

## New Approach Identifying Corrosion Effects besides Standardized Materials Testing

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received September 12, 2014; received in revised form October 20, 2014; accepted November 30, 2014

### Abstract

The corrosion resistance of waterglass-based putties is influenced considerably by the alkali modulus. The acid resistance of such putties is currently tested according to the standard DIN EN 993 – 16 and described by means of the measured change in weight. Dynamic Mechanical Analysis (DMA), a testing procedure to define the viscoelastic behavior of plastic materials, has brought about new findings on evaluation of the influence of the alkali modulus and the kind of damage resulting from corrosion caused by acids, with regard to mechanical behavior. Both applied test methods have revealed two different effects of corrosion: weight loss on the one hand, and a decrease in the storage modulus  $E'$ , on the other hand.

*Keywords:* Acid-resistant putties, corrosion, Dynamic Mechanical Analysis

### I. Introduction

To protect industrial chemical processing plants (e.g. systems for the preparation of acids or exhaust gas treatment) against acids, acid-resistant alkali waterglass-based putties are used as laying and jointing material to mechanically fix the ceramic lining. To have available a certain assortment of different efficient putties, it is of fundamental importance to know about the specific corrosion resistance of such materials to acid media. This makes it possible to assign characteristic service lifetimes to the respective materials.

The current test method to evaluate the acid resistance of putties (DIN EN 993 – 16) consists of determining the change in weight caused by corrosion. For that purpose, the standard defines the exposure of granular or fragmented material to boiling sulfuric acid (70 %) for six hours. After the samples have been washed and dried, the weight loss of the samples is documented.

This purely gravimetric method, however, cannot be used to determine structural changes to the materials. Aim of the performed studies was therefore to find a new approach to describe the changes in structural properties as a result of corrosion by means of Dynamic Mechanical Analysis.

The corrosion resistance of waterglasses is usually described in relation to the alkali modulus, which expresses the ratio of silicon dioxide and alkali oxide in waterglasses. For this reason, it was the objective of the performed studies to precisely define the actual correlation between level of the alkali modulus and the corrosion resistance of putties by extending the current test method.

Two standard potassium silicates with the same processing properties but a different alkali modulus were tested. For this purpose, the putties produced from these water-

glasses were exposed to varied concentrations of sulfuric acid for different periods of time. A comparative evaluation was made based on measurement of the weight loss as well as by means of Dynamic Mechanical Analysis.

#### (1) Waterglasses

Waterglasses are used in acid-resistant putties as binders, whose consolidation takes place as a result of chemical reactions with respective hardeners. The term “waterglasses” summarizes alkali silicate glasses with the general formula  $\text{Me}_2\text{O} \cdot n\text{SiO}_2$  either in the form of amorphous solids or in the form of dispersions of such glasses in water. Mainly waterglasses with proportions of sodium oxide and potassium oxide are of technical importance<sup>1,2</sup>. The ratio of silicon dioxide and alkaline oxide differs from waterglass to waterglass and is defined by the alkali modulus  $M$ <sup>3</sup>. The selection of the alkali cation and the alkali modulus is of considerable importance for the chemical behavior (e.g. corrosion resistance) and mechanical behavior (e.g. strength and rigidity) of waterglasses.

#### (2) Corrosion of waterglasses caused by acids

The corrosion resistance of waterglass-based putties is defined by the composition and the state of the amorphous bonding phase, which has been damaged and, thus, reduces the mechanical properties of the entire compound<sup>4</sup>.

Three fundamental damage mechanisms dominate the attack based on aqueous corrosion: formation of a gel layer, ion exchange and hydrolysis<sup>4,5,6,7</sup>. In most cases, these three mechanisms run parallel to each other to a varying extent. The prevailing pH value determines which of these three mechanisms is dominant. According to the studies in ref. 7, hydrolysis can be mainly observed in the neutral and alkaline pH range, whereas ion exchange and gel formation dominate in lower pH ranges.

