



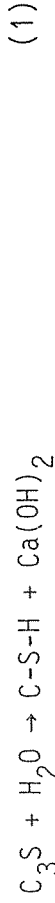
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As a result of a change from Ordinary Portland cement to blended cements, fly ash - and slag cements, in Norway, investigations have been made to compare these cements with Ordinary Portland cement. This paper presents results from investigations aiming at differences in degree of hydration, residual calcium-hydroxide, and water contents of pastes made from fly ash cement with - and without addition of condensed silica fume compared with Ordinary Portland cement. Possible effects of a plasticising agent in a cement - silica paste is discussed.

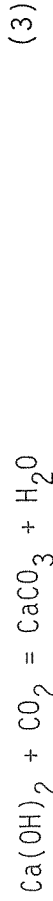
Key words: hydration, residual calciumhydroxide, water contents, cement pastes.

1. INTRODUCTION

It was of interest to examine the residual calciumhydroxide in pastes of blended cements because the pozzolanic reaction reduces the concentration of calciumhydroxide, and this reduction may be of great importance as to the durability of concrete and mortar when exposed to aggressive environments. The pozzolanic reaction (2) may simplified be written x



If the concrete is exposed to carbondioxide, the reduced contents of calcium-hydroxide in blended cements are still more reduced according to the reaction between calciumhydroxide and carbondioxide



and this may mean a reduced capacity of protecting the reinforcement against corrosion from blended cements compared with Ordinary Portland cement. If the concrete is exposed to sulphate attack, the reduced calciumhydroxide contents of a blended cement may be an advantage.

x cement chemistry nomenclature is used for C = CaO, S = SiO₂, A = Al₂O₃

2. TEST SPECIMENS AND PROCEDURE

The cements, which were used in this work, were produced and delivered by A/S NORCEM, and the condensed silica fume was supplied from Elkem a/s.

The chemical composition of the materials, according to the manufacturers, are given in TABLE 1.

Following mixtures were investigated,

1. Ordinary Portland cement 1)
2. Fly ash cement (10% fly ash) 2)
3. Fly ash cement (25% fly ash) 3)
4. 95% Ordinary Portland cement + 5% condensed silica fume
5. 95% Fly ash cement (10% fly ash) + 5% condensed silica fume
6. 95% Fly ash cement (25% fly ash) + 5% condensed silica fume
7. 70% Ordinary Portland cement + 30% condensed silica fume

Water: solid ratios of 0.5 and 0.7 were used.
The pastes were handmixed for a period of 3 minutes.

The mixtures were put into small polyethylene bottles and sealed. To avoid segregation of water and solid, the specimens were rotated during the first days of the hydration period, and then stored at room temperature. At certain intervals of time the hydration was stopped. The specimens were crushed, washed with cold ethanol and stored in ethanol at -20°C until they were analysed.

The pozzolanic reaction and residual calciumhydroxide of the specimens were followed by determination of $\text{Ca}(\text{OH})_2$ by means of thermogravimetry. The apparatus used for the analyses was NETZSCH 409 STA.

The hydrated pastes were dried at 105°C , pulverized and packed into alumina crucibles.

Alumina was used as reference material.

The heating rate was $20^{\circ}\text{C}/\text{min}$.

TG-sensitivity was $2 \text{ mg}/\text{cm}$.

DTA-sensitivity was 0.1 mV .

Driving gas: N_2 .

Later in the paper described as:

- 1) SP30
- 2) MP30 (10)
- 3) MP30 (25)

TABLE 1. Chemical composition of the materials

	SP30	MP30 (10)	MP30 (25)	Condensed silica fume	Fly ash
Loss on ignition	1.41 %	1.32 %	0.62 %	1.68 %	3.3 %
SiO ₂	20.20 %	23.03 %	28.85 %	96.0 %	49.0 %
Al ₂ O ₃	5.00 %	6.64 %	11.13 %	0.12 %	26.0 %
Fe ₂ O ₃	3.24 %	3.35 %	3.61 %	0.06 %	6.0 %
CaO	62.87 %	59.01 %	50.23 %	0.06 %	5.0 %
MgO	2.28 %	2.56 %	2.28 %	0.23 %	1.5 %
SO ₃	3.30 %	3.28 %	2.81 %	-	0.5-0.6 %
Insol. mat.	0.35 %	-	-	0.81 %	-
K ₂ O	1.13 %	1.05 %	0.95 %	0.41 %	0.8-0.9 %
Na ₂ O	0.36 %	0.26 %	0.35 %	0.12 %	0.25 %
Alk.	1.10 %	0.96 %	0.97 %	0.39 %	0.81 %
Free CaO	0.78 %	1.09 %	1.26 %		
C. (tot.)	3505 cm ² /g	4015 cm ² /g	4710 cm ² /g	1.37 %	
Blaine					

3.

RESULTS AND DISCUSSION

3.1 Hydration - pozzolanic reaction

The results from the thermogravimetric measurements, in mg Ca(OH)₂ as function of time are shown on fig. 1 and 2. From the curves it can be seen that the Ca(OH)₂-contents of all specimens increase during the first days of hydration. A comparison between Ca(OH)₂-contents as a function of the change in v/(c+s)-ratio, indicates an increase² in degree of hydration when water:solid ratio increases.

