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Deterioration of Bituminous Pavement Surfaces by Growth of Alum Crystals

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ABSTRACT

Some 1.5-in. bituminous pavements in Stafford County, Virginia, have developed numerous small domes from 2 to 4 in. in diameter and about 1 in. high. Each dome has a core of white, astringent-tasting crystals that are under the bituminous pavement and at the top of the subbase. The crystals appear to be closest in composition to pickeringite, a magnesium alum, which commonly results from the weathering of pyritic schists. The domes were observed primarily between vehicle wheel tracks and in areas of poorest drainage. The aggregate in the bituminous pavement is quartz sand and gravel and does not appear to be casually involved in the deterioration. The subbase aggregate is largely crushed biotite schist and granite and is from a quarry near Culpeper. Analyses of water in the quarry and of salts leached from stone piles indicate that the quarry is the probable source of the alum, and that the salts are in the subbase stone. It appears that salts concentrate under the bituminous pavement because water without the contained salts moves through the bituminous pavement, which appears to act as a semipermeable membrane. A particle count of subbase aggregate under the bituminous pavement indicates that the darker particles of biotite schist have produced local zones of capillarity in the subbase. This allows for water to be transmitted upward at certain spots, thus causing the salts to concentrate in mushroom-like masses under the bituminous pavement.

Work for the project described in this paper was done during August, September, and October 1982, and was financed by the General Crushed Stone Company. The objectives of this research were to (a) determine the cause of small mounds occurring in bituminous pavements in the area of River Ridge Estates, which is at the end of State Route 655 in Stafford County, Virginia, and (b) suggest remedies for minimizing the deterioration problem. The discussion in this paper concentrates on the causes.

The deterioration was first observed in 1981 and was brought to the attention of General Crushed Stone, which furnished the subbase aggregate. The Virginia Highway and Transportation Research Council (VHTRC) reported on the chemical composition of the substance associated with the deterioration in a memorandum dated October 1, 1981. Froehling and Robertson, Inc. (engineers and chemists), in a report dated December 31, 1981 (1), described the problem and made chemical analyses of salts that concentrated under the pavements. The Virginia Department of Highways and Transportation (VDHT) looked into the problem and took samples for investigation. In the fall of 1982 General Crushed Stone had samples of waters from the area analyzed by Environmental Systems Service, Ltd. of Culpeper, Virginia.

ROAD AND MATERIAL SPECIFICATIONS

The roads in which the deterioration occurs were constructed according to the following specifications.

1. Subbase, 6 in., type I, size no. 21A: "Type I aggregate base material shall consist of crushed stone, crushed slag, or crushed gravel; with or

without soil mortar or other admixtures. Crushed gravel shall consist of particles of which a minimum of 90 percent by weight of the material retained on the No. 10 sieve shall have at least one fractured face by artificial crushing" (2,p.99).

2. Size No. 21A consists of 100 percent passing a 2-in. sieve, 94 to 100 percent passing a 1-in. sieve, 63 to 72 percent passing a 0.375-in. sieve, 32 to 41 percent passing a No. 10 sieve, 16 to 24 percent passing a No. 40 sieve, and 8 to 12 percent passing a No. 200 sieve, according to VDHT specifications. Reports dated 1976 and 1977 of gradations of the subbase material used show gradations within the No. 21A ranges.

3. The soundness specifications for type I aggregate allow a maximum loss for 20 cycles of the freeze-thaw test (AASHTO T103) of 12 percent; for 5 cycles in the magnesium sulfate soundness test (AASHTO T104) the maximum allowable loss is 30 percent.

4. Seal or tack coat: An asphalt emulsion is "done after the surface is thoroughly compacted, cleaned of all dust, mud and foreign matter and the section to be sealed has been approved" (2,p.289).

5. Wear surface: It is a bituminous concrete plant mix, items S-5, ± 1.5 .

6. The subbase in General Crushed Stone's No. 26 crusher run and appears to be similar to No. 21A. A VDHT test form dated July 12, 1982, indicated that the stone had a magnesium sulfate soundness test loss of 17.2 percent, absorption of 0.8 percent, and Los Angeles abrasion test (AASHTO T96) loss at 500 rev. of 35.5 percent.

