DETERMINATION OF PORTLANDITE AND OTHER CEMENT COMPOUNDS IN HARDENED CEMENT PASTE AFTER SQUEEZING PORE SOLUTION WITH HIGH PRESSURE

BESTIMMUNG DES PORTLANDITANTEILS UND ANDERER ZEMENTINHALTSSTOFFE IN ZEMENTSTEIN NACH AUSPRESSEN VON PORENWASSER UNTER HOHEM DRUCK

DÉTERMINATION DE LA TENEUR EN PORTLANDITE ET AUTRES COMPOSANTS DES CIMENTS DANS LES PÂTES DE CIMENT DURCIES PAR EXTRACTION DE L'EAU INTERSTITIELLE PAR PRESSAGE SOUS HAUTE PRESSION

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SUMMARY

The present work shows, that squeezing pore water out of hardened cement pastes with different w/c-ratios allows to determine the quantity of pore solution. Balancing total water in hardened cement pastes with a w/c-ratio of 0,50 (Σ water of crystallisation (hydration water) + squeezed interstitial water in g/kg cement paste) leads to uncertainties less than 5 %. The ion balance of squeezed interstitial water proves that with high probability the squeezed water reflects the status of the interstitial water in hardened cement paste. With the complete squeezing of interstitial or pore solution with high pressure at room temperature it is possible to extract all soluble salts including $Ca(OH)_2$ solved in interstitial water with out disturbing the establishment of equilibrium (equilibrium concentration) of the salts in pore solution. The combination of squeezing and DTA allows the determination of Portlandite in hardened cement paste with a w/c-ratio of 0,50. The x-ray diffraction spectra of squeezed hardened cement paste prove the obtained results by DTA. The influence of $Ca(OH)_2$ in the hydrating solution in portland cement during and after the process of separating pore solution could be minimized.

ZUSAMMENFASSUNG

Die vorliegende Arbeit zeigt, daß durch Auspressen von Porenwasser mit hohem Druck aus Zementstein mit unterschiedlichen Wasser/Zement-Werten die Gesamtmenge an Porenwasser ausgepreßt werden kann. Der Fehler bei der Bestimmung der Gesamtwasserbilanz (Hydratwasser plus freies Porenwasser) liegt für einen Zementstein mit einem Wasser/Zement-Wert von 0,50 unter 5 %. Die Ionenbilanzen der ausgepreßten Porenlösungen belegen, daß mit hoher Wahrscheinlichkeit das so erhaltene Porenwasser die Verhältnisse im Porenwasser im Zementstein richtig widerspiegeln. Mit dem nahezu vollständigen Auspressen von Porenwasser bei hohem Druck und Raumtemperatur ist es möglich alle gelösten Salze im Porenwasser, einschließlich des $Ca(OH)_2$ ohne Störungen des Gleichgewichtszustands der Salze im Porenwasser aus dem Zementstein zu entfernen. Die Kombination von Auspressen und Differentialthermoanalyse erlaubt die Bestimmung des Protlanditanteils im Zementstein bei einem w/z-Wert von 0,50. Die Röntgenbeugungsspektren der Zementsteinproben bestätigen die Ergebnisse der DTA und zeigen, daß die Gehalte von Portlandit im Zementstein mit dem w/z-Wert korrelieren. Das Verfahren erlaubt es die Einflüsse von $Ca(OH)_2$ im Porenwasser auf die Hydratation von Portlandzement bei der Bestimmung der Phasenanteile zu minimieren.

RESUME

Le travail présent montre que l'extraction par pressage sous haute pression permet de déterminer la quantité totale d'eau interstitielle contenue dans des pâtes de ciment durcies ayant différents rapports eau/ciment. Pour une pâte de ciment durcie avec un rapport eau/ciment de 0,50, l'erreur commise lors de l'établissement du bilan des eaux (eau de cristallisation (eau d'hydratation) + eau interstitielle) est inférieure à 5 %.

Le bilan ionique de l'eau extraite montre qu'avec une forte probabilité, celle-ci reflète correctement la composition de l'eau interstitielle contenue dans la pâte de ciment durcie. Grâce à l'extraction sous haute pression à température ambiante, il est possible d'extraire tous les sels (y compris $Ca(OH)_2$) dissous dans l'eau interstitielle sans perturber l'équilibre (concentration d'équilibre) des sels. La combinaison du pressage et de l'analyse thermique différentielle permet de déterminer la teneur en Portlandite des pâtes de ciment durcies ayant un rapport eau/ciment de 0,50.

