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**Chemistry of Hydration of
Portland Cement**

By

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PORTLAND CEMENT

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Paper IV-3. Chemistry of Hydration of Portland Cement*

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Synopsis

The results of recent investigations have provided evidence for the presence of several aluminates and sulfoaluminates in hardened portland cement pastes. For some of these, little evidence for their presence had been obtained previously. Some indications have also been obtained as to the nature of the iron-bearing hydrates.

Information as to the water contents of the various hydrates formed can be obtained for certain drying conditions by statistical analysis of nonevaporable water data as a function of the composition parameters of the cement.

Along with X-ray and statistical results, free-lime data obtained by X-ray quantitative analysis can be combined with the oxide composition of a cement so that an estimated composition of a hydrated paste of that cement can be calculated. Most of our concepts about the rate of hydration of cement in pastes or concrete have been based on the rate of increase of strength, heat of hydration, and fixed water. Inferences concerning the rates of hydration of the individual components have been made from considerations of rate of change in heat of hydration, and in related physical and chemical properties of the hydration products. Direct measurement of these latter rates show that the inferences are not always true.

Recent data are presented on the heats of hydration of the different ASTM types of cements at ages from 3 days to 13 years at 0.40, 0.60, and 0.80 water-cement ratio. The significant influence of water-cement ratio on the rate of hydration of cement can be interpreted in terms of physical parameters of the hydrating paste. The effect of temperatures in the range of 4.4 to 110 °C on the rate of hydration of cement can be expressed by the Arrhenius equation.

As a first approximation, the intrinsic hydration characteristics of cements can be expressed in terms of the compositions of the cements, by least squares analyses of heat evolution and chemically combined water. Secondary changes of the hydrated calcium aluminate are indicated. Some aspects of the roles of gypsum, alkalis, glass content, and ignition loss of the original cement on heat evolution are considered.

Résumé

Les résultats de recherches récentes ont fourni des preuves de la présence de plusieurs aluminates et sulfoaluminates dans les pâtes de ciment portland durcies. Pour certaines d'entre elles, cette présence n'était jusqu'à présent que peu évidente. Des indications ont été également obtenues quant à la nature des hydrates ferriques.

Pour certaines conditions de séchage, on peut obtenir des informations concernant les teneurs en eau des différents hydrates formés, au moyen d'une analyse statistique des données de l'eau non-évaporable en fonction des paramètres de la composition du ciment.

Avec les résultats des rayons X et statistiques, les données de chaux libre obtenues par analyse quantitative des rayons X peuvent être combinées aux compositions oxydes d'un ciment de façon telle que l'on peut calculer une composition estimée d'une pâte hydratée de ce ciment. La plupart de nos concepts sur la vitesse d'hydratation du ciment dans les pâtes ou dans le béton ont été basés sur la vitesse de l'augmentation de la résistance, la chaleur d'hydratation, et l'eau fixée. Des déductions concernant les vitesses d'hydratation des composants individuels ont été tirées à partir de considérations sur la vitesse de changement dans la chaleur d'hydratation, et dans les propriétés physiques et chimiques, s'y rapportant, des produits d'hydratation. La mesure directe de ces dernières vitesses indique que les déductions ne sont pas toujours vraies.

Présentation est faite de données récentes sur les chaleurs d'hydratation des différents types de ciments selon les normes ASTM à des âges allant de 3 jours à 13 ans à un rapport eau-ciment de 0.40, 0.60, et 0.80. L'influence significative du rapport eau-ciment sur la vitesse d'hydratation du ciment peut être interprétée en fonction de paramètres physiques de la pâte qui s'hydrate. L'équation Arrhenius peut exprimer l'effet des températures allant de 4.4 à 110 °C sur la vitesse d'hydratation du ciment.

Comme première approximation, on peut exprimer les caractéristiques intrinsèques d'hydratation des ciments en fonction des compositions des ciments, par analyses aux écarts moindres quadratiques de l'évolution de la chaleur et de l'eau chimiquement combinée. Les changements secondaires de l'aluminate de calcium hydraté sont indiqués. Certains aspects du rôle du gypse, des alcalis, de la teneur en verre, et de la perte au feu du ciment original sur l'évolution de la chaleur sont considérés.

Zusammenfassung

Die Ergebnisse der neuesten Forschung haben gezeigt, daß mehrere Aluminate und Sulfoaluminat in gehärteten Portlandzementmassen vorhanden sind. Einige dieser sind früher nicht identifiziert worden, und man hat auch schon etwas über den Charakter der eisenhaltigen Hydrate ausfindig machen können.

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Man kann den Wassergehalt der verschiedenen Hydrate für gewisse Trocknungsbedingungen mit Hilfe einer statistischen Analyse, bei der das nichtverdampfungsfähige Wasser als Funktion der Zusammensetzungsparameter des Zementes ausgedrückt wird, bestimmen.

Durch eine Kombination der Röntgenbeugungsmessungen, der statistischen Resultate und der Werte für freien Kalk, wie sie durch quantitative Röntgenstrukturbestimmungen erhalten werden, und auch der Oxydzusammensetzungen kann man eine schätzungsweise Zusammensetzung der hydratisierten Paste eines solchen Zements errechnen. Die meisten unserer Ideen über die Hydratationsgeschwindigkeit des Zements in Pasten oder in Beton wurden durch ein Studium der Geschwindigkeit der Festigkeitszunahmen, der Hydratationswärme und des gebundenen Wassers erhalten. Die Hydratationsgeschwindigkeiten der einzelnen Verbindungen wurden von Betrachtungen, die sich mit den Hydratationswärmeveränderungen befassen, und auch mit verwandten physikalischen und chemischen Eigenschaften der Hydratationsprodukte, inter- und extrapoliert. Aber direkte Messungen dieser Veränderungen haben gezeigt, daß solche Inter- und Extrapolierungen manchmal zu Irrtümern leiten können.

Die letzten Messungen der Hydratationswärmen der verschiedenen ASTM-Typen der Zemente, die zwischen 3 Tagen und 13 Jahren alt waren, und mit Wasser/Zementverhältnissen 0,40, 0,60 und 0,80 angemacht worden waren, werden erörtert. Der bedeutungsvolle Einfluß des Wasser/Zementverhältnisses auf die Hydratationsgeschwindigkeit des Zements kann mit Hilfe der physikalischen Parameter der hydratisierenden Masse ausgedrückt werden. Der Temperatureffekt kann zwischen 4,4 und 110 °C für die Zementhydratationsgeschwindigkeit vermittelt der Arrhenius Gleichung ausgedrückt werden.

In erster Annäherung kann die körpereigene Hydratationskenngröße als Funktion der Zementzusammensetzungen ausgedrückt werden, wenn man die Methode der kleinsten Quadrate auf die Wärmeentwicklung und das chemisch gebundene Wasser anwendet. Das hydratisierte Kalziumaluminat zeigt sekundäre Veränderungen, die besprochen werden. Die Einflüsse des Gipses, der Alkalien, des Glasgehalts und des Gewichtsverlusts bei Rotglut des ursprünglichen Zements auf die Wärmeentwicklung werden besprochen.

Foreword

The difficulties encountered in the study of the chemistry of hydration of portland cement have been discussed many times, and are known only too well by all who work in this field. In spite of these difficulties progress is being made, even though the path to understanding may meander a bit.

The past work on the pure compounds found in cement has provided a foundation for the study of the hydration of cement itself, and the constant improvement in experimental techniques has made it possible to begin the study of hydration products in hardened pastes of portland cement. The chemistry of hydration of cement in hardened pastes has been emphasized in this review; perhaps it has been overemphasized. Many of the conclusions presented here are based on good evidence; others are admittedly tentative, but they are included in order to establish a basis for further discussion.

The paper is divided into three main sections: In the first section the composition of the hydration products of portland cement is discussed. In the second section the rate of hydration of cement, and the rate of hydration of each of the four major phases in cement is reviewed. In the third section the most recent information on the energetics of hydration is presented.

I. The Stoichiometry of the Hydration of Portland Cement

D. L. Kantro and L. E. Copeland

Status of the Problem as of 1952

By 1952, it had been established [1]¹ that the silica-bearing phases in portland cement react with water to form calcium silicate hydrates of two possible types, designated CSH(I) and C₂SH(II). These hydrates were observed and discussed by Taylor [2], many of his observations being in good agreement with earlier work. The similarity between CSH(I) and the natural mineral

tobermorite was pointed out by Claringbull and Hey [3] and discussed in detail by Bernal [1]. The C₂SH(II), while not in the tobermorite composition range, showed many similar properties. The X-ray diffraction diagrams of these two calcium silicate hydrates are so much alike that to distinguish between them is quite difficult. Hence it could not be ascertained at the time of the 1952 London Symposium whether either or both of these calcium silicate hydrates occurred in hydrated portland cement.

¹ Figures in brackets indicate the literature references at the end of this paper.

It had been surmised by a number of investigators that the 3:2 calcium silicate hydrate of the tobermorite series, that is, CSH(I), was the more likely product formed in the hydration of portland cements. That this is the case arises from the fact that it is this composition of solid which is in equilibrium with a saturated $\text{Ca}(\text{OH})_2$ solution [4]. If $\text{C}_2\text{SH}(\text{II})$ were to form, it would presumably be a metastable product. As far back as 1938, the 3:2 calcium silicate hydrate was considered to be the product of the hydration of the silicate phases of portland cement. For example, Bessey [5] arrived at this conclusion on the basis of free calcium hydroxide determinations on hydrated pastes.

Steinour, in his 1952 review [4], points out that the most probable reaction product of tricalcium aluminate, at least initially, is the tetracalcium aluminate hydrate, C_4AH_{13} . The cubic calcium aluminate, C_3AH_6 , if it forms at all, forms only slowly. He points out also that the hexagonal hydrate that forms has at times been reported as an intergrowth of a dicalcium aluminate hydrate and the tetracalcium aluminate hydrate, such that the overall $\text{CaO}:\text{Al}_2\text{O}_3$ ratio of the phase is 3.0.

In their discussion of Steinour's paper, Nurse and Taylor [6] cite evidence from X-ray diffraction for the presence of C_4AH_{13} . They also cite X-ray evidence for the cubic C_3AH_6 , but inasmuch as their observations were on a 22-year-old specimen, they concluded that the cubic hydrate was the result of a slow conversion of the tetracalcium aluminate hydrate.

There have been a number of investigations of calcium aluminoferrites and ferrites, and calcium ferrite hydrates have been prepared which are analogous to some of the calcium aluminate hydrates. The calcium ferrite hydrates form solid solutions with the corresponding calcium aluminate hydrates, but little experimental data

had been found that these solid solutions occur in hydrated portland cement pastes.

One problem that has received a great amount of attention for many years from cement chemists is that of the sulfoaluminates, and, to a lesser extent, sulfoferrites. These complex compounds arise from the interaction of the appropriate component of clinker with gypsum, added as a retarder. In general, either of two calcium sulfoaluminates may form, these being the calcium monosulfoaluminate, $\text{C}_2\text{A}\cdot\text{CaSO}_4\cdot 12\text{H}_2\text{O}$, and ettringite, $\text{C}_3\text{A}\cdot 3\text{CaSO}_4\cdot 31\text{H}_2\text{O}$. These compounds are also known as the low sulfate and high sulfate sulfoaluminate, respectively. As was pointed out by Steinour [4], equilibrium studies such as those made by Jones [7] indicate that ettringite forms during the early stages of reaction, but as further hydration of C_2A takes place, the low sulfate sulfoaluminate will form at the expense of the ettringite. Once all of the SO_3 has been used for this reaction, further hydration of aluminate should lead to a solid solution of tetracalcium aluminate hydrate and calcium monosulfoaluminate. However, at the time of Steinour's review, no direct observation of either sulfoaluminate in cement pastes had been made, and any conclusions drawn were strictly by inference. The ettringite observed in cracks and pores in old concrete or hardened paste was considered to be formed by secondary reaction due to exposure. More recently similar observations were made on old mortar exposed to air [8].

The calcium sulfoferrites corresponding to the low-sulfate and high-sulfate sulfoaluminates have been prepared individually [9]. The analogy of the sulfoferrites to the sulfoaluminates both in constitution and behavior has been pointed out. However, no identification of either of the sulfoferrites as a reaction product of cement, gypsum, and water under ordinary conditions of hydration could be made.

Methods of Investigation of the Chemical Reactions Occurring During the Hydration of Portland Cement

The qualitative and quantitative information concerning the hydration processes of portland cement have been obtained in several different ways. In general, however, regardless of what technique is being used, the cement paste may be treated in either of two ways. The observations may be made on the paste as a whole or the paste may be broken down into fractions such that one or more of these fractions may be enriched with respect to certain of the hydration products.

Nurse and Taylor [6] describe a method whereby the paste is ground to a powder and then ground in a suitable liquid such that a suspension of finest particles is formed. The suspension is removed from the coarse fraction and centrifuged to recover the fine fraction.

Differences in specific gravity of various constituents have also been used to effect separation.

Taylor [10] separated several fractions from finely ground pastes by centrifuging the material in bromoform and bromoform-benzene mixtures. Turriziani [11] used a sedimentation apparatus in which the suspending agent was amyl alcohol. Several fractions of different finenesses were obtained and division of these into subfractions by the specific gravity technique using bromoform-benzene mixtures was then performed.

The separation methods have certain difficulties associated with them. It has not yet been possible to separate a fraction consisting of a single hydration product, nor has it been possible to separate a fraction which contained all of a given substance that occurs in the paste, e.g., if a given fraction is shown to be enriched with respect to the iron-bearing component, it still will not contain all of the iron-bearing phases in the original

paste. Finally, there is the distinct possibility that the products of hydration may be altered by the separation process. Nurse and Taylor found C_3AH_6 in some of their fractions, but attach little importance to the result since the sample was heated at one stage of the procedure.

Perhaps the most fruitful investigations made of hydrated cement pastes, either whole or divided, are those using X-ray diffraction techniques. Most of the X-ray examinations of cement pastes made up to the present time have been by the Debye-Scherrer film technique. However, the recent development of the diffractometer now permits greater resolution and reveals important details heretofore unknown. It was with apparatus of this type that Kantro, Copeland, and Anderson [12] examined a group of well-hydrated portland cement pastes of various compositions. Although portions of these pastes were ground and dried, no treatment was given them to cause any unknown phase alteration. Fully hydrated pastes were used so that clinker lines would not interfere with the lines of the various hydrates. The hydrated pastes were examined both in saturated condition and in dried condition. The saturated specimens were small rectangular slices removed from the centers of the paste cylinders and polished smooth. The surfaces obtained contained no holes due to air bubbles inasmuch as the pastes were prepared by a vacuum-mixing technique [13] so that no air was entrained. Provisions were made to keep the specimen saturated during the entire X-ray observation. The remainder of the paste was ground to pass a 200-mesh sieve and dried either over $Mg(ClO_4)_2 \cdot 2-4H_2O$ or over ice at $-78^\circ C$ (see below). These dried powders were packed in small sample holders and their diffraction patterns observed in the usual manner. Some dry powder specimens were brought to equilibrium at other relative humidities prior to X-ray examination. This was accomplished by placing the sample in a desiccator over an appropriate saturated salt solution, evacuating the desiccator, and allowing the sample to stand under these conditions for at least 2 weeks.

One of the difficulties encountered by many investigators attempting to identify the hydration products of portland cement by X-ray diffraction techniques is the alteration or decomposition of certain of the hydration products as the result of drying.

Lines of some substances disappear and others shift to new positions. In view of this type of behavior, observations of both wet and dry samples produce more useful information than either type of observation alone. The assignment of a diffraction line to a particular material is often complicated by the presence of a second substance having a line in the same vicinity. However, when the water content of the paste is changed, such that some of the lines may shift while others do not, the identification of a particular hydrate in portland cement paste may be made not only

on the basis of the presence of lines at certain d -spacings, but also on the basis of the shifts the lines have when the paste is wetted or dried. Likewise, the lack of a line shift serves as a useful identifying feature in some cases.

Thermogravimetric and differential thermal analysis techniques have been applied to hydrated portland cement pastes. Taylor [10] used thermogravimetric analysis to show the relationship of the weight loss-temperature curve of a portland cement paste to those of various substances which may be hydration products. However, no definite conclusions may be drawn from the cement paste data, although they do indicate the type of result to be expected.

Recently Turriziani [11] used differential thermal analysis (DTA) in an investigation of the hydration products of portland cement. This method, however, like thermogravimetric analysis, in its present state of development suffers from certain shortcomings. Primary among these is that a number of possible cement hydration products have endotherms so close to the same position that, as Turriziani points out, "... the characterization of the individual components of the mixture is practically impossible." However, by observing samples under reproducible conditions, one can often derive information from the relative amplitudes of certain peaks.

Until recently, most of the investigations carried out with the electron microscope have been limited to the study of hydration products formed in a large excess of water. Such studies are subject to the "difficulties in verifying the indications relative to cement paste" mentioned by Steinour [4]. Surface replica techniques are now being used to study the structure of hardened pastes, and methods of sample preparation are being developed that may permit one to study the substances produced when cement hydrates as a paste. Selected area electron diffraction in conjunction with electron microscopy promises to be a most useful tool. Its greatest disadvantage is the inability to control the orientation of the extremely small crystallites found. Eventually electron diffraction patterns of crystals with known compositions will provide the information necessary to make certain the identification of the products of hydration of cement.

Although electron-optical investigations of the stoichiometry of portland cement hydration fall within the realm of this discussion, they have, for the most part, been omitted, inasmuch as the entire field of electron-optical investigations in cement chemistry is discussed elsewhere in this symposium.

Chemical analysis has and always will provide a great deal of necessary information in the study of cement hydration products. One of the techniques of chemical analysis widely used is the determination of free calcium hydroxide. The quantitative analysis for free calcium hydroxide by means of X-rays [14] provides an excellent means for determining the amount of crystalline

calcium hydroxide present in a given paste. If amorphous calcium hydroxide is also present [15], needless to say, it is not detected by the method.

All free calcium hydroxide, both crystalline and amorphous, may be determined by solvent extraction techniques. The Franke method [16] using a mixture of isobutyl alcohol and ethyl acetoacetate as the extraction solvent has been modified recently [17, 18] so that the total calcium hydroxide extracted may be corrected for the amount of calcium oxide removed from other substances in the mixture, provided this decomposition has proceeded slowly relative to the rate of solution of free calcium hydroxide. If the decomposition is rapid, however, no such correction can be made, and it is impossible to distinguish between extractable and free calcium hydroxide by this technique alone.

It therefore is quite advantageous to compare results of X-ray and solvent extraction calcium hydroxide determinations in order to obtain useful information about the hydrated cement paste system. Some results obtained by this method will be discussed in a later section.

The interpretation of the data obtained by the methods described above in quantitative or semi-quantitative terms requires that other chemical data be available. Among these are the oxide composition of the original cement, the compound

composition of the original cement and the bound water content of the hydrated paste.

The oxide analyses may be obtained by conventional analytical techniques. The potential compound composition of the cement may then be calculated according to the method of Bogue [19]. The determination of the actual composition of the cement may be carried out by means of X-ray quantitative analysis [20, 21]. This again, like the X-ray free lime determination, is an internal standard method.

The bound water content or nonevaporable water content of hydrated cement paste is a somewhat arbitrary value, depending upon the equilibrium water vapor pressure to which the material was dried. Although many methods of drying have been devised in the past only two will be considered in the ensuing discussions and these will be described here. The two methods differ mainly in the desiccant used, and hence in the equilibrium vapor pressure. One of the desiccants is a mixture of magnesium perchlorate dihydrate and tetrahydrate, which produces an equilibrium vapor pressure of 8μ . The other is ice at the temperature of dry ice having an equilibrium vapor pressure of $\frac{1}{2} \mu$. The method of vacuum drying specimens to the $\frac{1}{2} \mu$ level has been described in detail by Copeland and Hayes [22].

