

# THE DETERIORATING ACTION OF SALT AND BRINE ON REINFORCED CONCRETE.\*

BY

**HENRY JERMAIN MAUDE CREIGHTON,**

Department of Chemistry, Swarthmore College.  
Member of the Institute.

AT the present time, when concrete structures are being erected throughout the country for all manner of purposes, it is of the greatest importance that the limitations, the durability, and the causes of the deterioration of reinforced concrete should be thoroughly understood. Within the past few years the number of reinforced concrete structures has been increasing so rapidly that to-day concrete has replaced brick and stone to a large extent. Since most of our oldest reinforced concrete is not over fifteen to eighteen years old, who can predict, from so short a period of observation, its condition twenty-five or fifty years hence?

During the past few years there has been considerable discussion regarding the durability of concrete, and there exists a certain amount of disagreement on the matter. There appeared in *Engineering News* of April 4, 1912, wherein is published a report of the American Society for Testing Materials' meeting, the following sentence: "The report of the water-proofing committee brought about some excited discussions, during which several persons affirmed their belief in the imperishability of concrete and protested against any hint of any other possibility." However, though "it is no doubt true that many diseases can be cured by a practitioner who strenuously denies their existence and thus encourages the patient to resist and overcome them, it can hardly be expected that defective concrete walls or disintegrating piers can be strengthened by 'absent treatment,' however vigorous be the denial of the injury or however prominent the denier." It is much better to look facts in the face and attempt to find a remedy.

Sea-water, one of the agents which brings about the disintegration of concrete, attracted the attention of users of cement

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\* Communicated by Professor Creighton.

soon after it was first employed in marine construction. Although a great deal of non-reinforced concrete has withstood the action of the sea up to the present, and will probably continue to do so, still some of it has failed. Although the cause of this disintegration is not definitely known, Le Chatelier and others point out<sup>1</sup> that it can probably be ascribed to a reaction between the magnesium sulphate of the sea-water and the lime of the cement (formed during setting) and the alumina of the aluminates of the cement, the result being the formation of magnesium hydrate and calcium sulpho-aluminate, which crystallizes with a large number of molecules of water. Notwithstanding that the other components of sea-water have usually been considered as having little effect on concrete, attention has recently been called to the fact that both sodium chloride and magnesium chloride rapidly react with the silicates in concrete.<sup>2</sup>

In the laboratory it is possible to destroy, almost completely, small cylinders or other forms of concrete or cement mortar by the action of solutions of various salts. The "Action of the salts in alkali water and sea-water on cement" has been the subject of a lengthy investigation by Bates, Phillips and Wig, of the U. S. Bureau of Standards, and their results have been published<sup>3</sup> under the foregoing title. This investigation was undertaken in consequence of disintegration of concrete, through the action of water containing magnesium and sodium sulphates, occurring in several irrigation projects in some of the Western states; and for the purpose of determining the action of various single and mixed salt solutions on concrete and cement. The salt solutions were allowed to percolate through hollow cement cylinders closed at one end, and it was found that any cement mortar may be destroyed if a sufficient amount of salt accumulates and crystallizes out. It was also found that, in general, chloride solutions were more active than sulphate solutions in removing lime from concrete, but that mixed chloride and sulphate solutions were more active than solutions of single salts.

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<sup>1</sup> Le Chatelier, *Tonindustrie Zeitung*, 33, 931; Chandlot, "Ciments et Chaux Hydrauliques," p. 306; Michaelis, *Bul. de la Soc. D'Encourag. de l'Ind.*, June, 1897.

<sup>2</sup> Chandlot, *loc cit.*; Michaelis, *Bul. de la Soc. D'Encourag. de l'Ind.*, 682, 1890; D'Rohan, *Eng. Record*, July 20, 1910.

<sup>3</sup> Bur. of Standards, Techn. Paper 12, JOUR. FRANKLIN INST., 175, 65.

