DETERMINATION OF CONCRETE ADMIXTURES IN CONCRETE BY NMR SPECTROSCOPY

UNTERSUCHUNGEN ZUM NACHWEIS VON BETONZUSATZMITTELN IN BETONEN MIT NMR-SPEKTROSKOPIE

DETERMINATION D'ADDITIFS DE BETON PAR SPECTROSCOPIE DE RESONANCE MAGNETIQUE NUCLEAIRE

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SUMMARY

Based on investigations of typical components - active components and impurities - of common concrete admixtures like water reducers, retarders, plasticizers, mobile components and mobile decomposition products of active components resulting from reactions of concrete admixtures with concentrated alkaline solutions in porous water were determined. Cement mortar and concrete samples with admixtures (admixture concentration 0.5 and 2 % of cement content) were extracted/leached with different organic solvents and aqueous solutions at higher temperatures. The identification and quantification of relevant compounds in initial products and extracts were carried out by nuclear magnetic resonance spectroscopy (^{1}H NMR) as well as by gas chromatography/ mass spectrometry. The obtained data prove on one hand, that concrete admixtures are detectable in concrete with the methods chosen. On the other hand the data proves, that even under "worst-case"-conditions (grounded cement bound building material and extraction/leaching at higher temperatures for more than 5 d) only minor portions of active components and impurities are mobile in water. More than 70 % of the added admixture is irreversible bound to the concrete matrix. Besides small portions of active components mainly formiate and acetate can be detected in aqueous solutions. Of the listed dangerous substances only phosphoric acid tributyl ester can be detected in aqueous extracts of concrete and cement mortar in minor traces.

ZUSAMMENFASSUNG

Im Rahmen von Untersuchungen typischer Inhaltsstoffe handelsüblicher Betonzusatzmittel – Wirkstoffe und Hilfsstoffe – wurden mobilisierbare Wirkstoffanteile sowie mobilisierbare Abbauprodukte aus der Reaktion der Betonzusatzmitteln mit Zement bestimmt. Zementmörtel- und Betonproben mit einem Zusatzmittelgehalt von 0,5 bzw. 2% (bezogen auf den Zementgehalt) wurden mit verschiedenen organischen Lösungsmitteln sowie reinem Wasser bei erhöhten Temperaturen extrahiert bzw. eluiert. Die Identifizierung und Quantifizierung der relevanten löslichen Verbindungen in den Extrakten bzw. in den Zusatzmitteln selbst wurden mit Kernresonanzspektroskopie (^{1}H-NMR) sowie Gaschromatographie/ Massenspektrometrie durchgeführt. Die erhaltenen Ergebnisse zeigen einerseits auf, dass die eingesetzten Betonzusatzmittel mit den obigen Methoden in Betonproben sicher nachgewiesen werden können. Andererseits belegen die Ergebnisse, dass selbst unter extremen Bedingungen (zementgebundene Baustoffe in gemahlener Form und Extraktion bei erhöhten Temperaturen über einen Zeitraum von mehr als 5 Tagen) nur geringe Mengen an Wirk- und Hilfsstoffen über den Wasserpfad mobilisierbar sind. Über 70 % der eingesetzten Zusatzmittel werden irreversibel in die Zementmatrix eingebunden. Neben kleineren Anteilen an Wirkstoffen werden hauptsächlich Formiat und Acetat in den wässrigen Eluaten nachgewiesen. Von den als gefährlich eingestuften Substanzen kann in den wässrigen Eluaten der Beton- bzw. Zementmörtelproben lediglich Tributylphosphat in geringen Spuren nachgewiesen werden.

RESUME

Au cours des études de composants typiques d'additifs de béton commercials – des agents et des matériaux auxiliaires (moyens)- la fraction des additives mobiles ainsi que celle des produits de décomposition mobiles formés dans la réaction avec ciment ont été déterminées.

Des échantillons de béton et de mortier à ciment contenant 0,5 et/ou 2% d’additif (par rapport à la teneur en ciment) ont été extraits avec des différents solvants organiques ainsi qu'avec d’eau pure à températures élevées. L'identification et la quantification des composés soluble pertinents dans les extraits et/ou dans les additifs (produits originaux) ont été accomplies par la spectroscopie de résonance magnétique nucléaire (^{1}H NMR) ainsi que par la chromatographie de gaz/spectrométrie de masse (GC/MS).

