

## Ageing of Dry Cement Mixes for Finishing Purposes

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Dry building mixes, stored in the air, absorb water vapor and CO<sub>2</sub> gas and ageing because properties of binding materials, mostly Portland cement, deteriorate after its prehydration and carbonation. In this paper the ageing singularities of dry cement mixes for finishing purposes and additives for retarding this process has been determined. Ordinary and quickly hardening Portland cements absorb H<sub>2</sub>O and CO<sub>2</sub> more than white cement – about 70 % – 75 % and 30 % – 38 % per month of initial mass, respectively. White cement is more resistant to prehydration and carbonation, because it contains less C<sub>3</sub>A, C<sub>4</sub>AF and alkali, characterized initial activity. Dry mixes with white cement, although slower, but still worse after stored. Influence of routine dry mortar mixes ingredients and additives (methyl cellulose, pigments, sand and lime) on prehydration properties of the mixes for finishing purpose is not substantial. Significant positive influence comes from the addition of fatty acid salts (zinc stearate or sodium oleate). The dry cement mixes for finishing purpose has been recommended to hydrophobise with one of these additives, adding about 1 % by weight of cement during producing mixes.

*Keywords:* dry cement mixes, hydration, carbonation, strength.

### 1. INTRODUCTION

Portland cements used in the production of dry cement mixtures come a long way before they are used in construction. During that time they as well as the products being made and already manufactured from them are affected by various environmental factors as well as water vapours present and CO<sub>2</sub> gases present in the air, which alter the properties of the products. Phenomena of different Portland cements ageing have been scrutinised for quite some time now [1–5]. For instance, a survey [3] addressed the conditions of storage of two types of Portland cements. The Portland cements differed in their mineral content and the fineness of the grain. Stored in regular cement bags in the open air, the cement got considerably worse in 14 days. Surface samples (taken in a depth of up to 10 cm) deviated from control samples in terms of loss ignition (by up to 3 %), the demand for water to make dough of a normal degree of density, the bonding durations, etc. According to other author's [3] opinion, the main reason behind the alterations of the properties of Portland cements is the hydration of cement, whilst carbonisation has little effect. The speed of airborne hydration would increase linear with raising the C<sub>3</sub>A and alkali content; this was particularly relevant in terms of the alkali that form part of C<sub>3</sub>A. The resultant products are ettringite and singenite. Accelerated binding was observed when the cements were stored in airtight containers as well. C<sub>3</sub>AH<sub>6</sub> was found on the surface of the layer. An overview provides carbonization process of porous cementitious materials [6]. Gaseous carbon dioxide first dissolves in the pore solution mainly as HCO<sub>3</sub><sup>-</sup>. The CO<sub>2</sub> then react with dissolved calcium to precipitate calcite, CaCO<sub>3</sub>, as well as other CO<sub>2</sub>-based solid phases. The presence of carbonates in the pore solution can also lead to the formation of other solid phases, for example 3CaO·Al<sub>2</sub>O<sub>3</sub>·CaCO<sub>3</sub>·11H<sub>2</sub>O [7].

There are no stable capillary pores in dry cement mixtures. So the solid phases may be formation on surface of the particles. Our earlier work [5] has indicated that when Portland cement is exposed to air of 75 % – 80 % relative humidity, the binding speed decreases, the need for water to produce dough of normal density level goes up, the activity of the cement drops, especially on the onset of hardening. Exposure to humid air that is free of CO<sub>2</sub> gas also reduces the qualities of cement, but to a lesser extent. When cement is separately exposed to dry N<sub>2</sub>, O<sub>2</sub>, CO<sub>2</sub> gas present in the air by way of aeration, the binding speed changes slightly, yet the strength-related qualities remain virtually the same. A method [8] has been proposed to study the effects of air on the properties of cement. C<sub>4</sub>AH<sub>13</sub>, C<sub>3</sub>AH<sub>6</sub>, ettringite, singenite (K<sub>2</sub>SO<sub>4</sub>·CaSO<sub>4</sub>·2H<sub>2</sub>O) and new hydro-silicate compounds were found in cement that has been exposed to humid air with CO<sub>2</sub>. Working together with vapours present in the air, CO<sub>2</sub> produces R<sub>2</sub>CO<sub>3</sub>, RHCO<sub>3</sub>, CaCO<sub>3</sub> in cement. Production of mono-sulphate and singenite consumes the gypsum in the cement and therefore Portland cement hardens as if it did not contain any gypsum. That way, depending on the conditions of storage of Portland cement, its premature hydration can occur. Also, carbonisation of hydrating minerals can take place. As a result, the cement becomes less powdery, active and its other important properties deteriorate as well.

