DETERMINATION OF MOISTURE CONTENT IN HYDRATING CEMENT PASTE USING THE CALCIUM CARBIDE METHOD

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The calcium carbide method is used for measuring the moisture content in hydrating cement paste which could be considered as a measure of the course of the hydration process. The experimental measurements show that the readings on the acetylene manometer used for calculating the residual moisture content in the material increase with time significantly up to approximately six hours which is remarkably different from the measurements on the most of other materials such as bricks, gypsum, etc., where the final constant readings are achieved already after ten minutes. Two hypotheses for the explanation of this fact are proposed. The first consists in the assumption that calcium carbide reacts not only with free water but also with a part of water already bonded in the cement binder. The decomposition of ettringite in the reaction bottle accompanied by partial loss of bonded water, which becomes available for the reaction with calcium carbide should be the most probable mechanism in this case. The second hypothesis is based on the assumption that the delay in determining the final values of residual moisture content is caused by a slow release of water from cement gel due to the high bonding forces of water to the porous matrix in small gel pores. In any case, the relatively long time necessary for the achievement of final readings makes the application of calcium carbide method for monitoring the hydration process questionable because its main advantage, fast determination of moisture content, cannot be effectively utilized.

INTRODUCTION

Hydration processes of cement in concrete are accompanied by fast incorporation of free water into the cement binder. Monitoring the not incorporated (residual) water content in hydrating concrete mixture can therefore give useful information on the course of hydration starting with a defined content of water in the mixture.

Due to the rapidity of the process, not every common method is suitable for moisture measurements in hydrating concrete. The classical gravimetric treatment consisting in hot air drying at 105 °C cannot be employed because the reaction rates in hydration processes strongly depend on temperature. Vacuum drying at 20 °C is excluded automatically because moisture determination takes at least several days. Application of common electric conductivity methods or capacitive methods at lower frequencies (e.g. [1 - 4]) is questionable due to the high ion content in the hydrating mixture which makes it possible to obtain principally only qualitative data whose quantification is doubtful. The well established neutron absorption (e.g. [5, 6]) or NMR (e.g. [7-9]) methods cannot distinguish between chemically bonded and free water.

Therefore, we have basically two possibilities how to determine the moisture content. The first is water removal from the sample by washing out by a fluid which is soluble in water and nonreactive with cement, such as ethanol with ethylether [10] or isopropylalcohol

with ethylether, and subsequent gravimetric analysis. Another possibility is the application of well known fast and reliable methods such as microwave absorption (e.g. [11, 12]) or g-ray attenuation (e.g. [13]) techniques.

In the case we are interested only in laboratory measurements and do not require a nondestructive technique, the calcium carbide method could be employed in determining the moisture content in hydrating cement mixtures. The method is known for more than 40 years and some improvements were patented in 1989 [14, 15]. Currently is it commonly used for fast moisture field tests in soils. Its application for building materials is described for instance in [16, 17]. Portable devices working on the principle of calcium carbide method are usually presented as "Speedy Moisture Testers", examples of such devices are those of Mastrad, Soiltest or Riedel de Haën.

EXPERIMENTAL PART

The cement paste was prepared using Portland cement ENV 197-1 CEM I 42.5 R (Králův Dvůr, CZ) and water. The water to cement ratio $w = 0.3$ was chosen in our experiments. For moisture measurements, the CM device based on the calcium carbide method was employed (Janser Ltd., Brno, CZ).

The calcium carbide method (see [16] for details) is a direct procedure for the determination of the moisture content where the present water is initially

chemically converted and afterwards the moisture content is detected by a quantitative registration of the gaseous product. The method is based on decomposition of calcium carbide by water according to the exothermal chemical reaction

$$CaC_2 + 2\ H_2O \rightarrow Ca(OH)_2 + C_2H_2\ .$$
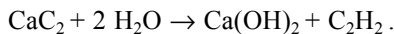
During this reaction, acetylene gas is produced whose pressure in a steel bottle can be measured. Knowing the acetylene pressure, the temperature and the volume of the reaction vessel, the amount of water necessary for the reaction can be calculated assuming the ideal gas behavior. In order to achieve better accuracy of moisture determination, producer of every CM device gives a pressure-moisture conversion table determined empirically which takes into account for instance the change of reaction volume by different quantities of the test material, deviations from the ideal gas law, etc. Example of such an empirical conversion table between the acetylene pressure and water content can be found in [16].

Practical measurements are performed in the following way. First, sampling is done using hammer and chisel, and the sample is crushed in an agate dish. In our measurements, we always used approximately 5 g of cement paste. Then, several steel balls, an ampoule with calcium carbide powder and the crushed sample are put consecutively into the pressure bottle, and the bottle is closed by the manometer head. The ampoule is broken by intense shaking of the bottle, and the sample is well mixed with the calcium carbide by continuous shaking for 2-5 minutes. After 10 minutes, the first pressure reading on the manometer is done. A better accuracy can be achieved by keeping the system in isothermal conditions. In our experiments, we used water bath with temperature $(25 \pm 1)\ ^oC$ where the bottle was placed.