According to a recent report<sup>4</sup> by J. L. Harrison, District Engineer, Iloilo, the cracking of reinforced concrete structures is markedly prevalent in the Philippine Islands. A study of this trouble has shown that not a single structure showing rusted steel has been free from salt, the percentage of which varies considerably. In view of this, engineers in the Philippines have been advised that not only is the use of salt water dangerous in concrete structures, but that beach sand and beach gravel should be employed only after having been thoroughly washed with fresh water.

The foregoing, and many other similar pieces of evidence, indicate that salt and brine exert a deteriorating action on concrete.

In this paper the writer wishes to give a brief account of observations on the deterioration of reinforced concrete by salt and brine, which were made by him, a few years ago, while examining a large number of reinforced concrete structures in different parts of the country.

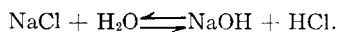
In order that the deteriorating action of salt water on iron may be better understood, the probable reactions which occur when this metal comes in contact with a salt solution will be briefly discussed.

When a piece of iron is placed in distilled water, it becomes negatively charged, since its electrolytic solution pressure (which is equal to  $1.2 \times 10^4$  atmospheres) causes atoms of the metal to pass into solution in the form of positively charged ions, leaving an equivalent number of negative charges behind on the bar of metal. In spite of the large electrolytic solution pressure of iron, only a vanishingly small quantity of it passes into solution in the form of ions, and, consequently, the bar of metal receives but a very small negative charge. This is due to the fact that when a ferrous-ion with its large positive charge ( $2 \times 96,500$  coulombs for every gramme-ion of the metal) leaves the bar of neutral metal the latter acquires a correspondingly large negative charge; it therefore becomes more difficult for a second ferrous-ion to go into solution, owing to the attraction between the unlike charges; and it is still more difficult for a third ion to leave the metal, and so on. Very soon, therefore, the negative charges upon the bar of metal become sufficient to prevent further fer-

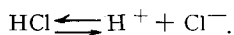
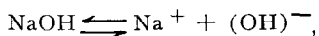
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<sup>4</sup> *Bulletin* of the Bureau of Public Works, October, 1916.

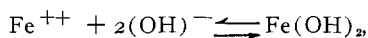
rous-ions from going into solution, and equilibrium occurs; and, unless these negative charges are removed from the metal, no more iron can pass into solution. Suppose, now, that common salt be added to the water containing the bar of iron. On dissolving, this electrolyte largely dissociates into its ions, and it may be assumed that hydrolysis takes place, although to a most limited extent, in accordance with the equation:



The concentration of these new substances being extremely small, they dissociate practically completely and give rise to negatively charged hydroxyl ions and positively charged hydrogen ions:



The hydroxyl ions then unite with the ferrous-ions, that have passed into solution from the bar of metal, to form undissociated ferrous hydroxide:



which gradually precipitates as an hydrated oxide. The presence of dissolved oxygen in the solution would, of course, gradually convert the oxide and ferrous hydroxide into the corresponding ferric compounds.

The negative charges upon the bar of iron, which were in equilibrium with the ferrous-ions before the addition of the sodium chloride, now attract the positively charged hydrogen ions, the electrolytic solution pressure of hydrogen being much less ( $9.9 \times 10^{-4}$  atmospheres) than that of iron and very much less than that of sodium ( $> 10^{43}$  atmospheres). In consequence of this attraction, hydrogen ions move towards the negatively charged iron bar, touch it and become neutral, gaseous hydrogen atoms. The negative charges on the bar being thus diminished, more iron enters the solution in the form of ferrous-ions, and the foregoing process occurs again, and so on. In this way the bar of iron gradually disappears and iron oxide and hydrated oxide accumulate.

The nascent hydrogen which is produced on the bar may be absorbed by the iron; it may be oxidized by the oxygen dissolved in the solution, or it may be liberated as a gas. In order to determine whether gaseous hydrogen is ever liberated under the foregoing conditions, the writer immersed a number of pieces of iron in dilute aqueous solutions of sodium chloride contained in glass tubes with a capillary top, and connected at the bottom with a small glass tube bent upwards at right angles. Before being introduced into the glass tubes, the salt solution was boiled to remove the air, and afterwards, before sealing off the tip of the capillary, a high vacuum was applied to the solution for some time. It was found that in all the tubes a grayish-green deposit slowly accumulated near the bottom, and at the end of several months a small quantity (0.1 to 0.2 c.c.) of gas had formed in three of the tubes. This gas proved to be mostly hydrogen.

