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# NEW AND POWERFUL METHOD FOR THE EVALUATION OF MULTIPARAMETER CORROSION TESTS

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Abstract:

A new method for the evaluation of corrosion and stress corrosion tests performed with cementitious materials has been developed. The method is based essentially on a transformation of the strength-time data obtained usually from corrosion experiments. Results of the application of the method to the evaluation of stress corrosion data from cement mortars in aqueous ammonium salt solutions are discussed.

Zusammenfassung:

Zur Auswertung von Korrosions- und Spannungskorrosionsversuchen bei zementgebundenen Baustoffen wurde ein völlig neues Verfahren entwickelt. Es basiert im wesentlichen auf einer Transformation der Festigkeits-Zeit-Kurven, die in Korrosionsversuchen üblicherweise erhalten werden. Ergebnisse der Anwendung des Verfahrens zur Auswertung von Spannungskorrosionsversuchen an Zementmörteln in wässrigen Ammoniumsalzlösungen werden diskutiert.

## 1. Introduction

Corrosion experiments with cementitious materials are usually performed by immersing suitable specimens in the media of interest and determining certain properties of these (for example strength) or of the media (for example concentration of some species) as a function of time. In the case of stress corrosion, mechanical stresses are applied in addition to the chemical attack or solely.

Even if the corrosion research aims at studying only a few parameters, for example the effects of w/c-ratio or type of cement in a medium of given composition, the test series rapidly become tremendously large, easily involving several hundreds of specimens.

As a consequence large amounts of data emerge from such tests which often cannot be presented in a well arranged manner or evaluated in a straightforward way.

As an example, the results of a series of stress corrosion experiments with portland cement mortars in ammonium sulphate solutions [1] are reproduced in fig. 1. These results have been obtained with a single type of specimen thus representing only one combination of type of cement, w/c-ratio, curing time, salt type, salt concentration and load level and a single material property, flexural strength.

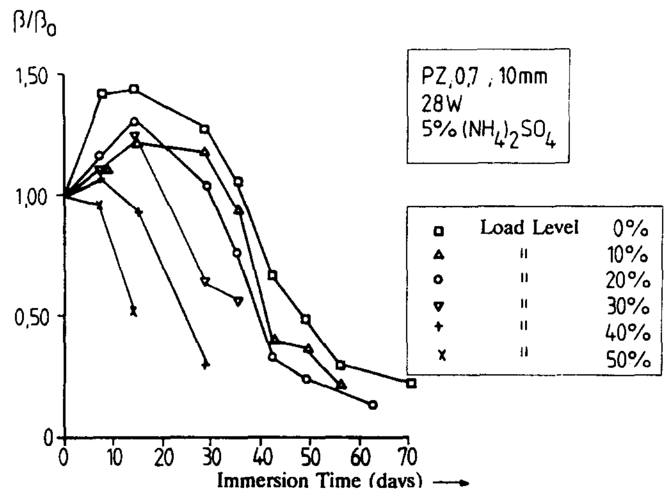


Fig. 1: Flexural strength $\beta$ related to initial flexural strength $\beta_0$ of mortar prisms immersed in 5% ammonium sulphate solution as a function of immersion time according to [1]

To study the effects of say w/c-ratio several series of this type with various w/c-ratios have to be performed and compared to each other. As every single w/c-ratio yields not only one single curve but a group of curves, the comparison becomes at least cumbersome. In general, following current practice, a detailed, often an arduous discussion is necessary to present all the facts in a well structured manner and draw the conclusions therefrom.

Whereas classical corrosion experiments may still be designed and evaluated by conventional methods, this is next to impossible for stress corrosion tests where the mechanical stress acts as an additional parameter affecting in general in a different manner each of the other parameters, referred to here as "specimen-" or "corrosion-" parameters respectively. In addition, for every load level applied every combination of the specimen- or corrosion-parameters must be studied.

For the evaluation of such experiments a new and comprehensive method has been developed, which is also suited for reducing the number of specimens in conventional corrosion tests without loosing valuable information. Maintaining the number of specimens allows obtaining additional information therefrom.

It is the purpose of this paper to present the new method in detail, explain the principles underlying the transformations involved and to outline further applications of the method.

The examples on which the method is demonstrated refer to stress corrosion tests on mortar specimens in various aqueous salt solutions which have been taken from [2].

