

INFLUENCE OF ALKALIES ON THE HYDRATION OF CEMENT

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Abstract

The setting of cement is closely related to the composition of mixing water solution. Rapidly dissolved alkalis, especially the alkali sulfates of the clinker, increase the pH-value and lower the calcium hydroxide concentration of the solution. This fact seems to increase the hydration velocity of the C_3A , particularly during the first minutes of hydration, before the dormant period stops further reactions. C_3A -rich cements with a lack of gypsum show rapid setting caused by formation of aluminate hydrates. With gypsum in excess rapid setting by formation of large amounts of ettringite may occur. The increase of the temperature in fresh concrete mixes has a similar effect on setting as an increase of OH^- -concentration caused by alkalis diluted from the cements. Rapid setting can be avoided by exact balancing of calcium sulfate contents by different provisions in the plant and by decreasing the temperature of fresh concrete.

1. Introduction

Consistency and workability of concrete depend on its composition. They are essentially influenced by the properties of the cement used, the cement content and the grading of aggregate. Additives used, time of mixing and temperature of fresh concrete as well as the time during which concrete is transported from the mixing plant to the building site and the continuous mechanical motions of the concrete during the transit may also be of practical importance.

In order to find out whether these factors are of major influence on practical application of cement, extensive studies have been carried out at the "Forschungsinstitut der Zementindustrie" since a longer time. The investigations at first were mainly focused on the effects of cement composition and manufacturing conditions on the setting of cement^{1,2,3}. More recent studies are concerned with

the effects of additives, temperature of fresh concrete and mechanical motions on the consistency of concrete. Further objectives of research are to examine whether the composition of the mixing water solution may effect the setting of cement.

2. Present state of investigations

The setting behaviour of the cement influences mainly the workability of the concrete and for this reason certain requirements have been standardized in the cement-producing countries. Chemical reactions between the cement constituents and the mixing water decisively influence the setting behaviour. The reaction products developing thereby bridge the water-filled space between the cement particles and by this build up a structure which gradually grows stronger with time. This formation of a structure lowers the consistency of cement paste, mortar or concrete.

In the first reactions which take place immediately after the addition of the mixing water nearly exclusively the tricalcium aluminate of the cement clinker and the calcium sulfate added to regulate the setting participate. Normally the reaction product formed is ettringite ($3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot3\text{CaSO}_4\cdot32\text{H}_2\text{O}$). In the case of insufficient calcium sulfate monosulfate ($3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{CaSO}_4\cdot12\text{H}_2\text{O}$) and tetracalcium aluminate hydrate ($4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot x\text{H}_2\text{O}$) are developed. Additionally, the alkali sulfate content of cement clinker, the alkalies in the hydrated portion of the C_3A and calcium hydroxide, formed by hydration of the free CaO or by an initial surface reaction of the calcium silicates are dissolved. The initial reactions which in most cases only last a few minutes are followed by a dormant period of 2 to 6 hours.

According to the older literature on this subject^{4,5,6,7)} the dormant period as well as set retardation were explained to result from the effect of gypsum. The interruption of the hydration reactions shall be caused by an ettringite cover on the surface of the aluminates. The reactions would start again as soon as the gypsum in solution has been consumed.

More recent investigations³⁾, however, have shown that the dormant period is not based on the effect of gypsum. The dormant period occurs with gypsum containing cements as well as with sulfate-free clinkers. The examinations also showed that the setting of cement already starts during the dormant period. In the presence of sufficiently high amounts of calcium sulfate 3 to 6 % by weight of ettringite normally are formed from the C₃A which reacted at the beginning of the hydration within the first minutes. The ettringite appears on the surface of the cement particles mostly in the form of fine crystals, smaller than 1 μm. Electron microscopic investigations showed that later on the ettringite grows by recrystallization or coarsening crystallization and that the ettringite crystals consequently begin to bridge the pore space. The recrystallization and the formation of a structure during the dormant period leads to the setting of the cement.

The investigations have indicated so far that the course of setting of a cement is determined by the type and the amount of hydration products which are formed during the first 5 minutes. Decisive for this are the influencing factors given in table 1.

