

DIFFUSION OF SODIUM INTO CONCRETE

by

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INTRODUCTION

The existence of the alkalis in the concrete has been found to be a cause of structural failure, for they react chemically with components of the concrete giving rise to nonuniform pressures (Stanton, 6). Alkalis, normally held to 0.7 per cent by specification, are to be found in concrete. In addition alkalis are believed to diffuse into the concrete from external sources. The manner of how the alkalis, particularly sodium, diffuse into various kinds of concrete is the subject of this work.

Chemical analysis and flame photometer methods had been used by others (Blackman, 2) to measure the alkalis which existed within the concrete. These measurements failed for two reasons. First, the amounts involved were quite small. Secondly, it was impossible to distinguish the sodium coming from an outside source and those already present. In order to eliminate the above difficulties, the method of using radioactive tracers (Spinks, 5) was chosen as the basis of the present study.

Former work at the Kansas State College using tracers in concrete was started in 1955 (Swanson, 7). A set of concrete samples of various aggregation was investigated. This paper describes a continuation of that work.

APPARATUS AND METHOD

Treatment of the Concrete Samples

Sixty concrete cylinders for this study were supplied by the

Applied Mechanics Department of Kansas State College. These cylinders involving fourteen varieties of aggregate were two inches in diameter and four inches long (Plate I). Their constituents are given in Table 1. After fabrication, they were subjected to a 30 day curing period in a conventional steam room and stored in the laboratory air for an additional 400 days.

In order to remove the irregularities on the surface resulting from the initial molding, 0.5 inch of the cylinder was cut off by a brick saw, and the resulting surface was ground by a surface grinder to make it as smooth as possible. The sides of the cylinders were coated with paraffin so that the sodium moved through the end surfaces only and thus the problem was reduced to a one-dimensional one.

Before the cylinders were put into the sodium solution, they were immersed in distilled water. It was observed that only during the first 24 hours of immersion was water taken up by the concrete in any appreciable quantity. However, the cylinders were kept in water for 34 days to insure complete saturation. This was to prevent the sodium from being carried into the concrete by causes other than pure diffusion.

Twelve cylinders were placed in a horizontal position into each of five stainless steel racks. The rack with the cylinders was then put into a glass battery jar. Each jar was filled with seven liters of 0.15 M. Na_2SO_4 plus three ml. of Na^{22}Cl having a specific activity of 0.0456 mc/ml (Plate II). The jars were covered by beeswax-coated wooden lids to minimize evaporation. Only

Table 1. Constituents of the concrete cylinders.

Identification	Cement	Gr. of Cement	Gr. of Blue River S. C.	Mix by Wt.	Additions
PDAC	Penn Dixie	300	1200	1:4	None
PDAL	" "	300	1200	1:4	N-Tair-R*
PDA2	" "	300	1200	1:4	N-Tair-R
PDCC	" "	214	1286	1:6	None
PDC1	" "	214	1286	1:6	N-Tair-R
PDC2	" "	214	1286	1:6	N-Tair-R
PDBC	" "	250	1251	1:5	None
PDB1	" "	250	1251	1:5	N-Tair-R
PDB2	" "	250	1251	1:5	N-Tair-R
PDB1F	" "	175	1251	1:5	30% sub fly-ash+N-Tair-R
MAC	Medusa	300	1200	1:4	None
MA1	" "	300	1200	1:4	N-Tair-R
MA2	" "	300	1200	1:4	N-Tair-R
MCC	" "	214	1286	1:6	None
MC1	" "	214	1286	1:6	N-Tair-R
MC2	" "	214	1286	1:6	N-Tair-R
MBC	" "	250	1251	1:5	None
MB1	" "	250	1251	1:5	N-Tair-R
MB2	" "	250	1251	1:5	N-Tair-R
MB1F	" "	175	1251	1:5	30% sub fly-ash+N-Tair-R

Grading of Blue River S. C.

Sieve	3/8	4	8	16	30	50	100
% Retained	0	18	45	60	80	93	95

6.5 gallons/sack all mixes

*air-entrainment.

small additions of water were necessary from time to time to keep the concentration of the solution constant.

The jars were then placed into an oven (Plate III), the temperature of which was maintained constant. A temperature of 99° F was chosen because this temperature of the oven could be maintained higher than that of the laboratory at all times, and it was low enough to keep the paraffin from being melted away from the cylinders.

EXPLANATION OF PLATE I

Two of the cylinders before being coated with paraffin.

PLATE I



EXPLANATION OF PLATE II

Concrete cylinders in battery jar containing radioactive solution.

PLATE II



EXPLANATION OF PLATE III

Battery jars placed in temperature controlled ovens.

PLATE III



The sixty cylinders representing fourteen different concrete types were placed into the solutions on August 13, 1954. The first group of twenty cylinders were taken out of the solution on May 13, 1955, corresponding to a diffusion period of 273 days or 2.38×10^7 seconds. One of the two ends of these cylinders were ground and measured as described later during the period from Oct. 1955 through Jan. 1956 (Swanson, 7). The remaining ends of these same cylinders were measured in a similar fashion during Jan. 1957 through June, 1957. The second group of six cylinders were taken out of solution on May 28, 1957, giving a diffusion time of 1018 days or 8.81×10^7 seconds. The third group of 20 cylinders were taken out on Nov. 27, 1957, giving a diffusion time of 1201 days or 10.4×10^7 seconds. The cylinders of the first group were rinsed with water upon being taken out of the solution. The second group of cylinders were washed only on one end. Both ends were left unwashed for the cylinders in the third group.

Grinding Method

The method of measurement required that the surface of the cylinder be counted for radiations from within the cylinder after successive thin layers of concrete were removed from end surface of the cylinder. A surface grinder was used for removing these layers. The cylinder under test was first secured to the moving table of the surface grinder by use of a vise. In the course of grinding, the grinding wheel together with the cylinder was enclosed by a plastic bag which was used to contain the radioactive concrete dust.

After each grinding operation, the plastic bag was removed. Countings were made without removing the cylinder from the vise (Plates IV, V, VI).

The thickness of the concrete layers removed during grinding was measured by the use of a depth gauge. The distance measured was that between the end of the cylinder and a reference brass ring fastened to a plywood plate which was in turn fastened to the vise. Six readings were taken at six different positions on the end of the cylinder. The average value was taken as the gauge depth. This value was then subtracted from the gauge depth taken when the cylinder had not yet been ground in order to get the true thickness of the removed layer.

The thickness removed between measurements ranged from 0.03 mm up to 1 mm.

Counting Method

The apparatus used to detect and record the activity consisted of a G-M tube having a window thickness of 1.6 mg/cm^2 and a Berkeley model 2000 decimal scaler. A special lead shield protected the G-M tube. Radiation entered the tube through a one inch diameter aperture adjacent to the tube window. Positioning of the tube was made reproducible by the use of special notches on the circumference of the shield. The notches were made identical with that of the plywood plate fastened to the vise and served as a centering guide. When the tube was appropriately placed, only the central portion of the end of the cylinder was counted.

EXPLANATION OF PLATE IV

Photograph showing plastic bag in position.

PLATE IV



EXPLANATION OF PLATE V

Photograph showing plastic bag removed and the G-M tube in position for taking a count.

PLATE V



EXPLANATION OF PLATE VI

Close up showing concrete cylinder in the vise, brass ring for depth measurements and plywood plate for centering of C-M tube.

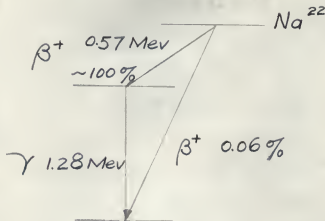
PLATE VI



Edge effects were thus avoided.

After each grinding, the plastic bag was removed and the end of the cylinder cleaned by a brush. Then a square of Kleenex was placed on it to prevent contamination of the tube.

Na^{22} emits positrons and γ radiations. It has a half life of 2.6 years and a decay system as follows (Hollander, et. al. 3).



The maximum range of the β^+ particles was about 220 mg/cm^2 . This corresponded to 0.85 mm of aluminum or concrete because they are approximately of the same density. The half thickness of concrete for 1.28 Mev γ rays is about 5.5 cm.

