

A STUDY OF THE MOVEMENT OF ALKALIES IN
PORTLAND CEMENT CONCRETE BY MEANS OF
RADIOACTIVE ISOTOPES

by

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INTRODUCTION

In 1940 T. E. Stanton (4, 5) first reported evidence of reaction between alkalis in cement (Na_2O and K_2O) and certain types of aggregate. Excessive expansion was noticed in certain concrete structures while others made with the same cement but different aggregate remained in good condition. In other structures concrete made with the above poor aggregate remained in good condition when a different cement was used. This discovery led to the belief that some constituent in certain cements reacted with some constituent in certain aggregates to form a product that gives rise to excessive expansions.

Since this first report by Stanton, deterioration of concrete attributed to this kind of alkali-aggregate reaction has been reported by many investigators in all parts of the world.

Experimenters have shown that abnormal expansions occur when high alkali cements are used with reactive aggregate. It has also been shown by measurement of expansion that alkali from a relatively highly concentrated zone will migrate to another zone in which the concentration is lower provided moisture conditions are agreeable. Another example of alkali migration is found in areas where alkali soil is present. Surface water may take up soluble alkali salts from the soil and upon entering the concrete carry alkali ions in solution to a position where harmful alkali-aggregate reaction may take place.

It is a known fact that concrete is a porous material; i.e., there exists small interconnected pores or capillaries. The movement of alkali through concrete can best be explained as due to

diffusion through these solution filled pores or capillaries. Diffusion will take place from a point of high concentration to one of lower concentration. For this reason it would be expected the alkalis would be lost from concrete that is stored in water. Conversely, it would be expected that a relatively low alkali cement concrete would take up sodium ions when stored in NaOH solution. Several investigators have shown this to be the case (1, 2).

It seems apparent then that for the alkali aggregate reaction to occur there must be present in the system, alkali, reactive aggregate, and if the alkalis are not distributed, free water must be available for the purpose of transporting alkali ions from one zone to another.

One of the most reliable and quickest methods for determining the extent of the alkali aggregate reaction is by the measurement of expansion of concrete beams subjected to alternate wetting at 70° F. and drying in air at 130° F. Even with this accelerated aging test a comparatively long time is taken for the reaction to manifest itself. Thus it may be concluded that the formation rate of harmful expansion product is very slow. For example a test specimen in which harmful aggregate reaction takes place may expand approximately one per cent in one year compared with a normal expansion of approximately 0.03 per cent in the same period of time.

One of the most widely accepted hypotheses for the mechanism of cement aggregate reaction is that of W. C. Hansen (1). It seems to be well established that the silicate ions in solutions

of alkali silicates tend to associate into complex ions. Due to the size of the silicate ion, diffusion through the hardened cement paste would be restricted while water and the ions and molecules of the alkali hydroxides would diffuse freely. These are the requirements of an osmotic pressure cell. Under these conditions alkali hydroxides would be drawn from solution outside the cell and a hydrostatic pressure would be built up against the confining cement paste. The possible equation for this reaction is as follows,



The method for reducing serious expansion that is currently receiving most attention is by the addition of pozzolanic materials. It has been shown by Scholer and Smith (3) that the use of certain pozzolanic materials in amounts of 20 to 30 per cent substitution for portland cement, will inhibit this reaction to a noticeable extent. The mechanism by which this is done is not clearly known.

PHASE I - MATERIALS AND METHODS

Phase I of this investigation was designed to see if it would be possible to cause alkali salts to migrate upward through concrete prisms that have their bases submerged in water, and their tops exposed to a warm dry atmosphere. A great bulk of the concrete used in the United States is placed with one or more surfaces in contact with the earth where it is subjected to saturation from ground water originating in the earth fill on which it is placed. This phase of the investigation attempts to simulate

the action of ground water rising by capillary action through a concrete structure; e.g., a highway or a sidewalk.

The materials and proportions used in sample preparation were:

1. Blue River Sand from Florena Switch, Kansas
2. A standard brand portland cement (type 1).
3. Radioactive Na^{22}Cl . (Details of gradation of aggregate, physical and chemical properties of the constituents are given in the appendix Table IV)

One part of cement to five parts of combined aggregate by dry weight was used with a water-cement ratio of 6.5 gallons per sack.

The prisms were designed to be neither impervious nor excessively permeable, and would be similar to much of the concrete that is used commercially in this area.

As a method of determining the diffusion of alkali ions in concrete, the unique properties of radioactive tracers were utilized. Since the chemical reactions of tracer sodium and normal sodium ions can be studied by observing the radiations given off by the radioactive material. The tracer method has two distinct advantages, one of which is the ease of detection of the position of the sodium ion without physically or chemically disturbing the concrete sample. Secondly the tracer method is at least as sensitive as flame photometer procedures for the determination of sodium ion concentration.

A radioactive isotope of sodium with a half life of 2.6 years

can be prepared by bombarding magnesium with deuterons. Sodium-22, decays by emission of positrons and gamma rays. Positrons are readily stopped by a small thickness of concrete. About one-half of the gamma rays from sodium-22 are absorbed in traversing two inches of concrete. The gamma rays which do pass through can readily be detected by Geiger-Mueller counters and by radioautographic techniques. Since the half life of sodium-22 is long, the activity and rate of diffusion can be measured for as long as twenty years.

PHASE I - EXPERIMENTAL

Four 2" by 2" by 12" concrete prisms were molded in the standard manner. A deposit of radioactive sodium chloride was placed in the center and approximately 1-3/4 inches from one end, while the concrete was in a plastic condition. To avoid evaporation from the 12 inch sides of the specimens, a brush coat of 156° F. melting point asphalt cement was heated and applied. A jacket of copper foil .001 inch in thickness was placed over the asphalt to further seal and to simplify the handling of the specimens.

The radioactive Na^{22}Cl was received from the Atomic Energy Commission as a liquid. This was evaporated to dryness and the radioactive materials deposited in solid form. Approximately 0.3 millicurie was placed in each concrete prism.

If water from the base permeates through the concrete, sodium ions should migrate through the capillaries in all direct-

ions to zones of lower concentration. Should this take place, probably the greatest migration would be in a downward direction to the relatively large volume of water in which the base of the specimen is submerged. Thus, it was the immediate purpose of this phase of the investigation to effect a redistribution of the radioactive sodium ion and to devise a suitable method of detecting this redistribution. In order to avoid destruction of the specimens, two methods were employed to detect this movement. One of these methods is by means of a photographic plate, and will be discussed later. The second method of noting redistribution is to record radiation received by a radiation survey meter as it was placed at various positions along the 12 inch side of the specimen. This method has to date shown only small changes in the redistribution of radioactive sodium in the specimens as the radiation meter shows considerable fluctuation for the same level of activity. Unless the sodium concentration increased by at least 20 per cent in a given section, this method would not detect it.

