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PREDICTABILITY GAP BETWEEN SCIENCE AND TECHNOLOGY OF CEMENTS: I. CHARACTERIZATION OF HYDRAULIC CEMENTS

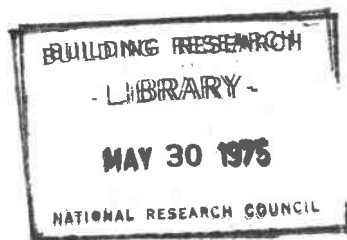
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by
P. J. Sereda and V. S. Ramachandran

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**L'ECART ENTRE LA SCIENCE ET LA TECHNOLOGIE EN CE
QUI CONCERNE LA PREDICTION DE L'EFFICACITE DES CEMENTS
I. LA CARACTERISATION DES CEMENTS**

SOMMAIRE

On distingue traditionnellement, en parlant de publications scientifiques, deux grandes catégories: les rapports de recherches originales et les exposés de synthèse sur les domaines de la recherche. Dans un cas comme dans l'autre il s'agit d'hommes de science communiquant avec d'autres hommes de science. Or si la science doit servir la technologie, il faut qu'il y ait communication ou transfert d'information efficace entre les deux. Nombreux sont ceux qui considèrent que ce transfert n'est pas très actif actuellement et que c'est là une des raisons de la difficulté que ressent la technologie à prédire l'efficacité des matériaux. Les auteurs envisagent la publication d'une série d'articles sur le besoin de faire un examen critique des exigences que comporte l'amélioration, grâce aux recherches futures, de ce genre de prédiction appliquée à la technologie des ciments. Le premier article de cette série aborde les problèmes de la caractérisation des ciments hydrauliques en fonction de leur réactivité, du rôle des adjuvants, de l'aire superficielle, de la modification des cristaux et de la composition chimique.



Predictability Gap Between Science and Technology of Cements: I, Characterization of Hydraulic Cements

P. J. SEREDA and V. S. RAMACHANDRAN

Division of Building Research, National Research Council of Canada, Ottawa, Canada

Scientific publications fall, traditionally, into two general categories: reports of original research and state-of-the-art reviews of areas of research. In both types, scientists communicate with other scientists. If science is to serve technology, however, there must be effective communication or transfer of information between the scientist and the technologist. At present, many believe that such transfer is not very effective and that this ineffectiveness contributes to the difficulty the technologist experiences in predicting the performance of materials. The authors plan a series of papers that will provide a critical assessment of what will be required if research is to improve predictability in the technology of cements. Part I discusses problems involved in the characterization of hydraulic cements in terms of reactivity, role of admixtures, surface area, crystal modification, and chemical composition.

I. Introduction

A PREDICTABILITY gap is said to exist when the degree of understanding of the nature of a material and the processes involving its formation and deterioration are inadequate to permit prediction of the effect of any change in the system. In such a situation any new material or modification of an old one must be tested to establish its acceptance for each specific use. If the science of materials is to serve technology adequately it must provide the basis for predicting the behavior of materials under all conditions of service. In many instances science has been able to explain the behavior of materials, but it has not yet been able to do so adequately for cements. The subject is complicated and knowledge as yet incomplete, so that treatment of the field appears to be hidden behind a facade of words.

Fifty-five years ago at the First International Symposium on the Chemistry of Cements, Henry Le Chatelier made the following statement "... it used to be said that bodies react because they have affinity for each other. The actual explanation of the hardening of cements is of an analogous kind. People evade defining what they call a colloid, but they seem to take the word in the sense of a body capable of hardening. And then the explanation comes down to this: cements harden because they have the property of hardening." This paper examines to what degree the situation described by Le Chatelier exists today and focuses attention on questions that still need to be answered if technology is to develop rapidly and in an orderly manner.

Cements occupy a very important basic position in the world economy.¹ Consumption of both cement and iron has been used as an index of the state of the technological development of a country. The term "cements" includes many inorganic cements, but this paper will deal only with plaster, lime, and portland cement because of their relative economic importance and close interrelation.

