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The comparison of properties of hydrophobized limestone powders produced in different methods

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Two methods have been used in order to manufacture hydrophobized lime powder. Materials obtained in these ways may be used as an anti-explosive agent in mining industry. It is important because a typical method of anti-explosive dust production is no longer profitable in modern quarries, so a new manufacturing method should be developed. The obtained modified samples were analyzed with the use of research methods originally applied in the powder technique. Moreover the adhesive force and shear stress were measured. The method for determining the hydrophobization index of samples was worked out as well. The obtained results enable us to make a characterization of lime dusts. All products are characterized not only by typical properties of water-resistant materials but also by properties suitable for fine materials.

1. Introduction

Powder materials are used in everyday life and in many industries. Their properties are quite different from those of massive solids, in particular there are cohesive interactions between fine particles. This effect determines the behavior of powders in many technological processes, e.g. fluidization, mixing or multiphase processes. Also during combustion, catalysis processes and solution, powders behave in a different way than the massive solids. The first ones are characterized by a large external surface and that is the reason why powders react more quickly with other ingredients, or why they better dissolve. It is known that the solids surface is often characterized by quite different properties than the matter inside. The knowledge of phenomena taking place on the solids surface has contributed to a huge technological development in the last years. In nature there are solids characterized by various surface properties. The hydrophobicity (the solids resistance against water) is one of the more interesting surface qualities. This property causes the materials not to be destroyed by moisture. People observed nature and started to protect their surroundings against moisture using first natural hydrophobic materials, and then modifying other materials towards their water-resistant properties. Materials characterized by hydrophobic properties are particularly applied in construction industry (Rokiel, 2006). But they are also used more specifically. In paper

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industry, for hydrophobization, the so-called sizing substances are applied. Lime dust is generally used as a method of precaution against coal dust explosions in mining industry (Polish Standard, 1994).

The decrease in wettability of solids characterized by large surfaces is achieved by coating final products with a hydrophobic layer (Buczek and Vogt, 2007) by means of painting, spraying or dipping bath. They are a group of construction materials modified by the addition of modifier in the production process. In the case of powders we do not find it easy to apply those modification methods.

2. Method and results

2.1 Material and manufacturing method

Lime dust from the Czatkowice Quarry (Buczek and Vogt, 2007) was used as a raw material. It is a good agent for research because it is possible to compare the properties of samples modified in this work to the properties of anti-explosive lime dust (PH) used in mining industry (Polish Standard, 1994). This product protects human life so its properties are very important and well-known. Such comparison enables us to define an index of hydrophobization for modified materials. Moreover, a typical method of hydrophobic dust production is no longer profitable in modern quarries. Accordingly, a new manufacturing method has been developed as described below.

In this work two methods of manufacturing of hydrophobic material are proposed: hydrophobization from stearic acid vapour and from silicone solutions. The first one consists in stearic acid vapour and dust countercurrent flow (Buczek and Vogt, 2007). The index of hydrophobization is easy to determine when stearic acid is used as a modifier. The manufactured sample (S_18) contains 0.18 % of stearic acid, being an acceptable level according to Polish Standard (1994). The second method consists in mixing raw dust with commercial silicone solution - SARSIL® H-15. SARSIL® silicone paints provide perfect protection of the facade against impact of atmospheric conditions. In the case of this modifier the authors had to work out the method for determination of hydrophobization C coefficient. The film flotation method (Fuerstenau and Williams, 1987) could be used if the commercial material (PH) was used as a comparative sample. The C coefficient defining to what extent the hydrophobic properties of the S_SH15 sample are different from the hydrophobic properties of the PH sample on contact with a suitable methanol solution was calculated from the equation 1, where f_{pi} and f_p are mass percentage of S_SH15 sample and PH sample floating on a selected (10, 20, and 60 % (w/w)) methanol solution surface respectively.

$$C\,[\%] = \frac{f_{pi} \cdot 100}{f_p} \tag{1}$$

The obtained results are listed in Table 1. The medium value of the C coefficient was calculated as the arithmetic mean of the results obtained for individual solutions.

Table 1 Hydrophobization coefficient

Solution concentration	10 %	20 %	60 %	
C [%]	92.2	87.7	75.4	$\bar{C}$ = 83.8

The average value of the C coefficient shows that the S_SH15 sample obtained sufficient hydrophobic properties in comparison with the PH sample. We can state that the second proposed method of hydrophobized lime dust manufacturing is useful.

