Construction and Building Materials 220 (2019) 396–402

Contents lists available at ScienceDirect

Construction and Building Materials

journal homepage: www.elsevier.com/locate/conbuildmat

Gypsum dehydration in cement and its impact on air-void structure in air-entrained concrete

Maciej Sypek [a], Rafał Latawiec [a], Waldemar Pichór [b,*]

[a] *Lafarge Cement S.A., Małogoszcz, Poland*
[b] *Faculty of Materials Science and Ceramics, AGH University of Science and Technology, Cracow, Poland*

HIGHLIGHTS

- Air-entrained concretes with cements of various gypsum dehydration level were tested.
- The AVA technique was used to test air-void structure of concrete.
- The effect of gypsum dehydration level on the air-void structure in concrete was observed.

ARTICLE INFO

Article history:
Received 8 February 2019
Received in revised form 29 May 2019
Accepted 2 June 2019
Available online 24 June 2019

Keywords:
Air-void structure
Gypsum dehydration
Air-entrained concrete

ABSTRACT

The compatibility of the admixture of cement and concrete is an important factor in the creation of high-quality concrete. Common problems involving the resistance of concrete to freezing and thawing drew the authors' attention to gypsum dehydration in cement. The influence of gypsum dehydration on the air-void structure of air-entrained concrete obtained with cement low in C_3A was examined. In all studied cases, the negative influence of gypsum dehydration was observed. It is believed that greater solubility and a higher solubility rate of hemihydrate result in higher early-stage Ca^{2+} and SO_4^{2-} ion concentrations, and thus cause alterations in the chemical admixture's mechanism of action.

1. Introduction

Concrete used in road surfaces and bridges in cold-winter regions is exposed to very severe conditions. Over the past several years, it has been observed that many types of concrete used in bridges in many countries have failed to meet industry standards [1]. The problem of the resistance of concrete to freezing and thawing has existed globally for some time [2]. Various methods to test the frost resistance of concrete have been developed [3,4]. The test methods used most commonly rely on the subjection of concrete samples to a cycle of freezing and thawing in water and/or de-icing salts. Powers [5] developed the concept of using the spacing factor and size of air voids as parameters used to ensure the frost resistance of concrete. The mechanism of air entrainment and the formation and stabilisation of air voids in fresh concrete has been described by many researchers, e.g. Folliard and Du [6]. Chemical admixtures known as air-entraining agents are used to produce air-entrained concrete. Air voids create empty spaces within the concrete which act as reservoirs for freezing water moving in the capillary pores [7]. Air-entraining agents are usually surfactants – molecules composed of a hydrophilic head, which may be either charged (ionic) or polar (non-ionic), and a hydrophobic hydrocarbon tail. Surfactants enhance foam creation and stability via several mechanisms, namely reduction of surface tension, separation of bubbles repelling each other due to steric interactions, and stabilisation of bubbles by micelles [8–10]. Other admixtures, mainly water reducers, are known to alter air-void structure. Nowadays, in the case of pumpable, air-entrained concrete, superplasticisers based on polycarboxylate ethers (PCE) are most commonly used. In this case, a strong air-entraining effect has been observed [11,12]. Lange and Planck [13] studied the mechanism underlying the air entrainment of PCE and came to the conclusion that excessive foaming behaviour on the part of PCE requires a foam stabiliser, which, in their case, was an unreacted monomer. Łaźniewska-Piekarczyk [12] examined the surface tension of solutions containing a PCE superplasticiser and/or an air-entraining agent and discovered that surface tension was similarly affected by both admixtures. Other plasticising admixtures based on naphthalene or melamine have also been proven to coarsen air-void structure [14]. Admixture interactions are mentioned by Folliard

---

* Corresponding author at: AGH University of Science and Technology, Faculty of Materials Science and Ceramics, Mickiewicza 30, 30-059 Cracow, Poland.
E-mail address: pichor@agh.edu.pl (W. Pichór).

https://doi.org/10.1016/j.conbuildmat.2019.06.011
0950-0618/© 2019 Elsevier Ltd. All rights reserved.

and Du, who, however, point out that, due to the complexity of modern admixtures, it is impossible to generalise about the effects of their interaction; instead, they should be experimentally examined [6]. The compatibility of cement and various admixtures has been extensively investigated; various incompatibilities have been observed, thus preventing the establishment of any general guidelines. Many authors point to the importance of three chemical properties of Portland clinker: C_3A content and crystal composition, alkali content, and type and content of sulphate-bearing materials [15–19]. These characteristics, in combination with different admixtures, can cause severe loss of fluidity, retardation of setting time, lack of strength, improper air-void structure, and others. All of these factors strongly affect the early hydration period, as they dissolve in cement pore solutions and form early hydration products.

