

The Agricultural Experiment Station
OF THE
Colorado Agricultural College

Destruction of Concrete by Alkali

BY

WM. P. HEADDEN

The Agricultural Experiment Station.

FORT COLLINS, COLORADO

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Destruction of Concrete by Alkali.

BY

WM. P. HEADDEN.

Cement has been found so generally serviceable and beset with so few disadvantages that its use is generally recommended without any reservation, and this confidence has been fully justified with but few exceptions so far as the limited literature at my disposal indicates.

The principal condition under which good portland cement has failed to fulfill the requirements of the structure in which it was used, seems to have been where the structure was exposed to the action of sea water. Such exposure has not resulted uniformly in the destruction of the cement, so that even this condition, i. e., the exposure to sea water, a solution comparatively rich in magnesian chlorid and sulphate, may not have been the determining factor in the trouble noted.

The following case of deterioration may be of some interest as it presents some new points. There were sent to me some months ago a number of fragments of tiling which had been laid but from eight to nine months. They had been disintegrated to such an extent that one of the samples was simply a white putty-like mass mixed with sand. There was nothing about this sample remotely suggestive of concrete. Another of the samples consisted of a fragment of the tile, the interior portions of which had been wholly decomposed, while there still remained an outer and inner portion in good condition, or comparatively so. Another sample had been attacked on the inner side leaving the mass of the tile outside of the zone of decomposition apparently sound. The line of decomposition was sharply limited and showed distinctly, but even in this case there remained a thin layer of cement on the inside.

I do not know whether the tile were running full of water or not, probably not, as the fragments seem to be parts of 16 or 18 inch tile. The importance of this point is simply this, that it would answer any question in regard to the separation of solid "alkali" salts on that portion of the tile above the water line. That such a separation of these salts should take place does not seem very probable in this case.

The point of attack so far as the samples at my disposal indicate, is either in the center of the cement mass or near the inner surface. In either case we are almost compelled to assume the action of the water, i. e., of the salts held in solution. At the same time we see the resisting power of the outside and inside surfaces, which are evidently richer in cement than the inner portion of the mass of the tile.

The sand used in making the tile was quite fine.* The proportion used was 5:1. We can readily see that the individual masses of cement in the interior mass of the tile must be small and readily attacked by solutions of salts capable of reacting with the cement.

It seems quite evident that the agents causing this disintegration of the cement must gain access to the interior portion of the mass of the tile

*I do not know the character of the water used.

in the form of a solution, but it is a question whether this solution is the same in strength and character as the water in the drain. I think that I have clearly shown in Bulletin 65 of the Colorado Experiment Station, page 34, that the water soluble portion of the soil is different from the salts held in solution in the ground water. Further in Bulletin 72, page 28 *et seq.* that the ground waters are different from the drain waters, and the action of these waters on the tile would vary somewhat according to the source of the solution which penetrated the mass of the tile.

The drain waters obtained, say at a depth of four feet, contain as a rule a smaller amount of salts in solution than the ground water. The salts present are the same but their relative quantities vary. The usual salts present in the ground waters are, sodic sulfate, calcic sulfate, magnesian sulfate, sodic carbonate, and sodic, in some instances also magnesian chlorid. In the drain waters we have the same salts but their relative quantities are different, the most notable feature being the relatively large amount of sodic carbonate.

The substances claimed to be the most active in effecting the disintegration of cement are the sulfates. In the case of sea water the explanation offered is that the lime of the cement decomposes the magnesian salts present in the water whereby the lime goes into solution and the magnesia is deposited in its stead, causing a bulging and disintegration of the work owing to its greater bulk. The principal magnesian salt in sea water is the chlorid, the deleterious action of which on cement is not established, but it has been shown that magnesian sulfate acts energetically.* The most active agent in decomposing concrete is the sulfuric acid of the sulfates carried in solution. Again solutions of gypsum have been shown to act detrimentally on concrete by forming with the tri-calcic aluminate a sulfo-aluminate.

