

Surface energy and fracture energy

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ABSTRACT: Properties of cement-based materials are governed by their nano-structure in general and by the interaction between the surfaces of the nano-particles with their hygral surrounding in particular. In this contribution local damage and nano-crack formation in the three-dimensional network of nano-particles is considered to be at the origin of crack formation. Macroscopic fracture energy can be considered to be the sum of a huge number of small energies consumed by nano-crack formation. Considering the physical process of nano-crack formation it is possible to predict the influence of variable environments on fracture energy. This hypothesis is verified by experimental investigations. The influence of aqueous NaCl solutions on strength, fracture energy and swelling has been determined. It is shown that values of fracture energy as determined in the laboratory are not conservative if applied for prediction of crack formation of reinforced concrete structures situated in marine environment. This fact is of major importance for durability and service life of reinforced concrete structures in marine environment.

1 INTRODUCTION

Fracture energy of different types of concrete has been measured by many authors by different techniques, and for many years by now (see for example Carpinteri et al. 2007). In the literature there are various standard test methods described such as direct tension test, three point and four point bending test, and wedge splitting test, which all may serve to determine fracture energy experimentally. In the fictitious crack model by Hillerborg (Hillerborg et al. 1976, Hillerborg 1985) fracture energy of concrete is introduced in a phenomenological way. The overall energy consumed by crack formation in sufficiently large specimens is considered to be a material property. Crack formation induced by shrinkage for instance can be predicted with this approach in a realistic way (Alvaredo 1994). In this global approach, however, physical processes involved in crack formation are neglected. For this reason the influence of changes of the environment on fracture energy cannot be taken into consideration directly and quantitatively. If a global approach is used, it is not clear and not of primary interest to know precisely what happens in the fracture process zone when a crack is propagating.

Conventional concrete is a composite material with mineral aggregates embedded in a cement-

based matrix. Most characteristic properties such as shrinkage or swelling and compressive or tensile strength are governed by the nano-structure built up by hydration products of cement. When a load is applied to the three-dimensional framework of nano-particles, a complex state of stress with local stress concentrations is built up. At sites where the stresses are above the local load bearing capacity, damage will occur by nano-crack formation. This process progressive damage leading to macroscopic cracks can be modeled numerically.

In this contribution the macroscopically observed fracture energy shall be linked with the elementary processes in the nano-structure. It will be shown that in this way it is possible to describe the influence of chemical composition of the pore solution on strength, fracture energy, and shrinkage or swelling at least phenomenologically.

2 FUNDAMENTALS

In a homogeneous ideal brittle material the Griffith criterion can be applied to describe crack formation. If we consider a nano-crack in the xerogel of the hardened cement paste with the length of $2c$ the critical stress σ is given by the following equation:

$$\sigma = \sqrt{\frac{2E\gamma}{\pi c}} \quad (1)$$

In Equation (1) E stands for the elastic modulus of the material around the crack and γ is the surface energy and at the same time the fracture energy on the nano-scale. Formation of one nano-crack can be considered to be the elementary step of accumulation of damage and finally crack formation. To create a macroscopic crack a huge number of nano-cracks have to be formed first.

If an external load is applied, early nano-cracks are formed at a macroscopic stress as low as one third of the load bearing capacity. With increasing load more and more cracks are formed and the length of existing cracks increases (see for example Zaitsev & Wittmann 1981). This process induces damage to the material, which can be observed by a gradual decrease of the stiffness or by increased capillary absorption (see for example Wittmann et al. 2006). Once the maximum stress is reached the density of nano-cracks is high enough and micro-cracks are formed by coalescence of nano-cracks. The density of nano and micro-cracks is particularly large in the so-called fracture process zone where the macroscopic crack will be formed finally.

On the nano-scale Equation (1) is certainly a good approximation to describe nano-crack formation or damage. Then the surface energy γ is the energy needed to break one link in the nano-structure. This value depends on the humidity of the surrounding atmosphere. Under usual conditions a water film is adsorbed on the surface of gel particles with a characteristic thickness Γ , which depends on the RH of the surrounding air. The reduction of surface energy due to an adsorbed water film is shown in Figure 1 (Setzer 1972). The surface energy γ_0 is at maximum in the completely dry state. Under these conditions strength is at maximum too as predicted by the Munich model (Wittmann 1976, 1977).