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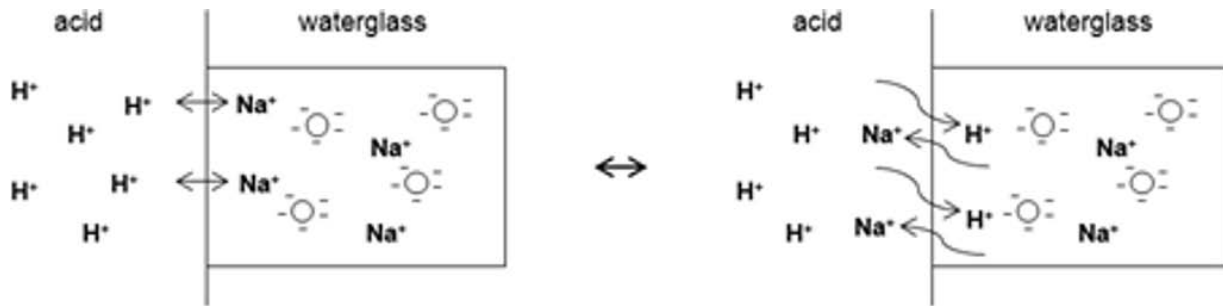


Fig. 1: Model of ion exchange.

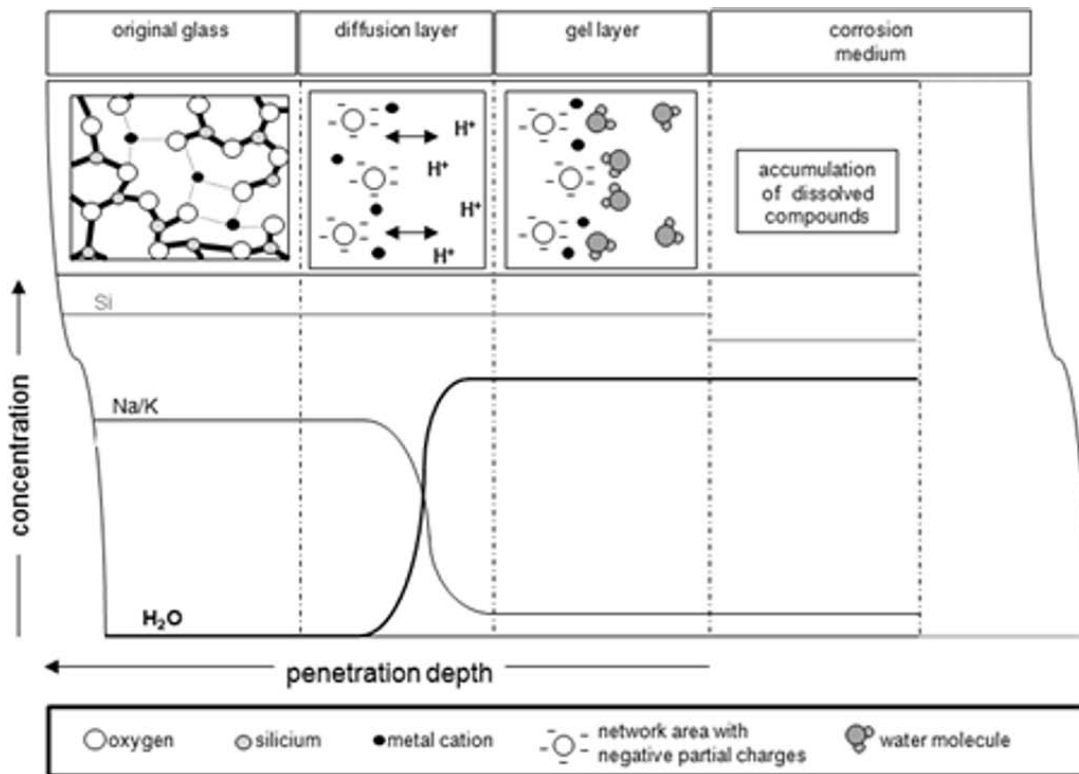


Fig. 2: Model of layer formation at the waterglass caused by corrosion at pH < 4<sup>8</sup>.