Les spectres de diffraction des rayons X des échantillons de pâte durcie confirment les résultats obtenus par analyse thermique différentielle et montrent que la teneur en Portlandite des pâtes de ciment durcies est corrélée avec le rapport eau/ciment. Ce procédé permet de minimaliser l'influence du $Ca(OH)_2$ de l'eau interstitielle sur l'hydratation du ciment Portland pendant la détermination des concentrations des différents composants.

1. INTRODUCTION

One of the possibilities of studying the influence of pore solution on hardening processes in cement is given by the analysis of squeezed pore solution combined with Differential Thermal Analysis and X-Ray Diffraction of hardened cement paste. In the past mainly hardened cement pastes with a cement/solvent-ratio (w/c) of 0,60 were used for experiments to squeeze pore solution [Schießl et al., 1997; VDZ, 1993-1993]. The present work shows some orientating results with cement pastes with w/c-ratios differing from 0,60 to 0,40.

To get knowledge of the influence of pore solution to hardening processes in cement paste, it is necessary to dry the hardened cement paste. This can happen in three different ways

- Drying the hardened cement paste at higher temperatures
- Extraction of pore solution with various organic liquids
- Squeezing the pore solution with high pressure

Normally drying processes as well as extraction processes influence the accuracy of the results [Ramachandran, 1984; Manns, 1975; Locher et al., 1976]. The difficulties to measure the residual moisture, as well as questions of the distribution of the soluble salts in pore solution and organic liquids in porous structure lead to uncertainties determining the mass equivalents in hardened cement paste. Especially the thermoanalytical determination of Portlandite [$Ca(OH)_2$ calziumhydroxide] is influenced by $Ca(OH)_2$ by pore solution. Relating to the drying conditions or to the water/liquid distributions different amounts of free, physicochemial or chemical bound water from hydrated cement compounds like Gypsum or Ettringite can be detected.

If it is possible to obtain the total amount of free pore solution by squeezing with high pressure, without disturbing the hardened cement paste structure it should be possible to detect the composition of cement paste and pore solution under reproducible conditions. Squeezing processes were normally carried out under room temperature. Under defined conditions (sample size, pressure) it should be possible to obtain a sample of hardened cement paste with small reproducible amounts of free pore solution. If pressure does not influence the mineralization or adsorption processes of water the determination of the contents of pore solution and cement paste will lead to reproducible results. The determination of the compounds in pore solution in combination with Different Thermal Analysis and X-Ray-Diffraction of hardened cement paste should give the opportunity to balance hydration processes.

Normally CO_2 from surrounding air has an influence to the mineralization in cement paste. The results of the present work were obtained by limiting this influence by excluding the contact of the cement paste with air during the hardening period, so only internal alkali-carbonate-reactions from dolomite or calcite contents of the cement influence the mineralization.

The possibility to examine cement paste without pore solution has the advantage to minimise the reaction of alkali in pore solution during the sample preparation (pulverising, drying). The squeezing procedure leads to samples of hardened cement pastes (age 28 days), which allow to determine the minerals formed in the cement paste by Differential Thermal Analysis (DTA) and X-Ray-Diffraction with few disturbances from remaining pore water. This method gives the possibility to calculate hydration degrees.

2. EXPERIMENTAL PROCEDURE

Three samples of cement pastes with different c/s-ratios (0,60, 0,50 and 0,40) were made with CEM I 32,5 R. After mixing the cement paste was filled in plastic bottles (250 ml) an the bottles locked air tight. To prevent demixing processes the bottles with the cement paste were shacked for 24 hours thoroughly. Afterwards the samples were stored in the plastic bottles locked air tight for 28 days at 20 °C.

After this storage period the plastic bottles were destroyed and the hardened cement paste samples squeezed with high pressure under reproducible conditions (500 N/mm²). The pore solution was collected without any contact to air and sensitive parameters like pH, conductivity, hydroxide and specific gravity measured immediately. The used squeezing apparatus (manufacturer: Fa. Böhler UDDEHOLM – special production) is shown in Figure 1. The other analysed parameters in the squeezed solution were Na^+, K^+, Ca^{2+}, Cl^-, SO_4^{2-}, NO_3^- and CrO_4^{2-}. The determination methods are mentioned in Table 1. In the squeezed cement pastes loss at red heat and sulphate (DIN EN 196) were analysed. The amount of hydration water, Portlandite and CO_2 were analysed by Differential Thermal Analysis (DTA) [Satava et al., 1975; Huppertz et al., 1999]. Additionally X-Ray-Diffractionsspectra were taken from each sample. This gave the possibility to compare the results obtained with both methods for Ettringite, Portlandite and CSH (calzium-silcate-hydrate)-phases in the hardened cement pastes.