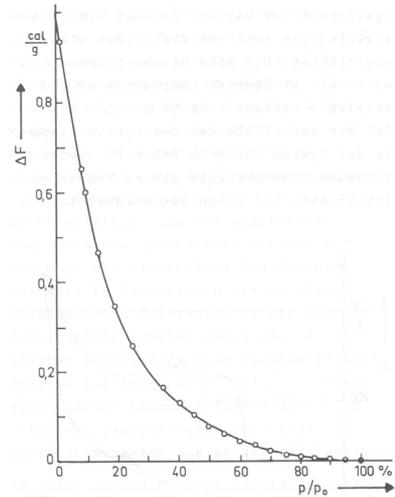
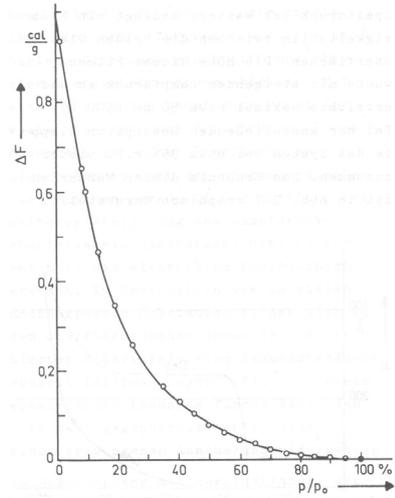
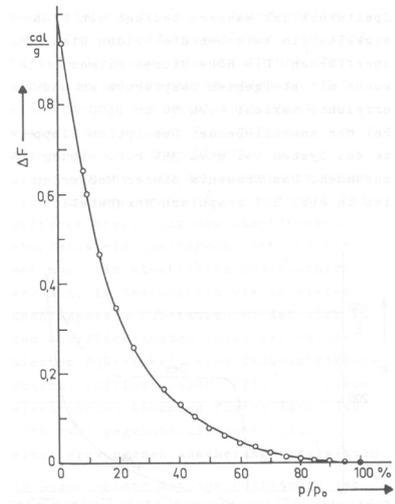
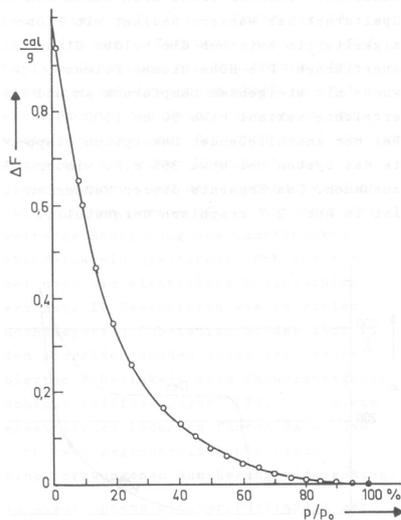


Figure 1. Decrease of surface energy γ in Equation (1) as function of relative humidity p/p_0 (Setzer 1972).

If we assume that by changing the moisture content all values with the exception of γ remain constant we obtain the following equation for the resulting change of strength:

$$\left(\frac{\sigma_h}{\sigma_0}\right)^2 = \frac{\gamma_h}{\gamma_0} = 1 - \frac{\Delta\gamma}{\gamma_0} \quad (2)$$

where σ_h stands for the strength at relative humidity h and σ_0 for the strength in vacuo, γ_h stands for the

surface energy at relative humidity h and γ_0 the surface energy in vacuo, $\Delta\gamma$ is the change of surface energy.

