Химия в интересах устойчивого развития **15** (2007) 169–173

Influence of Activation Method of Sorbents on Their Properties

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Abstract

The contribution describes chemical, physical and mineralogical properties of so-called Albanian (ore origin) leaching residuum from dumping ground of former Sered' Nickel Works (West Slovakia). The main mineral component of this residuum represents synthetic magnetite, which is known by its ability to sorb some substances. The changes in grain size and specific surface were studied as a function of grinding time and mill. The activation in ball mill during 25 min resulted in a two-fold increase in specific surface. Contrary to this fact, grinding in attritor led to a three-fold increase in specific surface already after 15 min, *i.e.* from 1.31 to 3.86 m^2/cm^3.

For adsorption tests and following magnetic filtration the leaching residuum ground in the solution of $K_4Fe(CN)_6$ was applied. Obtained results point to the fact, that magnetic sorbent prepared in such a way and magnetic filtration enable substantial reduction of ion concentration of heavy metals such as copper, manganese and zinc.

INTRODUCTION

Much attention is paid today to the application of magnetic sorbents in the treatment of water, contaminated by heavy metal ions [1].

Generally, magnetic sorbents can be divided into three groups:

1. Magnetic sorbent, which can be used as an individual phase able to bond the contaminants on its surface.
2. Magnetic sorbents in the form of special polycomponent materials made from magnetic particles and chemical substances with increased sorption capacity, such as ferromagnetic particles covered by polymers, magnetite captured on the outer surface of polyamine-epichlorohydrine resin and magnetite in polyacrylonitrile matrix.
3. Magnetic sorbent in the form of Fe-hydroxide and Fe-oxides can be precipitated *in situ* in water contaminated by heavy metals with increased Fe content.

Thus, the whole process of water treatment with application of magnetic sorbents consists of three basic steps:

a) sorbent preparation,

b) sorption of contaminants onto magnetic sorbent, and

c) magnetic separation or filtration, *i.e.* the process in which magnetic sorbent together with sorbed contaminants are removed from water.

The submitted contribution describes the properties of magnetite-bearing so-called Albanian leaching residuum, which comes from hydrometallurgical processing of Ni-laterite ore in the former Sereп Nickel Works (West Slovakia). A total amount of this residuum is running about 6 million tons. The dump of residuum occupies the farmland on the area of 54 hectares (0.54 km^2) [2]. An ability of magnetite to sorb the heavy metals is known and for this reason a pretreatment or activation of the residuum was tested in grinding mills. The sorption tests were focused on manganese, copper, and zinc.

Macášek and Bartoš [3] successfully applied the Albanian leaching residuum, which was activated by potassium ferrocyanide, in the process of radiocesium removal from soil. The utilisation of 5 % solution of $K_4Fe(CN)_6 \cdot 3H_2O$ at activation was performed with the aim to create a thin layer of this compound on the surface of residuum grains. The layer of potassium ferrocyanide on the surface of magnetite enhances affinity to radionuclides at their sorption, mainly as to isotope ^{137}Cs sorption from water suspensions and polluted soils. Naturally, an enlargement of active surface results in the increasing efficiency of ^{137}Cs adsorption. Moreover, a magnetic core of such a sorbent enables the application of magnetic filtration to separate the treated water off pollutant bonded on magnetic particles.

Similarly, the parameters of sorption process at removal of Cs^+, Sr^{2+}, Pb^{2+}, Eu^{3+} and TcO_4^- by means of the Albanian leaching residuum have been described by Hredzák *et al.* [4] and by Macášek *et al.* [5].

EXPERIMENTAL

Methods

Chemical analyses were performed using atomic absorption spectrometer SpectrAA-30 Varian. Iron was determined by titration.

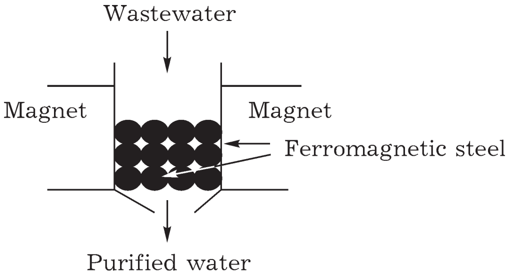

Fig. 1. Scheme of the magnetic separator used for wastewater purification.