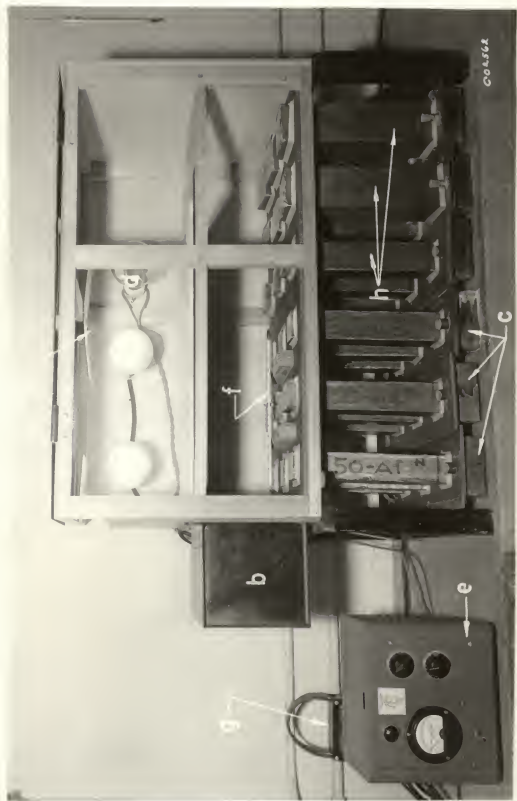
EXPLANATION FOR PLATE I

APPARATUS FOR INDUCING FLOW OF
WATER IN CONCRETE PRISMS

(Door Open)

- a. Cabinet
- b. Blower
- c. Pans containing water
- d. Light Bulbs (Heat Source)
- e. Thermocap Control
- f. Thermometer
- g. Transformer
- h. Concrete Prisms

PLATE I



EXPLANATION OF PLATE II

APPARATUS FOR INDUCING FLOW OF
WATER IN CONCRETE PRISMS
(APPARATUS IN OPERATION)

PLATE II



The apparatus used for this experiment is shown in Plates I and II. The concrete prisms were supported with the lower ends immersed in water while the upper ends were exposed to a draft of warm dry air. The blower is arranged to pull room air over three, two hundred watt light bulbs, and thence over the upper ends of the prisms. The thermocap control is arranged to actuate one of the three light bulbs, and was controlled by the thermometer. The temperature was arbitrarily set at 100° F.

For this experiment specimens 7, 8, and 9 were placed in the apparatus while 10 was left outside in laboratory air as a control specimen.

A camera was designed to strap along one 12 inch side of the prism. A small diameter wire was soldered on the copper covering for an index mark. Each time an exposure was made the camera was butted against this index wire. Thus each exposure was taken from the same position on the prism each time. Plate III, Fig. 1. and Fig. 2., show the camera attached to a specimen. The back-plate is removed ready for insertion of film. An exposure time of 24 hours was used in all of this phase of the work. Variations were held to a minimum by taking medical x-ray film from the same box and keeping conditions of exposure and development constant. An example of a print of a developed exposure is shown in Plate IV. It should be noted in viewing prints of the x-ray film that the exposed portion of the film appears light. When densities were determined negatives were used. The same exposed portion would appear dark on the negative.

EXPLANATION OF PLATE III

Fig. 1, Fig. 2

Camera attached to 2 in. x 2 in. x 12 in.
concrete specimen. "A" indicates end of
specimen with radioactive deposit. This
end is placed in $\frac{1}{8}$ in. of water.

PLATE III

A



FIG. 1.

A



FIG. 2.

EXPLANATION OF PLATE IV

Print of exposed x-ray film. The light portion corresponds to section of film at "hot" end of concrete prism.



Relative darkening of the developed plates were compared with a Leeds and Northrup recording densitometer. Densities were obtained from these recordings and plotted versus distance from hot end. By this means densities at any point can be compared monthly. An example of a typical densitometer recording is shown on Fig. 1. Figure 2 shows a plot of density vs. distance obtained from the densitometer recording.

PHASE I DISCUSSION

At the present time an increasing amount of activity has been detected in the pans. This indicated that a redistribution of the sodium ion was occurring. Unfortunately, no quantitative record has been kept to this activity, but enough information has been gathered to indicate that the concentration is increasing with time.

Although this method of detecting redistribution seems ideal, the results of eight months experimentation do not conclusively indicate movement upwards through the concrete. An examination of Fig. 2 will show that calculated densities fluctuate considerably from month to month. For example, specimen No. 10 shows at a distance of 9 units that the first reading has a density of 2.3, then 2.5 one month later, 1.6 another month later and 2.0 at the end of three months. Since it is difficult to conceive of such a change occurring one would suspect that the results obtained are in error. However, densities were closely reproduced several times when exposures were taken on two consecutive days. It is

urgent that this phase of the investigation be continued for a longer period of time since it has been established that the rate of movement of the alkali ion in this type of specimen would be very slow.

PHASE II MATERIALS AND METHODS

Phase II of this investigation was designed to study the distribution of radioactive sodium which permeated the walls of concrete cups. A comparison was made of distribution of sodium ions in plain portland cement and several fly ash substituted concrete cups. Also two samples were run in which the distribution of calcium ion was observed. In these cups solution of salts was maintained under a head of about 2.75 inches. Under these conditions the water percolating through the sidewall would be under a greater driving force than that of water percolating through the 2 by 2 by 12 inch prisms by capillary action, described in Phase I of this investigation. The smaller resistance of the cup walls (approximately 0.75 inch) compared to 12 inch distance of the prisms would show more readily the movement of water and, consequently, movement of alkali ions. An explanation of the mechanism by which a pozzolanic material inhibits alkali-aggregate reaction is needed.

The cement used was of the same type as that used in Phase I. The fly ash was from the Chicago area and had a fineness of 3000 to 4000 cm^2/gm (Blaine). The fly ash has a 44.9 per cent reduction of alkalinity as determined by reactivity tests with

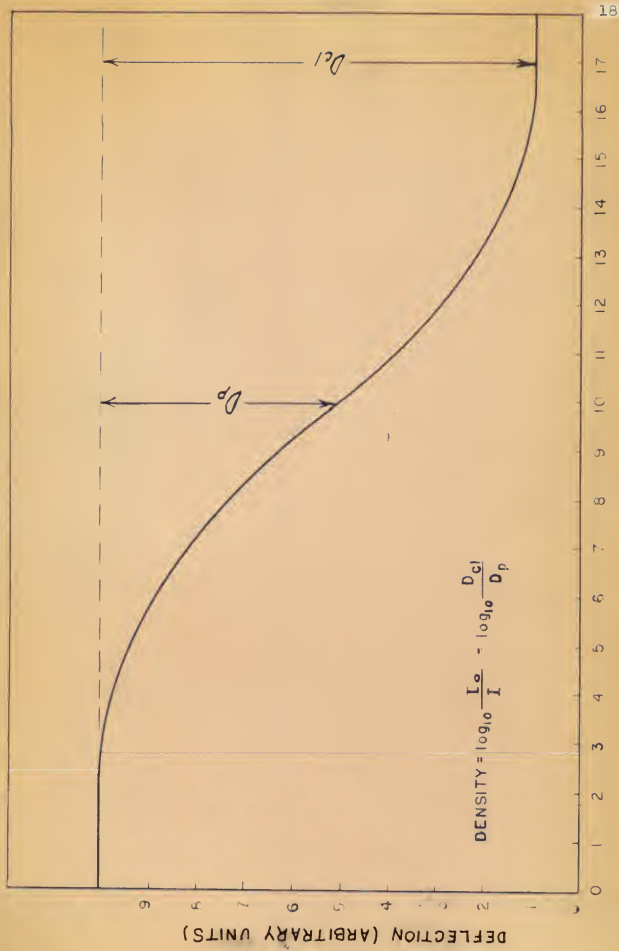
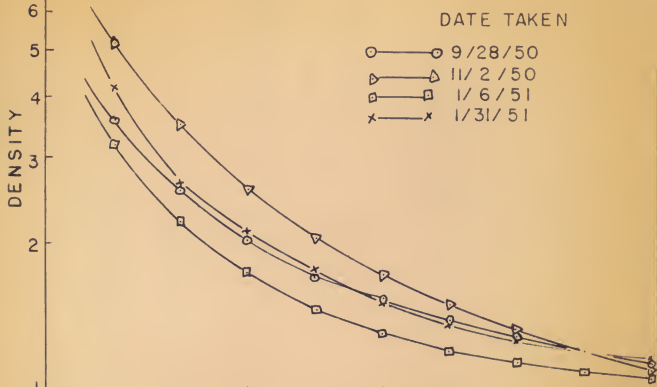