Ref. 6 and ref. 7 describe the formation of a gel layer at the glass surface, which is caused by hydration. This runs stable and is particularly dominant through the high H<sup>+</sup>-concentration at very low pH values (pH < 3). At pH values > 3, large proportions of the gel layer dissolve and damage the glass structure continuously.

Furthermore, ref. 7 proves that alkali ions are eluted from the gel layer and the glass microstructure under the influence of acids through ion exchange due to an inward diffusion of H<sup>+</sup> (Fig. 1).

These two damage mechanisms lead to a zonal layer formation at the contact surface of the waterglass with the corrosion medium (compare Fig. 2 below).

In the slightly acid (> pH 4) to neutral pH range as well as in the alkaline pH range, a dissolution of the silicate network can also be observed by splitting bonds over oxygen bridges through hydrolysis<sup>6,7</sup>. Of all above-mentioned mechanisms, this reaction causes the worst damage to waterglasses, because it represents the inversion of the con-

densation reaction during setting. Hydrolysis and condensation reaction are in equilibrium (Fig. 3).

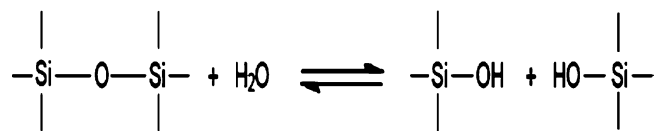


Fig. 3: Equilibrium reaction of the hydrolytic splitting at pH > 4.

The alkali modulus in particular determines corrosion resistance. The higher the proportion of SiO<sub>2</sub>, the higher is the corrosion resistance of the waterglass. This is based on the network-creating function of SiO<sub>2</sub>, whereas the alkalis act as network modifiers and break up the three-dimensional network<sup>9</sup>:

$$\text{Alkali modulus } M = \frac{\text{Network creator (SiO}_2\text{)}}{\text{Network modifier (Me}_2\text{O)}}$$

**II. Experimental**

The experimental studies were conducted with two potassium silicates with a different alkali modulus. In the

following these samples are designated K-A and K-B. K-A has an alkali modulus  $M = 1.4$ , and for K-B the alkali modulus is  $M = 1.1$ . Both are already commercially used and applied, for instance, in the acid protection sector. Typical putties were prepared with the waterglasses (Table 1). They reflected usual compositions as applied in practice. Silica sand with a grain band of  $0.355 \leq d \leq 0.09$  mm and silica flour with a grain band of  $0 \leq d \leq 0.163$  mm were used as fillers in each formulation. A traditional aluminium phosphate was used as the hardener.

**Table 1:** Overview of the sample materials.

Sample material	
waterglass K-A	waterglass K-B
$M = 1.4$	$M = 1.1$
filler I: silica sand	
filler II: silica flour	
aluminium phosphate hardener	

Two types of test pieces were subsequently produced for the studies, granular material and DMA bars.

For the preparation of granular sample material for testing according to DIN, the previously manufactured putties were broken in a jaw crusher, and the so-obtained coarse material was then ground in a roller mill. Grading fractions of  $0.6 \leq d \leq 0.8$  mm were obtained by means of double-screening. These fractions were washed with distilled water in accordance with the standard regulation to remove fine abrasive material. Afterwards, they were dried until a constant weight was achieved.

Furthermore test pieces of  $50 \times 10 \times 2$  mm<sup>3</sup> were extracted from the putties with a laboratory saw. The bars were also dried until a constant weight was achieved before the tests were started.

**(1) Testing according to DIN**

The corrosion resistance of the putties was determined according to the current standard DIN EN 993 – 16. The samples (granular material, DMA bars) were exposed to boiling 13.1-molar sulfuric acid for six hours (which corresponds to the standardized concentration of 70 %). After cool-down, the samples were washed with distilled water, dried at  $T = 110$  °C until a constant weight was achieved, and the weight loss of the sample was documented.