Among various reasons for the differences in the above-mentioned chemical properties of clinker, the dehydration of gypsum to hemihydrate is one that directly affects sulphate-bearing materials, as well as indirectly affecting C_3A; this is sometimes difficult to control or prevent. At temperatures between 75 and 110 °C, dehydration of gypsum leading to the creation of hemihydrate may occur in the cement mill or silo [20]. The initial rate of C_3A hydration is strongly influenced by the source of the sulphate being used; therefore it should be considered along with the type of sulphate-bearing material [21,22]. Hemihydrate, in comparison to gypsum, is characterised by greater solubility and a higher solubility rate; therefore, a higher initial ion concentration is expected in the pore fluid. Porchet [23] has shown this behaviour in conjunction with early C_3A hydration in the presence of different kinds of calcium sulphate. Many hypotheses concerning the mechanism of the action of calcium sulphate have been suggested; however, the mechanisms of retarding the C_3A reaction have not yet been fully elucidated. According to some authors, the action is due to the formation of a barrier layer caused by hydration products, consisting of a more or less permeable sulphoaluminate crystalline or non-crystalline layer on the C_3A surface, limiting the transport of water and ions [24]. Another hypothesis is that deceleration of C_3A hydration occurs due to the precipitation of calcium hydroaluminate or adsorption of the sulphate on C_3A [25]. Such disagreements in interpretation are probably due to the fact that the most of the phenomena occur at a very early stage, even during mixing. Łagosz shows that the effectiveness of retardation of the C_3A reaction in the presence of hemihydrate is less than when gypsum is used [26]. Additionally, the reaction product of the C_3A phase and hemihydrate is not analogous to the ettringite phase; thus the monosulphite-aluminate form of $C_3A{\cdot}CaSO_4{\cdot}11H_2O$ does not undergo the ettringite-monosulphate reaction. Moreover, if the cement contains a small amount of C_3A, the effect of increasing ion concentration in the pore solution is enhanced, as less C_3A is present to adsorb sulphate ions.

There are many factors affecting air-void structure in concrete: cement mineral composition, fine and coarse aggregates, chemical admixtures, water-cement ratio, mixing, transport, pumping, and many others. The chemical composition of cement, in terms of alkali or sulphate content, may have a negative influence on air-void structure [10].

In this study, the impact of cement composition, particularly the dehydration of gypsum in cement on the air-void structure of concrete, was considered. It is believed that gypsum dehydration in cement has significance in practical use when air-entrained concrete is produced and placed. The characteristics of the new cement, not considered previously in this context, are shown to constitute an important factor in the creation of a satisfactory air-void structure and, consequently, durable construction.

2. Materials and methods

2.1. Experimental programme

The correlation between freezing-thawing resistance and air-void structure as measured by AVA was investigated. The influence of gypsum dehydration on air-void structure was examined by means of a two-stage study of freshly-mixed concrete. The first stage was performed with a pure single compound of an air-entraining agent with a constant dosage; meanwhile, the level of cement gypsum dehydration was variable. The aim of this stage was to distinguish the impact of dehydration level on an admixture set and single surfactant. The second stage was conducted with constant slump and air content, whereas the level of cement gypsum dehydration and the admixture dosage were variable. Commercially available admixture sets were used. The aim of this stage was to observe the influence of the gypsum dehydration level in cement on air-void structure.

2.2. Materials

Cements with different levels of gypsum dehydration were prepared separately for each stage of the experimental programme by means of controlled heating of base cement in an oven. Three different batches of the cement CEM I 42,5 N-SR3/NA were used. The phase composition of clinker, the contents of sulphate-bearing materials, and the calculated gypsum dehydration level (GDH), time, and temperature of heating are shown in Table 1. The physical properties of the cements are shown in Table 2. Cements were given names according to the batch of cement used and degree of gypsum dehydration, e.g. C1/22 signifies that the mix was prepared with cement batch C1 and that the degree of gypsum dehydration was 22%.

Each cement batch was heated in several metal containers, each with a capacity of 20 kg. Following heat treatment, cement samples were left to cool. Each cement series was homogenised via mixing. The gypsum dehydration level (GDH) was calculated as follows:

$$GDH = (HH \cdot 172/145)/(G + HH \cdot 172/145) \tag{1}$$

where the molar mass of gypsum (G) was 172 g and of hemihydrate (HH) 145 g. No anhydrite was detected in any sample. Contents of Na_2O and K_2O were approximately 0.2 and 0.5%, respectively.

Table 1
Cement composition and calculated gypsum dehydration level (GDH).

Series/prepared cements		C_3S [%]	C_2S [%]	C_4AF [%]	C_3A [%]	CaO [%]	G* [%]	HH** [%]	GDH	SO_3 [%]	Treatment
C1	C1/22	59,4	20,4	13,3	1,3	0,4	3,0	0,7	0,22	2,54	not heated
	C1/42	59,2	19,9	14,1	1,2	0,4	2,8	1,7	0,42	2,50	16 h in 90 °C
	C1/56	59,0	20,1	13,5	1,3	0,5	1,5	1,6	0,56	2,54	20 h in 90 °C
C2	C2/42	60,0	16,4	16,0	1,0	0,5	2,8	1,7	0,42	2,54	not heated
	C2/61	59,9	17,1	15,4	1,0	0,5	1,5	2	0,61	2,49	16 h in 90 °C
	C2/81	59,4	16,6	16,2	1,0	0,4	0,7	2,5	0,81	2,42	20 h in 90 °C
C3	C4/29	58,9	18,5	16,9	1,1	1,0	2,6	0,9	0,29	2,47	not heated
	C4/69	59,0	17,8	16,7	0,8	0,6	1,4	2,6	0,69	2,55	16 h in 90 °C
	C4/74	59,3	18,2	16,5	1,0	0,6	0,9	2,2	0,74	2,53	20 h in 90 °C

* Gypsum.
** Hemihydrate.

