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Original Research

Effects of Commercial Modifiers on Flow Properties of Hydrophobized Limestone Powders

Elżbieta Vogt*

AGH University of Science and Technology, Faculty of Energy and Fuels,
Al. A. Mickiewicza 30, 30-059 Kraków, Poland

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Abstract

Limestone powder popularly used as an anti-explosive agent in the mining industry and as an absorbent for exhaust fume desulphurization in the energy industry, both of which take advantage of the powder's, favourable flow properties. In this project, evaluations of the influence of commercial modifiers on the flow properties of hydrophobized limestone powders were measured. The analysis was carried out on the basis of densimetric measurements with the use of a powder characteristics tester. It was stated that the hydrophobization process improves not only the waterproof properties of limestone powders, but also reduces cohesion and improves flow properties.

Keywords: limestone powder, hydrophobization, flow properties, densimetric measurements

Introduction

The use of limestone powders is popular with in the mining industry (as an anti-explosive agent) and in the energy industry (as an absorbent for exhaust fume desulphurization) [1-3]. Coal dust explosions are among the greatest hazards in coal mines and are catastrophes damaging environmental impact.

Limestone powders also are used in the road construction industry to produce building materials, as well as in the chemical industry, the animal feed industry, and the glass industry. The popularity of this material is due not only to its effectiveness but also its widespread availability in Poland, which has substantial reserves of this raw material, but which cannot be regarded as limitless due to the high rate of consumption. The mining industry can have a negative influence not only on the natural landscape, but can cause particular damage to mining area ecosystems. Therefore, all activities that reduce limestone consumption are beneficial for the environment. The modification of limestone products properties so that their water resistance is increased can reduce limestone consumption because of the enhanced durability against the environmental effects of hydrophobized material.

What is more, favourable flow properties like the flowability and floodability of limestone material are required in the above-mentioned practical uses. Unfortunately, the high comminution degree of limestone powders can cause cohesive interactions [4-8] between small particles. This phenomenon is responsible for electrifying and pasting of grains, which unfavourably influences the possibility of the application of limestone powders in the above-mentioned processes. This quality also unfavourably influences the progress of such processes as: storage, fluidization, pneumatic conveying, and mixing fine-dispersional materials in multiphase sets that are parts of manufacturing processes.

In order to maintain the limestone powder properties desired for a particular application and to eliminate negative features, fine-dispersional materials may be exposed to various types of hydrophobization [9-13]. Enriching powder materials with hydrophobic properties results not only in their increased moisture-resistance but also in their decreased agglomeration potential and reduced cohesive interactions between grains. Thus, by implication, the application of waterproof powders is more profitable.

*e-mail: vogt@agh.edu.pl

Unfortunately, the standard method of producing such powder by milling limestone with stearic acid is unprofitable in many modernized quarries and plants, and sometimes impossible due to the introduction of technological changes and implementation of modern mills. Consequently, new methods of obtaining waterproof limestone powder and new modifiers should be sought. To control the modification process a study of newly obtained material properties must be made. The acquired results allow assessing the direction of changes in limestone powder properties caused by the hydrophobization process. The correctly conducted process of hydrophobization should retain or improve the desired flow qualities of fine-dispersional raw material such as flowability and floodability.

Experimental Procedures

Analyzed Materials

The analyzed samples of limestone powder came from the Czatkowice Limestone Quarry [14, 15] and included: meal with a grain diameter smaller than 80 μm and sand with a grain size within the range 100-400 μm.

Typical commercial modifiers such as stearic acid, the Sarsil® H-15 silicone preparation produced by the chemical plant "Polish Silicones" Ltd, and the Bitumen Voranstrich-bituminous preparation produced by Köster Bauchemie AG Ltd, Kraków, were applied for powder hydrophobization.

Conditions for Conducting the Hydrophobization Process

The description of techniques used for the hydrophobization of limestone powder was discussed in earlier works by the author [16, 17]. The first hydrophobization method was carried out in a self-made and designed installation and it consisted of free sedimentation of the powder layer dispersed by stearic acid vapour in powder counter-current flow. The second method consists of mixing raw powder with a Sarsil® H-15 silicone preparation. It was determined to be the optimal modifier quantity. While the Bitumen Voranstrich preparation was used as a modifier, the powder was mixed with the preparation in a beaker. The preparation was diluted before use [18] at a weight:ratio of 1:2.

