It is suggested on the basis of /3/ that $w_{n,a.s.g}$ is about 30% of the dry weight of the a.s.gel. Then the amount of gel should be $G \sim 18 \cdot 0{,}3 = 60$ kg/m$^3$.

Another guess of the magnitude of G can be made from the amount of reactive material. The fine aggregate makes 760 kg/m$^3$. About 10% of this is reactive particles, i.e. 76 kg/m$^3$. Part of this material may react and together with calcium and water create gel of the same order of magnitude as calculated above.

## 4. CONCLUSIONS

Measurements of connected values of relative humidity and water content by weight make it reasonable to assume that alkali-silica-gel contributes essential to the selfdesiccation of seal-cured concrete with alkali-silica reactive aggregates.

Further research is needed to clear out the rules of calculation for the desorption curve of the alkali-silica-gel.

## REFERENCES

/1/ NIELSEN,A., BERTELSEN, N.H. & NILSSON, L-O.
Methods to determine moisture content in building materials and structures.
1. Int. Conf. on Mat. Science & Restoration. Esslingen, Sept. 3-8 1983.

/2/ BERGSTRÖM, S.G. & AHLGREN, L.
Calculation of absorption isotherms for concrete (In Swedish).
Nord. Betong. 1959, no. 2.

/3/ THAULOW, N. & KNUDSEN, T.
Quantitative microanalyses of the reaction zone between cement paste and opal.
Alk.aggr. symp. Reykjavik. Aug. 1975, p. 189 ff.

/4/ BARKAS, W.W.
The swelling of wood under stress.
Her Maj. Stat. Off. London 1949.

/5/ KROGH, H.
Examination of synthetic alkali-silica-gels.
Symp. on Alk.-aggr. reaction. Reykjavik. Aug. 1974, p. 131-163.

/6/ NILSSON, L-O.
Hygroscopic moisture in concrete.
Report TVBM 1003. Div. of Build. Mat., Lund Inst. of Tech. Lund, Sweden 1980.

/7/ NIELSEN, A.
Moisture measurements in a swimming pool wall (In Danish).
Tech. Inst., Building Technology. Taastrup 1982-08-23.

---

# MOISTURE EFFECTS ON THE ALKALI-SILICA REACTION

Lars-Olof Nilsson, Dr Sc., M Sc. Civ. Eng.

Lund Institute of Technology
Division of Building Materials
Lund, Sweden

## ABSTRACT

The moisture effects on the alkali-silica reaction have been studied by measurements of moisture distributions on some damaged structures and by several laboratory experiments with varying climatic conditions. Relative humidities of the concrete close to 90 % RH, at different temperatures, have been shown to be "critical", causing the most popouts.

A test method for popouts has been developed using the "moisture history" as an aid to reproduce the damages in the laboratory. The effect of some potential inhibitors has been studied with the test method, with promising results.

Key-words: popouts, moisture, relative humidity, test method

## 1. INTRODUCTION

Problems due to alkali-silica reactions in Sweden are new and coincide with the introduction of a high-alkali cement in the south of Sweden where an ordinary concrete aggregate contains reactive grains of opaline flint and sandstone. The problems occur only as popouts on certain structures and turn out to be a definite moisture problem as popouts have never been found on outdoor structures even when they are wet. Problems arise only on "moist indoor structures", that have had a certain history of moisture changes. The most frequently affected structure is concrete slabs on the ground. More than 9 out of 10 problems with popouts due to ASR are found on such a structure /1/.

Moisture effects on the alkali-silica reaction causing popouts have been studied in practice and in experiments. In this paper some damage investigations are summarized and some results of the laboratory work are shown. The pessimum effect of moisture is pointed out.

## 2. SOME DAMAGE INVESTIGATIONS

The moisture effects have been studied by measuring the moisture distribution on some damaged structures. The results from two cases are summarized below.

### 2.1 Case 1: An epoxy painted basement floor

Several large popouts (up to 60mm in diameter!) have occurred on an epoxy painted concrete floor in a basement. In different parts of the basement, the moisture distribution through the floor slab has been determined by measuring the relative humidity (RH) on samples taken at different depths, cf. /2/. Some results are shown in Figure 1.

