Hanne Krogh

Examination of synthetic alkali-silica gels.

Summary: In this project an investigation of the litterature accordingly to some factors which have an influence on the expansion is carried out. Moreover is given the composition of alkali-silica gels in concrete. The analyses are selected from the litterature.

From the litterature is mentioned results of the viscosity, the deformation and the volume of Na_2O-SiO_2 gel stated as a function of the water content of the gel.

In this project measurements of the water content of gels in equilibrium with a definite relative humidity for gels from the systems Na_2O-SiO_2, K_2O-SiO_2 and Na_2O-CaO-SiO_2 are carried out. The atmospheres chosen were 0.60 RH, 0.86 RH, 0.90 RH and 0.97 RH.

PREFACE

The examination of synthetic gels is carried out on the Danish Academy, Department of Chemistry and Engineering. The examination has been supported financial from the Danish Council for Scientific and Technical Research and from the Academy for Scientific and Technical Research.

I will like to thank for the financial support from the two foundations and for advice from the concrete laboratory Karlstrup and the Danish Academy, Department of Civil Engineering.

Hanne Krogh

REACTION OF SILICA AND ALKALIES

INTRODUCTION.

The cracking of concrete caused by alkali-silica reaktion is well known but the mechanism who causes it and the factors which determine the expansions are not well explained.

Expansion of concrete can be prevented if the aggregates not include reactive material as porous flint or opal or if the content of alkalies in the concrete is of a limited amount. Examinations in Germany (ref. 1) have shown that expansion of concrete will not occur if the content of alkalies is less than 3 kg Na_2O per cubic meter concrete. Expansion can also be prevented by using pozzolanes. Mixtures of pozzolanes-cement with maximum 35 per cent pozzolanes are used in U.S.A. (ref. 2).

Prevention of alkali-silica reaction by using not reactive aggregates will be difficult because of a limited amount of these materials. Lowering of alkalies in concrete means a lowering of the content of alkalies in the cement which will result in a higher price of the cement (for example is danish low alkali-sulphate resistant cement (Na_2O - eqv: 0-0.5%) more expensive than danish portland cement (Na_2O - eqv: 0.6-1%))

Addition of pozzolanes to danish cement will involve a marketing of a special cement and import of pozzolanes. (Blastfurnace slags are used in U.S.A. and Germany). Those things mentioned above will cause a higher price of the cement.

Use of road salt as NaCl can lead to an increasing possibility of alkali-silica reaction in concrete.

It is therefore of interest to identify the decisive factors for a destructive reaction in concrete and then to give preventive measures in an inexpensive way.

The aim of this project is an examination of synthetic gels with same compositions as alkali-silica gels in concrete (see table 1).

Measurement of water adsorption and viscosity of the gels will be carried out because they have a great influence on the size of expansion of concrete. The water adsorption is measured as the water content of the gels at equilibrium with a definite humidity (as for example 0.60 RH, 0.86 RH, 0.90 RH and 0.97 RH). The gels are taken from the systems $CaO-Na_2O-SiO_2$, Na_2O-SiO_2 and K_2O-SiO_2. The results of water adsorption are mentioned in p. 20. The report includes a short summary concerning to factors influencing the reaction of alkali-silica p. 2. Careful investigations of the litterature are done by S. Diamond (ref. 3) and D. Hirsche (ref. 4).

Factors which have an influence on the expansion are mentioned in p. 4 . Thorough examinations of factors influencing the expansion are done in Germany 1973 (ref. 1).

Properties of alkali-silica gels are summarised at p.10. The results from water adsorption are summed up at p. 18-20.

REACTION OF REACTIVE MATERIAL AND ALKALIES.

When the alkali-silica reaction has taken place in concrete the porous flint in the aggregates is complete converted to gel. Dense flint has only a reaction rim (ref. 5).

Experiments with opal (amorphous SiO_2, nH_2O) and with porous flint show that these materials are strongly attacked by base (ref. 1). The OH-ion breakes down the SiO_2-skeleton:

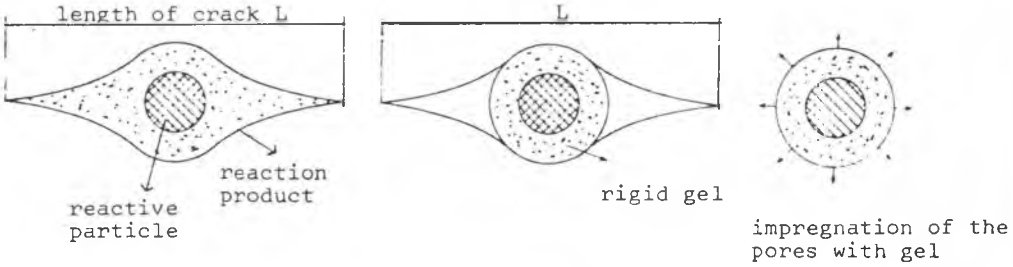
$$\equiv Si - O - Si \equiv + OH^- \rightarrow \equiv Si - O^- + HO - Si \equiv$$

The reaction rate depends on the amount of broken bonds in the lattice, on the available surface and on the pH of the pore fluid. (Opal is attacked faster than quartz because of the greater amount of broken bonds in opal than in quartz, and porous flint reacts faster than dense flint because of the greater surface). With increasing pH the solubility of SiO_2 increases. (Amorphous SiO_2 has a solubility of 500 ppm at pH = 10 and of 2.000.000 ppm (extrapolated) at pH = 13 (ref. 3). pH is about 13.4 in cement paste, when the cement has a high content of alkalies and about 12.5 when the cement has low to moderate content of alkalies (ref. 3)).

EXPANSION OF CONCRETE.

The cracking of concrete is due to the precipitation of a compound as e.g. $Na_2O, SiO_2 \cdot 9H_2O$ (ref. 6) or to the development of a gel. The gel takes in water and produces a pressure twice the tensile strength of concrete and creates a crack (ref. 7).