The Hydration Products of Portland Cement

The Calcium Silicate Hydrate

The results obtained from patterns of both wet and dry cement pastes [12] indicate that a calcium silicate hydrate of the tobermorite type is present, in agreement with the results reported by Taylor [10]. Only three diffraction maxima are observed for this substance. Bernal, Jeffery, and Taylor [23] report only two lines for the products of hydration of C_3S at room temperature. These were at 3.07 and 1.83 Å. More recently, Brunauer, Copeland, and Bragg [24] reported lines at 3.03, 2.82, and 1.83 Å from the products of the hydration of C_3S as paste at room temperature. It is possible that the 2.82 Å line was missed in the older work because it is a peak superimposed on the broad high angle shoulder of the 3.03 Å line, and as a result, would be difficultly detectable by a Debye-Scherrer technique. Brunauer, Kantro, and Copeland [15] have found that the calcium silicate hydrate produced by the hydration of C_3S as well as that by C_2S shows the same three diffraction lines.

The X-ray diffraction patterns of hydrated portland cement pastes have certain characteristics in common with those of hydrated C_3S and C_2S . The same three lines ascribable to calcium silicate hydrate in the pastes of the pure silicate compounds also appear in cement paste patterns. The characteristics of these lines in cement paste patterns are much the same as in the calcium

silicate paste pattern. There is a broad hump with a maximum in the vicinity of 3.05 Å. This peak is quite asymmetric, just as in the cases of C_3S and C_2S , falling off relatively sharply on the low angle side and much more gradually on the high angle side. In the wet slab patterns, the principal calcite line, at 3.03 Å [25], is superimposed on this peak.

The line found at 2.82 Å in calcium silicate hydrate patterns appears shifted to 2.78 Å in cement paste patterns. This shift is due to the presence of lines from other hydration products at about the same spacing. Among the substances contributing to the 2.78 Å peak is ettringite, with a line at 2.77 Å [26]. This line, however, would not be present in dry powder patterns. Although the ettringite pattern disappears when the sample is dried, the 2.78 Å line does not shift back to 2.82 Å. The low sulfate sulfoaluminate has a line in the vicinity of 2.78 Å [27, 28, 29]. Thus, the persistence, on drying, of the 2.78 Å line in substances showing no low sulfate sulfoaluminate, but only ettringite, as well as in substances showing the simultaneous presence of both indicates that sulfoaluminates are not solely responsible for the shift.

The 2.78 Å line in cement pastes appears to be somewhat stronger than that of the 2.82 Å line in pastes of hydrated calcium silicates. The shape is also somewhat different and is that shape to be expected if a line from a well-crystallized hydrate

were superimposed upon the 2.82 Å tobermorite line.

The 1.82 Å tobermorite line is easily distinguishable. The line appearing here is far too strong to be accounted for as the low sulfate sulfoaluminate line found by Midgley [27, 28] at 1.82 Å, while Fratini, Schippa, and Turriziani [29] do not report a low sulfate sulfoaluminate line at this spacing. No known hydration product other than tobermorite can give a line strong enough to account for the 1.82 Å spacing observed.

It can be seen from the above discussion that the same calcium silicate hydrate lines appearing in patterns of hydrated pastes of C_3S and C_2S are found in the patterns of hydrated portland cement pastes. Although these lines tend to characterize this hydrate as a tobermorite type, they constitute a set of data too meager in themselves to give any information as to the composition of this phase.

There are indications from other techniques as well that the calcium silicate hydrate in portland cement pastes is of the tobermorite type, e.g., the thermogravimetric curves of Taylor [10] and the differential thermal data of a number of investigators, most recent among these being Turriziani [11]. Finally, Gaze and Robertson [30] have identified tobermorite crystals as the product of hydration of a foamed mixture of portland cement and asbestos, using an electron microscope. The presence of tobermorite in this latter example is not conclusive that it is the product of ordinary paste hydration, however.

The calcium silicate hydrate which forms in portland cement pastes probably contains small amounts of impurities, primarily alumina. It was shown by Kalousek [31] that aluminum can be substituted for silicon in the tobermorite lattice without the substance losing its original identity. Compositions containing as much as 4 to 5 percent Al_2O_3 were prepared hydrothermally. A similar situation may exist in portland cement pastes during hydration at room temperature. Other substances such as alkali may also enter into the silicate structure [32].

The Calcium Sulfoaluminates

In the preceding paragraphs, several references were made concerning the presence of either the low sulfate calcium sulfoaluminate, the high sulfate calcium sulfoaluminate, or both. X-ray diffraction lines of both substances have been observed in hydrated pastes, sometimes separately and sometimes simultaneously. Table 1 lists the X-ray diffraction d -spacings observed with wet slabs of several cement pastes. Table 2 lists d -spacings observed with dried ground cement pastes.

The two strongest ettringite lines, at 9.73 and 5.61 Å [26] occur in positions not interfered with by other possible products of cement hydration. It can be seen in table 1 that whenever the 9.73 Å line appears in a hydrated cement, the 5.61 Å line also appears. In most cement pastes where they

appear, these lines are weak and the other ettringite lines are proportionately weaker so as to be obscured by normal background variation. However, in those patterns where the 9.73 Å line is more intense, some of the weaker lines such as 4.69 and 3.48 Å can be distinguished. The rather strong line occurring at 3.88 Å is somewhat obscured by a calcite line. However, as this calcite line is weak relative to the principal calcite line, at 3.03 Å, the 3.88 Å line found in all cement paste patterns showing 9.73 and 5.61 Å lines is easily seen to be too strong to be accounted for only as calcite.

As can be seen from table 1, the ettringite lines are found in pastes which have been cured for long periods of time. Thus the data for 10-year-old pastes made from cements of various compositions indicate the presence of a significant quantity of ettringite, except for those pastes made from cements high in C_3A . However, in pastes of one high C_3A cement, 15754, samples of which have been prepared under a variety of conditions, no ettringite is found except in the youngest paste observed, one which was hydrated for only 6 months. Thus it would appear that this cement behaves in the manner described by Taylor [10], in that ettringite forms at early ages, and then disappears. Taylor suggested that the disappearance of ettringite may be due to the formation of the low sulfate sulfoaluminate, which then dissolved in the C_4AH_{13} phase to form a solid solution.

On the other hand, ettringite has been observed in some cements, such as those mentioned above, even after long periods of curing. This type of behavior is in agreement with that observed by Turriziani [11], who found this material in pastes made from four different cement compositions, and hydrated at two different water-cement ratios, at ages from 7 days to 6 yr.

Considerably less success has been had in years past in identifying the low sulfate sulfoaluminate in portland cement pastes by X-ray diffraction techniques. Turriziani [11] was unable to find evidence for monosulfoaluminate in any of his specimens over the whole range of compositions, water-cement ratios, and times investigated. He concluded that if this material does form, it does so only at a very slow rate. Diffraction patterns for the compound $C_3A \cdot CaSO_4 \cdot 12H_2O$ have been reported by Midgley [27, 28] and Fratini, Schippa, and Turriziani [29]. The results are in reasonably good agreement. The principal diffraction peaks for this material are at 8.9 and 4.45 Å. The 8.9 Å line has been observed in certain of the wet slab patterns, the data for which are given in table 1. The 4.45 Å line appears in every one of these as well, but in addition, in patterns in which the 8.9 Å line does not appear. As will be seen later, this arises from the fact that a strong line from another phase also appears at 4.4 Å. The other lines of the calcium monosulfoaluminate are either too weak to be detectable in view of the difficulty distinguishable 8.9 Å line, or else other substances have lines appearing in the same locations, such

TABLE 1. X-ray d-spacings—hydrated cement wet slab and rewetted sample data

Specimen	C-88	C-54	C-87	C-75	C-75 *	C-66-K	C-66-O	C-61-C	C-33-1	C-33-1 *	C-31-1	C-32-1
Cement.....	15754	15754	15754	15754	15754	15754	15754	LTS-17	15622	15622	15497	15669B
Type.....	I	I	I	I	I	I	I	I	II	II	III	IV
Nominal W/C.....	.40	.55	.40	.65	.65	.70	.57	.70	.60	.60	.60	.60
Age.....	11 yr	11 yr	7 yr	7 yr	7 yr	11 mo	6 mo	1 yr	10 yr	10 yr	10 yr	10 yr
Spacings, A.....		8.9		8.9	9.0	9.0	9.7	9.8	9.8	9.8	9.7	9.8
	7.8	7.8	7.8	7.7	7.8	7.8	8.7	8.6	7.8	7.8	8.3	7.8
	5.09	5.06	5.09	5.09	(b)	5.09	5.66	5.68	5.64	5.66	5.64	5.64
	4.94	4.92	4.93	4.93	4.93	4.94	4.92	4.94	4.93	4.94	4.92	4.92
	4.41	4.38	4.43	4.39	4.40	4.41	4.39	4.41	4.39	4.40	4.41	4.20
	4.27	4.27	4.27	4.28	4.28	4.27	4.27	4.27	4.26	4.26	4.26	4.20
	4.00	4.00	4.03	4.02	4.02	4.02	4.02	4.02	4.04	4.04	4.02	4.02
	3.88	3.86	3.88	3.87	3.86	3.88	3.88	3.88	3.88	3.88	3.88	3.88
	3.79	3.78	3.77	3.77	3.77	3.78	3.81	3.81	3.81	3.81	3.81	3.81
				3.67	3.67				3.67	3.67	3.69	3.69
						3.50	3.50	3.50	3.48	3.48	3.49	3.49
	3.35	3.43	3.34	3.45	3.42	3.45	3.45	3.45	3.38	3.38	3.35	3.35
	3.31	3.30	3.31	3.31	3.32	3.32	3.32	3.31	3.35	3.32	3.31	3.36
	3.12	3.11	3.12	3.12	3.12	3.12	3.12	3.12	3.12	3.12	3.12	3.26
	3.05	3.04	3.05	3.05	3.04	3.05	3.05	3.05	3.05	3.05	3.05	3.05
	2.88	2.88	2.88	2.88	2.89	2.89	2.88	2.89	2.88	2.88	2.89	2.89
	2.78	2.77	2.78	2.84	2.78	2.83	2.79	2.78	2.78	2.78	2.77	2.84
	2.63	2.63	2.63	2.63	2.63	2.69	2.69	2.67	2.67	2.69	2.70	2.78
	2.60	2.58	2.59	2.59	2.58	2.63	2.63	2.63	2.63	2.63	2.63	2.63
	2.53	2.52	2.54	2.53	2.54	2.69	2.69	2.67	2.67	2.67	2.66	2.66
	2.50	2.50	2.50	2.49	2.49	2.54	2.54	2.54	2.54	2.53	2.53	2.53
	2.47	2.45	2.46	2.47	2.46	2.49	2.49	2.51	2.51	2.50	2.50	2.51
	2.43	2.43	2.43	2.43	2.42	2.46	2.46	2.46	2.46	2.45	2.45	2.45
	2.37	2.37	2.37	2.36	2.36	2.43	2.43	2.44	2.44	2.43	2.43	2.41
		2.31	2.31			2.36	2.37	2.37	2.35	2.35	2.36	2.36
	2.29	2.29	2.29	2.29	2.29	2.29	2.29	2.30	2.29	2.29	2.29	2.29
	2.27	2.26	2.27	2.27	2.26	2.27	2.26	2.27	2.27	2.27	2.26	2.26
	2.14	2.19	2.19	2.19	2.20	2.20	2.20	2.20	2.21	2.21	2.21	2.21
	2.10	2.10	2.10	2.10	2.10	2.14	2.14	2.14	2.15	2.15	2.14	2.16
	2.07	2.06	2.06	2.07	2.07	2.11	2.10	2.10	2.09	2.10	2.10	2.10
	2.01	2.01	2.02	2.01	2.01	2.07	2.07	2.04	2.06	2.06	2.06	2.06
	1.96	1.96	1.97	2.01	2.01	2.01	2.02	2.01	2.01	2.01	2.01	2.01
	1.932	1.929	1.931	1.931	1.930	1.96	1.96	1.96	1.96	1.96	1.96	1.97
	1.912	1.912	1.912	1.912	1.930	1.932	1.930	1.931	1.930	1.931	1.930	1.932
	1.881	1.875	1.879	1.879	1.875	1.912	1.912	1.912	1.912	1.912	1.912	1.912
	1.826	1.819	1.824	1.824	1.823	1.879	1.881	1.879	1.879	1.879	1.879	1.879
	1.799	1.796	1.799	1.799	1.798	1.823	1.823	1.823	1.824	1.823	1.823	1.823
	1.722	1.714	1.723	1.719	1.717	1.799	1.798	1.798	1.797	1.798	1.797	1.801
	1.690	1.688	1.689	1.690	1.688	1.723	1.723	1.723	1.720	1.720	1.717	1.717
	1.660	1.658	1.660	1.660	1.658	1.689	1.688	1.689	1.689	1.689	1.688	1.689
	1.639	1.635	1.638	1.638	1.638	1.662	1.662	1.662	1.662	1.662	1.662	1.665
			1.609			1.652	1.652	1.651	1.657	1.656	1.654	1.654
						1.635	1.638	1.639	1.636	1.638	1.638	1.634
						1.607	1.607					

* Shoulder on strong peak. Exact d-spacing not certain.
 b Badly obscured by strong peak. Spacing cannot be estimated.

* Dried sample, rewetted in a saturated atmosphere.

that assignment of the diffraction maximum to a particular substance would be questionable.

However, the low sulfate sulfoaluminate lines do not behave in the same way as ettringite, when the material is dried. Instead, the basal reflections shift to lower d-spacings, while the other lines show no significant change. Roberts [33] points out that upon drying over anhydrous CaCl₂, the low sulfate sulfoaluminate basal spacing contracts from 8.9 to 8.2 A. When this material is dried in CO₂-free air at 115° or *in vacuo* at room temperature to the half-micron level, the 8.9 A line, assigned 001 by Fratini, Schippa, and Turriziani [29], contracts to 8.2 A, and the line at 4.45 A, assigned 002, contracts to 4.1 A [34]. The 8.2 A line appears in the patterns of those pastes for which the wet slab pattern showed the 8.9 A line. In the past, the 8.2 A line has been attributed to the tetracalcium aluminate hydrate [10], but the fact that it appears only in patterns of material which, when dry, shows the low sulfate

sulfoaluminate line, indicates that it is this substance which is responsible for the line. Likewise, the 4.15 A line in dried powder patterns appears only when the 8.2 A line does. That the 4.4 A line does not disappear in dry powder patterns is due to the fact that another material, not affected by drying, contributes to it.

The lines of low sulfate sulfoaluminate appearing in dry powder patterns are strong and sharp, indicating that a significant amount of the material is present in the paste. This is true even for those pastes whose wet slab patterns gave low sulfate sulfoaluminate lines which were very weak. The weakness of the lines in wet pastes is due to the effect of carbonation.

Dried specimens of several of the pastes included in tables 1 and 2 were brought to equilibrium with various relative humidities. No significant changes were observed at humidities below 28 percent. However, in patterns of low sulfate sulfoaluminate-bearing samples, equilibrated at higher humidities,

TABLE 2. X-ray d-spacings—hydrated cement dried powder data

Specimen	C-75	C-49	C-61-C	C-33-1	C-33	C-33-1	C-31	C-32-1	C-32
Cement.....	15754	15754	LTS-17	15622	15622	15497	15497	15669B	15669B
Type.....	I	I	I	II	II	III	III	IV	IV
Nominal W/C.....	.65	.65	.70	.60	.60	.60	.60	.60	.60
Age.....	7 yr	5 yr	1 yr	10 yr	7 yr	10 yr	7 yr	10 yr	7 yr
Spacings, Å.....	8.2	8.2	8.2	8.2	8.2	8.2	8.2	8.2	8.2
	7.7	7.9	7.7	7.8	7.8	7.7	7.7	7.7	7.7
	5.47	5.48	5.45	5.47	5.43	5.45	5.45	5.47	5.48
	* 5.06	(b)	(b)	* 5.06	5.06	5.07	* 5.06	(b)	(b)
	4.92	4.95	4.91	4.92	4.92	4.92	4.92	4.92	4.92
	4.41	4.41	4.41	4.41	4.39	4.39	4.39	4.40	4.39
	4.09	4.10	4.07	4.09	4.08	4.08	4.08	4.08	4.08
	3.89	3.92	3.86	3.89	3.89	3.86	3.86	3.86	3.86
	3.62	3.62	3.62	3.66	3.66	3.66	3.66	3.66	3.66
	3.31	3.32	3.31	3.32	3.35	3.31	3.30	3.30	3.30
	3.12	3.12	3.12	3.12	3.12	3.12	3.21	3.12	3.18
	3.04	3.05	3.03	3.05	3.04	3.04	3.05	3.03	3.11
	2.92	2.92	2.92	2.92	2.92	2.92	2.92	2.92	3.03
	2.88	2.88	2.88	2.88	2.86	2.86	2.86	2.86	2.87
	2.78	2.78	2.78	2.78	2.77	2.77	2.76	2.79	2.78
	2.63	2.63	2.63	* 2.67	2.66	2.63	2.63	2.63	2.63
	* 2.60	2.59	2.60	2.60	2.58	2.55	2.58	2.58	2.58
	2.53	2.53	2.53	2.53	2.53	2.53	2.53	2.53	2.53
	2.49	2.46	2.48	2.46	2.45	2.45	2.47	2.47	2.45
	2.46	2.43	2.43	2.44	2.43	2.43	2.42	2.42	2.42
	2.43	2.35	2.35	2.35	2.35	2.35	2.35	2.35	2.35
	2.31	2.30	2.30	2.30	2.30	2.30	2.30	2.30	2.30
	2.26	2.26	2.26	2.26	2.26	2.26	2.26	2.26	2.26
	2.08	2.10	2.08	2.08	2.08	2.08	2.08	2.08	2.08
	2.05	2.05	2.05	2.06	2.05	2.05	2.05	2.05	2.05
	2.01	2.01	2.01	2.01	2.01	2.01	2.00	2.01	2.02
	1.93	1.93	1.93	1.93	1.93	1.93	1.93	1.93	1.93
	1.88	1.89	1.88	1.88	1.88	1.88	1.88	1.88	1.89
	1.82	1.82	1.83	1.82	1.82	1.82	1.82	1.82	1.82
	1.80	1.80	1.80	1.80	1.80	1.80	1.80	1.80	1.80
	1.72	1.72	1.72	1.72	1.72	1.72	1.72	1.72	1.71
	1.69	1.69	1.69	1.69	1.69	1.69	1.69	1.69	1.69
	1.65	1.65	1.65	1.65	1.65	1.65	1.65	1.65	1.65
	1.64	1.64	1.64	1.64	1.64	1.64	1.64	1.64	1.64
	1.61	1.60	1.61	1.61	1.62	1.62	1.62	1.62	1.64

* Shoulder on strong peak. Exact d-spacing not certain.

b Bably obscured by strong peak. Spacing cannot be estimated.

the 8.9 Å line appeared. It showed only as a shoulder on the 8.2 Å peak at 28.8 percent relative humidity, was about equal in intensity with the shrinking 8.2 Å peak at 33 percent relative humidity, and at 42 percent relative humidity, the 8.2 Å peak was a small shoulder on the 8.9 Å peak. These features are illustrated in figure 1. At higher humidities, the patterns appeared quite like the wet slab patterns, except that no significant amount of carbonation had occurred. As a result, the low sulfate sulfoaluminate lines were of intensities comparable to those of the lines in the dried powder patterns. That is, they were strong and sharp. Because of this, it was easy to distinguish the 4.45 Å sulfoaluminate line from a 4.40 Å line due to another phase (see below). This resolution is illustrated in figure 1. Furthermore, it can be seen from results in tables 1 and 2 and in figure 1 that while the 4.1 Å line in the dry material shifts to 4.45 Å in the wet material, the line at 4.0 Å reappears as well when the sample is rewetted. This corresponds to the line reported at 3.99 Å by Midgley [27, 28] and at 4.02 Å by Fratini, Schippa, and Turriziani [29].

Thus in figure 1, idealized patterns in the 9 Å and 4 Å regions are shown for pastes containing the dry form of low sulfate sulfoaluminate, the wet form, and an intermediate case (33 percent humidity) in which both forms appear simultaneously. The differences between wet slab and rewetted powder patterns show that low sulfate

sulfoaluminate reacts with CO₂ just as does Ca(OH)₂.

