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Northwest Expressway, Interstate Route 94. This view, west from Augusta Blvd., Chicago, Ill., shows a section of the reversible roadway for six lanes of traffic and the median shoulders for emergency parking.

IN THIS ISSUE

U.S. DEPARTMENT OF COMMERCE
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Characterization of Montmorillonite Saturated with Short-Chain Amine Cations

Part I—Interpretation of Basal Spacing Measurements

BY THE DIVISION OF PHYSICAL RESEARCH
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The clay mineral montmorillonite is widely distributed in soils and has a considerable effect on soil properties such as plasticity, strength, and volume change. Recently, various amines (cationic organic compounds, derivatives of ammonia) have been tried in soil stabilization, usually as supplementary additives with other stabilizers such as phosphoric acid. The following two articles present information on two aspects of the products obtained by treating a montmorillonite (Wyoming bentonite) with a number of these amines. The results presented are not of immediate practical value in application to field problems, but are basic in nature; they represent a part of a larger study investigating the nature and properties of soil clay minerals and their contribution to the engineering performance of soil materials. In the first article the data concern measurements of the basal spacings of the amine-saturated montmorillonite.

Basal spacing measurements were made by x-ray diffraction. Specimens prepared by saturating portions of the montmorillonite with a series of small aliphatic primary, secondary, and tertiary amine cations, and with quaternary ammonium cations were x-rayed while wet, after oven-drying, and after glycerol treatment. Observed basal spacings ranged from about 12 to 14 A., depending on the cation, indicating that a monolayer of cations always was interleaved between adjacent montmorillonite layers. The observed spacings are consistent with the concept that the cations were oriented with their minimum thickness in the c-axis direction, but it is possible that the smallest cations had a long axis in this direction and were partially embedded in the clay surfaces.

Montmorillonite saturated with cations containing up to four carbon atoms retained some sensitivity to water, as indicated by a slight contraction of the lattice on oven-drying and by rapid re-expansion on exposure to the humidity of the laboratory atmosphere.

For cations having a layer thickness less than glycerol, limited lattice expansion occurred when specimens were glycerol treated, usually to a spacing sufficient to accommodate a single layer of glycerol molecules. Apparently the cations functioned as pillars separating the montmorillonite layers, and the glycerol molecules expanded the lattice as necessary to enter the spaces between the pillars. However, two exceptions were noted: with methylamine-saturation both a one-layer and a two-layer complex of glycerol were present simultaneously in the same specimen; but in trimethylamine saturation two different, one-layer complexes were present. It is suggested that the glycerol in one-layer montmorillonite complexes may exist in two orientations, one causing a layer thickness of about 4.1 A., the other a thickness of about 4.6 A.

Introduction

THE PROPERTIES of montmorillonite saturated with large aliphatic amine cations have been studied fairly extensively in recent years, but relatively little work has been done with the smaller amine and quaternary ammonium cations. The present work represents an attempt to characterize the complexes formed on saturation of a montmorillonite with some of these smaller cations, particularly as to cation dimensions, packing of ions on the clay surface, and complexes formed by glycerol. This article includes information on the determination of basal spacings of the various complexes, and on the interpretation of the data in terms of the thickness and orientation of the cations and of the glycerol molecules.

Summary and Conclusions

It has been shown that montmorillonite saturated with any of a number of short-chain normal primary, secondary, or tertiary amine, or quaternary ammonium cations acquires a basal spacing characteristic of the formation of a complex consisting of a monolayer of cation pillars interleaved between adjacent layers of montmorillonite. The basal spacing is generally very regular, even with wet specimens, and the spacing is not significantly reduced by air-drying. Oven-drying causes slight contractions in spacing ranging from about 0.7 A. (angstrom unit, 10^{-8} cm.) for specimens saturated with the trimethylamine cation down to about 0.1 A. for those saturated with cations containing six or more carbon atoms. Upon re-exposure to the laboratory atmosphere, specimens that showed significant contractions on oven-drying underwent a rapid, partial re-expansion because of the sorption of water vapor.

Thicknesses of the cation layers estimated from basal spacings of the saturated clay were 0.2 to 1.1 A. smaller than the minimum clearance thicknesses measured from atom models. One- and two-carbon amine cations might have been present in other than minimum thickness orientation with respect to the basal plane and, if so, were partially embedded in the silica sheets.

The effect of glycerol treatment of the clay varied somewhat with the cation. For saturation with most of the smaller cations, basal spacings were obtained that are characteristic of the clearance thickness of a monolayer of glycerol molecules between the montmorillonite layers. However, with saturation by methylamine cations, at least part of the clay expanded to admit two molecular layers of glycerol. This may have been a reflection of the inhomogeneity of the Wyoming bentonite material, the fully-expanding portion perhaps having a lower layer-charge density than the remainder. With trimethylamine-treated clay, two distinct, one-layer complexes of glycerol occurred simultaneously in the same specimen. This also may have been an indication of the inhomogeneity of the montmorillonite.

In general, it is clear that with saturation by the smaller amine cations, glycerol penetrated the lattice and a complex consisting of

cation pillars and interpillar glycerol molecules was formed in the interlayer spaces, with the separation between adjacent montmorillonite layers being controlled by the glycerol molecules. Generally, the orientation of the glycerol molecules apparently corresponded to that observed in the normal two-layer glycerol complexes of montmorillonite, which had a Δ-value of about 4.15 A. per layer. Of the two, one-layer glycerol complexes with trimethylamine-saturated clays, one glycerol layer had a 4.2 A. Δ-value and the other a Δ-value of 4.6 A. This apparently indicated two different orientations of the glycerol molecules. The 4.6 A. Δ-value indicated an orientation corresponding to that for the one-layer glycerol complex for a sodium-saturated montmorillonite. With the larger tertiary amine cation and the quaternary ammonium cations, the changes in basal spacing observed for glycerol-treated specimens were minimal, and it was not possible to decide unequivocally whether the lattice actually had been penetrated by glycerol molecules.

Materials and Experimental Procedure

Volclay-brand Wyoming bentonite was used as a source of montmorillonite. The commercial product was fractionated by dispersion in water with sodium hexametaphosphate (Calgon) and sedimentation by centrifugation; the material coarser than 2-microns was discarded.

Amine cation-saturated specimens of the clay were prepared for x-ray diffraction by using 1-normal solutions of amine compounds as follows: methyl-, ethyl-, dimethyl-, diethyl-, di-n-propyl-, trimethyl-, triethyl-, tri-n-propyl-, and tri-n-butylamine hydrochloride. Saturations also were made with solutions of two salts, tetramethylammonium chloride and tetraethylammonium bromide. For each specimen an aliquot of the clay-water dispersion sufficient to yield about 100 milligrams of clay was used to prepare a thin film of clay as an oriented aggregate on a porous ceramic tile, by a centrifuge method (1).[2] Saturation was accomplished by passing five separate, 5-milliliter portions of the amine salt solution (50 times the exchange capacity) through the clay film and tile held in the suction device described in reference 1. The clay film was then washed five times by passing 20-milliliter portions of distilled water through the film and tile in the same manner.

The solutions of the primary, secondary, and tertiary amine hydrochlorides were prepared by neutralizing the appropriate amine with concentrated hydrochloric acid and diluting to 1-normal with distilled water. Corresponding solutions containing the quaternary amine cations were prepared directly from the two salts, tetramethylammonium chloride and tetraethylammonium bromide. The amines and quaternary ammonium salts were Eastman organic reagents.

X-ray diffraction patterns were recorded with a General Electric XRD-3 diffractom-

eter employing copper Kα radiation. These patterns were obtained for specimens when they were (1) wet, directly after the saturation and washing treatment; (2) air-dried; (3) oven-dried overnight at 110° C.; and (4) glycerol-treated.

For the glycerol treatment, an excess amount of glycerol was applied to the clay film: the specimen was placed over a supply of glycerol in a sealed container and tempered overnight at 70° C. After this tempering treatment, the specimens had substantially the same basal spacings as those treated with glycerol alone, but the tempering markedly improved the regularity of the sequence of basal reflections and greatly increased the intensity of the individual maxima.

Results and Discussion

Wet specimens

Basal spacings of the wet amine-cation saturated specimens are listed in table 1. The numbers given are averages calculated from several higher orders of reflection, and they occupy a restricted range of 12.6 to 14.2 A. For most specimens, the x-ray maxima were surprisingly sharp and well-defined, and they had a very regular sequence of reflections. This was in contrast to the x-ray maxima for wet specimens of the same montmorillonite saturated with inorganic cations; such specimens commonly exhibited only diffuse reflections lacking in higher orders. As the basal spacing of the montmorillonite structure itself was 9.4 A. and the thickness of a methyl group (2) is about 4 A., it is clear from the basal spacings, as shown in table 1, that no more than a monolayer of cations was present between adjacent layers of montmorillonite.

Air-dried specimens

Small reductions in the basal spacings of about 0.1 A. were caused by the air-drying of the wet amine-cation saturated specimens. The basal spacing data for the air-dried specimens were not included in table 1 because the effect of air-drying was so slight and the relative humidity had not been controlled.

Table 1.—Basal spacings of wet- and oven-dry amine-saturated montmorillonite

Cation	Basal spacings		
	Wet specimens	Oven-dried specimens	Difference
	A.	A.	A.
Methylamine	12.6	[1] 12.16	0.4
Ethylamine	12.94	[1] 12.66	0.3
Dimethylamine	12.94	[1] 12.52	0.4
Diethylamine	13.22	[1] 12.81	0.4
Di-n-propylamine	13.28	13.15	0.1
Trimethylamine	13.5	[1] 12.84	0.7
Triethylamine	13.40	13.26	0.1
Tri-n-propylamine	13.4	13.36	0
Tri-n-butylamine	13.6	13.51	0.1
Tetramethylamine	[2] 14	13.85	(2)
Tetraethylamine	14.2	14.17	0

[1] Averages of estimates based on higher orders of reflection, each order of reflection having been recorded individually immediately after a separate drying period.
[2] Diffuse nature of x-ray pattern of the second and higher orders precluded accurate estimation of basal spacing and of difference in spacing between wet- and oven-dry specimens

Oven-dried specimens

The basal spacings for the oven-dried specimens also are given in table 1. In the normal x-raying procedure, an oven-dried specimen was removed from the oven, mounted directly on the diffractometer, and the appropriate two-theta range (2° to as high as 60°) was covered in a continuous scan. This technique was satisfactory for specimens saturated with the larger amine cations; but, for those with the smaller cations, rapid adsorption of water vapor from the atmosphere caused considerable expansion of the lattice to take place while the diffraction patterns were being recorded. As appropriate accessory equipment was not available to prevent this adsorption and expansion during the x-raying, a special procedure to minimize the effect was adopted to record the patterns. The diffractometer was preset to within one-half a degree of the expected position for a given maximum, the specimen was removed from the oven and mounted immediately in the diffractometer, and the maximum was recorded. The specimen was then returned to the oven to remove the small amount of moisture that had been adsorbed during the recording period, and the procedure was repeated to record the next order of reflection. For each recording, approximately 1½ minutes elapsed between the removal of the specimen from the oven and the recording of the maximum; the specimen remained hot during this period.

The basal spacings with this procedure were estimated from four or five individual higher orders of reflection, which agreed within 0.05 A. for most specimens and within 0.10 A. for all. The regularity of spacing was comparable to that observed for specimens saturated with the larger cations, by use of the normal continuous scan procedure.

As shown in table 1, for clay specimens saturated with the smaller amine cations (up to four carbon atoms), the basal spacings were not fixed; the spacings for the wet specimens were from 0.3 to 0.7 A. higher than those for oven-dried specimens. It was clear that despite the amine saturation, water penetrated the interlayer spaces of specimens and slightly expanded the lattice. But when specimens were saturated with cations containing six or more carbon atoms, the result was virtually fixed basal spacings. The differences in spacings between wet and oven-dry specimens were not more than about 0.1 A.; these differences are consistent in direction and probably are not much greater than the experimental error.

Jordan (3) has shown that in the series of primary normal aliphatic amine cations those up to decylamine yield one-layer complexes with montmorillonite, although dodecylamine and larger cations form two-layer complexes. Little information is available in the literature concerning the size of cation at which a corresponding change takes place in the secondary or tertiary amine series. In this study, one-layer complexes were observed in specimens with the largest of the secondary and tertiary amine cations em-

ployed, di-n-propylamine and tri-n-butyl-amine. Although no further exploration was made in the secondary amine series, specimens saturated with the next higher member of the tertiary series, tri-n-amylamine, were examined and the basal spacing of approximately 18 A. indicated the presence of a two-layer complex.

Recently, a two-layer complex of methylamine- or dimethylamine-saturated montmorillonite was obtained by treatment of Wyoming bentonite with concentrated solutions of methylamine and dimethylamine hydrochloride (4). However, for these smallest two cations only one-layer complexes were formed when the clay was treated, as in this study, by repeated leaching of a thin film of clay with an excess of 1-normal solution of the hydrochloride. The effect was the same whether the clay film was x-rayed while still soaked with the amine hydrochloride solution or after thorough washing with distilled water. Presumably, therefore, formation of a two-layer complex with methylamine or dimethylamine requires that the clay be in contact with a solution more concentrated than 1-normal.

Little published information is available on basal spacings that could be used for comparison with the basal spacings observed in this study for the oven-dried specimens. Spacings generally 0.1 to 0.3 A. less than those recorded for this study have been cited (5, 6) for a montmorillonite that had been saturated with methylamine, dimethylamine, trimethylamine, tetramethylammonium, and tetraethylammonium cations, all of the specimens having been dried and outgassed under high vacuum. A spacing of 13.3 A. was reported (7) for both wet and air-dried specimens of a montmorillonite saturated with triethylamine cations, which is comparable to the 13.40 A. and 13.26 A. obtained in this study for a wet and an oven-dried specimen.

In discussing the basal spacings of clay-organic complexes, it has been customary to estimate the thickness of the organic layer by subtracting the theoretical thickness of the silicate layer (9.4 A. for montmorillonite) from the basal spacing measured by x-ray diffraction. MacEwan (8) called this estimate of the thickness of the organic layer the "Δ-value." Δ-values calculated in this way for the several amine and quaternary ammonium cations used in this study are presented in table 2. For comparison, also included are the corresponding minimum clearance thicknesses for the various cations; these were obtained by direct measurement of Fisher-Taylor-Hirschfelder atom models. Each Δ-value is somewhat smaller than the minimum clearance thickness measured from the model; the apparent contraction varied from 0.2 to 1.1 A. Similar effects have been observed for adsorbed organic molecules, as well as for cations (9, 10, 5). This apparent contraction of the organic layer has been variously ascribed to hydrogen bonding to the silicate surface, to partial keying into the silicate layer, or simply to compression exerted by the host montmorillonite lattice. Brindley and Hoffman (11) have reviewed and discussed this subject in considerable detail.

In the foregoing discussion of the basal spacing and apparent contraction data, it has been assumed that the adsorbed ions were oriented so as to present their minimum thicknesses in the direction perpendicular to the layers. However, another interpretation is likely for the smallest amines; that is, those containing only one or two carbon atoms. In a recent paper, Rowland and Weiss (4) have suggested that, when montmorillonite is treated with a relatively dilute solution of methylamine hydrochloride or dimethylamine hydrochloride, the adsorbed amine cations may be oriented with their long axis perpendicular to the silicate layers, the cations being partially embedded in the holes of the hexagonal oxygen rings of the silica sheets. The basal spacings observed in this study for these two cations, and also for the ethylamine cation, are consistent with either orientation—the increased clearance thickness required for these cations in their vertical orientation could have been compensated for by their being partially embedded in the 2.4 A.-deep oxygen-ring cavity. Evidence presented in part II of this article strongly supports the latter interpretation.

Glycerol-treated specimens

Basal spacings for amine-saturated montmorillonite specimens treated with glycerol are given in table 3. These spacings give no indication of the formation of two-layer complexes, except for specimens saturated with methylamine. X-ray diffraction patterns of specimens saturated with the methylamine cation and then treated with glycerol disclosed that both one- and two-layer complexes were present simultaneously. This simultaneous occurrence of the two types of complexes may possibly have been caused by the inhomogeneity of the bentonite with respect to layer charge density—that portion of the material with lower charge density tending to expand more readily than that with higher charge density, thus admitting two molecular layers of glycerol, but the higher charge density material tended to admit only one molecular layer. Beavers and Larsen (12) showed that a clay fraction of a Wyoming bentonite, analyzed electrophoretically by schlieren moving boundary procedures, behaved as though materials of two or more different charge densities were present.

The patterns of the glycerol-treated trimethylamine-saturated clay, although not showing the presence of a two-layer glycerol complex, were unusual in that they showed two distinct series of reflections and thereby indicated the simultaneous presence of two, different one-layer complexes—a predominant one having a basal spacing very close to 14.0 A., and another, representing only a small part of the clay, having a spacing of about 13.6 A. This variation also might be accounted for by inhomogeneity of the montmorillonite with respect to layer charge density. The x-ray diffraction patterns for all of the other cations showed only a single sequence of strong and well-ordered basal reflections, all for one-layer complexes. The basal spacings cited in table 3 are averages

Cation	Δ-value [1]	Minimum clearance layer thickness derived from model	Apparent contraction
	A.	A.	A.
Methylamine	2.8	3.7	0.9
Ethylamine	3.3	3.9	0.6
Dimethylamine	3.1	3.9	0.8
Diethylamine	3.4	3.9	0.5
Di-n-propylamine	3.7	3.9	0.2
Trimethylamine	3.4	4.5	1.1
Triethylamine	3.9	4.7	0.8
Tri-n-propylamine	4.0	4.8	0.8
Tri-n-butylamine	4.1	4.8	0.7
Tetramethylamine	4.5	5.3	0.8
Tetraethylamine	4.8	5.5	0.9

[1] Observed basal spacing of oven-dried specimen minus 9.4 A., the theoretical thickness of the montmorillonite layer.

calculated from four or five individual, higher orders of reflection. Agreement among the basal spacing estimates calculated from these individual orders of reflection is comparable to the agreement among basal spacing estimates for oven-dried specimens. For comparison with the basal spacings of the glycerol-treated specimens, the corresponding spacings for oven-dried specimens also are given in table 3. In general, the basal spacings for the glycerol-treated specimens are higher and vary with the size of the cation. With methylamine, the smallest cation, the spacing of the one-layer complex produced by the glycerol treatment is 13.6 A., which is about 1.4 A. higher than the spacings for the oven-dried specimens. For the other cations, differences between the spacings of the glycerol-treated and the corresponding oven-dried specimens decrease systematically with increasing size of the cation; the difference ranges from 1.2 A. for dimethylamine down to 0.1 A. or less for specimens saturated with cations having more than six carbon atoms. For the tetraethylammonium cation, the spacing of the glycerol-treated specimen is actually lower than that of the oven-dried specimen, by 0.1 A.

Table 3.—Comparison of basal spacings for glycerated and oven-dried specimens of amine-saturated montmorillonite, and Δ-values for the glycerated specimens

Cation	Basal spacings			Δ-value for glycerated specimens
	Glycerated	Oven-dried	Difference	
	A.	A.	A.	A.
Methylamine	13.60 and 18	12.16	1.44 and 6	4.2
Ethylamine	13.65	12.66	0.99	4.2
Dimethylamine	13.74	12.52	1.22	4.3
Diethylamine	13.40	12.81	0.59	4.0
Di-n-propylamine	13.40	13.15	0.25	4.0
Trimethylamine	13.99 and 13.6	12.84	1.16 and 0.8	4.6 and 4.2
Triethylamine	13.36	13.26	0.10	4.0
Tri-n-propylamine	13.47	13.36	0.11	4.1
Tri-n-butylamine	13.55	13.51	0.04	4.1
Tetramethylamine	13.96	13.85	0.11	4.6
Tetraethylamine	14.05	14.17	−0.12	4.6

Δ-values for the glycerol-treated specimens also are given in table 3. These specimens may be placed in two groups, one whose Δ-values averaged 4.15 A. and one whose Δ-values averaged 4.6 A. MacEwan (8) gave a Δ-value of 8.3 A. for the two-layer glycerol complex, which corresponds to a thickness of 4.15 A. for the glycerol molecule. He also observed a lower Δ-value of 3.8 A. for the one-layer glycerol complex of halloysite. Previously, the authors (13) reported that a one-layer glycerol complex of sodium-saturated montmorillonite had been obtained by heating the glycerol-treated clay. The basal spacing was 13.95 A., which corresponds to a Δ-value of 4.55 A. Thus, the Δ-values reported in table 3 are within the range of previously reported estimates derived from glycerol complexes. Examination of an atom model of the glycerol molecule revealed that a large number of possible conformations and orientations of the molecule can yield Δ-values within this range. Two different orientations or conformations of the glycerol molecules are suggested by the two distinct groups of Δ-values, and also by the two separate sequences of basal reflections observed for one of the cations in each of the two groups. The orientation causing a Δ-value of about 4.15 A. apparently corresponds to the state of the glycerol molecules in the normal two-layer glycerol complex; and the orientation causing the 4.6 A. Δ-value apparently corresponds to the orientation of the glycerol molecules in the one-layer glycerol complex of sodium-saturated montmorillonite.

