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CORRELATION BETWEEN FRACTURES TOUGHNESS AND ZETA POTENTIAL OF CEMENTSTONE
Ir.A.T.F.Neerhoff
CORRELATION BETWEEN FRACTURES TOUGHNESS
AND ZETA POTENTIAL OF CEMENTSTONE

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SUMMARY

A brief account is first given of the difficulties encountered when trying to make a proper choice of fracture-facilitating surface-active agents for cementstone. In this context we describe the "Rebinder-effect", the notion of zeta potential, and the present knowledge about the adsorption behaviour of calcium alumino silicates in alkaline aqueous environments. Comparison of the results of zeta potential measurements by means of electroosmosis, and measurements of the fracture toughness \( K_{lc} \), both performed on cementstone in aqueous electrolytic solutions of varying concentration which were kept saturated vs. calciumhydroxide, shows a distinct maximum for \( K_{lc} \) at the so-called "Iso Electric Point". A preliminary model is suggested to explain the observed behaviour of \( K_{lc} \) as a function of the concentration of the electrolytic solution.

I INTRODUCTION

A vast amount of literature exists about the chemical, physical and mechanical properties of cementstone (1,2,3,4). As far as is known however no definite results have been published up till now on the effects of environment on the intrinsic strength of the cementstone-gel during a fracture process.

Essentially cementstone is a short-range-order ionic lattice. Its structural units are formed by hydrated calcium silicate- and calcium alumino silicate crystallites. Due to the smallness of these crystallites (typically 10 Å to 1 μm) a relative large number of atoms is present a their surface. This will make every surface effect to a volume effect (5,6,7). For In-
stance the strength of the crystallites will undoubtedly be determined by their adsorbate (5,7), which mainly consists of water saturated vs. Ca(OH)₂. The crystallites themselves induce structural changes in their adsorbate at distances from the interface that greatly exceed molecular dimensions (8,9,10).

Forces between crystallites which increase the strength of cementstone are (1,3):
- London - van der Waals dispersion forces across pores smaller than about 5 Å
- primary chemical cross-links such as Si-O-Si or Si-O-Ca-O-Si
- hydrogen bonds
- pure mechanical entanglement of crystallites

Forces which decrease the strength of cementstone are:
- double layer forces due to a net electric charge of the crystallites
- penetration forces of water between crystallites

At increased crack velocities the visco-plastic behaviour of load-bearing water films becomes important. An important question further is whether the crystallites themselves will break (brittle failure) or whether they shear apart (ductile failure).

During a "fracture" process all the above mentioned forces act together. A theoretical strength- vs. structure-relationship of cementstone, containing in addition pores and microcracks in varying proportions, therefore seems to be impossible. As a matter of fact, even for "well-defined" silicates such a treatment is largely qualitative, and has only been possible for a very limited number of simple cases (11,12). Most realistic values of the excess-energy of solid fracture surfaces seem to be given by indirect measurements, such as the heat-of-solution method of Lipsett (13) which was applied on tobermorite by S. Brunauer (14). We shall therefore not attempt here to estimate a quantity such as the "surface energy of cementstone", whatever its microscopic definition may be.

In view of the expected difficulties in making a proper choice of fracture-facilitating agents for cementstone, the author felt it as a most valuable approach to investigate the applicability of the so-called "Rebinder-effect" (15) (A recent review of adsorption-sensitive fracture phenomena including the "Rebinder-effect" can be found in ref. 16, or see the paper by Dr. J.J. Mills, this conference). We shall now briefly discuss this effect as well as the notion of zeta potential with which it is closely related.

When a solid is immersed in an electrolytic solution it may obtain a net electric surface charge due to the preferential adsorption
of (potential-determining) ions from the solution (10). In fig. 1 these ions are supposed to have a positive charge. A thin (Stern-) layer of hydrated counter-ions also strongly adsorbed, stays behind in the liquid, just at the solid-liquid interface. After applying an electric field parallel to the interface the diffuse layer of electrolyte outside the so-called slipping plane (bearing a negative charge in fig. 1) will move. The liquid flow is proportional to the value of the electrostatic potential $\psi$ at the slipping plane which is known as zeta potential ($\zeta$), and which can be measured by the method of electroomosis. The concentration of electrolyte for which $\zeta = 0$ is called the Iso Electric Point (IEP). Now for most inorganic materials - whether crystalline or amorphous - there is a definite correlation between its plastic deformation characteristics and zeta potential, with the restriction that enough time is allowed for the adsorption equilibrium to be established (16). In fig. 2 such a correlation is depicted between microhardness and zeta potential as a function of concentration of electrolyte (i.e. the actual "Rebinder effect") (16).