Since the β^+ particle's range is short, its counting rate can be utilized for determining the distribution of this sodium 22. This requires two separate countings of each measurable situation. At the first counting, only a piece of Kleenex was placed between the tube and the cylinder. At the second counting an aluminum absorber was used to stop all the β^+ particles. The first counting was of the $\beta^+ + \gamma$ activity, while the second, γ alone. Subtracting these two values, the β^+ counting rate was

obtained; and it was considered proportional to the concentration of sodium at that point. A justification of this procedure had been given by Spinks (4), and an additional mathematical confirmation is presented in the discussion section.

Precautions

The activity of the dust was quite low as the maximum counting rate of the entire cylinder was only hundreds of counts per minute. A survey meter failed to show any reading higher than background in testing the dust. However, the following precautions were observed. The whole work was done in a small room constructed of a wooden frame and lined with cellulose acetate-coated, cotton-cord mesh, to prevent spreading of dust which might have been leaked out of the plastic bag. A lab coat and a dust mask were worn by the operator. A water filtered vacuum cleaner was used to clean the room after grinding each end of the cylinder.

RESULTS

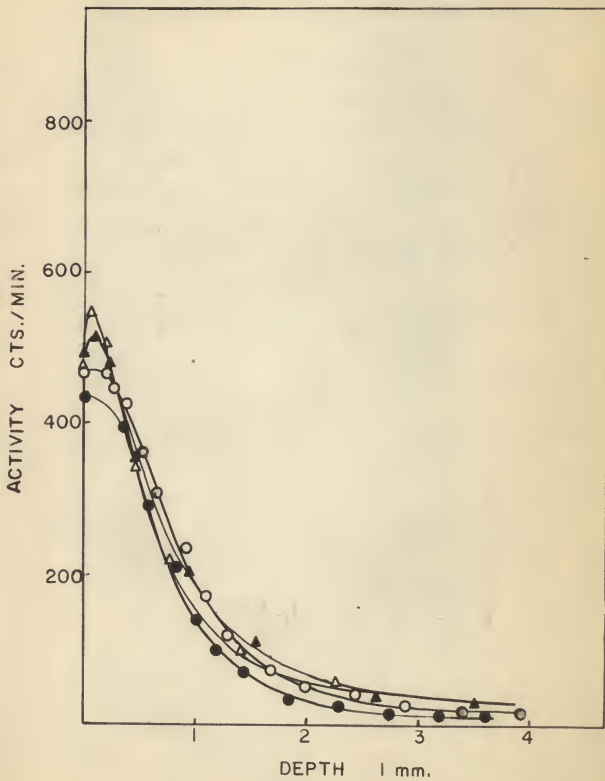
Since Na^{22} decays exponentially with time; and the data were taken at different times, they were corrected accordingly. Plates VII to XX are the corrected β^+ counting data for the cylinders. These curves represent data which were taken after 273 days of immersion, after 273 days immersion and subsequent storage for an additional year, after 1018 days, and after 1201 days. The diffusion constants and other important aspects of the graphs are tabulated in Tables 2 and 3, and a sample calculation of a

EXPLANATION OF PLATE VII

Graph of activity versus depth in concrete for cylinder PDAC.

- Period of diffusion: 273 days, from Aug. 13, 1954 to May 13, 1955.
Date when the activity was measured: Nov. 7, 1955.
- Period of diffusion: 273 days, from Aug. 13, 1954 to May 13, 1955.
Date when the activity was measured: Jan. 2, 1957.
- ▲ Period of diffusion: 1201 days, from Aug. 13, 1954 to Nov. 27, 1957.
Date when the activity was measured: Feb. 10, 1958.
- △ Period of diffusion: 1201 days, from Aug. 13, 1954 to Nov. 27, 1957.
Date when the activity was measured: Feb. 12, 1958.

PLATE VII

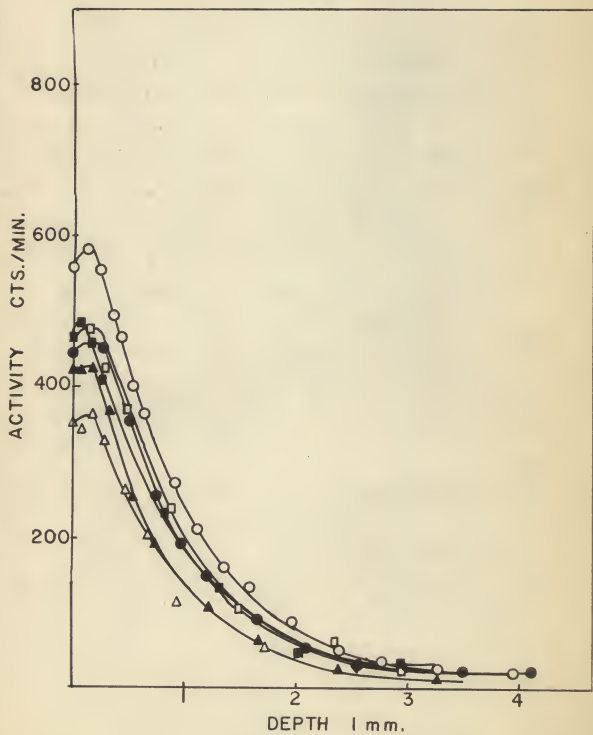


EXPLANATION OF PLATE VIII

Graph of activity versus depth in concrete for cylinder PDAL.

- Period of diffusion: 273 days, from Aug. 13, 1954 to May 13, 1955.
Date when the activity was measured: Nov. 9, 1955.
- Period of diffusion: 273 days, from Aug. 13, 1954 to May 13, 1955.
Date when the activity was measured: Jan. 9, 1957.
- Period of diffusion: 1018 days, from Aug. 13, 1954 to May 28, 1957.
Date when the activity was measured: July 15, 1957.
- Period of diffusion: 1018 days, from Aug. 13, 1954 to May 28, 1957.
Date when the activity was measured: Aug. 7, 1957.
- ▲ Period of diffusion: 1201 days, from Aug. 13, 1954 to Nov. 27, 1957.
Date when the activity was measured: Nov. 27, 1957.
- △ Period of diffusion: 1201 days, from Aug. 13, 1954 to Nov. 27, 1957.
Date when the activity was measured: Nov. 29, 1957

PLATE VIII

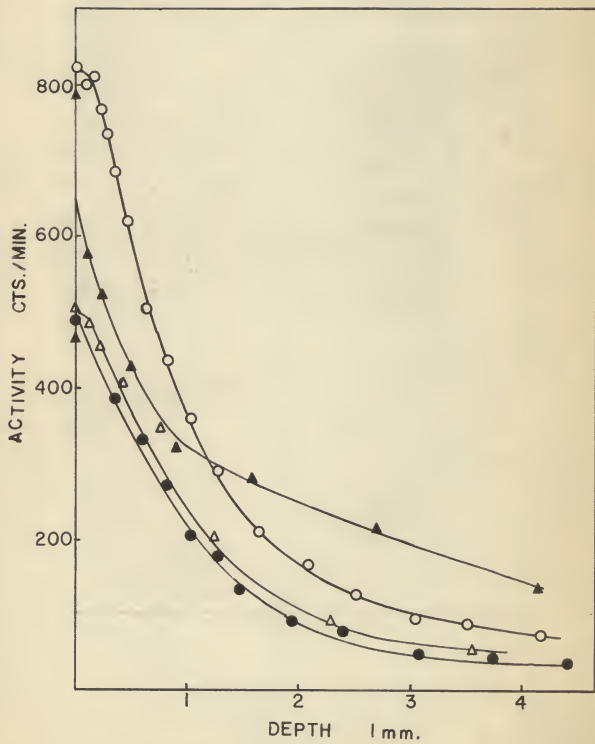


EXPLANATION OF PLATE IX

Graph of activity versus depth in concrete for cylinder PDCC.

