

*Dedicated to Professor Lisa Heller-Kallai on the occasion of her 65<sup>th</sup> birthday*

## **THERMAL MASS CHANGES OF PORTLAND CEMENT AND SLAG CEMENTS AFTER WATER SORPTION**

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### **Abstract**

A simple water sorption/retention (WS/WR) test, followed by stepwise static heating, was applied to the study of cement quality and the reactivity of its grain surface. The physically bound water and hence the specific surface both in the unhydrated and in the hydrated state were estimated as a function of the hydration time. Rehydration after heating at 220°C and contact with air was different in WS from that in WR samples, which indicates a difference in microstructure. XRD proved the formation of portlandite during the sorption test and eventual heating at 220°C, and its transformation into carbonates on contact with air, especially on heating at 400°C. The contents of these compounds were estimated from the mass difference between 400 and 800°C, which was compatible with the mass change between 220 and 400°C and this indicates surface reactivity. The test may serve for the routine study of cement.

**Keywords:** cement hydration, specific surface, water sorption

### **Introduction**

The results presented in this paper were obtained during a study of the behaviour of the cement-bentonite-water system, applied in civil engineering as impermeable screens. The purpose of this study was to explain the unusual behaviour of cement-bentonite-water suspensions, i.e. the strength of suspensions with Portland cement was smaller than that of mixtures with slag cements. The reasons for this were expected to be found in the differences in microstructure, which were intended to be studied by water sorption, XRD, SEM, thermogravimetry, etc. Appropriate measurements of properties were performed not only on mixtures, but also on parent materials. Results obtained for cements were surprising and are therefore treated separately below.

The behaviour of Portland cement was discussed at the 13th NSTAC Conference [1] and at the 9th International Congress on the Chemistry of Cement [2].

Methods derived for clays were applied here, i.e. the water sorption (*WS*) test and the water retention (*WR*) test successively at increasing  $p/p_0$  (*WS*) or at decreasing  $p/p_0$  (*WR*), and at normal atmospheric pressure, followed by step-wise static heating at definite temperatures, up to 800°C. As the water sorption is proportional to the specific surface,  $S$ , its value for the material under study may be calculated from the measured *WS* and/or *WR* values, using suitable coefficients. The results obtained are expected to be close to the value appropriate for this material when submerged in water. Its variability as dependent on pretreatment may also be inferred.

Smectites and other clay minerals indicated variations in water sorption and thermogravimetric behaviour depending on the pretreatment, e.g. mechanical processes, drying and wetting, freezing and thawing, etc., which could be explained by the influence on the microstructure: particle arrangement, particle thickness, interactions between structural elements, etc. [3]. It was previously shown that the mass loss on heating of bentonite powder was dependent on the conditions of prestorage of the sample: it was different after the *WS* test (successively increasing  $p/p_0$ ) than after the *WR* test (successively decreasing  $p/p_0$ ). The appearance of the samples both on a macroscopic and on a microscopic scale was also different [4]: (1) a loose arrangement of powder grains and a parallel particle arrangement inside the grain, as well as a smaller loss in mass on heating after the *WS* test, and (2) the dense packing of powder grains, the floc structure of particles inside a grain and the larger loss in mass on heating after the *WR* test.

The character of water sorbed in clays is comparatively well understood, but in cements the hydration mechanism is still not clear [5, 6]. Here, not only water sorption occurs, but also hydration and chemical bonding of water. These various types of water are classified in various terms, e.g. (1) Capillary water, water physically adsorbed on surfaces, water structurally associated with the solid (interlayer water) and hydroxyl water in the solid lattice ([7], p. 330). (2) Water of hydration, water adsorbed in the gel by set cement compounds and water present in capillary voids in set cement ([8], p. 274); as hydration proceeds, a rise in the content of gel water occurs and the content of capillary water drops. (3) Finally, the simplest distinction is between evaporable (e.g. at 105°C) and non-evaporable water ([8], p. 271). For simplicity reasons, this last distinction will be adopted in this paper.

It is assumed that, similarly as in clays, the surface of cement grains at  $p/p_0 = 0.8$  adsorbs a three-molecular water layer of thickness 8–9 Å [9], which remains in the system on desorption at  $p/p_0 = 0.8$ ; thus, the pores of diameter

about 20 Å are filled with water. At  $p/p_o = 1.0$ , a six-molecular layer is adsorbed [10], and the value of water sorption should therefore increase by a factor of two.

According to various authors, at complete hydration about 0.2 to 0.26 g H<sub>2</sub>O per g cement is non-evaporable ('chemically bound' [6, 8], p. 271). This depends on the constituents: for a paste 0.5 year old, the following values are given for non-evaporable water [7]: 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 and 0.213 for C<sub>4</sub>AF.

Larionova *et al.* [12] and Copeland *et al.* [13] found that in one year alite C<sub>3</sub>S is almost completely hydrated. Belite C<sub>2</sub>S displays a high degree of hydration after one year (0.68 g/g), which decreases after 7 years to 0.18 g/g. The degree of hydration of the remaining constituents decreases with time [13].

For the physically bound water (adsorbed water evaporating below 105°C), a value of 0.15 g H<sub>2</sub>O per g anhydrous cement is usually adopted [6, 11]. Thus, the total water content at complete hydration (evaporable and non-evaporable water) should amount to about 40%.

It is usually assumed that the water hydrating the gel has a density increased by about 10% due to the strong adhesion forces [11]. Such a densification of the adsorbed water may also be due to the 'surface tension' acting in sorption from the gas phase at a high  $p/p_o$  close to 1: the attraction of the adsorbed surface water molecules by internal molecular layers (and by the solid surface itself) is not balanced by the external molecular neighbours, as is the case in liquid water. The formation of a regular dense phase may be enhanced by prolonged constant temperature and constant  $p/p_o$ , as is the case in the *WS/WR* test.

For hydration occurring after the contact of cement with water, two possible hydration mechanisms will be mentioned here [8]:

(1) a 'through-solution mechanism', i.e. the dissolution of cement compounds, producing ions, which combine to precipitate the hydrated products (induction phase);

(2) direct 'topochemical' or 'solid-state' reactions, which result in higher rates of reaction, closer to those observed.

The first mechanism is supported by the SEM observations of pure or almost pure Ca(OH)<sub>2</sub> at the edges of some particles of III C-S-H gel separated from one-day-old Portland cement paste, this gel being considered to be a significant constituent of such pastes [14]. In soil-cement-water mixtures the XRD peaks of Ca(OH)<sub>2</sub> occur already on the second day of curing [15]. The Roman numbers designate the form of the gel; thus, I C-S-H gel is needle-like, II C-S-H is network-like and III C-S-H is gel-like. Ca(OH)<sub>2</sub> may precipitates on the grain surface and thus the through-solution mechanism may be followed by the topochemical mechanism.

The degree of bonding of water molecules increases 2–3-fold during the first month [15]. Alite is almost completely hydrated after one year, and belite is about 70% [12].

Cement hydration may be considered in analogy to the weathering of silicate minerals. Yariv [16] mentions three chemical reactions of the mineral: (1) with aqueous solution due to a non-equilibrium state, (2) among soluble species in the aqueous phase, (3) 'between the aqueous solution and stable and/or metastable species sorbed on the residual primary particles or forming an independent solid phase.'

On the basis of thermodynamic calculations, Yariv [17] is of the opinion that chemical weathering is governed mainly by reaction (1), i.e. aqueous dissolution, which should also relate to cement hydration, which may depend on the specific surface and its development during hydration.

## Experimental

### Materials

Three cements were investigated. These were supplied by J. M. Bijen INTRON and designated as: (1) cement 50, (2) cement A, and (3) cement 30.