2.2 Methods of measurement of powder properties

It is interesting to know how the modification process influenced the change of typical dust properties, e.g. flowability or volatility. The property mentioned as the second one is as well as hydrophobicity an important quality when we look at the possibility of using modified powders as an anti-explosive agent in mining industry.

2.2.1 Powder Characteristics Tester (PChT) – type PT-E, Ser. No. 901331

Parameters which were measured: bulk density, packed bulk density, compressibility, and angles of: repose, fall, difference, and dispersibility. Carr (1965) tried to evaluate powder's flowability and floodability in a numerical manner. The tables for the conversion of the measured figures into a common index were published. These parameters also allow us to calculate the Carr's or Hausner's (1967) ratios. The obtained results are listed in Table 2. The dust characteristics shown in Table 2 give us the possibility of determining the properties of material from the cohesion point of view. The compressibility value for the raw sample equals about 50 % and it is decreased slightly for the modified samples, but both the raw lime dust and the modified powders will settle in elbows, and the outlet will clog (Carr, 1965). The fall angle of all dusts is much bigger than 10 degrees so all the investigated samples have fairly high degrees of floodability (Carr, 1965). The values of the difference angles for both raw and hydrophobized dust are low, as in the case of cohesive materials. A great difference between the dispersibility values was found only in the case of raw and the S_18 samples. So the measurement of this one cannot be used for evaluating the degree of hydrophobization. The dispersibility for all samples is less than 50 % - that is substandard for easy flowing powders. The Hausner's ratios are bigger than 1.4, i.e. the three samples are characterized by all properties of cohesive powders. The Carr's ratios obtained during researches are much bigger than 30 and confirm the low flow rate of powder. Only compressibility could be used as the criterion for evaluating the degree of hydrophobization of modified dusts.

Table 2 The characteristics of raw and hydrophobized lime dusts

Characteristics	Raw	S_18	S_SH15
Bulk density [kg/m^3]	724	798	790
Packed bulk density [kg/m^3]	1475	1377	1414
Compressibility [%]	51	42	44
Repose angle [deg]	52	47	37
Fall angle [deg]	35	33	34
Difference angle [deg]	17	14	3
Dispersibility [%]	20	41	16
Carr's ratio [%]	50	42	44
Hausner's ratio	2.0	1.7	1.8

2.2.2 Shear tests

Some shear tests were performed to determine the effect of hydrophobization on the powders behavior characteristics. Data from shear tests is mainly an important basis for the design of reliable bulk solids handling equipment (Schwedes, 2003). Flowability testing may also be useful to compare similar bulk solids. However it is known that obtained results depend to a large degree on the way of running the test. A shear cell method according to Jenike (1964) and Institution of Chemical Engineers, (1989) was used and the shear tester was made in accordance to European Standard CEN (2003). The tester was 60 mm in diameter with the driving shaft providing the displacement velocity of 0.045 mm s^{-1}. The samples of all the materials were, in the first place, preconsolidated with a normal load applied (σ_r) and the sample was then pre-sheared until the steady state flow was obtained. To complete the full test of powder shearing, the preconsolidated sample was loaded with smaller normal stress and sheared again. Repetition of the test procedure with fresh samples, at constant normal load during the pre-shear (σ_r = 79.62 kPa), and varying normal loads during the proper shear with values equal to ($0.9\sigma_r$), ($0.68\sigma_r$), ($0.4\sigma_r$) and ($0.15\sigma_r$) respectively, made it possible to obtain additional points of tangent stress – shear displacement relationship as shown in Figure 1.

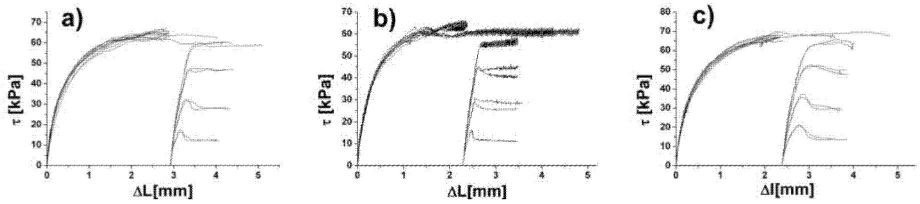

Figure 1 Comparison of tangent stress – shear displacement relationships obtained for a) sample of a raw material, b) S_18 modified sample and c) S_SH15 modified sample

The shear experiments performed and the data shown in Figure 1 were the basis for yield loci for the tested materials to be determined – Figure 2, and further, values of cohesion (C) and angle of internal friction (φ) of samples to be calculated – Table 3.