- Period of diffusion: 273 days, from Aug. 13, 1954 to May 13, 1955.
Date when the activity was measured: Nov. 15, 1955.
- Period of diffusion: 273 days, from Aug. 13, 1954 to May 13, 1955.
Date when the activity was measured: Jan. 29, 1957.
- ▲ Period of diffusion: 1201 days, from Aug. 13, 1954 to Nov. 27, 1957.
Date when the activity was measured: Feb. 5, 1958.
- △ Period of diffusion: 1201 days, from Aug. 13, 1954 to Nov. 27, 1957.
Date when the activity was measured: Feb. 3, 1958

PLATE IX

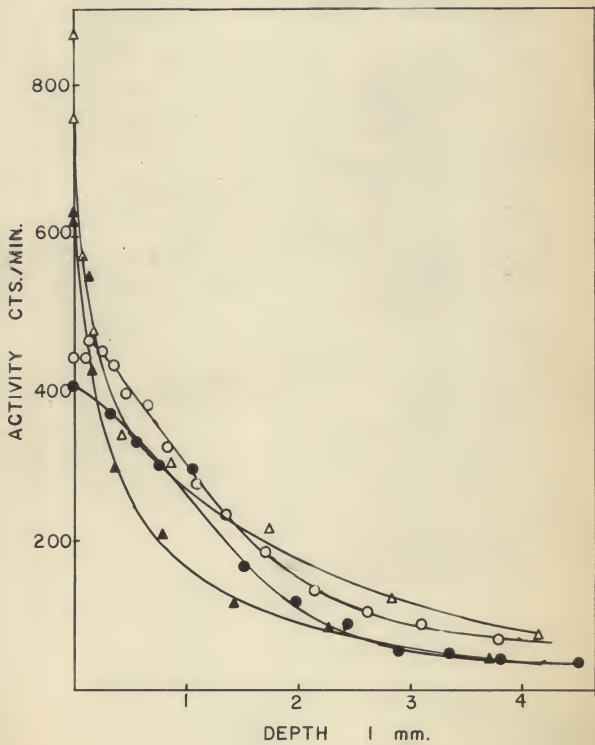


EXPLANATION OF PLATE X

Graph of activity versus depth in concrete for cylinder PDCl.

- Period of diffusion: 273 days, from Aug. 13, 1954 to May 13, 1955.
Date when the activity was measured: Nov. 21, 1955.
- Period of diffusion: 273 days, from Aug. 13, 1954 to May 13, 1955.
Date when the activity was measured: Feb. 8, 1957.
- ▲ Period of diffusion: 1201 days, from Aug. 13, 1954 to Nov. 27, 1957.
Date when the activity was measured: Jan. 31, 1958.
- △ Period of diffusion: 1201 days, from Aug. 13, 1954 to Nov. 27, 1957.
Date when the activity was measured: Jan. 29, 1958.

PLATE X



EXPLANATION OF PLATE XI

Graph of activity versus depth in concrete for cylinder PDBC.

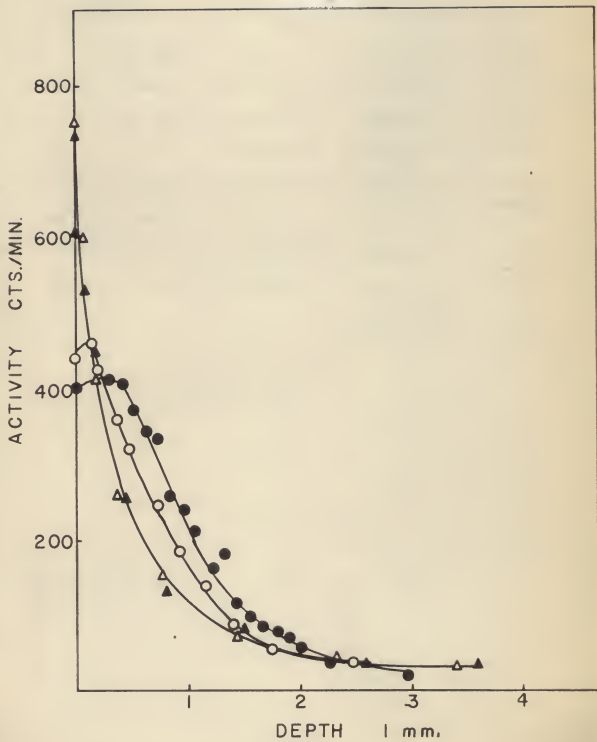
- Period of diffusion: 273 days, from Aug. 13, 1954 to May 13, 1955.
Date when the activity was measured: Oct. 28, 1955.
- Period of diffusion: 273 days, from Aug. 13, 1954 to May 13, 1955.
Date when the activity was measured: Feb. 27, 1957.
- Period of diffusion: 1018 days, from Aug. 13, 1954 to May 28, 1957.
Date when the activity was measured: Sept. 3, 1957.
- Period of diffusion: 1018 days, from Aug. 13, 1954 to May 28, 1957.
Date when the activity was measured: Aug. 26, 1957.
- ▲ Period of diffusion: 1201 days, from Aug. 13, 1954 to Nov. 27, 1957.
Date when the activity was measured: Jan. 19, 1958.
- △ Period of diffusion: 1201 days, from Aug. 13, 1954 to Nov. 27, 1957.
Date when the activity was measured: Jan. 22, 1958.

EXPLANATION OF PLATE XII

Graph activity versus depth in concrete for cylinder PDB2.

- Period of diffusion: 273 days, from Aug. 13, 1954 to May 13, 1955.
Date when the activity was measured: Oct. 12, 1955.
- Period of diffusion: 273 days, from Aug. 13, 1954 to May 13, 1955.
Date when the activity was measured: March 12, 1957.
- ▲ Period of diffusion: 1201 days, from Aug. 13, 1954 to Nov. 27, 1957.
Date when the activity was measured: Jan. 27, 1958.
- △ Period of diffusion: 1201 days, from Aug. 13, 1954 to Nov. 27, 1957.
Date when the activity was measured: Jan. 15, 1958.

PLATE XII

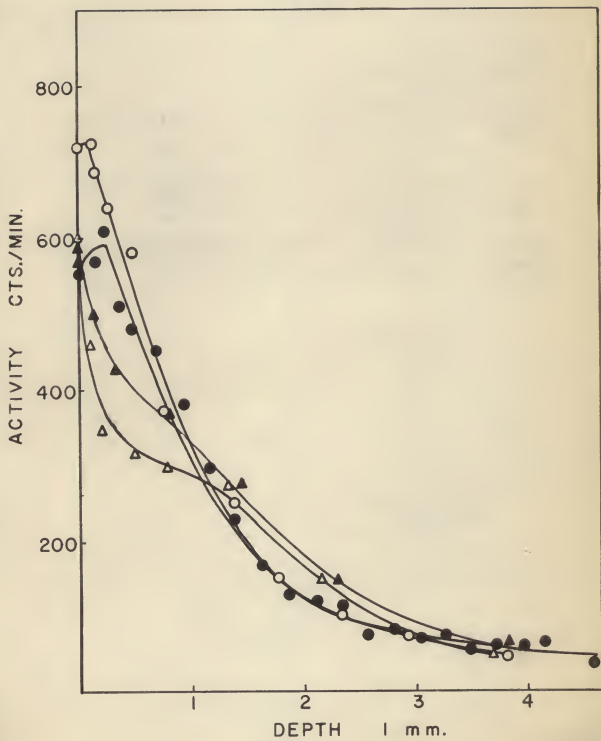


EXPLANATION OF PLATE XIII

Graph of activity versus depth in concrete for cylinder PDB1F.

- Period of diffusion: 273 days, from Aug. 13, 1954 to May 13, 1955.
Date when the activity was measured: Oct. 19, 1955.
- Period of diffusion: 273 days, from Aug. 13, 1954 to May 13, 1955.
Date when the activity was measured: March 20, 1957.
- ▲ Period of diffusion: 1201 days, from Aug. 13, 1954 to Nov. 27, 1957.
Date when the activity was measured: Jan. 11, 1958.
- △ Period of diffusion: 1201 days, from Aug. 13, 1954 to Nov. 27, 1957.
Date when the activity was measured: Jan. 9, 1958.