As for the pastes of fly ash cements a reduction in the Ca(OH)₂-contents are observed after 28 days of hydration, while a similar reduction² of the Ca(OH)₂-level can be seen between 7 and 14 days in pastes containing condensed silica fume. This means that the pozzolanic reaction giving an increase of calcium silicate hydrates occurs earlier in the hydration period when condensed silica fume is added compared with fly ash. As the calcium silicate hydrates contribute to the strength of the cement-paste, an increase in strength due to the pozzolanic reaction may be expected comparatively early in the hydration period with moderate addition of condensed silica fume in pastes. This agrees with measured strengths of compression which have been carried out on mortar prisms containing these blended cements (mixtures 1 to 6).^x

^x Discussion with Per Arne Dahl, FCB

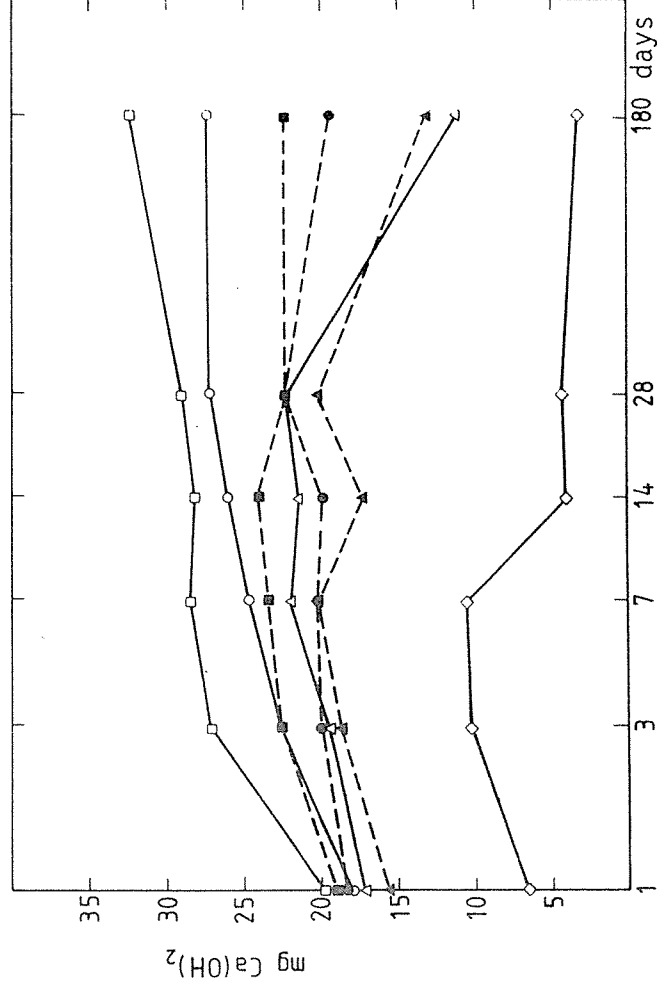


Fig. 1. Ca(OH)₂ contents (mg) in pastes given as function of time. w/(c+s) = 0.5

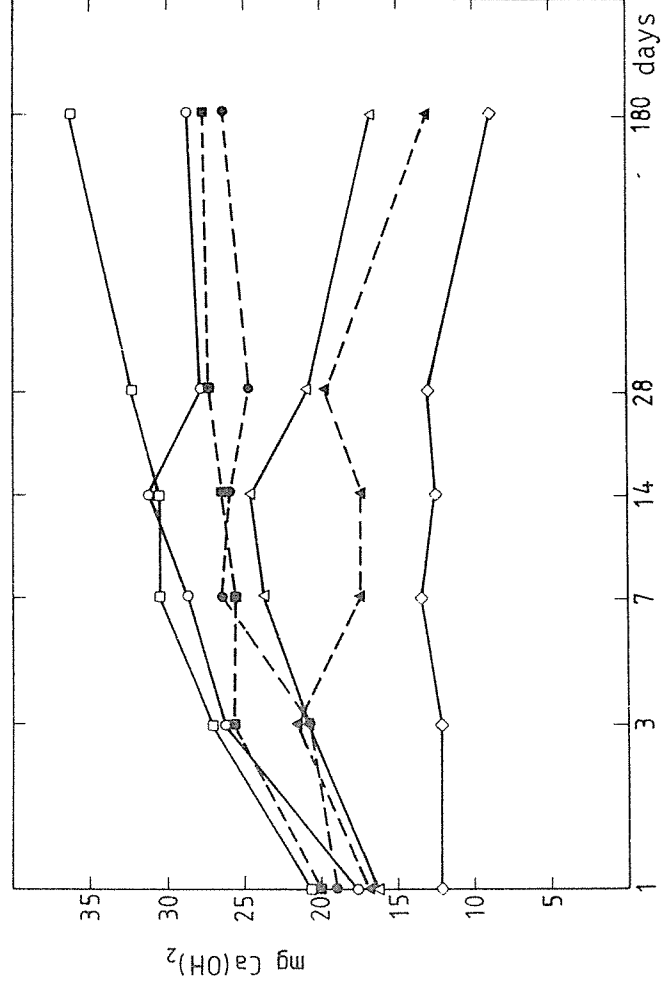


Fig. 2. Ca(OH)₂ contents (mg) in pastes given as function of time. w/(c+s) = 0.7

- SP-30
- MP-30 (10%)
- △ MP-30 (25%)
- ◇ 70% SP-30 + 30% silica
- 95% SP-30 + 5% silica
- 95% MP-30 (10%) + 5% silica
- ▲ 95% MP-30 (25%) + 5% silica

