Analysis of Rheological Models of Selected Cement Slurries

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Analysis of Rheological Models of Selected Cement Slurries

Cement slurries become more and more widely applicable in reinforcing and strengthening the rock mass. The processes taking place in fresh cement slurries were presented and their complex character analysed. The equations describing rheological models, e.g. cement slurries, were given. The selected cement slurries were analysed in laboratory conditions for various water-cement parameters and three temperatures. The obtained results were statistically analysed and the best fit of the rheological model to the individual cement slurries was shown.

Key words: *cement slurries, rheological model, plastic viscosity, cementing in drilling wells, water – cement parameter.*

Introduction

The development of the cement industry results in broader and broader offers of cement products. This is especially important for the individual customers who use cements in various technical and technological conditions. Three products of "Górażdże Cement S.A." were selected in view of their applicability in drilling and geoengineering works (Godet a kol, 2000). These are:

- Portland cement CEM I 52.5 R,
- Portland ash cement CEM II/A - V 32.5 R,
- low-alkaline metallurgical cement CEM III/A - 32.5 NA.

These cements were analysed in laboratory conditions. The rheological models were defined as they often have a decisive influence on the efficiency of strengthening and sealing operations in the rock mass.

Processes taking place in fresh cement slurries

Cement slurries are complex dispersion systems having considerable specific surfaces where complex time-related hydration reactions take place (Grzeszcyk,1991; Grzesczyk, 1988; Stryczek, 1998). The structure of such a system mainly depends on the water-to-cement ratio, ranging from 0.5 to 1.0, depending on the literature source. Other factors influencing the structure of the cement slurry are adsorption effects, existing surface charges and ionic concentrations (Grzesczyk, 1988).

High reactivity of cement, especially the clinker phase C_3A to the slurry fluid causes that during the experiment all the grains are covered with a layer of gel consisting of a mixture of hydrated silicates and calcium aluminosilicates.

The mutual mobility of grains is principally due to the quantity and type of products of this process at the initial stage of hydration. On the other hand, the chemical and mineral composition of non-hydrated cement grains affects the physical and chemical properties of the formed gel layer. The distribution of charge on the surface of colloidal particles and solid concentration determine intergranular forces and have an influence on ordering of grains in the shear structure, and so on the behaviour of the slurry when subject to external forces.

The formation of a layer of water having a regular structure on solid surfaces plays an important role in the formation of rheological properties of sealing slurries, cement slurries in particular. The inner zone having a regular structure gradually changes into a transient zone where the particles of the slurry are distributed at random, to become an external zone of water solution.

The size of the inner and transient zones decides about the viscosity of the sealing slurry. Depending on the magnitude of the surface solids charge the width of the diffusion zone and forces acting on ions in the remaining solution change as well. Owing to a considerable reactivity of cement phases to water, the rheological properties of the sealing slurry mainly depend on the type and quantity of cement hydration products (except for water- to-binder ratio and dispersion of hydraulic binder); the character of the clinker phase surfaces is of lesser significance here. Another factor influencing the structure of the fresh cement slurry is the mineral composition of cement, which eventually influences the course of hydration itself. In the course of cement hydration

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processes a considerable portion of gypsum gets to the slurry, and the liquid phase gets saturated with the ions Ca^{2+} and SO_4^{2-} and the alkalies contained in cement. Within a few minutes span of time a certain quantity of ettringite is formed. If it makes a compact layer on the grains of cement, it has no significant impact on the rheological properties of the slurry. The initial reaction of alite with water at the induction stage also does not influence the structure of the slurry when it is mixed to sever the hydrates from the surface of grains. After the induction period the crystallisation of calcium hydrate and accelerated hydration of alite result in a considerable growth of viscosity of the slurry. The rheological properties of the cement slurry gradually change with time.

In cements having small amounts of calcium trialuminate (C_3A) the solid phase is saturated with calcium sulphate, which acts as a strong flocculant. Besides it reduces solubility of calcium aluminates and enhances silicate hydration. At a considerable C_3A content ettringite crystallises and the sulfate ions content drops. To improve the rheological parameters of cement slurries gypsum can be substituted with a mixture of lignosulfonates and sodium carbonate.

The influence of initial chemical reactions on hydration processes and physical properties of cement slurry becomes even more vivid when the specific surface of cement is bigger. At the given water content in the slurry (w/c ratio), the cohesion force and strength to shear forces are bigger, the bigger is the specific surface of cement.