## 2. Fundamentals

### 2.1 General Aspects of Stress Corrosion of Cementitious Materials

Stress corrosion is defined as the synergetic interaction between corrosion (or chemical attack respectively) and mechanical stresses acting simultaneously on a material. This paper deals only with static mechanical loads. It has been shown [1] that mechanical loads significantly affect the corrosion of cementitious materials in aqueous solutions. Furthermore, there is some evidence that the stress corrosion might be symmetric with respect to chemical and mechanical effects, which means that if a chemical attack affects the mechanical properties then mechanical stresses could affect vice versa the chemical corrosion [1] in some way.

In general, corrosion occurs with cementitious materials then and only then when chemical reactions can occur inside the material. For stress corrosion to occur these reactions need not to be necessarily of an aggressive type themselves. For example, sodium chloride brines are known not to be aggressive with respect to cementitious materials provided other factors like frost etc. are absent. Nevertheless, cementitious materials undergo chemical reactions when brought into contact with sodium chloride solutions, the products of which are complex calciumchloroaluminates. If mechanical stresses act on cementitious materials immersed in sodium chloride brines, stress corrosion occurs, yielding to significantly reduced lifetimes in comparison to otherwise identically treated non-loaded materials.

Cementitious materials are porous materials. The corrosive reactions thus take place everywhere in the volume accessible to the attacking medium, depending on certain parameters like w/c-ratio and others. Being subjected to corrosion in aqueous salt solutions no localized corrosion centres exist, the average degree of degradation for cementitious materials is thus equal to the real degree of degradation of the material.

Due to the physico-chemical nature of hardened cement paste there are no localized corrosion centres, even if a given medium may react specifically with only one phase present in the material, for example sulphates which react preferably with the aluminate phases to form ettringite-type phases.

Stress corrosion is in general the more pronounced the more brittle a material is [4]. This is also true for cementitious materials. Non-brittle materials allow for a buffering of excessive local stress concentrations via plastic deformation. The ability of accumulating mechanical stresses somewhere in its volume is thus an absolute prerequisite for the onset of stress corrosion in a given type of material. As cementitious materials are brittle and local stress accumulation is possible by various mechanisms, they are subjected to stress corrosion.

Mechanisms causing stress corrosion with cementitious materials are [2]:

- increased accessability for the attacking medium of the immobile reactive centres inside the material due to the mechanical stress
- structural changes due to the formation of solid reaction products or the dissolution of structural components respectively

prevention of healing of freshly created structural defects due to the effects of mechanical stress.

## 2.2 Theory of stress corrosion

Recently, a theory of stress corrosion of cementitious materials based on the theory of activation processes has been developed [1,2].

According to this theory failure under stress corrosion conditions (load level $L = \sigma/\beta_0$) occurs after a time $\tau^L$, which hence represents the lifetime of the specimen, if [5-9]

$$(\tau^L)^{-1} = \text{const.} \exp -[(Q-C-S)/RT] \qquad (1)$$

where Q: Mean activation energy of the failure process of the undisturbed, unloaded, non-corroding material, C: Reduction of activation energy due to chemical attack (corrosion) acting during $\tau^L$, S: Reduction of activation energy due to mechanical stresses acting during $\tau^L$.

For $C = 0$ and $S = 0$ the lifetime of a non corroding, unloaded material is obtained. $S = 0$ and $C \neq 0$ corresponds to a corroding, unloaded material whereas $S \neq 0$ and $C = 0$ corresponds to a non-corroding material subjected to mechanical stresses.

Whereas $C = f(c,T)$ may be treated under practical conditions [1] as a constant characteristic for the corrosive medium, for S an expression of the form

$$S = \frac{X\sigma}{\beta_0 - \sigma} \qquad (2)$$

has been derived using a hypothesis from [10] where X is a material constant, $\sigma$ is the stress level acting on the material and $\beta_0$ is its initial strength.

Introducing eq.2 in eq.1 and doing some straightforward algebra results in

$$\ln(\tau^L) = A - \frac{B\sigma}{\beta_0 - \sigma} \qquad (3)$$

where A, B are constants related to the aggressivity of the medium (A) and the sensitivity of the material under consideration against stress corrosion (B). A detailed discussion of the properties of A and B is given in [1,2].

Eq.3 is symmetric in chemical and mechanical effects because they contribute independently to the reduction of life time of the material.

Due to the structure of eq. 3 a synergetic effect results when chemical and mechanical loads act simultaneously, because the relative effects of mechanical stress increase with increasing aggressivity of the attacking medium (decreasing A). Eq.3 is thus suited for the description of stress corrosion phenomena with cementitious materials [1].