3. RESULTS

Table 1 shows the results of the determination of different anions and cations in pore solution squeezed form hardened cement paste with different w/c-ratios. As expected increases the amount of sodium- and potassiumhydroxide in the pore solution with increasing ratios of cement. This leads to an increase of the pH-value and the conductivity in the analysed solutions. The calculation of the ion balance (sum anions and sum cations) demonstrates, that the total amount of soluble salts in pore solution was identified.

Table 2 shows the results of DTA and wetchemical analysis of the squeezed hardened cement paste and additionally the DTA results of the used cement (CEM 32,5 I R) . According to the known mechanisms about the hydration processes (hydration steps) the parameter hydrate water/ water of crystallisation bound at Portlandite and CSH (calcium silicate hydrate)-phases and gypsum, ettringite is mainly of interest.

Table1. *Compounds of squeezed pore solution from hardened cement paste with different w/c-ratios after storing the samples for 28 days at 20 °C air tight*

Mixture nr. w/c-ratio	1 0.60	2 0.50	3 0.40	Method of determination
pH-value	13.81	14.00	14.11	DIN 38 404 T5
Conductivity	96.9 mS/cm	117.2 mS/cm	164.0 mS/cm	DIN EN 27888
Specific gravity g/cm^3	1.074	1.073	1.082	
Na^+ mmol/l	27.2	31.9	38.6	DIN 1164
K^+ mmol/l	384.0	522.5	721.4	DIN 1164
Cl^- mmol/l	0.21	0.06	0.03	DIN 38 405 D1
NO_3^- mmol/l	0.19	0.22	0.03	DIN EN ISO 10304 T2 (D20)
SO_4^{2-} mmol/l	0.22	0.68	1.19	DIN EN ISO 10304 T2 (D20)
Cr(VI) mmol/l	0.18	0.19	0.29	DIN 38 405 D 24
OH^- mmol/l	410	554	760	DIN 38 409 T7
Ca^{2+} mmol/l	1.6	1.9	1.5	DIN EN ISO 11885 E 22
Σ cations mval/l	413	556	762	Calculated
Σ anions mval/l	411	555	761	Calculated
Σ Ions g/l	22,73	30,71	42,18	Calculated

Table 2. *DTA results for cement CEM I 32.5 and squeezed hardened cement paste with different w/c-ratios after storing the samples for 28 days at 20 °C air tight*

Mixture nr.	Cement	1	2	3
w/c-ratio		0.60	0.50	0.40
Loss on red heat m.-%	2.84	23.04	26.53	25.15
Hydrate water (total) M.-%	0.73	20.24	24.52	23.02
Water from Portlandite M.-%	0.35	4.89	4.55	4.19
CO_2 M.-%	2.05	2.15	1.70	1.82
SO_3 M.-%	2.57	2.02	1.91	1.95
Water of crystallisation without Portlandite M.-%	0.38	15.35	19.97	20.96
$CaCO_3$ M.-%	4.70	6.13	5.13	5.37

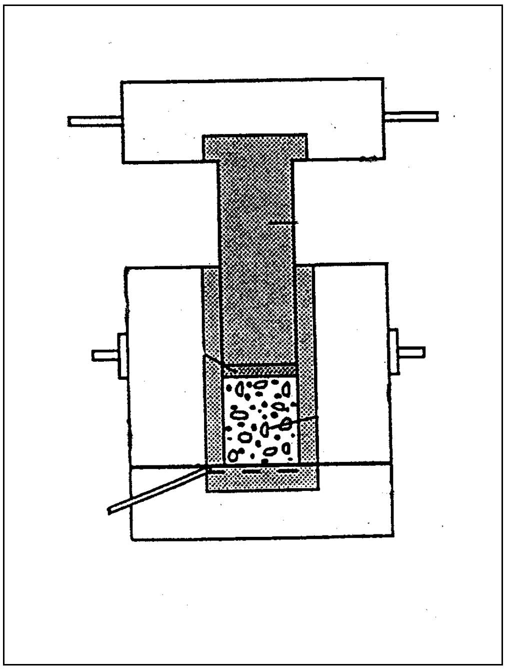

Figure 1. *Schematic outline of the squeezing apparatus (max. pressure 300 t) with a cement sample. Ejector pad and sample container steel 155 CrVMo*

