

Quantitative Microanalyses of the Reaction Zone  
between Cement Paste and Opal

by

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ABSTRACT

The chemical-mechanical transformation of reactive silica in concrete into alkali- or alkali-calcium silica gels has bearing on the possible expansion and disruption of the concrete. By the combination of scanning electron microscope, energy dispersive x-ray spectrometer and computer, the composition of the transition zone or reaction rim between cement paste and opal has been measured.

To a depth of 150  $\mu\text{m}$  the opal was converted to a calcium silicate hydrate with only a trace of alkali and a calcium to silica ratio of 0.7 : 1 on a molar basis.

Key words: Alkali-silica reaction, Gel, Quantitative analysis, Microprobe, SEMEX, Opal, Rim-corrosion

### Aim of investigation

In a contribution to the Transportation Research Board Meeting, January 1975, my colleague Dr. T. Knudsen and I demonstrated the possibility of carrying out chemical analyses of micro-volumes of alkali-silica gel by the combination of the scanning electron microscope, energy dispersive x-ray spectrometer and data processing by computer. The main conclusion of that investigation was that gel with high, up to 20 per cent of calcium oxide can be positively found by analysing gel deposited in the interior of concrete. A variation of the calcium oxide content was found going along a crack, in which the gel was found. A low level of calcium oxide content was seen in gel near to the reacted particle and a high level of this content in gel further away from the reaction place in the crack. These results will be published in Cement and Concrete Research Vol 5 No 5 in September 1975 [1]. Having established the analytical tool of SEMEX it seemed obvious to collect more pieces of information on what is going on between reactive silica and cement paste, primarily in relation to the role of calcium in this reaction.

### Experimental

Our SEMEX consists of a JEOL JSM U3 scanning electron microscope equipped with both a wavelength dispersive crystal spectrometer and an EDAX 707 energy dispersive spectrometer connected to a NOVA-minicomputer. Spectrum handling such as smoothing, back-ground subtraction and peak integration is performed on-line by the minicomputer to give the net intensities of x-ray lines emitted from the elements in the sample. To obtain quantitative results for chemical composition we correct for atomic number effect, absorption and fluorescence in the sample and compare with a standard of known composition. This is done off-line in a larger computer by the programme ZAFIB developed recently in our laboratory. All elements heavier than fluorine can be analysed for with the need of only a single standard. Water can not be detected directly but are calculated by difference. In this investigation opal was used as standard after checking the content of silica against a pure iron standard.

The reason for using the energy dispersive system instead of the crystal spectrometer is the ease of operation, the need for only a single standard, and most important, less damage to the specimen due to the lower beam current which is sufficient for the energy dispersive detector. Evaporation of sodium and potassium is a severe problem in wavelength dispersive work. The trade off by the EDAX detector is partly the overlapping of peaks from neighbouring elements but also the problem of diffuse electrons exciting atoms on a large area of the sample. By placing a piece of x-ray film in the sample holder it was established that the diffuse electrons hit an area outside a circle of 4 mm in diameter with the primary beam focused in the center. Other measurements showed the intensity of diffuse electrons to be 11 - 12 per cent of the well focused electrons.

The easiest way to avoid serious errors due to this fact is to cover the surface with graphite paper leaving only a few mm<sup>2</sup> of surface open for analyses.

In the quantitative analyses of the present investigation this was done.

Before running the ZAFIB programme the overlap of calcium  $K_{\alpha}$  by potassium  $K_{\beta}$  was corrected for.

A detailed description of the performance of the system SEMEX - ZAFIB including treatment of resolution, precision and accuracy is given in the article to be published in Cement and Concrete Research Vol 5 No 5 in September this year [1].

The sample used in the present investigation consisted of an opal cylinder embedded in cement paste.

The opal cylinder was drilled as a core 9 mm in diameter and 12 mm in length from a piece of milky white opal from the Faeroe Islands. The opal had a density of  $2.2 \text{ g/cm}^3$ , and an index of refraction approximately 1.45. By thermal analysis a dynamic water loss of 1.6 per cent was found between 20 and  $1000^\circ\text{C}$ . The water loss showed maximum rates at 100 and  $270^\circ\text{C}$ . Infrared spectroscopy showed a broad absorption between  $2900$  and  $3700 \text{ cm}^{-1}$  with maximum absorption at  $3400 \text{ cm}^{-1}$ . X-ray diffraction gave broad lines of  $\alpha$ -cristobalite with a trace of quartz.

