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# The effect of viscosity modifying agents on mortar and concrete

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#### **Abstract**

The influence of different viscosity modifying agents (VMA) on the flow properties and the rheology of self-compacting mortars is studied. Additionally, their effect on the early hydration of cement pastes and on the development of concrete strength is determined. Beside the inorganic VMA microsilica (MS) and nanosilica slurry (NS) organic VMA based on high molecular ethylenoxide derivate (EO), natural polysaccharide (PS) and starch derivate (ST) are used. The different VMA are combined with a superplasticizer (SP).

At constant water-to-binder ratio (w/b) the addition of VMA causes a decrease of mortar flow and an increase of flow time (V-funnel test). At the same time yield stress and plastic viscosity are increased. At a constant dosage of superplasticizer (SP) mixtures with VMA require a higher w/b to keep the same flow properties as the reference mixtures without VMA. In spite of the higher w/b flow time and plastic viscosity respectively are only slightly reduced. This property is especially beneficial for the production of stabilizer-type self-compacting concrete where the amount of fines can be reduced with the use of VMA. However, only the use of VMA PS and ST leads to smaller changes of flow when w/b is changed. The organic VMA show almost no influence on early cement hydration and the development of compressive strength. However, the inorganic VMA cause an acceleration of hydration and higher compressive strength at the age of 1 day.

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# 1. Introduction

A low water-to-binder ratio (w/b) of mortar and concrete is required for numerous applications to achieve improved strength and durability. The use of superplasticizers (SP) allows reducing w/b of mortar and concrete without significantly changing their flow properties [1]. However, several problems can show up when using SP. When the concrete or mortar flow is kept constant by the addition of SP, the flow time (V-Funnel) as measure of viscosity is increased [2], because the volume fraction of particles in the suspension increases.

By changing concrete flow properties using SP, problems in concrete production may result. For example, mixtures

with SP are very sensitive to small changes in the w/b increasing the probability of segregation and bleeding. This is often observed in the production of self-compacting concrete (SCC) [3,4]. On the one hand, viscosity modifying agents (VMA) can be used to enhance the resistance to segregation and bleeding [5–8]. On the other hand, their use enables a modification of the flow properties and rheology of mortar and concrete. This property can be used to optimize various types of concrete. Shotcrete for example demands a relatively high yield stress and a relatively low viscosity to control adhesion and rebound behavior respectively [9,10]. As another example, when concrete is pumped, a high viscosity of the mixture decreases the output at a constant pumping pressure.

The objective of this study is to investigate the effects of various VMA on flow properties and rheology. The tests are conducted on self-compacting mortars because they react sensitively to changes in composition. Additionally,

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the effects of VMA on early cement hydration and compressive strength of concrete are studied.

# 2. Materials

Ordinary Portland cement CEM I 42.5 N according to European Standard EN 197-1 was used as binder (Table 1). Different commercial available viscosity modifying agents were examined: the inorganic VMA microsilica (MS) and nanosilica slurry (NS), as well as high molecular ethylenoxide derivate (EO), natural polysaccharide (PS) and starch derivate (ST) as examples for organic VMA. In mortar and concrete mixtures, all VMA were applied in combination with a polycarboxylate type superplasticizer (SP) (Table 2). All dosages of liquid admixtures are referring to the aqueous solutions and not to the solid fraction. The solid content was measured according to European Standard EN 480-8 by drying the admixtures at 105 °C for 4 h.

The first test series was conducted on mortars. The volume of paste was kept constant at 57%. Natural sand (carbonates and silicates) with a grain size of 0-2 mm (0.0–0.5 mm: 53%, 0.5–1.0 mm: 26%, 1.0–2.0 mm: 21%) was used as aggregate. A mixer according to European Standard EN 196-1 at stage I (62.5 rpm) was used to prepare the fresh mortars. The dry mortar constituents were mixed for 1 min. The water with dissolved liquid admixtures was added progressively during the next 30 s. After continuing the mixing for 1 min it was stopped for 30 s in order to scrape off the material that had adhered to the sides of the mixing bowl with a plastic spatula. After that followed a second mixing period of 1 min. Seventy-five different mortar mixtures were produced. The type and amount of VMA added was varied while keeping the amount of SP constant at 1.0%. Reference mixtures were produced with no VMA but with the same dosage of SP. Water/binder ratio (w/b) was always changed in steps of 0.02. It was increased until the flow time (V-Funnel) was reduced below 2 s and decreased until the mortar flow reached a value below 200 mm maximum spread diameter. In the second test series the influence of the different VMA on compressive strength of concrete was determined. The concrete mixtures were made with 300 kg/m³ of ordinary Portland cement (Table 3) at a water/binder ratio of 0.50. Two reference concretes, one without any admixtures and one containing 0.4% SP were produced. 0.5% by mass of SP was added to the concrete mixtures containing VMA (dosage given in Table 2). Natural gravel (carbonates and silicates) with a grain size of 0–32 mm (0–4 mm: 38%, 4–8 mm: 16%, 8–16 mm: 16%, 16–32 mm: 30%) was used as aggregate.