The concept has been established (5, 6) that, in montmorillonite saturated with certain small amine cations, the cations act as "pillars" holding the individual montmorillonite layers apart to a spacing approximating the thickness of the individual cation. The pillars do not form a close-packed layer, and the interlayer space remaining between them is available for sorption of either polar or nonpolar gases. Also established was the fact that further expansion of the basal spacing of the amine-saturated montmorillonite can accompany sorption of certain polar gases whose molecules require greater clearance space than that provided by the amine cation pillars.

The results for the sorption of glycerol in this study are consistent with this pillar concept. For the smaller amine cations, penetration of glycerol molecules into the vacant interlayer spaces between the cation pillars apparently was accompanied by a lattice expansion to the clearance required to accommodate the glycerol molecules themselves. A mixed, one-layer complex of glycerol molecules and amine cations thus may be said to have been present. But, for the larger tertiary amine cations, interlayer separations established in the specimens by the cations themselves approached the clearance required to accommodate glycerol molecules. Adsorption of a monolayer of glycerol molecules in the interpillar spaces therefore would require little, if any, expansion of the lattice. As the changes in basal spacings for these cations were minimal (table 3), it is clear that not more than such a monolayer of glycerol molecules could have been adsorbed; but, it also is not possible to decide unequivocally whether penetration of glycerol into the interpillar spaces actually occurred. A similar uncertainty also applies for the quaternary ammonium cations.

Although similar x-ray data for glycerol-treated, triethylammonium-saturated montmorillonite had been interpreted (14) to indicate that glycerol molecules do not penetrate between the unit layers, results from this study indicate that such an interpretation is not necessarily correct. Whether any such penetration actually occurs is discussed more fully in part II.

REFERENCES

(1) *A New Method for Preparation and Treatment of Oriented-Aggregate Specimens of Soil Clays for X-Ray Diffraction Analysis,* by E. B. Kinter and Sidney Diamond, in *Soil Science,* vol. 81, No. 2, Feb. 1956, pp. 111–120.

(2) *The Nature of the Chemical Bond,* by Linus Pauling, 2d ed., 1940, Chapter V, Interatomic Distances and their Relation to the Structure of Molecules and Crystals, Sec. 24, Van Der Waals and Non-Bonded Radii of Atoms, p. 190.

(3) *Organophilic Bentonites; Part I.—Swelling in Organic Liquids,* by John W. Jordan, The Journal of Physical and Colloid Chemistry, vol. 53, No. 2, Feb. 1949, pp. 294–306.

(4) *Bentonite-Methylamine Complexes,* by R. A. Rowland and E. J. Weiss, a paper presented at the Ninth National Conference on Clays and Clay Minerals, Purdue University, Oct. 1960.

(5) *Sorption and Intercalation by Methyl Ammonium Montmorillonites,* by R. M. Barrer and J. S. S. Reay, Transactions of the Faraday Society, vol. 53, Part 9, Sept. 1957, pp. 1,253–1,261.

(6) *Activation of Montmorillonite by Ion Exchange and Sorption Complexes of Tetra-Alkyl Ammonium Montmorillonites,* by R. M. Barrer and D. M. MacLeod, Transactions of the Faraday Society, vol. 51, Part 9, Sept. 1955, pp. 1,290–1,300.

(7) *The Swelling of Organophilic Montmorillonites in Liquids,* by R. Greene-Kelly, The Journal of Colloid Science, vol. 11, No. 1, Feb. 1956, pp. 77–79.

(8) *Complexes of Clays with Organic Compounds: I—Complex Formation Between Montmorillonite and Halloysite and Certain Organic Liquids,* by D. M. C. MacEwan, Transactions of the Faraday Society, vol. XLIV, Part 6, June 1948, pp. 349–367.

(9) *Molecular Associations Between Montmorillonite and Some Polyfunctional Organic Liquids,* by W. F. Bradley, Journal of the American Chemical Society, vol. 67, No. 6, June 1945, pp. 975–981.

(10) *Sorption of Aromatic Organic Compounds by Montmorillonite: Part I—Orientation Studies,* by R. Greene-Kelly, Transactions of the Faraday Society, vol. 51, Part 3, March 1955, pp. 412–424.

(11) *The Orientation of Organic Molecules on Clay Mineral Surfaces,* by G. W. Brindley and R. W. Hoffman, a paper presented at the Ninth National Conference on Clays and Clay Minerals, Purdue University, Oct. 1960.

(12) *Electrophoresis of Clays by the Schlieren Moving Boundary Procedure,* by A. H. Beavers and B. L. Larson, Soil Science Society of America Proceedings: Division II—Soil Chemistry, vol. 17, No. 1, Jan. 1953, pp. 22–26.

(13) *Gravimetric Determinations of Monolayer Glycerol Complexes of Clay Minerals,* by E. B. Kinter and Sidney Diamond, in *Proceedings of the Fifth National Conference on Clays and Clay Minerals ,1956, Clays and Clay Minerals,* 1958, National Academy of Science—National Research Council, No. 566, pp. 318–333.

(14) *Pretreatment of Soils and Clays for Measuring External Surface Area by Glycerol Retention,* by E. B. Kinter and Sidney Diamond, in *Clays and Clay Minerals: Proceedings of the Seventh National Conference on Clays and Clay Minerals, 1958,* vol. 5, Pergamon Press, 1960, pp. 125–134.

Characterization of Montmorillonite Saturated with Short-Chain Amine Cations

Part II—Interlayer Surface Coverage by the Amine Cations

BY THE DIVISION OF PHYSICAL RESEARCH
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Introduction

IN MONTMORILLONITE saturated with certain short-chain amine and quaternary ammonium cations, it has been shown (1, 2)[2] that the amine cations are present largely as an incomplete monolayer between the unit layers of the montmorillonite, and the individual cations act as pillars in preventing collapse of the montmorillonite lattice when the clay is dried. Also, the space between the cation pillars has been demonstrated to be available for the sorption of both polar and nonpolar gases. In an attempt to measure the extent of the interpillar areas by applying the Brunauer-Emmett-Teller (B.E.T.) equation to their observed data for the sorption of gases, Barrer and Reay (1) found that the calculated areas were much lower than had been expected from the cation exchange capacity of the clay and the size of the cations. The principal reason adduced for this discrepancy was that the B.E.T. gas-sorption model seemingly did not apply to the unusual sorption conditions prevailing in the sterically restricted areas between the montmorillonite unit layers.

For montmorillonite and related substances that have been saturated with inorganic cations, the interlayer area can be measured conveniently by liquid-state sorption methods; polyhydric alcohols such as glycerol (3, 4) and ethylene glycol (5) have been used. With the glycerol method, a saturated sample of clay is treated with an aqueous solution of glycerol and, in a glycerol-vapor atmosphere maintained at slightly less than saturation, the water and excess glycerol are removed from the clay at a temperature of 110° C. A monomolecular layer of glycerol is retained by the clay, both on the areas between the unit layers and on the exteriors of the particles. Completion of the desorption of excess glycerol is signaled by the glycerol-treated clay's attainment of constant weight. The

A brief explanation of the basis for research with a montmorillonite clay saturated with a series of amine cations is included in the editorial appearing with the first article. In this Part II, the interlayer surface area of the clay that is covered by the amine cations is discussed.

Portions of Wyoming bentonite were saturated with a series of short-chain aliphatic amine and quaternary ammonium cations and the amine content remaining after washing was determined by combustion analysis. When the clay was saturated with amine cations containing one or two carbon atoms, the amine content of the clay was greatly in excess of its cation exchange capacity. This excess was thought to be either amine cations or uncharged amine molecules that had become partially embedded in the oxygen rings of the silica sheet surfaces. When the clay was saturated with the larger, tertiary amine cations, the amine content of the clay was slightly less than its exchange capacity, presumably because of the blocking of some exchange sites by steric interference.

Quantitative determination of the glycerol retained as a monolayer in glycerol-treated specimens of the amine-saturated clays showed that these clays retained considerably less glycerol than the untreated bentonite. The amounts of retained glycerol were employed to provide quantitative estimates of the interlayer clay surface remaining unoccupied between cation pillars. The percentage of unoccupied interlayer surface of the untreated clay ranged from about 75 percent for the clay saturated with methylamine to essentially zero for the clay saturated with the larger, tertiary amine cations.

The validity of the areas calculated from the glycerol retention data was indirectly confirmed by deriving estimates of the cross-section areas of the several cations from the reductions in the amount of glycerol retained. These experimentally-derived cross-section cation areas were in satisfactory agreement with the areas of the cations projected from atom models.

weight increase over the oven-dry weight of the clay represents the weight of the monolayer. By use of the monolayer weight and the coverage area assigned to the glycerol molecule, the surface area of the clay is estimated.

X-ray diffraction results included in part I of this article indicated that glycerol molecules, applied in the liquid state, also can penetrate interlayer spaces when montmorillonite is saturated with any one of a number of short-chain aliphatic amine cations, containing up to four carbon atoms. The entry of glycerol was revealed by an expansion of the basal spacing of the amine-cation saturated clay, which provided a separation of not less than about 4 A. between the unit layers. Analogous restricted lattice expansion caused by sorption of certain polar molecules on amine-treated montmorillonite also has been observed (1, 6).

In this study, the extent of the interpillar area of a montmorillonite saturated with a

series of short-chain aliphatic amine cations was estimated by means of the glycerol retention technique. The interpillar area, the total interlayer area of the untreated clay, and the number of amine cations present in each amine-saturated product, as determined by analysis, were used to estimate the area covered by the individual cations.

Summary and Conclusions

Wyoming bentonite was treated with solutions of the hydrochlorides of a number of short-chain aliphatic amines and two quaternary ammonium salts and washed with an acetone-water solution. Carbon analyses indicated that in most cases the cations were adsorbed and retained against washing in amounts consistent with the exchange capacity of the clay. However, for the one- and two-carbon amines, the adsorption was greatly in excess of the exchange capacity, although for the larger tertiary amines it was less than the exchange capacity.

Glycerol retention determinations indicated that the surface available to glycerol is greatly reduced by treatment with amine cations, the reduction being most pronounced for the larger cations. After allowing for glycerol retained on external surfaces, the remaining glycerol was interpreted as having been retained between the cation pillars in the interlayer spaces. From the glycerol retention figures, estimates were made of interpillar area ranging from more than 400 m.²/g. for the methylamine-treated clay to essentially zero for the clay treated with tri-n-butylamine.

Consequently, the difference in glycerol-retaining capacity between untreated bentonite and the amine-treated clay was ascribed to the interlayer area physically occupied by the amine cations. From the loss of glycerol-retaining capacity, the total area occupied by the cations and the average cross-section area per cation were calculated for each of the several amines. These experimental cross-section areas were shown to be in good agreement with coverage areas obtained from atom models of the individual amines. This agreement confirmed that the interlayer space not occupied by amine cations may be occupied almost completely by glycerol and, consequently, that the glycerol retention method provides an acceptable measure of the area between the amine cation pillars. The completeness with which glycerol fills the interpillar areas suggests that at least the larger cations possess some freedom of lateral adjustment in the interlayer space.

The distribution of cations within the monolayers was considered to be somewhat irregular, with the actual distances between adjacent cation sites deviating considerably from the calculated average distance of 7.7 A. Because of this irregularity, saturation treatments with cations such as tri-n-propylamine, which are large enough to occupy all of the interlayer surface of the clay on the basis of a complete exchange of cations, do not necessarily accomplish this coverage. On the one hand, the exchange of large cations was not complete because some of the sites that happened to be closely spaced may have been blocked; but at the same time, in regions of widely-separated sites, some of the interlayer area may still have been unoccupied. Upon glyceration a few glycerol molecules may therefore be adsorbed into the interlayer space; the probability of this presumably decreases with increasing layer charge of the montmorillonite. Because of this, saturation with triethylamine cations, which had previously been suggested as a means of preventing the penetration of glycerol into the interlayer spaces, was not completely effective with Wyoming bentonite. Estimates of the external surface of some soils and clays obtained by glycerol retention after such treatment thus may be slightly high.

Methylamine, ethylamine, and dimethylamine seemed to be adsorbed and retained by the clay in a manner somewhat different from the other amine cations, apparently being in perpendicular rather than parallel orientation with respect to the planar surface of the clay. The amount of methylamine adsorbed and retained corresponds to the number of oxygen ring cavities calculated to be present on the clay surface. It is thought that a full exchange complement of methylamine cations was partially embedded in those cavities which are associated with cation sites, and that amine in excess of this was similarly embedded in the remaining ones. The adsorption of excess amine was not accompanied by either the adsorption of chloride ions or by an observable drop in pH. Consequently, although it is clear that the excess amine was not adsorbed as molecules of amine salt, it is not certain whether adsorption was in the form of amine cations or as free amine molecules. The adsorption of the two-carbon amines was somewhat less than for methylamine, corresponding to occupation of all of the cavities associated with cation sites, plus only about half of the remaining ones. This lesser adsorption is thought to have been caused by the physical difficulty of the two-carbon amines in becoming suitably oriented for embedding in the cavities.

Preparation of Amine-Saturated Clay

The clay used in this study was Volclay brand Wyoming bentonite ground to pass the 200 mesh sieve; this clay contained about 85 percent montmorillonite and the remaining 15 percent was largely quartz and feldspar. This material was used as supplied, without fractionation or other purification. The group of amines used included a number of short-chain primary, secondary, and tertiary aliphatic amine cations and two small quaternary ammonium cations; these are listed in table 1. The clay was saturated with amine cations by using 1-normal solutions of the amine hydrochlorides prepared by neutralizing Eastman organic reagent amines with hydrochloric acid to a final pH of about 7. For saturation with the quaternary ammonium cations, 1-normal solutions of tetramethylammonium bromide and tetraethylammonium chloride, prepared from the corresponding Eastman salts, were used.

For each cation saturation, 50 milliliters of the amine salt solution (5 times the exchange capacity) was added to a 10-gram portion of the clay, and the mixture was stirred until the clay was thoroughly wetted. About 100 milliliters of distilled water was then added and the mixture was stirred vigorously for 10 minutes with a vibration mixer. The strongly-flocculated clay was sedimented by centrifugation, and the supernatant liquid was decanted and discarded. This treatment was performed five times, after which the clay was washed five times by a similar process with 150-milliliter portions of 9:1 acetone-water solution. The clay remained flocculated throughout the washing process and was easily separated from the wash liquid. The last supernatant liquid was tested with a silver nitrate solution to assure its being free of chloride ion. The washed clay was dried at room temperature, lightly powdered, and stored.

Determination of Amine Content

The several amine-saturated clay materials were analyzed for carbon content by the conventional dry combustion method. The amine content in milliequivalents per gram of clay (meq./g.) was calculated by use of the carbon content data and the theoretical carbon content of the individual amines; these data are given in table 1. For comparison with these data, the cation exchange capacity of the raw clay (0.91 meq./g.) was determined by the versenate titration method described by Jackson (7). The amine content of the saturated clay material varied greatly; the results fell into three groups, depending on the size of the amine used for the saturation: (1) The amine content of the clay saturated with the 1- and 2-carbon amines greatly exceeded cation exchange capacity of the clay, the content of methylamine being almost three times as great; (2) the amine content of clay saturated with amines containing from 3 to 8 carbon atoms was approximately equal to the cation exchange capacity; but (3) the amine content of clays saturated with amines containing 9 or more carbon atoms was somewhat less than the cation exchange capacity. The anomalously large amine content of the clay preparations saturated with the smaller amines will be discussed later in this article. The deficiency in amine content noted for clay saturated with the larger amines agrees with findings for other relatively large amines made by Hendricks (8), Slabaugh and Kupka (9), and others; apparently this deficiency was caused by a steric interference by the large cations—those involved early in the exchange process blocking the access of some of the other cations to the remaining exchange sites. Even after repeated treatments of the clay, some of the original cations apparently remain; therefore, the amine cations were present on the clay in amounts that are less than the full exchange capacity of the clay.

INTERPILLAR AREA

Glycerol Retention Determinations

Duplicate glycerol retention determinations were made for the untreated clay and for each of the amine-saturated and quaternary ammonium-saturated clay products, by use of essentially the same procedure reported earlier (4). Briefly, a 1-gram sample of clay was treated with 10 milliliters of a 5-percent aqueous solution of glycerol, the clay was brought to constant weight (the glycerol monolayer condition) by removal of water and excess glycerol, at a temperature of 110° C., in an atmosphere slightly less than saturated with glycerol vapor. The difference in the initial and final weight of the clay represented the glycerol retention or weight of the glycerol monolayer. These glycerol retention determinations are given in table 1. To provide a uniform basis of comparison, the data in terms of milligrams of glycerol retained per gram of amine-saturated clay were converted to the basis of milligrams per gram of untreated clay by using the carbon content data and the stoichiometric compositions of

Table 1.—Characterization of amine-saturated clay

Saturating cation	Carbon content,[1] based on oven-dry weight of amine-saturated clay	Amine content, based on oven-dry weight of untreated clay	Glycerol retention			Calculated interpillar surface area
			Based on oven-dry weight of amine-saturated clay[2]	Based on oven-dry weight of untreated clay	Reduction from amount of untreated clay	
	Percent	meq./g. [3]	mg./g.	mg./g.	Percent	m.²/g.
Untreated clay	----------	----------	----------	192[4]	----------	624[5]
Methylamine	2.46	2.35	128.5	137.4	29	431
Ethylamine	3.22	1.46	101.5	109.2	44	331
Dimethylamine	2.97	1.34	106.4	126.8	34	394
Diethylamine	4.16	.94	70.6	75.3	61	212
Di-n-propylamine	5.56	.89	54.9	59.5	69	156
Trimethylamine	3.08	.92	103.7	109.2	43	331
Triethylamine	4.16	.93	22.5	24.6	87	33
Tri-n-propylamine	7.30	.75	26.5	29.3	85	49
Tri-n-butylamine	8.83	.70	13.9	15.7	92	1
Tri-n-amylamine	9.98	.64	(6)	(6)	(6)	(6)
Tetramethylamine	4.26	.95	85.8	91.7	57	270
Tetraethylamine	7.60	.89	22.4	24.9	87	34

[1] Average of duplicate determinations, corrected for carbon content of untreated clay. Analyses performed by L. B. Hayes, chemist, Bureau of Public Roads.
[2] Average of duplicate determinations which agreed within 1.5 mg./g.
[3] The cation exchange capacity of the untreated clay is 0.91 meq./g.
[4] Average of six determinations on a sample washed five times with a 9:1 acetone-water solution.
[5] Complete interlayer surface area of untreated clay.
[6] Not determined; explanation given in text.

the amines. All the resulting data show that the amount of glycerol retained by the clay product had been substantially reduced by the amine treatment. The reductions ranged from about 30 percent to more than 90 percent of the amount retained by the untreated clay; these reductions increased generally with the increasing number of substituent alkyl groups and the length of the alkyl chains.

An effort was made to investigate the effect of even larger cations on clay; but the attempt to obtain similar glycerol retention data for the two, next larger cations in the tertiary series, tri-n-amylamine and tri-n-hexylamine, was unsuccessful. After the saturation and washing, the samples could not be brought to constant weight by oven-drying; they continued to lose weight slowly for several weeks. This weight loss was accompanied by the evolution of a characteristic amine odor, apparently caused by the desorption of amine molecules that had been adsorbed during the saturation treatment and not removed by the washing. Because of this difficulty, no further attempts were made to characterize tri-n-amylamine- and tri-n-hexylamine-treated montmorillonite by the glycerol retention technique.

