

## Viscosity of Cement Slurries as a Function of Solids Content

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### ABSTRACT

Apparent viscosity is the ratio between shear stress and shear rate. The Krieger-Dougherty equation was developed for suspensions of monodisperse particles and described the relation between apparent viscosity and the volume fraction of solids in suspensions. The Krieger-Dougherty equation has been shown to hold for a polydisperse system as cement paste and for a wide range of shear rates.

### INTRODUCTION

The results presented here is a part of the ongoing project "Rheological properties of cement based binders" running at SINTEF from 2002 to 2005. The project have a fundamental approach to find the parameters that govern the rheology of cement based binders, and this part describes the effect of water-to-cement ratio.

The continuous phase (often called matrix) in concrete is the suspension of Portland cement particles (average diameter about 15  $\mu\text{m}$ ), any mineral additives (e.g. silica fume with average particle diameter 0.15  $\mu\text{m}$ ) and aggregate fines (i.e. sand < 100  $\mu\text{m}$ ) dispersed in water containing plasticizing admixtures (poly-electrolytes or grafted polymers). This matrix again disperses coarser aggregate (i.e. sand, gravel and stones usually up to 20 mm). This study focuses on suspensions of Portland cement and water with some plasticizer. When cement and water is mixed, the slurry is

fluid and becomes progressively more viscous as the cement is not an inert particle but hydrates as a function of time. After a few hours it will set and behave as a solid with increasing strength.

The flow behaviour of matrix is important because it controls the flow behaviour, and hence the processability, of concrete. The viscosity of matrix is known to increase with increasing volume fraction of solids, and several empirical relationships between viscosity and cement content and fineness have been proposed<sup>1-3</sup> (as reviewed by Tattersall and Banfill<sup>4</sup> and by Struble<sup>5</sup>). These relationships have not found widespread use, probably because of their empirical basis. If a theoretically derived equation was shown to be valid, it could be used to model concrete matrix viscosity based on independently measurable parameters.

The flow behaviour of suspensions depends primarily on the concentration of particles and the extent to which the particles are flocculated. Viscosity increases with increasing volume fraction of solids and degree of flocculation. Of the many attempts to model the relationship between viscosity and solids fraction, probably the most successful has been the equation developed by Krieger and Dougherty<sup>6</sup>. This equation has been widely used because it has strong theoretical underpinnings and the physical significance of its parameters is known. The validity of this equation has

been established using rheological measurements on dispersed suspensions of spherical, monosized latex particles. A few publications have applied this equation to complex particulate systems, but only Struble and Sun<sup>7</sup> have formerly applied it to cement suspensions. However, they used unrealistic high amounts of plasticizer (5% dry admixture of cement mass) to secure full dispersion, while the present study used more realistic amounts (i.e. around 1% by mass of cement) and a high shear mixer.

### EXPERIMENTAL

In the first series, cement slurries were made out of a CEM I 42.5 RR<sup>8</sup> Portland cement and distilled water to form a series with volume fraction of solids ranging from 0.36 to 0.46 in increments of 0.02, corresponding to w/c ranging from 0.37 to 0.56. The pastes were blended in a high shear mixer and added 1.32% sodium lignosulphonate to ensure a good de-agglomeration. The mixing procedure was ½ minute mixing at high speed, 5 min rest and another minute mixing at high speed to avoid false set. Each slurry was 500 ml to minimise weighing uncertainties, but only 2 ml was transferred to the Physica MCR 300 Rheometer. The rest was used to filter off the liquid phase. The rheometer was set to 20°C and measured the down flow curve (shear stress versus shear rate) for shear rates ranging from 200 to 2 s<sup>-1</sup> after homogenisation for a few minutes at 100 s<sup>-1</sup>. The flow curves are shown in Fig. 1.

