THE EFFECTS OF GALVANIC CURRENT ON CONCRETE

AUSWIRKUNGEN VON ELEKTROLYSESTRÖMEN AUF ZEMENTMÖRTEL

LES EFFETS DU COURANT ELECTRIQUE SUR LE BETON

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Summary: The effects of galvanic current on chemical and physical properties of concrete have been investigated. Current densities in the range of strong cathodic overprotection (625mA/m²) have been applied to mortar for up to 322 days. As a result of current flow, the cathodic area shows a decrease of porosity and of (initially admixed) chloride, while Potassium and sodium concentrations do not increase substantially. The acidification of the anodic area due to oxygen and chlorine evolution increases porosity and dissolves cement lime. The transportation number of chloride is about 0.1 at an initial concentration of 2%/cement weight.

Zusammenfassung: Elektrolyseströme führen zu Veränderungen der chemischen und physikalischen Eigenschaften von Zementmörtel. Stromdichten in Höhe der zehnfachen kathodischen Schutzströme führen in chloridhaltigem Portlandzementmörtel an der Kathode zu einer Verdichtung des Gefüges. Die Chloridkonzentration nimmt im Kathodenraum deutlich ab, während die Alkalikonzentration nur unwesentlich ansteigt. Die Ansäuerung der Anodenumgebung führt zu einer Auflösung von CHS-Phasen und Calciumhydroxid. Die Überführungszahl für Chlorid liegt bei 0,1 für eine Chloridkonzentration von 2%/Zementgewicht.

Résumé: Des courants électriques ont des effets sur les proprietés chimiques et physiques du béton. Un courant d'une densité d'environs dix fois le courant de protection cathodique produit une diminution de la cocentration des chlorures aux environs de la cathode, pendant que la concentration d'alcali ne monte pas essentiellement. A la cathode, la porosité augmente, pendant qu'elle se diminue à l'anode. L'acidification de l'anode provoque la dissolution des phases CSH et de l'hydroxide de calcium.

Keywords: concrete repair, galvanic current, chloride removal, cathodic protection, electro-migration, porosity

1.1 Electrode Reactions

The dominating reactions at the anode in the potential range to be discussed are hydrogen evolution (1) and oxygen reduction (2). As consequence, the cathodic area will be alkalized.

$$2 \ H^+ \ + \ 2e^- \ \dashrightarrow \ H_2 \tag{1}$$
$$O_2 \ + \ 2 \ H_2O \ + \ 4e^- \ \dashrightarrow \ 4 \ OH^- \tag{2}$$

Oxygen evolution however will take place at the anode, producing an acidification. If the electrolyte contains choride, chlorine gas will evolve, reacting with water to form hypochloric acid and hydrochloric acid as follows:

$$2 \ H_2O \ \dashrightarrow \ O_2 \ + \ 4 \ H^+ \ + \ 4e^- \tag{3}$$
$$2 \ Cl^- \ \dashrightarrow \ Cl_2 \ + \ 2e^- \tag{4}$$
$$Cl_2 \ + \ H_2O \ \longrightarrow \ HCl \ + \ HOCl \tag{5}$$

1.2 Transport Reactions

Electric current is being transported by ions moving in the electric field. The amount of current, transported by each species of ions is given by the transport number (t+ resp. t-). The contribution of anions and cations is usually not the same, causing local changes of the chemical composition of the electrolyte. The change in composition of the anode and cathode electrolyte can be used for the determination of transport numbers.

In addition to the above mentioned transportation mechanisms, in porous systems like mortar or concrete, electroosmosis is possible: the electrolyte inside capillaries is moved by an electric force acting at the outer Helmholtz-layer of the solid/liquid interface.

Finally, diffusion is taking place whenever concentration differences occur. These mechanisms are further complicated by chemical reactions, adsorption/desorption of species, solution/precipitation phenomena a.s.o.

2. Experimental

The prismatic samples (4x4x16 cm) were composed of cement-mortar with addition of sodium chloride (table 1).

