

# MECHANISMS FOR THE CHANGES IN FLUIDITY AND HYDRATION KINETICS OF GROUTS AFTER MIXING

Keisuke Takahashi<sup>1\*</sup> and Thomas Bier<sup>2</sup>

<sup>1</sup> UBE Industries, Ltd., Research & Development Department, JAPAN.

<sup>2</sup> TU Bergakademie Freiberg, Institute of Ceramics, Glass and Construction Materials, GERMANY.

\*: corresponding author. [keisuke.takahashi@ube-ind.co.jp](mailto:keisuke.takahashi@ube-ind.co.jp)

## ABSTRACT

*Mixing and pumping both exert mainly shearing action to adversely affect rheology and hardening properties of cement-based grouts. However, little research conducted on the effects of shearing energies has focused on the mechanisms for such typical changes. This study examines the effects of mixing periods on fluidity and hydration kinetics of grouts with different dispersion conditions adjusted for super plasticizer doses. Our results identify hydration acceleration and a loss in fluidity occurring with increasing mixing energies, even in the case of fully dispersed grouts. From these findings, the mechanism responsible for hydration acceleration is pinpointed as the increase of active surface area to dissolution due to the destruction of the protective superficial layers of cement particles as well as a transition from flocculation to dispersion. The creation of new surfaces leads to further consumption of active super plasticizer in solution phase and to subsequent degrading changes in fluidity.*

**Keywords: Mixing energy; cement-based grout; fluidity; hydration kinetics**

## INTRODUCTION

Mixing and pumping processes of cement-based grouts and self-compacting concrete (SCC) are essential practices in industrial construction. Flawless integrity of construction demands that grouts and SCC have good fluidity and stable hardening characteristics due to their application in various construction methods involving earthquake resistance design and sewage drain rehabilitation. There are some instances<sup>1, 2</sup> where rheology and hardening properties of grouts and SCC undergo

degrading changes after excessive mixing and long distance pumping. Such deterioration will cause a quality loss of workmanship and result in filling problems and structural defects. Nevertheless, not much research on the mixing and pumping processes has been directed at the core reasons or mechanisms for these changes. Ouchi et al.<sup>3</sup> suggested that a change in the dispersion state of cement particles, or in other words, a transition from flocculation to dispersion leads to an extension of the cement surface area and to an increase in hydration rate and in consumption of super plasticizer in solution phase. The interstitial water in the flocculated cement particles may be released possibly due to the dispersion. These proposed factors for changes in the rheological properties and the hydration kinetics of grouts and SCC are widely accepted. In our earlier works<sup>4,5</sup>, we reported the effects of mixing and pumping energies on technological properties of grouts and proposed another mechanism for the changes in fluidity and hydration kinetics: the very fact that mixing and pumping both exert mainly shearing action meant that these could modify the interface of the cement particles — a change defined by the repeated processes of destruction and restoration of protective superficial layers consisting of the concentration gradient of  $\text{Ca}^{2+}$  ions and the coating of cement grains by metastable hydrates. This modification of the interface could also induce changes in the hydration kinetics and the rheological properties. However, there has been little data to prove the presence of the protective superficial layers and the destruction of the layers by shearing action. For the purpose of experimental demonstration of this phenomenon, our work examines the effects of mixing periods and mixing speeds on the properties of grouts with different dispersion conditions adjusted for the doses of super plasticizer by describing and measuring flow values, hydration kinetics, adsorbed amount of super plasticizer and BET specific surface area ( $S_{\text{BET}}$ ).

## EXPERIMENTAL

The experimental grouts contained CEM I 42.5 R, fine aggregate, polycarboxylic ether super plasticizer (PCE) and tap water in the proportions shown in Table 1. Prior to testing, cement, fine aggregate and PCE were pre-mixed (dry and hand mixing) and subsequently mixed with water in a beaker for a maximum of 7 min at 700 rpm (middle speed) and 1100 rpm (high speed) using a chemical stirrer. Glass beads with a grain size of 0.35-0.50 mm were used as the fine aggregate in order to inhibit the adsorption of PCE. The PCE dose for cement was increased to a maximum of 0.291 % by weight (dose A: 0.186 %, dose B: 0.256 %). Grouts with PCE dose B set closer to a fully dispersed state than grouts with PCE dose A. To observe the effects of mixing energies on the properties of almost fully dispersed grouts, the properties of grout A containing PCE dose A were compared to those of grout B containing PCE dose B.