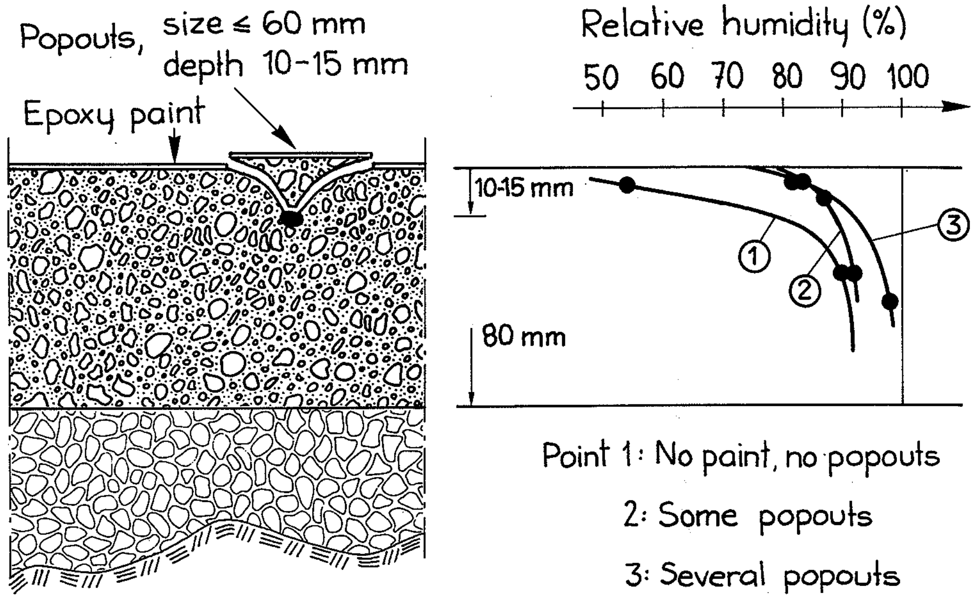

FIG. 1 Moisture distributions in "case 1": An epoxy painted basement floor

The concrete floor is wet towards the ground and there is a moisture flow upwards. Where the floor is not painted, however, the upper part of the floor slab is dry and no popouts have been created here. The epoxy paint has a certain resistance to moisture flow, depending on its thickness and quality. This results in higher moisture conditions in the upper part of the floor; around 90 % RH in the upper 20 mm, a little lower at the concrete surface.

Several very large popouts have occurred originating from reactive grains at a depth of 10 to 15 mm where the relative humidity is over 85 % RH but lower than 95 % RH. Closer to the surface the humidity is even lower and consequently no smaller popouts from this depth have been created.

### 2.2 Case 2: An epoxy painted floor in a heated hangar

At an epoxy painted hangar floor popouts, gel extrusions and deterioration of the paint film have occured. The moisture distributions were measured at different parts of the floor, see Figure 2.