The paste containing 70% SP30 and 30% condensed silica fume shows a low Ca(OH)_2 level throughout the whole period. After one day of hydration the paste with $v/(c+s)$ -ratio of 0.5 shows Ca(OH)_2 contents = 6.3% and with $v/(c+s)$ -ratio of 0.7 = 11.7% calculated as $W/W \times 100$ of the clinker fraction. The corresponding Ca(OH)_2 contents in pastes of SP30 are 13.1% and 15.3%. As other experiments have shown that the reduction of Ca(OH)_2 due to the pozzolanic reaction mainly takes place after 3 days of hydration /1/ the low Ca(OH)_2 contents observed after one day may imply an adsorption of water by condensed silica fume, and this adsorbed water will not be available for the immediate hydration of the clinker material in these specimens where no plasticising agents were used.

3.2 Residual calciumhydroxide

To compare the level of calciumhydroxide of the blended cements with SP30 the

$$\text{ratio: } \frac{\text{Ca(OH)}_2 \text{ pozzolanic pastes}}{\text{Ca(OH)}_2 \text{ SP30}} \quad (\text{Weight \%}) \text{ has been calculated for specimens}$$

having the same lengths of reaction time. The results are indicated as function of time on fig. 3 and 4. From these results following summary can be drawn with respect to the residual calciumhydroxide at 6 months of hydration,

$\text{MP30(10)} > \text{SP30} + 5\% \text{ condensed silica fume} > \text{MP30(10)} + 5\% \text{ condensed silica fume} > \text{MP30(25)} > \text{MP30(25)} + 5\% \text{ condensed silica fume} > \text{SP30} + 30\% \text{ condensed silica fume}.$

At 14 days of hydration it seems as if MP30(10) has a greater residual calciumhydroxide than SP30. This is most likely due to the larger spec. surface of the MP30(10) . Beyond that, the blended cements show relatively small differences from SP30. After 6 months' storing the Ca(OH)_2 -contents of MP30(10) are reduced by 10-20% compared with SP30. The corresponding reduction for MP30(25) is 50%. With moderate addition of condensed silica fume the residual calciumhydroxide is still more reduced, but there is no significant difference between SP30 and the two fly ash cements.

The results indicate a difference between the two pozzolanic materials, fly ash and condensed silica fume. In pastes containing fly ash the residual calciumhydroxide, compared with the corresponding one of Ordinary Portland cement, is reduced with increasing $v/(c+s)$, while an increase in $v/(c+s)$ shows an increase in residual calciumhydroxide in pastes containing condensed silica fume.

This difference between the pozzolanas may be due to the earlier mentioned adsorption of water by condensed silica fume.

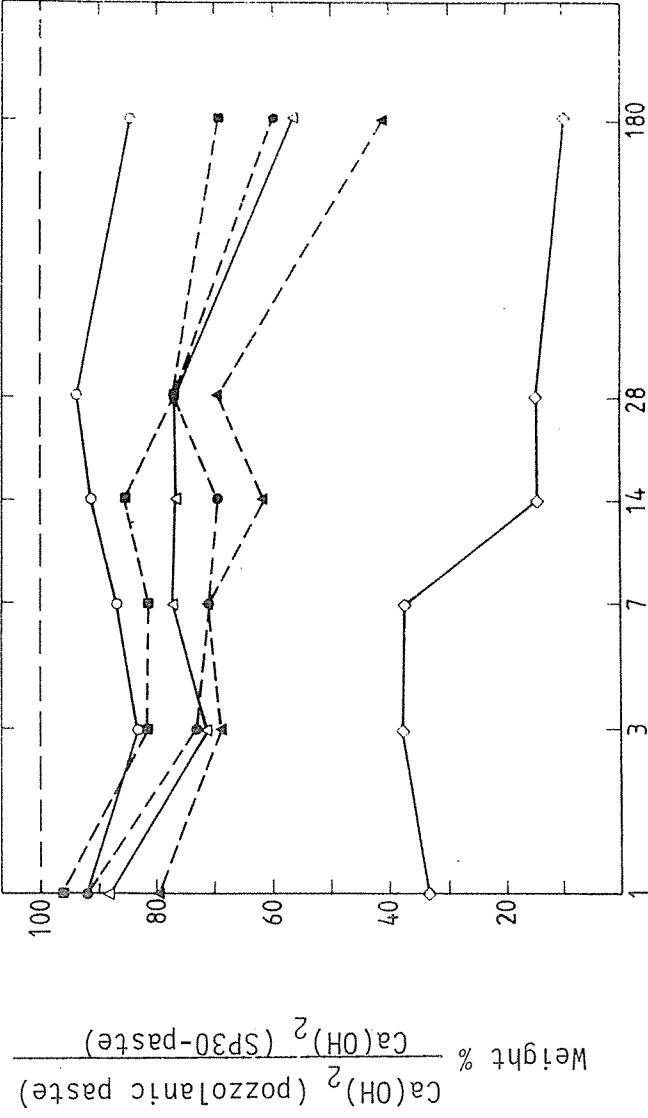


Fig. 3. Relation between Ca(OH)_2 contents in pastes of blended cements to Ordinary Portland cement as function of time. $w/(c+s) = 0.5$