7. The aggregate in the bituminous pavement is a tan-colored gravel and natural sand; it is largely quartz.

OBSERVATIONS

Nature of Deterioration

The deterioration consists of roughly circular domes in bituminous pavements. The domes are from 2 to 4 in. in diameter and are up to about 1 in. high. Usually some tension cracking has occurred at the top of the domes, apparently because of stretching of the pavement when it is domed upward. The domes tend to occur in groups, with the individual domes from a few inches to about a foot apart (Figure 1). (Note the tendency of the domes to occur in between the areas of the maximum number of wheel passes. Tension cracks occur at the top of the domes.) In



FIGURE 1 Distribution of deterioration domes in pavement.

places, the domes coalesce and the deterioration becomes general. The domes tend to occur toward the middle of pavement areas and where vehicle wheels do not make many passes.

At the center of each mound (mostly beneath the pavement, but in some cases working up into irregularities in the pavement) is a mass of fine-grained, white, crystalline salt with an astringent taste (Figure 2). (Note that the white salt is in the center of the dome, and none gets into the pavement.) Where the mounds coalesce, the crystalline material is more or less continuous (Figure 3). Where there were no salt domes, no white crystals were observed under the pavement.



FIGURE 2 Typical dome pried out of the pavement.

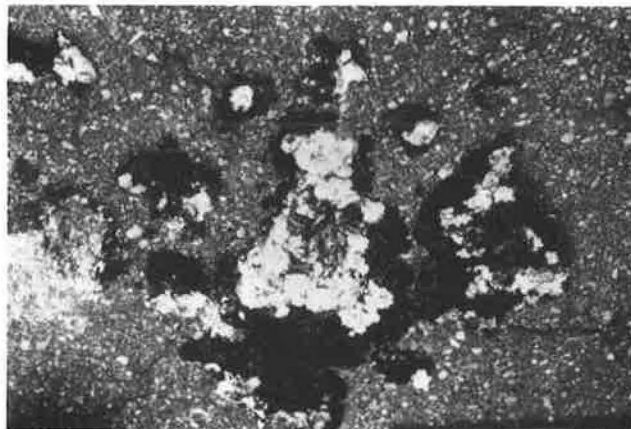


FIGURE 3 Zone of coalescing domes showing coalescing salt masses.

At two locations breached domes were observed (Figure 4). (Note that more typical unbreached domes occur around the breached dome.) Saline solution apparently had leaked through the dome, perhaps because of hydrostatic pressure from below. In each case a whitish concentration of salt was visible immediately around the dome and a damp-looking area about 6 to 8 in. in diameter ringed the dome.

The domes are what might be called "pavement salt domes" and, like salt domes that are found naturally in such places as the Mississippi delta, are caused by salt pushing upward from below. The doming in nature is caused by the upward movement of less dense salt from layers at depth penetrating the

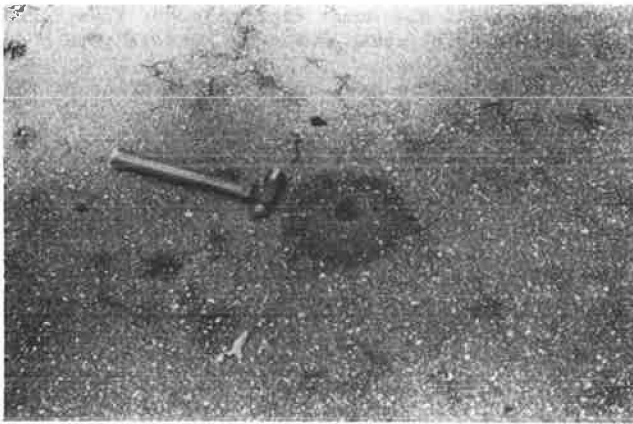


FIGURE 4 Breached dome from which salts apparently erupted to form a damp-appearing halo.

overlying sediments along vertical zones of weakness. In the present case, the salts are apparently forcing the pavement upward because of the growth of crystals.

Samples of bituminous pavement, the white salt, and base material were taken from 12 locations at two cul-de-sacs off River Ridge Lane, one called Ridge View Circle and the other Valley Lane. The samples were investigated under a zoom binocular microscope. The rock particles within the subbase under the mounds tend to be quite fine and sandy, and appear to be much finer than the original gradation. The larger particles tend to be about 1 in. across and consist of hard pieces of biotitic and muscovitic granitic gneiss and granite and deteriorated fragments of mica-schists with black, white, and tan micas. Some of the deteriorated schist contains metallic sulfides, probably iron pyrite (FeS_2), but the iron sulfide appears to be fresh. Some of the schistose particles observed were so weathered and disaggregated that they retained the form of particles only because they were held together by asphaltic material. They were, effectively, patches of sand. White crystals, about 0.125 in. long, apparently of the type associated with the deterioration, were observed within some of these disaggregated particles. In several cases the white crystalline material was found on top of the deteriorated schistose particles. The crystalline growths were not found directly on top of any fragments of granitic material.