Fig. 2, where life time data are plotted against all studied load levels in [1] ($L = \beta/\beta_0 = \sigma/\beta_0$) shows the good coincidence of theory and experiments [2].

## 3. The New Method

The theory outlined in the previous chapter and described in detail in [1,2] treats essentially the relationship between lifetime $\tau^L$, the applied load level L and various material parameters.

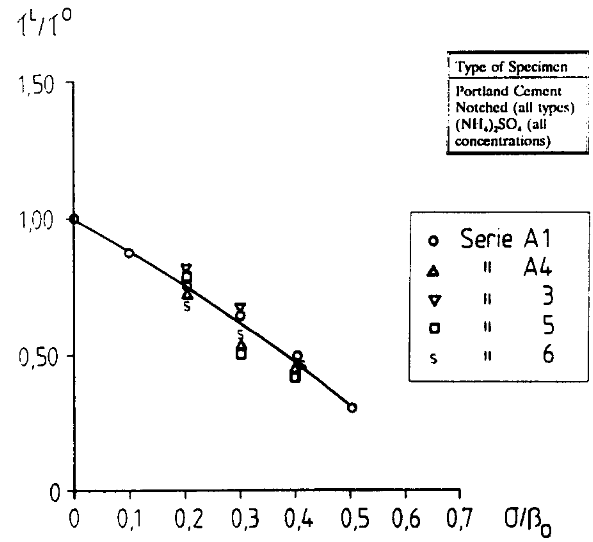


Fig.2: Comparison between theoretical prediction and experimental data for stress corrosion tests of cement mortars in ammonium sulphate solutions ($\tau^0$ = lifetime of unloaded specimens, $\tau^L$ = lifetime of specimens subjected to load level L).

A practical orientated evaluation should reveal the strength-time behaviour of the material subjected to stress corrosion and ideally allow for immediate practical applications.

Application of the theory outlined in the previous chapter leads to a simple transformation of the experimental data into a comprehensive presentation meeting these requirements. As an example the transformation will be demonstrated on the data shown in fig. 1.

Table I shows the lifetimes obtained for this series of tests [2]. The left column shows decreasing concentrations, i.e. the specimens were immersed in the salt solutions and kept there until the end of the test. The second column represents same tests where the solutions were renewed weekly.

Plotting now the relative strength $\beta/\beta_0$ versus the relative lifetime of the specimen $t/\tau^L$, where $\tau^L$ is the life time of specimens in solution under stress level L, results in a single curve for all curves of a group.

Fig. 3 shows this curve resulting from fig.1 and table 1.

Basically, this transformation normalizes the mechanical effects, i.e. the effects of the mechanical load acting on the corroding specimens. For every load level only one curve is obtained, thus reducing the volume of data from stress corrosion tests to that of normal corrosion tests where every combination of specimen- or corrosion-data respectively yields also one such curve. For the time being, this transformation is valid only for cementitious materials where the theory described in [1,2] applies. However there is evidence that this transformation may also apply for other non-metallic materials.

Table I: Lifetime data for the experiments shown in Fig. 1.

| Load Level L (%) | Lifetime $\tau^L$ (days) | |
|---|---|---|
| | solutions unchanged | solutions exchanged weekly |
| 0 | 49 | 45 |
| 10 | 43 | - |
| 20 | 39 | 33 |
| 30 | 33 | 25 |
| 40 | 24 | 21 |
| 50 | 15 | - |

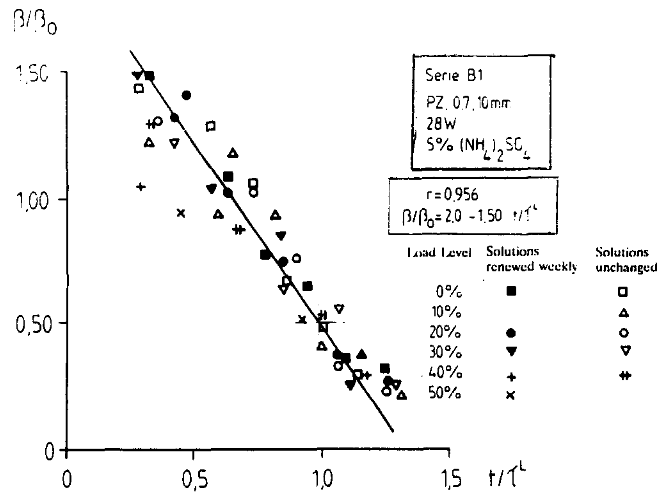


Fig.3: Transformed data and curve obtained from the data shown in fig. 1 and table I.

