

The influence of additives on rheological properties of limestone slurry

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Abstract. Limestone slurry appears in the lime production process as the result of rinsing the processed material. It consists of particles with diameter smaller than 2 mm and the water that is a carrier of solid fraction. Slurry is directed to the settling tank, where the solid phase sediments and the excess water through the transfer system is recovered for re-circulation. Collected at the bottom of the tank sludge is deposited in a landfill located on the premises. Rheological properties of limestone slurry hinder its further free transport in the pipeline due to generated flow resistance. To improve this state of affairs, chemical treatment of drilling fluid, could be applied, of which the main task is to give the slurry properties suitable for the conditions encountered in hydrotransport. This treatment consists of applying chemical additives to slurry in sufficient quantity. Such additives are called as deflocculants or thinners or dispersants, and are chemical compounds which added to aqueous solution are intended to push away suspended particles from each other.

The paper presents the results of research allowing reduction of shear stress in limestone slurry. Results demonstrate rheological properties of limestone slurry with and without the addition of modified substances which causes decrease of slurry viscosity, and as a consequence slurry shear stress for adopted shear rate. Achieving the desired effects increases the degree of dispersion of the solid phase suspended in the carrier liquid and improving its ability to smooth flow with decreased friction.

1. Introduction

Solid-liquid transport appears frequently in many industrial applications, like for instance in chemical engineering, mining industry and power plants. Such transport depends on several parameters, like: concentration of solid particles, slurry velocity, particles diameter, pipe diameter, terminal velocity, liquid and solids density, carrier liquid viscosity, flow geometry and rheological properties [1]. If limestone slurry is considered we recognize settling and non-settling flow. The settling flow can be with stationary or moving bed while the non-settling slurry flow can be homogeneous or pseudo-homogeneous. When all the particles have the same density, the larger particles always form the lower layer, however if the particle sizes are sufficiently different, the separation may appear. The non-settling slurries usually exhibit non-Newtonian character and they exhibit the yield stress. Those with very fine solid particles demonstrate increased viscous sublayer, which means that damping of turbulence may appear in the near-wall region. Slurry turbulence in the region close to a pipe wall was examined by scientists like Nouri and Whitelaw [2], Schreck and Kleis [3]. They concluded that ejection-sweep cycle is affected strongly by particles, and slip velocity decreases with solids concentration increase. A review of experimental studies on turbulence



modification by particles is given by many researchers [4,5,6,7]. In order to build mathematical model of such slurry flow, the starting point is to determine proper rheological model. In contrast with that, if slurry with coarse solid particles is considered, it is reasonable to assume the Newtonian model, as now one can measure rheology in such slurries [8].

The main objective of the research is to investigate reduction of shear stress in limestone slurry by applying selected chemical additives. A sufficient addition dosage significantly decreases the effect of particle size on the flow ability of limestone slurries. In order to find a best chemical additive for shear reduction in limestone slurry the influence of various doses of additives in relation to three arbitrary chosen solids concentrations of slurry, equals 30%, 40% and 50% by mass, is demonstrated. rheological behaviours of limestone slurry have been investigated using rotational viscometer.

2. Lime production process

During the lime production process the pipeline transport of limestone slurry is carried out. Limestone slurry arises from rinsing of stones during production process. Such slurry is a finely-granular solid phase and the water is added as a carrier liquid of the solid phase. It flows by turbulent traffic and is usually accompanied by moving bottom sediment. Limestone slurry is directed to the settling tank (natural reservoir), in which the solid-phase fraction sediments and the excess water, through the transfer system, is recycled back to the process of rinsing of stones.

One of the methods for reducing the frictional pressure loss and therefore the pump discharge pressure requirements, when transporting viscous, often non-Newtonian slurries and pastes in pipelines, is the method of reduction of the degree of flocculation of particles in the slurry using suitable chemical additives. Adding soluble ionic compounds to flocculated slurries can result in substantial pressure drop reduction in a pipe flow. The ionic compounds disperse the particles, thereby breaking up the flocculated particle network that gives rise to higher shear stresses in a pipe flow. In order to disperse particles, the charge on their surfaces needs to be of the same sign and the higher the charge the greater the repulsive forces between particles [9].