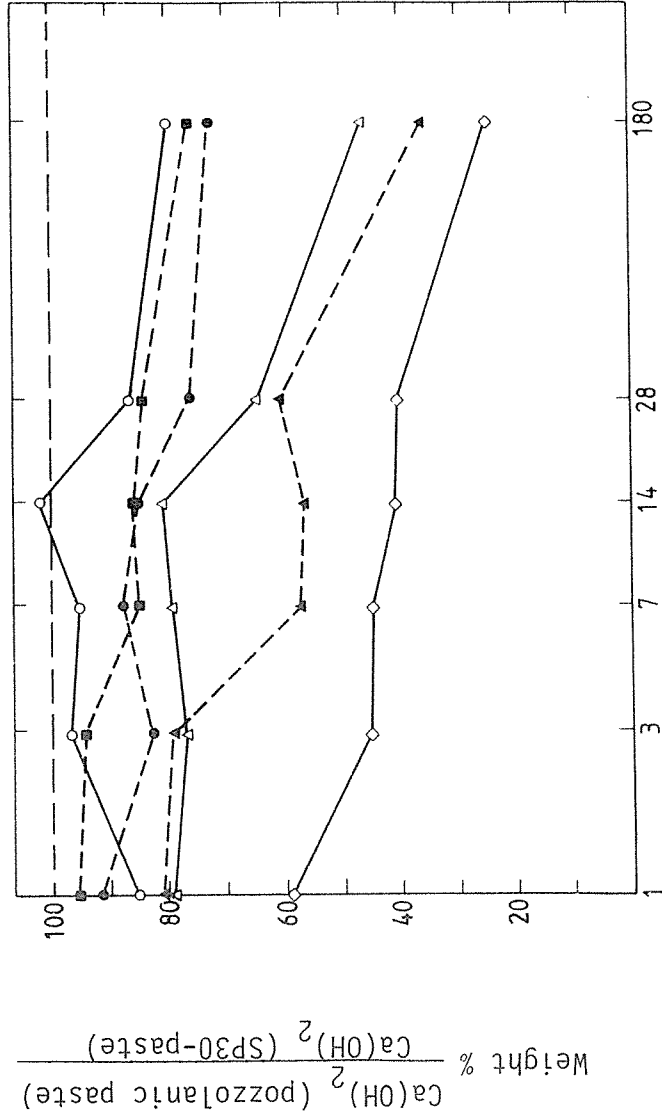


Fig. 4. Relation between Ca(OH)_2 contents in pastes of blended cements to Ordinary Portland cement as function of time. $w/(c+s) = 0.7$

- MP-30 (10%) ■ 95% SP-30 + 5% silica
- △ MP-30 (25%) ● 95% MP-30 (10%) + 5% silica
- ◇ 70% SP-30 + 30% silica ▲ 95% MP-30 (25%) + 5% silica

3.3 Possible effects of a plasticising agent in pastes containing condensed silica fume

The low amount of $\text{Ca}(\text{OH})_2$ after one day of hydration and the increase in the residual calciumhydroxide with increasing $v/(c+s)$ may mean an adsorption of water by condensed silica fume. The adsorped water thereby becomes inaccessible for the hydration of the clinker in these paste-specimens where no plasticising agents were used. Earlier investigations have shown that condensed silica fume loses its hydrofobic properties and coagulates when it is added to a saturated solution of calciumhydroxide. These coagulated silica particles most likely adsorb water as Grutzek et al. reported from their examinations on silica pastes using scanning electron microscopy (SEM) /2/, /3/. It has also been observed that addition of a plasticising agent has a dispersing effect on these coagulated silica particles in a saturated calciumhydroxide solution. This dispersing effect increases with increasing addition of plasticiser. This is tried illustrated on fig. 5.

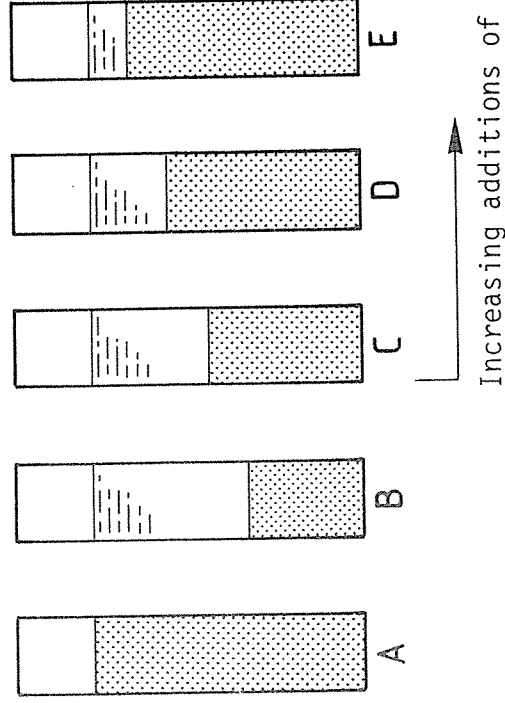
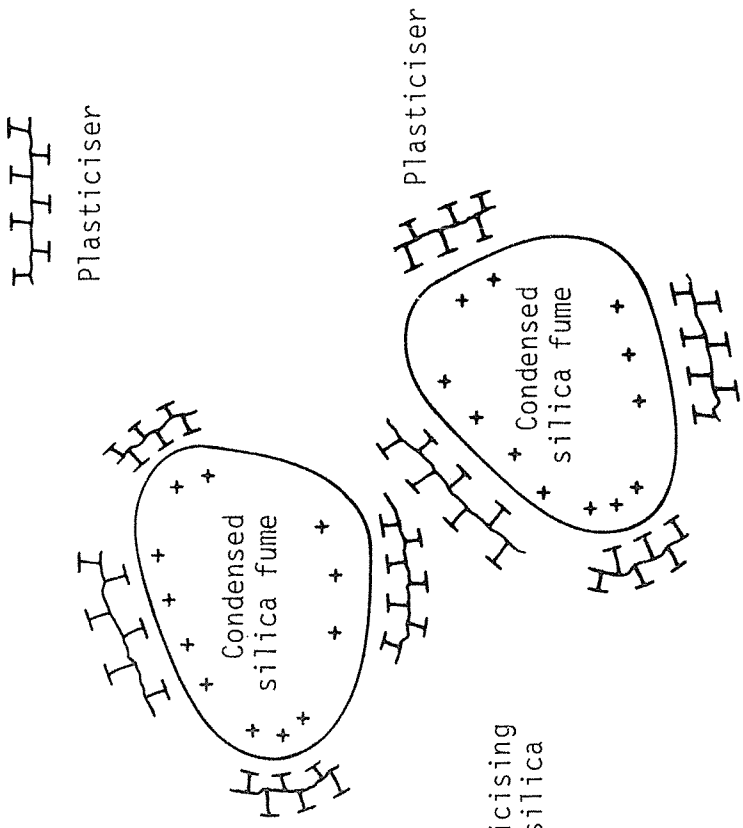