Having started producing dry cement mixes for different applications one can see that their properties change before they are actually put to use. Dry grouts and finishing plaster mixes contain a variety of specific additives [9, 10]. However, their purpose is usually to improve the plasticity of the grout and the way it binds with the base. Preservation of stability of mixes is a somewhat secondary thing.

The purpose of this paper is to investigate the ageing singularities of dry cement mixes for finishing purposes and to determine additives for retarding this process.

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## 2. MATERIALS AND METHODS

### 2.1. Materials

The study involved the use of white Portland cement from the Danish company ALBORG (“DC”). For comparison purposes, Portland cements I 42.5R by Cemex of Broceni (“BC”) and by JSC “Akmencementas”, (“AC”) were used. Their compositions are presented in Table 1.

**Table 1.** Chemical and mineral composition of Portland cements used, %

Portland cement component	Danish white Portland cement (DC)	Portland cement CEM I 42.5R	
		Cemex of Broceni (BC)	Akmencementas (AC)
SiO <sub>2</sub>	25	18.8	20.4
Al <sub>2</sub> O <sub>3</sub>	2.1	4.4	5.0
Fe <sub>2</sub> O <sub>3</sub>	0.3	3.2	3.8
CaO	61	61.5	62.6
SO <sub>3</sub>	2.1	3.2	2.2
MgO	0.6	3.8	3.7
Na <sub>2</sub> O <sub>ekv.</sub>	0.2	1.0	1.2
C <sub>3</sub> S	77	59	63.3
C <sub>2</sub> S	15	16.2	8.2
C <sub>3</sub> A	5	7.1	8.8
C <sub>4</sub> AF	1	9.1	12.7

Occasionally, other Portland cements were used as well as specified in the text: Portland cement with a limestone additive CEM II/AL 42.5N from Akmencementas, AB (“ACL”) and CEM I 42.5 N.

Furthermore, sand with grain size 0/1.6 mm by company Sakret and some other grout additives, like methyl-cellulose Welocel (“W”), pigment TiO<sub>2</sub>, slaked lime and quicklime containing 60 % Ca(OH)<sub>2</sub> and 80 % CaO, zinc stearate, etc. was used as well. On top of that, certain dry grouts from a retail chain were used too.

