POP-OUT FORMATION.
A LABORATORY STUDY WITH A SWEDISH OPALINE GRAVEL.

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1. SUMMARY

108 cement mortar specimens were made. The aggregate was always in the range
0.25 - 2.00 mm.
In 60 of the specimens, the aggregate of the mortar was non-reactive.
For the residual 48 specimens, a type of aggregate was choosen, which was
suspected of alkali-reactivity.

In each specimen was implanted one stone, suspected of reactivity, and
4.0 - 5.6 mm in size.

The cement of the mortar was pure portland cement, or was 1 - 10 per cent of
the cement replaced with Norwegian silica-fume.

Different programs for curing, drying, and and re-humidification were used.
Only in one of the 108 specimens, the implanted stone caused a pop-out (and
a big one). In this case, the fine aggregate was partly alkali-reactive.

In one of the specimens, the stone formed liquid alkali silicate gel, and a
wet spot appeared on the top surface of the specimen. The fine aggregate
was, in this case, non-reactive.

In seven specimens, the test stone reacted to a less degree. The reaction
zone between stone and mortar could be observed in a cut surface through the
specimen at the stone.

In the residual 99 specimens, the test stones had reacted still less.
Obviously, it was difficult to choose the test stone so that each stone had
the same reactivity. However, the results do not contradict the presumption
that silica-fume has a protecting effect upon a test stone of that size.

In mortar with reactive fine aggregate, the total population of reactive
grains was drastically increased. In cuts through such mortars, wet spots
and small pop-outs had dev lopped already after curing the specimen. This
was equally true, even when so much as ten per cent of the cement was
replaced by silica-fume. Small stones could not be protected by silica-fume.

Keywords: pop-outs, silicate-gel, silica-fume, grain-size.

1. BACKGROUND

In southern Scania, in Sweden, a number of cases with pop-outs have
occurred, since the local plant for low alkali cement had shut down.
Many laboratory tests have been performed in order to find the conditions
for formation of pop-outs. It was easy to get alkali silicate gel as a
reaction product, but only few big pop-outs have appeared.

The aim of this study was to find out the importance of the following five variables:

A. One reactive stone in mortar with
   non-reactive or reactive fine aggregate.

B. Cementing agent Slite Std Cement,
   pure, or replaced with 1, 2, 5, or 10 per cent of silica-fume.

C. Specimen cured
   at 100, or at 93 per cent relative humidity.

D. Cured specimen dried for 28 days
   at 20, or at 40 degrees Celcius.

E. Cured and dried specimen re-humidified
   in moist air, or partially immersed in water.

2. MATERIALS

A pop-out in a concrete floor is caused by, most often, one single stone, about 3 - 4 mm in size. A common source of concrete sand is Hasle-Bösarp, about 24 kilometers east of Trelleborg. A specimen of sand and fine gravel from this place was choosen for the present work.

2.1 The reactive test stone

From the test sand, a quantity of the fraction 4,0 - 5,6 mm was taken out by sieving. From this fraction, a number of stones were selected, which were rounded in form, white or grey in colour, and which contained weak components (chalk) and also hard components, such as opal and quartz. All test stones were dried, in order to make the pore system of each stone available for the alkaline pore liquid from the cement paste.

2.2 The aggregates of the mortars .

The aggregates of the main mortars always consisted of sand in the range 0.25 - 2.0 mm.

2.2.1 Non-reactive aggregate   (Series 1)

From a sample of Åstorp-sand (a quartz sand), the following fractions were taken out by sieving and mixed together in equal parts, by weight.

$$0.25 - 0.50 \text{ mm}$$
$$0.5 - 1.0 \text{ mm}$$
$$1.0 - 2.0 \text{ mm}$$

2.2.2 Aggregate with reactive silica   (Series 2)

From the concrete sand sample from Hasle-Bösarp, the same three fractions were taken as from the Åstorp sand. They were mixed in accordance with the natural grain size distribution of the test sand:

0.25 - 0.5 mm   31.3 per cent by weight
0.5 - 1.0 mm   53.3 "-
1.0 - 2.0 mm   15.4 "-

A visual examination indicated that the coarse fraction contained most of material, suspected for containing alkali reactive silica. The fine fraction contained only a small part of such suspicious grains. The medium fraction contained a moderate part of suspicious grains, and the residual parts of those two fractions mainly consisted of quartz grains.

2.2.3 Fine aggregate for top layer

The top layer of a concrete floor with pop-outs is often very weak. This layer may be formed on top of a fluid concrete mix, as a result of too long a vibration period, and it is most often rich in fine particles and water.

