Assessment of the usability of $Mg(OH)_2$ obtained from the solution after sphalerite leaching for the winning of polyetylene composition

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In this work obtaining of magnesium hydroxide from the solutions obtained during magnesium removal from zinc concentrates is presented. The received product was used for the winning of composites from polyethylene (PE) using extrusion and injection methods. The obtained composites were tested in terms of thermal stability (TG, DTG) as well as combustibility (LOI and thermovision camera). The preliminary results indicate the beneficial effect of the decrease of PE quality by magnesium hydroxide obtained by means of solution purification and precipitation of $Mg(OH)_2$ by means of soda lye.

Keywords: Magnesium hydroxide, polyethylene.

INTRODUCTION

The waste disposal problems concern Trzebionka Mining Works in Trzebinia, where two types of wastes are generated, the solid waste and wastewater. The main component of the solid waste is the powdered host rock (post flotation waste), whereas of wastewater – the dissolved MgSO₄.

Gravity separation, dense liquid separation and enrichment by flotation are applied to obtain zinc concentrate. Such material contains about 58 - 60% Zn and a relatively high amount of magnesium, even up to $1.5\%^{1-2}$. The reduction of magnesium content is realized by leaching with sulphuric acid according to reaction:

 $\label{eq:caCO3} \begin{array}{l} {\rm CaCO_3 \cdot MgCO_3} + 2{\rm H_2SO_4} \rightarrow {\rm MgSO_4} + {\rm CaSO_4 \cdot 2{\rm H_2O}} + 2{\rm CO_2} \end{array}$

In consequence, $MgSO_4$ is dissolved in water, whereas calcium sulphate is precipitated as gypsum. The obtained suspension passes to flotation for sphalerite recovery³⁻⁵.

It enables the reduction of the content of magnesium and calcium compounds into the concentrate for the amount of up to about 0.3%. Thereby zinc concentration in the product increases. The presence of Mg-compounds in the concentrate is disadvantageous for the metallurgical zinc production process.

The aim of this research was an attempt to dispose the wastewater generated in the process of magnesium removal from sphalerite. One of the ways is the precipitation of magnesium hydroxide.

Magnesium hydroxide $(Mg(OH)_2)$ is an important raw material in many industrial processes. In this work the magnesium hydroxide as the addition to the polyethylene was used.

Magnesium hydroxide decomposes endothermically with the formation of water at a decomposition temperature of 340 - 450°C, and it has been used as a promising environmental-friendly flame retardant in polymeric materials because it is halogen-free, nonvolatile, of low cost. Magnesium hydroxide can be synthesized with high purity and in a range of useful morphologies, responds well to surface modifiers and can be incorporated into most polymers by suitable processing methods⁶⁻⁷.

In our research we have prepared a series of polyethylene $(PE)/Mg(OH)_2$ composites containing 20 and 30 wt. % of

 $Mg(OH)_2$ by injection moulding and the thermal properties of the obtained composites were investigated by thermal analysis methods.

EXPERIMENTAL

Waste solution used for the experiment was composed of about 8 g of magnesium in 1 dm³, additionally of heavy metals of relative high concentration including the iron elements, zinc, lead and cadmium.

At the head heavy metals should be removed from this solution.

The chemical precipitation with CaO and solution aeration was tested to remove the metals. These operations were performed simultaneously. The optimum process conditions were as follows: addition of 0.3% CaO and two-hour aeration. It enables decreasing iron concentration below the limit of detection for spectrofotometric analysis and reduce the content of other metals to trace amounts.

The magnesium hydroxide from pure solution was precipitated during appropriate pH regulations. The sample of the magnesium hydroxide was determined by the X-ray diffraction method using Phillips diffractometer with X'Pert system, and the result of phase analysis is shown in Fig.1.

The analysis results confirmed that the samples contained pure magnesium hydroxide.

After filtration and drying the obtained $Mg(OH)_2$ with polyethylene in different proportion was mixed and the composite was investigated.

Thermogravimetric analysis was performed on a Netzsch TG 209 thermal analyser, operating in a dynamic mode at a heating rate of 10 K/min under air atmosphere.

For the differential scanning calorimetry (DSC) measurements a Netzsch DSC 200, operating at the heating rate of 10 K/min under air atmosphere, was employed. Prior to the use the calorimeter was calibrated with mercury and indium standards; an empty aluminium pan was used as reference.

RESULTS AND DISCUSSION

TG profiles of the degradation process of $PE/Mg(OH)_2$ composites are shown in Fig. 2

Magnesium hydroxide undergoes stoichiometric decomposition to magnesium (II) oxide and water. Polyethylene



Figure 1. X-ray diffraction pattern of the magnesium hydroxide



Figure 2. The TG profiles of PE/Mg(OH)₂ composites

degradation occurs by random chain scission, according to the free-radical mechanism⁸. For PE/Mg(OH)₂ composites containing 30 wt. % of Mg(OH)₂ there is an increase in the thermal stability, as evidenced by T_{onset} and T_{DTGmax} (Tab. 1).