D’une part les résultats prouvent que les additifs de béton appliqués peuvent être déterminés certainement par les méthodes choisies. D’autre part les résultats montrent que même à conditions très dures (mortier à ciment pulverisé et extraction à températures élevées pendant plus que 5 jours) il y a seulement peu d’agents et/ou de moyens qui peuvent être mobilisés. Plus que 70 % des additifs appliqués sont absorbés irréversiblement par le ciment. Des composés dangereux il n’y a que le tributylphosphate qui est déterminé en quantité minimale.

KEYWORDS: concrete admixtures, determination, NMR, leaching, environmental risks

1. INTRODUCTION

Concrete admixtures are added to concrete and mortar in concentrations of 0.5 – 2%, in order to influence defined characteristics of fresh and/or hardened concrete. In the following only active components and supplies of concrete admixtures used as water reducers, superplasticizers and retarders were regarded. The assigned raw materials are not considered as biologically easily degradable and may not directly discharged in discharge systems, ground- and surface water [1]. The presented investigation serves to identify mobile substances contained in different commercially available concrete admixtures for concrete in contact with ground water and offers a possibility to determine concrete admixtures in concrete. The experimental conditions of the chosen extraction methods in water and organic solvents allow to detect even minor mobile portions of the admixtures. The results of the presented study do give an outline of possible mobile components and/or degradation products of concrete admixtures leached out of concrete or cement mortar. The results cannot be directly transferred to conditions of leaching monolithic concrete bodies in contact with ground water.

2. INVESTIGATED CONCRETE ADMIXTURES

For the investigations 5 common concrete admixtures were selected. Manufacturer's data of active components of these concrete admixtures are given in the following table.

Table 1 : Concrete admixtures – Initial Products – Manufacturer's Data

Concrete admixture	Active component (manufacturer's data)
A	Acrylate copolymer + naphthaline sulfonate
B	Acrylate + lignosulfonate + naphthaline sulfonate
C	Naphthaline sulfonate
D	Polycarboxylate ester
E	Lignosulfonate + naphthaline sulfonate

The concrete admixtures were added to cement mortar and concrete (w/c = 0.5) in two different concentrations (0.5 and 2 % relative to the cement content). The maximum permissible dosages for these admixtures to cement are about 10 ml/kg (densities of the admixtures are approx. 1.1 g/cm^3) . A dosage of 2 % (relative to cement) corresponds thus to an overdosing of approx. factor 2 for concrete plasticizers and represents on the other hand the maximum concentration for superplasticizers. Moreover the selected different concentrations give information on the concentration dependent emission potential in the different polar extraction media.

3. EXPERIMENTAL RESULTS

3.1 Admixtures based on naphthaline sulfonate

Concrete admixtures based on naphthaline sulfonate can be identified by characteristic NMR fingerprints ($\delta = 7.5 - 8.3$; solvent D_2O) after extraction with organic solvents and aqueous solutions. The naphthaline sulfonates (derivatives of the naphthaline sulfonates) determined in water-, methanol- and acetone/H_2O-extracts of cement bound building material are modified compared to the naphthaline sulfonate of the initial products and differ also (chemically) from monomeric naphthaline sulfonate described in the literature which can be mobilized via the water path (comparison of spectra with Aldrich Library of ^{13}C and ^{1}H FT NMR Spectra, volume 2) (s. also [2]). A structure determination of these compounds could not be made with the selected methods. In extracts of dichloromethane (DCM) of hardened cement paste samples an additional non-polar compound on basis of naphtaline sulfonate can be determined. This compound is definitely not naphthaline. It can be determined in all naphthaline sulfonate containing admixtures investigated and differs chemically (proven by NMR spectra) from naphthaline sulfonate derivatives found in aqueous (polar) extracts. Compared to the total amount of naphthaline sulfonate in aqueous extracts the fraction soluble in DCM is about < 10 to 20 % of the total naphthaline sulfonate content. Naphthaline can neither be determined in DCM-extracts of initial products nor in cement mortar added with naphthaline sulfonate. Yet, naphthaline can be determined in small quantities (< 10 mg/kg concrete admixtures), if admixtures based on naphthaline sulfonate are treated with a strongly alkaline solution at higher temperatures for longer periods of time. This shows that naphthaline sulfonate containing concrete admixtures are no relevant source for naphthaline in ground water and leachate. All concrete admixtures (initial products) based on naphthaline sulfonate are contaminated with different organic solvents like cis and trans decahydronaphthaline (decalin) (admixtures B and C), different n- and cycloalkanes (admixtures A and E) or xylene as well as t-butyl-xylene (admixture A). The concentrations of these impurities are below 5 g/ kg admixture.