Fig. 5. Dispersion of condensed silica fume in,

- A) Distilled water
- B) Saturated solution of calciumhydroxide
- C, D and E) Saturated solution of calciumhydroxide with increasing additions of a plasticising agent.

It may be supposed that the plasticiser effects the silica particles in the same way as it effects cement grains. It adsorps on the surface and prevents an agglomeration. This effect is tried illustrated on fig. 6. The zetapotentials of condensed silica fume in saturated $\text{Ca}(\text{OH})_2$ solutions, fig. 7, also show the dispersing effect of the plasticiser on the silica fume particles. Because the plasticiser has greater affinity to silica fume than to cement /4/, the plasticising agent may reduce the adsorption of water on the silica fume particles, and thereby a greater part of the water becomes available for the clinker hydration.



X Fig. 6. Adsorption of plasticising agent on condensed silica fume particles.

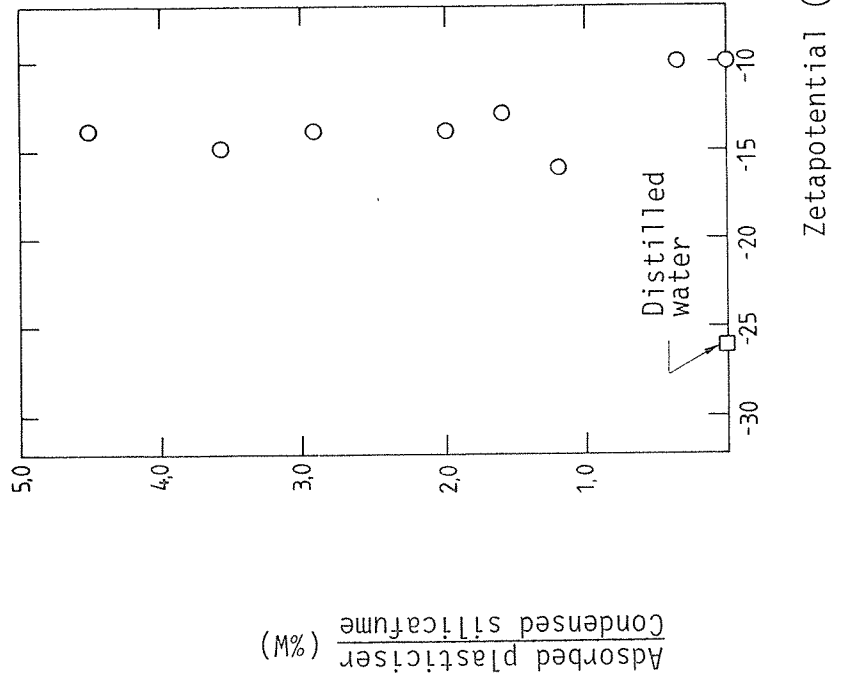


Fig. 7. Zetapotential in suspensions of condensed silica fume in distilled water and in saturated solutions of calciumhydroxide with increasing additions of a plasticising agent.

X The figure is copied from: P.C. Kreijger, "Plasticisers and dispersing admixtures." Proceedings Concrete International, London 1980.

3.4 Loss on evaporation and loss on ignition

It was of interest to determine the fractions of evaporable water and chemically bound water. Investigations had shown that the former fraction increased with increasing additions of pozzolanas /5/.

To determine the loss in weight 6 months' old specimens were dried at 110°C and then ignited at 900°C. The results calculated as % of dried material are shown in fig. 8.

