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Dr.-Ing. E. Eickschen, Dr.-Ing. C. Müller,
Research Institute of the Cement Industry, Duesseldorf, Germany

SUMMARY

There have been reports of problems that have arisen in practice during the production of air-entrained concrete when using plasticizers, especially those based on polycarboxylate ether (PCE). The total air content fluctuated and in individual cases the requirements for the air void parameters measured on the hardened concrete were not met in spite of the fact that the total air content of the fresh concrete complied with the requirements. The dependable adjustment of the micro air void structure, which prevents damage by freeze-thaw with or without de-icing salt is no longer possible. The extent to which interactions between air-entraining agent and plasticizer can affect the air void microstructure was investigated in a research project. The formation of air voids was tested in mortar and concrete with different combinations of admixtures and cements. The aim was to manufacture appropriate air-entrained concrete containing plasticizers by identifying "robust" admixture combinations that reduces the risk of unwanted air void formation. The interrelationships were incorporated in a model which makes it possible to give recommendations. The sequence of addition of air-entraining agent and plasticizer and the active agent of the air-entrainer have a decisive influence on the air void formation. Admixture combinations of air-entraining agent and plasticizer containing air-entraining agents based on natural active substances are considered more "robust" than variants with synthetic air entraining agents.

ZUSAMMENFASSUNG

Aus der Praxis wurde über Probleme bei der Herstellung von Luftporenbeton berichtet, insbesondere wenn Fließmittel auf der Basis von Polycarboxylatethern (PCE) verwendet wurden. Der Luftgehalt insgesamt schwankte und vereinzelt wurden trotz Einhaltung des Luftgehalts im Frischbeton die am Festbeton ermittelten Anforderungen an die LP-Kennwerte nicht erreicht. Die zielsichere Einstellung des Mikro-Luftporengefüges, das Frost- und Frost-Tausalzschäden verhindert, ist somit nicht mehr gegeben. In einem Forschungsvorhaben wurde untersucht, inwieweit Wechselwirkungen zwischen Luftporenbildner und Fließmittel die Luftporenbildung beeinflussen. Dabei wurde die Luftporenbildung an Mörtel und Beton mit unterschiedlichen Zusatzmittelkombinationen und Zementen erforscht. Ziel war die anforderungsgerechte Herstellung von Luftporenbeton unter Verwendung von Fließmittel durch Identifikation „robuster" LP-Bildner/Fließmittel-Kombinationen, die die Luftporenbildung nicht beeinträchtigen. Zur Erklärung der Wechselwirkungen wurde ein Modell erarbeitet und daraus Empfehlungen abgeleitet. Die Versuche zeigen, dass die Zugabereihenfolge von LP-Bildner und Fließmittel und die Wirkstoffbasis des LP-Bildners die Luftporenbildung stark beeinflussen können. Zusatzmittel-Kombinationen mit einem LP-Bildner auf natürlicher Wirkstoffbasis verhalten sich „robuster" als Kombinationen mit synthetischen LP-Bildnern.

(Translation by Robin B. C. Baker)

Interactions of air-entraining agents and plasticizers in concrete

Zusammenwirken von Luftporenbildner und Fließmittel in Beton

1 Introduction

The use of an air-entraining agent to achieve adequate resistance to freeze-thaw with de-icing salt is stipulated for concretes of exposure classes XF2 and XF3 with a w/c ratio of 0.55 and for concrete in exposure class XF4. Water-reducer or plasticizers are used so that the concrete can be worked longer and more easily. There have been reports of problems that have arisen in practice during the production of air-entrained concrete, especially when using plasticizers based on polycarboxylate ether (PCE). The total air content fluctuates and in individual cases the requirements for the air void parameters measured on the hardened concrete are not met in spite of the fact that the total air content in the fresh concrete complies with the requirements. This means that dependable adjustment of the micro air void structure, which prevents damage by freeze-thaw with or without de-icing salt, is no longer possible. So far there have been no systematic investigations into the action mechanisms that occur during simultaneous use of PCE-based plasticizers and air-entraining agents. The extent to which interactions between air-entraining agents and plasticizers affect the air void formation was therefore investigated in a research project in relation to the cement and the basis of the active substance in the admixture. An understanding of the interrelationships permits carefully controlled selection of robust admixture combinations and a reduction in the risk of unwanted air void formation.

2 Current state of knowledge

2.1 Air-entraining agents

It is usually necessary to add an air-entraining agent, which generates a large number of small, evenly distributed, air voids with diameters ≤ 300 µm, to concrete to achieve adequate resistance to freeze-thaw with de-icing salt. Soaps made from natural resins (wood resins) and synthetic raw materials (alcohol polyglycol ether sulfates, alkyl sulfates and sulfonates) have proved successful basic materials for air-entraining agents [1, 2]. Air-entraining agents belong to the group of surface-active substances, so-called tensides. The common characteristic of tensides is their hydrophobic/hydrophilic molecular structure. They consist of a non-polar, hydrophobic, branched or unbranched, hydrocarbon chain with 8 to 12 carbon atoms and a hydrophilic polar carboxyl, sulfate or sulfonate group. Air-entraining agents seldom consist of pure basic materials and are often mixtures of different starting materials [2].

The molecules of air-entraining agent dissolved in the cement paste stabilize the air bubbles introduced into the concrete by the mixing process. The polar hydrophilic part projects into the water (or the cement paste, ❱ Fig. 1) while the long-chain hydrophobic part lies in the air bubble. Other molecules are sorbed with the negatively charged polar group on positively charged parts of the cement or aggregate particle. This enables the air bubbles to attach themselves to solid particles and the stability of the air void system is improved [3]. Some of the rest of the air-entraining agent is precipitated in the pore solution. New air bubbles are stabilized continuously during the mixing. The air content rises until there is no more dissolved air-entraining agent in the pore solution. The good solubility of synthetic air-entraining agents means that a longer mixing time is necessary with high addition levels to fully activate the active substance. Air-entraining agents based on natural active substances are very largely precipitated in the pore solution and are therefore activated after a short mixing time, even with high addition levels [3].

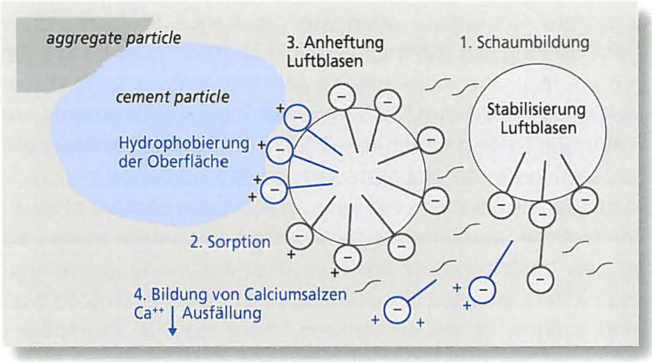


Figure 1: Action mechanisms of air void formation
1: Foam formation (stabilization of air bubbles)
2: Sorption of the air-entraining agent molecules and hydrophobing of the cement particles as a precondition for
3: Attachment of air bubbles to solid particles (improvement in the stability of the air void microstructure)
4: Precipitation in the pore solution by formation of insoluble calcium salts

2.2 Plasticizers

With plasticizers a distinction is made between classical plasticizers (based on melamine, naphthalene and lignin sulfonates) and polycarboxylate ethers (PCEs). The plasticizing action is dependent on sorption of the negatively charged plasticizer molecules on positively charged areas of the cement surface or initial hydration products. The action of the classical plasticizers is based on electrostatic repulsion but PCEs also cause a spatial (steric) separation of the cement particles. Both of them reduce the formation of agglomerates of cement particles and other fine solid particles. The active substances in classical plasticizers have a high charge density and are strongly sorbed onto solid particles in a short time. In contrast to classical plasticizers, PCEs have specific number of side chains that are distri-

Table 1: Requirements for the air void parameters in relation to the test [7]

Type of testing	Requirements for	
	Spacing factor in [mm]	Micro air void content in [vol. %]
Initial testing	0.20	1.8
Component testing	0.24	1.5
Effectiveness testing	0.20	1.5

Table 2: Overview of the plasticizers and air-entraining agents (concentrates) used

Admixture	Producer 1	Producer 2	Producer 3
PCE ready-mixed concrete	1 PCE (30.3)[1]	1 PCE (19.9)	1 PCE suitable for both areas of application (17.9)
PCE precast element	1 PCE (30.3)	1 PCE (29.1)	
Conventional plasticizer	Naphthalene sulfonate (39.7)	Melamine sulfonate (20.2)	–
Air-entraining agent	Wood resin soap (16.6)	Modified wood resin (19.4)	Synthetic tenside 1 (7.9)

[1] Values in brackets: solids or active substance content of the air-entraining agent or plasticizer in mass %

buted along a main chain. The sorption of the PCEs can be selectively altered by varying the charge density and the lengths of the main and side chains, so that a strong initial plasticizing effect or a longer workability of the concrete can be achieved [4–6]. PCEs can therefore be adapted to particular conditions of use (e.g. cement, fresh concrete temperature). However, changed marginal conditions can influence the effectiveness of the PCE and the workability time of the concrete.