FIG. 1. TYPICAL DENSITOMETER RECORDING OF RELATIVE DARKENING OF X-RAY FILM.

SPECIMEN NO. 9



SPECIMEN NO. 10 (CONTROL)

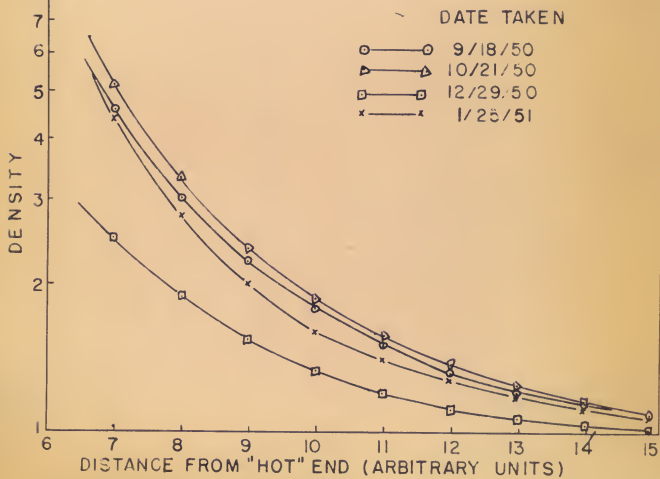


FIG. 2. DENSITY VS. DISTANCE

NaOH as outlined by the Bureau of Reclamation specifications for the Davis Dam project. Blue River sand of a size that would pass a No. 16 sieve and be retained on a No. 30 was used. A six gallon per sack water cement ratio, and a 1:3 cement to sand ratio was used. Here again the mix was designed to be neither impervious nor excessively permeable. Radioactive Na^{22}Cl the same as described in Phase I of this experiment was used. Radioactive $\text{Ca}^{45}\text{Cl}_2$ was used in two of the cups. Calcium-45 has a half life of 152 days and decays by the emission of beta particles. The beta particles would be absorbed by approximately 0.01 inch of concrete, and thus only those radioactive calcium ions very near the surface of the concrete are recorded.

PHASE II EXPERIMENTAL

The cups molded had the following dimensions; overall height, $3\frac{1}{2}$ inch, outside diameter $3\frac{1}{2}$ inches, inside diameter 2 inches.

A solution of radioactive Na^{22}Cl or $\text{Ca}^{45}\text{Cl}_2$ was added to the cups to a previously marked level line. This level was maintained throughout the run by the periodic addition of distilled water. A total volume of 80 cc was contained in each cup. The tops of all cups were covered with watch glasses. This did not form an airtight seal, but was used to restrict evaporation from the top surface. The cups were supported so that laboratory air at room temperature could circulate freely on all sides and bottom. Thus water passing through the side wall would soon evaporate. See Plate V, Fig. 1.

EXPLANATION OF PLATE V

Fig. 1. Concrete cups on rack

Fig. 2. Concrete cup broken in half.
Dotted line shows position of
film when exposure is taken

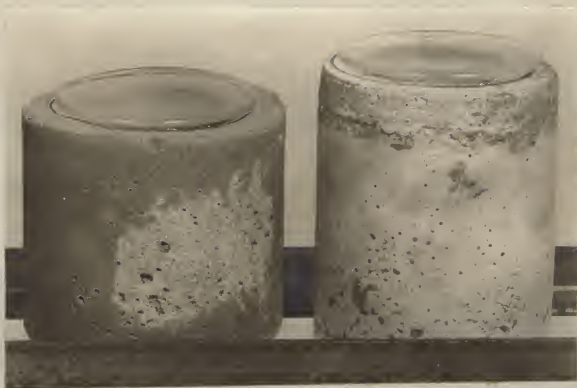


Fig. 1.

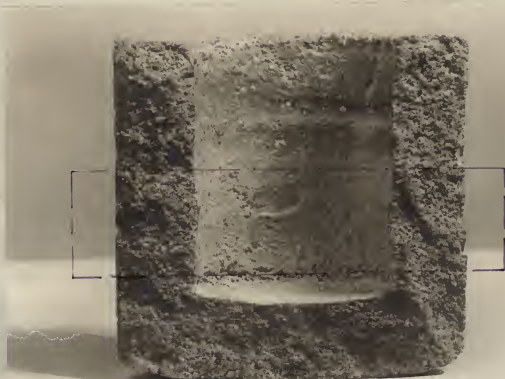


Fig. 2.

Table 1. Identification of concrete cups used in Phase II.

Identification :	Type of cure :	Type of mix :	Radioactive solution used :	Length of time in contact :	Average loss of water per day :
1 ₁ *	4 days moist room 2 days Lab. air	Plain concrete	Ca ⁴⁵ Cl ₂	28 days	4.3 cc
2 ₁ *	"	10% Fly ash	Na ²² Cl	28 days	9.4
1 ₂	30 Day Moist room	Plain concrete	Ca ⁴⁵ Cl ₂	57 days	1.3
2 ₂	"	"	Na ²² Cl	32 days	2.5
3 ₂	"	"	"	85 days	1.2
4 ₂	"	20% Fly ash	"	85 days	1.3
5 ₂	"	30% Fly ash	"	59 days	1.3
6 ₂	"	40% Fly ash	"	85 days	1.3

* Samples used in preliminary experiment

A preliminary experiment was run to give some indication of the time required for salts to migrate through the sidewall. Identification of cups and solutions used are shown as 1_1 , and 2_1 , in Table 1. After fabrication, these cups were allowed four days cure in the moist room, and two days cure in laboratory air. After this time radioactive solutions were added to the cups.

Due to the dry porous condition of the concrete, large amounts of water were initially absorbed into the sidewall structure. For example, cup 2_1 with Na^{22}Cl solution used 56 cc of water the first day. When equilibrium conditions were reached 2 to 3 cc per day were required. This constant value of 2 to 3 cc per day was thought to be lost mainly through evaporation from the sidewalls. A small amount of water would be taken up by the hydration of the cement and a small loss would also occur from the top surface around the watch glass.