PLATE XIII

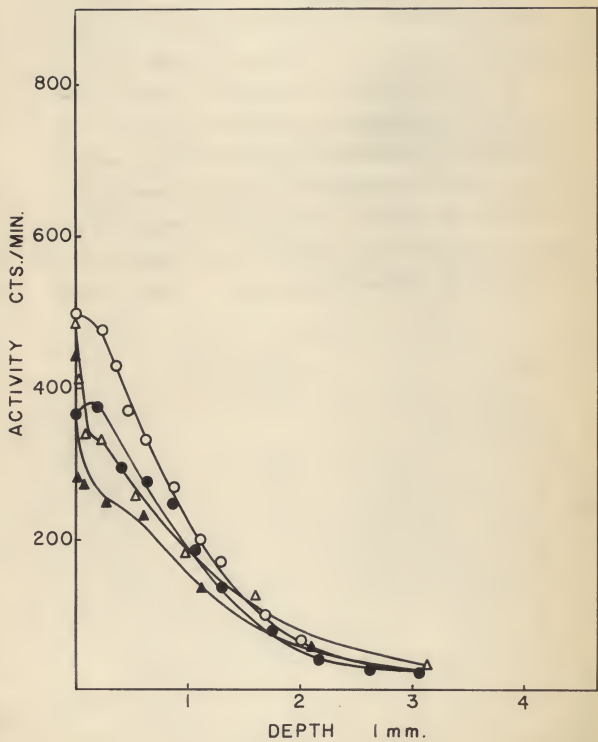


EXPLANATION OF PLATE XIV

Graph of activity versus depth in concrete for cylinder MAC.

- Period of diffusion: 273 days, from Aug. 13, 1954 to May 13, 1955.
Date when the activity was measured: Nov. 23, 1955.
- Period of diffusion: 273 days, from Aug. 13, 1954 to May 13, 1955.
Date when the activity was measured: Apr. 1, 1957.
- ▲ Period of diffusion: 1201 days, from Aug. 13, 1954 to Nov. 27, 1957.
Date when the activity was measured: Jan. 4, 1958.
- △ Period of diffusion: 1201 days, from Aug. 13, 1954 to Nov. 27, 1957.
Date when the activity was measured: Jan. 3, 1958.

PLATE XIV

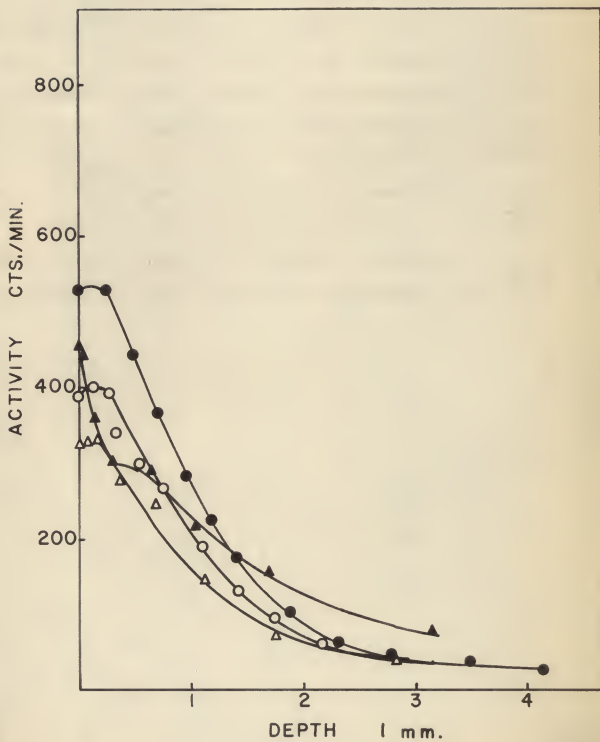


EXPLANATION OF PLATE XV

Graph of activity versus depth in concrete for cylinder MAL.

- Period of diffusion: 273 days, from Aug. 13, 1954 to May 13, 1955.
Date when the activity was measured: Nov. 27, 1955.
- Period of diffusion: 273 days, from Aug. 13, 1954 to May 13, 1955.
Date when the activity was measured: April 8, 1957.
- ▲ Period of diffusion: 1201 days, from Aug. 13, 1954 to Nov. 27, 1957.
Date when the activity was measured: Jan. 2, 1958.
- △ Period of diffusion: 1201 days, from Aug. 13, 1954 to Nov. 27, 1957.
Date when the activity was measured: Dec. 30, 1957.

PLATE XV

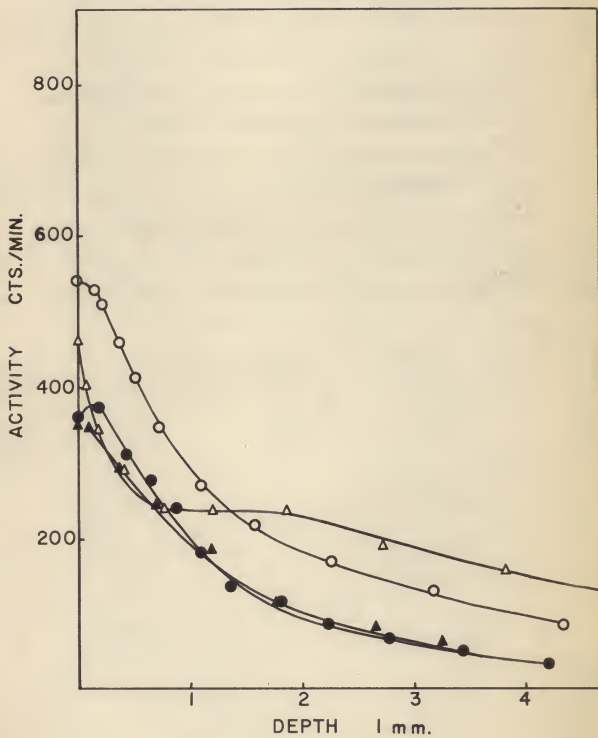


EXPLANATION OF PLATE XVI

Graph of activity versus depth in concrete for cylinder MCC.

- Period of diffusion: 273 days, from Aug. 14, 1954 to May 13, 1955.
Date when the activity was measured: Dec. 1, 1955.
- Period of diffusion: 273 days, from August 13, 1954 to May 13, 1955.
Date when the activity was measured: April 18, 1957.
- ▲ Period of diffusion: 1201 days, from Aug. 13, 1954 to Nov. 27, 1957.
Date when the activity was measured: Dec. 29, 1957.
- △ Period of diffusion: 1201 days, from Aug. 13, 1954 to Nov. 27, 1957.
Date when the activity was measured: Dec. 27, 1957.

PLATE XVI

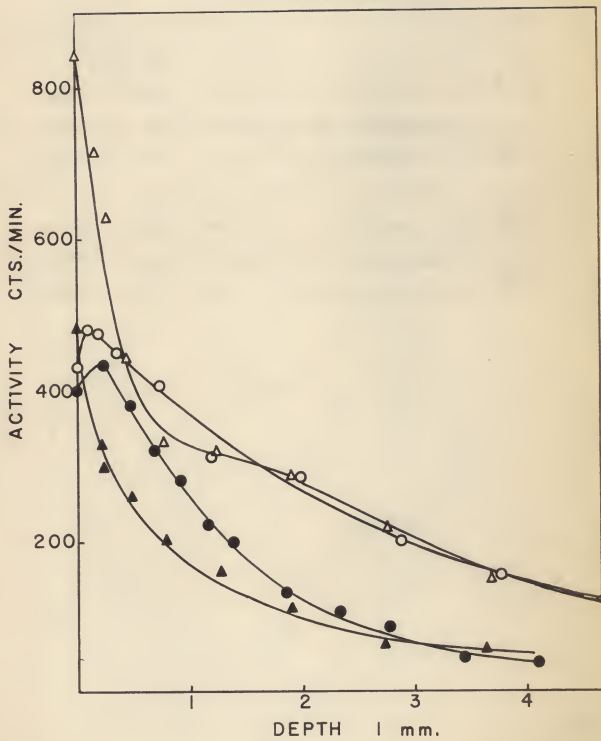


EXPLANATION OF PLATE XVII

Graph of activity versus depth in concrete for cylinder MC1.