(1) Portland cement CBR P-50, containing (XRD): calcium silicates, alite,  $\text{Ca}_3\text{SiO}_5$  ( $\text{C}_3\text{S}$ ), belite,  $\text{Ca}_2\text{SiO}_4$  ( $\text{C}_2\text{S}$ ), calcium aluminium silicate,  $\text{CaAl}_2\text{SiO}_6$  ( $\text{CA}_2\text{S}$ ) and possibly tobermorite,  $\text{Ca}_5\text{Si}_6\text{O}_{16}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ . Chemical composition: CaO 64.1%,  $\text{SiO}_2$  20.8%,  $\text{Al}_2\text{O}_3$  4.5%,  $\text{Fe}_2\text{O}_3$  2.81%,  $\text{K}_2\text{O}$  0.85%,  $\text{Na}_2\text{O}$  0.11%,  $\text{SO}_3^*$  3.2%, MgO 2.00%,  $\text{TiO}_2$  0.26%,  $\text{Mn}_3\text{O}_4$  0.06%,  $\text{P}_2\text{O}_5$  0.07%, loss on heating 0.80%. Net 99.5%.

(2) Slag cement CBR KL-A, with a slag content of 75%, of the chemical composition: CaO 47.3%,  $\text{SiO}_2$  28.6%,  $\text{Al}_2\text{O}_3$  9.2%,  $\text{Fe}_2\text{O}_3$  2.05%,  $\text{K}_2\text{O}$  0.60%,  $\text{Na}_2\text{O}$  0.11%,  $\text{SO}_3^*$  3.9%, MgO 6.96%,  $\text{TiO}_2$  0.40%,  $\text{Mn}_3\text{O}_4$  0.15%,  $\text{P}_2\text{O}_5$  0.00%, loss on heating 0.42%. Net 99.7% (Blaine 380  $\text{m}^2/\text{kg}$  [18]).

(3) Slag cement CBR LK 30 (Gent) with a slag content of 87%, Blaine 434  $\text{m}^2/\text{kg}$ . It also contains (XRD): calcite,  $\text{CaCO}_3$ , alite,  $\text{C}_3\text{S}$ , anhydrite,  $\text{CaSO}_4$ , and possibly tobermorite. Chemical composition: CaO 45.3%,  $\text{SiO}_2$  29.90%,  $\text{Al}_2\text{O}_3$  9.6%,  $\text{Fe}_2\text{O}_3$  1.62%,  $\text{K}_2\text{O}$  0.48%,  $\text{Na}_2\text{O}$  0.11%,  $\text{SO}_3^*$  4.2%, MgO 7.27%,  $\text{TiO}_2$  0.41%,  $\text{Mn}_2\text{O}_3$  0.18%,  $\text{P}_2\text{O}_5$  0.00%, loss on heating 0.84%. Net 99.9%.

## Methods

Cement samples of 5.0 g (in triplicate) were placed in aluminium containers measuring 2×3 cm. They were

(1) oven-dried for 1 day at 110°C for the WS test (WS<sub>0</sub> samples);

(2) untreated (air-dry) for the WS test (WS<sub>a</sub> samples);

(3) untreated (air-dry) for the WR test (WR samples);

and then placed in desiccators over appropriate solutions, i.e. in the WS test:

(I) at  $p/p_o = 0.5$  for 14–15 days (over saturated Mg(NO<sub>3</sub>)<sub>2</sub> solution);

(II) at  $p/p_o = 0.95$  for 14–15 days (over 10% H<sub>2</sub>SO<sub>4</sub> solution);

(III) at  $p/p_o = 1.0$  for 14 days (over distilled water), all at a constant temperature of 30°C and at normal atmospheric pressure. In the WR test, an inverse sequence of  $p/p_o$  conditions was applied (Fig. 1).

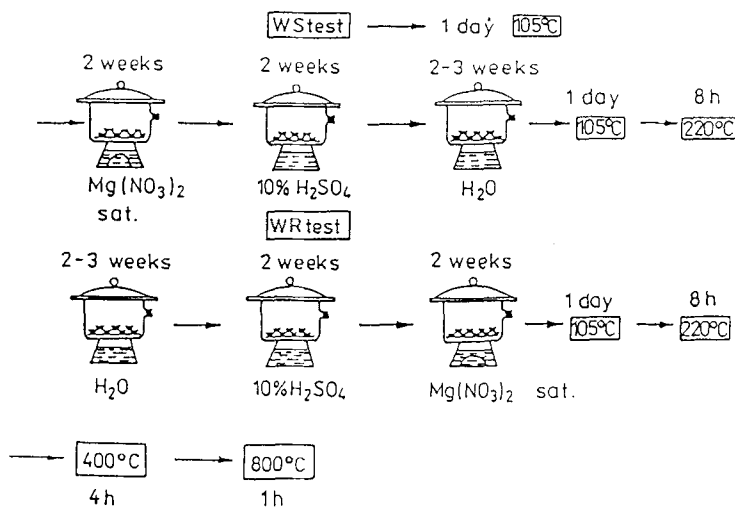


Fig. 1 Schematic representation of WS and WR test

At every change of the storage conditions, samples were weighed ( $W$ ) to calculate the water content. All the samples, including the untreated ones, designated here as UT (single sample), were subject to static heating at 110°C (1 day), 220°C (8 h), 400°C (4 h) and 800°C (1 h). After heating at 220°C, samples were transferred to ceramic crucibles and left overnight in a cool oven, which caused an increase in mass. Sorbed water content and change in mass on heating:

$$\Delta W = [W(T) - W_o]/W_o$$

were related to the initial mass  $W_0$  of the air dry cement at the air dry water content 0.3–0.5%.

A high increase in mass of  $WSa$  and  $WS_0$  at  $400^\circ\text{C}$  was observed (2 to 9%; in UT samples this increase was 0.5 to 1%). To check the reasons by XRD, another series II of the  $WS/WR$  test was performed on  $WS_0$ ,  $WSa$  and  $WR$  samples (single) of cement 50, placed at the beginning of the test into a ceramic crucible, and thus not transferred after heating at  $220^\circ\text{C}$  ( $W_0 = 0.5\%$ , whereas it was 0.3% in series I). Step III (storage over distilled water) was omitted. In this case, a continuous decrease in mass was observed on heating, this being almost linear with log temperature (Figs 2 and 3).

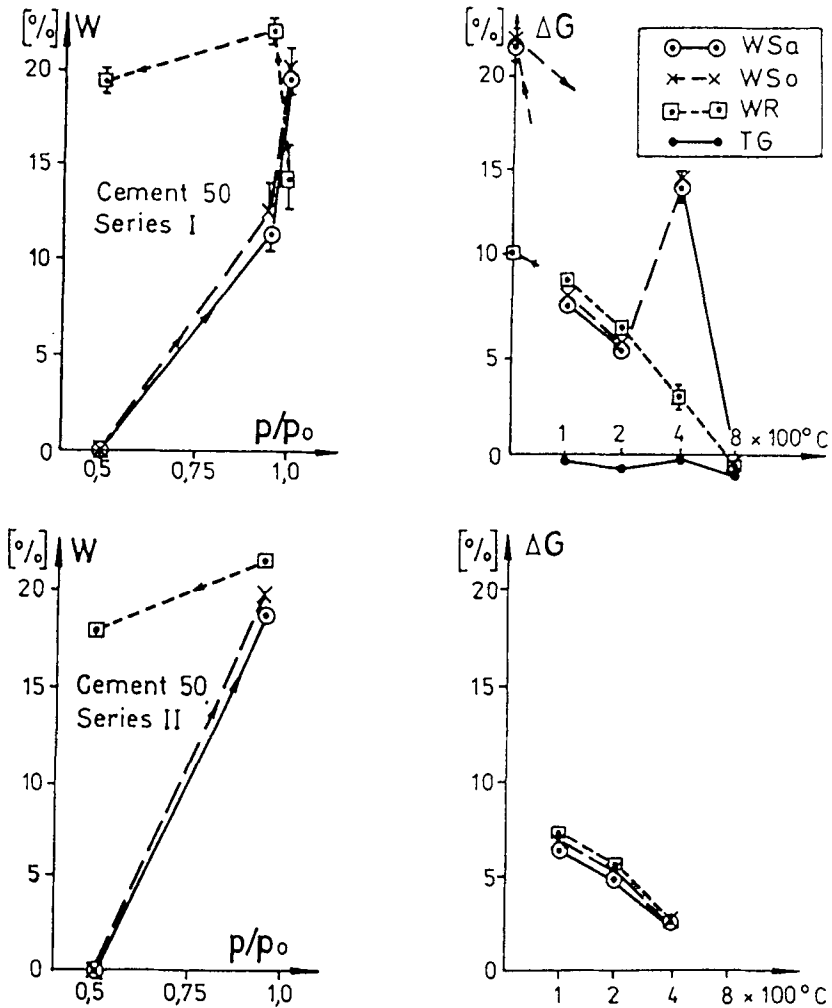


Fig. 2 Water sorption and thermal behaviour of Portland cement 50, series I and II [1]