In the third test series calorimetric measurements were made on cement pastes with w/b ratio 0.40 using the medium dosage of VMA and the same dosage of SP as in the first test series.

#### 3. Methods

#### 3.1. Flow properties

A cone according to European standard EN 1015-3 with an upper diameter of 70 mm, a lower diameter of 100 mm and a height of 60 mm was used to perform the mortar flow test and measure the resulting mortar flow (maximum spread diameter without shocking) [11]. In the mortar funnel test the flow time of the mixtures was determined (Fig. 1) [11]. The flow of the concrete was measured according to the European standard EN 12350-5 (flow table test with shocking). Its compactability due to the vibration with a poker was determined according to EN 12350-4. In this test the concrete is filled in a vessel and vibrated for 60 s. The compactability is derived from the decrease of height of the concrete in the vessel due to vibration.

# 3.2. Rheology

The flow behavior of cement paste, mortar and concrete (as other particle suspensions) can be in many cases described with sufficient accuracy by the Bingham model:

Table 1 Composition of the ordinary Portland cement CEM I 42.5 N

| CaO<br>(%) | SiO <sub>2</sub> (%) | Al <sub>2</sub> O <sub>3</sub> (%) | Fe <sub>2</sub> O <sub>3</sub> (%) | MgO<br>(%) | K <sub>2</sub> O<br>(%) | Na <sub>2</sub> O<br>(%) | SO <sub>3</sub> (%) | Loss on ignition (%) | Blaine<br>(cm <sup>2</sup> /g) | Density<br>(kg/m³) |
|------------|----------------------|------------------------------------|------------------------------------|------------|-------------------------|--------------------------|---------------------|----------------------|--------------------------------|--------------------|
| 63.5       | 19.8                 | 4.6                                | 2.5                                | 1.8        | 0.89                    | 0.10                     | 3.2                 | 2.66                 | 2680                           | 3.13               |

Table 2 Characterization of the admixtures and applied dosages for mortar tests, calorimetry<sup>1</sup>, and concrete tests

| Admixture | Substance                          | Total solid (%) | Dosage (mass% of c | ement)                                               |
|-----------|------------------------------------|-----------------|--------------------|------------------------------------------------------|
| VMA MS    | Microsilica                        | 100             | Mortar concrete    | 2.0/6.0 <sup>1</sup> /10.0 4.0                       |
| VMA NS    | Nanosilica slurry                  | 16.4            | Mortar concrete    | $0.5/1.0^{1}/1.5 \ 0.5$                              |
| VMA EO    | High molecular ethylenoxy derivate | 1.9             | Mortar concrete    | $0.5/1.0^{1}/1.5 \ 0.5$                              |
| VMA PS    | Natural polysaccharide             | 3.9             | Mortar concrete    | $0.2/0.4^{1}/0.8 \ 0.2$                              |
| VMA ST    | Starch derivate                    | 3.4             | mortar concrete    | $0.2/0.4^1 \ 0.2$                                    |
| SP        | Polycarboxylate                    | 31.0            | Mortar concrete    | 1.0 <sup>1</sup> , 0.4 (without VMA), 0.5 (with VMA) |