The Evaluation of Analyzed Materials Properties

The Evaluation of Hydrophobization Degree

It is difficult to find a simple research method which could be applied to determine the hydrophobization degree of powder materials modified with the use of various modifiers [19-21]. In the presented research it was possible to compare the hydrophobic properties of powders modified in the work with properties of industrial anti-explosive powder available on the market (PH – industrial anti-explosive limestone powder) [20]. A relative evaluation of the

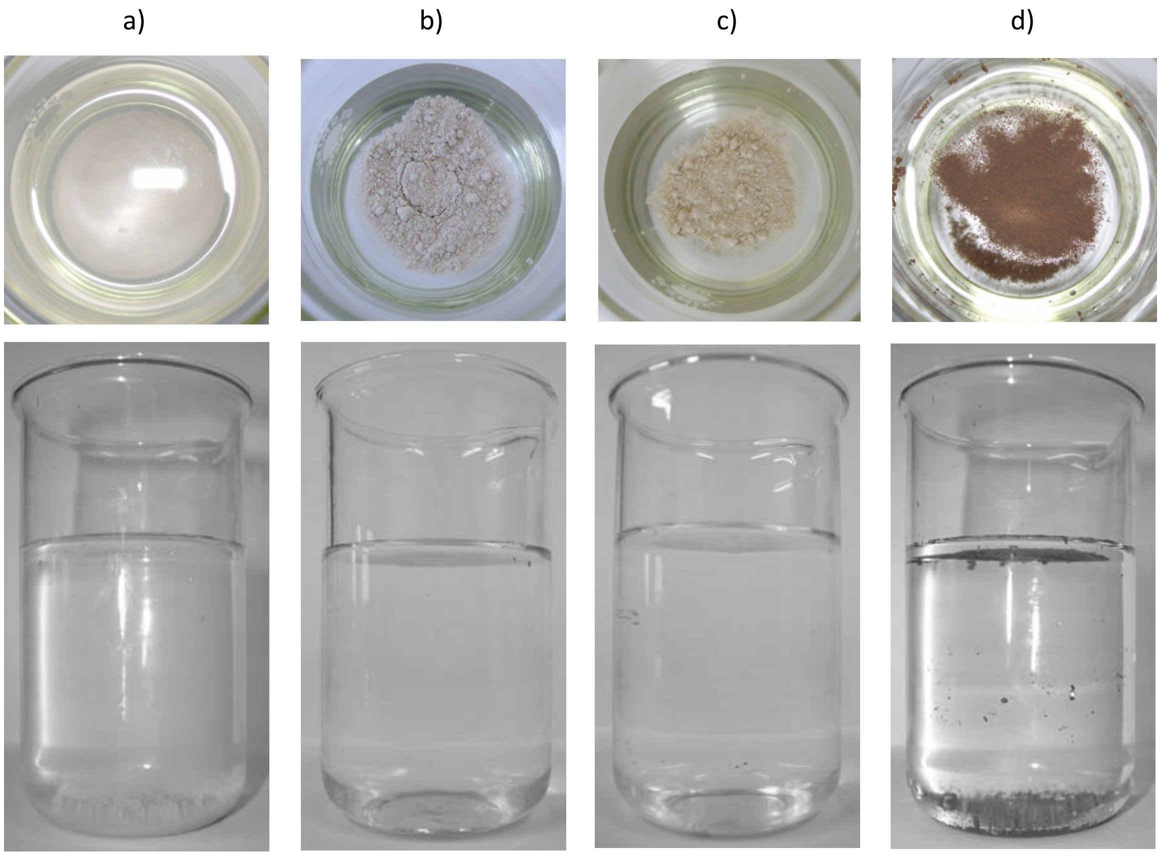

Fig. 1. The "floating on water" test. Limestone meal: a) raw, b) modified in stearic acid vapours, c) modified by mixing with the SARSIL® H-15 preparation, d) modified with the Bitumen Voranstrich preparation.

Table 1. Values of parameters characterizing raw and modified powders determined with the use of the powder characeristics tester apparatus and AccuPyc 1340.

Material	Modifier	Properties					
		ρ_b (g/cm³)	ρ_{pb} (g/cm³)	ρ_r (g/cm³)	C (%)	R (%)	I_H
Meal	Lack	0.724	1.475	2.764	50.9	20	2.0
Meal	Stearic acid	0.922	1.532	2.725	39.8	42	1.7
Meal	SARSIL® H-15	0.790	1.414	2.683	44.1	16	1.8
Meal	Bitumen Voranstrich	0.929	1.238	2.514	24.9	50	1.3
Sand	Lack	1.257	1.625	2.717	22.6	19	1.3
Sand	Stearic acid	1.383	1.675	2.706	17.4	19	1.2
Sand	SARSIL® H-15	1.278	1.511	2.674	15.4	15	1.2
Sand	Bitumen Voranstrich	0.906	0.999	2.549	9.3	23	1.1

hydrophobization degree of the analyzed materials was based on a very simple experiment, the so-called "floating on water" test.

