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Cementitious properties of metallurgical slags

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When sufficient crystals were present in the melt, the sample was quenched by switching off the power to the thermocouple. In this manner, a bead containing primary phase crystals was produced.

The crystal-containing bead was removed from the thermocouple by bending the arms and tapping the bead with a small agate pestle. The bead was then ground to a fine powder under alcohol in an agate mortar. The resulting powder was placed on a bristle and mounted in a 114.83×10^{-3} m diameter X-ray powder camera and subjected to copper radiation using a nickel filter. The power settings were 34 kV at 18 mA.

The crystalline phase thus determined was compared with the assumed phase as taken from Osborn, DeVries, et al. [18], and observations made during crystal growth. It was noted that some of the phase could be readily identified by the shape and character of the crystals. Spinel formed octahedrons, often distorted; melilite crystallized into tabular prisms; forsterite could be identified by its high degree of birefringence under Polarized light. The primary phases determined are given in Table IV.

III. EXPERIMENTAL PROCEDURE - CEMENT

3.1 Hydraulic Properties

Blast furnace slags in the crystalline state normally have no hydraulic properties. It is a matter of some debate why a crystalline blast furnace slag is non-hydraulic while a glassy slag of the same composition is. This anomaly is further compounded by the fact that the crystalline material in portland cement clinker, e. g., C_3S and C_3A, is highly reactive with water while these same cement clinkers in a less crystalline (more glassy) state, while still reactive, are so to a lesser extent [30]. Before a comparison of the hydraulic properties of portland cement and slag cement can be made, some insight into the overall reactions governing the hydration of both portland cement and slag cement is needed.

3.1.1 Hydration of Portland Cement

The four major active constituents of portland cement clinker are C_3A, C_4AF, C_3S, and C_2S given in declining order of reactivity. These compounds all react with water to yield hydration products, but at different rates and with the formation of different types of product.

3.1.1.1 Hydration of C_3S and Beta-C_2S

Both C_3S and beta-C_2S hydrate with water to form calcium hydroxide, and a calcium silicate hydrate of the form C_xSH_y. The calcium silicate hydrate may take the form of either crystals or a gel both of which are similar to the naturally occuring mineral tobermorite. Tricalcium silicate hydrates very rapidly upon contact with water while the C_2S reaction with water occurs very slowly [31].

The low resistance offered by C_3S to attack by water has been explained as being due to the high internal energy as well as the alkaline character of the compound. This condition is brought about by the rel-

ative sizes of the Si^{+4} and Ca^{+2} ions, variations in coordination numbers, and their requirements for electrical neutrality which is provided by oxygen ions [32]. These conditions give rise to a highly distorted structure containing many "holes" which causes the compound to hydrate readily [33]. The complete hydration of C_3S can be expressed:

$$2Ca_3SiO_5 + 6H_2O \longrightarrow Ca_3Si_2O_7 \cdot 3H_2O + 3Ca(OH)_2 \quad \ldots\ldots\ldots (1)$$

βC_2S yields identical hydration products, although the stoichiometry differs.

The amount of $Ca(OH)_2$ liberated during the reaction manifests itself in the crystalline and amorphous form both of which are precipitated. It is believed that the $Ca(OH)_2$ is largely responsible for the activation of slag cements when they are mixed with portland cement [17].

3.1.1.2 Other Hydration Reactions

Tricalcium aluminate (C_3A) hydrates immediately upon contact with water to yield primarily tricalcium aluminate hydrate (C_3AH_6). Additionally, C_2AH_8 and C_4AH_{13} may be formed. It is believed that C_3A must have a similar, although probably more distorted, structure than C_3S. This could result from variations in the coordination number of the aluminium ion. Hence C_3A contains a relative large proportion of free energy, rendering it highly reactive. Calcium hydroxide is also formed, but this often recombines with other reaction products [34].

The almost instantaneous hydration of C_3A which is accompanied by a rapid stiffening of the cement paste is often referred to as "flash set" and is generally undesirable. The reaction products are formed quickly and coat the unreacted grains so that further hydration is retarded. Additionally, the mortar becomes difficult to work. This is a particularly unwanted condition in portland cement as the C_3A hydration products may prevent the normal slower hydration of C_3S and C_2S from occuring. For this reason, gypsum is often added to retard the hydration

of C_3A thus preventing "flash set".