The ettringite lines appearing in wet slab patterns at 9.8 and 5.6 Å are absent in the dried powder patterns of these pastes. Rewetting these pastes at humidities up to 47 percent has no significant effect on the diffraction pattern. Rewetting at 100 percent relative humidity causes the ettringite lines to return. No significant amount of carbonation occurred with these rewetted samples, and yet the ettringite lines were of comparable intensities to those in the original wet slab patterns wherein considerably more carbonation occurred. Thus, if CO₂ reacts with ettringite, it does so sufficiently slowly so as not to affect the X-ray observations.

The low sulfate sulfoaluminate is found in pastes made from cements high in C₃A, but not in those made from cements low in C₃A. On the other hand, ettringite is the only sulfoaluminate found in pastes made from cements low in C₃A, while little if any of it is found in pastes of cements high in C₃A.

One of the cements low in C₃A discussed above is of especial interest in one respect, however. If the low sulfate sulfoaluminate were to have formed instead of ettringite, not enough Al₂O₃ would be present in the cement to react with all the SO₃. Under these circumstances, it is possible that a sulfoterrite might form. Malquori and Cirilli [35] have prepared calcium sulfoterrites analogous to

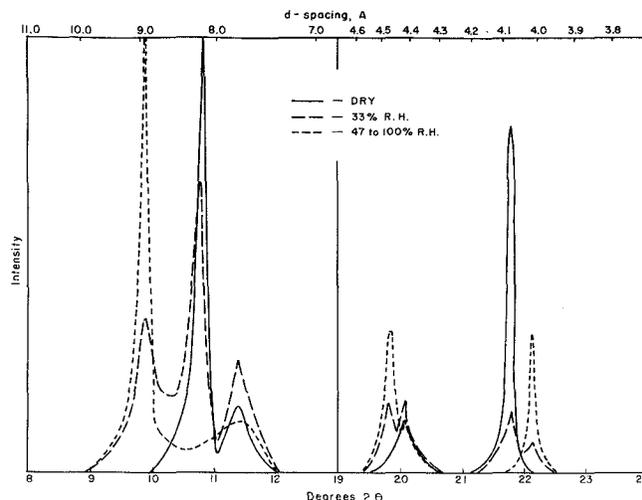


FIGURE 1. Calcium monosulfoaluminate lines in X-ray patterns of portland cement paste at different relative humidities.

the calcium sulfoaluminates which are found in hydrated portland cement pastes. The X-ray diffraction patterns of these sulfoferrites are, in general, very much like those of their sulfoaluminate analogs. As a result, the sulfoferrite compounds, were they present in portland cement pastes, would not be readily distinguishable from their aluminate counterparts. However, there is evidence that the iron-bearing phase in cement hydrates in a unique manner not involving SO_3 . This will be discussed in the next section.

The Calcium Aluminate and Calcium Ferrite Hydrates

The calcium aluminate and calcium ferrite hydrates have been reported as existing in hydrated cements in two different forms: cubic and hexagonal. The cubic hydrates are represented by the compounds C_3AH_6 and C_3FH_6 ; the hexagonal hydrates are represented by the compounds C_4AH_{13} and C_4FH_{13} . It was shown by earlier investigators such as Wells, Clarke, and McMurdie [36] that C_3AH_6 is the stable calcium aluminate hydrate in contact with solutions saturated with respect to calcium hydroxide. On the other hand, in none of the discussions of the stoichiometry of the hydration of portland cement is much evidence given for the presence of the cubic tricalcium aluminate hydrate. On the basis of evidence available at the time, Steinour [4] stated that "... initial formation of C_4AH_{13} in clinker and water paste seems much more probable than formation of cubic C_3AH_6 It is not impossible, however, that the cubic hexahydrate might form later." In recent X-ray investigations of portland cement pastes, Taylor [10] and later

Turriziani [11] report only the hexagonal tetracalcium aluminate hydrate, C_4AH_{13} ; they observed no cubic tricalcium aluminate hydrate in the pastes.

In the discussion to follow we shall review evidence that both cubic and hexagonal hydrates are present in hardened pastes and that the cubic phase at least is a solid solution of several substances. We shall discuss first the cubic and then the hexagonal hydrates.

It can be seen from the data in tables 1 and 2 that a group of lines appears distinctly in patterns of all cement pastes except the Type IV cement, which is quite low both in Al_2O_3 and in Fe_2O_3 , and even in patterns of this cement paste there is evidence of these lines. This group of lines appears at 5.07, 4.40, 3.32, 2.26, 2.01, and 1.72 Å, corresponding to six relatively strong C_3AH_6 lines reported at 5.14, 4.45, 3.37, 2.30, 2.04, and 1.75 Å by Midgley [27, 28], and at 5.13, 4.45, 3.36, 2.30, 2.04, and 1.75 Å by Burdese and Gallo [37]. The lines for the analogous iron compound, C_3FH_6 , are reported at 5.20, 4.54, 3.40, 2.33, 2.07, and 1.77 Å by Flint, McMurdie, and Wells [38] and at 5.18, 4.50, 3.41, 2.33, 2.07, and 1.77 Å by Burdese and Gallo [37]. More complete d -spacing data for these materials are given in table 3. The reported C_3AH_6 lines are all higher than those observed in the hydrated cement pastes, and the C_3FH_6 lines are farther removed from the observed lines. The spacings observed in cement pastes would not be those expected from C_3AH_6 , C_3FH_6 , or a solid solution of the two.

Burdese and Gallo [37] also report spacings for a partially dehydrated cubic tricalcium ferrite, C_3FH_2 . These spacings are 5.07, 4.38, 3.32, 3.10, 2.78, 2.53, 2.27, 2.01, and 1.72 Å in very good agreement with those observed in cement pastes,

TABLE 3. *d*-spacings reported for tricalcium aluminate and ferrite hydrates and corresponding spacings in some representative hydrated cement pastes

<i>hkl</i> [38] ^a	C ₃ AH ₆ [38]	C ₂ AH ₆ [27, 28]	C ₃ AH ₆ [37]	C ₃ AH _{3.75} [44]	C ₃ FH ₆ [38]	C ₃ FH ₆ [37]	C ₃ FH ₂ [37]	C-75	C-33-1
211	5.16(VS)	5.14(S)	5.13(MS)	5.03(VW)	5.20(M)	5.18(MS)	5.07(M)	5.09	5.06
220	4.47(M)	4.45(M)	4.45(M)	4.39(VW)	4.54(S)	4.50(S)	4.38(MW)	4.39	4.39
321	3.37(M)	3.37(M)	3.36(MW)	3.30(VW)	3.40(W)	3.41(MW)	3.32(W)	3.31	3.32
400	3.15(M)	3.15(M)	3.15(W)	3.09(VW)	3.19(S)	3.19(MS)	3.10(MS)	(b)	(b)
420	2.81(M)	2.82(MS)	2.81(MS)	2.77(VW)	2.85(S)	2.85(MS)	2.78(MS)	(b)	(b)
322			2.68(VW)		2.72(VW)		2.72(VW)		
422	2.56(VW)	2.57(W)	2.55(W)		2.60(M)	2.61(MW)	2.53(M)	2.53	2.53
431	2.46(W)	2.47(MW)	2.47(W)		2.50(VW)	2.51(W)	2.44(WW)	2.43	2.44
521	2.30(VS)	2.30(VS)	2.30(MS)	2.26(VW)	2.33(M)	2.33(MS)	2.27(W)	2.27	2.27
440	2.22(VW)	2.23(VW)	2.23(W)		2.26(W)				
611, 532	2.04(S)	2.04(S)	2.04(S)	2.01(VW)	2.07(M)	2.07(S)	2.01(S)	2.01	2.01
620	1.99(VW)	1.99(VW)	1.99(VW)		1.99(W)	2.02(W)	1.96(W)	1.96	
444	1.81(VW)	1.82(VW)	1.82(VW)			1.84(WW)	1.79(VW)	(b)	(b)
640	1.74(W)	1.75(MW)	1.75(MS)	1.72(VW)	1.77(M)	1.77(M)	1.72(M)	1.72	1.72
633, 552, 721	1.71(W)	1.71(W)	1.71(W)		1.73(W)	1.74(VW)	1.70(VW)		
642	1.68(M)	1.68(M)	1.68(S)	1.66(VW)	1.70(VS)	1.71(VS)	1.66(VS)	1.66	1.66
651, 732	1.60(VW)	1.60(M)			1.62(VW)				
800	1.57(W)	1.57(VW)	1.57(W)		1.59(W)	1.60(W)	1.55(W)		
840	1.40(W)	1.41(MS)			1.43(M)				

^a Numbers in brackets refer to literature cited at end of text.
^b Probably present, but overlapped by line from some other component.

as can be seen in table 3. The lines at 3.10 and 2.78, of course, are overlapped by strong lines of Ca(OH)₂ [39] and the calcium silicate hydrate, respectively. (It is to be pointed out here again that the strength of the 2.78 Å line is far too great to be accounted for on the basis of any aluminate or ferrite.) The compound C₃FH₂, however, is obtained by dehydration of C₃FH₆ at 250 °C [40]. It is difficult to imagine that a species normally formed by dehydration at relatively high temperatures should form at room temperature in a saturated aqueous system, unless some other substance were dissolved in it to stabilize it. Stabilization of solid phases under conditions far removed from equilibrium is not an unusual phenomenon, especially in cement chemistry; one merely need consider the case of β-C₂S. However, the more usual examples, such as β-C₂S, do not involve an aqueous solution phase.

From the kinetic data presented in another section of this discussion, it would appear that the ferrite phase in portland cement hydrates with no significant change in A/F ratio of the remaining unhydrated material. Hence, one might assume that the product of hydration may be a solid solution of a ferrite and an aluminate such that the A/F ratio of the solid solution is the same as it was in the original ferrite phase. Thus, if the original ferrite phase had an A/F ratio of unity, then the hydration product in question would presumably be an equimolar solid solution of a C₃F hydrate and a C₃A hydrate, the phase having the overall composition C₆AFH₂. On the basis of a statistical analysis of nonevaporable water data as a linear function of the composition parameters of a group of 27 cements (the water data being obtained from a group of well-hydrated cement pastes), the water content of such a phase is calculated to be 6 moles per mole of C₆AF; that is, the phase has the composition C₆AFH₆. This work, and the calculations leading to this result, will be discussed in detail in a later section. However, it is interesting to note that the water

results obtained are such as to indicate that no pure ferrite phase can form, and that solid solution with an aluminate is probably necessary.

The composition C₆AFH₆ can be considered to correspond to a solid solution of C₃FH₂ with an aluminate of composition C₃AH₄. The lattice of C₃AH₆ shrinks in a regular manner as water is removed [41, 42, 43] but the lattice remains cubic as long as the H/A ratio is greater than 1.5. One might expect a composition C₃AH₄ to have almost exactly the same lattice parameter as C₃FH₂. Indeed, this appears to be the case, since Burdese and Gallo report the lattice constant of C₃FH₂ to be 12.39 Å, and Köberich [44] gives the lattice constant of C₃AH_{3.75} as 12.37 Å. The X-ray *d*-spacings reported for this material are in reasonably good agreement with those of C₃FH₂ and those found in patterns of hydrated pastes as can be seen in table 3.

The estimation of the composition of this ferrite-aluminate solid solution phase is still a first approximation. The material is more likely to be a silica-containing member of the hydrogarnet series. The estimated water content would be expected to be low because it is replaced by silica as was described by Flint, McMurdie, and Wells [38]. Thus, if the estimated lattice spacing of 12.38 Å is taken into consideration, and it is still assumed that the A/F ratio of the material is 1.0, then the material corresponds to a hydrogarnet having a composition in the vicinity of C₆AF₂S₂H₈.

The lines ascribed to the proposed solid solution phase appear in wet slab as well as dry powder patterns, as is indicated by the data in tables 1 and 2. However, in almost all patterns, wet or dry, the 5.07 Å line is partly obscured by the 4.90 Å calcium hydroxide line [39]. In many cases a shoulder appears sufficiently distinctly so that a reasonable estimate of the *d*-spacing at 5.07 Å can be made. In a few other cases, however, the shoulder is not as distinct, and about all that can be said for such cases is that there is a line present, though fairly well hidden by the

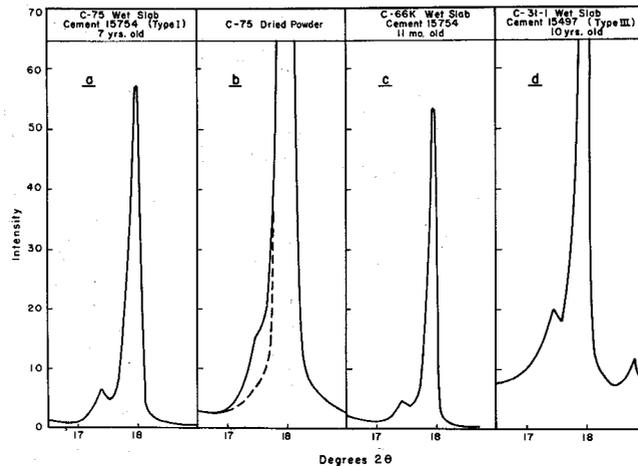


FIGURE 2. The appearance of the 5.07 and 4.40 Å lines in portland cement paste X-ray patterns.

calcium hydroxide line. Examples of these types are given in figure 2.

The X-ray pattern of this solid solution phase obtained from a sample of a well-hydrated paste of cement 15754 from which most of the calcium hydroxide had been extracted by means of water was somewhat more distinct. The 5.07 Å peak was almost completely undisturbed by the 4.90 Å calcium hydroxide line. The 3.11 Å line was too large to be accounted for by the remaining calcium hydroxide, and although little evidence for other substances containing aluminum or iron was found, the 2.78 Å peak was still too large to be caused only by the calcium silicate hydrate phase.

There is little evidence to show either a growth or decrease of the solid solution hydrate lines as a function of time. The lines appear in the pastes of cement 15754 at all ages reported in table 1. Hence, there is no indication that this hydrate would only be a product of hydration of the C_4AF phase after long periods of time. On the contrary, whatever amount of this hydrate is found would appear to have been formed at some early age, and to have remained unchanged thereafter.

In his DTA investigation Turriziani [11] was unable to detect any cubic phase, either C_3AH_6 , C_2FH_6 , or a hydrogarnet. He observed decomposition temperatures in the vicinity of 375 °C for C_3AH_6 and two members of the solid solution series $C_3AH_6-C_3AS_2$. However, if the hydrogarnet had an A/F ratio of 1.0, then the decomposition temperature ought to be in the vicinity of 240 °C [38]. An endotherm at this temperature may be difficult to detect when an endotherm also appears at 220 °C due to the presence of tetracalcium aluminate hydrate.

Many investigators in the past have reported the presence of a hexagonal tricalcium aluminate hydrate. Schippa and Turriziani [45] state that

it is impossible to form such a compound under conditions such as those that exist in a hydrating cement paste, and that the substance observed is actually calcium monocarboaluminate. All of the wet slab patterns show a line at 7.8 Å, corresponding to the principal line of calcium monocarboaluminate [46]. Much of this carboaluminate may have resulted from the carbonation of the wet slabs during handling. However, the pastes of cements high in C_3A have a 7.8 Å line with a pronounced asymmetry on the low-angle side, indicating the presence of another, weaker line at a higher d -spacing. In some high C_3A cement paste patterns, this asymmetry has developed into a shoulder such that the d -spacing of the peak causing it may be estimated. The value obtained, 8.3 Å, is very close to the position of the strongest line of tetracalcium aluminate hydrate, C_4AH_{13} , reported by Schippa and Turriziani [45] as 8.4 Å, and by Roberts [33] as 8.2 Å. In the wet slab patterns, this line is sufficiently weak that it is not expected that any of the other C_4AH_{13} lines, all of which are weaker than the 8.4 Å line, would be detectable. In some dried powder patterns, other lines are seen.

The principal peak of the iron analog of this aluminate, that is, C_4FH_{13} , occurs at 8.2 Å [47]. Thus, a solid solution of this material with the corresponding aluminate could produce a line at 8.3 Å. However, the determination of d -spacing from a shoulder of the type described is far too inaccurate to warrant any conclusion regarding the composition of the hexagonal phase.

In the dried powder patterns, the 7.8 Å line is much weaker, since very little if any carbonation has occurred during handling. The fact that no shift is observed in this line when the specimen is dried is in agreement with results obtained on a sample of pure calcium monocarboaluminate

which was dried to the half-micron level. The pattern of the dried pure compound showed no appreciable shift in line positions from those in the wet sample pattern [34], and was in reasonably good agreement with the spacings reported by Turriziani and Schippa [45, 46] and by Buttlar, Dent Glasser, and Taylor [48]. The carboaluminate line in dried samples, and in rewetted samples as well, is weak, indicating that not much of the material is present. That little, if any, CO_2 has entered the dried pastes is indicated by the fact that the principal calcite line is not observable.

Buttlar, Dent Glasser, and Taylor present diagrams of patterns of C_4AH_{13} after various drying treatments. These patterns indicate a shift in the basal reflection in the same way as was found for the monosulfoaluminate. When heated to 105°C , the C_4AH_{13} line at 8 Å shifted to 7.8 Å. Drying at 105°C is roughly equivalent to the vacuum drying condition described by Copeland and Hayes [22]. However, when C_4AH_{13} is dried *in vacuo* at room temperature [34], the basal line shifts from 8.4 Å, the wet state position [45], to 7.8 Å over a relatively short period of time. Continued drying for a much longer period of time (21 days) led to only a small weight loss relative to that in the first 3 days, but the basal reflection shifted to 7.4 Å, in agreement with the value reported by Roberts [33]. X-ray patterns of this material revealed only the 7.8 Å line unless special precautions were taken to eliminate all traces of water vapor, this being done by passing a dry nitrogen stream over the sample while the pattern was being obtained. Hence, it appears that very little water need be taken up by the well-dried C_4AH_{13} before the basal reflection shifts from 7.4 Å to 7.8 Å, so that in many cases, the line observed at 7.8 Å may represent either carboaluminate, C_4AH_{13} , or both. The reversibility of the hydration-dehydration process in C_4A hydrate was also noted by Roberts. However, there is always a small amount of CO_2 in any paste, most of which was present in the cement prior to hydration. If all this CO_2 were in the form of carboaluminate, there would, in most cases, not be enough present such that all of the tetracalcium aluminate hydrate potentially in the paste would be in the form of carboaluminate.

The diffraction maximum observed at 7.8 Å is not a strong, sharp peak, but rather a low, broad hump. This spacing is the basal reflection of the pseudohexagonal crystal [48], regardless of which of the two compounds it represents.

The Dependence of Water Content on Cement Composition

Nonevaporable water data have been obtained on a group of cements hydrated for times up to 13 yr [51, 52]. The cements used were those prepared for use in the "Long Time Study" project at the Portland Cement Association Research and

The fact that this reflection is poorly developed indicates that the crystals may be quite small and disordered, a condition somewhat akin to that of the CSH(I) produced by reaction of CaO and SiO_2 at room temperature. (The calcium silicate hydrate produced by the hydration of C_3S , of course, shows no basal reflection whatever [15, 24].)

There is some evidence that tetracalcium ferrite hydrate may also have a diffraction line at 7.8 Å. Various investigators have reported different basal reflections for C_4FH_7 , presumably because each investigated material with a different moisture content. Greening and Seligmann [47] found the basal spacing to be 8.2 Å for material in the saturated state. Watanabe and Iwai [49] report a value of 7.96 Å for somewhat drier material. Taylor [50] has X-ray data for a hydrate of the composition C_4FH_{10} which includes a basal reflection of 7.8 Å. However, even this material would presumably lose water on further drying to the $\frac{1}{2}\text{-}\mu$ level, and as a result, undergo further layer contraction. This would result in a downward shift of the basal reflection toward the 7.4 Å value reported for dried tetracalcium aluminate hydrate. There is no information available at present as to how rapidly this dried ferrite hydrate would pick up moisture.

