FURTHER EVALUATION OF DEICING CHEMICALS

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Severe corrosion of reinforcing steel and deterioration of concrete in reinforced concrete bridge decks caused by salt applied to the decks to control ice and snow have prompted a search for a noncorrosive deicing chemical suitable for maintenance use. Seventeen candidate chemicals have been evaluated. Tetrapotassium pyrophosphate exhibited good frost-preventing properties, and 2 years of limited field testing on bridge decks is reported. A skidding-car method of determining coefficient of friction is evaluated. The results of sodium formate used as a deicer and its detrimental effect on concrete are noted.

•CONSIDERABLE attention (1, 3, 4, 5, 11) has been given to the problem of bridge deck deterioration. In general, the results have shown that one of the most significant causes of rusting of the steel and spalling of the concrete is the use of salt for snow, ice, and frost control on bridge decks. In this respect, studies have been made to determine the feasibility of (a) the heating of bridge decks, thus reducing or eliminating the need for salt to prevent frosting or icing; (b) the use of waterproof membranes so that salt is prevented from coming in contact with the concrete; (c) the use of polymers or other penetration-type sealers to make concrete itself sufficiently waterproof so that chlorides may not be able to penetrate the concrete in a short time; and (d) the use of chemicals other than chlorides that not only will control ice and frost but also will be noncorrosive to either the steel embedded in the concrete or the concrete itself (2, 6, 7, 8, 9).

In a previous study, 17 different potential deicing chemicals were subjected to various laboratory and field tests (11). Of these 17 chemicals, only sodium formate and tetrapotassium pyrophosphate were found to be reasonably effective alternative deicing chemicals and yet not any more toxic or ecologically harmful than sodium chloride.

As a result of laboratory studies, tetrapotassium pyrophosphate (TKPP) was tested by highway maintenance forces at selected bridge locations. These bridges were "salted" to prevent frosting and not for the purpose of snow and ice removal. Because TKPP costs about 15 times as much as salt, its use was considered most appropriate for those locations where only the bridge deck is "salted".

Initially the work was oriented primarily toward a laboratory search for alternative deicing chemicals, with research personnel performing a minimum field evaluation to confirm the test results. This report presents the results of the use of the chemicals by maintenance personnel to determine if there were any operational difficulties. This report is the finalization of the original project. It gives the results of 2 years of field testing at selected locations, along with further evaluations of skid resistance and corrosion.

LABORATORY TEST DETAILS

PCC Durability

In order to determine to what degree the various deicing chemicals could adversely affect concrete, 84 portland cement concrete cylinders ($4\frac{1}{2} \times 9$ in.) with embedded gauge

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plugs at each end were subjected to alternate immersion tests. Changes in length and observations of physical distress were noted. The cylinders were made from 2 mix designs; one had 4½ sacks of cement per cubic yard at 2¾-in. slump and 5.8 percent entrained air, and the other had 7 sacks of cement per cubic yard at 4-in. slump with 4.5 percent entrained air. All cylinders were cured for a minimum of 28 days by complete immersion in tap water at room temperature, then oven-dried at 140 F for 28 days in a forced-draft oven. In one series the specimens were alternately completely immersed in the solutions for 7 days followed by oven-drying 7 days at 140 F. Changes in length and weight were measured and visual distress was noted after each cycle. In a second series, other specimens were continually partially immersed (2 in.) in the solutions with no oven-drying. Figure 1 shows the results of alternate immersion and oven-drying on length change for each of the solutions used. The following is a summary of these tests.

