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RESEARCH ARTICLE

THE STRUCTURE OF HAZARDOUS INDUSTRIAL WASTES

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ABSTRACT

The aim of this paper is to evaluate the structure of wastes from non-ferrous metals. Wastes from the production of metals were selected namely waste from the production of aluminum - red mud and the waste from the production of nickel - black nickel mud. Morphology of samples was documented by scanning electron microscope, phase analysis using diffraction techniques and the content of elements was determined by EDX analysis. The influence of pre-treatment of these wastes on the structure was also investigated. Activation of red mud and black nickel mud has increased the size of their specific surface area, which may have the positive influence of adsorption or catalysis. The pre-treatment of wastes has changed the surface properties mainly electrostatic, hydrophobic and hydrophilic. Activation creates a new surface structure and thus affects its properties. Activation has created a new surface structure. EDX analysis of the samples confirmed the higher percentage content of Fe and Al.

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INTRODUCTION

Red mud (RM) is considered as major industrial hazardous waste that causes environmental problems and generates multiphase problems in the society. The utilization of red mud is realistically a significant problem in the alumina industry (Samal *et al*., 2013). The integrated utilization of red mud has thus been intensively investigated, especially in terms of construction materials like cement, land fill etc (Wanchao *et al*., 2014). The waste materials obtained from the alumina industries and thermal power plant need necessary treatment and confined disposal to manage them properly (Borges *et al*., 2011). RM is a solid waste residue formed after the caustic digestion of bauxite ores during the production of alumina. Each year, about 90 million tonnes of red mud are produced globally. Red mud is a highly alkaline waste material with pH 10–12.5 mainly composed of fine particles containing aluminium, iron, silicon, titanium oxides and hydroxides. Due to the alkaline nature and the chemical and mineralogical species present in red mud, this solid waste causes a significant impact on the environment and proper disposal of waste red mud presents a huge challenge where alumina industries are installed (Pirkanniemi and Sillanpää, 2002, Ordóñez *et al*., 2002). RM is produced during the Bayer process for alumina production.

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Bauxite ores are usually a mixture of minerals rich in hydrated aluminium oxides. However, they also contain iron, silicon and titanium minerals. After the digestion of bauxite ores with sodium hydroxide at elevated temperature and pressure, aluminium oxide is dissolved in the solution and the solid residue is red mud. The amount of the residue generated, per tonne of alumina produced, varies greatly depending on the type of bauxite used, from 0.3 tonnes for high grade bauxite to 2.5 tonnes for very low grade. Yearly production of red mud in Slovakia was about 70 000 kg and supplies are estimated at 8 million tons (Legube, *et al*., 1999, Xu *et al*., 1999, Li *et al*., 2001). As red mud has a strong alkalinity, which will cause some potential risks to its reuse, pre-treatment to change the alkalinity will produce beneficial effects. In the past years, several methods have been proposed such as acid neutralization, seawater wash treatment, heat treatment and the combination of above three treatments. Acid neutralization is widely used for red mud treatment and this method can remove alkali metals and other inorganic impurities as well as some organics. It is generally found that acid neutralization can increase the surface area and pore volume, favouring adsorption. Heat treatment can decompose unstable compounds and organics, however, it can also cause particle aggregation or sintering (Shaobin *et al*., 2008). Utilization of red mud will produce significant benefits in terms of environment and economics by reducing landfill volume, contamination of soil and ground water, and release of land for alternative uses.

Moreover, it can be used to produce valued materials for other applications and thus saving natural resources (Wang *et al*., 2009, Sahu *et al*., 2011). Black nickel mud (BNM) was created by leaching of nickel and cobalt from lateritic iron-ore. The black nickel mud containing chromium oxide, silicon, aluminum, calcium and the rest nickel is essentially iron concentrate. In Slovakia nickel was produced from the Albanian iron-nickel ore with a nickel content of about 1 %. Annual production of black nickel mud was about 300 000 kg and supplies in Slovakia are estimated at 5.6 million tons (Václavíková *et al*., 2002, Kováčová *et al*., 2006).