The Munich model also predicts a length change if the moisture content changes (Wittmann 1976, 1977). The length change Δl of a specimen with length l_0 can be described by means of the Bangham equation (Bangham & Fakhoury and Bangham & Razouk):

$$\frac{\Delta l}{l_0} = \lambda(\gamma_0 - \gamma_h) \quad (3)$$

where λ is a material constant, which takes the stiffness of the material into consideration. By combining Equation (1) and Equation (3) we obtain:

$$\left(\frac{\sigma_h}{\sigma_0}\right)^2 = 1 - \frac{1}{\lambda\gamma_0} \frac{\Delta l}{l_0} \quad (4)$$

That means that the square of the related strength is linearly related to swelling. These relations are applicable to nano-porous materials in the range of RH < 60 %. In this range strength as well as swelling or shrinkage are controlled essentially by the change of surface energy. At higher relative humidity disjoining pressure dominates and should be taken into consideration separately (Wittmann 1976).

So far we have considered formation of one single nano-crack in hardened cement paste. When the density of nano-cracks becomes high enough micro-cracks are formed and finally macro-cracks. The energy necessary to form a macro-crack is obviously the sum of all nano-cracks which are necessary to be formed before failure. The Griffith criterion is not applicable in its simple form given by Equation (1) to cement based composite materials. But still surface energy γ is at the origin of all the elementary processes leading to crack formation. The sum of all small quantities of surface energy needed to form the huge number of nano-cracks necessary to create a real crack finally is the macroscopic fracture energy, which we determine with experimental methods.

Based on these considerations we can state that adsorption of water in the nano-structure reduces surface energy of gel particles and in an indirect way fracture energy as measured on the macro-scale. In marine environment salt water can penetrate into the pore space of concrete. As seawater and salt water in general have a higher surface energy as compared to water, we may expect that salt water and seawater reduce strength even more than pure water. In general strength and hygral length change depend on the chemical composition of the pore solution.

3 EXPERIMENTAL

Preliminary results have been published recently

(Wittmann et al. 2007). In this contribution new results shall be presented to broaden the experimental basis, which serves as verification of the above described relations.

Tests have been carried out on concrete and mortar specimens. For concrete broken natural gravel with a maximum diameter of 20 mm and local river sand with a maximum diameter of 5 mm were used. In order to obtain good workability 1% of a plasticizer related to the mass of cement was added. Ordinary Portland cement type 32.5 was used throughout. The composition of concrete is given in Table 1.

Table 1. Composition of concrete in kg/m³.

Cement	Gravel	Sand	Water	W/C
320	1267	653	160	0.5

Table 2. Composition of mortar in kg/m³.

Cement	Sand	Water	W/C
450	1350	225	0.5

Two types of concrete specimens have been prepared: (a) slabs with the dimensions of 400 x 400 x 36 mm for wedge splitting tests (WST) and (b) beams with the dimensions of 100 x 100 x 510 mm for three point bending tests (3PB). For tests to determine compressive strength cubes with an edge length of 200 mm have been cast.

In addition mortar with a maximum aggregate size of 5 mm has been prepared using the same type of cement. The composition of the mortar is indicated in Table 2. From the mortar the following two types of specimens have been produced: (a) slabs with the dimensions 400 x 400 x 36 mm for wedge splitting tests and standard prisms with the dimensions 40 x 40 x 160 mm for three-point bending tests. On the two ends obtained by three-point bending compressive strength of mortar has been determined.

All specimens were allowed to harden for 28 days in a humid chamber at T = 20 ± 2 °C and RH > 95 %. At the age of 28 days compressive strength and fracture energy have been determined. Part of the specimens was then dried in a ventilated oven at 105 °C for 14 days. At that time constant weight had been achieved. After cooling down to room temperature fracture energy has been determined again. Other samples were allowed to absorb water vapour after drying. They were placed in the laboratory atmosphere, which can be characterized by 20 °C and 75 % RH for at least two months. Other pre-dried samples were placed in liquid water or in seawater for 14 days. Then fracture energy has been determined by wedge splitting test and by three-point bending.

Similar tests have been run on mortar specimen. But on the standard prisms made of mortar hygral swelling was measured in addition.