3. Use of additives to dispersed particles in limestone slurry

In order to improve rheological properties of limestone slurry, the chemical processing is used, of which the main task is to give the slurry properties suitable for the conditions encountered in pipeline transport. Such processing consists of adding chemical compounds, usually polymeric substances. Quantity and quality of added substances is crucial, similarly to the character of its interactions with the slurry. Added substances should stabilize limestone slurry and strengthen its structure, which causes increase of degree of solid phase dispersion and improving its ability to create sludge. However, the main important task is to reduce viscosity of the slurry. In lime production process the viscosity increases as the result of saturation of the slurry by dust particles. Another significant issue is to prevent the sedimentation of solid particles on the wall of horizontal pipelines, which causes its clogging. To avoid this undesirable state of things slurry should have suitable fluency.

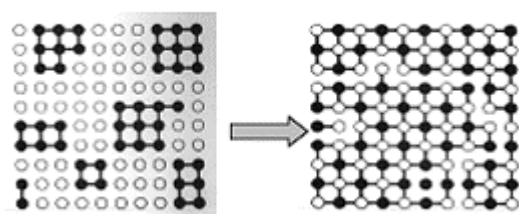


Figure 1. The mechanism of dispersion agglomerates of molecules occurring in the deflocculating process.

Source: <http://www.vekamaf.com.pl/>

Dispersing agents are commonly used in mining industry in order to reduce viscosity and yield stress of limestone slurry. Dispersants increase the liquidity of slurry through its rarefaction which enables introducing more solid particles to slurry without changing its fluency nature - Figure 1. Occurring inside the slurry structure process is explained by combining short chain links of dispersant

substances containing negative charge with the positive charge of solid particles by the action of electrostatic forces. After absorbing the polymeric substances occurs the neutralization of positive charge of solid particles which result in disappearing electrostatic forces between the molecule suspensions and polymer-molecular complexes are gaining a negative charge. It leads to the disintegration of aggregates of solid particles.

4. Experimental studies on influence of selected chemical additives on rheological properties of limestone slurry

4.1. Experiments

The first step in experiments was determination of the curve of grain for the slurry contaminated by dust processed raw limestone. Granulometric analysis was carried out on the laser diffraction particle analyzer for wet dispersion and particle size in the range from $0.01\mu\text{m}$ to $3500\mu\text{m}$. Measured particle sizes of the limestone slurry were in the range from $0.52\mu\text{m}$ to $143.9\mu\text{m}$. The value of average particle diameter in the tested slurry is close to $27\mu\text{m}$, which is presented in Figure 2.

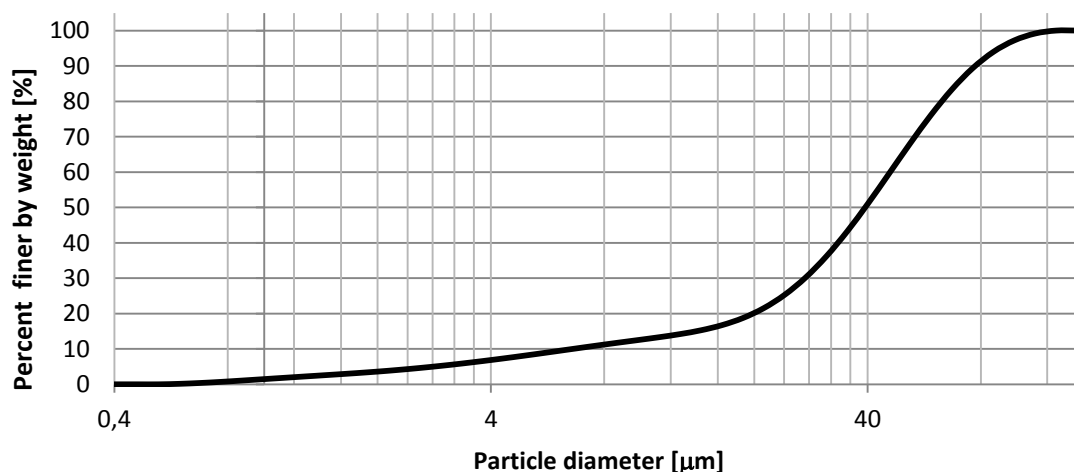


Figure 2. The grain size curve of limestone slurry. Measured by using Mastersizer 3000.

As the result of analysis, three types of fraction have been separated: fraction of clay, dust and sand. The highest percentage in the sample are the particles of dust fraction (64.19%) with diameter in the range of 2-50 microns. Clay fraction with an average grain diameter less than 2 microns is 3.38%, while the phase of sand with grain diameter greater than 50 microns is 31.98% of all particles, which is seen in Table 1.