Plaster is one of the oldest building materials. The pyramids of Egypt are among the most ancient structures, and between their gigantic blocks of stone may be found a cementing material made from calcined impure gypsum. Even today, in Canada, over one billion square feet (40 square miles) of walls and ceilings are

covered yearly by plasterboard. Lime was used as mortar in Greek and Roman times and is still important in construction, although portland cement and other cements have replaced it for many uses. By comparison, portland cement is a modern invention. Concrete made with cement and aggregate comprises, in quantity, the largest of all the man-made materials. Considering that 4 to 5% of cement is gypsum and that lime is a major constituent of hydrated cement itself, one wonders whether these materials should always be considered together under the general name of cements.

II. Hydraulic Cements

Characterization of unhydrated materials in such a way that significant similarities or differences in their behavior as cementing agents can be identified would provide a basis for judging when results can be meaningfully compared and when reproducible behavior can be expected. Unfortunately, this ideal has been achieved only in part with cements and cement compounds. For example, plasters and other cements from different sources, or even samples taken from the same source, vary in such properties as rate of hydration, induction period, setting, viscosity, strength, and response to admixtures. The same material will even behave differently following storage. It is often difficult, therefore, to compare results obtained in different laboratories.

Factors which may be responsible for such discrepancy in the behavior of cements are thermal history, particle size and shape, surface area and energy, porosity, and chemical composition (including the concentration and nature of minor impurities, density of nuclei, lattice imperfections, etc.). No known method will assess these factors to permit reasonably accurate prediction of reactivity.

(1) Reactivity: What Is It? What Controls It?

The very definition of reactivity, although taken for granted, is sometimes arbitrary. For example, a small amount of gypsum or lignosulfonate may retard the transformation of C_3A to C_3AH_6 ,* and excessive amounts may inhibit the formation of C_3AH_6 . On occasion, however, this inhibition has been termed a retardation of the reactivity of C_3A , which seems to indicate a lack of appreciation of the fact that in the presence of excessive amounts of gypsum or lignosulfonate a bulk reaction occurs, with formation of calcium sulfoaluminate hydrates or lignosulfonate complexes. In fact, most of the C_3A may have reacted with gypsum or lignosulfonate so that there is none left for conversion to C_3AH_6 .

An unresolved question is why one material will react at a rapid rate with H_2O and another will not. For example, the C_3S component in portland cement reacts much faster with water than does C_2S . Proposed explanations include: The coordination number of Ca is >6 , coordination of Ca is irregular, the existence of holes in the crystal lattice, and differences in the position of the Fermi level.

To test the relative reactivities of Ca^{2+} in some of the minerals, the well known Hedvall effect was applied to these systems.² The increased reactivity of a solid during, and as a consequence of, a crystalline transformation is commonly known as the Hedvall effect. When $AgNO_3$ is mixed with different proportions of CaO , $Ca(OH)_2$, C_3S , β - C_2S , and hydrated C_3S and is heated in a DTA apparatus, reaction occurs between $AgNO_3$ and Ca^{2+} . The reacted amount can be estimated from a quantitative determination of unreacted $AgNO_3$. The reaction of $AgNO_3$ with CaO , $Ca(OH)_2$, and hydrated C_3S is almost stoichiometric. Only 27% Ca present in C_3S and 6% Ca from C_2S reacted with $AgNO_3$. These data raise questions. Are C_3S and C_2S structures such that some Ca^{2+} is relatively more reactive owing to structural imperfections? Is there an increase

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* Cement chemistry nomenclature is used: C = CaO , A = Al_2O_3 , S = SiO_2 , F = Fe_2O_3 , H = H_2O .

in reactivity as the surface area is increased; does this represent the relatively more rapid reaction of C_3S with H_2O in the acceleratory stage; or does it have any other implications in the mechanisms of these reactions? Although the Hedvall effect has not been applied in gypsum chemistry, it may be useful in examining the reactivities of the products formed when the hemihydrate is heated to form soluble or insoluble $CaSO_4$.

The reactivity of a product is also very sensitive to the type of raw material from which it is made. Many examples confirm this, but the exact implications have not been clarified. In the formation of magnesium oxychloride cement it has been observed that MgO formed by calcination of magnesite is superior to oxide formed from most other sources. This behavior is analogous to the catalytic activity of chromium oxide gel used for dehydrogenation reactions. Among the preparations from various chromium salts, that precipitated from $Cr(NO_3)_3$ shows the maximum reactivity. Another example is the formation of CaO from different raw materials. The calcination of $CaCO_3$ yields a surface area of only 10 to 15 m^2/g . In the formation of oxides, generally, heating in vacuum results in a higher surface area. Heating $Ca(OH)_2$ in air or in vacuum gives a surface area of 25 to 30 m^2/g and 80 to 90 m^2/g , respectively.³ Most of these results have not been explained adequately.

