Influence of deflocculants on shear stress in hydromixture flow

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Abstract. The paper presents experimental studies on influence of two arbitrary chosen additives on wall shear stress in hydromixture, which consists solid particles of averaged diameter 0.05 mm. Experiments were performed for two mass concentration of solids equal to 20% and 43%. Measurements were performed for varied doses of deflocculants in three different proportions in wide range of shear rates. Experiments confirmed influence of chosen additives on decreasing hydromixture viscosity and as a consequence decreasing of shear stress. The analysed process is complex and strongly depends on doses of deflocculants and solids concentration. However, the rheological property of such mineral suspension is complex and there is no single parameter that can solely explain it. Physical and chemical properties affect on the level of interparticle interaction or aggregation and therefore it is useful to control them in industrial process such as transportation of slurries.

1. Introduction

Process of lime production causes that wasted minerals appears in large amount during rinsing process of lime stones. Wasted minerals are continuously transported to selected landfill using water as a carrier liquid. Unfortunately, the solids are transported with low solid mass concentration. That circumstances cause that such process requires much amount of water and energy to feed centrifugal pumps. To improve properties of hydromixture during its flow in pipeline, mechanical and chemical methods are considered to deal with. Mechanical methods are focused on especially designed grooves or mechanically deformed pipes. Chemical methods are using deflocculants mainly in order to decrease of hydromixture viscosity and as a consequence decrease shear stress. Presence of solid particles in a carrier liquid could increase or attenuate turbulence and depends on solid sizes, flow conditions and carrier liquid properties [1-5].

The paper presents method of increasing solids concentration of wasted minerals during its transportation by adding two components to hydromixture in order to reduce the wall shear stress in a flow.

2. Hydromixture flow

2.1. Types of hydromixture flow in pipeline installation

Horizontal flow of hydromixture consisting of fine solid particles and water, as a carrier phase, can occur in several ways. Due to several factors, like interaction between particles, particle diameter, critical velocity of a hydromixture at which the bottom sediment forms, and the rate of settling of solid particles, four different flow regimes can be distinguished [6]:
- homogeneous or pseudo-homogeneous flow, characterized by a homogeneous distribution of solid particles in a flow cross section,
- heterogeneous flow in which all particles remain in suspension or heterogeneous with bottom sediment moving by leaps,
- flow with moving bottom sediment (sliding bed),
- flow with stationary bottom sediment (fixed bed).

For hydromixture consisting of liquid and fine dispersed solid phase with a moderate ratio of particles density to the liquid phase density and at corresponding high flow rates, homogeneity of flow is usually assumed [7]. Such hydromixture can be classified as monophasic liquid with increased viscosity and density. When hydromixture flow with moderate velocity is considering we usually deal with pseudo-homogeneous flow. At sufficiently high velocities, the momentum forces dominate, while the share of other forces acting on particles is negligibly small. In this case, solids contained in hydromixture are evenly distributed in the flow cross-section [1]. For low flow velocities, bottom sediment appears, which can be fixed or sliding. The formation of bottom sediment is an undesirable phenomenon leading to a drop in flow rate or even clogging of pipeline.

Figure 1 presents the velocity distribution in horizontal pipeline of transported hydromixture in cross-section; average volume concentration of solid phase in the flow cross-section and transport concentration of solid phase in the unit of cross-section for mentioned flow types.

| Hydromixture velocity $v_r$ [m/s] | Volume concentration $C_v$ [%] | Transport concentration $C_{vt}$ [%] |
|----------------------------------|---------------------------------|-------------------------------------|
| Homogeneous                      | ![Homogeneous](image1)         | ![Homogeneous](image2)              |
| Heterogeneous with full suspension| ![Heterogeneous full suspension](image3) | ![Heterogeneous full suspension](image4) |
| Heterogeneous with rolling and saltation | ![Heterogeneous rolling and saltation](image5) | ![Heterogeneous rolling and saltation](image6) |
| Sliding bed                      | ![Sliding bed](image7)         | ![Sliding bed](image8)              |
| Fixed bed                        | ![Fixed bed](image9)          | ![Fixed bed](image10)               |

**Figure 1.** Types of hydromixture flow – horizontal pipeline [7].

2.2. Hydromixture flow in lime production process
Pipeline transport of fine-grained solid particles and water, named as hydromixture, appears in a lime production process. In the final stage, hydromixture is subjected 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. The research is focused on applying deflocculants with a defined composition and serve them to transported hydromixture in order to be able to increase solids concentration and making process economically efficient. This may also an effect on increasing the flow rate without increasing the energy consumption of the pumps or pumps system. Another advantage of proposed solution would be reduction of water consumption, which has been used as a carrier liquid.