2.3 Combined addition of air-entraining agent and plasticizer

The content of small voids is assessed by determining the micro air void content and the spacing factor in the hardened concrete. To ensure adequate resistance to freeze-thaw with de-icing salt the micro air void content must be at least 1.8 vol. % in the initial testing and the spacing factor must not exceed 0.20 mm [7]. Somewhat lower requirements are set when testing structures (❯ Table 1). Both parameters are determined in an elaborate test on the hardened concrete. As a rule the concrete will have an adequate content of small voids if the requirements for the total air content measured on the fresh concrete are met. If air-entraining agents and plasticizers are used simultaneously then, depending on type and quantity of the admixtures, there may be interactions between the two types of admixture that adversely affect the formation of air voids [8, 9]. As a consequence these concretes will have a lower content of small air voids ≤ 300 µm than stiff concretes for the same total air content [9]. The de-foaming agents contained in the plasticizer have been cited as the cause. The negative charges on the air-entraining agents and plasticizers can also cause competing reactions at the sorption sites on cement particles. It also has to be borne in mind that for the same total air content the soft air-entrained concretes (with or without the addition of plasticizers) already contain more large air voids than stiff concretes due to the nature of the production process.

This is because the air voids introduced during the mixing are not split up in the same way as when stiff concretes are mixed [12]. The total air content of soft air-entrained concretes and of air-entrained concretes that contain wetting agents or plasticizers is increased by 1 vol. % by increased addition of the air-entraining agent in order to ensure the resistance to freeze-thaw with de-icing salt. If it is proved during the initial testing that the air-entraining parameters comply with the limits then this safety margin is not necessary and a 1 vol. % lower air content is used. The air-entraining parameters always have to be verified for the F6 flow table spread class [7]. With simultaneous use of an air-entraining agent and a plasticizer/wetting agent an effectiveness test must also be used to show that the chosen combination achieves a spacing factor of ≤ 0.20 mm and a micro air void content of ≥ 1.5 vol. % in the hardened concrete.

The sequence in which the admixtures are added also affects the air void formation. If the plasticizer is added first, followed by air-entraining agent, then the air void system is

Table 3: Characteristic chemical and physical parameters of the cements used

Parameter		CEM I 42,5 N	CEM II/A-LL 42,5 N	CEM III/A 42,5 N-LH/NA
K_2O	mass %	0.88	0.85	0.91
Na_2O	mass %	0.13	0.09	0.23
Na_2O equiv.	mass %	0.71	0.65	0.83
SO_3	mass %	2.96	2.98	2.90
Blastfurnace slag content	mass %	–	–	50.6
Limestone content	mass %	–	14.0	–
Initial setting time	min	160	200	220
Water demand	%	27.0	29.0	30.0
Spec. surface area	cm²/g	3250	3680	4210
Compr. strength 2 d	N/mm²	25.1	26.2	17.0
7 d	N/mm²	42.4	39.9	34.6
28 d	N/mm²	56.5	49.3	52.1

formed in a softer concrete, which results in a coarser air void system. Sorption sites on the cement particles are also already occupied by plasticizer molecules, so less air-entraining agent is sorbed. There is the danger that air bubbles will not be attached to solid particles and will escape from the concrete during the compaction process, resulting in an unstable air void system. In practice the air-entraining agent is therefore added first, followed by the plasticizer. The effectiveness of the admixtures, and therefore the air void formation, is affected by numerous factors, such as concrete composition, concrete production, fresh concrete temperature and consistency of the concrete [10, 11]. In order to take the various parameters into account the quantities of admixtures to be added are determined in the preliminary testing and if necessary are adjusted to suit the actual construction conditions during the construction work.

3 Test procedure

3.1 Aim and extent of the tests

An understanding of the action mechanisms occurring during the production of air-entrained concrete with plasticizers reduces the risk of incorrect applications. The extent to which interactions between air-entraining agents, plasticizers and cement can affect the air void formation was therefore examined at the FIZ (Research Institute of the Cement Industry). Fine concretes (maximum grain size 4 mm) were produced with a specific air content and plasticizers were then added in several stages in order to show any possible de-foaming action in relation to the combination of starting materials. The air content and consistency of the content were determined after each partial addition. The air void formation in the fresh and hardened concrete (air void parameters) in relation to the combination of starting materials and the concrete age was also determined in concretes with a maximum grain size of 16 mm. The test results were used to develop a model to explain the air void formation during combined addition of air-entraining agents and plasticizers. The recommendations drawn from this for construction practice should ensure carefully controlled air void formation and reduce the risk of incorrect applications.

3.2 Starting materials

a) Admixtures (air-entraining agents and plasticizers)
With the help of three admixture producers five PCEs were selected as well as two plasticizers based on melamine and naphthalene sulfonates respectively to provide a link with previous experience (› Table 2). Two producers each provided one PCE for the precast element sector and one for the ready-mixed concrete sector, while the third producer provided a PCE that is used in both sectors. Although no detailed information was given about the compositions of the PCEs it is true that PCEs for the ready-mixed concrete sector have a longer plasticizing action than PCEs for the precast element sector. PCEs for ready-mixed concrete consequently tend to have a lower charge density and longer side chains than PCEs for the precast element sector with their trend towards higher charge densities and shorter side chains. Air-entraining agents based on different active substances were also supplied by the producers. The FIZ also selected one air-entraining agent based on natural active substances (modified wood resin, producer 2) and one based on synthetic active substances (alkyl polyglycol ether sulfate, synthetic tenside 1, producer 3) (Table 2). Because of its good solubility the synthetic air-entraining agent 1 remains active in the pore solution while the air-entraining agents based on natural active substances are to a great extent precipitated [3].

b) Cement
Three cements of the 42,5 N strength class were selected for producing the cements: CEM I, CEM II/A-LL and CEM III/A LH/NA (› Table 3).

c) Aggregate
0/0.1 mm quartz meal, 0/2 mm coarse Rhine sand and 2/4 mm quartz gravel were used for producing the fine concretes (maximum grain size 4 mm). 0/0.1 mm quartz meal and 0/2, 2/8 and 8/16 coarse Rhine sand with a grading curve in the centre of the A/B 16 grading curve area as defined in DIN 1045-2 were used for producing the concretes (maximum grain size 16 mm).

d) Mixing water
Düsseldorf mains water was used for producing the concretes.

3.3 Air void formation in fine concrete

The investigations on fine concretes (maximum grain size 4 mm, cement content 400 kg/m^3, w/c value 0.42) with a stiff initial consistency and an air content of about 5.5 vol. % were intended to determine whether a change in air content (e.g. a drop as a result of the de-foaming action of the plasticizer) occurs after addition of the plasticizer. The aggregate mix consisted of 6.9 vol. % of 0/0.1 mm quartz meal, 23.1 vol. % of 0/2 mm coarse Rhine sand and 70 vol. % of 2/4 mm quartz gravel. The aggregate content was 1 666.5 kg/m^3.

The cement and aggregate were mixed dry for 15 seconds in a 50 l mechanical mixer. The air-entraining agent was added to the mixing water immediately before the concrete was mixed. The mixing time after addition of all constituents was two minutes. The amount of each air-entraining agent added (› Table 4) was set so that with a mixing time of two minutes the air content of the fine concrete was 5.5 ± 0.5 vol. % when tested with a 1 l pressure vessel immediately after the end of mixing. Plasticizer was then added in several stages, each of 0.2 mass % w.r.t. cement (PCE) or 0.3 mass % w.r.t. cement (conventional plasticizer). The concrete was mixed for 30 seconds after each partial addition of plasticizer. Immediately after that some concrete was taken from the mixer to determine the air-void content (pressure equalization method as specified in DIN EN 12350-7) and the consistency (flow table spread on the Hägermann table as specified in DIN EN 459-2). The addition of plasticizer was continued in stages until the concrete exhibited strong signs of segregation in the mixer. In an additional test the consistency was also adjusted by the addition of water instead of with plasticizer. The w/c ratio was increased in stages of 0.02.