Table 1:
composition of mortar

cement PZ45F	150 g
sand	450 g
water	75 g
NaCl	5 g

Steel and titanium wires (embedded as shown in fig.2) were used as electrodes. Following 7 days curing at 100% humidity, the samples were subjected to a current of 1 mA (= 62,4 mA/cm² mortar resp. 200 mA/cm² electrode area) up to 322 days at 100% relative humidity.
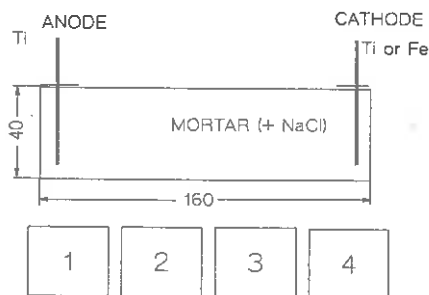
Fig.2: mortar samples

Potentials were measured by means of a calomel-electrode. The sodium, potassium and chloride-content was determined by means of AAS (Na,K) and potentiometrically after extraction with water (Cl) respectively.

The 322 days'sample was aditionally analysed by means of thermoanalysis (DTA), X-ray diffractometry and porosimetry. To study electrode-reactions, current-potential curves were measured in aqueous solutions.

3. Results

3.1 Electrode Reactions

The cathodic polarization curve of steel in mortar (saturated with water) is shown in fig.3: The plateau in the range of -500 to -1000 mV corresponds to the reduction of oxygen according to reaction 2, below -1000 mV superimposed by water decomposition (hydrogen evolution) according to reaction 1. Compared to the curves measured in aqueous solution, the oxygen reduction current is very low in mortar.
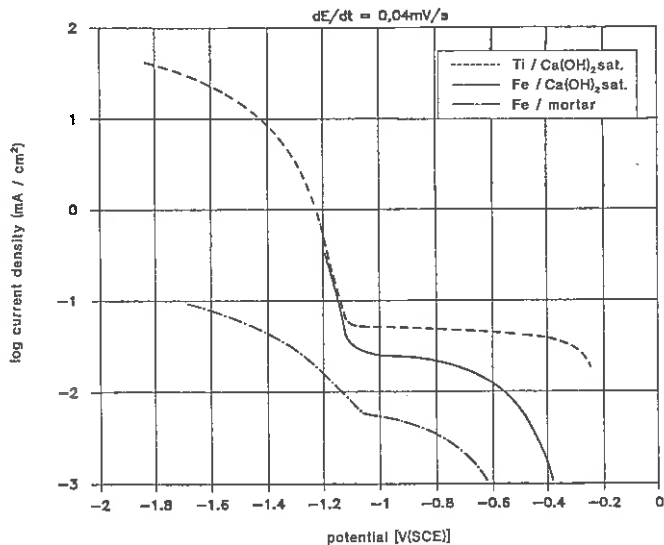
Fig.3: Cathodic polarization curves of steel in mortar,
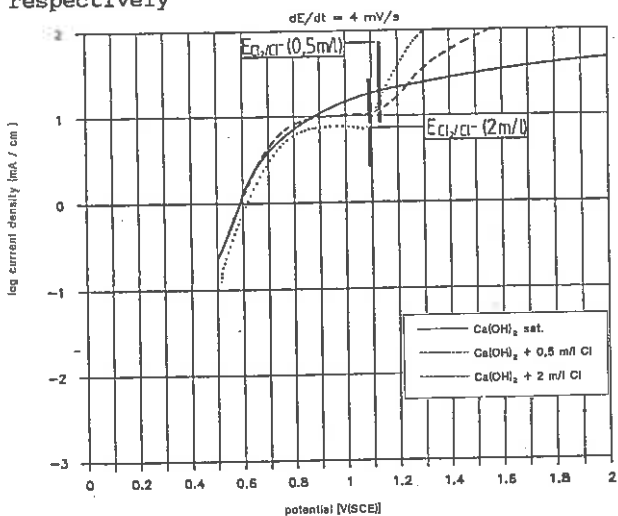steel and titanium in saturated solution of Ca(OH)2
respectively

Fig.4: Anodic polarization curves of titanium in $Ca(OH)_2$
sat. solution with and without addition of sodium
chloride.

