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Qualitative Explanation of the Fluidity of Fresh Concrete
by Miss Ir.W.L. Sluyter, Prof.Ir. P.C. Kreijger

1. Introduction

Fresh concrete is composed of several types of particles of varying dimensions dispersed in a fluid and especially characterized by a (practical) property called consistency or by others fluidity. This property may vary over a large range and is accompanied – due to heterogeneity – by phenomena like segregation and stability. Moreover fluidity is influenced by mixing-procedures, time and by admixtures.

Mostly cementpaste, mortar and fresh concrete are at macro-level considered as multiphase systems: air phase (bubbles), fluid phase (water) and solid phases (cement, aggregates) with different specific masses ($\approx 0$, 1000, 3100 and 2650 kg/m$^3$ respectively) which are the cause for segregation due to gravitation. In such a consideration also the distribution of the phases in the mixture(s) is different since only water is the continuous phase, the others being discontinuously, leading to a quite different fluidity of the phases themselves.

Despite these facts there is the demand that the mixture must contain the same amount of gravel-, sand-, cement particles, water and air per unit of volume, to be realised by the mixing-procedure.

It will be made clear that a stable mix of wished fluidity only can be reached by a proper use of the micro-level forces between particles and phases, realising the origin of the change in fluidity as effected by time and mixing and knowing in which way admixtures effect the micro-level forces between particles and phases.

To get a qualitative explanation of the fluidity of fresh concrete, the various aspects that play its role from macro- to micro-level are considered in fig. 1. This scheme is worked out in the succeeding paragraphs.
Fig. 1. - Analysis of the fluidity of fresh concrete

Macro level

Wished value of fluidity of fresh concrete

- overall effect in paste, mortar, fresh concrete
- effect of forces
  - sheering planes and sheering forces
  - rheological behaviour

change of fluidity

- effect of time
- stiffening effect

effecting the fluidity

- effect of mixing
- effect of admixtures
- type, dosing, time of adding

- mechanical influence
- physical influence
- chemical influence

Micro-level

- particle size/form
- distance-effect of forces
- amount of water with regard to particles
- air bubbles

- fluid:
  - ionising power
  - concentration and type of ions
  - surface tension

"Factory" where "fluidity" is manufactured
2. Forces between particles

The forces between the particles of various sizes, situated in a fluid can be distinguished as given in table 1.

<table>
<thead>
<tr>
<th>particle sizes (nm)</th>
<th>type of force</th>
<th>effect attracting</th>
<th>repulsing</th>
</tr>
</thead>
<tbody>
<tr>
<td>≈ 30 - 1</td>
<td>mechanical</td>
<td>none</td>
<td>none</td>
</tr>
<tr>
<td>1 - 0.1</td>
<td>capillary</td>
<td>yes</td>
<td>no</td>
</tr>
<tr>
<td>0.1 - 2.10^{-4}</td>
<td>flocculation</td>
<td>yes</td>
<td>no</td>
</tr>
<tr>
<td>2.10^{-4} - 10^{-6}</td>
<td>colloid(double layer)</td>
<td>no</td>
<td>yes</td>
</tr>
<tr>
<td>10^{-6} - 10^{-7}</td>
<td>true solutions</td>
<td>no</td>
<td>yes</td>
</tr>
<tr>
<td></td>
<td>(dissolving forces)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Determining factors:
- Particle size, form and gradation
- Min./max. distance between particles
- Amount of fluid per amount of particle
- Ionising power of fluid
- Type and concentration of ions in fluid
- Surface tension

If, for example, the fractions of the particles mentioned in table 1 are mixed with water and poured vertically through a chute on a porous bottom, fig. 2 gives schematically the rheological behaviour.

**Fig. 2** - Rheological behaviour of a mixture of particles and water poured vertically by means of a chute on a porous base.
2.1. Mechanical forces (particle size $\approx 30 - 1$ mm)

The gravel particles are crumbrous, the water very movable, the fluidity is good but segregation due to gravitation is optimum and the water disappears from the particles.

2.2. Capillary forces (particle size $\approx 1 - 0.1$ mm)

Capillary forces play its role for narrow capillaries, so for small particles and only if no excess of water is present. As a consequence of these forces a coherent mass exists.

During pouring, the mass flows in the form of lumps while amongst the planes of fracture real flow exists which breaks the coherent mass into smaller lumps.