Fig. 1: Influences on the setting of cement

| | |
|---|---|
| <p>1. <u>COMPOSITION OF CEMENT</u></p> <p>C₃A CONTENT</p> <p>TOTAL ALKALI CONTENT</p> <p>ALKALI SULFATE CONTENT</p> <p>TOTAL SULFATE CONTENT</p> <p>CALCIUM SULFATES: CaSO₄·2H₂O CaSO₄·1/2H₂O CaSO₄</p> | <p>2. <u>MANUFACTURING OF CEMENT</u></p> <p>COOLING RATE OF CLINKER</p> <p>STORAGE OF CLINKER</p> <p>CEMENT TEMPERATURE DURING GRINDING</p> <p>WATER INJECTION INTO MILL</p> <p>FINENESS OF CEMENT</p> <p>STORAGE</p> |
| <p>ADDITIVES</p> | |

Above all the amount and the reactivity of the C_3A and of the various calcium sulfates is of importance. The reactivity is mainly induced by the cement composition and the conditions during the production of the cement, such as for instance the velocity of clinker cooling, the temperature and the relative humidity during grinding and storage of the cement.

The reactivity of the clinker with the mixing water also determines the composition of the solution, that is how much alkalies, calcium hydroxide and sulfate the solution contains and which pH-value emerges. The literature gives differing data^{8,9)} on this subject. But these data allow no conclusions on the reason for the appearing differences. The composition of the solution is not only significant for the setting, but also for the development of strength¹⁰⁾, the alkali-aggregate reaction^{11,12)} and the reaction of pozzolans.

3. Cements

To examine the influence of the composition of the solution on the setting of the cement, several cements have been selected which differed in their contents of tricalcium aluminate, alkalies and calcium sulfate as gypsum ($CaSO_4 \cdot 2H_2O$) or semi-hydrate ($CaSO_4 \cdot 1/2H_2O$). In figure 2 the most important properties of the used cements are presented. Some of the cements were mixed from plant-made clinkers with calcium sulfates and others have been plant-made cements. The C_3A content calculated according to Bogue ranged from 10.9 to 13.4 % by weight and the total alkali content from 0.06 to 1.60 % by weight Na_2O -equivalent. The amount of alkalies in the clinker bound as sulfate ranged from 6 to 100 %. The laboratory mixed cements contained 1.5 to 5.0 % by weight of sulfate as gypsum or as semi-hydrate.

Fig. 2: Composition of cements

| | C_3A (BOGUE) [W-%] | $\sum Na_2O + 0.658 K_2O$ [W-%] | DEGREE OF SULFATISATION [%] | TOTAL SULFATE IN CEMENT [W-%] | SPEC. SURFACE [CM^2/G] BLAINE |
|--------------------------|-------------------------|------------------------------------|-----------------------------------|-------------------------------------|--------------------------------------|
| <u>LABORATORY</u> | | | | | |
| <u>MIXED CEMENTS</u> | | | | | |
| FROM CLINKER | | | | | |
| AW | 11.2 | 0.06 | 75 | | 4 000 |
| DM 100 | 13.4 | 0.83 | 100 | 1.5 - 5.0 | ± 100 |
| WO 2 | 11.9 | 0.94 | 6 | | |
| <u>TECHNICAL CEMENTS</u> | | | | | |
| PZ AG/68 | 12.0 | 0.80 | 31 | 2.6 | APPR. |
| PZ LA/68 | 12.8 | 1.60 | 45 | 3.1 | 3000 - 3500 |
| PZ B/350 | 12.9 | 0.31 | 14 | 3.4 | |
| PZ S/350 | 10.9 | 1.02 | 61 | 2.8 | |

4. Test results

4.1 Setting of cement

The change in the consistency of the laboratory-mixed cements of clinker "AW" and "DM 100", which is related to the setting, was measured with a penetrometer. The amount of the appearing ettringite, syngenite and secondary gypsum was determined with a DSC-calorimeter (Differential-Scanning Calorimeter) after 1 hour of hydration. The results of some of these investigations are illustrated in fig. 3 and 4. In the diagrams on the left the course of setting and on the right the new formed phases have been plotted versus the total sulfate content of the cements.

The sulfate was added to the cements as gypsum (continuous line) or as semi-hydrate (dashed line).