Fluidity was evaluated by flow value, which was measured using a  $\varnothing$  50 mm\*100 mm mini-slump cone based on EN 12706 and tested immediately after mixing. A calorimetric test as an index of hydration kinetics was carried out using the isothermal

conduction calorimeter of a triple type. The rate of heat evolution was monitored for 24 h. The amount of adsorbed PCE on cement surfaces was investigated using a total organic carbon (TOC) meter. Immediately after mixing the grout, the testing solution for TOC was separated from each sample by the centrifugation at 3000 rpm and 1880 G for 10 min. The resulting supernatant solution was filtered with a 0.45  $\mu\text{m}$  membrane-filter.  $S_{\text{BET}}$  was measured by an automatic surface area analyser using the volumetric gas adsorption technique. Prior to the  $S_{\text{BET}}$  test, Nitrogen purging was conducted for 3 h.  $\text{N}_2$  gas was kept at 40 °C. The specimens were frozen by immersion in liquid nitrogen immediately after the mixing and subsequently placed in a freeze drier overnight<sup>6</sup>. The energy expended during grout mixing, defined as the torque was measured using the chemical stirrer equipped with a torque detective servomotor system. The value of torque was recorded once every second. All tests were performed in a constant temperature room at 20 °C. Every test was repeated more than three times under the same conditions.

*Table 1. Proportions of the grouts (unit ; g)*

	<b>CEM I 42.5 R</b>	<b>Glass beads</b>	<b>PCE</b>	<b>Tap water</b>
Grout A	430	570	0.80 (Dose A)	180
Grout B			1.10 (Dose B)	

## RESULTS

Figure 1 (left) shows mixing energies used during grout mixing at 700 rpm and 1100 rpm as a function of mixing time. The mixing energies increased to a maximum value immediately after putting grout powders into water and thereafter decreased. According to Dils<sup>7</sup>, the optimal mixing time of a pan mixer varies between 30 and 180 s. Lowke<sup>2</sup> described three mixing phases that can be distinguished by the rate at which mixing energy is used: dispersion, optimum and overmixing (Fig. 1, right). Therefore, the time periods for mixing the grouts were predetermined at 1 min and 2 min to reflect optimal mixing and 7 min to reflect excessive mixing.

Figure 2 shows the adsorbed amount of PCE per gram of cement weight and flow value as a function of total PCE concentration (PCE dose). Grouts were mixed at 700 rpm for 2 min. As the PCE dose increased, the adsorbed amount of PCE increased and then leveled off with more than 2500 mg/L of total PCE concentration because of the supersaturated adsorption of PCE. The flow value became larger with an increase in the total PCE concentration. The adsorbed amount of PCE correlates with the dispersibility of particles<sup>8</sup>. Optimal mixing energies provide a complete dispersion of raw materials and admixtures<sup>2</sup>. From these findings, grout B mixed for 2 min (optimal duration) is defined as an almost fully dispersed mortar due to its supersaturated adsorption of PCE.

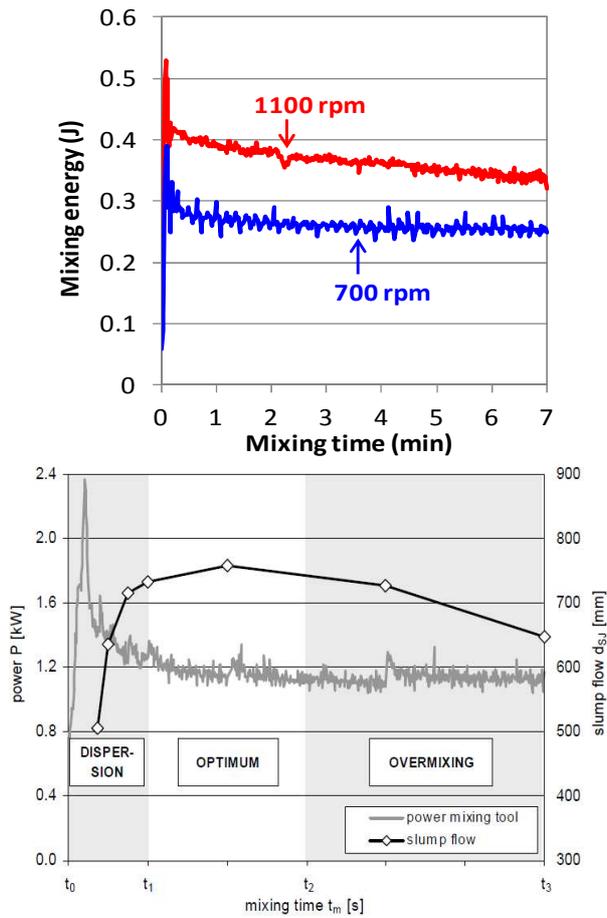


Figure 1. Mixing energies as a function of mixing time (left: measured, right: literature<sup>2</sup>)

