# WATER SATURATED SUPER-ABSORBENT POLYMERS USED IN HIGH STRENGTH CONCRETE

# WASSERGESÄTTIGTE SUPERABSORBIERENDE POLYMERE ALS ZUSATZ FÜR HOCHFESTEN BETON

# POLYMERES SUPER ABSORBANTS SATURES EN EAU UTILISES COMME ADJUVANTS POUR BETONS HAUTES PERFORMANCES

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## SUMMARY

As part of a DFG research program the influence of water-saturated admixtures and aggregates on high strength concrete attributes was investigated. Some of the results concerning super-absorbent polymers, used as admixture, are presented in the following sections.

## ZUSAMMENFASSUNG

Im Rahmen eines DFG-Forschungsprojektes wurde der Einfluss wassergesättigter Zusätze und Leichtzuschläge auf die Eigenschaften hochfester Betone untersucht. Einige der Ergebnisse, die mit superabsorbierenden Polymeren, verwendet als Zusatzmittel, erzielt wurden, werden im folgenden gezeigt.

## RESUME

Dans le cadre d'un projet de recherche DFG, l'influence sur les propriétés des bétons hautes performances des adjuvants et granulats légers saturés en eau a été analysée. Quelques résultats concernant les polymères super absorbants utilisés comme adjuvants sont présentés.

KEYWORDS: Super-absorbent polymers, high-strength concrete

# 1    INTRODUCTION

Internal water storage systems can be subdivided into two categories. Firstly there are the water saturated lightweight aggregates (LWA). They can be considered to be volume stable and they participate in the concrete strength. They have been closely examined by Reinhardt and Weber [1,2,3]. Secondly there are super-absorbent polymers (SAP). They came recently under investigation and it was expected that they perform likewise as internal water sources. For both water sources the determinant material parameters were investigated. Based on the found results an approach for modelling is presented.

# 2    MATERIAL PROPERTIES

## Polymer attributes

In 2000, Jensen [8,9] introduced a new possibility to avoid self-desiccation of high strength concretes by using super-absorbent polymers, which reduce autogenous shrinkage and early age cracking of concrete. The polymers extract water after they have been dryly added to the mortar or concrete mixture. They provide the absorbed water during hydration functioning as internal water source. SAPs were known and used much earlier mainly by the health care industry. These polymers can absorb up to 5000 times of their own weight of pure water. Picture 1 shows a polymer in dry and swollen state.
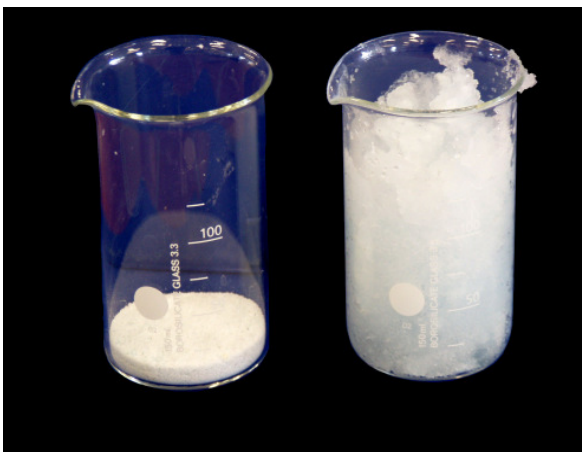


*Picture 1: The left side shows the dry polymer powder. The right cup shows the same amount of polymers after water absorption*

Different types of polymers are known to function as super-absorber. Most often polyacrylic acids are used since their water absorption ratio (water absorption in relation to self-weight) is higher than the one of other known polymers. The polymers are covalently cross-linked by di-functional molecules [10]. The swelling capacity of commercially available polymers is highly reduced in the presence of ions because ions can cause a collapse of the gel by over cross-