Other examples are available in which reactivity or sequence of reactions of a particular material hydrated under apparently similar conditions varies greatly. A study of the literature on the hydration of C_3A shows that the periods of appearance of the metastable aluminate hydrates and their conversion to the stable cubic hydrate vary over a wide range. Even at the same water/solid ratio the sequence of reactions may vary, depending on the amount of material and the geometry that is subjected to hydration.

The hydration and hardening mechanism has been one of the most debated topics in the field of cement chemistry; the history of the controversy has been well described by Bogue.⁴ At the present time, the unsolved problem is the relative importance of mechanisms involving dissolution and precipitation versus the in situ conversion mechanism. Recent electron microscopic investigations have added new information on this subject.

(2) Reactivity and the Role of Admixtures

Admixtures in one form or another are widely used to provide certain desirable qualities in portland cement or gypsum; several hundred types have been patented. In spite of their practical use, however, the detailed role of their action is not yet resolved. A reasonable knowledge would permit the production of tailor-made admixtures for particular needs. The following examples show that progress has been made with some admixtures in recent years, but obviously much more is required before the behavior of particular chemicals acting as accelerators or retarders can be predicted.

Calcium chloride is widely used as an accelerating admixture in concrete. It is generally assumed that in the hydration of tricalcium silicate $CaCl_2$ remains unaffected because no new compound containing $CaCl_2$ has been identified. A careful sequential examination of C_3S hydrated with different amounts of $CaCl_2$ indicates that $CaCl_2$ may exist in 4 or 5 forms, depending on the extent to which hydration has progressed. Free chloride adsorbed on the silicate surface, that chemisorbed on the C-S-H surface or penetrating the interlayer, and that firmly incorporated in the C-S-H lattice are possible states of chloride in hydrating C_3S .^{5,6}

Calcium lignosulfonate is one of the most common types of admixture used for reducing water requirements and retarding the set of cement. Adsorption-desorption isotherms on cement components in both aqueous and nonaqueous media have revealed certain interesting features. In a nonaqueous medium, C_3A and the stable C_3AH_6 adsorb almost no lignosulfonate, but the hexagonal phases irreversibly adsorb lignosulfonate. In an aqueous medium, both the hexagonal and cubic phases irreversibly adsorb calcium lignosulfonate.⁷⁻⁹ At high lignosulfonate concentrations, evidence indicates formation of a complex and precipitation of a basic calcium lignosulfonate. The action of lignosulfonate on the hydration of C_3S at early periods is related to the stability of the surface complex involving the silicate, lignosulfonate, and water.¹⁰

Triethanolamine, used in certain admixture formulations, has generally been termed an accelerator, but recent studies cast some doubt. Used alone with some portland cements, small amounts have little effect on either setting or hardening properties; in amounts $>0.05\%$, rapid setting and strength loss are pronounced. This behavior may be explained in terms of the accelerating influence of the amine on the C_3A + gypsum reaction and retardation of hydration of C_3S . The mechanism of its action may be traced to complexes.¹¹⁻¹³

These examples and others in the literature seem only to touch the surface of "admixture chemistry." Several theories regarding the action of admixtures have been proposed, but each explains only part of the picture. It seems reasonable to assume that the action of an admixture involves the combination of several mechanisms, the predominating one depending on the type of material, conditions of hydration, and period of hydration; these have yet to be resolved. It is to be expected also that more complications will arise with an admixture containing a combination of chemicals. This field is a challenge to the cement chemist.

(3) Surface Area of Hemihydrates

The difficulty of properly labelling a plaster may be appreciated by discussing surface area, only one of the factors that can be used for characterization. Gregg and Willing¹⁴ were the first to determine the surface area of gypsum heated to different temperatures, using N_2 , O_2 , and CCl_4 as adsorbates. They found two maxima in the surface area values, at 180° and at 280°C. The first inflection was attributed to the formation of hemihydrate, the second to the formation of anhydrite.