Experimental

Red mud and black nickel mud were pre-treated by chemical or non chemical ways:

- *Activated*: 190 ml of distilled water and 18 ml 31 % HCl were added to 10 g of mud. Suspension was 20 minutes heated by 100 °C and filled up with distilled water up to 800 ml. pH = 8 was reached by addition of 22 % NH_3. This suspension was 10 minutes heated at 50 °C, filtered and three times decanted with distilled water. The slurry was dried at 110 °C and annealed at 550 °C for 2 hours.
- *Non-activated*: 10 g of mud were filled up to 100 ml with distilled water. Suspension was mixed and filtered. Then slurry was dried at 110 °C and annealed at 550 °C for 2 hours (Pratt and Christoverson, 1982)

Morphology of samples was documented by scanning electron microscope TESLA BS 500 and JEOL JSM 7600F and phase analysis was carried using diffraction techniques from experimental data measured by X-ray Philips PW 1710 diffractometer using a Co anode and a secondary graphite monochromators. Electric energy required for these processes was obtained from photovoltaic panels.

RESULTS AND DISCUSSION

Based on the EDX analysis of samples of red mud (table 1) we can conclude that the results confirmed the higher percentage of Fe and Al, which can positively affect the adsorption and catalytic properties of waste and thereby predispose them to act as an alternative adsorbent or catalyst, respectively. Acid treatment and calcination can produce changes in thephysicochemical properties of RM that affect its catalytic activity.The effects of the acid treatment on the physicochemical properties of RM were examined. The RM consisted of numerous components. Main components were Fe and Al, with Na, Ti and Ca being the next mostprevalent ones. After activation of the surface of red mud the reduction of Ca, which is caused by a reaction of calcium ions with HCl, was observed.

Table 1. The results of EDX analysis of red mud in wt. %

	O	Al	Si	Ca	Ti	Fe
Non-acivated red mud	34,31	7,74	5,02	11,48	2,60	38,83
Acivated red mud	33,71	6,83	4,57	3,89	3,97	47,03

The similar phenomenon was observed by black nickel mud, where the concentration of Mg after activation reduced in the same way (table 2). Activation of the surface of black nickel mud caused no impact on it with the exception of decreased Fe content. In particular, the calcium and sodium contents in the RM and BNM samples treated with hydrochloric acid had decreased significantly.

Table 2. The results of EDX analysis of black nickel mud in wt. %

	O	Al	Si	Mg	Ca	Fe
Non-acivated black nickel mud	25,31	4,97	4,56	3,48	3,70	67,29
Acivated black nickel mud	26,71	4,06	6,60	0,89	1,17	58,03

X-ray diffractograms of activated and non-activated forms of red mud are almost identical. In red mud we have identified rutile (TiO_2), hematite (Fe_2O_3), limestone ($CaCO_3$), halloysite ($Al_2Si_2O_5(OH)_4$) and bayerit ($Al(OH)_3$) (Fig. 1, 2). In the case of black nickel mud mainly hematite, schorlomite $Ca_3(Fe, Ti)_2[(Si, Ti)O_4]_3$, calcite ($CaCO_3$), magnetite ($Fe_3O_4$) and sillimanite ($Al_2SiO_5$) (Fig. 3, 4) are presented. Activation caused a significant decrease of $CaCO_3$ and schorlomite. The content of crystalline compounds containing iron after activation decreases, probably due to thermal treatment. On the basis of X-ray analysis of waste samples we assumed, that due to the presence of certain metal oxides industrial wastes could be used as adsorbents or catalysts.