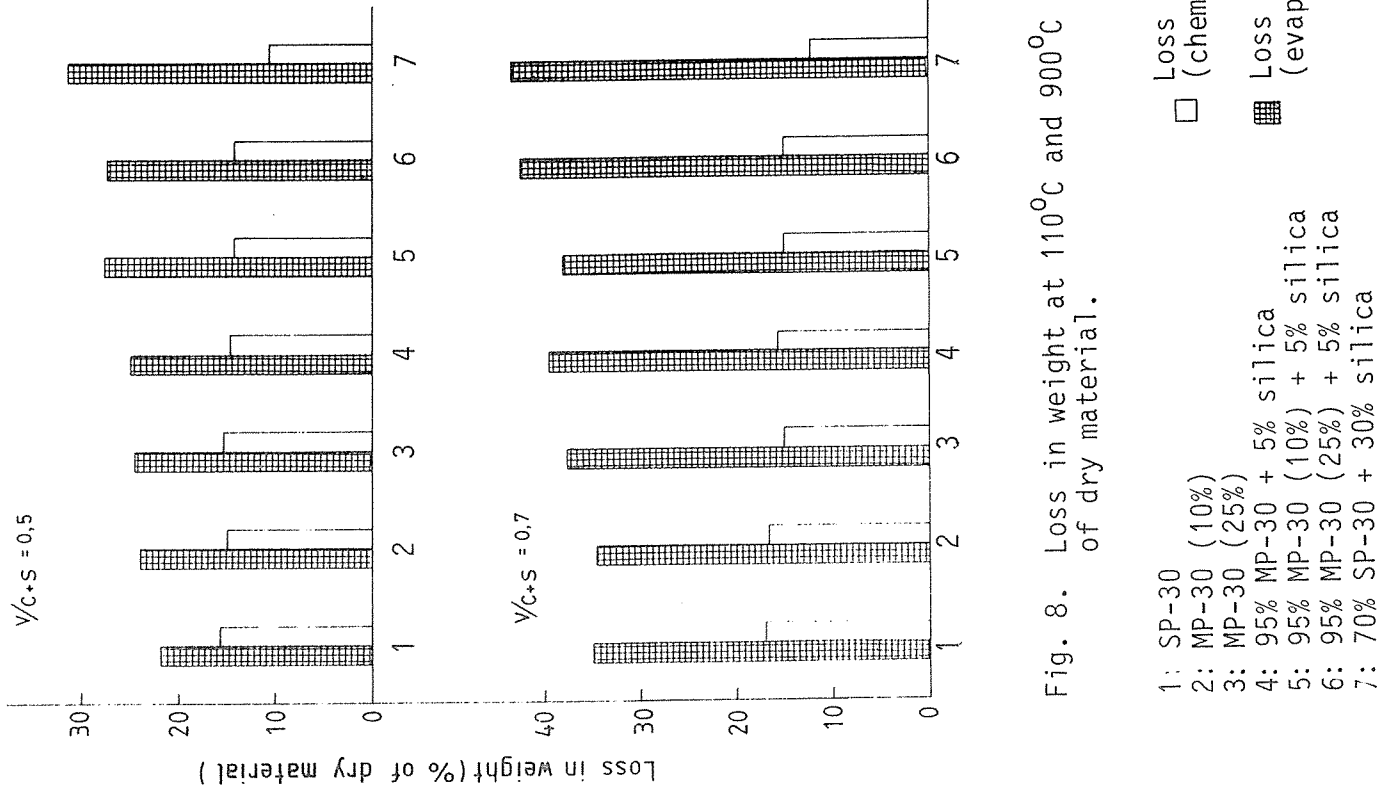


Fig. 8. Loss in weight at 110°C and 900°C in % of dry material.

- 1: SP-30
- 2: MP-30 (10%)
- 3: MP-30 (25%)
- 4: 95% MP-30 + 5% silica
- 5: 95% MP-30 (10%) + 5% silica
- 6: 95% MP-30 (25%) + 5% silica
- 7: 70% SP-30 + 30% silica

□ Loss in weight at 900°C (chem. b. water)
 ▨ Loss in weight at 110°C (evaporable water)

As the specimens have been stored sealed during the hydration period, it can be assumed that the loss in weight on drying represents mainly pore water and adsorbed water, and the loss on ignition represents the chemically bound water. The results state what Page and Vennesland /5/ found in their investigations on pastes of blended cements: It looks as if the pozzolanic reaction does not bind any water chemically, therefore an increase in addition of pozzolana may be followed by an increase of evaporable water.

Results from differential thermoanalytical examinations of the pastes are given in fig. 9 and 10. The paste containing 70% SP30 and 30% condensed silica fume, fig. 10c, exhibits an exothermic peak in the area of 800°C. This sharp peak cannot be observed with any of the other specimens. According to literature /6/, /7/ this peak indicates a calcium silicate hydrate of the type C-S-H(I) comparatively rich in silica. Due to its structure this type of calcium silicate hydrates adsorb more water than the more CaO-rich type C-S-H-(II). //

Raymert /8/ also found calcium silicate hydrates of the type C-S-H(I) in his investigations on fly ash cements. Grutzeck et al. /2/, /3/ reported a C-S-H-(I) phase from their studies on hydrating pastes containing condensed silica fume.

The increased quantity of evaporable water which has been found in pastes of blended cements may be due to the chemical composition and consequently to the structure of the calcium silicate hydrates, and for pastes containing condensed silica fume also to the water adsorbed on the silica.

One practical consequence of the larger quantity of evaporable water of pozzolanic cements may be an increased risk of drying shrinkage.