RESULTS AND DISCUSSION

Figure 1 shows the residual moisture content in the hydrating cement paste ($w = 0.3$, i.e., 23.08 wt.% of water) in dependence on the duration of the original hydration reaction for the first 3 days, determined by the calcium carbide method. The readings of acetylene pressure were always done after 10 minutes. The irregularities on the moisture vs. time curve are slightly higher than it would correspond to the precision of the manometer given by the producer (5 % for our range of readings) but they are still in a reasonable range taking into account possible additional errors due to weighing, interpolation in the pressure-moisture table and empirical character of this conversion table.

In our experimental measurements, we additionally analyzed the reliability of measured data obtained by the standard treatment recommended by the producer of the CM device. We have left the sample in the pressure bottle for a longer time, up to 40 hours, and recorded the
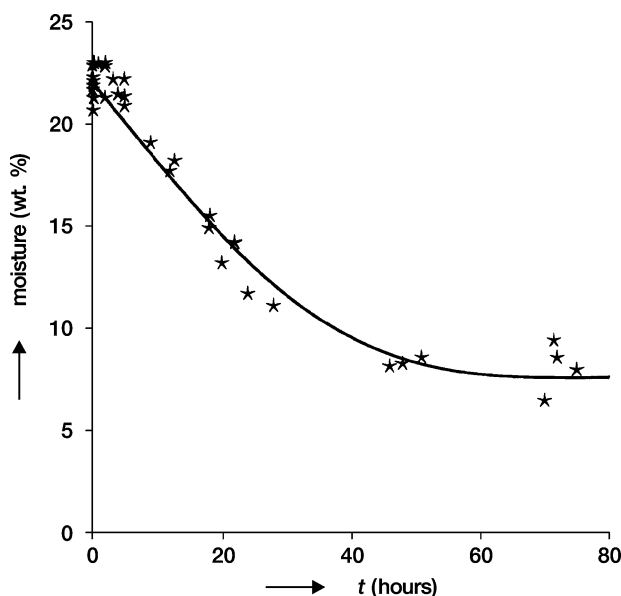

Figure 1. Dependence of residual moisture content in hydrating cement paste (w = 0.3, i.e. 23.08% kg/kg of water) on the duration of the original hydration reaction, beginning with the moment of adding water to cement. The pressure values used for the calculation of residual moisture content were measured always 10 minutes after initiation of acetylene formation.
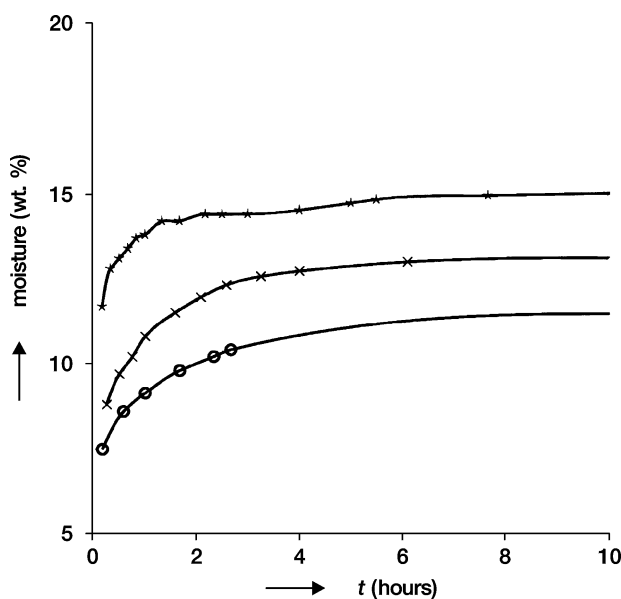

Figure 2. The time dependence of moisture data calculated from the continuous pressure readings on the manometer. The parameter in the key is the duration of the original hydration reaction between the moment of adding water to cement and the time of initiation of acetylene formation.
* - 24 hours, × - 72 hours, ○ - 197 hours.

data from the manometer. Figure 2 shows the time dependence of data measured by the manometer and recalculated to moisture content, the parameter in the key being the time between the moment of adding water to cement and the time of initiation of acetylene formation, i.e. the duration of the original hydration reaction. Apparently, the measured moisture content increases relatively fast up to 2 - 4 hours, and then the increase is much slower so that after 6 hours the changes of the measured moisture are practically negligible.

We have done test measurements on several other, more stable materials. We analyzed the behavior of bricks, for instance, and did not see any changes of measured moisture content after 10 minutes. Also, we investigated some materials containing crystalline bound water, among them anhydrite and gypsum. Again, we did not observe any changes in the recorded acetylene pressure for longer times than 10 minutes.

We have two possible hypotheses for the observed increase of measured moisture content in hydrating cement paste.

The first hypothesis consists in the assumption that the increase should not be awarded to free water, and that the remainder of calcium carbide began to react with water already bonded in the cement binder.

