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EXTRACTION OF $\text{Ca}(\text{OH})_2$ FROM PORTLAND CEMENT AND $3\text{CaO} \cdot \text{SiO}_2$ PASTES

by V.S. Ramachandran and G.M. Polomark

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SOMMAIRE

On décrit un procédé pour extraire la chaux libre des pâtes mures de ciment portland et de silicate de tricalcium. Cela exige l'exposition de minces disques de pâte à une solution aqueuse de Ca(OH)_2 en faisant en sorte que la concentration de CaO dans la solution reste de l'ordre de 9,5-12 mmole/L pendant toute la période d'extraction. La quantité d'hydroxyde de sodium restant dans le solide est estimée par calorimétrie de balayage différentielle et celle dans la solution par spectrophotométrie d'absorption atomique. L'étude des échantillons extraits au microscope électronique à balayage, au pycnomètre à hélium, par diffraction des rayons X, par porosimétrie au mercure et par thermogravimétrie indique que la méthode d'extraction n'a pas d'influence significative sur la phase C-S-H.

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Extraction of $\text{Ca}(\text{OH})_2$ from Portland Cement and $3\text{CaO} \cdot \text{SiO}_2$ Pastes

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(Paper received 9 March 1982 and accepted 7 October 1982)

A procedure for extracting free lime from mature pastes of Portland cement and tricalcium silicate is described. It involves exposure of thin discs of paste to an aqueous solution of $\text{Ca}(\text{OH})_2$ in such a way that the concentration of the solution remains in the range 9.5–12 mmol CaO dm^{-3} throughout the extraction period. Calcium hydroxide remaining in the solid is estimated by differential scanning calorimetry and that in the extractant is estimated by atomic absorption spectrophotometry. Investigations of the extracted samples by scanning electron microscope, helium pycnometry, X-ray diffraction, mercury porosimetry and thermogravimetry indicate that the extraction procedure has no significant influence on the C-S-H phase.

1. Introduction

In mature paste formed by the hydration of C_3S or Portland cement the predominant phases are calcium silicate hydrate, commonly referred to as C-S-H ($\text{C} = \text{CaO}$, $\text{S} = \text{SiO}_2$, $\text{H} = \text{H}_2\text{O}$), and calcium hydroxide. The C/S ratio of the C-S-H phase is approximately 1.4:1.6¹ but it may change with the physical and chemical characteristics of the unhydrated C_3S or cement, the water/solid ratio at which hydration takes place, temperature, and degree of hydration. Calcium hydroxide is present mainly in the crystalline form; a completely hydrated C_3S contains approximately 40% and hydrated Portland cement contains 20–25%.

Various characteristics of hardened pastes are determined by the nature and amounts of the C-S-H and CH phases and by the pore structure. The relative roles of the C-S-H and CH phases in hardened pastes are not, however, well understood. One approach is to study the characteristics of the hardened paste from which free $\text{Ca}(\text{OH})_2$ has been extracted. When used as an extractant for $\text{Ca}(\text{OH})_2$, water has been shown to attack the C-S-H phase.² Organic solvents can be used instead, but they may leach lime from the C-S-H phase.³

There is need for a technique for extracting $\text{Ca}(\text{OH})_2$ that will have minimal effect on the C-S-H phase. In the equilibria between the hydrous calcium silicates and lime solutions there is a range of concentrations of CaO in solution within which the C/S ratio of the solid stays at approximately 1.4:1.6. Equilibrium curves reported in the literature show some variation. At the Division of Building Research, National Research Council of Canada, a method was devised in which thin discs of hydrated pastes are exposed to a lime solution with a concentration at the lower end of this range. Increase with time in the concentration of CaO in the solution is monitored. Whenever the concentration exceeds a particular value it is decreased by dilution with water so that the pastes always remain within the chosen range of CaO concentration. As an alternative, the amount of free lime in the paste can be estimated and the solid/solution ratio adjusted so that during extraction the concentration of CaO in the solution does not exceed a value of 12 mmol dm^{-3} . Further, the stability of the C-S-H phase can be facilitated by leaving a small amount of free $\text{Ca}(\text{OH})_2$ in the paste.

This paper describes a procedure for extracting $\text{Ca}(\text{OH})_2$ from Portland cement and C_3S pastes.

