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Determination of water-to-cement ratio in freshly mixed rapid-setting calcium sulfoaluminate concrete using 2.45 GHz microwave radiation

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Abstract

This paper describes how 2.45 GHz microwave radiation can be conveniently and accurately used for the on-site determination of the water-to-cement (w/c) ratio in a batch of fresh rapid-setting concrete. Calcium sulfoaluminate cements are attracting attention because of their superior properties compared to traditional Portland cements. While w/c is an important factor in process control of Portland cement, it is a factor of crucial importance in rapid-setting cements containing calcium sulfoaluminate ($C_4A_3\bar{S}$). A main advantage of such concretes, in addition to their low permeability and high sulfate resistance, is their very early strengths. But because of these very early strengths, the traditional microwave tests approved by AASHTO for w/c control cannot be used. We describe a test allowing determination of w/c in a rapid-setting concrete. We present results on the accuracy of the technique in the laboratory and in the field during trial batches. In all cases, the accuracy of the microwave technique was excellent. The accuracy of the test has been shown to be $(w/c)_{measured}=(w/c)_{theoretical} \pm 0.03$ in the field, with an even higher accuracy of 0.01 in the laboratory. Therefore, it would be reasonable to set an upper quality limit of (w/c) + 0.05 for onsite quality control using microwave testing.

Keywords: Microwave processing; Fresh concrete; Drying; Sulfoaluminate; Rapid-setting cement

1. Introduction

The water content of a freshly mixed batch of concrete has important consequences on the properties of the concrete. Addition of excess water will result in higher porosity, lower strength and lower durability. Therefore, control of the water-to-cement (w/c) ratio is a necessary part of process control during concrete batching. This is true of Portland cement-based concrete but even more so for rapid-setting concretes. For example, in cements containing calcium sulfoaluminate $C_4A_3\bar{S}$, all the water added for hydration is actually used in the crystals of ettringite responsible for early strength development. Therefore, it is necessary to have all the water available to achieve the desired strength; therefore, a low w/c will be detrimental to strength. On the other hand, operators using such cements and unfamiliar with their unique chemistry are often tempted to increase the w/c ratio in order to improve workability and slump. Unfortunately, a high w/c ratio results in higher porosity hence lower strength and higher permeability.

Using the interactions between microwaves and cementitious materials to probe the structure of the cement or to enhance the kinetics of hydration is a relatively new field of study [1–8,10,11]. The interaction between materials and microwave for heating purpose is also attracting attention. For example, the interactions between microwaves and some transition metal oxides such as Fe_3O_4 can be used to fabricate fly ash bricks and tiles [8] or ceramic–metal composites [9]. Microwave losses in materials can generate very high temperatures in very short times. For example, Fe_3O_4 powder can be heated to 1200 °C in less than a minute in a home microwave oven. The frequency of the electromagnetic radiation in such an oven is 2.45 GHz, which is the optimum frequency for losses in the molecule of water. Therefore, microwaves

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will interact with a cement paste with (1) water and (2) microwave-susceptible solid phases in the cement. The power absorbed by a volume V of material in a microwave field is:

$$P = \int_V \sigma E^2 dV$$

where σ is the total effective conductivity and E is the electric field intensity (V/m). The conductivity σ is related to the effective relative loss factor $\varepsilon''_{\text{eff}}$ by

$$\sigma = \omega \varepsilon_0 \varepsilon''_{\text{eff}}$$

where ω is the pulsation and ε_0 the permittivity of vacuum. Therefore, the power absorbed per unit volume is

$$P = \omega \varepsilon_0 \varepsilon''_{\text{eff}} E^2 = \omega \varepsilon_0 \varepsilon_r' \tan\delta E^2$$

Assuming perfect insulation (no radiation or convection losses), the quantity of heat adsorbed for a temperature increase ΔT is:

$$Q_{\text{abs}} = \frac{mC_p \Delta T}{V} = \rho C_p \Delta T$$

where ρ is the density of the material and C_p its heat capacity. We can write

$$Pdt = \rho C_p \Delta T$$

And the temperature rate increase:

$$\frac{\Delta T}{dt} = \frac{\omega \varepsilon_0 \varepsilon_r' \tan\delta E^2}{\rho C_p} \quad (1)$$