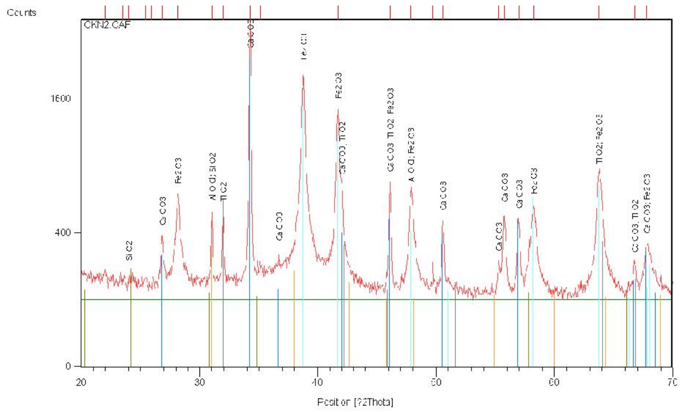

Fig. 1. RTG diffractogram of non-activated red mud

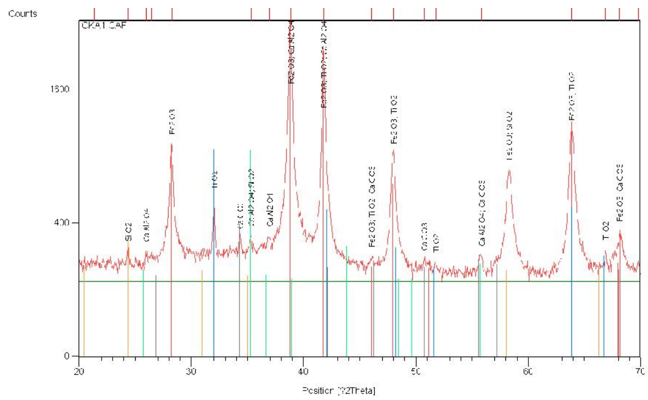

Fig. 2. RTG diffractogram of activated red mud

By examining the structure of red and black nickel muds using electron microscopy was found out that they contain different particles with the presence of crystalline structures. Acid-activated samples show the presence of new cavities and granular structure. The activation creates a new surface structure and thus affects its properties. Figure 5 shows the surface of non-activated red mud, which is relatively rough morphology with a set mostly consisting of micro-aggregates. Particle size ranges from 0.5 to 1 μm. Activation leads to the lees incurred particle surface morphology and smooth surface while creating a wrinkled (porous) structure (Fig. 6), which increased the size of its specific surface. This is mainly due to dissolution of salts present on the surface by used HCl.

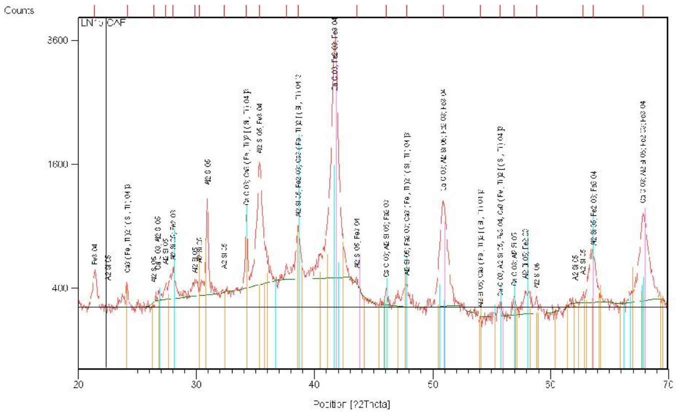

Fig. 3. RTG diffractogram of non-activated black nickel mud

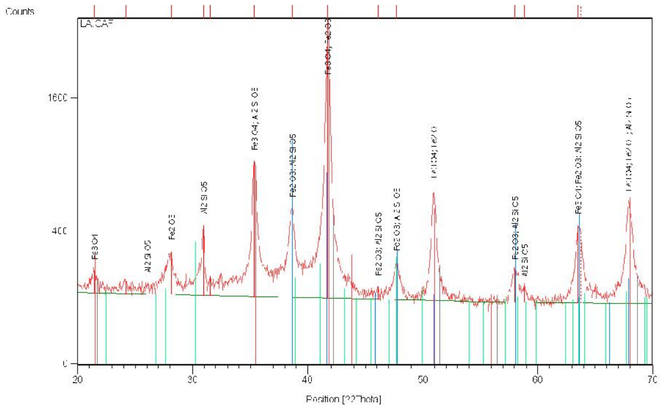

Fig. 4. RTG diffractogram of activated black nickel mud

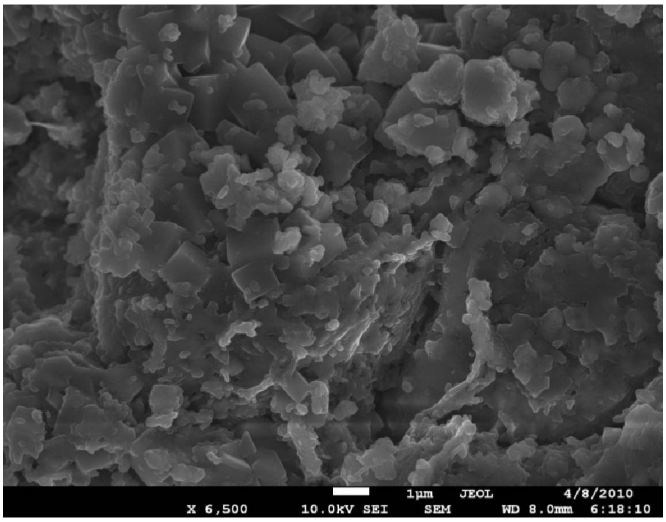

Fig. 5. The surface of non-activated red mud

For samples of black nickel mud, morphological difference from red mud samples could be seen. Surface layers of particles of black nickel mud also formed agglomerates microcrystalline formations, but their share is significantly lower than in red mud. Activation again caused a reduction in calcium phases, but iron oxides, which prevailed in black nickel mud, retain their original form.