Char residue is increasing also with an increase of the $Mg(OH)_2$ content which is a good promise for lower flammability of the composite⁹. Char reduces the diffusion of volatile products of polymer degradation out of polymer bulk; therefore the reduction in the rate of mass loss is observed. The introduction of anizometric impermeable

Mg(OH)₂ particles into polymer results in the formation of labyrinth in the bulk of the material that volatile products must escape. This effect also reduces the diffusion of atmospheric oxygen into the material during thermooxidative degradation. The mechanism of thermal stability improvement/ flammability reudction was also ascribed to the changes in the dynamics of polymer molecular motion. This effect involves the reduction of transport of reactive species in composite materials and causes changes in the kinetics of chemical reactions proceeding during thermal decomposition of polymer¹⁰.

Table 1. The TG parameters of the thermal degradation of PE/Mg(OH)₂ composites

Sample	T _{onset} [°C]	T _{DTGmax} [°C]	Char residue [%]
Mg(OH) ₂	334.6	366.9	68.07
PE	273.5	327.5	3.49
PE/20% Mg(OH) ₂	273.7	324.4	6.48
		372.6	
PE/30% Mg(OH) ₂	350.7	380.5	9.32



Figure 3. The DSC curves of $PE/Mg(OH)_2$ composites

From the DSC profiles of the $PE/Mg(OH)_2$ composites (Fig. 3) one can observe that incorporation of $Mg(OH)_2$ into the PE matrix causes a lowering of the polymer melting temperature due to the hindering of the crystallisation process; the heat of melting diminishes as well.

CONCLUSIONS

Thermal analysis of polyethylene (PE)/Mg(OH)₂ composites containing 20 and 30 wt. % of Mg(OH)₂, obtained by injection moulding, shows that upon an addition of Mg(OH)₂ into PE matrix there is an increase in the thermal stability, as evidenced by T_{onset} and T_{DTGmax}. Char residue is increasing also with an increase of the Mg(OH)₂ content which is a good promise for lower flammability of the composite. From the DSC profiles one can observe that incorporation of Mg(OH)₂ into polymer matrix causes a lowering of the polymer melting temperature due to the hindering of crystallisation process; the heat of melting diminishes as well.

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LITERATURE CITED

1. Szołomicki, Z. (1995). Chemical treatment of zinc concentrate, I Międzynarodowa Konferencja Przeróbki Kopalin, 14 – 17 Listopad 1995, Zakopane, Polska, (in Polish). 2. Janus, I. (2002). Economical review of flotation of waste storage. Chemical Works, Przedsiębiorstwo Handlowo – Usługowe "OŚ" s.c., Bytom, (in Polish).

3. Kowalski, Z., Żelazny, S., Włodarczyk, B. (2003). Conception reuse of waste solution from remove of magnesium from concentrate for magnesium sulfate production, Gospodarka Surowcami Mineralnymi, t 19, zeszyt specjalny, Wyd. IGSMiE PAN, Kraków, Polska, (in Polish).

4. Urbanowicz, M., Starowicz, M. (2004). Remove test of magnesium compounds from water waste generated after remove of magnesium from zinc concentrate, Praca Magisterska, Politechnika Krakowska, Kraków, Polska, (in Polish).

5. Kozak A., Fela K, Żelazny S., Jarosiński A. (2004). Remove of heavy metals from waste solution generated in enrichment of zinc and lead ores, VIII Konferencja "Recyklace Odpadu", 8 – 11 November 2004 (pp.37 – 42). Ostrawa, Czechy (in Polish).

6. Liu, P. & Guo, J. (2007). Organo-modified magnesium hydroxide nano-needle and its polystyrene nanocomposite. J. Nanopart. Res. 9(4), 669 – 673. DOI: 10.1007/s11051-006-9079-4.

7. Li, Z. & Qu, B. (2003). Flammability characterization and synergistic effects of expandable graphite with magnesium hydroxide in halogen-free flame-retardant EVA blends. Polym. Degrad. Stab. 81(3), 401 – 408. DOI: 10.1016/S0141-3910(03)00123-X.

8. Pielichowski, K. & Njuguna, J. (2005). Thermal Degradation of Polymeric Materials. Shawbury, UK: Rapra.

9. Grand, A.F. & Wilkie, C.A. (2000). Fire Retardancy of Polymeric Materials. New York, USA: Marcel Dekker.

10. Vyazovkin, S. & Dranca, I. (2004). A DSC study of aand b-relaxations in a PS-clay system. J. Phys. Chem. B. 108, 11981-11987. DOI: 10.1021/jp0487020.