4 RESULTS AND DISCUSSION

4.1 Strength and fracture energy of untreated concrete and after different hygral conditioning

Compressive strength as obtained after different curing conditions is shown in Figure 2. The concrete used for these test series had a compressive strength of 42.5 N/mm² at an age of 28 days. After drying the compressive strength had increased to 65.4 N/mm². This corresponds to an increase of 54 %. Part of this increase can be explained by further hydration at elevated temperature but the major part is due to increased surface energy of the nano-particles in hardened cement paste after removal of the adsorbed water layers. At 75 % RH humidity approximately two molecular layers of water are re-adsorbed. As a consequence compressive strength decreases again to a value of 54 N/mm². Finally the strength decreases even more if the specimens are water saturated. In fact they nearly reach the original strength.

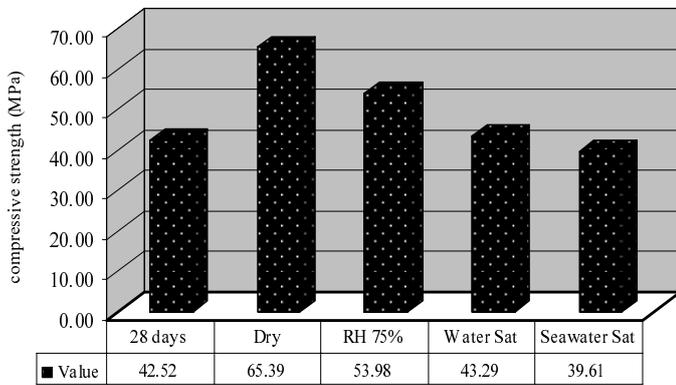


Figure 2. Compressive strength of differently conditioned concrete cubes.

But most interesting, the compressive strength decreases even more if the specimens are saturated with seawater. Water has a surface tension of 72.6 mN/m (Vargaftik et al. 1983) and surface tension of seawater has been measured to be 74.5 mN/m (see Table 3). That means the surface energy of the cement gel is even more reduced after saturation with seawater.

Table 3. Surface tension of water, aqueous solutions with 3 % and 5 % NaCl and seawater.

Liquid	Surface tension mN/m
Water	72.6
3 % NaCl	73.3
5 % NaCl	73.9
Seawater	74.5

In Figure 3 the force-CMOD diagrams as obtained by wedge splitting tests on concrete preconditioned in the same way as described above in context with the compression tests are shown. The curves

shown in Figure 3 are average values of at least three individual measurements. It should be mentioned here that the same tests have also been carried out with smaller slabs (200 x 200 x 40 mm). As results are essentially the same and because of space limits these results shall not be presented here but in a forthcoming paper. From the original data, as shown in Figure 3, fracture energy and strain softening have been determined by inverse analysis (Bretschneider et al. 2007).

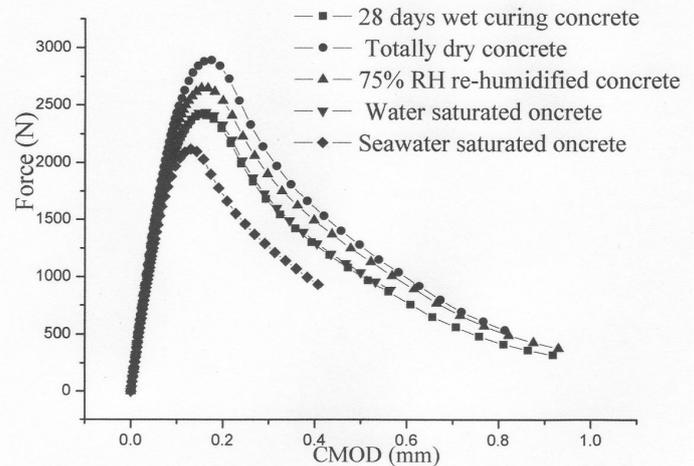


Figure 3. Force-CMOD diagrams as obtained by the wedge splitting test (WST) from concrete pre-conditioned in the same way as specimens prepared for compression tests (see Fig. 2).