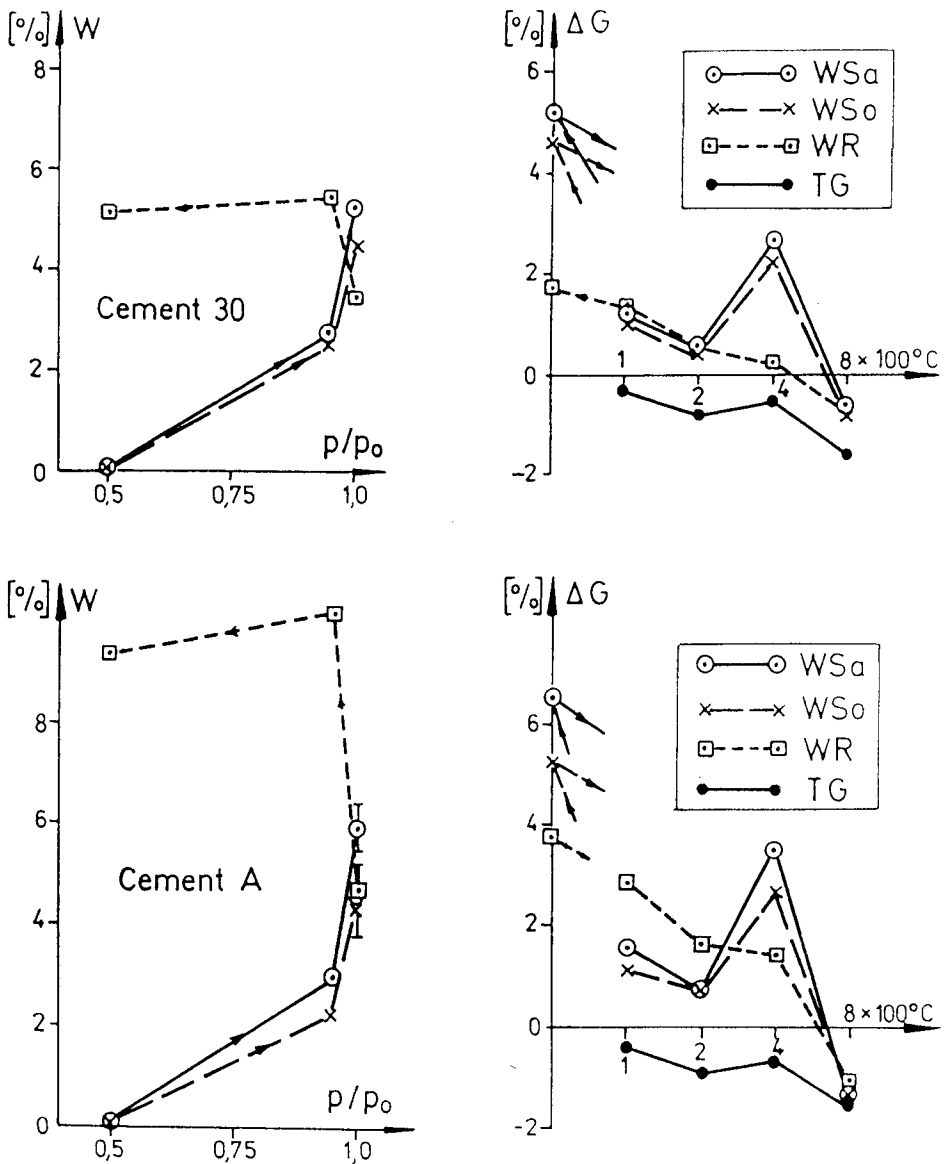
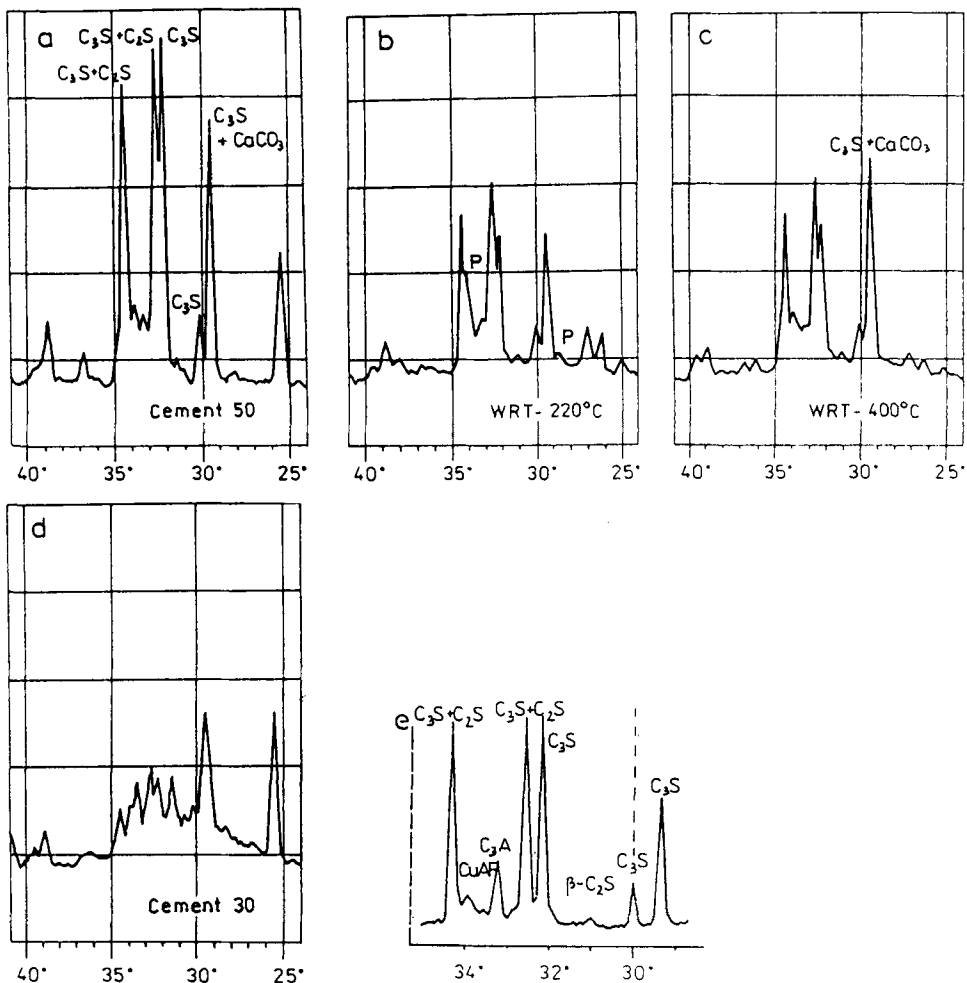


Fig. 3 Water sorption and thermal behaviour of slag cements A and 30

Selected samples after the WR test were studied by XRD. Results may be compared with those on series I only qualitatively and they should be checked in further study.