It was found that from this initial experiment that sodium ions were carried through the 24/32 inch sidewall in from 2 to 3 hours. Presence of sodium ions on the outer wall was detected by scraping a sample from the surface of the concrete and counting with a scaler. After 28 days the solution was removed and the specimen broken in half. Relative concentrations at various sections throughout the sidewall were determined by a photographic technique which consisted of placing x-ray film in contact with the broken surface. A print of such a film is shown on Plate VI. The position of this film with respect to the half section is shown Plate V, Fig. 2. Another method of checking relative con-

EXPLANATION OF PLATE VI

Radioautograph of Specimen 2

A - represents inside surface of cup

B - outside surface of cup

The light portion at outer surface B indicates that the highest concentration of sodium ion is at this surface.

PLATE VI



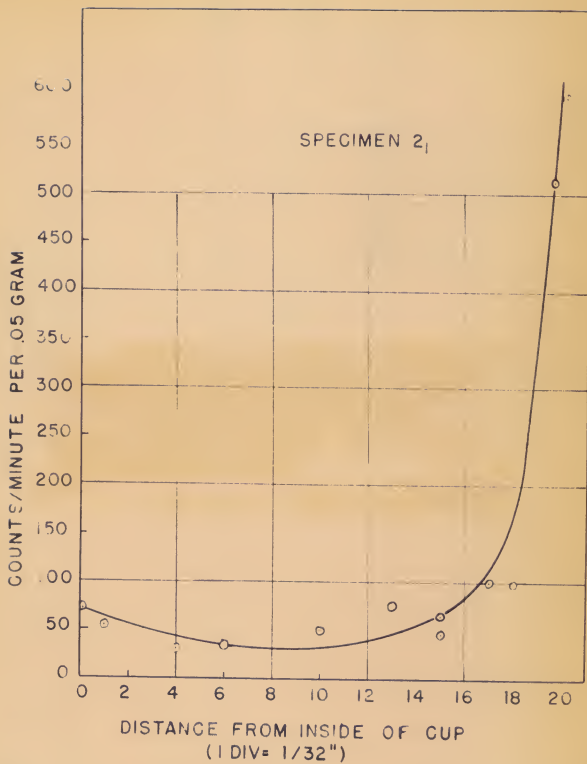
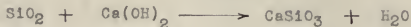


FIG 3. DISTRIBUTION OF RADIOACTIVE SODIUM-22 AT VARIOUS SECTIONS THROUGHOUT SIDEWALL.

centration was to remove samples from various sections throughout the sidewall and determine activity by means of a Geiger-Mueller tube and scaler. A plot of relative concentrations versus distance from inside of cup is shown Fig. 3.

It was thought that the extensive and rapid movement of the sodium ions through the sidewall was not due to diffusion from a high to a low concentration, but rather due to the sodium ions being mechanically transported through by the relatively fast moving water. In this case the water velocity was much greater than the rate of diffusion.

Specimen, containing $\text{Ca}^{45}\text{Cl}_2$ solution was also examined to determine the distribution of calcium ion throughout the sidewall. It was shown both by radioautograph and by taking small samples from the cross section and counting with a scaler that the calcium ion did not migrate to any great extent. (See curve 1, Fig. 4.) This is probably due to the formation of insoluble compounds with some constituent in the concrete. The reaction may take place as follows:



The calcium silicate formed is insoluble, hence no further movement would occur.

Results of this initial experiment indicate that the amount of sodium ion carried through the sidewall was in some manner proportional to the amount of water passing through. Due to lack of homogeneity in the concrete cups, different amounts of water

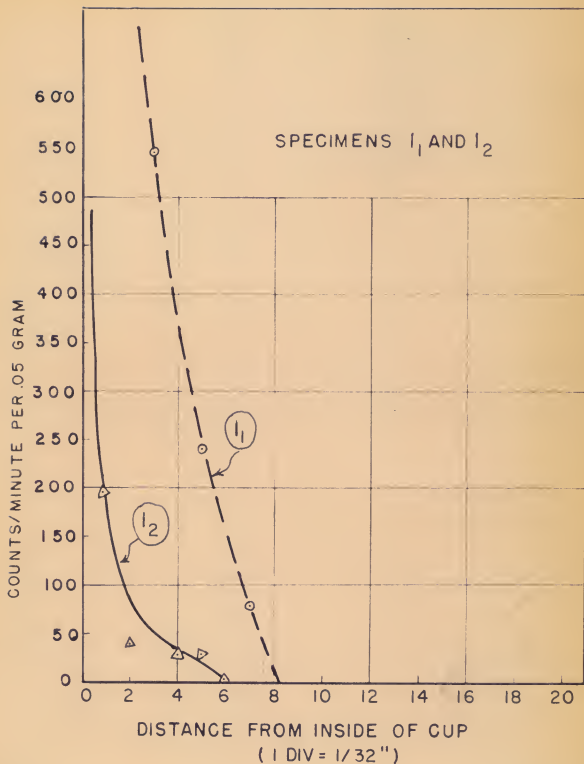


FIG. 4. DISTRIBUTION OF RADIOACTIVE CALCIUM-45 AT VARIOUS SECTIONS THROUGHOUT SIDEWALL.

were initially absorbed and different evaporation rates were established. Hence, any comparison of alkali distribution could not be made on the basis of time. A better comparison could be made when equal amounts of water had percolated through or when equal amounts of alkali ions had left the solution.

On the basis of this experiment six more cups were molded with the type of mix as indicated in Table 1. In order to eliminate the initial high absorption of solution these cups were given a thirty day cure in the moist room and were allowed no curing time in laboratory air. Distilled water was added to the cups until each had reached a constant rate of water loss. The water velocity through the sidewall was low, therefore any movement of sodium ions for this series would be due mainly to diffusion. Distilled water was added every other day to bring the level of the solution up to the previously marked level line. Solution concentration was determined once a week. This was done by pipetting 25 microliters of solution from each cup, evaporating on a copper disc and counting with a scaler. These samples were corrected each time with control samples taken at the beginning of the run so that half life corrections were not necessary. It was impossible to get an accurate check of the $\text{Ca}^{45}\text{Cl}_2$ solution for the reason that an insoluble precipitate formed on the surface. This precipitate was very radioactive which indicates that either $\text{Ca}^{45}\text{CO}_3$ was formed by CO_2 being absorbed from the air or that some anion from the concrete migrated to the solution and reacted with the calcium ion present.

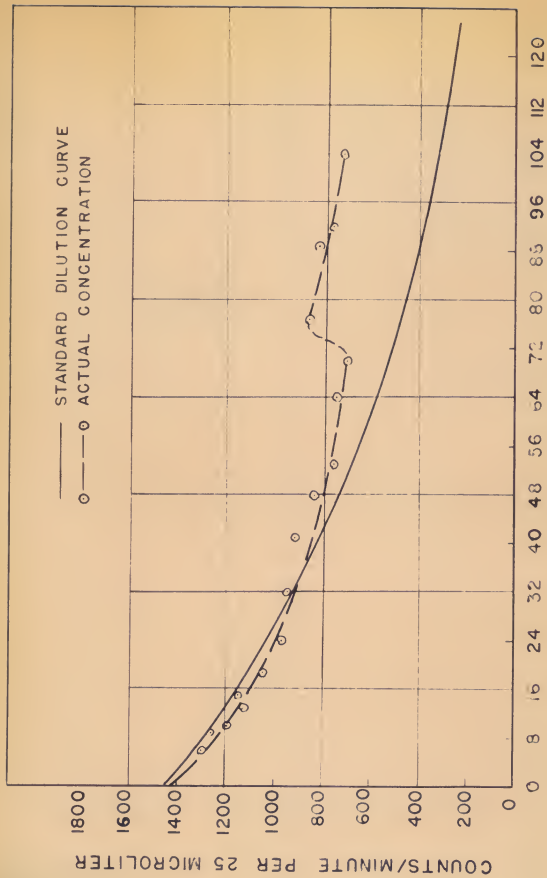


FIG. 5. VARIATION IN SOLUTION CONCENTRATION VS. CC. OF H₂O ADDED.