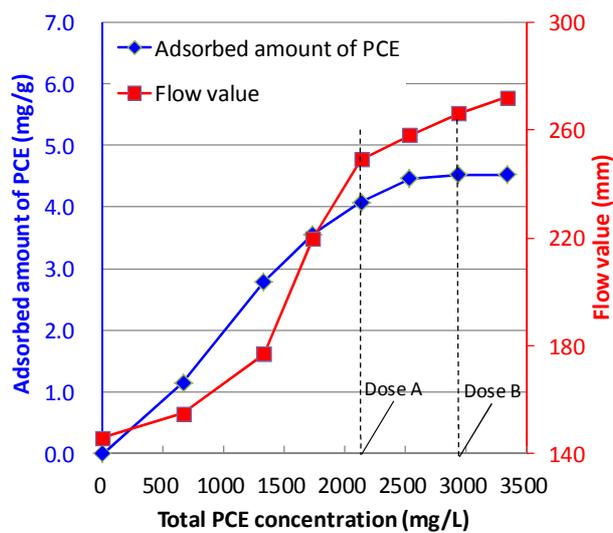


Figure 2. Adsorbed amount of PCE and flow value as a function of total PCE concentration

The effects of mixing periods and mixing speeds on flow values of grouts A and B are shown in Fig. 3. Mixing was predetermined at fixed durations of 1 min, 2 min and 7 min, and at speeds of 700 rpm and 1100 rpm. Flow values decreased with an extended mixing time and higher mixing speed, whereas the degradation rate of grout B was lower than that of grout A.

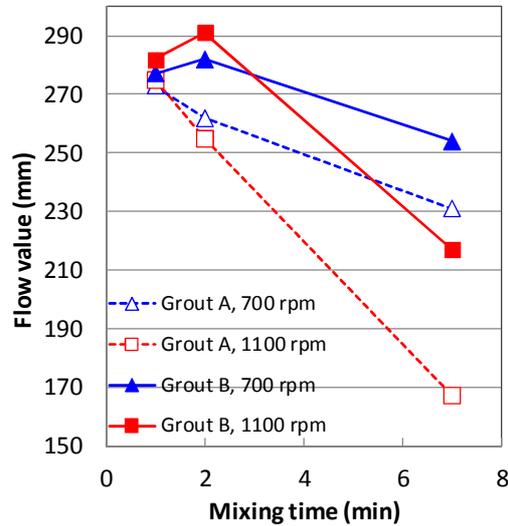


Figure 3. Flow value as a function of mixing time and mixing speeds

Heat release rates of grouts A and B as a function of time are plotted in Fig. 4 for mixing periods of 1 min and 7 min and mixing speeds of 700 rpm and 1100 rpm. With increased mixing duration and mixing speeds, the beginning of accelerated period was advanced and the second peak value of heat release curves increased. These effects of the mixing time and mixing speeds became less pronounced in grout B.