The experiment consisted of placing a small amount of powder on the surface of water in a beaker. The following were accepted as reference materials: raw limestone powder (zero hydrophobization degree) and hydrophobic limestone powder (PH – industrial anti-explosive limestone powder) originating from the Małogoszcz Limestone Quarry (100% hydrophobization degree). The hydrophobization degree of materials modified in the work was evaluated on the basis of the quantity of powder floating on the water surface for a specified period of time.

Analysis of Flow Properties

Many methods may be applied for the evaluation of powder flow properties. Carr [22] proposed an evaluation of flowability and floodability on the basis of the physical properties of a powder. Geldart and Wong [23], according to the classification described in [24], suggest that powders in group A and some in group C may cause flushing. Methods of measuring powder flow properties are strictly standardized. The parameters obtained through such experiments are used while designing elements of apparatus equipment used for storage, transporting, or feeding of disintegrated solid particles – operations that are part of many manufacturing processes. They are less frequently applied as a criterion for comparing properties of the modified materials, especially those whose properties slightly differ from each other.

One well-known method of typifying powders, from the point of view of their flow properties, is based on densimetric measurements and the Carr procedure [22, 25-27], as well as the parameters measured with the use of the powder characteristics tester apparatus, which allows calculating the flowability and floodability of such materials.

In order to evaluate how the applied modifiers influence the flow properties of the analyzed materials, the following densimetric values were determined for raw and modified limestone powders: loose bulk density (ρ_b) and packed bulk density (ρ_{pb}). The compressibility (C), which is equivalent to Carr's index [22] as well as the dispersibility (R) of powders, and Hausner's ratio (I_H) [28], which characterizes materials from a cohesiveness point of view, were all calculated on the basis of the obtained results. Powders with a ratio larger than 1.4 possess all the properties of a cohesive powder [28].

The obtained results allow one to determine the flow properties of the analyzed materials in a numerical manner. There are also special tables [25, 26] available that make it possible for the measured parameters to be assigned appropriate ranges in flowability and floodability index values. A particular index range is typical of powders with similar flow characteristics and similar requirements regarding the application of the specialist apparatus used during powder application.

The flowability index determines the degree of ease at which a powder changes from a stationary condition to a motion condition. Its high value indicates high flowability [29]. Floodability indicates how stable the powder's liquid-like flow is. A high floodability index value suggests that it is necessary to additionally equip the apparatuses with special seals to prevent the powder from uncontrolled flushing at the stage of designing storage and flow apparatuses [30]. Both indexes were determined on the basis of tabular specifications included in the user's manual of the powder characteristics tester [25] apparatus.

The obtained measurement results as well as those calculated on their basis parameters and real densities (helium) (ρ_r), determined with the use of the AccuPyc 1340 apparatus, are presented in Table 1.

The particular ranges of the flowability index [25, 26] may be assigned to the determined compressibility values. The floodability index was evaluated on the basis of the measured dispersibility values. Free-flowing powders demonstrate dispersibility of over 50% with the corresponding floodability index range of 80-100%.

Table 2. Values of compressibility and dispersibility calculated for raw and modified powders and their corresponding ranges of flowability and floodability index values.

Material	Modifier	Compressibility, dispersibility and their corresponding index values			
		C (%)	Flowability index	R (%)	Floodability index
Meal	Lack	50.9	0-19	20	60-79
Meal	Stearic acid	39.8	0-19	42	80-100
Meal	SARSIL® H-15	44.1	0-19	16	40-59
Meal	Bitumen Voranstrich	24.9	60-69	50	80-100
Sand	Lack	22.6	60-69	19	40-59
Sand	Stearic acid	17.4	70-79	19	40-59
Sand	SARSIL® H-15	15.4	80-89	15	40-59
Sand	Bitumen Voranstrich	9.3	90-100	23	60-79

Table 2 presents the compressibility and dispersibility values calculated for raw and modified powders and their corresponding ranges of flowability and floodability index values.

Discussion of Results

Hydrophobic Properties

On the basis of the observations of the powders floating on water, it can be concluded that the majority of materials after modification acquired hydrophobic properties at the level of the hydrophobic properties of the PH material. Poorer hydrophobic properties were found in the case of material hydrophobized with the Bitumen Voranstrich preparation. The hydrophobic properties of this substance quite quickly decline with the passing of time.