Fig. 2 Correlation between microhardness (h) and zeta potential ($\zeta$)
A striking feature of this type of correlations in fracture-experiments is the optimum value of the strength-parameter at the IEP. A speculative explanation states that the near-surface (1 - 10 μm deep) electronic properties, and therefore near-surface mechanical properties (such as mobility of dislocations and point-defects (17)) are influenced by a surface-charge, and therefore the solid is in its most stable bonded state at the IEP (18).

As for the adsorption behaviour of cementstone in electrolytic solutions no definite data are available in literature. From measurements of electromechanical bending (20) performed on cementstone one can deduce that the crystallites in saturated cementstone specimens bear a positive electric charge. Siskens (21) measured the zëta potential of various calcium silicates and calcium alumino silicates at a constant pH = 12.0 as a function of concentration of CaCl₂, by the method of electroosmosis. He found a sign reversal of zëta potential from a minus to a plus at concentrations of CaCl₂ varying from 1 to 10 mmole/litre. He also found that calcium- and hydroxyl-adsorptions mutually stimulate each other, resulting in a small net electric charge behind the slipping plane for ζ ≠ 0. With calcium alumino silicates extra adsorption sites for calcium ions occurred, which was ascribed to adsorbed aluminate (Al(OH)₄⁻) ions. By means of electrophoresis Stein (22) found for hydrated tobermorite that at the high ambient pH = 12.5 of saturated Ca(OH)₂ solution most of the surface silanol-groups will be dissociated, and due to the excess of calcium ions in the solution tobermorite has a positive surface charge. Hydrated C₃S (23) and Ca(OH)₂ have a positive zëta potential in saturated Ca(OH)₂ solution. Spierings (25) found a positive zëta potential for C₃A when hydrating in a 0.1 M solution of NaOH, and ascribed it to preferential adsorption of calcium ions, not fully compensated for by hydroxyl- or aluminate-ions. Cementstone, due to its inhomogeneous structure and chemical composition, probably will show an at random distribution of many different types of adsorption sites.

In the following selected measurements of zëta potential on cementstone and quartz first are described, using electroosmosis in aqueous electrolytic solutions, kept saturated vs Ca(OH)₂. The results and discussion will show amongst others the predominant role of calcium ions. Hereafter K₁c - measurements on double cantilever specimens of cementstone, when immersed in an electrolytic solution are described. The paper ends with an explanation of the observed correlation between K₁c and the log concentration of electrolytic solution.
II ZETTA POTENTIAL OF CEMENTSTONE AND QUARTZ

1. Experimental

Electroosmosis apparatus

The electroosmosis apparatus which was constructed from Pyrex glass is shown schematically in fig. 3. Grains of the solid which is to be examined (see below) fill the lower part of compartment (a) as a porous plug. They are surrounded by the electrolytic solution which also fills the remaining part of compartment (a). A dc current I is applied via non-gassing electrodes which consist of zinc rods (b) in saturated zinc sulphate solution (c). Compartment (d) contains a 0.5 M KNO₃ solution which separates the zinc sulphate solution from the solution in compartment (a). Glass balls (e) prevent the mixing of the liquids. Liquid flow is observed in precision bore tubes (f) by means of a travelling microscope. The temperature of the apparatus is kept constant at \((25.0 \pm 0.1)\) °C. Zeta potential is calculated from the Smoluchowski-equation (26):

\[
\zeta = \frac{\phi \eta_w \sigma}{\epsilon_w I}
\]

where:

\(\phi\) = liquid flow \((\text{m}^3\text{ s}^{-1})\)

\(\eta_w\) = viscosity of water at 25 °C = 8.904.10⁻³ kg m⁻¹ s⁻¹

\(\sigma\) = specific electric conductivity of the electrolytic solution \((\text{m}^{-1})\)

\(\epsilon_w\) = permittivity of water at 25°C = 6.629.10⁻¹² F m⁻¹

I = dc current through the porous plug (A)

Fig. 3 Electroosmosis apparatus
Samples

Cementstone grains were obtained by grinding a 28 days old sample which had a W/C - ratio of 0.30 in an agate ball-mill. The fraction with diameters smaller than 45 μm was sieved off wet with a small amount of water, and kept in a polyethylene bottle with a magnetic stirrer. For each measurement a small amount of this suspension was repeatedly mixed (more than 10 times) with fresh electrolytic solution, and decanted after 15 minutes. Equilibrium was observed by measuring the electric conductivity (HACH cond. meter, type DR/2) and the pH value (Beckmann pH meter type 123300 with blue glass combination electrode type 39501) of each decantate. With quartz the same procedure was followed as with cementstone.

