New scientific results

Prepared for the final discussion

**CHLORIDE ION BINDING CAPACITY OF CLINKER MINERALS AND
CEMENTS INFLUENCED BY STEAM CURING**

PhD Thesis

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1. REASON OF STUDY

1.1 Introduction

Chloride ion induced corrosion of steel reinforcement in concrete is more severe than the conventional surface corrosion. Chloride ions induce local corrosion that is especially dangerous for prestressing tendons. There are several methods of concrete technology to avoid that chloride ions penetrate till the reinforcement: like dense concrete cover or selection of cements that are able to bind more chloride ions.

1.2 State of research

Some of the cement clinker minerals, the calcium-aluminates can be bound chloride ions in form of Friedel's salt ($C_3A \cdot CaCl_2 \cdot H_{10}$). These parts of chloride ions that are bound do not induce corrosion of steel reinforcement. Interaction of chloride ions and cements can be modelled by studying directly the interaction of chloride ions and the clinker minerals. Several researchers studied chloride binding of clinkers when the chlorides were added to the mixing water. These studies indicated that calcium-aluminate clinkers bind chloride ions in form of Friedel's salt (Friedel, 1897; Balázs, 2001). Further studies were directed to the interaction of chloride ions and hydrated cements. These studies indicated that also hydrated aluminates are able to bind chloride ions (Neville, 1995; Balázs – Csizmadia – Kovács, 1997a; Balázs – Csizmadia – Kovács, 1997b).

2. PURPOSE OF RESEARCH

Purpose of research were to answer the following questions:

a) What is the influence of the curing temperature (natural hardening at 20ºC, steam curing at 60ºC or steam curing at 90ºC) on the hydration processes of calcium-aluminate clinker minerals and cements? (Semiplastic consistency was used.)

b) What are the influences of the curing temperature and gypsum content on the chloride ion binding of hydrated calcium-aluminate clinker minerals (C_3A and C_4AF)? (My experiments modelled the influence of de-icing salts. Tests with C_3A and C_4AF aluminate clinker minerals were carried out by adding various amount of gypsum.)

c) What is the influence of the curing temperature on the chloride ion binding of cements? Chloride ion binding capacity of cements in the function of test parameters. (Three different types of cements were studied.)

3. METHOD OF RESEARCH

Hydration process was studied by *thermal test (DTA/TG/DTG)* using Derivatograph Q-1500 D and *X-ray diffraction (XRD)* using Philips PW 3710 diffractometer. Simultaneous application of thermoanalytical methods and powder diffraction made possible to carry out detailed analysis of phase modifications. My observations were extended also with *scanning electron microscopy* using JEOL JSM-5500LV.

Splitting tensile tests were carried out to study changes in mechanical properties of clinkers and cements in addition to them compression tests were carried out on cements.

Samples were subjected to salt treatment (modelling influence of de-icing salts) after hardening which was reached by natural curing or steam curing starting at 28 days.

3.1 Tests with aluminates

Experimentally applied C_3A and C_4AF clinker/gypsum ratios are summarized in *Table 1.* where the nominator indicates the mass of cement clinker and the denominator indicates the mass of gypsum. Samples were prepared in $10 \cdot 10 \cdot 50$ mm steel moulds with the same consistency (semiplastic). *Test series 1. and 2.* were kept at room temperature ($22 \pm 1^{\circ}C$) by 100% relative humidity and were demoulded at 24 hours of age. Samples were then kept by 100% relative humidity at $22 \pm 1^{\circ}C$ temperature.

Samples of *test series 3. to 6.* were subjected to steam curing for 3 hours after casting. Steam curing of *test series 3. and 4* were carried out at $60^{\circ}C$ temperature on the other hand *test series 5. and 6.* were carried out at $90^{\circ}C$ both on atmospheric pressure conditions. Steam curing of C_3A samples started in 1 hour after casting and that of C_4AF clinker samples started in 2 hours after casting. After curing samples were cooled down in the steam curing device. Samples were demoulded at 24 hours of age. Samples were then kept by 100% relative humidity at $22 \pm 1^{\circ}C$ temperature.

Test series 2., 4. and 6. were subjected to salt treatment between 28 and 38 days of age. Salt treatment ment that: samples were cyclically kept for 10 days first 24 hours in salt solution then in 100% relative humidity. Concentration of salt solution was 10% NaCl solution (10g NaCl in 100 ml water). Samples were kept after salt treatment at $22 \pm 1^{\circ}C$ in 100% relative humidity.