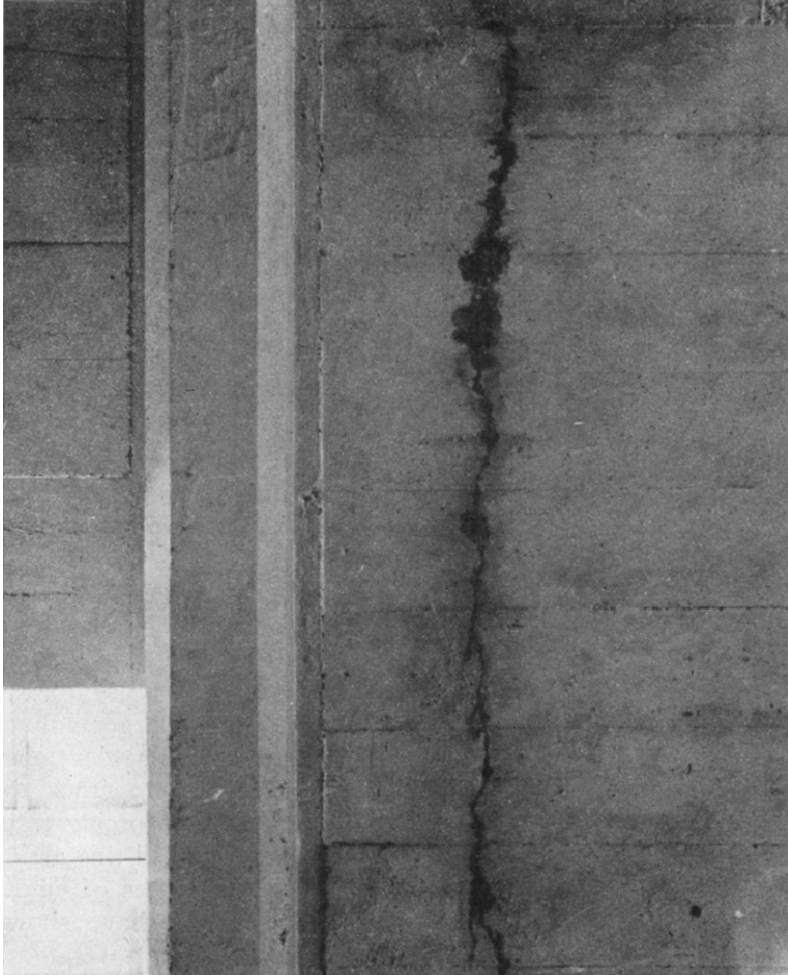
In addition to the corrosion of iron through the action of brine by the processes just outlined, auto-electrolysis may occur on account of the presence of segregated impurities which are responsible for the differences of potential established in certain areas. These potential differences bring about a galvanic action which causes the iron to go into solution at certain points with the formation of rust.

From what has been said, it is clear that reinforced concrete which comes in contact with brine or sea-water, unless rendered absolutely impervious, will commence to deteriorate as soon as the brine comes in contact with the reinforcing rods; for, as both iron oxide and the hydrated oxide occupy a larger volume than the corresponding amount of iron, there will be developed an enormous expansive force which is sufficient to crack the strongest concrete and force it away from the reinforcing rods. The more porous the concrete, the more rapidly will this action take place. Indeed, the writer is familiar with cases of cinder concrete structures, in contact with brine, which have shown signs of advanced deterioration at the end of a year.

Regarding the water-proofing of concrete, it should be pointed out that an impervious concrete is probably never obtained outside the laboratory. The average concrete is practically never water-proof. Although there are many substances on the market for rendering concrete water-proof, the majority of them

is far from satisfactory. A number of such instances has been investigated by Brown,<sup>5</sup> who points out that all water-proofing materials will sooner or later hydrolyze, crack, or disintegrate.