External surface

As indicated, part of the retained glycerol was considered to be present in channels between the amine cations in the interlayer spaces and the remainder of the glycerol was considered to be a monolayer on the external particle surfaces of the clay. Therefore, in estimating the extent of the interpillar area from these determinations, it was necessary to correct the total retention for the amount retained on external surfaces. In estimating the external glycerol, it seemed reasonable to postulate that the external surface areas of the several amine-saturated products were not significantly different from that of the untreated clay or from each other. The raw clay was treated directly with the amine

salt solution without prior dispersion, and flocculation was maintained throughout the saturation and washing treatments. Although mechanical agitation was a necessary part of the process, disruption of the primary particles was considered insufficient to have significantly affected the amount of the external surfaces. The external surface area of the untreated Wyoming bentonite material was 27 square meters per gram (m.²/g.) determined by the conventional B.E.T. method using nitrogen sorption.[3] An external surface area of 27 m.²/g. for untreated and unfractionated Wyoming bentonite, of the same grade and from the same source as that used in this study, also was cited by Mooney, Keenan, and Wood (10). Therefore, regardless of cation saturation, the figure of 27 m.²/g. was used as the external surface area of the clay in all subsequent calculations made during this study.

Coverage area per glycerol molecule

When calculating surface areas from glycerol retention data it was also necessary, in effect, to assign an area of surface coverage to the individual glycerol molecules. The assignment of such a coverage area for a sorbate molecule is commonly considered to be the least certain step in calculating surface area from adsorption data, whether by the B.E.T. or liquid-state sorption methods. Previously (4), a coverage area of 27 A.² had been assigned to the glycerol molecule; liquid density had been assumed for the glycerol monolayer and a molecular thickness of 4.5 A., as derived by x-ray diffraction, had been employed. A basal spacing leading to this same thickness was subsequently obtained for a monolayer glycerol complex of montmorillonite (11). A lesser monolayer thickness, approximately 4.1 A., has been observed (12) for glycerol-treated specimens of montmorillonite each of which had been saturated with one of a

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[3] This determination was kindly performed by Dr. Paul Seligmann, Portland Cement Association.

series of small amine cations. This thickness is the same as the average thickness of the glycerol molecule in a two-layer glycerol complex and was used by Jackson (13) when he computed a factor for estimating surface areas from retention results for both monolayer and duolayer glycerol complexes. With Jackson's computed factor, a slightly larger coverage area of 29 A.² was calculated for the glycerol molecule.

A scale model of the glycerol molecule was assembled from a Fisher-Taylor-Hirschfelder atom model kit. Measurements of clearance thickness and coverage area were made for various conformations of the molecule, the axis of the carbon chain being maintained in an orientation approximately parallel to the assumed basal clay surface. The molecular coverage areas were measured by placing the model on a sheet of paper, drawing a smoothed outline, and estimating the area of the described figure by cutting and weighing. A number of conformations having clearance thicknesses close to the 4.1 A. and 4.5 A., obtained experimentally, were examined. It was noted that more than one conformation could lead to the same thickness, and that each conformation could have a coverage area differing somewhat from others but with the same thickness. Coverage areas determined with the model generally were in the range of 27 to 31 A.², which indicated the reasonableness of the assigned areas of 27 and 29 A.²

Inasmuch as a unique conformation could not be assigned to a given layer thickness, it was impossible to select a unique measurement of coverage area corresponding to each of the two thicknesses. Therefore, a figure of 27 A.² as the coverage area for a glycerol molecule was employed in this study for surface area computations irrespective of the monolayer thickness. Correspondingly, it was calculated that 1 milligram (mg.) of glycerol in the form of a monolayer occupies 1.76 square meters (m.²) of external surface, and 3.53 m.² of surface area when interleaved between adjacent montmorillonite layers. Similarly, 1 m.² of external surface retains 0.568 mg. of glycerol, and 1 m.² of internal surface retains 0.284 mg. of glycerol.

Glycerol Retention Results in Terms of Interpillar Area

The interpillar areas were determined by use of the glycerol retention results (shown in column 5 of table 1) and the surface coverage factors set forth in the preceding paragraphs. To determine these areas, 15.3 mg. of glycerol per gram of clay, corresponding to the external surface (27 m.²/g. × 0.568 mg./m.² = 15.3 mg./g.), was subtracted from the glycerol determinations and the remainder multiplied by the factor for glycerol on internal surfaces, 3.53 mg. The results for both untreated clay and clay treated with each of the saturating cations are shown in the last column of table 1. Because of the natural impurities in the bentonite, the area of 624 m.²/g. is considered reasonable for the interlayer surface area of the untreated clay, although it is less than the area of from 760 to 800 m.²/g. commonly

ascribed to pure montmorillonite. All these data show that the interlayer area available to glycerol after the formation of amine-cation pillars is substantially less than that of the untreated clay. These areas are approximately 400 m.²/g. for methylamine and dimethylamine saturated clay; 300 m.²/g. for saturations with ethylamine, trimethylamine, and tetramethylamine; 150 to 200 m.²/g. for diethylamine and di-n-propylamine; and less than 50 m.²/g. for the larger tertiary amines and tetraethylamine. For clay saturated with tri-n-butylamine, it is apparent that no remaining interpillar surface is available to glycerol, the retention of 15.7 mg./g. being essentially the same as the 15.3 mg./g. expected for the external surface of the clay.

Some interlayer space apparently still was available for glycerol sorption even when the montmorillonite had been treated with such relatively large cations as triethylamine and tetraethylamine, for which an essentially complete exchange of cations had been accomplished; and with tri-n-proplyamine, for which the exchange had been somewhat less than the full exchange capacity. But, with the tri-n-butylamine, the more limited amine cation population apparently had occupied the interlayer space to such an extent that glycerol molecules were unable to enter.

Interpillar Coverage

An explanation of the interpillar coverage must rest on a realistic consideration of the distribution of cation sites with respect to the planar surface of the clay. Each cation in the monolayer of the amine-saturated clay is bonded to one of the two adjacent clay surfaces and occupies an area equal to its own cross-section on the surface to which it is bonded and at the same time it occupies an equal area on the other clay surface with which it is in contact. From the total surface area of the original clay and the cation exchange capacity (table 1), the average area available per exchange site was calculated as 120 A.²; consequently, half this area, 60 A.², is the cross-section area available per site. Based on two-thirds of a charge per unit cell, the theoretical total and cross-section area available for exchange per unit cell of montmorillonite would be 140 A.² and 70 A.², respectively. Therefore, as a first approximation, the cation positions may be visualized as distributed over the planar surface in the form of a rectangular net with a unit mesh area of 60 A.² in which the nodes, representing the centers of the cation postions, are 7.7 A. apart.

Obviously, for a glycerol molecule to enter an incompletely packed monolayer, such as that described in the preceding paragraph, sufficient room must be available between the individual cations. Examination of an atom model indicates that the smallest width of the glycerol molecule in an interlayer complex is approximately 5 A. Accordingly, if the cations were fixed in rigid positions 7.7 A. apart, a glycerol molecule could enter between them only if the width of the cations was less than 2.7 A. As this critical width is much

smaller than the Van der Waals diameter of a methyl group, saturation of the clay with any of the amine cations used in this study should almost exclude glycerol molecules from the interlayer spaces. But data from this study indicated that with most of the cations used for saturation, substantial numbers of glycerol molecules did enter and were retained in the interlayer spaces of the saturated clay. Thus, considering the distribution of cation positions in the monolayer as being of a fixed, geometrically-regular pattern is clearly inadequate.

If the individual cations were considered to have a degree of mobility sufficient to permit the entrance of some glycerol molecules, the process generally would be more in accord with the experimental results. However, unless the sum of the diameters of the cation and the glycerol molecule happened to be fortuitously close to the distance between cation sites, the resulting, mixed monolayer would still have a considerable unoccupied space, as the lateral adjustment of a cation to widen a channel sufficiently to accommodate a glycerol molecule would correspondingly constrict the opposite channel.

Possibly a more realistic consideration of the cation distribution is that the interlayer cations are located in association with the cavities of the oxygen rings of the silica sheets. Although the sources of charge deficiency in the octahedral or tetrahedral layers are not centered directly below these cavities, it has been demonstrated that small cations tend to enter the cavities when the clay is dried. There are two cavities for each planar face of the montmorillonite unit cell, and the total number for a montmorillonite of a given surface area may readily be calculated. The cation exchange capacity of the experimental montmorillonite suggests that slightly more than one-third of these cavities may have cations associated with them. It may be assumed that, although the arrangement of cavities themselves is highly regular in the silica sheets, the distribution of those that are associated with cations should be completely random. Moreover, because in a packet of unit layers, the stacking with respect to the a and b axes is known to be essentially random, the upper and lower oxygen rings that face on a given interlayer space are not normally superposed. Because of these factors, some of the cation sites must be quite closely spaced and others widely separated.

Accordingly, for saturation with an amine cation of moderate size, those cations occupying the more closely spaced sites might themselves effectively fill the space between the sites, although those on the more widely spaced sites might leave empty channels of much greater width than would be expected on the basis of a uniform spacing of the cations. A continuous distribution of channel widths would thus be expected, ranging from zero to relatively large dimensions. If the cations were fixed in position, some channels would be too narrow to accommodate glycerol molecules; however, if a certain degree of mobility of the cations is permitted to allow for lateral readjustment during sorption of the glycerol,

the resulting mixed, glycerol-amine cation monolayer might be almost completely efficient in occupying the interlayer space. On this basis, the area occupied by the pillars may be calculated as the total interlayer area (62 m.²/g. for clay of this study) minus the area found to be covered by glycerol molecules. Dividing this estimate of pillar area by the number of pillars present would yield a figure for the area occupied by an individual pillar and half of this would represent the cross section area of the pillar. Any vacant area remaining in the mixed monolayer would, on this basis, be erroneously allocated to cation occupation and, if the amount were significant, the cross-section areas determined experimentally in this study would be too high. Comparison of such experimental data with data obtained from atom models should provide a test of whether the vacant channel area is in fact negligible, and thus whether the glycerol retention technique provides an accurate measurement of interpillar surface area.

Calculation

In order to make this calculation for a given amine-treated clay it is necessary to estimate the number of cation pillars that are present. The total number of amine cations is readily calculated from the amine content, but it is necessary to correct for the cations that are present on external surfaces. Grim (14), apparently citing Hendricks, Nelson, and Alexander (15), suggested that about 8 percent of the exchange capacity of montmorillonite is associated with planar surfaces, the remainder being due to broken bond sites on the edges of the crystallites. However, A. Weiss (16) more recently obtained experimental evidence establishing that, for mica, vermiculite, and montmorillonite, cation exchange at near neutral pH values is associated exclusively with planar surfaces. Weiss' conclusion is adopted, the external portion of the cation exchange capacity may then be estimated from the internal and external surface areas by assuming (1) that the distribution of the cation exchange sites is the same for all planar surfaces, whether internal or external, and (2) that as clay crystals are usually much larger in the a and b directions than in the c direction, most of their external surface is of the planar type, and the small proportion of exchange sites attributed to the edges of the crystals may be ignored. As has been indicated, the external surface of the clay used in this study is 27 m.²/g., which is about 4 percent of the total surface. According to these assumptions, the external amine content would also bear this same relationship to the total amine content and, consequently, the internal or interlayer amine content would be about 96 percent of the total amount of amine found.

The interlayer area considered to be occupied by the amine cations was calculated for each of the several amine-treated products on the assumptions given in the preceding paragraph, and the determinations are listed in the second column of table 2. Also listed in table 2 are figures for the total number of cations per gram of clay, the estimated number

of pillars (96 percent of the total), the amount of interlayer area occupied per pillar, and the cross-section area of the pillar. The experimental estimates of cross-section area ranged from 8 A.² for methylamine to 77 A.² for tri-n-butylamine and, as expected, increased more or less regularly with increasing chain length and number of substituent alkyl groups.

Comparison of Estimates

To provide for the proposed comparison of the estimates of interlayer area with corresponding cross-section areas derived from atom models of the cations, a set of the models was assembled from the Fisher-Taylor-Hirschfelder kit. These models are designed to reproduce accurately the essential geometric features of the cations on a scale of 1 centimeter (cm.) to 1 A. Outline tracings of the coverage areas were made on paper, as illustrated for tri-n-propylamine in figure 1. As originally traced, the outlines contained a number of bulges and indentations, as indicated by the dashed line, but it was thought that smoothing and relaxing the outline, as indicated by the solid line, would provide a more realistic measurement. Areas enclosed within the outlines drawn on this basis were estimated by cutting and weighing, and are listed in the last column of table 2. Two types of orientation were used in positioning the models for outlining the coverage areas. For most of the cations, the orientation giving the minimum height was used; that is, with the carbon chain parallel to the planar surface of the clay. However, for the three smallest cations, which were thought to be partially embedded in the oxygen ring cavities, the areas were outlined when the models were oriented with the long axis perpendicular to the planar surface. Outlined areas for the three cations in parallel orientations were substantially higher than those cited in the table, 16 A.² for methylamine and 24 A.² for dimethylamine and ethylamine. Obviously, for these three amines the experimental estimates of cross-section area were in accord with those outlined with a perpendicular rather than a parallel orientation. The matter of perpen-

dicular orientation for these three cations is discussed in greater detail later in this article.

In general, there was a very good agreement between the cation areas derived experimentally and those derived from the models, the maximum deviation being only about 15 percent, except for methylamine. There was no indication that the experimental areas were systematically greater than those from the models, as would be expected if a substantial amount of vacant area were mistakenly ascribed to amine cation coverage because of incomplete penetration by glycerol. This consistently good agreement suggests that, for saturation with each of the amine cations, the amine cations and glycerol molecules occupied substantially all of the interlayer space, and it substantiates the validity of the measurement of interpillar area by glycerol retention. The virtually complete filling of the interpillar space by glycerol also supports the inference that, in general, the amine cations must have a considerable degree of mobility about the exchange sites; otherwise, they could hardly have arrived at such an efficient packing with the glycerol molecules.

Effectiveness of Triethylamine

In a previous study of the glycerol retention of soils and clays, Kinter and Diamond (17) used triethylamine saturation as a pretreatment designed to prevent the entry of glycerol into the interlayer spaces. From this study, however, although a full exchange complement of triethylamine cations was shown to have been adsorbed, the entry of a small amount of glycerol nevertheless appeared to have taken place. The glycerol retained after triethylamine saturation thus was not a strict measure of the external surface of this montmorillonite. In clays of a higher charge density, because of their larger number of exchange sites per unit of surface area, such widely-separated sites are less likely to occur than in the Wyoming bentonite. Therefore, a cation such as triethylamine might be large enough to fill completely the interlayer spaces of a clay with a higher charge density. As, in general, only a very small part of the internal surface


Figure 1.—*Characteristic outline of tri-n-propylamine cation model is represented by dashed line. The relaxed, solid outline was used to measure the cross-section area of the cation.*

of any montmorillonite is likely to be mistakenly classed as external surface by this procedure, the estimation of the amount of internal surface present in a given sample and, consequently, the content of expanding minerals should not be seriously in error.

Amine Content in Excess of Exchange Capacity

The carbon analysis data showed that the smallest amines were adsorbed in amounts well above the cation exchange capacity. This was further confirmed by ignition loss determinations interpreted by the method of McAtee (18). Morel (19), however, has reported the adsorption of methylamine only in amounts equal to or less than the exchange capacity, as did Cowan and White (20) for ethylamine. Grim, Allaway, and Cuthbert (21) and Cowan and White (20) have reported excess adsorption, but only for somewhat larger amines than the three small amines used in this study. Cowan and White (20) considered that the excess amine must be present either as molecules of the free amine or of the amine salt. Finding by analysis that their amine-treated clay did not contain adsorbed anions, they concluded that there had been no adsorption of amine salt molecules and that the excess therefore was present as free amine. Although they did not make pH measurements, they assumed that the adsorption of free amine had caused a lowering of the pH in their clay-amine salt solution mixture, as a consequence of the production of HCl according to the reaction:

$$RNH_3^+ \text{ saturated clay } + RNH_3Cl \rightleftharpoons$$
$$(RNH_3^+ \text{ saturated clay) } (RNH_2) + HCl$$
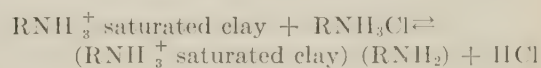
Grim and coworkers (21) found that sorption of excess amounts of dodecylamine from a dodecylamine acetate solution was accompanied by a drop in pH from 7 to 5.6. In this study, pH measurements were made on the mixture of dry clay and 1-normal methylamine hydrochloride solution, but the initial pH of 7 remained essentially unchanged.

Table 2.—**Experimental estimates of cation cross-section areas, and comparison of these areas with areas measured from outline of models**

Cation	A Estimate of interlayer clay surface covered by cation pillars [1]	B Total No. of amine cations per g. of clay ×10^20	C No. of cations assigned to interlayer spaces per g. of clay ×10^20 = B×0.96	D Interlayer clay surface covered per cation pillar = A÷C	Experimental estimate of cross-section area per cation = D÷2	Coverage area per cation from atom model outline
	m.²/g.			A.²	A.²	A.²
Methylamine	193	13.26	12.73	15.2	8	11
Ethylamine	293	8.78	8.43	34.8	17	17
Dimethylamine	230	8.07	7.75	29.7	15	17
Diethylamine	412	5.65	5.42	76.0	38	36
Di-n-propylamine	468	5.10	4.90	95.5	48	47
Trimethylamine	303	5.52	5.30	57.2	29	29
Triethylamine	601	5.57	5.35	112.3	56	48
Tri-n-propylamine	575	4.54	4.36	131.9	66	64
Tri-n-butylamine	623	4.20	4.03	154.6	77	83
Tetramethyl-ammonium	354	5.79	5.56	63.7	32	28
Tetraethyl-ammonium	590	5.36	5.15	114.6	57	50

[1] Original interlayer surface of clay (624 m.²/g.) minus interpillar surface covered by glycerol molecules.

To determine whether the amine content of the methylamine-treated clay, prepared and washed as previously described, was merely an intermediate stage in the process of removal of excess amine by hydrolysis, a newly-prepared methylamine-treated clay was subjected to successive centrifuge washing treatments with the acetone-water wash solution, and a portion of the clay was removed at each stage and analyzed by ignition for methylamine content. The results indicated that (1) 3.0 milliequivalents of amine per gram of clay were present on the treated product prior to washing; (2) after a single washing, the amine content had dropped to 2.1 milliequivalents per gram; and (2) as many as nine additional centrifuge washing treatments had not caused any further significant removal of the amine. Therefore, the amine obviously does not undergo significant hydrolysis on repeated washing; and thus, the washed sample whose carbon analysis is reported in table 1 must have been at equilibrium with respect to the amount of amine present. An x-ray spectrometric analysis of the same material indicated that it was essentially chloride-free. To check the possibility that chloride might initially have been adsorbed during the treatment and subsequently removed by the washing, the methylamine hydrochloride treatment and washing sequences were repeated on a fresh portion of the clay and the supernatant solutions analyzed for chloride. There was no indication of any adsorption of chloride by the clay at any stage.

Nature of adsorbed amine

In attempting to ascertain the nature of the excess adsorbed amine, it seemed reasonable to assume (1) that a complete exchange complement of amine cations was present in the methylamine-treated clay and (2) that amine in excess of this exchange complement could be present in one or more of three forms: additional amine cations, free amine or hydrated amine molecules, or un-dissociated molecules of the amine salt. For the excess to be present as amine cations would require that either an equal number of anions (chloride or hydroxyl) also be adsorbed to preserve the electrical neutrality of the solution or that the neutrality be preserved by a rather unlikely partial decomposition of the clay. As the analysis showed no adsorption of chloride, the excess definitely was not in the form of amine salt. Furthermore, because the pH was not lowered as would have occurred if hydroxyl ions had been adsorbed, it does not seem likely that the excess could have been in the form of cations. The remaining possibility—that the excess was free amine or hydrated amine molecules—also was not supported by the experimental data. If the excess adsorbed amine had been in the form either of free amine or of hydrated amine molecules, the reaction suggested by Cowan and White (20) would have applied, and a marked lowering of pH should have been observed. The specific form of the excess amine therefore remains in doubt.