Hydration products were studied by thermal tests and X-ray diffraction at 1, 7, 28, 90 and 180 days for C_3A clinkers and at 1, 7, 28, 56, 90 and 180 days for C_4AF clinkers. We were able to analyse differences in hydration processes after different curing for test series 1., 3. and 5. and to analyse chloride ion binding capacities for test series 2., 4. and 6.

Splitting tensile tests were carried out to follow changes of mechanical properties of calcium-aluminate clinkers.

Table1. Composition and curing of calcium-aluminate (C_3A or C_4AF) samples

| Test series	Mass ratio of calcium-aluminate to gypsum	Curing of samples
1.	10/0, 10/1, 10/2, 10/3, 10/4, 10/5	100% r.h. and 22˚C
2.	10/0, 10/1, 10/2, 10/3, 10/4, 10/5	100% r.h. and 22˚C then salt treatment
3.	10/0, 10/1, 10/2, 10/3, 10/4, 10/5	steam curing at 60˚C then 100% r.h.
4.	10/0, 10/1, 10/2, 10/3, 10/4, 10/5	steam curing at 60˚C then salt treatment
5.	10/0, 10/1, 10/2, 10/3, 10/4, 10/5	steam curing at 90˚C then 100% r.h.
6.	10/0, 10/1, 10/2, 10/3, 10/4, 10/5	steam curing at 90˚C then salt treatment
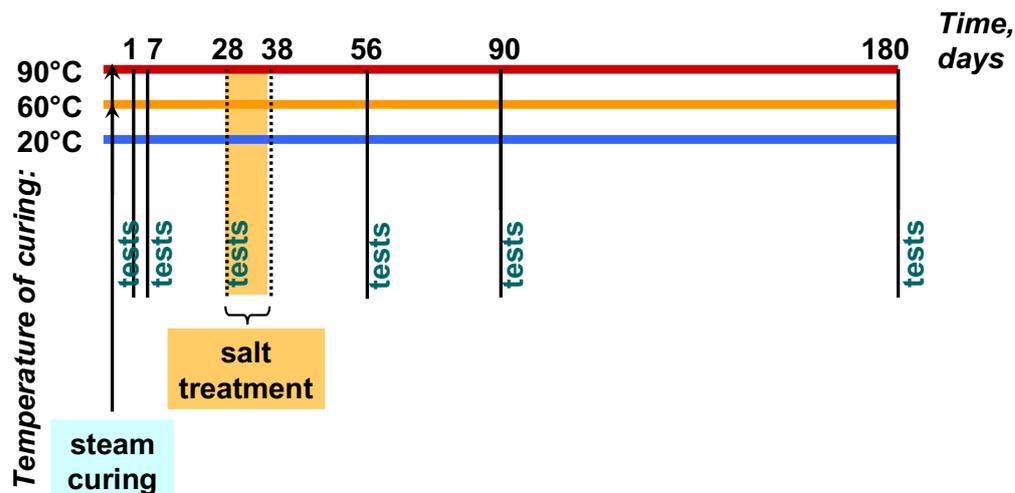
Fig. 1. Schematic representation of the experimental program

3.2 Tests with cements

Similarly to the tests by aluminate clinkers, tests were also carried out by the following 3 selected cements to study the influence of steam curing and salt treatment like for series 1 to 6 in *Table1:*

- 1: CEM I/A 42,5 N (OPC) – ordinary Portland cement
- 2: CEM III 32,5 N (GGBSC) – blast furnace slag cement (with 40% ground granulated blast furnace slag content)
- 3: CEM I 32,5 RS (SRPC) – sulphate resistant Portland cement.

Chemical compositions of cements are given in *Table 2.*

Table 2. Chemical compositions of cements

Components, m%	CEM I 42,5 N,	CEM III/A 32,5 N,	CEM I 32,5 RS,
SiO_2	19,81	26,41	20,69
Al_2O_3	5,64	6,07	3,61
Fe_2O_3	3,57	1,95	6,10
TiO_2	0,29	-	0,23
CaO	62,60	52,45	63,40
MgO	1,34	4,37	1,87
K_2O	0,61	0,65	0,17
Na_2O	0,09	0,17	0,33
SO_3	2,79	3,08	2,35
Cl	0,02	-	0,01
insoluble part	0,22	4,37	0,66

Sulphate contents of cements were not modified (hence the influence of various sulphate contents was not studied separately for the cements). The selected 3 cements contained C_3A and C_4AF clinkers in various proportions. Mineralogical compositions of cements according to Bogue are given in *Table 3*.