Mineral composition of residuum was studied by XRD using a device DRON-2.0, goniometer GUR-5 (Techsnabexport, Russia) at radiation FeK_α ($\lambda = 1.937$ Å), $U = 24$ kV, $I = 10$ mA.

Granulometric characteristics of the samples were measured using the Sympatec Helos laser diffraction particle size analyser (Germany). The apparatus was applied under the wet conditions in order to eliminate the aggregation during the measurement. The specific areas of the samples were measured by the BET method using Micrometrics Gemini 2360 apparatus. The material was ground in 5 % solution of $K_4Fe(CN)_6 \cdot 3H_2O$ in ball mill and attritor. A 20 ml of solution have been added per 100 g of the residuum. Thus, a sorbent in the form of paste was prepared and dosed to water contaminated by ions of Mn, Cu and Zn. A laboratory magnetic separator was used in the process of solid/liquid separation. Its principal

TABLE 1

Chemical analysis of the Albanian leaching residuum, %

Fe_{total}	Fe_{met}	Fe^{2+}	Fe^{3+}	Mg	Ca	Mn	Ni	Co	Cr	Ti	Al	Na	K	SiO_2
45.89	1.32	17.60	26.91	1.33	2.53	0.27	0.27	0.06	1.44	0.22	2.54	0.23	0.106	15.03

TABLE 2

Mineral composition of the Albanian leaching residuum

Mineral phase	Content, %
Magnetite $(Fe_{0.752}Mg_{0.202}Mn_{0.021}Ni_{0.020}Co_{0.005}O) \cdot Fe_2O_3$	54.09
Quartzite α-SiO_2	13.15
Wьstite FeO	8.02
Calcite $CaCO_3$	6.32
Ferropicotite $FeO \cdot (Cr.Al)_2O_3$	5.51
Corundum Al_2O_3	2.72
Na-feldspar	2.62
K-feldspar	0.78

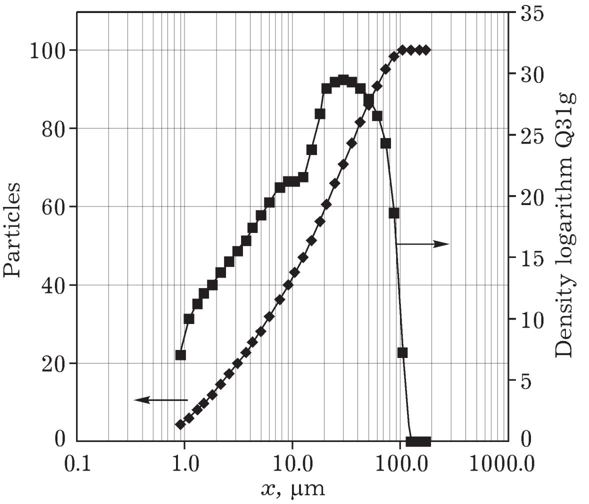

Fig. 2. Particle size analysis of the Albanian leaching residuum.

scheme is presented in Fig. 1. The diameter of the matrix canister was 40 mm and its length was 150 mm. The ferromagnetic steel balls with a diameter of 10 mm were used as a matrix. Magnetic induction was $B = 0.3$ T.

Materials

Chemical and mineralogical compositions of the Albanian leaching residuum are introduced in Tables 1 and 2, respectively. The grain size curves are illustrated in Fig. 2.

RESULTS AND DISCUSSION

Study of changes in grain size and specific surface

A time dependence of grinding on changes in grain size and specific surface was observed in the case of ball mill only. However, an application of attritor during 15 min resulted in obtaining better results as to grain size composition and specific surface. A decrease in grain