- Period of diffusion: 273 days, from Aug. 13, 1954 to May 13, 1955.
Date when the activity was measured: Dec. 5, 1955.
- Period of diffusion: 273 days, from Aug. 13, 1954 to May 13, 1955.
Date when the activity was measured: April 26, 1957.
- ▲ Period of diffusion: 1201 days, from Aug. 13, 1954 to Nov. 27, 1957.
Date when the activity was measured: Dec. 24, 1957.
- △ Period of diffusion: 1201 days, from Aug. 13, 1954 to Nov. 27, 1957.
Date when the activity was measured: Dec. 21, 1957.

PLATE XVII

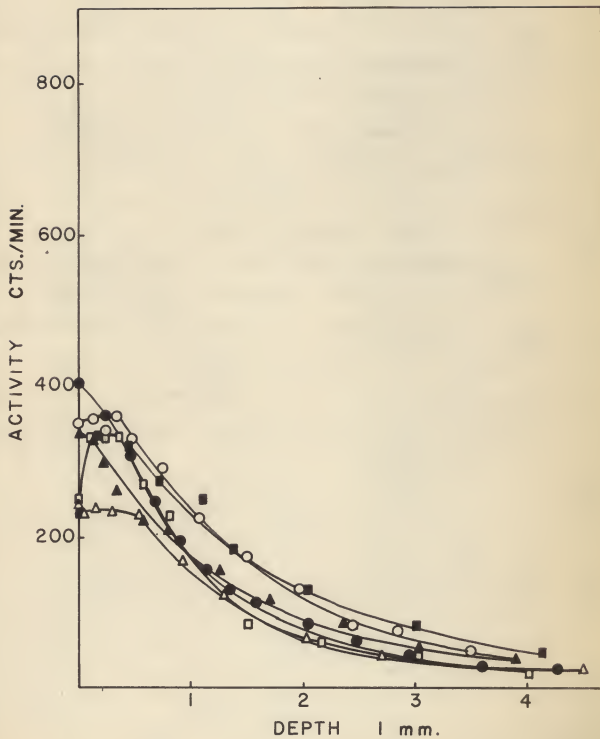


EXPLANATION OF PLATE XVIII

Graph of activity versus depth in concrete for cylinder MBC.

- Period of diffusion: 273 days, from Aug. 13, 1954 to May 13, 1955.
Date when the activity was measured: Nov. 2, 1955.
- Period of diffusion: 273 days, from Aug. 13, 1954 to May 13, 1955.
Date when the activity was measured: May 7, 1957.
- Period of diffusion: 1018 days, from Aug. 13, 1954 to May 28, 1957.
Date when the activity was measured: Aug. 19, 1957.
- Period of diffusion: 1018 days, from Aug. 13, 1954 to May 28, 1957.
Date when the activity was measured: Aug. 12, 1957.
- ▲ Period of diffusion: 1201 days, from Aug. 13, 1954 to Nov. 27, 1957.
Date when the activity was measured: Jan. 23, 1957.
- △ Period of diffusion: 1201 days, from Aug. 13, 1954 to Nov. 27, 1957.
Date when the activity was measured: Jan. 25, 1957.

PLATE XVIII

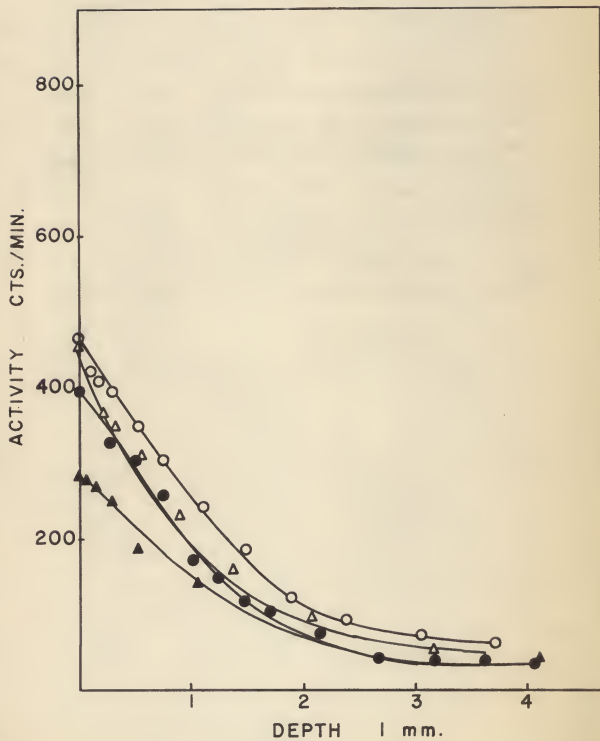


EXPLANATION OF PLATE XIX

Graph of activity versus depth in concrete for cylinder MB1.

- Period of diffusion: 273 days, from Aug. 13, 1954 to May 13, 1955.
Date when the activity was measured: Oct. 24, 1955.
- Period of diffusion: 273 days, from Aug. 13, 1954 to May 13, 1955.
Date when the activity was measured: May 13, 1957.
- ▲ Period of diffusion: 1201 days, from Aug. 13, 1954 to Nov. 27, 1957.
Date when the activity was measured: Dec. 10, 1957.
- △ Period of diffusion: 1201 days, from Aug. 13, 1954 to Nov. 27, 1957.
Date when the activity was measured: Dec. 4, 1957.

PLATE XIX



EXPLANATION OF PLATE XX

Graph of activity versus depth in concrete for cylinder MB1F.

- Period of diffusion: 273 days, from Aug. 13, 1954 to May 13, 1955.
Date when the activity was measured: Sept. 30, 1955.
- Period of diffusion: 273 days, from Aug. 13, 1954 to May 13, 1955.
Date when the activity was measured: May 23, 1957.
- ▲ Period of diffusion: 1201 days, from Aug. 13, 1954 to Nov. 27, 1957.
Date when the activity was measured: Dec. 1, 1957.
- △ Period of diffusion: 1201 days, from Aug. 13, 1954 to Nov. 27, 1957.
Date when the activity was measured: Nov. 30, 1957.

PLATE XX

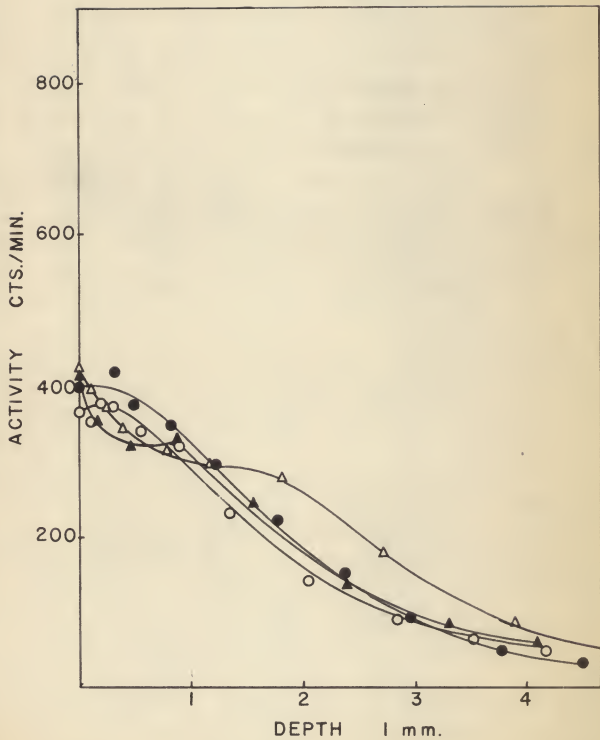


Table 2. Diffusion constants in 10^{10} cm²/sec.