Table 3. Mineralogical composition of cements according to Bogue and some of their further characteristics,

Components, m%	CEM I 42,5 N,	CEM III/A 32,5 N,	CEM I 32,5 RS,
C_3S	53,06	31,86	53,36
C_2S	16,54	9,92	15,36
C_3A	8,78	5,27	-
C_4AF	10,85	6,51	29,10
C_2F	-	-	0,73
setting regulators	4,74 $CaSO_4$	3,00 $CaSO_4$	4,00 $CaSO_4$
mineral component		~40,00 slag	
free lime	0,12	-	0,45
loss on ignition	3,38	2,03	1,00
LSF	93,99	-	92,67
SM	2,15	-	2,13
AM	1,58	-	0,59

Samples of cements were prepared by the required amount of water to rich the standard consistence (MSZ EN 196-3):

- 1. cement samples: w/c = 0,280,
- 2. cement samples: w/c = 0,305,
- 3. cement samples: w/c = 0,260.

Hydrated cement samples were studied with thermal tests and XRD at 1, 7, 28, 56, 90 and 180 days of age. SEM photos were taken at 180 days of age.

Changes in mechanical properties of cement samples were studied by splitting tensile tests and compressive tests.
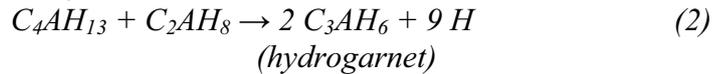
4. NEW SCIENTIFIC RESULTS

Normal characters give the text of the new scientific results, *and the italic characters give the explanations or the previous conclusions found in the literature.*

1st group of new scientific results ─ Influence of temperature of curing on the hydration

1.1 *Production of hydrogarnet (C_3AH_6) in C_3A cement clinker samples without addition of gypsum normally consists of two steps. In the first step*

$$2\ C_3A + 21\ H \rightarrow C_4AH_{13} + C_2AH_8 \qquad (1)\ reaction\ takes\ place.$$
$$(hexagonal\ hydrates)$$
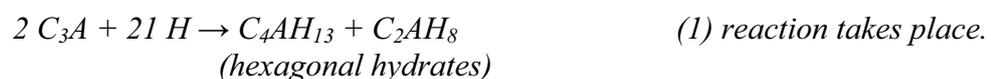
It is followed by the next reactions available in the literature

$$C_4AH_{13} + C_2AH_8 \rightarrow 2\ C_3AH_6 + 9\ H \qquad\qquad (2)$$
(hydrogarnet)

(Feldman–Ramachandran, 1966; Breval, 1976; Collepardi et al., 1978), or

$$3\ C_2AH_8 \rightarrow 2\ C_3AH_6 + AH_3 + 9\ H \qquad\qquad (3)$$
(hydrogarnet)
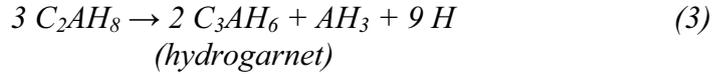
(Stein, 1965; Corstanje et al., 1973).

Steam curing of C_3A cement clinkers — prepared with semiplastic consistency and no addition of gypsum — does not lead to the complete reactions according to *Eqs. (2) and (3)*. Steam curing on high temperature (90ºC) in 1 day helps to produce further amount of hexagonal hydrates according to *Eq. (1)* in addition to hydrogarnet. Owing to the limited amount of water by the hydration of aluminate clinkers is limited, which observation is different from that available in the literature. In addition to hexagonal hydrates and hydrogarnet form solid solution in C_3A samples without addition of gypsum steam cured at 90ºC and tested in the age of 1 day.

Above 50 ℃ C_3AH_6 is also produced as primary compound in addition to C_4AH_{13} és C_2AH_8 since relatively high temperatures are favourable to the production of cubic hydrate favoured by high temperature of reaction like hydrogarnet (C_3AH_6) (Feldman – Ramachandran, 1966; Collepardi et al, 1978).