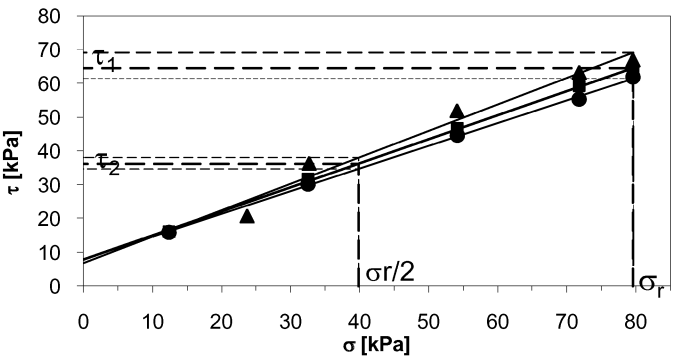

Figure 2 Shear stress – normal stress for tested materials: ■-raw, ●- S_18, ▲- S_SH15

Table 3. The cohesion and angle of internal friction calculated for test materials

	Raw	S_18	S_SH15
C [kPa]	7.92	7.89	6.81
φ [°]	35.4	33.9	38.1

Data from both the Figures and Table 3 show that the effect of surface modification on powders flowability measured with Jenike shear cell method is similar, with some difference, as far as the S_18 sample is concerned. In this case distinct oscillations in the shear stress during the sample shearing can be seen. The probable reason for this is the material compressibility. Molenda et al. (2001) indicated that oscillation could be considered as part of compaction-dilatation events occurring around the area of shear zones developed in the material during shearing. It can lead, among others, to strong vibration on silo walls and should be avoided as far as possible. From the obtained data it may be concluded that a proper way of lime dust modification is that leading to the S_SH15 sample. For this sample the cohesion is clearly smaller than for raw material and there is no stress oscillation during shearing. But on the basis of the results described earlier it is known that two modified samples obtained water-repellent properties. Some additional data reflecting the effect of surface modification on powders flowability (hydrophobization) would be obtained from direct capillary adhesion measurements and shear tests performed for powder samples with different wettability. It is difficult to formulate general conclusions on the basis of shear test results, concerning the hydrophobization state of lime dust. But it is worth thinking whether these results could be used to evaluate lime dust volatility. It seems possible on the basis of the angle of internal friction.

2.2.3 Measurement of capillary adhesive force

The adhesive force was measured for an array of about 250 individual particles (Figure 3) of the S_18 sample with technique described by Harnby et al. (1996). The coarse limestone particles (grain fraction: 0.385-0.400 μm) were contacted with metallic flat surface (50-100 μm roughness) in a humid atmosphere. For raw material the adhesive force appeared at humidity of about 60 %, then grew to value of 0.008 N at humidity of 95 %. The results obtained for modified material were negligible small and impossible to measure. This clearly indicates that the modified material lost its adhesive properties. These measurements were carried out only with metallic flat surfaces. It would be reasonable to measure adhesion with the use of lime plate; these investigations are planned to be performed in the near future.

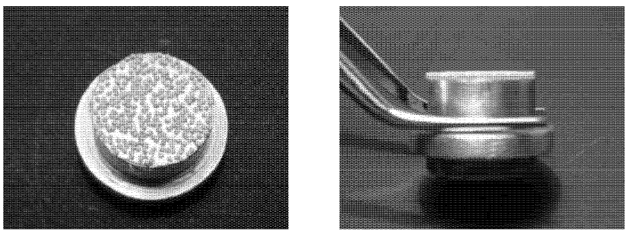

Figure 3 The array composed of particles placed on a tacky surface

3. Conclusions

The obtained results enable us to make a characterization of lime dusts used. However only two, from the used research methods are useful for evaluating the degree of hydrophobization of modified dusts, i.e. the film flotation method and PChT. The value of the compressibility could be used in the case of the latter method mentioned. Unfortunately the film flotation method is time-consuming and of little precise. The results obtained in different laboratories may differ from each other, but on the other hand, they give us the possibility of making the comparison of samples modified in different ways. On the basis of the shear test results it was not possible to determine the hydrophobization criterion. However it is noticeable that the way of modification is reflected in the obtained results. The adhesion force measurements show that the modified material lost its adhesive properties, but only on contact with metallic flat surfaces. It seems that this could be an interesting method of testing the hydrophobization degree for samples modified in different ways. But a more precise method of taking the measurement should be developed in the future. Additionally, the parameters obtained with the use of PChT enable us to estimate the flowability and volatility of dusts and give the possibility of determining the properties of lime dust from the cohesion point of view.

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