3.2 Admixtures based on polycarboxylates

Concrete admixtures based on polycarboxylate esters consist of an acid component (polyacrylate backbone) esterified with different polyols. For admixtures A and D the polyacrylate backbone is esterified with polyethylene glycols (resp. methylether derivatives of polyethylene glycol) of different chain length. With the methods chosen it cannot be differentiated whether besides esterified polyethylene glycol (derivatives) non esterified "free" polyethylene glycol is contained in the initial products. Both components, the polyacrylate backbone and the polyethylene glycol side chains are detectable in the tested initial products.

Admixtures which contain polyacrylate/polycarboxylate show characteristic ethoxy-compounds in water-, methanol- and acetone/H_2O (1:1) extracts (NMR-fingerprint at $\delta = 3.45 - 3.65$; solvent D_2O). These ethoxy compounds are essentially methylethers of polyethylene glycol and possibly nonsubstituted polyethylene glycols. This mixture on basis of polyethylene glycol will be described as polyethylene glycol (derivative) in the following. This class of compounds can be determined in the initial products and represents the main part of active components in concrete admixture D. The polycarboxylate/ polyacrylate backbone is not detectable in aqueous eluats and DCM-extracts. In concrete with admixtures based on polycarboxylate/polyacrylate only these characteristic ethoxy compounds (polyethylene glycols) are mobile. This portion of the admixtures can be originated either from an alkaline cleavage of the esters or it consists of "free" non esterified polyethylene glycols, which are already part of the original product. The substantially different results of the mobile quantities of polyethylene glycols for concrete admixtures B and D, regained in aqueous solutions (Fig. 2) clearly point out, that the chemical composition of the products (active components) is essential for the release of polyethylene glycols. Besides those polyethylene glycol derivatives p-toluenesulfonic acid can be determined in aqueous eluates of cement mortar treated with admixture D. The amount of mobile p-toluenesulfonic acid is less than 10 mg/kg cement.

3.3 Admixtures based on lignosulfonates

^1H NMR spectra of lignosulfonate are not very characteristic. Lignosulfonate of initial products B and E is detectable by ^1H NMR (NMR- fingerprint at $\delta = 6.6 - 7.1$; solvent D_2O). In aqueous and organic extracts of cement mortar treated with concrete admixtures B and E no significant hint for lignosulfonates can be determined. There are 3 possible reasons for this:

- the sensitivity of the applied method for compounds of this type is so low, that even larger mobile quantities cannot be detected
- the concentration of lignosulfonate in the initial products (B and E), which is relatively low compared to the concentrations of other active components in concrete admixtures, is so small that in fact no lignosulfonate is leached out
- or the solubility of the active component lignosulfonate in general is so low that lignosulfonate is practically not mobilizable via the water path.

3.4 Processing agents and impurities

Besides the active components concrete admixtures contain product-depending various processing agents (see table 2 and 3).