1.2 The stable hydrogarnet is not even produced by steam curing of aluminate clinkers (C_3A, as well as C_4AF) prepared with relatively high amount of gypsum (10/3, 10/4 and 10/5 clinker/gypsum). The hydration is characterized by equilibrium of ettringite and monosulphate (AFt – AFm).

2nd group of new scientific results — Chloride ion binding of C_3A and C_4AF cement clinkers

2.1 *Monosulphate can not be produced in aluminate (C_3A as well as C_4AF) samples without gypsum. In absence of monosulphate other hydrate phases are able to bind chloride ions.*

My experimental results on C_3A and C_4AF samples (prepared without gypsum and salt treated after hydration) indicated that Friedel's salt can not be produced from monosulphate; however, it is produced from the stable hydrogarnet. After salt treatment I observed considerable increase of the splitting tensile strength, which can be explained by the volumetric increase of Friedel's salt produced by hydrogarnet.
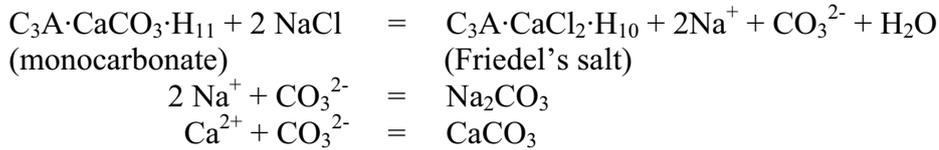
Density of Friedel's salt is smaller than the density of hydrogarnet; therefore, the decrease of the porosity induces the increase of the splitting tensile strength.

  ρ (Friedel's salt)   = 2,056 g/cm³   (Terzis et al., 1987),
  ρ (hydrogarnet)   = 2,520 g/cm³   (Révay, 1977).

2.2 *Calcium-monocarbo-aluminate AFm phases are produced in hydrated aluminate+gypsum samples that are not subjected to salt treatment. After salt treatment*

the calcium-monocarbo-aluminate phase can not be observed. Instead of it sodium-carbonate and calcium-carbonate are produced

I have experimentally shown that also the calcium-monocarbo-aluminate is able to bind chloride ions. This chloride binding in hydrated aluminate+gypsum samples leads to the production of sodium-carbonate and calcium-carbonate. I developed the following equation for this process:

$$C_3A \cdot CaCO_3 \cdot H_{11} + 2\,NaCl \quad = \quad C_3A \cdot CaCl_2 \cdot H_{10} + 2Na^+ + CO_3^{2-} + H_2O$$
$$\text{(monocarbonate)} \qquad\qquad \text{(Friedel's salt)}$$
$$2\,Na^+ + CO_3^{2-} \quad = \quad Na_2CO_3$$
$$Ca^{2+} + CO_3^{2-} \quad = \quad CaCO_3$$

In addition to it I observed that the production of calcium-carbonate is possible by partial ionic change of Na^+ ions originating from salt treatment and Ca^{2+} ions originating from the hydrated calcium-aluminate phases.

In contrary to the hydration of C_3S és C_2S clinkers, the hydration of C_3A and C_4AF clinkers is not followed by the production of $Ca(OH)_2$.

2.3 By using scanning electron microscopy I observed that in hydrated samples after salt treatment the released sulphate ions (produced from the reaction of sulphate-AFm phase, monosulphate and chloride ions) lead to secondary formation of ettringite and do not react with the available $Ca(OH)_2$ producing gypsum (Fig. 1).
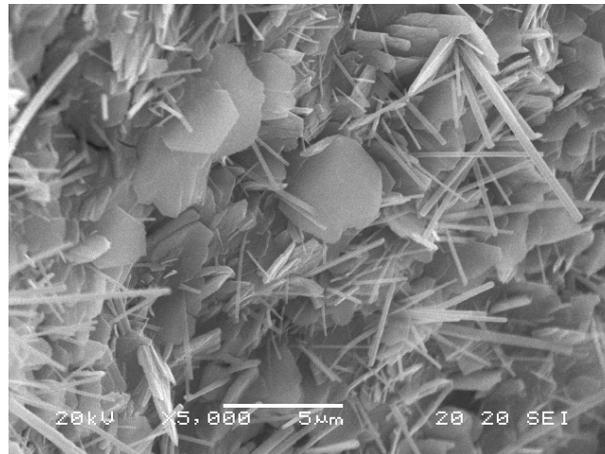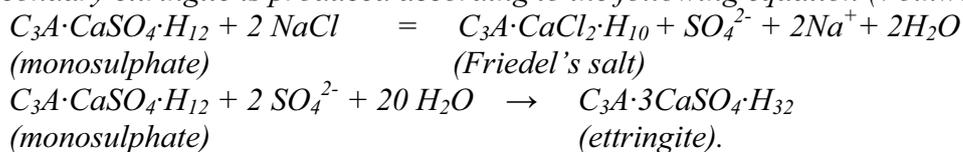