FIG. 1.

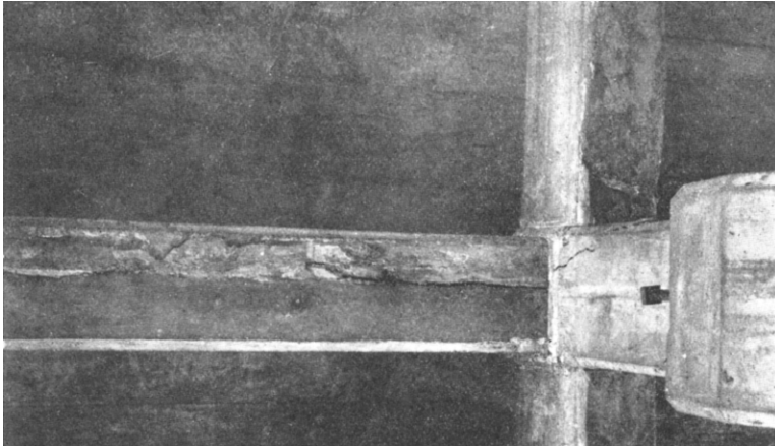


Since most concrete is more or less porous to moisture, and since iron undergoes gradual decomposition, in the presence of salt water, with consequent expansion in volume, it is to be

<sup>5</sup>*The Electrician*, 69, 915 (1912).

expected that reinforced concrete which comes in contact with brine or salt and moisture will ultimately disintegrate. It is not surprising, therefore, to find throughout the country reinforced concrete piers, sea walls, and buildings in the neighborhood of the ocean in various stages of deterioration. The cracks which occur in such concrete usually run parallel to the reinforcing rods. These cracks are very narrow at first, but as the decomposition of the iron progresses they become iron-stained, gradually increase in width, and, finally, the concrete is forced so far from the reinforcing rods by the pressure of the accumulating iron oxide that large pieces of it break off.

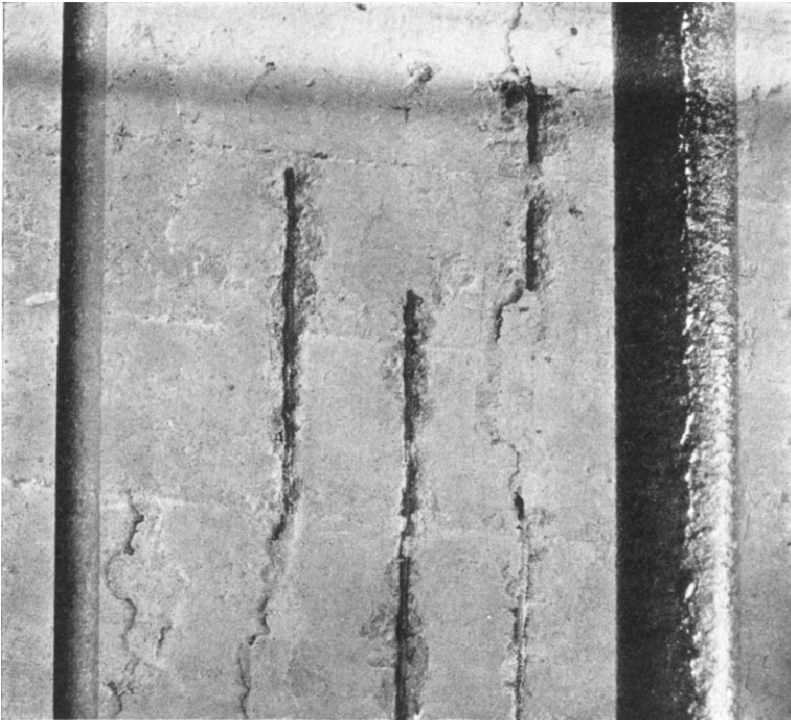
FIG. 2.



