

## Variations in water sorption and in thermogravimetry of a Portland cement

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### Abstract

Water sorption was studied at various relative humidity conditions, followed by step-wise static heating. Phase transformation to portlandite and calcite was found by XRD at unusually low temperatures. Cement quality and hydration reactions may be inferred from this investigation.

### 1. INTRODUCTION

This report is a part of the study in the reasons of behaviour of cement-bentonite-water system applied in Civil Engineering.

The problem of water sorption in clays is comparatively well understood, which is not the case in cements, where the hydration mechanism is still not clear [1], see [2]. The components of the total sorbed water content may be considered as: (1) physically bound, adsorbed water, escaping below 110° C, (2) hydrating water escaping below 400° C and (3) chemically bound water.

At  $p/p_o > 0.8$  a three molecular water layer of the thickness of 8-9Å is adsorbed by the surface of cement grains [3]. It remains in the system on desorption at  $p/p_o = 0.8$ . At full saturation of water vapour ( $p/p_o = 1.0$ ) a six molecular layer is adsorbed [4]. The physically bound water may amount to 0.15 g H<sub>2</sub>O per g anhydrous cement [5], [6], see [2].

An increased density by about 10% of the adsorbed water is usually assumed, due to strong adhesion forces [5] and to "surface tension" (capillary forces) at saturated water vapour pressure. This factor resulted in dense arrangement of bentonite powder grains [7]. In cements it may hinder full hydration.

Cement hydration may result from (1) liberation of Ca<sup>2+</sup> ions from the edges of grains followed by transformation into Ca(OH)<sub>2</sub> [8] and (2) after dissolution of anhydrous grains the hydration occurs and precipitation of hydration products on the grain surface [2].

About 0.2 to 0.26 g H<sub>2</sub>O per g cement is chemically bound at full hydration [2] and thus the total quantity of accumulated water may amount to 40%.

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The chemically bound water content depends on time and on cement constituent. Powers [5] gives the following values for half year curing [in g H<sub>2</sub>O per g cement]: 0.187 for alite C<sub>3</sub>S, 0.158 for belite C<sub>2</sub>S, 0.665 for C<sub>3</sub>A, 0.213 for C<sub>4</sub>AF. In one year alite is almost completely hydrated and belite – to about 70% [9], i.e. 0.688 g/g and after 7 years it decreases to 0.18 g/g [10].

To study cement quality the water sorption was measured at three relative water vapour pressures, followed by stepwise static heating. Results are interpreted in reference to broad experience in water sorption and TG of clay minerals. Some samples were subject to XRD study.

## 2. MATERIAL

Portland cement CBRP-50 was investigated, supplied by prof. J.M. Bijen (Delft). It contains (XRD): calcium silicates, alite Ca<sub>3</sub>SiO<sub>5</sub> (C<sub>3</sub>S) and belite Ca<sub>2</sub>SiO<sub>4</sub> (C<sub>2</sub>S), calcium aluminium silicate CaAl<sub>2</sub>SiO<sub>6</sub> (CA<sub>2</sub>S) and possibly tobermorite Ca<sub>5</sub>Si<sub>6</sub>O<sub>16</sub> (OH)<sub>2</sub> · 8 H<sub>2</sub>O.

## 3. METHODS AND RESULTS

### 3.1. Water sorption (WS) and water retention (WR) test:

Cement samples 5.0 g (tripple) in aluminium containers 2 × 3 cm were: (1) oven dried for one day at 110° C for WS test (WS<sub>o</sub> samples), (2) untreated (air dry) for WS test (WS<sub>a</sub> samples) and (3) untreated (air dry) for WR test (WR samples). All were placed in desiccators over appropriate solutions, i.e. in WS test: (I) at  $p/p_o = 0.5$  for 14-15 days (over the saturated Mg(NO<sub>3</sub>)<sub>2</sub> solution), (II) at  $p/p_o = 0.95$  for 14-15 days (over the 10% H<sub>2</sub>SO<sub>4</sub> solution) and (III) at  $p/p_o = 1.0$  for 14 days (over the distilled water), all at constant temperature 30° C and at normal atmospheric pressure.