1. Both 4½- and 7-sack concrete cylinders were not significantly affected after 41 cycles of wet-dry tests when alternately submerged in tap water.
2. Concrete cylinders cycled and fully submerged in a saturated sodium chloride solution were first observed to have scaling of the surfaces of all cylinders after the third cycle. A progressive deterioration of the surface continued for approximately 80 cycles. After 80 cycles, the deterioration was so severe that the test was discontinued. Typical deterioration of the 7-sack concrete that was alternately immersed in the sodium chloride solution is shown in Figure 2.
3. After 25 cycles in a 60 percent solution of TKPP, no deterioration was evident on either the 4½- or 7-sack concrete cylinders.
4. After 25 cycles in a saturated urea solution, only negligible surface scaling was observed on the 4½- and 7-sack concrete cylinders.
5. No adverse effect was noted on the cylinders that were partially immersed in tap water, saturated sodium formate, or saturated sodium chloride.
6. After 3 cycles of complete immersion and oven-drying in the sodium formate solution, the 7-sack concrete exhibited severe distress (Figure 3).

Sodium Formate and Asphalt Concrete

Asphalt concrete briquets were cycled between 7 days of immersion in a saturated sodium formate solution and 7 days of drying in a 140 F oven. One sample that was made up of approximately a 1¼-in. thick layer of asphalt concrete on top of a 1-ft square concrete block was also cycled. After 5 alternate wet and dry cycles, no serious deterioration occurred in the asphalt surfacing or briquets. There did not appear to be any loss of bond between the asphalt concrete and the concrete block. There was, however, severe deterioration of the exposed surface of the 1-ft square concrete block.

Effect of TKPP on Glass and on Asphalt Concrete

Preliminary tests on automobile windshield glass indicate that 30 percent solution of TKPP (with a corrosion inhibitor of sodium metasilicate) had no effect on the tested glass.

A limited test on asphalt concrete briquets that were cycled between immersion in a 60 percent TKPP solution and drying in a 140 F oven showed no apparent undesirable effects.

TKPP and the Corrosion of Steel

Steel immersed in a 5 percent solution of TKPP with a corrosion inhibitor consisting of 2 percent sodium metasilicate results in an insignificant corrosion rate of 0.053 mils per year. A 3 percent sodium chloride solution resulted in a corrosion rate of approximately 4 mils per year, and in distilled water the steel corroded at a rate of 6 mils per year.

It should be pointed out that TKPP is apparently not readily absorbed by concrete. Therefore, the corrosivity of this chemical to steel would probably be limited to bare steel on spray equipment or vehicles.

Figure 1. Elongation plot for concrete cylinders cycled in various saturated solutions.