Since numerous scientific investigations define the pH as a decisive factor for corrosion provoked by acids, comparative trials in 0.1-molar sulfuric acid were conducted as well. To be able to evaluate the corrosion process also with regard to the kinetic aspect, the total duration of exposure was increased, deviating from the standard regulation. The samples were each studied after 2, 6, 12 and 18 hours respectively.

The weight loss itself can, however, only provide limited information on the characteristic resistance to acids. It does not allow statements regarding the damaging mechanisms of the microstructure itself nor on the change in

the mechanical properties of the material. Consequently it is not possible to obtain detailed indications of the structural corrosion process, but only of the change in physical values. For this reason additional tests were performed by means of Dynamic Mechanical Analysis.

**(2) Dynamic Mechanical Analysis**

Dynamic Mechanical Analysis<sup>10, 11</sup> is a test method to study the viscoelastic properties as a function of temperature, time and frequency.

For this purpose an oscillatory force is applied to a sample (exciter signal), which can be applied in the form of elongation, shear or compression. This sinusoidal stress provokes an also sinusoidal but phase lag of strain of the sample material with changed amplitude (response signal). The phase shift and the comparison of the amplitude of both signals result in the complex modulus  $E^*$  of the material.

The complex modulus  $E^*$  is composed of the storage modulus  $E^I$  and the loss modulus  $E^{II}$ . It defines the rigidity of the test material:

$$E^* = E^I + E^{II}$$

The storage modulus  $E^I$  measures the elastic portion of the rigidity and describes the energy applied through mechanical strain, which can be stored and dissipated by elastic displacement. The energy, which transforms to friction heat through plastic displacement, is expressed as the loss modulus  $E^{II}$ .

The performed series of measurements included isothermal immersion tests. For this purpose a tank was attached to the DMA apparatus. The corrosion medium sulfuric acid (13.1 M and 0.1 M) was filled into this tank. During the measurement, the sample (bar) was completely immersed into the corrosion medium. This supplies exact details on the time course of damage and the change in mechanical properties involved. Duration of each individual test was 10 hours.

**(3) X-ray fluorescence analysis**

For characterization purposes, the chemical composition of the putties was defined by means of x-ray fluorescence analysis (XRF). For this purpose several samples were taken from the original putties produced as well as from the washed granular material. The influence of washing processes during sample preparation on the ratio of SiO<sub>2</sub> and K<sub>2</sub>O was determined in this way.

**III. Results**

**(1) Gravimetric analysis**

**(a) Granular test material**

Figs. 4 and 5 show the average weight loss of granular test material and DMA test bars after their exposure to sulfuric acid in various concentrations. The relative weight loss indicated is the quotient of the total weight loss relative to the starting quantity of un-exposed test material.

Upon analysis of the weight loss of the granular material (Fig. 4), neither tested waterglass exhibits a significant difference. It is obvious, however, that the less concentrated acid provokes a substantial and greater weight loss and thus a stronger defect than the stronger concentrated acid.