Fig. 1. Simultaneously developed hexagonal Friedel-salt plates and ettringite crystal needles, CEM III/A 32.5, SEM, magnification: 5000x, salt treated samples, at 180 days of age

Secondary ettringite is produced according to the following equation (Volkwein, 1987):
$$C_3A \cdot CaSO_4 \cdot H_{12} + 2\,NaCl \quad = \quad C_3A \cdot CaCl_2 \cdot H_{10} + SO_4^{2-} + 2Na^+ + 2H_2O$$
$$\text{(monosulphate)} \qquad\qquad \text{(Friedel's salt)}$$
$$C_3A \cdot CaSO_4 \cdot H_{12} + 2\,SO_4^{2-} + 20\,H_2O \quad \rightarrow \quad C_3A \cdot 3CaSO_4 \cdot H_{32}$$
$$\text{(monosulphate)} \qquad\qquad\qquad\qquad \text{(ettringite).}$$

2.4 I have experimentally shown that steam curing improves the chloride ion binding capacity of C_3A és C_4AF cement clinkers. Steam curing induces higher increase in chloride ion binding capacity for C_3A clinkers (Fig. 2), than for C_4AF clinkers (Fig. 3).
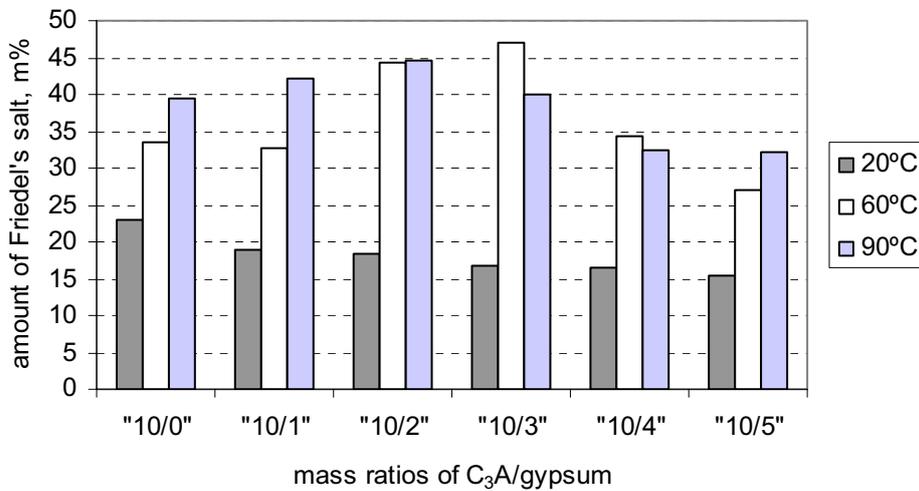

Fig. 2. Amount of Friedel's salt related to the mass of samples without ignition loss as functions of C_3A/gypsum mass ratio and curing temperature, m%
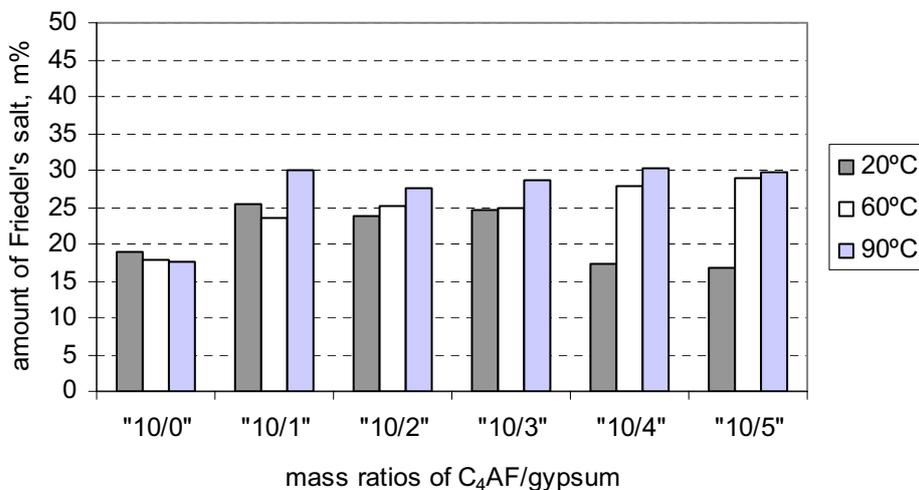