linking the polymers. This fact circumvented the use of SAPs in concrete until a new generation of stable polymers was recently developed and investigated. The used polymers were grinded to spherical particles with a medium grain size distribution of approximately 125 μm (Figure 1).
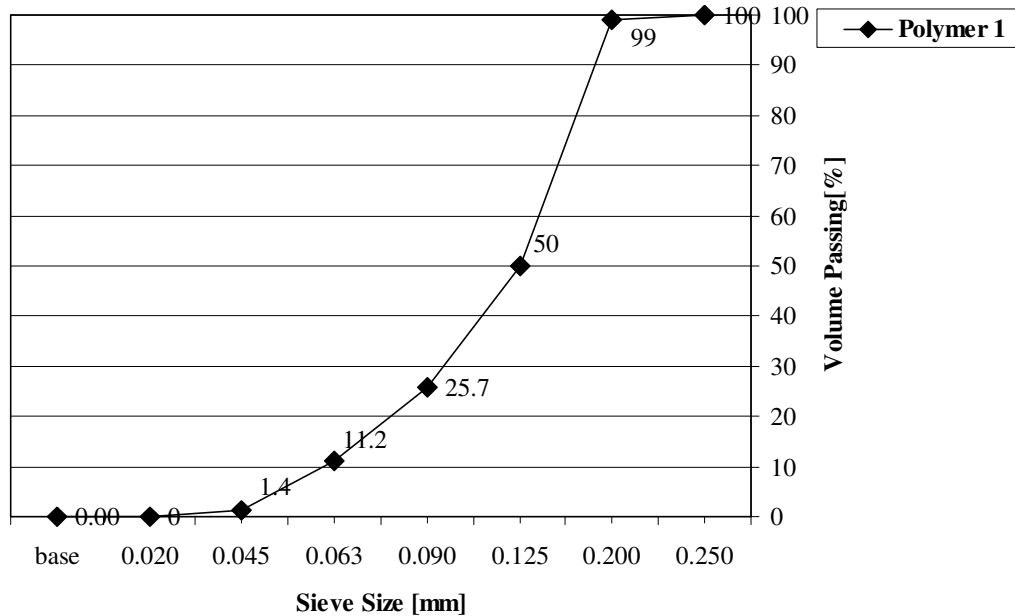


*Figure 1: Particle size distribution of a used super-absorbent polymer*

## Water absorption

The polymers influence the mortar or concrete on two different ways, dependent on the way how they get added to the mixture. Firstly, in case of being dryly inserted, they extract water from the fresh mix and by doing this the density of the matrix increases. Thereby they can consume such high amounts of water that their diameter increases dependent on their ability to consume water producing air pores with diameters of up to 400 μm. Secondly, they provide the absorbed water during hydration and act as an internal water source. For measuring the absorption capacity in an alkaline environment the polymer industry developed different testing procedures, for example the bag test [5]. Since no published research work of the behaviour of polymers under mixing conditions was found, a simplified testing procedure was developed. The absorbed water content of the polymers was determined by comparing different slump flow measurements of reference mixtures with varying water content with the one of the polymer mixture. Thus the absorption coefficient $\chi$ gets determined by the following equation:

$$\chi = \frac{m_{added}^{water} - m_{available}^{water}}{m^{polymers}} \qquad (1)$$

$\chi$ (ml/g): water sorption per gram polymer; m: mass (g)

The mass of available, remaining after absorption by the polymers, water ($m_{available}^{water}$) is identical to the water content of the reference mixture having a similar slump flow. The names of the reference lines in figure 3 refer to the added water amount. The mass of polymers and $m_{added}^{water}$ are taken from the polymer mixture.
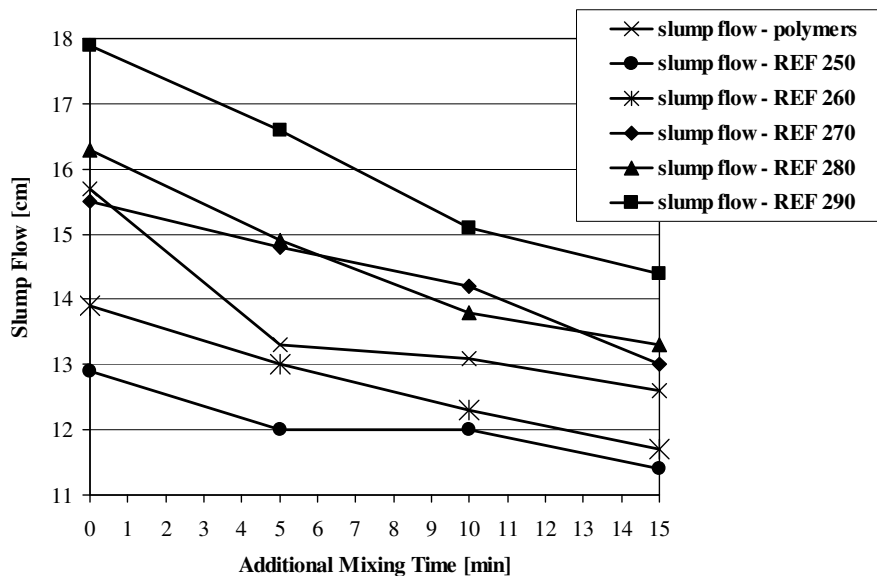


*Figure 3: Slump flow measurements of reference mortars, without any polymers, with different water content in comparison to a polymer-1 mortar containing 297 ml water and 0.6 g polymers.*