One hundred and twenty-three particles of subbase aggregate from under the blacktop mounds were taken from the material collected on September 16, 1982. All particles were from -1 to +0.125 in. in size. The particles were counted under a binocular microscope; 118 (96 percent) were fresh micaceous granite gneiss and granite, some with hornblende. Two particles in the -0.5 to +0.375 in. range were friable and consisted of a piece of rusty, weathered granite and a piece of biotite schist; the remaining three friable particles were from -0.375 to +0.125 in. and were biotitic schist. The fines were mainly quartz, muscovite and biotite mica, and feldspar.

As a check on the relative soundness of the biotite schist and granite from the quarry, two 10-cycle magnesium sulfate soundness tests (AASHTO T104) were run in the Dunn Geoscience Corporation laboratory, one on dark aggregate particles and one on light particles. The dark biotitic particles had a 32.4 percent loss; the light granitic particles a 15.4 percent loss. Most of the granitic particles that deteriorated were somewhat weathered.

Observations at Spotsylvania Quarry

Spotsylvania quarry is of medium size and has a stripped area of red-brown saprolitic material that is about 30 ft thick. Below the saprolite is weathered metamorphic rock that is porous, locally oxidized to a reddish brown, which was derived from a mixture of granite, micaceous granite gneiss, mica schist, and graphitic schist. Iron sulfides occur in some of the rock, particularly in the graphitic and micaceous schists. The top lift of the quarry is largely in weathered rock and is about 60 ft high. The next lift is 50 ft high and is largely in the extension of the more granitic zone, which is in the first lift but is fresher-looking. The finer grained schists and graphitic rocks are less common in lower lifts. The lowest lift is 50 ft and is mostly in blocky granite and has a sump and pumping station at its lowest point.

The fresh granites, granite gneisses, and schists tend to vary from light to dark gray--the color influenced largely by the amount of hornblende or black mica (biotite). Some of the graphitic rocks are locally almost black.

Seepages of water along fractures in the rock were observed in several areas, and salts that varied from white to brownish were precipitated around the seeps (Figure 5). The seeps were most obvious at the upper two lifts, but some seepage was noted at the lowest lift. The sump pump operates intermittently at the rate of about 600 gal/min, averaging about 50,000 gal/day. The water is pumped to a surface pond that empties into a local stream. The quarry is closed during winter months, during which time the water rises to a depth of 15 to 20 ft.



FIGURE 5 Salt efflorescence around water course, upper lift, Spotsylvania quarry.

Several piles of broken stone products were observed. One pile of stone near the weigh station was reportedly gray when much of it was laid down about 4 years ago, but it is now a tannish to rusty brown. Minor parts of the pile have been in place for about 6 months and are gray. Salt precipitates were minor and difficult to see in runoff areas below the piles.

Another pile of crushed stone was observed south of the maintenance shop. The pile, which had been in place for about 2 years, showed little tannish or brownish stain and was primarily a medium to dark gray. Biotite schist was abundant, comprising about 75 percent of the pile in local areas. Abundant salts were observed around ponded areas, and the salts cemented much of the interior of the pile,

particularly at the lower one-third (Figures 6 and 7). The salt crusts had an astringent taste. Some particles of biotite schist at the base of the pile were partially disintegrated.



FIGURE 6 Alum salt-covered Virginia size No. 19 aggregate particles, base of relatively fresh appearing aggregate pile, laid down 2 years, south of maintenance shop.



FIGURE 7 Salt-covered particles from pile shown in Figure 6.

CHEMISTRY OF SALTS AND WATERS

In a letter dated October 1, 1981, Gerry G. Clemena, research scientist for VHTRC, reported partial compositions for the white crystals associated with the deterioration of the pavements. Using X-ray fluorescence, he reported aluminum, manganese, nickel, sulfur, magnesium, iron, and calcium. He noted that the sulfur was in the form of sulfate and that the salt solution was quite acidic (5 percent H⁺ equivalent). Dissolution in water released gas, which he suspected was carbon monoxide. Based on X-ray diffraction, Clemena concluded that the substance is very likely a mixture of aluminum and other metallic sulfates. He concluded that the white substance is largely Al₂(SO₄)₃·18H₂O (alum plus some pseudo-alum). Clemena apparently concluded that the Mn, Ni, and perhaps the other metals are but minor components in a substance that is essentially alum.