Table 4: Quantities of air-entraining agent needed for an air content in the fine concrete of 5.5 ± 0.5 vol. %

Cement 42,5 N	Air-entraining agent	Quantity added in [mass %] w.r.t. cement
CEM I	Modified wood resin	0.150
	Wood resin soap	0.160
	Synthetic tenside 1	0.055
CEM II/A-LL	Modified wood resin	0.200
	Synthetic tenside 1	0.090
CEM III/A	Modified wood resin	0.300
	Wood resin soap	0.320
	Synthetic tenside 1	0.105

3.4 Air void formation in fresh and hardened concrete

3.4.1 Concrete compositions
Ten concretes (cement content 320 kg/m^3, w/c ratio 0.50, › Table 5) were produced in order to investigate the action mechanisms of air void formation in fresh and hardened concrete in relation to the combination of the air-entraining agent/plasticizer/cement starting materials. The quantities of admixtures added were laid down so that the concrete had an air content of 5.5 ± 0.5 vol. % and a flow table spread of 49 to 55 cm (consistency class F4) 30 minutes after production (precast element PCE) or 45 minutes after production (ready-mixed concrete PCE or conventional plasticizer based in naphthalene sulfonate). The concretes were produced with CEM I and CEM III/A cements in combination with the following admixtures (plasticizers and air-entraining agents):

- air-entraining agent: modified wood resin (producer 2), synthetic tenside 1 (producer 3)
- plasticizer: precast element PCE and ready-mixed concrete PCE (producer 2) as well as plasticizer based on naphthalene sulfonate (producer 1, only in combination with CEM III cement).

3.4.2 Production, storage and testing
The cement and aggregate were mixed dry for 15 seconds in a compulsory mixer. The mix volume was kept constant at about 180 litres. The air-entraining agent was added to the mixing water immediately before the concrete was mixed. Mixing was carried out for two minutes after the addition of water. The mixer was then stopped and concrete was removed for the planned fresh and hardened concrete tests. The plasticizer was then added and the concrete was mixed for a further

Table 5: Cement/admixture combinations (cement content 320 kg/m^3, w/c ratio 0.50)

No.	Cement 42,5 N	Plasticizer Type	Quantity added [mass %] w.r.t. cement: Plasticizer	Quantity added [mass %] w.r.t. cement: Active substance	Air-entraining agent Type	Quantity added [mass %] w.r.t. cement: Air-entraing agent	Quantity added [mass %] w.r.t. cement: Active substance	Active substance ratio plasticizer/ air-entraining agent
1	CEM I	PCE precast element 30 minutes[1)]	0.29	0.084	Mod. wood resin	0.075	0.0146	6
2			0.25	0.073	Syn. tenside 1	0.020	0.0016	46
3		PCE ready-mixed concrete 45 minutes[1)]	0.50	0.100	Mod. wood resin	0.085	0.0165	6
4			0.50	0.100	Syn. tenside 1	0.020	0.0016	63
5	CEM III/A	PCE precast element 30 minutes[1)]	0.30	0.087	Mod. wood resin	0.165	0.0320	3
6			0.29	0.084	Syn. tenside 1	0.040	0.0032	26
7		PCE ready-mixed concrete 45 minutes[1)]	0.55	0.110	Mod. wood resin	0.180	0.0350	3
8			0.50	0.100	Syn. tenside 1	0.040	0.0032	31
9		Naphthalene sulfonate 45 minutes[1)]	0.80	0.320	Mod. wood resin	0.200	0.0388	8
10			0.80	0.320	Syn. tenside 1	0.080	0.0155	21

[1)] Period from 30 or 45 minutes after end of mixing: air content 5.5 ± 0.5 vol. % and flow table spread 49 cm to 55 cm (F4)

minute. The moment after the one-minute mixing of the plasticizer was defined as the "end of mixing". Concrete for the planned investigations was taken after mixing in the plasticizer and 10, 20, 30, 45 and 60 minutes after the end of mixing. If there were signs of segregation the concrete was mixed again for 10 seconds before removing the fresh concrete.

The test pieces for the hardened concrete tests were compacted in steel moulds on a vibrating table. In order to determine the behaviour of the air-void parameters with time six cubes (edge length 150 mm) were produced from each of the ten concretes at the following times:

- after mixing in the air-entraining agent (two minutes mixing time),
- after mixing in the plasticizer (one minute mixing time) corresponding to the end of mixing, and
- 10, 30, 45 and 60 minutes after the end of mixing.

At these times the flow table spread was determined as specified in DIN EN 12350-5 and the air content was determined in the pressure vessel as specified in EN 12350-7. The air void vessel was compacted on the vibrating table. Three cubes (edge length 150 mm) were also produced either 30 minutes (precast element PCE) or 45 minutes (ready-mixed concrete PCE or naphthalene sulfonate) after the end of mixing (depending on the plasticizer used) to determine the 28 day compressive strengths.

After production the test pieces were stored for 24 ± 1 hours in a climatic chamber at an air temperature of 20.0 ± 2.0 °C and a relative humidity of 65 ± 5 % in their moulds covered with moist cloth. The test pieces were then removed from the moulds and stored and tested as follows:

a) Compressive strength
After they had been removed from their moulds three cubes with edge lengths of 150 mm were stored as specified in DIN EN 12390-2 in accordance with the national appendix. The compressive strengths were tested at 28 days as specified in DIN EN 12390-3.

b) Air void parameters
After they had been removed from their moulds the cubes intended for determination of the air void parameters were stored under water until they were seven days old and then stored in a climatic chamber until the moment when two slices were taken from each cube for determining the air void parameters as described in DIN EN 480-11.