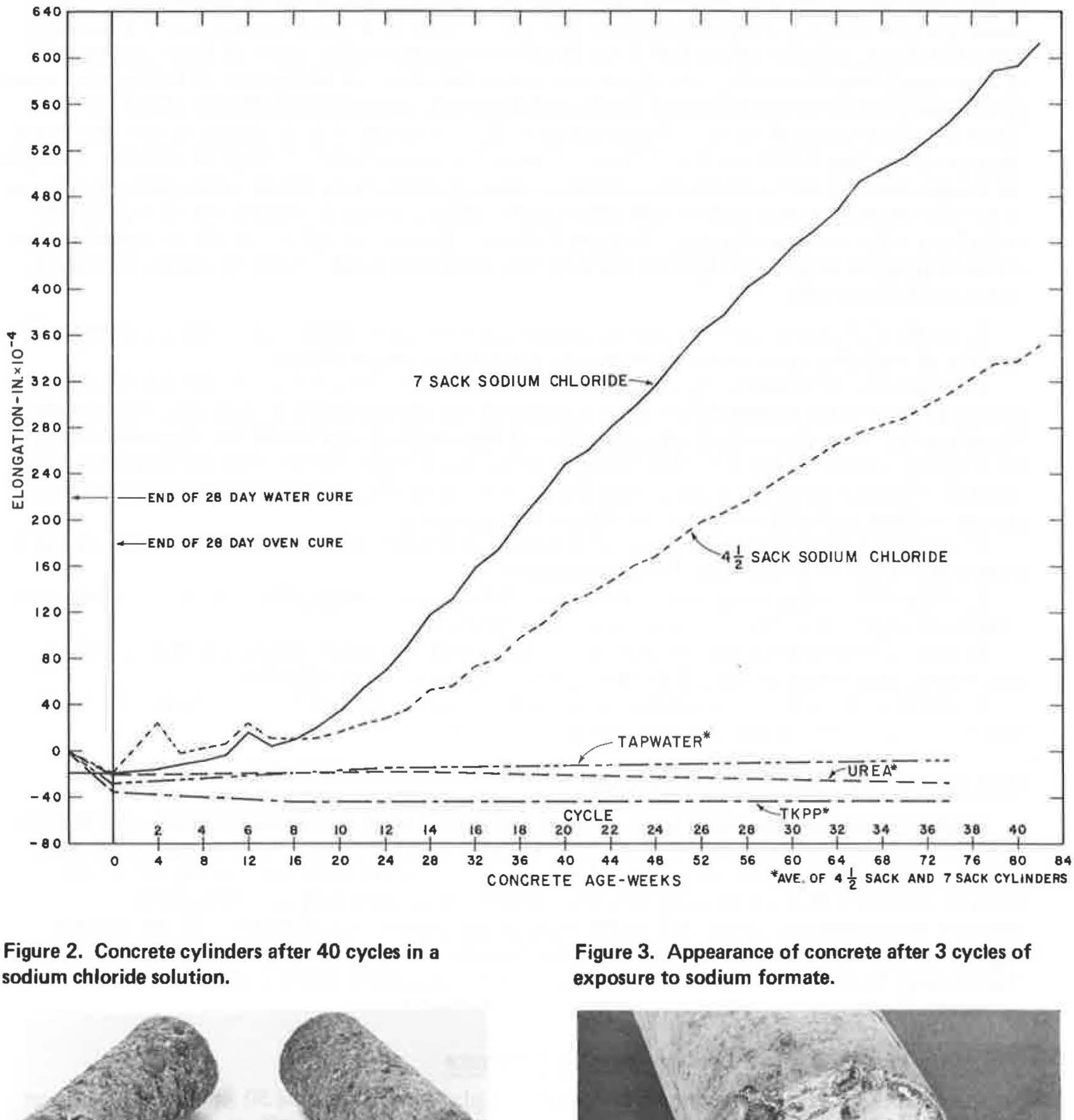

Figure 2. Concrete cylinders after 40 cycles in a sodium chloride solution.

Figure 3. Appearance of concrete after 3 cycles of exposure to sodium formate.

FIELD TRIAL OF TETRAPOTASSIUM PYROPHOSPHATE

The chemical TKPP underwent field trials during the winters of 1971 and 1972 in 7 geographic areas of California. The test areas included locations where only the bridge decks would become frosty and there was no snowfall and other areas where heavy snow and icing occurred. In the latter locations, TKPP was not effective in this test series because of the low temperatures encountered (below 25 F).

The following is a summary of the observations concerning the effectivness of TKPP in the various locations.

1. Russian River, Bridge 10-182, elevation 710 ft—TKPP was applied at a rate of 0.01 lb/ft^2 of deck and remained in place for 15 days. No frost occurred after application at this location. The chemical appeared to be "available" because there was evidence of formation of TKPP crystals upon evaporation of the water, and the pavement appeared wet in the early morning due to the deliquescent effect of the chemical. No evidence of pavement slipperiness was noted. A "wet" appearance of the deck has been evidence that TKPP has prevented or controlled frosting.

2. Grass Valley Creek, Bridge 5-10, PCC deck, elevation 2,200 ft, and Bridge 5-13, AC overlay, elevation 2,110 ft—A spray solution of 30 percent TKPP was applied at a rate of 0.01 lb/ft^2. Two days after the application, frost conditions were present as the temperature reached 27 F and the relative humidity was about 100 percent. The decks did not frost over; however, they were wet due to the deliquescent effect of the chemical. On both of these structures, at a later date, the TKPP powder was applied in conjunction with $1\frac{1}{2}$ yd^3 of sand. The wet sand froze to the bridge decks.