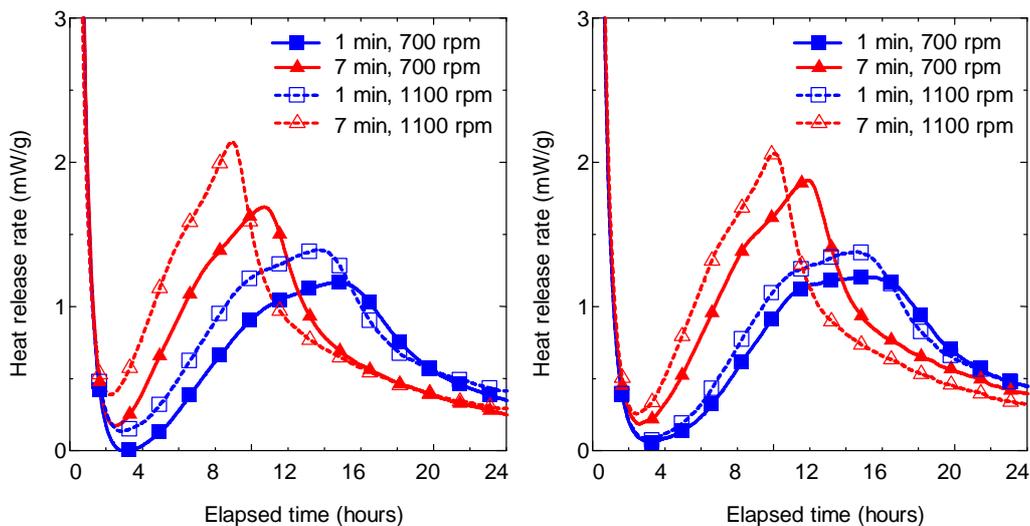


Figure 4. Heat release rates of grouts A (left) and B (right) as a function of time

Table 2 shows the adsorbed amount of PCE, residual amount of PCE in solution phase and  $S_{BET}$  of grouts A and B mixed for 1 min and 7 min at 700 rpm. As duration of mixing became longer, the adsorbed amount of PCE increased and thereby the residual amount of PCE decreased.  $S_{BET}$  increased significantly with an extended mixing time. Compared to grout A, the adsorbed amount of PCE and residual amount of PCE of grout B increased, however, the difference of the residual amount of PCE between 1 min and 7 min became smaller in grout B.

Table 2. Results of TOC test and  $S_{BET}$  test

	Mixing duration	PCE dose	Adsorbed PCE	Residual PCE	$S_{BET}$
	(min)	(mg/L)			( $m^2/g$ )
Grout A	1	2143	1718	425	1.78
	7		1872	271	4.11
Grout B	1	2946	1970	976	1.82
	7		2061	885	3.86

## DISCUSSION

Our results indicate that hydration acceleration, an increase in  $S_{BET}$  and a loss in fluidity occur with increasing mixing energies, even in the case of the almost fully dispersed grout (grout B). In a fully dispersed state, a further increase of surface area will not occur if cement grains are not further divided (milled) or early hydration products are not scraped at the surface by shearing energies. More precisely, the characteristic changes found after excessive shearing action can't be explained solely by a transition from flocculation to dispersion as was described in past studies. We reported the mechanisms for the changes in hydration kinetics: mixing and pumping could destruct protective superficial layers of cement particles exposed to dissolution and subsequently accelerate and increase the hydration rate<sup>5</sup>. In particular when the cement particles were put in contact with water, the  $Ca^{2+}$  ion concentration at the interface approaches the critical concentration. Damidot<sup>9</sup> defined this condition as the formation of an electrical double layer. Initial hydrates form the coating called metastable layer<sup>10</sup>. These layers slow down the dissolution rate. With excessive shearing forces during mixing and pumping, more surfaces of cement grains become exposed to dissolution and/or reaction. This is caused by abrasion of the initial hydrates on the cement surface and/or thinning of the electrical double layer. The damaged superficial layers are restored by further dissolution and precipitation. This repetition of destruction and of restoration increases the dissolution rate and accelerates the continual growth of hydrates. The cement surface ( $S_{BET}$ ) of both grouts A and B increased with an extended mixing time (Table 2). Figure 4 shows massive hydration commenced earlier and the second peak value of the heat release rate increased even in grout B as the mixing was prolonged and more rapid. These results demonstrate that initial hydrates scraped off by the shearing forces provide "seeds"

upon which more CH nucleate. The amount of the seeds could potentially increase with higher shearing forces. More seeds accelerate the hydrate rate and increase the second peak value of the heat release curve<sup>11</sup>. These changes in cement surfaces caused by excessive shearing energies likely occur in a fully dispersed state as well as in a flocculated state. The decrease of flow values could be explained by the formation of initial hydrates or by the insufficient adsorption of PCE, or by the insufficient residual state of unadsorbed PCE in solution phase, or by these phenomena occurring together. PCE adsorbs onto the initial hydrates and disperses cement particles due to electrostatic repulsions and steric hindrances<sup>12</sup>. As mentioned above, both the adsorbing active PCE and the initial hydrates form the metastable layer are being scraped off by the shearing action. The removed PCE is in an “inactive” state. Extended cement surfaces (adsorbed sites), provoked by the lengthened mixing, lead to an increase in the adsorbed amount of active PCE (Table 2). Adsorption of active PCE reduces the active PCE concentration (shown by the residual amount of active PCE) in solution phase. As the active PCE is in short supply, parts of the new surfaces are not covered by the active PCE, hence flow values decrease. The degradation rate of the flow value is lower in grout B because enough active PCE remains in solution phase and is available to adsorb onto the newly created superficial hydrates.