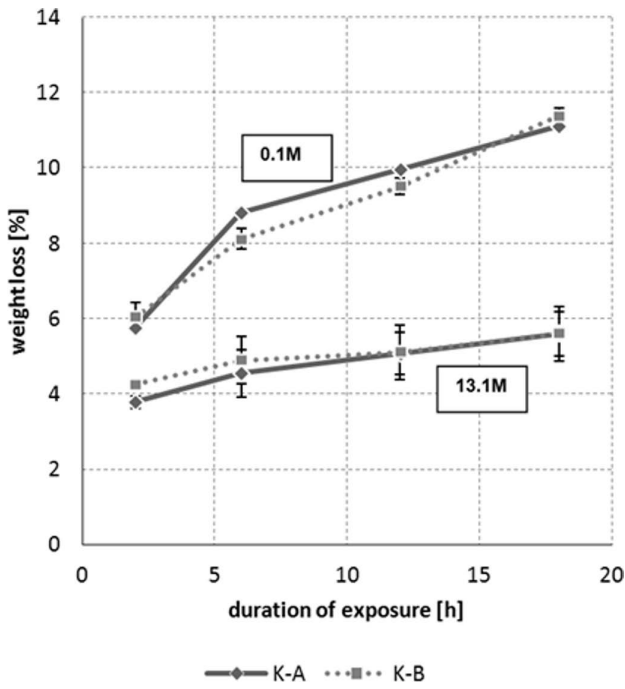


Fig. 4: Weight loss of the aggregates (granular material) after exposure to 13.1 M and 0.1 M sulfuric acid.

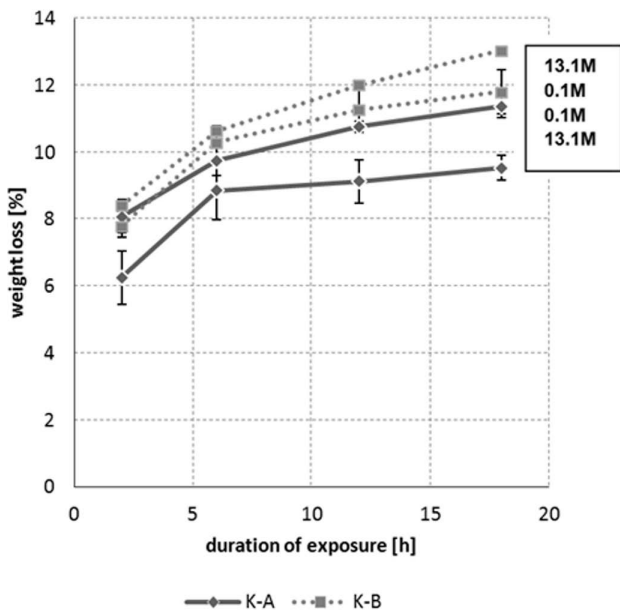


Fig. 5: Weight loss of the DMA bars after exposure to 13.1 M and 0.1 M sulfuric acid.

(b) DMA bars

The results of the exposed DMA bars differ significantly from those of the granular test material. As shown in Fig. 5, the weight loss of the bars caused by the acids is considerably higher. In addition there is a difference between the two samples K-A and K-B. Whereas after exposure to 0.1-molar sulfuric acid, K-B displays only a slightly stronger defect than K-A, the weight loss after testing in 13.1-molar sulfuric acid is extremely different. In the latter case the putty based on the waterglass with inferior alkali modulus shows a substantially stronger defect than the waterglass with the higher alkali modulus. The average weight loss caused by the 13.1-molar sulfuric acid is higher by 23 wt%.

(2) Structural analysis by means of the dynamic mechanical analysis

The results of the isothermal immersion tests reveal a decrease in the storage modulus  $E^I$  of the bars for both exposure media (Fig. 6). The greatest change in the slope of the curve is observed particularly at the beginning of the measurement. During the further course of the measurement, the curve flattens.