In this case, the most probable source of additional water for the reaction with calcium carbide would be in our opinion the decomposition of ettringite, an important crystalline sulphoaluminate hydrate of Portland cement. Its formation largely influences many application properties of concretes made from Portland cement such as setting, strength, deformation, durability, etc. [18, 19]. The concerned calcium sulphoaluminate $3CaO.Al_2O_3.3CaSO_4.31H_2O$ is formed during the hydration of cement by the reaction of gypsum with tricalcium aluminate, and it is also produced by the action of calciumsulphate on calcium aluminate solutions. It is also formed during the destructive attack of sulphate solutions on cement mortars and concretes.

Ettringite formed in cementitious materials can be partially or fully destroyed if material is heated at elevated temperatures (above 70 °C) and that ettringite can reform gradually in the material after a period of time delay when the material is destroyed at room temperature in a moist atmosphere (hence the term delayed ettringite formation). The 31 moles of water are retained until a vapour pressure below 0.7 mm at 20 °C is reached and it is reduced to 26 H_2O and 18 H_2O on drying at room temperature over anhydrous $CaCl_2$ and solid NaOH. Thermal dehydration leaves $7 - 8$ H_2O at 105-110 °C, $4 - 6$ H_2O at 145 °C and $2 - 3$ H_2O at 200 °C. The DTA thermogram of $3CaO.Al_2O_3.CaSO_4.$.$31H_2O$ is characterised by an endothermal decomposition at low temperatures with peak temperatures ranging from 110 °C to 180 °C.

The reaction of calcium carbide with water is very fast and highly exothermal. In the industrial production of acetylene from calcium carbide, it is even

recommended to add periodically cold water to keep temperature in the reaction vessel within the range of 60 - 70 °C because otherwise it could increase too much similarly as by reaction of burnt lime with water.

Therefore, we can say that the hypothesis on ettringite as a source of additional water for the reaction with calcium carbide sounds logical. On the slightly elevated temperatures and low water vapor pressure in the pressure bottle ettringite can loose a substantial part of its bonded water which is at that moment available for the reaction with the remainder of the calcium carbide.

The second hypothesis explaining the observed delay in achieving the final constant pressure reading is based on the assumption that the transport of water from the cement gel to the calcium carbide is so slow (in other words the strength of bonds of water to the gel is so high) that it takes these several hours.. We suppose that the rate of reaction between the calcium carbide and water in the bottle primarily depends on the availability of free water in this case. The main criterion of drying efficiency, namely the ratio of saturated vapor pressure to the actual vapor pressure in the drying chamber [20], is valid for the condition in the reaction bottle as well as in any other drying environment. The presence of calcium carbide keeps the vapor pressure inside the bottle at very low but still finite values which places limitations to the maximum bond strength which can be overcome. Therefore, also this hypothesis sounds logical because the gel pores have very small diameters, and the bond strength of water to gel is high which results in slower water removal from the pores.

CONCLUSIONS

The application of calcium carbide method for monitoring the hydration processes in fresh cement paste was found to be questionable because its main advantage, fast determination of moisture content, cannot be effectively utilized due to the relatively long time necessary for the achievement of final readings of the acetylene pressure in the reaction bottle necessary for the determination of the moisture content.

Acknowledgements

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URČENÍ OBSAHU VLHKOSTI V HYDRATUJÍCÍ CEMENTOVÉ PASTĚ POMOCÍ KARBIDOVÉ METODY

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Metoda založená na rozkladu karbidu vápníku je použita pro monitorování obsahu vody v hydratující cementové pastě, což může sloužit jako měřítko průběhu hydratačních reakcí. Experimentální výsledky ukazují, že hodnoty tlaku, naměřené na manometru, které se používají k výpočtu obsahu vlhkosti v materiálu, rostou s časem až do přibližně šesti hodin po zahájení produkce acetylenu, což je dosti odlišné od měření na většině jiných materiálů, jako je např. cihla nebo sádra, kde jsou konečné hodnoty tlaku dosaženy již po 10 minutách. V tomto článku navrhujeme dvě možné hypotézy pro vysvětlení tohoto faktu. První spočívá v předpokladu, že karbid vápníku reaguje nejen s volnou vodou, ale také s částí vody již zabudované v cementovém gelu. Nejpravděpodobnějším mechanismem by v tomto případě byla dekompozice ettringitu v reakční nádobě, doprovázená částečnou ztrátou vázané vody, která tak může jako volná vstoupit do reakce se zbylým karbidem vápníku. Druhá hypotéza je založena na předpokladu, že relativně dlouhá doba pro stanovení konečné hodnoty tlaku je způsobena pomalým uvolňováním vody z cementového gelu v důsledku existence dosti velkých vazebných sil mezi vodou a pevnou matricí v malých gelových pórech. V každém případě relativně dlouhá doba, potřebná ke stanovení konečné hodnoty vlhkosti v materiálu poněkud zpochybňuje použití této metody k monitorování hydratačních procesů cementu v betonu, protože metoda tím ztrácí svou hlavní komparativní výhodu, jíž je rychlost stanovení obsahu vlhkosti.