2.3. Physical properties of hydromixture
Sample of hydromixture used in experiments was procured from lime production process. In order to determine mass concentration of tested material, three samples of 100 ml each were collected and dried to obtain averaged values. Laboratory tests were carried out for two different mass concentrations of hydromixture equal to 20% and 43%. Mass concentration determines the percentage content of solids in total weight of hydromixture.

Granulometric analysis was carried out on the particle size analyser, named Mastersizer 3000, in the range from 0.01 to 3500 μm. Measured particle sizes of hydromixture were in the range from 0.5 to 163.5 μm. The averaged particle diameter was 45.5 μm. Table 1 shows percentage content of grain sizes with different particle diameter in tested hydromixture.

| Grain size (μm) | Content (%) |
|----------------|-------------|
| 0 ÷ 2          | 6.5         |
| 2 ÷ 50         | 82.4        |
| 50 ÷ 163.5     | 11.1        |

As the result of analysis, three types of fractions have been separated. Dust fraction with diameter in the range of 2-50 μm is the highest percentage in the sample (82.4%). Sand fraction with an average grain diameter greater than 50 μm is 11.1%, while the phase of clay with grain diameter smaller than 2 μm is 6.5% of all particles.

Chemically, tested hydromixture consists mostly of calcium oxide (CaO – 73.6%) and silicon oxide (SiO2 – 13%). Other chemicals included in sample are: MgO – 0.6%, Fe2O3 – 0.3%, Al2O3 – 1.1% and SO3 – 0.3%. Others, unidentified substances constitute about 11.1% of the sample.

2.4. Decreasing shear stress in hydromixture flow by using deflocculants
Deflocculants are used in order to reduce shear stresses in hydromixture and to improve conditions encountered during its flow in a pipeline. Adding thinners or any other chemical compounds to flowing medium is chemical processing. It is vital that quantity and quality of added substances should be adapted to physical and chemical properties of hydromixture. Very important is also character of interactions of deflocculants with hydromixture. Added substances should stabilize hydromixture and improve its ability to disperse solid particles in order to increase its fluency. However, the main task is to reduce viscosity of hydromixture and therefore the shear stress. In describing case, value of viscosity and shear stress increases as the result of saturation by dust particles derived from the processed raw material.

3. Experimental studies
The experiments were performed in Laboratory of Rheology at the Kielce University of Technology. To determine the effect of tested deflocculants on shear stress in hydromixture for adopted shear rates, a rotational viscometer Anton Paar MCR 302 was used. Measurements were carried out in systems of coaxial cylinders with measuring gap equals to 1.1 mm for samples of 18 ml volume in temperature of 20°C. Experimental studies included investigations of the influence of varied doses of deflocculants on
rheological properties of hydromixture. Additives were added in concentrations of 0.1%, 0.2%, 0.3%, 0.4% and 0.5%, according to dry mass of solid particles in three different ratio of each substance. Studies were carried out for hydromixture with two mass concentrations: 20% and 43% after 10 seconds of mixing with $\partial U/\partial y=200$ [1/s]. Measurements of shear stresses versus shear rates in the range from 1 to 1000 [1/s] were performed.

3.1. Characteristic of deflocculants used in the experiment

Compounds used in the experiments are calcareous groats and sodium water glass. These two substances are used as deflocculants – chemical additives intended to push away-suspended particles from each other and increase fluency of hydromixture.

Calcareous groats is a side-product of the lime production process. It is a remnant of lime slaking process by which the hydrated lime is formed. In the final step of lime slaking the hydration of lime and water mixture in suitable mixing chamber takes place. Waste materials that have not been slaked and unburned, sink at the bottom of the chamber. Next, they 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 selling as a finished product, while the remains of the separations are called calcareous groats [2].

Figure 2 and 3 presents image of the surface of calcareous groats made by scanning electron microscope. Figure 3 presents micro-scale features of tested sample made with 12000 magnifications after application of 10kV electron-accelerating voltage.