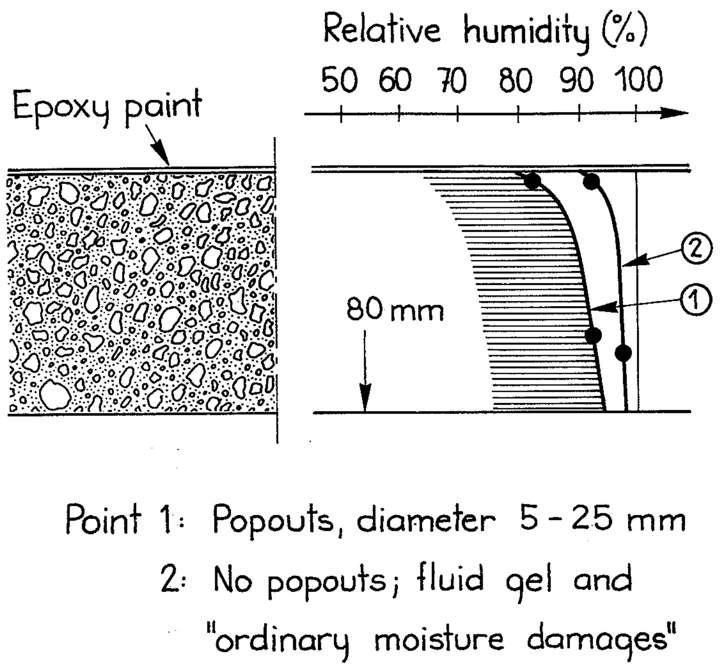

FIG. 2 Moisture distributions in an epoxy painted hangar floor

The hangar was built at a slope. Consequently the layer of sand beneath the concrete floor was only 0.15m at one end of the hangar but 0.5 to 1.0m at the other. This meant that there was a capillary suction of water to the slab at one end but only a much more limited moisture flow at the other. The epoxy paint had a high resistance to moisture flow resulting in a rather small moisture gradient over the slab.

Where the sand beneath the slab acted as a capillary break, the humidity in the upper part of the floor was around 90 % RH, resulting in several popouts. At the other end of the hangar the humidity was higher than 95 % RH and no popouts were created here, but a lot of gel extrusions through holes in the paint film was found. The film was also deteriorated by moisture. Too wet conditions obviously counteract the creation of popouts.

## 3. SOME EXPERIMENTAL RESULTS

Attempts to reproduce the damages incurred in practice have been made experimentally by using a concrete composition similar to the ones used in practice and expose the surface to a "history of climatic conditions" in a reproducible way.

Mortar specimens have been made using a high-alkali cement with an eqiuvalent alkali content of 1.04% and a sand, 0-8mm, containing 5-10 % opaline flint and sandstone in the fractions greater than 1 mm, with $w_o/C=0.7$ and aggregate/cement-ratio of 3.8. The surface was floated after a couple of hours and then steel trowelled. After a certain curing time at +20°C, the specimens were dried in various climates in climate rooms at +20°C and climate boxes. Finally the specimens were rewetted. The "moisture history" used, is shown in principle in Figure 3.

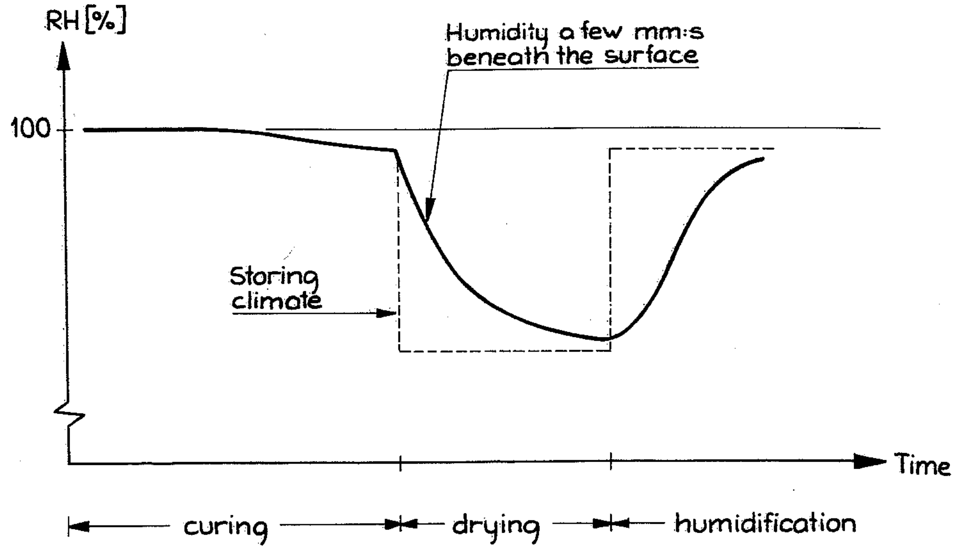

FIG. 3 Approximate "moisture history" for reactive grains close to the surface and the storing climate of the specimens.

Some of the results are published in /1/ and all of the experiments will be thoroughly described in /3/. Some examples of essential results are shown in TABLE I.