Table 3
Flow properties and rheological properties of mortar samples

| Гуре<br>VMA | Dosage<br>VMA mass% | w/b  | Mortar flow<br>(mm) | Flow time (s) | Yield stress<br>(Pa) | Plastic<br>viscosity<br>(Pa s) | Type<br>VMA | Dosage<br>VMA mass% | w/b  | Mortar flow<br>(mm) | Flow time (s) | Yield stress<br>(Pa) | Plastic<br>viscosity<br>(Pa s) |
|-------------|---------------------|------|---------------------|---------------|----------------------|--------------------------------|-------------|---------------------|------|---------------------|---------------|----------------------|--------------------------------|
|             | _                   | 0.36 | 193                 | 6.2           | 72                   | 37                             | EO          | 0.5                 | 0.46 | 264                 | 1.9           | 18                   | 7                              |
| _           | _                   | 0.38 | 220                 | 4.2           | 53                   | 22                             | EO          | 1.0                 | 0.40 | 195                 | 4.7           | 68                   | 21                             |
| _           | _                   | 0.40 | 243                 | 3.0           | 26                   | 14                             | EO          | 1.0                 | 0.42 | 224                 | 3.2           | 44                   | 14                             |
| _           | _                   | 0.42 | 250                 | 2.4           | 22                   | 11                             | EO          | 1.0                 | 0.44 | 244                 | 2.5           | 29                   | 11                             |
| -           | _                   | 0.44 | 275                 | 1.8           | 13                   | 8                              | EO          | 1.0                 | 0.46 | 260                 | 2             | 22                   | 9                              |
| _           | _                   | 0.46 | 290                 | 1.2           | 11                   | 5                              | EO          | 1.0                 | 0.48 | 282                 | 1.5           | 13                   | 6                              |
| -           | _                   | 0.48 | 320                 | 1.0           | 7                    | 5                              | EO          | 1.5                 | 0.40 | 187                 | 4.8           | 80                   | 22                             |
| MS          | 2                   | 0.38 | 196                 | 4.8           | 73                   | 25                             | EO          | 1.5                 | 0.42 | 218                 | 3.2           | 45                   | 14                             |
| ΜS          | 2                   | 0.40 | 223                 | 3.3           | 47                   | 16                             | EO          | 1.5                 | 0.44 | 235                 | 2.8           | 33                   | 12                             |
| ΜS          | 2                   | 0.42 | 246                 | 2.6           | 33                   | 13                             | EO          | 1.5                 | 0.46 | 256                 | 2             | 24                   | 8                              |
| ΛS          | 2                   | 0.44 | 267                 | 2.1           | 22                   | 10                             | EO          | 1.5                 | 0.48 | 264                 | 1.6           | 19                   | 6                              |
| ΜS          | 2                   | 0.46 | 281                 | 1.8           | 14                   | 7                              | PS          | 0.2                 | 0.38 | 197                 | 4.4           | 69                   | 22                             |
| ΜS          | 6                   | 0.40 | 188                 | 4.6           | 77                   | 22                             | PS          | 0.2                 | 0.40 | 234                 | 3             | 42                   | 16                             |
| ΜS          | 6                   | 0.42 | 213                 | 3.2           | 62                   | 18                             | PS          | 0.2                 | 0.42 | 253                 | 2.4           | 31                   | 12                             |
| AS          | 6                   | 0.44 | 232                 | 2.7           | 38                   | 15                             | PS          | 0.2                 | 0.44 | 269                 | 2             | 22                   | 9                              |
| 1S          | 6                   | 0.46 | 257                 | 2.1           | 21                   | 13                             | PS          | 0.2                 | 0.46 | 282                 | 1.6           | 15                   | 7                              |
| 1S          | 6                   | 0.48 | 271                 | 1.7           | 20                   | 7                              | PS          | 0.4                 | 0.38 | 192                 | 4.8           | 90                   | 25                             |
| 4S          | 10                  | 0.42 | 197                 | 4.0           | 80                   | 19                             | PS          | 0.4                 | 0.40 | 218                 | 3.5           | 49                   | 18                             |
| 4S          | 10                  | 0.44 | 209                 | 3.0           | 61                   | 16                             | PS          | 0.4                 | 0.42 | 238                 | 2.8           | 44                   | 13                             |
| AS          | 10                  | 0.46 | 232                 | 2.5           | 45                   | 11                             | PS          | 0.4                 | 0.44 | 252                 | 2             | 35                   | 9                              |
| AS          | 10                  | 0.48 | 266                 | 1.7           | 24                   | 9                              | PS          | 0.4                 | 0.46 | 272                 | 1.7           | 21                   | 7                              |
| NS.         | 0.5                 | 0.38 | 177                 | 5.5           | 87                   | 30                             | PS          | 0.4                 | 0.48 | 274                 | 1.4           | 17                   | 6                              |
| NS          | 0.5                 | 0.40 | 201                 | 4.0           | 61                   | 20                             | PS          | 0.8                 | 0.38 | 178                 | 5.8           | 126                  | 27                             |
| NS.         | 0.5                 | 0.42 | 222                 | 3.0           | 37                   | 14                             | PS          | 0.8                 | 0.40 | 202                 | 4.0           | 82                   | 23                             |
| IS          | 0.5                 | 0.44 | 241                 | 2.4           | 33                   | 11                             | PS          | 0.8                 | 0.42 | 223                 | 3.1           | 61                   | 15                             |
| IS          | 0.5                 | 0.46 | 268                 | 1.8           | 17                   | 7                              | PS          | 0.8                 | 0.44 | 241                 | 2.4           | 45                   | 12                             |
| IS          | 1.0                 | 0.40 | 197                 | 3.8           | 69                   | 21                             | PS          | 0.8                 | 0.46 | 256                 | 2.0           | 31                   | 8                              |
| IS          | 1.0                 | 0.42 | 221                 | 2.9           | 43                   | 14                             | PS          | 0.8                 | 0.48 | 263                 | 1.6           | 26                   | 7                              |
| IS          | 1.0                 | 0.44 | 245                 | 2.2           | 28                   | 10                             | ST          | 0.2                 | 0.40 | 190                 | 4.4           | 91                   | 22                             |
| IS          | 1.0                 | 0.46 | 257                 | 1.9           | 25                   | 8                              | ST          | 0.2                 | 0.42 | 211                 | 3.4           | 63                   | 17                             |
| IS          | 1.5                 | 0.42 | 177                 | 4.0           | 125                  | 16                             | ST          | 0.2                 | 0.44 | 225                 | 2.8           | 51                   | 13                             |
| S           | 1.5                 | 0.44 | 209                 | 2.8           | 79                   | 10                             | ST          | 0.2                 | 0.46 | 245                 | 2.2           | 33                   | 10                             |
| IS          | 1.5                 | 0.46 | 224                 | 2.3           | 55                   | 9                              | ST          | 0.2                 | 0.48 | 256                 | 1.8           | 22                   | 8                              |
| 1S          | 1.5                 | 0.48 | 245                 | 1.8           | 47                   | 7                              | ST          | 0.4                 | 0.42 | 194                 | 3.8           | 105                  | 17                             |
| EO          | 0.5                 | 0.38 | 176                 | 5.7           | 115                  | 27                             | ST          | 0.4                 | 0.44 | 210                 | 3.0           | 79                   | 14                             |
| EO          | 0.5                 | 0.40 | 206                 | 3.6           | 55                   | 16                             | ST          | 0.4                 | 0.46 | 229                 | 2.4           | 61                   | 12                             |
| EO          | 0.5                 | 0.42 | 230                 | 2.9           | 41                   | 14                             | ST          | 0.4                 | 0.48 | 231                 | 2.0           | 57                   | 11                             |
| EΟ          | 0.5                 | 0.44 | 250                 | 2.4           | 29                   | 12                             | ST          | 0.4                 | 0.50 | 248                 | 1.7           | 40                   | 9                              |