![Figure 2. Image of the surface of calcareous groats made by using Scanning Electron Microscope Phenom Pro X after application of 15kV electron-accelerating voltage.](image)

![Figure 3. Image of the surface of calcareous groats made in 12000 zoom by using Scanning Electron Microscope Phenom Pro X.](image)

| Element Number | Element Symbol | Element Name | Atomic Concentration | Error |
|----------------|----------------|--------------|----------------------|-------|
| 20             | Ca             | Calcium      | 13.1                 | 0.0   |
| 8              | O              | Oxygen       | 79.7                 | 0.1   |
| 6              | C              | Carbon       | 2.2                  | 0.9   |
| 53             | I              | Iodine       | 0.2                  | 0.0   |
| 7              | N              | Nitrogen     | 4.3                  | 2.1   |
| 12             | Mg             | Magnesium    | 0.5                  | 0.8   |
Table 2 includes results of measurements of chemical microanalysis made by Energy Dispersive X-Ray Spectroscopy in conjunction with SEM.

Another deflocculant used in experimental studies is well known dispersant sodium water glass (also liquid glass). Aqueous solution of sodium silicate is characterised by high viscosity and density even 20-70% more than the water. Table 3 presents main properties of this substance.

Table 3. Physical and chemical properties of sodium water glass.

| Properties                  | Na₂SiO₃                                      |
|-----------------------------|---------------------------------------------|
| Chemical formula            | Na₂SiO₃                                     |
| Appearance                  | thick liquid                                 |
| Density                     | 2.61 g/cm³                                   |
| Specific gravity            | 1.39 g/cm³ (20°C)                           |
| Melting point               | 1.088°C                                     |
| Solubility in water         | 22.2 g/100ml (25°C)                         |
| pH                          | approximately 11.3                          |

A mixture of calcareous groats and sodium water glass was added to hydromixture and used as deflocculants in experimental studies.

3.2. Results of measurements
The rheological theory of concentrated hydromixture is strongly related to the viscosity-dependence on the particle size. From this point of view, the investigation of rheological behaviour of tested raw material with respect to particle size and distribution is necessary.

![Figure 4](image-url) Dependence of the wall shear stress on different samples of deflocculants and its doses for three arbitrary chosen values of shear rates in hydromixture with two different mass concentrations.

The paper presents experiments on influence of two arbitrary chosen deflocculants, which are sodium water glass, denoted as d₁, and calcareous groats, denoted as d₂, on wall shear stress in tested
hydromixture. An average diameter of solids included in hydromixture was 0.05 mm. Solids concentrations in hydromixture was equal to 20% and 43% by mass. Measurements of wall shear stress for different shear rates in hydromixture with varied doses of mixed deflocculants were performed in the range of shear rates up to 1000 [1/s].

Figure 4 presents dependence of the wall shear stress on different samples of deflocculants for hydromixture with mass concentration 20% and 43% by mass. Measurements of wall shear stress for different shear rates in hydromixture with varied doses of mixed deflocculants were performed in the range of shear rates up to 1000 [1/s].

On the bases of presented results of experiments we can observe that influence of chosen additives on shear stress is complex and depends on solids mass concentrations of tested hydromixture and doses of deflocculant samples. As we can see, for hydromixture with 43% of solid mass concentration, the lowest wall shear stress refers to additive of deflocculants in proportion (2/3∙d1+1/3∙d2) for doses in the range of 0.1% to 0.5% for three arbitrary chosen values of shear rates, equal to (200; 600; 1000) [1/s].

Figure 4. Flow curve of hydromixture with mass concentration Cm=20% with additive of 0.1...0.5% of deflocculants measured after 10 seconds of mixing at ∂U/∂y=200 [1/s].

Figure 5 shows shear stress versus shear rate for raw hydromixture with deflocculants in proportions of (1/2-d1+1/2-d2). As we can see, the addition of combination of chosen chemicals at dose 0.1% and 0.2% in relation to dry mass included in hydromixture with Cm=20% do not improve its rheological properties but even worsen it. Addition of higher doses of deflocculants affect on reduction of shear stress arisen in hydromixture in wide range of shear rate. The largest decrease of shear stress was obtained after application of 0.5% of deflocculants into hydromixture. Results of measurements of generated shear stress and viscosity values for analyzed hydromixture are presented in Table 4.

