Effects of Lignosulfonates in Deicing Salts on the Penetration of Chloride Ions into Concrete

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Lignosulfonates are being used as corrosion inhibitors in highway deicing salts. Corrosion reductions of 50 to 80 percent have been reported for mild steel. Lignosulfonates act as both cathodic and anodic inhibitors. They remove oxygen from solution, form insoluble material on the corroding surface, and use its reducing ability to prevent oxidation of ferrous iron to ferric. Although lignosulfonates in deicing salts would be expected to protect exposed rebar in concrete, experiments were run to measure corrosion inhibition on rebar exposed by microcracks in concrete, and in undamaged concrete where corrosion occurs by chloride diffusion. Mortar blocks with cracks leading to the embedded mild steel electrodes were soaked in 3 percent sodium chloride and 3 percent magnesium chloride solutions, with and without 0.75 percent lignosulfonate. After 6 weeks, electrochemical measurements showed a 70 percent reduction in corrosion for the solutions with lignosulfonates. Wiss-Janey concrete test blocks were treated weekly for 1 year with 15 percent sodium and magnesium chloride solutions, with and without 3.75 percent lignosulfonate. Chloride penetration data indicated substantially lower chloride levels for blocks treated with salt solutions containing lignosulfonate. This experiment was repeated using small mortar cylinders that were treated with 3 percent sodium, magnesium, and calcium chloride solutions, with and without 0.75 percent lignosulfonates. Significant reductions in chloride levels were observed for samples treated with lignosulfonates. The proposed mechanism is the precipitation of lignosulfonates on or with calcium hydroxide to seal the pores in the surface. Depending on conditions, the life span of undamaged reinforced concrete structures could substantially increase if lignosulfonates were added to deicing salts.

Lignosulfonates, which have been used for many years in concrete admixtures as a water reducer, are now being added to road deicing salts to reduce their corrosiveness to mild steel (1–4). Lignosulfonates, mixed with rock salt, small amounts of magnesium chloride, and liquid magnesium chloride, have been used as inhibited deicing salts in 14 states (5–10).

Corrosion rate reductions of 50 to 80 percent have been demonstrated by coupon methods, polarization resistance, potentiodynamic scans, and cyclic potentiodynamic scans by Dr. Hagar at the University of Washington (unpublished data). These results have been confirmed by several laboratories (8–10).

All these various methods yield similar percent reductions in corrosion rates even though the values obtained by the different measuring methods may vary. Typically, a 3 percent sodium chloride solution with 0.75 percent calcium lignosulfonate yields a 60 percent reduction in corrosion rate compared to untreated salt for an aerated system as might be found using periodic coupon dipping, stirring, or salt spray. If the corrosion environment had restricted oxygen transport, as would be found in an unstirred solution or in a crack in concrete, reductions up to 80 percent could be expected.

Lignosulfonates appear to act as corrosion inhibitors by a combination of three different mechanisms. In solutions, lignosulfonates react with dissolved oxygen, removing it from solution and thereby inhibiting the cathodic reduction reaction at the surface of the metal. Salt solutions with 1 to 2 percent lignosulfonate have low measured oxygen content. Lignosulfonates react with the forming corrosion products to give an insoluble layer that prevents the migration of ferrous ions from the reaction site and oxygen to the reaction site, which inhibits both the anodic and cathodic reactions. Infrared spectra of corrosion products scraped off the metal surface shows the presence of lignosulfonates. Cyclic potentiodynamic scans using mild steel electrodes in deicing salts with lignosulfonates have shown that lignosulfonates lower the pitting tendency by about 66 percent.

The ability of the lignosulfonate to coat the corrosion site is proposed to account for this action. The third mechanism is the result of the reducing properties of lignosulfonates, which inhibit the oxidation of ferrous iron to ferric (Dr. Hagar, unpublished data). This mechanism is readily observed in corrosion experiments where the coupons with the lignosulfonate have a black coating, whereas those without are red (indicative of ferric hydroxide). Lignosulfonates appear to act as rust converters changing red rust to black rust.

Lignosulfonates in deicing salts should inhibit corrosion of exposed rebar in concrete structures if the mixture has easy access to the metal surface, that is, to regions where bulk water can reach the metal surface. The objective of this work was to first determine the effectiveness of lignosulfonate in reducing corrosion when access is by microcracks in the surface, which travel to the rebar. The second objective was to find out if lignosulfonates would benefit undamaged concrete when corrosion of the rebar is the result of chloride ion diffusion.