2. Experimental

2.1. Materials

The sample of tricalcium silicate used in this work had the following composition: CaO , 73.88%; SiO_2 , 26.17%; Al_2O_3 , 0.08%; free CaO (Franke), 0.46%. Mineralogical analysis was as follows: C_3S =99.33%; C_2S =0.00%; C_3A =0.21%. Blaine surface area was $3310 \text{ cm}^2 \text{ g}^{-1}$. The Portland cement, Type I, had the following compound composition: C_3S =46.5%, C_2S =24.6%, C_3A =10.4% and C_4AF =9.3%. Blaine surface area was $3279 \text{ cm}^2 \text{ g}^{-1}$. Calcium hydroxide for calibration purposes was obtained by calcining AnalaR Grade CaCO_3 to 1000°C for 3 h and hydrating the resulting CaO in distilled water. The purity of Ca(OH)_2 was checked by TGA and considered satisfactory for drawing the calibration curve.

2.2. Hardened pastes

Hydration of C_3S and Portland cement was carried out by mixing them with double-distilled water at a water/solid ratio of 0.8 and 0.5, respectively, in a plexiglas tube 12.7 cm long and 3.2 cm diam. Air voids during initial mixing on rollers were prevented by the vacuum method.⁴ After 1 day the samples were removed, placed in sealed glass tubes and hydrated in lime solution. The C_3S sample was hydrated for 5 years and the cement sample for 11 years.

2.3. Analysis

A differential scanning calorimetric cell (DSC), supplied as a module to a Du Pont 990 thermal analysis system, was used for obtaining thermograms from room temperature to 550°C . In each experiment 20 mg of the sample was heated in air at a rate of $10^\circ\text{C min}^{-1}$. For calibration purposes Ca(OH)_2 of known purity was mixed with C_3S in different proportions and endothermal peak areas were plotted against Ca(OH)_2 concentrations; peak areas were determined with a planimeter.

A Cahn balance was used to carry out thermogravimetric analysis; measurements were carried out in a vacuum at a heating rate of $10^\circ\text{C min}^{-1}$.

Microstructural examination was conducted on fractured pieces of the specimens using a Cambridge Stereoscan, Mark 2A. The specimens were given a conductive coating of carbon and gold.

Calcium in solution was estimated using a Perkin-Elmer 403 atomic absorption spectrophotometer. Estimation of CO_2 in a few samples was carried out as follows: carbon dioxide formed by

Figure 1. Amount of lime remaining in C_3S paste at different times of extraction.

the action of sulphuric acid on the substance (in a closed system) was absorbed by a standard $\text{Ba}(\text{OH})_2$ solution. The excess $\text{Ba}(\text{OH})_2$ was titrated against HCl using phenolphthalein as an indicator.

Porosity and pore size distribution of some samples were determined using an Aminco porosimeter capable of intrusion pressure up to 407 MPa.

X-ray examination was carried out with a Debye Scherrer camera. Microdensitometer traces were made from the X-ray films.

2.4. Extraction of $\text{Ca}(\text{OH})_2$

From the cylinders of hydrated C_3S cement thin discs 0.38 mm thick were sliced in ethanol in a dry box purged with N_2 . The sliced discs were dried at 80°C for 3 h in a vacuum and stored over magnesium perchlorate. They were then placed in a wire cage and left in contact with 5 dm^3 of lime solution containing $9.5\text{ mmol CaO dm}^{-3}$. The solution was stirred continuously with a magnetic stirrer. At different extraction times 1 cm^3 of the solution was taken and analysed for Ca by atomic

Figure 2. Amount of lime remaining in cement paste at different times of extraction.

Figure 3. DSC curves of cement paste exposed to different times of extraction.

absorption spectrophotometry. The concentration of CaO in solution did not exceed 12 mmol dm^{-3} . This procedure was continued until the DSC analysis of the solid showed almost no Ca(OH)_2 .

The amount of unextracted lime remaining in the sample of C_3S paste after different periods of extraction is plotted in Figure 1. As all lime was extracted within 12 days, extraction could be terminated between 9 and 12 days. The rate of extraction is very rapid in the early periods because of the ready accessibility of Ca(OH)_2 from the surface of the paste. If a thicker sample were taken, extraction would take longer.

Figure 2 gives the amount of Ca(OH)_2 remaining in a Portland cement paste after different periods of extraction. This paste had contained about 19% Ca(OH)_2 , of which 2% was converted to CaCO_3 . It takes somewhat longer to extract all free Ca(OH)_2 from Portland cement paste. Figure 3 gives the DSC curves for cement pastes subjected to extraction for 15 days. A gradual

Figure 4. Micrographs of unextracted and extracted C_3S pastes (A and C, unextracted; B and D extracted).

decrease in the intensity of the Ca(OH)_2 peak, occurring in the range of 450–475°C, signifies progressive depletion of Ca(OH)_2 . At 15 days about 96% Ca(OH)_2 had been extracted.