The fracture energy as obtained by inverse analysis of the force-CMOD diagrams shown in Figure 3 are compiled in Table 4. It can be seen that fracture energy of concrete increases considerably by drying. The increase of fracture energy by drying is slightly more than 20 %. But due to adsorption of water on the internal surface fracture energy decreases again after storage in air with RH = 75 %. The fracture energy is further reduced by water saturation. As one could have expected saturation with seawater reduces fracture energy even more than saturation with water as the surface tension of seawater is higher see Table 3).

Table 4. Fracture energy G_f in J/m² as determined by wedge splitting test (WST) and by three-point bending (3PB) on differently pre-conditioned concrete samples.

Moist. Cond.	28 days	dried	75 % RH	Water Sat.	Sea-water
WST	128	154	145	118	106
3PB	110	154	131	98	93

In Figure 4 results obtained by the three-point bending test are shown. The tendency is the same as already discussed in context of the results of the wedge splitting test shown in Figure 3. From the force-deflection diagrams shown in Figure 4 the fracture energy and strain softening has also been determined. All results are compiled in Table 4. The surface energy increases by 40 % by drying the specimens. But it de-

creases below the initial value obtained after 28 days wet curing. This is probably due to damage induced into the material during the drying process.

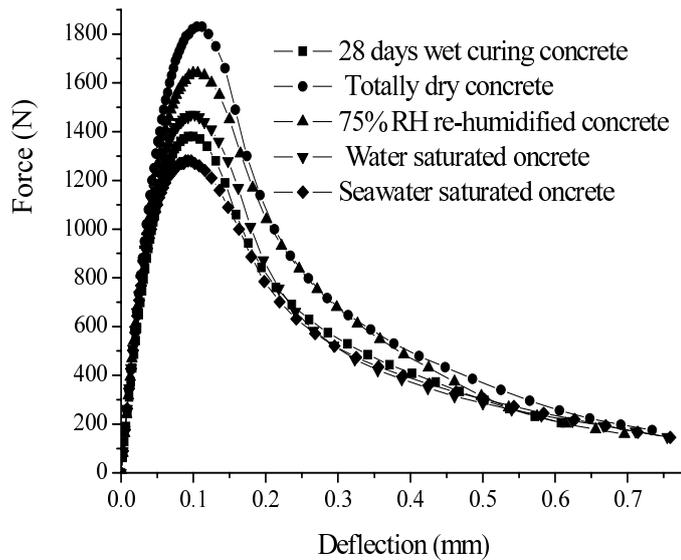


Figure 4. Force-deflection diagram as obtained by three-point bending test (3PB) on differently pre-conditioned concrete.

4.2 Fracture energy of mortar after different hygral conditioning

Concrete has been dried at an age of 28 days at 105 °C. After having cooled down to room temperature the specimens were immersed in water and in seawater respectively for 14 days. Some specimens, however, were surface impregnated with liquid silane before immersion in order to make the surface near zone water repellent. Then fracture energy has been determined in this case on small specimens.

The force-CMOD diagrams as obtained by wedge splitting tests are shown in Figure 5. From these data fracture energy and strain softening has been determined by inverse analysis. The initial fracture energy after 28 days wet curing was about 100 J/m². This value increased by drying to 127 J/m². The fracture energy measured on untreated concrete samples after immersion in water and seawater and the corresponding values measured on water repellent samples are compiled in Table 5. It can be seen that the fracture energy is strongly reduced in the untreated samples by immersion in water or seawater. Water repellent treatment prevents rapid water absorption by capillary action. But as the pores are not blocked water vapour can penetrate nevertheless.

The adsorbed water and capillary condensed water reduces gradually fracture energy but if the concrete surface is in contact with water or seawater temporarily only water repellent treatment provides a certain protection. Strength and fracture energy will be less reduced after water repellent surface impregnation.