Reagents used

The chemical compositions of the Dutch commercial cements we used are given in table I below. Fused quartz of pro analysi grade was obtained from Merck (Germany) as grains with a mean size of about 0.2 mm.

Table I Chemical compositions of cements (wt %)

<table>
<thead>
<tr>
<th>cement</th>
<th>CaO</th>
<th>SiO2</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>SO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Portland (Encilite-B)</td>
<td>64.9</td>
<td>20.7</td>
<td>5.1</td>
<td>2.3</td>
<td>2.6</td>
</tr>
<tr>
<td>Portland-blastfurnace (Robur-B)</td>
<td>50.6</td>
<td>26.0</td>
<td>11.0</td>
<td>1.5</td>
<td>2.6</td>
</tr>
</tbody>
</table>

Water used was twice destilled and boiled shortly before use (conductivity< 2 μmho/cm). All preparations were done in a glove-box under nitrogen atmosphere. The chemicals used were of pro analysi grade. ζeta potentials of portland cementstone, portland blastfurnace cementstone and quartz were measured with the following aqueous electrolytic solutions:

1. 0.100 M K₃Fe(CN)₆ sat. vs. Ca(OH)₂
2. 0.300 M K₃Fe(CN)₆ sat. vs. Ca(OH)₂
3. 0.250 M KCl, KBr, KI, KCLO₃, KBrO₃ and KNO₃ sat. vs. Ca(OH)₂.

Ca(OH)₂ was heated at 1100 °C for 24 hrs and ground in an agate mortar before use.
2. Results and discussion

In saturated Ca(OH)$_2$-solution (i.e. no second electrolyte added) zeta potentials $\zeta_0$ of portland cementstone, portland blastfurnace cementstone and quartz have a positive value (see figs. 1, 5 and table II below). This can most probably be ascribed to preferential adsorption of calcium ions on solid surfaces which bear a negative charge of their own (see also Introduction). Quartz is known to be covered by a thin layer of calcium silicate hydrate in the ambient medium (27). Its smaller value of $\zeta_0$ as compared with that of cementstone might be explained by the larger number of strong adsorption sites for calcium ions ("holes") of the latter, which has an intrinsic calcium- and alumina content. The larger value of $\zeta_0$ for portland blastfurnace cementstone as compared with that of portland cementstone might be ascribed to the larger alumina content of the former (see table I and also Introduction).

The porosity of cementstone and quartz (28) has as a consequence that calcium ions which adsorb on a pore wall pull their counter ions (which may not enter the pore) strongly against the outer solid surface. This reduces both the effective adsorption energy for calcium ions and the number of counter ions outside the slipping plane (i.e. zeta potential) (28). Grinding which transforms the solid surface from a crystalline to a glassy state (29) has the same effect as porosity (21); sharp protuberances on the solid surface increase zeta potential (39). The relative magnitudes of these effects with regard to our measurements are not yet clear.

![Graph](attachment:image.png)

Fig. 4 Zeta potential of portland cementstone (a), portland blastfurnace cementstone (b) and quartz (c) in an aqueous solution of K$_3$Fe(CN)$_6$ kept saturated vs. Ca(OH)$_2$
fig. 5 ζ-potential of portland cementstone (a), portland blast-furnace cementstone (b) and quartz (c) in an aqueous solution of $K_4Fe(CN)_6$ kept saturated vs. $Ca(OH)_2$

Table II ζ-potential values $\zeta_0$ in sat. $Ca(OH)_2$ - solution and slopes $S$ of the straight-line parts of the curves of figs. 4 and 5.

<table>
<thead>
<tr>
<th>solid</th>
<th>$\zeta_0$ (mV)</th>
<th>$S$ (mV/decade)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$K_3Fe(CN)_6$</td>
</tr>
<tr>
<td>portland cementstone</td>
<td>+ 21.0</td>
<td>-8</td>
</tr>
<tr>
<td>portland blastf. cementstone</td>
<td>+ 25.0</td>
<td>-9</td>
</tr>
<tr>
<td>Quartz</td>
<td>+ 19.3</td>
<td>-13</td>
</tr>
</tbody>
</table>

With increasing concentration of $K_3Fe(CN)_6$ (fig. 4) or $K_4Fe(CN)_6$ (fig. 5) ζ-potential curves of cementstone and quartz bend towards the log concentration axis, gradually passing into straight lines with slopes $S$ as given in Table II above. The larger charge of ferricyanide ions is clearly reflected into larger $S$-values. The straight line behaviour indicates - amongst others - that for each of the solid - liquid combinations of figs. 4 and 5:
a. There are no distinct (spatial separated) groups of sites with different adsorption behaviour (31).
b. There are no saturation effects such as were observed with anionic superplasticizers (to be published: see also ref. 24).