All mixtures contain 1.0% SP.

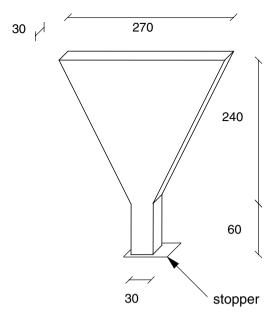


Fig. 1. V-funnel, measures in mm.

$$\tau = \tau_0 + \eta_{\rm pl} \cdot \dot{\gamma} \tag{1}$$

where  $\tau$  is the shear stress;  $\tau_0$  the yield stress;  $\eta_{\rm pl}$  the plastic viscosity and  $\dot{\gamma}$  is the shear rate.

In contrary to Newtonian fluids, where shear stress and shear rate are directly proportional, a minimum stress – the yield stress – is necessary for flow to occur. Above the yield stress the shear stress vs. shear rate curve has a constant slope that is generally termed as plastic viscosity.

The rheological properties of the mortars were measured on the same mixtures as mortar flow and flow time. A rheometer (Paar Physica MCR 300) was used in controlled shear rate mode. It was equipped with a ball measuring system, developed especially for cement pastes and mortars [12–14]. It allows the measurement of suspensions up to a maximum grain size of about 4 mm and is also used in other fields of applications like debris flow material [15]. A flow curve with shear rates varying from 0.001 to  $30 \, \mathrm{s}^{-1}$  was recorded. Yield stress and plastic viscosity were calculated according to the Bingham equation.

The measuring principle is shown in Fig. 2. Instead of a laminar flow, as in other geometries like plate—plate or cylinder, a displacement flow is caused by an eccentrically rotating sphere. The sphere moves in the mortar along the edge of the vessel covering a segment of about 300°. During this movement the speed of the sphere is increased and torque is measured.

According to [14] and also described in [15], the governing equations of the ball measurement system are as follows.

The movement of a sphere through a Newtonian fluid for Reynolds numbers Re < 1 can be expressed by the Stokes equation, assuming that the Stokes equation is also valid in the case of a non-Newtonian medium like a cement particle suspension:

$$F = 3 \cdot \pi \cdot \eta \cdot v \cdot D \tag{2}$$

where F is the force;  $\eta$  the dynamic viscosity of the fluid; v the velocity of the sphere; and D is the diameter of the sphere.

