SRB were transferred three times into the media which contained the test compound as the sole electron acceptor. The abiotic controls were carried out without the SRB application at the same conditions. The nefelometric method was used to determine the concentration of sulphates at 490 nm using the Spectromom 195 spectrophotometer. Soluble sulphide was analysed using a methylene blue method based on a colourimetric determination of dissolved H_2S and HS^- using *N*, *N*-dimethyl-*p*-phenylenediamine. The pH of the cultivation medium was determined using the PHM 210 MeterLab pH meter.

Results and discussion

The hydrogen sulphide production from the gypsum as the solid-phase electron acceptors during a 7-day period of SRB cultivation at using adapted (SRB – A) or non-adapted bacteria (SRB – N) is described in Fig. 1. Positive influence of the adaptation procedure was observed. The hydrogen sulphide amount in the case of adapted SRB using, in comparison with the non-adapted SRB was above double. Sulphates from gypsum were reduced by SRB according to equation (4) forming hydrogen sulphide. In abiotic controls (SRB – A (abiotic) and SRB – N (abiotic)) the negligible hydrogen sulphide production was observed.

$$2C_3H_5O_3Na + CaSO_4 \xrightarrow{SRB} 2CH_3COONa + CO_2 + CaCO_3 + H_2S + H_2O \quad (4)$$

The changes of sulphates and the hydrogen sulphide concentration at adapted SRB application and at abiotic control, when gypsum as the solid-phase electron acceptor was used is demonstrated in Fig. 2. Changes of corresponding pH values is shown in Fig. 3. The comparison of biotic and abiotic conditions documented the similar curve shape of changes of sulphates and hydrogen sulphide concentration, and pH values only during the first and second days (Figs. 2 and 3). Later the SRB presence caused the sulphates concentration decreasing and the hydrogen sulphide concentration increasing. In abiotic control after the second day sulphates and hydrogen sulphide concentrations changes were minimal. Also Fig. 2 documented the nutrient medium influence on the barite dissolving. Fig. 3 described the contrast of pH values changes between the SRB application and the abiotic control. Shift of pH values to alkaline zone was recorded at SRB presence. It corresponds with equation (4) because $CaCO_3$ as alkaline mater was produced. Abiotic conditions report consistent decreasing of pH.

The opposed results were observed at the adaptation of SRB using barite as the solid-phase electron acceptors (Fig. 4). Non-adapted SRB produced nearly decimal higher

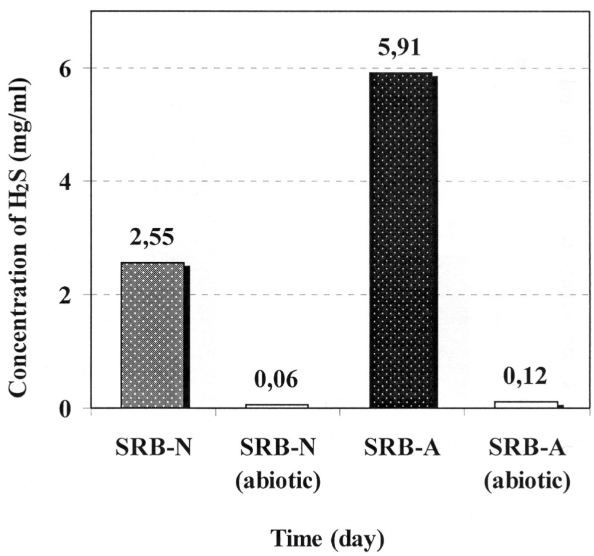

Fig. 1. Hydrogen sulphide production from gypsum by non-adapted sulphate-reducing bacteria (SRB-N) and adapted bacteria (SRB-A). SRB-A (abiotic), SRB-N (abiotic) – abiotic controls.

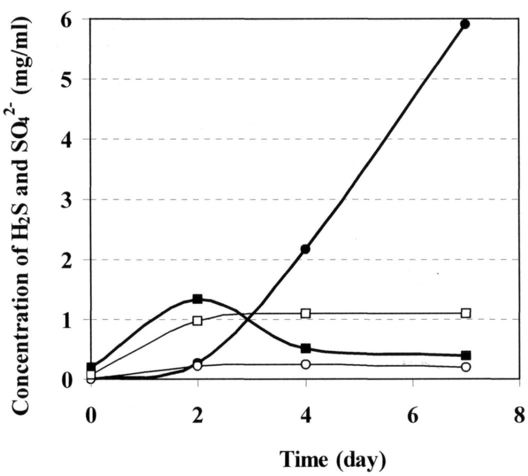

Fig. 2. Changes of sulphates (■)and hydrogen sulphide (●) concentration during adapted SRB cultivation and changes of sulphates (□) and hydrogen sulphide (○) in corresponding abiotic controls using gypsum as the solid-phase electron acceptors.

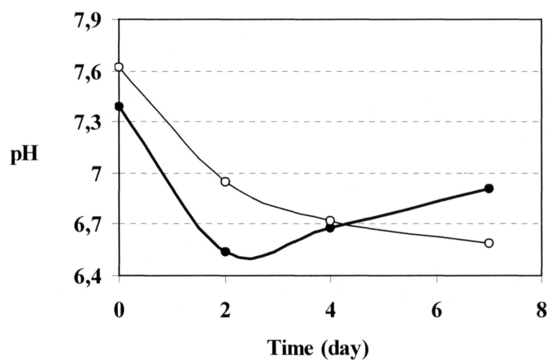

Fig. 3. Changes of pH values during adapted SRB cultivation (●) and corresponding abiotic control (○) using gypsum as the solid-phase electron acceptors.

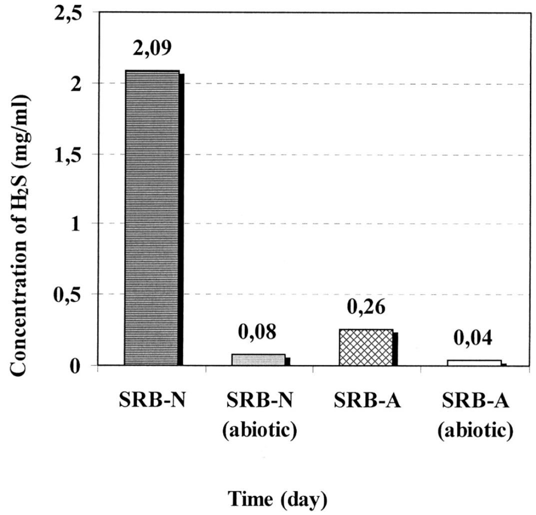

Fig. 4. Hydrogen sulphide production from barite by non-adapted sulphate-reducing bacteria (SRB-N) and adapted bacteria (SRB-A). SRB-A (abiotic), SRB-N (abiotic) – abiotic controls.

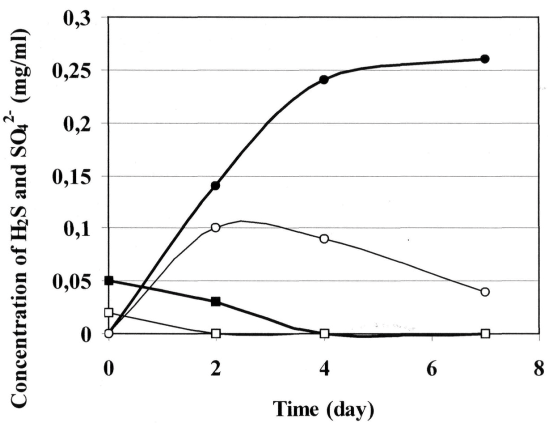

Fig. 5. Changes of sulphates (■) and hydrogen sulphide (●) concentration during adapted SRB cultivation and changes of sulphates (□) and hydrogen sulphide (○) in corresponding abiotic controls using barite as the solid-phase electron acceptors.

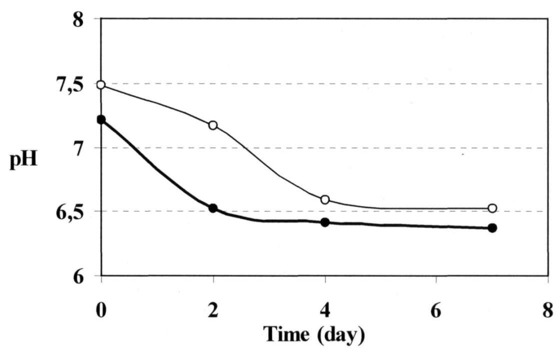

Fig. 6. Changes of pH values during adapted SRB cultivation (●) and corresponding abiotic control (○) using barite as the solid--phase electron acceptors.

concentration of hydrogen sulphide. At the moment we cannot explain of this fact. Probably the barium toxicity influenced on the SRB growth because the barium is generally toxic to bacteria, fungi, mosses and algae (Roza and Berman, 1971).

When the barium as the solid-phase electron acceptors was used the changes of sulphates and hydrogen sulphide concentration at adapted SRB application and at abiotic control shows Fig. 5. Changes of pH values at using SRB are shown in Fig. 6. The decrease of sulphate concentration and the increase of hydrogen sulphide concentration were observed in the case of SRB presence. At abiotic control allocated the decreasing of sulphates. After the initial minor increasing the hydrogen sulphide concentration showed the decreasing.

Equations (5) and (6) describe the biochemical reaction initiated by SRB in the presence of sodium lactate as an electron donor and $BaSO_4$ as an electron acceptor under anaerobic conditions at pH 7 according to Baldi et al. (1996).

$$\text{Na-lactate} + BaSO_4 \xrightarrow{\text{SRB}} \text{biomass} + BaCO_3 + BaS + CO_2 + H_2S \quad (5)$$

$$BaSO_4 + 2H_2S \rightarrow BaS + SO_2 + 2H_2O + S \quad (6)$$

Equation (5) suggests the biological decrease of the sulphate concentration and equation (6) the chemical trend, because produced hydrogen sulphide reduces $BaSO_4$ to BaS. These facts probably explain the zero concentration of sulphates in the Fig. 5. Experiments realized at biotic and abiotic conditions have documented the consistent decreasing of pH.

Conclusions

The study of the biological transformation of alkaline earth of metals sulphates ($CaSO_4$ and $BaSO_4$) confirmed that SRB obtained from the drinking mineral water Gajdovka could produce sulphide from the sulphate entity of gypsum and barite. The sulphate concentration decreased by the zero concentration in test cultures growing with $BaSO_4$ as the electron acceptor, possibly due to BaS precipitation by bacterially produced hydrogen sulphide. Hydrogen sulphide formation from the barite was the slowest when compared to gypsum as electron acceptor that is more soluble. Sulphate reduction with gypsum as the electron acceptor probably resulted in calcite formation ($CaCO_3$) but no precipitation of sulphide. With barite as the electron acceptor probably sulphide precipitated as BaS (galena), which is why the dissolved sulphide concentration remained low.

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Removal of sulphates from mining waters using the sulphate-reducing bacteria

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Abstract

The objective of this study was the experimental verification of the possibilities of the sulphate rich mining waters utilization as a source of sulphate for the cultivation of sulphate-reducing bacteria. The results of this process consist from the elimination of the sulphates from the waste waters and the biogenic hydrogen sulphide recovery. The acid mine drainage discharged from the shaft Pech located in abandoned ore deposit Smolník was used in this work.

Key words: wastewater treatment, sulphates, sulphate-reducing bacteria

Introduction

The sulphate rich waste waters are generated by a large spectrum of industrial processes including the paper and pulp production, sea food processing, potato starch production, tanneries, fermentation, fertilizers, ore processing and mining. Declining coal and metal mining industries have caused the problem of acid mine drainage (AMD) – the highly acidic, dissolved metals and sulphates containing waste waters. In the treatment of AMD a little attention has focused on the mitigation of dissolved sulphates. This may be attributed to its lower environmental risks – sulphates emissions are not a direct threat for the environment as sulphates are chemically inert, non volatile, non toxic and non bioaccumulative compounds. In general, organisms have a relatively high tolerance for sulphates. The consumption of the drinking water containing sulphates concentration in excess of 600 mgl^{-1} commonly results in laxative effects. The taste treshold for the most prevalent sulphates salts ranges from 250 to 500 mgl^{-1} (Davies et al., 2003; INAP, 2003). In term of the protection of aquatic life, sulphates toxicity is dependent on chloride and hardness concentrations of the water and it is different case by case (Davies et al., 2003; IDNR, 2009). However, the discharge of the sulphate-rich industrial waste water into the surface waters contributes to the increase of the corrosion potential of receiving waters and augments the total dissolved solid contents causing a problem with the cooling in the industries. Moreover, high sulphates concentration induces an unbalance in the natural sulphur cycle (Sarti et al., 2009).

Sulphates may be present in the waste waters at concentrations ranging from a few hundred to several thousand milligrams per liter and they should not be discharged into water bodies without sulphates removal. The current Government Regulation No. 296/2005 of the Slovak body of laws includes general requirements for the surface water quality in the Slovak Republic, where the recommended sulphates concentration is 250 mgl^{-1}.

Various treatment techniques of the mine waters have been developed during the recent time. The selection criteria for each of the processes are based on a number of technical, economical, environmental and legislative factors. The treatment processes removing sulphates include these categories: chemical treatment with the mineral precipitation, membrane technologies, ion exchange technologies and biological technologies (INAP, 2003).

The biological removal of sulphates from the waste waters can be realized by the way of anaerobical reduction to sulphide using sulphate-reducing bacteria (SRB). SRB are a heterogeneous group of microbes, which use sulphate as terminal electron acceptor. They use simple inorganic and organic compounds like hydrogen, lactate and acetate as electron donors (growth substrates) and reduce the sulphate to hydrogen sulphide as the end product by dissimilatory sulphate reduction pathway (Postgate, 1984).

Materials and analytical methods

Acid mine drainage

The investigation has been carried out at a laboratory scale, utilizing AMD discharged from the shaft Pech located at Smolník (abandoned and flooded Slovak sulphidic deposit), containing 2 150 mg/l sulphates. Before the use, many metals (Fe, Al, Mn, Zn and Cu) have been eliminated from AMD by selective sequential precipitation. These metals were removed by the precipitation in the form of hydroxides using sodium hydroxide as reagent and sulphides using bacterially produced hydrogen sulphide as reagent at the various values of pH (Mačingová et al., 2009).

Microorganisms

In the experiment the culture of the sulphate-reducing bacteria (genera *Desulfovibrio*) has been used, isolated from a mixed culture of SRB obtained from the mineral water Gajdovka (Košice, Slovakia). For their isolation and cultivation the selective nutrient Postgate´s medium C has been used (Postgate, 1984) at 30 °C at anaerobic conditions.

Analytical procedures

The nefelometric method was used to determine the concentration of sulphates at 490 nm using the Spectromom 195 spectrophotometer. The pH of the cultivation media was determined by the potentiometric method using the PHM 210 MeterLab pH meter.

Experimental procedure

Batch studies on sulphates removal from the pre--treated AMD using SRB were carried out using four reactors containing 250 ml modified nutrient Postgate´s medium C. The modification in each case was removing the sulphate containing salts from the prescribed media and adding 100 ml of pre-treated AMD containing the soluble sulphate. Here was also used the different growth substrates: sodium lactate according to prescribed media (sample marked La-Na I.), double volume of sodium lactate (sample marked La-Na II.), calcium lactate according to prescribed media (sample marked La-Ca I.) and double volume of calcium lactate (sample marked La-Ca II.). The pH value of nutrient medium was adjusted at 7.5 using 5 M sodium hydroxide. Each of the reactors was inoculated with 10 % of a 3-day SRB culture. The abiotic controls with substrates sodium lactate and calcium lactate respectively have been prepared (samples marked La-Na AC and La-Ca AC). The rest of the conditions for the growth were kept the same as that of the prescribed media.

The regular samples were taken every day over a week to monitor levels of sulphates.

Results and discussion

The aim of our work was the experimental verification of the possibilities of the sulphate rich waste waters utilization as the source of sulphate for the cultivation of SRB. During our study we obtained the evidence for the bacterial sulphate reduction to hydrogen sulphide:

(i) by formation of a black precipitate of FeS when sulphide is formed (for diagnostic purposes media contain a ferrous salt),

(ii) by decreasing of sulphates concentration in the nutrient mediums.

Figs. 1 and 2 show sulphate reduction kinetic when using substrates sodium lactate and calcium lactate respectively.

Results of our experiment demonstrate the high efficiency of the AMD treatment. Depend on the quality and quantity of used substrates there was reached 100 % (La-Na II.), 97 % (La-Ca II.), 61.39 % (La-Na I.) and 57.55 % (La-Ca I.) removing of sulphates by the dissimilatory sulphate reduction. In the abiotic controls the concentration of sulphates did not decrease. Fig. 3 shows the efficiency of sulphate elimination.

Technologies include SRB are promising for their ability to reduce soluble sulphates and produce high amount of hydrogen sulphide which has a great affinity to react with divalent metals to form of insoluble metal sulphides thus removing toxic metals from waste waters (Kaksonen et al., 2007). Sulphide precipitation of metals has been demonstrated to have several benefits over the usually used hydroxide precipitation, such as lower effluent metal concentrations, better thickening characteristics of the metal sludge and the possibility to recover valuable

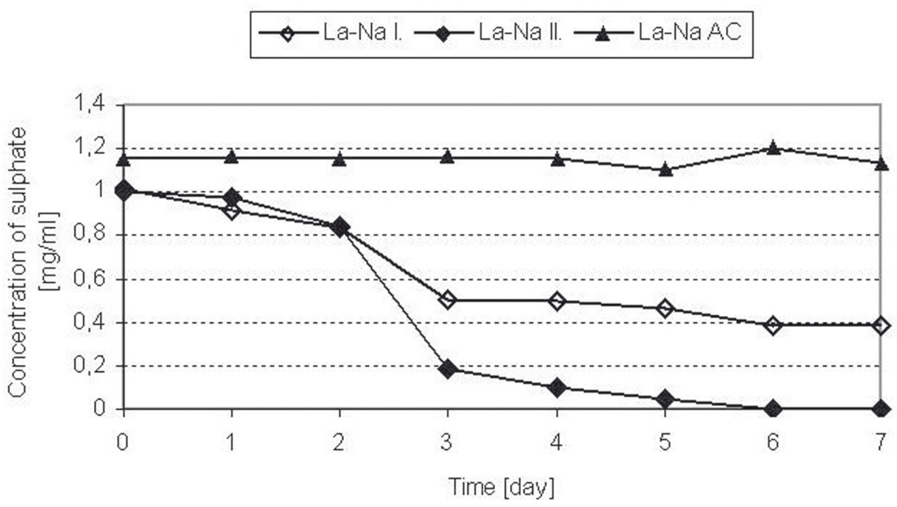

Fig. 1. Sulphate reduction kinetics using natrium lactate as substrate for cultivation of SRB.

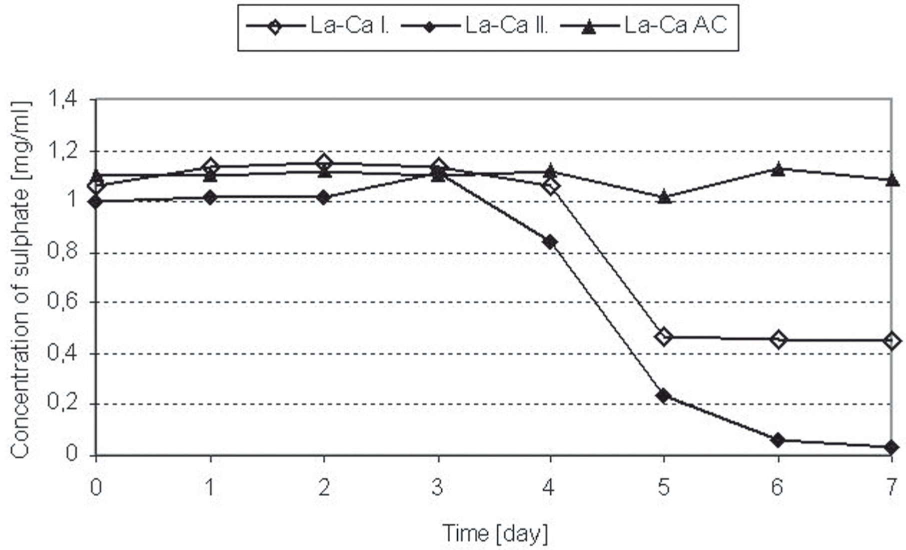

Fig. 2. Sulphate reduction kinetics using calcium lactate as substrate for cultivation of SRB.

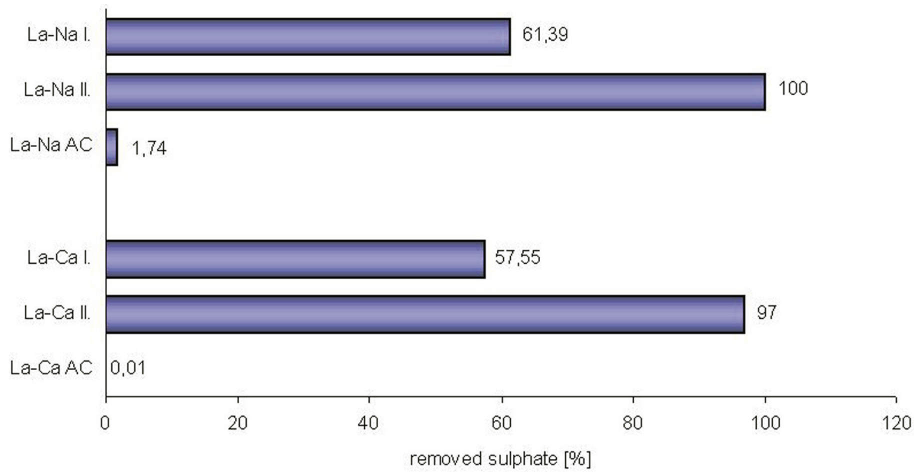

Fig. 3. Efficiency of removing of sulphate.

metals (Huisman et al., 2006). Obtained hydrogen sulphide may be also oxidized to elementary sulphur by way of chemical oxidation using ferric ions (Luptáková et al., 2002) or by Thiopaq gas purificating technology. This is a biotechnological process for removing H_2S from gaseous streams by absorption into a mild alkaline solution followed by the oxidation of the absorbed sulphide to elementary sulphur by naturally occurring microorganisms – Thiobacillus bacteria (THIOPAQ, 2004).

Conclusion

The possibility of utilization of the sulphate reducing bacteria to remove the sulphates from the waste water was the aim of our research. The sulphate concentration in six reactors contained modified nutrient Postgate´s medium with the pre-treated AMD as a source of sulphates were monitored during one week. Four reactors were inoculated with SRB cultures and two reactors without inoculation served as an abiotic control. A quantitative elimination of the sulphate (100 and 97 %) has been achieved in our experiment. Results have demonstrated the technical feasibility of the use of sulphate-reducing bacteria to biological sulphate removal from pre-treated AMD.

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Risk assessment for silver nanoparticles in environment

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Abstract

Nanotechnology, the science which offers great opportunities, involves manipulation and application of engineered particles or systems that have at least one dimension being less than 100 nm in length. Products of nanotechnology, e.g. silver nanoparticles are widely used in many industries due to their unusual properties, which are dependent on the nanometric sizes. Despite the fact that materials containing nanosilver are widely available, their possible impact on the human health and the environment is still not fully understood. Detailed information about the risk assessement for nanoparticles is required, especially data on the potential toxicity, routes of exposure and environmental effects, including application, transformation and bio-accumulation. The main aim of this paper is to present the possible negative interaction of nanosilver on the environment and toxicity to organism, as well as to draw attention to a new type of the waste – nanowaste and present probable ways to eliminate a destructive impact of nanoparticles.

Key words: nanotechnology, silver nanoparticles, risk assessment, toxicity, nanowaste, prevention

Introduction

Nanotechnology as a science about producing structures, devices and systems with one dimension between 1 and 100 nm is described as one of the key technologies of the present century. According to the National Nanotechnology Initiative of the U. S. government the main aim of this science is the research and development to understand and work with a matter at the atomic, molecular and supramolecular levels (Scott, 2007). In the other words the nanotechnology is focused on preparing the miniature products determined by the size of their elements. Nanoproducts e.g. nanoparticles exhibit completely new or improved properties based on specific characteristics such as size, distribution and morphology, if compared with the larger particles of the bulk material they are made of (Song and Kim, 2009). Using these unique features will allow to control many processes at the level of atoms and also offers opportunities to create new devices with unprecedented functionality (Świderski and Waszkiewicz-Robak, 2006).

Recently, the attention has been focused around the metallic nanoparticles which are widely used in the different areas of life due to their unusual properties (Panyala et al., 2008). One of the most important advantages of them is a large surface to the volume ratio with decreasing size of nanoparticles leading to increasing the chemical activity. Highly developed surface area has a significant effect on the adsorption properties, reactivity of nanomaterials, optical features and the other properties including antimicrobial activity (Song and Kim, 2009; Panighari et al., 2004).

Risks associated with nanotechnology

Though the research in nanotechnology continues apace, relatively little is known about the subsequent health effects of the exposure. Despite the fact that materials containing nanoparticles are widely available, one of the side effects of nanotechnologies is the release of nanomaterials to the environment. It may have a hazardous effects on the environment and living organisms, therefore the risk assessment of used nanomaterials is needed.

As mentioned, the nanomaterials show quite different features in comparison with the bulk materials and their toxicity may be different from that of the same chemical substance in the form of larger particles. There are examples where nanoparticles can produce toxic effects even if the bulk substance is nonpoisonous (Dowling, 2004). For example there is demonstrated that the ultrafine TiO_2 particles (20 nm diameter) elicited a persistently high inflammatory reaction in the lungs of the rats compared to the larger-sized particles (250 nm diameter) (Oberdörster et al., 1994). Also the research studies of Chae et al. (2009) suggest that two different silver forms (silver ions and silver nanoparticles) have various impact on the fish *Oryzia lapites*. The silver nanoparticles appear to be more toxic than the ionic form of silver which leads to cellular damage.

Due to smaller size, nanoparticles easier penetrate cells which is not always desirable, moreover they have increased surface so they are more reactive. Therefore more research on the toxicity of nanoparticles is needed, because besides the many advantages they can be also a threat. It should be noted that the potential risks of available nanoproducts are currently the subject of many different studies and toxicological effects are poorly understood despite rigorous risk control assessment (Hallock et al., 2009). To illustrate the problem, as an example there could be a new anti-bacterial material with the silver nanoparticles for the meat packing. The main advantage is the longer product shelf life and disadvantages include the uncertainty whether the silver nanoparticles might migrate from the packaging material into the meat. Another use of nanoscience with unexplained effects on the health of living organisms is a nanomaterial with the beta-carotene closed in small particles which better dissolves in the water, but experts still do not know the side effects of the nanoproduct (Siegrist et al., 2007). It is obvious that not all nanomaterials have a negative impact on the surrounding nature. Toxicity experiments of American researchers demonstrated that colloidal spherical silver nanoparticles and silver nanoprisms of 30 nm sizes are not cyto-, photo- or genotoxic to human skin HaCaT keratinocyte (Lu et al., 2010). However the risk assessment needs to protect the environment from the unwanted release.

Applications of silver nanoparticles

In recent years the nanostructured silver particles have been the subject of much intensive research. Already in 2007 at Woodraw Wilson International Center of Scholar there have been tested more than 500 commercial nanoproducts and 20 % of them contained silver nanoparticles (Lu et al., 2010).

At the beginning, silver was used for making ornament, but after the discovery of the extraordinary antimicrobial properties silver was utilized for preservation of food, water and milk and for the treatment of wounds and infections (Tien et al., 2008). Actually chemicals based on nanosilver are applied in electronic, optic, chemical and textile industries, as well as in pharmacy, cosmetology, medicine, food production and packing where they play a significant role as substrates for synthesis, catalytic materials, sensors, conductors, detergents or antimicrobial coatings (Xu et al., 2006; Siegrist et al., 2007; Chen et al., 2009; Lu et al., 2010). It is also possible to modify materials and raw materials by the deposition of the silver nanoparticles on the carrier or covering their different surfaces, whereby they shown deodorize, antistatic and impregnation properties (Zhang et al., 2007).