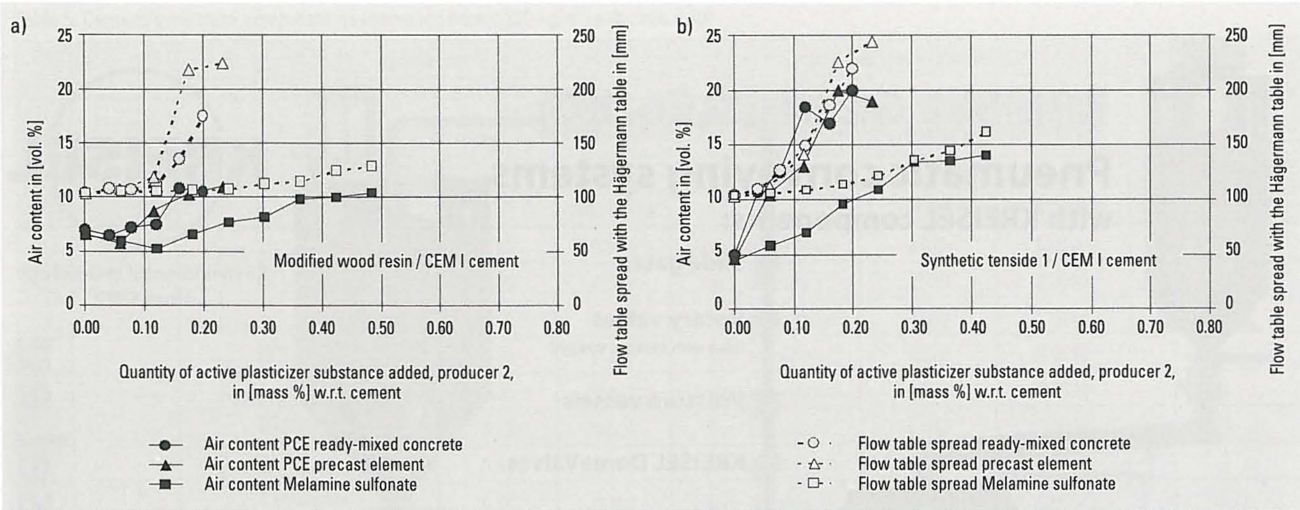
4 Test results

4.1 Air void formation in fine concrete

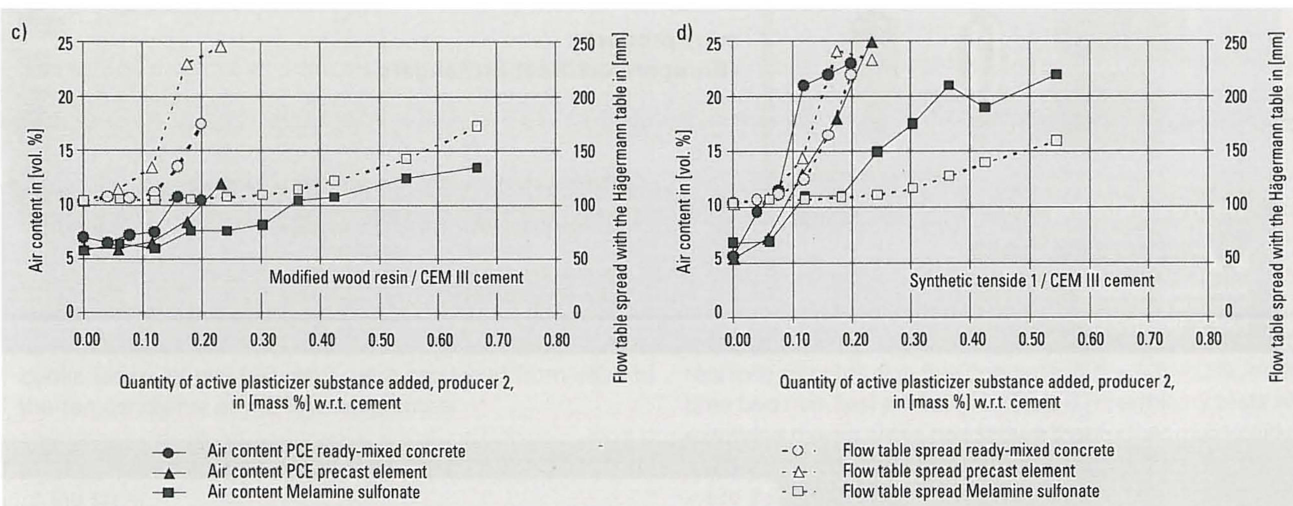
4.1.1 Required addition levels of air-entraining agent
The quantities of air-entraining agent needed to achieve the required air content in fine concrete (5.5 ± 0.5 vol. %, mixing time two minutes) are listed in Table 4. Preliminary tests with extended mixing times had shown that further mixing did not increase the air content and that the air-entraining agents were fully activated. The two wood resins required comparable addition levels. Substantially smaller addition levels were required for synthetic tenside 1 when compared with the natural air-entraining agents. Regardless of the type of active substance in the air-entraining agent higher addition levels were required for the CEM II and CEM III cements than for the CEM I cement. This is presumably due to the larger surface areas of the CEM II and CEM III cements, which lead to increased sorption of the air-entraining agents. The finenesses were 3250/3680/4210 cm^2/g Blaine (CEM I/ CEM II/B-S/CEM III/A cement, Table 3).

4.1.2 Influence of the plasticizer on air void formation
Examples of the influence of the plasticizer on air void formation are shown in Figs. 2a to 2d for combinations of the three plasticizers from producer 2 with the CEM I and CEM III cements and two air entraining agents (modified wood resin, synthetic tenside 1). Comparable results were obtained with the three plasticizers from producer 1 and the PCE from producer 3. The quantity of plasticizer added was increased in small stages of 0.20 mass % (PCE) or 0.30 mass % (melamine and naphthalene sulfonate) w.r.t. cement (mixing time of 30 seconds in each case). The air content and the flow table spread (Hägermann table) were determined after each partial addition. The air content and flow table spread are shown in Figs. 2a and 2d in relation to the total active substance in the plasticizer for better comparability of the plasticizers.

After the first and second partial additions of plasticizer a slight drop in air content or a constant air content were



Figures 2a and b: Air void formation and consistency relative to the type and addition level of the plasticizer from producer 2 when using CEM I cement: left – air-entraining agent based on wood resin, and right – tenside 1



Figures 2c and d: Air void formation and consistency relative to the type and addition level of the plasticizer from producer 2 when using CEM III cement: left – air-entraining agent based on wood resin, and right – tenside 1

recorded with the air-entraining agent based on natural active substance (Figs. 2a and 2c). After the third partial addition of plasticizer there was a universal increase in air content. With synthetic air-entraining agent 1 the air content always increased even after the first partial addition (Figs. 2b and 2d). The rise was substantially greater than with the natural air-entraining agent. The rise in air content was more strongly marked when using the PCE-based plasticizers than with the conventional plasticizers (e.g. melamine sulfonate). No appreciable differences were found between the PCEs (ready-mixed concrete and precast elements) or between CEM I and CEM II cements. With CEM III cement the rise was somewhat more strongly marked than with CEM I cement. No substantial drop in air content due to de-foaming action of the plasticizers was detected.

Combinations with the synthetic air-entraining agent and a PCE-based plasticizer exhibited a greater range of fluctuation in air content than combinations with natural air-entraining agents and conventional plasticizers. When the softer consistency was obtained by increased addition of water rather than with a plasticizer then the air content increased after each partial addition of water (❱ Fig. 3). The rise was somewhat sharper with CEM III cement. When the consistency was adjusted with plasticizer great differences in air void formation were established that depended on the type of active substance in the plasticizer (synthetic tenside: large rise, natural air-entraining agent: small rise). These differences did not occur when the consistency was adjusted by the addition of water or by changing the w/c ratio.

4.2 Air void formation in fresh and hardened concrete

4.2.1 Quantity of admixture added in relation to the combination of starting materials

The quantities of admixture added to achieve the required air content of 5.5 ± 5 vol. % or a flow table spread of 49 cm to 55 cm are listed in ❱ Fig. 4 left (air-entraining agents) and Fig. 4 right (plasticizers) and in ❱ Table 5. With CEM III cement the quantities added had to be increased for both air-entraining agents when compared with CEM I cement. The type of PCE had only a slight effect on the addition level of the air-entraining agent, and this applied to both types of cement. Concrete made with naphthalene sulfonate required the highest addition level of air-entraining agent. Ten-times higher concentrations of active substance were required with the natural air-entraining agent than with the synthetic tenside to achieve the required air content (Table 5), regardless of the chosen cement/plasticizer combination.

The amount of plasticizer required to obtain the desired consistency was not appreciably affected by the basis of the active substance in the air-entraining agent or by the type of cement (Fig. 4, right). A comparatively low (precast element PCE), moderate (ready-mixed concrete PCE) or high (naphthalene sulfonate) addition level was required, depending on the plasticizer. This sequence was also retained when the levels of active substance in the plasticizers were taken into account. The plasticizers were used with substantially higher addition levels of the active substance than for the air-entraining agents. The plasticizer/air-entraining agent ratio of active substances ranged between 3 and 8 (natural air-entraining agents) and between 21 and 63 (synthetic air-entraining agents).

4.2.2 Fresh concrete properties in relation to the combination of starting materials

4.2.2.1 Consistency

The flow table spread of the initial concrete after the air-entraining agent had been mixed in was about 35 cm (▸ Figs. 5a to 5e). After addition of the plasticizer the flow table spread increased to more than 60 cm. The fresh concrete was then kept covered in the mixer until the next test time (10 minutes after end of mixing). When signs of segregation occurred occasionally the concrete was mixed for 10 seconds immediately before the planned test time. The signs of segregation decreased with increasing concrete age due to the stiffening of the concrete. The PCE for the ready-mixed concrete sector and the plasticizer based on naphthalene sulfonate had a longer plasticizing action than the PCE for the precast element sector. The drop in flow table spread was more strongly marked with the precast element PCE. No major differences due to the cement or the air-entraining agent were detected.