Of course this equation only approximates the real temperature increase but is a good indication of the behavior of a material subjected to a microwave field. The microwave-absorbing properties of the cement paste will change as a function of temperature: As the mixture heats up, its dielectric constant increases and the dielectric losses also increase. Therefore, it should be pointed out that even as the paste has been almost completely dried up and very little water is left, the cement itself can couple with microwaves, and if left unchecked temperatures in excess of 1000 °C can be reached. Care must be taken in the experiment therefore in not exceeding the microwave processing time beyond that strictly required for the removal of water. At higher temperatures, weight loss in the material is due to carbonate or sulfates losses and would alter the accuracy of the measurement.

This paper is meant to provide a process by which, using microwaves, the amount of water contained in freshly mixed rapid-setting concrete can be retroactively determined. Such techniques have been used for Portland cement concrete but cannot be used without modification for rapid-setting cements. Such cements typically hydrate extensively within a much shorter time frame. Since water is used up during hydration to form ettringite crystals, one must prevent the hydration from taking place. Therefore, the process described below involves the addition of a large excess of citric acid, a well-known retarder of calcium sulfoaluminate cements. The mechanism of retardation involves adsorption of the carboxylic acid on the surface of the cement particles, thereby blocking hydration. The setting time can be substantially increased well beyond the timeframe of the microwave experiment, and this allows the microwave to effectively remove all water in the system.

It must also be stressed that this microwave test will remove all volatiles from the mixture. This includes all volatiles from any admixtures that were added and any moisture present in the starting material, whether or not it has been taken into account by the designer of the batch. Therefore, the microwave process has the potential of being a very accurate measurement of the w/c ratio. But its effectiveness still needed to be demonstrated, and this is the focus of the present effort. We endeavored to test the effectiveness by testing the process (1) in the laboratory to try and determine whether the accuracy of the test could reach the second decimal and (2) in trial batches on site to test whether sampling errors where significant.

2. Experimental

All experiments were carried out in a 900-W home microwave oven. The microwave oven was fitted with a turntable in order to allow averaging of the inhomogeneities in electric field density through the cavity. The concrete samples were placed in a 2 L Pyrex bowl. A scale with a readability of 1 g was essential to achieve the necessary precision of this test. The scale should be able to weigh at least 5000 g.

A sample of 1500 ± 100 g of thoroughly mixed concrete was placed in the bowl. A solution of 50 g of citric acid in 50 g of water was then added and mixed into the fresh concrete. The sample was weighed and covered with a woven fiberglass cloth. The concrete was then microwaved according to the schedule in Table 1. The schedule presented is the result of many trials. After each time interval, the sample was weighed and the mortar manually crushed and broken to prevent explosive release of water during the next microwave exposure interval. After a total of 25 min in the microwave, the concrete sample was then heated at 1-min intervals until the same weight is obtained twice. This concluded the experiment. It is important to stress that if the sample is exposed any longer to microwaves, further weight loss occurs. However, this weight

Table 1
Schedule of microwave testing

Microwaving interval (minutes)	Cumulative microwave exposure time (minutes)
0:30	0:30
0:30	1:00
0:30	1:30
0:30	2:00
0:30	2:30
0:30	3:00
1:00	4:00
1:00	5:00
5:00	10:00
5:00	15:00
5:00	20:00
5:00	25:00

loss is not related to water loss but to weight loss of carbonates and sulfates in the cement, releasing CO_2 and SO_x.