Table 2
Physical properties of cements.

Series/prepared cements		Fineness [cm^2/g]	Soundness [mm]	Standard consistency [%]	Setting time [min]		Compressive strength [MPa]	LOI [%]
					Initial	Final		
C1	C1/22	3272	0,0	28,8	240	350	52,8	1,28
	C1/42	3251	0,5	29,0	235	305	54,8	1,09
	C1/56	3225	0,0	29,4	250	320	56,2	1,20
C2	C2/42	3251	0,5	29,0	205	290	54,8	1,09
	C2/61	3232	1,0	29,0	195	285	53,8	1,09
	C2/81	3279	0,5	28,0	205	290	54,6	1,12
C3	C3/29	3051	0,5	28,7	240	295	48,9	1,28
	C3/69	3032	0,5	27,9	230	290	49,5	1,12
	C3/74	3110	0,5	28,6	230	300	48,8	1,14

Table 3
Admixtures information.

Admixture type	Admixture base	Admixture sets
AEA1	Vinsol resin – anionic polyelectrolyte	
AEA2	SLES – modern anionic surfactant	
SP1	PCE	Set 1 (commercial)
AEA3	Wood resin	
SP2	Polymeric type	Set 2 (commercial)
WR1	Lignosulfonate/gluconate	
AEA4	Combination of natural resins and synthetic tensides	

River sand and fractions 2/8 and 8/16 of crushed granite or dolomite were used. All the aggregate types met the requirements of EN 12620 and were proven to be frost-resistant. The water absorption of river sand, 2/8 granite, 8/16 granite, 2/8 dolomite, and 8/16 dolomite was 0.5, 0.7, 0.4, 0.5, and 0.4%, respectively. The pure air-entraining agents AEA1 and AEA2 were used in the first stage. Two commercially available polycarboxylate-type superplasticisers (SP1 and SP2), a lignosulphonate-based plasticiser (WR1), and two types of air-entraining agents (AEA3, AEA4) were used in the second stage. All of the admixtures used are described in Table 3, according to the relevant technical sheet or chemical compound name.

2.3. Concrete mixing procedure

Aggregates were dried in an oven and placed in a temperature-controlled room at 20 °C for at least 24 h before mixing. Aggregates were placed in the mixer. At the time of mixing, all aggregates were loaded into the mixer along with approximately half of the mixing water. This combination was mixed for 30 s to allow the aggregates to approach the saturated surface dry (SSD) condition and to ensure that they were evenly distributed. The cement and the remaining water were added and mixed for an additional 10 s. Then, the air-entraining agent, water reducer, and superplasticiser were added. Following the addition of the admixtures, the concrete was mixed for one minute. The resulting mixture was rested for 55 min and then mixed for an additional 30 s. Samples were tested for slump, total air content, and air-void structure, as measured by the AVA method. The concrete was rested for 55 min in order to simulate delivery time.

2.4. Test methods

It is assumed that the spacing factor proposed by Powers, along with A_{300} content, is an appropriate way to describe the air-void structure of concrete. The Powers spacing factor, which derives from a thesis on damage caused by hydraulic pressure during frost action, is an estimate of the longest distance to the air-void surface. The hydraulic pressure hypothesis is one of several theories concerning what happens during frost action; several researchers have questioned its validity, even though the spacing factor is a very popular evaluation criterion and is still used in many countries as an obligatory standard today. Standard requirements of various European countries which present a different approach to freeze-thaw resistance are presented in Table 4. Standard requirements concerning the spacing factor of air voids in hardened concrete are also used in the USA and Canada. American standards specify that the spacing factor should be lower than 0.2 mm [31]; Canadian standards state that in ordinary concrete this factor should not exceed 0.23 mm.

The air-void structure of concrete can be measured in either a fresh or hardened state. Air-void analysis of hardened concrete can be performed according to EN 480-11 [32] or ASTM C457 [33]; air-void analysis of fresh concrete can be performed using the AVA method [34] or the more recent SAM method [35]. Air-void analysis of hardened concrete is the most accurate method; however, the experience and accuracy of the operator are required in sample preparation [36]. The results of an air-void analysis of hardened concrete are obtained after the concrete is built in. Although the AVA method has some limitations, such as indicating a lesser value of air content than the air pressure method due to its inability to measure bubbles larger than 3 mm, the spacing factor measured via AVA can be used as an acceptance criteria for concrete [36]. The SAM method is relatively new on the market; to date only a few tests regarding this method have been published. The AVA method of measuring air-void structure has been chosen for this study because of its greater potential for use as a on-site quality control tool in comparison to air-void analysis of hardened concrete and because it is more proven than the SAM method. In order to improve and check the credibility of this method, a correlation between air-void structure measured by AVA method and freezing-thawing resistance was obtained.

Table 4
Standard requirements of different standards about air content and spacing factor.