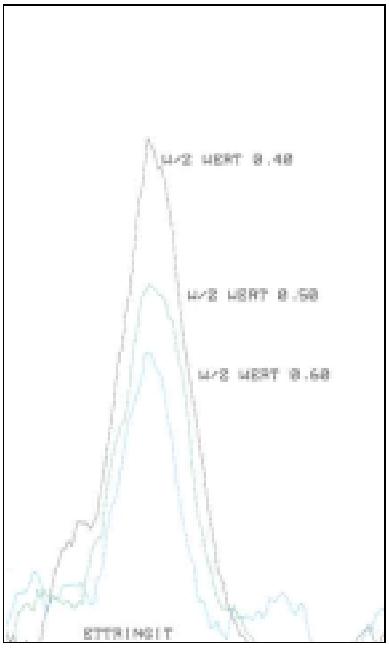

Figure 2. *Detail of X-Ray-Diffraction Spectra (Ettrinigte) for squeezed hardened cement paste (age 28 days) with different w/c-ratios*

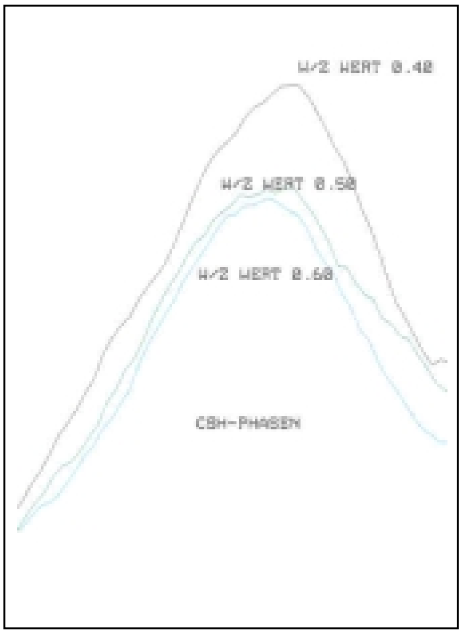

Figure 3. *Detail of X-Ray-Diffraction Spectra (CSH-phases) of squeezed hardened cement paste (age 28 days) with different w/c-ratios*

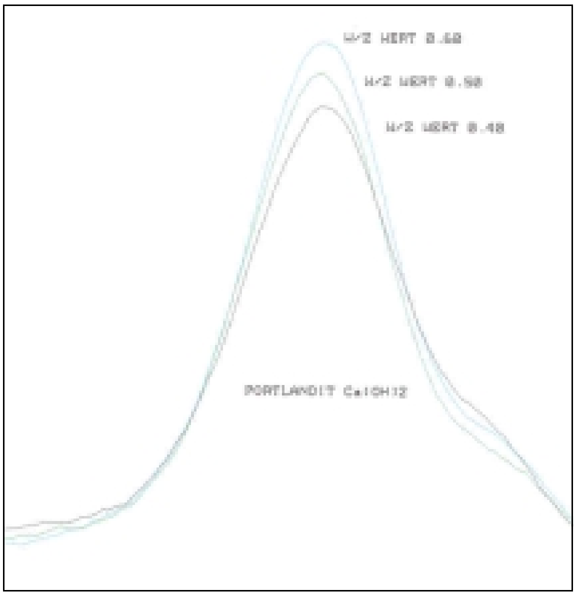

Figure 4. *Detail of X-Ray-Diffraction Spectra (Protlandite) of squeezed hardened cement paste (age 28 days) with different w/c-ratios*

Parallel to DTA and the wetchemical analysis X-Ray-Diffraction of the squeezed cement paste was carried out. Figures 2 to 4 show details of XRD-spectra of the hardened cement pastes with different w/s-ratios (Fig. 2 Ettringite peak; Fig. 3 CSH (calcium silicate hydrate)-phase; Fig. 4 Portlandite). These figures prove that the intensity of the XRD-signals are related to the w/c-ratios of the cement pastes.