Razouk *et al.*¹⁵ and Molony *et al.*¹⁶ subsequently observed only one maximum in the plot of surface area versus temperature of dehydration of gypsum. Gregg and Willing¹⁴ obtained values of 12 m^2/g with N_2 and 26 with O_2 , ascribing the lower value for N_2 to its larger diameter in relation to O_2 . Working with vacuum-heated gypsum, Molony *et al.*¹⁶ found values of about 3 and 12 m^2/g with N_2 and O_2 , respectively. Comparison of these results indicates that the magnitude and ratios of surface areas differ significantly for the two adsorbates.

It is not convincing to argue that the 4-fold difference in surface area obtained with N_2 and O_2 can be explained only on the basis of molecular diameter. The diameter of O_2 and N_2 molecules is 3.8 and 4.05 Å, respectively. If the explanation rests mainly on the inability of an N_2 molecule to penetrate pores <4.05 Å, then surface area determined with Ar (which has about the same molecular diameter as O_2) should be comparable to that determined with O_2 . On the contrary, however, Ar gives an area similar to that determined with N_2 .

Another discrepancy arises with the results of Gregg and Willing¹⁴ and Molony *et al.*¹⁶ The former heated the samples in air; Molony *et al.* heated them in vacuum. Literature on various materials indicates that samples heated in vacuum have much higher surface area than those heated in air.¹⁷ Razouk *et al.*,¹⁵ using cyclohexane as adsorbate, obtained a maximum surface area of ≈ 18 m^2/g for heated gypsum. The corresponding surface area, using N_2 as adsorbate, was reported earlier as 12 m^2/g by Gregg and Willing.¹⁴ Cyclohexane, having a cross-sectional area of 39 Å², should have shown a much lower value than N_2 , which has a cross-sectional area of only 16 to 17 Å².

The use of H_2O as the adsorbate in surface area determination of plaster introduces additional complications. Work on surface area of plasters has been done in this laboratory.¹⁸ The adsorption-length change isotherms of the dehydrated plaster (using H_2O as the adsorbate) initially show a region which could be attributed to the formation of the hemihydrate with some sorbed water. A method based on the Gibbs adsorption equation was worked out for estimating the quantity of sorbed water, thus allowing a calculation of the surface area by the BET method. A value of 12.3 m^2/g was obtained, compared to 11.4 obtained with methanol as the adsorbate.

The question of the surface area of gypsum plaster has definitely not been resolved. A more systematic means of defining the starting material in terms of method of heating, atmosphere, and other variables that may affect the area is needed. The work of Combe and

Table I. Surface Area of Cement (cm²/g)

Cement	Andreasen method		Wagner method	Air permeability	N ₂ adsorption
	Spherical	Cubical			
I	2310	2860	1790	2600	7,900
II	3110	3860	2270	4150	10,000

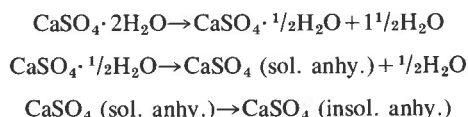
Smith¹⁹ in attempting to obtain a purer hemihydrate with reproducible properties offers promise, but more research is needed to establish their claims.

(4) Surface Area of Portland Cement

In studies concerning portland cement compounds such as C₃A, C₃S, C₂S, and the ferrite phase, surface area is generally obtained by the Blaine air permeability method. It too, however, has limitations and is not expected to measure the true surface area as accurately as more direct methods involving adsorption isotherms. Specific surface areas obtained by different methods using the same cement show large variations (Table I).²⁰ Determination of surface area using N₂ or Ar as the adsorbate is perhaps the closest approach to an absolute surface area measurement. It is therefore suggested that this method be used if reactivities are to be compared on the basis of surface area.