Standard	Requirement	Exposure class			
		XF1	XF2	XF3	XF4
EN 206-1 [27]	Air content [%]	–	>4,0	>4,0	>4,0
German Federal Ministry of Transportation ZTV Beton- StB 01 [28]	Air content (daily average) [%]	>5,0		>4,0	
	A_{300} [%]	>1,5		>1,8	
	Spacing factor L [mm]	<0,20		<0,20	
Austrian standard ONORM B 4710-1 [29]	Air content [%]	–	>2,5	>2,5	>4,0
	A_{300} [%]	–	>1,0	>1,0	>1,8
	Spacing factor L [mm]	–	–	–	0,18
Danish Standard DS. 2426 [30]	Air content in fresh concrete [%]	–		>4,5	
	Air content in hardened concrete [%]	–		>3,5	
	Spacing factor L [mm]	–		<0,20	
	Concrete resistance to surface scaling	–	good	good	good

In this paper, air content was determined using the pressure method according to EN 12350-7 [37]; slump was determined according to EN 12350-2 [38]. Air-void characteristics in fresh concrete were determined using an AVA-3000 Air Void Analyzer. The AVA method's error is estimated to equal 0.014 mm for spacing factor and 0.12% for A_{300}. Estimates are based on repeating measurements on several batches of identical concrete.

2.5. Concrete mixtures

In the first stage, six concrete mixes were prepared. The composition of the mixes were as follows: modified cement, 350 kg, aggregates: fine, 715 kg; 2/8 mm (granite), 513 kg; 8/16 mm (granite), 605 kg. The w/c ratio was 0.44. Dosages of admixtures were adjusted to achieve an air content of 7.4 ± 0.4% after 60 min (Table 5).

In the second stage of research, the nine different concrete mixes were the same as those used in the first stage. Admixture type and dosage are shown in Table 6. Dosages of admixtures were experimentally adjusted in order to achieve a slump of 130 ± 20 mm and air content either 6.0 ± 0.4% or 7.0 ± 0.4% after 60 min.

3. Results

3.1. Correlation between air void structure measured by the AVA method and freeze-thaw resistance

All results (presented in Figs. 1 and 2) correlating the spacing factor and content of air voids smaller than 300 µm (A_{300}) were achieved with the use of different concrete mixtures in constant conditions of temperature and humidity, using one AVA and one freeze-thaw chamber. The cement used in all mixtures was the same (CEM I 42,5N-SR3/NA). The results presented here lead to the conclusion that, for the tested concretes, in order to obtain concrete which fulfils the requirement of less than 20% loss of strength after 150 cycles of freezing and thawing, the spacing factor should be no higher than 0.30 mm and A_{300} no lower than 1%. Figs. 1 and 2 show the correlation between the AVA results and freeze-thaw resistance. For all results, AVA was operated by the same operator. According to Polish standards, concrete is considered freeze-thaw resistant when its loss of compressive strength after 150 cycles of freezing and thawing is no higher than 20%.

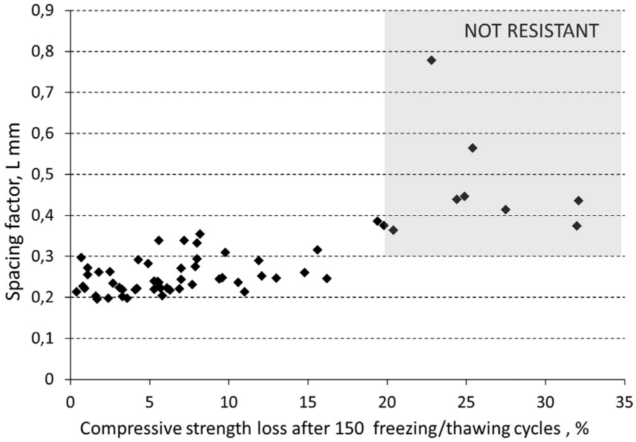

Fig. 1. Correlation between freezing-thawing resistance of different concretes and spacing factor measured by AVA based on earlier investigations of real commercial concretes.

Particular values of air-void characteristics are different from those developed by Powers; nevertheless, the correlation between them is strong.

3.2. Influence of gypsum dehydration on the behaviour of air-entraining agents

Table 7 presents detailed properties of concrete mixtures. Figs. 3 and 4 show the relationship between air-void structure and GDH for different AEAs. In the case of both AEAs, the spacing factor is severely affected by gypsum dehydration. On the other hand A_{300} is reduced only slightly in the case of SLES, significantly in the case of Vinsol resin. The air content of all mixes is similar and is not affected by the level of gypsum dehydration (Table 3).

Table 5
Concrete mixtures proportions in second study of research program.

Admixture	Cement	Admixtures type/dosage [% of cement mass]			Air content after 60 min [%]	Slump after 60 min [mm]
		SP	WR	AEA		
AEA3	C3/29	–	–	AEA3/0,760	7,4	30
	C3/69			AEA3/0,760	7,0	35
	C3/74			AEA3/0,760	7,4	50
AEA4	C3/29	–	–	AEA4/0,440	7,4	40
	C3/69			AEA4/0,440	7,8	50
	C3/74			AEA4/0,440	7,4	40

Table 6
Concrete mixtures proportions in first study of research program.