The crack will expand if the reaction products react with water and will then produce a sufficient pressure to extent the length of the crack. This necessary pressure (ref. 7) is descending ($\Longleftrightarrow \frac{dp}{dl} < 0$) when the reaction products are so viscous that they fill the crack without impregnating the cement paste (see fig. 1a).



a. Viscous reaction product $\Rightarrow \frac{dp}{dl} < 0$

b. Rigid reaction product $\Rightarrow \frac{dp}{dl} > 0$

c. Fluid reaction product $\Rightarrow dp = 0$

Fig. 1. The significance of the properties of the reaction products to the necessary pressure to increase the cracking.

This pressure increases ($\Longleftrightarrow \frac{dp}{dl} > 0$) when the reaction products are stiff and are not able to fill the crack completely (see fig. 1b). No pressure can be produced when the reaction products are fluid. They are then forced into the cement paste (see fig. 1c).

The viscosity of the reaction products is a function of the composition (as the weight ratio Na_2O/SiO_2) and of the water content (see p. 11-12).

From practice it is well known that the following factores have an great influence on the expansion:

a) The proportion of alkalies and reactive material.
b) The size of reactive material.
c) The amount of available water.
d) The temperature of concrete.

a The extent of expansion depends on the proportion of alkalies and reactive materials. Fig. 2 shows the effect of this proportion on the expansion.

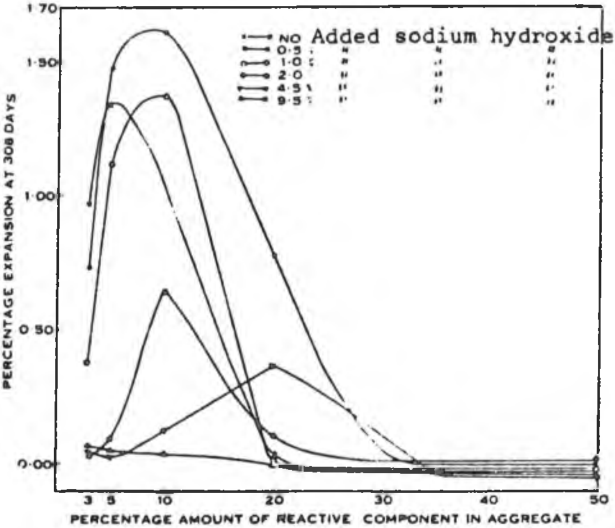


Fig. 2. The effect of the amount of reactive component in the aggregates on the expansion of motars containing various amounts of added sodium hydroxide (ref. 8).
(The cement used contained 0.50 wt % Na_2O and 0.14 wt % K_2O).

A small expansion will occur when the amount of alkalies is high in proportion to the amount of reactive material (e.g. 3-5 wt % reactive material and 4.5-9.5 wt % added NaOH in fig. 2). The explanation for this small expansion could be (ref. 8) that silica and alkalies react rapidly and form a product with a high mole ratio Na_2O/SiO_2. This reaction product adsorbs water and transforms by this to a fluid which penetrates into the mortar around the crack. No pressure is produced (see fig. 1c). Much reactive materials in the aggregates and a little amount of alkalies cause a small expansion (e.g. 20 wt % reactive material and 2 wt % added NaOH in fig. 2). In this case a great surface of silica can react with proportional small amount of Na^+-ions. Therefore the reaction product has a low mole ratio Na_2O/SiO_2 and the product is rigid (as in fig. 1b) causing a small expansion. Great additions of reactive material and of NaOH give a small expansion (see fig. 2). A lot of reaction product is produced but the product is rigid because of lack of water (ref. 8). The rigid product (as in fig. 1b) causes a small expansion.

Addition of sufficient pozzolanes decreases the expansion (ref. 2). The pozzolanes use up the alkalies without causing an expansion (ref. 3). Another hypothesis is that the pozzolanes increase the porosity of the mortar giving room for a greater volume (ref. 3).

b The dependence of concrete on the size of reactive material is shown in fig. 3. Experiments (ref. 9) indicate that the expansion increases down to a size of 20 µm of the reactive material. A very small size of reactive material causes the reaction to take place when the concrete is fresh and no expansion will occur.

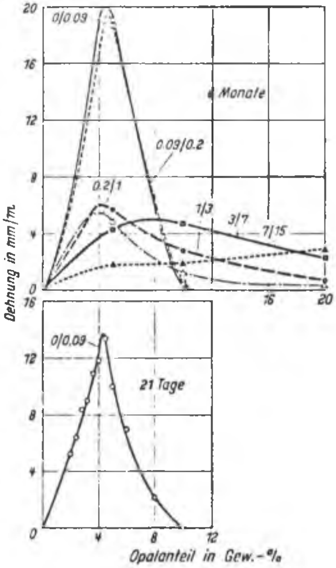


Fig. 3.

The effect of amount and size of reactive component in the aggregates on the expansions of concrete (ref. 1).

c The amount of available water effects as well the expansion (fig. 4). The reaction products take in water which is resulting in an expansion of the mortar.

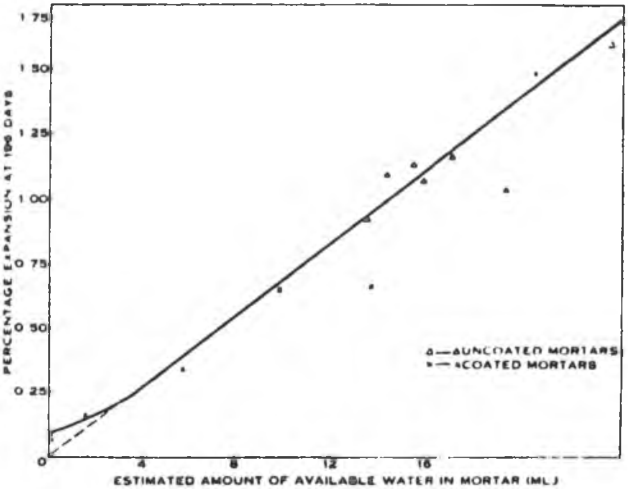


Fig. 4. The dependence of the expansions on the amount of available water in mortar (ref. 8).

d The extent of expansion depends also on the temperature of the concrete (fig. 5). The reaction rate increases with higher temperature. At a temperature rise of 10°C the reaction rate is doubled up.

