

Effect of Weathering on the Reactivity of Commercial Portland Cement

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Batches of freshly ground portland cement were exposed to the laboratory atmosphere and to CO_2 and/or water vapor for various lengths of time. The samples were then divided into two parts, one for immediate study and another for study after two months of storage. The reactivities of these cement samples (and of unexposed controls) were followed mainly by electron-optical techniques. The cement samples exposed to the laboratory atmosphere when tested immediately after exposure showed reactivities similar to that of unexposed cement, but the reactivities decreased markedly on storage. Dry CO_2 or water vapor alone was found to have no significant effect on the reactivity of cement. Exposure to humid CO_2 greatly increased the reactivity immediately after exposure; but on storage it decreased compared with the control.

•PREVIOUS WORK on the early stages of hydration of various types of commercial portland cement and corresponding mixtures of cement compounds showed that the course of the reaction was different in the two cases (1, 2). It was suggested that this difference might be due either (a) to differences in the thermal history during the manufacture of the commercial portland cements and the cement compounds, or (b) to the weathering action of moisture and/or carbon dioxide present in the atmosphere during storage of commercial cements. The effects of different heat treatments on the reactivity of various types of commercial portland cements have already been reported (3). They do not account for the main differences noted. The object of the present paper is to report subsequent work on the weathering of portland cement.

Hansen (4) has recently reviewed earlier investigations of the effects of weathering on the reactivity of portland cements. The main techniques used in these investigations were chemical analysis of the liquid phase extracted from the cement paste and measurement of the penetration of a Vicat needle. Hansen shows that there are contradictory reports of increasing and decreasing reactivity of portland cements due to aeration. All these results, though of considerable importance, are of an indirect nature. In the present study an attempt has been made to get direct evidence using electron-optical techniques.

SAMPLE PREPARATION

Ten-gram samples of ordinary portland cement, fresh from the cement mill, were spread out in thin layers and "weathered" in the following ways:

1. By aeration in the laboratory atmosphere for one to two weeks. These samples were made for a preliminary study to see if the results of the earlier work (1) could be reproduced.
2. By exposure to dry carbon dioxide with intermittent shaking.
3. By exposure to water vapor in a desiccator under vacuum. A saturated solution of $\text{Na}_2\text{Cr}_2\text{O}_7$ was used as humidifier (52% RH).
4. By exposure to humid CO_2 (52% RH).

5. By further exposure, after treatment as in (3), to dry CO_2 , as in (2).

In batches (2) to (5) samples were exposed for various times, from 24 hours to 7 days. All the samples were then divided into two parts, one for immediate study, the other for study after storage for two months in stoppered bottles

The electron-optical techniques used have been described previously (5). X-ray diffraction was used to substantiate the results of electron-optical study for some samples. A sample of unexposed cement was used as a control during the whole study.

RESULTS

The unexposed cement, over the whole period of the study, was found to react normally, i. e., some ettringite crystals were formed after 4 min hydration and more ettringite crystals were formed at 3 hr. Figure 1 shows a representative electron-micrograph of the unexposed cement after 4 min hydration.

The batches of cements exposed to the laboratory atmosphere, when studied just after exposure, showed reactivities similar to that of the unexposed cement. The same samples, when retested after storage in stoppered bottles, showed a reactivity similar to that of the commercial portland cements studied earlier (1). In these exposed and stored cements only surface reaction occurred during the first 4 min of hydration, and only a few ettringite crystals had formed after 3 hr. Figure 2 shows a representative electron-micrograph after 4 min. The reproducibility of the previous work (1) having been thus confirmed and the main effects shown to be due to weathering, the other samples were investigated. Batches (2) to (5) were made to determine if both moisture and carbon dioxide were necessary to produce these effects.

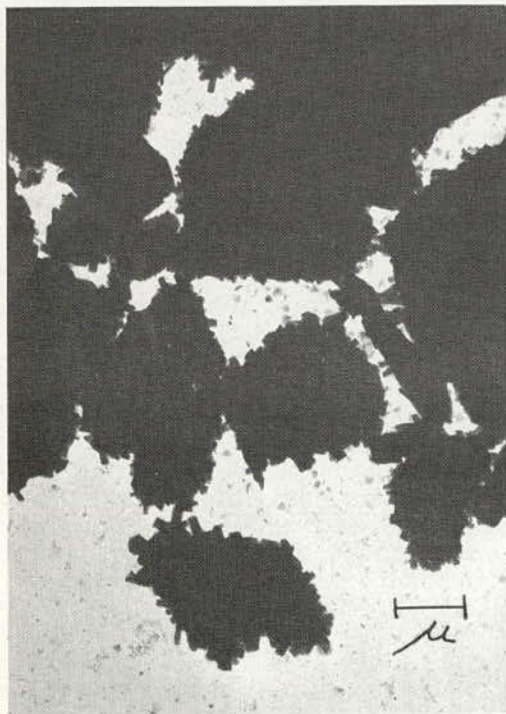


Figure 1. Unexposed cement, hydrated for 4 min, showing small crystals of ettringite.