3. Results and discussion

3.1. Lab results

In order to calculate the w/c ratio from the known mass loss of the sample, we must first calculate the amount of dry concrete, C_d:

$$C_d = W_c - (W_o - W_f - 50)$$

Here, W_c is the initial mass of the concrete sample (1500 ± 100 g), W_o is total initial mass of the sample (bowl + concrete + citric solution) and W_f is the total final mass of the sample (bowl + dry concrete). We must calculate the percentage of cement in our dry concrete sample, but first we need to find the mass of the water in the gypsum that has been added to the cement. This mass of water was calculated to be about 2% of the mass of the cement. Since the water in the gypsum has evaporated from our sample, we must subtract the mass of the water in the gypsum when calculating the percentage of cement, P_c, in our dry concrete sample.

$$P_c = \frac{0.98\ c_m}{0.98\ c_m + a}$$

where c_m is the mass of cement in the mix design and a is the mass of all the aggregate in the concrete. Then, calculate the weight of dry cement, c:

$$c = P_c \cdot C_d$$

Table 2
Water loss versus time for four w/c ratios in laboratory tests

Minutes	w/c (theoretical)			
	0.413	0.421	0.434	0.442
0	0	0	0	0
0.5	1	1	1	1
1	4	4	4	3
1.5	7	7	6	6
2	11	11	11	9
2.5	15	14	16	13
3	18	18	20	17
4	24	23	24	22
5	35	34	33	31
10	124	126	126	123
15	209	212	213	210
20	252	256	260	262
25	268	272	276	279
30	276	280	285	287
35	282	286	290	292
36	283	286	292	293
37	283		292	294
38				294
Measured w/c	0.414	0.422	0.438	0.443
Theoretical w/c	0.413	0.421	0.434	0.442

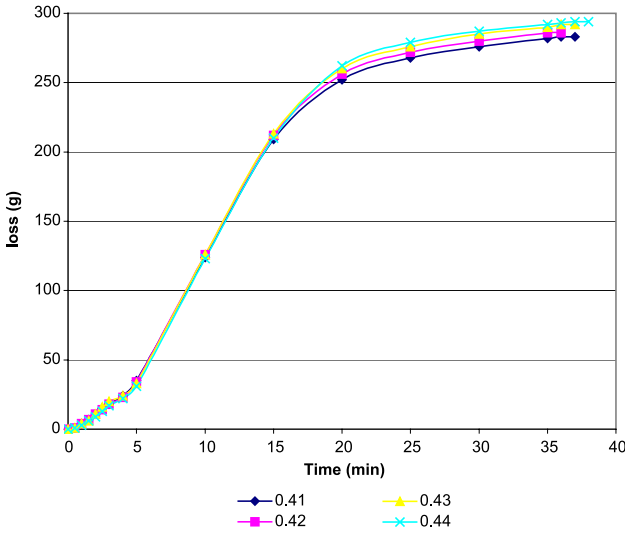

Fig. 1. Water loss versus time for several w/c ratios.

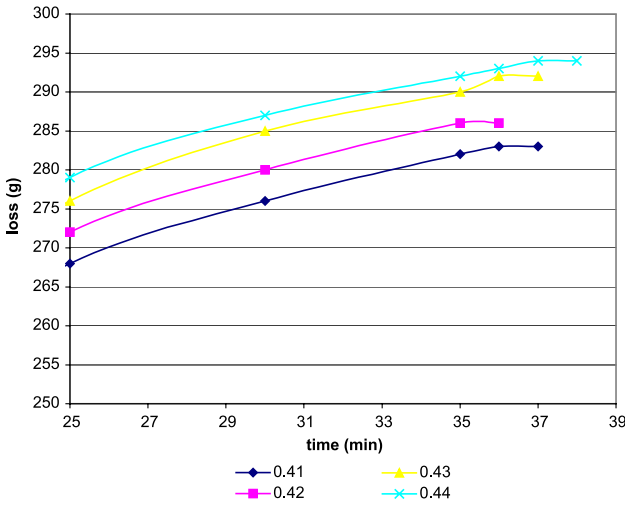

Fig. 2. Water loss versus time for several w/c ratios.