The cement used was from Akranes, Iceland. Chemical analysis showed an alkali content of 0.37 per cent as potassium oxide plus 1.65 per cent as sodium oxide. Nearly all potassium and one third of the sodium was water soluble.

The opal cylinder was surrounded by an 11 mm thick hull of cement paste mixed with a water-cement ratio of 0.4. After demolding, the specimen was stored over water at room temperature in a closed container. After 1 month gel was observed at the surface of the sample but cracks could not be seen.

After 8 months the sample was removed, dried at  $110^\circ\text{C}$ , embedded in epoxy resin, cut and polished, so that the interface between opal and cement paste was perpendicular to the polished surface. The surface was coated with carbon and examined by optical microscope and by scanning electron microscope.

Fig. 1 shows the polished sample.

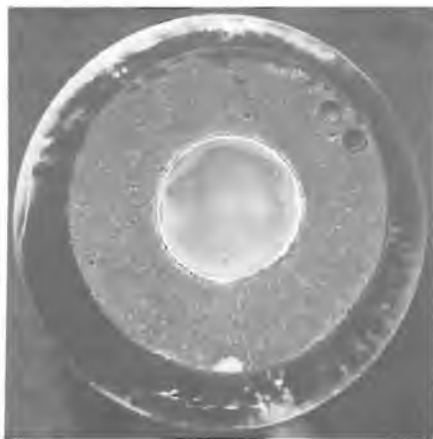


FIG. 1

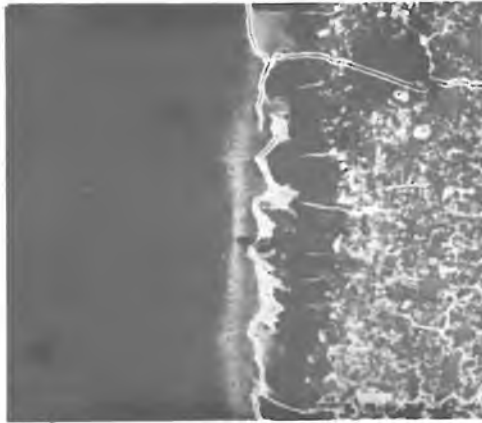
## Results

Optical examination of the polished sample in reflected light showed the center of the opal to be unaltered, homogeneous and transparent to some degree. To a depth varying between 0.2 and 1.5 mm from the interface to the cement paste, less transparent clouds were visible in the opal.

To a depth of 0.1 to 0.5 mm a white, opaque rim followed the periphery of the opal. A thin approximately 0.1 mm dark glassy rim adjacent to the original surface of the opal was seen. The cement paste in contact with the opal was brown in colour and appeared wet. This region extended 0.1 mm into the cement paste. In some places the brown region of cement paste was followed by a narrow, white zone of cement paste while in other places the brown colour fades out into normal looking cement paste. Unhydrated cement grains were visible. Some air voids close to the opal were partly filled by a colourless, transparent glassy material. Nine empty cracks radiated from the opal to the surface of the sample.

Whether these cracks are the result of expansion of the opal or shrinkage of the cement paste is not clear to us.

Examination with the scanning electron microscope clearly revealed the transition zone between opal and cement paste as seen in Fig. 2



**FIG. 2. Secondary electron image. 80x, 16kV, 0.6nA**

To the left opal with a smooth surface can be seen, and to the right the cement paste shows remains of unhydrated cement grains. The bright spots and lines in the paste are pores and cracks.

Inside the opal in a distance of 50 to 150  $\mu\text{m}$  from the original interface an irregular vertical crack is seen. This crack seems to follow a zone in the opal with a bright appearance probably due to higher porosity.

Some horizontal cracks beginning at the vertical crack and penetrating both the transition zone and the cement paste are also recognized.

The largest crack continues to the surface of the sample and is one of the radial cracks which were visible in the optical microscope.

The upper part of the field of Fig. 2 is shown in 300 times magnification in Fig. 3.