In some of the dried powder patterns, other lines of the hexagonal calcium aluminate hydrate are seen. The most important among these is at 3.9 Å, the 002 reflection. The carboaluminate has no line at 3.9 Å, but rather, one at 3.8 Å. This latter spacing appears in many wet slab patterns, along with a line at 3.9 Å caused by the presence of calcite. In the dry powder patterns, no calcite lines appear, and no line at 3.8 Å. However, a small line at 3.9 Å is found indicating that the hydrated aluminate is primarily C_4AH_{13} . The spacing at 3.9 Å is also one found with C_4FH_{10} [50]. Lines appear at 2.46 and 2.10 Å in the dried powder patterns, but these also contain contributions from other compounds, such as calcium monosulfoaluminate. The similarity of the pattern of this latter compound with that of tetracalcium aluminate hydrate is quite marked, with the exception of the locations of the basal reflections.

There remains the distinct possibility that the cement paste pattern lines attributed to monosulfoaluminate are in truth those of a solid solution of this material with the tetracalcium aluminate hydrate, but this would not obviate the fact that the evidence obtained indicates the presence of this latter material by itself.

Development Laboratories. The oxide compositions and the potential compound compositions of these cements were published by Lerch and Ford [53].

It was assumed that both nonevaporable water and surface area were dependent on linear functions of the cement composition parameters.

Thus:

$$w_n/c = k_1(\text{alite}) + k_2(\text{belite}) + k_3(C_3A) + k_4(F_{ss}) + k_5(CaSO_4) \quad (1)$$

where the k_i are constants and w_n/c is the nonevaporable water content in grams of water per gram of cement. The quantities (alite) and (belite) refer to the C_3S and C_2S phases as they occur in portland cement, each containing minor quantities of other oxides, primarily Al_2O_3 , as has been discussed by Jeffery (in the case of alite) [54], and in some recent publications on the quantitative analysis of portland cements by means of X-rays [20, 21]. The symbol F_{ss} represents the ferrite solid solution phase. All cement compound quantities may be expressed in grams per gram of cement.

It was shown in the quantitative cement analysis work that the compositions obtained from X-ray analysis did not differ significantly from those obtained from the potential compound calculation devised by Bogue [19] except in the case of C_3A . The C_3A values were lower in the X-ray determination because of the Al_2O_3 in the alite and belite phases; the alite phase was correspondingly higher because of this Al_2O_3 . Inasmuch as the ferrite solid solutions had A/F ratios near unity for the most part, the X-ray and potential values were in good agreement.

For the purposes of the calculations, it proved expedient to use potential rather than X-ray values because X-ray values were not available for all of the cements. Since the Al_2O_3 in the alite and belite phases probably behaves during the hydration process in much the same manner as the Al_2O_3 in C_3A , it is likely that no significant error is introduced by the use of potential data. Expressed in terms of the potential compound compositions, eq (1) becomes

$$w_n/c = a_1(C_3S) + a_2(C_2S) + a_3(C_3A) + a_4(C_4AF) + a_5(CaSO_4) \quad (2)$$

where the a_i are again constants in the equation.

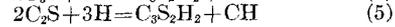
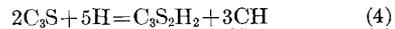
Since the quantity w_n/c in eq (2) is a linear function of the potential compound quantities, which, in turn, are linear functions of the oxides

[19], it follows that w_n/c is also a linear function of the oxides. Thus

$$w_n/c = b_1(CaO) + b_2(SiO_2) + b_3(Al_2O_3) + b_4(Fe_2O_3) + b_5(SO_3) \quad (3)$$

The coefficients in eq (2) have been evaluated by the method of least squares from data obtained from the "Long Time Study" (LTS) cements hydrated for 1, 6½, and 13 yr, at water:cement ratios of 0.4, 0.6, and 0.8, and dried to approximate equilibrium with the vapor pressure of water over a mixture of $Mg(ClO_4)_2 \cdot 2H_2O$ and $Mg(ClO_4)_2 \cdot 4H_2O$ (8 μ), or that of water over ice at $-78.5^\circ C$ (½ μ). The parameters of eq (2) were evaluated including the $CaSO_4$ term (5-parameter system) or omitting this term (4-parameter system). The results are shown in table 4. In this table, the age of the specimen is given in column 1, the water:cement ratio and method of drying in column 2, the number of parameters evaluated in column 3, the number of cements in the data set in column 4, the values of the parameters in columns 5, 7, 9, 11, and 13, and the standard errors of these parameters in columns 6, 8, 10, 12, and 14.

Investigations of the stoichiometry of the hydration of C_3S and C_2S [15, 24] have shown that the hydration reactions may be represented by the equations



the composition of the calcium silicate hydrate being given as that of the half-micron material. From these equations, it is seen that each gram of C_3S reacts with 0.197 g of water, and each gram of C_2S with 0.157 g of water. The constants, a_1 , in eq (2), obtained from the least squares treatment of the various sets of half-micron sample data, range from 0.199 to 0.208. It would therefore appear that in 6.5-year-old pastes, hydrated at relatively high water:cement ratios, for which these values were obtained, the C_3S is completely hydrated.

The constants, a_2 , obtained from these same data, range from 0.147 to 0.152. The fraction of C_2S hydrated, estimated as the ratio of the calculated value of a_2 to the theoretical value based on eq (5) is 0.951, on the average, for a

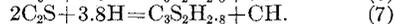
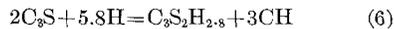
TABLE 4. Least squares coefficients from nonevaporable water data

Age	w_n/c & drying *	No. of parameters	No. of cements	a_1	σ_1	a_2	σ_2	a_3	σ_3	a_4	σ_4	a_5	σ_5
13 yr	0.4(P)	5	27	0.226	0.017	0.194	0.014	0.510	0.066	0.097	0.065	0.149	0.312
"	"	4	27	.230	.015	.196	.013	.522	.060	.109	.058		
6½ yr	0.8(P)	5	23	.228	.022	.193	.020	.478	.097	.151	.097	0.317	0.460
"	"	4	23	.234	.020	.197	.018	.509	.085	.184	.083		
"	0.8(D)	5	23	.211	.020	.154	.017	.571	.086	.190	.086	-0.120	0.410
"	"	4	23	.199	.018	.152	.016	.561	.075	.178	.073		
6½ yr	0.6(P)	5	24	.228	.020	.188	.018	.412	.090	.091	.079	0.607	0.409
"	"	4	24	.238	.020	.198	.017	.477	.081	.142	.074		
"	0.6(D)	5	24	.204	.015	.147	.016	.470	.083	.129	.074	0.243	0.380
"	"	4	24	.208	.017	.151	.015	.496	.072	.149	.063		
6½ yr	0.4(P)	5	27	.223	.018	.170	.015	.463	.070	.117	.069	0.503	0.333
"	"	4	27	.234	.017	.178	.015	.504	.066	.158	.065		
1 yr	0.4(P)	5	27	.212	.020	.155	.016	.363	.076	.067	.075	0.786	0.360
"	"	4	27	.228	.019	.168	.016	.429	.074	.132	.073		

* (P)—dried at 8 μ vapor pressure; (D)—dried at ½ μ vapor pressure.

6.5-year-old paste hydrated at a water:cement ratio of 0.6, and 0.974 for pastes of the same age hydrated at a water:cement ratio of 0.8. These latter values, however, must be considered as maximum values, inasmuch as there is usually somewhat more water in the calcium silicate hydrate phase than the two moles per mole of SiO_2 indicated by the two eqs (4) and (5), [15].

For 8- μ dried C_3S and C_2S pastes, the stoichiometric equations are [15]:



These equations predict the values of a_1 and a_2 to be 0.229 and 0.199, respectively. The values obtained indicate that for pastes hydrated at water:cement ratios of 0.4, after 1 yr, the C_3S is over 95 percent hydrated and after 6½ yr, it is completely hydrated. The C_2S is not so well hydrated, however, being, on the average, 81.4, 87.6, and 98.2 percent hydrated at 1, 6½, and 13 yr, respectively.

Inasmuch as the cements used in the least squares analysis are of widely different compositions, it must be pointed out that such a treatment is valid only for relatively well-hydrated pastes, wherein the effect of dependence of hydration rate on cement composition is no longer important.

Interpretation of the aluminate, ferrite, and sulfate nonevaporable water results is more difficult. In the first place, there are several possible products of hydration, and as has been shown, evidence has been obtained for the presence of some of them. Others may be present for which no evidence has as yet been obtained. As can be seen from the standard errors, the least squares parameters for the ferrite and sulfate are far less certain than are the C_3S and C_2S parameters. Furthermore, while there is no significant difference between the 4- and 5-parameter C_3S and C_2S results, the other parameters are strongly affected. The contribution of the sulfate in the 5-parameter calculation is absorbed primarily by the aluminate and ferrite parameters in the 4-parameter calculation.

The least squares results may be expressed in terms of oxides, according to eq (3). The parameters may then be converted to moles of water per mole of oxide. When this is done, the results for half-micron dried samples at a water:cement ratio of 0.8, rounded to whole numbers (except in the case of SiO_2) are $\text{H}/\text{C}=1$, $\text{H}/\text{S}=-0.5$, $\text{H}/\text{A}=5$, $\text{H}/\text{F}=-5$, and $\text{H}/\text{SO}_3=-2$. These values may be used to predict the water contents of the various possible products of hydration. For instance, a calcium silicate hydrate with a C/S ratio of 3/2 would have the composition $\text{C}_3\text{S}_2\text{H}_2$, just as was indicated from the potential compound parameters and the stoichiometric equations for the hydration of the pure silicates. Tetracalcium aluminate hydrate would have the composition C_4AH_9 , which is to be compared with

the compositions reported by Roberts [33] for tetracalcium aluminate hydrates dried under various conditions. Roberts gives H/A values of 11 for material dried over solid NaOH or anhydrous CaCl_2 , and values of 7 for material dried over P_2O_5 or at 120 °C.

The calcium ferrite hydrate case is not so simple. A tetracalcium ferrite hydrate would have a negative water content, which is, of course, absurd. However, if the aluminates and ferrites were in solid solution, physically possible, and not unreasonable, water contents are predicted.

The predicted water contents of the sulfoaluminates are, as was pointed out above, quite uncertain. The water-to-oxide ratios given above lead to the compositions $\text{C}_3\text{A}\cdot\text{CaSO}_4\cdot 7\text{H}$ and $\text{C}_3\text{A}\cdot 3\text{CaSO}_4\cdot 5\text{H}$. Lerch, Ashton, and Bogue [55] found water contents for these materials, dried at 110 °C, to be 6H and 7H, respectively. Roberts' recent work [33] indicates a value for the low sulfate sulfoaluminate of about 8H. If the least squares H/SO_3 value were -1 instead of -2, the predicted compositions of the sulfoaluminates would be $\text{C}_3\text{A}\cdot\text{CaSO}_4\cdot 8\text{H}$ and $\text{C}_3\text{A}\cdot 3\text{CaSO}_4\cdot 8\text{H}$. Thus, on the basis of experimental evidence, it appears that the H/SO_3 ratio should be somewhere between -1 and -2. Both these values fall well within the uncertainty limits determined statistically.

The evidence from the least squares calculations combined with the evidence obtained from the X-ray diffraction studies provides a strong indication that the alumina in C_3A reacts in a different manner from that in the ferrite phase. The cements low in C_3A shown in tables 1 and 2 both contain ettringite. On the other hand, those cements high in C_3A when hydrated contained the low sulfate sulfoaluminate. Thus, it appears that only when the A/F ratio in the cement is relatively high, does the low sulfate sulfoaluminate form. Steinoor points out, in his recent discussion of the setting of portland cement [56], that when the molar A/F ratio in a cement is less than 1.0, no retarder is needed. He also attributes flash set to the formation of a hexagonal calcium aluminate. Under the conditions obtained with the use of the high C_3A cements whose compositions are given in table 5, the presence of gypsum

TABLE 5. Oxide compositions of four portland cements

Cement type	15754 I	15622 II	15497 III	15669 IV
	Percent	Percent	Percent	Percent
SiO_2	20.67	22.44	19.83	27.51
CaO	62.03	63.81	63.41	63.73
Al_2O_3	6.13	5.88	5.21	1.95
Fe_2O_3	* 2.20	4.20	* 2.59	1.92
MgO	2.05	1.36	1.28	1.64
SO_3	2.37	1.59	1.82	1.82
Total.....	96.45	97.28	94.14	98.57
Free CaO	0.93	0.49	3.14	0.15
Na_2O17	.05	0.30	.05
K_2O16	.17	.40	.22

* The total Fe_2O_3 includes a small amount of FeO expressed as Fe_2O_3 .

prevents the formation of the hexagonal aluminate (presumably tetracalcium aluminate hydrate) by the formation of the sulfoaluminate. The first sulfoaluminate to form is ettringite, apparently, since of the X-ray patterns of pastes from cement 15754, only that of the youngest observed, a 6-month old specimen, showed ettringite. Taylor [10], too, studying a normal portland cement, observed initial formation of ettringite, with subsequent disappearance. It is interesting to note that a hexagonal phase ultimately does form, this however being the low sulfate sulfoaluminate. The molar A/F ratios in the two cements, 15754 and 15497, in which the monosulfoaluminate does form are 4.37 and 3.15, respectively.

On the other hand, the low sulfate sulfoaluminate does not form in cements 15622 and 15669 in which no significant amount of C_3A is present. The molar A/F ratios in these two cements are 1.45 and 1.59, respectively, or, when corrected for the alumina in the silicate phases, 0.81 and 1.34. It would appear from these results that no significant amount of alumina from the ferrite phase enters into a sulfoaluminate as long as enough alumina is available from other sources to combine with all of the SO_3 present to form at least the high sulfate sulfoaluminate.

Flint and Wells [57] observed that while C_3AH_6 was susceptible to attack by sulfate, hydrogarnets containing either iron or silica were quite resistant. It would appear from these considerations that the molar ratio of nonferrite alumina to SO_3 in a given cement would serve as an indication as to which sulfoaluminate forms ultimately. Thus, the high C_3A cements, which contain the low sulfate sulfoaluminate for the most part have SO_3 to nonferrite Al_2O_3 ratios of 0.7 and 0.6, respectively, while the low C_3A cements, which contain the high form for the most part have ratios 1.2 and 3.9.

It is therefore also likely that no sulfoferrites form in portland cement pastes, at least of cements within the wide composition range covered by those whose X-ray data are given in tables 1 and 2, and whose compositions are given in table 5. Furthermore, the least squares coefficients discussed above also indicate that there is no sulfoferrite, in that such a compound, either high form or low form, could not have a negative calculated water content, physically absurd. Of course, a solid solution of sulfoaluminate and sulfoferrite is possible as far as the least squares considerations go just as in the case of aluminates and ferrites.

II. Kinetics of the Hydration of Portland Cement

L. E. Copeland and D. L. Kantro

Introduction

The purpose of this section of the paper is to review our knowledge of the kinetics of hydration. Mechanisms of hydration may at times be mentioned but a discussion of mechanisms is not a principal objective.

The first kinetic studies of the hydration of portland cement were concerned with determining the strength of concrete and mortars as a function of time of curing. Useful information can be obtained from such studies, but their value for theoretical purposes is limited because the development of strength in concrete and mortar is influenced by many factors other than the rate of hydration of the cement in the mix. Knowledge of the rates of hydration of cement is just one step toward understanding the mechanism of hydration and the development of strength, but it is an important one.

Three general methods have been used in studying the kinetics of hydration of portland cement: (1) microscopic examination of hardened neat cement pastes after known curing times, (2) observations of changes in the physical and chemical properties of hardened pastes as a function of time, and (3) X-ray diffraction analysis of unhydrated cement in hardened pastes.

In general, the microscopic studies can be, and in some cases have been, interpreted to support Michaelis' theory of the hardening of portland cement in that the unhydrated clinker particles are found embedded in a gel which has no structure visible in the light microscope. The presence of all four major phases has been observed in these particles—even after 20 yr.

The measurement of several physical and chemical properties of pastes as a function of curing times has been made. In some cases inferences concerning the rates of hydration of the individual components of cement have been drawn from these measurements. It will become evident that some of these inferences are not justified.

In recent years new techniques have been developed. One of these, X-ray diffraction, offers about our best tool for measuring directly the rates of hydration of the individual phases in portland cement. At the present time the experimental error is large when compared with the experimental error of standard chemical methods of analysis, but significant results can be obtained. Further experience with the method will bring improved results. Perhaps other new techniques can also be applied to the problems.

Direct Microscopic Observations

Most of the microscopic examinations have been made on polished sections, or sometimes upon thin sections, of hardened pastes. But Anderegg and Hubbell [58] chose to develop a different technique for their work. They first passed cement through an air separator to obtain several fractions of cement with particles with a narrow size range. They then prepared pastes of these sized fractions, $w_0/c=0.4$, and cured them in contact with a small quantity of water. At each of several selected ages a small fragment was broken from each paste and dried in an oven to stop the hydration reactions by removing the water. Each fragment was then ground until microscopic evidence showed the material to be subdivided into small and uniformly sized particles. Specimens for microscopic examinations were prepared by placing these particles on a microscope slide in an oil with a refractive index of 1.67. Thus it was possible for them to tell whether or not a particle was hydrated by its refractive index, for if it is hydrated its refractive index is lower than that of the oil and vice versa. They counted thousands of particles (weighting the count by the size of the particles) and determined the volume fraction of hydrated cement from the number of hydrated particles relative to the total number of particles. They obtained the weight fraction hydrated by using the densities of the unhydrated cement and of the completely hydrated cement.

To check their results they determined the fraction of cement hydrated in samples prepared by mixing completely hydrated cement with unhydrated cement in known proportions. They reported results accurate to about 2.5 percent.

They proceeded then to calculate the depth of penetration of the water into cement particles. To do this they assumed that the shape of the original cement particles was the same as that of the unhydrated particles remaining in the paste, and made microscopic measurements to determine the size and shape of a great many cement particles. Typical results, given in table 6, were estimated for a cement with a known particle size distribution using their results on depth of penetration of water in sized fractions of clinker particles. They noted that their Type III cement appeared to hydrate no more rapidly than did their Type I cement.

These experiments were repeated [59] using pure compounds and mixtures of pure compounds. Pure C_2S hydrated much more slowly than did pure C_3S , which hydrated much more slowly than did pure C_3A . The addition of 10 percent C_4AF to either C_3S or C_2S caused the mixture to hydrate much more rapidly than either component of the mixture would hydrate when pure.

Brownmiller [60] examined polished sections of neat cement pastes cured for various times. From this examination he estimated that about $\frac{1}{2}$ of the cement remained unhydrated at the end of the first day. He compared the sizes of the particles

visible in the polished sections with the sizes of the particles of original cement and estimated that a 60μ particle decreased in size to about 45μ during the first day, that the depth of penetration was about $7\frac{1}{2}\mu$. At 7 days approximately 80 percent of the cement had hydrated, and at 28 days about 85 percent. Cements that were high in C_3S and C_3A were almost completely hydrated at the end of 7 days. He concluded that as hydration proceeds there is a uniform decrease in the size of the cement particles, and stated, "There is no microscopic evidence of the channeling of water into the interior of cement particles to selectively hydrate any single major constituent."

TABLE 6. Depth of penetration of water in clinker particles and the degree of hydration of a typical portland cement

Time (days)	Depth of penetration (μ)	Percent hydrated
1	10	24
7	47.2	82
28	78.1	85
90	-----	90

However, he did observe that different phases at the boundary of a particle did not hydrate at the same rates: e.g., C_3S hydrates more rapidly than C_2S , and some interstitial material hydrates very slowly indeed.

Rexford [61] used thin sections. He pointed out that accurate rates of hydration from such microscopic examination were very difficult to obtain; one needs to examine many fields and measure accurately with a Wentworth micrometer stage. He confirmed Brownmiller's conclusions that hydration proceeded from the boundaries of cement particles inwards towards the center at a comparatively uniform overall rate, which affected all the constituents of that particle more or less simultaneously. He stated further, "No indication of completed hydration of any one compound was ever observed although incipient selectivity was often visible around the periphery of a cement particle." His conclusions were based upon the examination of hardened pastes cured up to 6 months, and upon examination of concrete up to 20 yrs old.