In the second series, cement slurries were made out of CEM I 42.5 RR and CEM I 42.5 R-LA<sup>8</sup> Portland cement and distilled water to form a series with volume fraction of solids ranging from 0.40 to 0.45 in increments of 0.01 for the former and from 0.45 to 0.50 in increments of 0.01 for the latter. The mixing procedure was as for the first series, but now 1% sodium naphthalene sulphonate - formaldehyde condensate (denoted SNF) was used as a plasticizer by mass of cement. The rheometer was set to

20°C and measured the down and up flow curve (shear stress versus shear rate) for shear rates ranging from 200 to 2 s<sup>-1</sup> after homogenisation for a few minutes at 200 s<sup>-1</sup>. The down/up procedure was to check for hysteresis caused by agglomeration. The recording was repeated at time after water addition of 10, 30, 50, 70 and 90 min. As the down and up flow curves took 10 minutes to measure, the sample was rotated for 10 min at 200 s<sup>-1</sup> between each recording. The different characteristics for these 2 cements are shown in Table 1 and 2.

Table 1. Chemical analysis (%) of the Portland cements according to producer and minerals (%) by mass balance estimation.

Cement Type	CEM I 42.5 RR	CEM I 42.5 R-LA
<u>Chemical Analyses</u>		
CaO	61.98	63.15
SiO <sub>2</sub>	20.15	21.98
Al <sub>2</sub> O <sub>3</sub>	4.99	3.47
Fe <sub>2</sub> O <sub>3</sub>	3.36	5.13
SO <sub>3</sub>	3.55	2.26
MgO	2.36	1.56
Free lime	1.23	0.94
K <sub>2</sub> O	1.08	0.54
Na <sub>2</sub> O	0.42	0.21
Cr <sup>6+</sup> (ppm)	0.00	-
Carbon	0.04	-
Chloride	0.03	-
Loss on ignition	1.34	0.90
<u>Minerals by mass balance</u>		
Ca <sub>3</sub> SiO <sub>5</sub>	50.7	53.0
Ca <sub>2</sub> SiO <sub>4</sub>	19.5	23.0
Ca <sub>3</sub> Al <sub>2</sub> O <sub>6</sub>	7.5	0.5
Ca <sub>4</sub> Al <sub>2</sub> Fe <sub>2</sub> O <sub>10</sub>	10.2	15.6
CaSO <sub>4</sub>	7.7	4.9

Examples of down and up flow curves are shown in Figs. 2 and 3 for the CEM I 42.5 RR and CEM I 42.5 R-LA cements, respectively, at an age of 10 min. The first

cement shows only minor signs of hysteresis, while the latter cement surprisingly shows some hysteresis at the high shear rates, since agglomeration is expected to show up as hysteresis at low shear rates.

Table 2. Physical characteristics of Portland Cements according to EN 196

Cement type	CEM I 42.5 RR	CEM I 42.5 R-LA
<b>Fineness:</b>		
Grains +90 $\mu$ m	0.1%	0.0%
Grains +64 $\mu$ m	0.5%	0.6%
Grains -24 $\mu$ m	89.2%	86.6%
Grains -30 $\mu$ m	94.8%	93.3%
Blaine (m <sup>2</sup> /kg)	546	450
Water demand	32.0%	28.2%
Initial set time	115 min	100 min
$\sigma_c$ (MPa) <sup>a</sup> at		
1 day	32.7	21.7
2 days	39.9	32.5
7 days	49.3	46.1
28 days	58.9	62.0