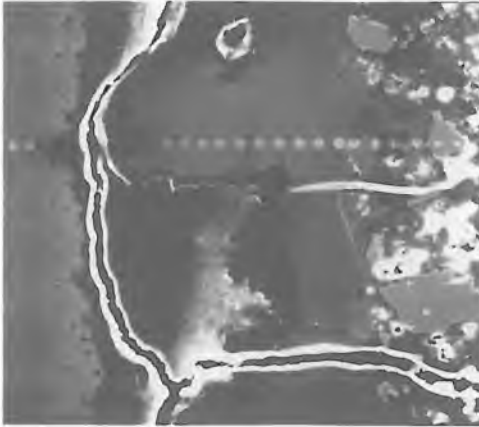


FIG. 3. Secondary electron image. 300x, 16kV, 0.6nA

It is apparent from this picture that the cracks are not gel-filled. Unhydrated cement grains and pores in the cement paste are now clearly visible. The original interface between opal and cement paste is supposed to be located where the unhydrated grains can no longer be seen. The horizontal row of bright spots each separated by  $10\ \mu\text{m}$  are contamination spots left by the stationary electron beam during the step-scanning measurement later described.

Fig. 4 shows the silicon distribution in the same field as Fig. 3.

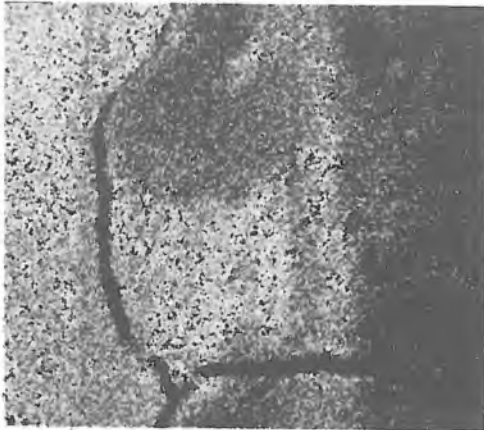


FIG. 4. X-ray image. Si-distribution, 300x, 25kV, 2nA, 2 x 100 sec. exp.

The higher the concentration of dots, the higher the silicon concentration in that area is on a weight per cent basis but not necessarily on a volume per cent basis. The upper area low in silicon in the otherwise silicon rich opal is relevant to the next picture showing the calcium distribution (Fig. 5).



FIG. 5. X-ray image. Ca-distribution, 300x, 25kV, 2nA, 2 x 100 sec. exp.

The calcium distribution is seen complementary to the silicon distribution.

Now the silicon low area in the opal is seen with a high content of calcium. The penetration of calcium into the opal appears to be a general phenomenon along the whole interface of opal to the cement paste. The depth of calcium penetration is up to 150  $\mu\text{m}$ .

The next picture (Fig. 6) shows the potassium distribution in the same area as the other distribution images.

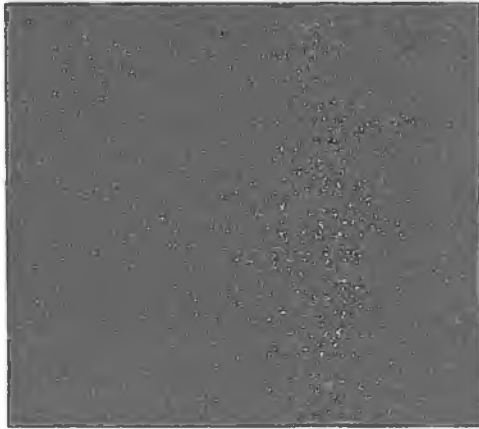


FIG. 6. X-ray image. K-distribution, 300x, 25kV, 2nA, 2 x 100 sec. exp.

Potassium was only found in low concentrations and mainly in a diffuse band covering the interface between opal and cement paste, with the larger part on the opal side. In the areas to the left and right of this zone the potassium concentration is under the detection limit caused by the continuous x-ray radiation giving rise to dots in these areas.

Surprisingly sodium was not detectable by this method which means that the sodium concentration is very low.

To inquire further into the concentration gradients across the interface between opal and cement paste line scan analyses for silicon, calcium and potassium were performed.