The Reynolds number is defined as:

$$Re = \frac{v \cdot D \cdot \rho}{\eta} < 1 \tag{3}$$

where Re is the Reynolds number and  $\rho$  is the fluid density. Torque and sphere velocity are given as:

$$M = F \cdot L_{\mathsf{h}} \tag{4}$$

$$v = \omega \cdot L_{\rm h} \tag{5}$$

where M is the torque;  $L_{\rm h}$  the distance between sphere and container center; and  $\omega$  is the angular velocity.

From Eqs. (2), (4) and (5) the torque  $M_1$  is given as:

$$M_1 = 3 \cdot \pi \cdot \eta \cdot \omega \cdot D \cdot L_b^2 \tag{6}$$

An additional torque  $M_2$  results from self-rotation of the sphere:

$$M_2 = \pi \cdot \eta \cdot \omega \cdot D^3 \tag{7}$$

The total torque M is

$$M = M_1 + M_2 = \pi \cdot \eta \cdot \omega \cdot (3 \cdot L_h^2 \cdot D + D^3) \tag{8}$$

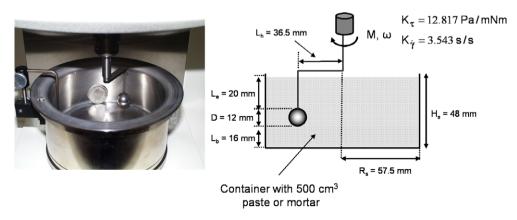


Fig. 2. Principle of a rheometer with a sphere measuring system according to Tyrach [14] (scheme adapted from [15]).

Dynamic viscosity is given as

$$\eta = \frac{\tau}{\dot{y}} \tag{9}$$

From Eqs. (8) and (9) the linear relationships for shear rate and shear stress can be derived.

$$\dot{\gamma} = \frac{\pi \cdot \tau}{M} \cdot (3 \cdot D \cdot L_{\rm h}^2 + D^3) \cdot \omega = K_{\dot{\gamma}} \cdot \omega \tag{10}$$

$$\tau = \frac{\dot{\gamma}}{\pi \cdot \omega} \cdot \frac{1}{3 \cdot D \cdot L_{\rm b}^2 + D^3} \cdot M = K_{\tau} \cdot \omega \tag{11}$$

This linear relationship was verified using different polymer solutions [14]. The proportionality factors are related to the geometry of the system (influence of the thin ball holder, container wall and bottom, etc.). Their values for the applied geometry are given in Fig. 2.

The ball measurement system has several advantages compared to conventional systems (e.g. cylinder or plate–plate), when used for building materials: wall slip and shear induced sedimentation are minimized. However it has to be kept in mind that the measuring time at high shear rates is quite short (between 10 s at a shear rate of  $0.001 \, \mathrm{s}^{-1}$  and  $0.1 \, \mathrm{s}$  at a shear rate of  $10 \, \mathrm{s}^{-1}$  in the applied measuring profile), because the ball does not perform more than one full round through the beaker. Therefore, a steady state of flow might not be reached in some cases.

# 3.3. Heat flow calorimetry

Isothermal heat flow calorimetry was carried out on cement pastes with w/b of 0.40 to determine the influence of the used admixtures on early cement hydration. One reference paste without any admixture was used, one paste contained only SP (1.0%) and the others 1.0% SP and VMA in the medium dosage of the mortar mixtures (Table 2). A conduction calorimeter (Thermometric TAM Air) was used for the experiments. About 6.00 g of cement were weighed into a flask and 2.40 ml of water or the admixture containing aqueous solution were added. The mixing was done by a small stirrer for 2 min. The flask was then capped and placed into the calorimeter. The heat flow was recorded for 72 h. Measuring temperature was 20 °C.

# 3.4. Strength development

Compressive strength was measured on concrete prisms  $120 \text{ mm} \times 120 \text{ mm} \times 360 \text{ mm}$  at the age of 1, 2, 7 and 28 days according to Swiss Standard SIA 162/1. Four specimens were tested per concrete and age. The specimens were stored at a temperature of 20 °C and a relative humidity of 90%.

#### 4. Results and discussion

The flow properties and the rheological properties of the mixtures studied are summarized in Table 3.