For these same decks, the normal application of chemical solution was applied and was reported to be effective for a period of 7 days because of the early morning wet-appearing decks. A second application of the chemical was made, and 3 days later the temperature was 22 F and frost was observed on the ground adjacent to the bridges. The bridges at this time were frost-free but wet-appearing. No pavement slipperiness was observed.

On Bridge 5-10, the average skid distance on dry pavement was 4.5 ft, while on wet pavement containing TKPP the average distance was 4.8 ft. On Bridge 5-13, the average skid distance was 3.5 ft on dry pavement and 4.5 ft on wet pavement containing TKPP.

3. Sacramento Weir, Bridge 22-32 with overlay—A 30 percent solution of TKPP was applied at a rate of 0.01 lb/ft^2 of deck surface. Immediately after applying the chemical, it was found that a pickup truck could quickly stop on the bridge. However, within 10 minutes after applying the chemical, a light application of sand was placed on the bridge deck. The sand caused the pickup truck to slide on the bridge deck when the brakes were applied. As soon as traffic whipped the sand from the traveled way, the deck was no longer slippery. Sand was not reapplied with the deicing chemical at this location.

Two days after the application of the chemical, the bridge was under frost conditions as the temperature was 29 F and frost was observed on the guardrails. The bridge deck had a wet appearance. It was necessary to salt and sand nearby bridges. At one time on this bridge, 1 day after the application of the chemical, the maintenance foreman reported that the pavement was slippery when the pavement appeared wet. The early morning temperature was about 27 F. It is possible that the chemical was too heavily applied when considering the residual chemical that was still in place on the deck. It was effective in preventing frost during frost conditions on this deck for a maximum period of 12 days when there was no rainfall.

4. Wheatland, Bear River Bridge, PCC deck, elevation 108 ft—One standard application of chemical was observed to be effective on this bridge for an estimated period of 19 days. Even though this bridge showed evidence of frost on the rails but not on the deck, during this time period another bridge about 7 miles away received 20 applications of salt and sand. This bridge had an average skid number SN_{40} of 46, while the skid distance on the dry deck was 4.8 ft. When wet with plain water the average distance was 6.4 ft, and when wet with a TKPP solution the average distance was 6.3 ft.

5. Hemet Valley Creek, Bridge 56-184, AC overlay, elevation 4,360 ft—One standard application of chemical was placed on this bridge deck at time intervals of 6, 9, and 7 days. During this period, the deck had a wet appearance in the early morning, with no

frost present on the deck. The minimum morning temperature was about 24 F for an estimated 4 days. Adjacent bridges required salt and sand for frost prevention. No slipperiness of the deck was observed by the maintenance personnel.

6. Bradley Overhead, Bridge 39-44, District 10, AC overlay, elevation 170 ft—TKPP was applied and thought to cause slipperiness. Use of the chemical was discontinued.

7. Sutter County, G. S. Housely Bridge, corrugated steel plank deck with AC riding surface—The bridge is a county-owned bridge that does not normally receive deicing chemicals. Therefore, TKPP was applied only to the northbound lane and the southbound lane was left untreated as a control. The typical method of applying the chemical is shown in Figure 4.

Two days after TKPP solution was applied, the southbound lane was frosty (no chemical) while the treated northbound lane was frost-free but wet. The air temperature was 29 F and the relative humidity was 90 percent. The typical appearance of this bridge during the test is shown in Figure 5.

The structure was maintained in a frost-free condition during the entire test period. The early morning temperatures did not fall below about 24 F.

The effect of using the chemical on the skid resistance of this deck surface is given in Table 1 for AC overlaid bridge deck.