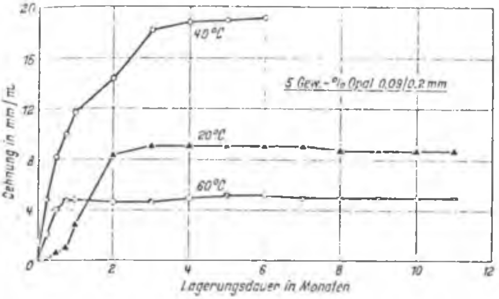


Fig. 5. The effect of the temperature of concrete on the expansion of concrete (ref. 1).

The viscosity of gels decreases at higher temperature. This can result in a smaller expansion if the reaction products get fluid (fig. 1c).

The possibility of an expansion of concrete excists, when the aggregates contain reactive material, a high content of alkalies in the cement and a moisture climate. In Iceland you have these conditions but only a little of the concrete expands in practice (ref. 2 and ref. 10). The explanation could be a low reaction rate and rigid reaction products, because of the low temperature.

ALKALI-SILICA GELS

COMPOSITION OF GELS.

The composition of alkali-silica gels found in concrete is mentioned in table 1. The gels come from the surface and the interior of the concrete. Some of the concrete has been placed close to or into the sea water.

The analyses can coarsely be classified into three groups (see table 1):

I Na_2O - SiO_2 with some K_2O
mole ratio $(Na_2O + K_2O)/SiO_2 \approx 0.3$
(analyse no 4, 7, 13 and 14).

II Na_2O - SiO_2 with a small amount of CaO
mole ratio $(Na_2O + K_2O)/SiO_2 \approx 0.2$
mole ratio $(CaO + MgO)/SiO_2 \approx 0.05\text{-}0.1$
(analyse no 1, 2, 6 and 15).

III CaO - SiO_2 with a small amount of Na_2O
mole ratio $(Na_2O + K_2O)/SiO_2 \approx 0.02$
mole ratio $(CaO + MaO)/SiO_2 \approx 0.2$
(analyse no 3).

A part of the gels belongs to intermediate groups.

Gel no.	Na_2O		K_2O		SiO_2		CaO		MgO		mole(CaO+MgO)/ mole SiO_2	mole(Na_2O+K_2O)/ mole SiO_2	Ref.
	wt %	mole %	wt %	mole %	wt %	mole %	wt %	mole %	wt %	mole %			
1	12.9	0.208			53.86	0.895	2.90	0.05	0.58	0.01	0.067	0.232	(12)
2	12.8	0.205			53.40	0.89	2.62	0.05	0.85	0.02	0.079	0.23	(12)
3	1.30	0.02	19.00	0.20	66.00	1.10	11.54	0.21	0.00		0.19	0.02	(13)
4	13.5	0.21	5.7	0.06	47.8	0.80						0.35	(14)
5	4.0	0.06	2.0	0.02	81.9	1.37	1.1	0.02			0.02	0.06	(11)
6	12.7	0.2	4.5	0.05	53.4	0.89	4.7	0.08			0.10	0.28	
7	19.9	0.32	6.5	0.07	58.7	0.98						0.40	
8	14.9	0.24	5.2	0.06	61.7	1.03	0.6	0.01			0.01	0.29	(15)
9	13.4	0.22	5.12	0.05	65.5	1.09	0.5	0.009	0.21	0.005	0.01	0.24	
10	12.4	0.20	4.9	0.05	69.9	1.16	0.3	0.005	0.5	0.01	0.02	0.22	
11	17.9	0.29	8.2	0.09	73.7	1.23	1.1	0.02	0.1	0.002	0.02	0.31	
12	9.4	0.15	4.1	0.04	72.8	1.21	1.3	0.02	0.2	0.005	0.02	0.16	
13	14.6	0.24	6.2	0.07	61.9	1.03			0.1			0.31	
14	16.2	0.26	5.7	0.06	56.8	0.95						0.34	
15	11.4	0.18	6.0	0.06	76.7	1.28	3.3	0.06			0.05	0.19	
16	8.2	0.13	4.1	0.04	56.1	0.94	17.4	0.31	0.2	0.004	0.33	0.18	
17	8.3	0.13	5.0	0.05	28.5	0.47	22.4	0.40	0.2		0.85	0.38	
18	0.15	0.002	0.53	0.005	33.2	0.55	58.0	1.04			1.88	0.001	(16)
19	0.22	0.003	2.59	0.02	38.8	0.64	47.6	0.85			1.31	0.04	
20	3.48	0.05	6.96	0.07	63.00	1.05	15.00	0.27	0.44	0.01	0.27	0.11	(17)
21	1.04	0.02	6.64	0.07	56.90	0.94	17.66	0.32	0.15		0.34	0.10	

Table 1. The composition of the alkali-silica gels taken from different references.

STRUCTURE AND PROPERTIES OF ALKALI-SILICA GELS.

The molecular weight of alkali-silicates. In aqueous solutions of alkali silicates the Si^{+4}-ion is coordinated with 6 OH^--ions (ref. 18). In solutions of sodium silicates with a mole ratio SiO_2/Na_2O = 1 only the monomer ($Na_2Si(OH)_6$) exists. Increasing the mole ratio monomer, dimer and polymer are present but in solutions of sodium silicate with a mole ratio SiO_2/Na_2O = 1 → 3.3 and at pH > 10.8 only the monomer of H_2SiO_3 exists (ref. 19). Polymerzation will even take place in thin solutions (concentration below 0.05 g/cm^3) of sodium silicate with a mole ratio SiO_2/Na_2O = 3.9. The molecular weight raises to 10.000 (ref. 20).

In solutions (conc. < 0.1 g/cm^3) of sodium silicates (mole ratio SiO_2/Na_2O = 3.3) the molecular weight is 320 found by experiments (ref. 19 and ref. 20). The molecular weight of $Na_2Si(OH)_6$ is calculated to 176 and the molecular weight of $H_2Si(OH)_6$ is calculated to 132. Solutions of sodium silicates with a mole ratio SiO_2/Na_2O = 3.3 is thought to consist of one part of $Na_2Si(OH)_6$ and 2.3 parts of $H_2Si(OH)_6$. The calculated molecular weight of this solution is then 146.

The molecular weight of solutions of potassium silicates with a mole ratio SiO_2/K_2O = 3.3 is found by experiments to 495 (ref. 18). The molecular weight of $K_2Si(OH)_6$ is calculated to 208 resulting in a calculated molecular weight of potassium silicate (mole ratio SiO_2/K_2O = 3.3) of 155.