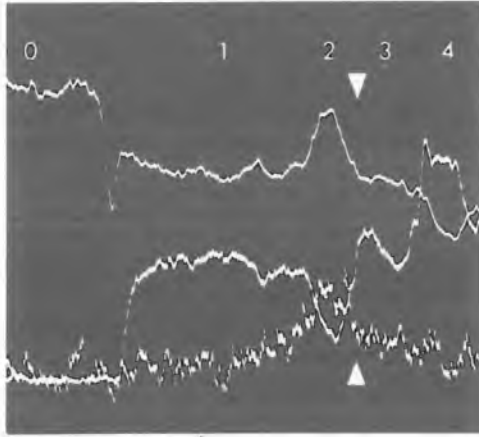


FIG. 7. X-ray line scan. Si, Ca, K.  $\times 300$

The upper curve in Fig. 7 shows the silicon concentration along a  $300\ \mu\text{m}$  line perpendicular to the interface. The middle curve shows the calcium concentration and the lower and more noisy curve shows the potassium concentration. The intensity of the elements are in different arbitrary scales and can not be compared directly. The original interface between opal and cement paste is marked. Going from left to right, high silicon concentration and absence of calcium and potassium shows pure opal (0). The sudden drop in the silicon signal is where the vertical crack is crossed. Now follows a zone (1) where an amount of calcium has penetrated the opal. This zone is gradually followed by a narrow zone (2) with less calcium but some potassium present and rich in silicon. Then comes a zone (3) of cement paste probably impregnated with lime rich potassium-silica gel. To the right is pure cement paste with no enrichment in potassium. The signals fluctuate due to inhomogenities such as pores and unhydrated grains in the cement paste.

Fig. 8 shows the results of step scan analyses along the same line with  $10\ \mu\text{m}$  intervals between points and 10 sec. analysing time. Peak heights of silicon (S) calcium (C) and potassium (K) are plotted in the same arbitrary scale against distance from the original interface between opal and cement paste. The zones described in Fig. 7 are visible. The penetration of calcium into the opal is to a depth of  $150\ \mu\text{m}$ . Notice that at the front of penetration the calcium concentration decreases over a distance of  $20\ \mu\text{m}$ . This is significant as the lateral resolution is better than  $2\ \mu\text{m}$ . Step scanning was repeated at another place on the specimen with the same qualitative result, and point analyses along the periphery of the opal confirmed the existence of these reaction zones.