In case of a (too) small amount of water capillary forces too are working between the contact points of the particles while the pores between the particles are filled with air. The surface tension of water assures the coherence of the mass.

2.3. Floculation (particle size $\approx 0.1 - 2.10^{-4}$ mm)

The surface of crystalline matter is covered with electrical charges especially at sharp edges and corners and these play a dominant role for small particles, leading to the forming of flocs by the attraction between the positive and negative charges (fig. 3). The coherence is determined by the force between the contact-points and by the amount of contactpoints per unity of mass-volume: the mass has to be pressed through the chute and stays in the form of a buttery consistency, the water in the flocs is immobilized, the pore volume of the flocs is high. Gravity has a very small effect because of the small sizes of the particles. Floculation is promoted by a fluid with a small ionising power (f.e. with kerosine up to $\approx 0.75$ l/kg, cement is stiff and buttery, while the same amount of water gives a very fluid mortar with strong segregation).

2.4. Colloidal forces (particle sizes $\approx 2.10^{-4} - 10^{-6}$ mm)

In fluids with a strong ionising power (water, alcohol) the repulsive forces of the double layer play a dominant role. By adsorption of water-molecules and a preference-ion the particle gets a surface charge:
zêta-potential (charge per unit of surface) which can be positive or negative. E.g. cement particles in water absorb Ca-ions and get a positive zêta-potential. As a consequence of the charge the particles attract ions from the fluid with an opposite charge and the so-called double-layer is formed. The particles repel each other if there is enough water to get some distance between the particles: fig. 4.

Since the specific surface of the particles is great, the need for water is high, the fluidity is good as well as the coherence. The effect of repulsive forces is greater, the smaller the particles are or the greater the density of the charges.

If less water is available, particles touch and hinder each other and flocculation occurs: the mass gets gel-like in stead of fluid and water is immobilised within the colloidal flocs: fig. 5.

Charge and sign of the colloidal particles are strongly influenced by the type and concentration of the ions in the fluid. The charge can be increased but also abolished in which case flocculation takes place (desalting).

If a mixture of particles is available with opposite charges, flocculation or coagulation takes place resulting in a less fluid and stiffer mass: fig. 6.

2.5 Forces of solution (molecular dimensions of "particles")

Although such ions in fact are no particles, they can be treated as the limit of the given sequence.
Positive and negative ions in a solution are strongly hydrated and there is practically no attraction between the charges, under condition of enough water. Fluidity and coherence are very good, the need for water is great: fig. 7. If there is not enough water, the ions are brought together, the charge-effects dominate and solid separation occurs.

In solution, the water shells give a kind of sterical hindrance or interference. Real sterical hindrance or interference occurs if inert large molecules are adsorbed on particles leading to shells of a thickness of some molecules, so the particles cannot approach each other more than a distance of about 2 times the shell-layer: fig. 8.

If (large) molecules of the solvent itself are adsorbed, this is called solvation, with water as fluid hydration.

Flocculation can be decreased or neutralised by sterical hindrance if the shell is thick enough to bridge the polar forces of the surface of the particles. This method can not be recommended for cement because in that case the sterical hindrance disturbs the setting of the cement.

2.6. Effect of forces between particles

From the foregoing, fig. 9 a/e compares the coherence and fluidity of the masses of the five groups of particles, (9 a,b), the water need of the particles, (9 c), the forces between the particles, (9 d) and the distances between the particles (9 e) in a certain qualitative way for each group of particles looked upon from the macro-level point of view. Seen from the micro-level point of view there is a subtle balance between attractive forces (van der Waals forces, better Hamaker forces) and (electrostatic) repulsive forces in the area of distances between (small) particles smaller than ≈ 1000 nm.
Apart from the distance, the zêta potential of the surfaces, the value of the charges involved, the dielectric constant of the fluid and the electrolyt concentration have their effect on the mutual relationship between these characteristics.

In general for this area of distances the smaller the distance is, the smaller the fluidity while it is possible to create circumstances in such a way that for greater distances equilibrium with a good fluidity exists (fig. 10)

One can conclude that fluidity of fresh concrete especially is influenced by the balance between flocculation and double layer effect (colloidal forces).