Although the adsorption of large amounts of long-chain amines and quaternary ammonium compounds on montmorillonite commonly has been attributed to Van der Waals bonding, it would not be expected that the very small amines could be held by such bonding against repeated washing of the clay or drying at 110° C. It would seem, therefore, that the retention of these small amines must involve an additional mechanism. One possible mechanism, as suggested by A. Weiss (16) is that free ammonia or small amine molecules could bond to montmorillonite by replacing water molecules in octahedral coordination around aluminum atoms exposed at the edges of the clay crystallites. Weiss determined experimentally that approximately 0.2 to 0.3 milliequivalent of ammonia per gram of montmorillonite can be held in this way. His mechanism thus does not account for the determination in this study of approximately 1.4 milliequivalents of excess methylamine.

An explanation more in accord with the experimental data of this study is that the adsorbed amine material, consisting of both the complement of cations equivalent to the exchange capacity and the excess amine, might have been partially embedded in the oxygen ring cavities of the clay surface. It is thought that such embedding may have accounted for the ability of the clay to retain the excess amine against the subsequent washing and drying treatments. The embedding would involve orientation of the amine more or less perpendicularly to the clay surface. This embedding and perpendicular orientation is in accord with the results (22) obtained from oscillating-heating x-ray diffraction experiments; in these experiments the methylamine and dimethylamine cations adsorbed by montmorillonite from solutions of moderate concentration were so located and oriented. For the methylamine, this orientation presumably would have either the amine group or the methyl group partially embedded in the cavity, with the remaining group located directly above, and the long axis of the amine would thus be perpendicular to the clay surface. A similar arrangement may be visualized for ethylamine except that, as the carbon-carbon bond of the ethyl group must maintain an approximately 110° angle with the carbon-nitrogen bond, the terminal group of the ethylamine must be offset from the perpendicular axis. For dimethylamine, as the amine group is in the middle of the molecule, one of the terminal methyl groups must be embedded in the cavity, the amine group must be located directly above, and the other methyl group must be offset to maintain the required bond angle.

As previously noted, the experimental cross-section areas given in table 2 strongly support this perpendicular orientation for these three amines. Also, as indicated in part I, x-ray diffraction measurements of the separation between the clay layers in montmorillonite saturated with these three amines were consistent with perpendicular orientation and embedding. Although the long dimensions of the amines as measured from models were from 1.6 to 2.3 A. greater than the observed distances between the clay layers, the 2.4-A.

depth of the cavities (23) is sufficient to permit this perpendicular orientation.

The specific amount of methylamine adsorbed also suggested an association of the amine with the cavities. From the widely-accepted Hofmann-Endell-Wilm structure, it may be calculated that there are approximately 1.6×10^{21} cavities per gram of pure montmorillonite. The analysis given in table 2 for the methylamine-saturated bentonite indicates that the amine content was equivalent to approximately 1.3×10^{21} methylamine cations per gram of clay. The bentonite used was not fractionated or otherwise purified; from the observed interlayer surface of 624 m.^{2}/g. as compared to the theoretical 760 m.^{2}/g. for pure montmorillonite, the bentonite was estimated to contain about 82 percent of montmorillonite. Accordingly, the expected number of cavities per gram of the bentonite would be about 1.3×10^{21}, which is in agreement with the amount of amine indicated to be present by the carbon analysis. It is noted, however, that for dimethylamine and ethylamine the estimates of the total number of amine cations per gram of clay, 0.81×10^{21} and 0.88×10^{21}, were considerably less than this. According to this interpretation, the cavities associated with exchange sites would have been fully occupied by amine cations, and the excess amine would have been sufficient to occupy only slightly more than half of the remaining cavities. In view of the restricted layer separations indicated by x-ray diffraction, even for wet amine-treated clay, the failure of the two-carbon amines to occupy all of the available cavities may have been due to the purely physical difficulty of becoming oriented so as to be able to enter the cavities.

REFERENCES

(1) *Sorption and Intercalation by Methyl Ammonium Montmorillonites*, by R. M. Barrer and J. S. S. Reay, Transactions of the Faraday Society, vol. 53, Part 9, Sept. 1957, pp. 1,253–1,261.

(2) *Activation of Montmorillonite by Ion Exchange and Sorption Complexes of Tetra-Alkyl Ammonium Montmorillonites*, by R. M. Barrer and D. M. MacLeod, Transactions of the Faraday Society, vol. 51, Part 9, Sept. 1955, pp. 1,290–1,300.

(3) *Surface Areas of Clay Minerals as Derived from Measurements of Glycerol Retention*, by Sidney Diamond and E. B. Kinter, in *Proceedings of the Fifth National Conference on Clays and Clay Minerals, 1956, Clays and Clay Minerals*, 1958, National Academy of Science–National Research Council, No. 566, pp. 334–347.

(4) *Gravimetric Determinations of Monolayer Glycerol Complexes of Clay Minerals*, by E. B. Kinter and Sidney Diamond, in *Proceedings of the Fifth National Conference on Clays and Clay Minerals, 1956, Clays and Clay Minerals*, 1958, National Academy of Science–National Research Council, No. 566, pp. 318–333.

(5) *Total Surface of Clays in Polar Liquids as a Characteristic Index*, by R. S. Dyal and

S. B. Hendricks, Soil Science, vol. 69, No. 6, June 1950, pp. 421–432.

(6) *The Swelling of Organophilic Montmorillonites in Liquids,* by R. Greene-Kelly, The Journal of Colloid Science, vol. 11, No. 1, Feb. 1956, pp. 77–79.

(7) *Soil Chemical Analysis, Chapter 4, Cation Exchange Determinations for Soils,* by M. L. Jackson, 1958, p. 64.

(8) *Base Exchange of the Clay Mineral Montmorillonite for Organic Cations and its Dependence upon Adsorption Due to Van der Waals Forces,* by S. B. Hendricks, Journal of Physical Chemistry, vol. 45, No. 1, Jan. 1941, pp. 65–81.

(9) *Organic Cation Exchange Properties of Calcium Montmorillonite,* by W. H. Slabaugh and F. Kupka, The Journal of Physical Chemistry, vol. 62, No. 5, May 1958, pp. 599–601.

(10) *Adsorption of Water Vapor by Montmorillonite: Part I. Heat of Desorption and Application of B.E.T. Theory,* by R. W. Mooney, A. G. Keenan, and L. A. Wood, Journal of the American Chemical Society, vol. 74, No. 6, Mar. 1952, pp. 1,367–1,371.

(11) *The Orientation of Organic Molecules Adsorbed on Clay Mineral Surfaces,* by G. W. Brindley and R. W. Hoffman, a paper presented at the Ninth National Conference on Clays and Clay Minerals, Purdue University, Oct. 1960.

(12) *Characterization of Montmorillonite Saturated with Short-Chain Amine Cations: Part I, Interpretation of Basal Spacing Measurements,* by Sidney Diamond and E. B. Kinter, a paper presented at the Tenth National Conference on Clays and Clay Minerals, University of Texas, Oct. 1961.

(13) *Soil Chemical Analysis —Advanced Course,* by M. L. Jackson, 1956, p. 336.

(14) *Clay Mineralogy,* by R. E. Grim, 1953, p. 384.

(15) *Hydration Mechanism of the Clay Mineral Montmorillonite Saturated with Various Cations,* by S. B. Hendricks, R. A. Nelson, and L. T. Alexander, Journal of the American Chemical Society, vol. 62, No. 6, June 1940, pp. 1,457–1,464.

(16) *Überdas Kationenaustauschvermögen der Tonminerale: Part II, Der Kationenaustausch bei den Mineralen der Glimmer-, Vermikulit-, und Montmorillonitgruppe,* by Armin Weiss, Zeitschrift für Anorganische und Allegemeine Chemie, vol. 297, No. 5–6, Dec. 1958, pp. 257–286.

(17) *Pretreatment of Soils and Clays for Measuring External Surface Area by Glycerol Retention,* by E. B. Kinter and Sidney Diamond, in *Clays and Clay Minerals, Proceedings of the Seventh National Conference on Clays and Clay Minerals, 1958,* vol. 5, Pergamon Press, 1960, pp. 125–134.

(18) *Inorganic-Organic Cation Exchange on Montmorillonite,* by J. L. McAtee, Jr., The American Mineralogist, vol. 44, Nos. 11 and 12, Nov.–Dec. 1959, pp. 1,230–1,236.

(19) *Observations sur la Capacité d'Echange et les Phénomènes d'Echange dans les Argiles,* by R. Morel, Bulletin du Groupe Français des Argiles, Tome X, Novelle Série No. 5, 1958, pp. 3–7.

(20) *The Mechanism of Exchange Reactions Occurring between Sodium Montmorillonite and Various n-Primary Aliphatic Amine Salts,* by C. T. Cowan and D. White, Transactions of the Faraday Society, vol. 54, Part 5, May 1958, pp. 691–697.

(21) *Reaction of Different Clay Minerals with Some Organic Cations,* by R. E. Grim, W. H. Allaway, and F. L. Cuthbert, The Journal of the American Ceramic Society, vol. 30, No. 5, May 1947, pp. 137–145.

(22) *Bentonite-Methyl Amine Complexes,* by R. A. Rowland and E. J. Weiss, a paper presented at the Ninth National Conference on Clays and Clay Minerals, Purdue University, Oct. 1960.

(23) *Sorption by Ammonium and Cesium Montmorillonites, and Ion Fixation,* by R. M. Barrer, and J. S. S. Reay, Journal of the Chemical Society, Part IV, 1958, pp. 3,824–2,830.

Materials and Construction
AASHO Road Test Film

A 16-mm. color film on the AASHO Road Test has been released by the Bureau of Public Roads. The 27-minute film, entitled *Materials and Construction,* describes the engineering characteristics of materials, the construction methods, and the quality control measures employed in building the facilities for the Ottawa, Ill., research project.

The AASHO Road Test comprised a huge outdoor research laboratory provided to study the behavior of pavements of varied composition and thickness and bridges of varied design under the application of controlled weights and frequencies of traffic. Extensive efforts were made to construct highly uniform facilities for the Road Test in order to relate performance of the pavements directly to design and loading. The film illustrates the several unusual construction methods employed and includes numerous animated graphs and charts showing materials' characteristics and the results of quality control testing.

The film was produced by Public Roads in cooperation with the Highway Research Board, which administered and directed the project for the sponsor, the American Association of State Highway Officials. The project was financed by the States, Public Roads, and industry with the cooperation of the Department of Defense. Public Roads photographers made a complete motion picture and still photo record of the Road Test from the beginning of construction in 1956 until the end of post-traffic testing in 1961. The present film covers the 1956–1958 period.

A second film, *Pavement Research,* is in production. This film will describe the tests made on the rigid and flexible-type pavements, the rationale for analysis of data, and the principal test results. Finished prints of this second film will be available early in the fall.

Prints of the film on *Materials and Construction* are available on a loan basis from the Bureau of Public Roads, Photographic Section, 1717 H Street NW., Washington 25, D.C. These prints may be borrowed by any responsible organization. There is no charge other than for express or postage fees. Requests should be submitted well in advance of the desired showing date, and alternate dates should be indicated, if possible. Immediate return is required. Inquiries about purchase of the film should be addressed to the Public Roads Photographic Section.

Resistance of Concrete Surfaces to Scaling by De-Icing Agents

BY THE DIVISION OF PHYSICAL RESEARCH
BUREAU OF PUBLIC ROADS

Reported[1] by WILLIAM E. GRIEB,
GEORGE WERNER, and DONALD O.
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This article presents the results of the continuation of tests made by the Bureau of Public Roads as part of its investigation of materials and procedures for protecting concrete pavements against the scaling and disintegration caused by the use of calcium chloride as a thawing agent for ice removal. Data are presented on the continuation of outdoor tests in which concrete slabs that previously had been exposed for two winters, 51 cycles of freezing and thawing, were continued for three additional winters through 154 cycles of freezing and thawing. For convenience, data reported in previous articles on the results of the first two winters of testing have been repeated in tables included in this article.

Data are also presented from an investigation made of the effect that protective coatings or admixtures might have on the control or prevention of scaling of the concrete caused by de-icing agents.

Introduction

AN ARTICLE on resistance of portland cement concrete to surface scaling by a de-icing agent (1)[2] appeared in a previous issue of this magazine, in which the results were reported on tests of small concrete slabs subjected to outdoor weathering. At the time of the previous article, the specimens had been exposed for two winters and subjected to 51 cycles of freezing followed by thawing by calcium chloride. Subsequently, exposure of some of the specimens was continued for three more winters; the slabs were subjected to a total of 154 cycles of freezing and thawing before the tests were discontinued. As the study continued, additional tests were made on similar specimens to study: (1) the effect of various protective coatings on the top surface of the concrete, and (2) the effect of admixtures in the concrete for the control or prevention of scaling.

Conclusions

Effect of air-entraining admixtures.—All of the air-entraining admixtures used were effective to different degrees in delaying the start of significant scaling. The salts of proteinaceous materials, and some of the synthetic detergents and some of the salts of wood resin, were less effective than the other air-entraining agents.

Effect of type of base.—The scaling of concrete was less pronounced when the concrete was cast in a mold with a sand base than when cast in a mold with a watertight metal base. No significant scaling was shown by air-entrained concrete cast on a sand base if the air content was more than 3 percent. Significant scaling was found on some air-entrained concrete cast on metal bases with air contents as high as 7.4 percent. For concrete containing 7.5 percent or more of air, no significant scaling developed regardless of type of base of mold. These findings are interpreted to mean that, if concrete containing the usual specified amount of air (3 to 6 percent) is placed on a waterproof base, scaling may develop if de-icing chemicals are used.

Effect of portland cement.—Concrete prepared with a low-alkali portland cement was more resistant to scaling than concrete prepared with a high-alkali cement.

Effect of slag cement.—No appreciable difference was found regarding resistance to scaling of concrete prepared with portland cement or portland blast-furnace slag cement from the same mill.

Effect of fly ash.—Concrete prepared with $5\frac{1}{4}$ bags of portland cement and $1\frac{1}{4}$ bags of low-carbon fly ash per cubic yard was equal in resistance to scaling to the concrete containing 6 bags of cement and no fly ash; and it was superior to concrete containing 4 bags of cement and 2 bags of fly ash. Fly ash of a high carbon content generally was inferior to low-carbon fly ash for use in concrete.

Effect of type of curing.—Concrete given no moist curing other than storage in room air at 50 percent relative humidity had better resistance to scaling than concrete given moist curing for 3 to 28 days. Membrane curing gave some protection against attack by calcium chloride as long as the film remained unbroken. Other types of curing materials applied shortly after the concrete was cast were of some benefit in delaying the development of scaling.

Effect of vacuum treatment.—Concrete subjected to a vacuum treatment on the exposed surface was more resistant to scaling than similar but untreated concrete.

Effect of surface treatments.—Protective surface treatments, usually applied 14 to 28 days after the concrete was cast, in general delayed but did not prevent the development of scaling.

Effect of silicone admixture.—An aqueous silicone solution used in proper amount as an admixture for concrete was effective in preventing scaling. The silicone admixture also increased the compressive strength of the concrete and caused a marked retardation of the setting time.

Effect of latex emulsion admixture.—An emulsion of polystyrene latex used as an admixture for concrete was effective in preventing scaling but the concrete so prepared contained 10 percent or more of air.

De-icing agents.—Of the several de-icing agents tested, calcium chloride was found to be the most effective and to cause less scaling of concrete.

Preventive measures.—In addition to the materials or treatments mentioned favorably in preceding paragraphs, scaling of concrete can be prevented or reduced by the elimination of waterproof coatings or sheetings on the subgrade, by the reduction of the water-cement ratio, and by permitting the concrete to dry before it is first frozen. For concrete placed shortly before freezing is anticipated, wet curing of the concrete should be minimized.

Description of Tests

A general description of the outdoor exposure test is, as follows:

● The slabs were 16 by 24 by 4 inches in depth with a raised edge or dam around the perimeter of the top surface. Except where noted, the slabs were cast in watertight molds with metal bases. The top surface of each was given a light broomed finish about $2\frac{1}{2}$ to

Figure 1.—Exposure area.

ours after molding and just prior to the application of the initial curing, if such was applied. Except when other methods of initial curing are noted, the slabs were covered with wet burlap for 24 hours and were moist cured for 2 or more days. The slabs were placed in the outdoor exposure area usually at an age of 28 or more days. Sometimes freezing and thawing was started immediately after exposure and sometimes it was started as much as 6 months later.

● The materials used were type I or IS cements, siliceous sands having a fineness modulus of 2.70 to 2.90, and a crushed limestone of 1 inch maximum size. The concrete was mixed and the slabs cast in accordance with standard laboratory procedures. The slump was 3 inches, plus or minus one-half inch, and, except where noted, the cement content was 6 bags per cubic yard. Both air-entrained and non-air-entrained concretes were included in these tests. The air content for air-entrained concrete was usually 5½ percent, plus or minus 1 percent.

● During cold weather when freezing was expected, the top surface of each slab was covered with one-fourth to one-half of an inch of water. The next morning after the water had frozen, commercial calcium chloride flakes were applied uniformly at a rate of 2.4 pounds per square yard of surface. After the ice had melted, usually about 3 or 4 hours later, the surface of the slabs was flushed with water from a hose to remove the chloride solution and to leave fresh water for the next freezing. Only one cycle of freezing and thawing was obtained each day. A view of the exposure area is shown in figure 1.

● The slabs were examined at intervals and rated for surface scaling. The ratings were based on visual observations of the extent and depth of the scaling. The slabs were washed thoroughly and loose mortar removed from the surface prior to rating. A general description of the numerical ratings is as follows:

0—no scale.

1—scattered spots of very light scale.

2—scattered spots of light scale with mortar surface above coarse aggregate removed.

3—light scale over about one-half of the surface.

4—light scale over most of the surface.

5—light scale over most of the surface, with a few moderately deep spots, where the mortar surface was below the upper surface of the coarse aggregate.

6—scattered spots of moderately deep scale.

7—moderately deep scale over one-half of the surface.

8—moderately deep scaling over entire surface.

9—scattered spots of deep scale with the mortar surface well below the upper surface of the coarse aggregate; otherwise moderately deep scaling.

10—deep scale over entire surface.

A rating of 5 or more would indicate significant or major scaling. The ratings given the slabs were based on the judgment of different observers at the various times that the observations were made, which accounts for occasional slight reversals. Typical examples of slabs with ratings of 2, 5, 7, and 10 are shown in figure 2.

RESULTS OF CONTINUATION OF PREVIOUSLY REPORTED TESTS

The outdoor exposure tests that were previously reported (1) through 51 cycles of freezing, followed by thawing with calcium chloride, were continued through 154 cycles. The results of these tests are given in tables 1 to 5 inclusive and continue the presentation of
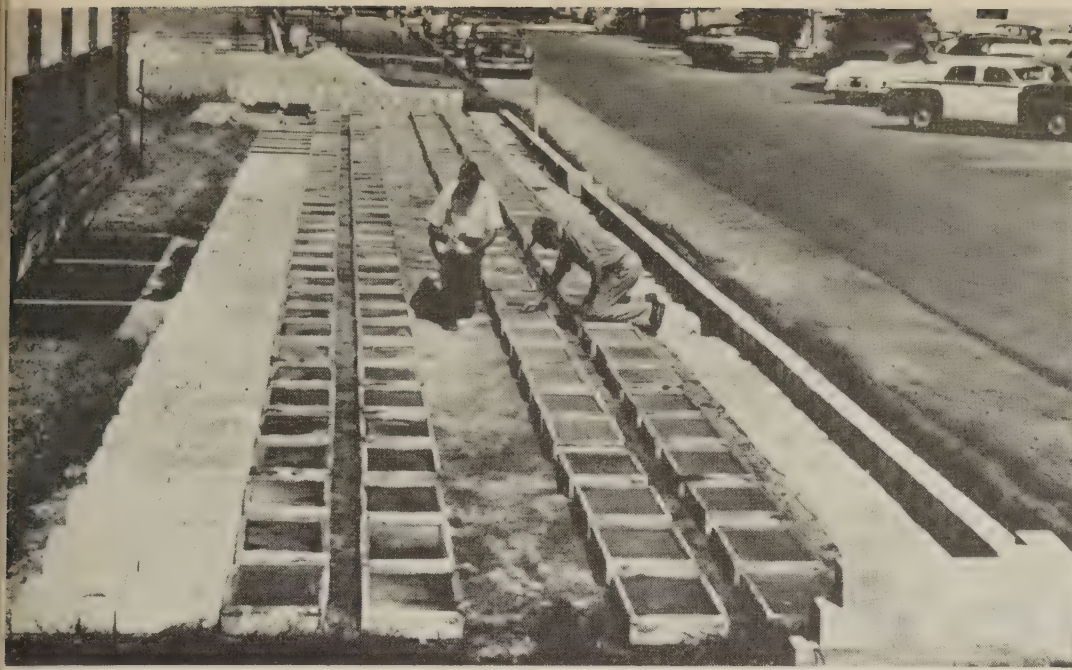
data reported in tables 16, 17, 19, 20, and 21 of the previous article. In addition, ratings are given here for 79, 131, and 154 cycles. At the end of each winter, many of the specimens that showed significant scaling, considered to be a rating of 5 or more, were discarded to make room for additional specimens.