X-ray step scan: Si, Ca, K

FIG. 8

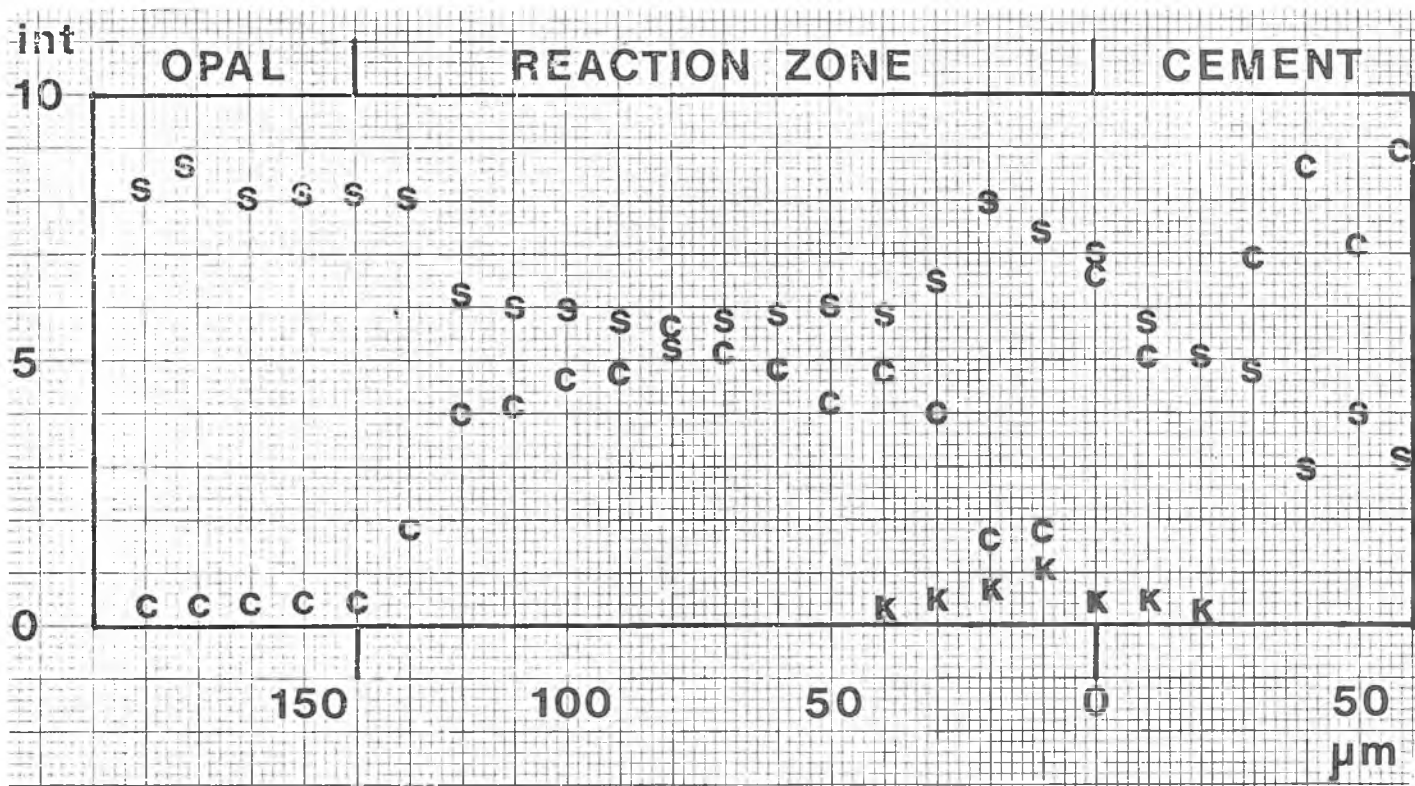




Fig. 9 shows the x-ray spectrum of a typical analysis of the lime rich zone. Only silicon and calcium are seen.

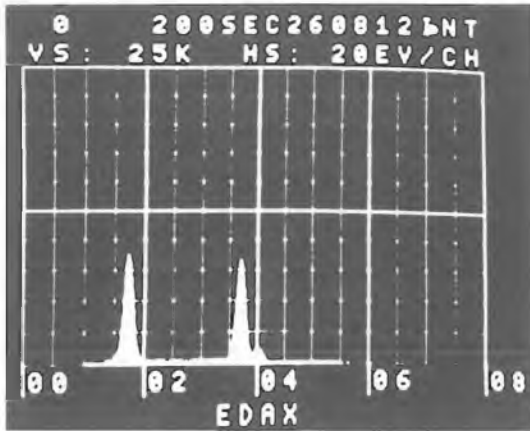


FIG. 9. Energy dispersive point analysis

Quantitative analyses were performed at selected points. The computer output of the ZAF-corrected results are shown in Figs. 10 - 15. The results are expressed as concentrations in weight per cent pure elements and as oxides. The sum of the oxides subtracted from 100 per cent gives an estimate of the water (or perhaps carbonate) content of the microvolume analysed. The results are also expressed on a molar ratio basis with silicon as 10. There is some variation in the composition of the calcium silicate hydrate formed in the reaction zone. The calcium to silicon ratio varies between 0.7:1 and 0.9:1.

## SEMEX-MIKROANALYSE

SEMEX-MIKROANALYSE  
 DATO 30/7/75 SIGNATUR NT

KV=16.0 TILT= 0 TAKE OFF=34

## STANDARDBETEGNELSE FE

SEMEX-MIKROANALYSE  
 GRUNDSTOF INTENSITET VÆGTPROCENT

JERN 68706.0 100.00

## PRØVEBETEGNELSE OPAL

SEMEX-MIKROANALYSE  
 GRUNDSTOF INTENSITET VÆGT% ,OXID

SILICIUM 85491.0 45.63 97.60  
 OXYGEN 0.0 54.37 97.60

FIG. 10

## SEMEX-MIKROANALYSE

SEMEX-MIKROANALYSE  
 DATO 30/7/75 SIGNATUR NT

KV=16.0 TILT= 0 TAKE OFF=34

## STANDARDBETEGNELSE OPAL

SEMEX-MIKROANALYSE  
 GRUNDSTOF INTENSITET VÆGTPROCENT

SILICIUM 85491.0 45.63

## PRØVEBETEGNELSE CA SI GEL

SEMEX-MIKROANALYSE  
 GRUNDSTOF INTENSITET VÆGT% ,OXID

SILICIUM 27595.0 15.90 34.02  
 KALIUM 278.0 0.16 0.20  
 CALCIUM 31978.0 20.33 28.44  
 OXYGEN 0.0 63.60 62.66

KEMISK FORMEL

SI 10.00  
 K 0.07  
 CA 8.96  
 O 70.21

FIG. 11

## SEMEX-MIKROANALYSE

-----  
 DATO 30/7/75 SIGNATUR NT  
 -----

KV=16.0 TILT= 0 TAKE OFF=34  
 -----

## STANDARDBETEGNELSE OPAL 45.63

-----  
 GRUNDSTOF INTENSITET VÆGTPROCENT  
 -----

SILICIUM 83061.0 45.63  
 -----

## PRØVEBETEGNELSE CA SI GEL

-----  
 GRUNDSTOF INTENSITET VÆGT% ,OXID  
 -----

SILICIUM 32182.0 18.94 40.52

KALIUM 192.0 0.12 0.14

CALCIUM 30211.0 19.85 27.78

OXYGEN 0.0 61.09 68.44  
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## KEMISK FORMEL