Ward [62] examined thin sections and came to somewhat different conclusions. He described two kinds of gel, one of which he called a "ground mass" gel that was interrupted by unhydrated clinker grains, calcium hydroxide crystals, and by small channels, and pores. Small crystalline particles of low birefringence were scattered throughout this gel. As the paste aged, a clear gel appeared to exude from the ground mass or to precipitate in the voids and channels.

He observed that C_2S and C_4AF were slow to hydrate and that many cement grains were shattered during the hydration. He identified the fragments as C_2S . He concluded that each

clinker grain does not hydrate in such a manner as to develop an individual coating of hydrate with subsequent uniting of these coatings.

The overall rate of hydration of cement observed in these microscopic studies agrees qualitatively with expectations based upon the rate of strength development. Anderegg and Hubbell tacitly assumed a mechanism of hydration that was supported later by the independent observations of Brownmiller and of Rexford. In answering a criticism of their paper, Anderegg and Hubbell show that they were aware that this assumption was not universally accepted, but argued that it is true. Actually, it is supported by the theory of hardening advanced by Michaelis, just as Brownmiller interprets his results to support Michaelis' theory.

There is a small difference between the compositions of the finely ground part and the coarser part of a cement, but if hydration proceeds by a more or less uniform diminution in the size of the cement grains, then the finer fraction would disappear first—probably during the first day. After

that time the composition of the unhydrated residue should change only slowly if at all.

Ward criticized the above views. He wrote of an apparent increase in the amount of C_2S in the hardened pastes and suggested that the individual phases react separately, then at a favorable concentration a general precipitation of gel occurs. But both concepts can be correct. The mechanism proposed by Ward could account for the initial setting of cement but by far the greatest amount of cement could be hydrated as Brownmiller and Rexford have described it. It is certainly true that if cement grains were "shattered" by hydration, this must have occurred before the paste hardened.

Ward observed shattering of C_2S grains in observing the hydration of the pure compound under the microscope. He noted that his pure C_2S showed a tendency to dust and suggested that perhaps the shattering was the result of the $\beta \rightarrow \gamma$ conversion. Is it possible that water could leach a soluble stabilizing agent out of the C_2S phase in portland cement, causing the same conversion with shattering of the cement grain?

Kinetics From Changes in Physical and Chemical Properties

Heat of Hydration

Many workers have determined the heat of hydration of portland cement as a function of time of curing. Woods, Steinour, and Starke [63, 64] were able to correlate such heats of hydration with the development of strength in mortars, and also found a good correlation between the rate of development of strength and the composition of the cement. Their primary motive was development of low heat cement, and therefore it was essential to their purpose to find a relationship between heat of hydration and composition of cement. For this they employed the method of least squares, assuming that at any given age each percent of each cement compound makes a fixed contribution to the heat evolution independent of the proportion of the compound in the cement. They were successful in accomplishing their objective. Other workers have generally followed their example. Davis, Carlson, Troxell, and Kelly [65] made similar studies of heats of hydration, and Verbeck and Foster [51] published initial results of an extensive investigation which is continuing. The latter authors included the effects of gypsum and both gypsum and glass in their computations.

By comparing the magnitudes of the respective "contributions" of each of the components to the heat of hydration, it can be inferred that the rates of hydration of the major components have the order C_3A , C_4AF , C_2S , C_2S . This order agrees with that obtained by comparing the rates of hydration of the pure components. The contribution of each component to the heat of hydration of completely hydrated cement paste is, within experimental error, the heat of hydration of the pure component.

Apparently no one working with heats of hydration has done more than draw qualitative conclusions concerning rates of hydration of the individual components from his data. If the assumption made tacitly in applying the principle of least squares to heat of hydration data is valid, the rates of hydration of the individual phases can be estimated. It will be instructive to consider this assumption.

Consider k cement pastes, each made with a cement different in composition from all the others. Let H_i be the heat of hydration of the paste made from 1 g of the i th cement and cured t days. Let X_{ij} be the weight fraction of component j in the i th cement, and $w_{ij}(t)$ be the weight of component j per gram of cement that has hydrated in t days. Let h_j be the heat of hydration of 1 g of component j . The heat of hydration of the paste can now be written:

$$H_i(t) = \sum_j w_{ij}(t) h_j. \quad (8)$$

The $w_{ij}(t)$ are unknown. In the application of the least squares principle to the k pastes, each hydrated t days, it is assumed that H_i can be written:

$$H_i(t) = \sum_j a_j(t) X_{ij}. \quad (9)$$

The coefficients $a_j(t)$ are called the contributions of the major components j to the heat of hydration. Eq (8) can be put into the form of eq (9) by multiplying and dividing each term on the right of eq (8) by X_{ij} , that is,

$$H_i(t) = \sum_j \frac{w_{ij}(t)}{X_{ij}} h_j X_{ij}. \quad (10)$$

Equations (9) and (10) are consistent if

$$a_j(t) = \frac{w_{ij}(t)}{X_{ij}} h_j \quad (11)$$

In applying the method of least squares to eq (9), it must be assumed that the $a_j(t)$ are independent of the compositions of the cements; consequently, $\frac{w_{ij}}{X_{ij}}$, the degree of hydration of component j , must be the same in all cement pastes at the time t . Also, the time derivative of the degree of hydration, which we shall call the fractional rate of hydration, must be independent of the composition of the cement used in making the paste. A mechanism could be devised to account for this behavior, but the validity of the assumption must be shown by evidence independent of heats of hydration.

Heats of hydration have been used in other ways to obtain information concerning rates of hydration. Steinherz [66] has recently noted that Anderegg and Hubbell [58] oversimplified their calculations on the depth of penetration of water in cement grains by their assumption concerning the shape of their particles. He presents a different approach based upon the measurement of a mean volume and weighted mean diameter of the particles and the assumption that the shape of the particles corresponds more closely to flattened cylinders than to spheres. He used the heat of hydration of the fraction of clinker grains he studied to estimate the amount of cement hydrated, and calculated a depth of penetration. He obtained results similar to those of Anderegg and Hubbell.

The effect to be expected of assuming that the components hydrate at equal fractional rates in cement has been shown by zur Strassen [67]. He considers two different conditions: (1) the rate of diffusion of water through the gel layer is so high that sufficient water is always present in the reaction zone to bring about conversion, or (2) that the reaction is impeded by the rate at which water can diffuse through the gel film being formed. He assumed that the particle size distribution of the original cement could be represented by a Rosin-Rammler size distribution with exponent 1.05. Using Verbeck and Foster's heats of hydration as a measure of the amount of cement hydrated, he calculated the depth of penetration of water into the cement particles and found that the rate followed the diffusion law at times up to 28 days for Type I cement, and times up to 7 days for Type III cements. Thereafter the rate became slower.

He also used the data of Schwiete and Knoblauch [68] on the heats of hydration of pure C_2S and pure C_3S and concluded that for C_2S the rate of reaction is constant up to about 80 percent conversion. For C_3S , after a short period when the rate is linear, the rate follows the diffusion law. He suggests that in cement the expected initial retardation of the hydration of β - C_2S is so

little reflected in the $\frac{V_m}{w_n}$ and $\frac{\Delta H}{w_n}$ ratios that the impression of a fully uniform rate of hydration is given. (V_m is the weight of water required to form an adsorbed layer one molecule thick.)

Nonevaporable Water

The nonevaporable water content (or any other good measure of fixed water) is a measure of the extent of hydration of cement in pastes, just as is the heat of hydration. As yet no extensive analysis concerning kinetics of nonevaporable water data has been made as has been done for heats of hydration. Actually there is little need to do so for it has been shown [51, 69] that there is a linear relationship between the two quantities. Least squares calculations based upon the same model as was used for heats of hydration would certainly give the same results.

The effect of the original water-cement ratio, w_o/c , upon the rate of hydration of cement can be seen by comparing nonevaporable water contents of pastes made from the same cement and cured under the same conditions, except for variations in w_o/c . Unpublished data from this laboratory show that w_o/c has little effect upon the rate of hydration during the first 3 or 4 days. After that, the smaller is w_o/c , the more rapidly the rate of hydration decreases. This effect is consistent with the widely accepted view that the rate of hydration is controlled in some manner by the rate of diffusion of reacting species through the gel.

Recently Taplin [70] has published similar, but more complete data, covering w_o/c ratios from 0.157 to 0.80. These data, figure 3, show the same effects when w_o/c is over 0.5, but in pastes where w_o/c is low, the rate of hydration for a short time is higher than in pastes where w_o/c is high. The slightly greater rate of hydration can probably be accounted for by the temperature of the pastes. The temperature of fresh pastes cast in molds and stored in a constant temperature room will rise several degrees above room temperature during the first 24 hr. The smaller the mass of the paste per gram of cement the greater will be this temperature rise, and the greater will be the effect upon the rate of hydration.

The effect of availability of water immediately after hardening is shown graphically in figure 4. The upper curve shows w_n/c for a paste with $w_o/c=0.6$ cured in contact with water at all times. The lower curve represents two samples of a paste made from the same cement with the same initial w_o/c , but cured under different conditions [71]. The pastes were placed under a bell jar for 48 hr after mixing. After that time, half of the paste was transferred to a sealed jar for the remaining curing time. The other half was wrapped with filter paper and placed in a covered tray in contact with a small amount of water. These two samples continued to hydrate at the same rate even though the total water content per gram of cement w_n/c , of the sample in contact with

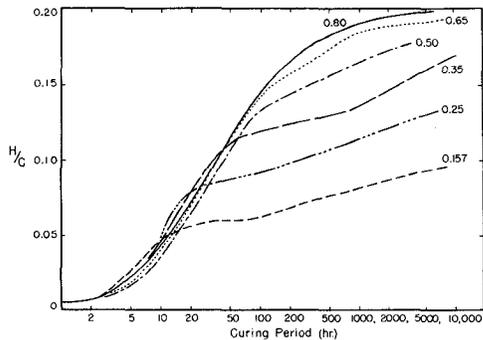


FIGURE 3. Effect of w_n/c upon rate of increase of combined water in portland cement pastes.

water increased to 0.64 at 200 days. The total water content of a sample cured continuously moist to the same nonevaporable water content, $w_n/c=0.20$, should be 0.652 [72]. The nonevaporable water content of 0.20 was attained in less than 28 days in the sample cured continuously moist.

The effect of the lack of an adequate supply of water during the first 2 days upon the rate of hydration was so great that the effect of w_n/c was almost eliminated. Pastes with $w_n/c=0.6$ hydrated only slightly more rapidly than pastes with $w_n/c=0.44$. It is important that the fresh paste has an adequate supply of water continuously if the maximum rate of hydration is to be maintained. Copeland and Bragg observed very little effect due to self-desiccation after the first 2 days, but their curing conditions missed the large effect shown in figure 4.

Specific Surface of Hardened Paste

In their study of the physical properties of hardened portland cement paste, Powers and Brownard [73] observed that the specific surface of hardened paste was a linear function of the nonevaporable water content. The data were not quite precise enough to show that the line definitely passed through the origin, but if there is an intercept, it must be small. Further data, obtained later, confirmed the linear relationship for pastes made from cement with normal composition. In pastes made from cements with high C_2S contents, V_m did not appear to be exactly proportional to w_n .

Rate of Formation of Calcium Hydroxide

A part of the nonevaporable water of hardened pastes is in the calcium hydroxide. Pressler, Brunauer, Kantro, and Weise [18] determined calcium hydroxide in a number of hardened pastes. One series of pastes was made from a cement low in C_2S ; another series was made from a cement high in C_2S . Pastes in each of these series were cured for intervals of time ranging from 1 day to several years. In the series made from the low- C_2S

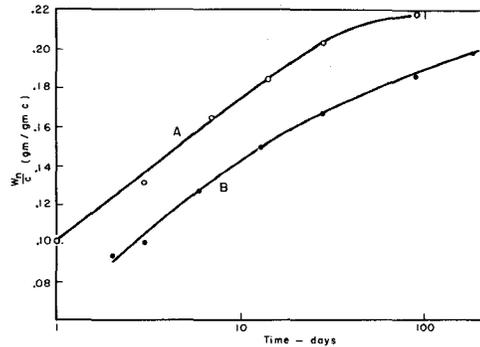


FIGURE 4. Effect of self-desiccation of portland cement pastes upon rate of hydration of the cement. A—cured continuously moist, B—self-desiccated.

cement, the calcium hydroxide produced in hydration was found to be a linear function of the nonevaporable water content. The relationship between the calcium hydroxide and nonevaporable water formed by hydrating the high- C_2S cement was decidedly curvilinear.

Discussion of Rates of Change of Physical Properties

Powers and Brownard [73] pointed out that if V_m is proportional to w_n , then the ratio of colloidal to noncolloidal products should be the same at all stages of hydration. To simplify the handling of their data, they assumed that V_m/w_n was constant. The linear relationship [51] between the heat of hydration and nonevaporable water, and also V_m , seemed to confirm the idea that the same kinds of hydration products were being formed at all stages of hydration. One of the authors (Copeland) pointed out that these linear relationships would be observed if the components in cement hydrated at the same fractional rates. It was recognized that this assumption could not be true during the initial stages of the reaction, but it might be true after the first 24 hr.

Brunauer [74], after a careful examination of heat of hydration data, observed that the heat of hydration of cements high in C_2S was not a linear function of the nonevaporable water. It was pointed out above that V_m/w_n is probably not constant in pastes made from these same cements, so if the assumption is true at all, it is limited to cements comparatively low in C_2S .

The assumption of equal fractional rates of hydration of the components in cement is different from the assumption made in applying the principle of least squares to heat of hydration data. In the latter case it is assumed that the fractional rate of hydration of each component is independent of the composition of the cement. The results of the least squares calculation show that the fractional rates of hydration are not equal to each other, so one or both of these assumptions is incorrect.

The heat of hydration studies exemplify the difficulty of inferring rates of hydration from the rate of change in physical and chemical properties. Different assumptions have been made and rates calculated from the same data: (a) The interpretation of least squares coefficients as the contribution to the heat of hydration by that component requires that the fraction of a component hydrated in a given interval of time be always the same and independent of the composition of the cements and accordingly the composition of the gel. This assumption seems to require that all cements become completely hydrated in the same period of time—that time required by the component with the lowest fractional rate of hydration.

X-Ray Diffraction Analysis

The rates of change in physical and chemical properties of portland cement pastes depend upon the rates of hydration of the components in cement, but the dependence is complex. The rates deduced from observing changes in properties depend upon the assumptions that are made in interpreting the data. The desire to find a method of measuring the rates directly prompted us to make our first attempts at X-ray analysis.

The first published attempt to use X-ray analysis to estimate rates of hydration directly is that of H. F. W. Taylor [10]. He prepared pastes of portland cement and hydrated them for periods of time up to 300 days. An attempt to separate the hydration products from the unhydrated cement with a dense liquid was not completely successful. Nevertheless, he examined Debye-Scherrer patterns of the fractions and concluded that C_3S hydrates much more rapidly in cement pastes than does C_2S , as is shown by his estimates of the weight fraction of C_3S in the silicates in table 7. He estimated that after 14 days curing, at least 50 percent of the cement had hydrated. The ignition loss indicated 61 percent hydration.

TABLE 7. Weight fraction of C_3S in silicates of the unhydrated residue of cement in pastes

Days	0	1	4	7	14	44	300
C_3S	60	50	30	25	20	<10	<5
$C_3S+\beta-C_2S$							

At the same time attempts were being made in this laboratory to use X-rays to analyze portland cement pastes; but only recently has acceptable precision in cement analysis been attained [21]. The method has been applied [75] to the analysis of two series of pastes made from different cements, the first, a cement of average composition, 15754, the second a cement low in C_2S and C_3A , 15669.

The same method of analysis was used for analyzing these pastes as is used for analyzing cements with one exception: the 511 line for silicon (the internal standard) was used instead of the 111 line used in analyzing the cements. The advantage of using this line at smaller spacing in pastes is two-fold: (1) there are no interfering lines from either

(b) The assumption of a uniform depth of penetration of water in cement grains can also fit the data as has been shown by Steinherz [66] and by zur Strassen [67]. The concept of a uniform depth of penetration is consistent with the assumption that the components hydrate at equal fractional rates. It is not supported in detail by direct microscopic examination, for as pointed out above [60, 61], C_2S and some interstitial material hydrate more slowly than C_3S and C_3A . But it is just this effect of the slower hydrating components covering C_3S and C_3A regions and preventing water from getting to them that could account for equal fractional rates of hydration for all components.

the cement or the hydration products for this line, whereas the 111 line is affected to some extent by the broad 3.06 Å line from the tobermorite and the adjacent 100 line from $Ca(OH)_2$; (2) after the pastes have hydrated a few days, the weaker 511 line matches better the strengths of the lines from the cement components. The intensity of this line relative to the 111 line of silicon is given as 0.17 by Swanson and Fuyat [25] and found by us to be 0.171 ± 0.002 for our sample of silicon.

The cement pastes were prepared with $w_0/c = 0.4$ and cured for intervals of time ranging from 2 hr to 6 months. The analyses of the four major phases unhydrated in each paste is given in table 8. The values reported are referred to the original weight of cement in the paste. Nonevaporable water contents are also given.

The degree of hydration of each component in the two series of pastes are compared in figure 5. Time is plotted on a log scale for convenience. Equal fractional rates of hydration for the components of a cement will be shown by coincidence of these curves. A cursory examination of the figures shows that the components of cement do not hydrate at the same fractional rate in either cement.

The degree of hydration of alite is plotted in figure 5(a). The alite in the normal portland cement does not hydrate at the same fractional rate as that in cement 15669, although probably this condition is realized within experimental error after about 28 days.

The degree of hydration of alite in cement 15669 increases more rapidly than in cement 15754, but the actual rate of hydration of alite in cement 15754 is more rapid than in cement 15669, as is shown in figure 6(a).

The results for belite are plotted in figures 5(b) and 6(b). The degree of hydration of belite at any time in cement 15754 is greater than in cement 15669, but again the actual rate of hydration is higher in the cement containing the more belite. The relatively large error in determining the amount of belite in the pastes made from cement 15669 makes the conclusion that the fractional rates are not equal somewhat less certain than for the case of alite.

TABLE 8. Composition of unhydrated residue in portland cement pastes (g component/g cement)

Time hydrated	Type I cement					Type IV cement				
	Alite	Belite	C ₃ A	F _{ss}	$\left(\frac{W_n}{c}\right)_{\frac{1}{2}}$	Alite	Belite	C ₃ A	F _{ss}	$\left(\frac{W_n}{c}\right)_{\frac{1}{2}}$
0	.531	.259	.069	.097	-----	.262	.627	.010	.058	-----
2 hr	.538	.248	.054	.064	.0108	.253	.605	.009	.068	.0000
6 hr	.416	.242	.060	.082	.0258	.194	.553	.007	.084	.0118
1 day	.308	.226	.025	.082	.0881	.105	.618	.003	.060	.0426
2 days	.222	.196	.021	.053	.1145	.063	.515	.004	.051	.0570
3 days	.179	.198	.016	.052	.1204	.052	.600	.005	.051	.0619
4 days	.150	.170	.012	.044	.1276	.054	.536	.007	.053	.0674
7 days	.119	.152	.013	.038	.1438	.041	.477	.006	.052	.0763
14 days	.079	.118	.008	.024	.1614	.031	.518	.001	.056	.0818
28 days	.059	.136	.001	.021	.1748	.025	.282	.000	.036	.1048
3 months	.023	.034	.001	.010	.1890	.006	.220	.000	.024	.1305
6 months	.008	.020	.000	.010	.1947	.004	.185	.000	.004	.1394

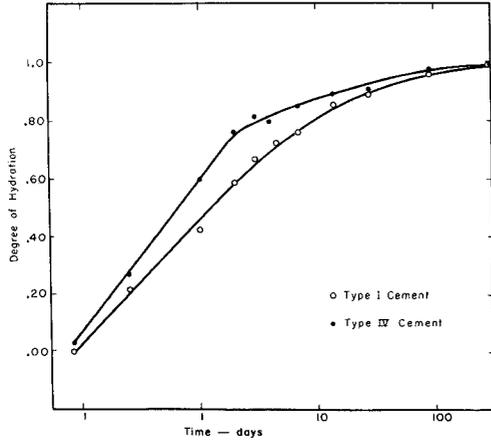


FIGURE 5a. Degree of hydration of alite in the two series of pastes.