The pH of the solutions in contact with the concrete was observed to be approximately 10.5 in every case.

A graph of solution concentrations versus cc of water added for specimen 4₂ is shown as a dashed line on Fig. 5. The data for this curve are shown in the appendix, Table 2. The solid line on Fig. 5 is a reference curve, which shows the results that would be obtained by replacing 1.3 cc of solution with 1.3 cc of distilled water each day. The volume of 1.3 cc was chosen since this was the average amount of water added each day. None of the curves varied appreciably from sample 4₂ so it is shown as typical.

Variations in the concentration curves may be due to several factors: (a) evaporation losses from the top surface; (b) water loss by hydration; (c) diffusion of ions; and (d) loss of water through sidewall pores or capillaries.

(a) and (b) The change in concentration caused by evaporation losses from top surface and water taken up by hydration would be represented by horizontal line, ie, a curve with a slope of zero.

(c) The change in concentration caused by diffusion of ions with no water loss would be represented by a curve with slope of -90° .

(d) The change in concentration as sodium ions are carried by the water which permeates the sidewalls would be represented by a reference curve.

It will be noted that during the early part of the run when

concentrations were high the values of concentration fell below the reference curve and at greater dilutions the values were above the reference curve. According to Fick's Law of Diffusion

$$P = -D \frac{\partial c}{\partial x} \text{ where}$$

P = quantity transferred / unit time / unit area of thickness

D = diffusion constant

$\frac{\partial c}{\partial x}$ = concentration gradient

This equation indicated that the rate that sodium ions leave solution is directly proportional to the concentration gradient. This fact was shown by the increasing slope of the concentration curve. After the concentration had decreased to a considerable extent the effects of diffusion would not be so pronounced. The dashed line shows an increase in concentration at approximately 75 cc of water added. This was obtained by the addition of two grams of non-radioactive NaCl. Prior to addition of the non-radioactive NaCl a large concentration of radioactive sodium was either adsorbed on the pore surface or perhaps held by a weak chemical bond. When non-radioactive sodium ions are added to the solution some of the radioactive sodium ions were replaced in the concrete and migrated to the solution where their increased concentration was detected by the counter, hence the abrupt rise in the curve at this point.

At various intervals of time, as shown in Table 1. the six cups were broken to determine distribution of sodium and calcium.

Plate VII shows the radi-autographs obtained by placing x-ray film in contact with the broken cup. Several cups were sawed

EXPLANATION OF PLATE VII

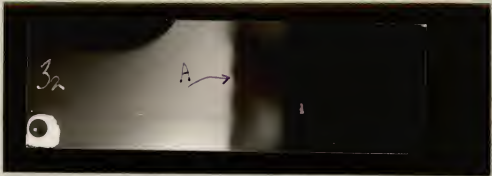
Radioautographs of Specimens 2₂, 3₂, 4₂, 5₂,
and 6₂

A - represents inside surface

B - represents outside surface



35



32

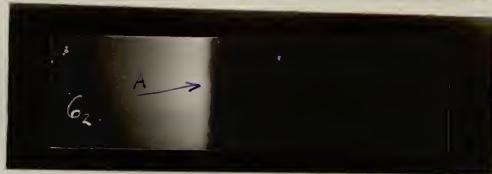
32



42



52



62

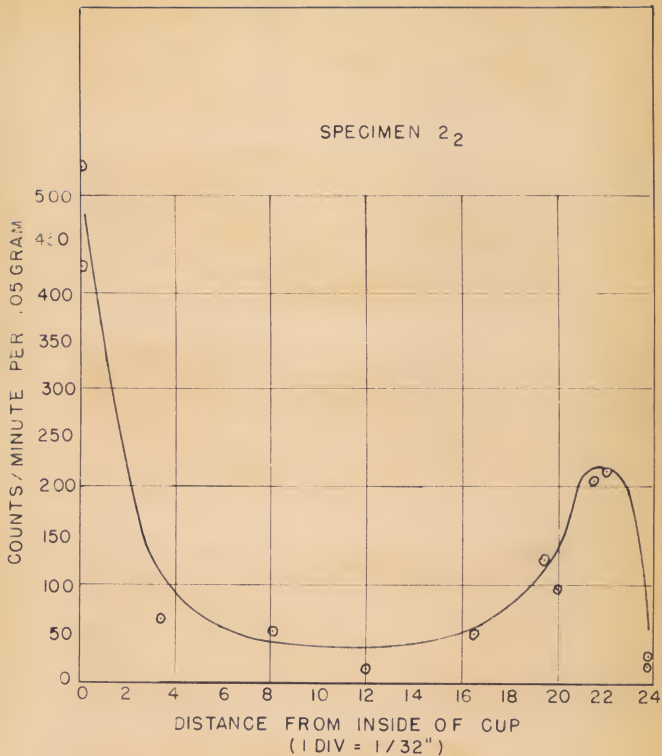


FIG. 6. DISTRIBUTION OF RADIOACTIVE SODIUM - 22
AT VARIOUS SECTIONS THROUGHOUT SIDEWALL.

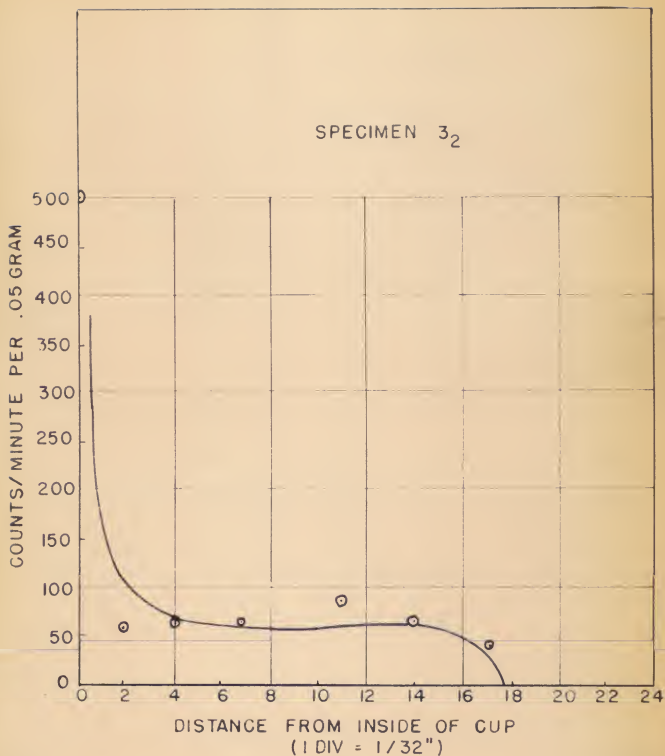


FIG. 7. DISTRIBUTION OF RADIOACTIVE SODIUM-22
AT VARIOUS SECTIONS THROUGHOUT SIDEWALL.