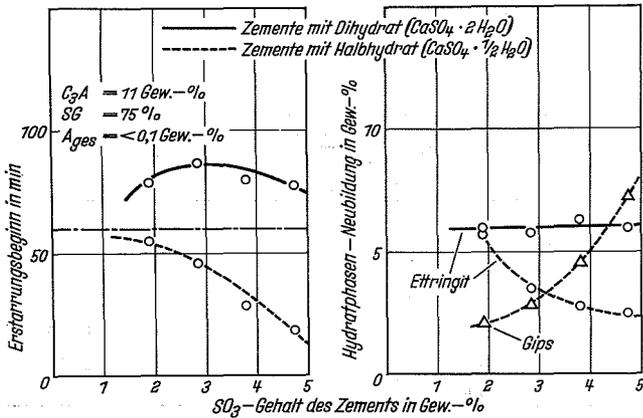


Fig. 3: Cements made from clinker "AW" - Setting and formation of hydrated phases.

In fig. 3 the results from cements "AW" which were rich in C_3A and poor in alkali are presented. Summarized the result is that the gypsum-containing cements set approximately after more than 70 minutes. With 3% by weight of SO_3 the setting time shows a flat maximum. During the first hydration which takes place before the dormant period begins, a nearly constant amount of approximately 6% by weight of ettringite independent of the amount of added sulfate was formed. Aluminate hydrates have not been estimated. If the cements contain semi-hydrate instead of gypsum how it may occur in the mill with grinding temperatures exceeding $80^\circ C$ or after a prolonged silo storage, gypsum is precipitated from the solution and rapid setting takes place. Because of the formation of this secondary gypsum the quantity of ettringite decreases.

Fig. 4 demonstrates the setting of cements made from clinker "DM 100". They mainly differ from the cements "AW" in a higher C_3A -content of 13% by weight and a medium-high total alkali content of 0.8% by weight Na_2O -equivalent. Similar to the cements "AW" the C_3A of the cements "DM 100" does not contain alkalis. Whereas the cements "AW" had a low total content, the alkalis of cements "DM 100" are completely bound as sulfate.

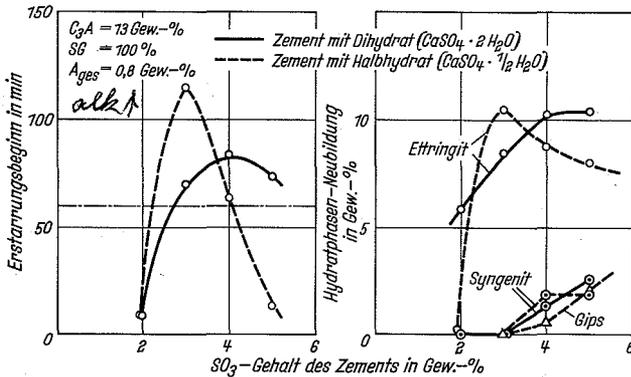


Fig. 4: Cements made from clinker "DM" - Setting and formation of hydrated phases

The gypsum-containing cements "DM 100" show a sharper maximum in the setting time at approximately 4 % by weight of SO₃. Cements poorer in gypsum content set more rapidly, since more aluminate hydrate and monosulfate are formed which build up a bridging structure. With a higher content of gypsum the cements change their consistency because of a formation of more than 10 % by weight of ettringite. "DM 100"-cements with semi-hydrate set in a similar way. But with high sulfate contents the excessive formation of ettringite is accompanied by a precipitation of secondary gypsum which together lead to rapid setting. Rapid setting caused by ettringite is especially favoured by such cements in which the C₃A has a still higher reactivity because of large amounts of alkalies in solid solution. Such a behaviour would show for example cements of the type "WO 2" according to fig. 1.

With the exception of the alkali content the cements "AW" and "DM 100" differ only slightly and yet both cements set in different ways. However, since the alkalies in the cements "DM 100" are exclusively present as alkali sulfate, it may be expected that they will go into solution and thereby affect their composition immediately after addition of the mixing water.