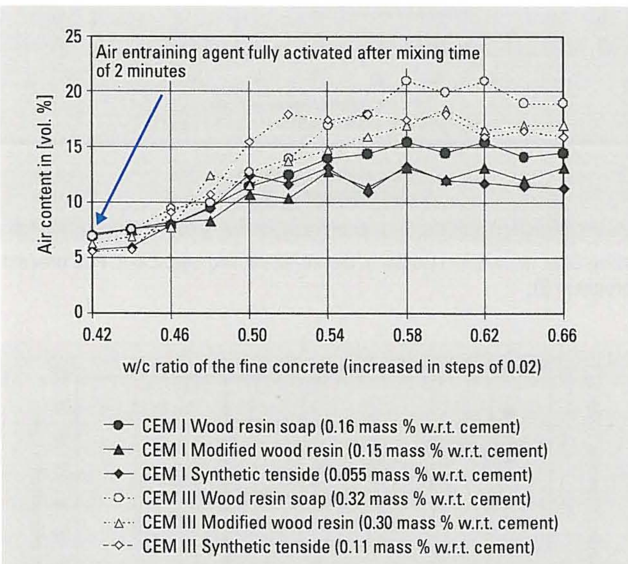


Figure 3: Air content of the fine concrete in vol.% relative to the extra water addition, the cement and the air-entraining agent (flow table spread w/c = 0.50 about 130 mm, w/c = 0.58 about 180 mm and w/c = 0.66 about 210 mm)

4.2.2.2 Air content

a) PCE-based plasticizer (▸ Figs. 5a to 5d)

The concretes made with the two PCE variants exhibited comparable time-dependent air void formation. The air contents of the concretes made with natural air-entraining agent of about 7 vol. % to 8 vol. % after the air-entraining agent had been mixed in were above the target value of 5.5 vol. % and the air contents of the concretes made with synthetic tenside of about 2.5 vol. % to 4.5 vol. % were below it. After the PCE had been mixed in (end of mixing) the air contents of the concretes made with natural air-entraining agents fell and those of the concretes made with synthetic air-entraining agent rose. With the natural air-entraining agent the drop in air content was less with CEM III cement than with CEM I cement. The rise with the synthetic tenside was more strongly marked with the CEM III cement than with the CEM I cement. No clear trend could be identified up to the test ages of 30 minutes and 45 minutes respectively after the end of mixing – the air content remained virtually constant. After that the air content fell until a test age of 60 minutes.

b) Plasticizer based on naphthalene sulfonate (Fig. 5e)

The concretes made with naphthalene sulfonate exhibited approximately comparable air void formation. The type of active substance in the air-entraining agents had no detectable significant influence such as was found with the PCE variants. The air content of about 8 vol. % to 9 vol. % after the air-entraining agent had been mixed in was far above the target value of 5.5 vol. %. After addition of the plasticizer (end of mixing) the air content was still about 8 vol. % and fell with increasing age of the fresh concrete.

4.2.3 Hardened concrete properties in relation to the combination of starting materials

4.2.3.1 Air void parameters

a) PCE-based plasticizers (▸ Figs. 6a to 6d)

After the addition of the air-entraining agent the concretes made with natural air-entraining agent exhibited lower spacing factors, corresponding to their higher air contents of

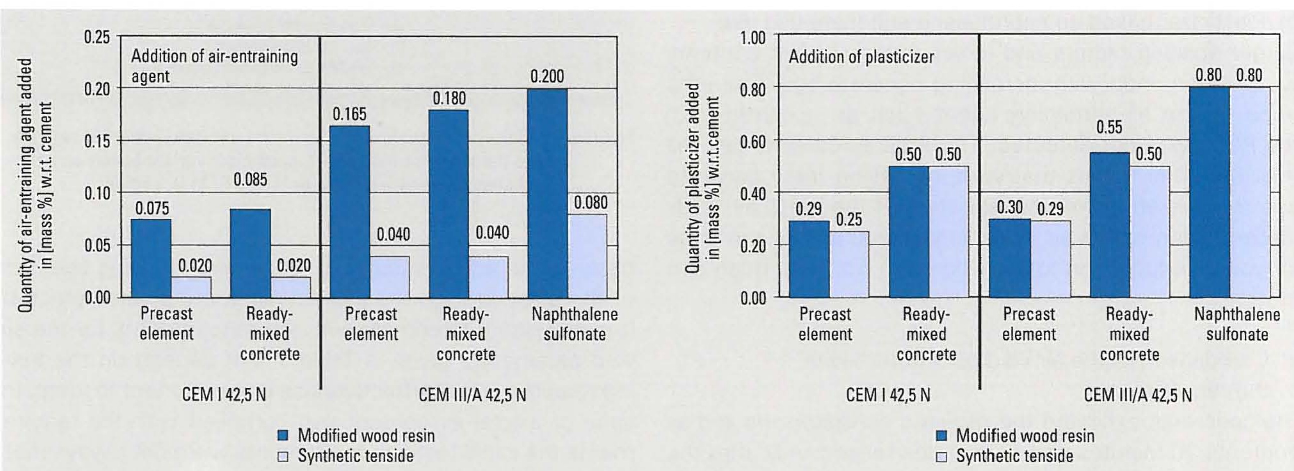
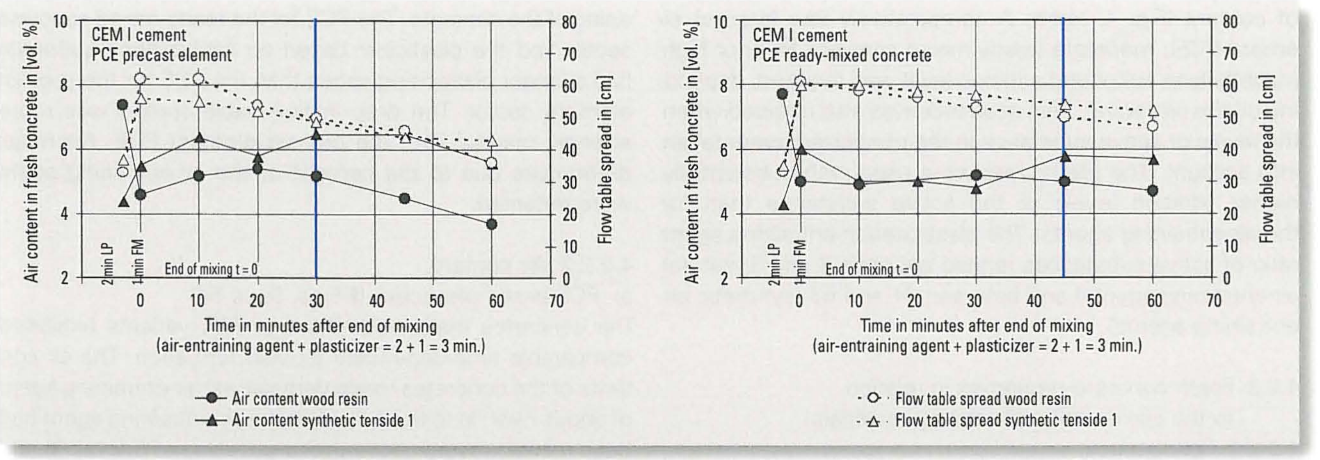
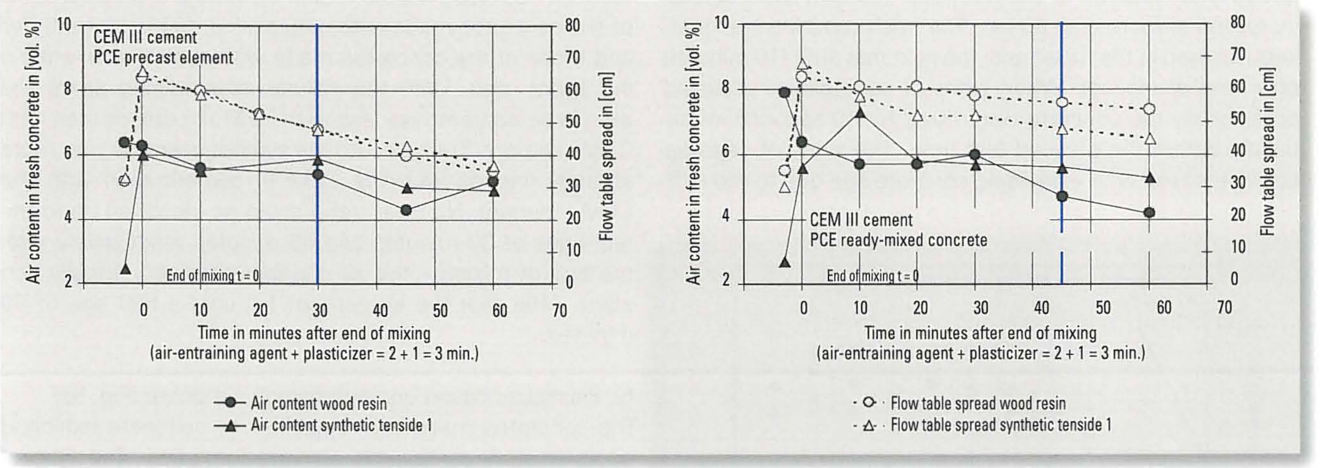