In many parts of the country to-day there are reinforced concrete structures housing industries that use large quantities of salt and brine, which are constantly spilled on the floors. In order to ascertain whether the concrete of such buildings has undergone any deterioration, the writer a few years ago examined a large number of them in different cities throughout the country. In practically all the buildings inspected, reinforced concrete floors which came in contact with brine had iron-stained cracks on the under side. Usually these cracks were very narrow, but they indicated, nevertheless, deterioration of the reinforcements, and would continue to grow as the disintegration of the iron progressed. Fig. 1, which is a photograph of the ceiling of a large reinforced concrete building in Detroit, the floors of which are

continually wet with brine, is a typical example of one of these iron-stained cracks in the early stages, and Fig. 2 shows a cracked horizontal beam supporting the floor of a reinforced concrete building in Chicago. In many instances the cracks were found to vary from  $\frac{1}{8}$  to  $\frac{1}{4}$  inch in width, and in some cases deterioration had progressed so far that large pieces of concrete had fallen, or were about to fall, leaving the badly corroded reinforcements

FIG. 3.

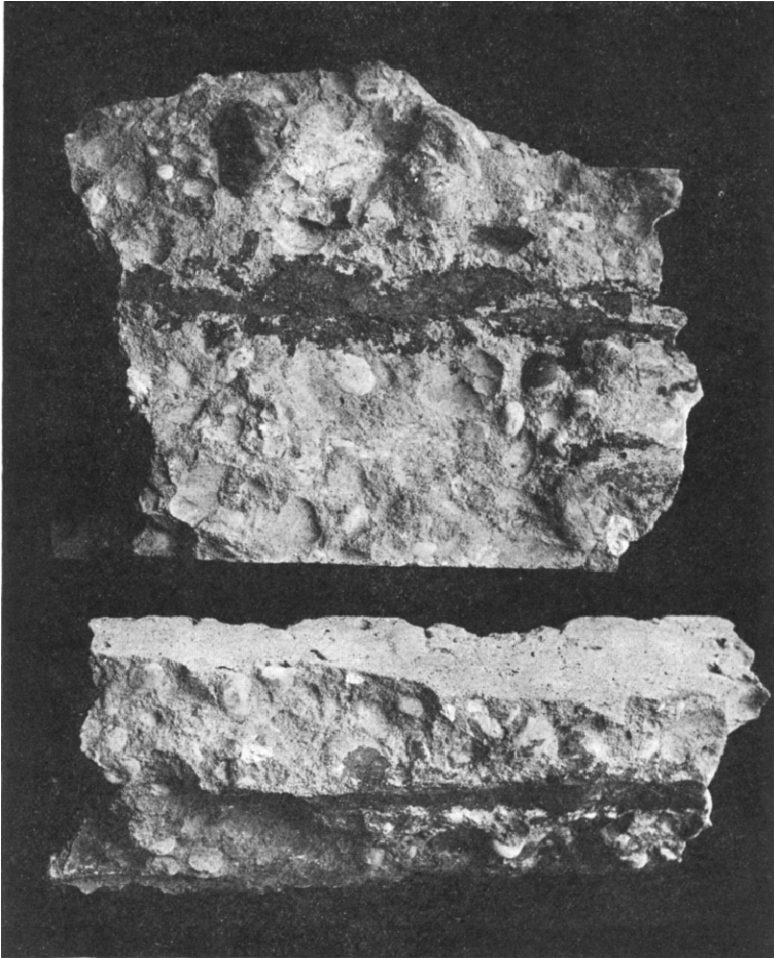


exposed, as illustrated by Fig. 3 (photograph taken in Buffalo). An examination of a number of pieces of this fallen concrete showed that in every case a quantity of iron oxide adhered to the concrete where it had come in contact with the reinforcing rods (Fig. 4), and that it was sometimes as thick as  $\frac{1}{8}$  inch. Where the concrete had broken away from the reinforcements, the latter were usually so badly corroded that it was possible to remove thick layers of oxide with the fingers. In a few cases the deterioration had progressed to such an extent that the rein-



forcements had been completely converted into oxide. Fig. 5 shows pieces of iron oxide,  $\frac{1}{8}$  to  $\frac{3}{16}$  inch thick, which were pulled away from corroded reinforcing rods or beams with the fingers.