4.2 Composition of the solution

The composition of the solution was determined after 1 h of hydration, that is during the dormant period of the cement. On the left of fig. 5 the obtained alkali contents and on the right the determined calcium oxide contents of the solution have been plotted. The measurements led to high alkali contents of 50 to 60 mmol/l in the solution of the cements "DM 100", whereas with the low-alkali cements "AW" virtually alkali-free solutions have been found.

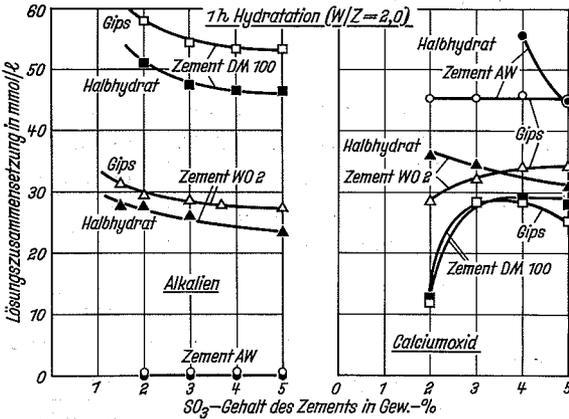


Fig. 5: Composition of the solution after 1 h of hydration

On the other hand the solution of the low-alkali cements "AW" contained fairly large amounts of calcium oxide, whereas the solution of the alkali-rich cements "DM 100" showed a altogether lower CaO-content, which increased with added calcium sulfate. The measurements did not show in the single case whether calcium hydroxide or calcium sulfate were dissolved. But according to the fact, that the pH-value of the high-alkali solutions was higher than that of low-alkali but Ca-rich solutions, the conclusion may be drawn that higher OH⁻ or alkali hydroxide contents in

solution lead to correspondingly lower amounts of calcium dissolved as calcium hydroxide according to the solution equilibrium of N. Fratini¹³⁾. The remaining calcium seems therefore to be dissolved as calcium sulfate, whose solubility - according to literature¹⁴⁾ - is said to be increased in solutions rich in alkali hydroxide.

Former investigations of the equilibrium in pure solutions of calcium hydroxide and alkali hydroxide^{15,16,17)} led to similar conclusions. The result of recent investigations in which alkali sulfates were added to alkali and calcium hydroxide containing solutions is shown in fig. 6.

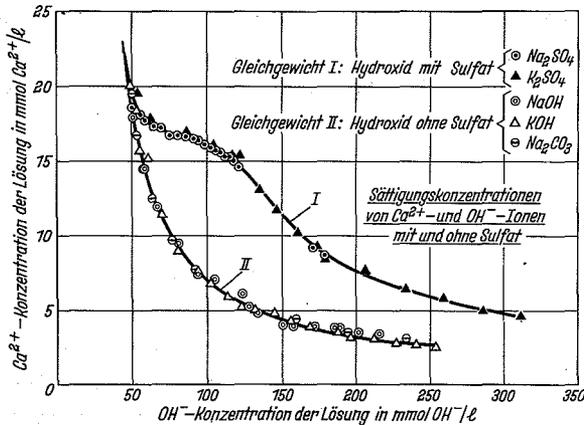


Fig. 6: Concentration of Ca^{2+} - and OH^- -Ions in saturated solutions with and without sulfate.

Curve II demonstrates that according to the mass action law the solubility of calcium hydroxide decreases with increasing OH^- -concentration added as NaOH or KOH. In the presence of sulfate (curve I), however, the Ca^{2+} -concentration of the solution decreases slower at higher OH^- -concentrations. The added alkali sulfate seems to react with the calcium hydroxide whereby alkali hydroxide besides gypsum and syngenite are formed. According to

DSC-analysis of the solid phase the gypsum remains in solution almost completely, apparently favoured by alkali hydroxide up to concentrations of approximately 100 mmol/l. From this result may be concluded that an increased calcium solubility in alkali and sulfate containing solutions is due to an increased gypsum solubility but not so much to a supersaturation of calcium hydroxide.

This result is of interest for the hydration of cement. In general the sulfate is almost completely consumed after 1 d by reaction with C_3A to ettringite and in that case the pore solution of a hardened cement paste is mainly influenced by the alkali and the calcium hydroxide content according to the equilibrium of curve II in fig. 6. The equilibrium between alkalis, calcium and sulfate may therefore be of importance only in the earliest stage of hydration in which the cement sets. This is suggested by tests performed with 3 plant made cements. The changes in the composition of the liquid phase were determined in relation to the time of hydration.