These results agree well with experimentally de-

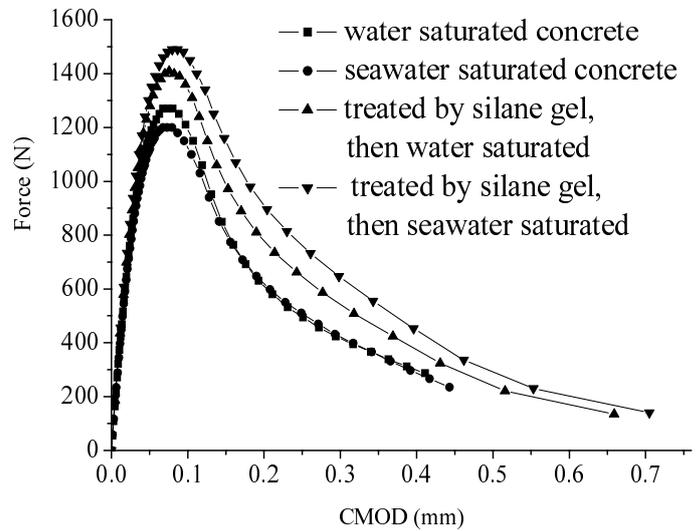


Figure 5. Force-CMOD diagram of neat and water repellent concrete immersed in water and seawater.

Table 5. Fracture energy in J/m² as measured on untreated and water repellent concrete samples immersed in water and in seawater.

	Untreated	Water repellent
Water	97.5	115.4
Seawater	93.3	122.0

termined compressive strength of similar treated concrete samples.

4.3 Fracture energy of mortar after different hygral conditioning

Similar tests as described above for concrete have been carried out on cement mortar specimens. The compressive strength obtained after different hygral conditioning is shown in Figure 6. It can be seen that the same changes as observed on concrete have been measured on mortar. Drying increases strength by 54 % but after re-humidification strength decreases again. As expected from the theoretical background most of the observed strength increase is reduced already after storage at 75 % RH.

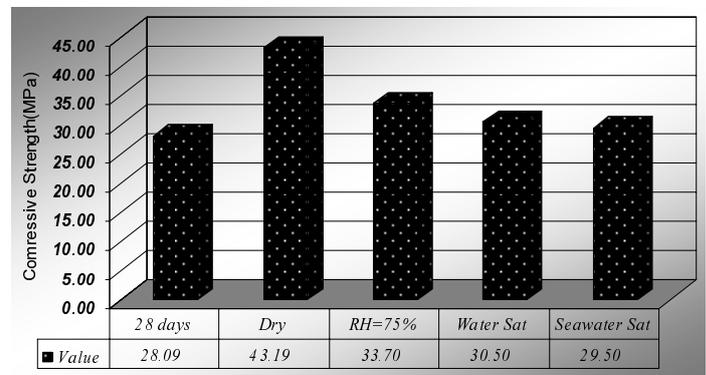


Figure 6. Compressive strength of mortar at an age of 28 days and after different hygral conditioning.

This is due to the fact that the first adsorbed layers reduce surface energy of the gel particles most

significantly (see Fig. 1). Again it is observed that strength of specimens saturated with seawater, which has a higher surface tension than tap water, is further reduced.

Fracture energy of mortar after different hygral conditioning has been measured the same way as on concrete samples by the wedge splitting test and by three point bending. The force-CMOD diagram is shown in Figure 7 and the force-deflection diagram is shown in Figure 8.