TABLE I. Specimens, thickness 8 cm, size 0.2x0.3m, sealed cured one week and then continuously stored in different climates for 1.5 years; then rewetted at 100 % RH

| Climate | Number of popouts (+ =after rewetting) | Size (mm) |
|---|---|---|
| +20°C 79 % RH | 1 (+1) | <5 (10) |
| 86 | 8 (+2) | <10 (15) |
| 91 | 5 | 5-15 |
| 93 | 4 (+1) | 10-50 (25) |
| 97 | 0 | - |
| +40°C 88 % RH | 20 (+1) | 5-20 (40) |
| 96 | 8 | 5-20 |

These and other results show that, in order to reproduce popouts, it is of essential importance to have a rather long drying time, at a relatively high humidity, and that a subsequent rewetting should only be slow or that there should only be a small humidity increase. The time needed is shortened very much by using a higher temperature during drying and the moisture dependence is somewhat changed at higher temperatures. At +40°C a higher relative humidity is needed to fill the pore system to the same degree as at +20°C in order to maintain the availability of alkalies by a continuous water phase.

The viscosity of the produced gel decreases when the humidity increases. The gel becomes more fluid and penetrates the surrounding cement matrix without causing any expansion or popout if the humidity is too high. The effect of moisture obviously has a pessimum close to 90 % RH at room temperature, cf. Figure 4.

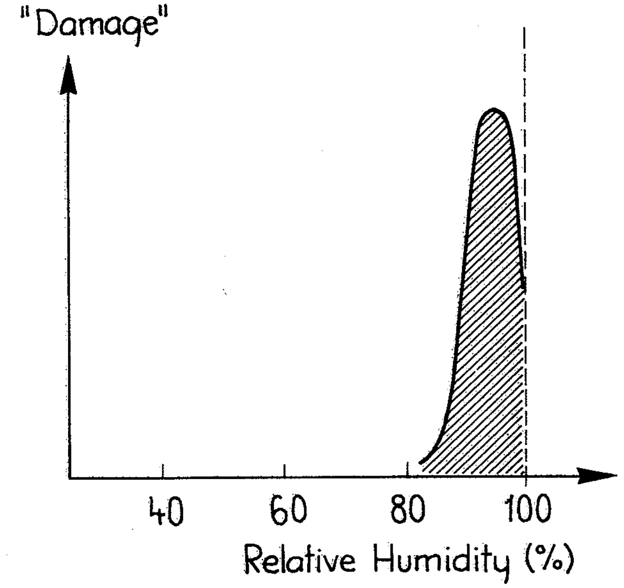

FIG. 4 The pessimum effect of moisture, in principle, at room temperature

Of course the effect of moisture is more complicated than shown in Figure 4. It is not only the continuously used humidity that matters, but the variation with time. Changes sometimes result in more popouts than a constant climate.

## 4. SUGGESTED TEST METHOD

To test the potential reactivity of combinations of cements and aggregates and the effect of potential inhibitors a test method has been outlined by using a number of testing climates close to the estimated pessimum humidity. Since the presence of reactive grains of different sizes and types sometimes is very limited the specimen size has been chosen rather big, 0.3x0.4x0.02 m, which means a total test surface of approximately 0.25 $m^2$. The specimens, the chosen climates and one of the climate boxes are shown in Figure 5.