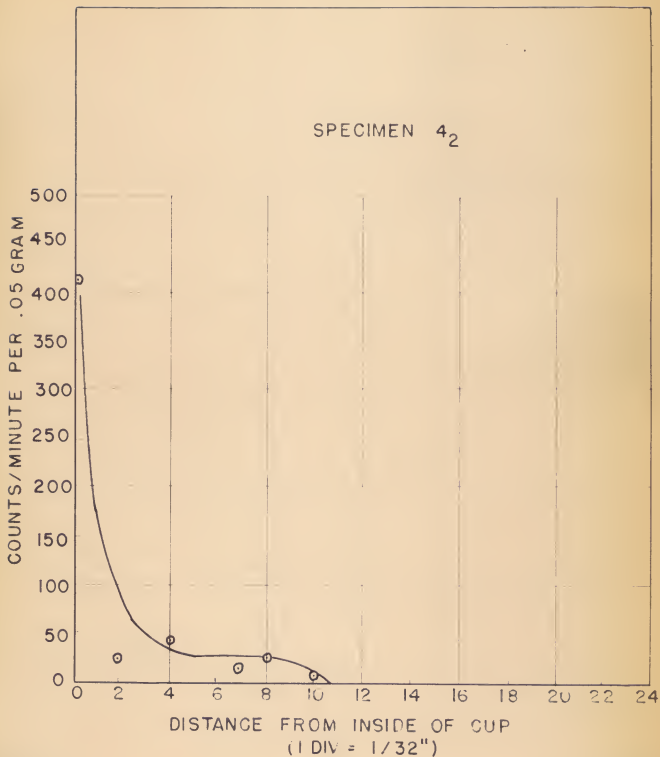


FIG. 8. DISTRIBUTION OF RADIOACTIVE SODIUM-22 AT VARIOUS SECTIONS THROUGHOUT SIDEWALL.

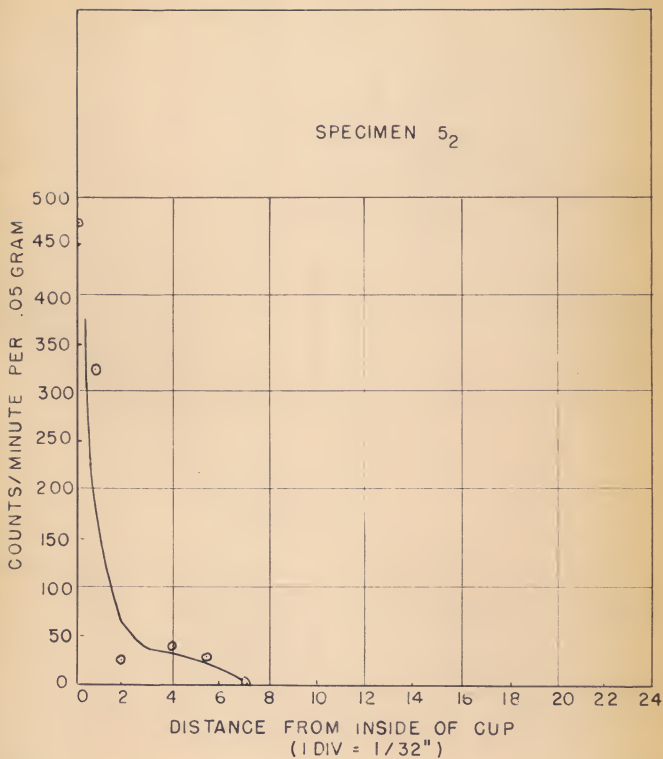


FIG. 9. DISTRIBUTION OF RADIOACTIVE SODIUM-22 AT VARIOUS SECTIONS THROUGHOUT SIDEWALL.

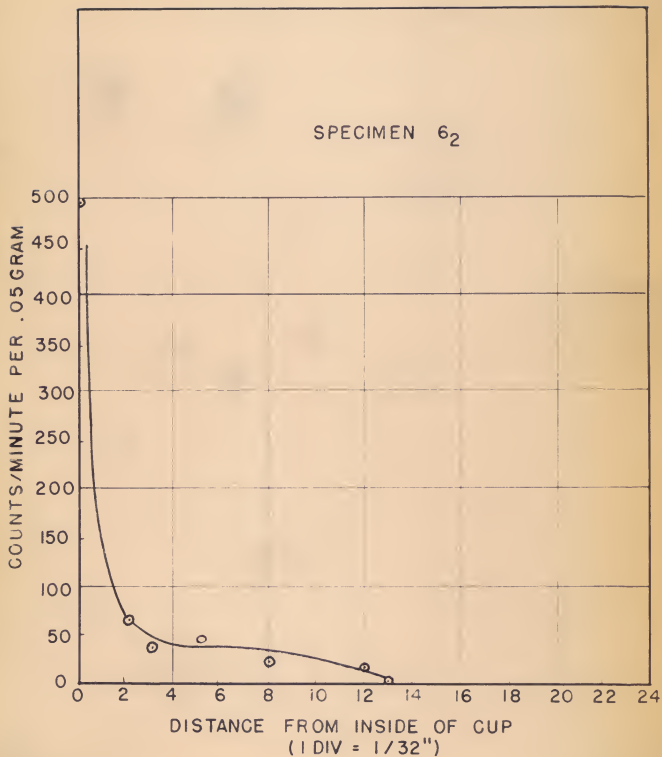


FIG. 10. DISTRIBUTION OF RADIOACTIVE SODIUM-22 AT VARIOUS SECTIONS THROUGHOUT SIDEWALL.

in half in order to obtain a smooth surface to place in contact with the film. This was done to eliminate uneven darkening of the film which occurs when film is placed in contact with irregular radiating surface. A comparison of films obtained by these two methods led to the conclusion that sawing does not permanently smear or spread the activity from one zone to another. In each case the freshly sawed concrete was brushed and washed thoroughly to remove loose dust.

Figures 6, 7, 8, 9, and 10 are graphs showing distribution of activity versus distance from inside wall for different samples which were taken from various sections. Data for these graphs are found in Table 3. in appendix. The relative concentrations were measured with a Geiger-Mueller tube and scaler.

PHASE II DISCUSSION

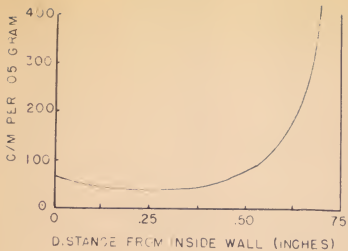
In general the curves showing relative concentration versus distance from the inside of the cups agree quite closely with the evidence shown in the radioautographs. The distance that ions were observed to migrate from the inside wall was approximately the same when measured by either of the two methods. Due to non-homogeneity of the concrete it is reasonable to expect that the ions would migrate further in one area than in another; i.e., channeling may occur. Since the radioautograph and the samples for counting were not taken from the same area a considerable variation could be expected. Due to difficulty in taking representative samples, and in weighing and measuring activity

the error for relative concentration at any one area may be as much as 10 to 15 per cent. In other words the ordinate on these curves may vary as much as 10 to 15 per cent from the values shown.