The anodic polarization curve of titanium in oxygen-
free solution of $Ca(OH)_2$ and NaCl shows oxygen
evolution, superimposed by chlorine gas evolution at po-
tentials above the equilibrium E_{Cl} $/Cl^-$ (E_{Cl} $/Cl^-=$
$1,36-0,059*\log a_{Cl^-}$). Oxygen evolution seems to be
inhibited in the chloride-containing solutions at
higher potentials, possibly due to adsorption of
chloride.

3.2 Electrode Potentials

Potential and instant-off potential vs. time are shown in
fig 5 for steel cathodes/titanium anodes and for titanium
anodes/titanium cathodes in fig 6 respectively. The anode
potential increases with time, reaching chlorine evolution,
while the cathode works in the range of cathodic
overprotection at about $-1,4$ V.
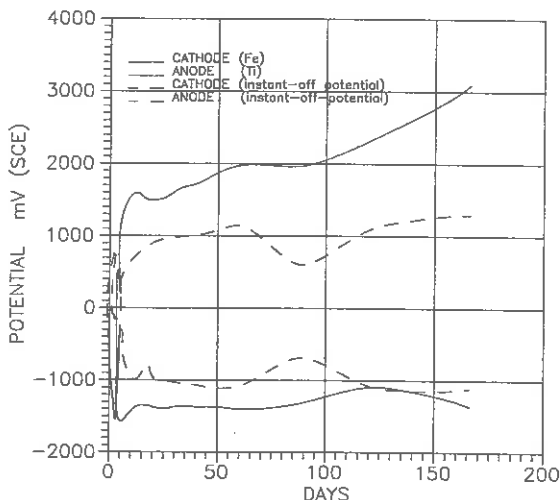
Fig.5: Potential and instant-off potential vs. time (anode:
titanium; cathode: iron)

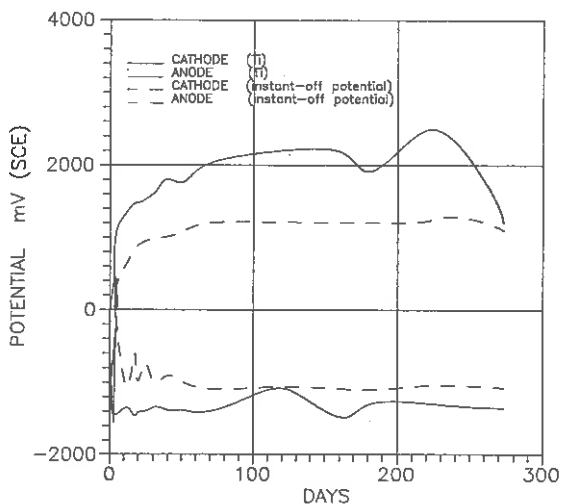Fig.6: Potential and instant-off potential vs. time (anode:
titanium; cathode: titanium)

3.3 Chemical Composition

Concentration profiles showing Cl-,Na and K-content after 0
and 273 days of current flow are shown in fig.7. The effect
of ion-migration is obvious. At the same time, the total
amount of chloride substantially decreases due to chlorine
gas evolution. The decrease of (total) sodium and
potassium-content is possibly caused by formation of
unsoluble alkali-silicate.