FIG. 4.

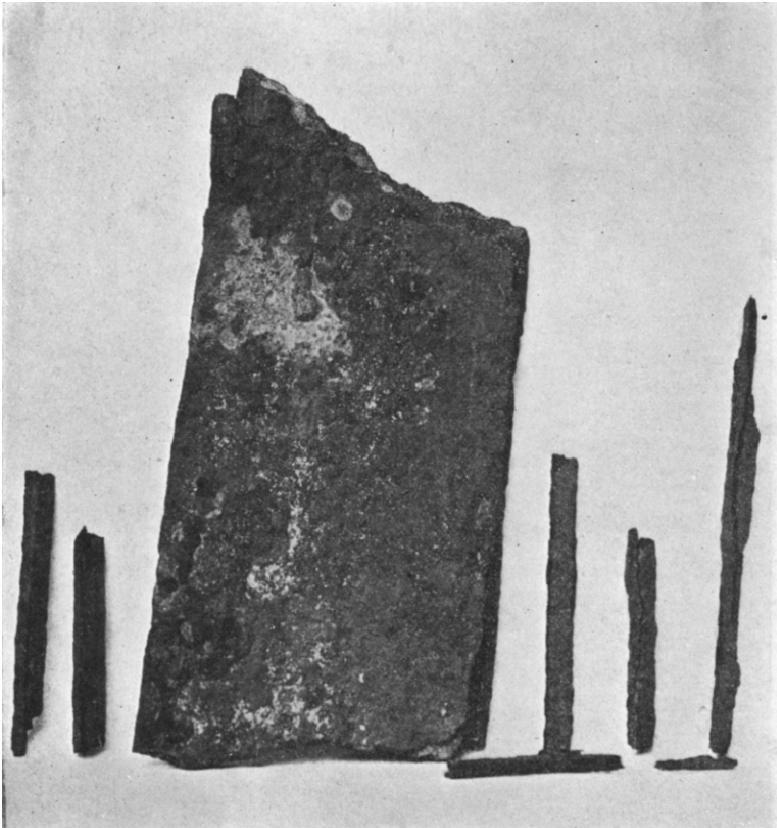


A few details regarding particular cases of deterioration met with in some of the reinforced concrete structures examined may be of interest.

The ceiling of a machine shop of a large reinforced concrete plant in East St. Louis was found to be very badly damaged.

This building, at the time of inspection, was about ten years old. The upper side of the ceiling was continually wet with brine, which constantly leaked through to the under side and wetted it in a number of places. On this ceiling large, brown iron-stains were numerous and in at least twenty places pieces of concrete had fallen, leaving badly corroded, net-iron reinforce-

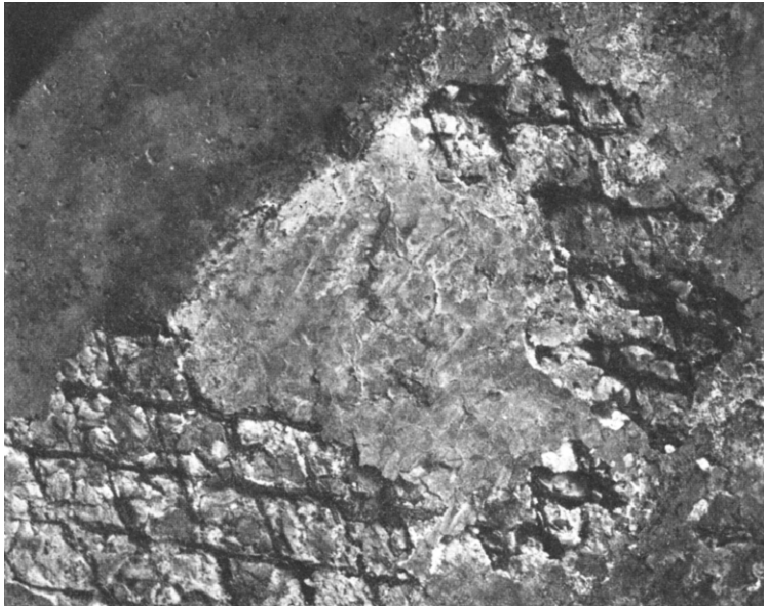
FIG. 5.