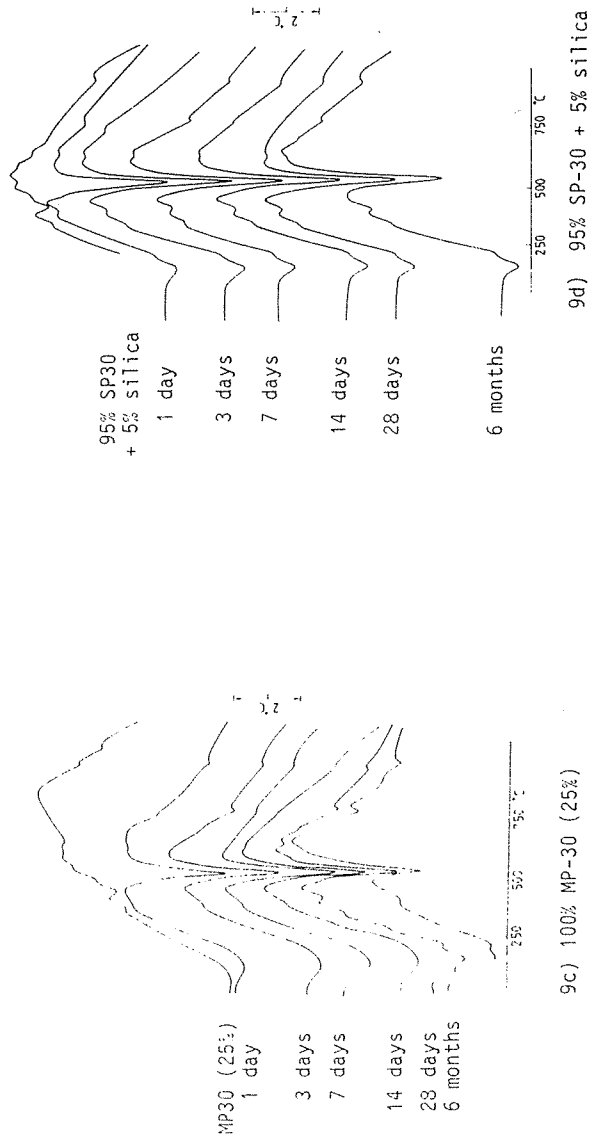
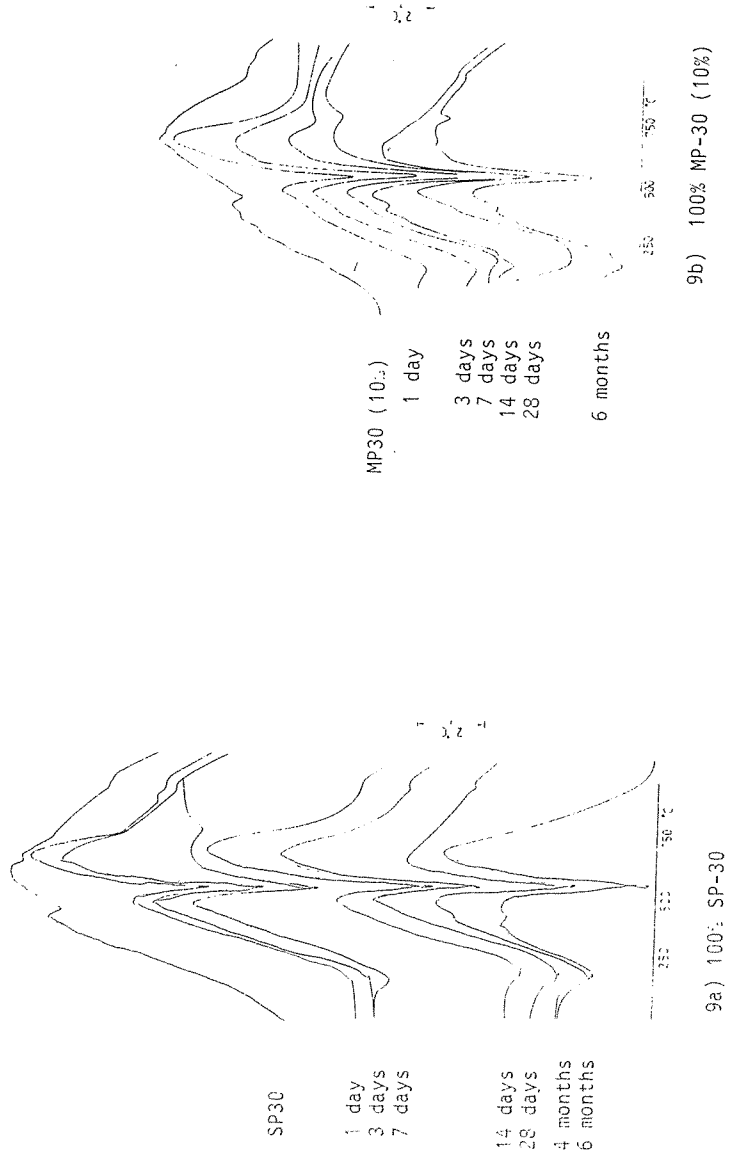


Fig. 9. DTA diagrams of pastes at these times of hydration, 1-, 3-, 7-, 14-, 28 days and 6 months.