Influence of the silver nanoparticles on living organisms

Particles with the dimension below 100 nm are synthesized not only in industrial prosesses, but also the nature enriches the environment by the different nanosized particles. They are generated by natural events such as volcanic eruptions, forest fires and they are components of fumes formed during the automobile exhaust or other industrial combustion reactions (Navarro et al., 2008; Hallock et al., 2009; Bystrzejewska-Piotrowska et al.,

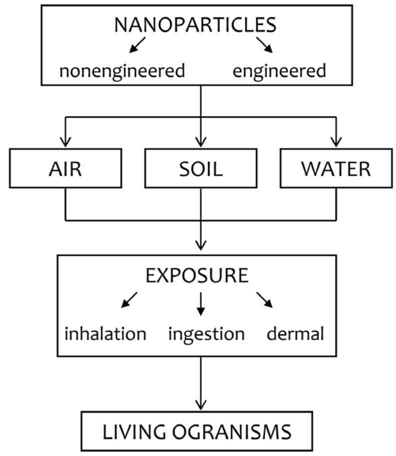

Fig. 1. Pathways of nanoparticles in the environment.

2009). In other words, people have always had contact with the nanoparticles of various origin. Rapid growing production of nanomaterials caused the increase of amount of nanomaterials in the environment, what which may have adverse effects on organisms.

Due to the multiplicity of routes of penetration into the body of organisms, many studies on the toxicity of nanoparticles on living organisms have been conducted. However, they do not give an unequivocal answer whether nanosilver harms, because some reports demonstrate the toxic effects on the health and another show that silver nanoparticles do not induce any negative consequences. There exist three main groups of exposures – inhalation, ingestion and skin absorption (Friedrichs and Schulte, 2007; Hoyt and Mason, 2008; Hallock et al., 2009). For the silver nanoparticles the most frequent is inhalation and skin absorption routes due to size, mass and shape of nanoparticles (Hyun et al., 2008; Larese et al., 2009).

It is found that silver metal and silver dressing has no negative effects (or even favourable) when is used in reasonable amounts, but many scientific reports prove that silver in various forms, also, nanosized silver is extremely toxic to some plants, fungi, bacteria, fish and mammalian cells (Panyala et al., 2008). It is shown that silver nanoparticles disintegrated cell membranes of bacteria e.g. *Escherichia coli* and *Staphylococcus aureus* and kill them (Martínez-Castañón et al., 2008). Moreover, as already mentioned silver especially silver nanoparticles causes changes in the expression of the stress-related genes of fish leading to disruption of metabolism and DNA damage (Chae et al., 2009). Other research showed that silver nanoparticles induced embryo-cytotoxicity in the mouse blastocysts and decrease their viability increasing apoptosis (Li et al., 2010). Cytotoxic effect of nanosilver was also demonstrated using the in vitro rat liver derived cell line (Hussain et al., 2005). It was noted that the presence of the silver and other nanoparticles leads to oxidative stress and interferes with mitochondrial function. Braydich-Stolle et al. (2005) estimated that silver nanoparticles already at 5 to 10 μg/ml concentration caused changes like necrosis and apoptosis of cells and drastically reduces mitochondrial activity. Further research suggests than nanoparticles can have a severe toxic effect on the male reproductive system by the capability to cross the blood-tests barrier (Panyala et al., 2008). Nanosized silver also easily pass through the blood-brain and skin barriers in the model animals (Borm and Kreyling, 2004).

On the other hand, there are reports of non-toxic effect of silver nanoparticles on living organisms like mentioned earlier tests results of nanosilver influence on the human skin HaCaT keratinocyte. Another example are studies on the nasal septum respiratory mucosa of rats. The animals exposure on the silver nanoparticles by inhalation exhibited the changes in the properties of the goblet cells in the respiratory system, but without toxicological significance (Hyun et al., 2008). Similar results were observed during experiments on mices, which shown lack of negative changes in the functionality of organism. Two different concentrations of the specially prepared silver nanoparticles were injected intra-peritoneally. Despite of penetration of the nanosilver across the blood brain barrier it was not observed toxicity. Additionally, silver nanoparticles apparently can be an alternative to conventional chemotherapy by increased neurotransmission and activity of the brain (Daniel et al., 2010).

It is true that organism´s response to the presence of nanoparticles may by different and in the vitro models there is a simplification of natural conditions, nevertheless each result can be a basis for the further assessing of the potential risk of exposure. The amount of potential applications of silver nanoparticles shows that more research is needed to improve nanomaterials and release them of any toxicity.

Influence of silver nanoparticles on the environment

It is believed that the development of nanotechnology may help to protect the environment by improving the water and food quality and reducing the energy consumption. Among the numerous applications of nanotechnology, there are already many that involve the environment. Using the iron nanoparticles for remediating of contaminated land and waters (Owen and Depledge, 2005; Tratnyek and Johnson, 2006), europium oxide nanoparticles for detecting the antrazine pesticide in the water (Małecka, 2007) or silver nanoparticles in the water treatment applications as antibacterial water filter (Lv et al., 2009) are only some examples.

However, there are also alarming reports concerning the uncontrolled release of nanomaterials (nanowastes) to the atmosphere, the soil and to the aquatic systems. Fig. 1 presents a schema of the nanoparticles pathways in the environment.

This problem also includes the silver nanoparticles. Based on several studies, it can be concluded that nanosilver appears to be a threat for natural ecosystems and thus indirectly to living organisms. Silver and silver nanoparticles exhibit toxic effect on human-friendly microbes like heterotrophic and chemolithotrophic bacteria in the soil, which play a major role in the nitrogen fixation and decomposition of inorganic matters (Panyala et al., 2008). The model for nanoparticles toxicity in aquatic system is in vitro culture of rainbow trout hepotocytes. There was investigated the influence of the different forms of silver on trout hepatocytes and the results showed that the nanosilver was highly cytotoxic and even at low concentrations nanoparticles reduced of metabolic activity and the membrane integrity (Farkaš et al., 2010). Moreover, researchers observed than silver nanoparticles were slightly higher toxic than silver ions. It is found that the silver nanoparticles toxicity was mediated by the silver ions – nanoparticles were interacting with the cells and thereby releasing a high number of ions directly inside the cells. Another example proving accumulations of nanosilver in the aquatic environments are experiments on zebrafish embryo. Silver nanoparticles increased apoptosis in nanoparticles-treated embryos and caused brain, heart, eyes injury and other serious damages (Navarro et al., 2008). Other reports demonstrated that, silver nanoparticles also have the negative influence on the phytoplankton. In the study of Miao et al. (2009) silver nanoparticles cause the inhibition to the cell growth of coastal marine diatom *Thalassiosira weissflogii*.

It should be paid an attention that some living organisms like fungi or plants also introduced silver nanoparticles into the soil environment. Extracellular biosynthesis has been shown e.g. in *Fusarium solani* (Ingle et al., 2009) and in the different plants as *Magnolia kobus* or *Ginko boloba* (Song and Kim, 2009).

Because the nanotechnology is a relatively young branch of science, the release of nanomaterials to the environment is still not fully understood. It is not known yet what concentration, size and shape of nanoparticles are toxic in different environments, what are mechanisms of the trophic transport and exposure routes, therefore the further research are absolutely needed.

Nanowaste – possible ways to eliminate it

New, rapidly developing science – nanotechnology leads to the formation of a new type of the waste – nanowaste. It contains collections of nano-objects like engineered particles, fibres or plates in the nanoscale. Due to the diversity of nanoobjects synthesized by the nature or researchers their potential threats to environment and the composition of the nano-waste is a very different. Depending on the amount, types and composition of the nano-objects the different quantities of nanowaste are produced (Allan et al., 2009). There exist four main types of nanowastes, which can act as an ecotoxicological hazard through the biodegradation or bioaccumulation in the food chain:

1. Pure materials,
2. Items contaminated with nanoparticles,
3. Liquid suspensions containing nanomaterials,
4. Solid matrices with nanomaterials (Hallock et al., 2009).

It is necessary to find how nanomaterials will be treated and disposed of after the end of their use, therefore the examination of the harmfulness must include: identification and quantification of the sources, determination of the environmental release pattern, establishment of concentrations in the environment, and examination of the potential bioaccumulation (Bystrzejewska-Piotrowska et al., 2009).

It is obvious that all the problems concerning the hazard evaluation of nanotechnology cannot be rapidly solved, but so far has been proposed many ideas for possible ways to eliminate them. Firstly, due to nanoparticles are 100 % respirable it could be considered to change of form. For example the reducing the airborne concentrations may be obtained by the receiving or handling nanomaterials only in wet form (Hoyt and Mason, 2008). An interesting idea about the removal of nanoparticles from the environment encompass a method developed by Iwashita et al. (2007). They elaborated a device for trapping nanoparticles by collision and attaching them by their surface. The trapping efficiency of the device for nanoparticles above 2 nm in size is more than 99.8 % at a low pressure. Another promising way to decrease of toxicity is the surface modifications by adding different functional groups or encapsulation. Interesting results of experiments conducted with the use of carbon nanotubes. Test consisted from the adding various chemical groups to an aqueous solution of the carbon nanotubes, which changed the surface structure of nanotubes. As a result, there was observed the reduction of mortality of the human skin cells from 50 % to more than a dozen (http://www.nanotec.org.uk). For the identification and observation (morphology, composition or interparticles relations, distributions of nanomaterials in the organisms) there is possible to use the fluorescent detection, surface plasmon resonance, photocatalytic detection and another analytical techniques (Silbergeld et al., 2010; Zhang and Fang, 2010).

Attention is also drawn to a nanowaste recycling, emphasizing segregation, nanowaste storage, recovery and reuse. Other ideas are based on the possibility of bioaccumulation of nanowastes (mainly nanoparticles) by plants, fungi and microorganisms as is the case with the heavy metals. It is believed that bioutilization may help to remediate the environment and protect fauna and flora (Bystrzejewska-Piotrowska et al., 2009).

Conclusions

New types of risks to the environment resulting from the release of nanomaterials on the environment should be considered. Therefore the potential risks of the silver nanoparticles and another nanomaterials are currently the subject of hundreds conducted studies. Numerous institutions are collecting data about ongoing research projects and the test results – e.g. the International Council of Nanotechnology – ICON, the Woodrow Wilson International Centre for Scholars, National Nanotechnology Initiative – NNI and other (Friedrichs and Schulte, 2007; Hoyt and Mason, 2008).

Considering the nanotechnology it is needed to look not only what damaged it causes, but what opportunities it offers. Phillipus Auroleus Bombastus von Hohenheim also referred to as Paracelsus created the classic toxicology maxim: "All things are poison and nothing is without poison; only the dose makes a thing not a poison." Currently, still is little known about the effects of the implementation of nanotechnology, however, it is estimated that in the future the world will develop, owing to nanotechnology, free of any threat.

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Biosorption of lead (II) ions by pretreated biomass of *Phanerochaete chrysosporium*

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Key words: heavy metals, biosorption, biomass

Abstract

Heavy metals are discharged from various industries such as electroplating, metal finishing, textile, storage batteries, mining ceramic and glass. As they pose serious environmental problems and are dangerous for human health, considerable attention has been given for the methods for their removal from the industrial wastewaters. At present, many technologies, such as sulfuration method, electrolysis, membrane and ion-exchange process, can be used for the treatment of wastewater polluted by the heavy metals. However, these methods are less effective and more expensive when heavy metal concentration in the wastewater is low, and some of them are easy to cause the secondary pollution. Removal of heavy metals by biosorption has many advantages, such as fast adsorption speed, removing heavy metal ions selectively under low concentration, high adsorption efficiency, wide range of pH and temperature, less investment and running cost. In addition, some heavy metals can be recovered.

Phanerochaete chrysosporium is a well-known white-rot fungus and it has a strong ability to degrade various xenobiotics and exist in bleaching effluents from pulp and paper mills. It could also be used to remove heavy metals from the wastewaters by adsorbing the metals on its mycelium. The treatment of native biomass improves its biosorption capacity, changes the possible binding groups. In this study the biosorption of heavy metals from aqueous solution on non-living mycelial pellets of *Phanerochaete chrysosporium* treated with caustic, heat and ethanol was studied using batch technique with respect to initial pH value, initial concentration and biomass dosage. *Phanerochaete chrysosporium* was grown in a liquid medium containing mineral and vitamin materials with a complex composition. The maximal adsorption capacity for lead removal was determined at pH 6. The kinetics of lead(II) removal and the relevance of adsorption isotherms for characterization of the uptake were examined. The biosorption process followed pseudo-second order kinetics. The adsorption data of heavy metals on the blank beads and treated biomass could be well described with Freundlich and Langmuir isotherm equation as well. The biomass of *P. chrysosporium* treated with ethanol revealed that it was mechanically stable and had increased adsorption capacity compared to caustic, heat and untreated cells.

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Metal mobilization from AMD sediments in connection with bacterial iron reduction

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Abstract

Ochreous sediments, dominated by schwertmannite mineral from the acid mine drainage effluent from the Smolník abandoned sulfide mine, and biogenic schwertmannite prepared under laboratory conditions, were subjected to leaching by the acidophilic iron-reducing bacterium *Acidiphilium* SJH. Different kinetics of the mobilization of sulfur and iron entities from the schwertmannite during the bacterial leaching indicated incongruent dissolution of the mineral. Due to bacterial iron reduction, all of the dissolved iron was in divalent state. Contrary to the progressive sulfate extraction, the leaching of iron showed saturation behaviour, caused either by the sorption of ferrous ions onto the mineral surface or by the precipitation and formation of new mineral phase. Mobilization of arsenic from the sediment in the early stage of leaching was followed by its later disappearance from the solution due to sorption or co-precipitation onto/with a newly formed iron mineral phase.

Chemical analysis of the acid mine drainage (AMD) water and related sediments formed from the stream revealed selective scavenging potential of the iron precipitates for arsenic and some other species. The iron oxidizing and iron reducing bacteria play a vital role in the successive dissolution and immobilization of elements in the mine drainage systems in connection with the biogeochemical destruction and reconstruction of metal sulfides, iron hydroxides and iron hydroxysulfate minerals.

Key words: AMD, schwertmannite, acidophilic bacteria, iron, sulfate, precipitation, oxidation, reduction

Introduction

Iron and sulfur oxidizing bacteria play an important role in the metal mobilization in AMD, as they accelerate the oxidation of iron and sulfur entities in the pyrite and other metal sulfides, leading to mineral dissolution and acid generation (Singer and Stumm, 1970; Nordstrom, 1982). On the other hand, bacterial oxidation of Fe^{2+} to Fe^{3+} affects the iron speciation and as a result of that it contributes to the formation of the secondary iron minerals. After the ferric iron in the AMD systems reaches saturation, it hydrolyses and precipitates in various forms of iron oxides and hydroxysulfate minerals. Schwertmannite (Eq. 1) is considered to be the major secondary ferric iron mineral that forms in moderately acidic (pH 2.8 – 4.5) sulfate waters impacted by AMD (Bigham et al., 1996).

$$8\ Fe^{3+} + SO_4^{2-} + 14\ H_2O \rightarrow Fe_8O_8(OH)_6SO_4 + 22\ H^+ \qquad (1)$$

Sediments of AMD recipients receive significant amount of iron, sulfur and other elements that co-precipitate with or adsorb onto these secondary mineral phases. The formation of these iron minerals may play an important role in the transient storage of metals.

Heterotrophic acidophilic bacteria, that occupy acid mine streams, have been shown to use the dissimilatory reduction of ferric iron to growth in oxygen-limited conditions (Coupland and Johnson, 2008). Reductive dissolution of solid ferric iron minerals by these bacteria causes mobilization and down-stream transportation of iron, sulfate and other potentially toxic elements associated with the precipitates through sorption or solid solution. The cycling of Fe between the oxidized and reduced solid phases thus involves successive solubilization and immobilization of elements from these transient storages. Iron oxides are in general compounds with low- to very low solubility. In natural environments, reductive dissolution is by far the most important dissolution mechanism (Cornel and Schwertmann, 2003).

In this work, heterotrophic bacterium *Acidiphilium* SJH was applied in the leaching test, as the ability of this bacterium to reduce both soluble and solid phase ferric iron has been reported previously (Bridge and Johnson, 2000).

Material and methods

Preparation of the minerals

Ochreous precipitates were collected from the sediments of AMD effluent from the shaft Pech that concentrates the majority of waters draining the flooded Smolník mine area.

The sediment was air dried at the ambient temperature, homogenized and stored in desiccators for further use.

The biogenic schwertmannite was prepared in the laboratory from ferrous sulfate solution ($FeSO_4 \cdot 7H_2O$) by its biological oxidation to ferric sulfate followed by the ferric iron hydrolysis and precipitation. Psychrotolerant iron-oxidizing bacterium *Acidithiobacillus ferrooxidans* SS3 (Kupka et al., 2007) was inoculated to the ferrous iron-containing medium. The schwertmannite formation was achieved in the absence of potassium and at low level of other monovalent cations to prevent the precipitation of jarosites (Wang et al., 2006; Gramp et al., 2008) salts medium for schwertmannite synthesis contained 1.6 mM $MgSO_4 \cdot 7H_2O$, 6.1 mM $NH_4H_2PO_4$ and 120 mM $FeSO_4 \cdot 7H_2O$ in 4.05 mM H_2SO_4. The initial pH of the medium was 2.8. The incubation was carried out at 4 °C in 500 ml flasks stored in cooling thermo cabinets and magnetically stirred at 180 rpm. Samples of the solutions were taken in intervals for the iron speciation, sulfate, pH and redox analysis. All synthesis conditions involved 10 days of equilibration before the samples of precipitates were separated from the rest liquid medium by centrifugation at 5 000 rpm, washed by distilled water and air dried.

Bacterial leaching

The leaching tests of the sediment samples were done with the iron reducing bacteria *Acidiphilium* SJH (Bridge and Johnson, 2000) in the special tubes with a screw cap and a septum. Each tube contained 0.05 g of dried sediment and 10 ml of liquid medium (final pulp density 5 g · l^{-1}). The medium contained (per liter) 6.25 g $(NH_4)_2SO_4$, 2.5 g $MgSO_4 \cdot 7H_2O$, 0.13 g tryptic soy broth, 0.9 g D-galactose, and 1 mL solution of the trace elements. The medium was acidified with 5M H_2SO_4 to final pH 2.5. The bacterial inoculum was taken from the aerobically grown culture. The cells were separated from the nutrient solution by filtration through a 0.20 μm pore size Milipore filter. Washed cell pellets were suspended in fresh medium and diluted to adjust the final cell concentration equal to optical density OD_{600} = 1.0. Ten milliliters of the cell suspension were added to each tube. The tubes were air tightly closed, and incubated dynamically on a rotator at 60 rpm in a thermostat at 25 °C. Experiments were carried out in triplicates and each series included one abiotic control.

Because of the observing anoxic conditions and excluding the sample contamination, the samples were taken in regular intervals through the cap´s septum by using sterile needles and syringes. The samples were filtered in order to separate the solid and liquid phases before analysis.

Chemical analyses

Chemical composition of the solid phases was determined by atomic absorption spectrometry (AAS) with GTA furnace after the digestion with concentrated nitric and hydrochloric acid (1 : 1) in a microwave digester. Ferrous iron was measured by o-phenantroline colourimetric method, ferric iron by UV-spectrophotometric method at λ = 300 nm. Sulfate concentration was determined by $BaCl_2$ nephelometric method. Concentrations of the total iron and arsenic in the leaching liquors were determined by AAS and pH and the redox potential of the solutions by the potentiometric method.

The XRD patterns were measured using a Philips PW 1820 powder diffractometer working in the 2Θ geometry with CuKα radiation. The JCPDS PDF database (JCPDS--PDF, 2004) was utilized for the phase identification.

Results and discussion

The XRD spectrum of the Smolník precipitate (Fig. 1) gave characteristic schwertmannite XRD pattern with 8 broad peaks and a high background, indicating poor crystallinity. The spectrum contained the phases: iron oxide sulfate hydroxide $Fe_{16}O_{16}(SO_4)_3(OH)_{10} \cdot 10H_2O$ (JCPDS 47--1775), iron oxide hydroxide FeO(OH) (JCPDS 13-87), and ferrihydrite $Fe_5O_7(OH) \cdot 4H_2O$ (JCPDS 29-712).

Chemical composition of the sediment is given in Tab. 1.

The two major elements of the precipitate are iron and sulfur. Schwertmannite, with the ideal formula $Fe_8O_8(OH)_6(SO_4)$, implies an Fe/S molar ratio of 8. However, the sulfate content is variable in natural samples of schwertmannite and varies from 10 to 15 wt.%, yielding Fe/S mole ratios ranging from 8 to 4.6 (Bigham et al., 1994; Murad et al., 1994; Bigham et al., 1996). The weight % of iron and sulfur in the "Smolník" precipitate (Tab. 1) are 44.89 and 5.53 respectively, yielding Fe/S molar ratio of 4.7. This value belongs to the range of naturally occurred schwertmannites published by Bigham et al. (1994).

Fe(III)-hydroxysulfates from the acid mine drainages have been shown to contain As, Cr, and a variety of the rare earth elements (Schroth and Parnell, 2005). Relatively high content of arsenic (0.28 wt.%) in the "Smolník" precipitates indicates their ability to accumulate oxyanions from the surrounding water. The concentration of arsenic in the AMD stream in which the precipitates were formed was 30 μg · l^{-1}. The concentration of iron and sulfate in the AMD was 380 mg · l^{-1} and 2 320 mg · l^{-1} respectively. The pH of the water was 3.9 and temperature 14 °C. Natural precipitates in the sediments of streams, where the water has attained a pH of 3 to 4, are dominated by schwertmannite.

Tab. 1
Chemical analysis of precipitates taken from AMD (shaft Pech) in Smolník abandoned mine (April, 2009)

Fe	S	Al	Ca	Mg	Na	K	As	Cu	Zn	Mn	Pb
%	%	%	%	%	%	ppm	%	ppm	ppm	ppm	ppm
44.89	5.53	0.38	0.1	0.07	0.02	47.5	0.28	112.5	72.5	35	16.8

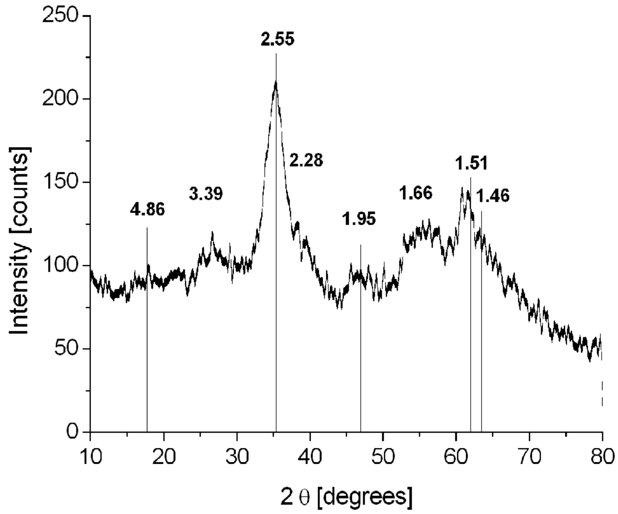

Fig. 1. X-ray diffractogram of precipitates collected from the shaft Pech in the Smolník abandoned mine. The d-spacing (Å) and peak positions for schwertmannite (PDF 47-1775) are given as vertical lines.

Schwertmannite was the major component of all collected and studied AMD precipitates formed between pH 2.5 and 4 by Murad et al. (1994).

Preparation of the biogenic schwertmannite from ferrous salt solution using psychrotolerant iron oxidizing bacteria *Acidiphilium* SS3 was done at 4 °C. Ferrous iron was completely oxidized to ferric iron within 10 days (Fig. 2A). The solution pH initially increased due to the acid-consuming iron oxidation. Subsequent reaction of ferric iron hydrolysis, leading to schwertmannite formation is acid producing and the final pH value depends on the extent of ferric iron precipitation (Fig. 2B).

Due to bacterial oxidation of Fe^{2+} to Fe^{3+} ferric iron eventually reached supersaturation with respect to

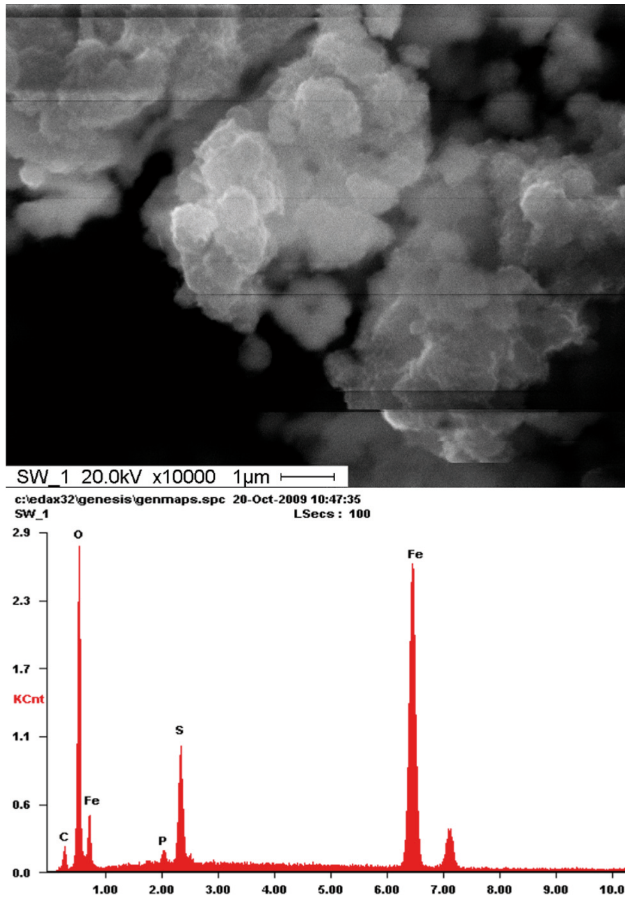

Fig. 3. SEM micrographs of biogenic Schwertmannite prepared in laboratory (top) and EDX analysis (bottom), which revealed 65.6 % Fe and 6.87 % S content in the mineral, yielding Fe/S molar ratio of 5.48. This value belongs to the range of naturally occurred schwertmannites published by Bigham et al. (1994).

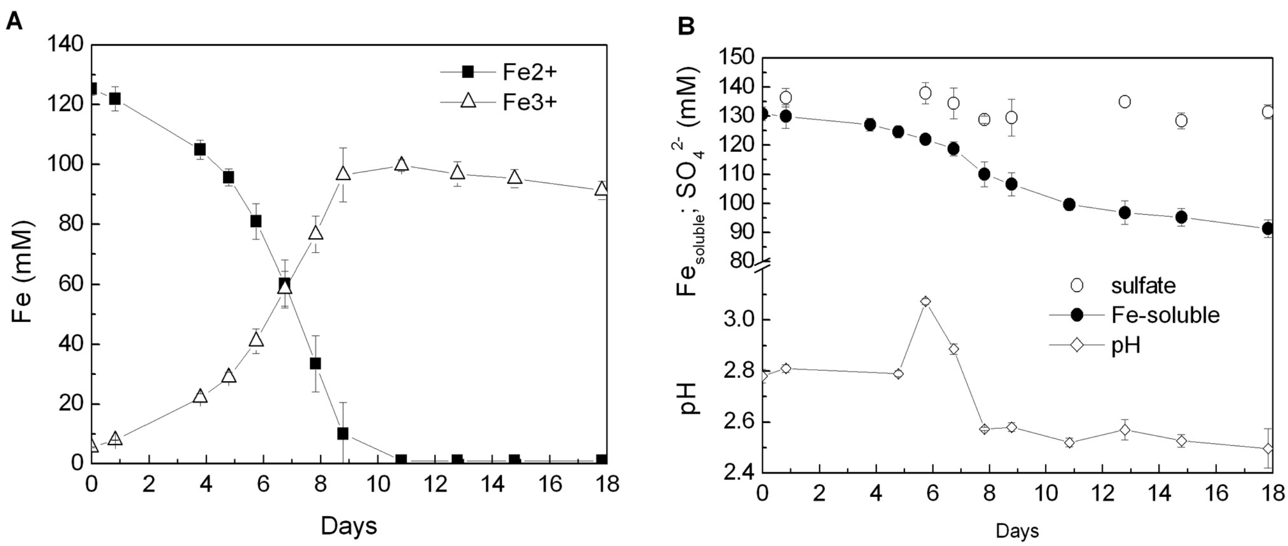

Fig. 2. Bacterial oxidation of Fe^{2+} to Fe^{3+} (2A), pH changes and precipitation of iron and sulfate in the course of schwertmannite formation (2B) at 4 °C. Symbols indicate averages ± standard deviations from triplicate flasks.

schwertmannite, which formation diminished iron and sulfate concentration in the solution. Schwertmannite was synthesized in the absence of potassium and other monovalent cations, to eliminate the formation of jarosite minerals. The SEM and EDX analysis of schwertmannite formed is done in Fig. 3. The XRD analysis of this reference schwertmannite sample revealed characteristic 8 broad peaks pattern (data not shown), similar to those in Fig. 1.