From their analytical work, Froehling and Robertson, Inc. (1) concluded that the white material

under the pavement (sample A) and the dissolved salt associated with the base material (sample B) had the compositions given in Table 1. A pH of 3.85 was observed, apparently in water in the base material. Mn and Ni were not observed, and Na was noted but not determined quantitatively.

TABLE 1 Analyses of Salts

Chemical Measured	Weight Percent	
	Sample A	Sample B
SiO ₂	29.75	18.40
Fe ₂ O ₃	1.54	0.87
Al ₂ O ₃	9.75	8.45
CaO	5.03	3.67
MgO	11.24	12.15
SO ₄	33.01	ND
S	11.02	13.53
LOI	31.08	ND

Note: Wet analytical work by Froehling and Robertson, Inc. (1). Sample A salt is from under a blacktop pavement, and sample B salt is dissolved from aggregate.

The chemistry, according to Froehling and Robertson, Inc. (1), appears to be somewhat more complex than that suggested by VHTRC. Their analyses are most consistent with alum family salts. However, the SiO₂ content is somewhat puzzling, is not a normal constituent of alums, and may have come from some sort of contamination.

Samples of water from several locations taken by General Crushed Stone personnel in the fall of 1982 were analyzed by Environmental Systems Service, Ltd. The report, dated September 8, 1982, is summarized in Table 2. Only the water from the sump in the quarry could potentially precipitate alum on evaporation.

TABLE 2 Analyses of Waters

Constituent	Weight Concentration (mg/L)				
	Quarry Sump	Plant Well	Pond Discharge	Black Top Plant Well	Water Dripping
Total alkalinity as CaCO ₃	80	26	5.6	68	16
pH (S.U.)	6.75 ^a	5.95 ^b	5.55 ^b	6.51 ^b	7.13 ^b
SO ₄	457	452	380	3	8
Cl	3.5	6.6	1.2	135	0.2
Al	117	0.02	0.18	0.05	0.12
Ca	92.6	73.6	69	1.09	1.13
K	21.2	10	13.2	1	0.7
Mg	40	50	31	2	0.9
Na	40	25	40	6.4	13

Note: Water analyses were made by Environmental Systems Service, Ltd. Locations are all at the Spotsylvania plant of General Crushed Stone.

^aAt 26°C.

^bAt 25°C.

Samples of the white salts taken by the author on September 16, 1982, were analyzed by the New York State Department of Health (NYSDH), which has made hundreds of analyses of saline waters in recent years in connection with another Dunn Geoscience project. The results are given in Table 3.

DISCUSSION OF CHEMISTRY

The waters that were analyzed have different histories and are from different locations and hence vary considerably (of course, they are also reported

TABLE 3 Analyses of Salts

Compound or Element	Weight (mg/L)		
	Salt on Stone ^a	GCS-C-4 ^b	GCS-D-1 ^c
Al	7,800	30,800	44,600
Cl	200	300	307
SO ₄	120,000	354,000	415,000
SiO ₂	24	63	48
Ca	50	70	70
Fe	280	1,010	1,480
Mg	13,900	46,800	52,300
MN	1,900	7,540	4,920
K	780	46	46
Na	1,400	108	340
Total	—	440,737	519,111

Note: Analyses were done by NYSDH.

^a This sample is from the size 19 pile near the maintenance shop.

^b This sample is from the cul-de-sac at the end of Ridge View Circle.

^c This sample is from the cul-de-sac at the end of Valley Lane.

differently). The most critical water analyses are of the quarry sump, the water dripping, and the salts. Although the concentrations are considerably different, the ratios of sulfates and the metals are similar (i.e., evaporating the dripping water would produce a composition that is similar to the sump water, and evaporation of the sump water could produce salts of the type observed). These waters are characterized by high sulfate and high Al, Mg, and Ca relative to sulfate. Evaporating water of this composition could produce a salt similar to that observed under the bituminous pavement roads.

The compositions of the pond discharge water and the water from the well at the plant are similar to that of the sump water, except for the much lower Al content. There is no explanation for this difference, although Al concentration is sensitive to pH and oxidation potential causing precipitation of aluminum hydroxides.