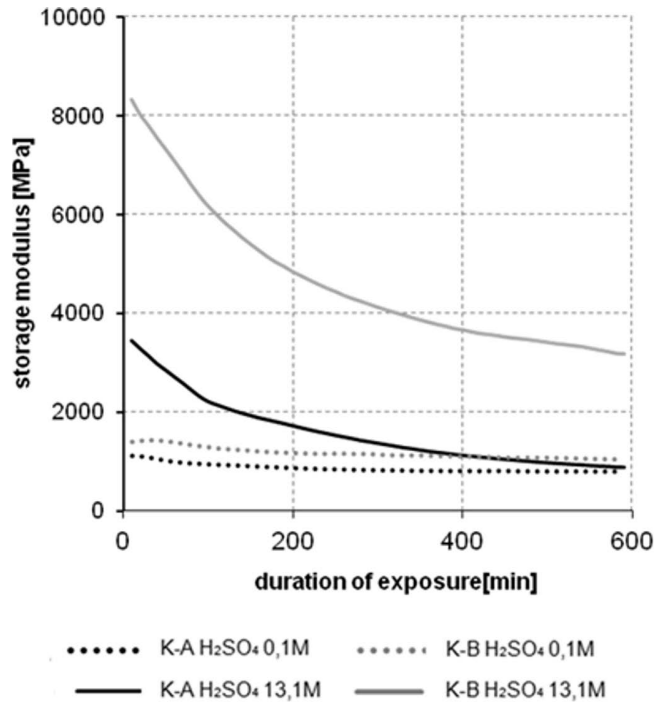


Fig. 6: Isothermal immersion test of both waterglasses when exposed to 13.1 M and 0.1 M sulfuric acid.

Moreover, the immersion test results as well as the DIN testing results display a dependence of the damage extent on the concentration of the acting acid. The 0.1-molar sulfuric acid causes the highest weight loss when testing according to DIN, whereas the 13.1-molar sulfuric acid provokes the strongest damage during the immersion tests. It becomes obvious that the decrease in storage modulus is much more intense with the stronger concentrated sulfuric acid than with the weaker concentrated acid.

Both samples K-A and K-B differ regarding their rigidity and thus in their absolute values of the storage modulus  $E^I$ . For this reason, analysis of the strength development over corrosion time can only be relative when comparing the corrosion process. To compare the samples exposed to different media, the starting and final values of  $E^I$  were, therefore, defined and normalized. The percentage decrease calculated via this comparison is shown in Fig. 7. It makes it obvious that the greatest decrease in storage modulus  $E^I$  is caused by the acid with stronger concentration. In addition, only slight differences can be observed when the two waterglasses are compared. However, it is striking that the decrease in storage modulus  $E^I$  of the waterglass with higher alkali modulus is more distinctive with both media. The reduction in mechanical strength caused by corrosion is more substantial for the waterglass with higher alkali modulus, independent of the corrosion medium used.

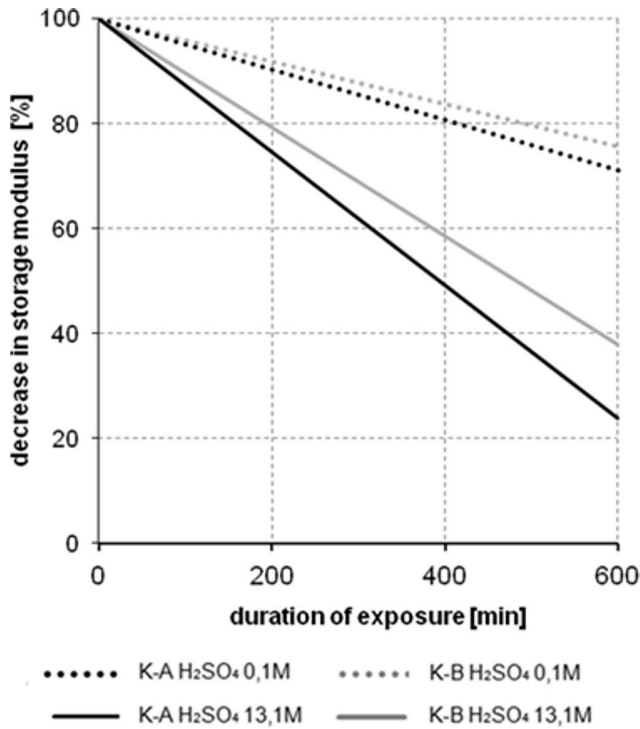


Fig. 7: Percentage decrease in storage modulus  $E'$  during immersion tests.