<sup>a</sup> Compressive strength of mortar

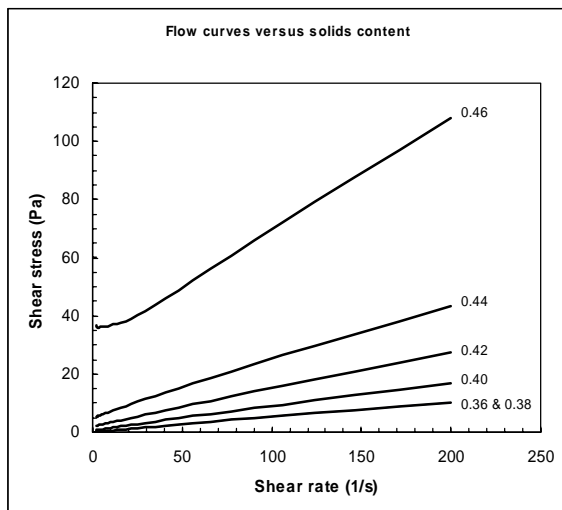


Figure 1 Flow curves for CEM I 42.5 RR cement pastes with lignosulphonate as a function of volume fraction of solids ( $\phi$ ).

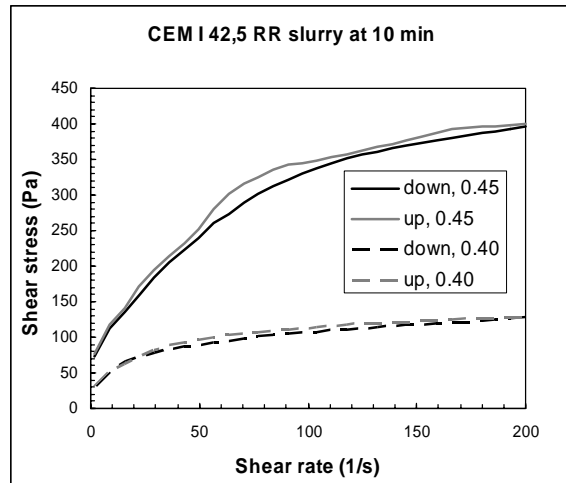


Figure 2. Example of down and up flow curves for CEM I 42,5 RR cement slurries with 1% SNF plasticizer for volume fractions of solids of 0.45 and 0.40 (upper and lower limit for the series).

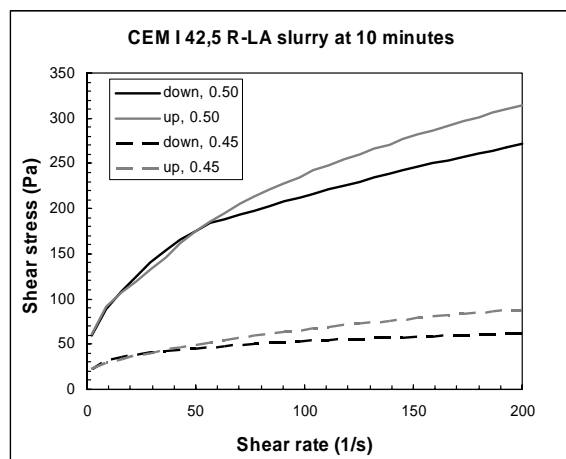


Figure 3. Example of down and up flow curves for CEM I 42,5 R-LA cement slurries with 1% SNF plasticizer for volume fractions of solids of 0.50 and 0.45 (upper and lower limit for the series).

## RESULTS AND DISCUSSION

The apparent viscosity,  $\eta \approx \tau / \dot{\gamma}$  ( $\tau$  = shear stress and  $\dot{\gamma}$  = shear rate), of fully dispersed slurries is a function of the volume fraction of solids,  $\phi$ , according to the Krieger-Dougherty equation<sup>6</sup>:

$$\frac{\eta}{\eta_c} = \left(1 - \frac{\varphi}{\varphi_m}\right)^{-[\eta]\varphi_m} \quad (1)$$

where  $\eta_c$  is the apparent viscosity of the continuous phase (1 cP for water at 20°C),  $\varphi_m$  is the maximum volume concentration of solids (about 0.65) and  $[\eta]$  is the intrinsic viscosity of the suspension given by

$$[\eta] = \lim_{\varphi \rightarrow 0} \frac{\frac{\eta}{\eta_c} - 1}{\varphi} \cong 5 \quad (2)$$

All independent variables; concentration, particle size distribution and particle shape, relate to the density at which particles are packed in suspension. Both  $\varphi_m$  and  $[\eta]$  depend on shear stress,  $\tau$ . For spherical particles  $\varphi_m$  is 0.63 at  $\tau \rightarrow 0$  and 0.71 at  $\tau \rightarrow \infty$ . There is no theoretical basis of calculating  $\varphi_m$  for polydisperse particles, but it can be obtained empirically from viscosity of suspensions at various volume fractions as was done for cement paste in the present study.