(5) Polymorphism of Calcium Sulfate Hemihydrate

Gypsum dehydrates in a series of steps:



Gypsum is dehydrated to the hemihydrate by several methods: in open pans or deep kettles, in rotary drums, under pressure in autoclaves, or without pressure in salt solutions. Two forms of hemihydrate have been reported, α , prepared by wet methods, and β , prepared by dry methods. The two forms differ in such properties as density, heat of solution and heat of hydration, refractive index, consistency with water, energy content, solubility, crystal size, surface area, and differential thermal behavior. In DTA the α form usually exhibits a sharp exothermic peak at a lower temperature than does the β form.²¹

Doubts have been expressed as to whether the differences in the properties known for the two forms justify their treatment as polymorphs. X-ray evidence suggests that the powder diagrams differ only with respect to the relative intensities of the peaks and minor differences in the broadening of the reflections. Additionally, no significant differences have been observed between the ir spectra for the two forms. The nuclear magnetic resonance investigation of α and β forms shows them to be similar except that the β form has more adsorbed water, due perhaps to higher surface area.

Evidence that the two forms are not polymorphs is presented by Bensted and Varma.²² Optical and electron microscopic studies indicate that the α hemihydrate is composed of larger crystals than the β variety. Thus, it seems possible that most of the differences in the properties of the two forms are due to difference in particle size. The ir spectra of α and β forms are similar, except that the β form shows sharper peaks. This difference is attributed to greater scatter-

ing from the better crystallized form. The difference disappears when the α form is well ground.

The X-ray diffraction patterns of the α and β hemihydrates differ only in the relative intensities of the lines.²³ In the reflections for the two forms there are no observable differences in positions of peaks, although the α form shows sharper peaks. If the α hemihydrate is ground, however, the reflections of the resulting material are identical with those for the β variety.

One of the popular techniques used to differentiate between the two forms is DTA, but there is disagreement on the intensity of the exothermic peaks. A broad exotherm appears at a higher temperature in the β form than in the α form. The differential thermogram of the ground α form is similar to that of the β form, confirming that grinding of the α form produces the β form.

This behavior suggests that the β form, produced by dry heating, promotes a poorly crystalline material with larger surface area than that produced by the α form, a precipitated material which is well crystallized. There seems to be no justification for treating α and β forms as if they have different crystal structures. For example, a polycrystalline, annealed sample of Ni shows sharp X-ray lines. If it is a cold-worked lattice, imperfections multiply and X-ray diffraction peaks are broadened. Despite structural, thermodynamic, and chemical variations brought about by such treatment, the deformed Ni is treated merely as undergoing stages of disorganization.²⁴ It should seriously be considered whether the two forms of hemihydrate should not in the future be considered as one.

(6) Polymorphism of C₃S

Cement minerals, although commonly designated as C₃S, C₂S, C₃A, and C₄AF, are far more complex systems consisting of solid solutions. The C₃S and C₂S phases in clinkers, for example, form solid solutions with impurities such as oxides of Al, Mg, and K. The C₃A phase may also form solid solutions with Na₂O, K₂O, etc.; composition of the ferrite phase may vary from C₆A₂F to C₆AF₂, with a median value near C₄AF.

Among the cement minerals, C₃S has the greatest number of allotropic forms. When it is heated, several transformations occur; much research has been done on the types of transformations, the temperature at which they occur, and energies involved. There is disagreement even on the number of detectable transformations. Table II gives the characteristics of reversible transformations of C₃S as interpreted by some investigators.²⁵⁻²⁷

Even where there is consensus on some of the better known allotropic forms, there is uncertainty regarding the relative reactivities and hardening behavior of the compounds. Some earlier work showed that they were practically the same, but recent work has cast doubt. Again, if characterization is to be achieved there must be agreement on the identification and importance of these allotropic forms.

(7) Volume Change with Hydration

Volume change accompanying the hydration of cements is of great practical importance, its measurement dating back to Le Chatelier.²⁸ The whole area of cement technology involving expanding and self-stressing cements is concerned with volume change on hydration. It is valid, therefore, to ask which parameters determine the apparent volume change of a hydrating system and why it does not seem to be related to the solid volume change associated with the hydration reaction but rather to the nature of the

Table II. Characteristics of the Reversible Transitions of C₃S

Approx. characteristic temp. of transformation (°C)	Nature of endotherm	Assignment			Heat of transformation (cal/g)
		Ref. 25	Ref. 26	Ref. 27	
585 ± 5	Broad valley	Triclinic I ⇌ triclinic II	$\alpha \rightleftharpoons \beta$ transition		0.6
917 ± 3	Sharp and most intense	Triclinic II ⇌ triclinic III	Triclinic ⇌ monoclinic	Triclinic ⇌ monoclinic	1.0–1.3
975 ± 3	Sharp, less intense	Triclinic III ⇌ monoclinic	Monoclinic ⇌ trigonal	Monoclinic ⇌ trigonal	0.5–0.6
990 ± 2	Very small peak*	Monoclinic ⇌ orthorhombic			0.05

* Detectable only with high-resolution DTA.