Figure 4: Quantities of admixture added: air-entraining agent (left) and plasticizer (right)



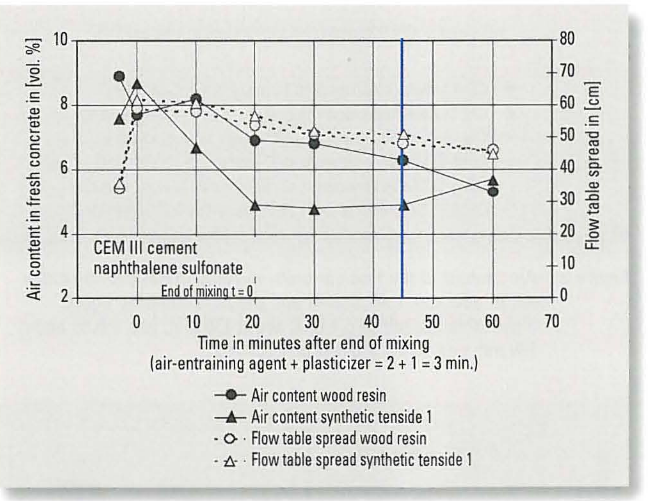
Figures 5a and b: Behaviour with time of the fresh concrete properties when using CEM I cement relative to the air-entraining agent: left, PCE precast element (producer 2) and right, PCE ready-mixed concrete (producer 2)



Figures 5c and d: Behaviour with time of the fresh concrete properties when using CEM III cement relative to the air-entraining agent: left, PCE precast element (producer 2) and right, PCE ready-mixed concrete (producer 2)

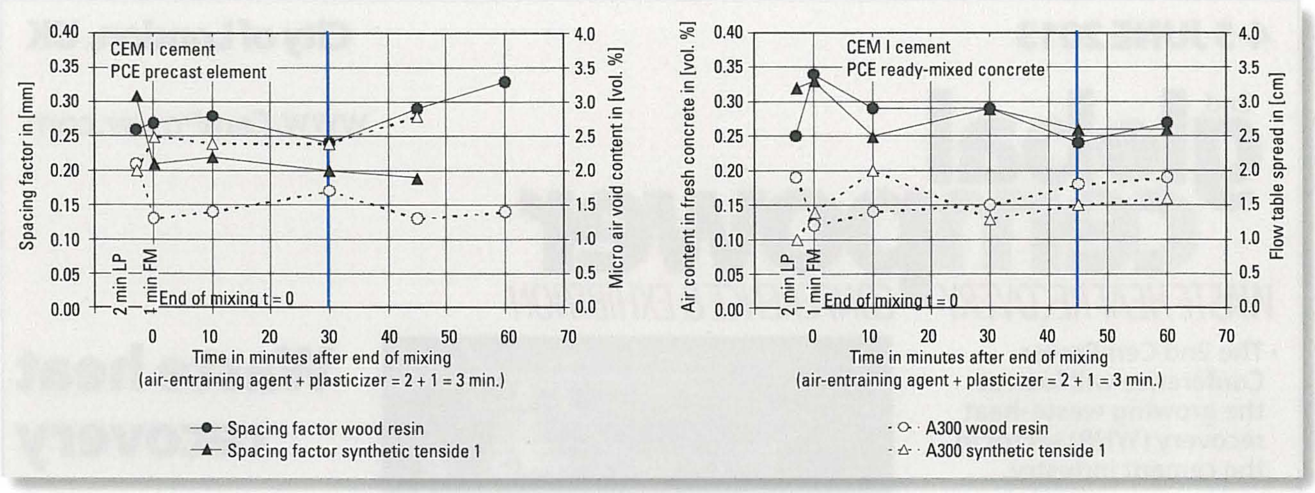
about 7 vol. % to 8 vol. %, and higher micro air void contents than the concretes made with synthetic air-entraining agents that also exhibited lower air contents (about 2.5 vol. % to 4.5 vol. %). In the concretes made with natural air-entraining agents the addition of the plasticizer caused a drop in air content combined with a deterioration in the air void parameters (Figs. 5a to 5d) and in the concretes made with synthetic tenside it caused an increase in air content combined with an improvement in the air void parameters. No clear trend could be detected in the period between the end of mixing (after addition of the plasticizer) and 60 minutes after the end of mixing.

b) Plasticizer based on naphthalene sulfonate (Fig. 6e)
Larger spacing factors and lower micro air void contents were determined with increasing concrete age. The influence of the air-entraining agent such as occurred with the PCEs was not detected. The total air content also fell (Fig. 5e). This means that with increasing fresh concrete age there is an increasing deviation of the small air voids (deterioration of the air void parameters) and of the large air voids (reduction in total air content) from the fresh concrete.

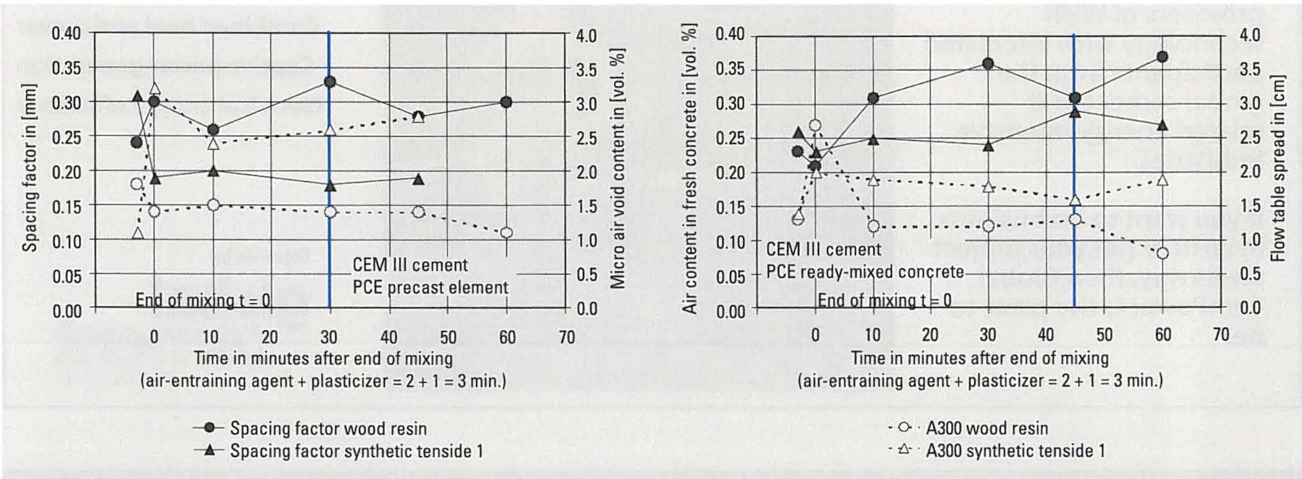


Figures 5e: Behaviour with time of the fresh concrete properties relative to the air-entraining agent: plasticizer variant based on naphthalene sulfonate (producer 1) and CEM III cement

c) Comparison of the air void parameters with the requirements
The concretes exhibited the required consistencies and air contents 30 minutes and 45 minutes respectively after the end of mixing. The air void parameters determined at these times are listed in ❱ Table 6. No systematic influence of the basis of the active substance of the air-entraining agent or of the plasticizer on the air-void parameters was detected. It is necessary to comply with the requirements for the air void parameters given in Table 1 that depend on the testing required (initial, effectiveness or component testing). In spite of a total air content that complied with the requirements the initial testing requirements were not always met. This applied both for combinations with PCEs and for variants with the plasticizer based on naphthalene sulfonate.