XRD was performed with a Siemens Kristalloflex D 500 instrument with Ni-filtered  $\text{CuK}\alpha$  radiation. Some identification work was done with a 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. The following samples were studied (Fig. 4): (a) cement 50, (b) cement 50 after the *WR* test and heating at  $220^\circ\text{C}$ , (c) cement 50 after the *WR* test and heating at  $400^\circ\text{C}$ , and (d) cement 30. Fragments of diffractograms are shown in Fig. 4; for comparison, a typical diffractogram of alite in Portland cement is also indicated (e), as published in [7].



**Fig. 4** XRD peaks of Portland cement 50, series II: (a) untreated (b) after *WR* test and  $220^\circ\text{C}$ , (c) after *WR* test and  $400^\circ\text{C}$ , (d) cement 30 (e) diffractogram of a typical alite in Portland cement from [7]



## Results

Qualitatively, all the cements under study behaved similarly, but the quantitative behaviour was dependent on the slag content. Also, oven-dry and air-dry samples indicated a similar sorption and weight loss on heating, though all these values were somewhat higher for slag cements in *WSa*, whereas for Portland cement they were higher in *WSo* (Table 1, Figs 2 and 3).

It is not surprising that the water content at  $p/p_o = 0.5$  (which is similar to laboratory conditions) was close to the air-dry water content, i.e. about 0.4%.

At  $p/p_o = 0.95$ , the water sorption was 2–3% for slag cements and 11–13% for Portland cement. Still higher water sorption was measured at  $p/p_o = 1.0$ , i.e. 4–6% for slag cements and 20% for Portland cement (series I). In series II, Portland cement sorbed almost as much water already at  $p/p_o = 0.95$ .

In all cases, the value determined in the *WR* test at  $p/p_o = 1.0$  was smaller than that measured at  $p/p_o = 0.95$  (by 1–5% for slag cements and by 8% for Portland cement). Only a small decrease in the content of sorbed water was observed in the *WR* test at  $p/p_o = 0.5$ : for Portland cement 19.5% was measured (as compared with 22.2% at  $p/p_o = 0.95$ ). For cement A, the difference was small (9.3% as compared with 10.2%), and for cement 30 the difference was negligible (5.2% as compared with 5.5%).

Only part of this sorbed water escaped at 110°C. The oven-dry mass of all the samples increased after the *WS/WR* test. The evaporable water was 3–4% for slag cements and 12% (series I) or 13–14% (series II) for Portland cement. The oven-dry mass of slag cements was 1–3% higher than the initial mass, while for Portland cement the corresponding value was 8–9% (series I) and 6–7% (series II).

The hydration water escaped partly at 220°C: the decrease in mass was 0.7–1.2% for slag cements and 2.4–2.5% for Portland cement, series I, whereas it was only 1.5% for series II, which indicated incomplete hydration.

On contact with air, the samples resorbed a little more water than their final mass in the *WS/WR* test (by 1% for slag cement A and by 1.6–2% for Portland cement). Also, the mass of *WSa* and *WSo* samples after heating at 400°C was higher than that at 220°C. The parent material (untreated sample, UT) increased in mass by 0.2 to 0.8% at 400°C.

When heated at 800°C, all the samples lost mass: 0.4–1.5% below the initial value in the air-dry state.

In diffractograms of cement 50, most of the peaks were present independent of the sample treatment, but their relative intensity varied (Table 2). Only the peak at 3.49 Å, observed for the untreated cement, disappeared after the *WR* test. This peak corresponds to tobermorite, whose presence in untreated cement is doubtful though.

Table 1 Water sorption properties and thermal change in weight,  $\Delta W$ , of cements at the initial weight  $W = 5.0$  g (except *UT* at 2.6–2.8 g), related to air dry weight (in percent)

Cement	Test	Water content / w%			$\Delta W$ / %				
		$p/p_0 = 0.5$	0.95	1.0	$T = 110^\circ\text{C}$ 1d	$220^\circ\text{C}$ 8h	rehydration	$400^\circ\text{C}$ 4h	$800^\circ\text{C}$ 1h
30	<i>WSa</i>	0.07	2.50	4.52	0.97	0.39	4.61	2.21	-0.77
		$\pm .02$	.03	.33	.09	.05	.20	.15	.08
$W_0 = .28\%$	<i>WR</i>	0.15	2.76	5.28	1.17	0.50	5.20	2.70	-0.60
		$\pm .02$	.19	.38	.10	.07	.28	.15	.10
$W_0 = .26\%$	<i>UT</i>	5.18	5.46	3.52	1.25	0.48	1.75	0.24	-0.69
		$\pm .20$	.21	.21	.17	.10	.14	.14	.07
<i>A</i>	<i>WSa</i>				-0.30	-0.81		-0.50	-1.10
		0.13	2.19	4.37	1.12	0.73	5.3	2.70	-1.46
$W_0 = .26\%$	<i>WR</i>	$\pm .09$	.23	.59	.16	.12	.51	.83	.49
		0.15	2.96	5.91	1.58	0.84	6.55	3.49	-1.31
$W_0 = .26\%$	<i>UT</i>	$\pm .02$	.06	.44	.14	.14	.32	.07	.06
		9.33	10.16	4.67	2.86	1.64	3.77	1.45	-1.10
$W_0 = .26\%$	<i>UT</i>	$\pm .21$	.24	.21	.07	.05	.04	.07	.13
					-0.34	-0.86		-0.62	-1.63

Table I Continued

Cement	Test	Water content / w%				T = 110°C 1d	220°C 8h	$\Delta W$ / % rehydration	400°C 4h	800°C 1h
		p/p <sub>0</sub> = 0.5	0.95	1.0	1.0					
50 series I W <sub>0</sub> = .30%	WSo	0.05	12.62	20.17	8.22	5.73	21.77	14.46	-0.43	
	WSa	± .02	1.43	.95	.43	.38	.48	.41	.12	
50 series II W <sub>0</sub> = .52%	WSo	0.11	11.41	19.65	7.93	5.35	21.55	14.14	-0.40	
	WSa	± .02	1.04	.71	.26	.18	.62	.37	.13	
50 series II W <sub>0</sub> = .52%	WR	19.51	22.17	14.33	9.07	6.65	10.54	4.07	-0.47	
	UT	± .48	.59	1.71	.27	.07	.11	.56	.11	
50 series II W <sub>0</sub> = .52%	WSo	-0.22	19.84	-	6.83	5.43	-	-0.05	-1.08	
	WSa	0.06	18.73	-	6.32	4.84	-	2.83	2.61	
50 series II W <sub>0</sub> = .52%	WR	17.88	21.62	-	7.27	5.66	-	2.64	2.64	

The relative intensities of some peaks and their changes after the *WR* test and heating at 220 and 400°C are shown in Table 2. The  $C_3S$  peak at 2.77 Å was arbitrarily chosen as reference.

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

## Discussion

During the *WS/WR* test, water sorption and hydration occurred to *C-S-H* gels, which were amorphous in the XRD study. Other reactions were indicated by this method and are quantitatively evaluated below from the mass changes on heating.

**Table 2** Relative intensities,  $I_r$  of XRD peaks of cement 50, series II after *WR* test and heating

Compound	Peak / Å	Relative intensity		
		Cement 50	<i>WR</i> 220°C	<i>WR</i> 400°C
Portlandite	4.92	–	0.30	–
Portlandite	3.10	–	0.194	–
Portlandite	2.64	–	0.657	?
$C_3S + CaCO_3$	3.025–3.03	0.75	1.00	1.42
$C_3S$	2.96	0.188	0.358	0.361
$\beta-C_2S$	2.87	0.038	0.194	0.194
$C_3S$	2.77–2.78	1.00	1.00	1.00
	its intensity	80%	33%	31%
$C_3S + C_2S$	2.74	0.962	1.373	1.278
$C_3Ac$	2.684	0.212	?	0.333
$C_4AF$	2.638	0.25	?	0.444

Thus, from the XRD data presented in Table 2, it may be inferred that the following reactions are possible:

(1) Portlandite is formed during the test, as its peaks appear in the sample *WR*, 220°C. Sanman [19] has shown that under hydrothermal conditions the main products of hydration of pure  $C_3S^x$  are  $C_2S$  hydrate and a considerable amount of  $Ca(OH)_2$ . This compound starts to decompose at 350°C, and it is fully dehydrated below 550°C [22, Criado].