All the samples, including the untreated ones (designated here as TG, single sample) were subject to stepwise static heating at 110° C (1 day), 220° C (8 h), they were transferred to ceramic crucibles (which operation caused an appreciable increase in weight) and they were further heated at 400° C (4h) and 800° C (1h), Fig. 1.

Sorbed water content and the change in weight on heating

$$\Delta G = [G(T) - G_o]/G_o,$$

were related to the initial weight of the air dry cement ( $W_o = 0.3\%$ ). The oven dry weight increased both after WS and WR test.

Surprisingly a high increase in weight was observed in samples WS<sub>o</sub> and WS<sub>a</sub> after the contact with air and heating at 400° C (about 9%), which was not the case in WR samples. Also the TG sample indicated a small increase (1%).

To check the reason by XRD another series II of WS/WR test was performed (single sample, ceramic crucibles,  $G_o = 2.6$  g,  $W_o = 0.5\%$ ), storing at  $p/p_o = 0.5$  and 0.95 only. In this case a smaller increase in oven dry weight was found and the weight at 400° C was in all samples smaller than that at 220° C. Selected samples series II after WR test were studied by XRD.

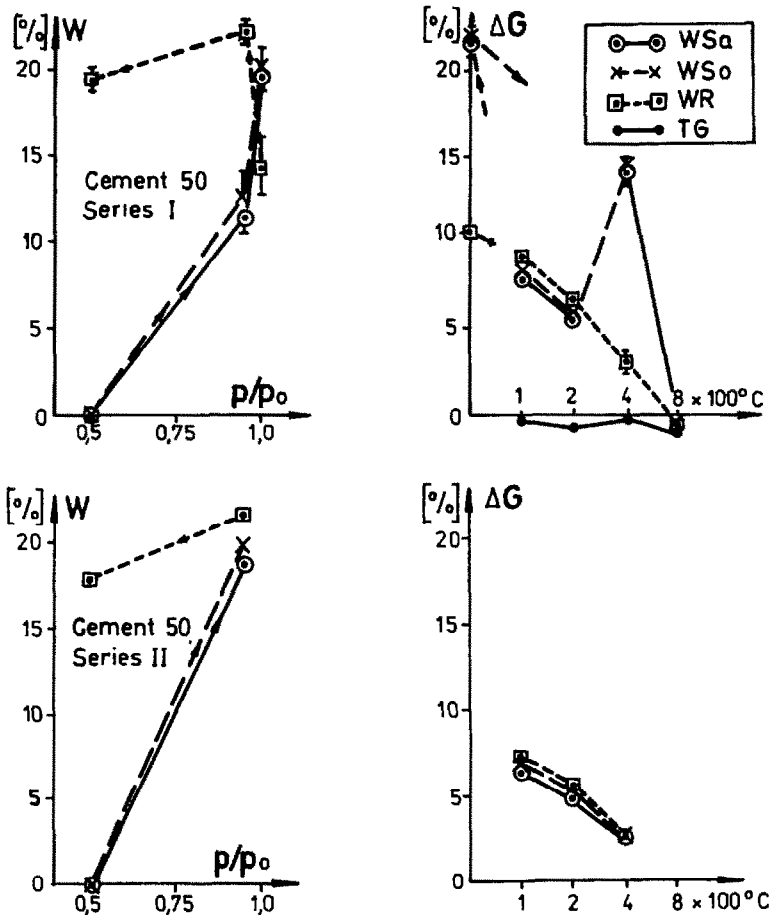


Fig. 1. Water sorption and thermal behaviour of cement 50, series I and II

3.2. XRD was performed by a Siemens Kristalloflex D 501, equipped with a graphite monochromator  $\text{CuK}\alpha$  and a computer SICOMP PC 16-20 with files of basal spacings of various standard minerals.

There were studied: (a) cement 50, (b) cement 50 after WR test and heating at  $220^\circ\text{C}$  and (c) cement 50 after WR test and heating at  $400^\circ\text{C}$ .