Now, to find the actual mass of the cement (c_o), we must add 2% to our value of c.

$$c_o = c + 0.02c = 1.02c$$

If there is any admixture in the mix, this admixture contains some organic liquids that evaporated during the test. Tests on silica-admixture mixes show that in some cases, approximately 80% of the admixture evaporates. Therefore,

$$P_{\mathrm{a}} = \frac{m_a}{c_{\mathrm{m}}}$$

where P_{a} is the percentage of admixture, and m_{a} is the mass of the admixture in the mix design.

Table 3
Trial batch data (John Wayne Airport)

	Trial	Batch 1		Batch 2	
		1	2	3	4
Mass of the bowl	W_B (g)	1294	1261	1256	1293
Mass of the concrete	W_c	1499	1538	1536	1492
Percentage of cement in concrete	P_c	0.173	0.173	0.200	0.200
	Minutes	Water loss			
	0	0	0	0	0
	0.5	0	0	1	2
	1	1	1	2	3
	1.5	2	2	2	5
	2	2	2	4	7
	2.5	5	3	4	9
	3	7	5	8	11
	4	10	8	9	14
	5	15	10	11	19
	10	83	75	67	82
	15	155	155	139	156
	20	199	204	202	214
	25	211	217	230	234
	30	218	226	243	242
	35	222	229	250	247
	36	224	231	251	249
	37	225	231	251	249
	38	225			
Total mass loss	$W_o - W_f$	225	231	251	249
(Total mass loss) − (100 g of added water)	$W_o - W_f - 100$	125	131	151	149
Mass of dry concrete	C_d	1374	1407	1385	1343
Mass of dry cement	c	237.70	243.41	277.00	268.60
Mass of water in gypsum	$0.02c$	4.75	4.87	5.54	5.37
Mass of cement before test	c_o	242.46	248.28	282.54	273.97
Mass of water before test	$W_o - W_f - 100 - 00.02c$	120.25	126.13	145.46	143.63
w/c ratio assuming no admixture	w_o/c_o	0.496	0.508	0.515	0.524
w/c ratio including admixture calculation	w/c	0.451	0.462	0.479	0.488
Average measured w/c		0.46		0.48	
Theoretical w/c		0.48		0.45	

Table 4
Trial batch data (Twining)

	Trial	1	2	3	4	5
Mass of the bowl	W_B (g)	1256	1258	1261	1293	1294
Mass of the concrete	W_c	1490	1491	1491	1486	1510
Percentage of cement in dry conc.	P_c	0.189	0.189	0.189	0.189	0.189
	Minutes	Water loss				
	0	0	5	6	6	4
	0.5	1	6	6	6	4
	1	3	7	7	7	5
	1.5	4	8	8	7	5
	2	6	9	8	8	6
	2.5	9	10	9	10	8
	3	12	11	10	11	9
	4	18	13	13	13	11
	5	28	20	18	19	16
	10	100	88	86	83	79
	15	142	140	145	141	140
	20	152	154	162	159	158
	21	155	157	165	162	161
	22	156	158	166	164	162
	23	158	160	168	165	164
	24	159	161	169	166	166
	25	160	162	170	168	167
	26	161	164	171	169	168
	27	162	166	172	170	169
	28	162	166	172	171	
	29				172	
	30				172	
Total mass loss	$W_o - W_f$	162	166	172	172	169
(Total mass loss) − (50 g of added water)	$W_o - W_f - 50$	112	116	122	122	119
Mass of dry concrete	C_d	1378	1375	1369	1364	1391
Mass of dry cement	c	260.44	259.88	258.74	257.80	262.90
Mass of gypsum in cement	$0.02c$	5.21	5.20	5.17	5.16	5.26
Mass of cement before test	c_o	265.65	265.07	263.92	262.95	268.16
Mass of water before test	$W_o - W_f - 50 - 0.02c$	106.79	110.80	116.83	116.84	113.74
w/c ratio assuming no admixture	w_o/c_o	0.402	0.418	0.443	0.444	0.424
Measured w/c ratio	w/c	0.390	0.405	0.429	0.431	0.411
Average measured w/c						0.42
Theoretical w/c						0.44

Therefore, the calculated w/c ratio in the mixed concrete is:

$$\frac{w}{c} = \frac{W_o - W_f - 50 - 0.02c - 0.8P_a c}{c_o}$$

Our first series of experiments was designed to determine the sensitivity of the test in the laboratory. We mixed four concrete mixtures with w/c ratios of 0.413, 0.421, 0.434 and 0.442.

