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#### Stress Corrosion of Cement Mortars in Ammonium sulfate Solution

Corrosion sous contrainte des mortiers de ciment dans des solutions de sulfate d'ammonium Spannungskorrosion von Zementmörteln in Ammoniumsulfatlösungen

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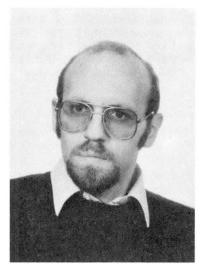
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Dr.-Ing. Erich Nägele, born 1953, received his master degree in chemistry at the University of Karlsruhe, FRG in 1978. He received his doctorate in civil engineering 1981. Dr. Nägele works now in the civil engineering department at the University of Kassel in the field of stress corrosion of non-metallic inorganic materials and on the electric properties of materials.



Norbert Dujardin, born 1950, received his civil engineering master degree at the University of Aachen. For 4 years he was involved in the design and calculation of pipe supports for nuclear reactors. For the last 3 years he has been working in the civil engineering department at the University of Kassel. His research is devoted to the stress corrosion of non-metallic inorganic materials and fracture mechanic of concrete.

#### SUMMARY

The effects of type of cement, of water/cement-ratio and of surface coatings on the stress corrosion of cement mortars in 5%- ammonium sulfate solution are reported. The effects observed for different cements and water/cement-ratios in stress corrosion correspond to the effects observed in classical corrosion, i.e. mechanical stresses are not present. Coated specimens, however, show a distinct decline in strength when a mechanical stress acts simultaneously to a chemical stress and when the coatings are destroyed by cracks. Thus, the use of coatings has to be reconsidered, taking into account stress corrosion.

#### RÉSUMÉ

Ce travail examine les effets du type de ciment utilisé, du rapport eau/ciment et de la protection des surfaces visà-vis de la corrosion sous contrainte des mortiers de ciment dans les solutions de sulfate d'ammonium. Les effets du type de ciment et du rapport eau/ciment sont les mêmes que pour une corrosion classique, s'il n'y a pas d'actions mécaniques. Des échantillons montrent une diminution de résistance marquée lorsque des actions mécaniques agissent simultanément à une action chimique et lorsque les couches superficielles sont détruites par fissuration.

# ZUSAMMENFASSUNG

In dieser Arbeit wird über den Einfluss der Zementart, des W/Z-Wertes und von Oberflächenbeschichtungen auf die Spannungskorrosion von Zementmörteln in 5%iger Ammoniumsulfatlösung berichtet. Die für die verschiedenen Zemente und W/Z-Werte beobachteten Effekte entsprechen denen bei normaler Korrosion, d.h. wenn zusätzliche mechanische Spannungen nicht vorhanden sind. Beschichtete Proben zeigen jedoch unter Spannungskorrosion einen starken Festigkeitsabfall, wenn die Beschichtung Fehler aufweist. Daher muss die Verwendung von Beschichtungen neu überdacht werden, wobei die Spannungskorrosion zu berücksichtigen ist.



#### 1 INTRODUCTION

Chemical attack and mechanical properties of cementitious materials are usually being studied separately. However, in practice, chemical attacks are common to load bearing structures, therefore the simultaneous action of chemical and mechanical stresses, known as "stress corrosion", has to be considered in any evaluation of the durability of cementitious materials. It has been shown that cementitious materials like many other building materials are also subjected to stress corrosion [1-5].

#### 2 EXPERIMENTAL

#### 2.1 Materials

The experiments were performed with mortar prisms 4x4x16 cm made according to the German standard DIN 1164. Three cements were used throughout the tests, a German Portland cement, PZ 35F (PC), a German blast furnace slag cement, HOZ 35L with a slag content of 50% by weight (BFC) and a German fly ash cement, FAZ 35L with a fly ash content of approximately 30% by weight (FAC). The analysis of the cements is given elsewhere I2-51. The aggregate was quartzitic German standard sand.