The measured apparent viscosity was fitted towards the volume fraction of solids after programming Eq. 1 into the spread sheet  $\Sigma$ -plot. The apparent viscosity of the liquid filtered from the pastes was estimated to 1.40 mPa·s using the parallel plates in the MCR 300 with a gap of 0.5 mm and was kept constant for all the pastes, although it could have been introduced separately for individual slurries in the spread sheet. The measured,  $\eta_{\text{meas}}$ , and calculated,  $\eta_{\text{calc}}$ , apparent viscosities together with the fitting parameters; maximum volume concentration of solids ( $\varphi_m$ ), intrinsic viscosity ( $[\eta]$ ) and regression factor ( $r^2$ ), are listed in Table 3 and 4 as a function of shear rate.

Table 3 Measured and calculated apparent viscosities ( $\eta_{\text{meas}}$  and  $\eta_{\text{calc}}$ ) at different shear rates ( $\dot{\gamma}$ ) for CEM I 42,5 RR cement slurry with 1.32% lignosulphonate as a function of solids fraction ( $\varphi$ ) together with the fitting parameters in Eq. 1 ( $\varphi_{\text{max}}$  and  $[\eta]$ ) and the regression factor ( $R^2$ ).

$\dot{\gamma}$ (s <sup>-1</sup> )		146		90.4	
$\varphi$	w/c	$\eta_{\text{meas}}$	$\eta_{\text{calc}}$	$\eta_{\text{meas}}$	$\eta_{\text{calc}}$
0.36	0.564	53	37	56	35
0.38	0.518	53	53	55	51
0.40	0.476	87	82	91	79
0.42	0.438	143	138	154	136
0.44	0.404	250	260	261	271
0.46	0.373	601	599	732	698
$\varphi_m =$		0.516		0.505	
$[\eta] =$		5.285		5.089	
$R^2 =$		0.9980		0.9967	

Table 4 Measured and calculated apparent viscosities ( $\eta_{\text{meas}}$  and  $\eta_{\text{calc}}$ ) at different shear rates ( $\dot{\gamma}$ ) for CEM I 42,5 RR cement slurry with 1.32% lignosulphonate as a function of solids fraction ( $\varphi$ ) together with the fitting parameters in Eq. 1 ( $\varphi_{\text{max}}$  and  $[\eta]$ ) and the regression factor ( $R^2$ ).

$\dot{\gamma}$ (s <sup>-1</sup> )		9.79		2.75	
$\varphi$	w/c	$\eta_{\text{meas}}$	$\eta_{\text{calc}}$	$\eta_{\text{meas}}$	$\eta_{\text{calc}}$
0.36	0.564	61	49	122	87
0.38	0.518	66	78	129	149
0.40	0.476	147	137	312	284
0.42	0.438	340	280	830	649
0.44	0.404	723	750	1980	2029
0.46	0.373	3750	3726	13100	12883
$\varphi_m =$		0.484		0.484	
$[\eta] =$		5.397		6.263	
$R^2 =$		0.9995		0.9997	

The curves for measured and calculated apparent viscosities at shear rates of 146 and 9.8 s<sup>-1</sup> are plotted in Fig. 4 and 5, respectively, to visualize the good compliance.