A few trial skid tests using the skidding-car test were made on the frosty side of this bridge. It was found that there was no significant difference in the skid distance between the frosty or wet bridge deck. However, this would not be true if the deck were icy or had a layer of snow. In this case, the frost apparently caused little danger to traffic as far as skidding was concerned.

FIELD SKID TESTING

Towed-trailer skid tests were performed using solutions of sodium chloride, TKPP, and urea on both concrete and asphalt pavements. Work with the towed skid test trailer (ASTM test method E 274-65T) showed that this method was not applicable for evaluating the effects of different solutions on pavement friction. This was because the test method requires the application of water, which overshadows the presence of the chemical. A skidding-car method was determined to be the best test available to maintenance superintendents for evaluating the effects of the solutions on pavement surfaces (10). Theoretical analysis and field tests suggest that if a vehicle that is traveling at 10 mph can stop in less than 8 ft of locked-wheel braking, the pavement can be regarded as not being slippery. Limited test results using the skidding-car method indicate that individual applications of up to 0.01 lb/ft^2 of 30 percent TKPP solution will not significantly affect the slipperiness of the roadway. However, much depends on the surface texture of the pavement, because even plain water can be a hazard with a smooth pavement.

Initially, the field tests of the TKPP solution encompassed the application of sand at the same time. It was found that the sand application itself caused the deck to be "slippery" and this operation was discontinued. Apparently sand is effective for packed snow and ice but not necessarily satisfactory for wet or frosty conditions except as a "blotter".

Because the commonly used skid testing devices did not show the true effect of the chemical, it was decided to try the skidding car method (10). This method consists of measuring the length of skid of a standard sedan with locked wheels. The automobile was equipped with a powder-actuated marking device connected to the brake pedal. The test speed used was 10 mph. The distance between a chalk mark on the pavement occurring at the instant of wheel lock and another one made after stopping is the measure of skid resistance. The specially mounted speedometer used to more easily control the test speed is shown in Figure 6; Figure 7 shows the special marking devices mounted on the automobile bumper.

After several trials, it was decided that a "go, no-go" test result for the effect of the deicing chemical on the pavement should be used. The criteria for the test were that the application of the chemical should not cause a serious degradation of the coefficient of friction of the pavement surface and the maximum average stopping distance

Figure 4. Application of 30 percent solution of TKPP.

Figure 5. Sutter County test bridge: 30 percent TKPP has been applied to right side of bridge; note frost on left side.

Table 1. Results of skid tests.

	Average Skid Distance (ft)[a]			
Bridge Deck	Dry	Wet (Water)[b]	Wet (Chemical)[c]	Wet (Chemical-Humidity)[d]
PCC	4.7 (13 tests)	6.3 (8 tests)	6.3 (20 tests)	6.6 (2 tests)
AC overlaid	5.4	5.7	6.8	7.1

[a]Braking distance when vehicle velocity is 10 mph.
[b]Sprayed to have continuous film of water.
[c]Immediately after applying 0.01 lb/ft^2 of TKPP.
[d]Deliquescent effect of chemical in producing a wet deck during high humidity.

Figure 6. Special speedometer mounted adjacent to the steering wheel to better control the 10-mph test speed.

Figure 7. Two-shot marking device mounted on test vehicle.

should not exceed 8 ft. In this regard, the following equation was used to calculate the maximum allowable stopping distance from a vehicle velocity of 10 mph:

$$f = \frac{V^2}{30S} \tag{1}$$

where

- V = miles per hour (10);
- S = distance traveled before stopping, feet; and
- f = coefficient of friction.

A value of 0.40 for the coefficient f was selected as being reasonably good.

Calculation using a speed of 10 mph and an f of 0.40 shows that the pavement would have a sufficiently great skid resistance if the vehicle does not skid more than about 8 ft when braking from a velocity of 10 mph.

As indicated by Table 1, the greatest influence on the skid distance on a portland cement concrete deck was whether it was wet or dry. In all cases, however, the average skid distance was less than 8 ft, and therefore the deck surface of these bridges was considered to be of adequate roughness for safe application of water or the deicing chemical used (TKPP).