ments exposed. In one place a piece of concrete twelve feet long and varying from two to eighteen inches in width had broken away. The reinforcements of this ceiling were imbedded at a depth of about  $\frac{3}{4}$  inch from the surface. Photographs of this ceiling are shown in Figs. 6, 7 and 8. Examples similar to these have been observed by the writer in Chicago, Kansas City, Detroit, and Buffalo.

At a plant in Kansas City there was found a very interesting cracked reinforced concrete pillar which supported a reinforced concrete platform at the top of an outside staircase. Large quantities of salt were used in the plant, and the platform was often wet with brine. The cracks on the pillar ran parallel to the longitudinal reinforcing rods. In some places the concrete had fallen away from the rods, which were badly corroded, and in others portions of the concrete were easily pulled away. A photograph of this pillar is shown in Fig. 9.

FIG. 6.



At another plant in this city there was a long outside platform, from which cars were loaded, covered by a reinforced concrete roof. At one end of this roof there was a pile of rock salt, which was partially protected from the weather by a wooden roof. Rock salt had been stored in this place for years. For a number of yards beyond where the salt was stored it had been spilled continually on the concrete roof, and, owing to rains, perhaps a quarter of the roof was frequently wet with dilute brine. On the under side of the roof, directly below this place, there were many brown iron-stains, wet patches, salt deposits, and in one place

FIG. 7.



the concrete had fallen, leaving the net-iron reinforcements exposed. These had deteriorated to such an extent that the outer portions crumbled on touching and some of the rods were easily pulled away. The area from which the concrete had fallen was at least one square foot. The individual rods of the exposed net-rein-

FIG. 8.

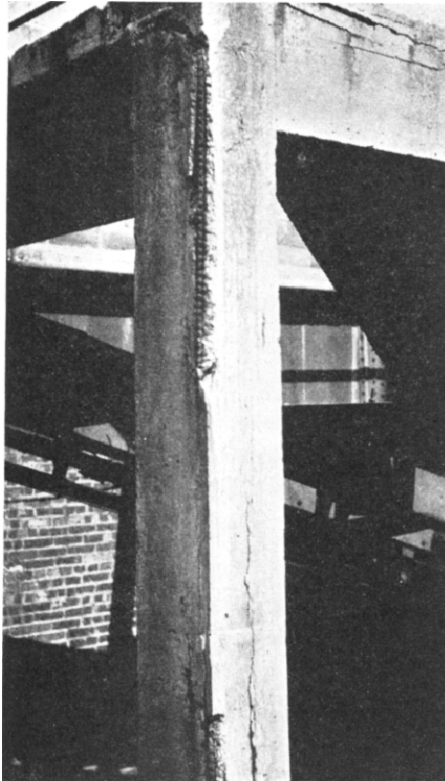


forcing, originally about  $\frac{1}{8}$  inch in diameter, had increased to about  $\frac{1}{4}$  inch in diameter, owing to the conversion of the iron into oxide. Some of these rods had disintegrated to such a degree that the sound iron core was less than  $\frac{1}{25}$  inch in diameter. Near where the concrete had fallen, it was evident that

the expanding reinforcings were gradually forcing the concrete downwards. At the far end of the ceiling, where salt had not been spilled above, there was no evidence of deterioration and the concrete was in an excellent condition.

At a third plant in Kansas City, a five-year-old, reinforced concrete, basement ceiling was found to be in a very bad condi-

FIG. 9.