Table III. Physicochemical Constants for Volume Changes in Cements

Component	Chemical composition	Possible transformation	Mol vol change (%)
Plaster	$\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$	$\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O} \rightarrow \text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	41.1
Gypsum	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$		
Lime (calcia)	CaO	$\text{CaO} \rightarrow \text{Ca}(\text{OH})_2$	90.9
Hydrated lime	$\text{Ca}(\text{OH})_2(\text{CH})$	$\text{Ca}(\text{OH})_2 \rightarrow \text{CaCO}_3$	11.2
Calcite	CaCO_3	$\text{CaO} \rightarrow \text{CaCO}_3$	121.9
Periclase	MgO	$\text{MgO} \rightarrow \text{Mg}(\text{OH})_2$	117.2
Brucite	$\text{Mg}(\text{OH})_2$		
Tetracalcium aluminate hydrate	$4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 19\text{H}_2\text{O}$	$\text{C}_4\text{AH}_{19} \rightarrow \text{C}_3\text{A} \cdot 3\text{CaSO}_4 \cdot 31\text{H}_2\text{O}$	93.8
Ettringite	$3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 31\text{H}_2\text{O}$		
Tricalcium silicate	$3\text{CaO} \cdot \text{SiO}_2$	$\text{C}_3\text{S} \rightarrow \text{C-S-H} + \text{CH}$	64.4
Calcium silicate hydrate (C-S-H)	$\text{Ca}_3\text{Si}_2\text{O}_7 \cdot 3\text{H}_2\text{O}$		

hydrated product and conditions of hydration (Table III). The very small expansion during the hydration of cement contrasts with the expansion of hydrating plaster and, even more dramatically, with the expansion of CaO or MgO hydrated by vapor phase. The ratios of expansion on hydration of portland cement:hemihydrate: CaO are in the order of 1:10:100, as measured on compacts.

A study of volume change readily shows that an explanation of this phenomenon must be based on the mechanism of structure formation of the hardening cements. Examination of the expansion of plaster during hydration, in which initial porosity as well as temperature at which hydration occurs has great influence, indicates that many factors are responsible.²⁹ The greater expansion occurring at lower temperature has been linked with the very much smaller crystals formed at the low temperature. This fact does not, however, explain the mechanism any more than it does for supersulfated cement, where ettringite crystals of different size seem to alter expansion.

Work done in this laboratory on measurement of volume change, using compacts of unhydrated material, is significant because it offers not only a test for unsoundness in lime (where MgO contributes to expansion due to delayed hydration) but also a technique for the study of the mechanism of volume change.³⁰ The technique is simple and is adaptable to a variety of materials and a range of conditions. For example, it can be used to hydrate compacts in vapor atmosphere at various temperatures, including high pressure autoclaving, and it is adaptable for liquid hydration. The technique was most useful in the investigation of white-coat plaster failure on a wall where the adjacent wall had not failed. In compacts formed from the failed white-coat plaster material, autoclave expansion was 5.4%, whereas the corresponding expansion for the sound plaster was 15.4%. The difference was that the MgO in the failed plaster had hydrated much more than that in the sound plaster owing to differences in exposure to moisture.³⁰

The present authors consider that volume change on hydration is in some way related to the property of accommodation during structure formation. In other words, the fact that portland cement does not expand significantly on hydration is related to the ability of the products to displace one another, densifying the structure without exerting much stress on the existing structure. The question of when a hydrating cement will expand and when it will not is not predictable at present, and further study is required.

III. Hydrated Cements

The requirement for characterization of hydrated cements is the same as for unhydrated starting material. Behavior can be predicted only on the basis of clearly defined basic properties and understanding of the various processes. Unfortunately the situation is even more confused for hydrated cements.