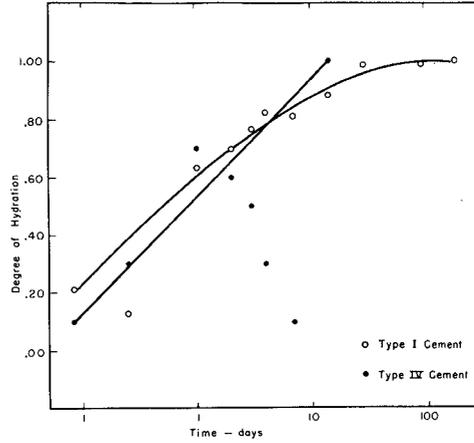


FIGURE 5c. Degree of hydration of tricalcium aluminate in the two series of pastes.

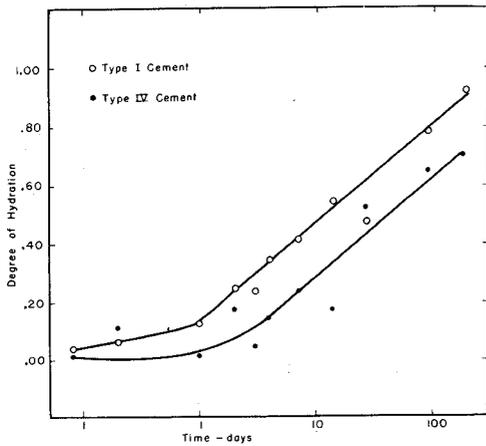


FIGURE 5b. Degree of hydration of belite in the two series of pastes.

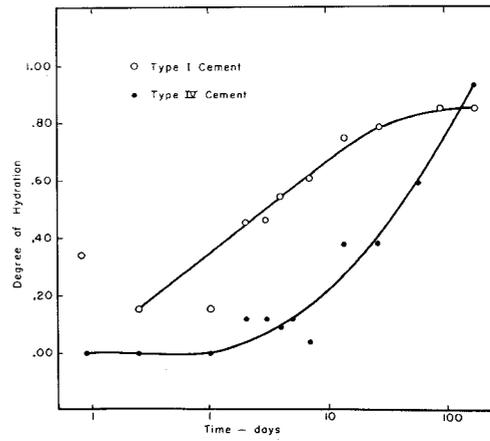


FIGURE 5d. Degree of hydration of ferrite solid solution phase in the two series of pastes.

The degrees of hydration of C_3A in the two cements are the same within experimental error, figure 5(c). There is only 1 percent C_3A in cement 15669, and this small quantity is difficult to determine precisely. The C_3A results for cement 15754 present a consistent trend, and most of the C_3A results on cement 15669 agree with the same trend. The screening of C_3A from water may be responsible for the fact that its absolute rate of

hydration, figure 6(c), is so much lower than the rate of hydration of C_3S .

The greatest difference in the fractional rate of hydration of a component in these two cements is shown by the ferrite solid solution phases, figure 5(d). Perhaps a difference in the composition of the phase is partially responsible, although there is, as yet, no way of knowing how the composition of the ferrite phase affects its rate of hydration in cement. The A/F ratio of the F_{ss} phase in cement 15754 is 1.44. That in cement 15669 is 1.22. It was observed that the strongest ferrite line did not shift in position as hydration progressed; consequently, the composition of the unhydrated residue is the same as that of the original component. The absolute rate of hydration of the ferrite solid solution phase, as well as its fractional rate, is lower than that of any other component.

The X-ray analyses are certainly not as precise as one would like, and probably not as precise as will be obtained in subsequent studies. They are precise enough to show without question that the major phases in portland cement do not hydrate at equal fractional rates; but in the discussion to follow it will be seen that the observed rates of hydration are consistent with the empirical relations that formed the basis for the assumption of equal fractional rates of hydration for all the components.

One of these empirical relations was the proportionality between V_m and w_n , and another the proportionality between the heat of hydration and w_n . Powers and Brownard [73] recognized that V_m might not be strictly proportional to w_n , but assumed proportionality to simplify the treatment of their data. The best straight line through the data does not pass through the origin, but has a small positive intercept on the w_n axis. This

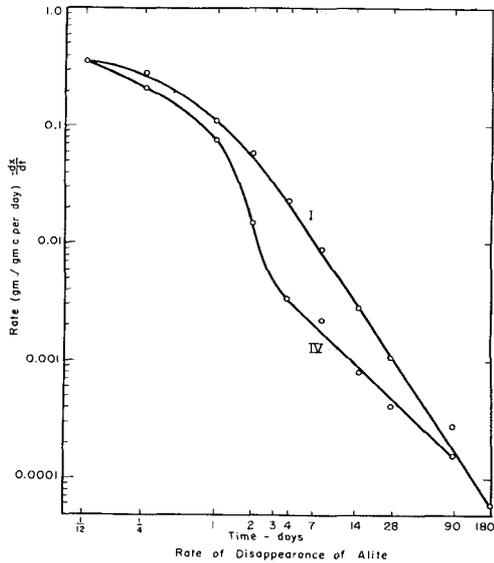


FIGURE 6a. Rates of hydration of alite in Type I and IV cements.

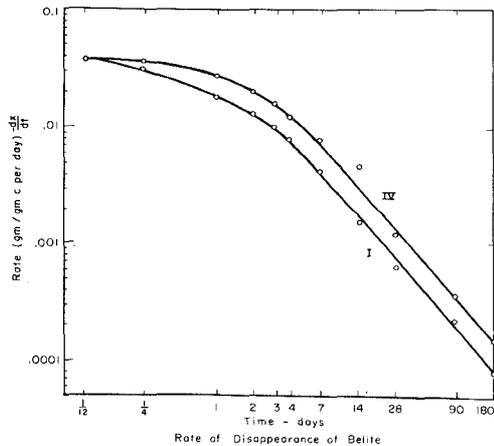


FIGURE 6b. Rates of hydration of belite in Type I and IV cements.

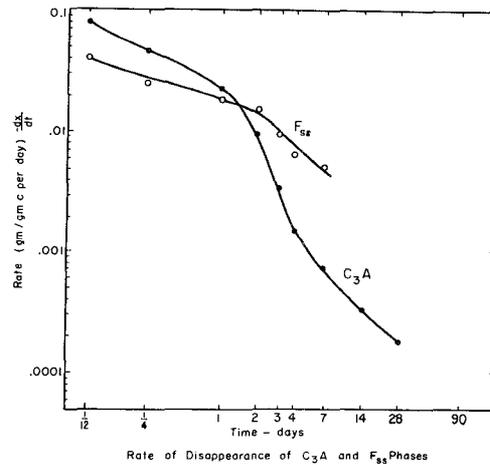


FIGURE 6c. Rates of hydration of tricalcium aluminate and calcium aluminoferrite solid solution in Type I cement.

relationship is discussed in detail in another paper in this symposium.

Calculations were made to compare the X-ray results with the data of Verbeck and Foster [51]. To do this, the least squares coefficients for the heat of hydration of cement at 6½ years were used with amounts of each component that had hydrated in each paste as determined from the X-ray analysis. Similarly, the nonevaporable water and the amount of water adsorbed at 36 percent relative humidity in pastes dried over $Mg(ClO_4)_2 \cdot 2H_2O$ were calculated from the respective least squares coefficients for fully hydrated pastes and the X-ray analyses. The data are plotted in figure 7. The two lines are the lines drawn by Verbeck and Foster in their figures 6-7. The calculated heats of hydration agree very well with the heat of hydration line for Type I cement. The calculated adsorptions are slightly below the line drawn by Verbeck and Foster, but well within the range for Type I and Type III cements as determined by them.

There is no equation relating V_m of a paste to the composition of the cement used in making the paste. Instead of calculating V_m , the water adsorbed at 36 percent relative humidity was calculated and is plotted as a function of the nonevaporable water for pastes dried at the vapor pressure of water at $-78^\circ C$ in figure 8. The data fall on a line with a slight curvature, but if the observed values of w_n had been used, the scatter would have been great enough to obliterate the curvature. A straight line through the origin gives a pretty good fit to the points. The slope of the straight line has the value 0.42. This is a reasonable value since for this cement $V_m/w_n = 0.31$. The best straight line through the data would not pass through the origin, but would give a small positive intercept on the w_n/c axis, as is observed experimentally.

The rates of hydration give satisfactory agreement with the empirical relationships between properties of hardened pastes. Since the major phases hydrate at fractional rates different from each other, one may question the significance of the expression "degree of hydration" as applied to cement and the meaning of terms such as "maturity factor" for pastes, mortars, or concrete. These concepts are important practically, even though they may not be precisely defined theoretically.

The ratio of the heat of hydration of a cement paste to the heat of hydration of a fully hydrated paste from that cement has been used as a measure of the "degree of hydration" of the cement in the paste. The ratio of the nonevaporable water to the maximum nonevaporable water has been used for the same purpose in our laboratories.

The "degree of hydration" of the cement in each of the pastes used in this investigation was calculated by adding together the amounts that had hydrated of the four major phases and dividing by the original cement content of the paste. In figure 9, the values are plotted as a

function of the ratio of the observed w_n/c divided by the maximum w_n/c for the cement. The function is not quite linear, but the ratios give a fairly

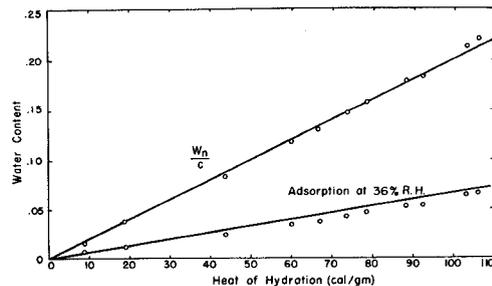


FIGURE 7. Relationship between heat of hydration, nonevaporable water, and water sorption at 36 percent relative humidity.

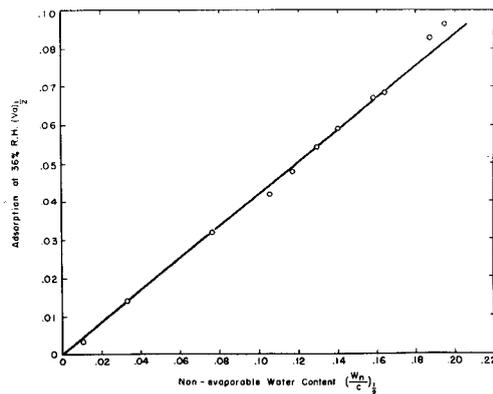


FIGURE 8. Relationship between $\left(\frac{w_n}{c}\right)^{1/2}$ and water sorption at 36 percent relative humidity.

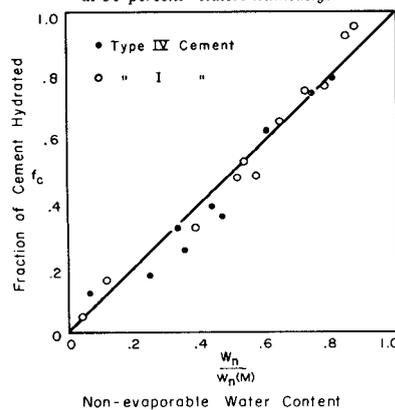


FIGURE 9. Relationship between the degree of hydration of cement and $\left(\frac{w_n}{c}\right)^{1/2}$ in hardened pastes.

reliable estimate of the degree of hydration, particularly when the cement is over 50 percent hydrated.

Because of near linearity between w_n and the heat of hydration, and also w_n and the surface area, any of these may be used as estimates of the degree of hydration of cement.

Analysis of pastes with X-ray diffraction promises to be a most useful tool for investigating rates of hydration of the individual constituents of cement. The preliminary work shows that the fractional rates of hydration of the four major compounds are not equal to each other. Further, the fractional rate of hydration of any chosen component, except possibly C_3A , is not the same, for all cements, but does depend upon the composition of the cement. The reliability of the X-ray analysis has been shown by calculating the heat of hydration, nonevaporable water, and the amount of water adsorbed at 36 percent relative humidity. The relationships between these calculated quantities were the same as has been observed from measurements of these properties on hardened pastes. Although these relationships are probably not exactly linear, they are sufficiently close to being linear that any of them may be used to estimate the "degree of hydration" of the cement in a paste.

Effect of Temperature

The study of the effect of temperature upon the rate of hydration of cement has been limited, for the most part, to the study of the effect of temperature upon either the heat of hydration or the development of strength in concrete. As a result of these studies, several functions have been proposed with which one may estimate the maturity of concrete after curing under prescribed conditions of time and temperature.

Saul [76] defined the maturity of concrete "as its age multiplied by the average temperature above freezing it has maintained," and concluded that concretes of the same mix will have approximately the same strength at the same maturity, whatever combination of time and temperature produce that maturity. Bergstrom [77] concluded that the base temperature should be -10°C instead of the freezing point. Thus the maturity should be calculated from the temperature, θ , and the time, t , by the equation

$$M = \int_0^t (\theta + 10) dt \quad (12)$$

Plowman [78] found that concrete hydrated slowly at -10°C , but that hydration ceased at -11.7°C , and recommended this latter temperature as the base temperature.

Rastrup [79, 80, 81] examined heat of hydration data and assumed that the hydration of cement proceeded very much as most chemical reactions proceed. He concluded that the heat of hydration of a variable temperature process could be compared with the heat of hydration determined

at a predetermined constant temperature, θ_a , by use of the time-temperature function

$$\tau_a = \int_0^t 2^{\left(\frac{\theta - \theta_a}{10}\right)} dt \quad (13)$$

The Saul-Bergstrom function corresponding to Rastrup's use of a time-temperature function is

$$\tau_a = \int_0^t \left(\frac{\theta + 10}{\theta_a + 10}\right) dt \quad (14)$$

Nykänen [82, 83] performed an extensive series of tests to determine a time-temperature function. He observed that a sharp decrease in the rate of hydration of concrete occurred as the temperature dropped below 0°C , and that the composition of the cement affected the time-temperature function. He modified Bergstrom's function to

$$M = \Sigma k(\theta - \theta_b) \Delta t \quad (15)$$

where θ_b is the base temperature at which hydration ceases, and k is a factor the value of which depends upon the temperature of the concrete and the composition of the cement.

For temperatures above 0°C , $k=1$; for temperatures below 0°C , $k=0.2$ to 0.4 , depending upon the composition of the cement. The base temperature, θ_b , ranged between -10 and -15°C , depending upon the composition of the cement.

These time-temperature functions serve for approximate calculations and are probably good enough for practical purposes. McIntosh [84] points out some of the shortcomings of these functions; when they are applied to concrete cured continuously at low temperatures, an estimate based on maturity calculated from -10°C leads to an overestimate at low maturities and an underestimate at high maturities. The error at low maturities can be partly alleviated by calculating maturity from the time the concrete starts to gain strength instead of from the time of mixing. But the time-temperature functions cannot account for the fact that concrete cured initially at low temperature and later at normal temperature can develop a higher compressive strength than concrete cured continuously at a normal temperature. Bernhardt [85] shows that the maximum strength developed in a concrete is not independent of its temperature during curing.

Danielsson [86] points out that if a time-temperature function exists, the composition and morphology of the hydration products of cement must be independent of the temperature at which they were formed, but depend only upon the state of hydration or, what amounts to the same thing, upon the value of the heat of hydration, H . The value of dH/dt would depend upon θ and H alone, and would not depend upon the temperature-time path by which H was reached. Also, values of dH/dt for two different temperatures would have a fixed ratio for the same H . He found, experimentally, that at low H this last condition was

approximately true, but that at high H the condition did not hold. Consequently, a time-temperature function should not be more than an approximation. He also found that dH/dt was not independent of the time-temperature path by

which H was reached. This indicates that the composition and properties of the hydration products depend upon the temperature of the hydration process as do the findings of McIntosh and Bernhardt mentioned above.

III. Energetics of the Hydration of Portland Cement

George Verbeck

Introduction

Numerous studies have been made of the heat evolved when cement reacts with water and various methods of measurement of heat liberation have been used, depending upon the purpose of each investigation.

Where the primary interest is in temperature rise of concrete for use in massive structures, large adiabatic calorimeters have been used, thereby obtaining directly the information desired without assumptions as to the heat capacity of the paste and aggregate components of the concrete or the effect of temperature history of the concrete on the heat actually evolved. However, most studies of the energetics of cement hydration have involved measurements directly on cement paste.

For the study of the early stages of hydration, conduction calorimeters can be used most advantageously. Such devices permit the continuous and accurate recording of the rate of heat liberation from an age of about $\frac{1}{2}$ hr to perhaps 3 days of hydration; this technique is usually supplemented by a simple "bottle" calorimeter for measurements

prior to $\frac{1}{2}$ hr. The magnitude, number, and times of appearance of the heat liberation "peaks" that are observed during this early period assist in the understanding of the various chemical reactions taking place and of the influence of various factors, such as hydration temperature, gypsum content, and accelerators and retarders on the properties of pastes and concrete at both early and later ages.

After the first few days of hydration, the rate of heat liberation becomes very low and direct measurement of heat evolution is difficult. The heat of solution method developed by Woods, Steinour, and Starke [63] is most useful for heat of hydration measurements for hydration periods from about 3 days to any desired age.

It is not the present purpose of this paper to consider studies of the heat evolution during the initial reactions. The discussion to follow will concern the various aspects of cement hydration as revealed by the heat of solution technique for hydration periods from 3 days to 13 yr.

Heat of Hydration at Ages of 3 Days to 13 Years

The data previously published by Verbeck and Foster [51] have been substantially augmented in a continuing study of the heat of hydration characteristics of cements. Data are now available for the heat of hydration characteristics of 27 plant-produced portland cements corresponding to ASTM Types I, II, III, IV, and V cements for hydration periods up to 13 yrs and at 0.40, 0.60, and 0.80 water-cement ratios by weight. For the immediate purpose only the average results obtained for each of the different ASTM types of portland cement will be considered.

Data on the average heats of hydration of the different types of cement for ages from 3 days to 13 yr are presented in table 9 and figure 10. The cement pastes used in these tests were prepared at an initial water-cement ratio of 0.40 by weight and were hydrated in sealed vials until tested. In general, only small increments of heat were evolved between the $6\frac{1}{2}$ and 13 year test ages. For the Type III cements very little, if any, heat was evolved during this period, the -0.1 cal/g observed being well within expected experimental error.

TABLE 9. Average heats of hydration of the different ASTM types of cements

0.40 water-cement ratio; cured at 21° C.

ASTM cement type	No. of cements averaged	Heat of hydration at age indicated, cal/g						
		3 days	7 days	28 days	3 mo.	1 yr	6½ yr	13 yr
I.....	8	60.9	79.2	95.6	103.8	108.6	116.8	118.2
II.....	5	46.9	60.9	79.6	88.1	95.4	98.4	100.7
III.....	3	75.9	90.6	101.6	106.8	114.2	120.6	120.5
IV.....	4	40.9	50.1	65.6	74.4	80.6	85.3	87.3

It should be noted that the average heat of hydration characteristics of the different ASTM types of cement are in keeping with the purposes for which each was designed. At early ages, the average heat of hydration of the Type III cements (high early strength) were significantly greater than the Type I cements (normal) although at 13 yr the heats of hydration are comparable. At all ages through 13 yr, the average heat of hydration of the Type IV cements (low heat) is significantly below the average of the Type II

cements (moderate heat) which in turn evolves less heat at all ages than the Type I (normal) cements.

It should be emphasized that the particular plant-produced cements in this study were specifically selected to include cements possessing a wide range of characteristics within each ASTM type classification. The individual cements within each of the different ASTM types therefore show differences in heat evolution characteristics. The data shown in figure 11 represent the maximum, minimum, and average heats of hydration of the different ASTM types of cement at the various ages. These results show that each cement type has a reasonably separate and distinct range in heat of hydration at the various ages and that, in general, only moderate overlapping occurs between the various types. The greatest range among the cements of any type occurs among the Type I cements, presumably in part because of the greater number of cements included in this classification and in part because the specifications for Type I cement (normal or general purpose portland cement) are purposefully less restrictive than for the other types of cements designed for more specific purposes.