Therefore, sealing slurries can have various rheological parameters. The flow curves can be either inversible or they can form hystereses. This can be caused, among others, by the fact that the destruction processes dominate in the slurry when the measuring times are short and reconstruction processes prevail when the measuring times are longer. Therefore, in fresh sealing slurries the destruction of the structure under the influence of shear in the viscosity meter overlaps with its reconstruction by cement hydration products.

Rheological models of cement slurries

The sealing slurries used for drilling purposes are mostly treated as non-Newtonian fluids (Kemblowski, 1973), (Wilkinson, 1963).

For non-Newtonian fluids the course of the flow-curve is either straight and out of the centre of the system or curvilinear.

Generally, depending on their recipes, cement slurries can be grouped according to their rheological parameters:

- generalised Newtonian fluids,
- Bingham's fluids (plastic-viscous),
- fluids having both plastic-viscous and pseudoplastic properties.

Recently numerous attempts have been made to describe the flow curve of generalise Newtonian fluids with the use of respective mathematical models. These models are crucial for analytical solutions of questions related to the flow of non-Newtionian fluids, especially in the conditions of a drilling well, soil porous medium and fractured rock mass.

The simplest mathematical rheological model describing the flow of Newtonian fluids is the so-called exponential model proposed by Ostwald de Waele (Kemblowski, 1973), (Wilkinson, 1963).

The exponential model by Ostwald de Waele is the simplest mathematical rheological model for the generalised Newtonian fluid having only two easily determinable constants (k;n), called rheological parameters. The dependence of shear stress (τ) on shear rate (γ) in this model has the following form:

$$\tau = k \, . \, \gamma^n \qquad [Pa] \qquad (1)$$

where: k - parameter defining the measure of consistency (viscosity);
the bigger is k the more viscous is the fluid; Pa s,
n - parameter defining the measure of distortion of a fluid from the Newtonian fluid; for generalised
Newtonian fluids n<1; dimensionless.

The main disadvantage of the model lies in the fact that k depends on the exponent n as k equals to (force) x $(time)^n$ / $(length)^2$. The coefficient k changes qualitatively and quantitatively for various fluids, whereas rheological parameters n and k have a physical sense only when treated jointly.

M. Reiner stated that the exponential model is not a rheological equation of state but only an empirical interpolation formula, which fails to be valid beyond the interpolation.

To improve the description of the experimental data, numerous authors suggest mathematical rheological models having more complex structure than exponential equations. These models describe the relation between the shear stress τ and shear rate γ for all rheostable liquids, which have no yield point, both diluted and densified with shear.

The rheologically stable fluids with yield point are called plastic-viscous fluids. Bingham's plastic-viscous liquid belongs to this group. For this liquid the flow curve in the form $\tau = f(\gamma)$ is a straight line which does not meet the origin the coordinates system. This liquid is described by the rheological equation in the form:

$$\tau = \tau_y + \eta_p \cdot \gamma \qquad [\mathrm{Pa}] \qquad (2)$$

where: τ - static stress; Pa,
τ_y – yield point; Pa,
η_p – plastic viscosity; Pa s,
γ - shear rate; Pa s.

The parameters τ_y and η_p in this model are rheological parameters, which can be determined experimentally.

On the basis of the Bingham's model one may doubt whether it is possible or not for any real system to strictly meet the above relation. Therefore, cement slurries are treated as nonlinear plastic-viscous liquids.

According to Van Wazer et al. (Kemblowski, 1973), (Wilkinson, 1963) in their paper on the character of flow, when the yield point τ_y is exceeded it is often the rheological parameters of the medium which are most crucial. A suspension with high solid concentration in a Newtonian liquid may exhibit properties similar to the properties of Bingham's liquid. The same suspension in a liquid exhibiting, e.g. the dilution effect under shear will usually have a nonlinear flow curve with the concurrent yield point.

Besides, the Bingham's model does not fully represent the behaviour of a liquid for small and for high rates of shear. In turn, the Ostwald de Waele's exponential model provides less pieces of information about the rheological parameters for small shear rates. In the conditions of high shear rates, certain inadequacies can be encountered.

Sealing slurries, especially the cement-based ones, have:

- the yield point,
- nonlinear flow curve.

Therefore, Lauzon and Reid (Kemblowski, 1973) suggest that the rheological parameters of fresh cement slurries might be described by another rheological equation, i.e Casson's equation in the form (Wilkinson, 1963):

$$\sqrt{\tau} = \sqrt{\tau_y} + \sqrt{\eta_{pc} \cdot \gamma} \qquad [\mathrm{Pa}] \qquad (3)$$

to supplement the analysed models.