## 2.2 Specimens

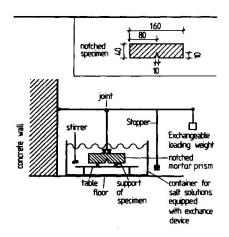
The specimens were made with the general composition aggregate : cement : water = 3:1:w/c. Hence the contents of cement and aggregate were kept constant in all experiments.

The specimens were made with notches 10mm depth, 45° opening angle by pressing a suitable wedge into the fresh mix. A detailed overview of the tests is given in table 1. The specimens were cured for 28 days under water before immersed into the aggressive media.

#### 2.3 Test Procedure and Test Program

The mortar prisms were immersed into 5%-ammonium sulfate solutions and loaded with load levels up to 50% of their initial flexural strength, which was determined prior to immersion. The loading device is shown in fig. 1. It is decribed in more detail in [2-5].

Unloaded specimens were stored in the same containers, so loaded and unloaded specimens were stored in the same solutions and under the same conditions. The load levels applied to the respective series may be taken from table 1, where the test program is summarized.



Loading Device

Fig.1: Loading Device for Stress Corrosion Tests



Table 1: Test Program

Series No.	Effect investigated	Type of Specimen	Load levels (%)
1	Type of Cement	W/C≃ 0,7; PZ, HOZ, FAZ	0 30
2	W/C-Ratio	PZ , HOZ W/C=0,55; 0,65;0,75	0 30
3	Surface Treatment and Coating	PZ , W/C=0,7 Sand blasted PUR-coated EP-coated	O

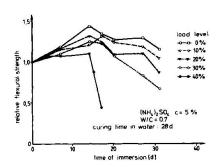
#### 3. RESULTS AND DISCUSSION

Due to the limited space available not all results can be presented and discussed here. Thus only a brief survey on the most important features of the stress corrosion of cementitious materials is given and those topics most important for building practice are discussed briefly. Further details may be found in [2-5].

## 3.1 Stress Corrosion Phenomena in Aqueous Solutions

Fig.2, where the relative flexural strength is plotted versus the immersion time, shows some results of stress corrosion experiments from series 1 in 5%- ammonium sulfate solutions. Strength first increases due to chemical reactions like the formation of calciumsulfoaluminmates etc. and then decreases due to the formation of gypsum which causes sulfate expansion. If a mechanical stress acts simultaneously to the chemical one the initial strength development is

Fig.2: Stress Corrosion of Portland Cement Mortars



Effect of Load on Strength Development

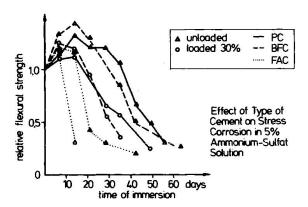
diminished and the deterioration of the specimens occurs at earlier times. At very high load levels no initial strength increase is observed. Thus, stress corrosion leads to a significant decline in flexural strength for loaded specimens compared to unloaded ones. The higher the load the earlier failure occurs. Similar results are obtained for other media [2,3,5]. Thus it may be concluded, that cementitious materials are subjected to stress corrosion in many common aggressive aqueous solutions.



## 3.2 Effect of Type of Cement

Fig.3 shows the effect of type of cement. Stress corrosion occurs for all types of cement investigated.

Fig. 3: Effect of Type of Cement on Stress Corrosion of Mortars



The type of cement affects the life time i.e. in ammonium sulfate solution the portland cement and the blast furnace slag cement specimens show a higher life time compared to the fly ash cement specimens respectively, because in the corrosion times involved the higher Ca(OH)<sub>2</sub> content of the portland cement and the blast furnace slag cement pastes acts as a buffer. The strength decline is most pronounced for the fly ash cement. For the loaded specimens the same behaviour is observed. Portland cement and blast furnace slag cement show nearly the same strength decline with immersion time, whereas the fly ash cement showns very rapid failure. Thus, in stress corrosion the effect of the type of cement is the same as in ordinary corrosion of cementitious materials.