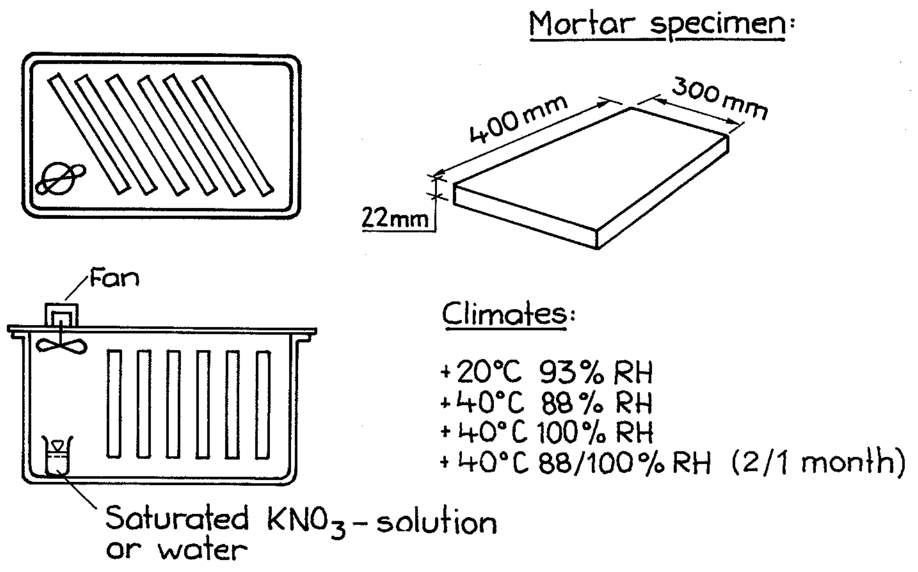

FIG. 5 Specimen, climate boxes and climates used in the test method.

Some sands, cements and potential inhibitors have been tested with the suggested method. The results after six months are summarized in TABLE II as numbers of popouts and their size. The mix proportions were: "cement":water: aggregate equals 1:0.66:4.77, where the amount of "cement" sometimes is a high-alkali cement mixed with various additional materials.

The sand HB is known to produce popouts in practice but no popouts have ever been reported where the sand R has been used, even if it contains reactive grains. With the HB-sand popouts were created in all of the testing climates, but with the unharmful R-sand very few popouts were obtained and in one climate only.

Of the three sands with unknown behaviour in practice, sand Sö must be classified as "unharmful", since no popouts whatsoever have been created. The other two, B and Hv, can be described as harmful or "possible sources of popouts".

All the tested cements have been producing popouts in all the testing climates. The potential inhibitors, slag, fly-ash and silica-fume, have been tested with a large amount of the high-alkali cement replaced. The effect may be mainly caused by the decreased total alkali content. Fly-ash and silica-fume seem to be promising inhibitors; only very small or very few popouts were created, and only in some of the testing climates. Other mix proportions, taking the desired concrete quality into consideration, should also be tested before use in practice.

TABLE II. Results from the suggested test method

| VARIABLES | | NUMBER OF POPOUTS (size in mm) after 6 months | | | | |
|---|---|---|---|---|---|---|
| | | Testing climate (after 2 months sealed curing) | | | | |
| | | Sealed at+20 C | 93%RH at+20 C | 88%RH at+40 C | 88/100%RH at+40 C | 100%RH at+40 C |
| Sands: (cement S) | | | | | | |
| HB | number<br>size | 1<br>(10) | 3<br>(5-10) | 12<br>(5-10) | 19<br>(5-20) | 19<br>(5-15) |
| R | number<br>size | 0 | 0 | 0 | 3<br>(5-10) | 0 |
| Sö | number | 0 | 0 | 0 | 0 | 0 |
| B | number<br>size | 1<br>(10) | 5<br>(8-15) | 3<br>(5-15) | 11<br>(4-15) | 6<br>(4-20) |
| Hv | number<br>size | 1<br>(10) | 3<br>(3-10) | 1<br>(16) | 17<br>(8-15) | 2<br>(7-10) |
| Cements: (sand HB) | | | | | | |
| S | number<br>size | 1<br>(10) | 3<br>(5-10) | 12<br>(5-10) | 19<br>(5-20) | 19<br>(5-15) |
| D | number<br>size | 9<br>(6-15) | 18<br>(5-10) | 5<br>(5-15) | 11<br>(3-10) | 23<br>(5-15) |
| Ss | number<br>size | 11<br>(5-15) | 18<br>(5-25) | 5<br>(8-30) | 13<br>(5-15) | 10<br>(8-20) |
| P | number<br>size | 1<br>(8) | 3<br>(5) | 11<br>(5-10) | 11<br>(5-10) | 4<br>(10-30) |
| Additional materials: | | | | | | |
| 40 % slag added | number<br>size | 1<br>(5) | 2<br>(2-5) | 15<br>(3) | 20<br>(3-5) | 25<br>(3-5) |
| 30 % slag -"- | number<br>size | 1<br>(3) | 1<br>(5) | 3<br>(3-5) | 16<br>(5-10) | 8<br>(5-15) |
| 35 % fly-ash -"- | number<br>size | 1<br>(3) | 0 | 0 | 0 | 3<br>(2) |
| 4 % Si-fume -"- | number<br>size | 0 | 0 | 0 | 0 | 2<br>(15) |
| $w_o$/C = 0.4 | number<br>size | 16<br>(3-10) | 26<br>(3-15) | 27<br>(5-8) | 40<br>(3-20) | 36<br>(5-25) |

