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THE INFLUENCE OF TIME OF RHEOLOGICAL PARAMETERS OF FRESH CEMENT SLURRIES**

1. INTRODUCTION

The rheological properties of sealing slurries are very important at the stage of designing and realization of works related to the sealing and reinforcement of the ground rock mass with the use of drilling technologies. For providing high efficiency of the works related to the sealing of casing pipes in deep wells and the rock mass with borehole injection methods, the rheological parameters of sealing slurries should be selected depending on [1,2]:

- reservoir conditions of ground and rocks to be sealed,
- geometry of borehole and circulation system,
- interactions between the stream of injected slurry and the resulting flow resistance, especially in the sealed medium.

Meeting these criteria is connected with finding out a rheological model and determining rheological parameters for the assumed model. The correctly determined rheological parameters allow for calculating a definite flow resistance for the assumed [5,6,8,9]:

- technological parameters of slurry,
- range (character) of flow (laminar, turbulent or piston).

Despite numerous laboratory experiments and analyses performed by various scientific and research units, the sealing slurries have not been fully systematized in view of their rheology for 20 years. This is mainly connected with the fact that the rheology of

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sealing slurries is very complex and depends on a number of such physicochemical factors as [3,4,10]:

- specific surface of cement and granulation of admixed inorganic hydraulic binders making up the sealing slurry,
- water/cement and water/hydraulic binder ratios,
- composition of chemical and mineral hydraulic binder,
- chemical composition of working fluid,
- presence and chemical composition of additives and admixtures in the slurry recipe,
- way and dynamics (time and rate) of slurry mixing,
- temperature of slurry,
- hydration rate,
- measurement conditions and method.

2. RHEOLOGICAL PROPERTIES OF FRESH CEMENT SLURRIES

The rheological properties of fresh cement slurries are important because of their effect on, e.g. [2,6,10]:

- slurry binding,
- consistency,
- stability,
- selection of technology of sealing slurry injection into a medium,
- flow resistances caused by circulation system.

Sealing slurries, especially the cement-based ones, are concentrated dispersive systems containing solid molecules of well developed specific surface. Such systems have very complex rheology, which is obviously connected with already mentioned factors, but also with hydration reactions taking place in the slurry in a function of time.

Owing to the size of cement grains, fresh cement slurries started to be considered as dispersive systems. The structure of such a system largely depends on the mass ratio of water and dry cement (and its granulation) and consequently the specific surface. The physicochemical properties of the slurry structure are also influenced by forces acting on cement grains and water molecules, which in turn, are affected by [1,4,5,6]:

- surface charge,
- ionic concentration in slurry,
- adsorption.

Similar to other systems, cement grains undergo coagulation and when the solid phase content is appropriate, they form a continuous coagulation structure. In simplified models discussing the structure of fresh cement slurries, the hydration products tend to be ignored.

The complexity of the water/cement systems results in considerable difficulties in interpretation of rheological results obtained by various investigators. This is mainly caused by the fact that rheologically cement slurries are non-Newonian fluids where the phase composition additionally changes during the ongoing hydration of cement particles. For this reason the rheological properties of modelled structures do not correspond to the results of measurements of real systems.

The big activity of cement, especially the klinker phase C_3A on working fluid, causes that all grains are covered with a layer of gel composed of a mixture of hydrated silicates and calcium aluminosilicates.

The mutual mobility of grains is mainly the result of the quantity and type of hydration products produced at the initial stage. The chemical and mineral composition of non-hydrated cement grains affects the physicochemical properties of the gel film. The distribution of the charge on the surface of colloidal molecules and concentration of the solid phase is determined by intergrain forces. Besides it orders the grains in the coagulation structure and so influences the behavior of the slurry under external forces.

The formation of a water film of an ordered structure on the surface of solids is important for the generation of rheological properties of sealing slurries, especially the cement-based ones. The external well-ordered zone gradually enters an intermediate zone, where the working fluid molecules are distributed randomly, and then external zone of water solution.

The magnitude of internal and intermediate zones is determined by the viscosity of the sealing slurry. The width of the diffusive layer and forces acting on the ions in the solution change, depending on the magnitude of the solids surface charge. Owing to the high reactivity of cement phases against water, the rheological properties of the sealing slurry (apart from water/binder ratio and dispersion of hydraulic binder) mainly depend on the type and amount of hydration (cement) products, whereas the character of surfaces of klinker phases is of less importance.