It can be concluded from the calculations that some polymerization has taken place as the calculated molecular weights are smaller than the molecular weights found be experiments.

Gels prepared from solutions of sodium silicates with a mole ratio SiO_2/Na_2O = 3.35 are composed of small particles of polymers of SiO_2. Each particle contains 2-5 units SiO_2 (ref. 21).

pH of solutions of alkali silicates. pH increases in these solutions with the mole ratio and with the concentration. pH of solutions of Na_2O-SiO_2 (ref. 18) is:

mole ratio SiO_2/Na_2O	weight ratio SiO_2/Na_2O	Na_2O wt %	SiO_2 wt %	pH	η P at 20 °C
1.65	1.60	19.5	31.2	12.8	70
2.06	2.00	18.0	36.0	12.2	700
2.58	2.50	10.5	26.3	11.7	0.5
2.99	2.90	11.0	31.9	11.5	9.6
3.32	3.22	8.9	28.7	11.3	1.8
3.87	3.75	6.8	25.5	10.8	2.2

Table 2. pH and the viscosity of solutions of Na_2O-SiO_2 (ref. 18).

pH of solutions of K_2O-SiO_2 (ref. 18) is:

mole ratio SiO_2/K_2O	weight ratio SiO_2/K_2O	K_2O wt %	SiO_2 wt %	pH	η P at 20 °C
2.83	1.80	16.4	29.5	12.15	13.0
3.30	2.10	12.5	26.3	11.70	10.5
3.45	2.20	9.05	19.9	11.55	0.07
3.92	2.50	8.3	20.8	11.30	0.4

Table 3. pH and the viscosity of solutions of K_2O-SiO_2 (ref. 18).

The pore structure of gels depends on pH (ref. 22).

pH	V_s	O_H	r_{av}
	cm^3/g	m^2/g	Å
3	39	57	21.2
5	102	73	43.9
7	235	117	62.2
8	202	98	69.6
10	43	14	97.8

Table 4. The surface area and the average pore size of the silica gels.

V_S : adsorbed amount of N_2 at saturation.

O_H : surface area calculated from the adsorption isotherm.

r_{av}: the average pore radius. The maximum of the curve $\frac{dV}{dr}$ drawn as a function of r represents the average pore size. The curve $\frac{dV}{dr}$ comes from the adsorption isotherm (V as function of r) by differentiation of the isotherm

The gels in table 4 are prepared from a solution of potassium silicate (weight ratio SiO_2/K_2O = 1.7). The gels are precipitated from the solution at 20 °C by use of 2N H_2SO_4 at different pH. The gels are washed with 3 l water and dried at 120°C. The starting solutions had a concentration of SiO_2 of 0.7 mole/l.

The viscosity of the gels is a measure of the mechanical resistance which determines the size of expansion (see fig. 1 p. 3).

v/t	Na_2O	η ved 20 °C
g water/g dry gel	wt %	Poise
1.80	8.25	1
1.72	8.50	3
1.64	8.75	7
1.57	9.00	20
1.50	9.25	160
1.43	9.50	1000

Table 5. The viscosity of gel with a mole ratio Na_2O/SiO_2 = 0.29 (ref. 20).

The figures in table 5 originate from curves, showing the viscosity as a function of water content, and the reading of these curves makes it only possible to mention the viscosity with two ciffers.

The mechanical resistance of gels is measured in ref 23. These measurements are carried out on blocks of gels with a thickness of 2.5 mm.

v/t	Load	Deformation	Volume of gel
g water/g dry gel	g/cm^2	cm	cm^3
2.61	30	0.175	1.26
1.82	300	0.107**	1.02
1.35	6000	0.099**	0.75
1.25	500	0.109**	0.78
0.71			0.55
0.42	6000	0.064***	0.41
0.35	6000	0.015***	0.40
0.29	6000	0.000***	0.30
0.16	6000	0.000***	0.26
0.09*	-	-	0.21

* At this water content the material is a white, opaque solid, not a clear gel.

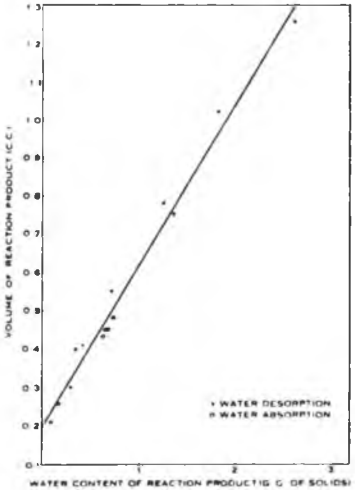
** Flowed very slowly and cracked under high loads.

*** Cracked without flowing.

Table 6. The correlation of water content in gels with the volume and the mechanical resistance of the gels (ref. 23).

The gels in table 6 consist of Na_2O and SiO_2. The definite composition is not given but the mole ratio SiO_2/Na_2O of the gels used (in ref. 23) varies between 5 to 6.

The volume of gels depends on the water content of the gels. In fig. 6 the water content (v/t) is given as g water per g dry gel.



start point: 1.26 cm^3 gel
with a weight 1.56 g
and a content of solid of 0.4329 g

Fig. 6. The dependence of the volume of reaction product on the water content (expressed as g water per g dry material).

The greatest expansion occurs when the gels fill the crack completely with out impregnating the mortar (see fig. 1a p 3). Gels with a mole ratio Na_2O/SiO_2 = 0.29 and a water content (v/t) smaller than 1.57 have a viscosity (table 5) as 100 % glycerol (or 15 P). These gels will probably behave as the reaction product shown in fig. 1a. Gels with a mole ratio Na_2O/SiO_2 = 0.20 to 0.17 and a water content (v/t) higher than 0.70 flow under load, with a smaller water content the gels crack without been deformed. One could therefore expect the maximum expansion when water content is between 0.70 and 1.57 of gels with the composition mentioned above. (The gels in table 5 and the gels in table 6 have probably not the same composition but you must ignore it because no measurements of the viscosity of the gels in table 6 exist).