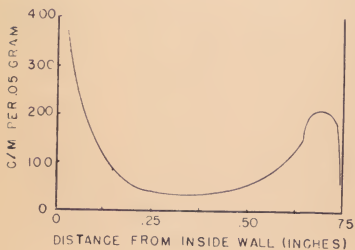
The curves for specimens 4₂, 5₂ and 6₂ (fly ash substituted samples) do not develop a noticeable trend, however a comparison of any one of these with the curve for sample 3₂ (no fly ash) clearly shows that sodium ions do not migrate as far in fly ash substituted concrete as in plain concrete. These samples all had approximately the same average daily water loss so could be considered to have the same permeability. Specimen 3₂, 4₂ and 6₂ were in contact with the solution for 85 days while 5₂ was in contact 59 days.

A comparison of distribution for specimens with different permeabilities; i.e., different average daily water loss rates is shown by study of curves for specimens 1₁, 2₂ and 3₂, which are reproduced on Fig. 11. In specimens 1₁ and 2₂ the large migration of sodium ions is due mainly to the effect of high velocity of water through the capillary channels rather than due to diffusion; i.e., transport is by mechanical action.

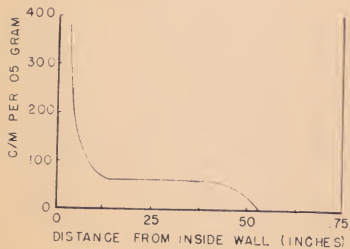
This same effect of greater migration in more permeable specimens was also noted for the cups containing calcium ion in solution. (See Fig. 4.) Even though the calcium ion reacts chemically to form an insoluble compound a greater movement was noted in specimen 1₁. The average water loss per day for specimen 1₁ was 4.3 cc/day and for specimen 1₂ was 1.3 cc/day.

SPECIMEN 2₁

9.4 CC. PER DAY WATER LOSS

SPECIMEN 2₂

2.5 CC. PER DAY WATER LOSS

SPECIMEN 3₂

1.2 CC. PER DAY WATER LOSS

FIG. II. DISTRIBUTION OF RADIOACTIVE SODIUM-22 AT VARIOUS SECTIONS THROUGHOUT SIDEWALL.

Specimen 2₂ shows a high concentration of sodium ion approximately 2/32 inch from the outside wall of the cup. This is thought to be due to vaporization of the water at this point as it permeates from the inside to outside wall. All of the sodium ions in solution at this point will be deposited, which accounts for the high relative concentration. A careful examination of the radioautograph for specimen 2₁, shown on Plate VI, also shows this high concentration of sodium ion just inside the outer wall. This is represented by the light portion of the film at the two points marked "B".

CONCLUSIONS

Even with the specimens arranged so that the rate of diffusion is augmented by the mechanical transportation of ions due to a relatively high water velocity a very long time is required for any noticeable movement of ions. For example, it took 85 days for sodium ions to migrate slightly over $\frac{1}{2}$ " in specimen 3₂. In this case only a relatively small concentration of sodium was detected. With this information regarding the slow rate of movement and the small concentrations involved it is reasonable to expect that only a very slight redistribution of sodium ion would occur within 8 months time in the 2 x 2 x 12 inch prisms described in Phase I. Perhaps several years would be required before positive movement could be detected.

The effects of permeability are shown above in the discussion of cup specimens 1₁, 2₂, and 3₂. It is well known that any

Improvement in imperviousness will increase the desirable properties of portland cement concrete.

These experiments were begun without any previous knowledge of the rate of movement of alkalies in portland cement concrete. Although it was known^v that pozzolanic materials inhibited the alkali-aggregate reaction it was not known to what extent migration would take place. Because of this these experiments were designed first of all to cause a redistribution of radioactive ions and secondly to determine a suitable means of detecting this redistribution.

The two methods described for detecting redistribution of the radioactive ions are both quite positive proof of movement. For this work the two methods are in very good agreement.

By use of a form of Fick's Law of diffusion and a slight variation in this experiment the diffusivity constant for the concrete could be determined. This could be accomplished by placing the concrete cups in a water bath so that the outside water level would be equal to the inside water level. The hydrostatic head would thus be balanced. This would eliminate the flow of water through the concrete and pure diffusion would take place. Such factors as solubility and compound formation that would be observed in various systems would place limitations on the magnitude of the diffusion potential with the result that diffusivity would be expected to vary over a considerable range.

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APPENDIX

Table 2. Solution concentration versus cc of water added.

Date	Time : : elapsed : : (days) :	Specimen #22 : : H ₂ O Activity : : (c/m) :	Specimen #32 : : H ₂ O Activity : : (c/m) :	Specimen #42 : : H ₂ O Activity : : (c/m) :	Specimen #52 : : H ₂ O Activity : : (c/m) :	Specimen #62 : : H ₂ O Activity : : (c/m) :
	: added : : (cc) :	: added : : (cc) :	: added : : (cc) :	: added : : (cc) :	: added : : (cc) :	: added : : (cc) :
11/8	0	1459	1459	1459	1459	1459
11/13	5	10.5	1300	8.0	8.0	6.0
11/15	7	17.5	1065	11.0	1219	1194
11/16	8	19.5	1031	10.0	1154	1124
11/18	10	23.5	976	13.0	1087	1053
11/20	12	27.5	948	15.0	1051	1080
11/22	14	32.5	882	19.0	1000	952
11/27	19	40.5	728	24.0	897	847
12/4	26	57.0	665	32.0	866	807
12/11	31	72.0	587	41.0	850	707
12/12	32	72.0	560			
12/18	38			48.0	692	627
12/22	42			53.0	718	585
1/3	54			64.0	661	525
1/8	59			70.0	592	493
1/15	63			77.0	806	83.0
1/25	73			89.0	750	94.0
1/26	74			90.0	764	95.0
2/6	85			104.0	718	

Note. Activities as given are; counts/minutes per 25 microliter of solution

Table 3. Data for determination of activity at various sections throughout sidewall.

Sample #1 ₁	Ca ⁴⁵ Cl ₂ solution	Plain concrete	
Distance from inside wall	c/m	Sample weight	c/m per .05 gram
1/32 inch	320	.0151 gm.	1060
3/32	190	.0174	546
5/32	25	.0052	240
7/32	12	.0077	78
9/32	0	--	0

Sample #2 ₁	Na ²² Cl solution	10% Fly ash	
Distance from inside wall	c/m	Sample weight	c/m per .05 gram
0 inch	8	.0055 gm.	73
1/32	5	.0046	55
4/32	15	.0246	30
6/32	6	.0038	34
10/32	23	.0218	50
13/32	35	.0212	75
15/32	20	.0153	65
15/32	8	.0090	45
17/32	22	.0110	100
18/32	52	.0262	99
20/32	200	.0120	833
21/32	1317	.0409	1610

Table 3. (cont.)