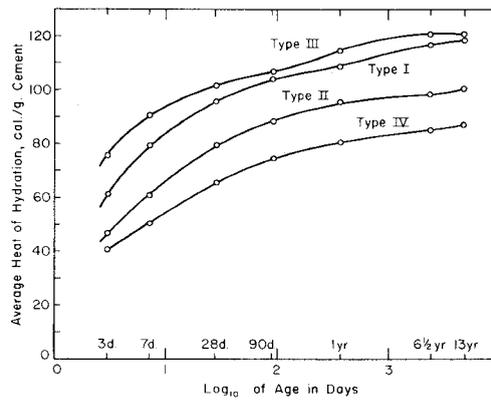


FIGURE 10. Average heats of hydration of different ASTM types of cement at various ages. (0.40 water-cement ratio; cured at 21 °C.)

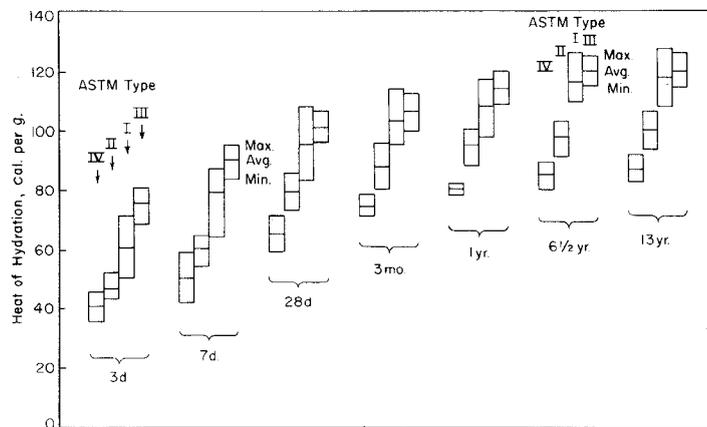


FIGURE 11. Comparison of ranges in heats of hydration of the different ASTM types of cement. (0.40 water-cement ratio; cured at 21 °C.)

Effect of Water-Cement Ratio

The hydration of cement is accompanied by an increase in the volume of solids within the hydrating paste, the volume of the hydration product being greater than the volume of cement from which it was produced. The hydration product steadily increases in volume and fills the capillary void space within the paste, the initial volume of which is established by the original water-cement ratio of the paste. If the capillary void space originally present is small (low water-cement

ratio) this space can become completely filled with hydration products and hydration will cease even though a substantial fraction of the cement remains unhydrated.

Some published information on the influence of water-cement ratio on heat evolution is available in the data of Carlson and Forbrich [87]. These data were limited to a single cement for ages ranging from 3 days to only 28 days. Their data indicate that the original water-cement ratio

has a great influence on the heat of hydration of the cement as shown in table 10. An increase in water-cement ratio from 0.30 to 0.50 increased the heat of hydration by 14 percent at 3 days and 23 percent at 28 days.

The effect of water-cement ratio on heat of hydration might be expected to vary among cements having different hydration characteristics and compositions and in addition to become most pronounced at the later ages when the hydration of cement is more nearly complete. Because of the reported magnitude of the influence of water-cement ratio on heat of hydration and the practical and theoretical significance of such effects, the heat of hydration studies at 0.40 water-cement ratio presented in table 9 were extended to include measurements of pastes having water-cement ratios of 0.60 and 0.80 by weight.

In order to prepare hardened paste specimens having these high water-cement ratios it was necessary to prevent the segregation (bleeding) of water from the pastes while still plastic by slowly rotating the sealed vials containing the paste until setting occurred. To determine whether rotation of the fresh paste altered hydration of the cement as suggested by Carlson and Forbrich, redeterminations were made of the heat evolutions of five different cements at 0.40 water-cement ratio using this rotation technique for comparison with the previously obtained "static" results.

Such comparisons have since been made for hydration periods from 3 days to 6½ yr. The initially rotated vials were hydrated at 23 °C as compared to 21 °C for the earlier static vial tests. The average difference between results obtained by these two methods was ±2.8 cal/g when comparing each cement at each age and averaged -0.2 cal/g for all cements at all test ages. This is considered to be a satisfactory agreement. The rotated vial tests were initiated several years after the static vial tests. Because of this lapse of time, the five cements were resampled and their heats of solution and ignition losses redetermined when the rotated vial tests were begun. The average deviations of the heats of solution and ignition losses of the cements were ±2.1 cal/g and ±0.06 percent respectively. Thus it may be concluded

TABLE 10. Effect of water-cement ratio on heat of hydration

Carlson and Forbrich [87]			
Water-cement ratio, wt.	Heat of hydration at age indicated cal/g		
	3 days	7 days	28 days
0.30	45.7	58.3	74.3
.40	49.2	61.8	82.9
.50	52.3	69.8	91.4

that rotation of the specimen vials and hydration at the slightly elevated temperature did not significantly affect the heat evolutions of the cements. The differences that were observed in heats of hydration can be considered to be due to experimental errors and to differences in the heats of solution of the unhydrated cements caused by differences in the ignition losses of the two samples of each cement used.

Comparisons will now be made of the effect of water-cement ratio on the heat of hydration of cements representing different ASTM types at ages up to 6½ yr. Such data are shown in table 11.

It is readily apparent from the data that heat evolution is significantly influenced by water-cement ratio. During the early stages of hydration, an increase in water-cement ratio from 0.4 to 0.8 had only a slight effect on hydration and heat liberation of the Type IV cements, but produced a significant effect, an increase of 14 percent, in the heat of hydration of the Type III cements at 3 days. The greatest differences in heat of hydration occur at intermediate hydration ages, the exact age for the maximum difference depending upon the type of cement and occurring at earlier ages for the more rapidly hydrating cements. The increase in heat of hydration resulting from an increase in water-cement ratio from 0.4 to 0.8 was a maximum of 19.5 cal/g for the Type III cements at 90 days, and was a maximum of 14.2 cal/g for the Type IV cements at 1 yr, a very substantial effect which should be considered when evaluating cements for mass concrete. These increases in heat evolution exceeded the heat yet to be evolved from those ages to the 13-yr test age for the 0.4 water-cement ratio pastes.

TABLE 11. Effect of water-cement ratio on average heats of hydration of different ASTM types of cements cured at 21 °C

ASTM cement type	No. of cements averaged	Water-cement ratio	Heat of hydration at age indicated, cal/g						
			3 days	7 days	28 days	90 days	1 yr.	6½ yr.	13 yr.
I	8	0.40	60.9	79.2	65.6	103.8	108.6	116.8	118.2
		.60	65.8	87.7	107.1	114.7	120.0	123.1	----
		.80	66.3	89.4	111.6	119.5	122.2	125.0	----
II	5	.40	46.9	60.9	79.6	88.1	95.4	98.4	100.7
		.60	49.6	61.3	83.5	94.8	102.1	104.6	----
		.80	49.3	64.3	84.7	99.2	106.8	106.1	----
III	3	.40	75.9	90.6	101.6	106.8	114.2	120.6	120.5
		.60	86.1	103.6	119.9	124.4	127.3	127.2	----
		.80	86.7	105.0	121.0	126.3	130.0	130.6	----
IV	4	.40	40.9	50.1	65.6	74.4	80.6	85.3	87.3
		.60	43.2	53.5	66.6	78.7	90.4	92.5	----
		.80	41.7	52.8	69.8	82.5	94.8	96.4	----
All	20	.40	55.65	70.52	86.50	94.44	100.54	106.47	107.99
		.60	60.28	76.64	95.02	103.98	110.70	112.97	----
		.80	60.19	78.14	97.92	108.20	114.04	115.40	----

Although at the 6½-yr test age the average heat of hydration of all cements at 0.8 water-cement ratio was 8 percent greater than at 0.4 water-cement ratio, it should be noted that the rate at which heat was evolved at the later ages was greatest for the low water-cement ratio pastes; between the 1- and 6½-yr test ages, the 0.4 water-cement ratio pastes on the average liberated 5.9 cal/g while the 0.8 water-cement ratio pastes liberated only 1.4 cal/g. These differences indicate that the major effect of water-cement ratio in the range of 0.4 to 0.8, is not primarily to limit the maximum degree of hydration and hence heat liberation, but rather to influence the rate of hydration.

Interesting comparisons of the effect of the different water-cement ratios on the corresponding rates of hydration can be made if it is assumed: (1) that the heat of hydration observed at 6½ yr for the 0.8 water-cement ratio paste represents complete hydration of the cement, a very reasonable assumption and, (2) that the rate or degree of hydration of the 0.8 water-cement ratio pastes at the various ages represents hydration of cement as unimpeded by surrounding reaction products as can be expected at rational water-cement ratios. With these assumptions, at each of the test ages and water-cement ratios, the amount of unhydrated cement present can be estimated from the difference between the heat of complete hydration and the heat of hydration at each test age. The fraction of this unhydrated cement which was actually hydrated during the subsequent test interval can be calculated from the increment of heat evolved during the subsequent test interval. Such fractions when compared to the fraction of hydration for the 0.8 water-cement ratio paste for the corresponding age increment yield the relative rate of hydration during the various test age intervals of the 0.4 and 0.6 water-cement ratio pastes compared to the assumed ideal at 0.8 water-cement ratio.

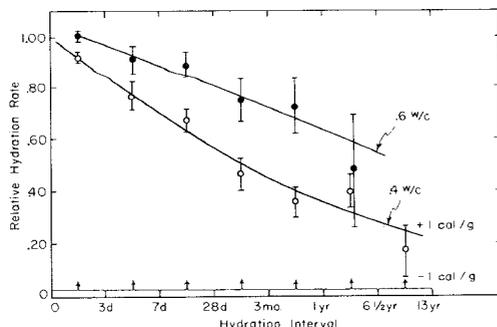


FIGURE 12. Average effect of water-cement ratio on rate of hydration at various ages.

Such comparisons for the average of all 20 cements are made in figure 12 for the various test periods. For presentation an arbitrary time scale has been used and the essentially linear nature of the relationships that appears with the use of this scale is not significant. The influence of a calorimetric error of ± 1.0 cal/g in heat of hydration on the comparisons at the various ages is shown and emphasizes the sensitivity of the calculated relative hydration rate, particularly at the later ages.

It is apparent that the water-cement ratio significantly affects the inherent rate of hydration of the cements. The 0.6 water-cement ratio pastes hydrated more slowly than the 0.8 water-cement ratio pastes and this retardation became more pronounced at the later test ages. During the 1- to 6½-yr test interval to 0.6 water-cement ratio pastes hydrated only 50 to 60 percent as fast as the 0.8 water-cement ratio pastes. The 0.4 water-cement ratio pastes were retarded at all ages to an even greater extent and during the 6½- to 13-yr test interval, hydrated only about 25 percent of the remaining unhydrated cement, whereas in the 0.8 water-cement ratio pastes any unhydrated cement would have been completely hydrated.

The influence of water-cement ratio on rate of hydration appears readily interpretable. The hydration of cement requires the diffusion of water through the hydration products to the surface of the unhydrated cement and the diffusion of reacted material away from the reaction site. The hydration product which is laid down in the liquid surrounding the unhydrated cement serves to retard the diffusion of these materials and hence retard the hydration of the cement. At a particular water-cement ratio the retardation of hydration should increase as hydration proceeds due to the increasing amounts (concentrations) of hydration product present. Such effects can be seen in figure 12. As the original water-cement ratio of the paste is reduced, the concentration of hydration product is increased; this increased concentration further retards the hydration of the cement.

The effects of progressive hydration and of water-cement ratio can be combined to express this concept of retardation due to increasing concentrations of hydration product in a manner similar to the "gel-space" ratio used by Powers [88]. The relative rates of hydration of cement at 0.4 and 0.6 water-cement ratio previously shown in figure 12 at the various test intervals are compared in figure 13 with their corresponding average gel-space ratios. It can be seen that this concept approximately expresses the retarding effects observed. A second approximation to the relationship could be made by a correction for the moderate retardation that must have occurred at the later stages of hydration of the 0.8 water-cement ratio pastes for which a maximum gel-space ratio of 0.59 is calculated.

It should be kept in mind that although the gel-space ratio may approximately express the concentration of hydration gel for any particular cement or average of cements, it would not be ex-

pected to quantitatively express the gel concentrations when comparing different cements since the amount of gel produced per unit of heat evolved depends to some degree on the composition of the cement. Additional empirical correlations between the relative hydration rates and other fundamental parameters of the hydrated paste can also be obtained.

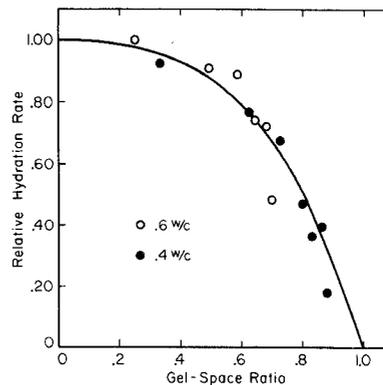


FIGURE 13. Average effect of gel-space ratio on rate of hydration of pastes of different water-cement ratios and ages from 3 days to 13 yr.

Effect of Temperature

The information available on the influence of temperature on degree and rate of hydration is not as extensive as desired, particularly as regards the higher water-cement ratios for extended hydration periods. However, the available data very satisfactorily reveal the effect of a wide range of temperatures on hydration rate of pastes of 0.4 water-cement ratio.

Heat of hydration data obtained by Carlson and Forbrich [87] using a "standard" cement at 0.4 water-cement ratio cured at temperatures of 4.4, 23.3, and 40 °C for ages from 3 to 90 days are shown in figure 14. The large increase in heat evolution during the early stages of hydration produced by increase in temperature is evident. It would appear from these data, for pastes of 0.4 water-cement ratio, that the temperature affects only the rate of hydration, the results obtained at the 28 and 90 day test periods suggesting equal ultimate heats of hydration at some later age.

It is interesting to quantitatively compare the early rates of hydration at the different temperatures; these rates may be taken as relative to the heat of hydration at one day and estimated from the curves in figure 14. For most chemical reactions the dependence of the kinetic reaction rate, K , upon reaction temperature T°_K , is expressed by the Arrhenius equation, $\ln K = -\frac{E}{RT} + \text{const.}$, in which E represents the "activation energy" and R is the gas constant. As may be noted in figure 14, the observed relationship between $\log K$ and $1/T$ is essentially linear and hence the relative reaction rates observed at the different temperatures are related in the manner required by the Arrhenius equation.

Additional information of a somewhat different nature is available from the studies in this laboratory [52] over the temperature range of 4.4 to

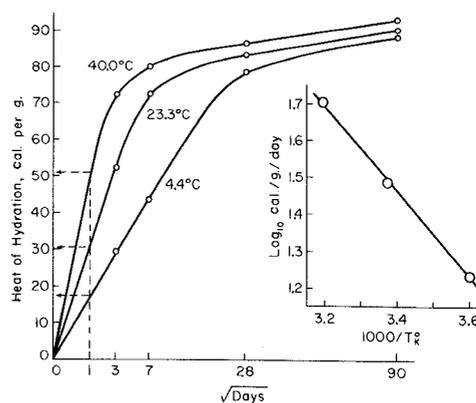


FIGURE 14. Effect of temperature on hydration of cement. Data from Carlson and Forbrich [87].

110 °C. Two different cements, ASTM Type I and Type IV, were hydrated at the preselected temperatures for the lengths of time required to produce approximately the same degree of hydration in the pastes of each cement, as estimated from heat of hydration and nonevaporable water measurements. The relative rates of hydration at the different temperatures are inversely related to the time required at each temperature to reach the equivalent degree of hydration. Such data are shown in table 12. Although the degrees of hydration attained for the various tests of each cement are not identical, they are believed to be sufficiently alike to permit the direct calculation of rate of hydration as shown in the table. Evaluation of these results on the basis of the Arrhenius equation is shown in figure 15. It may be observed

that an acceptably linear relationship is obtained for each cement over this wide temperature range. The relationship for the Carlson and Forbrich data shown in figure 14 is reproduced in figure 15. It is important to note that all three of the linear relationships obtained are essentially parallel, indicating that these cements do have the same "activation energy" although they have a very wide range in calculated potential compositions and inherent rates of heat liberation.

TABLE 12. Effect of temperature, on rate of hydration, of cement.

0.40 water-cement ratio.						
ASTM cement type	Hydration temp. °C	Hydration period, days	Heat of hydration cal/g	Hydration rate cal/g/day	Log ₁₀ hydration rate	$\frac{1}{T^{\circ}K}$
I	110.0	1	92.35	92.35	1.965	0.00261
	71.0	2	98.02	49.01	1.690	.00290
	43.4	3	93.05	31.02	1.492	.00316
	21.0	9	96.43	10.71	1.030	.00340
	4.4	11	83.22	7.57	0.879	.00360
IV	110.0	1	56.51	56.51	1.752	0.00261
	71.0	2	56.49	28.24	1.451	.00290
	43.4	3	49.44	16.46	1.216	.00316
	21.0	8	47.48	5.93	0.773	.00340
	4.4	11	41.89	3.81	0.581	.00360

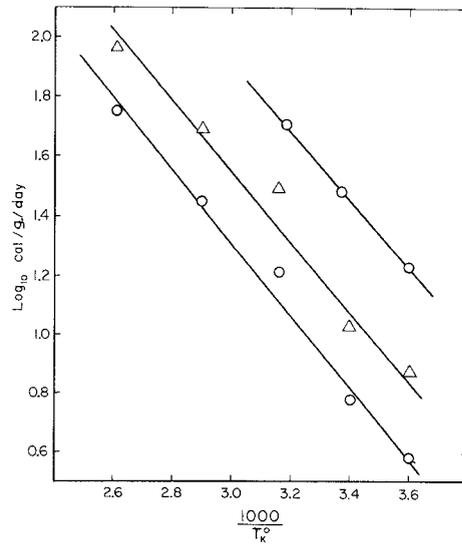


FIGURE 15. Relationship of log "reaction rate" and $1/T^{\circ}K$ for cements over temperature range from 4.4 to 100° C.

Effect of Moisture Content—Heats of Adsorption and Wetting

The heat of hydration of a cement, as normally measured, represents the total heat evolution that is usually of direct practical interest. However, this heat consists of two separate factors representing the energy change due to chemical reactions and the heat of the simultaneous adsorption of water on the colloidal hydration product. For a well hydrated cement, perhaps 80 percent of the energy released is due directly to the chemical reactions, i.e., the formation of "hydrates," while 20 percent of the energy represents the "wetting" of the large surface area of this colloidal product, this "wetting," of course, being necessary for the continuation of hydration. The relative amounts of these energies depend to some degree upon the chemical composition of the cement. The heat of adsorption of the hydration product is of considerable practical and theoretical interest.

In its most practical aspect, it appeared possible that unevaluated heat of adsorption effects could influence the heat of hydration measurements of cement with resulting errors in estimation of the degree of hydration of the cement from such data. Copeland and Bragg [71] have shown that hydrating past specimens, sealed to prevent uptake of water, become "self desiccated," the relative humidity within such pastes decreasing as the cement hydrates, with the decrease being most pronounced for pastes of low water-cement ratio.

The lowest relative humidity they observed was 94 percent in a paste of 0.44 water-cement ratio at 1 yr. It would appear probable that pastes of 0.40 water-cement ratio cured 6½ or 13 yr might have relative humidities significantly below this value. In addition to self desiccation, a cement paste can lose further increments of moisture during the crushing, grinding, screening, and weighing procedures required in the preparation of paste samples for heat of solution measurements. These considerations suggest that the relative humidity of 0.40 water-cement ratio pastes at the later test ages, such as shown in table 9, might be as low as 80 or 90 percent. The heat of solution of a paste at 80 percent relative humidity is greater than that of a more nearly saturated paste, the additional increment representing the heat of wetting of the surface from perhaps 80 to 100 percent relative humidity. This greater heat of solution of the hydrated but partially dried paste reduces the apparent heat of hydration of the paste. Powers and Brownyard [69] report the heat of wetting of paste equilibrated by adsorption to 80 percent relative humidity to be as great as about 6 to 7 cal/g cement. An "error" of this magnitude in determination of the heat of hydration of low water-cement ratio pastes at later ages if neglected could introduce a significant error in estimation of degree of hydration of the cement from such data.