Table 1. Percentage content of grain fraction in limestone slurry. Measured by using Mastersizer 3000.

Fraction	Clay	Dust	Sand
Grain diameter [μm]	< 2	$2 \div 50$	> 50
Percentage content	3.38%	64.19%	31.97%

Chemically tested limestone slurry consists mostly of calcium oxide (CaO – 73.64%) and silicon oxide (SiO_2 - 13%). Other chemicals included in particulate form part mineral are as follows: MgO –

0.61%, Fe_2O_3 – 0.32%, Al_2O_3 – 1.11% and SO_3 – 0.28%. Humidity of tested samples was 96.67%. Density of solids is 2720 kg/m^3 .

Laboratory tests were carried out for three different mass concentrations of limestone slurry: 30%, 40% and 50%. Mass concentration (C_m) determines the percentage content of solids in total weight of limestone slurry (1):

$$C_m = \frac{m_s}{m_s + m_l} \cdot 100\% \quad (1)$$

where:

C_m – mass concentration of solid particles (%)

m_s – mass of the solid phase (kg)

m_l – mass of the liquid phase (kg)

Sampling material needed to measure solid phase mass concentration took place by collecting and drying three samples of 100 ml each to obtain the averaged values.

4.2. Compounds used in the experiments

In the final stage of lime production process, slurry is subjected to sedimentation in order to separate the solid phase from it. Sludge collected on the bottom of the tank after gravity thickening is directed to the sedimentary reservoir located at a considerable distance from the plant. Its further transport by pipeline system is difficult because of its rheological properties. Applying suitable chemical additives in proper dose are intended to push away suspended particles and increase its fluency. To the group of such substances, called deflocculants, belongs among others sodium water glass. It is an aqueous solution of sodium silicate having the characteristic of colloid or polymer, high viscosity and density 20% - 70% more than the water.

Another dispersant used in experimental studies is known as calcareous groats. This substance is byproduct of limestone production process and so far has not found its industrial application. Calcareous groats is a remnant of lime slaking process by which the hydrated lime is formed. In the final step of lime slaking takes place the process of hydration lime and water mixture in suitable mixing chamber. The waste materials in form of heavier particles of the lime that have not been slaked and unburned lime stone sink at the bottom of the chamber and are periodically removed outside by the trigger aperture located in the lower chamber of the mixer. Obtained hydrated lime is subjected to two-stage separation process in order to separate it from contaminants. Hydrated lime is a finished product, while the remains of the separation are called calcareous groats and is presented in Figure 3.



Figure 3. Substance arisen as a result of limestone production process - calcareous groats. Made with a digital camera.

A mixture of these two substances (sodium water glass and calcareous groats) added to limestone slurry can act as dispersant. Its task is to repel particles in suspension from each other to dilute, which would facilitate its further transportation by pipeline. The analyzed substance is formed by mineral particles with grain diameter less than 1.8 mm and average particle diameter equals 240 μm . Chemically calcareous groats mostly consist of the calcium and magnesium oxide (70.81%), silicon dioxide (1.52%) and alumina (0.84%). Other substances (25.91%) are minor contamination caused by the hydration of lime and water mixture. The chemical composition of hydrated lime is shown in Table 2.

Table 2. Analysis of the chemical composition of calcareous groats and limestone slurry.
Source: Laboratory of TRZUSKAWICA S.A.

Chemical composition	Calcareous groats [%]	Limestone slurry [%]
CaO	70.58	73.64
MgO	0.23	0.61
Fe ₂ O ₃	0.56	0.32
SiO ₂	1.52	13
Al ₂ O ₃	0.84	1.11
SO ₃	0.36	0.28
other	25.91	11.04

4.3. Methods of measurements

To test the effect of selected chemical additives on the rheological properties of limestone slurry laboratory tests were carried out. They included investigations of the influence of varied doses of sodium water glass and calcareous groats on limestone slurry. The concentrations of additives were 0.1%, 0.2%, 0.3%, 0.4%. Compounds were applied in the ratio 1:1 each substance in order to obtain the wanted dose. The study included measurements of rheological properties of limestone slurry in three mass concentrations: 30%, 40% and 50% after applying chemical additives. Measurements were carried out on rotational viscometer in the measuring system of the coaxial cylinders with the gap 1.1 mm. The tests were performed at 20°C for samples having volume of 18 ml. The experiments were focused on comparison of shear stress versus shear rate for different quantity of chemical additives in the range of the shear rate from 1 to 300 s^{-1} .