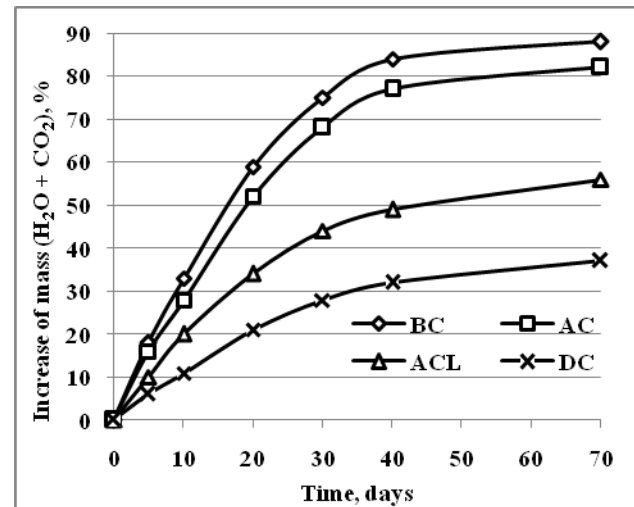
### 2.2. Methods

To establish the absorption levels of airborne vapours and CO<sub>2</sub>, layers of powder material about 2 mm thick were made and placed on a pre-weighed platter into an enclosed environment with relative humidity of air of 90 % – 95 % and room temperature of 18 °C ± 2 °C. The platters with the material were weighed to determine the increment in mass. Moreover, a special device (a capsule) [8] was used, which was filled with a certain amount (1.5 kg) of material with air blown through it using a compressor. The air humidity was 70 %. Samples of aerated cement were taken to establish increments in mass, CO<sub>2</sub> and activity levels.

The activity of cement was also surveyed following a certain period of container storage. To determine the effects of hydrophobic treatment, 3 mixes of grout were made and kept opened for 5 days (in layers 3 mm – 5 mm thick) in a room with relative humidity of 70 % – 75 % and temperature of 17 °C – 18 °C. After that, the strength of the samples made was established following a specified period of hardening (without storage and after that).

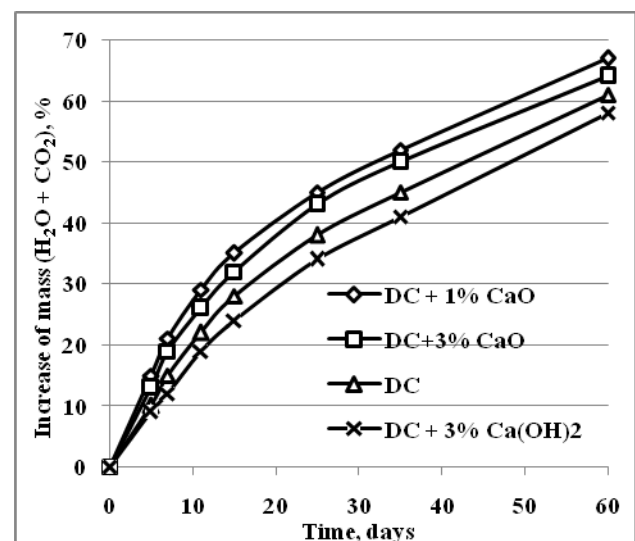
## 3. RESULTS

Fig. 1 shows the binding of vapours and CO<sub>2</sub> gas present in the air by different Portland cements.



**Fig. 1.** Absorption of airborne vapours and CO<sub>2</sub> gas by different Portland cements

The most intensive absorption of active components of air has been observed for Portland cement CEM I 42.5 R as it contains the largest amount of compounds that absorb humidity and CO<sub>2</sub>. Such compounds are identified [5] to be C<sub>3</sub>A, alkali and C<sub>4</sub>AF. As recently published [13–15] the moisture is observed intensively by orthorhombic C<sub>3</sub>A, C<sub>4</sub>AF as well as CaO, CaSO<sub>4</sub>·0.5H<sub>2</sub>O and CaSO<sub>4</sub>. CEM II/AL 42.5 has been seen to absorb less of the above elements as this cement has a lower clinker content. White Portland cements absorb less H<sub>2</sub>O and CO<sub>2</sub> just because they contain much less C<sub>3</sub>A, C<sub>4</sub>AF and alkali. For instance, the Danish Portland cement C<sub>3</sub>A only contained 5 % and 1 % of C<sub>4</sub>AF. The alkali content under Na<sub>2</sub>O<sub>ekv.</sub> was in a range of 0.2 % – 0.3 %. White Portland cement from Akmencementas, AB (“AC”) was used as well. It absorbed less H<sub>2</sub>O + CO<sub>2</sub> than DC due to its larger grain size.