Figure 5. Flow curve of hydromixture with mass concentration Cm=20% with additive of 0.1...0.5% of deflocculants measured after 10 seconds of mixing at ∂U/∂y=200 [1/s].

Table 4. Measured values of shear stress and viscosity generated in hydromixture with mass concentration of 20%.

| Shear Rate [1/s] | Cm 20% | Cm 20% + 0.5%·(1/2-d1+1/2-d2) |
|------------------|------------------|-----------------------------|
|                  | Shear Stress [Pa] | Viscosity [Pa·s]            | Shear Stress [Pa] | Viscosity [Pa·s] |
| 1000             | 3.350             | 0.00335                     | 2.680             | 0.00268            |
If higher mass concentration of hydromixture is considered ($C_m=43\%$) we can observe clear decrease of shear stress for all doses of deflocculants in full range of shear rates. The best influence on decrease the shear stress we can notice for dose of 0.5% of sodium water glass and calcareous groats in relation to dry mass of hydromixture. Data presented in Figure 6 demonstrate shear stresses in hydromixture, which includes deflocculants in proportions of $(1/2 \cdot d_1+1/2 \cdot d_2)$.

![Figure 6. Flow curve of hydromixture with mass concentration $C_m=43\%$ with additive of deflocculants from 0.1% to 0.5% measured after 10 seconds of mixing at $\partial U/\partial y=200 \ [1/s]$.](image)

Experimental data presented in Table 5 show observable decrease of viscosity and shear stress using dose of deflocculants equals to 0.5% in proportions of $(1/2 \cdot d_1+1/2 \cdot d_2)$.

| Shear Rate [1/s] | $C_m 43\%$ | $C_m 43\% + 0.5\% \cdot (1/2 \cdot d_1+1/2 \cdot d_2)$ |
|-----------------|-------------|--------------------------------------------------|
| 1000            | 7.850       | 6.220                                            |
| 900             | 7.310       | 5.560                                            |
| 800             | 6.760       | 4.990                                            |
| 700             | 6.210       | 4.440                                            |
| 600             | 5.640       | 3.900                                            |

| Shear Rate [1/s] | $C_m 43\%$ | $C_m 43\% + 0.5\% \cdot (1/2 \cdot d_1+1/2 \cdot d_2)$ |
|-----------------|-------------|--------------------------------------------------|
| 1000            | 0.00785     | 0.00622                                          |
| 900             | 0.00812     | 0.00618                                          |
| 800             | 0.00845     | 0.00624                                          |
| 700             | 0.00888     | 0.00635                                          |
| 600             | 0.00940     | 0.00651                                          |
Results of experiments confirmed that influence of additives on shear stress is strongly depending on proportion and doses of deflocculant in samples. In order to decrease viscosity in hydromixture, and as a consequence the shear stress, proper proportion of additives related to dry mass of hydromixture has to be applied.

4. Conclusions
Influence of solids concentration of hydromixture on rheological properties is significant since various ranges of solids concentration can lead to different types of flow curves. Rheological behaviour of tested hydromixture is pseudo-plastic (shear-thinning). The degree of its pseudo-plasticity increases with increasing solids concentration. Results of research proved that addition of small amount of suitable thinner can improve flow-ability of hydromixture by decreasing its viscosity. This can enhance the energy efficiency of hydromixture transport.

Presented analysis of the influence of various doses of sodium water glass and calcareous groats gave response to a question regarding the amount of substances needed to apply in hydromixture with mass concentrations equal to 20% and 43% in order to reduce flow resistance and then to increase solids concentration. Generally, after addition of 0.5% of deflocculants in proportions of \((1/2 \cdot d1 + 1/2 \cdot d2)\) by mass, the viscosity of hydromixture is lowest in both mass concentrations. The gradual increase of deflocculant from 0.1% up to 0.5% leads to reduction of shear stress in all investigated ranges of shear rates.

Additives used in the research are easy to access and are commercially cheap. Proposed solution can decrease shear stresses in hydromixture flow for about 20% for both mass concentrations. Such reduction causes that it is possible to decrease energy consumption for further transportation of hydromixture to natural reservoir, and decrease volume of water serving as a carrier liquid.

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