SI 10.00

K 0.04

CA 7.35

O 56.62

FIG. 12

## SEMEX-MIKROANALYSE

-----  
 DATO 30/7/75 SIGNATUR NT  
 -----

KV=16.0 TILT= 0 TAKE OFF=34  
 -----

## STANDARDBETEGNELSE OPAL

-----  
 GRUNDSTOF INTENSITET VÆGTPROCENT  
 -----

SILICIUM 83061.0 45.63  
 -----

## PRØVEBETEGNELSE CA SI GEL

-----  
 GRUNDSTOF INTENSITET VÆGT% ,OXID  
 -----

SILICIUM 31908.0 18.79 40.19

KALIUM 310.0 0.19 0.23

CALCIUM 29968.0 19.70 27.56

OXYGEN 0.0 61.33 67.99  
 -----

## KEMISK FORMEL

SI 10.00

K 0.07

CA 7.35

O 57.31

FIG. 13

## SEMEX-MIKROANALYSE

\*\*\*\*\*  
 DATO 30/7/75 SIGNATUR NT

KV=16.0 TILT= 0 TAKE OFF=34  
 \*\*\*\*\*

## STANDARDBETEGNELSE OPAL

\*\*\*\*\*  
 GRUNDSTOF INTENSITET VÆGTPROCENT

SILICIUM 83061.0 45.63  
 \*\*\*\*\*

## PRØVEBETEGNELSE CA K SI GEL

\*\*\*\*\*  
 GRUNDSTOF INTENSITET VÆGT% +OXID KEMISK FORMEL

GRUNDSTOF	INTENSITET	VÆGT%	OXID	KEMISK FORMEL
SILICIUM	60502.0	34.26	73.29	SI 10.00
NATRIUM	132.0	0.38	0.51	NA 0.13
KALIUM	2626.0	1.72	2.08	K 0.36
CALCIUM	9452.0	6.44	9.00	CA 1.32
OXYGEN	0.0	57.20	84.88	O 29.31

\*\*\*\*\*

FIG. 14

## SEMEX-MIKROANALYSE

\*\*\*\*\*  
 DATO 30/7/75 SIGNATUR NT

KV=16.0 TILT= 0 TAKE OFF=34  
 \*\*\*\*\*

## STANDARDBETEGNELSE OPAL

\*\*\*\*\*  
 GRUNDSTOF INTENSITET VÆGTPROCENT

SILICIUM 85491.0 45.63  
 \*\*\*\*\*

## PRØVEBETEGNELSE GEL IN PASTE

\*\*\*\*\*  
 GRUNDSTOF INTENSITET VÆGT% +OXID KEMISK FORMEL

GRUNDSTOF	INTENSITET	VÆGT%	OXID	KEMISK FORMEL
SILICIUM	33565.0	19.20	41.06	SI 10.00
KALIUM	700.0	0.42	0.51	K 0.16
CALCIUM	22404.0	14.38	20.11	CA 5.25
OXYGEN	0.0	66.01	61.69	O 60.37

\*\*\*\*\*

FIG. 15

Table 1 summarize typical results. Zone 1 is the broad band of calcium silicate hydrate formed inside the opal showing nearly 28 per cent of calcium oxide. In zone 2 the analysis with the maximum of potassium content was taken. Even so there is only 2 per cent potassium oxide and 0.5 per cent sodium oxide present, close to the original opal surface. The analysis in zone 3 is located in what seems to be gel-impregnated cement paste.