**Fig. 2.** The effect of slaked lime and quicklime on vapour and CO<sub>2</sub> gas in white Danish Portland cement

**Table 2.** Effects of certain grout mix additives on vapour and CO<sub>2</sub> gas absorption levels in white cement (DC) at relative humidity of 90 % – 95 % and temperature of 18 °C ±2 °C

Cement marking and additives	Water and CO <sub>2</sub> absorption, %, after a number of days			
	7	14	28	35
DC, additive-free	15	28	38	49
DC + 3 % CaO	17	29	45	50
DC + 3 % Ca(OH) <sub>2</sub>	12	24	38	48
DC + 1 % TiO <sub>2</sub>	13	25	36	46
DC + 0.5 % “W”	14	30	50	55
DC + 1 % “W”	13	23	39	48
DC + 0.5 % ZnSt	3.5	5.5	5.5	5.5
(DC/S = 1:1)	8.7* (4.3)	22* (11)	30 (15)	34 (17.4)
(DC/S = 1:1) + 0.5 % ZnSt	0	3.2* (1.6)	3.2 (1.6)	3.2 (1.6)
(DC/S = 1:1) + 2% ZnSt	0	0	0	0
(DC/S = 1:3) + 1% “W”	11*	23* (5.7)	27.7 (6.9)	38.2 (9.7)

\* – % of cement mass; percentage of mix mass is given in brackets.

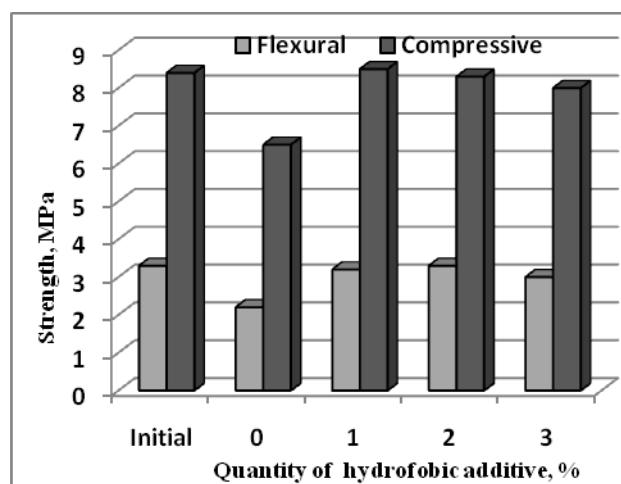
To some extent, water vapour and CO<sub>2</sub> gas absorption is affected by additives that are normally used in the making of dry grout mixes. Plaster and finishing mixes very often have sand and slaked lime or quicklime added. As it illustrated in Fig. 2 and Table 2, quicklime increases vapour and CO<sub>2</sub> absorption, because the finely dispersive CaO is very active with respect to vapours and CO<sub>2</sub> gas. Their reaction produces Ca(OH)<sub>2</sub> and CaCO<sub>3</sub>. The additive of hydrating lime suppresses the absorption of vapours and CO<sub>2</sub>. The white pigment TiO<sub>2</sub> has negligible and usually remissive effect. The additive of methyl-cellulose, which usually accounts for 0.5 % to 1.5 % of cement weight, does not have any significant effect either. Vapour and CO<sub>2</sub> absorption is materially affected by the hydrophobic additive zinc stearate, which amounts to roughly 1 % of cement weight.

Apart from cement, one of the key ingredients in dry group mixes is sand. Sand attenuates Portland cement in a grout mix to at least double the volume. As a result, a cement/sand mix absorbs less vapours and CO<sub>2</sub> comparing to sand-free Portland cement. Sand imbues cement with a certain sort of protection against atmospheric effects. Adding zinc stearate or other fatty acidic salts to a cement/sand mix apart from other components produces good results. The study involved certain laboratory and commercial finishing grout mixes.

The breakdown of the M 10 class grout made in a laboratory is as follows: 18 % white cement, 2 % hydrating lime (powder), 80 % quartz sand of Anykscai.