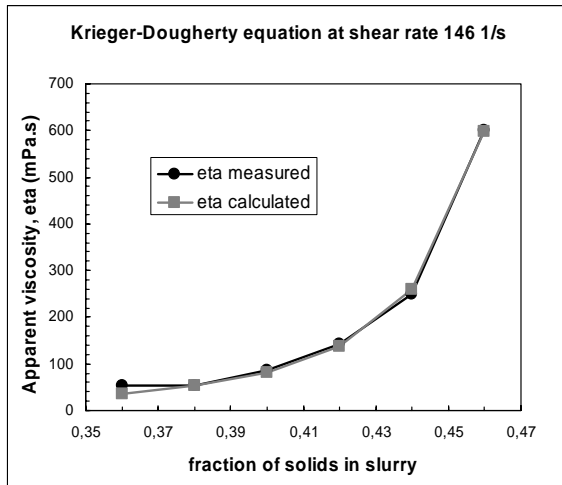


Figure 4 Measured and calculated (Eq. 1) apparent viscosity ( $\eta$ ) for cement slurries as a function of volume fraction of solids ( $\phi$ ) at a shear rate ( $\dot{\gamma}$ ) of  $146 \text{ s}^{-1}$ .

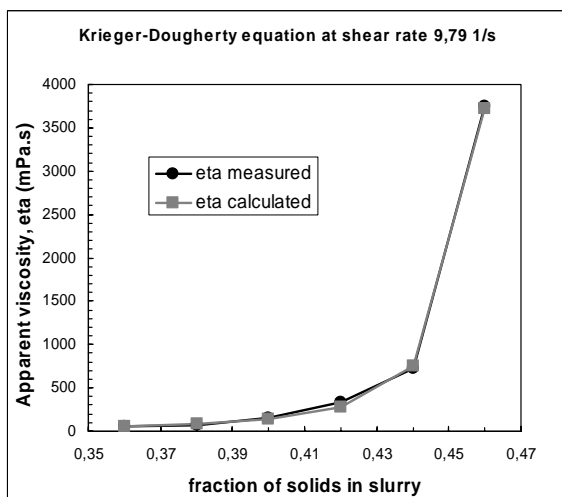


Figure 5 Measured and calculated (Eq. 1) apparent viscosity ( $\eta$ ) for cement slurries as a function of volume fraction of solids ( $\phi$ ) at a shear rate ( $\dot{\gamma}$ ) of  $146 \text{ s}^{-1}$ .

The maximum volume concentration of solids,  $\phi_{\max}$ , is slightly lower than expected (0.65) and it seems like it decreases with decreasing shear rate (and thereby shear stress). The intrinsic viscosity,  $[\eta]$ , found for the cement slurry is as expected (i.e.  $\approx 5$ ).

For the second series of cement slurries, an effort was made to measure the viscosity of the filtered water phase using an Ostwald viscometer. The result was 0.891 and 0.868 mPa.s for the CEM I 42,5 RR and the CEM I 42,5 R-LA cements, respectively. Initial attempts to keep the  $\eta_c$  of Eq. 1 constant gave a good fitting ( $R^2 = 0.98-0.99$ ) in  $\Sigma$ -plot, but ridiculous values of  $\phi_{\max} > 1$ . The next attempt included setting the restraint  $\phi_{\max} < 1$  and let the viscosity be a variable too. These results for the age of 10 min are shown in Tables 5 and 6 as function of shear rate for the CEM I 42,5 RR cement and in Tables 7 and 8 for the CEM I 42,5 R-LA cement.

Table 5 Measured and calculated apparent viscosities ( $\eta_{\text{meas}}$  and  $\eta_{\text{calc}}$ ) at different shear rates ( $\dot{\gamma}$ ) for CEM I 42,5 RR cement slurry with 1% SNF plasticizer as a function of solids fraction ( $\phi$ ) together with the fitting parameters in Eq. 1 ( $\phi_{\max}$  and  $[\eta]$ ) and the regression factor ( $R^2$ ).