Admixture	Cement	Admixtures type/dosage [% of cement mass]			Air content after 60 min [%]	Slump after 60 min [mm]
		SP	WR	AEA		
Set1	C1/22	SP1/0,56	–	AEA1/0,040	6,8	120
	C1/42	SP1/0,63		AEA1/0,035	6,8	120
	C1/56	SP1/0,62		AEA1/0,040	7,0	140
Set1	C2/42	SP1/0,57	–	AEA1/0,036	6,2	150
	C2/61	SP1/0,64		AEA1/0,035	6,0	140
	C2/81	SP1/0,51		AEA1/0,035	6,1	150
Set2	C2/42	SP2/0,34	WR1/0,12	AEA2/0,050	7,0	130
	C2/61	SP2/0,36	WR1/0,12	AEA2/0,050	7,0	150
	C2/81	SP2/0,41	WR1/0,12	AEA2/0,050	7,0	160

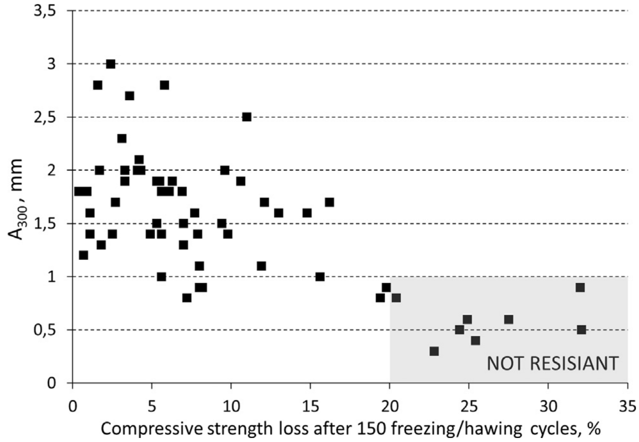

Fig. 2. Correlation between freezing-thawing resistance and A_{300} measured by AVA.

3.3. Influence of gypsum dehydration on concrete mixes with similar air content and slump

Table 8 presents detailed properties of concrete mixtures. Figs. 5 and 6 show the air-void characteristics of samples of fresh concrete with different cement and admixture sets. Trend lines were generated according to the best fit to the data. In all analysed cases, A_{300} decreased and spacing factor increased with increasing gypsum dehydration levels. The linear relationship between air-void structure and gypsum dehydration level is confirmed by coefficients of determination ranging from 0.75 to 0.99 (particular values are shown in Figs. 5 and 6).

4. Discussion

Thermal treatment of cement changed the dehydration levels of gypsum. The authors observed that the total content of sulphate-bearing materials varied within a range of ±25% between batches of the same cement with different dehydration levels. This is attributed to the absolute error in Rietveld analysis. The sulphate content of different cement mixes was similar.

Chatterji [39] has pointed out that the two AEAs used in the first stage of the research programme are of different types. Vinsol resin reacts with a calcium hydroxide solution of cement paste to precipitate insoluble calcium slats that collect on water-air-cement grain and thus cause both air entrainment and bubble stability. This type does not reduce surface tension. SLES lowers surface tension and thus causes air entrainment.

In a comparison of the two AEAs, A_{300} is similar; however, the spacing factor is lower in the case of SLES. This may suggest that the air-void structure generated by SLES consists of air voids with lesser diameters than those generated by Vinsol resin.

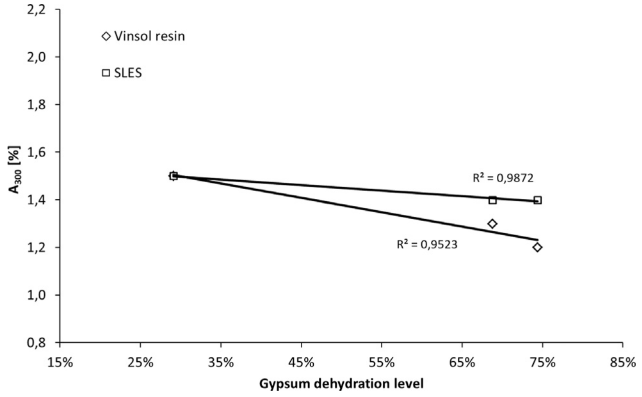

Fig. 3. A_{300} factor examined by AVA versus gypsum dehydration level for different concrete mixtures with pure air-entrainment admixtures (AEA's) and C3 cements.

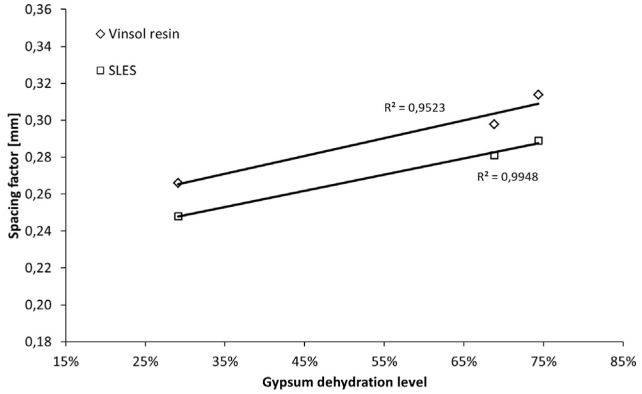

Fig. 4. Spacing factor L examined by AVA versus gypsum dehydration level for different concrete mixtures with pure air-entrainment admixtures and C3 cements.

The difference in the size of the smallest generated bubbles may be the cause of differences in the influence of gypsum dehydration on A_{300} in cases of different AEAs. Gypsum dehydration causes, instead of the smallest bubbles, bubbles with greater diameters irrespective of the type of AEA. The strong influence of SLES on spacing factor and its weaker influence on A_{300} may be caused by its prevention of the creation of the smallest air bubbles and its formation instead of larger pores, albeit pores with diameters below 0.300 mm. With regard to Vinsol resin, similarly to SLES, larger pores are formed instead of the smallest air bubbles. Unlike SLES, these pores are characterised by diameters greater than 0.300 mm; thus both A_{300} content and spacing factor are significantly affected.