(2) Calcite,  $CaCO_3$ , starts to form at 220°C (25% increase in the relative intensity of the  $C_3S + CaCO_3$  peak at 3.03 Å) and its formation proceeds at 400°C (the relative intensity is almost double that in pure cement). This is an unusually low temperature, as 85 to 95% of pure  $Ca(OH)_2$  transforms into  $CaCO_3$  be-

tween 400°C and about 700°C, depending on the partial pressure of CO<sub>2</sub> (20 to 760 torr [22,]).

(3) The carbonation observed here occurs at the expense of C<sub>3</sub>S: the relative intensities of the C<sub>2</sub>S peaks and the C<sub>2</sub>S+C<sub>3</sub>S peaks increases markedly (by 50% and by 30–40%, respectively).

The mass changes in particular temperature ranges will be discussed below and used for the calculation of certain values characterizing the cement under study. Experience acquired in investigations of clays and clay minerals will be applied here.

(1) The total increase in mass during the *WS/WR* test, resulting from storage for about one month at high relative humidity and at constant temperature, represents mainly all forms of water accumulated in the cement sample. Some hydrolysis of Ca-ions and/or CaO to Ca(OH)<sub>2</sub> also occurs: portlandite XRD peaks were observed after the *WR* test (Fig. 4, Table 2). Some carbonation of Ca(OH)<sub>2</sub> may also take place, which would result in an increase in mass by a factor dependent on the molecular weight ratio CO<sub>2</sub>/H<sub>2</sub>O. All these effects (including the initial water content) amount to 6–10% for slag cement and 20–22% for Portland cement (Table 3).

(2) Water evaporable at 110°C, *W<sub>e</sub>*, represents water adsorbed on the external surface and is proportional to its area; it also contains a proportion of the water sorbed in the interlayer space. *W<sub>e</sub>* (110°C) amounts to 4–7% for slag cement and 12–14% for Portland cement.

(3) The total non-evaporable water represents (a) water sorbed on internal (interlayer) surfaces, needing a higher thermal energy for escape (at least 220°C) and amounting to 0.4–1.2% for slag cement and 2.5% for Portland cement, (b) the hydration of C–S–H-gel and other possible gels, whose water should escape below 400°C; probably at least a part of this water is adsorbed on interlayer surfaces (see a), (c) hydrolysis of CaO and/or Ca-ions to Ca(OH)<sub>2</sub>, which may form at the edges of C–S–H gel, as shown in [14] (see Introduction). Indeed, XRD peaks of portlandite were present in diffractograms of Portland cement 50, series II, *WR*, 220°C (Fig. 4b, Table 2), (d) constitutional water in gypsum, CaSO<sub>4</sub>·2H<sub>2</sub>O, escapes below 220°C.

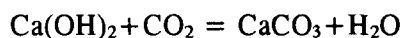
(4) On contact with air, rehydration occurred and the sample mass after the *WS* test did not differ much from that on first hydration, whereas after the *WR* test it was much smaller (by 1/3 to 1/2).

The difference between rehydration and first hydration for *WS* sample A amounts to 0.6–0.9%, whereas for sample 50 it is higher, i.e. 1.6–1.9%. Either carbonates or portlandite formed during contact with air (compare Table 2).

**Table 3** Interpretation of test results for cements [in %;  $W_0$  air dry water content]

Value measured	$p/p_0$	Test	Time/ weeks	$WSa$	$WSa$	$WS_0$	$WS_0$
				30	A	50 I	50 II 0.95
1. Max mass increase $W_0 + WS(1.0)$	1.0	WS	4	5.6	6.2	20.5	20.4
	0.95	WR	4	5.7	10.4	22.5	22.1
2. Evaporable water, $W(1.0) - W(110^\circ\text{C})$ $W_e$ $W(1.0) - W(220^\circ\text{C})$	1.0	WS	4	4.1	4.3	12.0	13.0
	0.95	WR	4	4.2	7.3	13.1	14.4
		UT	–	0.30	0.34	0.33	
	1.0	WS	4	4.8	5.1	14.4	14.4
	0.95	WR	4	5.0	8.5	15.5	16.0
		UT	–	0.81	0.86	0.83	
3. Nonevaporable $W(110^\circ\text{C})$ $W(220^\circ\text{C})$		WS		1.2	1.6	8.2	6.8
		WR		1.3	2.9	9.1	7.3
		WS		0.5	0.8	5.7	5.4
		WR		0.5	1.6	6.6	5.7
4. Resorbed after $220^\circ\text{C}$ (total)		WS		5.2	6.6	21.8	
		WR		1.8	3.8	10.5	
5. Carbonation $W(400-220^\circ\text{C})$		WS		2.2	2.7	8.7	-2.6
		WR		-0.2	-0.2	-2.6	-2.2
		UT		-0.3	-0.2	-0.8	
6. $\text{CO}_2$ escape $W(400-800^\circ\text{C})$		WS		3.3	4.8	14.9	
		WR		0.9	2.6	4.5	
		UT		0.6	1.0	1.0	
7. Net mass loss $W(800^\circ\text{C}) - W_0$		WS		0.3	1.0	0.1	
		WR		0.4	0.8	0.2	
		UT		0.8	1.3	0.8	

(5) Up to  $400^\circ\text{C}$ , this resorbed water escapes, together with the rest of the non-evaporable water from the interlayer spaces, the 'gel water', and the transformation of portlandite into calcite also occurs, resulting in a net mass increase of 2% for slag cements  $WSa$  and 9% for Portland cement  $WS_0$ : the escaping water molecule has a lower molecular weight than the reacting carbon dioxide molecule:



The XRD peak of portlandite, which was observed in the sample heated at  $220^\circ\text{C}$ , disappeared after heating at  $400^\circ\text{C}$ . Below or at this temperature, port-

landite is transformed into calcite, which could be detected as the increase in intensity of the 3.03 Å peak of  $C_3S$  (Fig. 4c, Table 2). This results an increase in mass. In the parent material (untreated sample, UT) the weight increase at 400°C was 0.2 to 0.8%. Thus, some  $Ca(OH)_2$  might be present in the parent material; otherwise, it was formed during the *WS/WR* test. The increase in mass of series I between 220 and 400°C was 2.2–2.7% for slag cement and 9% for Portland cement. This did not take place either in the *WR* test or in series II, where the water sorption was measured at  $p/p_0 = 0.95$  only and for a shorter time, and thus all the values were somewhat smaller (Tables 1 and 3). At 400°C, a mass loss of 2.2–2.6%, was observed in series II, but the presence of carbonates due to their formation from  $Ca(OH)_2$  is possible (XRD, Table 2). The mass gain resulting therefrom may be balanced by the mass loss due to dehydration.

(6) It can be assumed that carbonates, which were formed throughout the whole test, decomposed on heating at 800°C: the final sample mass is close to the initial mass of the cement sample (a little lower, by 0.4–1.6%). This temperature may seem too low for such a decomposition (924±4°C is indicated in [23]), but it should be kept in mind that in this case the possible carbonates may be extremely fine and their behaviour may therefore be exceptional. Thus, the content of these carbonates may be estimated from the change in mass between 400 and 800°C, subtracting the mass decrease within this temperature range for the untreated sample. This is assumed to represent the escape of  $CO_2$  from the decomposition of newly formed carbonates. In the *WS* test, this value was 2.7%, 3.8% and 13.9% for cement 30, A and 50, respectively, whereas it was much smaller after the *WR* test, i.e. 0.3%, 1.6% and 3.5%, respectively (as compared with 0.6–1% for the UT sample, Table 3). The amount of carbonates would be 2.27 times higher (the ratio of molecular weights for  $CaCO_3/CO_2 = 100/44$ ). They were formed from  $CaO$  activated during the *WS/WR* test, their content amounting to the values mentioned above multiplied by a factor of 1.27 (the ratio of the molecular weights of  $CaO/CO_2 = 56/44$ ).