# 4.1. Flow properties

At a constant w/b all VMA cause a decrease of the mortar flow and an increase of the flow time (first series). As an example, the effect of VMA PS is shown in Figs. 3 and 4. The changes are dependent on the type and dosage of the VMA. This can be illustrated by the increase of w/b needed for the mixtures with VMA to achieve the same mortar flow as the reference mixtures ("water demand"/Fig. 5). The mixtures with VMA MS and VMA PS display a linear change of water demand with increased dosages. The increase from 0.5 to 1.5 mass% of VMA EO results in a smaller change of the water demand than the increase from 0.0 to 0.5 mass%. Changing the dosage of VMA NS from 0.5 to 1.0 mass% has no significant effect. A dosage of 0.2 mass% of VMA ST significantly affects water demand, but

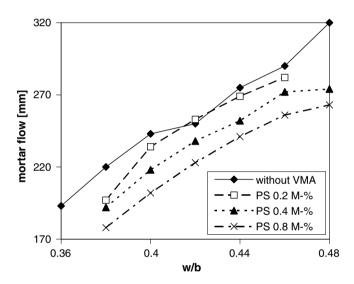


Fig. 3. Typical change of mortar flow with the addition of VMA (VMA PS = natural polysaccharide) at different w/b.

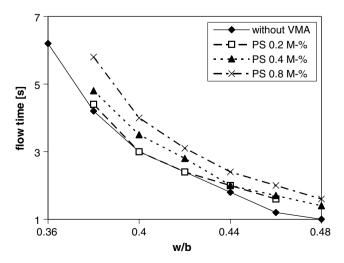


Fig. 4. Typical change of flow time with the addition of VMA (VMA PS = natural polysaccharide) at different w/b.

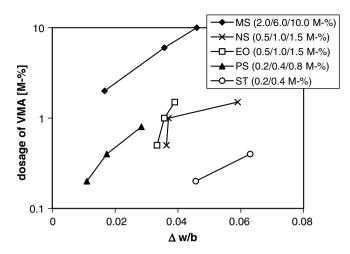


Fig. 5. Average increase of w/b required for the series with VMA to reach the same mortar flow (200, 225 and 250 cm) as the reference series without VMA

the change caused by the increase to  $0.4~\mathrm{mass}\%$  is much smaller.

The susceptibility of the mortar flow on changes of w/b is influenced by the addition of VMA. The gradient of the curves mortar flow vs. w/b (as shown in Fig. 3 for VMA PS) was calculated for the different VMA and dosages (Table 4). In general, the inorganic VMA MS and NS and the organic VMA EO show a bigger gradient and VMA PS (0.4% and 0.8%) and VMA ST a smaller gradient than the mixtures without VMA. These differences are relatively small. However, they indicate that variations of w/b in the production of concrete cause more pronounced changes of flow properties when VMA MA, NS and EO are used compared to VMA PS and ST.

In order to see, if the addition of VMA causes a change in the relationship between mortar flow and flow time, mixtures with dosages of VMA causing a similar water demand are compared to the reference mixtures (Fig. 6). The addition of VMA does not cause a significant change in the relation of these two parameters. At an equivalent mortar flow, the flow time of the mixtures with VMA is slightly decreased. However, it has to be kept in mind that the mixtures with VMA need an increase of w/b of about 0.035 to reach the same mortar flow as the reference mixtures (Fig. 5). Consequently, mixtures with VMA show a very similar flow properties as the mixtures without VMA at a considerably higher w/b. The difference between a decrease of w/b and the addition of VMA on flow properties can be shown when the two are compared starting with the same

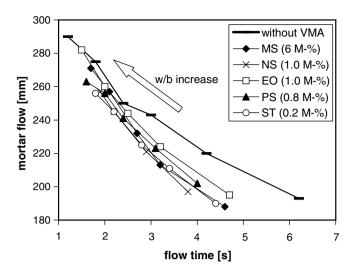


Fig. 6. Relation of mortar flow versus flow time for mixtures with dosages of VMA resulting in a comparable water demand.

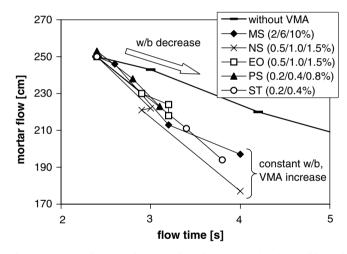


Fig. 7. Change of mortar flow and flow time caused by the addition of VMA at a constant w/b of 0.44 compared to the change caused by a decrease of w/b of the reference mixtures without VMA.

mixture (Fig. 7). The addition of VMA increases flow time significantly less than a reduction of w/b. There are no obvious differences between the different VMA.

Flow and compactability of the concrete (second series) show no systematic change due to the addition of VMA (Table 5). The used dosages of the different VMA are relatively low though. Additionally, the used methods are not very sensitive to small changes in composition.