From behaviour of the polymer mixture it can be concluded that the water uptake is ongoing between the measurement at 0 and 5 minutes. The slope of the curve changes after 5 minutes additional mixing time and resembles afterwards to the one of stiffening reference mortar. The final slump flow is close to the mixture containing 270 ml water. Thus the water uptake can be estimated with about 45 ml/g polymer for polymer-1. For the third type of polymer, polymer-3, the water absorption was measured with about 10 ml/g. Assumed that the polymer particles are spherical and the water uptake increases the volume steadily, the radius of a swollen polymer will increase by $\sqrt[3]{\chi}$. The medium sieve passing was measured with 125 micrometers. Thus, the emerging pores will have diameters between 270 and 445 μm. Indirectly the effect of polymers can be shown by the resulting densification of the mortar matrix. The second examined polymer was in alkaline environment unstable. It is a commercially available product.

## Water desorption

The desorption behaviour of polymers is mainly governed by diffusion. For most of the drying process the water delivery rate is constant and dependent on the relative humidity, e.g. at a humidity of 40 % the rate was measured to be 0.10 ml/min and for 80 % the rate dropped down to 0.032 ml/min.

## Mercury Intrusion porosity measurement

The mercury intrusion porosity measurements (MIP), as Figure 4 shows, point up the smaller amount of pores at a radius of 0.04 µm for the mixture with polymers. The total measured pore volume was smaller for the polymer mixture. However, the air pores left after desorption of the polymers were not measured since the maximum size measurable by mercury intrusion is 58 µm.
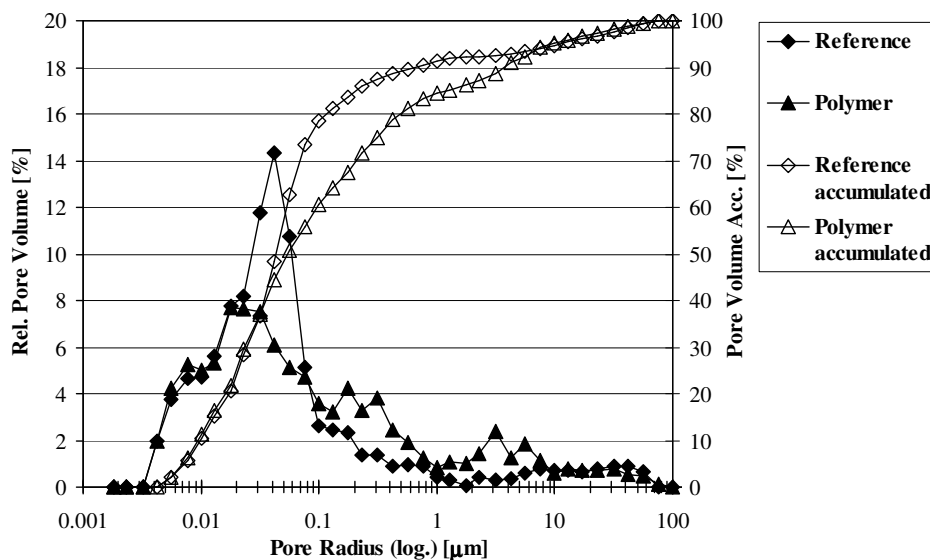


*Figure 4: MIP results for a reference and a polymer-1 mortar*

## Compressive strength

The compressive strength development of mortars mixed with different w/c-ratios and different types of polymers (Figure 5) did not show any significant difference between mixtures with or without polymers. If porosity is taken into account by a Bal'sin [7] calculation the difference in the compressive strength of the mixtures with polymer-2 and -3 compared to the reference mixture disappear. Except for polymer-1 the compressive strength of a mixture after 28 days were very close to each other. The smaller value for polymer-1 can be ascribed to the influence of larger pores on the compressive strength. Recent research work showed that not all pore sizes have an equal influence on the strength. Larger pores lead to higher strength reduction [6]. This could be an ex-