Another factor influencing the structure of of fresh sealing slurry is the chemical structure of cement, which consecutively affects the course of the hydration process. As a result of cement slurry hydration, a considerable part of gypsum gets to the solution and the liquid phase is saturated with Ca^{2+}, SO_4^{2-} and alkalies from the cement. In a few minutes time some amount of ettringite is formed. If it creates a compact film around the grains, it will not have any serious influence on the rheological properties of the slurry. The initial reaction of alite with water in the induction period does not affect the structure of the slurry when hydrates are severed from the grain surface in the process of mixing. Only after the induction period the crystallization of calcium hydroxides and accelerated hydration of alite bring about a considerable increase of viscosity of the slurry. The rheological properties of cement slurry undergo fast changes in time.

In low C_3A cements the liquid phase is saturated with calcium sulphate which acts like a strong flocculent, lowering the solubility of calcium aluminates and accelerating the hydration of silicates. At a high C_3A ettringite is crystallized and sulphate ions content decreased.

For improving the rheological parameters of cement slurries, gypsum may be substituted with a mixture of lignosulphonates and sodium carbonate.

Better visible is the influence of preliminary chemical reactions on the hydration process and physical properties of cement slurry, the bigger is the specific surface of cement. The higher are the coherence force and resistance to shear forces at a given water content in the slurry (w/c ratio), the higher is the specific surface of cement.

Other compounds having influence on the rheological properties of cement slurry are the following [3,4,6]:

- potassium sulphate – causes momentary increase of viscosity in the slurry;
- carbon in fly ashes added to cement – neutralizes the effect of plasticizers through the adsorption of plasticizing particles on the porous coke structure; its participation is limited by standards to 5%;
- contaminations in calcium: clay content retards the hydration processes due to the presence of humic acids; too high dolomite content results in undesired reactions with alkali. The pulverized calcium to less than 10 μm of grain size produces a positive result on the rheological properties and workability of fresh slurry.

Henceforth, sealing slurries may differ in their rheological properties. The rheological curves may be reversible or may show a hysteresis. This may be caused, among other factors, by the fact that in short measurement times the destruction of slurry structure dominates, whereas in longer time – its reconstruction prevails. Therefore, in fresh cement slurries the destruction of structure under the influence of shearing processes in the viscometer overlaps with reconstruction processes by cement grains hydration.

3. METHODICS OF LABORATORY EXPERIMENTS

Laboratory experiments of rheological parameters of cement slurries were based on the following standards:

1. PN – EN 197 – 1: 2002, Cement. Part 1. Composition, requirements and congruence criteria for common-use cement.
2. PN – EN ISO 10426 – 1. Oil and gas industry. Cements and materials for cementing boreholes. Part 1. Specification.
3. PN – EN ISO 10426 – 2. Oil and gas industry. Cements and materials for cementing boreholes. Part 2: Analysis of drilling cements. 2003.

The laboratory experiments were aimed at determining the influence of the function of time on changes of rheological properties of fresh cement slurries based on Class G drilling cement. The following variables were accounted for:

a) w/c ratio,
b) measurement of time (from the moment of making the slurry).

4. PREPARATION OF SEALING SLURRIES FOR LABORATORY ANALYSES

The water/cement ratios for the analyzed slurries equalled to 0.45; 0.55 and 0.65. Cement was weighed on electronic scales (erroneous indications ±0.1% of weighed substance). The slurry was prepared with the use of a 1 liter mixer (1 quart) with powered from the bottom and equipped with paddle mixers (fig.1).

The temperature of working water (tap water), dry cement and that of the mixer and mixing elements was 23°C ±1°C (73°F ±2°F).

Cement for sealing slurries (in line with standards ISO 25911-1 and ISO 3310-1) was sifted through three wire sieves of square mesh eyes: 1.0; 0.20 and 0.08 mm. Slurries were made only of sifted cement. Cement for slurries was so fine that the leftovers did not exceed 2% on a sieve of 0.20 mm mesh and were under 20% on a sieve of 0.08 mm.