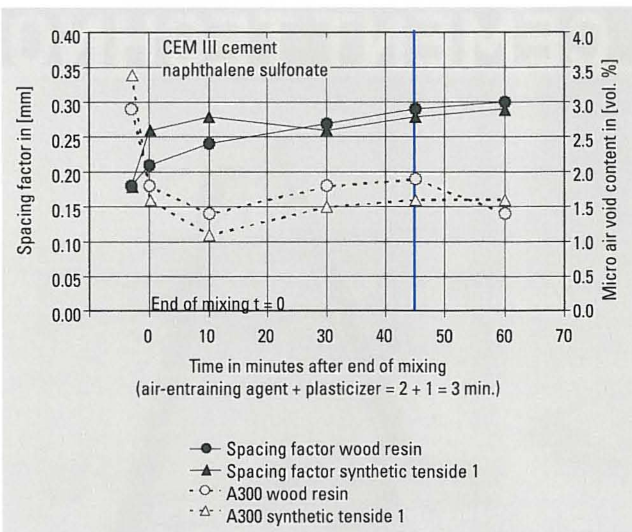


Figures 6a and b: Behaviour with time of the air void parameters when using CEM I cement relative to the air-entraining agent: left, PCE precast element (producer 2) and right, PCE ready-mixed concrete (producer 2)



Figures 6c and d: Behaviour with time of the air void parameters when using CEM III cement relative to the air-entraining agent: left, PCE precast element (producer 2) and right, PCE ready-mixed concrete (producer 2)

The reason for this is not a de-foaming action with certain admixture combinations but the consistency of the concrete. A flowable consistency (class F5, flow table spread of 58 cm to 62 cm) had to be established immediately after mixing in the plasticizer in order to achieve the desired very soft consistency (F4, flow table spread 49 cm to 55 cm) after 30 or 45 minutes. Experience shows that the good workability does in fact facilitate the introduction of air voids but it makes it harder to comply with the required air void parameters.



Figures 6e: Behaviour with time of the air void parameters relative to the air-entraining agent: plasticizer variant based on naphthalene sulfonate (producer 1) and CEM III cement

4.2.3.2 Compressive strength

The 28-day compressive strengths lay between 38 N/mm^2 and 45 N/mm^2 (Table 6). No systematic influence of the admixture combination of air-entraining agent and plasticizer was detected. The compressive strengths of the concretes made with CEM III cement were slightly below those of the concretes made with CEM I cement, corresponding to the strengths in the cement standard test (CEM I: 56.6 N/mm^2 and CEM III/A: 52.1 N/mm^2, Table 3).

5 Modelling

5.1 General

A model that explains air void formation in relation to the cement and the active substances on which the admixtures are based was developed from the test results taking account of the practical experience and findings concerning the mode of operation of air-entraining agents and plasticizers. The conclusions only apply to the variants that were tested as, because of the wide extent of the test, it was only possible to include a limited number of combinations. The concrete production was also taken into account in addition to the starting materials. An understanding of the relation-

Table 6: Air void parameters and compressive strength relative to the cement/admixture combination

No.	Cement	Admixture		Air void parameters		Air content of hardened concrete	28-day compressive strength
		Plasticizer	Air-entraining agent	Micro air void content	Spacing factor		
				[vol. %]	[mm]	[vol. %]	[N/mm²]
1	CEM I	PCE precast element	Mod. wood resin	1.7	0.24	7.0	45.1
2			Syn. tenside 1	2.4	0.20	7.1	40.5
3		PCE ready-mixed concrete	Mod. wood resin	1.8	0.24	6.4	44.3
4			Syn. tenside 1	1.5	0.26	6.8	41.5
5	CEM III/A	PCE precast element	Mod. wood resin	1.4	0.33	6.6	40.4
6			Syn. tenside 1	2.6	0.18	7.5	38.3
7		PCE ready-mixed concrete	Mod. wood resin	1.3	0.31	5.0	40.4
8			Syn. tenside 1	1.6	0.29	6.0	41.4
9		Naphthalene sulfonate	Mod. wood resin	1.9	0.29	6.7	38.0
10			Syn. tenside 1	1.6	0.28	6.4	40.5

ships involved has made it possible to make practical recommendations (see Section 6).

5.2 Starting materials

5.2.1 Admixtures

Air-entraining agents based on natural active substances (vinsol resin) and a synthetic tenside (active substance alkyl polyglycol ether sulfate) were used in the concrete tests. Because of its poor solubility vinsol resin is to a large extent precipitated in the pore solution. On the other hand, the synthetic tenside has a very good solubility even when large quantities are added. Conventional plasticizers and PCE were used as the plasticizers. The classical plasticizers based on melamine and naphthalene sulfonates have a high charge density and within a short time are sorbed strongly onto positively charged areas of the cement particles or initial hydration products. The PCEs have lower charge densities than the classical plasticizers. The PCEs for the ready-mixed concrete sector are intended to maintain the workability over an extended period and therefore have lower charge densities than the PCEs for the precast element sector. The consequence is that less PCE is sorbed with the result that large quantities of PCE are present in a dissolved state in the pore water and are available for redispersion and for maintaining the workability.

5.2.2 Cement

As a rule, concretes made with CEM III cement require larger quantities of added air-entraining agent to adjust the air content than concretes made with CEM I cement. The larger surface area of the finer CEM III cement causes increased sorption of the air-entraining agent molecules.

5.3 Mixing the concrete

5.3.1 Addition of the air-entraining agent

The mixing sequence was taken into account in the modelling: the air-entraining agent is mixed in first and then the plasticizer is added. Immediately after the cement and water are mixed positive calcium ions settle on cement aggregate particles or are present dissolved in the pore solution. Part of the air-entraining agent dissociated in the mixing water is sorbed on positively charged areas of the solid particles. Another part reacts with the calcium ions present in the pore solution. The calcium salts that are formed have different solubilities depending on the active substance. The calcium salts of the air-entraining agents based on vinsol resin are very sparingly soluble and are largely precipitated in the pore solution. Because of its good solubility the calcium salt of the alkyl polyglycol ether sulfate active substance remains active in the pore solution. The air introduced during the mixing process is stabilized by the molecules of the air-entraining agent. The air bubbles attach themselves to the solid particles. After the two-minute mixing time the air-entraining agent is fully activated and a stable air void microstructure has formed. If excess air-entraining agent has been added as the result of a shortened mixing time during production then small amounts of active substance (natural air-entraining agent) or large amounts (synthetic air-entraining agent) remain active in the pore solution. During any subsequent mixing process (e.g. rotating drum in a truck mixer) the air bubbles become stabilized, with the result that the air content can rise if a readily soluble tenside is used [3].

5.3.2 Addition of the plasticizer (first air-entraining agent, then plasticizer)

Like the air-entraining agents the plasticizer has a negative charge and is sorbed onto solid particles. After the addition of the plasticizer varying amounts (depending on the charge density of the plasticizer) of the air-entraining agent molecules are displaced from the solid particles and return to the pore solution. Air bubbles are also destroyed during the mixing process and further air-entraining molecules are transferred to the pore solution.

a) PCE-based plasticizers

The air void formation is hardly affected by the nature of the PCE (ready-mixed concrete or precast element). After the PCE has been added, sorbed molecules of air-entraining agent are displaced from the cement and aggregate particles. Because of the higher proportion of sorbed air-entraining agent with CEM III cement the amount of air-entraining agent molecules released is higher with CEM III cement than with CEM I cement. The formation of air voids while the PCE is being mixed in is heavily influenced by the basis of the active substance in the air-entraining agent.

– Air-entraining agents based on natural active substances

After the PCE has been mixed in the air content drops because the sorbed air-entraining agent molecules are displaced and some attached air bubbles become detached. Because of their low solubility the air-entraining agent molecules that have been released are precipitated in the pore solution and can no longer stabilize any air bubbles. With the natural air-entraining agent it is therefore necessary, before the PCE is added, to set up a higher air content than required in order to offset the drop after addition of the PCE. The high air content also initially produces better air void parameters. After the plasticizer has been mixed in, both small and large air bubbles escape from the fresh concrete. As a consequence the air content falls and the air void parameters deteriorate.

– Air-entraining agents based on synthetic active substances
The air-entraining agent molecules released during the addition of PCE are readily soluble and therefore remain active in the pore solution. Air bubbles introduced while the PCE is being mixed in become stabilized and increase the air content. To compensate for this it is therefore necessary, before the PCE is added, to set up a lower air content than required. This also results in unfavourable air void parameters. Small and large air bubbles become stabilized during the addition of PCE. This causes an increase in air content and improved air void parameters.

b) Plasticizers based on naphthalene sulfonate
A substantially higher air content than required had to be established before the plasticizer was added, regardless of the active substance in the air-entraining agent. This needed very large quantities of air-entraining agent compared with the concretes made with PCE. After addition of the plasticizer the air content is reduced and the air void parameters deteriorate, regardless of the active substance on which the air-entraining agent is based. One reason for this could be a de-foaming action of the plasticizer that would then have to affect the two air-entraining agents equally, regardless of the active substance. However, no appreciable de-foaming action was detected in the tests with fine concrete.