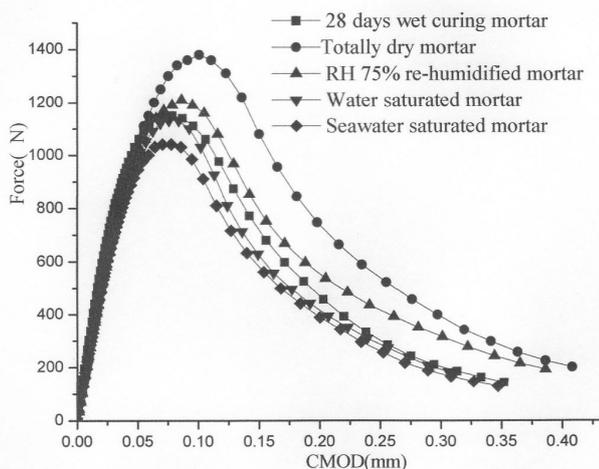
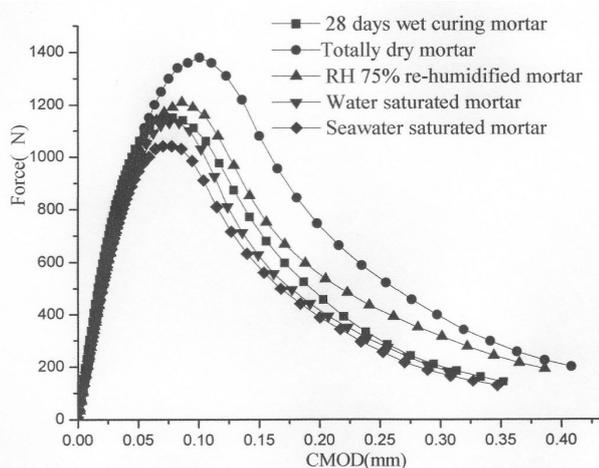


Figure 7. Force-CMOD diagram as measured on mortar samples, which were differently conditioned before the test.

From Figures 7 and 8 fracture energy and strain softening have been determined by inverse analysis (see Brettschneider et al. 2007). The fracture energy as obtained on the wet cured specimens at an age of 28 days, after drying at 105 °C for 14 days, after re-humidification in an environment with RH = 75 %, after water saturation and after saturation with seawater is compiled in Table 5. The trend observed on concrete samples after hygral preconditioning and described above is the same for mortar. Results are confirmed.

In all cases it could be shown that strength and fracture energy are highest in the dry state. The surface energy of the cement gel is at maximum under these conditions. Few adsorbed water layers lower the surface energy significantly. By water saturation

the surface energy is further lowered but by a comparatively small amount. This can be explained by the relation shown in Figure 1. If concrete or mortar samples are saturated with seawater, strength and fracture energy are lowered even more than by saturation with tap water as the surface energy of seawater is higher as compared to surface energy of water.

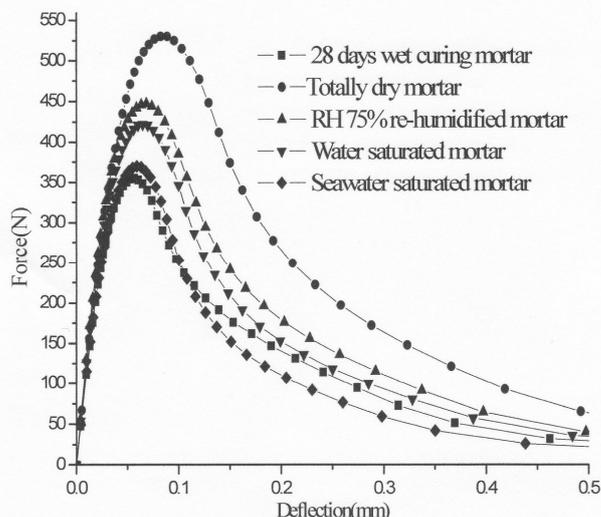


Figure 8. Force-deflection diagram as obtained by three-point bending test on differently preconditioned mortar prisms.

Table 5. Fracture energy of mortar as determined under different hygral conditions.

Hygral Cond.	Wet cur. 28days	Dried 105 °C	Re-humid. 75 %	Water Sat.	Sea water Sat.
WST	62.9	89.3	74.8	57.5	53.2
3PB	60.1	95.5	74.2	60.2	58.6

Similar results have been described in a recent publication (Wittmann et al. 2007). Ogishi (Ogishi et al. 1986) was probably the first to describe this phenomenon. More recently Matsushita & Onoue (2006) have studied the influence of surface energy on strength under static and dynamic loading.

All individual nano-cracks in the xero-gel can be formed with less energy if the surface is covered with a water layer, hence at lower stress level. As mentioned before, the integral over the energy consumption of all individual events leads to the macroscopic fracture energy. This depends in the first place on the moisture condition but also on the stress distribution in a given sample. Nano-cracks are preferentially being formed in the volume under high stress.