INITIAL DISTRIBUTION OF Cl,Na,K
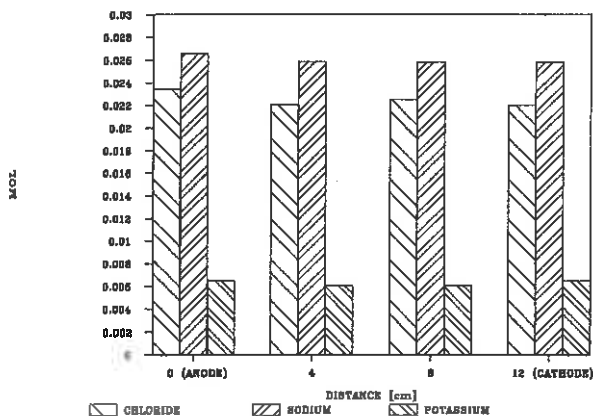
DISTRIBUTION OF Cl,Na,K
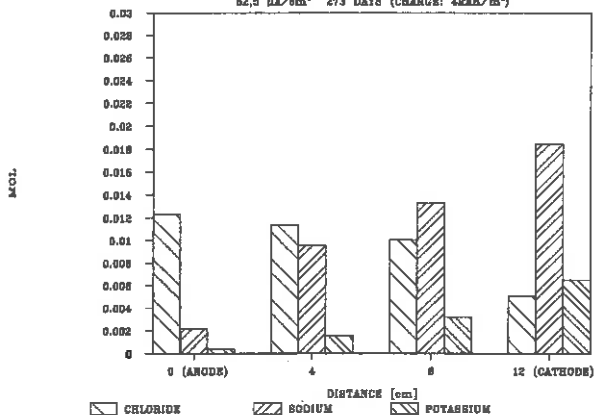### 52,5 μA/cm² 273 DAYS (CHARGE: 4kAh/m²)

Fig.7: Concentration-profile of Cl,K,Na after 273 days of
current flow compared to a 100 days old sample not
subjected to current.

The concentration changes vs. time are shown in fig. 8.
With increasing time, the effect of diffusion increases and
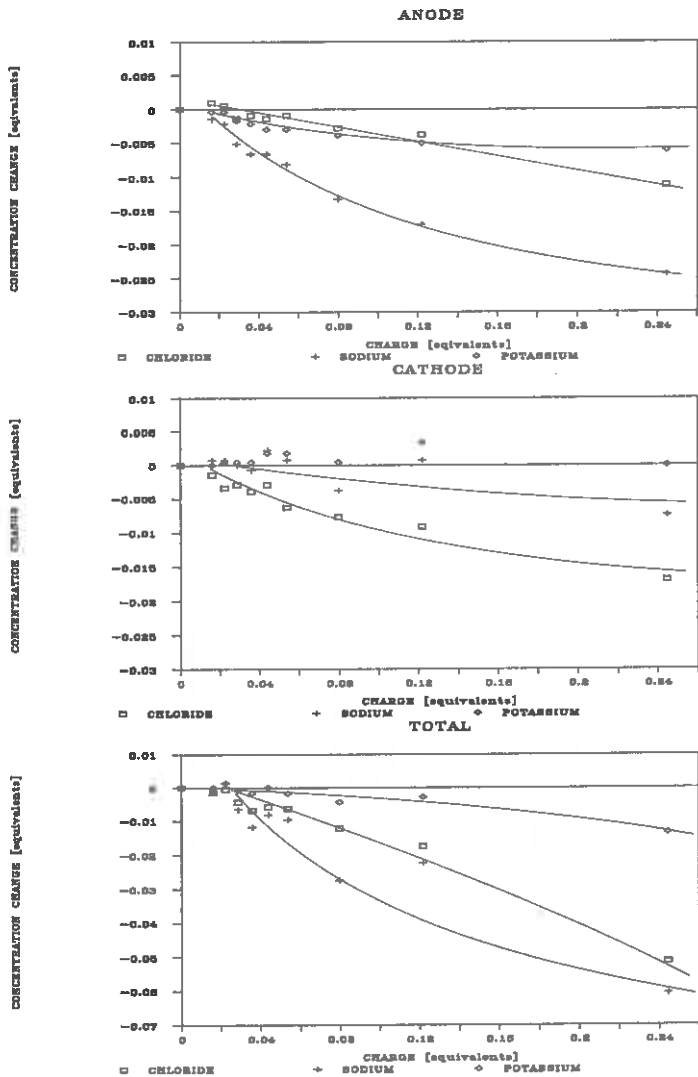migration is thus less effective.