The water acting on these tiles whether it be ground water or drain water is very bad. One of the two small samples sent to me contained 1252.6 grains per imperial gallon, of which 493.5 grains were sulfuric acid (SO_3) with an extremely large proportion of magnesia. The other contained 542.3 grains per imperial gallon, with 42.31 grains of magnesian oxide or 7.8 per cent. of the total solids. I have examined a number of waters from this section and find the ground water uniformly heavily laden with the sulfates of lime and soda with comparatively large quantities of magnesia, especially if the water comes from near the surface as it necessarily must in the case of drain waters. In addition to the above constituents, there is uniformly some carbonate present which for the present purpose we may consider as sodic carbonate.

We have then an ample supply of these substances present which are known to act deleteriously upon cement, i.e. the sulphates, a portion of which is magnesian sulfate, and in addition there is so much sodic carbonate present that its action cannot be neglected.

For the present I will assume that the cement used was at least an average Portland cement with not more than two per cent. of calcic sulfate added. Assuming this to be correct, the action of the waters on the tile shows an interesting line of action.

A preliminary examination of the white decomposition product indica-

*Taylor & Thompson Concrete Plain and Reinforced P. 401.

ted the presence of a large amount of water, also of considerable quantities of sulfuric and carbonic acids. The decomposed mass was washed with distilled water to remove as much sand as possible. Examination of the wash water showed that it had taken sulfuric acid, lime and soda into solution. The portion soluble in distilled water may have been partly derived from other sources but probably came, for the most part, from the altered cement. The wash water, therefore, was evaporated to dryness and the residue added to the insoluble portion and the whole dried at 60°C. The material thus prepared was submitted to analysis with the following results; with which is also given an analysis of a sample of the same brand of cement.

PORTLAND CEMENT DECOMPOSED BY ACTION OF ALKALI
WATER

| Original Cement | Decomposition Product* | Same calculated on water free basis | |
|--|---------------------------|--|--------------|
| SiO ₂ | 22.55 | 10.98 | 14.16 |
| SO ₃ | 1.29 | 15.56 | 20.07 |
| CO ₂ | 1.07 | 9.39 | 12.16 |
| Cl ₁ | not det'd | 0.51 | 0.65 |
| P ₂ O ₅ | | trace | |
| CaO | 59.86 | 29.14 | 37.58 |
| MgO | 1.75 | 5.79 | 7.46 |
| Al ₂ O ₃ | 5.88 | 2.08 | 2.68 |
| Fe ₂ O ₃ | 4.83 | 2.51 | 3.23 |
| Mn ₃ O ₄ | 0.21 | trace | |
| Na ₂ O | 0.76 | 1.27 | 1.63 |
| K ₂ O | 0.63 | 0.29 | 0.38 |
| H ₂ O Ignit. less CO ₂ | 0.72 | (22.48) | |
| | <hr/> 99.55 | <hr/> 100.00 | <hr/> 100.00 |

The loss on ignition in the analysis of the decomposition product agreed fairly well with that obtained by difference, but owing to the presence of alkalis, carbonates and sand the results of direct ignition are not to be relied upon except to show that the difference indicates the amount of water present with reasonable accuracy.

The composition of the water acting on this tiling may safely be assumed to be represented by the following analysis of a sample of Arkansas river water, essentially a return water, taken at Rocky Ford.

The summation of the analysis presents a rather large excess over one hundred which gives an excess of about one grain in the total amount of salts present. The excess of bases shown in the analysis as combined is not necessarily due to bad analytical work. The waters of our mountain streams show an excess of acids over the bases, but the alkalis forming efflorescences on our soils and alkaline waters, frequently show an excess of the bases, but seldom so large as in this case.

*6.01 per cent. sand deducted.