(3) Characterization by means of XRF

Table 2 shows the chemical composition of the prepared putties. Their main component is  $SiO_2$ , which is introduced primarily with the silica sand and silica flour fillers but also with the waterglass. The table also shows the different content of  $K_2O$  depending on the different alkali modulus of the two putties. The analysis reveals further the two components of the introduced hardener, i.e.  $P_2O_5$  and  $Al_2O_3$ .

Table 2: Chemical composition of the waterglasses (indicated in wt%).

Components	K-A		K-B	
	original putty	washed granular material	original putty	washed granular material
$SiO_2$	9.80	96.19	89.45	95.83
$P_2O_5$	3.95	1.41	4.47	1.57
$K_2O$	2.78	0.95	3.49	1.07
$Al_2O_3$	1.71	1.20	1.85	1.28

There are significant differences between the original putties and the washed granular material. Approximately two thirds of the alkali oxide quantity (K-A: 66 wt% and K-B: 69 wt%) are eluted through the contact with water during sample preparation. The hardener proportion also decreases.

IV. Discussion

(1) Gravimetric analysis

(a) Granular test material

The DIN-testing of the granular sample material does not show any considerable differences between the two batches with different alkali modulus. This is due to premature damage caused by the standard elution of alkalis during sample preparation. This is manifested by the comparison of the XRF analyses of untreated putties in standard condition and the washed granular material. These studies show considerable differences in the alkali oxide content. The proportion of  $K_2O$  after elution is only a third of the original concentration, because the potassium is eluted with the distilled water, which leads to a premature damage of the glass structure. The reason for this is the decrease in the network's stability.

The remaining proportion of alkali oxides in the waterglasses is reduced to a large extent, so they only play a minor role in corrosion during subsequent testing. Owing to this premature damage this test method cannot detect differences in the corrosion resistance between the samples with different alkali content. This proves a fundamental weak-point of DIN-testing, confirming that this method alone is not sufficient to define the influence of the alkali modulus.

(b) DMA bars

To minimize the impact of water during washing processes, exposure tests were conducted with the previously produced DMA bars, since these had less contact with water on account of their different preparation. Whereas the granular material was washed a number of times to remove fine abrasive material, the DMA bars were prepared using a water-cooled laboratory saw which causes minor abrasive material. Therefore an extra washing process was not necessary.

The bars display distinct differences between both batches. The waterglass with an elevated alkali modulus is more severely damaged by the 0.1-molar acid than by the 13.1-molar acid. The condensation-hydrolysis equilibrium is responsible for this effect, since it depends strongly on the pH according to ref 7. In the slightly acidic pH range the equilibrium is on the hydrolysis part whereas it is on the condensation side for the strongly acidic range. Since hydrolysis represents the process with the strongest damage to the network, as it leads to direct separation of bonds involved in the network, a stronger weight loss is measured with exposure to a 0.1-molar sulfuric acid compared to exposure to the 13.1-molar acid.

In the case of the waterglass with a lower alkali modulus, the opposite effect is observed. The stronger weight loss is provoked by the stronger concentrated acid. This is related to the differences in the alkali modulus of the tested waterglasses. The waterglass K-B with an alkali modulus of  $M = 1.1$  has a higher proportion of potassium oxide than K-A with  $M = 1.4$ . Owing to the higher content of  $K_2O$ , the waterglass-consisting bonding phase of the K-B putty has a more alkaline character than the matrix of the K-A sample. When interactions between the bonding phase and the



13.1-molar sulfuric acid take place, the resulting pH milieu is therefore higher as in case of the sample with lower alkali content. It is possible that in this case a limit value of the pH is achieved, which has an impact on the condensation-hydrolysis-equilibrium and shifts it in the direction of hydrolysis. Consequently, the 13.1-molar sulfuric acid can bring about a stronger defect.

A further possibility for the stronger damage can be related to the impact of potassium on the silicate lattice. Alkali oxides act as network modifiers in glass. This means that the network is interrupted in these areas. A higher content of alkali oxides leads to more defects in the network. If a further splitting of bonds occurs during corrosion, larger areas can dissolve in the network, which has been damaged more seriously anyhow. The consequence is a stronger weight loss.