Osmotic pressure. Measurement of the osmotic pressure of a 38 wt % (v/t = 1.63) solution of sodium silicate (mole ratio Na_2O/SiO_2 = 0.29) gives 550 psia (or 39 kp/cm^2). (ref. 11). The maximum pressure measured with the used apparatus was developed within 4 days. The development of pressure seemed not to have ceased yet.

Pressure of 2100 psia (or 148 kp/cm^2) is measured in cement paste with opal (ref. 24). The cement contained 1.10 wt % Na_2O and 0.9 wt % K_2O. 4 g opal (size between 0.84-1.19 mm) was added to the cement paste (v/c = 0.4).

The tensile strength of standard mortar prisms of portland cement is 70 kp/cm^2 after 28 days (ref. 25). The developed pressure can twice exceed the tensile strength of mortar and the possibility of the formation of a crack exsists.

EXPERIMENTS.

In this project the water adsorption and the viscosity of some synthetic gels from the systems Na_2O-SiO_2, Na_2O-CaO-SiO_2 and K_2O-SiO_2 are measured. The water adsorption is a measure of the swelling properties of the gels and thereby indicates the possibility of producing a pressure and the viscosity of the gels is a measure of the mechanical resistance.

COMPOSITION OF SYNTHETIC GELS.

The composition of synthetic gels (in table 7) are chosen from the knowledge of analyses of gels (see table 1).

COMPONENTS/TYPE OF GEL→	Na_2O-(CaO)-SiO_2	Na_2O-SiO_2	K_2O-SiO_2	(Na_2O)-CaO-SiO_2	(Na_2O)-(CaO)-SiO_2
SiO_2	1 mol	1 mol	1 mol	1 mol	1 mol
CaO	0.03 mol			0.3 mol	0.03 mol
Na_2O	0.3 mol	0.33 mol		0.03 mol	0.03 mol
K_2O			0.33 mol		

Table 7. The desired composition of the synthetic gels.
(The real composition of the gels in table 8).

PREPARATION OF GELS.

Preparation method. The gels are prepared by ion exchange of a solution of sodium silicate (100 g Na_2O, SiO_2, $9H_2O$ i 1 l water) through an ion exchanger on H^+-form. The amount of K_2O is added as a solution of KOH and the amount of CaO as a solution of $Ca(OH)_2$.

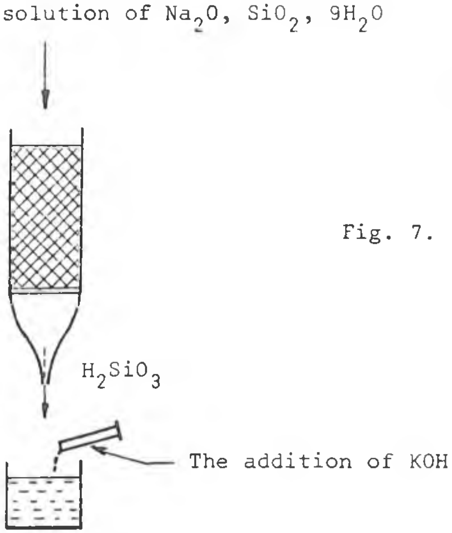


Fig. 7. The preparation of K_2O-SiO_2 gel.

The solutions are evaporated at 60°C under constant stirring untill a jelly-like mass appears.

The K_2O-SiO_2 gel and the Na_2O-SiO_2 were clear all the time (table 8). The gel of Na_2O-(CaO)-SiO_2 became cloudy in time. Immediately after addition of $Ca(OH)_2$-solution the gel of (Na_2O)-(CaO)-SiO_2 and of (Na_2O)-CaO-SiO_2 were unclear. The gels marked I, II, III and IV (table 8) are evaporated with the supply of N_2 to avoid carbonation of the gels.

Composition of gels. The gels are analysed for SiO_2, Na, K and Ca (table 8). SiO_2 is determined by gravimetry (described in Appendix I). The method of decomposition of gels is given in Appendix II. Na and K are analysed by flame fotometry (apparatus PE 305). As standard solution are respecktively used a solution of NaCl (conc. 1000 ppm) and a solution of KCl (conc. 1000 ppm). Ca is analysed by atomic absorption (apparatus PE 305). As standard solution is used a solution of $CaCO_3$ (conc. 500 ppm).

TYPE	COMPOSITION (mole ratio)			PREPARATION		APPEREANCE	WATER ADSORPTION			
MRK:	Na_2O/SiO_2	K_2O/SiO_2	CaO/SiO_2	pH of starting solution	g water per cent dry gel		0.60 RH (NH_4NO_3)	0.86RH (KCl)	0.90 RH ($BaCl_2,2H_2O$)	0.97 RH (K_2SO_4)
A K_2O-SiO_2	0.029	0.29	i.m.	11.7→10.7	96 %					
F "	i.m.	0.31	i.m.	10.9	244 %	CLEAR	36.8(8dg)	51.0(13dg)	74.4(12dg) 69.4(13dg)	357(13dg) 244(10dg)
IV "	i.m.	0.31	i.m.	i.m.	149 %	CLEAR	34.8(10dg)	57.2(10dg)	79.9(10dg)	247(10dg) 224(17dg)
B Na_2O-SiO_2	0.31	i.m.	i.m.	11.6→10.7	66 %					
I "	0.29	i.m.	i.m.	11.2	92.7 %	CLEAR	27.9(8dg)	38.1(13dg)	50.9(13dg)	250(13dg)
K "	0.28	i.m.	i.m.	10.8	203 %				78.5(24dg)	243(11dg)
III "	0.40	i.m.	i.m.	10.9	185 %	A LITTLE CLOUDY	37.4(10dg)	58.1(10dg)	78.4(17dg)	208(24dg) 217(17dg)
D Na_2O-(CaO)-SiO_2	0.33	i.m.	0.025	11.1→11.2						
J "	0.40	i.m.	0.027	10.3→10.9	337 %	A LITTLE CLOUDY			87.7(12dg)	248(11dg)
II "	0.35	i.m.	0.039	10.8	411 %	WHITE, OPAQUE	31.3(10dg)	43.9(10dg)	58.3(10dg)	212(17dg) 207(8dg)
C CaO-(Na_2O)-SiO_2	0.010	i.m.	0.79	i.m.	5800 %					
E "	0.019	i.m.	0.44	i.m.	3.7 %					
I "	0.047	i.m.	0.32	10.6	2887 %	HETEROGENOUS, CLOUDY	8.2(24dg) 23.1(16dg)	27.3(24dg)	52.3(10dg)	120(24dg) 143(17dg)
H (CaO)-(Na_2O)-SiO_2	0.048	i.m.	0.031	i.m.	1270 %	HETEROGENOUS, CLOUDY	40.6(41dg)	53.0(48dg)	75.6(52dg) 85.2(52dg)	122(51dg) 152(80dg)

i.m.: not measured

dg : days

Table 8. Composition of the prepared gels.