The measured volumes of working fluid, being a result of the assumed w/c ratios, were poured into the mixer cup. After 15 seconds the pre-weighed mass of cement was added to the working water and mixed at the rotational speed of 4 000 rpm ±200 rpm. Then the mixing was continued at a speed of 12 000 rpm ±500 rpm for 35 s ±1 s. Thus prepared slurry was subjected to the successive analyses in the shortest possible time.

Fig. 1. Two-speed mixer for preparing sealing slurries

The laboratory experiments aimed at determining the rheological parameters of fresh sealing slurries covered the following measurements:

- rheological properties (plastic viscosity, apparent viscosity, yield point) – with the use of a rotational viscometer equipped with coaxial cylinder Chan – 35 API Viscometer – Tulsa, Oklahoma, USA EG.G Chandler Engineering, of twelve rotational speeds (600, 300, 200, 100, 60, 30, 20, 10, 6, 3, 2, 1 rpm, corresponding to the shear rates: 1022.04; 511.02; 340.7; 170.4; 102.2; 51.1; 34.08; 17.04; 10.22; 5.11; 3.41; 1.70 s^{-1});
- building a rheological model – the optimum rheological model of sealing slurries was selected after determining the rheological curve, on the basis of which the results of measurements could be best described in a coordinates system: tangential stress (τ) – shear rate (γ).

The rheological parameters for particular models were determined with the regression analysis method. The optimum rheological model was established on the basis of statistical tests for a given sealing slurry recipe.

The following rheological models were analyzed [2,7,10]:

- Newton model $\tau = \eta \cdot \left(-\frac{dv}{dr}\right)$,
- Bingham model $\tau = \tau_y + \eta \cdot \left(-\frac{dv}{dr}\right)$,
- Ostwald de Waele model $\tau = k \cdot \left(-\frac{dv}{dr}\right)^n$,
- Casson model $\sqrt{\tau} = \sqrt{\tau_y} + \sqrt{\eta} \cdot \sqrt{\left(-\frac{dv}{dr}\right)}$,
- Herschel–Bulkley model $\tau = \tau_y + k \cdot \left(-\frac{dv}{dr}\right)^n$,

where:

n – exponent,
k – consistency coefficient, Pa · s^n,
τ_y – yield point, Pa,
η – dynamic coefficient of viscosity of Newton model; plastic viscosity for Bingham model, Casson's plastic viscosity for Casson model, Pa · s,
$\frac{dv}{dr}$ – shear rate gradient – γ – s^{-1}.

For the effect of facilitating calculation related to establishing optimum rheological models of analyzed slurries, the ‘Rheo Solution’ software was used. This program is owned by the Department of Drilling and Geoengineering, faculty of Drilling Oil and Gas Engineering AGH-UST [7,8]. The sealing slurries were made of Class G HRS drilling cement imported from Germany. The mineral composition of analyzed Class G cements is presented in Table 1.

Table 1

Mineral composition of Class G drilling cement used for laboratory experiments

Component	Content in Class G drilling cement (API), [%]
C_3A	1.20
C_4AF	15.50
C_3S	51.00
C_2S	19.30
$C_4AF+2 \cdot C_3A$	19.60

The analyses of rheological parameters of fresh cement slurries were performed after 10 min, 1h, 2hrs and 3 hrs from the moment of making the slurry.

5. RESULTS OF LABORATORY EXPERIMENTS

The analytical results of influence of tangential stresses on shear rate of fresh sealing slurries based on Class G drilling cement are presented in Table 2.

Table 2

Tangential stresses read out from a rotary viscometer for w/c ratios 0.45, 0.55, 0.65 and for measurement time 10, 60, 120 and 180 minutes from making the sealing slurry