Air-Entraining Admixtures

The effects of air-entraining admixtures on the resistance of concrete to scaling are shown in tables 1 and 2. All of the non-air-entrained slabs had severe scaling at 17 cycles and were given a rating of 10 (deep scaling over entire surface) by 39 cycles. With some exceptions, the slabs with the air-entraining admixtures had excellent resistance to the action of calcium chloride. Poor resistance to scaling was shown by the slabs cast on metal bases that had been prepared with the admixtures classified as salts of proteinaceous materials, some of those classified as salts of wood resin, and some classified as synthetic detergents. No tests were made to determine the relative size and number of entrained air voids caused by the various types of air-entraining admixtures. Large voids might explain the poor resistance that was shown by some of these concretes.

Table 1 gives the results for slabs cast on metal bases, and table 2 gives the results for slabs cast on sand bases. A comparison of the data given in tables 1 and 2 shows that, generally, the action of calcium chloride was less severe on air-entrained concrete cast on sand bases than on similar concrete cast

RATING 2

RATING 5

RATING 7

RATING 10

Figure 2.—Examples of typical ratings used to evaluate surface scaling of specimens subjected to outdoor freezing and thawing by calcium chloride.

on watertight metal bases. Sixteen of the 55 slabs cast on a metal base had significant scaling. Only one of the 16 slabs cast on a sand base had similar scaling, but the concrete of this slab contained only 2.6 percent of air.

Half of the specimens, as shown in tables 1 and 2, were prepared with cement A, and the other half were prepared with cement B. A comparison of the results indicates that the air-entrained slabs with cement B in general were not as severely attacked as those containing cement A. Nearly the same number of slabs prepared with each

cement showed significant scaling. Of the air-entrained specimens that showed significant scaling, those prepared with cement A had air contents of 5.5 to 7.4 percent, and those prepared with cement B had air contents of 2.6 to 6.0 percent. The lower air contents for slabs with cement B tended to mask the effect of this cement on the concrete's resistance to scaling. The data indicate that, for equal air content, slabs prepared with cement B had better resistance to scaling than those prepared with cement A. One significant difference between the cements was the alkali content. Cement A had a

high alkali content of 1.09 percent, expressed as sodium oxide, and cement B had an alkali content of only 0.14 percent. The chemical analyses of these two cements are given in table 1 of reference 1. These slabs of air-entrained concrete had very little additional scaling after 51 cycles. Only once was the increase in numerical rating more than two for specimens carried through 154 cycles.

Use of Fly Ash

The effect of fly ash, as a replacement for part of the cement, on the resistance of con

Table 1.—Effect of air-entraining admixtures on resistance of concrete to scaling for slabs cast on metal bases [1]

Admixture number [3]	Cement A								Cement B							
	Air, per-cent	Rating after freezing and thawing [2] for cycles—							Air, per-cent	Rating after freezing and thawing [2] for cycles—						
		12	17	39	51	79	131	154		12	17	39	51	79	131	154
BASE MIX: NO AIR-ENTRAINING ADMIXTURE																
None	1.8	6	10	10	10	out	------	------	1.0	4	8	10	10	out	------	-----
Do	2.1	1	5	10	10	out	------	------	2.1	8	10	10	10	out	------	-----
Do	1.8	8	10	10	10	out	------	------	1.1	8	10	10	10	out	------	-----
Do	1.9	6	10	10	10	out	------	------	1.1	8	10	10	10	out	------	-----
Do	1.0	8	10	10	10	out	------	------	0.6	3	10	10	10	out	------	-----
SALTS OF WOOD RESIN																
1	6.1	1	1	1	2	2	2	2	5.7	0	1	1	1	3	3	3
2	7.3	1	1	3	6	out	------	------	5.7	1	1	2	3	4	4	5
3	6.0	1	1	2	2	3	3	3	6.5	1	1	2	2	2	2	2
4	6.1	1	3	6	7	out	------	------	6.0	1	1	2	3	4	5	5
6	4.9	1	1	1	2	3	3	3	6.6	1	1	2	2	3	3	3
7	6.3	1	1	1	1	3	3	4	5.1	1	1	2	3	3	3	3
30	5.7	1	1	1	1	2	2	2	7.8	2	2	2	2	3	3	3
31	4.0	1	2	2	3	4	4	4	5.6	1	2	2	3	4	3	4
32	6.4	0	1	1	1	2	2	2	6.4	1	1	1	2	3	3	3
SYNTHETIC DETERGENTS																
12	6.7	1	2	2	4	4	4	5	5.6	0	1	1	2	2	3	3
14	5.4	1	1	2	3	3	4	4	4.6	1	2	2	2	2	3	3
17	6.3	0	1	3	5	out	------	------	4.8	1	5	7	8	7	7	7
26	8.4	0	1	1	1	2	2	2	4.9	1	1	1	1	2	2	2
26	5.6	1	1	7	9	out	------	------	------	------	------	------	------	------	------	-----
SALTS OF SULFONATED LIGNIN																
18	7.0	1	1	1	2	2	2	2	5.5	1	1	1	1	2	2	2
19	3.7	1	1	1	2	3	3	3	2.8	2	4	5	7	7	out	-----
21	5.1	1	1	1	2	2	3	2	5.5	0	1	2	2	2	3	2
SALTS OF PETROLEUM ACIDS																
11	7.4	0	1	2	4	4	6	6	6.7	1	1	1	1	3	3	2
27	6.5	1	1	1	1	2	2	2	4.1	1	1	1	3	4	5	5
27	------	------	------	------	------	------	------	------	5.1	1	1	2	2	3	3	3
SALTS OF PROTEINACEOUS MATERIALS																
24	5.5	1	1	4	9	out	------	------	4.3	1	2	4	8	out	------	-----
25	6.3	0	1	3	6	out	------	------	4.1	1	1	2	6	out	------	-----
FATTY AND RESINOUS ACIDS AND THEIR SALTS																
8	7.6	0	1	1	3	3	3	3	8.4	1	1	1	1	2	2	2
8	------	------	------	------	------	------	------	------	4.3	1	1	1	5	6	6	7
9	6.8	1	1	1	2	2	2	2	5.6	1	1	2	2	3	2	2
10	6.7	0	1	1	2	2	2	2	5.5	1	1	1	2	2	2	2
ORGANIC SALTS OF SULFONATED HYDROCARBONS																
23	7.5	1	1	1	2	2	2	2	5.6	1	1	1	3	4	4	4
MISCELLANEOUS																
33	5.7	1	1	1	2	3	3	2	4.5	1	2	2	2	2	3	3
34	5.7	1	1	1	2	3	4	3	6.9	1	1	1	1	3	3	3

[1] Continuation of tests reported in table 16 of reference 1. Slabs were made from February to June 1952, were stored in moist air for 30 to 120 days, and all slabs were stored in exposure area in July. The slabs were 6 months or more old when freezing and thawing started.
[2] Each rating represents one slab.
[3] Numbers 1 through 27 correspond to those given in reference 4.

Admixture number [3]	Cement A									Cement B							
	Air, per-cent	Rating after freezing and thawing [2] for cycles—								Air, per-cent	Rating after freezing and thawing [2] for cycles—						
		12	17	39	51	79	131	154			12	17	39	51	79	131	154
BASE MIX: NO AIR-ENTRAINING ADMIXTURE																	
None	1.1	1	8	10	10	out				0.6	4	8	10	10	out		
SALTS OF WOOD RESIN																	
2	5.0	1	2	2	2	3	3	3		6.0	1	1	1	2	3	3	2
SYNTHETIC DETERGENTS																	
12	3.7	1	2	2	2	3	3	3		4.5	1	1	1	2	3	3	3
15	6.7	1	2	2	2	3	3	3		4.8	1	1	1	1	3	3	3
SALTS OF SULFONATED LIGNIN																	
19	3.5	1	1	2	2	3	3	2		2.6	1	1	2	3	5	5	5
SALTS OF PETROLEUM ACIDS																	
27	4.3	1	2	2	3	4	4	4		4.3	1	1	1	2	3	3	2
SALTS OF PROTEINACEOUS MATERIALS																	
24	4.5	1	2	2	3	4	4	4		3.7	1	1	2	2	3	3	2
FATTY AND RESINOUS ACIDS AND THEIR SALTS																	
10	4.3	1	2	2	2	3	3	3		4.2	1	2	2	2	3	3	3
ORGANIC SALTS OF SULFONATED HYDROCARBONS																	
23	5.3	1	2	2	3	3	3	3		6.1	1	1	1	1	3	3	3

[1] Continuation of tests reported in table 17 of reference 1. Slabs were made in June 1952, were stored in moist air for 30 days, then were stored in exposure area. Slabs were more than 6 months old when freezing and thawing started.
[2] Each rating represents one slab.
[3] Numbers correspond to those given in reference 4.

crete to scaling is shown by data in table 3. Four different fly ashes were used in these tests; each fly ash was used as a replacement for 33⅓ percent of the cement in a 6-bag mix for both air-entrained and non-air-entrained concrete. Fly ashes A and B had carbon contents of 0.2 and 0.6 percent, respectively; fly ash X had a carbon content of 5.0 percent, and fly ash Y had a high carbon content of 12.2 percent.

All of the slabs prepared with non-air-entrained concrete had poor resistance to attack by calcium chloride, regardless of whether fly ash was used as a replacement for part of the cement. All showed moderately deep scaling over the entire surface, with a rating of 8, after only 17 cycles of freezing and thawing. The use of air-entrainment increased the resistance of the concrete to scaling but the addition of fly ash to the mix did not prove beneficial. Better results were obtained with the fly ashes A and B, which had low carbon contents, than with those having a higher carbon content.

Type of Curing

Table 4 gives the ratings of concrete slabs cured by different methods. Two rounds of slabs of non-air-entrained concrete and one round of slabs of air-entrained concrete were cast outdoors on different days. Considerable difference in the resistance to scaling was observed between the two rounds of non-air-entrained concrete. All of the slabs in round one showed better resistance than those of round two. This difference might have been caused partly by the daily differences in atmospheric conditions such as relative humidity, temperature, wind velocity, and sunshine. Because of the poorer resistance of round two of the non-air-entrained concrete, differences in the resistance to scaling caused by curing were more apparent. Therefore,

Table 3.—Effect of fly ash on resistance of concrete to scaling for slabs cast on metal bases [1].

Cement	Fly ash [3]	Air, [4] percent	Rating after freezing and thawing [2] for cycles—						
			12	17	39	51	79	131	154
A	None	1.0	5	8	10	10	out		
	A	1.0	6	8	10	10	out		
	B	1.0	6	8	10	10	out		
	X	1.0	7	8	10	10	out		
	Y	1.0	6	8	10	10	out		
A	None	4.0	1	2	2	3	4	6	6
	A	4.6	2	3	3	4	5	5	6
	B	5.4	3	4	4	4	5	out	
	X	4.9	4	6	7	7	8	out	
	Y	4.3	4	6	6	7	8	out	
B	None	1.0	3	8	10	10	out		
	A	1.0	4	8	9	10	out		
	B	1.0	4	8	10	10	out		
	X	1.0	6	8	10	10	out		
	Y	1.0	5	8	10	10	out		
B	None	6.8	1	2	2	2	3	4	3
	A	4.0	1	2	4	4	5	5	6
	B	3.3	5	6	7	7	out		
	X	3.9	6	8	8	8	out		
	Y	5.8	6	8	8	8	out		

[1] Continuation of tests reported in table 19 of reference 1. Slabs were made in June 1952, were stored in moist air for 30 days, then were stored in exposure area. Slabs were more than 5 months old when freezing and thawing started.
[2] Each rating represents one slab.
[3] When fly ash was used, 33⅓ percent of the cement was replaced by an equal volume of fly ash.
[4] Air content in non-air-entrained concrete was calculated.

Table 1.—Effect of curing on resistance of concrete to scaling [1]

Type base	Initial curing [3]	Surface treatment [4]	Admixture	Rating after freezing and thawing [2] for cycles—						
				12	17	39	51	79	131	154
NON-AIR-ENTRAINED CONCRETE [5]—ROUND 1										
Metal	None	None	None	1	1	1	1	3	3	3
Sand	do	do	do	0	1	1	1	2	2	2
Do	Burlap	do	do	0	1	1	1	3	3	3
Do	do	Lubricating oil	do	0	1	1	1	3	3	3
Do	do	None	Lubricating oil	0	1	1	1	3	3	3
Do	Paper	do	None	0	1	1	1	3	3	3
Do	Membrane A	do	do	1	1	1	1	3	3	3
Do	Membrane B	do	do	1	1	1	1	3	3	4
Do	Lubricating oil	do	Lubricating oil	0	1	2	2	4	4	5
NON-AIR-ENTRAINED CONCRETE [5]—ROUND 2										
Metal	None	None	None	1	2	4	6	out		
Sand	do	do	do	1	2	2	3	4	7	9
Do	Burlap	do	do	1	3	3	4	7	10	out
Do	do	Lubricating oil	do	0	1	1	1	3	6	8
Do	do	None	Lubricating oil	1	1	2	2	4	4	5
Do	Paper	do	None	1	2	4	9	out		
Do	do	Lubricating oil	do	0	1	3	5	8	10	out
Do	Membrane A	None	do	0	1	1	4	8	10	out
Do	Membrane B	do	do	0	1	1	2	3	4	9
Do	Lubricating oil	do	Lubricating oil	1	1	1	5	4	3	4
Do	Lubricating oil	do	do	0	1	2	3	4	3	3
AIR-ENTRAINED CONCRETE [6]										
Metal	None	None	Vinsol resin	0	1	1	2	4	3	3
Sand	do	do	do	0	1	1	1	3	3	3
Do	Burlap	do	do	1	2	2	2	4	4	4
Do	do	do	Used crankcase oil	0	1	1	1	3	3	4
Do	Paper	do	Vinsol resin	0	1	1	1	3	3	3
Do	Membrane A	do	do	0	1	1	2	3	3	3
Do	Membrane B	do	do	0	1	2	2	3	3	4
Do	Used crankcase oil	do	Used crankcase oil	0	2	2	2	3	3	4

[1] Continuation of tests reported in table 20 of reference 1. All slabs were made outdoors in July 1952, were removed from molds after 3 days, and then were stored in exposure area. Slabs were more than 4 months old when freezing and thawing started.
[2] Each rating represents one slab.
[3] Curing was applied 1½ hours after casting. Sheet materials or burlap were removed after 3 days.
[4] Surface protective treatment was applied after 28 days.
[5] Air content of non-air-entrained concrete was approximately 2 percent.
[6] Air content of air-entrained concrete was approximately 4½ percent.

this discussion is limited to the results obtained for round two and to the air-entrained concrete.

The tests for round two on non-air-entrained concrete without curing showed that the slabs cast on sand bases had better resistance to scaling than the slabs cast on metal bases. The slabs on which paper was used for curing had the poorest resistance. The slabs on which lubricating oil was used, both for curing and as an admixture for the concrete, were the most resistant to scaling of any of the other slabs cast for round two. These protective surface treatments delayed the scaling of the concrete only slightly; this was indicated by the large differences in the numerical ratings at 51 and 154 cycles. Membrane curing materials also delayed the scaling only slightly.

No significant scaling occurred on any of the air-entrained concrete slabs. Therefore, it was not possible to distinguish between the relative effects of any of the curing methods or air-entraining agents used. The amount of entrained air, and not the means of obtaining it, appears to be the factor governing the attainment of durability.

Vacuum Treatment

Comparisons between slabs that were finished in the usual manner and those to which the vacuum process was applied are given in table 5. Non-air-entrained concrete slabs were cast in molds with metal bases and in molds with damp sand bases. The air-entrained slabs were all cast in molds with sand bases. One-half of the slabs were finished in the usual manner and the other half were given the vacuum treatment. The slabs given the vacuum treatment were struck off in the usual manner and then the entire surface of the slab was covered with a vacuum pad. A vacuum of 18 to 25 inches of mercury was applied to the plastic concrete for about 30 minutes. All slabs were then moist cured with wet burlap for 3 days. The non-air-entrained concrete slabs cast on sand bases and vacuum treated had better resistance to scaling than those that were cast on metal bases and vacuum treated. The application of the vacuum process to the non-air-entrained concrete was beneficial in reducing the amount of scaling.

The air content of the air-entrained concretes varied from 2.6 to 10 percent. Only the slab with the lowest air content of 2.6 percent and placed by the conventional method had poor resistance to scaling. All of the air-entrained concrete slabs that were subjected to the vacuum process had equal or greater resistance to scaling than the corresponding slabs that had been placed by the conventional method.

Summary of Previous Tests

In general, the increases noted in scaling between the 51 cycles and the 154 cycles of freezing and thawing, at which point the tests were terminated, were not great enough to cause any material change in the previous conclusions (1). These continued tests indicated that 50 cycles of freezing and thawing—exposure for two average winters in a climate similar to that of Washington, D.C.—usually would be sufficient to indicate the resistance of concrete test specimens to scaling caused by the use of calcium chloride.

NEW OUTDOOR TESTS

Portland Blast-Furnace Slag Cement

A comparison was made between concrete prepared with portland cement and concrete prepared with portland blast-furnace slag cement (2). In these resistance to scaling tests, ten cements were used: a type I por-

Table 5.—Effect of vacuum surface treatment on resistance of plain or air-entrained concrete to scaling [1]

Air, percent	Type base	Surface treatment [3]	Rating after freezing and thawing [2] for cycles—						
			12	17	39	51	79	131	154
1.0	Metal	None	1	1	8	10	out		
1.0	do	do	1	4	10	10	out		
1.0	do	Vacuum	1	2	4	6	7	7	out
1.0	do	do	1	4	7	10	out		
1.0	Sand	None	1	1	9	10	out		
1.0	do	do	1	4	10	10	out		
1.0	do	Vacuum	1	1	2	4	5	8	out
1.0	do	do	0	1	2	3	4	4	3
2.6	do	None	1	1	2	4	4	5	out
2.6	do	Vacuum	0	1	2	2	3	3	3
3.2	do	None	1	1	2	2	3	3	3
3.2	do	Vacuum	0	1	1	1	2	2	2
5.2	do	None	0	1	2	2	2	2	2
5.2	do	Vacuum	0	1	1	1	2	2	1
6.1	do	None	1	1	2	2	3	3	3
6.1	do	Vacuum	0	1	1	1	1	1	0
7.0	do	None	1	1	3	3	4	3	3
7.0	do	Vacuum	0	1	1	2	3	4	3
10.0	do	None	0	1	1	1	3	3	3
10.0	do	Vacuum	0	0	0	0	1	1	1

[1] Continuation of tests reported in table 21 of reference 1. All slabs were made outdoors in September 1952, were cured with wet burlap for 3 days, and were then removed from molds and stored in the exposure area. Slabs were more than ... months old when freezing and thawing started.
[2] Each rating represents one slab.
[3] Vacuum was applied to top surface of plastic concrete for one-half of an hour immediately after the molding.

land and a type IS portland blast-furnace slag cement from each of five mills. Portland blast-furnace slag cement is defined as an intimately interground mixture of portland cement clinker and granular blast-furnace slag. The same clinker was used in the manufacture of the two types of cement from the same plant. Concrete slabs were made with mixes containing 5½, 6½, and 7½ gallons of water per bag of cement. The corresponding cement contents were approximately 6.0, 5.0 and 4.2 bags per cubic yard of concrete, respectively. The air content of this concrete varied from 4.3 to 6.1 percent. These concrete slabs were moist cured for 28 days and then were stored in the exposure area from 2 to about 40 days before freezing occurred. They were exposed to freezing and thawing through two winters, for a total of 55 cycles. The ratings of the slabs after 20, 35, and 55 cycles are shown in table 6. Each rating shown is an average of the ratings for two slabs. This table also shows the equivalent alkali content of the cements and the amount of slag used in the manufacture of the slag cement.