In the case of concrete mixes with air-entraining agents and plasticising admixtures, it has been observed that mixes contain

Table 7
Fresh concrete mixtures properties in first stage of research program.

Admixture	Cement type	Slump after 10 min [mm]	Slump after 60 min [mm]	Air content after 10 min [%]	Air content after 60 min [%]	AVA results after 60 min			
						Spacing factor [mm]	A_{300} [%]	Air void content in concrete [%]	Specific surface [mm^{-1}]
AEA3	C3/29	35	30	7,0	7,4	0,266	1,5	3,7	19,8
	C3/69	40	35	6,6	7,0	0,298	1,3	3,9	17,5
	C3/74	45	50	6,6	7,4	0,314	1,2	3,9	16,6
AEA4	C3/29	40	40	7,2	7,4	0,248	1,5	3,8	21,5
	C3/69	50	50	7,2	7,8	0,281	1,4	4,2	18,0
	C3/74	40	40	7,2	7,4	0,289	1,4	4,0	17,7

Table 8
Fresh concrete mixtures properties in second stage of research program.

Admixture	Cement type	Slump after 10 min [mm]	Slump after 60 min [mm]	Air content after 10 min [%]	Air content after 60 min [%]	AVA results after 60 min			
						Spacing factor [mm]	A_{300} [%]	Air void content in concrete [%]	Specific surface [mm^{-1}]
Set 1	C1/22	110	120	5,3	6,8	0,221	1,9	4,3	22,6
	C1/42	100	120	5,5	6,8	0,222	1,8	4,5	22,1
	C1/56	100	140	6	7	0,245	1,5	3,9	21,2
Set 1	C2/42	150	150	5,4	6,2	0,202	2,0	3,8	25,8
	C2/61	120	140	5,3	6,0	0,239	1,5	3,2	24,1
	C2/81	120	150	5,3	6,1	0,243	1,5	3,6	22,2
Set 2	C2/42	100	130	4,7	7,0	0,231	1,6	4,0	22,0
	C2/61	110	150	4,8	7,0	0,271	1,3	4,0	19,0
	C2/81	110	160	5,0	7,0	0,332	0,9	4,3	15

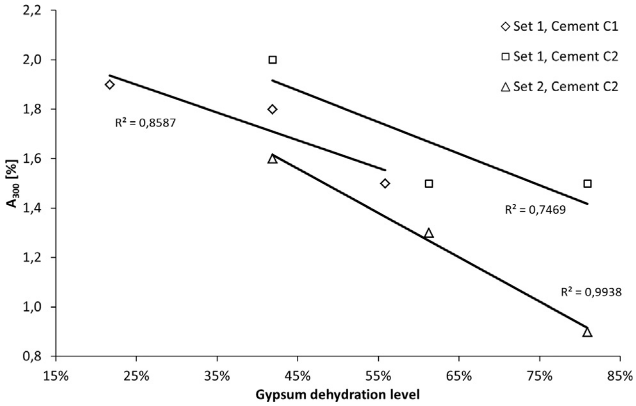

Fig. 5. Influence of gypsum dehydration level on A_{300} for different concrete mixtures with Set 1 or Set 2 admixtures and cement C1 or C2 examined by AVA.

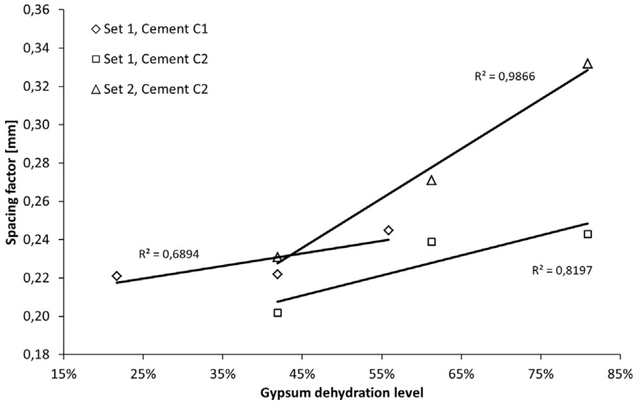

Fig. 6. Spacing factor L examined by AVA versus gypsum dehydration level for different concrete mixtures with Set 1 or Set 2 admixtures and cement C1 or C2.

differing amounts of admixtures in order to maintain similar slump and air content. Admixtures, especially superplasticisers based on PCE, are known to entrain air [11,12]. Therefore gypsum dehydration may change the air-void structure; however, gypsum dehydration may itself be a secondary effect. The primary effect may be a change in workability, which results in the necessity for a different amount of SP. The direct relationships of air-void structure on one hand and admixture dosage and GDH on the other point to the conclusion that it is gypsum dehydration that affects this structure.

Due to different admixture sets, the influence of the addition of lignosulphonate water reducer to concrete mix cannot be clearly identified. Differences in the steepness of Sets 1 and 2 with cement C2 trend lines points towards the conclusion previously reached by other papers, i.e. that lignosulphonate water reducer coarsens air-void structure [13].