Other calcium aluminates, CA, $C_{12}A_7$ and CA_2, normally found as constituents of high-alumina cements (used as refractory cement and in applications where a rapid set is desired) also hydrate rapidly to form CAH_{10}, C_2AH_8, C_4AH_{13}, and other calcium aluminate hydrates. These usually transform to the more stable hydrate C_3AH_6. In addition to these hydrates which take the form of precipitated crystals, AH_3, a gel, is usually formed [35].

Tetracalcium aluminoferrite (C_4AF) also hydrates rapidly but does not give a flash set. The hydration products have been shown to be C_3AH_6 and amorphous substances believed to be hydrated CF [35].

3.1.1.3 Hydration Products

The products of hydration can be an amorphous gel, a precipitated crystalline material, or a dissolved compound. During the course of hydration, any of these conditions may exist. Precipitates may redissolve, gels may react to yield crystalline or dissolved compounds. Of most interest are the products resulting from the hydration of C_3S, namely $Ca(OH)_2$ and those compounds having the form C_xSH_y, the tobermorites.

Tobermorites formed during hydration vary in their C/S ratio from about 0.8 to about 1.9 [31] based on molar percentages. They take the form of crystals (plates, needles, fibres, foils, etc.) or nearly amorphous gels. The C/S ratio in tobermorite is dependent upon the amount of free Ca^{+2} available during formation. Generally tobermorite formed from C_3S has a higher C/S ratio than that formed from C_2S [31]. Tobermorite also may abstract Mg^{+2} and Al^{+3} ions from solution during its formation.

Slag cements particularly rich in Al_2O_3 may hydrate to yield gehlenite hydrate, i. e., C_2ASH_8, and hydrogarnet, i. e., $C_3A(S,H_2)_3$. These products are less common than the tobermorite.

3.1.2 Hydraulic Properties of Crystalline Slags

Slags in the crystalline state have no natural hydraulic properties, with the exception of those containing βC_2S which are weakly hydraulic. Crystalline slags containing the gamma phase C_2S hydrate even more slowly. Slags containing crystalline C_2S may, however, be prone to falling.

Other crystalline components of slag fail to hydrate because the binding energy of the crystals is strong enough to prevent association of the crystal components with water. Somewhat of a paradox arises, though, when crystalline slag and crystalline portland cement clinker are compared. The former will not hydrate, while the latter readily hydrates.

This enigma can be partially explained by referring to the composition of the crystalline slag as compared with that of the clinker. None of the primary constituents of portland cement clinker (except C_2S) are present either as primary or secondary phases in crystalline blast furnace slag. It has already been shown that the hydraulic properties of cement clinker are due to its peculiar crystalline arrangement, and blast furnace slags are not of a composition which would yield crystals similar to those encountered in portland cement. Thus the binding energy of the crystals in blast furnace slag is apparently sufficient to preclude hydration, i. e., the internal energy of blast furnace slags is less than that of portland cement clinker.

Solacolu [22] points out that the difference in energy considerations between a crystalline slag and the same slag in the glassy state is small, and therefore can be discounted as a reason for the hydraulic inactivity of crystalline slags. Glassy slags without hydraulic properties, he concludes, consist of inactive and quasi-crystalline phases while in those which have hydraulic properties an active quasi-crystalline phase is present. His view is supported by the discontinuities in the iso-strength lines of glassy slag cements as they cross

a phase boundary.

Baldwin [12], quoting Toporov and Volkomski, points out that certain slag cements containing a high percentage of alumina (30 - 50 per cent Al_2O_3) only exhibit hydraulic properties when the slag is in the crystalline state. This is probably due to the formation of C_3A. In order to have this crystalline phase present in the slag, the slag must be processed in such a way that nucleation and crystal growth can occur. The phase C_3A can only occur in slags having a very low (less than 10 per cent) silica content which places them out of the range of normal metallurgical slags.

3.1.3 Hydraulic Properties of Glassy Slags

Slags of a suitable composition which are in the glassy state will hydrate quite readily, provided a suitable activator is present. In the case of portland cement-slag mixtures, activation of the slag is due to reaction (1) (page 43) which occurs rather rapidly with the liberation of sufficient amounts of $Ca(OH)_2$ to activate the slag. Slags can be activated by the addition of a base such as $Ca(OH)_2$, KOH, NaOH or a sulphate compound such as gypsum [2]. It is the cation, however, which provides the activation.