When the water content of the concrete was 6½ or 7½ gallons per bag, severe scaling was observed on all slabs by the end of 35 cycles of freezing. The concretes prepared with 6½ gallons of water were more resistant to scaling than those with the greater water content, but these differences in scaling were insignificant. The air content of all these concretes was more than 4.3 percent. From results of these tests, it appears that, even with air-entrained concrete, the water content of the concrete prepared with types I and IS cement is of primary importance in its resistance to scaling caused by the action of de-icing agents.

For the concretes containing 5½ gallons of water per bag of cement, considerable differences were noted between the resistance of the concretes prepared with both types of the cements from different sources. The concretes prepared with each of the two types of cement from sources A and B (all four with low alkali content) had very good resistance to scaling—much better than the concretes containing cement from the other three sources. Concretes containing the cements from sources C and E had the poorest resistance to scaling (three of these four cements had a high alkali content). This general trend indicated that cement with a low alkali content will furnish concrete with better resistance to scaling than cement with a high alkali content. However, concretes containing the two types of cement from source D did not conform to this trend; no reason was apparent for the relatively poor resistance to scaling of the concrete prepared with the cement from source D, which had a low alkali content.

From these tests very little difference was shown in the resistance to scaling of the concretes prepared with a portland cement and those prepared with the portland blast-furnace slag cement from the same source. Averages for all 10 cements, which reflect the influence of the water-cement ratio on the severity of

Table 6.—Effect of portland blast-furnace slag cement on resistance of concrete to scaling [1]

Cement				Rating after freezing and thawing [2]								
				5½ gallon mix			6½ gallon mix			7½ gallon mix		
Source	Type	Slag [3]	Alkali [4]	20 cycles	35 cycles	55 cycles	20 cycles	35 cycles	55 cycles	20 cycles	35 cycles	55 cycles
		Percent	Percent									
A	I		0.32	0	0	1	4	7	9	7	8	10
A	IS	45	.37	0	1	1	4	7	9	4	9	9
B	I		.19	1	2	2	4	7	9	6	8	9
B	IS	45	.22	1	2	2	4	9	9	6	9	10
C	I		.32	2	3	8	4	6	6	8	9	10
C	IS	25	.61	2	6	7	6	9	9	6	9	10
D	I		.21	1	2	4	8	9	10	9	9	10
D	IS	40	.22	4	6	7	7	9	10	8	9	10
E	I		.82	2	5	8	2	8	9	8	9	10
E	IS	35	.75	4	6	7	6	9	9	9	9	10

[1] These slabs cast on metal bases were made September to November 1956, were stored in moist air for 28 days, and then were stored in exposure area. The air content of the concrete varied from 4.3 to 6.1 percent, see reference 2. The slabs were from 30 to 70 days old when freezing and thawing started.
[2] Each rating is an average of observations for two slabs.
[3] Percent of slag used in manufacturing type IS cement.
[4] Equivalent alkalies as Na_2O.

the concrete's scaling are shown in figure 3. From these data, it appears that, to obtain resistance to frost and de-icing agents, the water content of concrete must be held to the smallest possible amount.
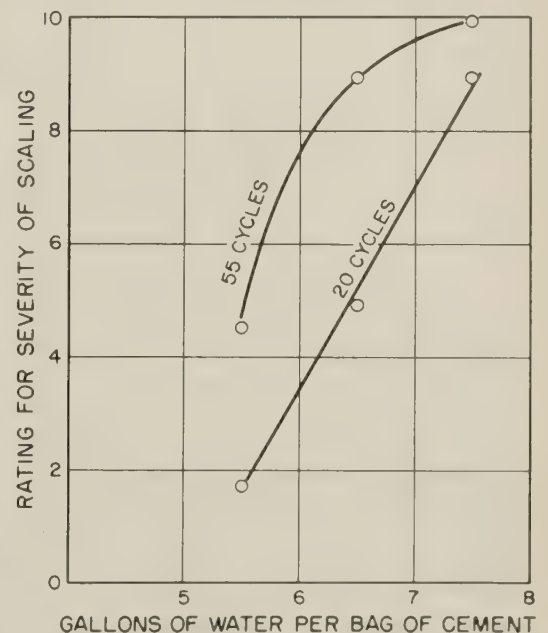
Silicone Surface Coatings

Two series of tests were made to study the effect that coatings of silicone solutions on the surface of concrete have on increasing the resistance to scaling caused by de-icing agents. In the first series, ten variables were included, as shown in table 7. The concrete had an air content of 3 percent. The slabs to which no initial curing was applied were stored in laboratory air, having a temperature varying from 70° F. to 90° F. and a relative humidity of from 30 to 60 percent. Initial curing was applied approximately 3 hours after the specimens were molded, and the surface treatment was applied from 14 to 28 days later. When three coats of surface treatment were applied, the first was applied 14 days after molding, the second at 21 days, and the third at 28 days. When only one coat was used, it was applied at 28 days.

Two different silicones were used. Silicone A was soluble in mineral spirits; silicone B was a water-soluble silicone from a different producer. The silicones were used at a rate of 1 gallon of a 2-percent solvent or aqueous solution per 100 square feet of surface. This amount was recommended by each producer. The membrane curing agent was applied at a rate of 1 gallon per 200 square feet. The specimens were stored in laboratory air for 30 days prior to being placed in the exposure area, when freezing started immediately. These slabs were exposed for five winters, and they were subjected to a total of 155 cycles of freezing and thawing by calcium chloride as the de-icing agent.

Three specimens were cast for each variable. The average ratings of the three slabs for each variable after 50, 90, 107, and 155 cycles of freezing and thawing are shown in table 7. These tests showed that the specimens given

7 days of initial moist curing usually had poorer resistance to scaling than the specimens that had no deliberate initial curing. The silicone surface treatments were sometimes of benefit in reducing the amount of scaling, one application of the treatment appeared to give better resistance to scaling than three applications.

When a silicone solution was used for curing (applied about 3 hours after molding) and no other surface treatment was applied very little scaling developed. Approximately the same results were obtained when a liquid membrane-forming curing agent was used. When three coats of silicone surface treatment were used in addition to the silicone used as a curing agent, more scaling occurred but the amount was still rated as slight. Supplementary tests have shown that the solution of silicone B would not meet the water-retention requirements for liquid membrane-forming curing materials (3). No appreciable difference was

Figure 3.—Influence of water-cement ratio on severity of scaling. Averages for 10 cements.

Table 7.—Effect of silicone coatings on resistance of concrete to scaling—series one

Initial applied curing [1]	Surface treatment [3]	Rating after freezing and thawing [2] for—			
		50 cycles	90 cycles	107 cycles	155 cycles
None	None	2	2	2	2
7 day moist	None	4	4	5	6
None	1 coat silicone A	1	1	1	1½
None	1 coat silicone B	1	1	1½	1½
7 day moist	do	2	2	2	3
None	3 coats, silicone B	3	2	3½	3½
7 day moist	do	3	3	4	3½
Silicone B	None	2	2	1	1½
Do	3 coats, silicone B	2	2	3	3½
Membrane	None	1	½	½	½

[1] Initial curing was applied 3 hours after molding. Slabs cast on metal bases were made in January 1955, were stored in laboratory air for 30 days, and then were stored in exposure area and immediately subjected to freezing and thawing. Air content was 3 percent.
[2] Each rating is an average of observations for three slabs.
[3] Surface treatment was applied 14 to 28 days after molding. Silicone A was mineral spirits soluble, and silicone B was water soluble.

Table 8.—Effect of silicone coatings on resistance of concrete to scaling—series two

Initial applied curing [1]	Surface treatment [3]	Rating after freezing and thawing [2] for—		
		10 cycles	20 cycles	40 cycles
None	None	½	½	1
3 days moist	None	½	1½	3½
None	Silicone C	½	1½	6
3 days moist	do	1½	3	8
None	Silicone D	1	2	6
3 days moist	do	½	2	5
None	Silicone E	0	3½	6
3 days moist	do	½	3	6½
None	None	0	½	1½
3 days moist	None	2	3	4½
None	Silicone F	½	1	2
3 days moist	do	2	3	5
None	Silicone G	1½	4	5
3 days moist	do	½	2	2½

[1] Initial curing was applied about 3 hours after molding. Slabs cast on metal bases were made November or December 1958, were stored in laboratory air for 15 days, and then were placed in exposure area and subjected to freezing within one week. Air content varied from 5.2 to 6.1 percent.
[2] Each rating is the average of two tests for the silicone treated slabs and of three tests for the control slabs.
[3] Surface treatment was applied 14 days after molding; silicones D and F were water soluble; silicones C, E, and G were mineral spirits soluble.
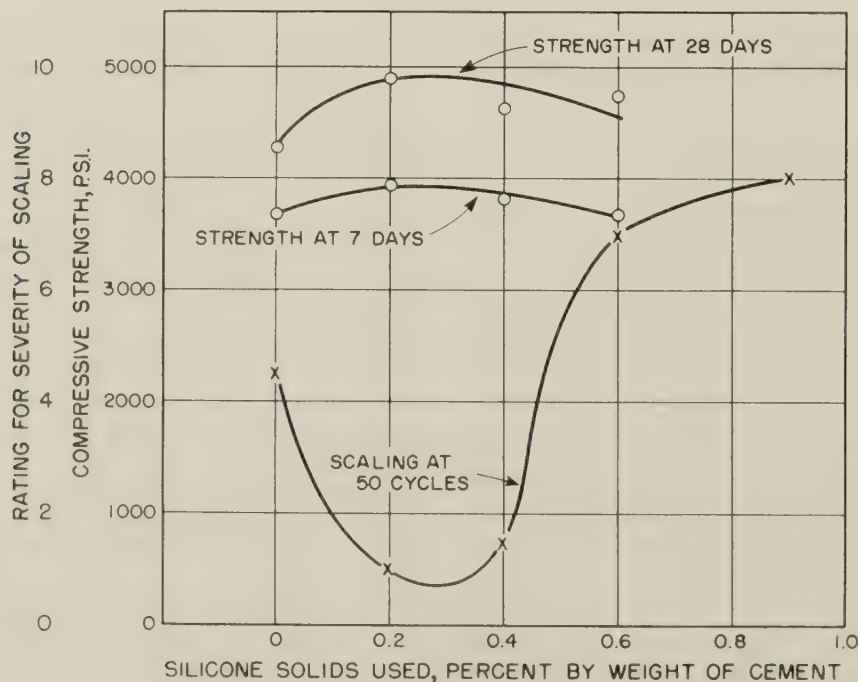
noted between the resistance to scaling for concrete treated with silicone A and that treated with silicone B. All of the concrete slabs in this series had relatively good resistance to scaling. Only one group of slabs showed significant scaling after 155 cycles of freezing and thawing; these slabs were given 7 days of initial moist curing and no surface treatment.

A second series of tests was made to study the effect of the use of five different silicone solutions. These silicones were used as surface protective coatings, and only one application was made. They were applied 14 days after molding, at the rate recommended by the manufacturers. The five silicones included both those soluble in water and those soluble in mineral spirits, and they were obtained from three producers.

The test slabs were made on two different days, and control slabs without silicone surface treatment were made on each day. The air contents of the concretes varied from 5.2 to 6.1 percent. Half of the slabs were given no initial moist curing, and the other half were moist cured for 72 hours. The slabs were stored in laboratory air for 15 days and then were placed in the outdoor exposure area and were subjected to freezing within a few days. The slabs were exposed for 1½ winters for a total of 40 cycles of freezing and thawing.

The ratings after 10, 20, and 40 cycles are given in table 8. Each rating is an average of the ratings on two slabs for each of the silicone treatments and on three control slabs. Most of the slabs that were given no initial moist curing had better resistance to scaling than those that were moist cured for 72 hours. The use of silicone surface coating was of no benefit in preventing scaling. Except for one set of two slabs, after 40 cycles of freezing and thawing the scaling of the silicone treated slabs was greater that that of the corresponding untreated slabs. No appreciable difference was noted in the resistance of eight of the ten sets of slabs treated with the different silicones. The eight sets of treated slabs all showed significant scaling after 40 cycles of freezing, whereas none of the untreated slabs had scaling of this extent.

Although the concrete for the second series of tests had a greater air content than that of series one, its resistance to scaling was poorer. The concrete slabs of series two were subjected to freezing and thawing at an age of about 20 days whereas those of series one were subjected to freezing and thawing at an age of 30 days. The two series were made about 3 years apart and different shipments of the cement were used, which might have accounted for some of the differences in resistance to scaling of the concrete between the two series.

Silicone as an Admixture

A preliminary series of tests was made to determine the effect of a silicone solution as an admixture for concrete on its resistance to scaling. In these tests, one of the water soluble silicone solutions included in the silicone surface tests was used. The mixes used in these tests included the control mix without silicone, and mixes prepared with 0.2, 0.4, 0.6, and 0.9 percent of silicone solids by weight of the cement. The air content for the mixes varied from 4.3 to 7.0 percent.

Table 9.—Effect of a silicone admixture on resistance of concrete to scaling

Silicone [1], percent	Air content, percent	Rating after freezing and thawing [2] for—		
		20 cycles	35 cycles	50 cycles
None	5.6	2	4	4½
0.2	5.0	1½	1	1
0.4	7.0	1	1	1½
0.6	4.3	4	5	7
0.9	5.0	5	5½	8

[1] Silicone solids by weight of cement.
[2] Each rating is an average of observations for two or three slabs. These slabs, cast on metal bases, were made in November 1958, were moist cured for 3 days, were stored in laboratory air for 11 days, and then were stored in exposure area and subjected to freezing within 5 days.

Figure 4.—Effect of a silicone admixture on scaling and compressive strength of concrete.

Table 10.—Effect of a silicone admixture on properties of concrete [1]

NO SILICONE
ADMIXTURE,
RATING 5

0.2%
SILICONE
ADMIXTURE,
RATING 1

0.4%
SILICONE
ADMIXTURE,
RATING 2

0.6%
SILICONE
ADMIXTURE,
RATING 7

0.9%
SILICONE
ADMIXTURE,
RATING 10

Figure 5.—Effect of silicone admixture on resistance of air-entrained concrete to scaling. Photographed in 1961 after 50 cycles of outdoor freezing and thawing by calcium chloride.

Silicone [2]	Slump	Air content	Retardation of set [3]	Compressive strength at—		
				7 days	14 days	28 days
Percent	Inches	Percent	Hours	P.s.i.	P.s.i.	P.s.i.
None	2.8	5.2		3,690	3,870	4,280
0.2	3.1	5.3	4.0	3,930	4,540	4,900
0.4	3.3	5.7	6.3	3,820	4,340	4,620
0.6	2.5	4.9	5.5	3,680	4,390	4,740

[1] Proportions by dry weight were 94–205–295 pounds; cement content was 6.0 bags per cubic yard; water content was 5.8 gallons per bag.
[2] Silicone solids by weight of cement.
[3] Determined by Proctor penetration test using load of 500 p.s.i. Retardation is delay in hardening of concrete containing silicone as compared to concrete without. Concrete without silicone had initial set of 5.0 hours.

All of the slabs were moist cured for 3 days and were stored in laboratory air for 11 days more and then were placed in the exposure area. They were subjected to freezing within 6 days after being placed in the exposure area. These slabs were exposed for $1\frac{1}{2}$ winters and were subjected to a total of 50 cycles of freezing and thawing. The ratings of these slabs after 20, 35, and 50 cycles of freezing and thawing are given in table 9.

Tests also were also made to determine the effect of the silicone as an admixture on the retardation of set and the compressive strength of concrete. The results of these tests are shown in table 10. The results of the tests for scaling and those for strength at 7 and 28 days are shown in figure 4. It will be observed that minimum scaling and maximum strength of concrete are indicated for a mix containing silicone solids in an amount of about 0.3 percent by weight of the cement. Photographs of typical slabs with silicone and the reference concrete slabs after 40 cycles of freezing and thawing are shown in figure 5.

The silicone admixture had the effect of increasing the time of set of the concrete. As shown in table 10, 0.2 percent of silicone solids required 9.0 hours for the concrete to reach initial set as measured by a Proctor penetration load of 500 p.s.i. but concrete

without the silicone admixture reached this degree of set in 5.0 hours. Increasing the amount of silicone tended to increase the setting time.

Miscellaneous Tests

A floor sealer, which had been tried experimentally by one of the State highway departments to prevent scaling, was applied as a curing agent and tested to determine its effectiveness on the resistance of concrete to scaling. The resistance to scaling of concrete cured with this material was compared with the resistance of concrete cured with wet burlap for 7 days and with the resistance of concrete cured with a liquid, membrane-forming curing material. Non-air-entrained concrete was used. The liquid curing materials were applied at two rates, 1 gallon per 100 square feet and 1 gallon per 200 square feet, approximately $2\frac{1}{2}$ hours after the slabs were cast. The slabs were placed in the outdoor exposure area at an age of 14 days, and freezing did not occur for about a week. The slabs were exposed for 2 winters and were subjected to 50 cycles of freezing and thawing.

The ratings after 20, 35, and 50 cycles of freezing and thawing by the use of calcium chloride as a de-icing agent are shown in table 11. Each rating is an average of the observations for two slabs. After 35 cycles of freezing and thawing, there was no appreciable difference in the ratings of any of the slabs; none showed any significant scaling. The slabs on which the floor sealer was applied had slightly better resistance than the other slabs. At 50 cycles, all of the slabs showed significant scaling; the ones on which the floor sealer was applied still had the best resistance and the moist cured slabs the poorest. No appreciable difference was noted in the scaling between the slabs on which the floor sealer and the liquid, membrane-forming curing materials were applied at the rate of one gallon per 200 square feet and those on which they were applied at the rate of one gallon per 100 square feet.

Tests were made on the two liquids used as curing agents to determine whether they met the requirements for water retention (3). These tests showed that the floor sealer did not meet the requirements and that the membrane-forming compound did. The weathering tests showed slightly better results for the floor sealer than for the curing material.

Use of Emulsified Polystyrene Latex

In this phase of the investigation, emulsified polystyrene latexes were used as a curing agent, as a surface protective coating, and as an admixture for concrete. Three different latexes were used as curing agents; one was used as a protective surface treatment; and one was used as an admixture. The control specimens without latex were moist cured for 7 days. For initial curing, the latex was applied to the slabs $2\frac{1}{2}$ hours after molding. Surface treatments or protective coatings were applied to the slabs at an age of 14 days. No water retention tests were made on the latexes. The concrete was non-air-entrained except when the latex was used as an admixture. Concretes prepared with the latex admixture entrained either 10 or 20 percent air without the addition of an air-entraining agent. When a latex was used as a curing material or as a surface treatment, it was applied at two rates, 1 gallon per 200 square feet and 1 gallon per 400 square feet. One slab was tested for each rate. The specimens were stored in laboratory air for 15 days then placed in the exposure area. Freezing started within a week. The slabs were exposed for $1\frac{1}{2}$ winters for a total of 40 cycles of freezing and thawing.

The ratings of the slabs at 10, 25, and 40 cycles are shown in table 12. The ratings are averages for two slabs on which the same latex was applied at the two different rates. The ratings for the control slabs and for those having the latex admixture were also averages for two slabs. After only 10 cycles

Table 11.—Effect of a floor sealer and a membrane curing material on resistance of concrete to scaling

Initial curing material	Rate of application, sq. ft./gal.	Rating after freezing and thawing [1] for—		
		20 cycles	35 cycles	50 cycles
Moist [2]		3	3	$9\frac{1}{2}$
Floor sealer	100	2	2	$6\frac{1}{2}$
Floor sealer	200	2	2	6
Membrane curing	100	2	$3\frac{1}{2}$	8
Membrane curing	200	2	3	8

[1] Each rating is an average of observations for two slabs. These slabs, which were cast on metal bases, were made in November 1956, stored in laboratory air for 14 days, and were then placed in the exposure area and subjected to freezing and thawing within a week.
[2] The slabs were moist cured for 7 days.