3. Discussion

To discover whether the extraction procedure would be satisfactory for preparing C_3S or cement paste that is virtually Ca(OH)_2 -free, further experiments were conducted to establish whether the method has any effect on the matrix of the hardened pastes.

3.1. Scanning electron microscopy

Scanning electron micrographs of extracted and unextracted C_3S paste samples representing two locations and two magnifications are shown in Figure 4. The surface of the unextracted paste indicates practically no cavities whereas the sample from which Ca(OH)_2 was extracted contains cavities of various shapes and sizes. There is no evidence of any other significant change in the matrix.

3.2. Helium pycnometry

The helium flow technique involves the normal pycnometric measurement of the solid volume of a body at a pressure of 2 atmospheres. The rate at which helium penetrates the body immediately following application of pressure provides information about some of its structural features. The helium flow curves (volume as a function of time) for the extracted and unextracted cement pastes are similar,⁵ indicating that extraction of lime does not alter the structure of the C-S-H phase.

Densities of extracted and unextracted paste specimens have also been plotted as a function of water loss from the 11% r.h. condition. The curves of the unextracted and extracted specimens were similar, again indicating no change in the C-S-H structure.

Figure 5. Densitometer tracings of C_3S paste (— C_3S paste, --- extracted C_3S paste).

3.3. X-ray diffraction

Figure 5 shows densitometric curves of C_3S paste with predominant peaks at 0.49, 0.265, 0.192 and 0.179 nm representing crystalline Ca(OH)_2 . A broad peak of low intensity at about 0.31 nm signifies Ca(OH)_2 and C-S-H. The Ca(OH)_2 -free paste reveals no Ca(OH)_2 lines, but the peak at 0.307 nm from the C-S-H phase persists. There is no development of any new phase following removal of Ca(OH)_2 .

3.4. Pore structure

The extraction of Ca(OH)_2 from C_3S and cement pastes should result in an increase in the porosity of the samples (Figure 6). Before extraction C_3S paste has a porosity of 27.1% which increases to 50.5% after extraction. The difference of 23.4% should be explained by the removal of Ca(OH)_2 . By knowing the density of Ca(OH)_2 , the amount of Ca(OH)_2 extracted and the apparent volume of the samples, the volume of extracted Ca(OH)_2 can be computed. This value was 23.2%, which was close to the determined value of 23.4%, suggesting that removal of Ca(OH)_2 does not alter

Figure 6. Mercury porosimetric curves of C_3S paste (--- extracted, — unextracted).

Figure 7. Mercury porosimetric curves of cement paste (--- extracted, — unextracted).

the original pore structure of the paste significantly. The curves also indicate that pores vacated by $\text{Ca}(\text{OH})_2$ were mainly in the size range $0.05\text{--}3\text{ }\mu\text{m}$ in the C_3S paste and that most of the pores occupied by neither CH nor C-S-H were in the range of 0.003 to $0.05\text{ }\mu\text{m}$.

For the cement paste, the extracted sample had a higher porosity and it appeared that most pores vacated by $\text{Ca}(\text{OH})_2$ were also in the size range $0.003\text{--}0.05\text{ }\mu\text{m}$ (Figure 7). There was a 2% difference between calculated and determined values of porosity for Portland cement paste.

3.5. Thermogravimetry

The thermogravimetric curves of C_3S paste and paste from which $\text{Ca}(\text{OH})_2$ has been extracted are shown in Figure 8. The weight loss due to $\text{Ca}(\text{OH})_2$ occurs in the temperature range $350\text{--}450^\circ\text{C}$. The amount of $\text{Ca}(\text{OH})_2$ computed from weight loss corresponds to 36.7%. For the extracted sample, the weight loss in this temperature range was lower. This sample, however, shows a continuous loss of weight throughout the temperature range of the study, indicating that in C_3S or cement paste the thermogravimetric method may overestimate $\text{Ca}(\text{OH})_2$ by 2–3%. This recalculated figure is close to the DSC estimation of 33% $\text{Ca}(\text{OH})_2$.

Figure 8. Thermogravimetric analysis of C_3S paste (--- extracted, — unextracted).

4. Conclusions

In the extraction of $Ca(OH)_2$ from C_3S and Portland cement pastes a lime solution appears to be less detrimental to the C-S-H phase than water or organic solvents. The method, which is based on the equilibrium concentrations of lime with respect to calcium silicate hydrates, was extended to Portland cement pastes because the dominant phase in these pastes is C-S-H. The use of thin samples and avoidance of over-extraction of $Ca(OH)_2$ ensures that the non- $Ca(OH)_2$ phases are not detrimentally affected.

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