Reductive dissolution of the iron precipitates

Fig. 4 shows bacterial leaching of AMD sediment and biogenic schwertmannite. The reductive dissolution of ferric hydroxysulfate (schwertmannite) $Fe_8O_8(OH)_6(SO_4)$, releases ferrous iron and sulfate and generates net alkalinity (Eq 2).

$$3Fe_8O_8(OH)_6(SO_4) + C_6H_{12}O_6 + 6H_2O \rightarrow 24Fe^{2+} + 6CO_2 + 3SO_4^{2-} + 42OH^- \quad (2)$$

In the course of bacterially mediated dissolution of ferric iron minerals, Fe^{III} from the solid phase accepts electrons from the oxidation of organic matter. Reduction of Fe^{III} to Fe^{II} destabilizes the coordination sphere of the iron, both as a result of the loss of charge and because of the larger size of the bivalent iron ion and thus induces detachment of iron as Fe^{2+} from the structure (Cornel and Schwertmann, 2003). The higher initial rate of the iron extraction was observed at laboratory prepared schwertmannite (Fig. 4 closed symbols) compared to iron extraction from the AMD sediment (Fig. 4 open symbols). The concentrations of dissolved iron, from which Fe^{2+} was the dominant iron species, reached approximately 16.5 mM (913 mg · l^{-1}), which corresponds to 31.6 % yield. The rate of the leaching gradually decreased and reached zero after 5 days at pure schwertmannite and 20 days in the case of AMD sediment sample. Laboratory studies of bacterial reductive dissolution of the crystalline ferric iron oxides typically revealed only minor degrees of the iron extraction (Phillips et al., 1993; Bridge and Johnson, 2000; Roden et al., 2000). There are a number of reasons of decelerating the iron dissolution rate. The mineral surface passivation due to the accumulation of surface bound divalent iron is assumed to be the major factor prohibiting the complete dissolution of mineral in batch systems (Roden et al., 1999, 2000). Adsorbed and exchangeable iron fraction of the solid phase was not quantified in these experiments. Unlike dissolved iron, the concentration of sulfate does not follow asymptotic behaviour and gradually increased in the observed interval (data not shown), indicating incongruent dissolution of the mineral phases. The high initial concentration of sulfate (approx. 120 mM) in the medium prohibited the exact determination of net sulfate extraction from the mineral phase during the leaching. Mobilization of arsenic from the Smolník sediment was observed in the early stage of leaching (Fig. 4B), followed by its disappearance from the liquid phase after 12 days.

Schwertmannite is a poorly crystalline, metastable mineral that transforms spontaneously to goethite, releasing all its structural sulfate and producing protons (Eq. 3) (Bigham et al., 1996).

$$Fe_8O_8(OH)_6SO_4 + H_2O \rightarrow 8FeOOH + 2H^+ + SO_4^{2-} \quad (3)$$

Transformation of the mineral schwertmannite to thermodynamically more stable goethite was observed in laboratory conditions at room temperature during 543 days (Bigham et al., 1996). In the presence of the iron reducing bacteria, the degradation of the parent iron mineral is accelerated and the reconstruction of the new mineral phase could be substantially affected due to the alteration of the ion speciation and the abundance of divalent iron

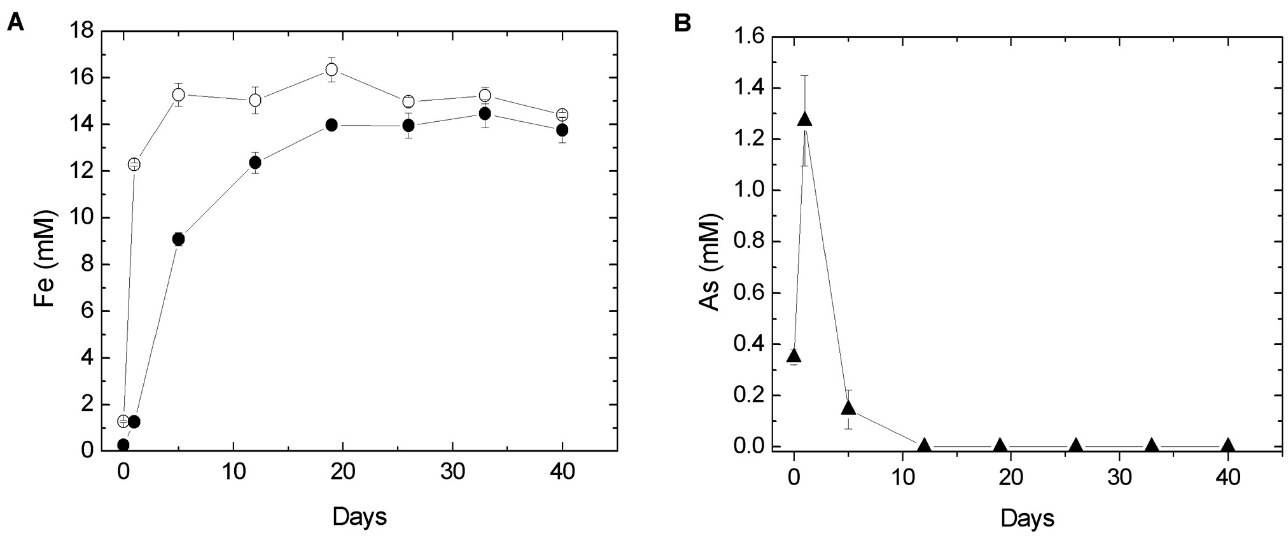

Fig. 4. Mobilization of iron and arsenic in the course of bacterial reductive dissolution of iron hydroxysulfate minerals. 4A extraction of iron from the biogenic schwertmannite (open symbols) and AMD sediment (closed symbols). 4B mobilization of arsenic from the AMD sediment in the course of bacterial leaching. Symbols indicate averages ± standard deviations from triplicate flasks.

species. Besides goethite, the formation of other phases is possible. At higher pH, which is achieved due to alkalinity producing reaction 2, the formation of magnetite is more likely as accumulation of this mineral has been observed during anaerobic bacterial iron reduction.

Conclusions

Bacterial oxidation of ferrous iron to ferric iron in the acid mine effluents contributes to attenuation of dissolved species in these systems. As ferric iron concentration in the solutions increased, it eventually reached supersaturation and co-precipitates with sulfate to the form of insoluble iron hydroxy sulfates. Schwertmannite is considered to be the major secondary ferric iron mineral that forms in the moderately acidic sulfide mine waters. The XRD pattern of both, the Smolník AMD precipitate and biogenic schwertmannite prepared in the laboratory corresponds to published X-ray spectra of AMD precipitates taken from other sites, where schwertmannite was the dominant Fe(III) mineral phase (Bigham et al., 1990). Chemical analysis of the Smolník sediment has proved retention of arsenic, Al, Cu, Zn and Pb from AMD stream and hence the capacity of iron precipitates for the transient storage of iron, sulfur and heavy metals. The paragenesis of ochreous AMD minerals and the fate of associated species depend on immediate environmental conditions. The cycling of Fe between oxidized and reduced solid phases may also involve solubilization or immobilization of associated potentially toxic metals or other ions during mineral destruction and transformation.

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Utilization of the waste and its mixtures in the technical land reclamation

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Key words: waste, land reclamation, Prestab and fly ash stabilisate

Abstract

Effects of the black coal underground mining are manifested in the mining landscape of the Ostrava-Karviná region in the form of earth´s ground deformations being accompanied by the deformations of all the way to the destruction of the surface structures. To deal with the black coal underground mining consequences it is necessary to provide the enormous volumes of the filling materials, especially in places where the waste rock and tailings from the preparation processes are short.

The utilization of the waste for the technical land reclamation is decided in the individual localities and based on the local risks as well as the legislative restrictions (the requirements for the harmful substance contents in the waste, which may be used on the ground surface, are specified in the Decree No. 294/2005 Coll. on conditions for the waste disposal in the waste disposal sites and its utilization on the ground surface, as amended by the Decree No. 383/2001 Coll., on details for the waste handling).

Therefore, firstly there is necessary to identify the own waste or waste mixtures with following laboratory and pilot tests. Only then, it is possible to determine, whether the waste may be applied in the locality in question for the technical land reclamation purposes.

Out of the range of the waste possibly suitable for the use on the ground surface, the choice of samples of "future" filling materials was narrowed to three available commodities: waste from the metallurgical primary production (blast-furnace slag), waste from the power--engineering (fluid fly ash, fly ash stabilisate), and waste from the chemical industry (production of titanium white).

First, the waste samples underwent the laboratory analyses and pilot tests. The objective was to prepare such mixtures of materials which could be used in the deposition on the ground surface or could be certified as materials suitable for technical land reclamation.

The following waste mixtures were prepared: Prestab + fly ash, Prestab + fly ash + slag, slag + Prestab, fly ash + slag, Prestab + fly ash stabilisate. In total, in the laboratory 41 samples of different mixtures of the above mentioned waste types were prepared. Gradually, all the proportions were mixed using a CAT M318 machine. After mixing, the individual figures of the inert material of about 1.5 m were formed. Such prepared, mixed volumes underwent a travel compaction experiment using a CAT D6H dozer.

Pilot tests helped to recommend a mixture of the slag and Prestab in the proportion 1.5 : 1 and a mixture of Prestab + fly ash stabilisate in the proportion 1 : 1.5. Using the proportions in question, the mixtures appear as no problem both in terms of handling as well as suitability for deposition on the ground surface within remediation and land reclamation work.

On the grounds of the laboratory analyses, only the mixture of Prestab and fly ash stabilisate can be recommended as it complied with the top admissible harmful substance concentrations in the waste solids in accordance with Appendix No. 10 to Decree No. 294/2005 Coll. Only in that case it is possible to consider certification of the mixture as a filling material for the land reclamation. Receiving a certificate should contribute to a simplification of the preparatory phase of ground shaping and remediation constructions.

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Possibilities of using a magnesite fines waste as an important mineral resource

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Abstract

Magnesite is a valuable material with the broad utilization mainly as the refractory and basic substance. During the mining, beneficiation and thermal treatment of magnesite the large amounts of its fines are lost despite of its high grade quality. This fact is caused by the impossibility of fines upgrading using a heavy media washing. Moreover, thermal treatment of the fines in rotary furnace is also controversial. Magnesite and/or periclase fines are formed during the sintering in the rotary and shaft furnaces and they are usually collected from the flue dusts using special filters.

The paper is focused on an enhancement of the magnesite fines recovery from preparation and beneficiation lines as well as from the thermal treatment of coarse magnesite where the flue dusts are formed. Thus, firstly, the sources of magnesite fines are identified according to processing plant flowsheet. Secondly, the possibilities of their upgrading are presented. The structure and properties of magnesite fines, economic and environmental aspects of their use and new concepts of thermal plant are considered. Proposed concepts are based on reducing the amount of the dust waste and designing the new technologies, which enable effective thermal treatment of these materials and thus a full-value application of these technologies. New development was aimed at an improvement of the magnesite fines thermal treatment.

Key words: magnesite fines, new concept of thermal treatment

Introduction

Magnesite industry produces the basic refractory materials necessary in the metallurgical and cement industries. Chemically pure magnesite contains 47.8 % MgO and 52.2 % CO_2. The principal harmful components are represented by CaO, SiO_2, Fe_2O_3, which unfavourably influence its quality from the technological point of view, because only the magnesia (MgO) is a utility component. These impurities often occur in the magnesite deposit as accompanying minerals, namely the dolomite, calcite and quartz. Magnesite from the Jelšava deposit is typical by the higher iron content due to the isomorphous replacement of magnesium by iron in its lattice. This ferroan magnesite is called breunnerite – $(Mg_{0.9–0.7}Fe_{0.1–0.3})CO_3$ (up to 9 % FeO) and it is a member of magnesite – siderite isomorphous series (Šalát and Ončáková, 1966). The magnesite in Jelšava deposit is accompanied above all by dolomite.

Owing to the high losses of the utility component in wastes during beneficiation and calcination a new technique is proposed. Universal technology of magnesite fines recovering is as follows: gaining, beneficiation, dressing, calcinations, calcinate upgrading, calcinate final treatment (Staroň and Tomšů, 1992).

Magnesite fines recovering

Magnesite fines can be recovered from wastes of beneficiation plant and from the flue dust of the shaft and rotary furnaces (Fig. 1). Raw magnesite upgrading in the heavy media suspensions is aimed at an obtaining of suitable qualitative parameters of the feed to thermal units. Contents of impurities in the magnesite fractions bellow 40 mm as a dependence on the grain size are given in Tab. 1 (Anonymous, 1998). Only the fractions above 0.2 mm are subjected to washing in the heavy suspensions. Subsequently, upgraded material with the grain size above 1 mm is fed to rotary furnaces. As it can be seen in the flowsheet in Fig. 1 a significant amount of fines is removed from the technological process. These fractions have a very high potential for increasing the usability of mined out raw material.

Thermal treatment of magnesite fines

The magnesite flue dust forms during the calcination and sintering in the shaft and rotary furnaces. Raw magnesite with the grain size of 40 – 200 mm is sintering in the shaft furnaces. Rotary furnaces are working on the counter-flow heating system. Cap of the furnace on the clinker output forms hot bulb in which is situated the burner into which the fuel and primary combustion air is supplied. Material movement in the rotary furnaces is provided by its rotation. Thermal processing of magnesite includes the following steps: preheating, decarbonization, sintering and cooling. Firstly, the drying (removing of presented H_2O) and preheating of the feed is performed. Subsequently, the decomposition of magnesite (decarbonization) starts at the temperature 399 °C according to equation:

$$MgCO_3 = MgO + CO_2$$

The decomposition of $CaCO_3$ begins at the temperature 600 °C. During decomposition the mass loss of the feed attains approximately 50 % (CO_2). The product is a high--cavernous caustic magnesite with the porosity above 45 %. It does not have qualities of the refractory material and that is why the temperature must be increased so the sintering process occurs. To obtain dense sintered product, the temperature should be above 1 600 °C. Fine fractions are formed in the calcinations stage by decrepitation.

Exploitability of co-products originated after the heat treatment

Basic property of the breunnerite is the high break down of its grains through the decarbonization process called decrepitation. Owing to the contra current working mode of the shaft and rotary furnaces a large amount of the flue dust is typical. Their granulometry and chemistry depends on parameters of the thermal treatment. By calcination at 1 000 °C caustically calcinated magnesite is obtained. Such clinker has a high reactivity and its surface area attains tenths m^2/g. Decrepitation of crystalline types of magnesite through the calcination process is acceptable effect.

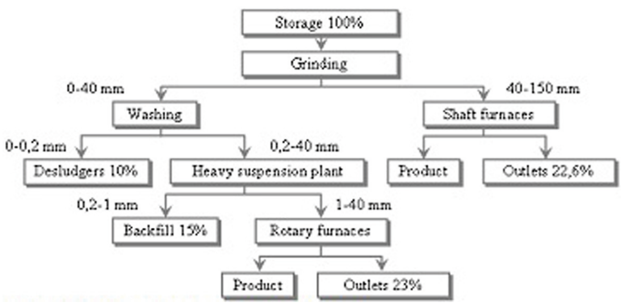

Fig. 1. Sources of fine granular magnesite fractions.

Accompanying minerals are practically undecomposed up to 900 °C and for this reason they can be separated by screening. Especially the fractions below 1mm, which are rich in MgO may be simply obtained and in such way can contribute to increased utilization of the raw material.

The calcination of breunnerite at temperatures above 750 °C results in the magnesioferrite formation as a substantial part of the calcinated material. Thus, a part of the calcinated material becomes ferromagnetic and can be magnetically separated. Calcination has to be controlled in conditions suitable for the magnesioferrite creation with sufficiently long time for its formation. The magnetic separation of calcinated material is usually carried out at a magnetic field induction of 0.1 – 0.2 T. The separation efficiency depends on CaO content, i.e. on dolomite content in the feed. Naturally, the separation sharpness can be unfavourably influenced by the intergrowth of magnesite and dolomite. Generally, described technique enables iron removing from the magnesia and in such way to obtain valuable product.

Improvement of thermal approaches

The economic recovery of the valuable minerals using the thermal treatment is influenced by the energy consumption and costs, which cover a pollution control (Repiský, 1997).

Present technologies

Shaft and rotary furnaces produce the dust in an amount of 15 – 20 % and 30 – 35 % of the fed material, respectively. For this reason their improvement was focused on the decreasing of the dust creation. Basic solution is to increase the furnace thermal efficiency. In the case of the shaft furnaces it was achieved by rearranging of the combustion system. The homogenization of the sintering temperature through the furnace cross section can result in the decreasing of the dust formation by 25 %.

So in the case of rotary furnaces the complex rearrangement results in 40 % reduction of the dust formation. For instance the flue dust amount was decreased by 25 % only by the increasing of material layer thickness. Despite of very favourable chemical composition of the flue dust its high value of loss on ignition makes the waste from it. It is caused by the contra current process, i.e. formed dust can not by separated and it is subsequently mixed with not fully calcinated dust from previous sections.

Tab. 1
Contents of impurities in magnesite fractions bellow 40 mm

Fraction (mm)	Content (%) CaO	Fe_2O_3	SiO_2	Al_2O_3	Lost on ignition LOI (%)
0 – 0.2	5 – 7.5	4.5 – 6	2.0 – 7	1.5 – 3.0	47 – 49
0.2 – 1	3 – 5	3.6 – 4.0	0.3 – 2.0	0.1 – 0.3	48 – 50
1 – 5	8 – 12	3.5 – 3.8	0.3 – 0.8	0.2 – 0.3	48 – 50
5 – 10	10 – 16	3.4 – 3.7	0.5 – 1.5	0.4 – 0.8	48 – 50
10 – 40	14 – 20	3.0 – 3.5	0.5 – 1.2	0.3 – 0.6	48 – 50

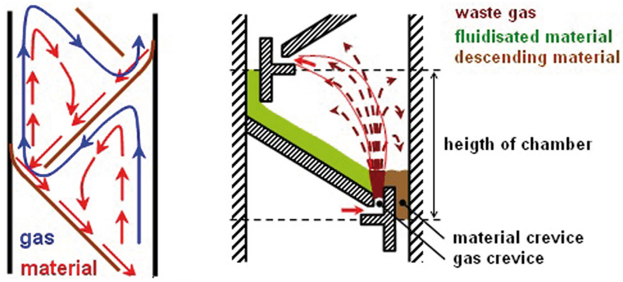

Fig. 2. Fluidization principles in the microfluid furnance.

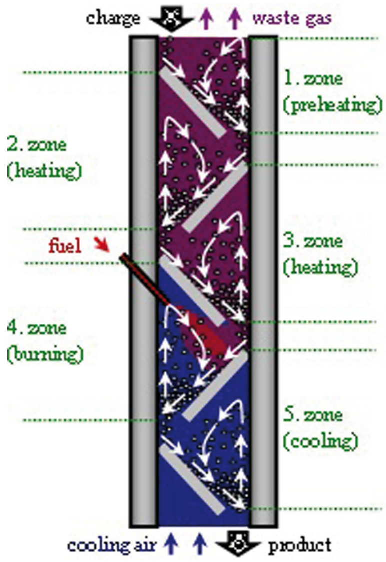

Fig. 3. Microfluid furnance.

Fig. 4. Experimental microfluid furnance.

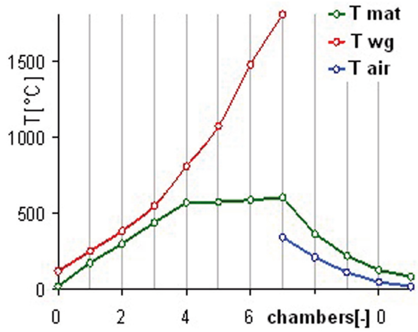

Fig. 5. Simulation of experimental microfluid furnance.

New thermal devices

Microfluid furnace

Microfluid furnace is based on hydromechanical fluidization principle (Fig. 2). Furnace consists of fluidization chambers in the counter current arrangement (Fig. 3). Material is fed from the upper part of the furnace and is discharged at its lover part. Material is gradually dried, heated, calcinated and cooled. Gas flow – cooling air is in the upward direction. It enables independent fluidization and material flow to the subsequent chambers. Furnace process is executed as follows. Fine-grained material is fed from the upper end of the furnace. It passes through the drying zone, preheating zone, heating zone, burning zone and cooling zone. Product discharge is at the lower end, where cooling air is introduced. Heat generation is in one or more combustion chambers (Koštial et al., 2007).

Experimental microfluid furnace (Fig. 4) has 9 fluidized chambers, which are providing: drying, heating, calcination and cooling of material. Burner is placed in the 7th chamber. A verification of functionality and operational parameters of furnaces were performed. Obtained results were used for the calibration of mathematical model. The specific capacity attained 652 kg of product per 1 m^3 of the furnace. The specific gas consumption was of 127 m^3/t.

Full-scale microfluid furnace was designed using the calibrated mathematical model (Fig. 5). The furnace has vertically 11 chambers, a burner is placed in the 7th chamber. Volume output of microfluid furnace is 1.88 m^3/t. For the comparison a volume output of the rotary furnace is about 70 m^3/t. Calibrated mathematical model is utilized for the simulation and for design requirements (Mikula et al., 2009).

High speed rotary furnace (HSRF)

The high speed rotary furnace performs thermal treatment of the fine grain materials in the fluidized layer created on the principle of mechanical fluidization. Mechanical fluidization carries out through the centrifugal and gravitational forces. Formation of fluidized layer depends on material parameters, equipment and conditions of fluidized process. Filling of the furnace space with particles at different revolutions of furnace is illustrated

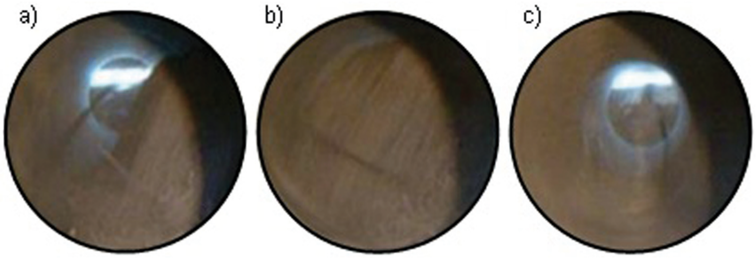

Fig. 6. Material fillingrate by the mechanical fluidization. a – low, b – optimal, c – high-speed.

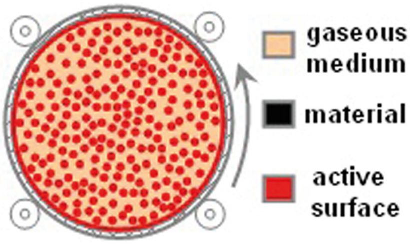

Fig. 7. Material distribution through the furnace cross-section.

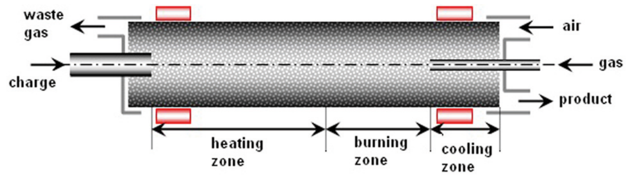

Fig. 8. Scheme of the high revolutions rotary furnance.

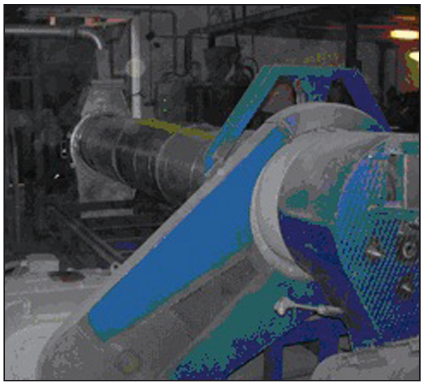

Fig. 9. The high revolutions pilot rotary furnance.

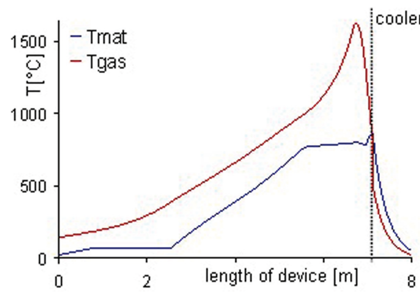

Fig. 10. Simulation of experimental device.

in Fig. 6. Active surface of the feed is determined from the surface of the fluidized particles, which are allocated at cross-section of the furnace (Fig. 7).

The major advantage of this unique technology of the raw material thermal treatment is a formation of dispersed layer, which allows a perfect contact of gaseous media with the surface of processed material particles. Material fluidization brings a significantly increase of the intensity in the heat and mass transfer. For the calcination of magnesite it is possible to reduce existing facility approximately tenfold. The main advantage of proposed solution is that ratio of the substances can be relatively in the large scale (Koštial et al., 2007).

Experimental research was carried out in the pilot HSRF. The working part of the furnace creates a cylinder with diameter 600 mm and length 5 500 mm. Rotation speed of furnace can be continuously changed by power drive in the range of 0 – 60 rpm. The material is fed to the furnace by the screw conveyor. Material is fluidized after entering the furnace. At the output side of the furnace material is taken away by the screw conveyor and on this side natural gas is supplied through the diffuse burner. Furnace is thermally divided into the cooling area, combustion area, heating area and pre-heating area. The high intensity of the heat transfer due to the mechanical fluidization enables to integrate all these operations into one facility (Fig. 8).

The pilot high speed rotary furnace is in Fig. 9. Based on these experimental results mathematical model of the furnace was calibrated. Using the mathematical model simulation a full scale operating high speed rotary furnace for the calcination of magnesite was designed (Fig. 10). Internal diameter of the furnace is 1.3 m, length 8 m and volume output is 10.9 m^3/t (Mikula et al., 2009).

Conclusion

The paper presented the possibilities of utilization enlargement of magnesite fractions 0 – 1 mm and the flue dust particles from the thermal treatment of magnesite. It also described a formation of the fine fractions and possibilities of their processing, which are based on the application of existing and new developed technologies.

In the shaft furnaces it is possible to increase their thermal efficiency. So, the achieved decreasing of the dust formation was by 25 %. In the case of the rotary furnaces the complex rearrangement results in 40 % reduction of the dust formation. For the calcination of fine fractions new types of thermal facilities – microfluid furnace a high-speed rotary furnace were developed. Thermal treatment in these furnaces is performed in fluidized layer. Accomplished studies have confirmed, that these conceptually new thermal units have very high efficiency during the treatment of grainy and dusty material and they enable to perform the calcination process on the border of technological optimum. These proposed solutions are verified in the pilot and full scale operating conditions.