As potassium ions do not adsorb specifically on oxidic surfaces, the main mechanisms which lower zeta potential and change its sign in figs. 4 and 5 probably will be:

1. super - equivalent adsorption (30,32) of ferro- or ferricyanide ions on surfaces which are positive of their own due to adsorbed calcium ions
2. Desorption of calcium ions from these surfaces

Both mechanisms are strongly suggested by the observed raise of pH with increasing ferro- or ferricyanide concentration (see figs. 6 and 7 below), which indicates a (weak) complex formation between these anions and calcium ions. The solubility of Ca(OH)₂ was also found to increase with increasing concentration of potassium-ferrocyanide or potassiumferricyanide. Especially mechanism 2. above can account for the larger slope S for portland blastfurnace cementstone as compared with that for portland cementstone (see table II). The largest S-value for quartz can be explained by its lower bond energy towards calcium ions, due to which desorption of the latter is enhanced.

In order to obtain additional information about the adsorption behaviour of cementstone and quartz we measured their zeta potentials in a 0.250 M solution of KCl, KBr, KI, KCIO₃, KBrO₃ and KNO₃ respectively, which were kept saturated vs. Ca(OH)₂.

![Fig. 6 pH of K₃Fe(CN)₆-solution, Fig. 7 pH of K₄Fe(CN)₆-solution kept saturated vs. Ca(OH)₂](image-url)
Fig. 8 Zeta potential of portland cementstone (+), portland blast-furnace cementstone (o) and quartz (•) in various 0.250 M solutions of potassium salts, kept saturated vs. Ca(OH)$_2$

The results are shown in fig. 8 above, where we have arranged the anions in the order of their increasing ability to lower zeta potential. No specific reactions (colour changes, phase separations, crystallite growth etc.) were observed between cementstone and the solutions of figs. 4, 5 and 8. The order of the anions in fig. 8 reasonably agrees with the order of their increasing nucleophilicity, such as is reflected by their increasing hydration enthalpy (33), or the decreasing strength of their respective acids (34). Deviations may be due to both sterical factors and partly dehydration of adsorbed anions. No differences could be detected (i.e. $\delta$ pH < 0.02) between the pH-values of the solutions of fig. 6 and a saturated Ca(OH)$_2$-solution. Probably only weak coulombic adsorption of the anions occurs on the positive surfaces at the present concentration.

This effect is the strongest for portland blastfurnace cementstone, as can be expected from its largest value of $\zeta_0$ in a saturated Ca(OH)$_2$-solution (see Table II). The results obtained with the anions of fig. 8 again emphasize the importance of the adsorption mechanisms 1. and 2. above.
III FRACTURE TOUGHNESS OF CEMENTSTONE IN AN ELECTROLYTIC SOLUTION

1. Experimental

Fracture toughness $K_{lc}$ of portland cementstone and portland blastfurnace cementstone was measured as a function of the concentration of an aqueous $K_3Fe(CN)_6$ solution which was kept saturated vs. Ca(OH)$_2$. We used double cantilever beam specimens, whose webs were immersed in the solution (see fig. 9). The web was made as to conform such a profile that its increasing width exactly compensates for the effect of increasing crack length upon the critical load $F_c$. The relationship between $K_{lc}$ and $F_c$ is given by (35):

$$K_{lc}^2 = \frac{12 F_c^2}{b h^3 k}$$

where:

- $K_{lc}$ = fracture toughness (N m$^{-3/2}$)
- $F_c$ = critical load (N)
- $h$ = cantilever beam height (m)
- $b$ = cantilever beam width (m)
- $k$ = constant (m$^{-1}$)

Fig. 9 Double cantilever specimen, fractured in direct tension while immersed in an electrolytic solution (a), and cross-section of the specimen (b).
As $K_{1C}$ is a constant the crack will propagate at a constant load $F_c$ (see fig. 10). Slow stable crack growth was allowed by loading the specimen in direct tension at a constant displacement rate of 0.30 $\mu$m/s. Our tensile machine, which was especially constructed for this purpose, was provided with adjustable springs to compensate for the specimen weight, as well as pendulous grips. The load on the specimen could be detected with an accuracy of 1% (Inductive transducer HBM type Q3 and oscillator/demodulator HBM type MC1-A).