(I) Chemical Composition

(A) *Does $\text{CaSO}_4 \cdot \frac{2}{3}\text{H}_2\text{O}$ Exist?*: The decomposition of dry $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ results in the formation of a hydrate containing $\leq 8\%$ H_2O , whereas the stoichiometric proportion for hemihydrate is 6.2%. On the basis of DTA and other evidence, it has been suggested that a compound of composition $\text{CaSO}_4 \cdot \frac{2}{3}\text{H}_2\text{O}$ exists.³¹⁻³⁴

Using sorption isotherms on dehydrated gypsum with H_2O as the adsorbate, several workers have found that water content increases rapidly up to that required for hemihydrate formation at very low water vapor pressures, followed by an almost horizontal plateau.^{18,35-37}

Feldman and Sereda¹⁸ found that a plot of length change versus weight uptake for a compact of dehydrated plaster showed a low slope corresponding to that of hemihydrate formation and a steep slope covering a region for further uptake of water. If it is assumed that the water in excess of $\frac{1}{2}\text{H}_2\text{O}$ is also zeolitic, then there should not have been a deviation from the slope for the formation of the hemihydrate. The form of water taken up in excess of $\frac{1}{2}\text{H}_2\text{O}$ is less clear. Saito³⁸ and Goto *et al.*³⁹ believe that it exists as capillary-condensed or physically adsorbed water. Basing their results on the plot of length change versus p/p° , Feldman and Sereda¹⁸ argued that at higher humidities, in addition to capillary condensation and adsorption, chemisorption occurs (followed by the formation of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$). The desorption branch was irreversible up to very low vapor pressures, suggesting this possibility.

(B) *$\text{H}_2\text{O}/\text{SiO}_2$ in the C-S-H Product*: The chemical composition of the hydrated products of CaO , $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$, high alumina cement, etc. has been reasonably well established. Several complex compounds have been identified in the formation of a magnesium oxychloride. The chemical composition of the hydrated silicates in portland cement paste is still, however, not known with certainty, especially the number of water molecules associated with the calcium silicate gel. Water may exist in capillary voids or in adsorbed or hydrated states. Difficulties arise in distinguishing between adsorbed and combined water. A firmly bound, adsorbed water molecule may be more strongly held than loosely held but combined H_2O .

The $\text{H}_2\text{O}/\text{SiO}_2$ ratio of the C-S-H phase is generally given as 1.5. This ratio was not determined experimentally but is based on arbitrary drying procedures at a vapor pressure of dry ice (5×10^{-4} mm Hg) or at 8×10^{-3} mm using $\text{Mg}(\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$ and $\text{Mg}(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$. The formula for the C-S-H product is given as $\text{Ca}_3\text{Si}_2\text{O}_7 \cdot 3\text{H}_2\text{O}$, which is supposed to convert to $\text{Ca}_3\text{Si}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ when dried at 5×10^{-4} mm Hg. It has also been assumed that 1 mol H_2O driven out during drying is not regained when the material is rewetted. It should be noted that 3.0 mol were obtained by rounding off the calculated value of 2.54 based on the assumptions made.⁴⁰ Another assumption implied in the calculations but yet to be proved is the calculation of surface area using H_2O as adsorbate.^{41,42}

Attempts have been made to determine the stoichiometry of hydrated C_3S by conditioning the sample at 11% rh (drying from 100% rh), which was found to be a better base than the D-dry state.⁴³ Hydrated C_3S was exposed to different humidities and the equilibrated samples were analyzed by DTA and TG to assess, qualitatively and quantitatively, the types of H_2O in the paste. Taking into account surface area, free lime, and carbonation, the stoichiometry of the bottle-hydrated C-S-H gel at 11% rh was $3.28\text{CaO} \cdot 2\text{SiO}_2 \cdot 3.92\text{H}_2\text{O}$. There was also evidence of higher hydrates at higher humidities.

This result indicates that the stoichiometry of hydrated portland cement is a variable, and this fact must be accounted for when comparing results using different preparations.