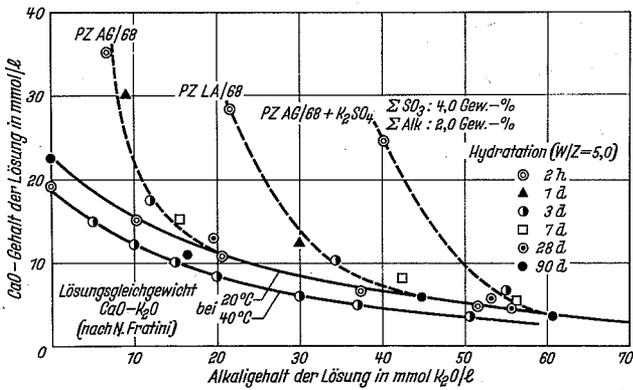


Fig. 7: Influence of time and temperature on the equilibrium between calcium and alkalis in the solution of cement pastes.

The results in fig. 7 demonstrate that all solutions contained after 2 hours of hydration large amounts of CaO which far exceed the CaO/K₂O-solution equilibrium. The high sulfate content found simultaneously in the same solution leads to the conclusion that the increased Ca²⁺-solubility is mainly caused by gypsum. After subtracting the amount of CaO equalling the analyzed SO₃ content the measuring points almost exactly fall to the equilibrium curve. On the other hand the Ca²⁺-solubility was reduced by prolonged hydration and the measuring points were the more approached to the equilibrium curve as the sulfate of the solution was consumed by reaction with the aluminate of the clinker. With prolonged hydration the points furthermore shift to higher alkali contents. That is due to the fact that with advancing hydration mainly of the C₃A still more alkalis are liberated, shifting the equilibrium of the solution correspondingly. Finally, the diagramm shows as a result of the literature¹³⁾ that the solubility of calcium hydroxide is reduced by rising temperatures too.

5. Conclusions

The obtained results lead to the following conclusions: Evidently the time during which a cement sets is closely related to the composition of the mixing water solution. This has been exemplified by the different behaviour of 2 cements which differed only in their content of alkali sulfate. Although both clinkers contained the relatively inactive cubic aluminate, more C₃A, however, reacted during the first minutes in the presence of higher alkali contents and with higher pH-values in the solution. If there was a lack of gypsum, mainly aluminate hydrate was formed resulting in rapid a) setting. With a too big supply of sulfate excessively large amounts of ettringite developed also leading to rapid setting.^{a)} It seems to be that with higher amounts of ettringite already a relatively small increase in the crystal size by coarsening crystallization is sufficient to bridge the water-filled pore space and thereby build up a structure.

Higher amounts of alkalies in the clinker, particularly of alkali sulfates, which are rapidly dissolved, lower the calcium hydroxide concentration of the solution, thereby increasing the hydration velocity of the C_3A prior to the dormant period. The possibility of rapid setting therefore always exists, if such cements are not perfectly balanced in their sulfate content. Similar results were found by P.K.Metha^{18,19)}, when he investigated the properties of high early strength cements. In that case, however, the accelerating effect of alkalies is desirable. It has been pointed out by W. Lieber²⁰⁾ too that the reaction of the C_3A can be speeded up substantially with high OH^- -concentrations in the mixing water solution. These results lead to the conclusion that the operation characteristics of additives and their application in concrete technology could by this way more effectively be tested.

According to these investigations an increase in temperature of the fresh concrete has much the same effect as an increase in OH^- -concentration caused by alkalies.

In view of the workability of concrete it can be deduced from the results that it is above all important to retard the hydration of the C_3A sufficiently within the first 5 minutes. This can be done in normal cases, for instance, by well regulated cement properties, by decreasing the temperatures of fresh concrete and by reduced motions in transit.