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Microbial communities in the mining water and bioremediation

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Key words: acid mine drainage, bioremediation, heavy metals, sulphate,
sulphate-reducing bacteria

Abstract

Acid mine drainage (AMD) is a serious environmental problem resulting from the extensive mining of sulphidic ore. The exposure of pyrite and non-pyritic sulphidic minerals to both oxygen and water results in the acidic and sulphate rich wastewater. The old mines at Slovinky in the Western Carpathians, Slovakia, demonstrate such situation. AMD communities contain fewer prokaryotic lineages than many other environments. AMD communities are characterized by a very limited number of distinct species, probably due to the small number of available metabolically beneficial reactions. To prevent the formation or the migration of the AMD from its source is generally considered to be the preferable option, although this is not feasible in many locations, and in such cases there is necessary to collect, treat, and discharge mine water. There are various options available for the AMD remediating, which may be divided into those that use either chemical or biological mechanisms to neutralize AMD and to remove metals from the solution. The roles of algae and fungi, the natural residents of AMD and its attenuator are not emphasized adequately in the mine water research. This review examines the role of these microorganisms (bacteria, algae and fungi) and documents their activities in the holistic form in the mine water environment.

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Removal of arsenic using synthetic magnetite: Desorption study

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Abstract

Synthetic magnetite (Fe_3O_4) was studied as a sorbent for the removal of arsenic from the model aqueous solutions. The sorbent was prepared by the co-precipitation of Fe(II) and Fe(III) under alkaline conditions. The effect of pH, initial arsenic concentration and a the contact time of magnetite and arsenic were investigated in the batch adsorption-equilibrium experiments. Maximum sorption capacity of magnetite obtained at pH 3.5 was 46.7 mg/g. Desorption of arsenic loaded on magnetite was studied under various experimental conditions.

Key words: arsenic, iron oxide, magnetite, sorption, desorption

Introduction

Arsenic is an ubiquitous element. Due to its toxicity it is considered as a high-priority pollutant. Arsenic contamination of the water supplies has become one of the major problems. Even small concentrations of arsenic in the drinking water may have adverse health effects. Known consequences include cancer, pigmentation changes, hyperkeratosis, neurological disorders, cardiovascular diseases and conjunctivitis (Mandal and Suzuki, 2002). Therefore, the World Health Organization (WHO) recommended to reduce the maximum contaminant level (MCL) of arsenic in the drinking water to 10 μg/L from an earlier value of 50 μg/L (WHO, 2004). In natural waters the arsenic can be found in a wide range of concentrations from less than 0.5 μg/L to more than 5 000 μg/L (Smedley and Kinniburgh, 2002).

Arsenic occurs in –3, 0, +3 and +5 oxidation states. In the water environment the most predominant forms are trivalent arsenite As(III) and pentavalent arsenate As(V). Redox potential (Eh) and pH are the most important factors controlling arsenic speciation. Generally, As(V) is more prevalent in the surface waters while As(III) occurs in anaerobic ground waters (Václavíková et al., 2008). Arsenic occurs in both organic and inorganic forms in natural waters. Organic arsenic may be produced by biological activity, mostly in the surface waters, but is rarely quantitatively important. The inorganic forms of arsenic are more toxic then its organic forms. Arsenic is more difficult to be removed when it occurs in As(III) form (Smedley and Kinniburgh, 2002).

Arsenic can be removed by various treatment methods, such as coagulation and flocculation, precipitation, ion exchange, reverse osmosis, membrane and adsorption technologies. Among them, coagulation/precipitation followed by filtration is the most commonly used technique. Ion exchange is effective in As(V) removal but may not be suitable for As(III) removal. The use of reverse osmosis and the membrane technologies is quite expensive compared to other methods (Pokhrel and Viraraghavan, 2007; Václavíková et al., 2008). Adsorption processes are commonly applied and show a good efficiency to cost ratio for arsenic removal. Sorbents based on iron compounds are the most commonly used. Several iron (III) oxides/oxyhydroxides, such as amorphous hydrous ferric oxide (FeOOH), poorly crystalline hydrous oxide – ferrihydrite, goethite (α-FeOOH) and akaganeite (β-FeOOH) are promising sorbents for the removal of both As(V) and As(III) from aqueous solutions. Other commonly used sorbents based on iron oxides/oxyhydroxides are e.g. iron oxide-coated sand, granular ferric hydroxide, iron--coated cement, iron-coated alumina and the magnetically modified zeolite. Most treatment methods discussed above are more effective in removal of arsenic from the water containing high initial arsenic concentrations (usually >100 mg/L). However, they fail to remove arsenic concentrations below the new decreased limit (10 μg/L) (Mohan and Pittman, 2007). Therefore, there is a tremendous demand for the developing of inexpensive efficient methods for the removal of arsenic species from the drinking water. Sorption methods are still considered promising, in regard to the cost/efficiency factor and new sorbents are being developed with the aim of obtaining the new target limit (Václavíková et al., 2008).

After the arsenic sorption there is a problem how to deal with used sorbents. Generally, there are two main options for dealing with arsenic waste materials:

- Desorption and regeneration of materials
- Solidification/stabilization followed by the disposal of treated wastes.

Desorption can help to regenerate the adsorbent. A successful desorption process must restore the adsorbent close to its initial properties for the effective reuse for further arsenic removal. Desorption and regeneration is a critical consideration and contributor to process costs and metal(s) recovery in a concentrated form. Desorption of arsenic from exhausted sorbent is usually achieved using several eluents. Selection of the eluent depends on the arsenic adsorption mechanism and the nature of the adsorbent (Mohan and Pittman, 2007). The most commonly used arsenic eluents are sodium hydroxide (Cumbal et al., 2003; Guo and Chen, 2005; Kundu and Gupta, 2006) and strong acids (Say et al., 2003).

Solidification/stabilization transforms potentially hazardous liquid/solid wastes into the less hazardous or non-hazardous solids before deposing these solids in secure landfills. This solidified/stabilized waste must strictly follow leachability regulatory requirements prior to the disposal. According to USEPA, a waste is deemed as hazardous material if the arsenic concentration in the Toxicity Characteristic Leaching Procedure (TCLP) leachate exceeds 5 mg/L (Leist et al., 2000; Mohan and Pittman, 2007). Several solidification/stabilization processes have been studied to form satisfactory storable solids. These included fixation with Portland cement (Akhter et al., 1990), Portland cement and fly ash (Chu et al., 1991), Portland cement and silicates (Leist et al., 2003), etc.

Materials and methods

Reagents

Analytical grade chemicals were used in all experiments. Model solutions were prepared by the dissolving of $Na_2HAsO_4 \cdot 7H_2O$ (Fluka) in deionized water. The pH of the solutions was adjusted with the suitable concentrations of analytical grade NaOH and HNO_3.

Preparation and characterization of sorbent

Synthetic magnetite was prepared by co-precipitation of Fe(II) and Fe(III) in the presence of NH_4OH. Surface area and pore volume measurements (Gemini 2360, Micrometrics Instruments Corporation, USA), zeta potential measurements (ZetaPlus, Brookhaven Instruments, USA) and magnetic properties measurements (KappaBridge KLY-2, Geofyzika Brno, CZ) were used for materials characterization. The characteristics of sorbent are given in Table 1.

Sorption experiments

The sorption properties of synthetic magnetite were tested under batch conditions. The effect of pH, initial arsenic concentration and contact time of sorbent and arsenic solution were studied. The experiments were performed at constant temperature 23 ± 1 °C in a rotary shaker set at 30 rpm and equilibrium time 24 hours. The arsenic quantity in solutions was determined by AAS (Varian 240 RS/240 Z, Australia) before and after the sorption experiments. The amount of the arsenic sorbed (mg) per unit mass of magnetite (g) q_{eq}, was calculated using the Eq. (1)

$$q_{eq} = \frac{C_0 - C_{eq}}{C_s} \qquad (1)$$

where C_0 and C_{eq} are initial and equilibrium arsenic concentrations (mg/L), respectively and C_s is the sorbent concentration in solution (g/L).

Tab. 1
The characteristics of synthetic magnetite

Surface area (m^2/g)	125.7
Total pore volume (cm^3/g)	0.212
pH_{PZC}	6.5
Magnetic susceptibility (10^{-6} SI units)	702 778

Desorption experiments

Desorption experiments were carried out to study the influence of eluent on to arsenic desorption from the solid adsorption residues. The sorbent used for sorption of 100 mg/L of arsenic solution was separated from the solution by centrifugation, washed gently using deionized water to remove residual arsenic on the surface and dried. After that, it was mixed with desorption agents: deionized water, 0.5 M Na_3PO_4, 1 M KNO_3, 1 M NaCl, 1 M $MgSO_4$, 1 M HNO_3 and 0.1, 0.5 and 1 M NaOH. The mixtures were shaken for 24 hours and the filtrates were analysed to determine the arsenic concentration after desorption.

Results and discussion

Effect of pH on As(V) sorption

The pH of adsorption medium is the most important factor influencing the sorption capacity of the sorbent. It is related to the adsorption mechanism onto the adsorbent surface and reflects the nature of physicochemical interaction of the species in solution and the adsorptive site of adsorbent (Aksu and Gönen, 2004). The effect of pH on the removal of As(V) within the range of 2 – 9 is given in Fig. 1. The initial arsenic concentration was 100 mg/L and

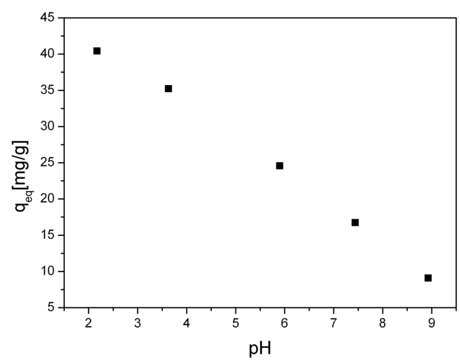

Fig. 1. The effect of pH.

the sorbent concentration was 2 g/L. The removal of As(V) from the aqueous solution decreased with increasing pH and the greatest arsenic uptake was observed at pH 2. The equilibrium As(V) uptake was 40.4 mg/g at this pH value. However, in this case, magnetite was dissolved and iron was detected in filtrates. For this reason, pH 3.5 has been chosen as optimum pH value for all sorption experiments. At pH 3.5 no iron was found in the solution and equilibrium As(V) uptake was 35.2 mg/g.

As mentioned before, pH plays an important role in the solution chemistry. In acidic environment, where the maximum As(V) removal was observed, the As(V) form predominates as the single negatively charged $H_2AsO_4^-$. In this pH range the magnetite surface is positively charged. So, the attractive electrostatic forces between the negatively charged As(V) species and the positively charged magnetite surface favour the sorption. The point of zero charge of the sorbent was found at pH 6.5 (see Tab. 1). Above this pH of magnetite surface is negatively charged and the double negatively charged form of $HAsO_4^{2-}$ predominates. The electrostatic forces are repulsive but sorption still takes place due to the existence of specific forces.

The effect of pH at As(V) sorption by the magnetite has been studied by several authors, as well. Yean et al. (2005) studied As(V) sorption by the magnetite nanoparticles (20 and 300 nm) and they also confirmed the pH dependence of As(V) removal. The maximum sorption capacity of 20 nm magnetite particles was 11.4 and 6.0 mg/g for pH values 4.8 and 8.0, respectively. The maximum sorption capacity of 300 nm magnetite particles was 1.1 and 0.8 mg/g for pH values 4.8 and 6.1, respectively. Chunming and Puls (2008) tested samples of eight commercial available magnetites for arsenic removal and confirmed the pH dependence of As(V) sorption. The sorption of As(V) was more favourable below pH 5.6 – 6.8. Decreasing of As(V) removal by the natural magnetite with increasing pH was observed by Giménez et al. (2007) as well.

Effect of initial As(V) concentration

The effect of initial arsenic concentration (20 – 200 mg/L) was studied with 2 g/L sorbent concentration, ambient temperature and pH values 3.5, 5.0 and 7.0. Sorption isotherms were fitted using the Freundlich model:

$$q_{eq} = K_F C_{eq}^{1/n} \quad (2)$$

where q_{eq} is amount sorbed per unit mass of sorbent (mg/g) and C_{eq} is the equilibrium concentration (mg/L). K_F and *1/n* are Freundlich constants related to adsorption capacity (mg/g) and adsorption intensity, respectively; the larger value of K_F the greater adsorption capacity. The *n* value is called heterogeneity factor and its value is in the range from 0 to 1. The more heterogeneous surface, the *1/n* value is closer to zero.

The maximum sorption capacity was 46.7, 37.3 and 27.0 mg/g for pH values 3.5, 5.0 and 7.0 respectively. As it is expected, the K_F value decreases with increasing pH. The K_F value was 23.5, 13.4 and 8.9 for pH values 3.5, 5.0 and 7.0 respectively. The *1/n* values indicate favourable adsorption of As(V) onto magnetite. Distribution coefficients R^2 values show a good agreement of the model to the experimental data (Štefušová, 2009).

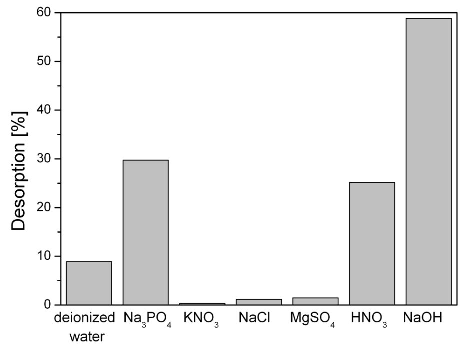

Fig. 2. The effect of various eluent agents on As(V) desorption.

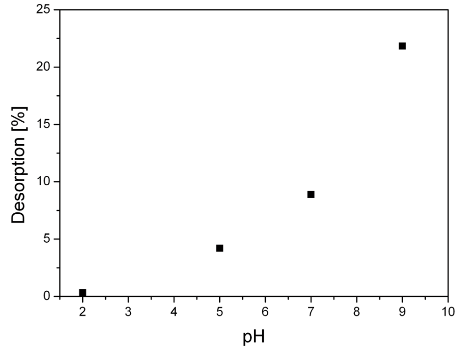

Fig. 3. The effect of pH on As(V) desorption.

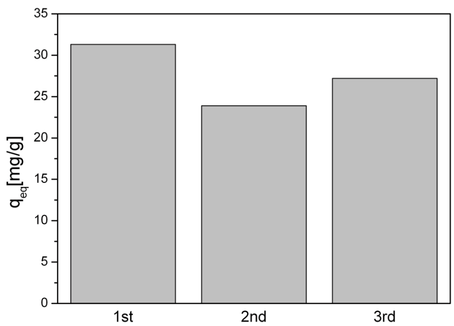

Fig. 4. Sorption capacity of magnetite in three sorption cycles.

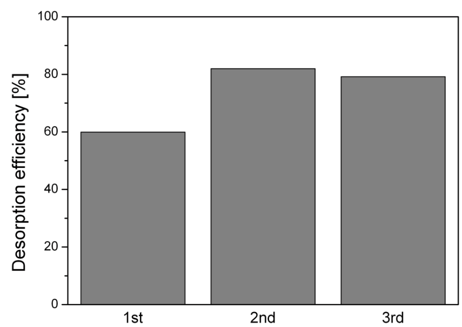

Fig. 5. Desorption efficiency of As(V) in three desorption cycles.

Effect of contact time of sorbent and As(V)

The kinetics of As(V) removal from the aqueous solution was studied with an initial arsenic concentration of 100 mg/L, sorbent concentration 2 g/L and pH 3.5. Initially, the uptake of As(V) was very fast within the first 1 h of treatment and the adsorption equilibrium was obtained after 5 h (Štefušová, 2009).

Desorption studies

Several eluents were used to study As(V) desorption ability from magnetite. Fig. 2 shows that the desorption efficiency varies with desorption agents.

The preliminary study has shown that the desorption of As(V) in deionized water is strongly influenced by pH of solution. The desorption efficiency was enhanced with increasing pH and the maximum desorption was observed at pH 9.0 (21.3 %). The effect of pH on As(V) desorption is given in Fig. 3. Zhang et al. (2007) studied the effect of pH on As(V) desorption from the ferric activated carbon and the pH dependence of As(V) desorption was also confirmed. The maximum desorption (97.3 %) was observed at pH 13 – 14.

Phosphates, sulphates, chlorides and nitrates are the major co-existing anions influencing the arsenic mobility in the waters (Mohan and Pitmann, 2007; Henke, 2009). The desorption efficiency of KNO_3, NaCl and $MgSO_4$ was not significant (less than 1.5 %), while the desorption with Na_3PO_4 was more effective (29.7 %). The negligible effect of nitrates, chlorides and sulphates on As(V) desorption from gibbsite and goethite was confirmed by Ladeira and Ciminelli (2004) as well. The desorption of As(V) from goethite in the presence of phosphates and sulphates was studied by O´Reilly et al. (2001). The desorption efficiency of phosphates was around 35 %, while the desorption efficiency of sulphates was less than 2.5 %.

Desorption efficiency using 1 M HNO_3 was 25.2 % but in this case magnetite was dissolved and iron was determined in filtrate (402.7 mg/L). The most effective desorption agent of As(V) from magnetite was NaOH. Preliminary desorption study using NaOH (from 0.1 to 1 M) has shown that the effect of ionic strength of NaOH is negligible and the desorption efficiency of As(V) from magnetite is ranged between 58.4 and 63.1 %.

The reusability of the sorbent was tested in three sorption-desorption cycles. Fig. 4 shows the sorption capacity of the sorbent (initial As(V) concentration 100 mg/L). Fig. 5 shows the desorption efficiency of As(V) from the As-magnetite matrix using 0.1 M NaOH. The 1st sorption cycle was obtained using the fresh sorbent. The results have shown that there were only negligible losses in the sorption capacities of magnetite. The drop of removal efficiency of As(V) with the number of cycles was 11 and 4 % in 2nd and 3rd sorption cycle, respectively. On the other hand, the desorption efficiency increases with the number of cycles by about 20 % after 2nd and 3rd cycle.

Conclusion

Low cost adsorbent based on synthetic magnetite with good removal capacity of As(V) from the waters has been developed. The maximum capacity of sorbent was 46.7 mg/g with initial As(V) concentration of 200 mg/L and optimum pH 3.5. The adsorption process was fast and equilibrium was obtained after 5 h. The desorption study confirmed that the sodium hydroxide is the most effective eluent of As(V) from the magnetite. The tested sorbent was reused in three sorption-desorption cycles with minimum changes on its sorption properties. Due to its low cost, easy preparation and good removal efficiency, synthetic magnetite seems to be a promising material for the environmental applications.

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Examination of geopolymer materials properties formed via alkali activation of black coal ashes with a high content of loss on ignition

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Key words: fly ash, geopolymer, compression strength, frost-resistance

Abstract

The utilization of the fly ashes in Slovakia is lower than in other countries and dumping of the fly ashes prevails. The dumping changes chemical and phase composition of the fly ashes and so it decreases possibilities for their utilization. Fly ashes are mainly used in building industry, where the content of loss on ignition (LOI) is limited due to standards. Black coal fly ashes produced in Slovakia have a high content of loss on ignition – more than 20 % – so they straight utilization in the building industry is not possible. The current possibility for their utilization is in geopolymer synthesis. Products with 28-day compression strength of 35.7 MPa and 180-day compression strength of 55.0 MPa were obtained by the alkali activation of fly ashes with 23.25 % LOI with 8 wt.% Na_2O and their next hardening in the temperature of 80 °C during 6 hours. Products have a great frost-resistance and aggressive environments resistance (NaCl and H_2SO_4 solutions).

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Hydrometallurgical treatment of exhausted alkaline batteries

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Abstract

On a resource management level, batteries could be considered as a metal source of the secondary origin, ore of secondary raw materials, because of their high content in useful metals, such as zinc and manganese. Moreover, disposal of spent batteries constituted a serious environmental problem in terms of the heavy metals content, when these devices are disposed off in an inadequate way.

Main processes applied for the treatment of the batteries are based on pyrometallurgy, involving the high energetic consumption and pollution, and on hydrometallurgy, which is less expensive and lower energy demanding.

The experiments in the presented work were based on the technology well know in mineral processing and metal dissolution by the hydrometallurgical processes for Mn-Zn recovery from wastes, constituted by spent alkaline batteries.

The results have demonstrated the technical feasibility of the application of the mentioned technologies; in fact, high recovery of manganese and zinc dissolved in the solution were achieved (over 90 %).

Key words: hydrometallurgical processes, wastes, alkaline batteries, metals recover, Zn, Mn

Introduction

Disposal of spent batteries represents an increasing environmental problem in terms of the heavy metals content when these devices are disposed off in inadequate way (Vegliò et al., 2003).

On a resource management level, batteries could be considered as a metal source of the secondary origin. Valuable metals such as zinc and manganese can be recovered. The use of recycled metals in battery production instead of virgin metals has the positive environmental impacts through the reduced energy use and reduced pollution related to the mining of the virgin sources (Vatistas et al., 2001).

The topic is reflected in the current European legislation by the Council Directive 91/157/EEC on batteries and accumulators containing dangerous substances (Ubaldini et al., 2009). Many batteries and accumulators of the alkaline and zinc-carbon types are still deposited on landfills or incinerated, instead of being collected and recycled (Beolchini et al., 2009).

The purpose of the proposal of 21 November 2003 for a Directive of the European Parliament is to reduce the quantity of spent batteries and accumulators and to set European targets for collection and recycling (Ubaldini et al., 2008a).

The proposal applies to all batteries and accumulators, unlike the current legislation (Directive 91/157/EEC). The ultimate disposal of industrial and automotive batteries and accumulators by incineration or landfilling is prohibited. Once this directive is in force, Member States will have more than five years for achieving a minimum average collection target equivalent to 160 grams per inhabitant per year for spent portable batteries and accumulators (Ubaldini et al., 2008b).

Several processes for the recycling of batteries were proposed, mainly in Europe, and the pyrometallurgical processes are the most used (Ubaldini et al., 2000). As for secondary raw material exploitation, in the literature different processes for manganese and zinc recovery from the exhausted cells have been reported (Vatistas et al., 2001; De Michelis et al., 2007; Ubaldini et al., 2008a; Ubaldini et al., 2008b; Ubaldini et al., 2009).

In this work, a complete flow-sheet for treatment of spent batteries has been outlined, starting from disassembling and physical separation of the component of the spent batteries. The attention of the investigation has been focused to the subsequent chemical dissolution of the metals, purification and recovery, carried out by the hydrometallurgical processes.

Materials and methods

Characterization and physical process

The disassembly of the batteries was done with a cutting mill model Retsch RM 2000. The size fraction less than 2.5 mm was sent to the part of the process devoted to the recovery of components other than zinc and manganese, while the size below is directly air separated. For the separation of the magnetic materials, drum magnetic separator model Sala was used at a field intensity of about 0.2 T. The separation of the different specific gravity materials was carried out in a dry vertical elutriator, while Eriez eddy current magnetic separator was employed for separation of non-ferrous metals. The size fraction +2.5 mm was sent to the micronization step. In this phase a hammer mill was used.

The alkaline Zn/MnO_2 consists of Zn anode, MnO_2 cathode, KOH electrolyte solution and separators. The cathode includes manganese dioxide, carbon (graphite) particles that enhance the conductivity of the cathode, and a binder. The anode can be formed of a gel including zinc particles. The separator (fibrous materials) is disposed between the cathode and the anode. Other constituents of the battery are an external plastic cover, steel needle and cap, a plastic disc and paper separators.

Fig. 1 shows the characteristics of spent alkaline batteries utilized and the powder composition, analysed at the end of the physical process.

Basic sample for experimental texts has been analysed by the X-ray diffraction (XRD), utilizing an automatic diffractometer Bruker mod. D8 Advance. The results show that the following main crystalline mineralogical species are present, in order of decreasing abundance: zincite (ZnO), quartz (SiO_2), manganese oxide (Mn_2O_3), calcium manganese oxide ($Ca_4Mn_2O_7$), sylvite (KCl) and potassium oxide (KO_2).

Quantitative chemical analysis was conducted by Inductively Coupled Plasma Mass Spectrometry (ICP-MS), using a Perkin-Elmer apparatus mod. Elan 6000. Results have shown that powder was composed mainly by 45 % MnO_2, 15 % Zn, 5.9 % K, 0.61 % Ni and 0.7 % Fe.

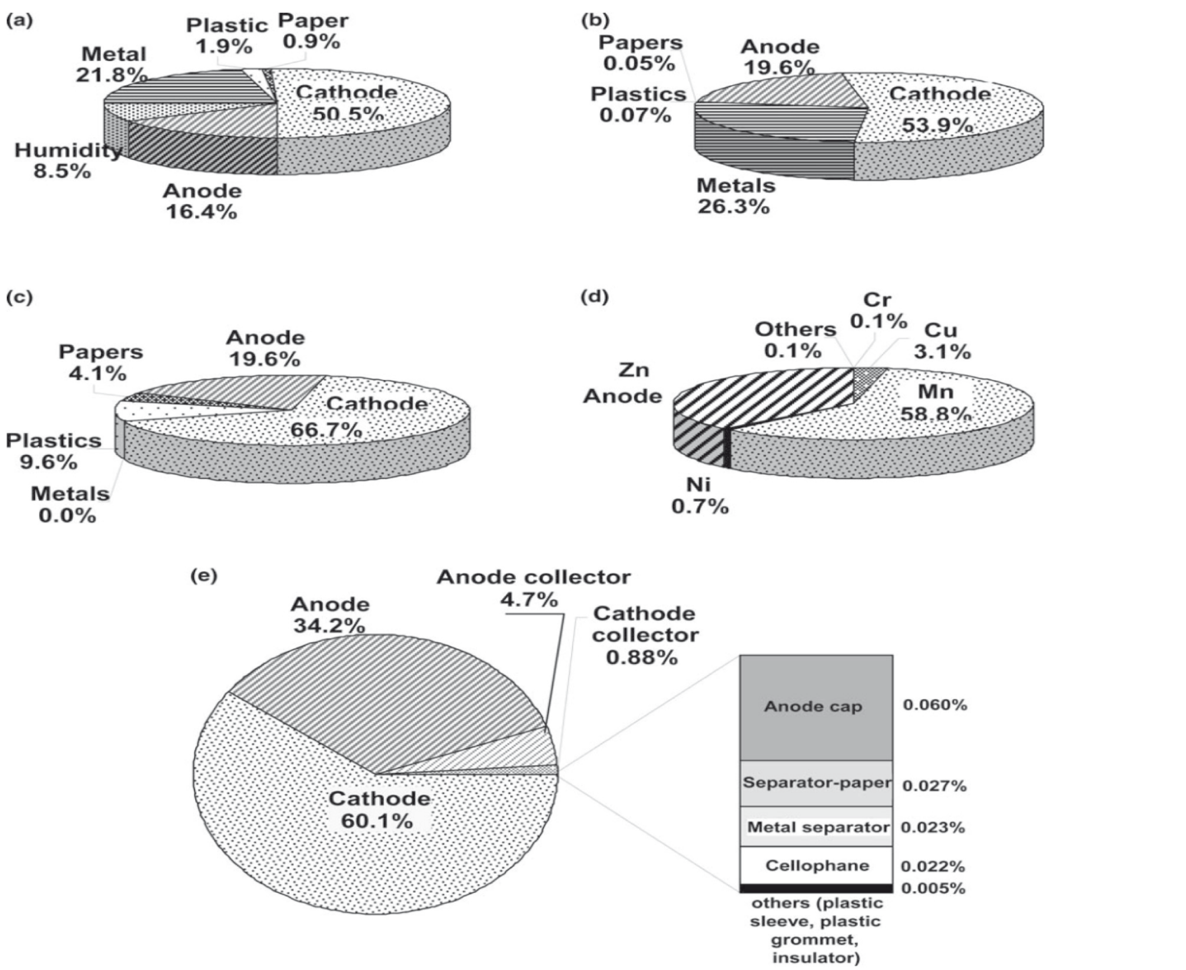

Fig. 1. Characteristics of spent alkaline batteries. (a) components and materials, (b) contribution of the components in the composition of the ash, (c) contribution of the components to lower heating value, d) metal content. Other inclusions: As, Cd, Co, Hg, Pb, Sb, Si, Ti, V. (e) Heavy metals in the components (Ubaldini et al., 2009).