Most of the peaks are present independent on sample treatment, but their relative intensities vary. Only the tobermorite peak at  $3.49\text{ \AA}$ , observed in the air dry cement, disappeared after WR test and heating at  $220^\circ\text{C}$ .

Some peak intensities are presented in Table 1, related to the alite peak intensity at  $2.77\text{ \AA}$ .

$$I_r = I(\text{peak})/I(2.77\text{ \AA}),$$

Table 1.

Relative intensities of XRD peaks of cement 50, series II, WR

Compound	Peak Å	Relative intensity <i>I</i> / <i>r</i>		
		Cement 50	WR 220° C	WR 400° C
Tobermorite	3.49	0.375	—	0.08
Portlandite	4.92	—	0.30	—
	3.10	—	0.194	—
	2.64	—	0.657	?
C <sub>3</sub> S + CaCO <sub>3</sub>	3.025-3.03	0.75	1.00	1.42
C <sub>3</sub> S	2.96	0.188	0.358	0.361
β-C <sub>2</sub> S	2.87	0.038	0.194	0.194
C <sub>3</sub> S its intensity	2.77-2.78	1	1	1
		80%	33%	31%
C <sub>3</sub> S + C <sub>2</sub> S	2.74	0.962	1.373	1.278
C <sub>3</sub> Ac	2.684	0.212	?	0.333
C <sub>4</sub> AF	2.638	0.25	?	0.444

#### 4. DISCUSSION

At  $p/p_o = 0.5$  no hydration occurs and the content of sorbed water (0.4%) is almost equal the air dry water content (0.3%). Adsorbed water covers the external specific surface by an about two molecular layer, compare clay minerals, which would indicate the external specific surface  $S = 2 \text{ m}^2/\text{g}$ .

At  $p/p_o = 0.95$  a partial hydration takes place, causing an increase in specific surface (some chemical bonding is also possible) and WS is now 11-13%. At  $p/p_o = 1.0$  the almost double value of WS 19-20% may be interpreted either as water sorption on this higher specific surface (six molecular layer, instead of three molecular layer, see Introduction, [3] and [4]), and/or as further proceeding of hydration. In WR test lower values were measured at  $p/p_o = 1.0$ , i.e. 14%, which increased to 22% at  $p/p_o = 0.95$  and changed only to 19.5% at  $p/p_o = 0.5$ . If the difference of 2.5% is considered as monomolecular water layer on the external specific surface expanded during the test, which water escaped on lowering of  $p/p_o$ , then

$$S = 0.025 \text{ cm}^3/\text{g} : 3 \text{ Å} = 63 \text{ m}^2/\text{g}.$$

The differences in water sorption measured in WR and WS test correspond to differences in sorption time. This may be the cause of lower WR than WS values at  $p/p_o = 1.0$  but there may exist also geometric hindrances, due to either (1) "surface tension" or to (2) cementation of cement grains at the sorbed water content (some chemical bonding). For geometrical hindrances speaks low value of resorption after heating at 220° C of WR samples (see below).

After heating at 110° C all the samples retained a part of accumulated water, which was somewhat higher in WR (9%), than in WS test (8%) and only about one third of this water, i.e. 2.5% escaped at 220° C (there remained 6.6% and 5.6% respectively). This retention could be due to following reasons:

- (1) sorption on internal surfaces needing higher thermal energy to escape,
- (2) hydration of C-S-H gel and other eventual gels. This water should escape below 400° C.
- (3) formation of portlandite, which was detected by XRD in the sample heated at 220° C. Sanman [11] has shown that under hydrothermal conditions the main products of hydration of pure  $C_3S^x$  are  $\alpha$ - $C_2S$ -hydrate and a considerable amount of  $Ca(OH)_2$ .