$\dot{\gamma} \text{ (s}^{-1}\text{)}$		145		90.8	
$\phi$	w/c	$\eta_{\text{meas}}$	$\eta_{\text{calc}}$	$\eta_{\text{meas}}$	$\eta_{\text{calc}}$
0.40	0.476	807	786	1156	1127
0.41	0.457	924	964	1333	1394
0.43	0.421	1552	1512	2214	2184
0.44	0.404	1917	1942	2786	2771
0.45	0.388	2552	2547	3535	3550
$\phi_m =$		0.568		0.687	
$[\eta] =$		5.847		8.727	
$\eta_c =$		13.71		6.019	
$R^2 =$		0.9979		0.9985	

From Table 5 and 6 it can be seen that the fitting to the Krieger-Dougherty equation (Eq. 1) is quite good ( $R^2 \approx 0.99$ ), but the estimated viscosity of the continuum phase (i.e. water) becomes very high. Furthermore, both the maximum volume concentration of solids,  $\phi_{\max}$ , and the intrinsic viscosity,  $[\eta]$ , gets reasonable

values at high shear rates, but they increases as shear rate decreases.

Table 6 Measured and calculated apparent viscosities ( $\eta_{\text{meas}}$  and  $\eta_{\text{calc}}$ ) at different shear rates ( $\dot{\gamma}$ ) for CEM I 42,5 RR cement slurry with 1% SNF plasticizer as a function of solids fraction ( $\phi$ ) together with the fitting parameters in Eq. 1 ( $\phi_{\text{max}}$  and  $[\eta]$ ) and the regression factor ( $R^2$ ).

$\dot{\gamma}$ ( $\text{s}^{-1}$ )		43.0		22.5	
$\phi$	w/c	$\eta_{\text{meas}}$	$\eta_{\text{calc}}$	$\eta_{\text{meas}}$	$\eta_{\text{calc}}$
0.40	0.476	2019	2060	3271	3317
0.41	0.457	2349	2465	3689	3854
0.43	0.421	3767	3574	5555	5243
0.44	0.404	4372	4330	6133	6143
0.45	0.388	5186	5271	7111	7218
$\phi_{\text{m}} =$		0.868		0.963	
$[\eta] =$		9.583		8.683	
$\eta_{\text{c}} =$		12.10		37.31	
$R^2 =$		0.9914		0.9870	

Table 7 Measured and calculated apparent viscosities ( $\eta_{\text{meas}}$  and  $\eta_{\text{calc}}$ ) at different shear rates ( $\dot{\gamma}$ ) for CEM I 42,5 R-LA cement slurry with 1% SNF plasticizer as a function of solids fraction ( $\phi$ ) together with the fitting parameters in Eq. 1 ( $\phi_{\text{max}}$  and  $[\eta]$ ) and the regression factor ( $R^2$ ).

$\dot{\gamma}$ ( $\text{s}^{-1}$ )		145.0		90.8	
$\phi$	w/c	$\eta_{\text{meas}}$	$\eta_{\text{calc}}$	$\eta_{\text{meas}}$	$\eta_{\text{calc}}$
0.45	0.388	397	455	574	641
0.46	0.373	588	567	857	812
0.48	0.344	959	934	1355	1339
0.49	0.330	1283	1243	1762	1747
0.50	0.317	1699	1708	2291	2304
$\phi_{\text{m}} =$		0.585		0.727	
$[\eta] =$		4.904		8.846	
$\eta_{\text{c}} =$		6.808		1.298	
$R^2 =$		0.9944		0.9962	

As seen from Tables 7 and 8, the fitting to the Krieger-Dougherty equation (Eq. 1) is also quite good ( $R^2 \approx 0.99$ ) for the CEM I

42,5 R-LA cement slurry, but the estimated viscosity of the continuum phase (i.e. water) varies from reasonable to high depending on shear rate. Furthermore, both the maximum volume concentration of solids,  $\phi_{\text{max}}$ , and the intrinsic viscosity,  $[\eta]$ , gets reasonable values at high shear rates, but they increases as shear rate decreases.