The results are given in Table 2 as weight loss with respect to time. This original experiment involved using a citric acid solution comprised of 50 g citric acid and 100 g water to block hydration of the cement. Therefore, it took longer than the usual 25–30 min to completely evaporate the water. Figs. 1 and 2 summarize these results. Fig. 1 shows the entire experiment while Fig. 2 simply shows the last several minutes of the test to stress that indeed the test is able to differentiate between w/c ratios differing by the second decimal only. The overall shape of the curve shows three regimes: the release of water is slow at first (in accordance with Eq. (1)) because the heat capacity of the water-rich paste is high. As water evaporates, the weight loss rate reaches a steady state regime before reaching a third stage where the weight loss rate decreases until all the water has been removed from the sample.

The data are presented in Table 2 and show that the theoretical and measured w/c ratios are identical to the second decimal. In other words, all the water added is recovered by microwave testing. The test was also clearly able to measure a difference in w/c ratio of 0.01. The key factor in being able to differentiate between w/c ratios separated by less than 0.02 is simply the ability to weigh a sample of 1500 g with an accuracy of 1 g or less. Therefore, it merely requires the use of a balance of sufficient accuracy.

3.2. Trial batches

One concern was that conditions in the laboratory are not always reproducible in the field. A particular concern was sampling: a sample tested is not necessarily representative of the mix design. For example, a sample of concrete might contain a few more large aggregates than the ideal mix. In this case, the weight of the nonvolatile might be larger than the theoretical mix. Another possible source of inaccuracies is the presence of admixtures. These admixtures can have a significant volatile content. These volatiles will be removed during the microwave test but obviously should not be measured as water. In order to verify if the accuracy of the laboratory test was reproducible in the field, we tested the microwave process onsite in trial batches in which the mix design was accurately known and compared the results of the test to the mix design. The results are shown in Tables 3 and 4. The calculations are made at the bottom of each table. We tested the admixtures used in this trial batch separately and found that under the conditions of microwave testing (mixtures of silica and admixtures), they contained about 80% volatiles.

In Table 3, two batches with different w/c ratios were tested. For each batch, the experiment was repeated twice. Batch 1, the measured w/c was 0.46 ± 0.01, the theoretical w/c was 0.48. In Batch 2, the measured w/c was 0.48 ± 0.01 for a theoretical w/c = 0.45. Therefore, the accuracy of the test is a little lower in the field than it was in the laboratory but fits well within an error of 0.04. Additional data in Table 4 show an average for five measurements of w/c of 0.42 ± 0.03 for a theoretical of 0.44 thus here again within the error of 0.03. Therefore, it appears that the size of the sample (1500 g) is large enough so that slight variations in the amount of aggregate sampled do not affect the calculation of w/c.

4. Conclusion

We have shown that it is possible to measure the w/c ratio of fresh rapid-setting concrete using a microwave-drying test. The test can be carried out using a household microwave oven. Due to the specificity of rapid-setting concrete, the test requires blocking hydration of the cement using a carboxylic acid such as citric acid. Attention must be paid to all ingredients that have been placed in the mix, such as this additional amount of retarder or any admixture. This is consistent with the fact that the microwave test will remove all volatiles from the mix, including those that were not taken into account in designing the mix. The accuracy of the test has been shown to be $(w/c)_{measured}=(w/c)_{theoretical} \pm 0.03$ in the field, with an even higher accuracy of 0.01 in the laboratory. Therefore, it would be reasonable to set a quality limit of w/c ± 0.05 for onsite quality control using microwave testing.

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