On top of that, methyl-cellulose in the amount of 0.2 % of the cement weight as well as varying amounts (ranging from 0 % to 3 % of the cement weight) of the hydrophobic additive of zinc stearate or sodium oleate were added. Samples (sized 4×4×16 cm) were formed of mix that has been freshly made or kept in open containers in a room with relative humidity of 70 % – 75 % and temperature of 17 °C – 18 °C. Fig. 3 shows the effects of the hydrophobic additive on the mechanical strength of the grout (by flexural and compressive) after 7 days of hardening) considering pre-hydration of the mix. We can see that in five days of pre-hydration the non-hydrophobic mix has lost around 22 % of its strength against

compressive and roughly 33 % of the strength against flexural. Following the addition of 1 % to 3 % of hydrophobic additive, the strength of the grouts after pre-hydration remained virtually the same (Fig. 3).



**Fig. 3.** The strength of samples of the laboratory grout (M 10) with hydrophobic additive content of 0, 1, 2 and 3 % after 5 days of pre-hydration against bending and compressive strength, MPa, after 28 days of hardening. The initial strength does not include pre-hydration and additives

It actually takes hydrophobic additive in the amount of about 1 % of the cement mass to protect the grout from the effects of humid air. No significant difference between the effects of zinc stearate and sodium oleate has been observed, yet large (3 % and more) concentrations of these additives slightly reduce the hardening of the grout as they inhibit the reaction between cement and water.

Table 3 shows the results of studies of reactions between commercial grout mixes with humid air. We can see that commercial plaster mixes can be resilient to pre-hydration and carbonisation too.

Insulation system reinforcement plaster exhibits a certain degree of resilience as well. They both contain a hydrophobic additive (sodium oleate). However, dry cement glue tends to get old. One of the conventional Portland cements, CEM I 42.5N was aerated using air of

**Table 3.** Absorption of vapours and CO<sub>2</sub> gas in some commercial grout mixes, %, at relative air humidity of 90 % to 95 % and room temperature of 20 °C ±2 °C

Grout name	Water and CO <sub>2</sub> absorption, %, after a number of days			
	7	14	28	90
White cement/lime plaster M 5	1.7	2.1	4.0	4.5
Grey cement/lime plaster M 5	2.0	2.5	2.6	4.0
Insulation system reinforcement plaster	0.5	2	3.1	3.1
Glue for polystyrene and mineral wool panels	13	20	24	25.8
Tile glue	4.3	8.0	9.0	10.8

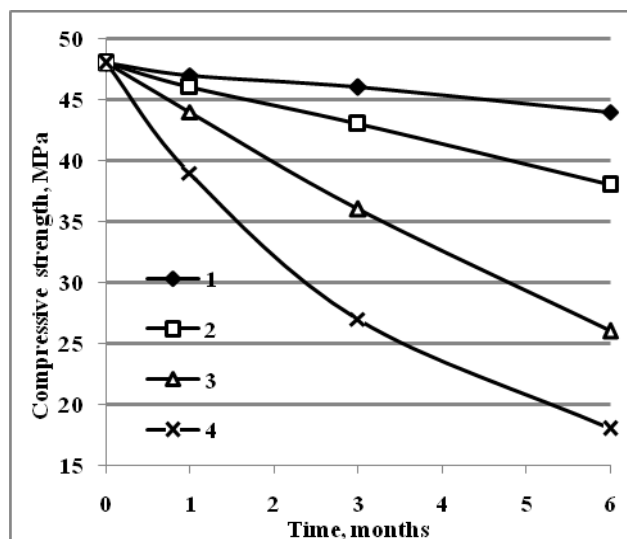
**Table 4.** Results of aeration of Portland cement CEM I 42.5N at relative air humidity of 70 % and temperature of 20 °C ±2 °C

Aeration duration	Air input, m <sup>3</sup> /kg	Increment in cement mass, g/kg	Products absorbed, g/kg		Residual cement strength, %, after aeration
			CO <sub>2</sub>	H <sub>2</sub> O	
0	0	0	0	0	100
5 min	0.06	9	4	5	96
15 min	0.18	25	12	13	90
30 min	0.36	33	15	18	86
60 min	0.75	50	26	24	62
3 h	2.25	66	32	34	56
10 h	7.5	120	63	57	23

70 % relative humidity and a special device – a capsule [5, 8]. The aeration was done on 1.5 kg of cement. The compressed air pressure was 1 ata and the debit was 0.037 m<sup>3</sup>/s. The results are shown in Table 4.