Fig.8: Concentration changes produced by current flow
(anode, cathode and over all) vs. time

3.4 Changes within solid phases

After 322 days of current flow, the mortar near the anode
gets a spongy appearance, showing non adherent particles of
brownish colour, while the cathode area shows white stains
(fig. 9).

The thin section (fig.10a) shows total loss of lime phases
within about 3mm distance around the anode. At the cathode
no visible changes are to be found (fig 10b). The X-ray-
diffractogram shows total loss of $Ca(OH)_2$ near the anode
(fig.12). This result is confirmed by DTA (fig.11).

Fig.9: View of a specimen subjected to 1 mA current for 322
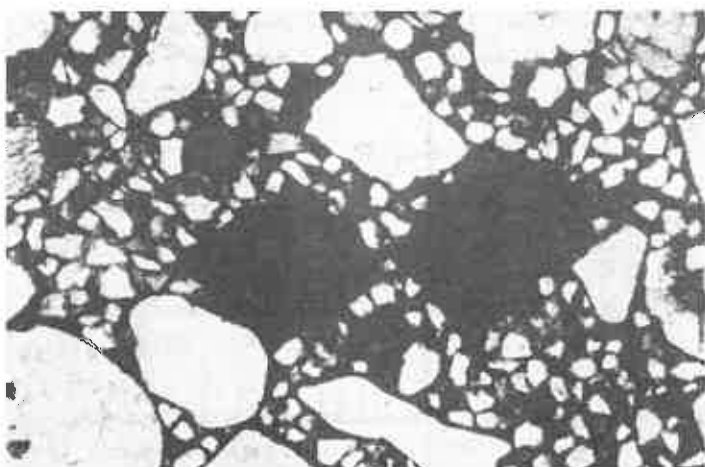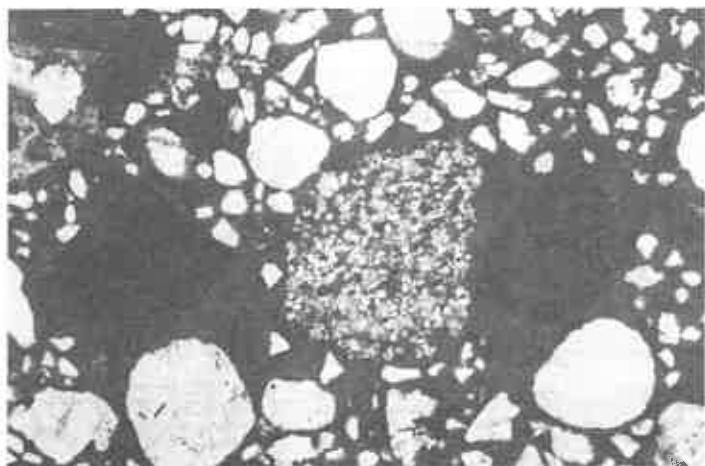days (1: anode; 4: cathode)

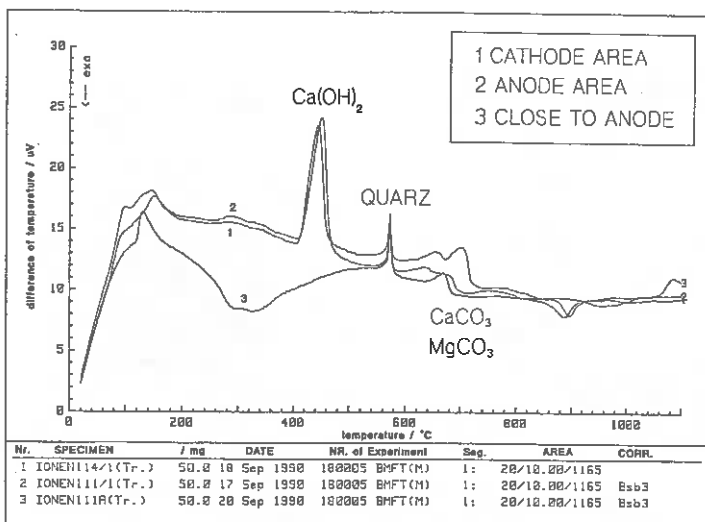Fig.10: Thin section across anode (above) and cathode
        (below)