(7) When heated at 800°C, all the samples lost mass 0.4% to 1.6% below the initial value. Thus, all the adsorbed and hydration water escaped throughout the heating procedure, and any carbonates formed previously decomposed during the final heating stage. There was some net decrease in mass on heating to 800°C, this being somewhat higher for UT sample (on subtraction of the air-dry water content it was 0.8%, 1.3% and 0.8% for samples 30, A and 50, respectively) than for *WS/WR* samples (0.3–0.4%, 1–1.2% and 0.1–0.2%). If the dehydration of gypsum is considered, these values should amount to the  $SO_3$  content multiplied by a factor of 0.45 (the molecular weight ratio  $2H_2O/SO_3 = 36/80$ ), i.e. 1.9%, 1.8% and 1.4%, respectively. The difference between these values may be due to incomplete decomposition of the carbon-

ates. It is interesting to note that for the *WR* samples the decrease in mass is almost linear with log temperature.

(8) The estimation of the values discussed above is presented in Table 4, i.e. the carbonates formed during the test, CaO and Ca(OH)<sub>2</sub> activated during the test, and the residual gel water, evaporating between 220 and 400°C. The latter value is overestimated, as some carbonates may form below 220°C (Table 2).

**Table 4** Quantitative estimations from the balance of mass loss [%]

Value	Test	30 WS <sub>a</sub>	A WS <sub>a</sub>	50 I WS <sub>o</sub>	50 II WS <sub>o</sub>
1. CO <sub>2</sub> escape W(400–800°C)	<i>WS</i>	3.3	4.8	14.9	
	<i>WR</i>	0.9	2.6	4.5	
	<i>UT</i>	0.6	1.0	1.0	
2. CO <sub>2</sub> accumulation W(400–220°C) (and H <sub>2</sub> O escape)	<i>WS</i>	2.2	2.7	8.7	–2.6
	<i>WR</i>	–0.2	–0.2	–2.6	–2.2
	<i>UT</i>	–0.3	–0.2	–0.8	
3. W(400–220°C) calc. from (1)×0.59, i.e. (CO <sub>2</sub> –H <sub>2</sub> O)/CO <sub>2</sub>	<i>WS</i>	1.95	2.83	8.70	
	<i>WR</i>	0.53	1.53	2.66	
	<i>UT</i>	0.35	0.59	0.59	
4. Hydrating water escape 220–400°C calc. (3)–(2)	<i>WS</i>	–0.2	0.1	0.1	
	<i>WR</i>	0.7	1.7	5.3	
	<i>UT</i>	0.6	0.8	1.4	
5. Gypsum dehydration 110–220°C calc. 2H <sub>2</sub> O/SO <sub>3</sub> =36/80=0.45	SO <sub>3</sub>	4.2%	3.9%	3.2%	
	×0.45	1.89	1.76	1.44	
6. W(110–220°C) measured	<i>WS</i>	0.7	0.7	2.5	1.4
	<i>WR</i>	0.8	1.2	2.4	1.6
	<i>UT</i>	0.5	0.5	0.5	
7. (5)–(6)=water uptake* or loss in dehydr. if <0	<i>WS</i>	1.2	1.1	–1.1	0
	<i>WR</i>	1.1	0.6	–1.0	–0.2
	<i>UT</i>	1.4	1.3	0.9	

\* (7) >0 indicates some water uptake, e.g. formation of Ca(OH)<sub>2</sub> from CaO; (7) <0 indicates water loss in dehydration e.g. from interlayer spaces.

(9) Both these components, i.e. C–S–H gel and calcite, may participate in the cementation of separate particles or grains. It was found for a mud cemented by various additives that the strength was correlated with the loss in mass on heating (a) between 110 and 400°C (static heating), which depends on the content of hydrated gel, most probably calcium aluminate silicate hydrate, and (b)



between 20 and 1000°C (dynamic heating in TG), which also depends on the carbonate content [20, 21].

To a first approximation, the increase in mass measured during the WS/WR test will be considered here as due to sorbed water only and it will be interpreted in analogy with the values obtained for clay minerals, where the water evaporable at 220°C was assumed to be a measure of the specific surface. In both cases, it is considered that the water sorption/retention is proportional to the specific surface, though the values of the coefficients applied may seem doubtful.

**Table 5** Quantitative estimations of compounds formed during test [%]

Value	Test	30	A	50 I
		WS <sub>a</sub>	WS <sub>a</sub>	WS <sub>o</sub>
1. CO <sub>2</sub> escape = W(400–800°C)– UT(400–800°C)	WS	2.7	3.8	13.9
	WR	0.3	1.6	3.5
2. CaCO <sub>3</sub> formed in test: (1)×2.27 CaCO <sub>3</sub> /CO <sub>2</sub> = 100/44 = 2.27	WS	6.1	8.6	31.6
	WR	0.7	3.6	7.9
3. Ca(OH) <sub>2</sub> needed: (2)×0.74 Ca(OH) <sub>2</sub> /CaCO <sub>3</sub> = 74/100	WS	4.5	6.4	23.4
	WR	0.5	2.7	5.8
4. Ca(OH) <sub>2</sub> dehydration of (3) W(220–400°C) = (3)×0.24, i.e. H <sub>2</sub> O/Ca(OH) <sub>2</sub> = 18/74 = 0.24	WS	1.1	1.5	5.6
	WR	0.1	0.6	1.4
5. –W(220–400°C) measured	WS	2.2	2.7	8.7
	WR	–0.2	–0.2	–2.6
	UT	–0.3	–0.2	–0.8
6. Net CO <sub>2</sub> accumulated, (4) + (5), compare (1)	WS	3.3	4.2	14.3
	WR	–0.1	0.4	–1.2
7. ‘Gel water’ escaping 220–400°C (6)–(1)	WS	0.6	0.4	0.5
	WR	–0.4	–1.2	–4.7
8. CaO activated in sorption CaO/CO <sub>2</sub> = 56/44: (1)×1.27	WS	3.4	4.8	17.7
	WR	0.4	2.0	4.4

From experiments on smectitic clays, there was assumed (1) a constant ratio of the quantity of water sorbed on the external specific surface,  $S$ , of platey clay particles to the total water sorption, amounting to about 0.41, and a constant ratio of the total to the external specific surface:  $S(\text{total}) = 6 S$ , (2) a definite thickness of the sorbed water layer on the external surfaces: bimolecular at  $p/p_o = 0.5$ , of increased density, and three-molecular at  $p/p_o = 0.95$  [24].

Table 6 Calculation of specific surface [ $m^2/g$ ,  $W_0$  = initial water content]

Value	Eq.	$p/p_0$	Coefficient $m^2/g H_2O$	$WSa$ 30	$WSa$ A	$WSO$ 50 I	$WSO$ 50 II	Sorption time
I. From total mass increase:								
$W_0 + WS$	[1]	0.5	585	2.5	2.4	2.4	3.4	2 w.
$W_0 + WS$	[2]	0.95	390	12	13	50	79	2 w.
$W_0 + WR$	[2]	0.95	390	22	41	88	86	4 w.
$W_0 + WR$	[3a]	0.95	1111	64	116	250	246	4 w.
$W_0 + WS$	[3]	1.0	555	31	34	114		4 w.
$W_0 + WS$	[3a]	1.0	1111	62	69	227		4 w.
$W_0 + WR$	[3a]	0.5	1111	61	107	220		6 w.
$W_0 + WR$	[1]	0.5	585	32	56	116		6 w.
$WR (0.95-0.5)$	[5]		3333	9.2	28	89	125	6 w.
II. From evaporable water content:								
$W_c (110^\circ C)$	[3]	1.0	555	23	24	67		4 w.
$W_c (220^\circ C)$	[3]	1.0	555	27	28	80		4 w.
$W_c (110^\circ C)$	[3a]	1.0	1111	46	48	133		4 w.
$W_c (220^\circ C)$	[3a]	1.0	1111	53	56	160		4 w.