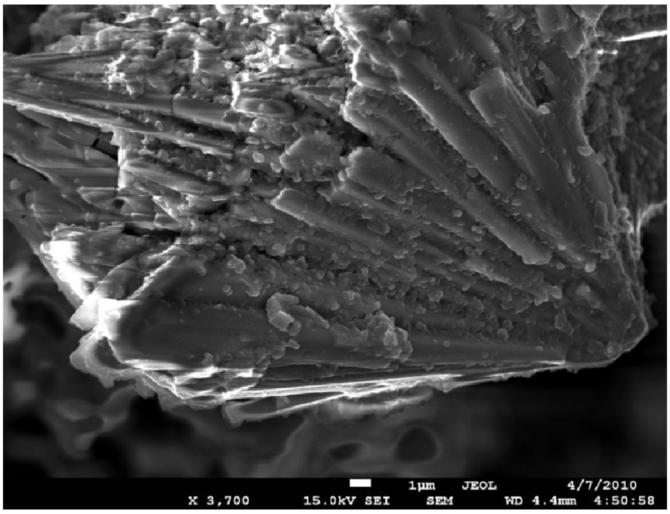

Fig. 6. The surface of activated red mud

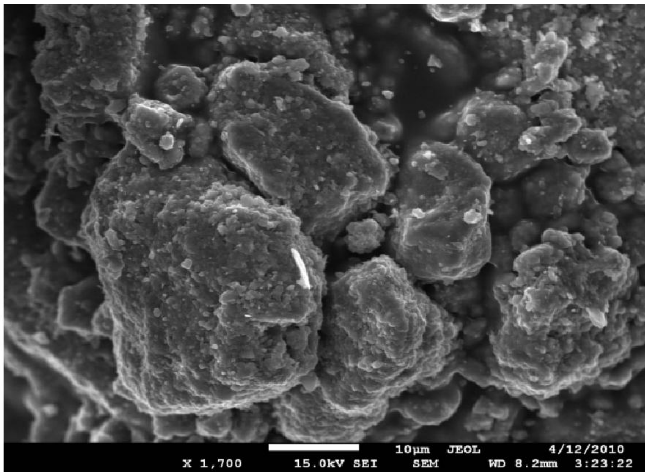

Fig. 7. The surface of non-activated black nickel mud

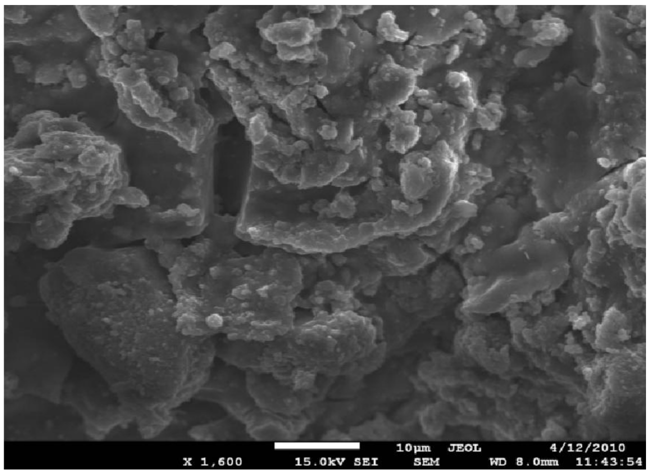

Fig. 8. The surface of activated black nickel mud

The change of the specific surface area after activation was less significant than in red mud. A comparison of Fig. 7 and 8 shows that the activation of the surface of black nickel mud caused significant fragmentation of particles, that ultimately increased the specific surface area mainly due to a reduction in particle diameter.

Conclusion

Activation of red mud and black nickel mud has increased the size of their specific surface area, which may have the positive influence of adsorption or catalysis. The pre-treatment of wastes has changed the surface properties mainly electrostatic, hydrophobic and hydrophilic. Investigating the structure of red mud and black nickel mud by scanning electron microscopy was found out, that they contain different particles in the presence of crystalline structures. Acid activated samples show the presence of new cavities and roughened surface structure mainly due to the dissolution of salts on the surface using HCl. It can therefore be concluded that activation creates a new surface structure and thus affects its properties. Studying the X-ray diffractograms of activated and non-activated forms of red mud and black nickel mud was determined that activation of red mud lead to a significant reduction in $CaCO_3$ content and activation of black nickel mud caused a significant decrease of $CaCO_3$ and schorlomite. EDX analysis of the samples confirmed the higher percentage content of Fe and Al, which will positively affect the adsorption and catalytic properties of these wastes.

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