Consequently these forces also can be used best to control the fluidity of the fresh concrete which means that flocculation forces have to be weakened (f.e. by an admixture) and/or double layer effects have to be increased (f.e. by increase of the amount of small particles)

![Fig. 9 - Effect of forces per group of particles](image)

![Fig. 10 - Effect of distance on interaction energy between particles](image)
2.7. Sliding planes and shear forces.

The foregoing (2.6) also is effected by the (macroscopic) forming of sliding planes through the larger particles under the influence of shear forces (fig. 11). As a consequence dilatation occurs, porosity increases with a lesser filling of the pores with fluid and so a higher shear force results. Therefore by preference sliding will occur at a flat plane (mould, measuring device etc).

On the other hand a shear force that disrupts the cementflocs will lead to decreased shear force. After stopping the shear force, the flocs recover (thixotropy). In both cases (flocculation, dilatation) a yield stress is necessary to start movement, which is not the case for colloidal and true solutions.

Fig. 12 gives the macroscopic consequences of the foregoing, expressed in the well known shear stress - shear rate diagram. Hydration, 1h after adding water and mixing, leads to about 1.5 times greater viscosity and yield value.

3. Fluidity of mortar and fresh concrete

Fresh concrete includes particle sizes from 30 mm (gravel) to 10⁻⁷ mm (dissolved ions), while in mortar the max. particle size is about 5 mm. Therefore all factors mentioned separately under 2 are now working together. While in the system of the smallest size of particles a good coherence goes together with a good fluidity (see fig.9), now in the system of all particle sizes the small size by its good fluidity has as a consequence the sedimentation of the large particles in this fluid matrix and thus a bad coherence. On the other hand for an optimum coherence (by strong flocculation), the fluidity is bad. This fluidity can be increased by adding more water as well as by increasing the amount of smallest particles however at the price of a decreased coherence.
So one needs a compromise between fluidity and coherence. Fig. 13 gives coherence, fluidity and water need of the composite particle system as affected by the various groups of particles. So for a given mortar or fresh concrete the fluidity can be adjusted on the macro-level by grading and water content and on the micro-level by the ratio between the flocculating forces and the colloidal forces (double layer effect). The stronger the last mentioned forces are, the better the fluidity (fig. 14a) and the less need there is for compaction energy since the coherence is decreased (fig. 14b).

**Fig. 13** - Coherence, fluidity and water need of a composite particle system as effected by particle size.

**Fig. 14a**

- Flocculation forces
- Increased fluidity
- Colloidal forces (stronger)
- Min. vibration energy (without sedimentation)

**Fig. 14b**

4. Measures for increasing the fluidity

Increasing the fluidity of fresh concrete in principle means decreasing the flocculating forces and increasing the deflocculating forces (increasing the effect of double-layer) for which the following measures can be given:

a. to increase the \( \frac{w}{c} \) ratio (and consequently increasing the distance between particles)

b. to use high speed mixing (stirring, grinding)

c. to vibrate (flocculation is removed, however temporary)

d. to add deflocculation agents (with great \( \zeta \)-potential) which increase the effect of the double layer.

e. to add large molecules which are adsorbed by the cement particles (sterical hindrance)

f. to add very fine (<10\( \mu \)) particles (of positive great \( \zeta \)-potential) like fly ash, trass etc.
g. to add air bubbles (with the help of air entraining agents), acting as ball-bearings.

h. to decrease the surface tension of the water in the mix by adding admixtures.

These measures have to be looked upon in connection with the natural occurring stiffening effect of fresh cement paste, mortar and concrete as function of time since this effect can be influenced too (fig. 15).

The natural stiffening effect mainly is the consequence of the (chemical) hydration of the cement particles since already after 3-5 min (lime and) ettringite (are) is formed so the cement particles get a watery gell-like ettringite-shell which decreases the distance between the cement particles and increases the attracting forces (the water is immobilised, gets a lower viscosity) On the other hand cement particles may stick to aggregate particles which also decreases fluidity. So there is a gradually decrease of fluidity already during the dormant period (1-2h) before the chemical reaction of the calcium silicates starts which lead to the forming of more and more fine fibres with time during which process we speak of the setting of cement: that is an arbitrarily chosen point of time during this silicate hydration action. This stiffening is inherent to cement hydration, it only can be avoided if the ettringite forming is retarded (f.e. by a waterreducing retarder see 5.2.e).