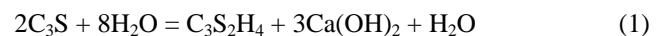
As we can see from the results presented in Table 4, in 10 hours of being subjected to aeration the Portland cement has absorbed some 12 % of H<sub>2</sub>O and CO<sub>2</sub>, more or less each. The strength under crushing starts to drop significantly after 30 minutes of aeration, when over 25 g/kg H<sub>2</sub>O + CO<sub>2</sub> has been absorbed.

A study of strength fluctuations was also performed on cement under storage conditions. Portland cement CEM I 42.5R was used here (Fig. 4).

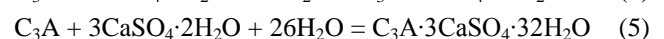
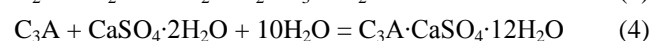
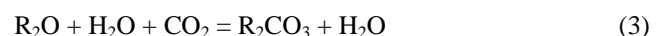


**Fig. 4.** Decrease in the activity levels of Portland cement CEM I 42.5R under storage conditions: 1 – while stored in a plastic bag in a heated room; 2 – while stored in a paper bag in a heated room; 3 – while stored in a paper bag in an unheated room; 4 – while stored in a paper bag in an unheated warehouse

Plastic and paper bags were used for storing cement. Filled with cement, they were stored in a heated and an unheated room. The study results have shown that the activity of cement decreases mostly when it is kept in paper bags in an unheated room. All these results lead to a conclusion that when exposed to humid ambient air with CO<sub>2</sub> gas present at all times, Portland cement undergoes pre-hydration. New compounds occurring next to cement under hydration become carbonised. The processes can be expressed as the following equations of reactions [6, 7]:



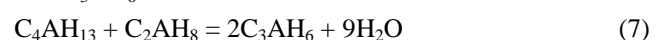
Ca(OH)<sub>2</sub> formed during prehydration of the Portland cement, but the carbonation reduces its amount. Experimental evidence of calcium hydroxide reaction upon calcite [11].



The following reaction occurs in parallel:



The resultant compounds are unstable and transform into C<sub>3</sub>AH<sub>6</sub>:



These aluminates do not form thick film on the surface of clinker particles, do not alter the binding times of cement but rather expend the active portion of cement. These and other reactions take place on the surface of minerals. The virtually insoluble CaCO<sub>3</sub> (calcite) forms on the surface of cement particles. Alkaline carbonates inhibit the solvency of Ca(OH)<sub>2</sub> and precipitate calcite out on the surface of minerals. Monosulphoaluminates and C<sub>3</sub>AH<sub>6</sub> occur too quickly. The Portland cement after aeration with dry air, as was referred [5], does not change its properties.

The first specification to proceed the mentioned reactions is the hydration of Portland cement. So, the opinion, declared in [3], on the role of hydration and carbonation is considered to be true. Therefore, cement undergoes accelerated binding and the resultant new compounds reduce the activity and powder-like properties of cement. The cement lumps. Yet white Portland cement is more resilient to pre-hydration due to the fact that it has a low C<sub>3</sub>A content and is virtually free from any C<sub>4</sub>AF and alkaline oxides ( $\text{Na}_2\text{O}_{\text{ekv.}} = 0.2 \%$ ).

#### 4. CONCLUSIONS

1. Compared to conventional Portland cement, white Portland cement hydrates and carbonises more slowly in humid air and absorbs 20 % – 30 % less H<sub>2</sub>O and CO<sub>2</sub> from the air. An exceptional property of many white cements is that they have a low C<sub>3</sub>A and alkali content and contain almost no C<sub>4</sub>AF. Therefore, such white cements are more resistant to pre-hydration and carbonation.

2. Non-hydrophobic dry finishing grouts, just like their white variety lose their positive properties over periods of storage in humid air conditions because premature hydration and carbonation worsen the properties of their main component, which is cement.