If the theories of the structure of the active components of portland cement clinker (C_3A and C_3S, primarily) proposed by Bernal et al [33] and the quasi-crystalline state of glassy slags proposed by Volacolu [22] are acceptable, the nature of the mechanism of the hydration of glassy slags may be clarified. Studies by Keil [1] indicate that glasses which, if crystalline, would form C_2MS_2, will undergo a hydration reaction with water alone, while a glass falling into the C_2AS field requires an activator.

Apparently the cation (Ca^{+2}, in the case of $Ca(OH)_2$) of the ionized activator is capable of modifying the quasi-crystalline structure of the slags rendering their composition similar to the tricalcium com-

pounds (silicate and aluminate) in portland cement. Such a replacement mechanism is a surface phenomenon which allows the dissolution of the surface layer of atoms of the slag. The hydration reaction which then occurs forms insoluble salts namely tobermorite, ettringite, calcium aluminium hydrate and others [2], which are precipitated from solution. In an agitated suspension, however, new unreacted surfaces are continually being exposed permitting complete hydration of the slag.

3.2 Activation Requirements of a Slag

There are differences of opinion between various authors about the amount of activator to use with slag cements [1,2,30,36,37]. The calcium hydroxide liberated by the portland cement mixed with the slag is usually relied upon for activation of the slag. The amount and grade of portland cement in the slag cement does not vary from one batch of slag to the next in commercial operations thus no provision is made for the different activation requirements of different slags. If the Ca^{+2} ion activates the glassy slag in the manner discussed in Section 3.1.5, then surely a different amount of activator should be required for each slag depending upon its composition. For this reason, a test was undertaken to determine if in fact the amount of activator used affected the resulting strength of the slag.

3.2.1 Determination of Activator Requirements

A commercial slag cement was obtained and used for this test. The chemical analysis results of this slag are shown in Table III. Samples of this milled, granulated slag were activated with various percentages of calcium hydroxide, by replacing the slag with an equivalent amount of the activator. Small test cylinders were prepared by the method discussed in Section 3.3. These were crushed according to the procedure discussed in Section 3.4. These results are shown in Table VI.

A graph was plotted (Figure 3) of strength versus per cent cal-

TABLE VI.

STRENGTH OF STANDARD BLAST FURNACE SLAG ACTIVATED WITH SELECTED PERCENTAGES OF CALCIUM HYDROXIDE

Per Cent $Ca(OH)_2$ Added.	Strength - N x $10^4/m^2$			
	7 Days	14 Days	28 Days	56 Days
1	190	300	480	1050
2	280	400	1000	1700
4	320	490	750	840
6	560	710	880	760
8	650	800	980	880
12	780	920	1060	1090
16	760	990	1140	1150
20	720	930	1070	1060
24	730	920	1060	1100
32	780	980	1050	1110