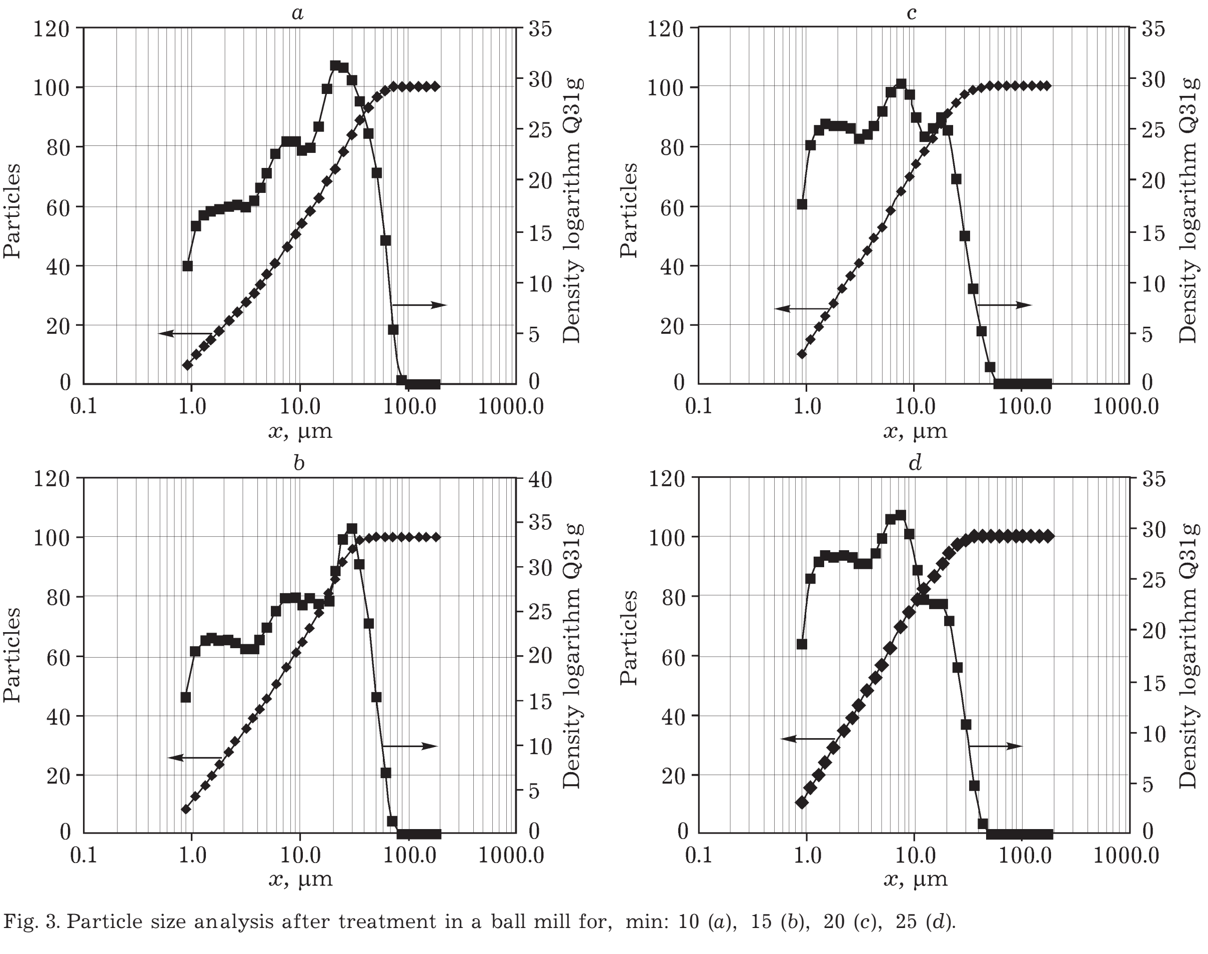

Fig. 3. Particle size analysis after treatment in a ball mill for, min: 10 (*a*), 15 (*b*), 20 (*c*), 25 (*d*).