### (2) Structural assessment by means of Dynamic Mechanical Analysis

The results of the dynamic mechanical analysis show a decrease in storage modulus  $E^I$  owing to corrosion. This reduction can be taken analogically as a measure for the extent of damage. The stronger the decrease in the storage modulus  $E^I$ , the greater is the loss in mechanical strength.

The worst defect can be observed with exposures to 13.1-molar sulfuric acid. This behavior can be explained with the network's hydration. Particularly at low pH values, water settles down to the outer material surface which has mostly negative partial loads. This is even favored by the high  $H_3O^+$  concentration. The hydration results in the opening and electrostatic destabilization of the network as well as in the dissolution of small proportions of the network<sup>6</sup>. The so-formed gel layer during hydration reduces the mechanical strength of the putties considerably, being the cause for a decrease in the material's complex modulus  $E^*$ .

It is further observed that the waterglass with a higher alkali modulus shows a comparably stronger decrease in storage modulus  $E^I$  than the waterglass with an inferior alkali modulus. The storage modulus has a direct correlation with the material's rigidity, which is substantially influenced by the cross-linking of the waterglasses' glass structure. The degree of cross-linking is particularly influenced by the hardening of the waterglasses. Differing decrease can, thus, be attributed to the variations during consolidation of the putties caused by the difference in alkali modulus.

To give reasons for the varying decreases in storage modulus with regard to deviations during the hardening process, the following model is outlined:

1. Setting is principally initiated by the alkaline range of waterglasses, leading to a de-polymerization of the aluminium phosphate hardeners<sup>1,12</sup>.
2. The higher pH of the potassium silicate with an inferior alkali modulus leads to stronger de-polymerization.
3. Phosphate components are made available for the formation of the glass network through de-polymerization of the hardener. Stronger de-polymerization brings about formation of excess phosphate components acting as network creators.

4. The amount of phosphate components correlates with the cross-linking in the glass microstructure. The more network creators are made available, the stronger cross-linking can be.
5. An increased availability of phosphate components for a waterglass with low alkali modulus results in a stronger cross-linking of the glass microstructure. The higher degree of this cross-linking is the reason for better strength and consequently a higher storage modulus of the waterglass with the inferior alkali modulus.

### V. Conclusions

The studies conducted show that it is not possible to make a global and overall statement regarding the dependence of acid corrosion on the alkali modulus. Both applied test methods have revealed two different appearances of corrosion: weight loss on the one hand, and decrease in storage modulus  $E^I$ , on the other hand.

The test results reinforce the statements on the weight loss often made in literature. A higher proportion of  $SiO_2$ , i.e. a higher alkali modulus, leads to better resistance. This can be proven by the exposure of the DMA testing bars. Testing of aggregates according to DIN can, however, not sufficiently prove the correlation between alkali modulus and weight loss because of elution of alkalis during sample preparation.

Furthermore it is shown that this partial statement of DIN testing does not take into account the variations in mechanical strength and thus corrosion behavior. Dynamic Mechanical Analysis can provide a first approach. This type of testing reveals a correlation between the alkali modulus and damage that has never been defined before. Contrary to the statements in literature, it can be proven that the decrease in storage modulus  $E^I$  is worse with an elevated alkali modulus, thus leading to stronger damage caused by corrosion.

For this reason, the impact of the alkali modulus on the corrosion resistance of waterglasses must be interpreted in a new way. In general, it should be seen in correlation with the studied defects.

As a consequence, future studies will have to examine which of the two corrosion effects is of greater importance for the use of acid-resistant putties. Since strong dependence of corrosion on the pH of the applied medium was detected as well, and corrosion varied with distinct alkali moduli, further studies are necessary to define the damage parameters and the material developments based on them.

### Acknowledgement

The authors wish to acknowledge the Stiftung Rheinland-Pfalz für Innovation for financial support.

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