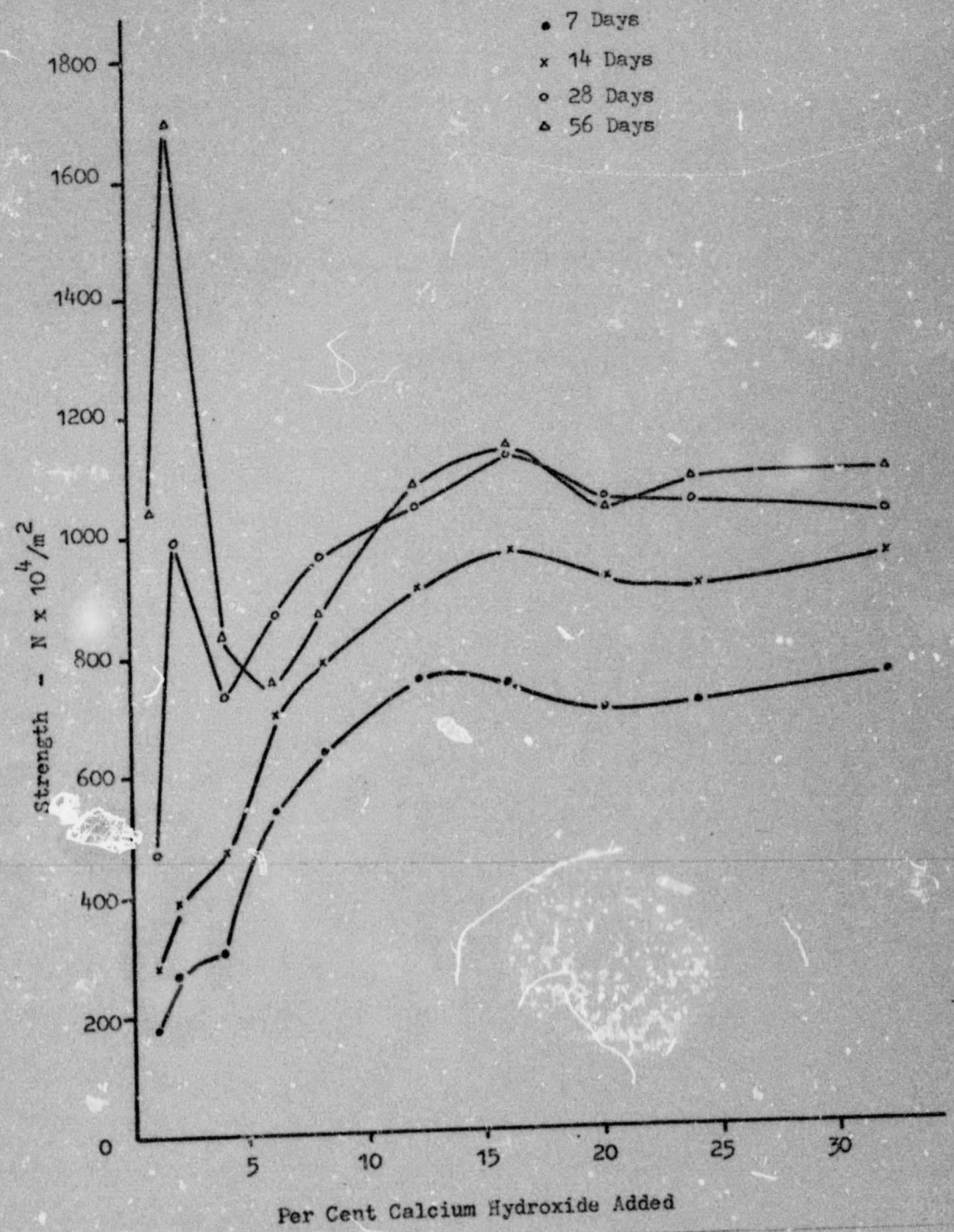


Figure 3. Effect of the Amount of Calcium Hydroxide Activator on the Strength Developed By Standard Blast Furnace Slagment

cium hydroxide activator at the various time intervals. The unusual peak that resulted at about two per cent $Ca(OH)_2$ addition at 28 and 56 days caused some speculation as to exactly which amount of activator produced the maximum strength. The peak is so sharp, and covers a wide range of activator values that another test using the same slag cement with various percentages of activator, viz., 0 to 3½ per cent in one-half per cent steps was undertaken. The results of this test are shown in Table VII, and pictured in Figure 4. These results define the area in question more clearly and indicate that a 1½ per cent addition of $Ca(OH)_2$ appears to be the optimum amount of activator addition. Further, the time-strength curves including the 112-day strengths had flattened out as would be expected (Figure 5).

In addition to the formation of relatively insoluble crystals and hydrogels, a certain amount of $Ca(OH)_2$ is liberated during the hydration of cements. It is believed that the presence of lime over and above that liberated by the hydration process prevents the hydrogels from forming an insoluble coating on the slag grains. Thus during initial hydration, when the hydration products are relatively simple, i. e., hydrates having only one or two molecules of each species per unit cell, insoluble gels are formed and precipitate on the surface of the unreacted slag grains inhibiting further reaction. When lime is present, however, in excess of the requirements for mono- and di-molecular hydration compounds, further reaction of these compounds yielding products as $C_5S_6H_5$, $C_3AS_3H_x$, and $C_3A_2S_3H_x$ occurs. These products contain more lime than is available from the initial slag and are more crystalline in nature than the hydrogels initially formed. Thus they do not tend to coat the slag grains completely.

The addition of an amount of $Ca(OH)_2$ in excess of that required for the formation of the more crystalline hydration products may have one of two effects, depending upon the amount in excess. As the crys-

TABLE VII.