## CONCLUSIONS

Setting out to clarify the mechanisms for the changes in fluidity and hydration kinetics of grouts after a shearing action such as mixing and pumping, the influences of mixing energies on technological properties of grouts with different dispersion conditions adjusted for the doses of super plasticizer were studied on a laboratory scale. Mixing grout over longer periods and at higher speeds results in: flow values decreasing, massive hydration commencing earlier, the second peak values of heat release curves increasing,  $S_{BET}$  increasing and the residual amount of PCE in solution phase decreasing. This was observed even in the case of the almost fully dispersed grout that contained a supersaturated amount of PCE and was mixed for an optimal duration.

Our findings support the concept of the presence of the protective superficial layers and the destruction of the layers by shearing action. That is, with excessive mixing energies, new cement surfaces are created by either removing initial hydrates or by thinning of ion concentration gradient and subsequently the dissolution (hydration) rate increases. As a consequence, more plasticizer adsorbs onto the new surfaces. If there are not enough plasticizer molecules dissolved in solution phase, part of the new surfaces can't be covered by the plasticizer; hence a loss in fluidity occurs.

The key mechanism responsible for hydration acceleration can be conclusively identified as the increase of active surface area to dissolution due to the destruction of the protective superficial layers of cement particles as well as a transition from

flocculation to dispersion. The creation of new surfaces leads to further consumption of active super plasticizer, thereby leading to subsequent degrading changes in fluidity.

## LIST OF REFERENCES

1. *Martinez-Ramirez S. et al., Behavior of repair lime mortars by wet deposition process, Cement and Concrete Research, Vol. 28, No. 2, 1998, pp. 221–229.*
2. *Lowke D. and Schiessl P., Effect of mixing energy on fresh properties of SCC, Proceedings of the 4<sup>th</sup> international RILEM symposium on self-compacting concrete, Chicago, USA*
3. *Ouchi M. and Tsutsui K., Change in flowability of self-compacting concrete due to pumping, Concrete Research and Technology, Vol. 29, No. 2, 2007, pp. 79–84*
4. *Takahashi K. and Bier Th., Effects of mixing energy on placing properties of injection grouts in formed in place pipes, Proceedings of the 29<sup>th</sup> international conference on trenchless technology, Berlin, 2011, DVD-ROM*
5. *Takahashi K., Bier Th. and Westphal T., Effects of mixing energy on technological properties and hydration kinetics of grouting mortars, Cement and Concrete Research, Vol. 41, No. 11, 2011, pp. 1167–1176*
6. *Korpa A. and Trettin R., The influence of different drying methods on cement paste microstructures as reflected by gas adsorption, Cement and Concrete Research, Vol. 36, No. 4, 2006, pp. 634–649*
7. *Dills J. et al., Influence of mixing procedure and mixer type on fresh and hardened properties of concrete: a review, Materials and Structures, Vol. 45, No. 11, 2012, pp.1673–1683*
8. *Uomoto, T. et al., Study on the dispersing effect of polycarboxylate-based dispersant, Concrete Research and Technology, Vol. 21, No. 2, 1999, pp. 79–84*
9. *Damidot D. et al., Kinetics of tricalcium silicate hydration in diluted suspensions by microcalorimetric measurements, J. Am. Ceram. Soc., Vol. 73, No. 11, 1990, pp. 3319–3322*
10. *Gartner E. and Gaidis J., Hydration mechanisms, J. Skalny ed., American Ceramic Society, Westerville, 1989, pp. 95–125*
11. *Thomas J. et al., Influence of nucleation seeding on the hydration mechanisms of tricalcium silicate and cement, J. phys. Chem, Vol. 113, No. 11, 2009, pp. 4327–4334*
12. *Plank J., PCE Superplasticizers – chemistry, applications and perspectives, Proceedings of the 18<sup>th</sup> Internationale Baustofftagung, Weimar, 2012, pp. 91–102*