			Periods of diffusion					
			273 days		1018 days		1201 days	
			1st	2nd	1st	2nd	1st	2nd
Cement	wt.	Additions	end	end	end	end	end	end
Penn	1:4	None	*2.1	2.26			0.458	0.346
Dirle			1.21	1.72			0.218	0.318
"	"	N-Tair-R	*3.1	2.24	0.54	0.356	0.670	0.570
			1.25	1.86	0.451	0.272	0.623	0.526
"	1:5	None	*3.1	1.75	0.369	0.405	0.450	0.472
			0.93	1.46	0.325	0.356	0.42	0.386
"	"	N-Tair-R	*3.3	2.12			0.170	0.092
			1.57	1.67			0.170	0.092
"	"	30% sub fly- ash+N-Tair-R	*5.6	2.43			1.02	1.35
			2.90	2.08			0.98	1.00
"	1:6	None	*4.6	2.73			1.01	1.45
			2.09	2.32			0.96	1.16
"	"	N-Tair-R	*6.3	8.33			0.471	0.230
			5.71	5.19			1.09	0.230
Medusa	1:4	None	*3.2	2.61			1.19	0.787
			3.04	2.28			0.787	0.686
"	"	N-Tair-R	*4.0	3.11			0.761	0.895
			2.81	2.70			0.761	0.83
"	1:5	None	*4.3	5.08	1.55	0.708	0.77	0.971
			2.61	4.46	1.30	0.450	0.77	0.711
"	"	N-Tair-R	*3.4	6.36			0.77	1.04
			3.04	6.36			0.77	0.711
"	"	30% sub fly- ash+N-Tair-R	*10.0	7.32			1.4	1.88
			9.01	4.63			1.4	2.65
"	1:6	None	*5.5	2.52			1.14	0.795
			3.33	2.52			1.14	5.03
"	"	N-Tair-R	*4.3	17.1			0.512	0.585
			4.24	17.1			7.43	1.02

*calculated by Swanson (5)

The second value of "D" of each end corresponds to a different method of determination of Co. (See Appendix)

Table 3. Gamma activity at surface of the cylinders, cts/min.

Cement:	Mix: by: wt.:	Additions:	Period of Diffusion			
			273 days		1201 days	
			1st end	2nd end	1st end	2nd end
Penn	1:4	None	*122	140	174	160
Dixie	"	N-Tair-R	*148	104	156	154
"	1:5	None	*113	128	143	147
"	"	N-Tair-R	*128	108	152	163
"	"	30% sub fly- ash+N-Tair-R	*274	219	243	260
"	1:6	None	*173	211	203	276
"	"	N-Tair-R	*141	169	284	186
Medusa	1:4	None	*115	127	160	153
"	"	N-Tair-R	*200	116	158	196
"	1:5	None	*151	166	172	154
"	"	N-Tair-R	*139	163	148	130
"	"	30% sub fly- ash+N-Tair-R	*274	225	346	307
"	1:6	None	*187	306	314	204
"	"	N-Tair-R	*226	246	305	204
Average			168	173	212	191
				170		201

*Taken by Swanson (7)

diffusion constant is given in the Appendix.

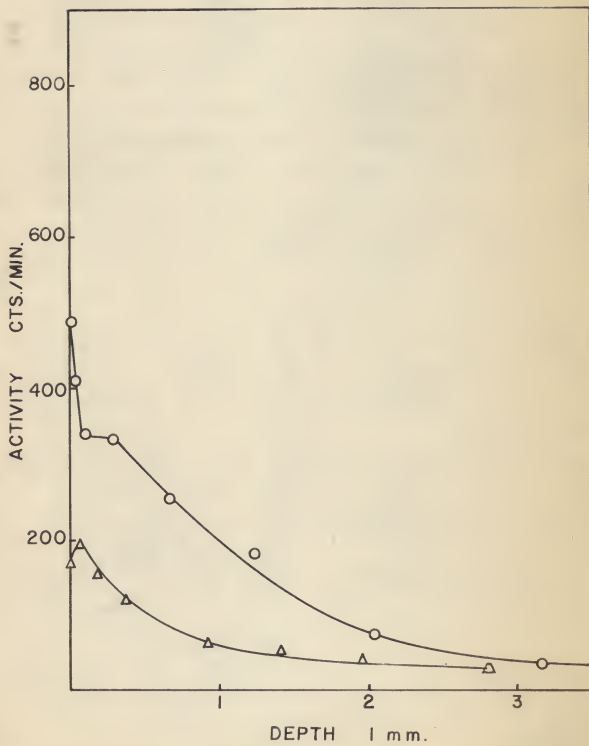
A short immersion period experiment was performed with a cylinder whose two ends had been previously ground for measuring concentrations. The depth to which the sodium had reached was ground off. The procedure of the previously described experiments was repeated, including an immersion period in distilled water. A short Na^{22} diffusion period of 24 hours was then allowed. The concentration curve obtained in this way is shown in Plate XXI as compared with a curve corresponding to diffusion period of 1201 days. It should be observed that the initial value of the concentration

EXPLANATION OF PLATE XXI

Graph of activity versus depth in concrete for cylinder MAC, showing the result of the short period immersion experiment.

- Period of diffusion: 1201 days, from Aug. 13, 1954 to Nov. 27, 1957.
Date when the activity was measured: Jan. 3, 1958.
- △ Period of immersion: 1 day, from April 14, 1958 to April 15, 1958.
Date when the activity was measured: April 15, 1958.

PLATE XXI



of one day's diffusion had reached half of that of 1201 days' diffusion.

The following comments can be made concerning these results and accompanying observations:

1. For a specific type of concrete the concentration curves were essentially independent of the times of immersion and of storage.

2. Individual variations among the concrete specimens were related to the apparent surface roughness or porosity.

3. While not statistically significant, the average γ ray measurements of the concrete specimens appeared to increase with time of immersion.

4. Large differences between initial counting rates for washed and unwashed cylinders were observed. These differences occurred only at the surface, at a depth less than 0.2 mm.. Surface sodium was removed from unwashed cylinders by wiping with a tissue paper swab.

5. The differences among the concentration curves of cylinders of small aggregate-cement ratio were small. Larger differences were observed among the concentration curves for those of larger aggregate-cement ratio.

6. No appreciable radioactivity was found in the cylinder over 5 mm. from the cylinder surface.

7. The amount of sodium diffused into cylinders of Penn Dixie cement was in average smaller than that diffused into cylinders of Medusa cement.

8. The amount of sodium diffused into cylinders containing the flyash was greater than for those which did not.

DISCUSSION

Theoretical Consideration and Justification of the Method of Obtaining the Concentration of the Sodium by the Counting Rate of the Intensity of β^+ Radiation

If the condition of diffusion is such that it follows the Fick's law, i. e.

$$P = - D \nabla C \quad (1)$$

where P = quantity of sodium passing through a surface perpendicular to the gradient of C at a point (x, y, z) per unit time,

D = diffusion constant,

C = concentration which is a function of coordinates.

Then in our problem of one-dimension and semi-infinite solid, the concentration as a function of time and depth assumes the form (Barrer, 1).

$$1 - \frac{C}{C_0} = \frac{2}{\sqrt{\pi}} \int_0^\alpha e^{-y^2} dy \quad (2)$$

where C = concentration at x,

C_0 = concentration at the surface of the concrete,

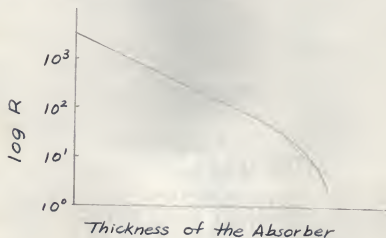
$$= x/2(Dt)^{\frac{1}{2}}$$

x = depth,

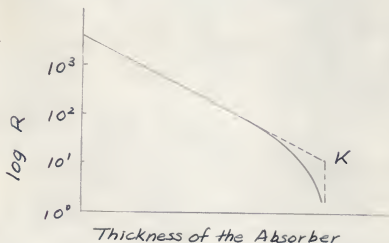
t = diffusion time.

Thus if we can find C(x), we can find α . From the known value of a corresponding x and t, the diffusion constant, D, can be calculated.