SEMEX ANALYSES		ZONE		
		OPAL	1	2
Na <sub>2</sub> O			0.51	
SiO <sub>2</sub>	97.60	40.19	73.29	41.06
K <sub>2</sub> O		0.23	2.08	0.51
CaO		27.56	9.00	20.11
H <sub>2</sub> O	2.40	32.02	15.12	38.31

TABLE 1

### Discussion

The results of this investigation are surprising to us and raise many more questions than easy answers. Lime rich alkali silica gels and reaction zones have always been subject to discussions. Words like »safe gel», »boundary layer», »semipermeable membrane» and »competitive diffusion» are brought into mind. Our results are not complete enough to form basis for an extension of the understanding of the alkali silica reaction but a theory should be able to explain the observed phenomena to be generally accepted.

It is expected that the calcium ion concentration in the pore liquid of our sample was very low due to the high alkali-content, and why calcium is found in so high concentration in the reaction zone instead of sodium or potassium is the key question.

Recently Hirche [2] showed enrichment of calcium in the surface of flint embedded in mortar and exposed to a strong sodium and potassium hydroxide solution.

Hirche suggested that the transport of ions into silica grains takes place through two distinct fundamental mechanisms. In large and middle-sized pores solvated ions can enter, retaining their hydration hulls, and migrate to the inner pores according to differences in chemical potential. In small pores or along lattice defects, ions can enter only after being at least partly stripped off their hydration hulls. Taking into consideration the occupancy of the lattice boundary surfaces with silanol groups, Hirche suggested a possible transport mechanism to exist resembling the conduction mechanism of protons in water.

The full implication of the last mechanism we tentatively speculate is the possibility of a much faster transport of ions into silica than diffusion suggests.

In 1950 Jones and Vivian [3] detected dark rim zones about 50 microns thick formed just inside the surface of their reacting opal grains as early as after 4 days. Jones and Vivian reported that the width of these rims did not increase substantially after their initial formation and attributed them to a secondary calcium-bearing reaction product thought to be formed between the primary reaction product and the hydrated cement paste.

Exactly when the rim seen in the present investigation was formed, and whether the rim would have grown progressively inward from the periphery of the opal cylinder, by further moist curing, or not, can not be stated with any degree of certainty. The sample represents but a single point in time of the reaction history with a given set of experimental parameters. However, our quantitative microanalyses show beyond doubt the occurrence of a calcium silicate hydrate with a molar calcium to silicon ratio around 0.8:1. This calcium silicate hydrate occurs as a 50 to 150  $\mu\text{m}$  wide reaction zone on opal embedded in cement paste.

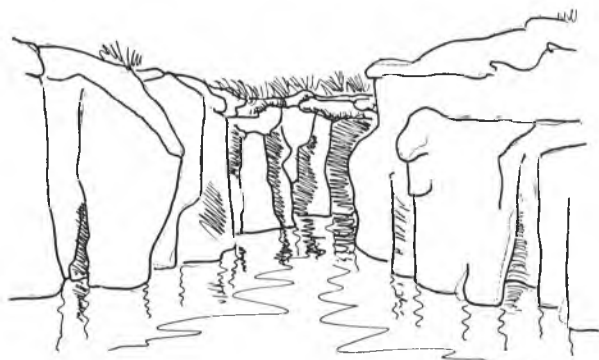
Expansion tests with mortar mixed with the same cement and crushed fractions of the same opal showed large expansion and cracking after 1 month by the method described by Diamond and Thaulow [4].

### Conclusion

The observation of the present investigation of a broad reaction zone of calcium silicate hydrate on opal in cement paste combined with our recent findings [1] of up to 20 per cent calcium oxide in gel deposited in cracks in concrete, call for a reexamination of the role of the calcium ion in the alkali-silica reaction.

Litterature

- 1) Knudsen, T. & Thaulow, N.: »Quantitative Microanalyses of Alkali-Silica Gel in Concrete», *Cement and Concrete Research*, 5(1975):5
- 2) Hirche, D.: »Die Alkali-Kieselsäurereaktion», Rheinisch-Westfälischen Technischen Hochschule, Aachen 1972, 355 pp.
- 3) Jones, R. H. & Vivian, H. E.: »Studies in Cement-Aggregate Reaction — IX: Some Observations on Mortar Containing Reacting Aggregate», CSIRO, Melbourne 1950, p. 1 - 12 — Series: Bulletin No. 256
- 4) Diamond, S. & Thaulow, N.: »A Study of Expansion Due to Alkali-Silica Reactions as conditioned by the Grain Size of the Reactive Aggregate», *Cement and Concrete Research*, 4(1974):4, p. 591 - 607



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Aug. 75 G. L. W.