References

- [1] Sprung, S.: Einfluß der Mühlenatmosphäre auf das Erstarren und die Festigkeit von Zement.
Zement-Kalk-Gips 27 (1974) H. 5, S. 259/267
- [2] Locher, F.W. und S. Sprung: Einflüsse auf das Erstarren von Zement.
Tonind.-Ztg. 98 (1974) H. 10, S. 273/276
- [3] Locher, F.W., W. Richartz und S. Sprung: Erstarren von Zement. Teil I: Reaktion und Gefügeentwicklung.
(to be published in Zement-Kalk-Gips)
- [4] Lerch, W.: The influence of gypsum on the hydration and properties of Portland Cement pastes.
Proc. Amer. Soc. Test. Mat. 46 (1946) S. 1252/1292
- [5] Steinour, H.H.: The setting of portland cement. A review of theory, performance and control.
PCA Bull. 98, 1958
- [6] Schwiete, H.E., U. Ludwig und P. Jäger: Untersuchungen im System $3\text{CaO}\cdot\text{Al}_2\text{O}_3\text{-CaSO}_4\text{-CaO-H}_2\text{O}$.
Zement-Kalk-Gips 17 (1964) H. 6, S. 229/236
- [7] Ludwig, U.: Über die Einflußnahme verschiedener Sulfate auf das Erstarren und Erhärten von Zementen.
Zement-Kalk-Gips 21 (1968) S. 81/90; S. 109/119, S. 175/180
- [8] Greenberg, S.A. und V.S. Mehra: Discussion Proc. 4th Int. Symp. on the Chem. of Cement, Washington 1960.
US GPO Washington 1962, S. 378/384
- [9] Longuet, P., L. Burglen und A. Zelwer: La Phase Liquide du Ciment Hydrate.
Rev. des Matériaux 676 (1973) S. 35/41

- [10] Billhardt, H.W.: Über den Einfluß der Alkalien und des Sulfats auf das Erhärten von Zement (Vortragsreferat). Zement-Kalk-Gips 24 (1971) H. 2, S. 91
- [11] Diamond, S.: A review of alkali-silica reaction and expansion mechanism. 1. Alkalies in cements and in concrete pore solutions. Cement and Concrete Research 5 (1975) S. 329/346
- [12] Diamond, S.: Pore solutions and alkali-aggregate attack. Symposium on Alkali-Aggregate-Reaction - Preventive Measures, Reykjavik 1975, S. 165/179
- [13] Fratini, N.: Ricerche sulla calce di idrolisi nelle paste di cemento, Teil 1. Ann. Chim. 39 (1949) S. 41/49
- [14] Golovatyj, R : l.c. Linke, W.F.: Solubilities - Inorganic and Metal-Organic Compound. Vol. I, 4th Edition, D. van Nostrand Comp. Inc. Princeton, N.J., Toronto, London, New York 1958, S. 673
- [15] Hein, H.: Die chemische Zusammensetzung der flüssigen Phase im Portlandzement - Normenbrei. Tonindustrie-Ztg. 56 (1932) H. 50, S. 632/634
- [16] Hansen, W.C. und F.E. Pressler: Solubility of $\text{Ca}(\text{OH})_2$ and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ in dilute alkali solutions. Ind. Eng. Chem. 39 (1947) H. 10, S. 1280/1282
- [17] Lawrence, C.D.: Changes in composition of the aqueous phase during hydration of cement pastes and suspensions. Highway Res. Bd. Spec. Rep. 90, S. 378/391, Washington D.C. 1966
-
- [18] Mehta, P.K.: Effect of lime on Hydration of Pastes containing Gypsum and Calcium Aluminates or Calcium Sulfoaluminate. J. Amer. Ceram. Soc. 56 (1973) Nr. 6, S. 315/319

- [19] Metha, P.K.: Scanning electron micrographic studies of Ettringite formation.
Cem. and Concr. Res. 6 (1976) S. 169/182
- [20] Lieber, W.: Wirkung anorganischer Zusätze auf das Erstarren und Erhärten von Portlandzement.
Zement-Kalk-Gips 26 (1973) H. 2, S. 75/79

The number of persons receiving health services in the United States in 1970 was estimated to be 1.1 billion, or 1.1 billion persons.

Approximately 1.1 billion persons received health services in the United States in 1970. This figure is based on data from the National Health Survey, which is a representative sample of the United States population.