Hydrometallurgical process

Mixture of the cathode (manganese oxides) and the anode (zinc oxides and electrolytic solution) materials in form of the powder was extracted and treated, while the potassium contained was dissolved (Ubaldini et al., 2008a; Ubaldini et al., 2008b).

All the experimental tests shown in this paper were carried out with the washed powder. Leaching tests were conducted to evaluate the leaching behaviour of the metals under the different conditions of solid/liquid ratio, temperature, sulphuric acid concentration and oxalic acid concentration, according to previous studies (De Michelis et al., 2007), conducted by 2^4 Factorial design. For each test the solution mixture was freshly prepared and washed battery powder in 100 ml of H_2SO_4 solution, by dissolving the required amount of analytical grade oxalic acid (OA) and adding washed battery powder in 100 ml of H_2SO_4 solution.

At the end of each test, pH was measured and the mixtures were filtered to separate undissolved material from solution, washed and put in the oven at 100 °C. After 24 h solid residues were recovered and weighed to evaluate the weight loss.

A leaching solution containing 30 g · dm^{-3} Mn and of 70 g · dm^{-3} Zn, after precipitation and cementation phase (data not reported here) has been utilized for electrowinning tests (Ubaldini et al., 2008a, b; 2009).

A cylindrical glass laboratory cell of 200 cm^3 in volume has been used. The cell was equipped by a thermostatic water jacket connected with the thermostatic bath, magnetic system for stirring and three electrodes: as cathode, a platinum mesh; as an anode, a spiral of platinum wire; as a reference, a saturated calomel electrode (SCE).

During MnO_2 deposition, the working electrode (W) was the anode and the cathode was the counter electrode (C). During Zn deposition, the W was the cathode, while the anode was the C. In both processes, the reference electrode was constituted by SCE, to permit an electrolytic process at controlled potential.

The cell was connected to a potentiostat-galvanostat (AMEL mod. 555B), equipped with an instrument system for automatic control of the process parameters at the constant potential conditions. By analysing the residual solution with ICP-MS, the purity of the MnO_2 and Zn deposition was monitored, while the deposit was analysed by XRD.

Electrowinning experiments were carried out in potentiostatic operations at constant anodic potential and stirring conditions.

Results

Results of the leaching experiments, elaborated by the analysis of the variance (ANOVA), demonstrate the high efficiency of the studied process. In any case, 70 % of manganese and 100 % of zinc were extracted after 5 h, at 80 °C with a 20 % of pulp density, 1.8 M sulphuric acid concentration and 59.4 g/L of OA.

Tab. 1
Main experimental levels of the parameters obtained for MnO_2 recovery

Parameters	Levels
Cathode Vs. SCE (V)	1.5 – 2.0
Cell voltage (V)	–2.5/–3.3
Current intensity (mA)	1 000 – 1 800
pHi	0.5 – 0.6
Bath temperature (°C)	90 – 95
Electrolysis time (h)	6 – 8
Stirring conditions (rpm)	200 – 250

Tab. 2
Main experimental levels of the parameters obtained for Zn recovery

Parameters	Levels
Cathode Vs. SCE (V)	–1.40/–1.5
Cell voltage (V)	3.5 – 3.9
Cell voltage (V)	1 300 – 1 600
pHi	2 – 3
Bath temperature (°C)	30 – 40
Electrolysis time (h)	6 – 8
Stirring conditions (rpm)	200 – 250

Tab. 3
Main results achieved by the hydrometallurgical process (leaching-electrowinning tests)

Species	Leaching y (%)	Electrowinning y (%)	η (%)	E (kWh/kg)
MnO_2	95.05	94.35	43.00	4.63
Zn	98.10	95.50	67.43	5.59

y – extraction yield (leaching) and electrodeposition yield (electrowinning)
η – faradic current yield
E – energetic consumption

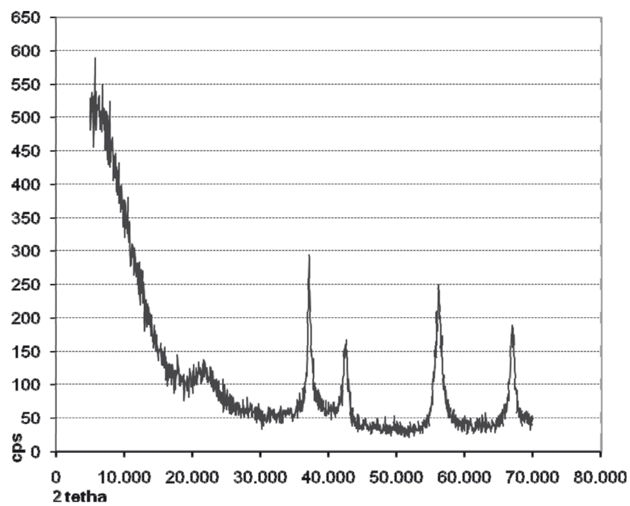

Fig. 2. The main identified peaks of MnO_2 were as follows: 294, 167, 250 and 190 cps.

At the end of the leaching process, a manganese and zinc sulphate solution has been obtained (30 g · dm^{-3} Mn and of 70 g · dm^{-3} Zn), together with the other dissolved metals (Fe, Si, Cr, Al and other trace elements).

Tabs. 1 and 2 show the best experimental level of the parameters obtained during Mn and Zn electrolysis.

Main results attained by the hydrometallurgical process (leaching-electrowinning) have been reported in Tab. 3.

Such as demonstrated by the X-Ray Diffraction Spectrum reported in Fig. 2, MnO_2 and Zn deposit at the high degrees of purity was achieved (> 92 %).

Discussion

The removal of potassium permits the elimination of the interference during electrowinning and the reduction of consumption of sulphuric acid in the leaching step.

The experimental results of leaching stage showed that the maximum extraction yields of zinc and manganese cannot be reached simultaneously: in fact, the high OA concentration required to dissolve manganese oxides causes the precipitation of zinc oxalate.

If the manganese reduction is carried out after the zinc leaching/electrowinning, manganese recovery was higher (increasing from 70 to about 95 % MnO_2). In this case, after the Zn-electrodeposition, finalized to the Zn recovery, the solution can been recirculated to the leaching stage to added OA for Mn reduction.

Processing of the experimental data by ANOVA indicates that for the Mn extraction yield, the most significant combinations are three: oxalic acid concentration, that has a strong positive effect on dissolution of insoluble Mn, sulphuric acid concentration (positive) and the combination of oxalic acid concentration with the temperature that has a negative effect on the extraction yield (precipitation of dissolved Mn as oxalate).

Also for the Zn extraction yield, the most significant combinations are three: oxalic acid concentration, which has a strong negative effect (precipitation of zinc oxalate), combination of temperature with oxalic acid concentration and, finally, the combination of acids with pulp percentage.

Purification before electrowinning has been carried out by the precipitation-cementation, with the aim to eliminate other dissolved metals. Iron represents the major impurity when Zn and MnO_2 are deposited in the electrowinning step, so it has been precipitated by an alkaline reagent.

Conclusions

Results have demonstrated the technical feasibility of the application of hydrometallurgical technologies for Zn and Mn recovery from exhausted batteries.

A quantitative recovery of manganese (about 90 % MnO_2) and zinc (about 94 % Zn) has been achieved at the end of the complete leaching-electrowinning circuit.

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Influence of selected parameters on nickel bioleaching from spent Ni-Cd batteries

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Abstract

Bioleaching is an effective way of obtaining heavy metals from the waste containing heavy metals. High yield of leaching process can be achieved by selecting appropriate parameters. The goal of this work was the study of leaching conditions and their effects on the Ni recovery from discarded Ni-Cd batteries. The experiments studied the impact of the quantity of the waste, the impact of bacteria *Acidithiobacillus ferrooxidans (AF)* and the mixture of *Acidithiobacillus ferrooxidans* and *Acidithiobacillus thiooxidans (AT)* bacteria, the impact of bacteria adaptation and temperature on the yield of Ni. The amount of nickel in the solution has increased with increasing temperature as well as by the use of adapted bacteria. The recovery achieved during the experiment, being in the range 33 – 84 %, confirms the dependence of nickel amount in solution at selected conditions. The highest yield was achieved under the following conditions: ratio L : S = 100, temperature 30 °C and usage of the adapted mixture of bacteria.

Key words: bioleaching, recycling, Ni-Cd batteries, *Acidithiobacillus ferrooxidans*, *Acidithiobacillus thiooxidans*

Introduction

Unprocessed discarded nickel-cadmium batteries pose a danger to the environment, mainly due to the high content of heavy metals. On the other hand, due to the high content of these metals, they are a suitable source for nickel and cadmium recovery. The content of these metals in batteries in comparison with the content of Ni and Cd in the primary raw material is much higher.

Nickel-cadmium battery is composed of three layers: a cathode, anode and a steel container. Positive electrode consists of nickel hydroxide, negative electrode consists of cadmium. In the charged state:

• The active material of positive electrode consists of nickel oxide-hydroxide – NiO(OH). During the discharging process following reaction at the positive electrode takes place:

$$2NiO(OH) + 2H_2O + 2e^- \rightarrow 2Ni(OH)_2 + 2OH^- \qquad (1)$$

• Negative electrode is composed of cadmium – Cd. During the discharging the following reaction takes place on negative electrode:

$$Cd + 2OH^- \rightarrow Cd(OH)_2 + 2e^- \qquad (2)$$

At charging process given reactions appear vice versa.

Separator containing electrolyte separates both electrodes. Alkaline aqueous solution of potassium hydroxide (KOH) is commonly used as an electrolyte.

In the recent years, several technologies were developed to process and to obtain usable materials from discarded Ni-Cd batteries (Bartolozzi et al., 1995; Freitas et al., 2005; Rudnik et al., 2007). Among the newer methods of heavy metals obtaining from used Ni-Cd batteries are bioleaching processes. Bioleaching processes are less expensive and as effective as traditional techniques of the heavy metals obtaining. More species of microorganisms have an ability to tolerate the presence of heavy metals in solution (Nemati and Webb, 1997) and they have the ability to dissolve heavy metals and transform them into ionic form, e.g. bacteria *Acidithiobacillus ferrooxidans*, *Acidithiobacillus thiooxidans* or bacteria of the genus *Acidiphilium* (Ballester et al., 1992; Cabrera et al., 2005).

Leaching process and thus its yield can be influenced by choosing appropriate parameters and conditions of leaching. Several authors (Cerruti et al., 1998; Nogueira et al., 2004; Zhu et al., 2003) examined the effect of temperature, type of leaching medium and amount of the waste (Nemati et al., 2000; Shen et al., 2001) on the efficiency of the bioleaching process. By optimizing of leaching conditions it is possible to increase the yield of the process and reduce its cost.

Not only conditions of leaching process but also the treating of the waste before leaching affect the yield of heavy metals. Method of crushing or grinding affects the granularity and morphology of particles that reflects in the amount of metal in solution and in required time to achieve maximum yield.

The aim of this paper was to analyse the influence of selected parameters on Ni leachability. The experiment was realized at different temperatures, two types of leaching medium and different ratios of L : S (100, 40 and 20) were used.

Experimental materials and methods

Grinded electrodes from discarded Ni-Cd batteries were used for the leaching experiments and solution of *Acidithiobacillus ferrooxidans* bacteria and the mixture of *Acidithiobacillus ferrooxidans* and *Acidithiobacillus thiooxidans* bacteria were used for bioleaching.

Electrode powder was manually separated from the rest of the battery and crushed to grain below 40 μm. Totally 19 to 20 g of powder was obtained from one battery. Powders treated this way were used in the leaching experiments in the amount 10, 25 and 50 g/l.

Leaching medium was prepared as follows:

• Adapted and non-adapted bacteria *Acidithiobacillus ferrooxidans* – 180 ml 9K nutrient solution and 20 ml solution of the bacteria were added into 9K nutrient solution,

• a mixture of adapted and non-adapted bacteria *Acidithiobacillus ferrooxidans* and *Acidithiobacillus thiooxidans* in quantity of 20 ml of bacteria mixture (10 ml

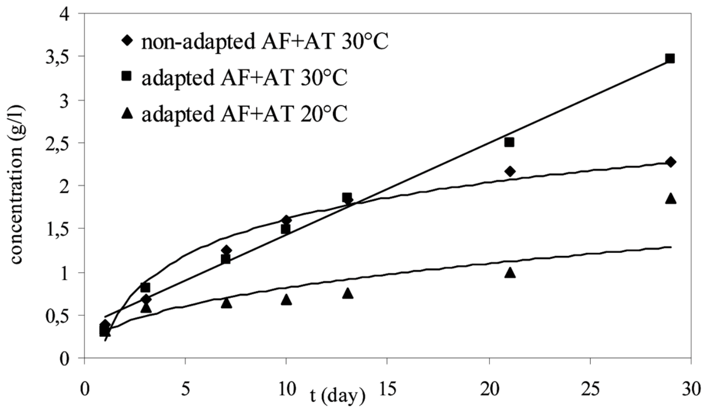

Fig. 1. Influence of adaptation and temperature on Ni bioleaching by bacteria *Acidithiobacillus ferrooxidans* (AF).

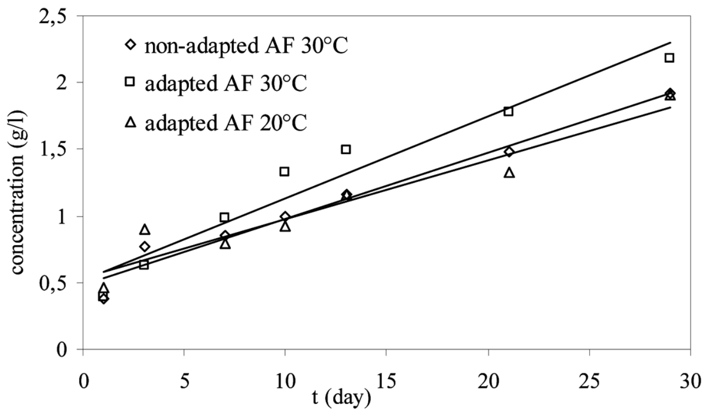

Fig. 2. Influence of adaptation and temperature on Ni bioleaching by the mixture of bacteria *Acidithiobacillus ferrooxidans* and bacteria *Acidithiobacillus thiooxidans (AF + AT)*.

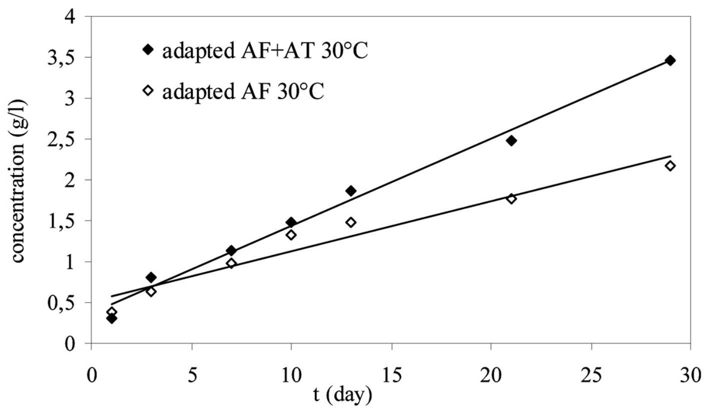

Fig. 3. Dependence of Ni concentration in solution on leaching medium type.

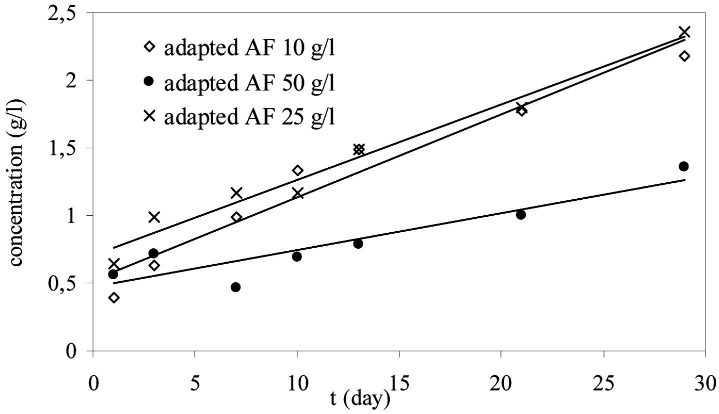

Fig. 4. Influence of L : S on nickel leaching by 30 °C.

AF + 10 ml AT) in 180 ml 9K nutrient solution was added into 9K nutrient solution.

The experiment was carried out at 20 °C and 30 °C. 2 g of electrode powder were added into the prepared solutions with adapted and non-adapted bacteria *Acidithiobacillus ferrooxidans* and a mixture of bacteria. All leaching experiments lasted 28 days and samples were taken at the following intervals: 1, 3, 7, 10, 13, 21, 28 days. The nickel content in the samples was estimated by AAS analysis.

Results and discussion

The average composition of the electrodes before leaching, determined by AAS analysis is provided in Tab. 1. Electrodes are mixture of nickel, cadmium and iron, the contents of nickel was approximately 40 %, cadmium 17 % and Fe 4.5 %.

The results of AAS analysis, Fig. 1, confirm that the higher temperature and the adaptation of bacteria help to increase the efficiency of the Ni leaching.

Assuming that all amount of Ni is leached into the solution and according to Tab. 1, the maximum achievable amount of nickel in the solution is 4.1 g/l (100 % of Ni from battery). The amount of Ni 2.2 g/l in the solution has been achieved after 28 days of leaching at temperature 30 °C and with using adapted bacteria *Acidithiobacillus ferrooxidans.* This is 54 %. The lowest yields of Ni were obtained at the temperature of 20 °C.

In the case of using the mixture of bacteria *Acidithiobacillus ferrooxidans* and *Acidithiobacillus thiooxidans* (AF and AT), Fig. 2, better results were obtained using adapted bacteria and leaching at a higher temperature (30 °C). In this experiment the amount of Ni in leaching solution reached 3.5 g/l, it is 84 % of Ni leaching efficiency.

Tab. 1
Chemical analysis of spent Ni-Cd battery electrode
(average compound)

Ni (%)	Cd (%)	Fe (%)
41.1	16.7	4.5

Comparison of the leaching efficiency at the temperature 30 °C in the adapted mixture of bacteria to adapted bacteria *Acidithiobacillus ferrooxidans* only: The analysis of results shows that using a mixture of bacteria it is possible to achieve higher yields than in the case of leaching in solution with adapted bacteria *Acidithiobacillus ferrooxidans* only, Fig. 3. While by leaching in solution with the bacteria *Acidithiobacillus ferrooxidans* was reached only 54 % efficiency of Ni leaching, using the mixture of bacterial allows to reach the leaching efficiency 84 %.

Comparison of the influence of the solid phase amount on leaching of nickel at 30 °C to usage bacteria *Acidithiobacillus ferrooxidans* is in Fig. 4. Comparing the ratios L : S = 100 to 40, it is obvious that the amount of Ni in solution is about the same ~55 % in both cases. However, increasing the concentration of solid components to 50 g/l, L : S = 20 leads to sharp decrease of leaching ability of solution. Under these conditions was reached only 33 % leachability of nickel after 28 days of leaching experiment. This confirms that the increase in the quantity of toxic substances in the solution causes a decrease of bacteria vitality that reflects in their ability of leaching. Probably, increasing of the concentration of the waste by the process of adaptation of bacteria could lead to achievement of the higher amount of heavy metals in solution. However, these assumptions need further experimental verification.

Conclusions

Crushed electrode powder from the discarded Ni-Cd batteries was leached at different temperatures, different ratios L : S and in four different leaching medias:

- 9K solution with adapted bacteria *Acidithiobacillus ferrooxidans*,
- 9K solution with non-adapted bacteria *Acidithiobacillus ferrooxidans*,
- 9K solution with a mixture of adapted bacteria *Acidithiobacillus ferrooxidans* and *Acidithiobacillus thiooxidans*,

• 9K solution with a mixture of non-adapted bacteria *Acidithiobacillus ferrooxidans* and *Acidithiobacillus thiooxidans*.

The results of the experiments are as follows:

1. The yield of Ni in leaching solution increases with increasing temperature;

2. The yield of Ni increases by using of adapted bacteria;

3. The highest amount of Ni in the solution, 93 %, was achieved using the mixture of adapted bacteria *Acidithiobacillus ferrooxidans* and *Acidithiobacillus thiooxidans*;

4. Reducing of L : S ratio, i.e. increasing the amount of electrode powder in a solution, causes a decrease of Ni dissolution, which implies that the concentration of toxic substances in the solution may raise above the tolerance limits of the bacteria.

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Comparison of conventional and microwave assisted leaching of zinc from the basic oxygen furnace dust

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Abstract

Basic oxygen furnace (BOF) dust is a hazardous metallurgical waste generated in the collection of particulate material during the steel making processes. The occurrence and recovery of metallurgical wastes from the steelmaking and the iron making processes are nowadays a great problem, mainly due to their big amount and environmental pollution by the heavy metals potential. The aim of this work was to carry out a chemical, physical, structural, and morphological characterization of these waste materials and subsequently to find out the best suitable method for the hydrometallurgical treatment. Experimental work includes full plant experiments. Extraction conditions like the effect of the microwave power, leaching agent, acid concentration, S/L ratio and the extraction time of the zinc removal efficiency were evaluated. The main goal is to set the best conditions for the transfer zinc into the solution while the iron should remain in the solid phase.

Key words: basic oxygen furnace dust, extraction, microwave assisted leaching, zinc recovery

Introduction

The primary source of iron as a feed to iron and steel facilities comes from the oxide ores containing minerals such as hematite (Fe_2O_3) and magnetite (Fe_3O_4), which usually carry a negligible amount of the non-ferrous metal as an impurity. However, some scrap is always used as a secondary source of iron and is usually carries zinc in significant amounts. Scrap originates from a variety of sources such as old cars, cans, bridges, rails and demolished buildings and in most cases it is in galvanized form, which accounts for the presence of zinc. Low vaporization temperature of zinc causes it to accumulate in the furnace off-gasses in the form of small dust particles. Regardless of the source, build-up of zinc in the steel making processes is not desirable due to its adverse effect on the process performance and eventual quality of steel. Fig. 1 represents the expanding tendency of the world steel production which is evidently associated with the waste production. It is estimated that each year, 5 – 7 million tones of the basic oxygen furnace (BOF) sludge is generated worldwide. A sludge stream is produced from the furnace dusts carried away with off-gases that are directed to scrubbers for cleaning prior to their release. This sludge is generally disposed as landfill. Two concerns here are related to the cost of landfill and the loss of iron units. Recovery of iron at acceptable zinc grade is an attractive option as long as it can be done economically. It was suggested that if the final zinc content of BOF sludge can be reduced to below 0.4 % (wt.), it can be directly recycled in the iron-making or steel-making process (Smith et al., 2000).

At U.S.Steel Košice, s.r.o., a steel factory in Slovakia, after the removal by the wet scrubber, the fine dust is allowed to settle in a pond, where it is stored until a suitable processing technique is available. Leaching of Zn may cause contamination of groundwater; moreover, government regulations no longer tolerate longterm storage of waste on industrial areas. Several possible treatment processes for the recycling and recovery of basic oxygen furnace dust are under investigation, e.g., pyrometallurgical processes (Asadi Zeydabadi et al., 1997; Das et al., 2007). The construction of prototypes for these processes is however very expensive, working costs are high and only large quantities of the dust with a relatively high Zn concentration can be processed economically.

The fine particle fraction of the BOF dust as obtained at U.S.Steel Košice, s.r.o., has Zn content about 9.3 %; nevertheless the percentage of the zinc depends on the charge. Hydrometallurgy is therefore, in our opinion, a more suitable alternative, offering the advantage that it can be used for wastes with a low Zn concentration. This paper describes a hydrometallurgical process to remove the Zn from dust in order to recycle the Fe and to recover the Zn. First, the BOF dust was characterized: the total composition was determined, and data from an extraction procedure were obtained.

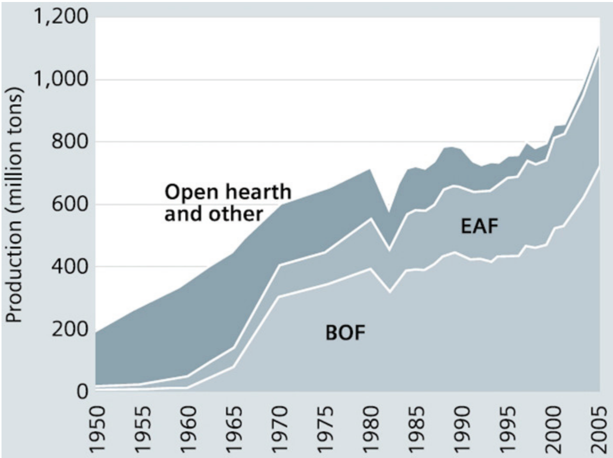

Fig. 1. World steel production.

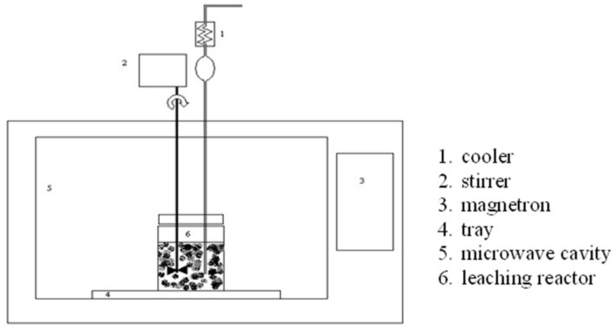

Fig. 2. Schematic diagram of the microwave leaching system.

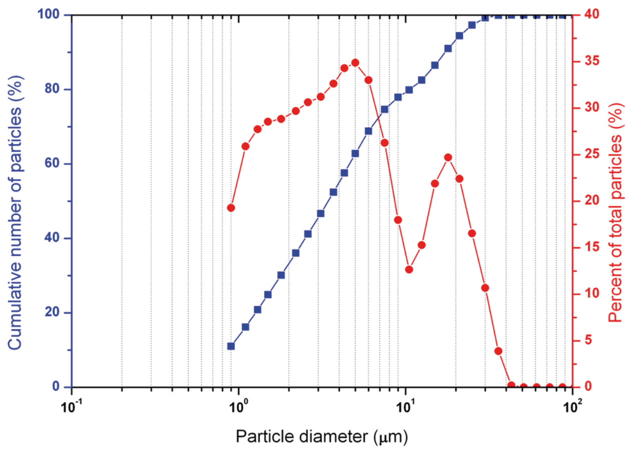

Fig. 3. Particle size distributions of the BOF dust used.

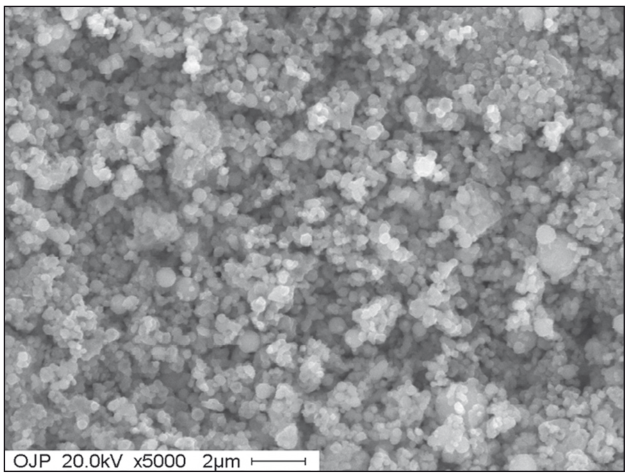

Fig. 4. Scanning electron micrograph of BOF dust particles.

Materials and methods

A BOF dust sample from the Steelmaking Company U.S.Steel Košice, s.r.o., was used in this investigation. First, the BOF dust was characterized: the total composition was determined, and data from an extraction procedure were obtained. The investigation was carried out by using granulometric analysis, chemical analysis, scanning electron microscopy (SEM) with EDX, X-ray diffraction (XRD) and Mössbauer spectroscopy to completely characterize the BOF dust sample.