In order to simulate this top layer, a mortar was composed with especially fine aggregate. From a quarrying plant at Hardeberga, 5 kilometers east of Lund, in Scania, a sample of practically pure quartz dust was taken. The dust was dried and sieved through a 0.5 mm sieve.

2.3 The cement mixture

A sample of Slite Standard portland cement was used, containing 1.25 per cent of potassium oxide (K_2O), and 0.22 per cent of sodium oxide (Na_2O). The total content of alkaline metal oxides, calculated as sodium oxide, was 1,04 per cent, and they mainly existed as sulphates.

The effectiveness of Norwegian silica-fume as a suppressor of alkali silica reactions, was tested by replacing some of the cement with the same weight of silica-fume. The following mixes of cement and silica-fume were used for the test specimens:

Cement mix, parts of weight		Designation of specimen Type of aggregate		Note
Cement	Silica-fume	Non-reactive	Reactive	First figure in designation gives the type of aggregate
100	0	10	20	
99	1	11	–	Second (and third) figures
98	2	12	22	give the percentage of
95	5	15	25	cement, replaced with
90	10	110	210	silica-fume

3. THE TEST MORTAR

For each designation, the main and top mortars must be mixed for twelve test specimens.

3.1 The main mortar

The mortar was mixed, in units of weight, from:
   Cement, or cement mix   1.0
   Water   0.7
   Sand mixture   3.6

130 milliliters, or 290 grammes, of the mortar mix was used for each specimen.

The non-reactive and the reactive sand mixtures had different grains and different grain size distributions. Still the same weight mix was used. Silica-fume had a tendency to make the test mortar more cohesive. Still all the mixes could be handled in quite the same manner as those with pure cement, when mixing and moulding the mortar.

3.2 The top layer mortar

The mortar for the very weak top layer was mixed, in units of weight, from:
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     Cement, or cement mix   1.0
     Water                   1.2
     Top layer dust          3.36
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6.3 milliliters, or 15 grammes, of mortar was used for each specimen. Part of the cement could be replaced with silica-fume without changing the weight composition of the mortar.

4. THE TEST SPECIMENS

4.1 The main mortar

The mortar was moulded in, at least, four consecutive layers in polystyrene beakers. Each layer was compacted on a vibrating table.

4.2 Implantation of the test stone

In the central point of the top surface of each one of the ready compacted mouldings, one test stone was placed.

4.3 Application of the top layer

As soon as the top layer mortar was mixed, the beaker was given a short vibration period, and the test stone was pressed down into the main mortar with a pair of tweezers, so that the stone was just covered.

Now the top layer mix was applied to a average thickness of 2 millimeters (6.3 milliliters or 15 grammes), and the beaker was given a short period of vibration for making the top surface smooth.

5. THE CURING

5.1 Stripping

The beaker was placed in a desiccator with pure water in the bottom space. After one day the beakers were stripped off from the specimens.

5.2 Marking. Grinding the top surface

The stripped test specimens were marked on the mantle surface (the ink must be lime proof).
Six specimens of each designation were given the letter "-A" after the designation number and the residual six specimens the letter "-B".
At last, the six specimens with the same letter were numbered "-1" to "-6".

The specimens were given still one day curing in a desiccator with pure water in the bottom space. Then, the top surface of each specimen was ground to smoothness with wet grinding paper nr 120. Water was used for rinsing.

5.3 Final curing

For final curing, the marked and top-smoothed specimens were separated into two groups. All specimens were cured for further 26 days at about 20 degrees Celcius, and then each specimen with the last figure "-1" was cut with a diamond saw, flushed with kerosine. The cut followed the axis of the the test specimen so that the test stone was cut also.

5.3.1 The "-A-group" (100 per cent RH)

The specimens marked "-A-" were stored in a desiccator with pure water in the bottom space.

5.3.2 The "-B-group" (93 per cent RH)

The "-B-specimens" were stored in a box, the humidity of which was controlled by wet potassium nitrate (KNO_3) in a bowl. The air was kept in movement by a fan, and the motor was placed above the lid, in order to avoid undesired heating of the test specimens.
It is essential that the solution <u>and</u> the solid salt keep contact with the air in the box all the time, or the control of the humidity will get lost.