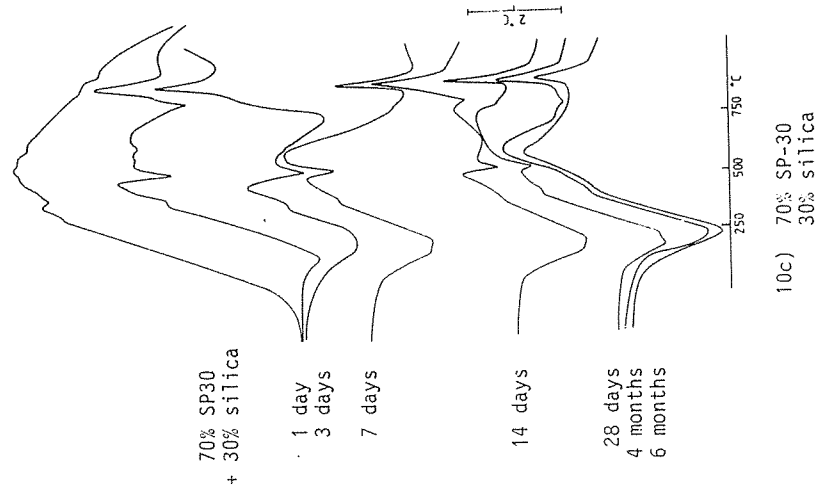
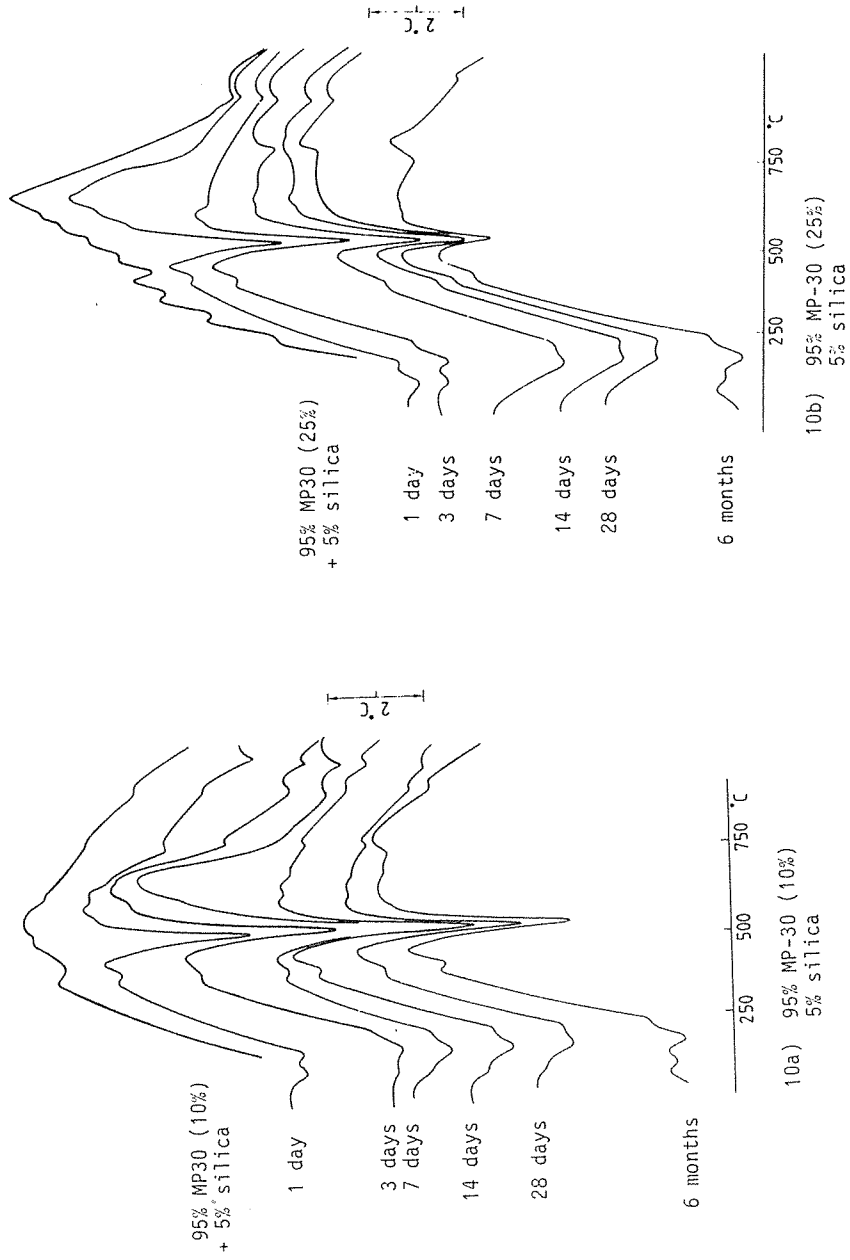


Fig. 10. DTA diagram of pastes at these times of hydration, 1-, 3-, 7-, 14-, 28 days and 6 months.

4. CONCLUSIONS

The investigation indicates following results:

- the rate of hydration, estimated from the contents of Ca(OH)_2 , shows no significant difference between SP30 and MP30 during the first 14-28 days of the hydration time. After 28 days the pozzolanic reaction takes place and reduces the Ca(OH)_2 phase of MP30.
- pastes containing condensed silica fume show a reduction in Ca(OH)_2 contents earlier in the hydration period than pastes containing fly ash.
- residual calcium hydroxide in blended cements is reduced with increasing additions of pozzolanas.
- compared with SP30 the silica pastes showed an increase in level of basicity with increasing $v/(c+s)$ while pastes containing fly ash show a reduction.
- addition of pozzolanic material gives larger quantity of evaporable water.
- paste made of 30% condensed silica fume and 70% SP30 indicates the presence of a silicate hydrate of the type C-S-H(I).
- the results from this investigations show rather small differences between SP30 and the MP30 (10) and MP30 (25).

Acknowledgement

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