Table 8 Measured and calculated apparent viscosities ( $\eta_{\text{meas}}$  and  $\eta_{\text{calc}}$ ) at different shear rates ( $\dot{\gamma}$ ) for CEM I 42,5 R-LA cement slurry with 1% SNF plasticizer as a function of solids fraction ( $\phi$ ) together with the fitting parameters in Eq. 1 ( $\phi_{\text{max}}$  and  $[\eta]$ ) and the regression factor ( $R^2$ ).

$\dot{\gamma}$ ( $\text{s}^{-1}$ )		43.0		22.5	
$\phi$	w/c	$\eta_{\text{meas}}$	$\eta_{\text{calc}}$	$\eta_{\text{meas}}$	$\eta_{\text{calc}}$
0.45	0.388	1021	1143	1689	1945
0.46	0.373	1547	1432	2551	2378
0.48	0.344	2286	2312	3680	3614
0.49	0.330	3047	2980	4578	4496
0.50	0.317	3860	3883	5555	5629
$\phi_{\text{m}} =$		0.730		0.835	
$[\eta] =$		8.510		9.146	
$\eta_{\text{c}} =$		2.961		5.257	
$R^2 =$		0.9935		0.9883	

By comparing slurries with  $\phi = 0.45$  in Table 5 with 7 and in Table 6 with 8, it can be seen that the CEM I 42,5 RR cement slurries has much higher apparent viscosities than CEM I 42,5 R-LA slurries. This is essentially because the first cement has a higher specific surface (546 versus 450  $\text{m}^2/\text{kg}$  as seen from Table 2) and a higher content of the most reactive cement phase,  $\text{Ca}_3\text{Al}_2\text{O}_6$  (7.5% versus 0.5% from Table 1). This means that the hydration activity on the surface of the grains will be much higher for CEM I 42,5 RR than for CEM I 42,5 R-LA. This may give trouble when Eq. 1 is used to study the effect of time since viscosity partly increases due to the conversion of liquid into solids and actual increases  $\phi$  from the nominal value (i.e. what was

weighed in) to an unknown real value that only can be estimated by measuring chemical bound water as a function of time for the slurries. Such corrections should be included in future work. The obtained liquid viscosity,  $\eta_c$ , the maximum volume fraction of solids,  $\phi_{max}$ , and intrinsic viscosity,  $[\eta]$ , as a function of time have been plotted in Figs. 6, 7 and 8, respectively.

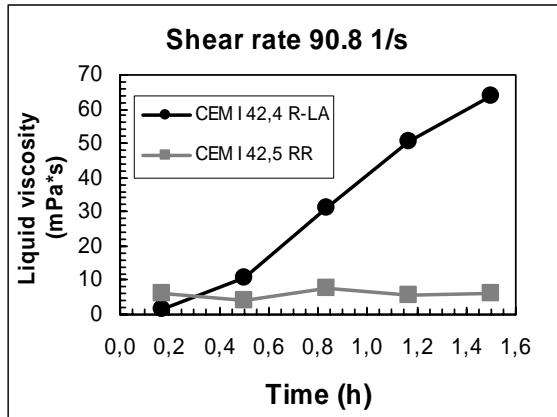


Figure 6 Liquid viscosity,  $\eta_c$ , for cement slurries as a function of time for a shear rate of  $90.8 \text{ s}^{-1}$ . Hydration is not corrected for.