6. DRYING AT 85 PER CENT RELATIVE HUMIDITY

The drying was performed in one box for 20 degrees Celcius and another for 40 degrees. The same salt was used for booth temperatures: potassium chloride (KCl). The boxes were equipped with fans, quite like the box for 93 per cent RH. The air in the box must contact the solid salt and also saturated solution all the time

6.1 Drying at 20 degrees Celcius

The specimens marked "-2" and "-4" from each designation and curing group, were carried over to the box for 20 degrees Celcius.
After 28 days, the storing was interrupted. The specimen marked "-2" were cut along the axis of each specimen, and also through the test stone.
The specimens marked "-4" was carried over for re-humidification.

6.2 Drying at 40 degrees Celcius

The specimens marked "-3", "-5", and "-6", from each designation and curing group, were carried over to the box in the oven for 40 degrees Celcius.

During the last period, this box happened to crack, so that the potassium chloride solution dried out. Wiskers developed from the chrystal bed, so that saturated potassium chloride solution was carried over to the specimens
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          210-A-3     210-B-3     210-A-5     210-B-5
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and to parts of the edge of the top surface of 25-A-3.

After 28 days drying, the specimens marked "-3" were cut trough the test stone, and the specimens marked "-5" and "-6" were carried over for re-humidification.

7. RE-HUMIDIFICATION OF THE TEST SPECIMENS

These processes started at an age of 56 days.

7.1 Re-humidification in moist air

All specimens marked "-4" and "-5" were carried over to a desiccator with pure water in the bottom space.
Since no stirring of the air was arranged, the specimens needed much time for adaptation of their humidity to the new type of storing.
The specimens were kept observed and, if no changes happened, they had to stay in moist storing for several months.

7.2 Re-humidification in a flat dish with a thin layer of water

This treatment was intended to simulate the case when, e.g., a floor is to be treated with magnesium fluosilicate solution.
All specimens marked "-6" were picked out for this type of storing. The duration was, principally, the same as for the moist air storing, but the access of water to all parts of the specimens was essentially better.

8. OBSERVATIONS

8.1 The behaviour of the single test stone

In one single case, designation 20-B-3, the reactive test stone caused a pop-out. The fine aggregate was reactive.
The curing was performed mainly at 93 per cent RH. The drying at 85 per cent RH took place at 40 degrees Celcius.

After cutting, the half specimens were stored in moist air att room temperature. Five weeks later, the stone had grown up about 1,5 millimeters from the cut surface. Still the top layer had cracked loose from the main volume of the half specimen.

In one other case, designation 10-B-4, the reactive stone has caused a wet spot after the drying period. The fine aggregate was non-reactive. The curing was performed mainly at 93 per cent RH.
The drying at 85 per cent RH took place at 20 degrees Celcius

After cutting, the specimen was stored for five weeks in moist air. Liquid gel flowed out over the surrounding mortar, and the stone changed into a wet fine sand.

In seven cases the cut test stone showed milder signs of gel formation, without any mechanical harm to the test mortar, and without any visible wet spots on the top surface of the specimen. In the following table, these specimens are put together in order of decreasing reactivity.

The line "Gel form" shows how far the gel liquid had spread over the surroundings, or whether only a brown border had formed around the surface of the cut stone.
The line "Stone char." shows the hardness of the cut stone surface. "Hard" tells about a content of quartz, "weak" about a chalky character.

Design.	12-B-3	10-B-3	20-A-5	11-B-5	11-A-5	10-A-1	25-B-6
Gel form.	5 mm	3 mm	3 mm	1.5 mm	0.75 mm	border	border
Stone char.	hard	hard	rel h	weak	rel h	hard	weak

A test stone may very well feel hard, and still be able to generate a rather large volume of liquid gel.
Small amounts of silica-fume, in a range up to 2, possibly 5, per cent of the cement mixture, do not totally inhibit the reaction between silica and alkali.

8.2 Signs of reactions in specimens with reactive fine aggregate

The number of wet reaction spots on the saw cut surfaces are put together in the following table, as average values from all specimens with common last number.

Nr	History	Spots on 25 cm^2	Pop-outs on 25 cm^2
-1	Just cured	7	1
-2	Dried 20 degr.	7	4
-3	Dried 40 degr.	6	2
-4	20 degr, air hum.	7	2
-5	40 degr, air hum.	6.5	2
-6	40 degr, wet stored	12	2

In the cut surfaces, most grains which are able to react seem to do so already during the 28 days curing period, irrespective of 93 or 100 per cent RH. Re-humidification in a thin layer of water, however, seems to increase the number of reaction sites significantly.
The contents of silica-fume in the cement mixture does not seem to influence the number of reacting grains in the cut surface.

Reaction spots on the top or mantle surfaces of the specimens mainly develop during the re-humidification.