Fig. 3. Amount of Friedel's salt related to the mass of samples without ignition loss as functions of C_4AF/gypsum mass ratio and curing temperature, m%

2.5 In cases of low gypsum content (samples of 10/1 and 10/2 aluminate clinker/gypsum mass ratio) after salt treatment not only Friedel's salt but also Kuzel's salt (sulphate containing chloride-AFm compound) are produced. The Kuzel's salt increases the amount of chemically bound chloride ions (Figs. 4 and 5). Production of Kuzel's salt is not followed by the production of secondary ettringite and not induces reduction of tensile splitting strength.
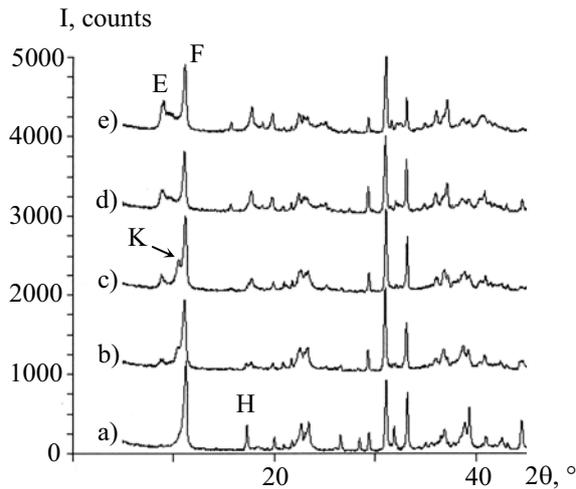
Fig. 4.
XRD patterns of 90 days
C$_3$A/gypsum samples,
steam curing at 60ºC,
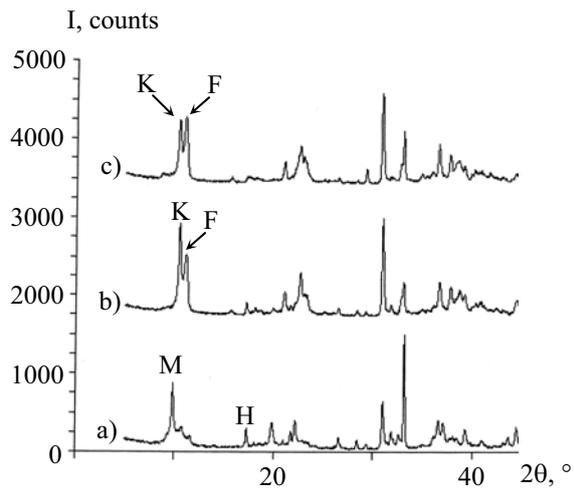C$_3$A/gypsum mass ratios:
a) - e) 10/1-től 10/5

Fig. 5.
XRD patterns of hydrated
10/2 C$_3$A/gypsum samples,
C$_3$A/gypsum mass ratio: 10/2,
steam cured at 90ºC
  a) before salt treatment, at 28 days
  b) salt treated, at 90 days
  c) salt treated, at 180 days

(Notations: F – Friedel's salt, K – Kuzel's salt, E – ettringite, H – hydrogarnet, M – monosulphate)

In cases of relatively high gypsum content (samples of 10/3, 10/4 and 10/5 aluminate clinker/gypsum mass ratio) after salt-treatment chloride ions are bound only in form of Friedel's salt, which may lead to secondary ettringite formation owing to the release of sulphate ions. Secondary ettringite formation is followed by swelling which leads to reduction in splitting tensile strength.

### 3rd group of new scientific results ─ Chloride ion binding of cements

3.1 I have experimentally shown that steam cured cements (concretes) are able to bind more chloride ions than non-steam cured (naturally hardened) cements (concretes). Amount of bound chloride ions is higher in samples steam cured at 90ºC compared to samples steam cured at 60ºC.