4.4 Fracture energy, strength, and hygral length change

The influence of change of surface energy on strength of an ideal brittle material can be described by means of the Griffith criterion (see Equation (1)). In cement-based materials macroscopic fracture energy

is the sum of a huge number of elementary processes, which can be described by means of Equation (1) and therefore fracture energy, can be assumed to be proportional to surface energy. The influence of change of surface energy on hygral length change is given by the Bangham equation (see Equation (3)) as predicted by the Munich model (Wittmann 1976, 1977). By combining Equation (1) with Equation (3) a relation between strength decrease and hygral length change is obtained (see Equation (4)).

In Figure 9 the square of the bending strength and the square of the compressive strength [N^2/mm^4] as obtained on samples saturated with water, aqueous solutions with 3 % and 5 % of NaCl and seawater are shown. Depending on the surface energy of these liquids the surface energy of mortar is reduced. The reduction of surface energy obviously leads to a reduction of both bending and compressive strength.

It should be mentioned at this point that the interpretation presented in this contribution is a simplification of the real situation, primarily because the influence of disjoining pressure has not been taken into consideration separately Wittmann 1976, 1977).

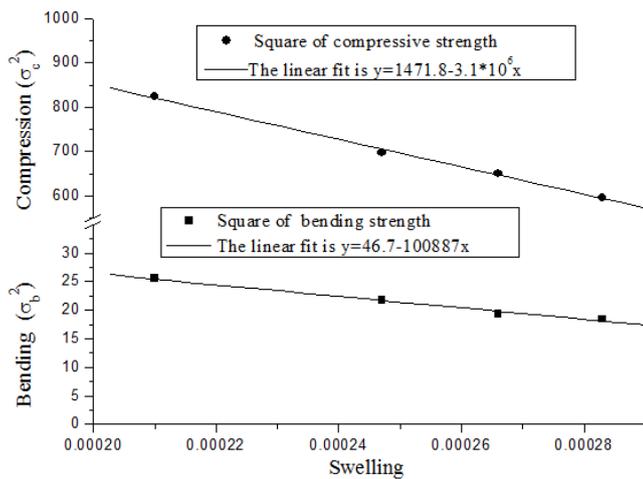


Figure 9. Square of compressive and bending strength as function of the swelling strain after saturation with water, aqueous solutions with 3 and 5 % NaCl and seawater.

The influence of surface energy on strength and swelling is dominant in the humidity range between 0 % and approximately 70 %. In the case of saturation, however, the influence of dissolved ions on disjoining pressure and hence on strength and swelling cannot be neglected (Wittmann 1976, Setzer 2007). To quantify this effect further tests are necessary.

5 CONCLUSIONS

It has been shown that strength and fracture energy depend on surface energy of the hydration products of cement in cement based materials such as con-

crete and mortar. Surface energy can be changed significantly by changing the hygral conditions. Surface energy and strength as well as fracture energy are at maximum in the completely dry state. One or two adsorbed water layers reduce surface energy of the hydration products significantly. This leads to a remarkable reduction of strength and fracture energy.

Fracture energy can be considered to be the sum of a huge number of small quantities of surface energies consumed by formation of individual nano-cracks in the xero-gel.

Seawater in contact with hydration products reduces surface energy even more than pure water as the surface tension of seawater is bigger. This effect has to be taken into consideration if crack formation in reinforced concrete structures situated in marine environment is to be predicted. Durability of concrete structures depends strongly on prevention of crack formation.

The reduction of strength and fracture energy of concrete in temporary contact with water or seawater as for instance in the splash zone can be limited by water repellent surface treatment.

The observed behavior has been predicted by the Munich Model (Wittmann 1976, 1977)). On this basis the reduction of fracture energy can also be linked with hygral length change such as swelling. A strong correlation between strength decrease and swelling has been confirmed.

Reduction of strength and fracture energy of cement based materials is of particular importance for durability and service life of reinforced concrete structures in marine environment.

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