After the short contact with air of the samples heated at 220° C their weight increased pronouncedly: to the value somewhat higher (by 2%) than the final value after WS test (and to about half the final value in WR test). This may be attributed to some geometrical-spacial reasons: water sorption process created some pores in the gels, which became emptied at 110° C and 220° C but were "water thirsty" (or "CO<sub>2</sub> thirsty"?). They were filled again during the short contact with atmospheric air. Weight higher by 2% with respect to the final WS value may represent portlandite, which formed during the whole procedure: if its specific density is 2.24 g/cm<sup>3</sup>, then its content should be  $2(1 + 1/1.24)\% = 3.6\%$ .

The higher weight of the sample after heating at 400° C as compared to that after heating at 220° C is attributed here to adsorption of CO<sub>2</sub> from atmospheric air and formation of carbonate, i.e. calcite (XRD, Table 1). In case of both WS samples the weight increase amounts to 8.6-8.7%, of adsorbed CO<sub>2</sub>. Thus the CaCO<sub>3</sub> created would be:  $(40+12+48)/(12+32) = 2.27$  times more, i.e. 19.5-19.7%. All this carbonate decomposes at 800° C and the final weight is close to the initial sample weight.

In series II, where samples were stored in water vapour at lower  $p/p_o$  only and thus for a shorter time and also were not in contact with atmospheric air after heating at 220° C, all the values measured were somewhat smaller: water retained at 110° C was 6.3-7.3%, decreasing by 1.5% at 220° C. At 400° C the  $\Delta G$  decreased to 2.6-2.8%, but the presence of carbonate is possible (XRD, Table 1). Here the weight gain could have been balanced by weight loss in dehydration.

These considerations show the possibilities created by the procedure described above but they need further study as the results are very sensitive to testing conditions, sample pretreatment etc.

## 5. CONCLUSIONS

Portland cement during storage in water vapour sorbs water, which quantity depends on time and relative humidity conditions. This water is partly retained on heating at 110° C, 220° C and 400° C and it is lost only about 800° C.

There are indications that after the water sorption :

- (1) portlandite forms at 220° C ( samples heated to lower temperature were not studied),
- (2) calcite forms at 400° C (possibly even at lower temperature) and it decomposes at 800° C,
- (3) sample heated at 220° C accumulates quickly water (and possibly CO<sub>2</sub>) from atmospheric air in quantity up to equal that at the end of WStest or half its value.

Water sorption followed by thermogravimetry may be useful in studying cement quality and reactions occurring on hydration. Such a study is worth the effort also because the unusually low temperature of the thermal reactions, discussed above, may be applied in designing of storage of solar energy [12].

## 6. REFERENCES

1. A.R. Ramahandran et al., Symp. on Microstructural Development During Hydration of Cement, Boston, Mat. Res. Soc. 1986, Proc. Vol.85, p.33-38.
2. K. van Breugel, Simulation of Hydration and Formation of Structure in Hardening Cement-Based Materials, 1991, Techn. Univ. Delft
3. T.C Powers, C&C Ass., London, 1968, p. 319-344, Ibid. [623].
4. J. Hagymassy et al., J. of Colloidal and Interface Science, 1969, Vol. 29, Nr 3, p.152-155.
5. T.C. Powers et al., J. of American Concrete Institute, 1946/ 1947, Part 1-9.
6. F. Keil, Zement, Springer Verlag, 1971.
7. E.T. Stepkowska and S.A Jefferis, Thermochimica Acta, 1987, Vol. 114, p. 179-186.
8. E.E. Lachowski & S Diamond, Cement and Concrete Research, 1983, Vol. 13, p. 177-185.
9. Z. Larionova, L. Nikitina and V Garashin, Phase composition, microstructure and strength of cement stone and concrete, Stroyizdat, 1977, Moscow, (in Rus.)
10. L.E. Copeland et al., Proc. 6th Intern. IAEG Congress, 1990, Balkema, p. 3147-3154.
11. Z. Sanman, Silikaty, 1964, Vo. 8, p.185-195.
12. J.M. Criado, M. Macias, A. Macias-Machin, 1991, Report of Instituto de Ciencia de Materiales, 41072 Sevilla, Spain.