4.4. Results of measurements

Figure 4 shows generated in the samples shear stress values for adopted shear rate. Received measuring points demonstrate the properties of limestone slurry with mass concentration of 30% after adding various doses of combination of sodium water glass and calcareous groats in proportion 1:1. As a reference for received points of additives in amounts of 0.1%, 0.2%, 0.3% and 0.4% related to the dry matter contained in the slurry a curve for pure limestone slurry was used.

As we can see, the addition of combination of chosen chemicals at dose 0.3% and 0.4% does not improve rheological properties of slurry but even worsens it. Addition of lower doses of additives affects reduction of shear stress in wide range of shear rates. The largest decrease of shear stress in slurry was obtained after applying an amount of 0.2% of chosen additives, which means that the dose of best proportion is of 0.1% of each substance: sodium water glass and calcareous groats in relation to dry mass of limestone slurry.

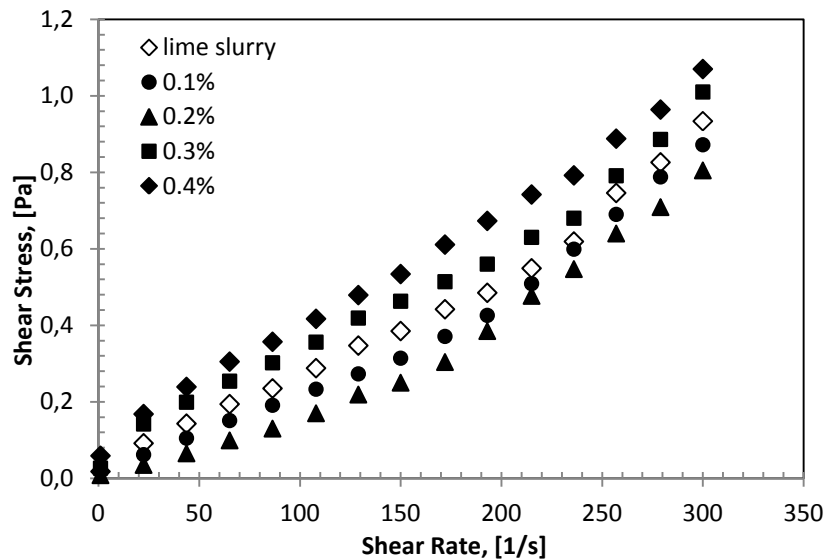


Figure 4. Influence of various doses of sodium water glass and calcareous groats on shear stress values in limestone slurry with mass concentration $C_m = 30\%$. Measured by using rotational viscometer MCR 302.

If high mass concentration of limestone slurry is considered ($C_m = 40\%$) we can observe a clear decline of shear stress even for small doses of compound mixture (0.1%, 0.2%, 0.3%) for shear rate in the range from $300 \text{ [s}^{-1}]$ to $1 \text{ [s}^{-1}]$. The best influence on decreasing the shear stress can be noticed for dose of 0.1% of sodium water glass and calcareous groats. The highest stress values were measured in the sample with 0.4% of proposed mixture of substances, which Figure 5 demonstrates.

It is worth mentioning that experimental data, which are presented in Figure 5, show that for the shear rate higher than $260 \text{ [s}^{-1}]$ observable increase of the shear stress appears. This could be due to the fact that transitional flow regime appears for such a high shear rate and for the gap between the rotor and the cylinder equal 1.1 mm .