STRENGTH OF STANDARD BLAST FURNACE SLAG ACTIVATED WITH SELECTED PERCENTAGES OF CALCIUM HYDROXIDE

Per Cent $Ca(OH)_2$ Added	Strength - N x $10^4/m^2$				
	7 Days	14 Days	28 Days	56 Days	112 Days
0	Developed insufficient strength for water immersion				
0.5	190	260	390	760	1160
1.0	210	320	460	1170	-
1.5	350	440	910	1700	1980
2.0	320	420	1040	1690	1900
2.5	350	450	770	1370	1620
3.0	210	350	730	1100	1430
3.5	300	440	730	1220	1590

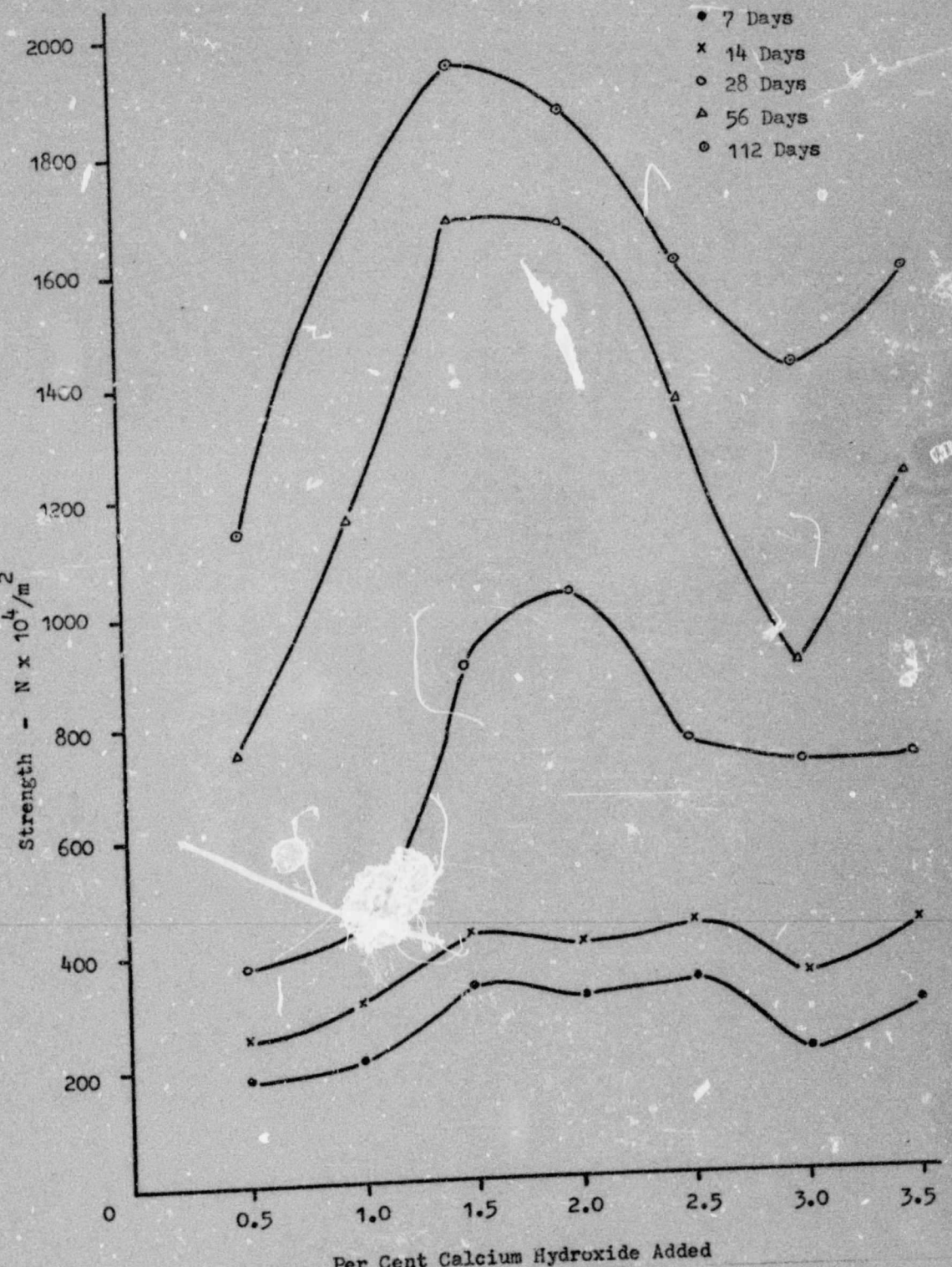


Figure 4. Effect of the Amount of Calcium Hydroxide Activator on the Strength Developed By Standard Blast Furnace Slagment

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