Table 4
Gradient of the curve "mortar flow versus w/b"

| Series                           | No VMA | VMA MS                      | VMA NS                           | VMA ED                          | VMA PS                         | VMA ST             |
|----------------------------------|--------|-----------------------------|----------------------------------|---------------------------------|--------------------------------|--------------------|
| Dosage (%)/<br>gradient of curve | -/988  | 2/1070<br>6/1050<br>10/1150 | 0.5/1110<br>1.0/1020<br>1.5/1095 | 0.5/1100<br>1.0/1050<br>1.5/960 | 0.2/1025<br>0.4/837<br>0.8/864 | 0.2/775<br>0.4/645 |

Table 5
Flow and compactability of the concrete mixtures

| Mixture            | No admixtures | Only SP | VMA MS | VMA NS | VMA EO | VMA PS | VMA ST |
|--------------------|---------------|---------|--------|--------|--------|--------|--------|
| Concrete flow (cm) | 33            | 54      | 41     | 43     | 56     | 62     | 47     |
| Compactability     | 1.23          | 1.05    | 1.08   | 1.12   | 1.04   | 1.03   | 1.07   |

Dosages of SP are shown in Table 2.

#### 4.2. Rheology

Yield stress and plastic viscosity of the mortars increase when VMA are added and w/b ratio is kept constant. As an example, the effect of VMA PS is shown (Figs. 8 and 9). The changes in yield stress and plastic viscosity caused by the different VMA and dosages are very similar to the changes in mortar flow and flow time (see Figs. 3 and 4).

A comparison of yield stress versus plastic viscosity (using the same mixtures as in the comparison between

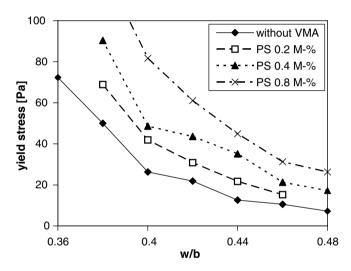


Fig. 8. Typical change of yield stress with the addition of VMA (VMA PS = natural polysaccharide) at different w/b.

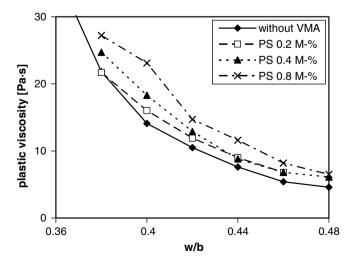


Fig. 9. Typical change of plastic viscosity with the addition of VMA (VMA PS = natural polysaccharide) at different w/b.

mortar flow and flow time, see Fig. 6) shows that the addition of VMA causes a change in the relation between these two parameters (Fig. 10). With a decrease of w/b, yield stress increases more compared to the reference mixtures at an equivalent plastic viscosity. The differences are relatively small, although the w/b of the mixtures with VMA is significantly higher. This is in good agreement with the comparison between mortar flow and flow time of the same mixtures. However, some differences between the effects of the different VMA are indicated in the rheological results. VMA PS causes the strongest increase of yield stress and VMA MS the lowest. This trend is present as well when the effects of a decrease of w/b and an addition of VMA are compared (Fig. 11). However, a reduction of w/b causes a bigger increase of plastic viscosity at an equivalent yield stress than an addition VMA (Fig. 11).

In order to keep mortar flow constant when VMA are added, the w/b can be increased as shown here. The other possibility is to keep the w/b constant and increase the dosage of SP. With this approach the same relative changes of yield stress and plastic viscosity between the different VMA can be expected. But because SP mainly reduces yield stress, the resulting mixtures would have a significant higher plastic viscosity than the mixtures where the w/b was increased to keep the mortar flow constant.

#### 4.3. Heat flow calorimetry

The cement used in this study reaches its main hydration peak 11.3 h after mixing if no admixtures have been added

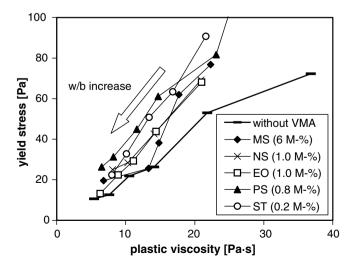


Fig. 10. Relation of yield stress versus plastic viscosity for mixtures with dosages of VMA resulting in a comparable water demand.

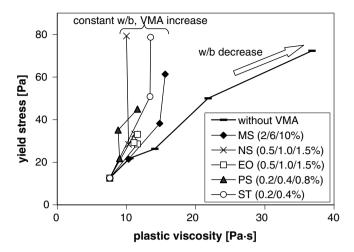


Fig. 11. Change of yield stress and plastic viscosity caused by the addition of VMA at a constant w/b of 0.44 compared to the change caused by a decrease of w/b of the reference mixtures without VMA.