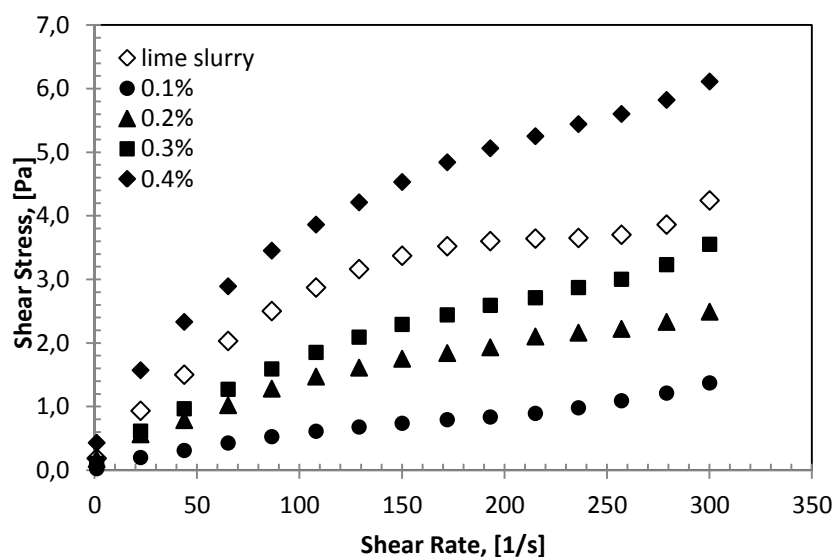


Figure 5. Influence of various doses of sodium water glass and calcareous groats on shear stress value in limestone slurry with mass concentration $C_m = 40\%$. Measured by using rotational viscometer MCR 302.

If slurry with solids concentration equalling 50% by mass is considered (Figure 6) we can see that there is no decrease of the shear stress if chemical additives are included. This lack of influence probably results from very small amounts of added substances in relation to dry matter content in slurry with such high mass concentration. Only a dose of 0.4% of proposed substances has an effect on slight decrease of received stresses values. But even this amount resulted only in approach the analyzed curve to the graph of pure limestone slurry without any additives. It is also interesting that the effect of using a dose of 0.1% and 0.4% is almost the same. It seems necessary to carry out laboratory studies for higher concentrations of used additives in order to find optimal dosage.

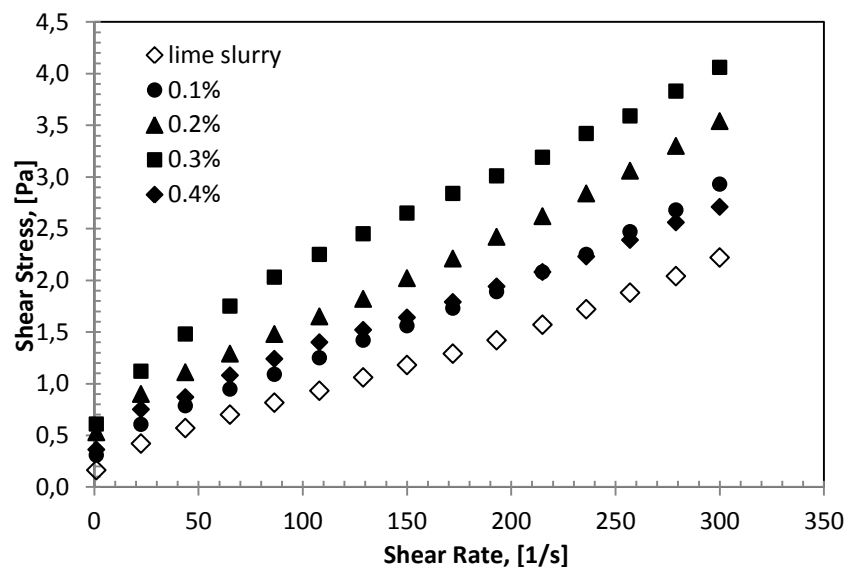


Figure 6. Influence of various doses of sodium water glass and calcareous groats on shear stress value in limestone slurry with mass concentration $C_m = 50\%$. Measured by using rotational viscometer MCR 302.

5. Conclusions

The analysis of the influence of various doses of sodium water glass and calcareous groats on rheological properties of limestone slurry gives to some extent a response to the question regarding the amount of substances needed to apply to slurry with $C_m=30\%$ and $C_m=40\%$ to reduce flow resistance. However, it seems to be necessary to perform tests in a wider range of doses of additives to limestone slurry with a mass concentration of solid particles equal to 50%.

The presented results of the research show how it is difficult to predict the effect of modifying chemical substances on the tested material. In order to stabilize rheological parameters of slurry, a dosage of additives should be selected appropriate to mass concentration of solids included in limestone slurry. Simple viscosimetric tests allow a proper selection of kind of mineral compounds. It should be noted however, that the chemicals used in the research are easy to access and they are cheap. We proved the positive influence of such chemical additives for reduction of frictional head loss in pipeline transportation of slurry in the range of solids concentration from 30% to 40% by mass. Reduction of frictional head loss makes it possible to decrease energy consumption for transportation of one tone of dry slurry per hour.

6. References

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