TABLE 3

Changes in grain size and specific surface

Grinding mill	Time, min	Yield (mass %) of undersizes			Specific surface, m^2/cm^3
		−10 μm	−40 μm	−63 μm	
None	0	42.34	79.47	91.90	1.31
Ball Fritsch	10	52.77	91.08	99.15	1.76
	15	63.55	99.24	100.00	2.19
	20	72.28	99.34	100.00	2.47
	25	77.36	99.93	100.00	2.63
Attritor	15	99.79	100.00	100.00	3.86

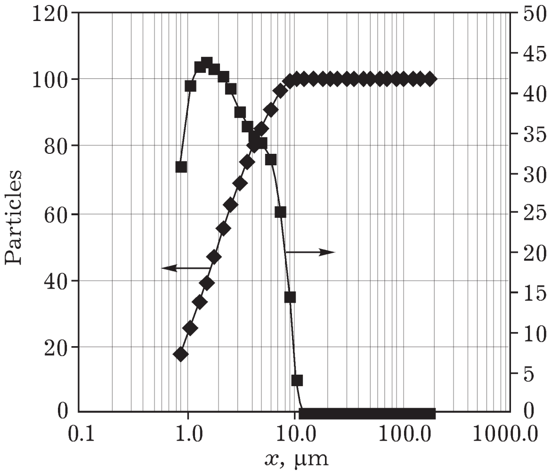

Fig. 4. Particle size after treatment in attritor for 15 min.

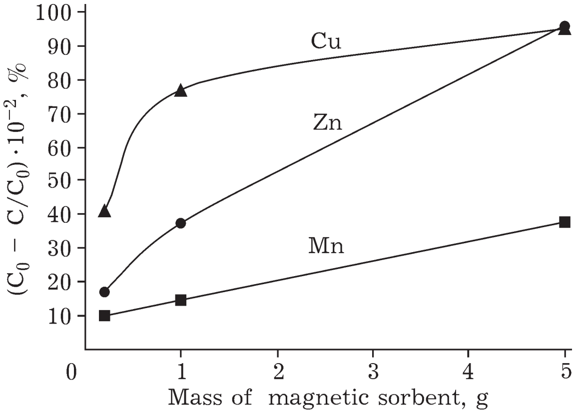

Fig. 5. Effect of the amount of magnetic sorbent on the magnetic separation efficiency of heavy metal ions. C_0 is initial concentration of heavy metal ions, C is final concentration of heavy metal ions.

size as the time dependence can be observed in Fig. 3, *a–d* as a shift of tops of the distribution curves to the left side, *i.e.* to the zero value.

These results are summarised in Table 3. A 100 mass % yield under 63 μm was attained after 15 min of activation and the specific surface enhanced almost two times. Contrary to this fact, grinding in attritor led to a threefold increase in specific surface already after 15 min, *i.e.* from 1.31 to 3.86 m^2/cm^3 (Fig. 4).

Magnetic filtration of contaminated waters

An influence of sorbent with maximal attained specific surface on the cation content in water is introduced in Fig. 5. After magnetic filtration a significant reduction of Cu and Zn concentration to the value of 3.7 μg/ml was achieved by adding 5 g of magnetite-bearing paste per 1 l of contaminated water.

CONCLUSION

The contribution describes chemical, physical and mineralogical properties of so-called Albanian (ore origin) leaching residuum from dumping ground of former Sereď Nickel Works (West Slovakia).

The residuum, *i.e.* magnetite-bearing material can be considered to be potential sorbent and for this reason the changes in grain size and specific surface were studied as the dependence of applied grinding mill and comminution time in the case of ball mill. Moreover, to increase its affinity to heavy metals a 5 % solution of potassium ferrocyanide was used during activation in grinding mills. A magnetic sorbent in the form of paste consisting of magnetic core and active layer on the surface of grain was prepared in this way.

It was proved that specific surface increases with the time of activation. The best results were achieved under application of attritor. The specific surface increased almost three times, *i.e.* from 1.31 to 3.86 m^2/cm^3.

The sorption tests and following magnetic filtration being focused onto removal of Zn, Mn and Cu ions from water resulted in the significant reduction of their concentration, namely, in the case of Zn it was by 93 %.

The experiments on magnetic filtration were performed at the same diameter of ferromagnetic balls. Thus, it is possible to consider optimisation of ball diameter and their distribution in filtration zone, which can result in increasing filtration efficiency. Naturally, it is also necessary to investigate the influence of suspension flow velocity through the filtration zone in more detail.

Acknowledgement

The authors are grateful to the Slovak Grant Agency for Science (grant No. 2/5150/25) and to the Ministry of Education of the Slovak Republic (Task of the State Program No. 2004 SP 26 028 0C 01) for financial support.

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