The white salt under the road, according to VHTRC and NYSDH, is primarily an aluminum magnesium sulfate as is the salt taken from the bottom of the stone pile south of the maintenance shop at the quarry. The salt appears to be closest to the magnesium alum, pickeringite [MgSO₄·Al₂(SO₄)₃·22H₂O]. Dana and Ford (3,p.764) state that pickeringite is "formed by the weathering of pyrite-bearing schists." Variations in the composition of alum salts are quite common, and there appears to be considerable room in the lattice for such miscellaneous ions as Mg, Ca, K, and Na.

The compositions of the water in the sump and in the drip are probably highly diluted versions of the water in the rock. Rainwater and water that moves through the red-brown saprolitic overburden are probably fairly pure and more like the water of the well at the blacktop plant (Table 2). Such water seeping through fractures, and rainwater falling directly into the quarry, must considerably dilute the salt-rich water in the rock.

The changes that occur in the rock below the saprolitic overburden may be of the following type. Pyrite (FeS₂) reacts with water and oxygen to form ferrous sulfate and sulfuric acid:



The sulfuric acid along with additional acids from normal air (carbonic, sulfuric, and nitric mostly) attack the feldspar, biotite, and other silicates to remove Al, Mg, and Mn along with minor alkali. With decrease in acidity as the acids are used up, the ferrous iron (Fe⁺²) oxidizes and precipitates as Fe(OH)₃, thus staining the rock brown. In

humid, warm climates the Al⁺³ is usually slightly more mobile than Fe⁺³, as indicated by the tendency for iron oxides to concentrate above aluminum oxides in weathering zones.

The chemical process of forming the weathered saprolite from silicate rock is slow, and the currently observed conditions have required millions of years of weathering. However, surface oxidation of iron sulfides usually occurs more rapidly than silicate weathering and may occur in relatively few years, geologically speaking. Even this process usually requires prolonged periods (many thousands of years) for completion. Apparently little oxidation of iron sulfide occurs under the pavement because unoxidized, fresh, yellow iron pyrite was observed in some of the sandy material in the subbase. Apparently any alum in the subbase was brought in with the aggregate.

The acidity of the waters varies because of dilution, chemical reactions, and the acidity of rainwaters. Keeping Al⁺³ in solution requires an acidic environment because acidity decreases Al⁺³, hydrolyzes, and goes to Al(OH)₃, which may precipitate or remain in suspension as a colloid.

GENERAL DISCUSSION AND CONCLUSIONS

The domes in the bituminous pavements are clearly associated with the growth of magnesium alum sulfate crystals. The alum masses grow at the interface between the subbase and the asphaltic pavement, preferring, possibly, to grow above particles of deteriorated rock in the base course. Sorptive effects enhanced by salts and the growth of the alum crystals within the schistose particles probably combine to cause their deterioration, thus breaking the particles down to a sand in many cases. (No sound pieces of biotite schist were observed in the base course aggregate.)

Precipitation of salts is often the result of a salt solution becoming supersaturated because of evaporation of the solvent. Quite probably evaporation can only occur off the top of the pavement. It is clear that the salt-rich water does not usually reach the surface of the pavement because salts are not visible at the surface (except where a mound has been breached), nor are salts observed within the pavement. In fact, the pavement does not appear to lose any integrity, which it probably would do if salts were growing within it.

Because water gets through the blacktop but salt does not, the pavement is apparently acting as a semipermeable or relatively impermeable membrane that transmits water but not its contained salts. When water moves to the surface of the pavement to evaporate, the salt apparently cannot get through, is left behind, and concentrates. Very probably the particles of mica schist start deteriorating before the salts saturate, and these particles are reduced to sand-size debris. The virtual absence of mica schist particles below the salt crystals is an indication of the probable efficiency of the deterioration process. The zones where such particles existed then become zones where capillary water is pulled to the top of the subbase after the water level has lowered around these sandy debris zones. Kovacs (4) calls such a zone the open capillary zone. Figures 8 and 9 show how the process of deterioration may operate.