Hence, the following coefficients were derived for the calculation of the specific surface from  $WS$  under definite relative water vapour pressure conditions:

$$S = WS ( p/p_o = 0.5) \times 585 \text{ m}^2/\text{g H}_2\text{O} \quad (1)$$

$$S = WS ( p/p_o = 0.95) \times 390 \text{ m}^2/\text{g H}_2\text{O} \quad (2)$$

The difference in coefficients results from the difference in thickness of the sorbed water layer.

Appropriate considerations should check (1) how far these coefficients may be applied to calculation of the specific surface of cement and (2) the temperature of evaporation of the internally sorbed water. In clays, most of this water escapes at 220°C. Without these considerations, the absolute values presented in Table 6 may seem questionable, but their relative magnitudes cannot be doubted.

To a first approximation, these coefficients will be accepted as correct in the discussion presented below. The more so since a similar thickness of adsorbed water is assumed for cement at  $p/p_o = 0.95$ , as it is in clays [9] (see Introduction).

At  $p/p_o = 1.0$ , a six-molecular layer is probable [10], of thickness  $6 \times 3 \text{ \AA} = 18 \text{ \AA}$ . Thus, if this assumption concerns the total specific surface:

$$\begin{aligned} S(\text{total}) &= WS ( p/p_o = 1.0) : (18 \times 10^{-8} \text{ cm}) = \\ &= WS ( p/p_o = 1.0) \times 555 \text{ m}^2/\text{g H}_2\text{O} \end{aligned} \quad (3)$$

The calculated values may differ from those obtained from Eq. [2], which relates to the external specific surface only.

If a three-molecular water layer were assumed, the result would be double:

$$\begin{aligned} S(\text{total}) &= WS ( p/p_o = 1.0) : (9 \times 10^{-8} \text{ cm}) = \\ &= WS ( p/p_o = 1.0) \times 1111 \text{ m}^2/\text{g H}_2\text{O} \end{aligned} \quad (3a)$$

It should be mentioned that the specific surface of cement may also be estimated from the water sorption at  $p/p_o = 0.35$  in the BET method, assuming a monomolecular water layer [8]:

$$S = a_1 V_m N / M$$

where  $a_1$  is the surface area occupied by one water molecule in the monolayer ( $10 \text{ \AA}^2$ ),  $V_m$  [in g gas per g solid] is the amount of water sorbed at  $p/p_o = 0.35$  (g gas per g solid),  $N$  is the Avogadro number and  $M$  is the molecular weight of water, i.e. 18 g/mol:

$$S \text{ (total)} = WS (p/p_o = 0.35) \times 3.33 \times 10^3 \text{ m}^2/\text{g H}_2\text{O} \quad (4)$$

This coefficient is 5.7 times higher than that in Eq. (1) for the external specific surface, due to (1) the difference in  $p/p_o$  conditions and (2) the difference in the considered specific surface, i.e. external (Eq. (1)) or total (Eq. (4)). Further the values calculated from Eq. (4) and water sorption are 3–5 times higher than those measured by the BET method and  $N_2$  adsorption, which estimates the external specific surface only. Thus, in cements the ratio of the total to the external specific surface is probably somewhat smaller (3–5) than in clays (6).

As mentioned above, the choice of proper coefficients and a proper method of drying needs further study.

Results are presented below of calculations using the above formula. As already indicated, to a first approximation the total increase in mass during the  $WS/WR$  test is considered to be here due to water adsorbed on both the external and the internal surfaces, and it is used for calculation of the specific surface.

This value for air-dry cements, calculated from the increase in mass, including the initial water content:  $W_o + WS (p/p_o = 0.5) = \sim 0.4\%$  and from Eq. (1) is about  $2.4 \text{ m}^2/\text{g}$  for series I, whereas for Portland cement, series II it is somewhat higher, i.e.  $3.4 \text{ m}^2/\text{g}$  for  $WSa$  (and only  $1.8 \text{ m}^2/\text{g}$  for  $WSo$ ), which is correlated with the higher initial water content.

Without an increase in specific surface area, the water sorption at  $p/p_o = 0.95$  would be about 1.5 times higher than that at  $p/p_o = 0.5$  (three- and bimolecular layer, respectively), whereas in the case under study after 2 weeks a much bigger increase in water sorption was measured, i.e. 2–3% for slag cements and 12–13% for Portland cement, series I, and 19–20% for series II. If the values of  $S$  are calculated from Eq. (2), adding to  $WS (0.95)$  the air-dry water content, the following will be obtained:

10 to 13  $\text{m}^2/\text{g}$  for slag cements

46 to 50  $\text{m}^2/\text{g}$  for Portland cement, series I and

75 to 79  $\text{m}^2/\text{g}$  for Portland cement, series II

It should be mentioned that the air-dry water content,  $W_o$ , was 0.3% for series I, and 0.5% for series II. The increase of  $W_o$  by a factor of 1.7 was accompanied by an increase by a similar factor of the water sorption at this

$p/p_o = 0.95$ , and of the specific surface calculated therefrom. Almost twice this water sorption was measured after another 2 weeks at  $p/p_o = 1.0$ , i.e. 4–6% for slag cements and 20% for Portland cement (which in series II sorbed as much water already at  $p/p_o = 0.95$ ). This is in agreement with the double increase in water sorption postulated by Hagymassy *et al.* [10], i.e. a six-molecular water layer at  $p/p_o = 1.0$ , as compared with a three-molecular water layer at lower  $p/p_o$  [9]. On the other hand, the longer sorption time (at  $p/p_o = 1.0$ ) could have resulted in further cement hydration and an increase in specific surface. The more so since in the *WR* test a similar influence of the sorption time was observed in spite of the decrease of  $p/p_o$  from 1.0 to 0.95. The bulk of the sorbed water was retained at  $p/p_o = 0.5$ . The final water content as measured in the *WR* test at  $p/p_o$  was only about 0.9 times smaller than the maximum water content, measured at  $p/p_o = 0.95$ .

Thus, in the *WR* test the amount of sorbed water decreased for Portland cement from 22.2% at  $p/p_o = 0.95$  to 19.5% at  $p/p_o = 0.5$ , for slag cement A from 10.2% to 9.3%, and for cement 30 from 5.5% to 5.2%. If a three-molecular water layer is adsorbed in the first case [9] and a bimolecular one on the external surface (of increased density, compare clay minerals [24]) in the second case, then the difference in retained water:

$WR(0.95) - WR(0.5) = 22.2\% - 19.5\% = 2.7\%$ , represents a monomolecular layer of water, and thus the specific surface of the hydrated cement may be calculated:

$$S = [WR(0.95) - WR(0.5)] : 3\text{\AA} = \\ = [WR(0.95) - WR(0.5)] \times 3333 \text{ m}^2/\text{g H}_2\text{O} \quad (5)$$

This difference is 0.3%, 0.9% and 2.7% for cement 30, A and 50, respectively, and thus the external specific surfaces are 9, 28 and 89  $\text{m}^2/\text{g}$ , respectively. These are somewhat higher than the values calculated from *WS* and Eq. (2), corresponding to a longer sorption time, but the agreement is satisfactory.

If water retained at  $p/p_o = 0.5$  is considered to be distributed in an approximately three-molecular layer on the total surface (overestimation for the external one), then from *WR* (0.5), adding the air-dry water content (5.5%, 9.6% and 19.8%, respectively, and from Eq. (3a), the total specific surface may be calculated as  $S_t = 61, 107$  and  $220 \text{ m}^2/\text{g}$  for cement 30, A and 50, respectively. Thus, the total specific surface calculated in this way is 2.5–6 times bigger than the external one. From *WR* (0.95) and Eq. (3a), it would be  $S_t = 64, 116$  and  $250 \text{ m}^2/\text{g}$ , respectively.