When TKPP was applied with a hand sprayer on a relatively smooth asphalt-covered bridge deck, 1 skid out of 5 was greater than 8 ft. A series of 4 tests where the bridge deck surface was wet (from high humidity) resulted in 1 skid out of 4 being over 8 ft. In this case the very old irregular surface of the bridge combined with the hand application of the chemical produced puddles of chemical and water on the surface and resulted in some of the tests exceeding a distance of 8 ft. In some cases where skid resistance of the deck surface is already borderline, the application of the deicing solution (or water) can lower skid resistance below the desired level.

If the skid test shows that a wet or dry deck can result in a skid distance exceeding 8 ft, then the application of any liquid, including plain water, can create a hazard. For example, on the Bear Creek Bridge in District 10, the average skid distance on the dry deck was 11 ft, and when wet with a TKPP solution, the average distance was 22 ft.

The skidding-car test can be used in other ways. For example, in 1 isolated test, the effectiveness of multiple applications of sand on skid resistance on compacted snow was investigated. It was found that there was no significant improvement on skid distance when sanding was done 3 times instead of once.

It is probable that the skidding-car test may be useful in determining when to request the skid trailer to determine the skid number of a pavement or to set up a priority for the chip sealing of a pavement to improve the skid number.

DISCUSSION OF RESULTS

Based on this study, it appears that in some cases salting and sanding of bridge decks may be done as a matter of "insurance" rather than as a result of actual need. For example, in one maintenance area it was found that the actual application rate of salt was an average of 0.001 lb/ft^2 of deck area. This amount of salt is ineffective for the prevention of hazardous frost conditions. However, the multiple application of the salt is the cause of much bridge deck deterioration.

Based on a preliminary study, TKPP appeared to be an effective frost-preventing chemical for temperatures greater than about 25 F on bridge decks. In addition, if there was no rainfall, it was found to be effective for periods of up to 2 weeks without reapplication.

In this second study, it was difficult to evaluate the relative effectiveness of the TKPP on California state highway bridges. This is because, for safety reasons, the chemical had to be applied to the whole surface of the bridge deck. Therefore, even though conditions were such that frost would form on the rails but not on the deck, testing of frost prevention was inconclusive. No "control" area could be provided wherein part of the deck would not receive application of the chemical. However, testing on half of a county bridge deck confirmed that TKPP was effective in preventing frost.

These results do not negate the fact that in previous work an application of the liquid TKPP to a dry pavement would, by itself, melt about 1 in. of ensuing snowfall. However, because of the high cost of TKPP, it is only considered for use on bridge decks to inhibit formation of frost where temperatures rarely go below 25 F. Chloride-type salt still remains the most economically feasible method for controlling ice on the many miles of highway pavement in snow areas.

The tests show that a 30 percent solution of TKPP applied at a rate of 0.01 lb/ft^2 of bridge deck surface is an effective frost preventative in mild climates. However, whether or not the chemical affects the slipperiness of the pavement more than water does depends on the smoothness of the pavement and perhaps the thickness and hardness of the frost layer if it is present.

At present it is not appropriate to make a cost comparison between the use of salt and TKPP to control frosting of decks. In one maintenance area it is estimated that, because of the lasting effect of TKPP, a maintenance crew could reduce the number of salting patrols by more than 50 percent by using the TKPP solution. Also, the patrols could be made during normal working hours instead of beginning them at 4:00 a.m.

It should be emphasized that TKPP is only being considered for those locations that are free of ice and snow. Such areas are normally the valley locations in California, where only the bridge deck frosts over and requires the use of a chemical to control frosting.

In the previous work it was observed that the most effective use of any tested deicing chemical was to apply it in liquid form before the conditions of frost and snow. Once the snow was packed, however, crystals of a deicer were needed to penetrate and break up the physical structure of the ice or snow.

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