A 10 g sample of BOF dust was mixed with 10 ml of deionized water. After 10 minute the sample was filtered and the acidity was measured using a pH meter (12.33). The granulometric analysis of BOF dust was evaluated by the Helos/LA Sympatec (Germany). The chemical characterization of BOF dust was focused in the determination of majority elements as Fe, Zn and Ca. The analysis was executed by using atomic absorption spectroscopy Varian Spectr AA-30 (Australia).

Mineralogical composition of samples was determined by XRD using a Philips PW1820 Automatic Powder Diffractometer with Cu Kα radiation. Powder samples were measured on the range of 20 – 80°2θ with a scan step 0.05° and fixed counting time of 2 s for each step. The pattern was analysed by using the Powder Cell software and the PDF database was used for the phase identification. Mössbauer spectroscopy measurements were carried out with a ^{57}Co/Rh γ-ray source (Germany) at the room temperature. The velocity scale was calibrated relative to ^{57}Fe in Rh. Recoil spectral analysis software was used for the quantitative evaluation of the Mössbauer spectra. Scanning electron microscopy (SEM) with the energy-dispersive X-ray (EDX) was executed to get additional knowledge of the BOF dust particle structure, morphology and chemical composition.

Leaching studies to determine optimum operational conditions such as efficiency, solid-liquid (S/L) ratio, leaching reagents, reaction time, in the reactor with volume of 300 ml were performed. In all experiment 10 – 20 g of BOF dust sample were used depending on the S/L ratio. Using conventional method, the samples were leached with sulphuric acid at temperature between 30 °C and 80 °C. The leaching reactor was dipped in a water bath and was covered to keep an S/L ratio constant. Mechanical stirrer with a constant stirring speed 350 rpm was used to mix the sample with a leaching agent. In the case of microwave assisted leaching a microwave oven Whirlpool AVM 434 with a power range from 90 to 650 W at frequency of 2.45 GHz was used. A schematic diagram of the microwave-leach system is presented on Fig. 2. About 5 ml solution was removed at convenient time intervals, filtered and analysed for zinc by atomic absorption spectroscopy.

During the microwave leaching process a mechanical stirrer was used to mix the BOF dust sample with a leaching agent, with a stirring speed 350 rpm, however the leaching reactions in higher power range were very violent and the stirring was not required. After the acquired leaching time the temperature of the solution was measured immediately with a manual non-contact thermometer Raynger MX4.

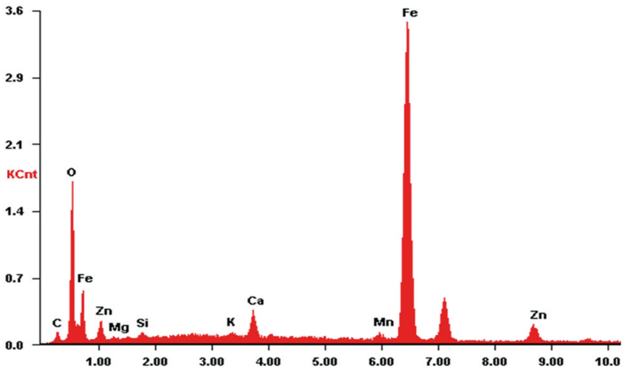

Fig. 5. EDX analysis of BOF dust sample.

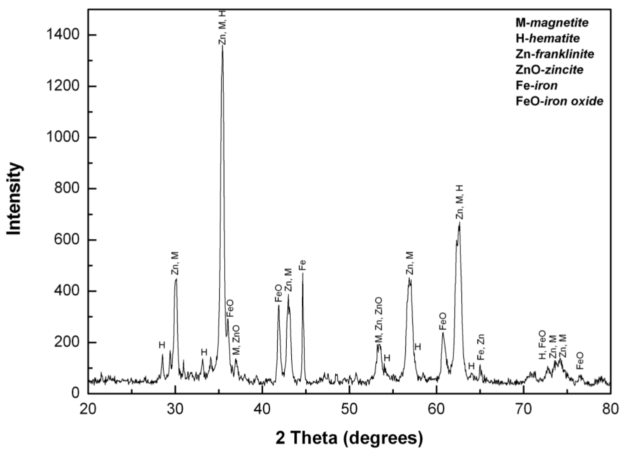

Fig. 6. X-ray diffraction pattern of BOF dust sample.

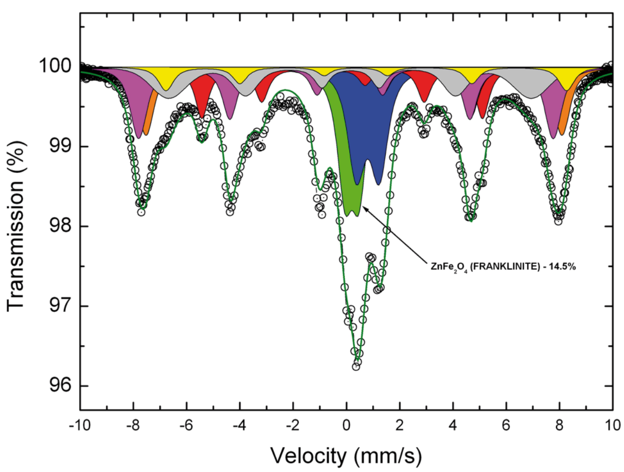

Fig. 7. Mössbauer spectrum of BOF dust.

In all the experiments, the zinc concentration and dissolution percent was determined by AAS. The effects of parameters on the zinc dissolution were studied. Results of these experiments are described in the following sections.

Results and discussion

BOF dust is alkaline, in our case with a pH range 12.33. The particle size distribution of the examined BOF dust is

Tab. 1
Chemical composition of BOF dust

Component	Fe	C	SiO_2	CaO	MgO	Zn	Pb
(mass %)	49.87	0.97	0.87	7.50	2.68	9.37	0.24

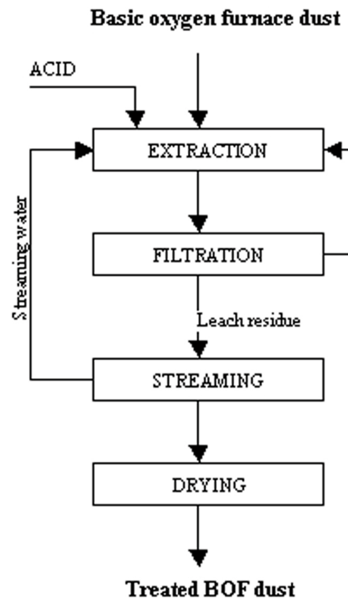

Fig. 8. Leaching diagram of the BOF dust.

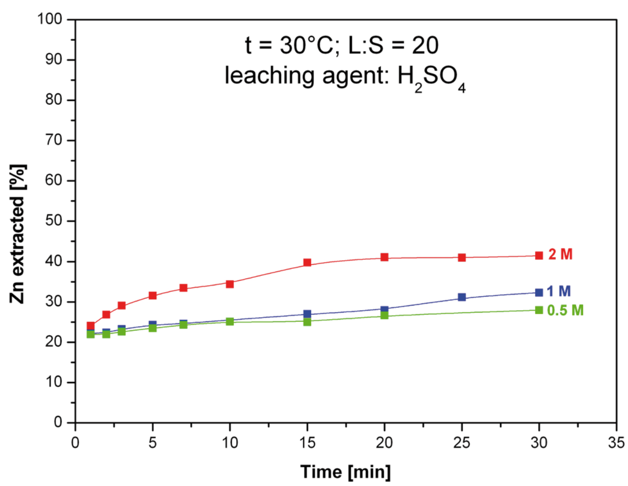

Fig. 9. Zinc dissolution percentage as a function of acid concentration on leaching time at 30 °C.

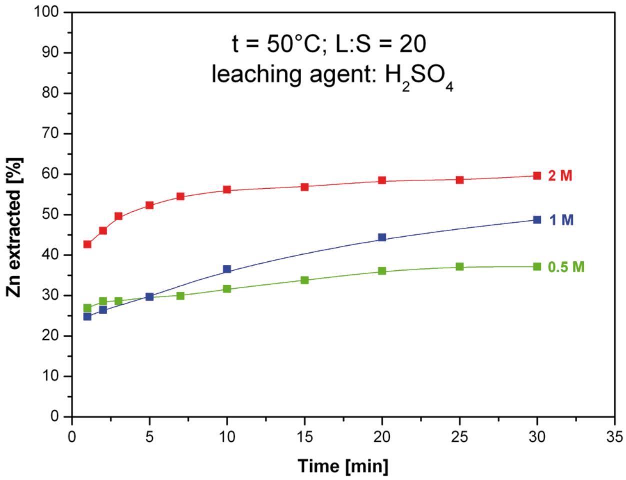

Fig. 10. Zinc dissolution percentage as a function of acid concentration on leaching time at 50 °C.

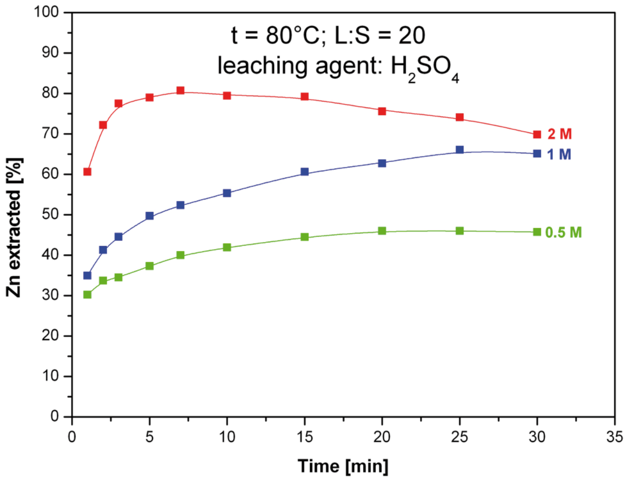

Fig. 11. Zinc dissolution percentage as a function of acid concentration on leaching time at 80 °C.

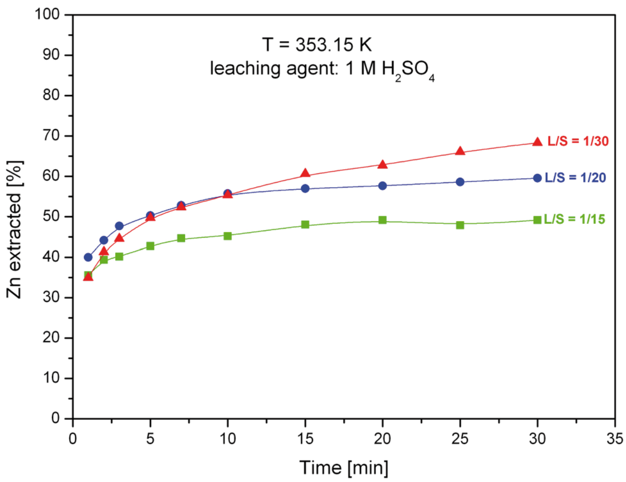

Fig. 12. Zinc dissolution percentage as a function solid/liquid ratio.

given in Fig. 3. It presents a heterogeneous distribution of particle size and contains two major size fractions: a fine grained portion (1 – 10 μm) and a coarser part (10 – 36 μm). As also known that the metals are more concentrated in the fine fraction of the waste (Machado et al., 2006), but mesh analysis was unsuccessful to separate fractions from the sludge, which could contained markedly different amount of zinc as the average composition.

It was found that 50 % of it was below 3.5 μm, whereas the majority (100 %) of the particles was below 36 μm. Scanning electron microscopy (SEM) with the energy--dispersive X-ray (EDX) was executed to get additional knowledge of the BOF dust particle structure, morphology and chemical composition. By the SEM observation (Fig. 4), the dust shape could be approximately spherical with some agglomerated parts. The SEM picture with EDX spectra are shown in Figs. 4 and 5.

The chemical composition of BOF dust depends mainly on the quality of steel scrap processed and the type of steel was found. Tab. 1 presents the chemical composition of the major elements of the BOF dust used. Beside iron and zinc, the dust is characterized by the relatively high content of calcium oxide, whose presence should be attributed to the lime added to the steelmaking furnace.

The X-ray diffraction pattern of the BOF dust is shown in Fig. 6. Four major phases were identified: franklinite, magnetite, hematite and iron oxide. Zinc in the examined BOF dust is in the forms of zinc oxide as zinc ferrite (franklinite – $ZnFe_2O_4$), whereas iron is mainly in the form of franklinite and magnetite (Fe_3O_4). Furthermore, iron, hematite, calcite and zincite are also present as minor constituents.

Iron ores are the source of iron oxide and magnetite phases. The amount of zinc is depending on the ratio of galvanized scrap utilized during the steelmaking process. Calcite is originated from limestone which is additional material added to the furnace.

Additionally, less crystalline oxides of Fe, Al, Zn, Pb, and other metals could be present in this fraction. The presence of Zn minerals, due to their low amount could however hardly be detected. To confirm the Zn-Fe phase the Mössbauer spectroscopy was used. The Mössbauer spectrum of BOF dust sample is displayed on Fig. 7.

As it was mentioned before, zinc in BOF dust is present as $ZnFe_2O_4$ (franklinite) and less amount in the form of zinc oxide ZnO (zincite). Iron is present, except of franklinite, mostly as magnetite, Fe_3O_4. The ZnO does not cause any problems to neither alkaline nor acid leaching. However, zinc ferrite is considerably refractory against leaching. Although alkaline leaching seems to be advantageous (due to the low iron leaching) and it requires relatively concentrated leaching medium (Kelebek et al., 2004). On the other hand the acid leaching does not need so concentrated solution as the alkaline one, but iron is partially transferred into solution in this case. However, choosing the sulphuric acid leaching route, the highly reactive species of zinc are dissolved. After the purification of the leach liquors, the metal from the leach solution can be recovered by the different methods such as precipitation, crystallization, solvent extraction, ion exchange, electrowinning etc.

The schematic diagram of the leaching process is demonstrated in Fig. 8.

The reactions of the main species occurring in the sample and their stoichiometry can be stated as follows (Havlík et al., 2004):

$$ZnO + H_2SO_{4\,(aq)} \rightarrow ZnSO_{4\,(aq)} + H_2O \tag{1}$$

$$ZnFe_2O_4 + 4H_2SO_{4\,(aq)} \rightarrow ZnSO_{4\,(aq)} + Fe_2(SO_4)_3 + 4H_2O \tag{2}$$

$$ZnFe_2O_4 + H_2SO_{4\,(aq)} \rightarrow ZnSO_{4\,(aq)} + Fe_2O_3 + H_2O \tag{3}$$

In respect of the quantity of present important substances in the BOF dust, the analysis was oriented mainly on zinc extraction. Moreover, in one case the comparison of zinc and iron extraction at chosen conditions and possibility of their selective extraction was studied. Results achieved from the kinetic study of leachability of zinc into the solution. Effect of acid concentration and temperature on zinc leachability by conventional heating is shown in the Figs. 9 – 11. The results showed that the rates of zinc dissolution are dependent on the acid concentration and temperature. The percentage of the zinc extraction increases with increased sulphuric acid concentration and temperature up to 2M where 80 % of zinc was extracted after 7 minutes at temperature 80 °C.

The leaching efficiency of zinc is dependent on the S/L ratio. Fig. 12 shows the Zn extraction efficiency depending on the S/L ratio. Decreasing the amount of the BOF dust sample in the leaching reactor the Zn dissolution percentage has increasing tendency.

The effect of the temperature and microwave energy was studied using a modified domestic microwave oven with power levels 90, 160, 350, 650 W. In this case the temperature is dependent on the time of leaching period. In every case of the microwave assisted extraction process the temperature of the leaching solution in the beginning was at room temperature. The results are shown in Fig. 13.

The comparison between the conventional and microwave assisted leaching of the zinc dissolution percentage is shown in Fig. 14. We can conclude that the dissolution rate of zinc is strongly dependent on the temperature and in the case of microwave assisted leaching on the microwave power.

The nature of the zinc species that is easily solubilized by the acid leaching is not clear. It is speculated, however, that it involves zinc oxide in a greater proportion in the coarse fraction of the dust sample than zinc ferrite. Likewise, the inability of the fines for the zinc leaching is probably related to the presence of the zinc ferrite in much greater proportion than the zinc oxide. For the verification purposes, these points may require additional characterization work for the sludge sample currently tested. Initial batch of the dust samples indicates the presence of zinc oxide by XRD technique only as a minority phase.

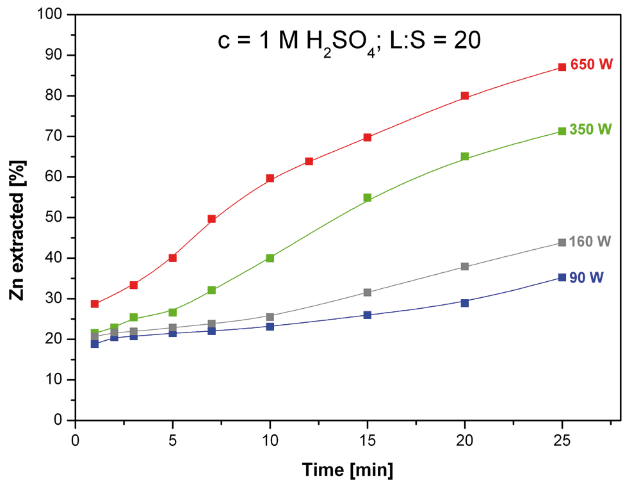

Fig. 13. Zinc dissolution percentage as a function of microwave power.

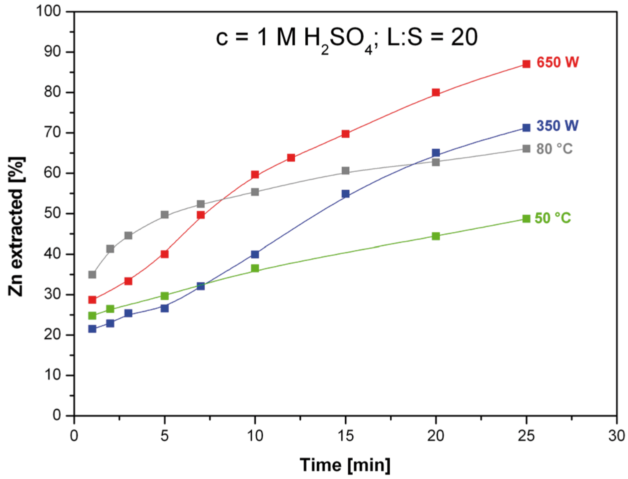

Fig. 14. Comparison of zinc leaching curves between conventional and microwave assisted leaching.

Conclusion

Recovery and separation of metals, especially zinc, from BOF dust is a practical idea in steelmaking industries. The fact that it is not possible to recycle this waste material directly or to reject it as landfill, makes it necessary to consider the proposed process used in this work, for obtaining a non-hazardous residue, which can be stored without problem or can be recycled. The characterization of a solid metallurgical waste using many different techniques increase the reliability in the results and also give more conditions to decide about the best possible recycling method.

Conventional and microwave assisted acid extractions were adopted to evaluate the efficiency of the zinc removal from the industrial dust. The percentage of the extraction of zinc increased with the acid concentration and temperature (microwave power). At higher temperatures, the dissolution rates were faster and more zinc was dissolved. These experimental results demonstrated that the most important factors in the acid extraction were the acid concentration and temperature. In the case of temperature the particles only react when they collide. When a substance is heated particles gain more kinetic energy and collide more frequently thus speeding the rate of reaction. Raising the temperature of reactants will speed up a chemical reaction since activation energy is achieved easily. The reaction is highly exothermic due to the alkaline nature of the sample. Harsher chemical conditions involving a higher dose of acid, high temperatures and the use of an appropriate catalyst would probably cause a dissolution of the greater amounts of zinc. However, this will probably be at the expense of the greater loss of iron units. Ability to recycle BOF dust is economically and environmentally advantageous.

Microwave treatment of BOF dust resulted in very rapid dissolution of the zinc phase. Leaching was completed within minutes, while the conventional leaching process needed much time and more electric energy in the heating process. For the comparison in the case of conventional leaching at temperature 80 °C the energy consumption was 0.8 kWh in the case of microwave assisted leaching at power level 350 W was 0.2 kWh. With the microwave heating the zinc recoveries were 10 – 20 % higher than those observed with conventional leaching. The effect of power level was significant. At the higher power levels, the dissolution rates were faster and more zinc was dissolved. The higher dissolution rate and also the higher zinc recoveries in the microwave leaching process could be attributed to one or more factors: – superheating of the liquid, – interaction of the microwaves with the BOF dust particles in the solution.

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Biological methods for the biodegradable waste removal

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Key words: biodegradable waste, organic fertilizer, biological treatment waste

Abstract

According to the EU directives and the state law, Poland as an EU member is obliged to the vast limitation of the quantity of storage communal waste. The fulfilling those obligations is available only on the way of scientific research in searching new treatment methods which give the products useful for another user and will be accepted on economical aspect. For the disposal of mixed communal wastes among the others, the installations for mechanical and biological treatment can be taken into consideration for substances biodegradable and typical biological methods for extracted biomass. The paper presents requirements related to the treatment products and assessments of possibility in the receiving of its suitable properties.

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Removal of lead(II) and cadmium(II) ions by immobilized waste yeast from the wastewater

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Key words: biosorption, lead and cadmium ions, biomass

Abstract

Heavy metal pollution has become one of the most serious environmental problems today. The intensification of industrial activity during recent years is greatly contributing to the increase of heavy metals in the environmental, mainly in the aquatic systems. Cadmium and lead are heavy metals, which pose serious health hazards through the entry into the food chain by anthropogenic pathways.

Biosorption, using biomaterials such as bacteria, fungi, yeast and algae, is regarded as a cost-effective biotechnology for the treatment of the high volume and low concentration complex wastewaters containing heavy metal(s) in order of 1 to 100 mg/L. Using immobilized biosorbent as a column material the biosorption of the heavy metals could be studied in the flow system under the dynamical conditions. The immobilization of the biosorbent by the biotic or synthetic polymer raised the mechanical substance stability, as well as the size-distribution, porosity, proof against the environmental effect of the biosorbent. Immobilized fungal cells may be re-used, immobilization reduces the cell wastes, minimizes the loss of product and facilitates the product recovery, in particular when in situ product removal is performed.

In the present study our aim was to optimize the composition of *Saccharomyces cerevisiae* biomass immobilized in the calcium alginate matrix. The biosorbent is brewery waste fungal cells. Decreasing the calcium alginate concentration, the adsorption capacity increase of *Saccharomyces cerevisiae* was obtained. The maximum biosorption capacity of the fungal biomass in the wastewaters, based on the dry weight, was determined under pH controlled conditions by varying the following experimental parameters: heavy metal concentration, biomass dosage, pH, adsorption time and temperature.

Equilibrium and kinetic investigation of cadmium (II) and lead (II) sorption in aqueous suspension were determined varying the calcium alginate and biomass concentrations in biosorbents using the batch technique.

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Geovestník

Informačný spravodajca pre geológiu, baníctvo, úpravníctvo a životné prostredie

Príloha časopisu Mineralia Slovaca, roč. 42, č. 3

Košice - Slovakia

Recyklácia odpadov – Waste recycling XIV.

Košice 2. – 3. 12. 2010

Mária Kušnierová
Institute of Geotechnics of Slovak Academy of Sciences, Watsonova 45, SK-043 53 Košice, Slovak republic

Medzinárodná konferencia ***Recyklácia odpadov*** má svoju históriu a vývoj. Jej I. ročník sa konal v roku 1997 na pôde Vysokej školy báňskej v Ostrave z iniciatívy jej zakladateľa a hlavného garanta, prof. Ing. Petra Fečka, CSc., ktorý bol v tom čase zástupcom vedúceho Inštitútu environmentálního institutu. Na základe rozhodnutia vedeckého výboru sa táto – pôvodne česká – konferencia v roku 2001 pretransformovala na medzinárodnú s ustanovením, že každý rok bude jedna z troch účastníckych strán poverená jej organizáciou. Garantom konferencie sa za poľskú stranu stal pán prof. Ing. A. Jarosinski

The history of the series of International conferences ***Waste recycling*** started in 1997, when the first conference, owing to the initiative of its founder and the main guarantee Prof. Dipl. Eng. Petra Fečka, PhD., being that time the deputy of the head of the Environmental Institute of the VŠB – Technical University of Ostrava, was held in this university. In 2001, based on the decision of the conference´s scientific committee, the originally Czech conference obtained an international extent and each year the logistics has started to be provided by one of three participating countries. Prof. Dipl. Eng. A. Jarosinski from the Politechnika Krakowska became the Polish guarantee z Politechniky Krakowskej a za slovenskú stranu doc. Ing. Mária Kušnierová, PhD., z Ústavu geotechniky SAV v Košiciach.

V dňoch 2. – 3. 12. 2010 sa v Košiciach uskutoční XIV. ročník konferencie ***Recyklácia odpadov***. Bude to už po tretíkrát, čo metropola východného Slovenska privíta odborníkov z oblasti úpravy a spracovania odpadov. Po prvýkrát sa konferencie zúčastnia aj kolegovia z Maďarska a je predpoklad, že v budúcnosti aj oni rozšíria medzinárodný organizačný tím na kompletný „višegrádsky".

Úlohy organizátora tohtoročnej XIV. konferencie sa zhostil tím vedeckých pracovníkov z Ústavu geotechniky SAV v Košiciach v zložení: Ing. Mária Praščáková, PhD., Ing. Slavomír Hredzák, PhD., Ing. Alena Luptáková, PhD., Ing. Oľga Šestinová, Ing. Jana Jenčárová, Ing. Lucia Ivaničová, PhD., RNDr. Eva Mačingová, Katarína Stuchlá a Helena Vašková pod vedením doc. Ing. Márie Kušnierovej, PhD., ako garantky konferencie:

Vedecký výbor konferencie pracoval v zložení:

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doc. RNDr. Peter Andráš, CSc., GÚ SAV, Slovensko
doc. Ing. Vladimír Čablík, PhD., VŠB – TU, Ostrava, Česká republika
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prof. Inž. Jaroslav Jarosinski, PK, Krakow, Poľsko
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Ing. Zoltán Németh, PhD., Mineralia Slovaca, Slovensko
Ing. Ondřej Procházka, CSc., Waste forum, Česká republika
Ing. Miroslav Mračko, Odpady, Slovensko
prof. Inž. Barbara Tora, PhD., AGH, Krakow, Poľsko

Konferencie sa v tomto roku zúčastní 105 účastníkov. Odprezentovaných 64 odborných článkov bude publikovaných podľa zamerania v recenzovaných odborných časopisoch Mineralia Slovaca, Waste forum a Odpady, ktoré sú zároveň mediálnymi partnermi konferencie.

Konferenciu ***Recyklácia odpadov/Waste recycling XIV.*** podporili reklamní partneri:

of the conference and Assist. prof. Dipl. Eng. Mária Kušnierová, PhD., from the Institute of Geotechnics of the Slovak Academy of Sciences in Košice, the Slovak guarantee.

On 2. – 3. 12. 2010 the XIV. International Conference will be held in Košice. In total it will represent third meeting of experts from the area of dressing and elaboration of the waste, being held in the metropolis of Eastern Slovakia. For the first time the conference will be attended by the colleagues from Hungary and there is an expectation that Hungary will enlarge the territorial extent of the conferences´s series for the complete "Visegrad" area in the future.

This year´s XIV. International Conference was organized by the team of scientific workers from the Institute of Geotechnics of the Slovak Academy of Sciences in Košice: Dipl. Eng. Mária Praščáková, PhD., Dipl. Eng. Slavomír Hredzák, PhD., Dipl. Eng. Alena Luptáková, PhD., Dipl. Eng. Oľga Šestinová, Dipl. Eng. Jana Jenčárová, Dipl. Eng. Lucia Ivaničová, PhD., RNDr. Eva Mačingová, Katarína Stuchlá and Helena Vašková led by the guarantee of the conference Assist. prof. Dipl. Eng. Mária Kušnierová, PhD.