The water content of gels after preparation. The water content is determined as the weight loose after drying in a heating chamber at 120°C at least in a couple of days. The water content in table 8 is given as g water per 100 g dry gel.

WATER ADSORPTION.

The measurements of the water adsorption of gels are carried out at 25°C at different humidities (table 9). The different atmospheres are obtained by use of saturated salt solution.

RH	°C	salt
0.60	25	NH_4NO_3
0.86	"	KCl
0.90	"	$BaCl_2$, $2H_2O$
0.97	"	K_2SO_4

Table 9. The relative water pressure of saturated salt solution (ref. 26).

Samples of the gels are placed in a desiccator with saturated salt solution in the bottom and with a stirrer at the top. (fig. 8). The same humidity is obtained all over the desiccator by covering the sides with a filter paper dipping into the salt solution.

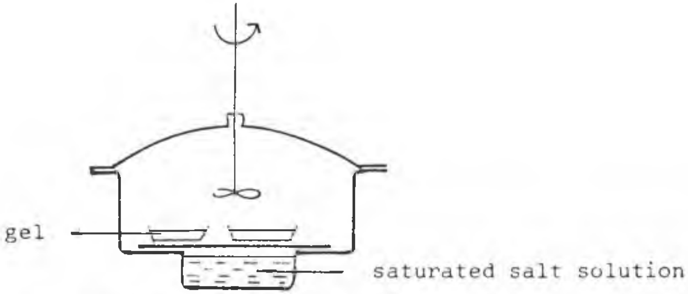


Fig. 8. The desiccator used to water adsorption.

The results are given in table 8, table 10 and Appendix III.

TYPE OF GEL	COMPOSITION mole ratio			WATER ADSORPTION g water per 100 g dry gel			
	K_2O/SiO_2	Na_2O/SiO_2	CaO/SiO_2	0.60 RH	0.86 RH	0.90 RH	0.97 RH
K_2O-SiO_2 (F + IV)	0.31(0)			36(1)	54(3)	75(3)	276(29)
Na_2O-SiO_2 (I+K+III)		0.32(0.04)		33(5)	48(10)	69(9)	230(10)
Na_2O-(CaO) -SiO_2 (J+II)		0.38(0.03)	0.033 (0.006)	31(e.m.)	44(e.m.)	73(15)	222(13)
(Na_2O)-CaO-SiO_2		0.047 (e.m.)	0.32 (e.m.)	16(7)*	27(e.m.)	52(e.m.)	132(12)
(CaO)-(Na_2O)-SiO_2		0.031 (e.m.)	0.048 (e.m.)	41(e.m.)	53(e.m.)	80(5)	137(15)

The ciffer in parenthesis gives the standard deviation of the average of the measurement ($s_{\bar{x}}$).

e.m. : single measurement

* see Appendix III-3.

Table 10. Composition and water content of the gels.

In appendix III the water contents are given as a function of time. The average water content is stated in table 10 and in table 8 a single measurement of the water content after a definite time is mentioned.

The small reproducibilities (the relative standard deviations in some case greater than 10 %) are due to variations of the composition of the gels and to carbonation of the gels in the desiccator. The K_2O-SiO_2 carbonates easily and becomes cloudy.

Experiments with removal of CO_2 frem the air were carried out. The air was bubbled through a circulating KOH solution (40 wt %) but is was not enough to avoid carbonation of K_2O-SiO_2 gel at 0.90 RH.

In appendix III is mentioned the time when gels become cloudy. A carbonation of gels cause a smaller water content.

In fig. 9 the water content of gels is shown as a function of relative humidity. The results are mainly obtained by desorption (see the water content of gels at preparation in table 8).

Equilibrium is obtained within 14 days for the gels of Na_2O-SiO_2, K_2O-SiO_2 and $(Na_2O)-(CaO)-SiO_2$ (see appendix III). Equilibrium is hardly not obtained for the gels of $(Na_2O)-(CaO)-SiO_2$ and $(Na_2O)-CaO-SiO_2$ within 50 days (see appendix III).

DISCUSSION

Adsorption isotherms. At 0.86 RH the adsorption isotherm strongly ascends due to condensation of water in the capillary pores. The size of these pores is calculated from the KELVIN equation:

$$\ln \frac{p_1}{p_o} = \frac{2M \cdot \gamma}{R \cdot T \cdot \rho \cdot r}$$

p_1 : the water vapour pressure across a curved surface.
p_o : the water vapour pressure across a plane surface.
M : molecular weight (g/mol)
γ : the surface tension of water (dyn/cm)
R : gas constant (erg/mol K)
T : temperature (K)
ρ : density (g/cm^3)
r : radius (cm)

For water at 25°C are $M = 18$ g/mol, $\gamma = 71.97$ dyn/cm and $\rho = 0.997$ g/cm^3.
$R = 8.31 \cdot 10^7$ erg/mol K.