Table 2: Identified components of concrete admixtures (initial products) – results according to nuclear magnetic resonance spectroscopy (^{1}H NMR)

Concrete admixture – manufacturer's data	Content of active components (residue after drying) in %	Content of active components – fraction of naphthaline sulfonate (according to ^{1}H NMR) in g/kg concrete admixture semiquantitatively	Components of concrete admixture (detected by ^{1}H NMR)
A Acrylate copolymer + Naphthaline sulfonate	26	approx. 100	Naphthaline sulfonate Polyacrylate Formiate Acetate Methanol Isopropanol
B Acrylate + Lignosulfonate + Naphthaline sulfonate	29	approx.65	Naphthaline sulfonate Lignosulfonat Polyacrylate Polyethylene glycol (derivative) Formiate, Acetate, Methanol Isopropanol
C Naphthaline sulfonate	21	approx.100	Naphthaline sulfonate Formiate, Acetate, Methanol Isopropanol
D Polycarboxylate ester	34	- -	Polycarboxylate Polyethylene glycol (derivative) p-Toluenesulfonic acid
E Lignosulfonate + Naphthaline sulfonate	42	approx.105	Naphthaline sulfonate Formiate, Acetate, Methanol Isopropanol Lignosulfonate (side component)

Besides ubiquitous compounds such as formiate and acetate, organic solvents like n- and cycloalkanes, methanol and isopropanol, aromatic compounds such as xylene and t-butyl-xylene can be determined in the initial products. Most of these solvents are impurities within the trace range (< 100 mg/kg concrete admixtures). Exceptions are t-butyl-o-xylene and decahydronaphthaline (decalin). The ubiquitous compounds formiate and acetate are part of almost all admixtures (except admixture D) and can be determined in all aqueous extracts/leachates, including concrete or cement mortar without admixtures, in differing concentrations. The determined concentrations of formiate and acetate leached out of cement mortar range from < 5 mg/kg for cement mortar without admixtures up to 30 mg/kg for cement mortar treated with admixtures based on naphthaline sulfonate. Besides concrete admixture D, a superplasticizer of the new generation, phosphoric acid tributylester is detectable in all aqueous eluats as well as in all in all examined admixtures. This admixture (D) contains p-toluenesulfonic acid as processing agent, which can be detected in aqueous leachates. Due to the sample preparation easily volatile compounds such as methanol, isopropanol, n- and cycloalkanes cannot be detected in the leachates. Impurities of cement like mineral oil hydrocarbons can be detected in all DCM extracts.

Table 3: Volatile components of concrete admixtures (Headspace gas chromatography/ mass spectrometry)

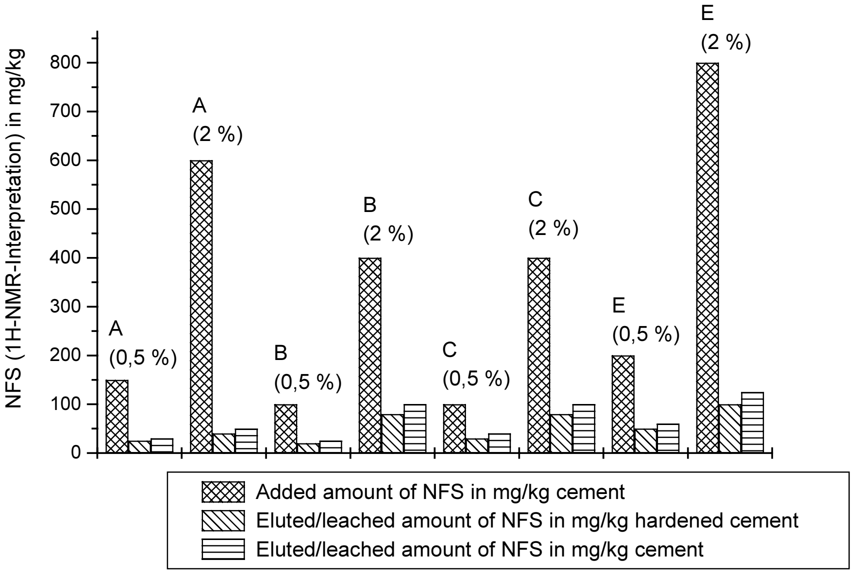
Concrete admixture	Volatile components (headspace technique)
A	Methylcyclopentane, ethylcyclopentane, cyclohexane, methylcyclohexane, dimethylpentane, xylene, t-butyl-o-xylene
B	cis- trans decahydronaphthaline (decalin)
C	cis-, trans decahydronaphthaline (decalin)
D	No volatile components detected
E	Methylcyclopentane, ethylcyclopentane, cyclohexane, methylcyclohexane, dimethylpentane
Pure active components	
Lignosulfonate (pure active components)	No volatile components detected
Naphthaline sulfonate (pure active components)	Decane, cis-, trans decahydronaphthaline (decalin)