Table 12.—Effect of an emulsified polystyrene latex on the resistance of concrete to scaling

Initial curing [1]	Surface treatment [3]	Admixture	Air content, (calculated) percent	Rating after freezing and thawing [2] for—		
				10 cycles	25 cycles	40 cycles
Moist_____	None_____	None_____	2	8	9	10
Moist_____	Latex No. 1_____	None_____	2	4½	9	10
Latex No. 1____	None_____	None_____	2	4½	5½	8½
Latex No. 2____	None_____	None_____	2	3½	3½	7½
Latex No. 3____	None_____	None_____	2	4	6	7½
None____	None_____	Latex No. 1 [4]_____	10	0	0	1
None____	None_____	Latex No. 1 [5]_____	20	0	0	½

[1] Initial curing was applied approximately 2½ hours after molding. Wet burlap was applied to moist cured slabs for 7 days.
[2] Each rating is an average of observations for two slabs. The slabs cast on metal bases were made in December 1956, were stored in the laboratory 15 days, and then were placed in the exposure area and subjected to freezing and thawing within a week.
[3] Surface treatment was applied 14 days after molding.
[4] Latex was added to the mix at a rate of 2.4 gallons per bag of cement.
[5] Latex was added to mix at a rate of 4.1 gallons per bag of cement, as recommended by the producer.

of freezing and thawing, the control slabs were severely scaled and had an average rating of 8, at 40 cycles the rating was 10.

There was no appreciable difference in the scaling of the slabs when the three latexes had been used as curing materials; the ratings after 10 cycles were from 3½ to 4, and at 40 cycles they were from 7½ to 8½. When a latex had been used as a surface protective coating, the ratings were slightly higher. These tests indicate that materials of this type, when used on the surface of the concrete, are effective only in slightly delaying the scaling. However, when a latex had been used as an admixture, excellent resistance to scaling was obtained. The excellent resistance of this concrete probably was caused by the high air content entrained by the latex. Similar results were obtained for concrete containing 10.0 percent air, as shown in table 5.

Additional Tests With Fly Ash

In the original series of tests for the resistance to scaling of concrete containing fly ash, tests were made on concrete in which one-third of the cement was replaced by an equal volume of fly ash (2). This is a larger amount of fly ash than usually would be used in paving concrete. In the second series of tests, the concrete was prepared with three-fourths of a bag of cement in a 6-bag mix replaced by 1⅓ bags of fly ash. The amount of sand used in the mix was reduced to compensate for the increased volume of concrete. This mix was one that had been recommended for paving concrete by a producer of fly ash.

In this series of tests, a fly ash with 0. percent carbon (B) and a fly ash with 11. percent carbon (Y) were used with two type I portland cements. Both air-entrained and non-air-entrained concretes were used. The ratings on slabs cast from these mixes are shown in table 13; each is an average of the ratings for two slabs.

As would be expected, all of the slabs, with and without fly ash, that had an air content of only 1.0 percent showed severe scaling after only 15 cycles of freezing and thawing. Slabs containing 4.5 percent or more air showed moderate to severe scaling after 40 cycles when the high carbon fly ash had been used. The least scaling occurred on the slab of concrete that had been prepared with cement E, fly ash B (low carbon content) and a cement content of 5¼ bags per cubic yard. The concrete prepared with this low carbon fly ash had durability equal to that of the concrete prepared without fly ash.

NEW LABORATORY TESTS

Effect of Thawing Agents

A limited laboratory series of tests was made to determine the effect of various thawing agents on the scaling of concrete and on the rate of thawing of the ice on the concrete. In this series of tests, the specimens used were similar to those used in the outdoor tests except that they were only 6 by 12 by 2 inches thick. The same mix was used for all specimens. The concrete was prepared with crushed stone coarse aggregate of one-half inch maximum size. The cement content was bags per cubic yard and the air content was percent. The specimens were moist cured for 7 days, and then stored in laboratory air for 14 days prior to the beginning of the freezing and thawing test. The procedure used for these tests was, as follows: A fixed volume of water was placed on the top surface of each specimen and the specimens placed on racks in the laboratory freezer; cold air at a temperature of 0° F. was circulated over the specimens. After the water had frozen, the specimens were removed from the freezer and placed in laboratory air at a temperature of 70° F. to thaw. The thawing agents were spread over the ice-covered surfaces at a rate of 2.4 pounds per square yard. After the ice had thawed, the surface was washed and fresh water was placed on the slabs. The specimens were exposed to freezing from about 4 p.m. until 9 a.m. the next day and were thawed from 9 a.m. until 4 p.m. the same day.

The length of time required for the ice to thaw and the amount of scaling on the exposed surface of the concrete were determined periodically. The results of these observations are given in figure 6. Each result given is the average for tests on five slabs. Five thawing agents were used in these tests: calcium chloride flakes, sodium chloride, a mixture of equal parts by volume of calcium chloride and
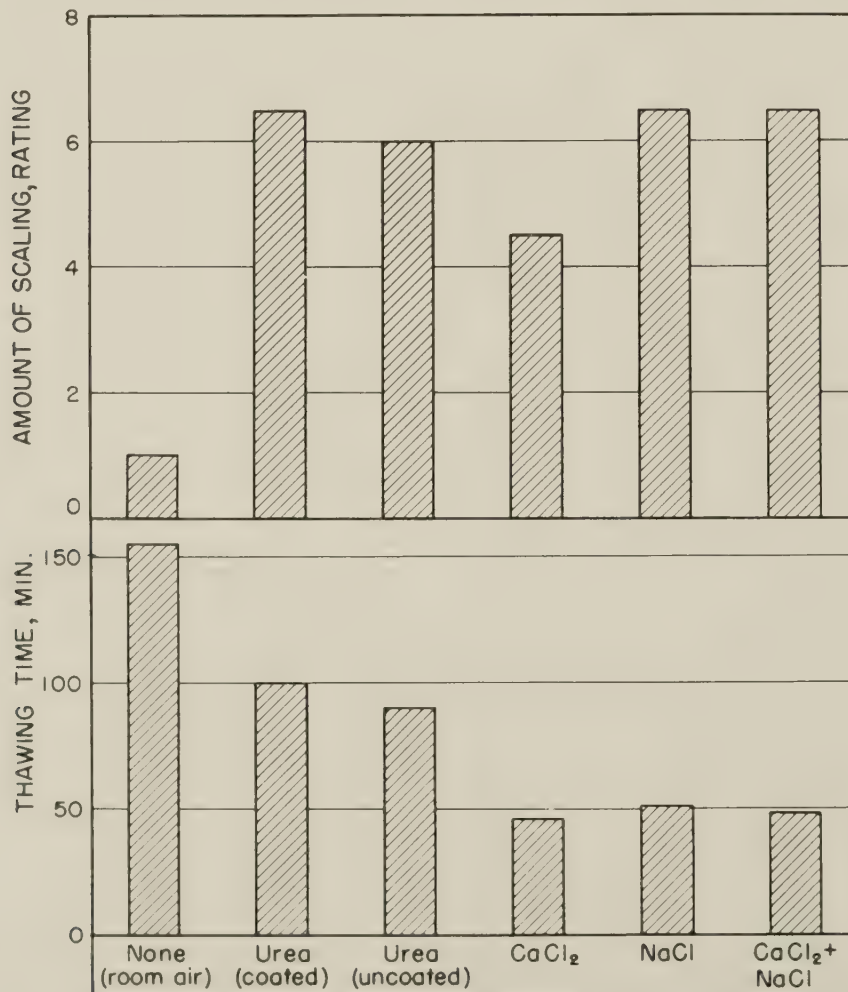
Figure 6.—*Effect of de-icing agents on rate of thawing and amount of scaling of concrete containing 6 percent of air.*

Cement			Fly Ash		Air	Rating after freezing and thawing[1] for—	
Source	Type	Content	Source	Amount		15 cycles	40 cycles
		Bags/cu. yd.		Lb./cu. yd.	Percent		
B	I	6	None	None	1.0	7	10
B	I	5¼	B	100	1.0	7	10
B	I	5¼	Y	100	1.0	10	10
E	I	6	None	None	1.0	9	10
E	I	5¼	B	100	1.0	9	10
E	I	5¼	Y	100	1.0	10	10
B	I	6	None	None	5.3	2½	4½
B	I	5¼	B	100	4.5	3	4½
B	I	5¼	Y	100	4.5	4½	7
E	I	6	None	None	4.8	2	4
E	I	5¼	B	100	6.2	2	3
E	I	5¼	Y	100	5.3	5	7½

[1] Each rating is an average of observations for two slabs. These slabs were cast on metal bases in April 1957, were stored in moist air for 28 days, and then were stored in the exposure area. Slabs were more than 6 months old when freezing and thawing started.

odium chloride, urea in a commercial de-icer of prilled pellets coated with clay, and urea in uncoated, shotted pellets. For comparison no thawing agent was used on one set of slabs; they were thawed in the laboratory at room temperature. The time required to melt the ice on the surface of the slabs varied from 46 minutes for the specimens on which calcium chloride had been used as a thawing agent to 155 minutes for those on which no thawing agent had been used. Calcium chloride, sodium chloride, and a mixture of the two, were much faster in thawing the ice than the agents containing either type of urea.

Of the five thawing agents, calcium chloride appeared to be the most effective and the least harmful to the concrete. The average rating of the specimens on which calcium chloride had been used was 4½ after 75 cycles of freezing and thawing. Less scaling was observed for these specimens than for the specimens on which the other thawing agents had been applied. The specimens on which no thawing agent had been used showed very little scaling and after 75 cycles they had an average rating of 1.

Age of Concrete When Frozen

Throughout the several series of tests, the results obtained appeared to have been influenced by the amount of water in the concrete when freezing occurred. The results, reported in tables 1 and 2, showed that less scaling occurred for the specimens cast on a sand base than for those cast in a waterproof mold with a metal base. There is no question but that the sand base removed some of the water required to lubricate the concrete mix, and the test specimens so cast contained less free water when frozen than those cast on metal bases. In other series of tests, it was not possible to prepare all of the specimens on the same day because of the limitations of the molds and manpower available; consequently, some specimens were older and probably contained less free water than others.
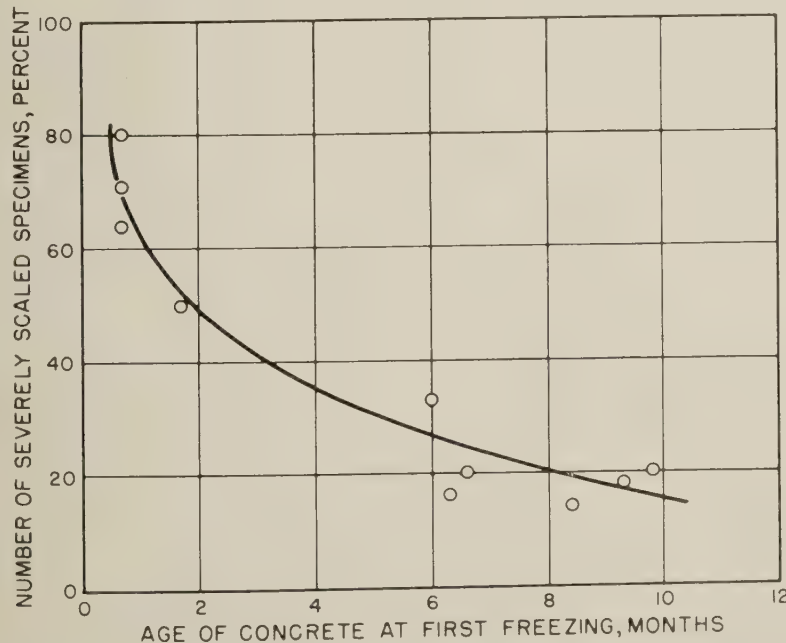
No tests were made to determine the amount of the free water in the hardened concrete specimens when they were first subjected to freezing. However, the age of the concrete of all specimens at first freezing is known. If it may be assumed that the amount of free water in the hardened concrete varied inversely with the age of the concrete at first freezing, a relation of some interest may be developed. To this end, test results for all of the specimens cast on steel bases and having an air content of 4.0 percent or greater were summarized, and the percentage of significantly scaled slabs at 50 cycles of freezing and thawing were plotted against the age of the concrete at first freezing. This is shown in figure 7. Because of the marked differences in controlling variables in the various series of tests, only a general trend might be expected to be shown. This trend does indicate that concrete subjected to freezing and thawing at an early age is most liable to suffer serious scaling. From this, it may be stated that for concrete placed when freezing is imminent, scaling can be minimized if wet curing of the

concrete is curtailed. The use of wind shields to permit the gradual removal of moisture from the concrete may in this case be preferable to the use of surface curing materials or wet curing methods.

REFERENCES

(1) Factors Affecting Resistance of Portland Cement Concrete to Scaling Action of Thawing Agents, by A. G. Timms, PUBLIC ROADS, vol. 28, No. 7, Apr. 1955, pp. 143–157.

(2) Final Report of Tests of Concrete Containing Portland Blast-Furnace Slag Cement, by W. E. Grieb and George Werner, PUBLIC ROADS, vol. 31, No. 9, Aug. 1961, pp. 183–193.

(3) Liquid Membrane-Forming Compound for Curing Concrete, ASTM C 309–58, in 1961 Book of ASTM Standards, including Tentatives: Part 4, Cement, Lime, Gypsum, Mortar, Concrete, Mineral Aggregates, Bituminous Materials, Soils, pp. 825–827.

(4) Evaluation of Air-Entraining Admixtures for Concrete, by F. H. Jackson and A. G. Timms, PUBLIC ROADS, vol. 27, No. 12, Feb. 1954, pp. 259–267.

Figure 7.—Effect of the age of the concrete when first frozen on the severity of scaling.

Table 14.—Effect of thawing agents on scaling of concrete and rate of thawing of ice in laboratory freezing and thawing tests

Thawing agent[1]	Thawing time,[2] minutes	Rating after freezing and thawing[3] for—		
		25 cycles	50 cycles	75 cycles
None	155	1	1	1
Urea, coated	100	5	6	6½
Urea, uncoated	90	5	6	6
CaCl₂	46	4½	4	4½
NaCl	51	5	6	6½
CaCl₂ and NaCl	48	5	6	6½

[1] Thawing agents were used at a rate of 2.4 lb. per square yard of surface.
[2] Time necessary for ice on surface to melt in laboratory air at 70° F.
[3] Each rating is an average of observations for five, 12- by 6- by 2-inch slabs. The slabs were cast on metal bases, were moist cured for 7 days, then were stored in laboratory air for 14 days prior to start of freezing. Air content was 6 percent.

Speed Estimation on Residential Streets

BY THE TRAFFIC OPERATIONS RESEARCH DIVISION
BUREAU OF PUBLIC ROADS

by **RICHARD D. DESROSIERS,**
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The study reported in this article was undertaken to determine with what degree of accuracy residents are able to estimate the normal operating speed of vehicles traveling on suburban streets. This information is expected to be useful to traffic engineers and law enforcement officers in acting upon the many complaints received about speeding cars and trucks in residential areas.

Various factors that might affect the estimations were considered in relation to the type of vehicle for which the speed was being estimated. Conclusions for this study were reached after a statistical analysis of the data collected. However, these conclusions were deemed to apply only to the areas studied because of the limited data collected.

The fieldwork for this study and initial analysis of the data collected were accomplished by a group of Junior Engineers [1] of the Bureau of Public Roads, during 1961, as part of their training.

Introduction

A PROJECT to study the accuracy with which residents estimate the normal operating speeds of vehicles traveling over residential streets was conducted by the Bureau of Public Roads in a selected area in Washington, D.C., in 1961. A passenger car and a panel truck were driven at three controlled speeds of 15, 25, and 35 miles per hour (m.p.h.) and 935 estimates of the speeds at which the vehicles were traveling were made by 160 residents. Generally, the speeds at which the test vehicles were traveling were underestimated. Of the 935 estimates, 42 percent were underestimates, 22 percent were overestimates, and 36 percent were correct estimates, to the nearest 5 m.p.h.

Summary

No general conclusions concerning the accuracy with which speed estimates are made for vehicles on residential streets could be reached because of the limited scope of this study and the data collected. However, the following observations were made: (1) Thirty-eight percent of the estimates of the speed of the passenger car were correct to the nearest 5 m.p.h.; and 34 percent of the estimates of the speed of the panel truck were correct to within 5 m.p.h. (2) More of the observers underestimated the speeds at which both vehicles were traveling than overestimated these speeds. (3) As the travel speeds increased the observers made greater absolute estimating errors in m.p.h. but their percentage error in estimating generally decreased. (4) The age of the observers or the type of vehicle (passenger car or panel truck) had no apparent effect on the mean absolute error made by the observers. (5) Whether the observers had small children seemingly had no effect on the accuracy of their speed estimations, those with and without small children made estimates with a similar degree of accuracy.

In this study no attempt was made to separate the residents who might have complained about speeding traffic, and it is possible that speed estimates from such a group of complainers might provide different results. It is suggested that those conducting future studies of the accuracy of speed estimation might consider using variables such as night interviews; a noisy vehicle; a sportscar; and/or a greater speed range, for example 10 to 50 m.p.h.

Procedure

Two vehicles, a 1959 sedan of a popular make and a panel truck were used as test vehicles for this study. The sedan was chosen because of its size, style, and familiarity to the general public. The truck was a type commonly used for home delivery of bread, milk, and similar commodities. Tests were conducted in which each of the vehicles was being operated at speeds of 15, 25, and 35 m.p.h. These operating speeds were selected because they represent the range of normal operating speeds of vehicles traveling on residential streets. Both the truck and the sedan were operated at each of the speeds so that the estimates for different types of vehicles could be compared.