The heat of wetting was determined at the 13-yr test age for all pastes of 0.40 water-cement ratio reported in table 9. In addition to the customary determination of the heat of solution of the partially desiccated paste, a sample of the paste was wetted and equilibrated and then introduced into the calorimeter using a specially designed capsule for heat of solution measurements. For the cements of 0.40 water-cement ratio at the 13-yr test age, the average heat of wetting was determined to be only 0.9 cal/g cement. Since even smaller heats of wetting could be anticipated in tests at higher water-cement ratio and earlier ages further use of this special technique was not considered necessary.

In addition, the heats of adsorption and desorption of hydrated cement paste are of considerable theoretical interest. Unfortunately, only a modest amount of information is available on the heat of adsorption. The data obtained by Powers and Brownyard [69] regarding heat of adsorption of hydrated pastes is most instructive and also serves to reveal the need for additional information.

These data, shown in figure 16, were obtained by the heat of solution method for pastes dried to the nonevaporable water state (magnesium perchlorate) and then equilibrated at various relative vapor pressures. It can be observed that the relationships obtained for these two cements are similar and that each relationship appears to consist of two discrete portions each of which is a linear function of water content. These data imply that two different classes of water are sorbed on hydrated paste, the types of water having distinctly different "heats of adsorption" but yet each type having a constant differential heat of adsorption over the entire range of water contents in which it operates. In addition, there appears to be a rather abrupt discontinuity in the relationships observed, which would not be anticipated if only simple surface adsorption were involved. It should be further noted that the total heat of adsorption, taken as the difference between the heat of solution of the pastes at the nonevaporable water state and the heat of solution extrapolated from the observed relationships to the total water content at 100 percent relative humidity, is approximately 30.4 cal/g for cement 16186 and 30.8 and 30.9 cal/g for cement 16189, A, B, and C rounds respectively. This apparent equality in the total heat of adsorption of these

pastes is of considerable significance since the degrees of hydration of the two pastes were materially different; the original water-cement ratios of the pastes being the same.

These observations of the "heat of adsorption," are analogous to recent observations in this laboratory of the drying shrinkage of cement pastes in the absence of carbonation. These shrinkage studies of hydrated pastes yield similar implications; the shrinkage-moisture content relationships of pastes between 100 and 0 percent relative humidity consistently demonstrated that there are two distinctly different types of water desorbed, each type of water having a constant shrinkage-water loss ratio over its operative range.

It is well established that various hydrated compounds in cement, the calcium aluminates and calcium sulfoaluminates, at least, will dehydrate and lose chemically combined water in this general range of relative vapor pressures. These results indicate the importance of the energy changes which accompany adsorption and desorption, particularly in their contribution to a full understanding of the volume changes of cement paste.

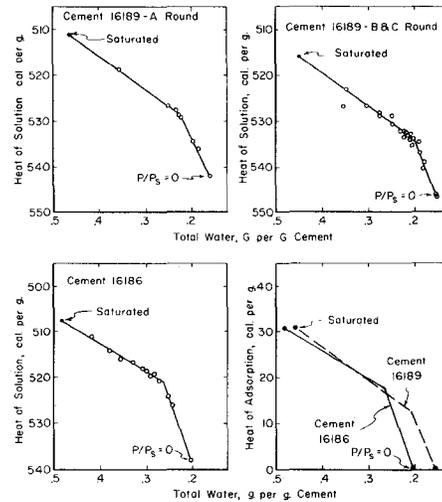


FIGURE 16. Heats of solution and adsorption of pastes containing various amounts of adsorbed water. Data from Powers and Brownyard [69].

Intrinsic Characteristics of Cement

It is apparent from the data presented in figures 10 and 11, and from numerous other studies of the heat of hydration of cement, that cements differ significantly in heat evolution characteristics, both as to total ultimate heat evolution and the rate at which this heat is liberated. It is believed that the causes of these different heat evolution characteristics in cements are understood, at least to a semiquantitative degree. Factors causing these differences include the composition of the cement,

the fineness of the cement, partial prehydration of cement, glass content, and alkali and gypsum contents. The influence of some of these factors will now be discussed.

Cement Composition

As a first approximation it is apparent that the heat liberated by a cement during complete hydration is approximately the sum of the heats of com-

TABLE 13. Heats of complete hydration of individual compounds

Anhydrous compound	Product	Heat of hydration, cal/g anhydrous compounds	
C ₃ S	C ₃ S+3H ₂ O	120	Lerch & Bogue [89]
C ₃ S	C ₃ S+2H ₂ O	62	Lerch & Bogue [89]
C ₃ A	C ₃ A·6H ₂ O	207	Lerch & Bogue [89]
C ₃ A	C ₃ A·6H ₂ O	214	Thorvaldson, Brown & Peaker [94]
C ₃ A	C ₃ A·8H ₂ O	235	" " " "
C ₃ A	C ₃ A·10·2H ₂ O	251	" " " "
C ₃ A	C ₃ A·11·6H ₂ O	261	" " " "
C ₃ A	C ₃ A·3CaSO ₄ ·32H ₂ O	347	Lerch & Bogue [89]
C ₄ AF		100	Lerch & Bogue [89]
CaO	Ca(OH) ₂	278.9	Thorvaldson, Brown & Peaker [95]

plete hydration of the individual compounds present or calculated to be present in the cement. The individual chemical compounds have significantly different heats of complete hydration as is shown in table 13. The heat evolved by C₃S is only 62 cal/g whereas the heat of hydration of C₃A is at least 207 cal/g, with C₃S and C₄AF having intermediate values. Cements having high C₃A (and C₃S) contents have significantly higher heats of complete hydration than cements low in these constituents and high in C₂S content.

The various compounds differ not only in heat of complete hydration but also in rate at which they hydrate; it has been generally observed that those compounds with high heats of complete hydration, C₃A and C₃S, also hydrate much more rapidly than C₂S, which has a low heat of hydration.

It is of interest to interpret the observed heats of hydration of different cements at various periods of hydration in terms of the composition of the cements. Various investigators [63, 65, 51] have used the method of least squares for this purpose. The coefficients obtained by such least squares analyses need to be interpreted with considerable care because of the several assumptions that are involved. Least squares analyses can be performed on the basis either of calculated compound composition or of oxide analysis. Since the calculated compound composition can be expressed by linear relationships with the oxide composition, least squares analyses on both bases are mathematically equivalent. Therefore, a least squares analysis in terms of calculated compound composition that produces heat coefficients that correspond to the heats of hydration of the individual compounds, and that collectively will closely reproduce the heats of hydration of the cements, does not require that the assumed or calculated compounds in reality exist. In addition, the least squares method assumes that the various compounds hydrate independently as has been discussed in the second main section of this paper.

Since it is not expected that the inherent hydration characteristics for any particular compound or phase would be identical in the various cements because of differences in actual composition and grain size of that phase among the different cements, the coefficients obtained for the various compounds will represent only the average coefficient for that compound among the different cements.

The results of least squares analyses of heat of hydration results at various ages obtained by Woods, Steinour, and Starke [63] with laboratory prepared cements are shown in table 14 and are compared with the heats of complete hydration for the pure compounds as reported by Lerch and Bogue [89]. The coefficients obtained for the compounds at the later ages acceptably correspond to the heats of complete hydration of the individual compounds. In addition, the coefficients obtained at the early ages conform qualitatively, at least, to the intrinsic reactivity of the individual compounds in that C₃S and C₃A react rapidly whereas C₂S reacts slowly. Therefore, the heat of hydration coefficients obtained by least squares analyses appear to have a real significance in relation to both the rate of hydration and the total heat evolutions of the individual compounds. These cements were laboratory ground with a constant amount of gypsum from laboratory prepared clinker having a very low alkali content.

TABLE 14. Results of least squares analysis of heats of hydration of cements

Com- pound	Least squares coefficients. Heats of hydration, cal/g compound						Heats of complete hydration, (Lerch & Bogue [89]) cal/g compound
	From Woods, Steinour, and Starke [63, 64]						
	3 days	7 days	28 days	3 mo	6 mo	1 yr	
C ₃ S	98	110	114	122	121	136	120
C ₂ S	19	18	44	55	53	62	62
C ₃ A	170	188	202	188	218	200	207
C ₄ AF	29	43	48	47	73	30	100

The least squares analyses previously reported by Verbeck and Foster [51] for commercially prepared cements at 0.40 water-cement ratio hydrated up to 6½ yr have now been extended to include analyses of results obtained after 13 yr of hydration and new results obtained for pastes of 0.60 and 0.80 water-cement ratio. Results obtained at 0.40 water-cement ratio are shown in table 15 and are compared with the data of Lerch and Bogue [89] for the heats of complete hydration of the pure compounds. The heat coefficients obtained for C₃S, C₂S, and C₄AF with these commercial cements are in close agreement with the reported heats for complete hydration. However, the coefficient obtained for C₃A is considerably

TABLE 15. Results of least squares analysis of heats of hydration of cements

Compound	Least squares coefficients, heat of hydration at water-cement ratio and age indicated							Heats of complete hydration (Lerch & Bogue [89]) cal/g compound
	cal/g compound—0.40 W/C and 21 °C.							
	3 day	7 day	28 day	90 day	1 yr.	6½ yr.	13 yr.	
C ₃ S	58	53	30	104	117	117	122	120
C ₂ S	12	10	25	42	54	53	59	62
C ₃ A	212	372	329	311	279	328	324	207
C ₄ AF	69	118	118	98	90	111	102	100

greater than that obtained for the formation of C₃AH₆, 207 cal/g, but approximates the heat of hydration of C₃A, 347 cal/g of C₃A, to form C₃A·3CaSO₄·32H₂O, as reported by Lerch and Bogue.

Analyses by least squares can be based on various models and many have been evaluated. The coefficients shown in table 15 were derived on the following assumption:

$$(1) H_t = a (\% C_3S) + b (\% C_2S) + c (\% C_3A) + d (\% C_4AF)$$

in which H_t = heat of hydration at a given age.

However, and particularly in view of the high coefficient that was obtained for C₃A, additional postulations were made as follows:

- (2) Formation of C₃A·CaSO₄·12H₂O
 $H_t = a (\% C_3S) + b (\% C_2S) + c (\% C_3A - 1.125\% SO_3) + d (\% C_4AF) + e (\% SO_3)$ and
- (3) Formation of C₃A·3CaSO₄·32H₂O
 $H_t = a (\% C_3S) + b (\% C_2S) + c (\% C_3A - 3.375\% SO_3) + d (\% C_4AF) + e (\% SO_3)$

The results of such analyses are shown in table 16,

TABLE 16. Results of least squares analyses of heat of hydration data including the formation of calcium sulfoaluminates

Compound	Least squares coefficients—cal/g compound, 0.5 W/C—1 yr		
	eq (1)	eq (2)	eq (3)
C ₃ S	124	128	125
C ₂ S	76	91	81
C ₃ A	325	396	384
SO ₃		-602	672
C ₄ AF	95	152	121

where it may be noted that these additional assumptions did not assist in revealing further details of the nature of the hydration reactions and the accompanying heat evolutions.

Of the various assumptions evaluated, perhaps the most instructive concerned the role of clinker alkalis on heat evolution. Newkirk [90] has reported that K₂O and Na₂O in portland cement

clinker form the compounds KC₂₃S₁₂ and NC₈A₃. Least squares analysis based on calculated potential compound compositions, including the formation of these alkali substituted compounds produced the coefficients shown in table 17.

TABLE 17. Comparison of least squares coefficients for alkali substituted compounds at early and late ages

Compound	Least squares coefficients, cal/g compound, 0.5 W/C—16 cements		
	3 days	1 yr	6½ yr
C ₃ S	92	130	134
C ₂ S	22	73	76
KC ₂₃ S ₁₂	57	62	74
C ₃ A	127	310	325
NC ₈ A ₃	4	322	288
C ₄ AF	-17	88	71

Comparisons of the coefficients obtained at 1 yr and at 6½ yr for C₃S and KC₂₃S₁₂ or for C₃A and NC₈A₃ suggest that at complete hydration the heat contributions of the presumed alkali substituted compounds are similar to the heat contributions of the unsubstituted compounds. However, at the age of 3 days the heat contributions of the substituted and unsubstituted compounds appear significantly different, suggesting a significant effect of alkalis, directly or indirectly at early ages.

Further elucidation of the nature of the reactions by least squares studies based on such relatively direct postulations may not be possible; Lerch [91] has shown that heat evolution depends in part and in a rather complicated way upon the mutual effects of C₃A content, fineness, alkali content, and gypsum content of the cement.

There is evidence indicating that the heat contribution coefficients of the individual compounds derived by the method of least squares have an additional significance. The amount of combined water (the nonevaporable water content) in a hydrated cement paste, can be used as a further index to the degree of hydration of cement. The nonevaporable water content, w_n/c , was determined for all the cements at all test ages and for all water-cement ratios, simultaneously with the heat of hydration measurements previously discussed. Least squares analysis of this information in a manner similar to that used with the heat of hydration results is most instructive. The number of moles of water associated with each mole of the clinker compounds can be derived by such analysis and compared with the heat contributions derived for the same test conditions, as is shown in figure 17. These relationships reveal that the derived coefficients for heat contributions and for moles of combined water for both C₃S and C₂S approximate as a limit a point closely corresponding to the ultimate heat of hydration and water content of the products C₃S+3H₂O and C₂S+2H₂O respectively. For less than complete hydration, it can be observed that both the derived heat coefficients and the combined water coefficients indicate

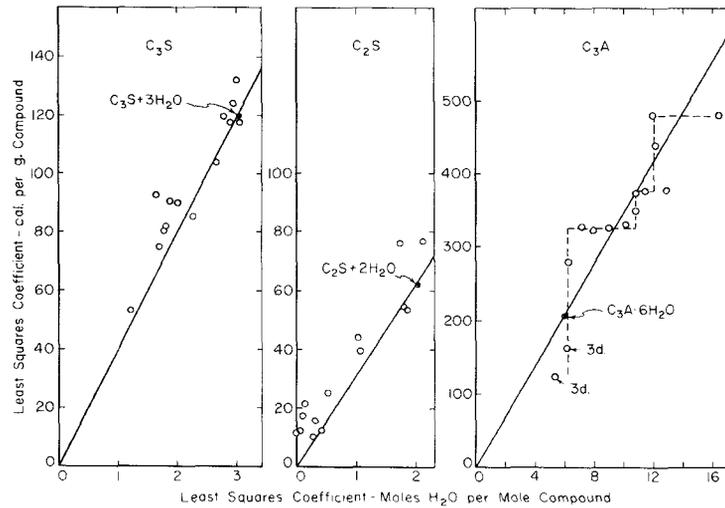


FIGURE 17. Comparison of least squares coefficients for heat evolution and combined water of C_3S , C_2S , and C_3A .

approximately the same degree of hydration of the compound, in further support of the significance of heat contributions derived by least squares.

The relationship obtained for C_3A indicates that both the derived heat contribution and combined water for this compound exceed the ultimate heat of hydration and water content of $C_3A \cdot 6H_2O$ except at the earliest test age, 3 days. The relationship obtained suggests an irregular relationship (dashed line) corresponding to hydrates higher than $C_3A \cdot 6H_2O$. More detailed study suggests that higher hydrates are formed which slowly reconvert to lower hydrates as the cement continues to hydrate with time. Such a relationship as shown in figure 18 supports the

possibility of slow secondary changes in the C_3A hydrated product, where it can be seen that both the heat coefficients and combined water coefficients reflect similar changes with time.

It is believed that the degree to which the derived heat coefficients and combined water coefficients permit equal estimates of the degree of hydration and of observed secondary changes serves to support the significance of such derived coefficients. However, there are several other factors which can contribute to or alter heat evolution and which are not normally included in least square analysis. Cement constituents such as free calcium oxide and magnesium oxide will hydrate with evolutions of heat that usually are not considered in least squares analysis. In addition, the glass content of the clinker and the ignition loss of the original cement, which represents a degree of partial prehydration and carbonation of the clinker minerals have not usually been considered but do have a significant effect on the heat of solution of the original cement.

The effect of glass content on heat of solution and heat of hydration as reported by Lerch [92, 93] and shown in table 18 is most interesting. The average increase in heat of hydration observed with an increase in glass content is 7.9 cal/g at the 28-day test age. This increase corresponds within experimental error with the 6.8 cal/g increase in heat of solution of the original cement. These data suggest that the observed increase in heat of hydration is due solely to the increased energy content of the clinker with an increase in glass content and that although the glass phase during hydration eventually attains the same state as the corresponding crystalline phase, the glass phase hydrates less rapidly than the crystalline phase.

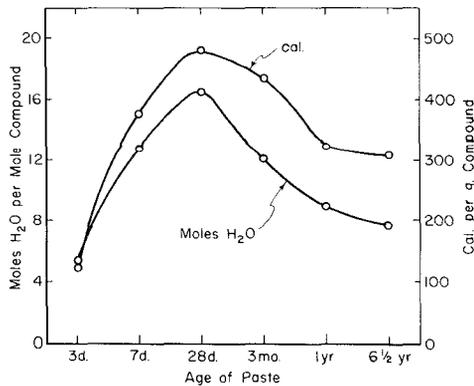


FIGURE 18. Least squares coefficients for heat evolution and combined water of C_3A at various ages. 0.80 water-cement ratio pastes.

TABLE 18. Effect of glass content on heat of solution and heat of hydration

Orig. cement	Average heat of solution [92] cal/g			Average heat of hydration [93] cal/g		
	3 days	7 days	28 days	3 days	7 days	28 days
638.8	564.2	552.4	544.9	74.6	86.4	93.9
641.9	567.2	555.0	546.0	74.7	86.9	95.9
645.6	570.9	554.7	543.8	74.7	90.9	101.8

The heats of solution of the original cements and hence the observed heats of hydration also depend significantly upon the partial prehydration of the original cement. Studies at this laboratory [52] have shown that the ignition loss of a cement represents loss of chemically combined water and CO₂ and loss of evaporable water, the latter presumably associated with the calcium sulfate in the cement. The amounts of CO₂ and of these different classes of water vary appreciably among cements and as shown in table 19 signifi-

TABLE 19. Range and analysis of losses on ignition and the corresponding corrections to heats of solution of 27 commercial cements

Range	Ignition loss	Combined water	CO ₂	Evaporable water	Correction to heat of solution of original cement, cal/g
Maximum	1.90	1.11	0.33	0.49	+9.5
Average	0.82	0.45	.17	.19	+3.5
Minimum	.35	.13	.08	.00	+0.4

cantly affect the heats of solution of the cements and hence the observed heats of hydration. An

approximate correction can be made to the heats of solution of cements from measurements of the CO₂ content and the content and distribution of the water within the cement assuming that the combined water and CO₂ have reacted with calcium oxide and that the original cement should have an evaporable water content corresponding to the dihydrate of the CaSO₄ in the cement. Approximate corrections calculated on this basis for 26 cements are significant in amount and variability as shown in table 19.

Results of a least squares analysis based on a selected group of these cements in which the correction for heats of solution of the original cements ranged from +0.7 to +4.9 are compared in table

TABLE 20. Results of least squares analyses based on uncorrected and corrected heats of solution of original cements

Basis of analysis	Least squares coefficients heats of hydration, cal/g compound 0.80 water-cement ratio, 6 1/2 yr			
	C ₃ S	C ₂ S	C ₃ A	C ₄ AF
Uncorrected heats of hydration	132	77	321	73
Corrected heats of hydration	137	81	325	62

20, with results of a similar analysis based on the uncorrected heats of solution.

It is observed that the coefficients for C₃S, C₂S, and C₃A were higher for the corrected heat analysis, indicating that the chemically combined water and CO₂ do not react primarily with either the C₃S or C₃A component of the cement. Other studies indicate some relation between the amounts of free CaO and alkali in the various cements and the amounts of combined water and CO₂ which they contain.

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**Bulletins Published by the
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100. **"List of Published Bulletins and Papers of the Research Department,"** May, 1959 (Also lists earlier research papers of the Portland Cement Association).
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