4. DISCUSSION

A comparison of solvents of different polarity used for extraction/leaching shows that modified solvents like methanol or acetone/water do not improve the mobility of characteristic compounds. All characteristic compounds found in extracts/leachates with modified solvents can also be detected in (pure) aqueous solutions. Hence, pure water and dichloromethane as solvents are sufficient for the determination of characteristic mobile compounds in concrete with admixtures. Despite limitations regarding the accuracy of ^{1}H NMR spectra on water basis the following conclusions can be made:

- About 5 – 30 % of the added amount of active components are in principle mobile when leaching grounded cement mortar added with different admixtures with water for a longer period of time at higher temperatures (5 d at 60 °C). The amounts of leached admixtures are in general less than 100 mg active components per kg cement. Transferred to concrete and an average dosage of admixtures of 0.5 % about 3 – 8 mg of active components and/or their derivatives per kg concrete are mobile under the "worst-case" conditions chosen.

Figure 1: Amount of applied naphthaline sulfonate (NFS) and corresponding amount of NFS found in aqueous solutions of hardened cement paste (w/c = 0.5) with 0.5 and 2 % admixtures.



- An increase of the dosage of the concrete admixture (factor 4) correlates for nearly all mobile compounds (active components) with an increase of the mobilized amounts (factor 2 –6) (Fig. 1).
- Besides the active components of the concrete admixtures and their degradation products (derivatives of naphtaline sulfonate or derivatives of polethylene glycol) only phosphoric acid tributylester used as antifoaming agent, p-toluenesulfonic acid and ubiquitous formiate, acetate and mineral oil hydrocarbons are mobile in aqueous media. Other organic compounds cannot be detected neither with polar (water) nor nonpolar (dichloromethane) solvents. Mobilizable amounts are generally < 5 mg/kg for tributylphosphate and 20 – 30 mg/kg for formiate and acetate, respectively (Table 4).

Figure 2: Amount of applied polyethylene glycol (derivative) and corresponding amount of polyethylene glycol (derivative) found in aqueous solutions of hardened cement paste (w/c = 0.5) with 0.5 and 2 % admixtures.

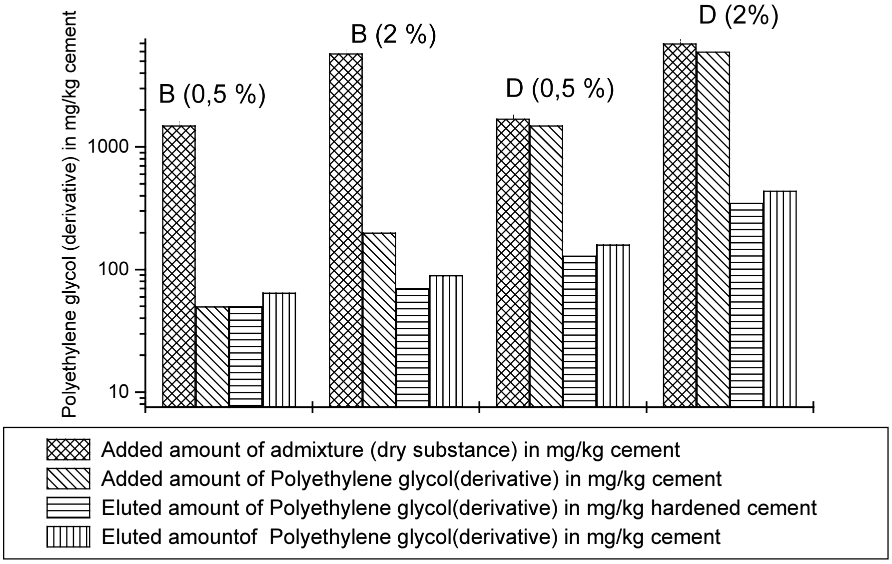


Table 4: Active components of concrete admixtures in the fresh cement mixtures and in aqueous solutions of hardened cement paste.