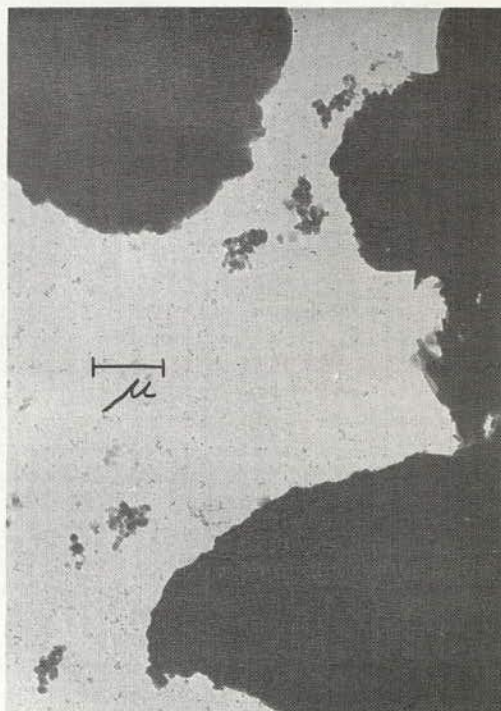


Figure 2. Cement exposed to the laboratory atmosphere for 7 days, stored for 2 months and then hydrated for 4 min; no ettringite formation is visible.



Figure 3. Cement exposed to humid CO_2 for 24 hr, then hydrated for 4 min immediately after the exposure; large crystals of ettringite have formed.

4-min sample, and only a few ettringite crystals were visible in the 3-hr sample. A few gypsum crystals were visible in the 4-min sample.

The cements of batch (5) behaved like those of batch (4).

DISCUSSION

From the results it appears that dry carbon dioxide or moisture alone does not change the reactivity of commercial portland cement very much. The presence of moisture and carbon dioxide together, however, increases the reactivity of commercial portland cement at first, but on long storage the reactivity is very much decreased. Thus we may expect that commercial portland cements tested just after grinding will have a reactivity similar to that of a mixture of cement compounds, except that the reactivities of the alumina and iron-bearing phases will be somewhat different from that of the pure compounds (3).

During storage the commercial cements will be exposed to the weathering action of both moisture and carbon dioxide present in the atmosphere. The results from sample (1) seem to show that prolonged weathering under normal commercial storage conditions is equivalent to the experimental conditions of a short period of accelerated weathering followed by storage in stoppered containers. If this is the case, it should be possible to find enhanced or depressed reactivity in commercial cements depending on the length of storage and the degree of weathering.

It is tempting to speculate that the change of reactivity on exposing cement to moist CO_2 is due to the initial formation of a layer of soluble $\text{Ca}(\text{HCO}_3)_2$. Decrease in the reactivity of the exposed cement on storage may be due to conversion of soluble $\text{Ca}(\text{HCO}_3)_2$ to a layer of insoluble CaCO_3 . Further work is necessary to test this hypothesis. However, it appears certain that it is the state of combination of the CO_2 in a

Cements of batch (2) exposed to dry CO_2 up to 7 days did not show appreciable change in reactivity compared to the unexposed cement. Storage in stoppered bottles did not affect the reactivity of these cements. The effect on reactivity of moisture in the absence of CO_2 , batch (3), was also negligible.

The effect of humid CO_2 on the reactivity of cement was remarkable. The reactivity was greatly enhanced in all cases by the exposure to humid CO_2 . The ettringite type of crystals formed after 4 min hydration were much larger than those formed in the case of unexposed cement at the corresponding time. Figure 3 shows a representative electron-micrograph of such a cement after 4 min hydration. Only a few of the well-formed needles gave electron diffraction patterns, but these patterns were similar to those reported by Gard for natural ettringite (6). By 3 hr the ettringite formation seemed to be completed. The X-ray diffraction diagram of the 3-hr sample showed moderately strong lines of ettringite, whereas the corresponding diagram of unexposed cement showed only a trace of ettringite.

When the above cements were retested after storage in stoppered bottles, the reactivity was again changed. No crystals of the ettringite type were formed in the

cement sample, rather than the total amount present, which is important in determining the reactivity of the cement.

If the present results are substantiated by other workers, they can be used to reconcile some of the contradictory reports in the literature.

Powers and Steinour (7, 8) showed that cement paste, soon after preparation, begins to act as one continuous flocculated mass. The bleeding rate of the paste is remarkably constant for a considerable period, which they interpreted as indicating that no radical change is taking place in the physical state of the paste. These results seemed to be confirmed by other investigators (9, 10). On the other hand, Russian workers could not find any such "dormant" period (11). Czernin (12) also could not find such an effect and called for some other explanation for the so-called dormant period. In view of the results of the present paper it seems these workers may have been studying the hydration of cements at different stages of weathering and got apparently contradictory results.

Bogue (13), in discussing the effects of various heat treatments of the clinker, has drawn attention to the considerable effect that early hydration rates have on the structure and physical properties of cement pastes, e.g., bleeding rate, degree of compaction, early strength, permeability, etc. The effects of weathering are likely to be even more important in producing such variations in structure and physical properties. Some of these effects are presently under investigation.

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