Fig.11: Differential thermo analysis of mortar (1: cathode area 0-4 cm; 2: anode area 0-4cm; 3: anode area 0-2mm) following 322 days of current flow
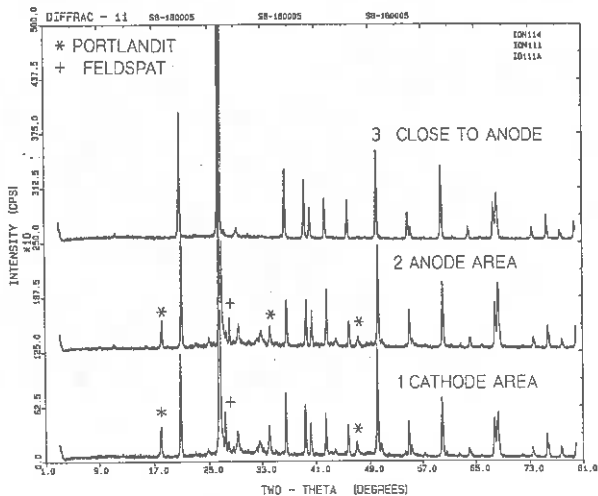

Fig.12: X-Ray diffraction pattern of mortar (1: cathode area 0-4 cm; 2: anode area 0-4 cm; 3: anode area 0-2 mm) following 322 days of current flow

Porosity data (pore size-distribution and nitrogen absorption) are summarized in fig. 13. Porosity increased around the anode and decreased at the cathode. The decrease is at the most obvious with pores of less than 4 μm radius.
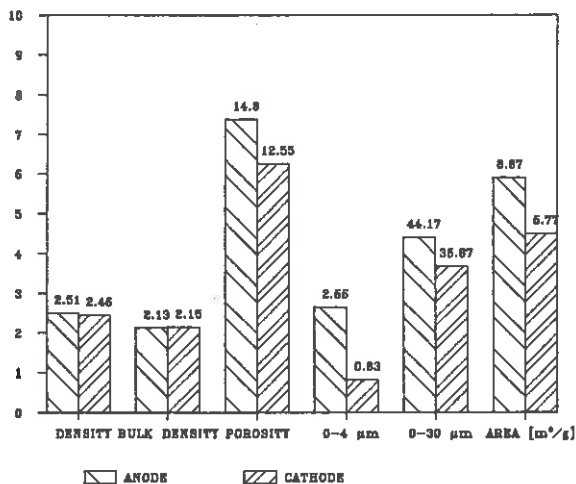

Fig.13: Porosity and nitrogen absorption data of mortar following 322 days of current flow

4. Discussion

By means of direct current, considerable migration effects are produced in concrete. The amount of electrical charge/total charge transported by one species of ions, calculated from the (initial) slope of the concentration vs. time plot in fig. 8 is as follows: 6.5 % for potassium, 16,6% for sodium and 10% for chloride, most of the electric charge thus beeing transported by hydroxide-ions and not by the species studied here.

A remarkable amount of chloride is set free as chlorine gas. About 20% of the current is consumed by this reaction. Thus, an additional driving force (concentration gradient) helps chloride transporting from the cathodic to the anodic end of the specimen.

It is interesting to note that the potassium and sodium concentration does not increase at the cathode, as should be expected. The explanation is possibly precipitation of non-soluble alkali-silicate.

At relatively high current densities, as used in the experiment, complete dissolution of Ca(OH)2 and CSH-phases around the anode (up to a short distance of about 3 mm from the electrode) is taking place due to the action of hypochloric and hydrochloric acid.