Now the first mentioned measure (increase of \(\frac{w}{c}\) ratio needs no further explanation, therefore the following is restricted to the effect of mixing and vibration and to the effect of admixtures.

4.1. Effect of mixing and vibration

Dry cement itself is a flocculated mass in which the cohesion forces mainly are due to van der Waal's forces (in this case more than 100 times greater than gravity forces). If water is poured on cement the contact points between the particles stay the same despite capillary water suction which wets the cement particles and a stiff mix is the result, so no mixing and no fluidity.

The aim of mixing is to get a homogeneous mass in which everywhere the same ratio exists between the amounts of the various particles,
water and air and, as well to disperse (mechanically) the cementflocs in order that wetting of the total surface of these particles is possible and physical and chemical reaction can take place. Physical effects are the forming of double layers (due to Ca\(^{++}\)-ions from the lime that is formed directly after contact between cement and water) by which deflocculation is improved so that after stopping the mixing, the flocculation forces can not be restored (fig. 16). This process also occurs during vibration so that in this stage a good fluidity exists.

During this "agitating" the formed hydration products are sheared off mechanically which in principle leads to accelerated hydration but consequently also to accelerated stiffening (fig. 17).

An optimum mortar fluidity arises if first cement and water are mixed and during further mixing sand is added. For fresh concrete the sequence of adding is not so important because of the grinding of the gravel particles which provides a very intensive mixing.

**Fig. 16** - Effect of mixing on forming of double layers: increased fluidity.

**Fig. 17** - Effect of mixing on stiffening of fresh concrete

4.2. **Effect of admixtures**

a. The addition of mineral powders (very fine particles < 10 \(\mu\)) increases the amount of colloidal particles repelling each other under condition of being charged positively by the adsorption of Ca-ions.

b. Retarders of cementshydration influence the behaviour regarding time since the stiffening effect caused by hydration does not occur and consequently the original fluidity is kept for a longer time. Most effective are retarders of C\(_3\)A-reactions by preventing the grow of gell-like ettringite layers. Of course also the setting is retarded which sometimes may be beneficial.
c. Accelerators increase hydration and therefore may effect a quick stiffening although the forming of effective double layers also is increased.
In a mortar with portland blast furnace cement with high slag content, calcium chloride provides high fluidity because of the extra Ca-ions adsorbed on the fine slag particles and besides because of the slower hydration of this type of cement compared to portland cement.

d. Lowering of the surface tension of water decreases the flocculation forces between the particles and so increases fluidity of the mix. If however this decreased surface tension is the result of a product formed by a chemical reaction with the lime in the mix (fe. NH₃ which lowers the surface tension of lime water) and the formed Ca-salt is insoluble (fe. ammonium carbonate; - sulphate, -phosphate leading to Ca carbonate, -sulphate, -phosphate) these last mentioned products are flocculating ones which decrease the fluidity. If however soluble Ca-salts are formed, the fluidity stays increased by decreased surface tension.

e. Surface active agents contain a hydrophobic C-chain, a hydrophobic group (with O-, S and/or N atoms in it) and mostly one or more polar groups (–COO⁻, –SO₃⁻ or –OSO₄⁻). They are either entraining agents, being mainly active at the air-water interface (stabilizing of air bubbles), or fluidifiers (also called plasticizers or plastifiers) being mainly active at the solid-liquid interface. The agents are adsorbed at these surfaces with an orientation of the molecules that defines the effect.

- So an air entraining agent is an anionic one with a non-polar chain which makes cement hydrophobic by adsorption in such a way that the non-polar chain is directed to the water and the negative ion adsorbed by the cement particle, (fig. 18) This admixture so promotes flocculation while the air bubbles adhere to the cement particles (the best condition for a regular partition) giving an increased yield value, but acting as ball-bearings during flow. An overdosing prevents hydration as no water can reach the cement in such a case.

Fig. 18 - Action of air-entraining agent
(anionic with non-polar chain)
If however the chain of such anionics is polar, these polar parts are adsorbed by the cement particles, charging the cement particles negative with mutual repulsion decreasing the flocculation (cement is dispersed) while the cement particles stay hydrophylic. Water can be reduced while an overdosing does not effect hydration, the air bubbles are isolated (fig. 19). Also the so called super-plastifiers belong to this class (see g) Some of these admixtures preferably are absorbed on C₃A - and C₄AF-parts of the cement particles (e.g.lignosulphonates) and therefore then retard the setting (waterreducing retarders) and consequently also the stiffening.