ACKNOWLEDGEMENT

The author acknowledges the assistance of the staff at the Division of Building Materials, Lund Institute of Technology, in carrying out the experimental work. The research was financed by a grant from CEMENTA AB, Sweden and the National Swedish Board for Technical Development.

REFERENCES

/1/ Nilsson, L-O (1981), "Pop-outs Due to Alkali-Silica Reactions - A Moisture Problem?". Proc of 5th Int Conf on Alkali-Aggregate Reaction in Concrete. Cape Town, South Africa, March/April 1981

/2/ Nilsson, L-O (1980), "Hygroscopic Moisture in Concrete - Drying, Measurements and Related Material Properties". Division of Building Materials, Lund Institute of Technology/University of Lund, Sweden. Report TVBM-1003.

/3/ Nilsson, L-O & Peterson, O (1983), "Alkali-Silica Reactions in Sweden - A Moisture Problem Causing Popouts on Concrete Floors". Div of Build Mat, Lund Institute of Technology. To be published.

# DISSOLUTION AND HYDRATION OF $C_3A$-$Na_2O$ SOLID SOLUTIONS

I. Jawed, Manager, Analytical Department
L. Struble, Scientist
J. Epp, Research Assistant

Martin Marietta Laboratories
Baltimore, Maryland U.S.A.

## ABSTRACT

This presentation highlights the dissolution and hydration data obtained on several $C_3A$ preparations in solid solution with varying amounts of $Na_2O$. Almost all $Na_2O$ present in the solid solution was released into the liquid phase of the hydrating system within a few hours, indicating nearly complete dissociation and hydration of the solid solution. With increasing $Na_2O$ content in the solid solutions, the concentration of CaO decreased and that of $Al_2O_3$ increased in the liquid phase. The effect was apparently independent of the source of $Na_2O$. The $Na_2O$ concentrations in the liquid phase were unaf-fected when the solid solutions were hydrated in the presence of $C_3S$. The data show that the hydration of solid solutions is not significantly affected by the incorporation of different amounts of $Na_2O$.

Keywords: cement, alkali, liquid phase, $C_3A$

## INTRODUCTION

Alkalies in portland cement clinker have become increasingly important for two principal reasons: firstly, they can become incorporated in the structure of clinker minerals resulting in several polymorphs or solid solutions of different hydration reactivities with subsequent effect on the mechanical properties of cement and concrete; secondly, their presence in the concrete pore fluid may lead to the well-known alkali-silica reaction. Until recently, the subject of hydration reactivity of clinker minerals as a result of alkali incorporation has received relatively little attention [1-5]. Also, only limited and indirect evidence is available concerning, if and to what extent, the distribution of alkalies among cement phases affects the alkali-silica reaction. Although correlations between alkali content of cement and alkali-silica expansion have been reported [6-9], there appears to be no published data relating the alkali content of individual clinker minerals and the alkali-silica expansion.

Since hydration of portland cement is essentially a dissolution-precipitation process, the rate of hydration and dissolution of various alkali-containing cement clinker minerals is of great importance for both reasons mentioned above. The nucleation and precipitation of hydration products is affected by the composition of the liquid phase of the hydrating system. It is, therefore, of special interest to determine how the alkali content of clinker minerals would affect the concentration of alkalies and other species in the liquid phase of the hydrating system. Of all cement clinker minerals, tricalcium aluminate ($C_3A$) is the most reactive with water and can also incorporate substantial amounts of alkalies in its structure. This note describes some initial studies on the hydration and dissolution of $C_3A$ phases containing various amounts of $Na_2O$ in solid solution.