3.2 Various cements have various chloride ion binding capacities. Chloride ion binding capacity of tested cement sin decreasing sequence (both for steam cured and non-steam cured samples) (Fig. 6. a, b, c):
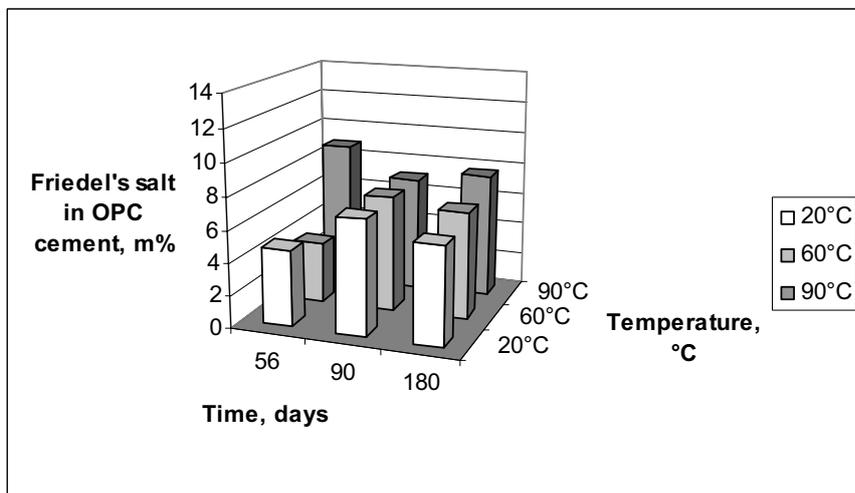 1. CEM III/A 32,5 N (GGBSC)
  2. CEM I 42,5 N (OPC)
  3. CEM I 32,5 RS (SRPC).

Among the above cements CEM III/A 32,5 with 40 mass% of slag (GGBSC) are able to bind the highest amount of chlorides. Among the above cements the lowest amount of chlorides are bound by the CEM I 32,5 RS cement (SRPC).
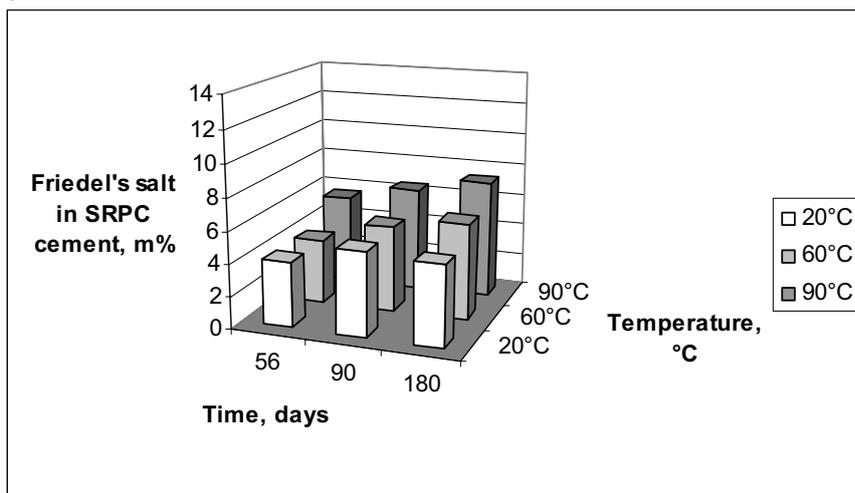
a)
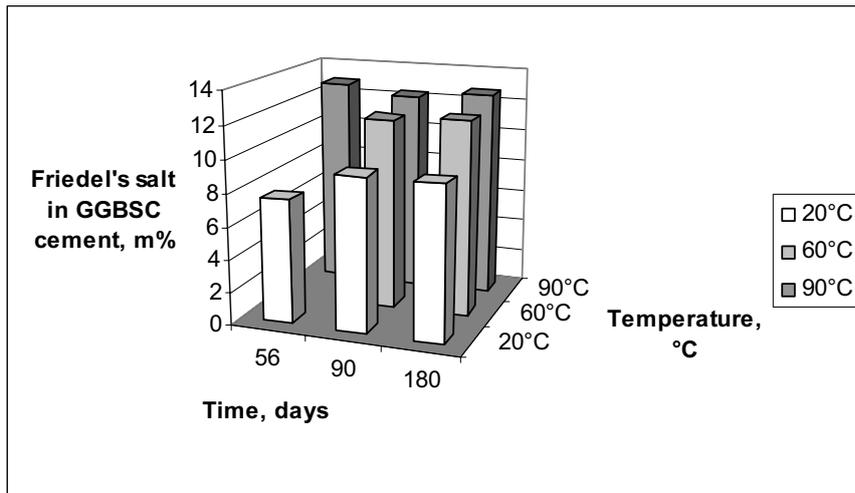
b)

c)