Shear rate, s^{-1}	Tangential stresses read out from rotary viscometer, mPa											
	Measurement after 10 minutes			Measurement after 60 minutes			Measurement after 120 minutes			Measurement after 180 minutes		
	w/c=0.45	w/c=0.55	w/c=0.65	w/c=0.45	w/c=0.55	w/c=0.65	w/c=0.45	w/c=0.55	w/c=0.65	w/c=0.45	w/c=0.55	w/c=0.65
1.7	5.1	2.0	2.0	5.1	3.1	2.6	5.6	3.1	3.1	6.1	3.6	3.6
3.4	6.1	3.1	3.1	6.6	4.1	3.1	7.2	3.6	3.6	7.2	4.1	4.1
5.1	6.6	4.1	3.6	7.7	5.1	3.6	8.7	4.6	3.6	9.7	5.6	4.1
10.2	9.2	4.6	4.1	10.7	5.6	4.1	11.8	5.6	4.1	12.3	6.6	4.1
17.0	12.3	5.1	4.6	14.3	6.6	4.6	15.8	6.6	4.6	16.9	8.2	4.6
34.1	16.9	6.1	5.1	19.9	7.2	5.6	22.0	7.7	5.6	25.0	9.2	5.6
51.1	18.9	6.6	5.6	23.5	8.2	6.1	26.1	8.7	6.6	29.6	10.2	7.2
102.2	24.0	8.2	7.2	30.1	9.7	7.7	33.7	11.2	8.7	36.8	12.8	9.7
170.3	28.6	11.2	8.7	36.8	12.3	10.2	40.9	13.3	11.2	48.5	16.4	12.8
340.7	39.3	17.9	11.8	51.6	19.4	12.8	57.7	20.4	14.3	69.0	22.0	15.8
511.0	49.1	23.0	13.8	64.9	25.6	15.8	72.6	28.1	17.4	82.8	30.7	18.9
1022.0	77.2	35.8	20.4	98.1	36.8	23.5	113.4	41.9	25.0	127.8	46.0	27.1

The mathematical parameters of rheological models of cement slurries of various water/cement ratio are presented in tables 3 and 4. The rheological parameters were calculated for the following models:

- Newton model,
- Bingham model,
- Casson model,
- Ostwald de Waele model,
- Herschel-Bulkley model.

Table 3

Parameters of rheological models of cement slurry for w/c ratios 0.45, 0.55 and 0.66 after 10 and 60 minutes from the time of making the slurry

Parameters of rheological models		Values of rheological model parameters					
		for 10 minutes			for 60 minutes		
		w/c= 0.45	w/c= 0.55	w/c= 0.65	w/c= 0.45	w/c= 0.55	w/c= 0.65
Newton model	Newton's dynamic viscosity [Pa · s]	0.0864	0.0395	0.0237	0.1110	0.0418	0.0271
	Correlation coefficient [-]	0.8573	0.9087	0.6859	0.8721	0.8527	0.7486
Bingham model	Plastic viscosity [Pa · s]	0.0686	0.0325	0.0171	0.0896	0.0329	0.0201
	Yield point [Pa]	11.4698	4.4951	4.2538	13.8549	5.7480	4.5068
	Correlation coefficient [-]	0.9762	0.9893	0.9742	0.9726	0.9847	0.9766
Ostwald de Waele model	Consistency coefficient [Pa · s^n]	3.6551	1.6919	1.8514	3.8219	2.4171	1.9279
	Exponent [-]	0.4181	0.4001	0.3182	0.4550	0.3540	0.3296
	Correlation coefficient [-]	0.9866	0.9559	0.9741	0.9947	0.9523	0.9715
Casson model	Casson's viscosity [Pa · s]	0.0423	0.0197	0.0086	0.0590	0.0183	0.0105
	Yield point [Pa]	6.0564	2.4479	2.7348	6.6983	3.4141	2.8108
	Correlation coefficient [-]	0.9924	0.9981	0.9950	0.9895	0.9967	0.99
Herschel-Bulkley model	Yield point [Pa]	4.931	2.8725	2.5089	3.9475	3.7305	2.5837
	Consistency coefficient [Pa · s^n]	1.1345	0.2066	0.3138	1.8781	0.2763	0.3328
	Exponent [-]	0.5956	0.7321	0.5814	0.5624	0.6920	0.5954
	Correlation coefficient [-]	0.9967	0.9983	0.9975	0.9984	0.9973	0.9985
Apparent viscosity at 1022.04 [s^{-1}], [Pa · s]		0.0755	0.0350	0.0200	0.0960	0.0360	0.0230

Table 4

Parameters of rheological models of cement slurry for w/c ratios 0.45, 0.55 and 0.66 after 120 and 180 minutes from the time of making the slurry

Parameters of rheological models		Values of rheological model parameters					
		for 120 minutes			for 180 minutes		
		w/c= 0.45	w/c= 0.55	w/c= 0.65	w/c= 0.45	w/c= 0.55	w/c= 0.65
Newton model	Newton's dynamic viscosity [Pa · s]	0.1267	0.0467	0.0292	0.1442	0.0514	0.0318
	Correlation coefficient [-]	0.8874	0.8888	0.7414	0.8847	0.8615	0.7350
Bingham model	Plastic viscosity [Pa · s]	0.1033	0.0378	0.0217	0.1178	0.407	0.0235
	Yield point [Pa]	15.0814	5.7507	4.8901	17.0322	6.9076	5.3424
	Correlation coefficient [-]	0.9766	0.9871	0.9714	0.9718	0.9854	0.9665

Table 4. cont.