The concentration was approximated by the β^+ activity curve as mentioned previously. This was determined as follows: In experiments with Na^{22} using aluminum absorbers, the resulting absorption curve was observed as follows:



This experimental curve was approximated by straight lines as follows:



This assumption of an exponential attenuation of the β^+ rays to a maximal value of range was within the accuracy of the experiment, particularly, since the major differences between the curves occur

at K where the contribution to the total count is small. It was assumed that the sodium which was located at a depth larger than a certain limit, say, Δ , contributed nothing to the total counting rate. Assume also that the concentration curve is to be designated by $\rho = \rho(x)$. If ρ is multiplied by the cross section of the cylinders, from which counts are to be observed and which is a constant in this case, the product represents the amount of sodium in unit length of the cylinder. We shall use this as the definition of concentration, $C(x) = S \rho(x)$ in the following discussion. The corrected for efficiency counting rate, $R(a)$, taken at a position, (a) , is

$$R(a) = \int_a^{a+\Delta} C(x) e^{-\mu_\beta(x-a)} dx \quad (3)$$

where μ_β was the absorption constant for the β^+ particles. Differentiating this equation with respect to a ,

$$\frac{dR(a)}{da} = \mu_\beta \int_a^{a+\Delta} C(x) e^{-\mu_\beta(x-a)} dx + C(a+\Delta) e^{-\mu_\beta \Delta} - C(a) \quad (4)$$

Since Δ was defined as above, it was reasonable that any term $C(a)$ multiplied by $e^{-\mu_\beta \Delta}$ would be negligibly small. By changing a into x , the equation reads:

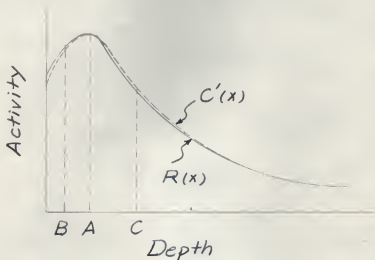
$$\frac{dR(x)}{dx} = \mu_\beta R(x) - C(x) \quad (5)$$

Since equation (2) involved only the ratio of two concentrations, only the relative values of $C(x)$ were important. Allowing

$C(x) = \mu_\beta C'(x)$, equation (5) became

$$C'(x) = R(x) - \frac{\frac{dR(x)}{dx}}{\mu_\beta} \quad (6)$$

A typical curve of counting rate was drawn below and a concentration curve was also shown which was exaggerated to show the relationship between the two curves.



The physical meaning of the above equation may be explained as follows: In case that the concentration was constant, the counting rate would also be constant; and this counting rate may be used to represent the concentration except for a multiplicative factor. This was the case for points adjoining A in the above figure, where the two curves intersect. At point B, the concentration was increasing. Due to more β^+ particles coming from the depth, the counting rate was higher than the normalized concentration. For a similar reason the counting rate at C was smaller.

Actually, the absorption constant for β^+ particles was large, so the counting rate ratios could be used to approximate the concentration ratios.

Gamma Activity and the Amount of Sodium Ions Diffused Into the Concrete

The total amount of sodium diffused into the concrete was equal to the area under a concentration versus length of cylinder curve and thus proportional to the area under the β^+ counting rate curve. This could be and was measured directly. More surprisingly, the γ activity at the surface was found to be proportional to the total amount of sodium diffused into the concrete. This could be justified as follows:

Let the concentration be $C(x)$, and the amount of sodium located between the surface and the point of depth X be A , then

$$A = \int_0^X C(x) dx \quad (7)$$

Assume that the efficiency of the G-M tube for γ rays to be η and that the intensity of γ ray attenuates exponentially. The γ ray counting rate, R_γ will be,

$$\begin{aligned} R_\gamma &= \eta \int_0^X C(x) e^{-\mu x} dx \\ &= \eta \int_0^X C(x) \left(1 - \mu x + \frac{\mu^2 x^2}{2} - \dots \right) dx \end{aligned} \quad (8)$$

Since $C(x)$ was quite small at a depth of 0.5 cm., the contribution of essentially all the sodium particles is included if X is set equal to 1 cm.

The γ ray half thickness was 5.5 cm., therefore

$$\mu = \frac{0.693}{5.5} = 0.126 \text{ cm}^{-1}$$

Thus the terms in the expansion of $e^{-\mu x}$ could be neglected except

for the first two. Again

$$0 < \int_0^1 \mu x C(x) dx < \int_0^1 \mu C(x) dx$$

$$\int_0^1 \mu x C(x) dx = \mu \theta \int_0^1 C(x) dx \quad \text{where} \quad 0 < \theta < 1$$

$$R_\gamma = \int_0^1 \eta C(x) dx - \int_0^1 \eta \mu x C(x) dx = \eta(1 - \mu \theta) \int_0^1 C(x) dx \\ = \eta(1 - \mu \theta) A$$

Since η , μ and θ are constants, this shows that the γ ray counting rate at the surface is proportional to the total amount of sodium diffused into the concrete.

Explanation of the Results

The curves given in the preceding section showed that the concentrations were approximately the same irrespective of the times of exposure of the cylinder to the solution and times of subsequent storing. The diffusion constant, "D", was therefore not constant as it was supposed to be. The observations that the concentration curve depended largely upon the surface conditions of the concrete specimen and that the increase of the average γ ray activity with time, which implied an increase of sodium diffused into the concrete, led to the belief that the results were due to the combination of at least two different processes. The following hypothesis appears to explain these observations:

The surface of the concrete is porous with pores of various lengths having components perpendicular to the surface of the cylinder. The lengths of these porous components would undoubtedly have some form of a statistical distribution. Water could enter the concrete to a depth through these pores without difficulty. The

results of this movement was observed as the cylinders were placed into distilled water at the first step of the experiment. When the cylinders were then put into the active sodium sulphate solution, the sodium moved promptly into the concrete since the rate of diffusion of sodium ions in water is fast. This was confirmed by the short immersion period experiment.

After and during the completion of the above mentioned process, a second stage or type of diffusion involving an actual diffusion into the cement probably occurred. Some idea of the concentration due to this diffusion should be obtainable by subtracting the concentration of a cylinder having a long period of diffusion from that of the same type of cylinder having a short period, 24 hours, of diffusion. The results of such a determination are not valid, however, due to the variation in the effective surface area due to porosity as one moves away from the actual surface.

The average increase of γ ray activity between cylinders of a diffusion period of 1201 days and that of 273 days was only about 30 cts/min. This is limited evidence that long term diffusion processes do occur.

There, also, existed large difference between initial counting rates for the washed and unwashed cylinders. This difference occurred only at the surface, at a depth less than 0.2 mm. For the cylinders which were rinsed after being taken out of the solution, the concentration of the surface was less than that under the surface. If the cylinders were left unwashed, some of them still

presented that peculiarity, but some of them gave very high concentration at the surface. If these surfaces were simply wiped by wet paper, the counting rate diminished appreciably. This proved that, in these cases, the sodium was actually exposed on the surface and could easily be taken away by rinsing or wiping. Thus the concentration of this region could not represent a property of the concrete. Presumably a like situation existed on the internal surfaces of the pores.

The concentration in the portion of the cylinder of depth from 0.2 mm. to about 3 mm. generally dropped from the initial value to a very low activity. The distribution of the sodium in this region was thought to be dominated by the porosity of the surface. It was this porosity which held the solution in the concrete and increased the effective area through which the sodium might diffuse and upon which they may collect. There were only small differences between concentration curves of cylinders of 4:1 aggregate-cement ratio but larger differences between those of 6:1 aggregate-cement ratio. This was presumably due to the increased porosity and inhomogeneity of large ratio aggregate-cement concrete specimens.

Within the cylinder at depths greater than 3 mm., the concentration maintained a low value; and it was observed to keep that value for large values of x . The counting rate of β^+ was below 30/min.; and the background, around 20 cts/min., was comparatively high.

The amount of sodium diffused into the cylinders of Penn Dixie cement was in average smaller than that into Medusa cement.

The addition of fly ash to concrete seemed to increase the sodium movement, resulted in more activity being observed in the cylinders. These observations were in conformity with the results obtained previously (Swanson, 7).

CONCLUSIONS

It was found that the sodium concentrations within the cylinders were approximately the same, although the cylinders of the first group had a diffusion period of 273 days and those of the second and third groups had a diffusion time of 1018 and 1201 days respectively. The concentration was also seen not to be influenced by storage time out of solution. The concentration curves all had the general feature that they start from a high initial value, then dropped to a low value before levelling off. The diffusion was thought due to a two stage diffusion action. In the first stage, sodium diffused into the water which was held in pores connecting to the surface of the concrete. This sort of diffusion was fast and was completed in a few days. The second stage or type of diffusion which apparently represented an actual movement of the sodium through the concrete was slow. Within the accuracy of this method, only an increase of the total γ activity with time was observed. A diffusion constant of the order of $10^{-8} \text{ cm}^2/\text{sec}$ may be associated with the faster diffusion and $10^{-10} \text{ cm}^2/\text{sec}$ or smaller with the slower diffusion.