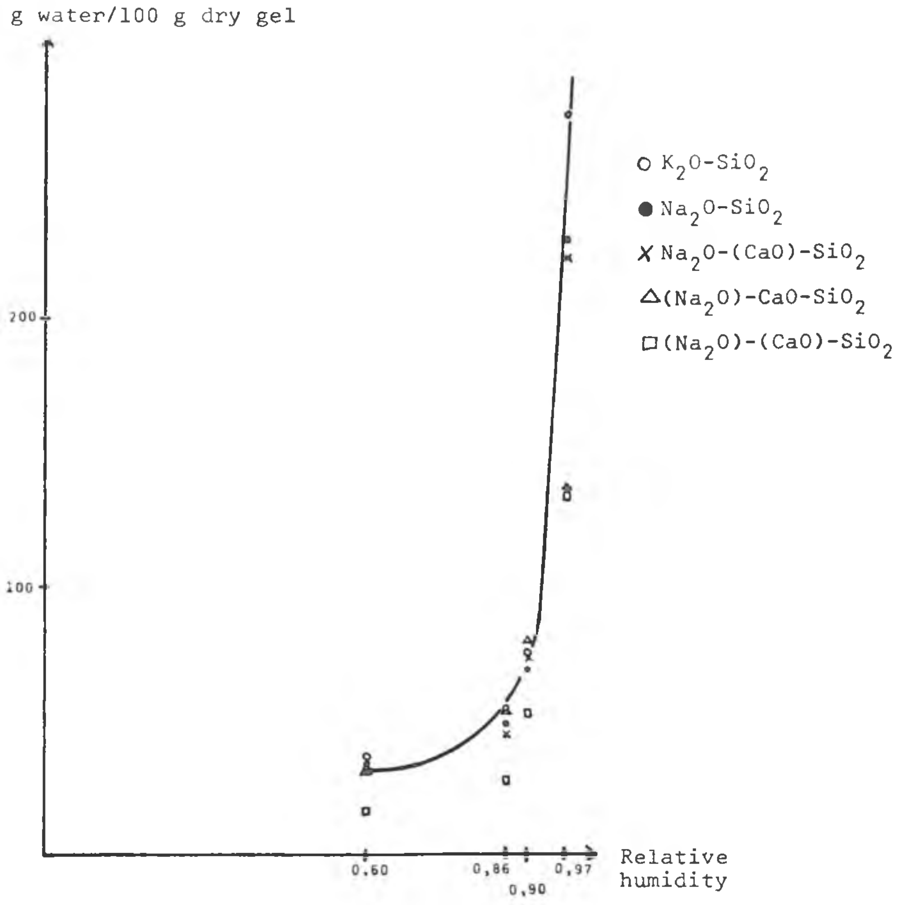


Fig. 9. The water content in gels at equilibrium as a function of relative humidity.

Relative humidity RH	The pore radius (r) Å
0.60	20
0.86	69
0.90	99
0.97	340

Table 11. Calculated pore radius from KELVIN equation.

The curves (fig. 9) indicates a great amount of coarse pores in gels of $(Na_2O)-(CaO)-SiO_2$ and of $(Na_2O)-CaO-SiO_2$. These two types of gels can be considered as inert accordingly to the water vapour as they looked dry and were rigid even at a high relative humidity opposite the other types of gels.

The average pore radius of SiO_2 gel varies with the method of preparation (table 12).

Name of silica gels (SiO_2)	The average pore radius Å	Ref.
"Aged" silica gel	r > 400	27
Fresh gel	13-24	
	60-134	
silica gel E	200	28
" BXK	100	
" B-300	85	
" K	80	
" 21	70	

Table 12. The average pore radius of silica gels taken from different references.

Comparing these above mentioned results with the results in table 4 there is an indication of a high pH causes a great amount of coarse pores. This makes the great amount of coares pores in the synthetic gels probably.

The magnitude of the water content of gels of $(CaO)-(Na_2O)-SiO_2$ and of gels of $(Na_2O)-CaO-SiO_2$ at saturation is the same as in fig. 10.

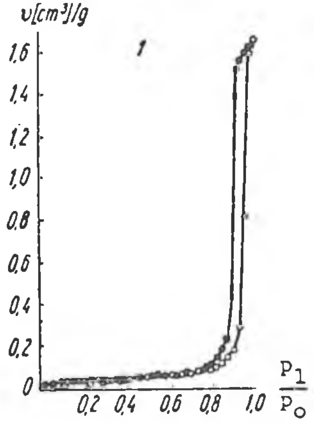


Fig. 10. The water adsorption isotherm of silica gel E (ref. 28).

From above mentioned it is possible that the gels of $(Na_2O)-(CaO)-SiO_2$ and of $(Na_2O)-CaO-SiO_2$ only adsorb water without reacting with it.

The gels of Na_2O-SiO_2, of K_2O-SiO_2 and of $Na_2O-(CaO)-SiO_2$ react with water vapour. They are rigid at 0.60 RH and fluid at 0.97 RH. The viscosity of the gels is not measured.

The swelling properties of the gels. The gels are produced under a pressure (p) necessary to create a crack ($\Leftrightarrow p > 2 \cdot \sigma_t$ see ref. 7). When the crack is formed the pressure is relieved resulting in a sudden expansion of the gels as seen in fig. 11.

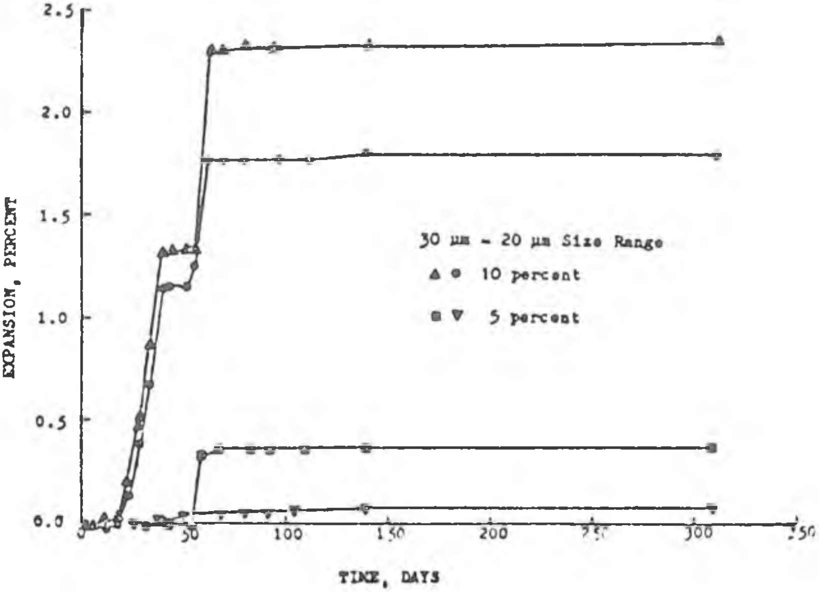


Fig. 11. Expansion vs. time for mortar mixed with 10 percent and with 5 percent of opal of size between 30 µm and 20 µm in the aggregate. Each curve represents the length change of a single specimen. (ref. 9).