The results show that gypsum dehydration in low-C_3A cement may have a strong negative influence on concrete air-void structure. Gypsum hemihydrate is characterised by both greater solubility and a higher solubility rate in comparison to dihydrate, which may result in increasing ion concentration in early pore solution and altered hydration of C_3A. Increasing ion concentration in early pore solution may be especially magnified in the case of low-C_3A cement, as not much substance is present to adsorb those ions. The authors suspect that if gypsum dehydration plays an important role in the compatibility of cement and air-entraining admixtures, gypsum content is equally important, as it carries Ca^{2+} and SO_4^{2-} ions. One area for future research in the scope of gypsum dehydration is measurement of the ion concentration in pore solutions of cement with dihydrate and hemihydrate. Another aspect for study is whether SO_3 content plays a role similar to that of gypsum dehydration.

The air-entraining mechanism was previously explained by Folliard and Du [6]. The highly ionic surface of cement particles during early hydration, mostly due to ettringite and allite, attracts other ionic compounds such as the ionic head of the air-entraining admixture. The part of the air-entraining admixture adsorbed on ettringite contributes little to proper air entrainment, as stated by Folliard and Du. The same authors state that bubbles that have already formed should adhere to cement particles due to ionic forces and stabilise foam. These two hypotheses are somewhat contradictory. Ionic species, especially multivalent, are known to alter the working mechanism of surfactants in concrete. Dodson [40] points out that an increase in electrolyte content results in the reduction of electrostatically-induced disjoining pressure. This results in turn in impaired ability to reduce surface tension and generate air bubbles small enough to ensure concrete freeze/thaw resistance.

All of the examined air-entraining agents are based on an anionic type of surfactant. This group of surfactants is most sensitive to the presence of electrolytes. Other types of surfactants, i.e. amphoteric and non-ionic, are more resistant to high ion concentrations [10]. Different types of air-entraining agents should be examined in subsequent studies in order to determine whether all of them are vulnerable to gypsum dehydration. Even though the AEAs examined here were all anionic, the influence of gypsum dehydration was not commensurately strong. Probably the structure of a particular surfactant is also an important factor to be taken into account when the influence of the level of gypsum dehydration is examined.

5. Conclusions

The influence of gypsum dehydration on air-void structure was examined and proved to be significant and difficult to control. The results of the studies on various chemical admixtures presented here may confirm that increasing levels of gypsum dehydration lead to coarsening of the air-void structure. The authors suspect that gypsum dehydration results in higher concentrations of SO_4^{2-} and Ca^{2+} ions in early pore solutions, especially in low- C_3A cement. In the case of air-entrained concrete, gypsum dehydration in cement should be taken into consideration and scrupulously avoided. Further studies should include ion concentrations, different sources of sulphate-bearing materials such as anhydrite, the influence of SO_3 content in cement, and the vulnerability of different types of surfactants, especially non-ionic and amphoteric, to gypsum dehydration. The authors observed that micro- and nano-interactions between cement and concrete admixtures, especially PCE superplasticisers, air-entraining agents, and de-foamers, have not been explained in detail. Since the quality of modern concrete is usually defined by the compatibility of these factors, it would be extremely useful to take a detailed look at these issues.

Declaration of Competing Interest

None.

Acknowledgements

This research has been partly supported by the EU Project POWR.03.02.00-00-I038/16-00.