(Fig. 12). The SP causes a strong retardation of cement hydration. The maximum heat flow of the mix containing only SP as admixture occurs after 27.1 h. The silica-based inorganic VMA microsilica (VMA MS) and nanosilica (VMA NS) accelerate hydration with respect to the mixture containing only SP. Nanosilica (peak maximum after 20.6 h) accelerates stronger than microsilica (peak maximum after 24.2 h), although its dosage is much lower. Microsilica may act as nucleation sites for calcium hydrox-

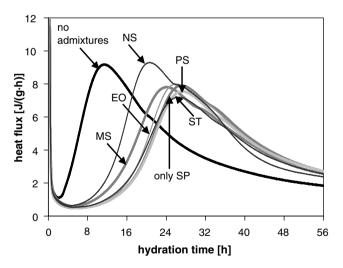


Fig. 12. Isothermal heat flow calorimetry of cement pastes with VMA and SP.

ides subsequently accelerating hydration [1]. This effect seems to be even more pronounced with nanosilica because of its higher surface area.

The organic based VMA do not influence the early hydration when compared with the mixture containing only SP (time of maximum heat flow: VMA EO 26.0 h, VMA PS 27.1 h, VMA ST 26.5 h).

# 4.4. Compressive strength

When comparing compressive strength at an age of 1 day, the concrete without any admixtures and the mixtures with the inorganic VMA microsilica and nanosilica in combination with the SP show the highest values (Table 6). After 28 days the values are similar for all mixtures except for the concrete without any admixtures that reaches a significantly lower strength.

The development of early strength is congruent with the calorimetric data. Microsilica is consumed at an early age [16]. Therefore its effect on compressive strength is not apparent any more at an age of 28 days. The same seems to apply to nanosilica. The relative low compressive strength of the mixture without SP at age of 28 days might be due to a worse distribution of cement particles. Thus, the quantity of hydrates needed to obtain a given strength is increased [17].

# 5. Conclusions

In regard to the methods used, the changes caused by the addition of VMA can be characterized either with mortar flow and flow time or with yield stress and plastic viscosity.

However, the rheometer with the chosen set-up is better suited to record the influence of admixtures on mortars because yield stress and plastic viscosity are influenced more by changes in composition than mortar flow and flow time. At constant w/b, VMA decrease mortar flow and increase flow time (V-funnel test) and cause an increase of yield stress and plastic viscosity. While such an increase can be achieved as well by a reduction of the w/b, the increase in yield stress in relation to plastic viscosity caused by the addition of VMA is much stronger.

The different VMA influence rheology in a very similar way. However, at an equivalent plastic viscosity, VMA PS causes the highest increase in yield stress and VMA MS the lowest. The effect of the other VMA lies between these two.

Development of compressive strength at w/b 0.50

| Mixture                     | No admixtures | Only SP | VMA MS | VMA NS | VMA EO | VMA PS | VMA ST |
|-----------------------------|---------------|---------|--------|--------|--------|--------|--------|
| f <sub>c</sub> 1 day (MPa)  | 14.2          | 12.8    | 15.8   | 16.7   | 11.9   | 10.2   | 11.9   |
| f <sub>c</sub> 2 day (MPa)  | 26.1          | 28.1    | 27.1   | 29.4   | 26.6   | 25.1   | 27.2   |
| f <sub>c</sub> 7 day (MPa)  | 41.5          | 44.3    | 45.3   | 48.7   | 46.2   | 46.6   | 45.9   |
| f <sub>c</sub> 28 day (MPa) | 47.2          | 55.2    | 57.0   | 55.7   | 54.7   | 56.5   | 55.5   |

All VMA enable the production of mortar and concrete at higher w/b without significantly changing flow properties and rheological properties compared to the reference mixtures without VMA. This is especially beneficial for the production of stabilizer-type SCC where the amount of fines can be reduced with the addition of VMA. However, only VMA PS and ST make SCC less susceptible to changes in w/b.

The studied VMA can be used as well for shotcrete and pumped concrete, because an addition of VMA and a simultaneous increase of w/b cause a decrease of plastic viscosity. Therefore, the output at constant pump pressure of shotcrete and concrete can be increased.

However, the addition of VMA can be combined with the addition of an appropriate amount of SP keeping w/b constant. In this case the yield stress will be unchanged, while the plastic viscosity is increased. The advantage of this approach versus the sole addition of SP is that the amount of cement used does not have to be increased to keep the volume of paste constant.

The inorganic silica-based VMA MS and NS accelerate early cement hydration with respect to the use of SP alone as determined by isothermal heat flow calorimetry. As a result, concrete compressive strength at the age of 1 day increases. The organic VMA show no obvious influence on early cement hydration. Compressive strength at an age of 28 days is not affected by the use of VMA in the used dosages.

In summary, VMA represent an important tool to control flow properties and rheological properties of cement based materials. The variation of w/b, the addition of SP and VMA all change flow properties and rheological properties in a different way. Therefore, various types of mortar and concrete can be optimized by using different combinations between these three possibilities.

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