The rheological parameters of the Casson's model are as follows:
τ_y – yield point; Pa,
η_{pc} – Casson's viscosity; Pa s.

In the case of complex recipes for sealing slurries, the Casson's model with exponent 0.5, also fails to satisfactorily describe the experimental flow curves. Better results are obtained for other exponents. Hence the Casson's model can be generalised as follows:

$$\tau^{\frac{1}{n}} = \tau_y^{\frac{1}{n}} + (\eta_{pc} \cdot \gamma)^{\frac{1}{n}} \qquad [\mathrm{Pa}] \qquad (4)$$

where: τ_y, η_{pc}, and n are rheological parameters.

Laboratory experiments

Laboratory experiments were carried out for the selected cements in order to establish the influence of:

- water-to-cement ratio,
- temperature of the sealing slurry on rheological parameters of sealing slurries, and to select the appropriate model.

The measurement of the rheological parameters of cement slurries was made with a rotary coaxial-cylindrical viscosity meter of Chan 35 API Viscometer type, 12 rotation rates, i.e. 600, 300, 200, 100, 60, 30, 20, 10, 6, 3, 2 and 1 rot/min, which corresponds to the respective shear rates (γ): 1022, 511.2, 340.8, 170.4, 102.5, 51.1, 34.08, 17.04, 10.22, 4.11, 3.41, 10.71 s^{-1}.

The following cements were used for making sealing slurries (Gonet et al, 2000):

- Portland cement CEM I 52.5 class,
- Portland ash cement CEM II/A – V 32.5 R class,
- low-alkaline metallurgical cement CEM II/A NA class.

The water-to-cement ratio (w/c) for the analysed cement slurries were 0.4, 0.5, 0.6, 0.8, 1.0, 1.2 and their temperatures were:

- 5^{0}C (±2^{0}C) [278 K],
- 20^{0}C (±2^{0}C) [293 K],
- 50^{0}C (±2^{0}C) [333 K].

Cements used for sealing slurries were sieved (0.20 mm and 0.08 mm square grid) (Polish standard PN-85/G-02320 “Cements and cement slurries to be used for cementing in drilling wells”). Tap water was applied.

Water was measured and poured to the container. A high rate electric mixer was switched on. The measured quantity of cement was admixed by 15 to 30 seconds. The mixing time was about 3 min. Thus prepared substance was poured to the measuring cup of the rotary viscosity meter Chan 35 type and the rheological parameters measured (shear rate 1022 s^{-1} to 1.7 s^{-1}).

To determine the rheological parameters of the analysed cement slurries in the function of the assumed models the obtained data were statistically analysed. Using the least squares method and dependences presented in (Kembłowski, 1973; Wilkinson, 1963; Volk, 1973), the following rheological parameters were determined for:

- Bingham’s model,
- Ostwald de Waele’s model,
- Casson’s model.

High correlation values for the above rheological model were obtained for these three cements for the water-cement parameters, ranging from 0.4 to 1.2 in temperatures 278, 293 and 323 K (Volk, 1963).

The rheological model was selected based on the calculated correlation coefficient. The most favourable fits of the rheological models to the obtained laboratory results were given in Tables 1 to 3.

Tab.1. Parameters of cement slurry and Bingham’s model.

Cement type	Water-to-cement ratio	Temperature K	Plastic viscosity Pa·s	Yield point Pa	Correlation coefficient
CEM I 52,5R	1.2	278	0.0076	0.477	0.9963
CEM I 52,5R	1.0	293	0.0100	0.718	0.9966
CEM I 52,5R	1.2	293	0.0086	0.618	0.9995
CEM II/A-V 32,5R	0.8	278	0.0135	1.012	0.9947
CEM II/A-V 32,5R	1.0	278	0.0088	0.220	0.9973
CEM II/A-V 32,5R	1.0	293	0.0112	0.449	0.9956
CEM II/A-V 32,5R	1.0	323	0.0121	1.708	0.9859
CEM/A-32,5 NA	0.8	278	0.0164	1.263	0.9986
CEM/A-32,5 NA	1.0	278	0.0089	0.531	0.9967
CEM/A-32,5 NA	1.2	278	0.0071	0.309	0.9974
CEM/A-32,5 NA	0.8	293	0.0183	3.393	0.9919
CEM/A-32,5 NA	1.0	323	0.0083	2.749	0.9814
CEM/A-32,5 NA	1.2	323	0.0059	0.623	0.9894

Tab.2. Parameters of cement slurry and Ostwald de Waele’s model.