Unlike the situation with the PCEs, no dependence of the air void formation on the basis of the active substance was detected. The reason is possibly the high charge density of the naphthalene sulfonate, which leads to greater sorption of the plasticizer. As a result more air-entraining agent molecules and attached air bubbles are displaced from the solid particles. With the combination of PCE with synthetic tenside new air bubbles become stabilized while the PCE is being mixed in and the air content rises. This is not the case with the variants containing naphthalene sulfonate. The reason is presumably that newly formed air bubbles are no longer able to attach themselves because the naphthalene sulfonate is more strongly sorbed than the PCE and the sorption sites are occupied by the plasticizer. As a consequence the air void microstructure is not stable – both small air bubbles (deterioration of the air void parameters) and large air bubbles (reduction of the air content) escape from the fresh concrete with increasing age.

c) Air void system
The requirements were not always met in an initial test even though the total air content complied with the requirements. This applied both for combinations with PCE and for combinations with the plasticizer based on naphthalene sulfonate. For the variants examined the reason lay not in a de-foaming action with certain air-entraining agent/plasticizer combinations but in the consistency of the concrete. A flowable consistency had to be established immediately after addition of the plasticizer in order to achieve the desired very soft consistency (F4, flow table spread 49 cm to 55 cm) after 30 minutes or 45 minutes. This means that the air void formation took place in a concrete with a flowable consistency and experience shows that this makes it harder to form an air void system with air void parameters that comply with the requirements. Conventional plasticizers may only be effective for a limited time so these are added to the truck mixer on the construction site before delivery. Because of their good plasticizing action PCEs are often added directly at the concrete plant. Alongside the greater sensitivity of the PCEs this may possibly be a reason for the adverse effect on air void formation reported from practice.

5.3.3 Changing the sequence of adding the admixtures
If, with the same addition quantities of admixtures, the sequence "first air-entraining agent, then plasticizer" is changed (e.g. simultaneous addition of the admixtures or "first plasticizer, then air-entraining agent) the air voids are formed in a concrete with a softer consistency, which facilitates the introduction of air voids. With the same addition quantity of admixtures the air content then inevitably rises. An irregular sequence of admixture addition increases the scatter of the air content, especially if a readily soluble air-entraining agent is used. Air-entraining agents based on natural active substances are substantially more robust in this respect.

5.3.4 Addition of the plasticizer on the construction site
In the laboratory trials the plasticizer was added during the production of the concrete. In practice the plasticizer is often added to the truck mixer on the construction site at the point of placement. The air content may rise if at this time the concrete contains a fairly large quantity of unactivated air-entraining agent (caused by addition of excess air-entraining agent due to a shortened mixing time).

6 Conclusions and practical recommendations

6.1. Conclusions
There have been reports of problems that have arisen in practice during the production of air-entrained concrete when using plasticizers, especially those based on polycarboxylate ether (PCE). The total air content fluctuates and in individual cases the requirements for the air void parameters measured on the hardened concrete are not met in spite of the fact that the total air content in the fresh concrete complies with the requirements. The extent to which interactions between air-entraining agents and plasticizers can affect the air void microstructure was investigated in a research project. Improved understanding of the action mechanisms during combined use of the two admixtures permits carefully controlled selection of "robust" admixture combinations and a reduction in the risk of unwanted air void formation.

Fine concretes were produced with an air content of about 5.5 vol. % and plasticizer was then added in several stages to estimate the influence on air void formation and a possible de-foaming effect of the particular air-entraining agent/plasticizer/cement combination. The air content was determined after each addition stage. Concretes with an air content of about 5.5 vol. % and a flow table spread corresponding to consistency class F4 were then produced with selected air-entraining agent/plasticizer/cement combinations.

No instance of a de-foaming action of the plasticizer was found in the investigations on fine concretes. The air content increased with rising addition level of plasticizer. The extent of the increase was low when using air-entraining agents based on natural active substances, while a greater increase was recorded with the synthetic tenside. The reason for the different air void formation is that air-entraining agents are passed back into the pore solution after the addition of the plasticizer. Air bubbles are stabilized while the plasticizer is being mixed in. With a sparingly soluble natural air-entraining agent most of the air-entraining agent that has been "released" is precipitated and there is only a slight increase in air content. The air content can increase more sharply with a readily soluble synthetic tenside.

The concrete tests were used primarily to investigate the influence of the air-entraining agent/plasticizer/cement combination and the age of the fresh concrete on the air content and the air void parameters. First of all the quantities of air-entraining agent and plasticizer added that were needed to achieve the required air content and the desired workability were established. With the air-entraining agents the synthetic air-entraining agents proved to be substantially more effective regardless of the chosen cement/plasticizer combination. More air-entraining agent had to be added to the CEM III cement than to the CEM I cement. The nature of the PCE had no appreciable influence on the quantity of air-entraining agent added, and this applied to both cements. The greatest quantities of air-entraining agent were required for concretes containing naphthalene sulfonate. The quantity of plasticizer needed to achieve the required consistency was not appreciably influenced by the active substance in the air-entraining agent or by the type of cement. The smallest quantity of plasticizer was needed with the PCE precast element and the largest with the naphthalene sulfonate. The PCE ready-mixed concrete lay in the middle.

The behaviour with time of the air void formation (fresh and hardened concrete) was determined after the air-entraining agent was mixed in, after the addition of the plasticizer (end of mixing) and then 10, 30, 45 and 60 minutes after the end of mixing. The concretes with the two PCEs (ready-mixed concrete and precast element sectors) exhibited similar behaviour patterns with respect to the development with time of the air content and the air void parameters. After the one-minute mixing of the PCE (end of mixing) a drop in air content combined with a deterioration of the air void parameters was established when using the air-entraining agent based on a natural active substance, and with the synthetic air-entraining agent there was a rise in air content and improvement in the air void parameters. With the natural air-entraining agent the drop in air content was less when using the CEM III cement than with the CEM I cement. With the synthetic air-entraining agent the increase was more strongly marked with the CEM III cement than with the CEM I cement. When using naphthalene sulfonate the air content fell and the air void parameters deteriorated after addition of the plasticizer regardless of the type of active substance in the air-entraining agent.

The requirements for the air void parameters were not always met in spite of a total air content that satisfied the requirements. This applied both to combinations with PCEs and with plasticizers based on naphthalene sulfonate. The cause of this is not a de-foaming action with certain admixture combinations but the consistency of the concrete. Immediately after the plasticizer has been mixed in a flowable consistency (class F5, flow table spread 58 to 62 cm) had to be established to achieve the very soft consistency required (F4, flow table spread 49 to 55 cm) after 30 or 45 minutes. Experience shows that the good workability does in fact assist the introduction of air voids, but it makes it more difficult to maintain the required air void parameters.

6.2 Practical recommendations

The interrelationships described in the model make it possible to give the following recommendations to the industry carrying out the construction work and to the producers of admixtures and mixing plants:

a) Producers of air-entrained concrete:
construction industry or ready-mixed concrete plants

Assuming the same quantities of admixtures the sequence of addition of air-entraining agent and plasticizer has a decisive influence on the air void formation. During the production of the concrete care must be taken in practice to ensure that the chosen mixing sequence and mixing time are retained. The air-entraining agent should be added first and then the plasticizer. If there are changes in the quantity of air-entraining agent (overdosing) and the mixing sequence then fairly major effects can be expected, especially with air-entraining agents based on synthetic active substances due to their good solubility. The air content may increase if there is subsequent input of mixing energy (e.g. during transport in the mixer truck with rotating drum or during placement with a screw conveyor). This is particularly the case if plasticizer is added subsequently to the mixer truck on the construction site. The better workability then once again assists the air void formation. A large proportion of air-entraining agents based on natural active substances are precipitated in the pore solution, so any influence, e.g. from overdosing, has less effect. Admixture combinations of air-entraining agent and plasticizer containing air-entraining agents based on natural active substances are therefore considered "more robust" than variants with synthetic air entraining agents.

b) Admixture industry

The air-entraining agents based on natural active substances are less inclined to re-activation. The disadvantage is that the air content can often only be raised with high addition levels. With a synthetic active substance component the air void formation could be improved without appreciably increasing the re-activation potential. More robust air void formation could possibly be achieved with air-entraining agent mixtures of synthetic and natural active substances when used together with plasticizers.

c) Construction machinery industry

The mixing plants should be equipped with two admixture dispensing systems and the control programme should be designed so that the dispensing devices can be operated by the mixer operator independently of one another. The time of addition should be freely selectable.

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