planation for the performance of the polymer-1 mortar. Polymer-2 was a polymer that should have collapsed during hydration hence a small difference was measurable for all examinations. This difference can be a result of a slightly smaller slump flow caused by a stiffer mortar matrix, compared to the reference mixture, due to the water absorption that occurred until the critical ion concentration was reached and the polymers collapsed.
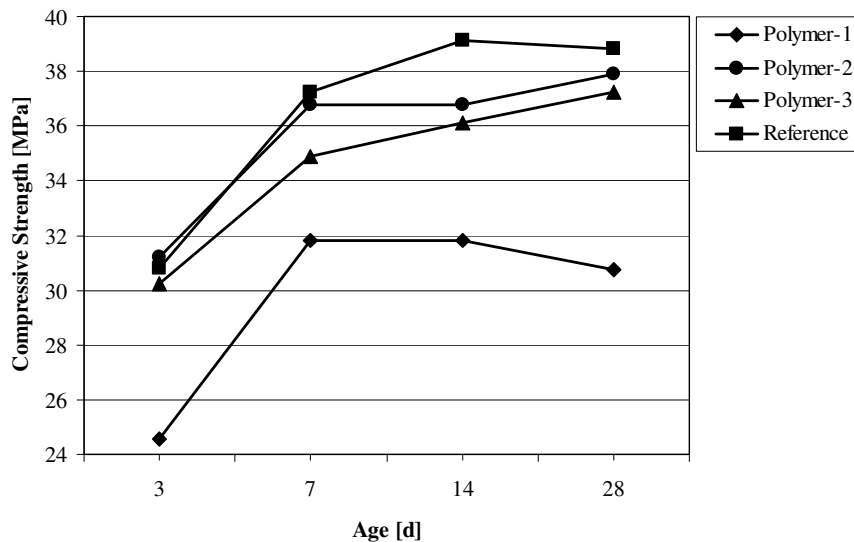


*Figure 5: Compressive strength development of a mixture with polymers and a reference mixture. All mixtures were produced with a w/c-ratio of 0.55.*

## Freeze- thaw resistance

By adding polymers of a known particle size distribution and absorption ratio the pore sizes developing during the water uptake can be estimated. Based on the assumption that air pores smaller 300 µm improve the freeze-thaw resistance a CDF test with a polymer-3 concrete was performed. The medium particle size was 125 µm and the absorption ratio 10 g/g. The resulting air pores had an estimated size of approximately 270 µm. The aspired exposure class was XF4. Table 1 shows the used concrete mixtures. The average spacing between two polymer particles was approximately 11 mm.

*Table 1: Used concrete mixtures for CDF*

|  |  | Reference mixture | Polymer mixture |
|---|---|---|---|
| Cement (CEM I 42.5) | kg/m$^3$ | 333.4 | |
| Water | l/m$^3$ | 160.3 | |
| Water / cement-ratio |  | 0.48 | |
| Superplasticizer (FM/BV 375) | g/m$^3$ | 500 | 2000 |
| Polymer content (polymer-3) | g/m$^3$ | - | 1300 |
| 0 - 2 mm | kg/m$^3$ | 518 | |
| 2- 4 mm | kg/m$^3$ | 263 | |
| 4 – 8 mm | kg/m$^3$ | 371 | |
| 8 – 16 mm | kg/m$^3$ | 586 | |

For the determination of the scaling resistance a CDF test was used. There-fore 28 cycles freezing and thawing were performed. Each cycle lasted 12 hours. After 2, 6, 14 and 28 cycles the test specimens were cleansed by ultrasonic and weighed. Figure 6 shows the results of the test.
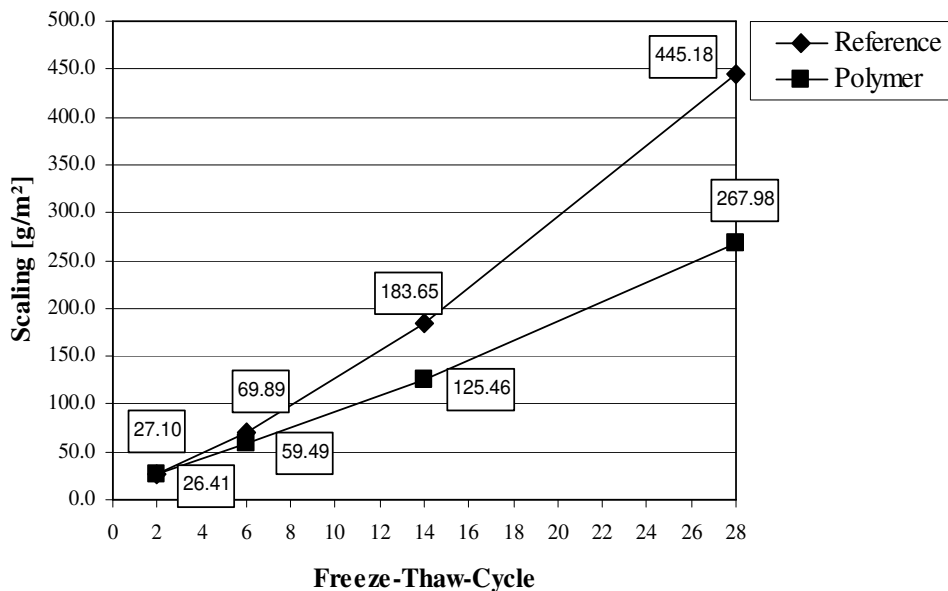


*Figure 6: Results of scaling determination*

The average density of the tested specimens for the reference mixture was 2.36 kg/dm$^3$ and for the polymer mixture 2.33 kg/dm$^3$. Table 2 shows the results of the strength tests after 29 days.