ACKNOWLEDGMENT

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APPENDIX

DETERMINATION OF THE INITIAL CONCENTRATION, C_0

Since the concentrations near the surface were thought not a property of the concrete, it should be ignored in calculating the diffusion constant "D". Two methods were used to determine C_0 . The first one was to extrapolate the curve until it intersects with the coordinate. The intersection thus obtained was considered the initial point of the curve. In the second method, the position where the extrapolation began to deviate from the experimental curve was taken as the actual surface of the concrete. This latter method resulted in values as seen in Table 2 which were roughly one-half of those calculated by the first method. Probably the second method is more nearly correct.

Sample Calculation

The $\beta^+\gamma$, γ , and β^+ ray activity curves for cylinder MAC were drawn on Plate XXII. Table 4 was obtained by using C as the initial point.

The first two columns were obtained from Plate XXII and $(1 - \frac{C}{C_0})$ was then calculated. By using a table of probability integrals α could be obtained using the value of $(1 - \frac{C}{C_0})$. The value of α was then plotted against x as shown in Plate XXIII. In general the plot of α against x was not a straight line desired but curved as shown. The initial slope was chosen as the value of (x/α) . Substitution of this in the formula

$$D = \frac{1}{4t} \left(\frac{x}{\alpha} \right)^2$$

where t is the diffusion period allows one to calculate D.

Table 4. Beta activity versus depth for cylinder MAC.

x mm.	C cts/min	$1 - \frac{C}{C_0}$	α
0	335	0	0
0.2	283	0.155	0.1382
0.4	238	0.290	0.2630
0.6	194	0.421	0.3923
0.8	154	0.540	0.5225
1.0	119	0.645	0.6547
1.2	90	0.731	0.7816
1.4	70	0.791	0.8884
1.6	60	0.821	0.9503
1.8	51	0.848	1.013
2.0	44	0.869	1.067
2.2	40	0.881	1.103
2.4	36	0.892	1.137
2.6	32	0.905	1.181
2.8	30	0.911	1.203

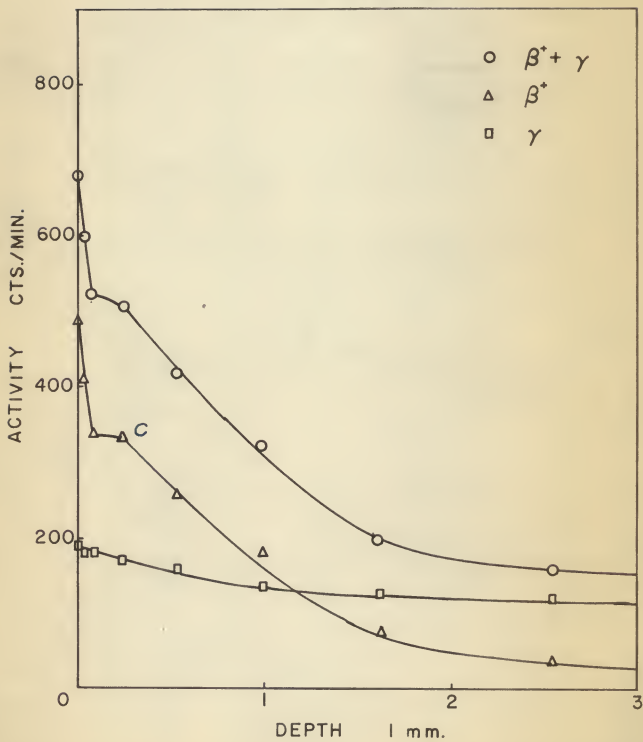
EXPLANATION OF PLATE XXII

Graph of $\beta^+ + \gamma$, γ and β^+ activities versus depth in concrete for cylinder MAC.

Period of diffusion: 1201 days, from Aug. 13, 1954 to Nov. 27, 1957.

Date when the activities were measured: Jan. 3, 1958.

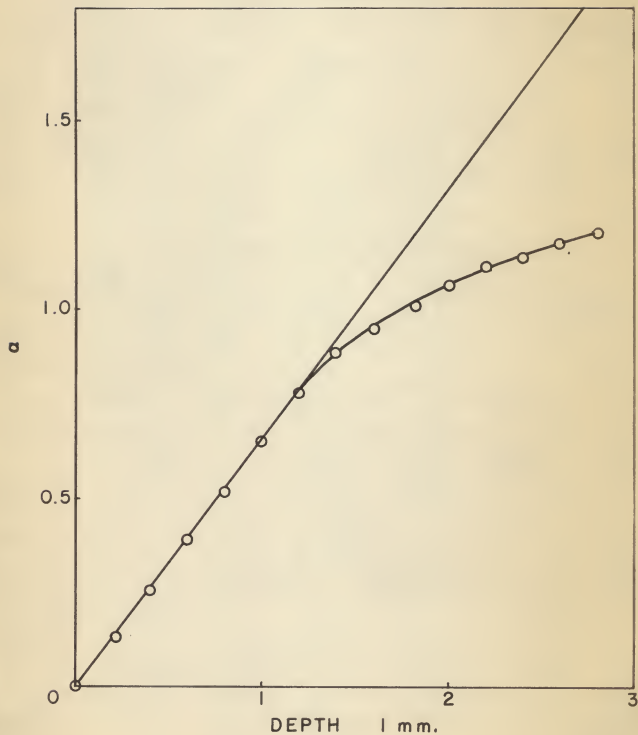
PLATE XXII



EXPLANATION OF PLATE XXIII

Graph of α versus depth in concrete for cylinder MAC.

PLATE XXIII



DIFFUSION OF SODIUM INTO CONCRETE

by

SHIH CHI CHANG

B. S., National Taiwan University, Taiwan, China, 1955

AN ABSTRACT OF A THESIS

submitted in partial fulfillment of the

requirements for the degree

MASTER OF SCIENCE

Department of Physics

KANSAS STATE COLLEGE
OF AGRICULTURE AND APPLIED SCIENCE

1958

The purpose of this thesis was to investigate the method by which sodium diffuses into the various types of concrete by using a radioactive tracer method. Lateral surfaces of concrete specimen in the form of cylinders were coated with paraffin. These cylinders were then immersed in a solution which consisted of 0.15 M. Na_2SO_4 and labelled with Na^{22}Cl so as to allow diffusion through the end surfaces of the cylinders.

The first group of cylinders consisting of one of each variety of concrete was immersed in the solution for a period of 273 days. An end of each of the cylinders of the different types of concrete was then ground away and the concentration of the diffused sodium within the concrete was measured. The second ends were measured after a year of storing in the laboratory air. The second and third groups, having a diffusion time of 1018, 1201 days respectively, were then measured in a comparable fashion.

Na^{22} is a positron emitter accompanied by γ ray radiation. If a G-M tube is placed in front of the cylinder, both β^+ and γ rays can enter the ionization chamber. The activity thus measured corresponds to $\beta^+ + \gamma$ rays. When an aluminum absorber was placed between the cylinder and the counter to stop all the β^+ particles, γ ray activity alone was recorded. The difference of these two countings gave the β^+ ray activity. As the β^+ particles have a short range in concrete, their activity at a point was considered proportional to the concentration of sodium ions at that point. This procedure of counting the β^+ activity at the cylinder's surface was repeated after thin layers of the cylinder were ground off.

Thus a curve of counting rate versus distance from the end of cylinder was determined.

All the counting rate curves obtained for a particular kind of concrete were approximately the same irrespective of the different diffusion periods and the time of subsequent storage. It was, however, observed that the curves mentioned above depended on the apparent roughness or porosity of the surface. Furthermore, an increase of the average γ ray activity with diffusion time was observed. This was thought to be an indication that the total sodium content within the concrete cylinders increased with time.

From these observations, we concluded that the diffusion was presumably composed of two types of action. At first, sodium diffused into the water through the pores connected to the surface of the concrete specimen. The rate of this diffusion is large, of the order of 10^{-3} cm²/sec. The actual diffusion of sodium through the cement is of the order of 10^{-10} cm²/sec. or smaller.