ANALYSIS OF ARKANSAS RIVER WATER, TAKEN AT ROCKY FORD

Total solids per imperial gallon 156.4 grains.

| Analytical results. | per cent. | Combined | Grs. Imp. Gal. |
|-----------------------------|-----------|-------------------|----------------|
| SiO ₂ | 0.428 | Calcic sulfate | 64.942 |
| SO ₃ | 48.299 | Magnesian sulfate | 27.994 |
| CO ₂ | 1.858 | Potassic sulfate | 0.942 |
| Cl | 4.667 | Sodic sulfate | 32.449 |
| Na ₂ O | 18.662 | Sodic chlorid | 12.044 |
| K ₂ O | 0.326 | Sodic carbonate | 7.007 |
| CaO | 17.090 | Sodic silicate | 1.358 |
| MgO | 5.993 | Ignition | 6.797 |
| Ignition | 4.346 | | |
| Sum | 101.669 | Sum | 153.533 |
| Oxygen equiv. to Chlorin... | 1.051 | Excess sodic oxid | 3.832 |
| Total | 100.618 | Total | 157.365 |

The ground waters of the Arkansas valley have essentially the same composition; they of course, vary in the amounts of mineral matter, total solids, held in solution. The two small samples of drain water sent with these tiles illustrate this very well, one of them carried 1252.6 grains, while the other carried less than one half as much, 542.3 grains in an imperial gallon.

The salient featurers in the composition of the salts present in the ground waters of this section are the large amount of sulfates and the presence of carbonates. The amount of chlorine or the corresponding chlorids is not large and are probably subordinate agents in the alteration of the cement.

Mr. R. Feret says*; "No cement or other hydraulic product has yet been found which presents absolute security against the decomposing action of sea water." Further, "The most injurious compound of sea water is the acid of the dissolved sulfates." Again the same writer says; "It is noteworthy, however, that chloride of magnesia is almost without action, while the sulfate of magnesia acts energetically upon cement. * * *"

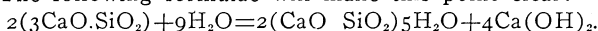
It has further been established by Candlot, Michaelis and Deval working independently, that calcic sulfate unites with calcic aluminate forming a hydrated sulfo-aluminate which expands greatly on crystallizing and is soluble in water.

It is assumed that magnesian sulfate acts upon the calcic hydrate set free by the setting of the tri-calcic silicate, forming calcic sulfate which is then capable of uniting with the calcic aluminate with bad results.

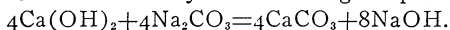
The ground waters found in the lower portions of our irrigated sections contain a mixture of the sulfates of soda, lime and magnesia, with which there is usually associated some carbonate. Some of these waters are essentially solutions of sodic sulfate with a little sodic carbonate; others especially drain waters contain calcic and magnesian sulfates with some carbonate, possibly sodic carbonate.

*Taylor & Thompson Concrete Plain & Reinforced. P. 400.

The knowledge of the fact that our drain waters contain carbonates led me to try the action of a mixture of sodic sulfate and carbonate on the coarsely ground concrete. This mixture attacked the cement rapidly yielding a white decomposition product rich in carbonic acid. This result is no other than what we would expect. If the tri-calcic silicate in setting really liberates four molecules of calcic hydrate, as we suppose the reaction should be accompanied by the liberation of a corresponding amount of sodic hydrate. The following formulae will make this point clear:



The calcic hydrate liberated or very loosely held can readily act on the sodic carbonate as indicated by the following simple formula;



The sodic hydrate thus freed is capable of further attacking the silicates and possibly the aluminates, carrying silicic acid, alumina and lime into solution, probably as hydrated silicates. The treatment of the cement with a mixed solution of sodic carbonate and sulfate showed that it is a fact that calcic carbonate is formed and also that silicic, alumina and lime do go into solution and that too without the aid of free carbonic acid.

No care was taken to make the solution of mixed salts even approximately of the same strength, as the ground waters, and no ratio between the salts was observed, simply, that the solution was a weak one; two to three grams of sodic carbonate to the liter with five or six grams of the sulfate. The time of the experiment was 14 hours. The time was short, and the solution not as rich in salts as some of our ground and drain waters. The tiles on the other hand are exposed to the action of similar solutions, some weaker but others stronger from the time of being laid till taken out, in this case eight to nine months. In view of these considerations it is not strange that the mass of concrete should be softened and destroyed.