References

[1] L. Czarnecki, J. Deja, K. Flaga, J. Jasiczak, W. Kurdowski, J. Małolepszy, W. Radomski, J. Śliwiński, Frost resistance of concrete in bridge structures (in Polish), Budownictwo, Technologie, Architektura 69 (2015) 1.
[2] M. Pigeon, J. Marchand, R. Pleau, Frost resistant concrete, Constr. Build. Mater. 10 (1996) 339–348.
[3] M.J. Setzer, P. Heine, S. Kasparek, S. Palecki, R. Auberg, V. Feldrappe, E. Siebel, Test methods of frost resistance of concrete: CIF-Test: Capillary suction, internal damage and freeze thaw test—Reference method and alternative methods A and B, Mater. Struct. 37 (2004) 743–753.
[4] L. Basheer, J. Kropp, D.J. Cleland, Assessment of the durability of concrete from its permeation properties: a review, Constr. Build. Mater. 15 (2001) 93–103.
[5] T.C. Powers, Void space as a basis for producing air-entrained concrete, J. Proc. 50 (1954) 741–760.
[6] L. Du, K.J. Folliard, Mechanisms of air entrainment in concrete, Cem. Concr. Res. 35 (2005) 1463–1471.
[7] D.A. Whiting, M.A. Nagi, Manual on Control of Air Content in Concrete, Portland Cement Association, Skopie, 1998.
[8] B. Feneuil, O. Pitois, N. Roussel, Effect of surfactants on the yield stress of cement paste, Cem. Concr. Res. 100 (2017) 32–39.
[9] I. Cantat, S. Cohen-Addad, F. Elias, F. Grane, R. Höhler, O. Pitois, F. Rouyer, A. Saint-Jalmes, Foams: structure and dynamics, OUP Oxford, 2013.
[10] V.S. Ramachandran, Concrete Admixtures Handbook: Properties, Science and Technology, 2nd ed.,,, William Andrew, 1996.
[11] E. Eickschen, C. Müller, Interactions of air-entraining agents and plasticizers in concrete, Concr. Technol. Rep. 2012 (2010).
[12] B. Łaźniewska-Piekarczyk, P. Miera, J. Szwabowski, Plasticizer and superplasticizer compatibility with cement with synthetic and natural air-entraining admixtures, IOP Conf. Ser.: Mater. Sci. Eng. 245 (2017) 032094.
[13] A. Lange, J. Plank, Study on the foaming behaviour of allyl ether-based polycarboxylate superplasticizers, Cem. Concr. Res. 42 (2012) 484–489.
[14] F. Saucier, M. Pigeon, P. Plante, Air-void stability, part III: field tests of superplasticized concretes, Mater. J. 87 (1990) 3–11.
[15] P.C. Aitcin, C. Jolicoeur, J.G. MacGregor, Superplasticizers: how they work and why they occasionally don't, Concr. Int. 16 (1994) 45–52.
[16] W. Prince, M. Espagne, P.C. Aıtcin, Ettringite formation: A crucial step in cement superplasticizer compatibility, Cem. Concr. Res. 33 (2003) 635–641.
[17] S. Jiang, B.G. Kim, P.C. Aıtcin, Importance of adequate soluble alkali content to ensure cement/superplasticizer compatibility, Cem. Concr. Res. 29 (1999) 71–78.
[18] S. Hanehara, K. Yamada, Interaction between cement and chemical admixture from the point of cement hydration, absorption behaviour of admixture, and paste rheology, Cem. Concr. Res. 29 (1999) 1159–1165.
[19] C. Jolicoeur, M.A. Simard, Chemical admixture-cement interactions: phenomenology and physico-chemical concepts, Cem. Concr. Compos. 20 (1998) 87–101.
[20] N.B. Singh, B. Middendorf, Calcium sulphate hemihydrate hydration leading to gypsum crystallization, Prog. Cryst. Growth Charact. Mater. 53 (2007) 57–77.
[21] F.J. Tang, F.P. Glasser, Influence of sulphate source on Portland cement hydration, Adv. Cem. Res. 1 (1988) 67–74.
[22] E. Sakai, J.K. Kang, M. Daimon, Influence of superplasticizers on the very early hydration of $Ca_3Al_2O_6$ in the presence of gypsum, $CaSO_4 \cdot 0.5\ H_2O$ and CaO, Cem. Sci. Concr. Technol. 56 (2002) 36–41.
[23] S. Pourchet, L. Regnaud, J.P. Perez, A. Nonat, Early C_3A hydration in the presence of different kinds of calcium sulfate, Cem. Concr. Res. 39 (2009) 989–996.
[24] J. Havlica, D. Roztocka, S. Sahu, Hydration kinetics of calcium aluminate phases in the presence of various ratios of Ca^{2+} and SO_4^{2-} ions in liquid phase, Cem. Concr. Res. 23 (1993) 294–300.
[25] P.W. Brown, L.O. Lawrence, G. Frohnsdorff, Kinetics of the early hydration of tricalcium aluminate in solutions containing calcium sulfate, J. Am. Ceram. Soc. 67 (1984) 793–795.
[26] A. Łagosz, J. Małolepszy, Tricalcium aluminate hydration in the presence of calcium sulfite hemihydrate, Cem. Concr. Res. 33 (2003) 333–339.
[27] EN 206-1 Concrete – Specification, performance, production and conformity (2013).
[28] ZTV Beton – StB 01 Bundesministerium fur Verkehr, Abteilu StraBenbau, Zusatzliche Technische Vertragsbedingungen und Richtlinien tur den Bau von Fahrbahndecken aus Beton, Ausgabe 2001, FGSV Verlag, Koln 2001 (in German).
[29] ONORM B 4710-1:2002 Beton – Teil 1: Festlegung, Herstellung, Verwendung und Konforrnitatsnachweis (Regeln zur Umsetzung der ONORM EN 206-1) (in German).
[30] DS 2426:2004 Concrete – Materials – Rules for application of EN 206-1 in Denmark (in Danish).
[31] 201.2R, A.C. Guide to Durable Concrete, American Concrete Institute (2016).
[32] EN 480-11 Admixtures for Concrete, Mortar and Grout – Test Methods – Part 11: Determination of Air Void Characteristics in Hardened Concrete (2014).
[33] ASTM C 457-98 Standard practice for microscopical determination of air-void content and parameters of the air-void system in hardened concrete (2000).
[34] GERMANN INSTRUMENTS A/S, Air Void Analyzer Instruction, (available at http://germann.org/products-by-application/air-void-system-parameters/ava).
[35] M. Tyler Ley et al., Determining the air-void distribution in fresh concrete with the Sequential Air Method, Constr. Build. Mater. 150 (2017) 723–737.
[36] K. Wang et al., Improving Variability and Precision of AirVoid Analyzer (AVA) Test Results and Developing Rational Specification Limits, InTrans Project Reports 149 (2008).
[37] EN 12350-2 Testing fresh concrete – Part 2: Slump test (2009).
[38] EN 12350-7 Testing fresh concrete: Air content – Pressure methods (2009).
[39] S. Chatterji, Freezing of air-entrained cement-based materials and specific actions of air-entraining agents, Cem. Concr. Compos. 25 (2003) 759–765.
[40] V.H. Dodson, Concrete Admixtures, 3rd ed., Springer Science & Business Media, New York, 2013.