Ostwald de Waele model	Consistency coefficient [Pa · s^n]	4.1652	2.2095	2.0848	4.3492	2.6900	2.2904
	Exponent [-]	0.4604	0.3869	0.3289	0.4767	0.3742	0.3260
	Correlation coefficient [-]	0.9923	0.9595	0.9733	0.9963	0.9637	0.9698
Casson model	Casson's viscosity [Pa · s]	0.0684	0.0223	0.0116	0.0806	0.0232	0.0127
	Yield point [Pa]	7.2311	3.2173	3.0038	7.7680	3.9984	3.2537
	Correlation coefficient [-]	0.9916	0.9977	0.9940	0.9880	0.9972	0.9907
Herschel-Bulkley model	Yield point [Pa]	5.1402	3.5952	2.4779	3.7670	4.3832	2.5454
	Consistency coefficient [Pa · s^n]	1.7306	0.2875	0.4558	2.5396	0.3490	0.5485
	Exponent [-]	0.5939	0.7063	0.5622	0.5586	0.6890	0.5482
	Correlation coefficient [-]	0.9979	0.9980	0.9994	0.9986	0.9972	0.9978
Apparent viscosity at 1022.04 [s^{-1}], [Pa · s]		0.1110	0.0410	0.0245	0.1250	0.0450	0.0265

Models with the highest correlation coefficient were accepted as the best rheological models. In all cases the Herschel-Bulkley model turned out to have the best fit. The obtained rheological models are presented in figures 2 to 4.

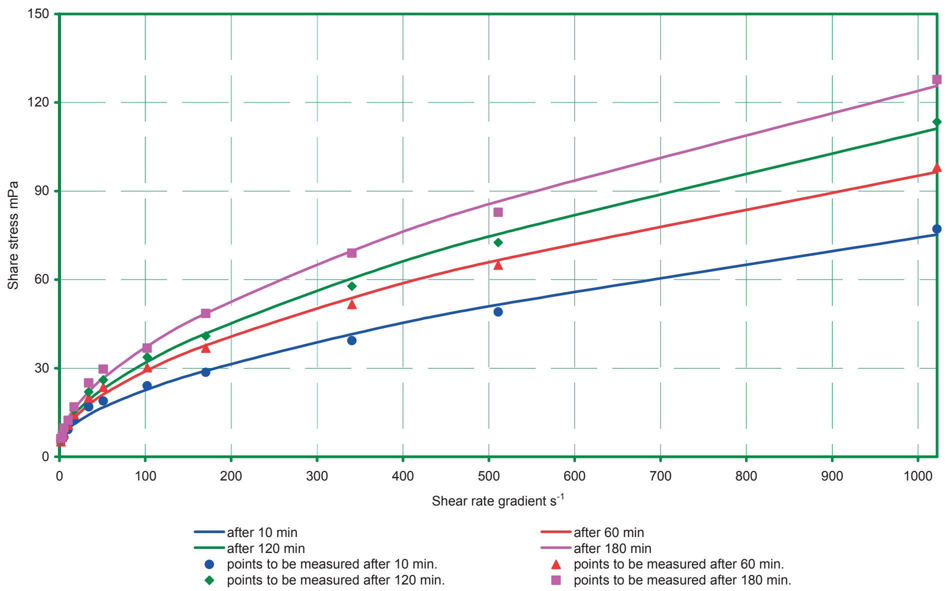

Fig. 2. Rheological models represented by Herschel-Bulkley curves for sealing slurries having w/c ratio 0.45; measuring time equal to 10, 60, 120 and 180 minutes from the moment of making the slurry