Fig. 19 - Action of fluidifier (also called plasticizer or plastifier)
(anionic with polar chain)

Although mostly too expensive for concrete technology, cationics with non-polar chain could be used and then are adsorbed in two layers on the cement particles in stead of the Ca⁺⁺-ions leading to positively charged cement particles which repel each other and so lead to greater fluidity (fig. 20) Air bubbles are isolated.

Fig. 20 - Action of cationic with
non polar chain
Non-ionics (phenolglycol or ethylenephenolaethers) which are not charged are fluidifying because of the many dipoles in the molecule, whereas the aether group is the hydrophylic part and the phenol group (with C-chain) the hydrophylic part (fe. C₉H₁₉C₆H₄[OCH₂-CH₂]ₙ-OH).

After adsorption at the cement particles (which stay hydrophylic) they cause deflocculation while sterical hindrance (see fig. 8) is possible, leading to greater fluidity (fig. 21). Air bubbles are isolated and during flow act as ball bearings.

**Fig. 21 - Action of non-ionics**

f. Flocculating or thickening admixtures increase as well yield value as viscosity and thus act opposite to fluidifiers (or plasticisers). These admixtures act either in promoting the flocculation forces (fe in de-charging double layers) or immobilising the water phase. (one can compare the effect to that of gelatine) The consequence is that the coherence and stability of the fresh concrete is increased and segregation is decreased.

g. The so called super-plasticizers (or super-fluidifiers, see also ad e) are anionics of colloidal size (molecular weight ≈ 20 000) with a great amount of polar groups in the chain (N and O) while the "anion" consists of about 60 - SO₃⁻ groups/molecule (fig. 22).

**Fig. 22 - Model and action of super plasticiser**
The cement particles are strongly charged (−) in this way. By an increased zêta-potential (see 3.4) of negative sign and by their size (sterical hindrance) there is a high repulsing effect causing a strongly increased fluidity. Intensive mixing is favourable for the action. They even act after some time of hydration and one can imagine this is caused by deflocculating the watery ettringite-shell around the cement particles: the small ettringite needles are freed from their watery shell by the adsorption of the admixture molecules. (fig. 23)

![Diagram showing the hypothesis of the effect of superplasticizers on cement particles](image)

Fig. 23 - Hypothesis of the effect of superplasticizers on cement particles that are hydrated already somewhat.

h. The time of action of an admixture is restricted since the adsorbed agents become built in the watery ettringite-shell which grows in thickness with time (fig. 24)

![Diagram showing the effect of time on the action of an admixture](image)

Fig. 24 - Effect of time on the action of an admixture
Therefore the dosing of the admixture depends on the time of adding, f.e. the admixture can be added at the building site instead of being added at the ready mixed-concrete plant. The results will be better while the dosing may be smaller (on condition the admixture gets a good partition over the total mix).

The amount of admixture per unit volume of cement or mixing water (concentration) normally is proportional to the effect of the admixture. However for higher concentrations undesired side-effects may occur but also the main effect may change with the dosing. Therefore the concentration is very important and must be restricted to a certain value which is related to the type of cement used (portland cement with high or low C₃A-content, portland blastfurnace cement with high or low slag content, fineness of the cement).

Since all these characteristics of the cement also vary for one type of cement, the effect of an admixture is hardly reproducible, apart from the effect of the intensity of mixing (see 5.1) which is illustrated in fig. 25. Here the effect of the type of mixing is given with regard to the fluidity, characterised by slump and flow table.

![Fig. 25 - Effect of a fluidifier on slump versus time for various mixing procedures.](image)

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Fig. 25 - Effect of a fluidifier on slump versus time for various mixing procedures.
Slump is a measure for the fluidity without vibrations, flowtable-diameter includes them. Mix A is mixed only 1.5 min. With and without fluidifier stiffening occurs (7 cm/10 min) but with fluidifier the slump stays much higher (~ 7 cm). This is also true for the flowtable-diameter. Mix D is mixed most intensive. Slump and flowtable-diameter decrease with time but strongest for the mix with fluidifier. Without admixture even a somewhat greater slump and flowtable-diameter is got after some time: admixture against mixing procedure!

6.5 Selected Literature.

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