The hydrostatic pressure or swelling pressure is calculated like the osmotic pressure:

$$p \cdot V_o = \div RT \ln \frac{p_1}{p_o}$$

p : swelling pressure
V_o : molar volume of the fluid (here water)
p_1 : water vapour pressure across the gel
p_o : water vapour pressure at a definite temperature(here 25°
R : gas constant
T : temperature

$$p \cdot V_o = \div RT \ln(RH)$$

RH : relative humidity

$$dp = \div \frac{RT}{V_o} \, d \ln(RH)$$

$$\Delta p = (p_1 - p_2) = \div \frac{RT}{V_o} \ln \frac{RH_1}{RH_2}$$

$$p_1 - p_2 > 0 \Longrightarrow RH_1 < RH_2$$

A reduction of the hydrostatic pressure in the gel ($p_1 \rightarrow p_2$) causes the gel to try to be in equlibrium with an atmosphere of a higher relative humidity ($RH_1 < RH_2$).

A calculation of the expansion caused by the water adsorption of the gel. The necessary pressure to crack the mortar is about twice the tensile strength (ref. 7):

$$\Delta p = 2 \cdot \sigma_t = 2 \cdot 70 \text{ kp/cm}^2 = \frac{2 \cdot 70}{1.033} \text{ atm.} = 136 \text{ atm.}$$

$$\Delta p = \div \frac{RT}{V_o} \ln RH; \ \Delta p = 136 \text{ atm.} \Longrightarrow RH = 0.90$$

When the gel is produced at 0.90 RH the water content (v/t) is about 0.70 (fig. 9) and the volume is 0.495 ml (fig. 6). The cracking of the mortar results in a relief of the pressure on the gel and the gel expands. Only the volume change to when the gel has a water content of 1.57 has an effect (see the argument on p. 14). The volume at water content of 1.57 is 0.86 (fig. 6).

The change of volume is then:

$$\frac{\Delta V}{V} = \frac{0.86-0.495}{0.495} = 0.75$$

When the expansion occurs in all directions the change of length is:

$$\frac{\Delta V}{V} \approx 3 \cdot \frac{\Delta L}{L} \Rightarrow \frac{\Delta L}{L} = 0.25$$

When the prism contains 10 vol % gel the maximum expected length change is 2.5 %. Measurements of the length change gives 3.26 %, 2.87 % and 2.13 % ($\bar{x}$ = 2.75 %) of a prism, where 10 % of the aggregates is opal in the size between 44 µm - 30 µm. The data of the mortar were v/c = 0.4 and aggregates/cement = 0.8 (ref. 9).

A calculation of the length change (theoretic).

If all the opal in the above mentioned mortar reacts and forms a gel with the composition of $Na_2O/SiO_2 = \frac{1}{3.3}$ and with the water content of the gel at 0.70 without expansion of the prism you can calculate the maximum expected expansion.

Density of the gel at the water content v/t = 0.7 (see fig. 6): $\frac{0.4329 \cdot 1.7}{0.495}$ = 1.49 g/cm^3

The amount of produced gel: $\frac{0.08 \cdot 4.3 \cdot 1.7}{3.3 \cdot 1.49}$ = 0.12 cm^3

The volume of cement: $\frac{1}{3.1}$ = 0.32 cm^3

The volume of inert material (quartz) $\frac{0.8 \cdot 0.9}{2.6}$ = 0.28

The volume of water: = 0.40

Total volume = 1.12 cm^3

vol % of the gel: $\frac{0.12}{1.12} \cdot 100 = 11$ % $\Rightarrow$ length change: 2.7 %

The example indicates that expansion can be related only to the water adsorption of the gel. The water content was changed from v/t = 0.70 (RH = 0.90) to v/t = 1.57. In the calculation I have ignored the volume change by the production of the gel but this is probably a little expansion.

CONCLUSION.

From the experiments it can be concluded that the gels of Na_2O-SiO_2, of K_2O-SiO_2 and of Na_2O-(CaO)-SiO_2 are swelling. (The gels have a great water content at 0.97 RH, fig. 9).

The gels of (Na_2O)-(CaO)-SiO_2 and of (Na_2O)-CaO-SiO_2 are not swelling because the water content of these gels is 1.3 at 0.97 RH (fig. 9). (The water content is expressed as g water per 100 g dry gel). This water content is of the same magnitude as the water content of gels at saturation mentioned in the litterature. Further these gels stayed rigid even at 0.97 RH.

It looks like that the deformation properties of gels of K_2O-SiO_2 and of Na_2O-SiO_2 are different. Measurements of these properties have not yet been carried out. Perhaps this phenomenon can explain the smaller expansion of mortar when K_2O is the dominating alkali oxids than when Na_2O is it.

From the knowledge of the water adsorption and the viscosity of gels with a known composition you are able to determine which reaction products will give an expansion and then coarsely to calculate the maximum expected expansion. Therefore when a reaction between silica and alkalies occurs you must know the composition of the reaction products before you can predict an expansion and then give advice to prevent it.

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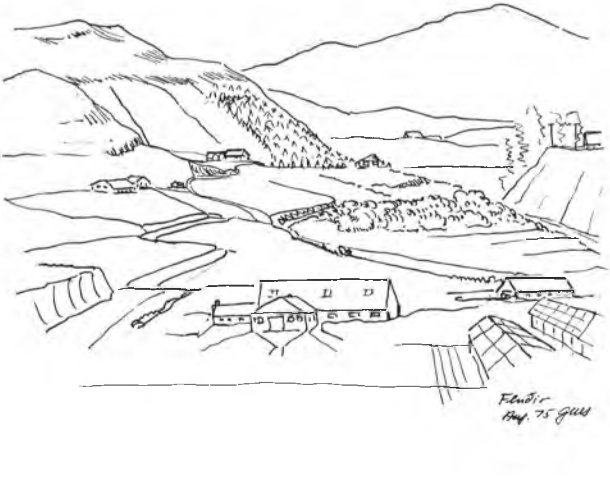
Due to lack of space Appendix I, II and III are omitted.



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