Scientific committee of the conference:

Prof. Dipl. Eng. P. Fečko, PhD., VŠB – TU, Ostrava, Czech Republic
Assist. prof. Dr. Peter Andráš, PhD., GÚ SAV, Slovakia
Assist. prof. Dipl. Eng. Vladimír Čablík, PhD., VŠB – TU, Ostrava, Czech Republic
Dipl. Eng. Slavomír Hredzák, PhD., ÚGt SAV, Košice, Slovakia
Prof. Dipl. Eng. Jaroslav Jarosinski, PK, Krakow, Poland
Visit. prof. Dipl. Eng. Víťazoslav Krúpa, DrSc., ÚGt SAV, Košice, Slovakia
Dipl. Eng. Zoltán Németh, PhD., Mineralia Slovaca, Slovakia
Dipl. Eng. Ondřej Procházka, PhD., Waste forum, Czech Republic
Dipl. Eng. Miroslav Mračko, Odpady, Slovakia
Prof. Dipl. Eng. Barbara Tora, PhD., AGH Krakow, Poland

This year 105 participants attended the conference. Altogether 64 scientific papers are published, being divided by their scope into three reviewed scientific journals: Mineralia Slovaca, Waste forum and Odpady (Waste), representing simultaneously the medial partners of the conference.

The conference ***Waste recycling XIV.*** is supported by the following partners:

Magistrát mesta Košice

Municipality of the town Košice

Ústav geotechniky Slovenskej akadémie vied, Košice

Institute of Geotechnics of Slovak Academy of Sciences, Košice

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Institute of Geotechnics of Slovak Academy of Sciences,
Watsonova 45, SK-043 53 Košice, Slovak republic

Abstract: *The paper presents the history, evolution, the main scope and activities, as well as the recent headquarters of the Institute of Geotechnics of the Slovak Academy of Sciences in Košice, Slovakia. The Institute is divided into following departments: Dept. of Mineral Biotechnologies, Dept. of Physical and Physical-Chemical Mineral Processing Methods, Dept. of Destruction and Construction Geotechnics, Dept. of Environment and Hygiene in Mining, Dept. of Mechanochemistry, as well as the service departments of the Central Laboratory and the Machine Service. The departments are equipped with the up-to-date laboratory and the pilot scale processing facilities. During the recent 10 years the Institute in national and international level solved 12 APVV/APVT projects, 1 project of the State Program of the Investigation and Development, 2 state projects, 52 VEGA projects, 2 EU FP projects, 2 NATO projects, 1 COST project, 20 projects of bilateral and multilateral cooperation, 1 project of the Centre of excellence of the Slovak Academy of Science as well as further projects focussed on practical application and used by the public administration. The total number of solved projects reached 100. The main recent activity of the Institute is its implementation as a research partner for the projects of the agency of the Ministry of Education, Science, Research and Sport of the Slovak Republic for the Structural Funds of EU.*

Key words: *geotechnics, biotechnologies, mechanochemistry, mining, projects, Centre of excellence*

História a vývoj

Začiatok základného výskumu v banských vedách v rámci Slovenskej akadémie vied možno datovať do obdobia jej vzniku – rok 1953. Ako prvá organizačná jednotka v SAV pre banský výskum bola v roku 1954 zriadená komisia pre baníctvo, neskôr, v roku 1955, z nej bol rozhodnutím Predsedníctva SAV, založený kabinet baníctva SAV. V tomto období mal kabinet 1 vedeckého pracovníka a 1 inžiniera I. stupňa.

Od 1. januára 1957 bol kabinet baníctva SAV premenovaný na laboratórium baníctva SAV, ktorého pracovisko bolo 11. apríla 1957 presťahované do Košíc, čím sa začala písať košická história ústavu. Miestnosti pre pracovníkov laboratória poskytla Banícka fakulta Vysokej školy technickej v pavilónoch nachádzajúcich sa v Parku Komenského. Laboratórium malo ku koncu roka 5 pracovníkov, 4 s vysokoškolským a 1 so stredoškolským vzdelaním.

V rokoch 1959 – 1961 bola na Solovjevovej (teraz Watsonovej) ulici realizovaná výstavba budovy pre Laboratórium baníctva SAV a Laboratórium hutníckej technológie SAV. Keď bola budova v roku 1961 odovzdaná do užívania, malo Laboratórium baníctva SAV 25 zamestnancov. Dňa 1. januára 1962 bolo pracovisko premenované na Ústav baníctva SAV a ten sa stal samostatnou rozpočtovou jednotkou.

Počas svojej existencie prešiel Ústav ďalšími reorganizáciami a koncepčnými zmenami, ktoré opäť vyvolali nielen zmeny jeho názvu, ale aj zmeny v počte pracovníkov. Napríklad v roku 1986 mal Banícky ústav SAV už 64 kmeňových pracovníkov, z toho bolo 21 vedeckých (6 DrSc., 15 CSc.), 7 vedecko-technických, 8 odborných s vysokoškolským vzdelaním, 23 odborných so stredoškolským vzdelaním a 5 ostatných pracovníkov.

V súčasnosti má Ústav celkovo 66 kmeňových zamestnancov, z toho 41 vedeckých pracovníkov (3 DrSc., 38 CSc./PhD., a to 3 profesorov, 2 docentov, 3 vedúcich vedeckých pracovníkov, 21 samostatných vedeckých pracovníkov – kat. 2a, 17 vedeckých pracovníkov – kat. 2b), 3 odborných pracovníkov VŠ, 18 odborných pracovníkov ÚS, 4 ostatných pracovníkov a 8 doktorandov v dennej forme doktorandského štúdia. Smerné číslo dané zriaďovateľom je 54. Šiesti pracovníci sa úväzkovo podieľajú na riešení projektov, traja sú na dlhodobých stážach v zahraničí. Priemerný vek pracovníkov Ústavu je 45,05 roka (muži 36,40; ženy 45,93).

22. 11. 1954	komisia pre baníctvo SAV
15. 10. 1955	kabinet baníctva SAV
1. 1. 1957	laboratórium baníctva SAV
5. 11. 1962	Ústav baníctva SAV
31. 12. 1966	Ústav vlastností hornín SAV
1. 1. 1976	Banícky ústav SAV
1. 5. 1993	Ústav geotechniky SAV

Riaditelia

Ing. Eugen Stacha	1955 – 1958
JUDr. Ing. Karol Ugor, CSc.	1958 – 1965
RNDr. Jozef Kupka, DrSc.	1965 – 1967
akademik Tibor Kolbenheyer	1967 – 1969
Ing. Vincent Mihalík, CSc.	1969 – 1974
prof. Ing. Ľudovít Kovanič, DrSc.	1975 – 1987
prof. Ing. Félix Sekula, DrSc.	1987 – 1998
hosť. prof. Ing. Víťazoslav Krúpa, PhD.	od r. 1998

Zameranie

Ústav geotechniky Slovenskej akadémie vied je vedeckou organizáciou s príspevkovou formou hospodárenia. V rámci organizačnej schémy SAV je Ústav geotechniky SAV zaradený do I. oddelenia vied o neživej prírode, do skupiny Technické vedy.

V rámci akreditácií ústavov SAV v roku 2007 Ústav geotechniky SAV obhájil kategóriu *A*. V zmysle platných predpisov vydalo Ministerstvo školstva SR pre Ústav *Osvedčenie o spôsobilosti vykonávať výskum a vývoj*.

Ústav geotechniky SAV je organizačne rozdelený do 5 výskumných oddelení, ďalej do 2 servisných tímov a organizačno-technického útvaru, ktoré svojou činnosťou podporujú výskum realizovaný vo vedeckých oddeleniach.

Základný účel a predmet činnosti je definovaný v článku I. Zriaďovacej listiny č. 468/G/12/2008 zo dňa 28. 7. 2008:

1. Ústav svojím zameraním pôsobí v oblastiach: vedy o Zemi a environmentálne vedy, environmentálne inžinierstvo, environmentálna biotechnológia a nanotechnológie. Vykonáva základný výskum geologických a geotechnických aspektov kontinuálneho porušovania horninového masívu a skúmania stability podzemných diel a objektov, transportu energie a hmoty v procese dezintegrácie horniny; základný výskum zákonitosti tvorby tuhých disperzií v mikro- a nanorozmeroch a modifikácie ich vlastností fyzikálnymi, mechanickými, chemickými, biotechnologickými postupmi a postupmi nanotechnológií; základný výskum interakcii fáz v disperzných sústavách a pri ich šírení v pracovnom a životnom prostredí.

2. Ústav sa cieľovo orientuje na využitie teoretických poznatkov z uvedených oblastí na rozpracovanie princípov špičkových technológií v oblastiach: rozpojovania hornín, komplexného spracovania nerastných surovín, odpadov a materiálov mineralurgickými a hutníckymi postupmi, monitorovania vybraných zložiek životného a pracovného prostredia a environmentálnych, chemických a geologických zmien na skládkach odpadov s cieľom ekologickej revitalizácie.

3. Ústav poskytuje poradenské a expertízne služby, ktoré súvisia s jeho hlavnou činnosťou.

4. Ústav uskutočňuje doktorandské štúdium v zmysle všeobecne platných právnych predpisov.

5. Ústav zabezpečuje publikáciu výsledkov vedecko-výskumnej činnosti prostredníctvom periodickej a neperiodickej tlače. Vydávanie periodickej a neperiodickej tlače sa riadi uzneseniami Predsedníctva SAV.

Aktivity Ústavu geotechniky SAV za posledných 10 rokov na národnej a medzinárodnej úrovni zahŕňajú riešenie 12 projektov APVV/APVT, 1 Štátneho programu výskumu a vývoja, 2 štátnych objednávok, 52 projektov VEGA, 2 projektov rámcových programov EÚ, 2 projektov NATO, 1 projektu COST, 20 projektov bilaterálnej/MVTS spolupráce, 1 projekt Centra excelentnosti SAV a 7 projektov zmluvného výskumu pre prax a verejnú správu – spolu 100 projektov.

Najdôležitejšou aktivitou v súčasnosti je zapojenie sa Ústavu ako partnera do riešenia projektov Agentúry Ministerstva školstva, vedy, výskumu a športu SR pre štrukturálne fondy EÚ:

– Centrum excelentného výskumu získavania a spracovania zemských zdrojov,
– Centrum excelentného výskumu získavania a spracovania zemských zdrojov – 2. etapa,
– Centrum excelentnosti progresívnych materiálov s nano- a submikrónovou štruktúrou – nanoCEXmat,
– budovanie infraštruktúry Centra excelentnosti progresívnych materiálov s nano- a submikrónovou štruktúrou – nanoCEXmat II,
– Slovenská výskumno-inovačná platforma pre trvalo udržateľné surovinové zdroje,
– Centrum excelentnosti pre integrovaný výskum geosféry Zeme,
– Ústavy SAV v Košiciach – modernizácia infraštruktúry a vnútorného vybavenia učební pre lepšie podmienky vzdelávania.

Súčasné vedenie ústavu

riaditeľ: hosť. prof. Ing. Víťazoslav Krúpa, DrSc.
štatutárny zástupca riaditeľa: Ing. Slavomír Hredzák, PhD.

vedecký tajomník: prof. RNDr. PETER BALÁŽ, DrSc.
predseda vedeckej rady: Mgr. MARCELA ACHIMOVIČOVÁ, PhD.

Vedecké oddelenia Ústavu geotechniky SAV

Oddelenie minerálnych biotechnológií

Vzniku oddelenia predchádzal proces schválenia nového výskumného smeru (biologicko-chemické metódy úpravy surovín), ktorý bol zavŕšený v roku 1985 Dr. h. c., prof., Dr. Ing. Františkom Špaldonom, DrSc., členom – korešpondentom SAV. Do roku 1992 bol výskum v tomto smere realizovaný v oddelení fyzikálno-chemických metód úpravy. Samotné oddelenie vzniklo organizačnými zmenami v roku 1992 pod vedením doc. Ing. Márie Kušnierovej, PhD.. V súčasnosti sa pracovníci oddelenia zaoberajú štúdiom v oblastiach:

- ***objasnenia procesov biologicko-chemickej oxidácie a transformácie sulfidov*** pre vývoj environmentálnych technológií ich spracovania s využitím autochtónnych a fyziologicky adaptovaných baktérií *Acidithiobacillus ferrooxidans* a *Acidithiobacillus thiooxidans*. Objasnené boli deje biologicko-chemickej oxidácie a transformácie arzenopyritu, pyritu, antimonitu, tetraedritu, galenitu, sfaleritu a chalkopyritu. Vyvinutá bola napríklad technológia biologicko-chemickej úpravy a získavania Au z refraktorných Au-As-Sb-Fe rúd z Pezinka a neextrakčnej aplikácie mikroorganizmov v procesoch selektívnej bioflotácie;
- ***zisťovania faktorov ovplyvňujúcich metabolické funkcie a interakcie baktérií s minerálnym povrchom***, ktoré umožňujú korigovať rýchlosť a účinnosť biolúhovacích procesov v extrakcii Fe ako hlavného nežiaduceho prvku nerudných surovín (kaolínov, kremenných pieskov, živcov, zeolitov a popolčekov);
- ***štúdia štádií biochemického zvetrávania horninotvorných minerálov*** v oblasti rudných a nerudných ložísk, identifikácie jednotlivých bakteriálnych druhov metódami molekulárnej techniky izolácie DNA;
- ***štúdia paragenézy sekundárnych železitých minerálov (oxihydroxidov a hydroxysíranov) v kyslých banských vodách*** v procese zvetrávania sulfidov;
- ***štúdia sorpcie a ko-precipitácie katiónov a oxyaniónov z banských vôd vo forme biogénnych železitých minerálov;***
- ***štúdia metabolizmu a aplikácie síran redukujúcich baktérií*** v procesoch eliminácie ťažkých kovov a síranov z kyslých banských vôd, úpravy a spracovania nerastných surovín a ich odpadov a biologicko-chemickej prípravy nanosorbentov na báze sulfidov;
- ***štúdia biodiverzity autochtónnych acidofilných baktérií*** *Acicdithiobacillus ferrooxidans*, *Acidithiobacillus thiooxidans* a *Leptospirillum ferrooxians* v podmienkach opustených a v dôsledku útlmu zatápaných banských diel, ako aj starých banských záťaží po ťažbe sulfidických rúd na Slovensku, z ktorých sa postupne vytvárajú prírodné geobioreaktory, produkujúce pre životné prostredie vysoko rizikové kyslé banské drenážne vody s pH okolo 2 s vysokou mineralizáciou a obsahom ťažkých a toxických prvkov;
- ***štúdia biokorózie stavebných materiálov*** v spolupráci so Stavebnou fakultou TU Košice;
- ***štúdia biodegradácie organických polutantov***, predovšetkým ropných uhľovodíkov a polyaromatických uhľovodíkov (PAH) v pôdach a vodách. V spolupráci s firmou Environcentrum, s. r. o., bola vyvinutá metóda monitorovania kinetiky biodegradačných procesov ako v laboratóriu, tak aj v podmienkach *in situ* – v prostredí ekologickej havárie, alebo v podmienkach *ex-situ* – na dekontaminačnej stanici;
- ***štúdia vplyvu autochtónnej mikroflóry*** na priebeh exogénnych dejov v deponiách energetických odpadov – popolčekov a na premeny uhoľnej hmoty z pohľadu zmien jej sorpčných vlastností;
- ***štúdia biologicko-chemickej oxidácie hutníckych odpadov s obsahom Fe*** s cieľom prípravy Fe nanodisperzií priemyselne využiteľných ako sorbentov a pigmentov;
- ***pedagogickej činnosti*** v oblasti 2. a 3. stupňa vysokoškolského štúdia na Fakulte BERG, Hutníckej fakulte a Stavebnej fakulte TU v Košiciach a VŠB v Ostrave (ČR).

Oddelenie je súčasťou (partnerom) Centra excelentnosti pre integrovaný výskum geosféry Zeme, ITMS kód 26220120064. V rámci Centra sa podieľa na riešení aktivity 3.3 štúdium biogeochemických procesov a environmentálnych aspektov ochrany baníckej krajiny. Buduje sa laboratórium geomikrobiológie s plánovaným prístrojovým vybavením: HPLC-MS, GC-MS, ICP-MS, TOC/TN, IC, fluorescenčný mikroskop, analyzátory Hg, analyzátory veľkosti častíc a povrchu, laboratórium molekulovej biológie s RT-PCR, bioanalyzátorom pre gélovú elektroforézu na čipoch a ďalšie.

Špecifické vybavenie oddelenia

- bioreaktor pre aeróbnu a anaeróbnu kultiváciu baktérií s analýzou plynov (O_2, CO_2)
- becton-Dickinson, Cockeysville, USA – mikrobiologický identifikačný systém pre druhovú identifikáciu bakteriálnych kultúr izolovaných z environmentálnych matríc
- PCR termocyklér, Techne, pre polymerázovú reťazovú reakciu (PCR)
- optický mikroskop Nikon Eclipse 400 pre pozorovanie, morfologickú identifikáciu a fotodokumentáciu skúmaných mikroorganizmov
- vysokoteplotná laboratórna pec VP 02/16 pre teplotné spracovanie materiálu do teploty 1 600 °C
- fluidný – tryskový mlyn 100AGF s triedičom 50 ATP, Alpine, pre prípravu ultrajemných disperzií
- laboratórne sušiarne, sterilizačné autoklávy a biologické termostaty
- spektrofotometer Spektromom 195
- membránový filtrátor Fritsch
- vákuová rotačná odparovačka
- odstredivka Hettich Zentrifugen Universal 320
- veľkokapacitná trepačka
- 50 l temperovaný reaktor pre biologicko-chemické lúhovanie suspenzií
- automatický titrátor TitraLab 850 v spojení s PC-programom TitraMaster 85 pre štúdium neutralizačných

kriviek AMD, precipitačných reakcií, zmien pH a Eh v priebehu experimentov

- interná zbierka acidofilných mikroorganizmov izolovaných z kyslých banských vôd
- interná zbierka baktérií druhov *Bacillus*
- interná zbierka sulfát-redukujúcich baktérií

Vedúci oddelenia:
MVDr. Daniel Kupka, PhD.
E-mail: dankup@saske.sk
Tel.: +421 55 7922624

Oddelenie fyzikálnych a fyzikálno-chemických metód úpravy nerastných surovín

Oddelenie vyvíja nové princípy fyzikálnych metód úpravy nerastných surovín na báze magnetických, magnetogravitačných, gravitačných, elektrických a termických postupov. Skúma základné fyzikálne, fyzikálno-chemické a chemické vlastnosti rúd, nerudných materiálov a kovonosných odpadov metalurgického priemyslu.

Technické vybavenie oddelenia

- čeľusťové a valcové drviče
- nízkointenzitný magnetický rozdružovač LAURILA
- valcové (keramické, kovové, resp. guľové a tyčové) mlyny, vibračný mlyn VM-1
- vysokointenzitné magnetické rozdružovače: JONES, VMR-1, MSB-300, MECHANOBR, WEDAG
- trepačky TE III a laboratórne sitá s okatosťou v rozsahu 5 μm – 60 mm
- izodynamický magnetický rozdružovač FRANTZ-COOK
- poloprevádzková hydrocyklónová stanica
- magnetohydrostatický rozdružovač FGS-1
- elektrostatický rozdružovač STURTEVANT, typ O. H.
- špeciálne upravené mikrovlnné pece
- prístroj na meranie magnetickej susceptibility – Kappabridge KLY-2

Vedúci oddelenia:
Ing. Slavomír Hredzák, PhD.
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Oddelenie deštrukčnej a konštrukčnej geotechniky

Oddelenie rieši problémy monitorovania, optimalizácie a rozpojiteľnosti hornín pri rotačnom vŕtaní, rezaní a plnoprofilovom razení v kontexte s fyzikálno-mechanickými a pevnostnými charakteristikami hornín, stabilitnými problémami a nákladovosťou rozpojovacích procesov.

Technické vybavenie oddelenia

- experimentálny stand pre rotačné vŕtanie s nástrojmi priemeru do 70 mm
- lis do 2000 kN
- SOMET zariadenie pre meranie opotrebovania diskov a valivých dlát
- lis do 50 kN
- automatizované systémy monitorovania pre laboratórne experimentálne práce a pre podmienky *in situ*

Vedúci oddelenia:
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Oddelenie životného prostredia a hygieny v baníctve

V oblasti základného výskumu sa oddelenie zaoberá štúdiom banského aerosólu. Poznáva vlastnosti tuhej minerálnej fázy a na základe kvalitatívnej a kvantitatívnej mineralogickej analýzy hodnotí riziko vplyvu banského aerosólu z aspektu fibrogenity. Navrhuje vhodné spôsoby technickej prevencie pri banských prácach. Sleduje imisnú záťaž prírodného prostredia, odhaľuje a hodnotí hlavných znečisťovateľov antropogénneho pôvodu pomocou sedimentačnej a aspiračnej metódy.

Technické vybavenie oddelenia

- dozimeter (Dräger AG Lubeck Germany)
- TET MM6 2000
- prístroj TESTO 452
- analyzátor TMA (Trace Mercury Analyzer)
- odberová aparatúra s čerpadlom a rotametrom
- prachometer s príslušenstvom
- odberové aparatúry a spektrofotometre Spekol s výbavou

Vedúci oddelenia:
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Tel.: +421 55 7922609

Oddelenie mechanochémie

Činnosť oddelenia je zameraná na mechanochemickú modifikáciu štruktúry a vlastností tuhých látok (jednoduchých oxidov, nerozpustných solí, zložitých oxidov spinelového typu, zliatin na báze Fe), poznávanie zákonitostí mechanochemickej syntézy a na definíciu odlišností medzi mechanicky predaktivovanými a mechanicky syntetizovanými tuhými látkami. Zaoberá sa štúdiom fyzikálno-chemických princípov odsírovania na báze odsírovacích aditív s využitím vlastných surovín Slovenska a princípov zušľachťovania uhlia s cieľom jeho komplexnejšieho využívania. Venuje sa aj extrakcii úžitkových kovov z rúd, koncentrátov a odpadov rôznej proveniencie. Vyvíjajú sa tu nové postupy zhodnocovania nerastných surovín s využitím princípov mechanochemického lúhovania, mechanoredukcie a mechanosyntézy.

Technické vybavenie oddelenia

- vibračné sitovacie zariadenie Analysette 3
- vibračný mlyn
- laserový granulometer HELOS s mokrou a suchou dispergačnou jednotkou (0,9 – 170 μm)
- laserový granulometer Nanophox – Sympatec – (10 nm až 10 μm)
- dezintegrátor UDA
- zariadenie COULTER COUNTER TA II
- planetárny mlyn Pulverisette 4 FRITSCH s výbavou
- zariadenie GEMINI 2360 na meranie povrchu (BET) a objemu pórov
- planetárny mlyn AGO-2 a AGO-5
- RTG difraktometer D8 Advance BRUKER – AXS
- HPLC – chromatograf
- derivatograf C/PC MOM
- Attritor LME 0,75 (Netzsch, Nemecko)
- Attritor LME 4 (Netzsch, Nemecko)
- sklenený autokláv

Vedúci oddelenia:
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Tel.: +421 55 7922603

Servisné oddelenia Ústavu geotechniky SAV

Centrálne laboratórium

Centrálne laboratórium analytickej chémie a fyzikálnych metód analýzy je zamerané na chemickú analýzu vzoriek dodaných grantovými kolektívmi, riešiteľmi vedecko-technických projektov a obchodných zmlúv metódami klasickej chemickej analýzy a atómovou absorpčnou spektroskopiou (AAS). Podieľa sa na riešení odborných úloh a publikačnej činnosti, spojených s využitím metód analytickej chémie

Technické vybavenie oddelenia

- prístroj VARIAN AA240FS s príslušenstvom: Zeeman AAS240Z s programovateľným dávkovačom vzorky PSD120 (Programmable Sample Dispenser), grafitová pec GTA120 (Graphite Tube Atomizer) a zariadenie pre vyvíjanie pár VGA-77 (Vapor Generation Accessory)

Vedúca oddelenia:
RNDr. Dana Gešperová
E-mail: gesper@saske.sk
Tel.: +421 55 7922617

Dielňa

Pracovníci dielne vykonávajú odborné práce na kovoobrábacích strojoch (sústruh, brúska), podieľajú sa na vývoji a konštrukcii technických zariadení i prístrojov a na ich obnove. Podľa potrieb vykonávajú bežnú údržbu laboratórnych a iných zariadení v Ústave. Podľa výkresovej dokumentácie, popisu postupu prác a na základe konzultácie s riešiteľmi projektov realizujú individuálnu remeselnú kusovú výrobu a úpravy zariadení pre výskum podľa požiadaviek riešiteľov.

Technické vybavenie oddelenia

- sústruhy – SU I 50, SU 32, MN 80
- frézy – FA 2U, HM 45
- stojanové vŕtačky – stĺpová veľká – φ 50 mm, stĺpová malá – φ 13 mm
- brúsky – univerzálna nástrojová N1, stojanová TM 26R
- mechanické pákové nožnice
- ohýbačka plechu
- zakružovačka
- elektrická zváračka RTB-3
- súprava na zváranie plynom
- strojová píla – dĺžka pílového listu 300 mm
- ručné náradie

Vedúci oddelenia:
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Tel.: +421 55 7922630

Organizačno-technický útvar

Útvar zabezpečuje pre všetky výskumno-riešiteľské kolektívy a vedenie Ústavu ekonomickú a legislatívnu agendu, korešpondenciu, materiálne zabezpečenie výskumu a prevádzky Ústavu. Podlieha štatutárnemu zástupcovi riaditeľa.

Sekretariát:
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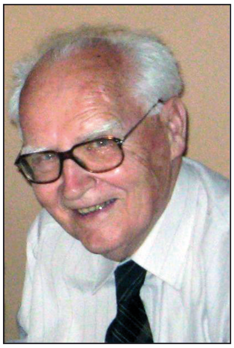
LAUDATIO

Nestor slovenského úpravníctva – The doyenne of the Slovak mineral processing

Pán Dr. h. c. prof. dr. Ing. František Špaldon, DrSc., 90 ročný

člen – korešpondent SAV

Corresponding Member of the Slovak Academy of Sciences celebrates 90th jubilee



Narodil sa 20. 7. 1920 v Čadci. Postupne absolvoval štúdiá na Gymnáziu v Žiline a následne v rokoch 1937 až 1942 na ČVUT v Prahe, neskôr na Univerzite v Záhrebe a na Univerzite v Ľubľane. Vysokoškolské štúdiá ukončil s výborným prospechom na Montanuniversität v Leobene, Rakúsku, kde v roku 1943 úspešne obhájil aj doktorskú dizertačnú prácu v oblasti úpravníckych technológií. V rokoch 1943 – 1952 pracoval v Handlovských uhoľných baniach, najskôr ako prevádzkový inžinier, vedúci závodu a neskôr ako hlavný inžinier bane v Novákoch, kde získal množstvo praktických skúseností a poznatkov, a v roku 1951 sa stal externým docentom novovznikajúcej Baníckej fakulty SVŠT v Bratislave. Tam začal so systematickým budovaním Katedry úpravníctva a ako jeden zo zakladateľov BF VŠT s ňou prešiel v roku 1952, už ako riadny zamestnanec, do Košíc. V roku 1955 bol menovaný zastupujúcim profesorom a následne v roku 1957 riadnym (najmladším) profesorom. V roku 1968, po obhajobe doktorskej dizertačnej práce, mu bol udelený vedecký titul doktora vied SAV. Významnú činnosť a veľký prínos pána profesora pre slovenskú vedu v obore úpravníctva ocenila SAV v roku 1983 udelením titulu člena – korešpondenta SAV.