The specimens, which had a $W/C$ - ratio of 0.30, were cast in stainless steel molds. The web was formed by a thin polished and razor-edged steel plate of the appropriate profile, which slid into the grooved sides of the molds. After curing for 1 day at a relative humidity of 90% the specimens were left to hydrate in a saturated Ca(OH)$_2$-solution until they were tested after 28 days. All preparations and measurements were performed in a climatized room at a temperature of $(25.5 \pm 0.2) ^\circ C$. All reagents used were of the same quality as with the electroosmosis experiments (see paragraph II), and precautions were taken to avoid contamination by CO$_2$ from the air.

2. Results and discussion

Fig. 11 shows the behaviour of $K_{1C}$ which we measured for portland cementstone and portland blastfurnace cementstone as a function of log concentration of $K_3Fe(CN)_6$, and which we shall call the "$K_{1C}$-log c correlation". Each point of the curves of fig. 11 corresponds with the average $K_{1C}$ - value of six samples which we took from six consecutive casts by means of a permutation procedure (36 samples were cast and tested for both curves).
For both types of cementstone there is a distinct maximum value of $K_{lc}$ at concentrations, which correspond with their respective isoelectric points (IEP) such as measured by means of electroosmosis (see paragraph II). The overall variation of $K_{lc}$ amounts to about 6%. From the average time $\Delta t\approx 100$ sec. we measured between the onset of stable crack propagation and final failure, and the length of the web (see fig. 10) we estimate as an upper limit for crack velocity a value of about 100 $\mu$ m/s. This should make continuous diffusion of the electrolytic solution to the crack tip possible (36).

The observed "$K_{lc}$ - log c correlation" proves - amongst others - that in the accessible part of the microfractured zone of cementstone a non-negligible amount of bonds probably are present whose strengths influence $K_{lc}$.

IV A MODEL FOR THE "$K_{lc}$ - LOG C CORRELATION"

An explanation for the observed behaviour of $K_{lc}$ as a function of ferrocyanide concentration a model is proposed in which two elementary mechanisms are thought to influence strength - determining bonds of cementstone. These mechanisms will be defined as Type I and Type II respectively (see fig. 12).
Type I mechanism causes $K_{lc}$ to decrease with increasing $\log c$, and includes short-range chemomechanical processes which occur on the plane of direct contact between the crack-tip material and the electrolytic solution. Such processes might be for instance (see Fig. 13):

1. Stress corrosion of surface Si-O-Si-bonds due to the increase of the pH-value of the solution with increasing ferrocyanide concentration (see paragraph II.2). This process is well-known in glass-science (36,37,38).
2. Dissolution of calcium ions under stress from surface Si-O-Ca-O-Si-bonds due to complex-formation with ferrocyanide ions from the solution (see paragraph II.2).
3. Lowering of the surface-energy of calciumhydroxide-crystals present in cementstone.

Fig. 13 Chemomechanical attack on surface bonds (Type I)
The negative charge acquired by the solid surface with the processes 1. and 2. above can (partly) be compensated for by means of adsorption of calcium ions from the solution.

**Type II mechanism is a long-range electrostatic process** which causes $K_{lc}$ to have a maximum at the IEP. In order to make this process plausible we must assume that:

1. Part of the fracture process just beyond the crack-tip occurs by shearing-off of anionic silicate complexes (29,40,41,42,43, and see also paragraphs I and II) which are linked together by means of relative weak and polarizable bonds such as Si-O-Ca-O-Si-bridges (see fig. 14).

2. Due to a non-zero charge of the compact part of the electrical double layer in the liquid (i.e. $\zeta \neq 0$) these bonds become polarized to such an extent that the mechanical energy which is needed to break them is reduced (37,38). For large values of $|\zeta|$ the polarization probably reaches a saturation value (see fig. 12).

Now the extension of a diffuse charge layer is proportional to the inverse square of the electrical carrier concentration (10,44,45). The electric conductivity of the solid material in the present case is smaller by several orders to magnitude (19,46) than that of the electrolytic solution with which it is brought into contact. This will result in a penetration-depth of an electrostatic field into the solid from the order of 1 micron, which is a typical value for a semiconductor in a 0.01 M electrolytic solution (45). As compared with the submicron-dimensions of the silicates-complexes (see paragraph I) this penetration-depth is very large. However, when estimating to which degree the interlinking bonds become polarized, there is the magnitude of the electrostatic field in the solid as a missing factor, since we cannot measure the electrostatic potential at the solid-liquid interface.
Concluding remarks.

When proposing the above model the author was aware of its preliminary character. However, it indicates some paths on should follow in selecting experiments which support it, and prepare the way to the optimization of the observed strength-concentration relationship.

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