Cement type	Water-to-cement ratio-	Temperature K	Plastic viscosity Pa·s	Yield point Pa	Correlation coefficient-
CEM I 52,5R	0.4	278	11.767	0.4087	0.9968
CEM I 52,5R	0.5	293	5.7125	0.5114	0.9988
CEM I 52,5R	0.6	293	3.7075	0.4540	0.9969
CEM I 52,5R	0.6	323	11.341	0.3691	0.9783
CEM I 52,5R	0.8	323	4.9035	0.3778	0.9905
CEM I 52,5R	1.0	323	1.6238	0.4055	0.9945
CEM II/A-V 32,5R	1.2	293	0.0294	0.8704	0.9905
CEM II/A-V 32,5R	0.5	323	3.5569	0.5353	0.9968
CEM II/A-V 32,5R	0.6	323	2.1945	0.5526	0.9955
CEM II/A-V 32,5R	0.8	323	1.4943	0.4562	0.9928
CEM/A-32,5 NA	0.4	293	10.158	0.4685	0.9946
CEM/A-32,5 NA	0.5	293	4.1930	0.5121	0.9985
CEM/A-32,5 NA	0.6	293	3.2087	0.4614	0.9968
CEM/A-32,5 NA	1.0	293	0.9159	0.3593	0.9837
CEM/A-32,5 NA	1.2	293	0.3704	0.4874	0.9867
CEM/A-32,5 NA	0.6	323	2.9236	0.4498	0.9938

Tab.3. Parameters of cement slurry and Casson's model.

Cement type	**Water-to-cement ratio**	**Temperature K**	**Plastic viscosity Pa·s**	**Yield point Pa**	**Correlation coefficient**
CEM I 52,5R	0.5	278	0.0564	7.454	0.9944
CEM I 52,5R	0.6	278	0.0310	4.344	0.9964
CEM I 52,5R	0.8	278	0.0135	1.002	0.9996
CEM I 52,5R	1.0	278	0.0091	0.232	0.9982
CEM I 52,5R	0.4	293	0.4782	8.987	0.9980
CEM I 52,5R	0.8	293	0.0135	1.020	0.9992
CEM I 52,5R	0.5	323	0.1358	13.813	0.9939
CEM I 52,5R	1.2	323	0.0057	1.153	0.9954
CEM II/A-V 32,5R	0.4	278	0.0957	4.609	0.9978
CEM II/A-V 32,5R	0.5	278	0.0361	2.671	0.9995
CEM II/A-V 32,5R	0.6	278	0.0208	1.379	0.9987
CEM II/A-V 32,5R	1.2	278	0.0067	0.002	0.9944
CEM II/A-V 32,5R	0.4	293	0.1378	4.639	0.9959
CEM II/A-V 32,5R	0.5	293	0.0459	2.720	0.9960
CEM II/A-V 32,5R	0.6	293	0.0202	1.553	0.9070
CEM II/A-V 32,5R	0.8	293	0.0099	0.455	0.9948
CEM II/A-V 32,5R	0.4	323	0.1746	9.706	0.9936
CEM II/A-V 32,5R	1.2	323	0.0022	0.112	0.9911
CEM/A-32,5 NA	0.4	278	0.2782	8.885	0.9993
CEM/A-32,5 NA	0.5	278	0.0659	5.135	0.9983
CEM/A-32,5 NA	0.6	278	0.0257	2.082	0.9984
CEM/A-32,5 NA	0.4	323	0.2578	7.666	0.9971
CEM/A-32,5 NA	0.5	323	0.0784	5.074	0.9919
CEM/A-32,5 NA	0.8	323	0.0087	1.741	0.9957

Conclusions

- Rheological parameters of the analysed slurries significantly depend on the water-to-cement ratio, temperature and type of cement used, especially at low water-to-cement ratios.
- Bingham's, Ostwald de Waele's and Casson's models well describe the cement slurries prepared from the Portland cement CEM I 52.5 R, Portland ash cement CEM III/A V 32.5 and low alkaline metallurgical cement CEM III/A 35.2 NA in view of water-to-cement ratios changing from 0.4 to 1.2 and temperatures from 278 to 323 K.
- Having assumed that the highest value of the correlation coefficient is critical for the choice of the cement, the following can be stated:
    - Bingham's model is most frequent for water-to-cement ratios ranging between 0.8 and 1.2,
    - Ostwald de Waele's model often describes cement slurries made in temperatures 293 and 323 K,
    - Casson's model much better describes cement slurries based on lower water-to-cement ratios (0.4 to 0.8) than on high rations (1.0 to 1.2).

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