Za jeden z jeho najväčších prínosov od roku 1951 možno označiť vybudovanie Katedry úpravníctva na Baníckej fakulte VŠT v Košiciach a s tým súvisiace založenie i systematické rozvíjanie študijných oborov: úprava úžitkových nerastov a neskôr, v roku 1974, aj medziodborového štúdia ochrana životného prostredia v ťažkom priemysle. Pre uvedené študijné obory spracoval aj základné učebné texty v podobe odborných kníh a skrípt, spočiatku samostatne, potom aj s odborníkmi, ktorých sám vychoval.

Treba uviesť, že táto katedra bola po dlhé roky považovaná za špičkovú v európskom meradle a podieľala sa aj na vysokom kredite absolventov Baníckej fakulty VŠT v Košiciach. Počas svojej 32-ročnej práce na Baníckej fakulte VŠT v Košiciach pôsobil aj vo významných akademických funkciách, a to: prodekan pre pedagogiku (1953 až 1957), prorektor VŠT (1958 – 1960), dekan (1960 – 1962, 1966 až 1969), rektor VŠT (1969 – 1972).

Vedecké aktivity počas pôsobenia na Baníckej fakulte VŠT možno zhrnúť do štyroch oblastí, a to: vypracovanie matematických a grafických metód hodnotenia účinnosti rozdružovania, spracovanie minerálnych suspenzií z úpravní, rozdružovanie magnezitových surovín so zameraním na odstraňovanie železa a úprava priemyselných odpadov.

Od roku 1984 pracoval na Baníckom ústave SAV, kde svoju vedeckú činnosť zameral a napokon aj úspešne zavŕšil kreovaním a schválením nového výskumného smeru v oblasti úpravníctva – biologicko-chemické metódy úpravy surovín – a vytvoril priestor pre rozvoj nových progresívnych metód v oblasti úpravníctva.

Pán profesor Špaldon počas svojej praxe vypracoval a publikoval sám, prípadne so spoluautormi, viac ako 150 odborných článkov, vedeckovýskumných štúdií a bol spoluautorom rady patentov. Nemožno nespomenúť – jeho rozsiahlu činnosť ako oponenta rady odborných štúdií pre rôzne komisie vlády, nehovoriac o nespočetnom množstve posudkov diplomových, kandidátskych habilitačných, inauguračných, doktorandských a iných odborných prác, ktoré boli základom pre ďalší vedecký rast mnohých odborníkov v danej oblasti.

Je takmer nemožné presne vyčísliť počet študentov, diplomantov, ašpirantov, neskorších docentov, profesorov a doktorov vied, na výchove ktorých sa pán profesor podieľal a v živote ktorých zanechal hlbokú stopu vysokého odborného kreditu. Pán prof. Špaldon bol vždy aktívny, precízny, prísny pri výchove študentov, ale ako oponent, a to až doposiaľ, je mimoriadne láskavý. Preňho bol vždy na prvom mieste odborný rast a permanentný záujem o svetový pokrok v obore úpravníctva. Tomu napomáhal do veľkej miery aj jeho vysoký odborný kredit, akceptovaný nielen svetovou úpravníckou verejnosťou, ale aj prestížnymi odbornými pracoviskami, o čom svedčia aj početné pozvania na pracovné a prednáškové pobyty (USA, Belgicko, Brazília, Bulharsko, Francúzsko, bývalá Juhoslávia, Kanada, Maďarsko, Nemecko, Švédsko, Taliansko, Veľká Británia) a napokon aj členstvá v medzinárodných úpravníckych komitétoch, ktoré po dlhé roky – od roku 1970 do roku 1988 – vykonával. Túto svoju medzinárodnú činnosť operatívne využíval aj na transfer najnovších poznatkov do svojej pedagogickej činnosti, a preto ho právom možno označiť za nestora slovenského úpravníctva. V zmysle Komenského definície učiteľa ako človeka, ktorý povzbudzuje ducha slobodného premýšľania a rozvíja aj cit k osobnej zodpovednosti, ho my všetci, jeho študenti a spolupracovníci, ktorých život obohatil, považujeme za nášho veľkého učiteľa.

S úctou a prianím dobrého zdravia a ďalších príjemných rokov života

Slovenská úpravnícka obec, Vaši žiaci, spolupracovníci a priatelia

Mária Kušnierová

Vybrané aktivity jubilanta – Selected activities

Členstvá – Memberships

– člen – korešpondent SAV, ČSAV,
– Vedecké kolégium vied o Zemi a vesmíre,
– Rada štátneho programu základného výskumu II.,
– Medzinárodný vedecký komitét pre prípravu medzinárodných kongresov o úprave rúd,
– predsedníctvo komisií pre obhajoby kandidátskych dizertačných prác v odbore úpravníctvo,
– komisia pre obhajoby doktorských dizertačných prác v odbore baníctvo,
– Vedecká rada Baníckeho ústavu SAV v Košiciach – predseda,
– Slovenská banícka spoločnosť ZSVTS,
– Zväz banských inžinierov Juhoslávie.

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Ing. Štefan Jakabský, PhD., šesťdesiatpäťročný

Greetings to 65th jubilee

Narodil sa 19. augusta 1945 v obci Nový Salaš, okres Košice-okolie. Vyrastal v Michaľanoch. Po ukončení Strednej priemyselnej školy stavebnej v Košiciach v roku 1964 pokračoval v štúdiu na Baníckej fakulte Vysokej školy technickej v Košiciach v odbore úpravníctvo. Štúdium úspešne ukončil v roku 1968 ako banský inžinier.

Ako vynikajúceho študenta si ho na prácu v Ústave vlastností hornín SAV (neskôr premenovaný na Banícky ústav SAV, v súčasnosti Ústav geotechniky SAV) vytypoval bývalý riaditeľ ústavu, Ing. Vincent Mihalík, CSc.

Svoju odbornú kariéru v Ústave začal študijným pobytom vo funkcii asistenta v roku 1968. Od roku 1970 pôsobil ako odborný asistent, neskôr ako interný ašpirant (1973 – 1976) a samostatný odborný pracovník (1976 až 1978). Na jeho vedeckom raste sa podieľali dvaja školitelia, Ing. Vincent Mihalík, CSc. a Ing. Stanislav Zaťko, CSc. Kandidátsku dizertačnú prácu obhájil v 1978 na Hornickom ústave ČSAV v Prahe. Následne mu bol v roku 1979 Baníckou fakultou VŠT v Košiciach udelený titul kandidát technických vied (CSc.). Potom do roku 1983 pracoval v postavení vedeckého pracovníka. V tom istom roku mu bol Slovenskou akadémiou vied priznaný kvalifikačný stupeň IIa – samostatný vedecký pracovník – a v roku 1987 sa stal vedúcim oddelenia úpravy úžitkových nerastov (v súčasnosti oddelenie fyzikálnych a fyzikálnochemických metód úpravy nerastných surovín).

Od jeho príchodu do Ústavu je jeho vedecká a odborná práca zameraná na teoretické aspekty a aplikáciu fyzikálnych a fyzikálnochemických metód na úpravu úžitkových nerastov. Riešil problematiku magnetického rozdružovania, elektroseparácie, gravitačnej úpravy a skusovania – aglomerácie a peletizácie jemnozrnných koncentrátov.

Už vo svojej dizertačnej práci objasnil niektoré problémy polygradientného magnetického rozdružovania, ktoré boli neskôr využité pri návrhu nového rozdružovača. Podieľal sa na vývoji magnetického rozdružovača VMR-1, skúmal vplyv sprievodných hornín rudnianskeho ložiska na magnetické rozdružovanie sideritových rúd, realizoval výskum magnetického rozdružovania rôznych druhov práškového železa, venoval sa výskumu uplatnenia supravodivých magnetov v procese úpravy nerastných surovín.

V roku 1981 ako prvý v Československu pripravil feromagnetickú kvapalinu, naprojektoval magnetohydrostatický rozdružovač a položil tak základy nového smeru v úpravníctve – rozdružovanie v magneticky polarizovateľných kvapalinách.

Neskôr, v rámci spolupráce s výrobnou sférou, ako zodpovedný riešiteľ úloh aplikovaného výskumu úspešne postupoval na objasnení prechodu antimónu do prchavej fázy pri pražení tetraedritových koncentrátov, podieľal sa na výskume a poloprevádzkovom testovaní lúhovania tetraedritových koncentrátov v alkalickom prostredí. Ďalšie jeho výskumné aktivity boli zamerané na optimalizáciu procesu mletia keramických surovín, kvalitu praženia nižnoslanskej rudy, optimalizáciu magnetického rozdružovania praženca a úletov z rotačných pecí v Nižnej Slanej, odstraňovanie popola a síry zo slovenských hnedých uhlí v hydrocyklóne a deferitizáciu karbonátových a silikátových surovín.

Aktuálne sa venuje aplikácii mikrovlnnej energie na spracovanie primárnych surovín, minerálnych medziproduktov a odpadov, ako aj aplikácii nanočastíc oxidov železa v environmentálnych technológiách.

Výsledky svojich vedecko-výskumných aktivít publikoval s kolegami v dvoch monografiách a v troch kapitolách monografií. Je autorom a spoluautorom 65 článkov vo vedeckých a odborných časopisoch, 220 príspevkov v zborníkoch vedeckých konferencií doma i v zahraničí a taktiež vyše 80 výskumných správ a expertíz pre potreby praxe. Na jeho práce bolo zaznamenaných 101 ohlasov.

Jubilant bol zodpovedným riešiteľom 10 domácich vedeckých projektov a 4 medzinárodných projektov. Pod jeho vedením úspešne ukončilo štúdium 8 doktorandov.

Popri svojej práci spolupracoval, resp. spolupracuje s kolegami v akadémii, tu možno uviesť Ústav experimentálnej fyziky SAV, Košice, Ústav materiálového výskumu SAV a Elektrotechnický ústav SAV, Bratislava. Významná bola a je jeho spolupráca s Technickou univerzitou v Košiciach – Fakulta BERG, Hutnícka fakulta a Letecká fakulta – a taktiež s Katedrou jadrovej chémie Prírodovedeckej fakulty UK, Bratislava.

V rámci domácej spolupráce, orientovanej prakticky, treba na prvom mieste uviesť bývalé Železorudné bane, neskôr ŽELBA, a. s., Spišská Nová Ves a osobitne závod Rudňany, s ktorým bola výskumnícka činnosť jubilanta veľmi úzko spätá. Potom možno menovať Siderit, s. r. o., Nižná Slaná, SABAR, s. r. o., Markušovce, Slovenské magnezitové závody, a. s., Jelšava, SLOVMAG, a. s., Lubeník, Hornonitrianske bane Prievidza, a. s., bývalé VSŽ, a. s., Košice, ÚVR, s. r. o., Košice, PETRA-ARTEP, s. r. o., Košice a KERKO, a. s., Košice.

Zo zahraničných partnerov treba spomenúť Institut environmentálního inženýrství, Hornicko-geologická fakulta, VŠB-TU, Ostrava, Ústav chemických procesů AV ČR, Praha, Katedru chémie, Aristotelova Univerzita, Thessaloniki, Grécko, Katedru environmentálneho inžinierstva a vedy, Univerzita Clemson, Južná Karolína, Katedru chémie a biochémie, Štátna univerzita Nové Mexiko, Las Cruces, Úpravnícky ústav Akadémie vied /FIA/, Freiberg, Nemecko, Fakultu baníctva a geológie, Univerzita v Belehrade, Srbsko, Ústav aplikovanej fyziky, Národná akadémia vied Bieloruska, Minsk, Spojený ústav geológie, geofyziky a mineralógie, Sibírske oddelenie Ruskej akadémie vied, Novosibirsk, Výskumný ústav komplexného využitia nerastných surovín (IPKON RAN), Moskva, Ústav mechaniky horninového masívu, Poľská akadémia vied, Krakov, Fakultu chemického inžinierstva Birminghamskej univerzity, Ústav stavebných vied Eduarda Torroju, Madrid, Gipromaš-ugleobogaščenie, Lugansk, Ukrajina, Divízia úpravy nerastných surovín – De Beers, Johannesburg, JAR.

Jubilant je dobre známy vo vedeckých kruhoch a v baníckej obci ako skúsený výskumník a organizátor rozličných vedeckých aktivít a podujatí.

V mene kolegov vyslovujeme jubilantovi úprimnú vďaku za jeho obrovský prínos v prospech slovenského baníctva, úpravníctva a slovenskej vedy.

Do ďalšieho života prajeme jubilantovi veľa tvorivých síl, pevné zdravie a pohodu v rodinnom kruhu i na pracovisku.

Slavomír Hredzák

Funkcie a členstvá – Appointments and memberships

– vedúci oddelenia fyzikálnych a fyzikálno-chemických spôsobov úpravy (1987 – 2010),

– spoločná odborová komisia pre obhajoby doktorandských dizertačných prác v odbore hutníctvo kovov,

– komisia pre obhajoby kandidátskych dizertačných prác v odbore úpravníctvo,

– Ústavná rada Baníckeho ústavu SAV (neskôr Ústavu geotechniky SAV) v Košiciach,

– Vedecká rada Baníckeho ústavu SAV (neskôr Ústavu geotechniky SAV) v Košiciach,

– redakčná rada časopisu Magnetic and Electrical Separation (1999 – 2003),

– komisia č. 6 Vedeckej grantovej agentúry Ministerstva školstva SR a SAV (VEGA) pre stavebníctvo, architektúru, baníctvo a geotechniku (2002 – 2008),

– Slovenská banícka spoločnosť ZSVTS.

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Vereš, J., Orolínová, Z., Mockovčiaková, A., Jakabský, Š. & Bakalar, T., 2010: Removal of nickel by natural and magnetically modified bentonite. *In: Václavíková, M., Vitale, K., Gallios, G. P. & Ivaničová, L. (eds.): Water Treatment Technologies for the Removal of High--Toxity Pollutants, Book Series: NATO Science for Peace and Security Series C: Environmental Security, Springer Netherlands, ISSN 1874-6519, ISBN 978-90-481-3495-3 (Print) 978-90-481--3497-7 (Online), 289 – 294.*

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Zlepšovacie návrhy a patenty – Proposals for innovation and patents

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Hosť. prof. Ing. Víťazoslav Krúpa, DrSc., šesťdesiatročný

Greetings to 60th jubilee

Narodil sa 28. októbra 1950 v Martine. Rané detstvo trávil na Martinských holiach, ako školák vyrastal už v Košiciach. Po maturite na Strednej všeobecnovzdelávacej škole pokračoval v štúdiu na Elektrotechnickej fakulte Vysokej školy technickej v Košiciach v odbore silnoprúd, v špecializácii elektrické teplo a elektrochémia. Štúdium úspešne ukončil ako elektrotechnický inžinier v roku 1974.

V tom istom roku sa zamestnal vo Výskumnom ústave elektrických strojov točivých v Košiciach na pozíciu technického asistenta. Už o rok bol prostredníctvom konkurzu vybratý na študijný pobyt do Ústavu vlastností hornín SAV (neskôr premenovaný na Banícky ústav SAV, v súčasnosti Ústav geotechniky SAV), kde pôsobí dodnes. Po ukončení študijného pobytu bol v roku 1978 prijatý na internú vedeckú ašpirantúru vo vednom odbore dobývanie ložísk, úsek geotechniky. Pod vedením svojho školiteľa, prof. Ing. Félixa Sekulu, DrSc., ukončil ašpirantúru obhajobou kandidátskej dizertačnej práce na tému *Matematické modelovanie diamantového vŕtania na základe standového výskumu*, čím mu bol udelený titul kandidát technických vied (CSc.) a zaradil sa medzi vedeckých pracovníkov Ústavu.

Neustály hlad po vedomostiach vyústil do postgraduálneho 4-semestrálneho štúdia na Katedre technickej kybernetiky Elektrotechnickej fakulty VŠT, Košice v odbore mikropočítače a aplikácie počítačových systémov. Získané vedomosti neskôr úspešne využíval pri štúdiu a opise procesu rozpojovania hornín. V roku 1987 mu bol Slovenskou akadémiou vied priznaný kvalifikačný stupeň IIa – samostatný vedecký pracovník – a v roku 1997 stupeň I. – vedúci vedecký pracovník. V roku 1998 bol úspešný v konkurze na miesto riaditeľa Ústavu geotechniky SAV a v tejto funkcii, aj po ďalších troch konkurzoch, pôsobí naďalej. V roku 2000 mu bol SAV priznaný kvalifikačný stupeň špičkový odborník a v roku 2002 mu bola priznaná vedecká hodnosť doktor technických vied (DrSc.).

Od nástupu do SAV bola predmetom jeho odbornej, vedeckej a výskumno-realizačnej činnosti problematika rozpojovania hornín, konkrétne matematické modelovanie procesu rozpojovania hornín diamantovými vŕtacími korunkami, optimalizácia procesu rotačného vŕtania, vývoj monitorovacích a optimalizačných sústav pre vŕtacie súpravy, vývoj monitorovacích a optimalizačných sústav pre plnoprofilové raziace stroje (WORS), matematické modelovanie interakcie diskovej hlavy raziacich strojov s horninovým masívom, mechanika strojného razenia (IKONA). V poslednom období sa podieľa na prácach spojených s aplikáciou metódy fuzzy pri modelovaní výkonu plnoprofilových raziacich strojov, ako aj hodnotením efektívnosti plnoprofilového razenia.

Jubilant bol zodpovedným riešiteľom 12 výskumných úloh a projektov. Výsledky výskumu neustále publikuje. Je autorom a spoluautorom 3 monografií, 1 vysokoškolskej učebnice, 56 článkov vo vedeckých časopisoch (z toho 20 v zahraničných) a 108 príspevkov v zborníkoch domácich i zahraničných odborných podujatí. Na jeho práce bolo zaznamenaných 345 ohlasov. Taktiež je spoluautorom 63 výskumných správ, má potvrdených 22 realizačných výstupov pre prax. Recenzoval 4 monografie a učebnice, 47 článkov pre vedecké a odborné časopisy, 36 článkov v zborníkoch, 36 projektov a správ, ako aj 27 kvalifikačných prác.

Jubilant je činný aj pedagogicky, je hosťujúcim profesorom na Technickej univerzite v Košiciach, členom komisií pre štátne záverečné skúšky, spoločných odborových komisií pre doktorandské štúdium, školiteľom doktorandského štúdia a konzultantom diplomových prác. Pod jeho vedením získali titul CSc./PhD. štyria ašpiranti/doktorandi.

V rámci spolupráce jubilanta s akademickou obcou je potrebné spomenúť nasledovné inštitúcie: Fakulta BERG, Stavebná fakulta a Letecká fakulta TU v Košiciach, Hornicko--geologická, Strojní a Stavební fakulta VŠB-TU, Ostrava, Ústav geoniky AV, ČR, Sergo Ordzhonikidze, Moscow, Geological Prospecting Institute of Moscow, State University (MGRI), A. A. Skotchinsky Institute of Mining Engineering (IGD) RAS a Istanbul Technical University – Mining Engineering Dept.

Z podnikateľských subjektov treba uviesť Banské stavby, a. s., Prievidza (teraz SKANSKA), Hydrotunel, s. r. o., Bojnice, Váhostav – tunely a špeciálne zakladania, a. s., Žilina, ZŤS – Výskum a vývoj, a. s., Dubnica nad Váhom, Doprastav, a. s., Bratislava, Inžinierske stavby, a. s., Košice, INGEO – ighp, s. r. o., Žilina, GEOFOS, s. r. o., Žilina, Geoexperts, s. r. o., Žilina, Cadeco, s. r. o., Žilina, Nafta Gas, a. s., Malacky, UNIGEO, a. s., Ostrava, Best Drilling Chemicals BDC – Morava, s. r. o., Břeclav.

Hosť. prof. Ing. Víťazoslav Krúpa, DrSc. je dobre známy vo vedeckej, ako aj v baníckej komunite. Je skúseným riadiacim pracovníkom a organizátorom výskumu.

V mene kolegov vedcov, baníkov a geotechnikov mu želáme veľa zdravia, nových tvorivých nápadov i osobných úspechov!

Slavomír Hredzák

Funkcie a členstvá – Appointments and memberships

– riaditeľ Ústavu geotechniky SAV v Košiciach,
– predseda rady riaditeľov košických pracovísk SAV,
– Vedecká rada Fakulty BERG TU v Košiciach,
– Vedecká rada Stavebnej fakulty TU v Košiciach – čestný člen,
– Vedecké kolégium SAV pre elektroniku, materiálový výskum a technológie,
– zahraničný člen Ruskej Akadémie montánnych vied – akademik,
– odborová komisia pre odbor 21-04-9 Dobývanie ložísk nerastov a geotechnika,
– odborová komisia pre odbor 5.2.32 Ťažba nerastov a inžinierske geotechnológie,
– odborová komisia pre odbor 5.2.36 Banská mechanizácia, doprava a hlbinné vŕtanie,
– odborová komisia pre odbor 5.2.38 Získavanie a spracovanie zemských zdrojov,
– garant predmetu Geotechnické inžinierstvo v študijnom programe 3. stupňa Teória a navrhovanie inžinierskych stavieb, Stavebná fakulta TU Košice,
– národná skupina International Society for Rock Mechanics (ISRM),
– Slovenský tunelársky komitét (ITA/AITES),
– viceprezident Slovenskej baníckej spoločnosti ZSVTS,
– Dozorná rada Slovenskej banskej komory,
– vicecechmajster Košického baníckeho spolku,
– redakčná rada medzinárodného vedeckého časopisu Acta Montanistica Slovaca,
– redakčná rada časopisu Stavebnej fakulty TU v Košiciach Pozemné komunikácie a dráhy

Ocenenia – Awards

– vzorný pracovník SAV (1982),

– Čestná plaketa rektora Vojenskej leteckej akadémie gen. M. R. Štefánika v Košiciach za zásluhy o rozvoj a výstavbu akadémie (2000),

– pamätná medaila pri príležitosti 10. výročia založenia Fakulty výrobných technológií TU v Košiciach so sídlom v Prešove (2002),

– vyznamenanie Za zásluhy o Slovenskú banícku spoločnosť (2005),

– strieborná medaila Zväzu slovenských vedecko-technických spoločností (2005).

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Krúpa, V. & Lazarová, E., 2002: Energetické aspekty opotrebovania rozpojovacích nástrojov. *Acta Montan. Slov., 7, 1, 5 – 11.*

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Prof. Ing. Peter Fečko, CSc., päťdesiatročný

Greetings to 50th jubilee

Narodil sa 21. 6. 1960 v Stropkove. Gymnaziálne štúdiá absolvoval v Prešove. Po ich ukončení v roku 1979 začal študovať na Baníckej fakulte Vysokej školy technickej v Košiciach. Štúdium úspešne ukončil s ocenením dekana v roku 1983 v obore úprava nerastných surovín so špecializáciou na ochranu životného prostredia. V roku 1984 nastúpil na miesto asistenta na Katedru úpravnictví Hornicko-geologickej fakulty Vysoké školy báňské v Ostrave. Pre skvalitnenie svojej pedagogickej práce sa rozhodol absolvovať externé štúdium vysokoškolskej pedagogiky na Filozofickej fakulte Univerzity Palackého v Olomouci, ktoré úspešne ukončil v roku 1989. V rokoch 1995 – 1996 absolvoval Evropské inženýrske studium životního prostředí na Technickej univerzite v Drážďanoch a v roku 1999 absolvoval Integrierte Mangement fur Fach- und Fuhrungskaräfte aus der Tchechischen Republik. V roku 1991 úspešnou obhajobou kandidátskej dizertačnej práce na Baníckej Fakulte VŠT v Košiciach získal titul kandidáta technických vied (CSc.). Už v tomto čase sa v rámci svojej výskumnej práce intenzívne zaoberal progresívnymi biologicko-chemickými metódami úpravy a v danej oblasti vypracoval aj habilitačnú prácu, na základe ktorej mu bola v roku 1995 udelená akademická hodnosť docent (doc.). V roku 2002 bol na základe inauguračnej prednášky, zameranej na kreovanie nového študijného smeru biotechnológií v úprave surovín, menovaný prezidentom Českej republiky za vysokoškolského profesora (prof.). Aj keď pedagogická a vedecká práca vypĺňa celý mimoriadne aktívny život pána profesora Fečka, okrem nej zastával počas uplynulých rokov významné funkcie v transformačne sa meniacich podmienkach vysokého školstva. Na počiatku to bolo vo vedení Katedry úpravníctva, neskôr, dve funkčné obdobia pracoval ako prodekan fakulty a v súčasnosti pôsobí ako vedúci oddělení odpadového hospodářství a biotechnológií v Inštitúte environmentálního inženýrství HGF VŠB-TU, Ostrava, ktoré založil. Profesor Fečko je neúnavným propagátorom najnovších poznatkov formou nespočetného množstva aktívnych účastí na svetových kongresoch, vrátane usporadúvania vlastných medzinárodných konferencií: Mineral Processing and Environment a Recyklácia odpadov, ktoré v tomto roku zaznamenali svoj XIV. ročník a na ktorých sa zúčastňujú mnohí významní vedci a odborníci z celého sveta. Ku skvalitneniu výučby v novozavádzaných progresívnych smeroch prispel pán profesor vydaním 16 monografií a vysokoškolských textov. Participujúc na vydaní ďalších skrípt a monografií, vytvoril podmienky na ich sprístupnenie študentom.

Veľmi významná je jubilantova publikačná činnosť, na ktorej sa podieľal nielen samostatne, ale vo veľkej miere aj so širokým okruhom spolupracovníkov a ktorá doposiaľ zahŕňa 18 odborných článkov, registrovaných v medzinárodných databázach ISI (CC, Scopus), a ďalších 426 odborných prác, publikovaných v rôznych odborných časopisoch a zborníkoch.

Hodnotenie pána profesora Fečka ako špičkového odborníka v obore úpravníctva potvrdzujú aj početné akceptácie zo strany medzinárodnej vedeckej komunity tým, že ho menovala do mnohých redakčných rád odborných vedeckých časopisov. Rovnako boli a stále sú oceňované aj pedagogické kvality pána prof. Fečka, a to v medzinárodnom meradle, formou pozvaní na prednáškové turné, ako napríklad na: University of Mining & Technology (Beijing), Universidad del Valle (Columbie), The Universidad Industrial de Santander (Columbie), The University of Petroşani (Rumunsko) a jeho periodického pôsobenia na Univezitách v Srbsku, Chorvátsku, Turecku a Poľsku.

Pán prof. Ing. Peter Fečko, CSc., je hybnou silou rozvoja a pokroku nielen na svojom pracovisku, ale je veľmi aktívny aj v medzinárodnej spolupráci, ktorú často iniciuje a systematicky buduje s prestížnymi pracoviskami na celom svete. Pre nás je potešiteľné, že na jednom z popredných miest je spolupráca s naším Ústavom geotechniky SAV v Košiciach, ktorá vyústila do mnohých spoločných projektov, monografií, publikácií a do usporadúvania periodických medzinárodných konferencií s názvom Recyklácia odpadov.

Pán profesor Fečko je aj napriek svojej pracovnej vyťaženosti mimoriadne veselý človek s veľkým srdcom, vždy pripravený pomôcť. Pri príležitosti jeho významného jubilea, 50-ych narodenín, mu prajeme pevné zdravie, veľa preňho charakteristického neskrotného optimizmu, tvorivých síl, pracovných a osobných úspechov v kruhu jeho študentov, kolegov a priateľov.

Mária Kušnierová

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– Vedecká rada Vysokej školy banskej – Technické univerzity v Ostrave,
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– Oborová rada doktorského studia studijního programu P2102 – nerostné suroviny, oboru 2102V009 – úpravníctví na Hornicko-geologické fakultě VŠB-TU, Ostrava,
– komisia pre štátne záverečné skúšky pre študijný odbor 3904R022 – zpracování a zneškodňování odpadů na Hornicko--geologickej fakulte VŠB-TU, Ostrava,
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– redakčná rada časopisu International Journal of Coal Preparation and Utilization, USA,
– redakčná rada časopisu Iranian Journal of Biotechnology, Iran,
– člen – korešpondent Medzinárodného organizačného výboru medzinárodných kongresov úpravy uhlia (Coal Preparation Congresses) za Českú republiku.

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