The reaction spots may be a grain, which generates a gel liquid, spreading to the surrounding. Sometimes, part of a grain may shoot up and form a "micro pop-out".
Cracks may originate from a reaction spot on the top or mantle surface, and mainly when five percent of the cement was replaced with silica-fume. In no case, there occurred any cracks on specimens, stored in a thin layer of water.

A contamination of a test specimen with potassium chloride resulted in "map cracking", even when so much as ten per cent of the cement was replaced with silica-fume.
The contamination also was followed by an increased number of reaction sites, and the attacked grains may be placed in the top or mantle surface, or in surfaces shaped by cutting. No re-humidification was necessary.

9. DISCUSSION

It is reasonable to presume that the chemical and physical laws for alkali silica reactions are the same, whether the particles are small or big.

The fact that only one single pop-out has developped from the 108 test stones in this work may be explained in different ways.

1. It was difficult to choose test stones with quite equivalent reactivity.

2. A sufficient content of silica-fume in the cement mixture may protect the test stone against the alkalinity of the cement, even if the stone is strongly reactive.

3. The pop-out in the specimen "20-B-3" may have been promoted by the rapidly available silica in the fine aggregate of the mortar. This may increase the quotient silica/alkaline metal oxides in the gel, which makes the gel more viscous at a given water content.

4. In a practical concrete, the combination "20-B-3" seems to be much more probable than "10-B-4", with all reactive silica concentrated in the test stone. This combination probably will promote the formation of a gel with low viscosity, which easily escapes through the pore system of the mortar.

5. The calcium content of the gel is claimed to be important for the capacity of a gel to shape a crack in the surrounding mortar, or concrete, by absorbing water.
This observation seems to be reasonable, but probably there is no direct causal connection. Primarily, a high quotient silica/alkaline metal oxides in the gel will reduce the pH-value of the gel, and this will increase the calcium ion concentration of saturated calcium hydroxide (or cement) solution. This way, the conditions for building calcium ions into the gel have been improved.
A gel with a very high quotient calcium/alkaline metal ions is probably similar to normal hardened cement paste, and does not expand very much.

6. Tests were made with a scanning electron microscope with EDAX to find out whether the gel composition in the two specimens "10-B-4" and 20-B-3" were different. The tests were, however, not successful. The microscope could not analyse the gel substance separated from the non-reactive grains from the attacked test stone or from the surrounding mortar.

7. Ten per cent replacement of cement with silica-fume did not protect the fine reactive grains in the mortar. The most reasonable explanation may be that the small reactive grains from the choosed gravel pit at Hasle-Bösarp, most abundant in the fraction 1.0 - 2.0 mm, have completed their reaction with the alkaline metal hydroxides before the silica-fume has reduced the alkalinity of the mortar water.
On the other hand, most experiance show that the fine reactive grains from this gravel pit are not abundant enough to be able to damage concrete seriously.

C.D. Pomeroy

This session clearly demonstrated the need for specialists who could use highly sophisticated equipment in the study of the underlying factors that control the reactions between certain aggregates and alkalis. Progress with such special methods calls for both dedication and enthusiasm from the individual workers and the four speakers showed both attributes.

However it is not easy for specialists to communicate with a general audience and it was suggested that at any future congress on the subject the specialists be provided with an opportunity to meet together, in small groups, and to report only their general conclusions to the main meeting. It was possible that some of the most advanced techniques were understood by only a small proportion of the audience.

Dr Micheline Regourd, however, gave a clear exposition on X-ray diffraction, electron microscopy and microprobe methods, especially for use in the examination of the matrix-aggregate interface and she stressed the relevance of her work to the practising engineer. Such methods are important in the study of the influence of modifications to cement formulation, or of the inclusion of fly ash or slag into the cement upon the hydration mechanism.

The work described by the different speakers showed how difficult it can be to classify an aggregate as reactive or inert, and this was particularly apparent in the work reported by Olaf Peterson who found it difficult to identify pieces of aggregate that would 'pop-out' as a consequence of reaction.

It is important to have experts available who are skilled in modern techniques that can be used to study the complex reactions that take place as cements hydrate and as the cement reaction products react with the aggregates. The role of the petrographer in classifying the aggregates is also extremely important, as Dr Dolar Mantuani so enthusiastically stressed. However these various skills must be directed towards practical solutions to the problems that the concrete structural designer or contractor faces and a dialogue between the research worker and the user needs to be given greater priority by research worker and user alike. Only in this way will real progress be made in ameliorating the problems that have arisen from the use of alkali reactive aggregates.