In all cases, the water sorption at  $p/p_o = 1.0$  in the *WR* test was smaller than that at  $p/p_o = 0.95$  (by 2–5% for slag cements and 8% for Portland cement).

This means either that 2 weeks was not enough for complete hydration, or that there were geometrical hindrances due to (1) 'surface tension' in the case of water sorption in fully saturated water vapour, or to (2) cementation of the cement grains (some chemical bonding caused by dissolution of surface ions in the sorbed water). This 'surface tension' may cause some densification of the powder grain arrangement (here cement grains, or the bentonite grains described in paper [4]). Geometrical hindrances are suggested by a lower value of resorption after the heating of *WR* samples at 220°C (see below). Such a densification decreases the availability of adsorption sites and thus decreases the maximum amount of sorbed water. The effects of 'surface tension' and of capillary forces [11] may be decreased or cancelled when the system is submerged in water or when sorption proceeds from the liquid phase.

If the evaporable water escaping at 110°C is considered to be water adsorbed in a three-molecular layer, then from Eq. (3a):

at  $W_e = 3.2\text{--}4.3\%$ , it is  $S_t = 36\text{--}48 \text{ m}^2/\text{g}$  for slag cements

at  $W_e = 10.4\text{--}12\%$ , it is  $S_t = 115\text{--}133 \text{ m}^2/\text{g}$  for P. cement, series I

at  $W_e = 12.4\text{--}14.3\%$ , it is  $S_t = 138\text{--}159 \text{ m}^2/\text{g}$  for P. cement, series II

If the evaporable water escaping at 110°C after the *WS* test at  $p/p_o = 1.0$  and the *WR* test at  $p/p_o = 0.95$  is considered to be water adsorbed on the surface in a six-molecular layer, then from Eq. (3) the following values would be calculated: 18–24, 58–66 and 69–80  $\text{m}^2/\text{g}$ , i.e. half the values calculated from Eq. (3a). These are somewhat too low and a three-molecular layer is more probable. At full hydration, the value of  $S_t = 200 \text{ m}^2/\text{g}$  dry mass of cement is given [8].

Table 6 presents values of specific surfaces calculated from the various equations mentioned above. Most reasonable and consistent results for hydrated cement were obtained for the external specific surface from *WS/WR* and Eq. (2), from *WR* (0.95) and *WR* (0.5) and Eq. (5), and for the total specific surface,  $S_t$ , from *WS* (1.0) and Eq. (3a), and from *WR* (0.95) and Eq. (3a),  $S_t/S$  being 2.5–6.

Here, it should be mentioned again that the increase in mass after transfer of the samples into ceramic crucibles is very interesting: the mass of *WS* samples is close to that after termination of the *WS* test (somewhat higher), whereas after the *WR* test it is approximately half the final value.

It may be inferred that the pores created and filled with water during the *WS/WR* test and evacuated on oven drying were hydrophilic (or 'carbonate-

philic') and were filled with the appropriate substance at somewhat increased density in *WS* samples and subject to geometrical hindrances in *WR* samples.

In *WS* samples, series I, the mass on heating at 400°C was higher than that at 220°C, most probably due to carbonate formation during the contact of the sample with air and/or during the sample heating (this was not observed either in the *WR* test or in series II). The conditions of this phenomenon need explanation: whether it depends on the duration of contact with water vapour or on the water content before the start of heating or on the age of the sample (formation of carbonates at grain edges) or on some other factors. Anyway, this phenomenon after appropriate study could be used for the characterization of cement, and thus it is worth while to continue research in this direction.

There are suggestions that the reversible transformations  $\text{CaO}/\text{CaCO}_3$  and  $\text{CaO}/\text{Ca}(\text{OH})_2$  are among the best candidates for the storage of high-temperature heat and thus solar energy [22]. A detailed study of the phenomena presented here seems promising.

## Conclusions

The water sorption/retention (*WS/WR*) test may be a sensitive and valuable tool for the assesment of cement quality and for the study of hydration and carbonatization reactions. After the *WS/WR* test, the oven-dry mass of cement increased pronouncedly; it returned to the initial mass at about 800°C. After the *WR* test, cement at  $p/p_o = 0.5$  retained only a little less water than it sorbed at  $p/p_o = 0.95$ , which was higher than that at  $p/p_o = 1.0$ , and the sample mass decreased almost linearly with log temperature. There is a possibility of the formation of portlandite during water sorption/retention and/or heating at 220°C. There is also a possibility of the transformation of portlandite into carbonate at about 400°C. All the phenomena mentioned above depend on the storage time and conditions. They may be utilized in the storage of solar energy; cement quality and the reactivity of its components may also be estimated.

Suggestions are given here concerning the quantitative estimation of the compounds mentioned above.

(1) From the total mass increase during the *WS/WR* test, the net amount of all forms of water may be estimated after the given sorption time.

(2) Evaporable water (at 220°C) represents most of the physically bound water. Generally no more than 0.5% remains at this temperature, escaping at 400°C.

(3) After heating at 220°C and contact with air, rehydration occurs, equal to that before heat treatment (*WS*) or to half this value (*WR*). This indicates the availability of the adsorption sites.

(4) During *WS/WR*, some CaO is activated to form Ca(OH)<sub>2</sub> at room temperature and/or 220°C and it either decomposes or forms CaCO<sub>3</sub> at 400°C on contact with air. Thus, the sample mass after the procedure mentioned above and heating at 400°C may be higher than that at 220°C, which was not observed in *WR*.

(5) Carbonates which were formed after the sorption test at 400°C decompose completely at 800°C. Thus, both temperatures are unusually low. The quantities of carbonates and reactive CaO may be calculated from the mass changes (a) between 220 and 400°C, and (b) between 400 and 800°C, which should be compatible.

(6) The external specific surface,  $S$ , may be calculated from *WS* or *WR* at  $p/p_o = 0.95$ , using the coefficient 390 m<sup>2</sup>/g H<sub>2</sub>O, which assumes (a) a three-molecular water layer on the external and internal surfaces, and (b) a ratio of the total to the external specific surface equal to 6. Hydration and  $S$  evidently depend on the sorption time.

(7) The total specific surface,  $S_t$ , may be calculated from *WS* ( $p/p_o = 1.0$ ) or *WR* ( $p/p_o = 0.95$ ) with a similar assumption of a three-molecular water layer. Thus, the coefficient is 1111 m<sup>2</sup>/g H<sub>2</sub>O. The ratio  $S_t/S$  calculated therefrom ranges between 2.5 and 6.

The quantitative estimations suggested above need verification and should be critically discussed. Water sorption from the gaseous phase represents different hydration conditions than that from the liquid water phase in the cement-water system, in which case geometrical hindrances may occur. This may hinder water evaporation, and thus the dehydration may be shifted to higher temperatures. Simultaneous tests are advisable to check how far the results are comparable.

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**Zusammenfassung** — Zur Untersuchung der Zementqualität und der Reaktivität seiner Kornoberfläche wurde ein einfacher Wassersorptions/-retentionstest (WS/WR), gefolgt von schrittweisem statischem Erhitzen angewendet. Die Menge physikalisch gebundenen Wasser und somit die spezifische Oberfläche sowohl im unhydratierten als auch im hydratierten Zustand wurden als eine Funktion der Hydratierungszeit geschätzt. Rehydratierung nach Erhitzen bei 220°C und Kontaktieren mit Luft ist für WS- und für WR-Proben verschieden, was eine Differenz der Mikrostruktur anzeigt. Röntgendiffraktion belegt die Bildung von Portlandit während des Sorptionstests und schließlichem Erhitzen bei 220°C sowie seine Umwandlung in Karbonate durch den Kontakt mit Luft, besonders beim Erhitzen bei 400°C. Der quantitative Anteil dieser Substanzen wurde anhand der Massendifferenz zwischen 400 und 800°C geschätzt, was mit der Massenänderung zwischen 220 und 400°C vereinbar ist und dies zeigt die Oberflächenreaktivität an. Dieser Test kann als Routineuntersuchung für Zement dienen.