Fig. 6. Amount of Friedel's salt related to the mass without ignition loss as functions of age and curing
temperature, m%
a) CEM III/A 32,5 N (GGBSC)
b) CEM I 42,5 N (OPC)
c) CEM I 32,5 RS (SRPC)

3.3 I have experimentally shown that the improved chloride ion binding capacity of slag Portland cements is owing to the chloride binding capacity of slag content. I have experimentally shown that the steam cured granulated slag itself is also able to bind chloride ions, even if its hydration was not in the typical environment of cements with high pH value. Chloride ion binding capacity of slag is provided by the hydration of the aluminate containing components of the glass phases. In addition to it I have shown that sulphate content (in my tests gypsum content was 5 mass %) produce a decrease in chloride ion binding capacity of slag.

5. POSSIBLE APPLICATIONS OF THE RESULTS

Concrete is normally subjected to de-icing salts when most of the cement minerals have been already transformed into hydrates. With the presented research I was able to analyse the complicated chemical processes of C_3A and C_4AF clinker minerals mixed with various amounts of gypsum. The samples hardened either naturally or were steam cured and additionally were subjected to salt treatment.

In addition to these results, I shown the process of chloride ion binding on 3 cements of different compositions during the formation of Friedel's salt.

All of these results are especially important by the selection of appropriate cements for road and bridge constructions.

My favourable experimental results on steam cured concretes are important because a considerable part of the reinforced concrete elements are prepared by steam curing.

I also propose to make the non-structural parts of bridges subjected to de-icing salt by using slag Portland cements.

6. FUTURE WORK

As a future extension of my test results, I suggest to study the chloride ion binding capacities of cements that include various amounts of silica fume, slag, metakaolin or trass.

My tests were carried out with law water-cement ratios. For comparison I suggest to make similar tests with various cements applying law water-cement ratio and admixtures. Also for them both the hydration process and the chloride ion binding capacity should be studied.

My results with steam cured specimens give support to analyses of concrete technology that consider the produced hydration heat (accelerated curing).

7. NOTATIONS

H   = H_2O
A   = Al_2O_3
C   = CaO
F   = Fe_2O_3
S   = SiO_2
C_3A ($3CaO \cdot Al_2O_3$)   tricalcium aluminate
C_4AF ($4CaO \cdot Al_2O_3 \cdot Fe_2O_3$)   tetracalcium aluminate-ferrite (brownmillerite)
C_3S ($3CaO \cdot SiO_2$)   tricalcium silicate (alite)

C_2S	$(2CaO \cdot SiO_2)$	dicalcium silicate (belite, β-larnite)
CH	$(Ca(OH)_2)$	calcium hydroxide (portlandite)
$CaSO_4$		calcium sulphate (anhydrite)
$CaCO_3$		calcium carbonate (calcite, vaterite)
AH_3	$(2\ Al(OH)_3)$	aluminium hydroxide
$CaSO_4 \cdot 2H_2O$		gypsum
C_3AH_6	$(3CaO \cdot Al_2O_3 \cdot 6\ H_2O)$	hydrogarnet
C_4AH_{13}		hexagonal hydrate
C_2AH_8		hexagonal hydrate
$C_3A \cdot 3CaSO_4 \cdot H_{32}$		ettringite (calcium trisulpho aluminate)
$C_3A \cdot CaSO_4 \cdot H_{12}$		monosulphate (calcium monosulpho aluminate)
$C_3A/F \cdot CaCl_2 \cdot H_{10}$		Friedel's salt (or its iron analogue)
$C_3A/F \cdot 0,5CaSO_4 \cdot 0,5CaCl_2 \cdot H_{12}$		Kuzel's salt (or its iron analogue)
$C_3A \cdot CaCO_3 \cdot H_{11}$		monocarbonate (calcium monocarbo aluminate)

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9. ACKNOWLEDGEMENTS

10. PUBLICATIONS FROM THE TOPIC OF THE THESIS

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