Using the results of these rather crude experiments we may interpret our analyses as indicating that the cement has been deprived of silicic acid; it originally contained 22.50 per cent. but the hydrated decomposition product contains only 10.98 per cent or 14.16 per cent calculated on a water free basis. While the ratio of the weight of the decomposition product to the original weight of the cement is not known, there is no evidence that there has been any increase in the weight which would invalidate the preceding observation and a second experiment with cement and a solution containing sodic sulfate and carbonate leaves no question about the removal of silicic acid, alumina and lime by waters containing these salts. The analyses also suggest the removal of a relatively large amount of lime. The cement contains 59.56 per cent. of lime while the alteration product contains but 37.58 per cent. (calculated on a water free basis). Further the ferric and aluminic oxids have been reduced to about one half as much in the decomposed cement as there was in the original. The sodic sulfate, more particularly the calcic and magnesian sulfates which are present in the ground water will at the same time act on the tri-calcic aluminate, forming the sulfo-aluminate $2(3\text{CaO} \cdot \text{Al}_2\text{O}_3) + 5\text{CaOSO}_3$, which crystallizes with 60 molecules of water and is soluble. That these reactions really have taken place is indicated by the increase of the sulfuric acid SO_3 which amounts to 20.07 per cent. and likewise of the carbonic acid which amounts to 12.16

per cent. of the water free decomposition product, while they amount to only about 1.0 per cent. each in the original cement.

That the magnesian sulfate also participates in producing the deterioration is indicated by its presence in the altered cement to the extent of about five times the amount present in the original; i.e. 7.46 per cent. in the water free alteration product against 1.75 per cent. in the original.

The changes effected in this case are quite consonant with the views quoted excepting the formation of so large a proportion of carbonate, evidently calcic carbonate due to the action of the sodic carbonate in the ground water. The presence of sodic carbonate in a solution so rich in lime may seem improbable, but this has been shown to be not only possible, but a fact.

This alteration product differs materially from those produced by the action of sea water on the works at Aberdeen and analyzed by Prof. Brazier (Redgrave and Spackman, *Calcareous Cements*, p. 285.) according to which the chief decomposition products were calcic carbonate with calcic and magnesian hydrates, while the amount of the sulphuric acid was scarcely altered at all. The analyses indicate a removal of the ferric and aluminic oxids from the interior portions of the work, and an increase of them in the outer portions. The authors after giving the analyses justly make the following statement: "We may observe with respect to these analyses that both in the case of the original cement and the deteriorated concrete, there are many matters which we are quite unable to reconcile."

The action of the ground waters seems to have been one of chemical change converting the lime of the cement into a sulfate and carbonate accompanied by the removal of silicic acid, alumina and lime and totally destroying the cohesiveness of the concrete.

The samples of deteriorated tiles sent to me do not justify any inferences whatever in regard to the part that may have been played by the expansive force of newly formed crystallizable compounds. The thickness of the tile and the amount of material involved is so small that this factor is negligible and the results presented are probably wholly due to chemical action.

This subject is of some importance as concrete structures, bridges, culverts, foundations, etc., are being erected in places where they will be subjected to the action of such waters.

Most of the cretaceous shales are, so far as my observation goes, rich in alkalis, calcic sulfate, etc., and concrete foundations laid in these may be acted on prejudiciously.

As the work in this article was about completed, I received Bulletin 69 of the Montana Experiment Station. The attention of the writers of this bulletin, E. Tappan Sannatt, and Edmund Burke, was called to the deterioration of the cement mortar used in the construction of the sewer system of Great Falls, Montana, by the City Engineer, C. W. Swearinger.

This bulletin gives some excellent illustrations of deteriorated mortar and a general description of the conditions as they found them, also some suggestions relative to their local conditions and recommendations in regard to foundations and other structures made of concrete, but there is no chemical work done on the cement and the products of its alteration. Such work is promised for some future time.