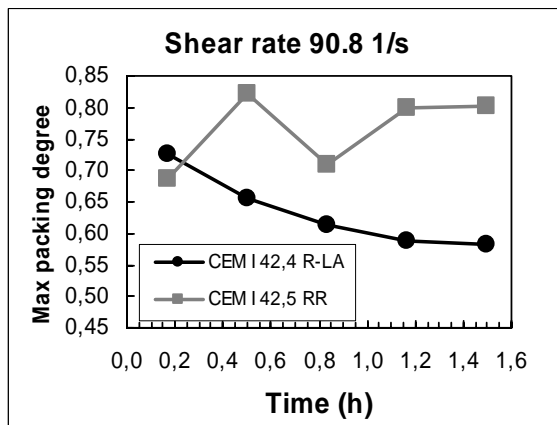


Figure 7 Maximum volume fractions of solids,  $\phi_{max}$ , for cement slurries as a function of time for a shear rate of  $90.8 \text{ s}^{-1}$ . Hydration is not corrected for.

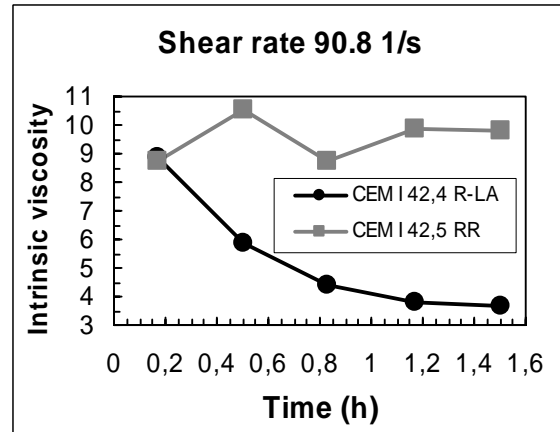


Figure 8 Intrinsic viscosity,  $[\eta]$ , for cement slurries as a function of time for a shear rate of  $90.8 \text{ s}^{-1}$ . Hydration is not corrected for.

By studying Figs. 6, 7 and 8 carefully it can be seen that the variables in the Krieger-Dougherty equation seems to be strongly coupled. When liquid viscosity,  $\eta_c$ , is adjusted up, both maximum volume fraction of solids,  $\phi_{max}$ , and intrinsic viscosity,  $[\eta]$ , are adjusted down. Care should be taken to trust in local minima in  $R^2$  in correlations without judging the obtained parameters.

There are some differences between the cements in the time behavior that probably can be attributed to the consumption of water by hydration. Remember that the more solids there are in suspension, the more sensitive it will be to hydration. Increasing “liquid viscosity” with increasing time for CEM I 42,5 R-LA cement slurries and not for CEM I 42,5 RR cement slurries is probably due to the higher solids content in the former ( $\phi$  ranging from 0.45 to 0.50) than in the latter ( $\phi$  ranging from 0.40 to 0.45). In particular since CEM I 42,5 RR chemically speaking should have higher hydration activity than CEM I 42,5 R-LA. This can only be sorted out by actually determining the chemically bound water and correct the solids volume fractions accordingly.

## CONCLUSION

The Krieger-Dougherty equation is able to describe the influence of solids concentration on apparent viscosity of cement slurries well. Measurements shortly after mixing, using high shear mixer and plasticizers to ensure good dispersion gives reasonable values for the variables, in particular if the shear rates are not too low ( $> 90 \text{ s}^{-1}$ ). Maximum volume fractions of solids,  $\phi_{\text{max}}$ , arrive then at 0.5 - 0.6 and intrinsic viscosity,  $[\eta]$ , at about 5, but both may increase as shear rate decreases. Only liquid viscosity seems to be estimated too high, but this can be due to immediately absorbed water onto the grains shifting the nominal solids fractions to higher values.

Cement is not an inert powder towards water and surface hydration on cement grains will also alter the nominal values of solids volume fractions to unknown real values as a function of time. The apparent viscosities can still be described by the Krieger-Dougherty equation, but the variables may arrive at ridiculous values. The only way of getting around this is to actually measure the amount of chemical bound water in the slurry and correct the solids fractions before fitting. Slurries with high solids content will be affected more than slurries with low solids content.

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