*Table 2: Results of the strength tests*

| [N/mm$^2$] | | Reference mixture | Polymer mixture |
|---|---|---|---|
| Compressive strength | Average | 65.6 | 67.3 |
| | Standard deviation | 0.39 | 1.42 |
| Tensile strength | Average | 6.4 | 5.1 |
| | Standard deviation | 0.30 | 0.44 |

The scaling test did show a significant reduction of scaling. After 28 cycles the total amount of scaling was 445 g/m$^2$ for the reference mixture and 267 g/m$^2$ for the polymer mixture that is 40 % less than the value for the reference mixture. The slightly higher compressive strength is within the range of the standard deviation thus the polymer admixture did not have a negative effect on the concrete strength presumably the strength was increased by the dense concrete matrix structure. The results of the porosity distribution measured by mercury intrusion are very similar to the ones presented in figure 4. The result for the total porosity was for the polymer mixture 57 mm$^3$/g and 62 mm$^3$/g for the reference mixture. Since the density of the reference mixture was the higher one the measurement might not be representative but it shows that the difference is just a very small one.

## 3    MODEL

The influence of super-absorbent polymers was modelled based on Du-COM [4]. DuCOM calculates for a representative distribution of cement grains and a maximum free growth radius for each grain which is dependent on the total amount of free water. To consider the presence of dryly added polymers the equations describing the initial situation were changed. Equally distributed cement grains have a packing density of 0.74 under the assumption of face-centred cube packing. If water is present the distance between two cement grains is equal to s. This is the free growing radius for each hydrating cement grain too. The influence of polymers can be considered by a reduction of the free water content and a resulting smaller distance between the cement grains.

$$s = 2 \cdot r_{Cementgrain} \cdot \left( \sqrt[3]{0.74 \cdot \frac{V_{Cube}}{V_{Cement}}} - 1 \right) \tag{2}$$

r: cement grain size; s: distance between two cement grains, $V_{cube}$: volume of reference element; $V_{Cement}$: volume of cement

The cement size distribution is simplified and a smeared approach calculates the medium size of a grain based on the Blaine value. The volume of a reference element ($V_{Cube}$) consists of cement and water. The volume of water changes as equation 3 shows. The initial water being present is dependent on the water/cement-ratio, the polymer/cement-ratio and the mass of cement used.

$$V_{Water} = \left( \underbrace{\frac{m_w}{m_c}}_{\frac{w}{c}-\text{ratio}} \cdot m_c \cdot \frac{1}{\rho_w} \right) - \left( \chi \cdot \underbrace{\frac{m_P}{m_c}}_{\frac{p}{c}-\text{ratio}} \cdot m_c \cdot \frac{1}{\rho_w} \right)$$

$$V_{Water} = \frac{m_c}{\rho_w} \cdot \left( \frac{m_w}{m_c} - \chi \cdot \frac{m_p}{m_c} \right) \tag{3}$$

$\rho_W$: water density; $m_i$: mass (g); Index i: c: cement; w: water; p: polymer; $\chi$ (ml/g): water sorption per gram polymers

## 4    CONCLUSION

The use of super-absorbent polymers did improve the freeze thaw resistance significantly. The compressive strength tests did not show a detrimental influence. On the contrary, the polymer mixture strength was slightly higher than the strength of the reference mixture. The mercury intrusion examinations did show a decrease of small pores while the total pore volume did not change. This is the result of a compacted concrete matrix by the water absorption of the polymers. The water absorption takes place during the mixing procedure, which can result in a mixture with significantly reduced slump flow. For high strength concrete with small water/cement ratios the amount of needed superplasticizer is increased. Examinations to investigate the influence on the shrinkage behaviour are currently performed. A preliminary model of the polymer influence on the concrete matrix structure was introduced. Examinations of a polymer mixture compared with reference mixtures with different water/cement ratios should prove the correctness of the model. The performed mortar tests did show that the absorption ratio and the particle size distribution of polymers have a significant

influence. A high absorption ratio may cause a stiff mixture and inserts a high amount of large pores resulting in a lower compressive strength.

The future research will investigate the shrinkage behaviour of polymer mixtures and further improve the model to account for changing material attributes due to desorption of water filled polymers.

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