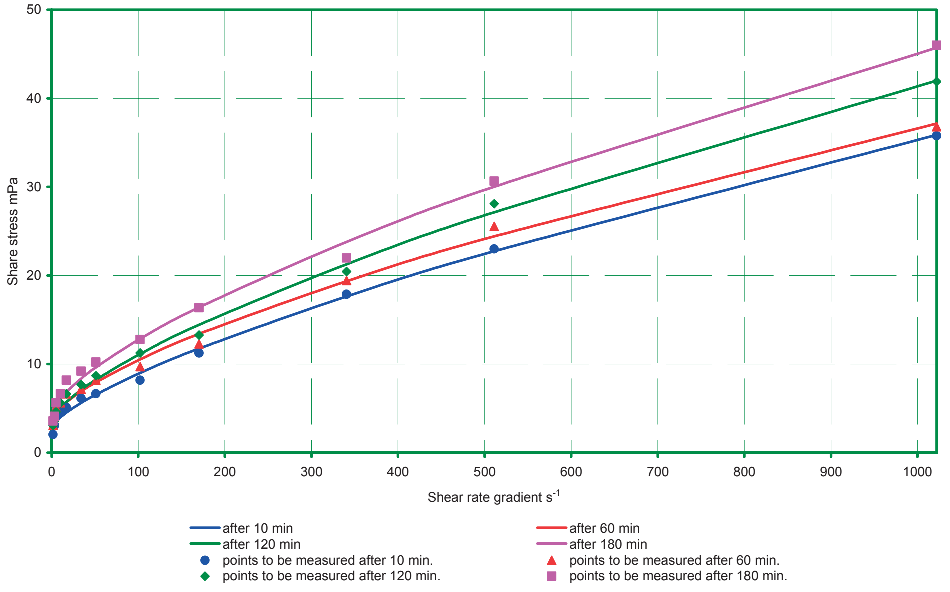

Fig. 3. Rheological models represented by Herschel-Bulkley curves for sealing slurries having w/c ratio 0.55; measuring time equal to 10, 60, 120 and 180 minutes from the moment of making the slurry

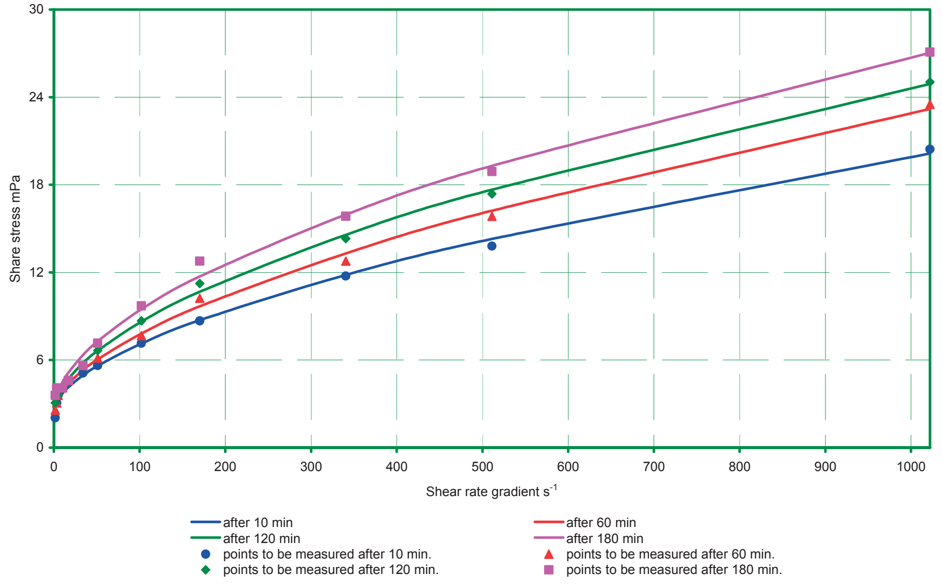

Fig. 4. Rheological models represented by Herschel-Bulkley curves for sealing slurries having w/c ratio 0.65; measuring time equal to 10, 60, 120 and 180 minutes from the moment of making the slurry

The analysis of the data obtained in the course of experiments reveals that the slurries had thixotropic properties – rheological parameters were changing with time. With time of shearing the cement slurry samples started to be degraded in their inner structure. After leaving the slurry still, its structure was restored. The lowering of apparent viscosity with the increase of shear rate is caused by the ordering of cement grains. At a defined shear rate the cement grains reach the state of being ordered and the rheological curve becomes a straight line.

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