(3) Density of Cement Paste

The density value quoted in the literature for a given material is accepted without much question because it depends simply on mass and volume; that for hydrated portland cement is no exception. Few realize that an accurate assessment of density of hydrated portland cement is one of the most important factors in determining porosity and in assessing durability and strength. Density has traditionally been measured at the D-dried state by means of a pycnometer, using a saturated solution of $\text{Ca}(\text{OH})_2$, but this method has some drawbacks. A logical method that least interferes with the solid is use of the helium pycnometer,⁴⁴ which has shown that porosity and density values are overestimated when the aqueous solution method is used. At the D-dried state, densities are 2.28 and 2.61 g/cm³, respectively, for the helium and aqueous solution methods, whereas corresponding values determined at 11% rh are 2.34 and 2.35 g/cm³.

These results illustrate that density of portland cement paste is not a unique value. It depends on the method used for its determination and on sample history, a fact that must be recognized in all evaluations of material properties requiring density value.

(4) Surface Area of Cement Paste

Some of the implications of determination of surface area in unhydrated cements have been discussed. Determination of surface area of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ is less complicated than that of hydrated portland cement. Whereas hydration of hemihydrate results in a bonding agent with a decrease in the surface area, there is a large increase in surface area when portland cement clinker is hydrated.

There is controversy over the significance of using H_2O as an adsorbate in determining surface area of hydrated portland cement. It is an important question, for correct interpretation facilitates a correct concept of the model of the cement paste and helps to explain various physical and mechanical properties. It is known that with water as the adsorbate the surface area of portland cement paste is $\approx 200 \text{ m}^2/\text{g}$, whereas with N_2 surface area decreases to 50% of this value or less. Calculation with H_2O assumes that the adsorption isotherm is reversible up to a relative vapor pressure of ≈ 0.35 , whereas there is good evidence that adsorption-desorption curves for water vapor on cement paste are not identical at low relative pressures. Apparently, part of the water is taken up by the interlayer structure of the cement gel. NMR data seem to confirm this concept. It is hoped that this important question will be studied further so that a correct model for cement paste will be possible.

It is relevant to mention that the surface area of a hydrated product depends not only on the nature of the starting material but also on the method of hydration and on the detailed determination procedure. For example, hydration of CaO in water yields $\text{Ca}(\text{OH})_2$ with a surface area of $\approx 10 \text{ m}^2/\text{g}$, but CaO hydrated in water vapor can have a surface area as high as $40 \text{ m}^2/\text{g}$.

It should also be noted that surface area may change when a hydrated product is aged in water vapor owing to agglomeration. Calcium hydroxide, with a surface area of $\approx 40 \text{ m}^2/\text{g}$, shows a decreased value of $29.2 \text{ m}^2/\text{g}$ after drying at a relative water vapor pressure of 0.25 for 15 h.⁴⁵

It is generally known that surface area of a cement paste determined using water vapor gives a reasonably constant value independent of method of preparation and history. Surface area determined with N_2 gives values that differ for different preparations and accounts for changes occurring as a result of sample history and aging processes.⁴⁶ Recently it has also been confirmed in our laboratories that surface area values determined with N_2 vary with the exact procedure of drying: rate and severity, including wetting and drying cycling. This variation indicates that the N_2 method reveals changes in the material due not only to its history but also to its treatment during the determination. This method appears to be an excellent means of characterizing surface changes.

IV. Conclusions

This paper has assessed the properties and behavior of cements; it has examined whether the characterization of the starting or unhy-

drated materials and present knowledge of the processes of hydration and structure formation are sufficient to permit prediction of the final properties of the products. It is concluded that there are still many "gray" areas in present knowledge and, therefore, that prediction of the behavior of the final products is not yet possible. Questions not yet resolved are summarized as follows:

(1) The characterization of hydraulic cements (unhydrated, starting materials) is not adequate to ensure that comparison of results obtained from different source materials and different workers is valid: (a) There is no agreement on how surface area of hemihydrate should be measured. (b) The reactivity and the factors that determine it are not adequately defined; the question, "What is reactivity?" will remain unanswered until the precise mechanisms of hydration reactions are known (this question applies equally to all cements).

(2) The characterization of hydrated cements is equally unresolved: (a) There is much controversy regarding determination of surface area, especially that of hydrated portland cement, and its significance. (b) The precise chemical and mineralogical composition of some hydrated cement constituents remains obscure: precise lime/silica ratio, location of lime in the microstructure, effect of admixtures, etc. (c) The density of hydrated cement appears to vary with the method of measurement and the history of the sample.

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