So that the interviewer would be able to record the actual speed of the test vehicle as it passed the observer, a code system was prearranged in which 6- by 6-inch cards with three different letters of the alphabet on them were used. The driver of the test vehicle selected the speed at random, either 15, 25, of 35 m.p.h., and placed the appropriate card

Table 1.—Mean absolute and percentage errors in speed estimating

Speed	Errors—			
	Passenger car		Truck	
	m.p.h.	Percent	m.p.h.	Percent
15	−3.3	−22	−3.4	−23
25	−3.7	−15	−5.0	−20
35	−6.1	−17	−5.4	−15
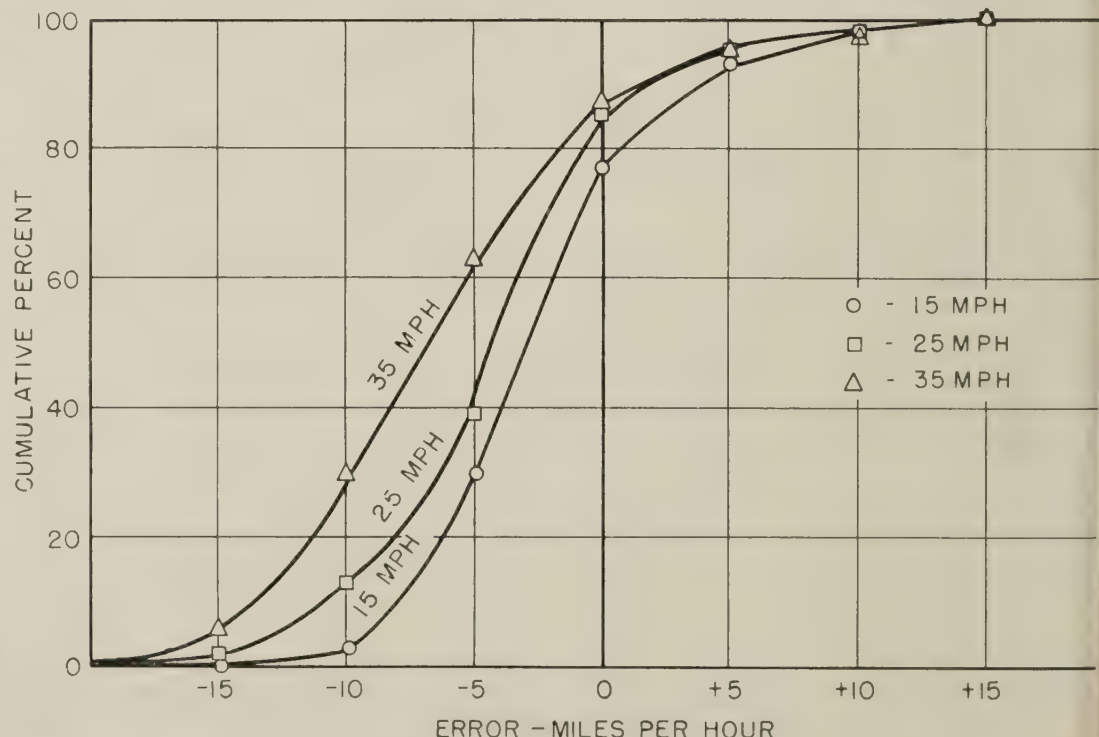
Figure 1.—Cumulative errors in speed estimates for the passenger car at 15, 25, and miles per hour.
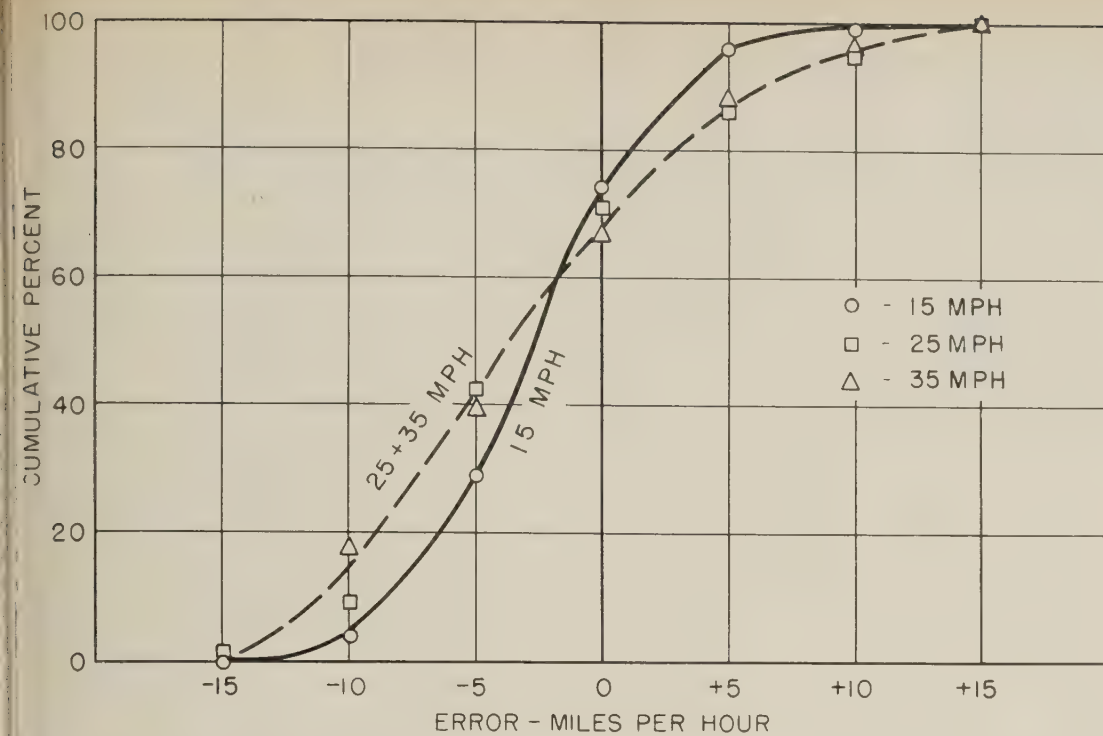
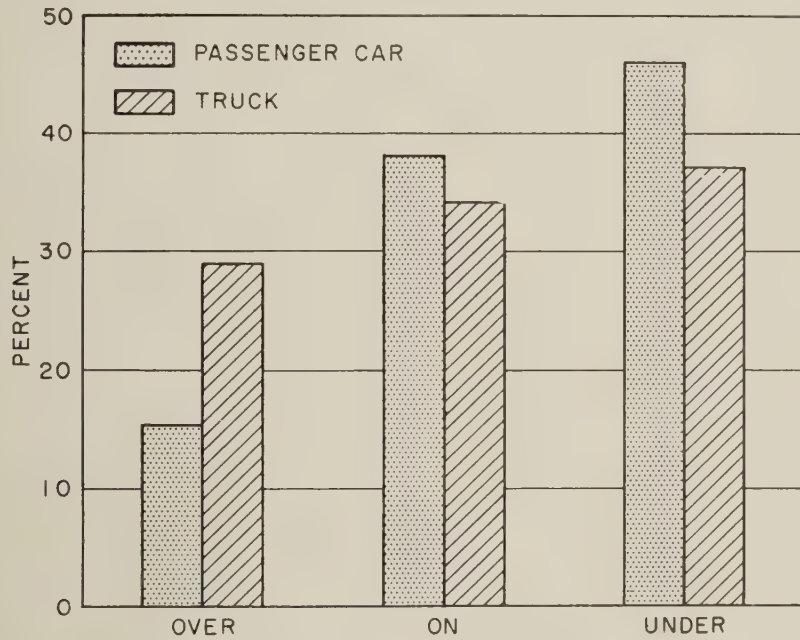Figure 2.—Cumulative errors in speed estimates for the truck at 15, 25, and 35 miles per hour.

Figure 3.—Percentage of speed estimates over, on, and under for all three test speeds combined.

in the windshield of the test vehicle. Thus the interviewer was able to record the code for the actual speed of the test vehicle at the same time he recorded the estimate made by the observer, and without giving any clue that might affect the observer's speed estimate.

The only pattern followed was that the truck always preceded the passenger car.

Test location

Upper-, middle-, and lower-income neighborhoods of different population densities

were selected for the test areas. Within these areas, four residences in each block were selected arbitrarily and the occupants asked to participate in the study. Site selection was limited to locations with the following listed physical characteristics: sufficient sight distance at minor intersections to permit safe crossing, straight-aways long enough for the truck to obtain the required speed, streets wide enough to permit the test without obstructing other traffic, dwelling units situated so that the observers easily could see the vehicles from his or her front door, and turn-around areas for vehicles away from children's play areas. Other factors that might have influenced the speed estimates were recorded by the interviewer: Posted speed limit, parked vehicles, sex and estimated age of the observer, and whether any children 10 years of age or under were in the family.

Observers

Interviewers contacted potential observers and read the following statement: "I am a highway engineer with the U.S. Bureau of Public Roads. We are conducting a Speed Estimation Research Project along this street in front of your house. We would like to engage your cooperation in estimating the speed of our sedan and truck as they pass directly in front of your house."

Those contacted and consenting to participate in the study were given instructions, as follows: "The truck and sedan are marked by large signs on the front stating: 'Speed Research Vehicle.' I will point out the vehicle as it approaches so there will be no identification errors. Each vehicle, the sedan and the truck, will make three passes. Each pass will be at a different speed. We want you to estimate the speed of each vehicle as it passes directly in front of your house, and as you make your estimation I will record it here on this form. We ask only one question other than the speed estimation and that is, 'Do you have any children under 10 years old?'"

A total of 160 observers made 935 individual speed estimates. Most of these estimates were made to the nearest 5 m.p.h. and when they weren't, the interviewer rounded off the estimate to the nearest 5 m.p.h.

Cumulative frequency of errors representing a minimum of 150 observations are shown by the curves in figures 1 and 2. These curves indicate the distribution of errors to have been

Table 2.—Influence of children 10 years of age or under on observers' speed estimates

Observers	Speed estimates—					
	Over		On		Under	
	Car	Truck	Car	Truck	Car	Truck
	Pct.	Pct.	Pct.	Pct.	Pct.	Pct.
With children 10 or under	16	26	36	35	48	39
Without children 10 or under	17	33	42	33	41	34

Table 3.—Cumulative percentages of correct speed estimates out of a total of 6 estimates per observer

Correct speed estimates	Cumulative percentage of estimates correct to within—		
	2½ m.p.h.	7½ m.p.h.	12½ m.p.h.
	Percent	Percent	Percent
6	1	44	85
5 or more	6	66	94
4 or more	21	81	98
3 or more	38	92	98
2 or more	66	97	100
1 or more	84	99	100
0 or more	100	100	100

fairly normal for the passenger car for each of three test speeds and for the truck when its speed was 15 m.p.h.; but, the error curves for the truck's speed at 25 and 35 m.p.h. indicate a greater variation in speed estimates. The mean absolute error in miles per hour made by the observers increased as the traveling speed of the vehicles was increased, but the percentage error generally decreased, as is shown in table 1. When all the errors were averaged, the results were negative; that is, the average observer underestimated the speed for all three test speeds for both vehicles. The number of errors made in estimating the speed of the passenger car were nearly identical when its speed was 15 and 25 m.p.h., but the number of errors increased greatly when the speed was increased to 35 m.p.h. As can be seen by figure 3, more underestimates than overestimates were made for the speeds of both vehicles. This was especially true for the passenger car: 46 percent of the estimates were under its speed, and only 16 percent of the estimates were over. Corresponding figures for the errors in estimating the speed of the truck were 37 percent and 29 percent, respectively.

A comparison of the percentage of speed estimates that were over, on, and under the actual speeds is shown for both the car and truck in figure 4. The chi square significance test was applied between the estimates that were over and under the actual speed for each vehicle at each of the three speeds. Significant differences (0.05 level) were obtained for the passenger car estimates when its speed was 25 and 35 m.p.h. No significant differences were obtained for either the passenger car, when its speed was 15 m.p.h., or for the truck at any of the three test speeds. Significance at the 0.05 level means that there are less than five chances in a hundred that the observed differences could have occurred by chance alone.

Prior to this study, it had been thought that people with small children might tend to overestimate the speeds at which vehicles were traveling. It is very evident from the data shown in table 2 that such a hypothesis was not supported by this study. Estimates of observers with small children were similar in accuracy to those of the observers without small children; approximately 65 percent of the observers had small children in their household. Neither did the age of the observer seem to have had an effect on the degree of accuracy. The ages of the observers that had been estimated by the interviewer were divided into ten-year age groupings. Consideration of the speed estimates revealed no apparent differences between these age groups in the absolute error in estimating speed.

Of the 935 estimates, 42 percent were under the speed of the vehicle, 22 percent were overestimates, and 36 percent were correct to the nearest 5 m.p.h. Although those interviewed had not been instructed as to what range should be employed in their estimating, nearly all observers estimated to the nearest 5 m.p.h. If a smaller estimating unit had been used, such as 1 m.p.h., the percentage of correct estimates would have been reduced.
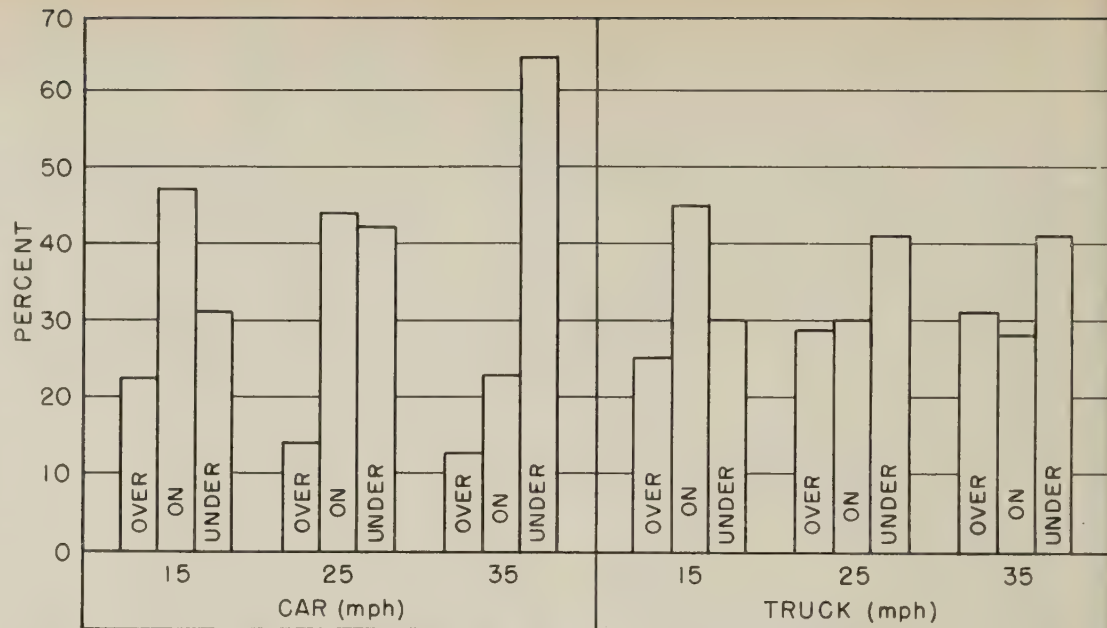

Figure 4.—Percentage of speed estimates over, on, and under for passenger car and truck at each test speed.

With most of the speed observations having been made to the nearest 5 m.p.h., a correct answer was actually 0 plus or minus 2½ m.p.h. Likewise, observation of 5 and 10 m.p.h. errors were actually 5 plus or minus 2½ m.p.h. and 10 plus or minus 2½ m.p.h. The upper (maximum) limits of these errors were used to construct table 3. The data here clearly show that the number of correct observations increased with an increase in the acceptable error, until 85 percent of the observers were never in error by more than 12½ m.p.h. Such figures apply only to the speed range used for this study, 15, 25, and 35 m.p.h., and any extrapolations to higher or lower speeds might lead to erroneous conclusions. The curves shown in figure 5 were constructed from the data of table 3. The use of these curves can be shown best by the following example. In estimating speeds within a 5-mile range, 18 percent of the observers were accurate every time (100 percent) and 38 percent were accurate 80 percent of the time.

The data collected were further examined to determine whether some individuals always estimate better than others. If at least four of the six speed estimates made by an observer were under the correct speed of the vehicle and none of the estimates were over, the subject was considered to have been an under estimator. If at least four speed estimates were over and none were under, the subject was considered to have been an overestimator. If at least four of the estimates were correct, the subject was considered to have been a correct estimator. On this basis, 34 percent of the observers always underestimated, 1 percent always overestimated, and 20 percent were always correct. The remaining 32 percent of the observers could not be placed in any one of these three groups because of the inconsistent pattern of their estimating.
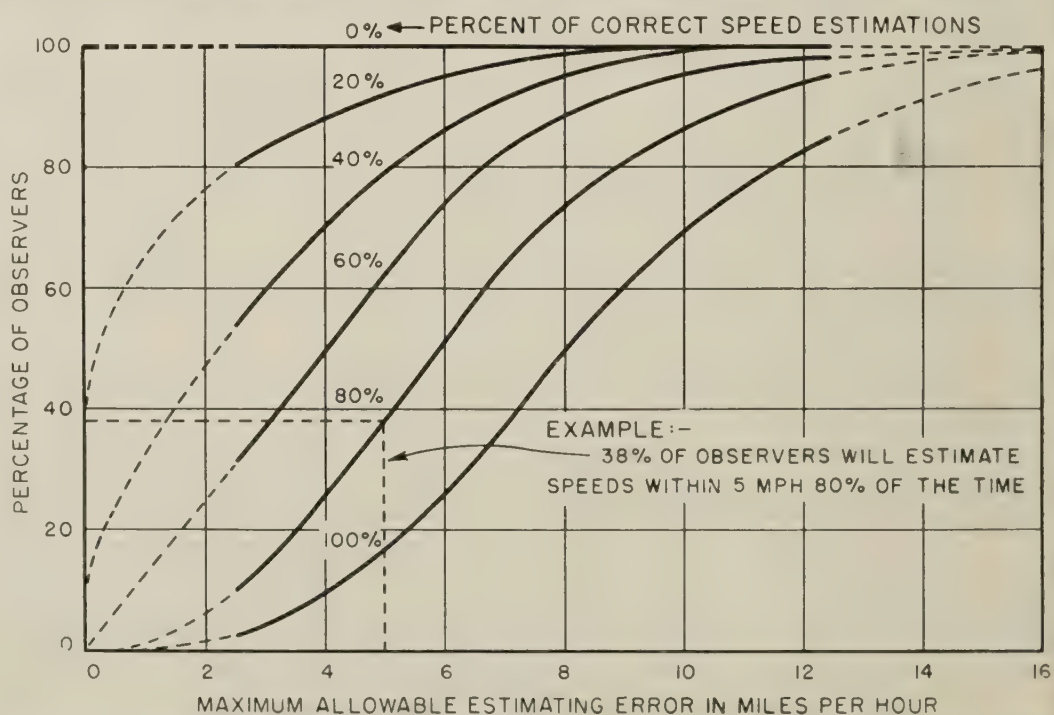

Figure 5.—Percentage of correct speed estimates as a function of the maximum allowable estimating error, and the percentage of observers.

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1951, 35 cents. 1955, 25 cents. 1958, 30 cents. 1959, 40 cents. 1960, 35 cents. 1961, 35 cents. (Other years are now out of print.)

REPORTS TO CONGRESS

Factual Discussion of Motortruck Operation, Regulation and Taxation (1951). 30 cents.

Federal Role in Highway Safety, House Document No. 93 (1959). 60 cents.

Highway Cost Allocation Study:
First Progress Report, House Document No. 106 (1957). 35 cents.

Final Report, Parts I–V, House Document No. 54 (1961). 70 cents.

Final Report, Part VI: Economic and Social Effects of Highway Improvement, House Document No 72 (1961). 25 cents.

The 1961 Interstate System Cost Estimate, House Document No. 49 (1961). 20 cents.

U.S. HIGHWAY MAP

Map of U.S. showing routes of National System of Interstate and Defense Highways, Federal-aid Primary Highway System, and U.S. Numbered Highway System. Scale 1 inch equals 80 miles. 25 cents.

PUBLICATIONS

Aggregate Gradation for Highways: Simplification, Standardization, and Uniform Application, and A New Graphical Evaluation Chart (1962). 25 cents.

America's Lifelines—Federal Aid for Highways (1962). 15 cents.

PUBLICATIONS—Continued

Classification of Motor Vehicles, 1956–57 (1960). 75 cents.

Design Charts for Open-Channel Flow (1961). 70 cents.

Federal Laws, Regulations, and Other Material Relating to Highways (1960). $1.00.

Financing of Highways by Counties and Local Rural Governments: 1942–51 (1955). 75 cents.

Highway Bond Calculations (1936). 10 cents.

Highway Capacity Manual (1950). $1.00.

Highway Statistics (published annually since 1945):
1955, $1.00. 1956, $1.00. 1957, $1.25. 1958, $1.00. 1959, $1.00. 1960, $1.25.

Highway Statistics, Summary to 1955. $1.00.

Highway Transportation Criteria in Zoning Law *and* Police Power and Planning Controls for Arterial Streets (1960). 35 cents.

Highways of History (1939). 25 cents.

Hydraulics of Bridge Waterways (1960). 40 cents.

Increasing the Traffic-Carrying Capability of Urban Arterial Streets: The Wisconsin Avenue Study (1962). 40 cents.

Landslide Investigations (1961). 30 cents.

Manual for Highway Severance Damage Studies (1961). $1.00.

Manual on Uniform Traffic Control Devices for Streets and Highways (1961). $2.00.

Parking Guide for Cities (1956). 55 cents.

Peak Rates of Runoff From Small Watersheds (1961). 30 cents.

Road-User and Property Taxes on Selected Motor Vehicles, 1960. 30 cents.

Selected Bibliography on Highway Finance (1951). 60 cents.

Specifications for Aerial Surveys and Mapping by Photogrammetric Methods for Highways, 1958: a reference guide outline. 75 cents.

Standard Specifications for Construction of Roads and Bridges on Federal Highway Projects, FP–61 (1961). $2.25.

Standard Plans for Highway Bridge Superstructures (1956). $1.75.

The Identification of Rock Types (revised edition, 1960). 20 cents.

The Role of Aerial Surveys in Highway Engineering (1960). 40 cents.

Transition Curves for Highways (1940). $1.75