Sample # 1 ₂ Ca ⁴⁵ Cl ₂ solution		Plain concrete		
Distance from inside wall		c/m	Sample weight	c/m per .05 gram
o	inch	824	.0342 gram	1205
1/32		65	.0166	196
2/32		10	.0122	41
4/32		9	.0159	28
5/32		8	.0125	32
6/32		0	--	0

Sample # 2 ₂ Na ²² Cl solution		Plain concrete		
Distance from inside wall		c/m	Sample weight	c/m per .05 gram
o	inch	94	.0086 gram	546
o		168	.0199	422
o		255	.0132	965
3/32 - 4/32		15	.0146	52
8/32		16	.0156	51
12/32		7	.0314	11
16/32 - 17/32		11	.0109	50
19/32 - 20/32		39	.0153	127
20/32		80	.0420	95
21/32 - 22/32		99	.0230	215
22/32		122	.0264	231
24/32		5	.0153	16
24/32		10	.0250	20

Table 3. (cont.)

Sample #3 ₂	Na ²² Cl solution	Plain concrete		
Distance from inside wall		c/m	Sample weight	c/m per .05 gram
0	inch	187	.0187 gram	500
2/32		27	.0232	58
4/32		38	.0307	62
7/32		37	.0277	67
11/32		53	.0305	87
11/32		39	.0218	89.5
14/32		34	.0255	67
17/32		6	.0077	39
18/32		0	--	0

Sample #4 ₂	Na ²² Cl solution	20% Fly ash		
Distance from inside wall		c/m	Sample weight	c/m per .05 gram
0	inch	174	.0212 gram	410
2/32		10	.0212	22
4/32		14	.0207	34
7/32		4	.0229	10
8/32		15	.0294	25.5
10/32		2	.0351	3
11/32		0	--	0

Table 3. (concl.)

Sample #5 ₂	Na ²² Cl solution	30% Fly ash		
Distance from inside wall		c/m	Sample weight	c/m per .05 gram
0	inch	111	.0123 gram	450
1/32		90	.0142	320
2/32		10	.0276	18
4/32		14	.0189	37
5/32 - 6/32		8	.0180	22
7/32		0	--	0

Sample #6 ₂	Na ²² Cl solution	40% Fly ash		
Distance from inside wall		c/m	Sample weight	c/m per .05 gram
0	inch	168	.0172 gram	490
2/32		24	.0185	65
3/32		13	.0176	37
5/32		10	.0111	45
8/32		10	.0220	23
12/32		7	.0234	15
13/32		0	--	0

Table 4. Physical properties of sand-gravel.

Specific gravity	2.62
Absorption	0.5 percent
Unit weight (dry rodded)	116.4 lb. per cu. ft.
Sieve analysis	Per cent retained
No. 4	16
No. 8	45
No. 16	60
No. 30	79
No. 50	96
No. 100	99

Physical properties of cement

Normal consistency	25 percent
Specific surface	3380 Sq. cm. per gm. (blaine)
Autoclave (soundness)	0.102
Initial set	4 hrs. 50 min.
Final set	6 hrs. 00 min.
Tensile strength	370 lb. per sq. in. (3 days)

Chemical analysis

Silicon dioxide	20.77 percent
Aluminum oxide	5.90
Ferric oxide	2.82
Calcium oxide	63.23
Magnesium oxide	2.77
Sulfur trioxide	2.30
Sodium oxide	0.28
Potassium oxide	0.59
Insoluble residue	0.38
Ignition loss	1.07

A STUDY OF THE MOVEMENT OF ALKALIES IN
PORTLAND CEMENT CONCRETE BY MEANS OF
RADIOACTIVE ISOTOPES

by

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B. S., Kansas State College
of Agriculture and Applied Science, 1947

AN ABSTRACT OF A THESIS

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KANSAS STATE COLLEGE
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ABSTRACT

Evidence of reaction between alkalis in cement and certain types of aggregate have been reported. Differences in expansion were noticed in certain concrete structures while others made with the same cement but a different aggregate remained in good condition. These observations have led to the belief that some constituent in certain cements reacted with some constituent in certain aggregates to form a product that showed excessive expansion.

Deterioration of concrete attributed to this kind of alkali-aggregate reaction also has been claimed.

Experimenters have shown that abnormal expansions occur when high alkali cements are used with reactive aggregates. It has also been shown by measurement of expansion that alkali from a relatively highly concentrated zone will migrate to another zone in which the concentration was lower provided moisture conditions were favorable.

A method for reducing severe expansion by the addition of pozzolanic materials in amounts up to 20 to 30 per cent substitution for portland cement has been suggested. The mechanism which explains this is not clearly known.

The rate or the extent to which alkali ions migrate in either plain or pozzolanic substituted concrete is not known. This program was undertaken in order to gain more information on the rate and extent of diffusion of sodium and calcium ions in various concrete specimens. Utilization of the unique properties of radioactive tracers was made. Since the chemical reactions of tracer ions and

normal ions are exactly the same, the path and rate of movement of the normal ions can be studied by observing the radiations given off by the radioactive material.

Phase I of this investigation was designed to see if it would be possible to observe the migration of sodium ions upward through 2 x 2 x 12 inch concrete prisms that had their bases submerged in water, and their tops exposed to a warm dry atmosphere. This simulated the action of ground water rising by capillary action through a concrete structure; e.g., a highway or sidewalk. Radioactive Na^{22}Cl was placed near the base of the prisms. As water from the base permeated through the prism it is expected that the radioactive sodium ion would diffuse through capillary channels away from the deposit. This movement was detected by a photographic technique, which consisted of placing a camera with x-ray film along a 12 inch side of the specimen for a twenty-four hour exposure. Gamma rays from the Na^{22}Cl darken or expose portions of this film and relative darkening was compared with a recording densitometer. In this manner densities could be compared at various intervals of time. An increasing amount of activity was detected in the water at the base of the prisms which indicated that sodium ions were migrating downward.

Although this method of detecting redistribution seems ideal, the results of eight months with this photographic technique do not conclusively indicate a redistribution, however investigations for a period of time is recommended.

Phase II of this investigation, was made to study the distri-

bution of radioactive sodium and calcium ions that were caused to permeate the 3/4 inch walls of concrete cups. Radioactive Na^{22}Cl and $\text{Ca}^{45}\text{Cl}_2$ solutions were added to plain portland cement and fly ash substituted concrete cups. After various lengths of time these cups were broken to determine the distribution of radioactive ions throughout the sidewall. Relative concentrations were determined by two methods; first a photographic technique which consisted of placing x-ray film in contact with the broken surface, the second by removing samples from sections throughout the sidewall and determining the activity by means of a Geiger-Mueller tube. The two methods were in very close agreement.

It was determined that the rate and extent of migration depended primarily upon the permeability of the specimen. Any improvement in imperviousness will reduce the extent and rate of diffusion. In all specimens the rate of diffusion was very slow. When diffusion takes place in the concrete cups the rate of movement would be less than $\frac{1}{8}$ inch in three months. All of the specimens that contained fly ash showed a decrease in the rate and extent of migration of the sodium ion. No trend was established when amounts of fly ash substitution were varied.

Calcium ions did not show any appreciable movement in either high or low permeable specimens. This is probably due to the formation of insoluble compounds with some constituent in the concrete.

With a slight variation in this experiment diffusivity constants could be obtained for alkalis in concrete. Such factors as solubility and compound formation place limitations of the magnitude of the diffusion potential with the result that diffusivity would be expected to vary over a considerable range.