4. DISCUSSION

Table 3. *Calculation of the components of pore solution in hardened cement paste with w/s ratio of 0.50 after storing the samples for 28 days at 20 °C air tight*

Mixture Nr.	2
w/c-ratio	0.50
Mass squeezed pore solution in g (measured)	18.588
Mass cement paste after squeezing in g (measured)	309.8
loss on heat of squeezed cement paste in m.-% (measured)	26.53
loss on heat of cement (CEM 32,5 I R) in m.-% (measured)	2.84
Mass cement (minus loss on heat) in cement paste in g (calculated)	227.6
Mass cement used for the admixture in the cement paste in g (calculated)	234.3
Pore solution in g/kg cement (calculated)	79.33
Specific gravity of pore solution g/ml (measured)	1.073
Pore solution in ml per kg cement (calculated)	73.9
Pore solution in g per kg cement (calculated)	73.5

Based on the results shown in Table 1 and 2 it is possible to calculate the amounts of water in the different physical, physicochemical or chemical bounding forms in hardened cement pastes. One example for the method to calculate these basic data for the hydration situation in hardened cement paste is shown in Table 3 and 4 for a cement paste with a w/c-ratio of 0,50.

Based on these results it is possible to balance the total water (pore solution, water of crystallisation) in hardened cement paste. Table 4 gives an example for a hardened cement paste with a w/c-ratio of 0,50.

Table 4. *Balance of the amount of pore solution and water of crystallisation in hardened cement paste. Admixture 2 with w/c- ratio 0.50 after storing the samples for 28 days at 20 °C air tight*
The w/c-ratio of 0,50 give the theoretical value of 333 g H_2O/kg cement paste

Admixture Nr. 2	
w/c-value	0.50
Σ water of crystallisation (hydration water) per 1 kg cement paste in g/kg (DTA-results; see Table 2)	245
Squeezed pore solution in the hardened cement paste in g/kg cement paste (calculated, see Table 3)	74
Σ water of crystallisation (hydration water) + squeezed pore solution in g/kg cement paste	319
Difference from theoretical value (333g H2O/kg cement paste) in g (in %)	14 (1.4 %)

The present results demonstrate, that squeezing is a very good possibility to balance the water distribution in hardened cement pastes. The determination of hydration water (Σ water of crystallisation (hydration water) + squeezed pore solution in g/kg cement paste) has an uncertainty of less than 2 %. This demonstrates that uncertainties from the determination of pore solution could not affect the determination of hydration water by DTA in hardened cement paste after squeezing. Squeezing the pore solution can be used as a basic method to calculate the hydration degree of a hardened cement paste with a w/c-ratio of 0,50.

If the cement pastes are calibrated on the loss on heat status (initial weight minus loss on heat = 100 %) it is possible to compare the DTA results for different compounds of the hardened cement paste with the results obtained by x-ray Diffraction.

In Table 5 all results are related to the loss on heat status so that the contents of different cement phases in hardened cement pastes can be compared.

Table 5. *Contents of water of crystallisation, Portlandite, SO_3 and $CaCO_3$ in different hardened cement pastes with the w/c-ratios 0,60, 0,50 and 0,40 calibrated to the loss on heat status (initial weight minus loss on heat = 100 %).*

Admixture- Nr.	CEM 32,5 I R	1	2	3
w/c-ratio		0.60	0.50	0.40
Σ water of crystallisation (hydration water) for Ettringite/Gypsum and CSH (Calzium-Silikate-Hydrate) M. %	0.15	13.51	20.61	19.16
Portlandite [$Ca(OH)_2$] M.-%	1.48	26.13	18.71	17.23
$CaCO_3$ M.-%	4.80	6.35	5.26	5.53
SO_3 M.-%	2.65	2.62	2.60	2.61

These results shown in Table 5 are comparable with the results of X-Ray-Diffraction (see Fig. 2 to 4). Both methods prove, that the content of portlandite in hardened cement pastes increases with the w/c-ratio, while the content of Ettringite/Gypsum and CSH decrease with increasing w/c-ratios. Under the given conditions the chosen method allows the accurate determination of the amount of Portlandite in hardened cement pastes (age 28 days), resulting from hydration of different cement compounds.

With the complete squeezing of pore solution with high pressure under normal conditions (room temperature; compare results in Table 1 and 4) it is possible to extract all soluble salts including $Ca(OH)_2$ solved in pore solution with out disturbing the establishment of equilibrium (equilibrium concentration) of the salts in pore solution. This procedure should prevent the influence of Ca^{2+} and OH^- in the hydrating solution on the hydration process of C_3A, C_4AF and C_2S in Portland cement [Ramachandran, 1984] during and after the process of separating pore solution.

The results also prove, that lower w/c-ratios lead to higher contents of Ettringite, resulting from an absolute higher quantity of sulphate in the admixture [Locher et al., 1983].

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