In Figure 8 note the nature of water in the soil-moisture zone (4). The critical area during salt concentrations in subbase road conditions appears to be Kovacs' open capillary zone, where concentrations of finer materials cause water to move upward more readily. Figure 9 shows that when the

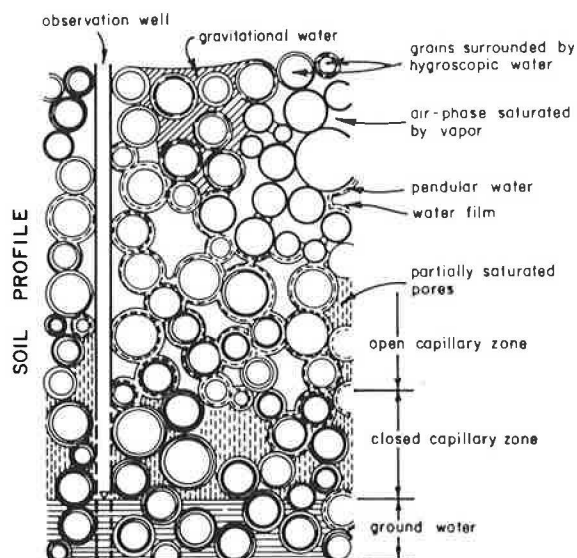


FIGURE 8 Types of water in soils.

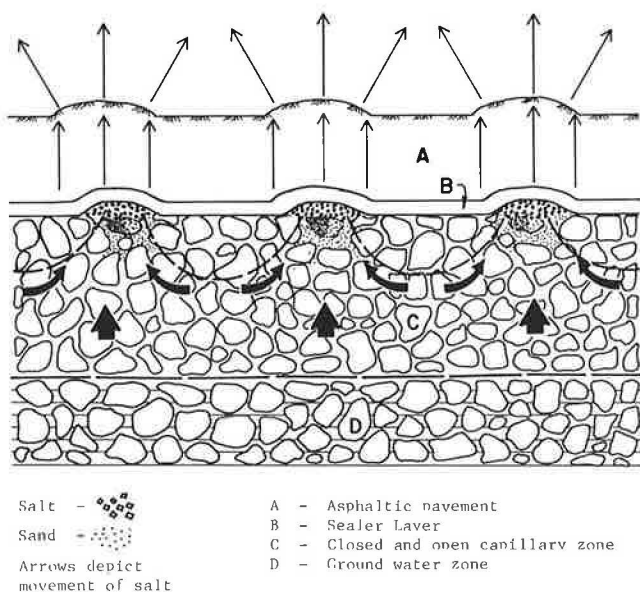


FIGURE 9 Mechanism of salt doming.

unsound particles under the pavement have disintegrated, they become, effectively, zones of fine sand within the subbase. During dry seasons when the level of groundwater drops to zone D, these sand patches become open capillary zones (see Figure 8) at the top of the closed capillary part of zone C. Evaporation off the surface of the pavement is apparently concentrated above these zones. Salt begins to precipitate directly under the seal as water without salt is pulled through the pavement to evaporate from the surface. The growing salt crystals dome the pavement upward.]

The saline solution above these capillary zones

becomes supersaturated and the contained alum salts precipitate. Cooling at night may possibly be a factor that starts the initial crystallization. The original points or zones of supersaturation appear to be above what were micaceous particles. Thus crystallization appears to begin at the top of the particles where they are in contact with the pavement where the salts, in effect, are filtered from the water. Once crystals begin to grow, they grow upward as water evaporates from the top of the pavement. This process presumably continues until all available salt in the base material is used up.

The particles of micaceous (and/or graphitic?) rocks disintegrate as the micaceous particles warm and cool in the presence of saline waters. This sort of accelerated deterioration is common and is the probable cause of much of the deterioration of rock in the New York State freeze-thaw test in 10 percent NaCl solution. It has been shown that the saline solution in many of the least sound rocks in New York State never freezes because no heat of freezing is detected in differential thermal analysis. The deterioration process is related to increased expansion and contraction on cooling and warming in the presence of saline solution (5,6).

Crystals of salt growing within the deteriorating particles may accelerate the process similarly to the deterioration of rocks in sulfate soundness tests (although the subbase material may never dry completely as in the tests). The particles of mica-rich rocks are so disintegrated by this process that much of the micaceous sand under the pavement may well result from the breakdown of such rocks. The deterioration process is so effective that the only mica schist particles that were seen were friable and readily disintegrated when handled.

Although salt domes of this type have apparently been observed elsewhere in Virginia, their full extent is not known. Whether such a process might operate in D-cracking of portland cement concrete pavements, as has been suggested (7), is also not known.

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