3. The regular additives of dry grouts like CaO, Ca(OH)<sub>2</sub>, TiO<sub>2</sub>, methyl-cellulose only exercise an insignificant effect in pre-hydration. Hydrophobic additives like fatty acid salts (zinc stearate, sodium oleate, etc.) provide a certain degree of improvement in this regard. Ordinary finishing grouts require an addition of hydrophobic additive in the amount of roughly 1 per cent of the cement weight.

#### REFERENCES

1. **Savinkov, N.** Hydration Cement in the Air *Concrete and Reinforced Concrete* 3 1978: pp. 32–33 (in Russian).
2. **Hoffmann, N.** Einfluß der Langeitlagerung von Zement auf die Gebrauchselgenschoften *Baustoff Industrie* 1 1987: pp. 9–11.
3. **Richarts, W.** Einfluß der Lagerung auf die Eigenschaften des Zement *Zement-Kalk-Gips* 2 1974: pp. 67–74.
4. **Acheenko, B., Galperina, T.** Physical Properties of Flid Cement *Cement* 1 1987: pp. 14–16 (in Russian).
5. **Vektaris, B., Andriušienė, J.** Change of Properties of Cements in Pneumotransporting Process *Cement* 8 1981: pp. 12–15 (in Russian).
6. **Glaser, F., Marchend, J., Samson, E.** Durability of Concrete – Degradation Phenomena Involving Determinal Chemical Reactions *Cement and Concrete Research* 38 2008: pp. 226–246.  
<http://dx.doi.org/10.1016/j.cemconres.2007.09.015>
7. **Barret, P., Bertrandie, D., Bean, D.** Calcium Hydrocarbo-natiunate, Carbonate, Aliumina Gel and Hydrated Aliuminales Solubility Diagrams Calculated in Equilibrium with CO<sub>2</sub> and with Na<sup>+</sup> aq Ions *Cement and Concrete Research* 13 1983: pp. 789–800.  
[http://dx.doi.org/10.1016/0008-8846\(83\)90080-7](http://dx.doi.org/10.1016/0008-8846(83)90080-7)
8. **Andriušienė, J., Vektaris, B.** Method Determinating Properties of Cements *Bulletin of Invetions* 41981: Aut. certificate 800140 (in Russian).
9. **Meshkov, P., Mokin, V.** Optimization Methods of Dry Building Mixes *Building Materials* 5 2000: pp. 12–14 (in Russian).
10. **Misnikov, D., Puchova, A.** Hydrophobisation of Dry Buildings Mixes by Additives from Biological Materials *Building Materials* 10 2004: pp. 2–4 (in Russian).
11. **Culturone, G., Gebartian, E., Hurtas, M. O.** Forced and Natural Carbonation of Lime-based Mortars with and without Additives: Mineralogical and Textural Changes *Cement and Concrete Research* 35 2005: pp. 2278–2289.  
<http://dx.doi.org/10.1016/j.cemconres.2004.12.012>
12. **Maltese, C., Pistolesi, C., Bravo, A., Cella, F., Cerulli, T., Salvioni, D.** A Case History: Effect of Moisture on the Setting Behaviour of a Portland Cement Reacting with an Alkali-free Accelerator *Cement and Concrete Research* 37 2007: pp. 856–865.
13. **Dubina, E., Black, L., Sieber, R., Plank, J.** Interaction of Water Vapour with Anhydrous Cements *Minerals Advances in Applied Ceramics* 109 2010: pp. 260–268.
14. **Enke, D., Ruckriem, M., Schreiber, A., Adolphs, J.** Water Vapour Sorption on Hydrophilic and Hydrophobic Nanoporous Materials *Applied Surface Science* 256 2010: pp. 5482–5485.
15. **Dubina, E., Wadso, L., Plank, J.** A Sorption Balance of Water Vapour Sorption on Anhyrous Cement Minerals and Cement Constituents *Cement and Concrete Research* 41 2011: pp. 1196–1204.

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