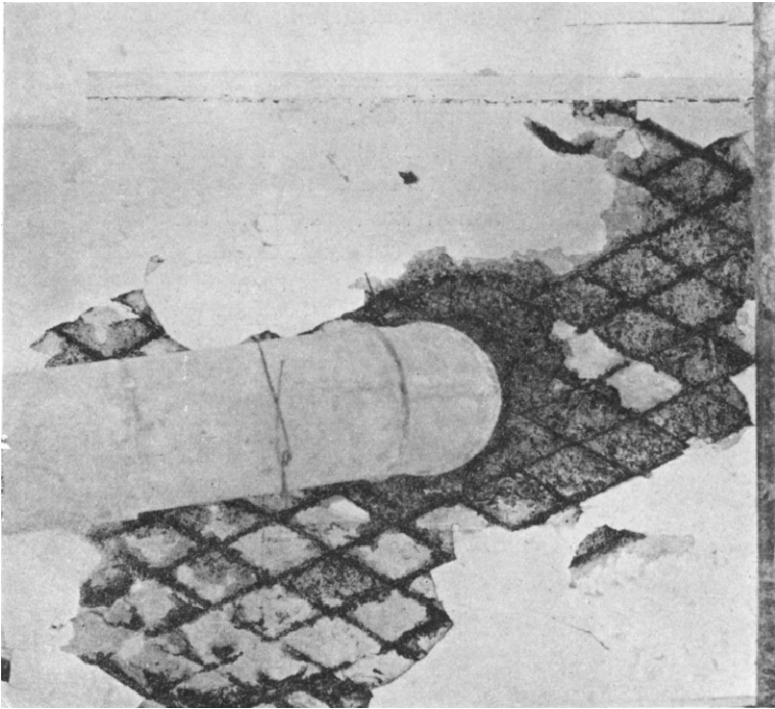


tion. This ceiling was reinforced with  $\frac{3}{4}$ -inch twisted iron rods. The floor above was more or less wet all the time, and, in places, salt came in contact with the water, forming brine. There were many cracks on this ceiling, some of which were sufficiently wide to insert a lead-pencil. One such crack was twenty to thirty feet in length. In several places large pieces of concrete had fallen, leaving corroded reinforcements exposed.

In one place a large piece of concrete which was almost dropping and which weighed about twenty-five pounds was easily pulled away from the reinforcements. The under side of this, as is usually the case, had a large portion of the corroded reinforcements adhering to it.

The writer examined a building in Kansas City which contained a large quantity of reinforced cinder concrete that came into contact with considerable amounts of brine. This concrete,

FIG. 10.



which was thirty years old, was in a very damaged condition, and in many places very large pieces had fallen.

In one of the Chicago plants examined, a whole floor had collapsed about a year previously, owing to the weakening of the reinforcements by disintegration.

Similar cases to the foregoing have been found by the writer in a number of cities in different parts of the country. An excellent example of deterioration of reinforced concrete found in Buffalo is shown in Fig. 10.

When concrete construction is carried out in winter, it is sometimes the practice to add salt to the concrete to prevent freezing, often as much as twenty per cent. being added. The writer has examined a number of reinforced concrete structures where salt had been mixed with the concrete during construction. As is to be expected, where the concrete comes in contact with water or moisture, there are manifold evidences of deterioration; but, on the other hand, where the concrete has been kept dry no damage has been observed.

The following conclusions are drawn by the writer from his investigations of the action of salt and brine on reinforced concrete:

1. All concrete which is not water-proofed in some way is more or less porous to water and brine.

2. Brine readily softens the surface of concrete and, therefore, more easily penetrates to the reinforcements, on which it exerts a disintegrating action that, owing to the attendant expansion, gradually weakens the concrete, causing it to crack and split, and in some cases to fall away from the reinforcements.

3. The more porous the concrete, the more rapid the disintegration of the reinforcements through the action of brine.

4. Reinforced concrete floors which come in contact with brine will gradually develop leaks. These will be followed by incrustations of discolored salt on the under side, where, later, iron-stained, hair cracks will develop running parallel to the reinforcements. As the deterioration progresses, the cracks will widen and, owing to the great expansive force of the accumulating iron oxide, the concrete will be gradually pushed from the corroded reinforcements and ultimately fall.

DEPARTMENT OF CHEMISTRY,  
Swarthmore College,  
July 27, 1917.