# 3.3 Effect of Water/Cement-Ratio

Due to the fact that cementitious materials in ammonium sulfate solution are subjected to two entirely different forms of corrosion failure, namely the dissolving attack and the sulfate expansion attack the effect of the water cement ratio depends also on the type of cement. Fig.4 shows the effect of the w/c-ratio for portland cement and fig.5. for blast furnace slag cement prisms both unloaded and loaded with a load level of 30% of initial strength. The decline of strength becomes

Fig.4: Effect of W/C-Ratio on Stress Corrosion of Portland Cement Mortars

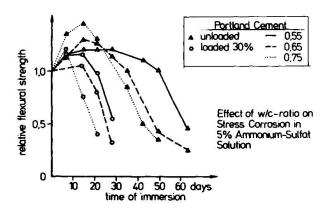
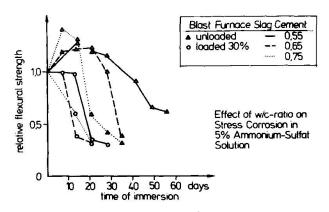




Fig.5: Effect of W/C-Ratio on Stress Corrosion of Blast Furnace Slag Cement Mortars

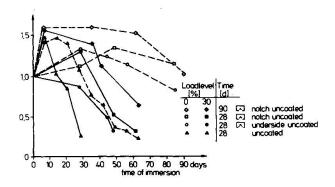


more distinct with increasing w/c-ratio for loaded and unloaded specimens. Thus, in general the effect of w/c-ratio on stress corrosion is the same as during ordinary corrosion without mechanical stresses. However, when a mechanical stress is superimposed onto the chemical stress the differences in strength development seem to become smaller than those observed with unloaded specimens. Furthermore, it can be seen from fig's. 4 and 5 that the initial increase in strength increases with increasing w/c-ratio, i.e. with increasing capillary porosity. This is an indication that the initial strength increase of mortar specimens stored in ammonium sulfate solution is due to the formation of new phases inside the pore volume.

## 3.4 Effect of Surface Coating

Fig.6 shows the decline of flexural strength of differently coated notched cement mortar prisms /6/. The coating prevents an attack on the coated areas of the specimen. Thus, the corrosion resistance of coated specimens is signifikantly higher than that of uncoated ones. The more of the specimens surface is covered by the coating the better is the performance under corrosion. However, the picture is quite different under stress corrosion conditions. The coated specimens, both those with the tensile side uncoated and those with only the notch region uncoated show extremely distinct load effects. This means, that if a coating has some failure points i.e. cracks, through which the aggressive medium can penetrate, these areas are the starting points of a severe stress corrosion, which under load, can reduce the life time of the structure to values of the unprotected material. The effect is observed for both types of coatings studied thus far, namely notch-free and one side free-coatings. It seems therefore to be necessary to reconsider the use of coatings at least for highly load bearing structural members subjected to a chemical attack.

Fig. 6: Effect of Coated Mortar Prisms under Stress Corrosion 5% Ammonium-Sulfat Solution





#### 4.SUMMARY AND CONCLUSIONS

Stress corrosion leads to significant reductions in strength of cementitious materials subjected to simultaneously acting mechanical and chemical stresses. Several media, amongst which are ammonium and sodium sulfate have been shown to cause stress corrosion. Severe reductions in strength and life time are the consequence of this process. In general, most of the important parameters of concrete technology affecting corrosion resistance also affect stress corrosion behaviour in about the same manner. An additional deleterious effect of stress corrosion has been discovered with coated specimens. Cracks and other failures in the coating result in an enhanced stress corrosion reducing the life-time of a coated structure to that of an uncoated one. Stress corrosion is further assumed to be responsible for the large differences known to exist between conventional laboratory studies, neglecting the effects of mechanical stresses on chemically attacked cementitious materials. It is therfore urgently necesseary to study the observed effects in more detail and to incorporate stress corrosion in the standards and evaluation procedures of durability of cementitious materials.

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