The hydrophobic properties of the modified sand were evaluated similarly to the case of limestone meal. All the modified materials floated on the water surface up to the moment of complete water evaporation. This testifies that they acquired good hydrophobic properties.

Real Density

It is noticeable (Table 1) that modified materials are characterized by lower values of real density than raw powders. This fact is a positive effect of the modification process. Owing to the fact that the modification process does not increase a powder's weight, their flow properties should be superior to those of raw powders.

Flowability Index

It can be observed that the modification process resulted in reduced compressibility of all materials, which should beneficially influence their flowability. However, the material characteristics carried out on the basis of the available tables of index values demonstrates that modified meals (with the exception of the meal modified with the Bitumen Voranstrich preparation) constitute the same group of materials as raw meal, and they may be assigned the same range on the flowability index [25, 26]. Such a qualification suggests that during the flow, the materials have a tendency to settle in pipe elbows and clog their outlets. However, it may be assumed that in the case of modified powders (of lower compressibility) flow disturbances upon storage and conveyance will be present on a smaller scale than in the case of a raw material. The flowability of the meal modified with the bituminous preparation, however, improved dramatically. In this case, the phenomenon of bridging, which can be observed in silos, will take place on a minimal scale.

Sands are generally characterized by higher flowability index values than meals. This qualifies them to be part of the group of materials with very good flowability as they do not require fixing special apparatuses to counteract the disturbances of flush in silos. The modification process additionally improved the properties of sands – it can be observed that all hydrophobic sands are characterized by a higher flowability index than raw sand.

Floodability Index

Both meals modified with stearic acid and the bituminous substance are characterized by dispersibility, thereby allowing one to assign the highest range of floodability index values to these materials (Table 2). In the case of these materials, the necessity may arise to implement special precise seals of apparatuses suitable for use with powders [30]. The determined dispersibility of the remaining materials is generally comparable for raw and modified materials. Therefore, it appears that in such a situation it would be better to apply dispersibility directly instead of the floodability index as the criterion for the evaluation of a powder's flow properties. Such an approach toward the issue allows one to more precisely estimate material properties on the basis of the measured values. It is especially true since, according to Svarovsky [31], it is dispersibility that is the principal value applied to assess a powders' vertical flow ability, characterizing the tendency of a grain material layer to transform to a powder condition. In this context, the influence of the modification processes on the flow nature of powders can be evaluated already on the basis of very small changes of dispersibility.

Taking into account the fact that generally the limestone meal modified with stearic acid and the meal and sand modified with the bituminous preparation achieved a considerable increase in the dispersibility value in relation to the raw material, it should be assumed that precisely these modifiers are best for improving the flow properties of powders.

Hausner's Ratio

The values of Hausner's ratio calculated on the basis of experimental data (Table 1) for all meals, with the exception of the meal modified with the bituminous preparation, are larger than 1.4 [28], which testifies that both the raw material and the modified one possess the properties of a cohesive powder. However, it can be observed that the modification process resulted in a decrease in cohesive interactions between grains, and this is demonstrated by the lower value of Hausner's ratio for hydrophobic materials.

Raw sand is characterized by a lower value of the ratio than the limit value for cohesive materials, but similarly as in the case of the meal, the modification process led to a decrease in Hausner's ratio, i.e. to reducing cohesive interactions.

Conclusions

The conducted series of tests allowed one to determine basic properties of powder, such as: loose and packed bulk density, compressibility, and dispersibility. It also made it possible to calculate Hausner's Ratio [26, 27], i.e. the parameter applied in modern techniques of a powder materials' evaluation [29]. The obtained results were used to assess the direction of changes of flow properties of limestone powders that were caused by the hydrophobization process. Familiarity with such characteristics is useful for the designing of devices and apparatuses suitable for use with powder materials or for the proper execution of such processes.

On the basis of the obtained results, one may conclude that the change of hydrophobic properties of limestone powder exerts a beneficial influence not only on their water-resistance, but it also reduces their cohesive properties and improves their flow properties, and this in turn enhances their feeding, conveying, and storage. It also was established that the hydrophobization processes with the use of stearic acid and the Bitumen Voranstrich preparation as modifiers had the most beneficial effect as far as flow properties of limestone powders are concerned. The modification process maintained the limestone powders' flow abilities. The application of waterproof powders is more profitable than the use of raw limestone material.

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