Concrete admixture added 1)	Content of active component - fraction of naphthaline sulfonate (derivative)2)	Content of active component - fraction of polyethylene glycol (derivative) 2)	Amounts of water-soluble active components and supplies in mg/kg hardened cement paste (w/c = 0.5)		
in % relative to cement	in mg/kg cement	in mg/kg cement	Naphthaline sulfonate (derivative)	Polyethylene glycol (derivative)	Tributyl phosphate
A (0,5)	150	n.d.	25	< 20	< 5
A (2)	600	n.d.	40	< 20	10
B (0,5)	100	50	20	50	< 5
B (2)	400	200	80	70	10
C (0,5)	100	n.d.	30	< 20	< 5
C (2)	400	n.d.	80	< 20	< 5
D (0,5)	n.d.	1500	n.d. *	130	n.d. *
D (2)	n.d.	6000	n.d. *	350	n.d. *
E (0,5)	200	n.d.	50	< 20	< 5
E (2)	800	n.d.	100	< 20	approx. 5

n.d. = not detectable

* not contained in the initial product

1) addition of initial product

2) calculated of ^{1}H NMR

Altogether, for admixtures based on naphthaline sulfonate the maximum amounts of active component detected in aqueous solutions by NMR, are about 20 –30 % of the originally applied amounts of active component. These amounts exceed values given by other authors [2,3,4] by a factor of approx. 2. These differences can be attributed to higher temperatures and the substantially longer times of leaching used in this investigation. In our opinion the values presented here give an upper limit for the amounts of active components which can be leached out of cement bound building materials with admixtures.

For concrete admixtures based on polycarboxylate as active components only polyethylene glycol (resp. methylether derivatives of polyethylene glycol) is mobile in aqueous solutions. The corresponding regaining rates differ however substantially depending on the specific concrete admixture used and vary between 50 and 5 %, whereby the maximum amount of mobile polyethylene glycol reaches 350 mg/kg hardened cement paste (Fig. 2).

5. CONCLUSION

Mobilizable fractions of admixtures of cement-bound building materials and the amount of mobile reaction products were determined. Cement mortar and concrete were extracted with different organic solvents and aqueous solutions. The identification and quantification of the relevant soluble compounds in admixtures and extracts were carried out by nuclear magnetic resonance spectroscopy (^{1}H NMR) as well as by gas chromatography/ mass spectrometry.

In the following some essential results are compiled briefly:

- The components of concrete admixtures can be characterized by ^{1}H NMR and GC/MS: Active components as well as side components can be identified and quantified.
- Active components of concrete admixtures applied in concrete and/or cement mortar samples can be determined by characteristic fingerprints in the ^{1}H NMR spectra of aqueous solutions and/or organic extracts.
- An increase of the dosage of the concrete admixtures correlates with an increase of the mobilized amounts.
- For admixtures based on naphthaline sulfonate the naphthaline sulfonates determined in aqueous extracts of cement bound building materials are modified compared to the naphthaline sulfonates of the initial products.
- For admixtures based on polycarboxylate/polyacrylate only polyethylene glycol is mobile in aqueous solution. The other part of the active components – the polycarboxylate backbone – is not detectable in aqueous extracts of concrete or cement mortar.
- Besides the active components of the concrete admixtures only tributyl phosphate as well as ubiquitous formiate, acetate and mineral oil hydrocarbons are mobile in aqueous media. Other organic compounds are not detected.

- Data indicate that environmental risks of cement-bound building materials with admixtures can be considered as low.

REFERENCES

[1] Deutsche Bauchemie e.V. : *Betonzusatzmittel und Umwelt* Sachstandsbericht Mai 1999.

[2] Herb, H.: *Zur Moblisierung von sulfonathaltigen Betonzusatzmitteln aus Zementstein*, Dissertation Universität Karlsruhe, 2001.

[3] Spanka, G., Thielen, G.: *Untersuchungen zum Nachweis von verflüssigenden Betonzusatzmitteln und deren Sorptions- und Eluationsverhalten* Beton 45 (1995) S. 320-327.

[4] Ruckstuhl S.: *Environmental exposure assessment of sulfonated naphthalene formaldehyde condensates and sulfonated naphthalenes applied as concrete superplasticizers*, Naturwissenschaften ETH Zürich, Nr. 14477, 2002.