Furthermore, for $t/\tau^L <= 1{,}4$ a straight line is obtained with sufficient accuracy for all experiments performed thus far in ammonium salt solutions. Fig. 3 further shows that for the series of tests performed in constant concentrations and decreasing concentrations respectively the same curve is obtained.

This transformation, in the following referred to as " τ-transformation", allows a concise evaluation of corrosion and stress corrosion experiments. In addition, some very interesting results on stress corrosion of cementitious materials have been obtained from its application.

In all cases studied thus far, the stress levels of a series of stress corrosion tests are transformed onto a common curve depending on characteristic parameters of the medium and the specimens. This was the original objective of evaluating the stress corrosion experiments in such a manner.

From the point of view of the $\tau$-transformation a mechanical stress acting simultaneously to a chemical one in a stress corrosion experiment shifts simply the relative life time of a given specimen towards higher values. Unloaded specimens hence represent realisations of low $\tau/\tau^L$-values whereas loaded specimens represent higher ones. Going from corrosion to stress corrosion thus can reduce the time needed for a given series of tests.

The higher the load level applied to a specimen the higher relative life times are realised in the experiment.

Thus, a stress corrosion experiment gives a comprehensive picture of the corrosion behaviour of a cementitious material in a short period of time because all $t/\tau^L$-values, i.e. the whole range of possible lifetimes of a given type of specimen in a given medium can be studied in a single experiment.

However, the most striking and entirely surprising result of the evaluations with this new method was the fact that there are no individual curves for each combination of medium/specimen but that there exists only a small number of common master curves, depending only on a few parameters. For example, the curve in fig. 3 is valid for notched specimens in aqueous ammoniumsulfate solutions. It is independent from the concentration of the solution, the notch type and depth, the type of cement and for portland cement in ammoniumsulfate solution also independent from the w/c-ratio. Such master curves are also known for glass [3].

At our present state of knowledge, the master curves seem to depend only on the type of salt, the presence of notches and on fly ash in the concrete.

This general constancy of the master curves for stress corrosion cannot be derived from the theory outlined above at our present state of knowledge, which only predicts the elimination of the load effects but not the surprising fact of the existence of only a few general mastercurves.

Having established their existence, the constancy of the master curves allows further, to use loaded specimens for accelerated corrosion tests without changing the corrosion mechanisms to be studied.

The performance of accelerated but close-to-reality corrosion tests for cementitious materials has now become possible. If corrosion experiments are performed with loaded specimens, the duration of a test is significantly reduced by a factor up to five depending on medium and load level applied, without being subjected to dangers like altered mechanisms for example due to elevated temperatures or concentrations. Environmental conditions, temperatures and concentrations can hence be studied in the desired practical case in short time.

Because of the existence of the master curves, one load level is sufficient to obtain the desired data, thus reducing the necessary efforts further.

## 4. Summary

For ammonium salt solutions all data obtained thus far can be subjected to a transformation called $\tau$-transformation. For all load levels a common master curve results, which is equal

for all series and depends solely on the type of medium, the existence of notches in the specimens and wether the mixture contains fly ash additions. All other parameters studied, namely the concentration of the solutions, form, type and depth of notches, type of cement (according to German standards), curing time, w/c-ratio etc. do not affect the master curve.

The $\tau$-transformation allows a compact and easy presentation of the results and an easy comparison of data which otherwise could only be represented by groups of curves.

The constancy of the master curves allows, having established their existence, to use loaded specimens for accelerated corrosion tests without changing the corrosion mechanisms to be studied by for instance high temperatures or other means of acceleration.

The constancy of the mastercurves cannot be derived from the theory at our present state of knowledge, which only predicts the elimination of the load effects but not the surprising fact of the existence of only a few general master curves.

Furthermore, the master curves can be treated as straight lines with sufficient accuracy. The data of the master curves established thus far for ammonium salt solutions are summarized in table II.

Table II: Data of the master curves of stress corrosion for cementitious materials

| Medium | Conc. (wt-%) | Notches | Other | Slope | Intercept |
|---|---|---|---|---|---|
| $(NH_4)_2SO_4$ | 0.1 - 10 | Yes | - | -1.50 | 2.0 |
| | | No | - | -0.86 | 1.36 |
| | | Yes | Fly Ash | -1.30 | 1.80 |
| $NH_4NO_3$ | 0.1 - 10 | Yes | - | -0.70 | 1.20 |

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