CORROSION INHIBITION-CRACKED MORTAR

Mortar cylinders were prepared from one part Type I/II portland cement to two parts sand at a 0.4 w/c ratio and 6 percent air entrainment. The cylinders were 2.7 cm in diameter and 8 cm long with a 0.5-cm-diameter nail cast in each to simulate reinforced concrete. On curing, small hairline cracks formed,

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that were assumed to travel to the embedded nail. The top half of the cylinder and all but the tip of the protruding nail were painted with epoxy paint. The 5-month-old mortar cylinders were submerged halfway into 15 percent sodium and magnesium chloride solutions, with and without 3.75 percent lignosulfonate at pH 7. The corrosion currents were measured using a potentiodynamic scan by the Tafel technique with an EG&G Princeton Applied Research Model 273 potentiostat with Model 342 computer system.

The results of the scans in Table 1 present approximately a 70 percent reduction in corrosion current for 15 percent magnesium chloride with 3.75 percent lignosulfonate after 2 and 6 weeks, and for 15 percent sodium chloride with 3.75 percent lignosulfonate after 6 weeks, compared with salts with no lignosulfonates. This is the amount of corrosion inhibition that was expected on the basis of previous coupon and electrochemical studies.

CORROSION INHIBITION ON UNDAMAGED CONCRETE

Lignosulfonates in deicing salts will inhibit the corrosion of rebar if the lignosulfonates can reach the surface of the metal. Using the Wiss-Janey test procedure (11), concrete blocks were prepared and treated with deicing salts, with and without lignosulfonates, to see if corrosion inhibition could occur when access to the rebar is by diffusion through the concrete.

The test blocks were prepared from a commercial sack concrete mix using the amount of water specified. They were 17.8 cm × 30.5 cm × 30.5 cm (7 in. × 12 in. × 12 in.) with two layers of rebar. The top set of rebar was 2.54 cm (1 in.) from the surface. Salt solutions (15 percent) with and without 3.75 percent calcium lignosulfonates were ponded on the blocks weekly for 1 year. The solutions were renewed on Mondays and removed on Fridays, and the surface was rinsed with plain water. The potential between the rebar layers, the copper to copper sulfate electrode potential between the surface and the first rebar level, and the ac resistance between rebar layers were measured weekly.

Only the test block treated with sodium chloride showed electrical activity. The potential between the rebar levels became more negative after the 1st week, maximizing at −700 mv in 5 weeks. In 12 weeks, the potential was almost back to zero. Because none of the other blocks changed, it was suspected that the sodium chloride test block had a passage to the rebar.

The test blocks were then analyzed after 1 year for chloride penetration. The blocks were cut in half and samples were then drilled out at different depths. The results for the 15 percent sodium chloride blocks, with and without 3.75 percent calcium lignosulfonate, are shown in Figure 1; the magnesium chloride blocks are shown in Figure 2. Although both sets of data show a large amount of scatter, the blocks with lignosulfonate present showed significantly decreased levels of chloride.

Chloride diffusion was reduced by about 50 percent. That degree of reduced penetration is significant in terms of lifetime of a bridge. Additional tests using mortar cylinders were run to confirm this effect.

The cylinders were 6 cm in diameter and 9 cm long. The mortar was prepared with one part Type I/II portland cement and two parts sand with a 2.4 fineness modulus at a 0.4 water/cement (w/c) ratio. Air entrainment was 6 percent. After sitting in the mold for 2 days, the mold was removed and the
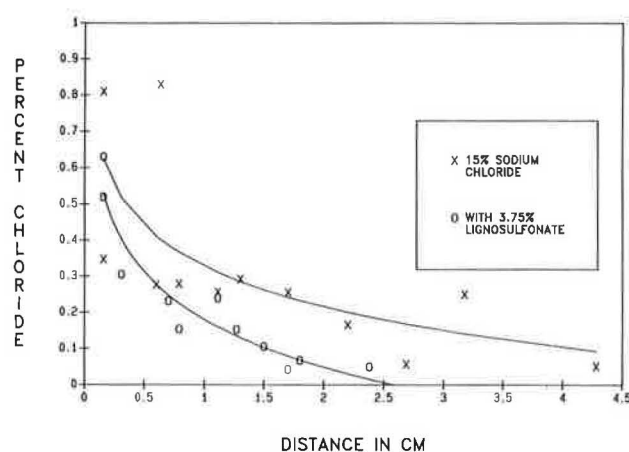

FIGURE 1   Chloride penetration into Wiss-Janey test blocks using 15 percent sodium chloride solutions.

TABLE 1   CORROSION INHIBITION OF LIGNOSULFONATES IN DEICING SALTS ON MORTAR BLOCKS WITH FINE CRACKS

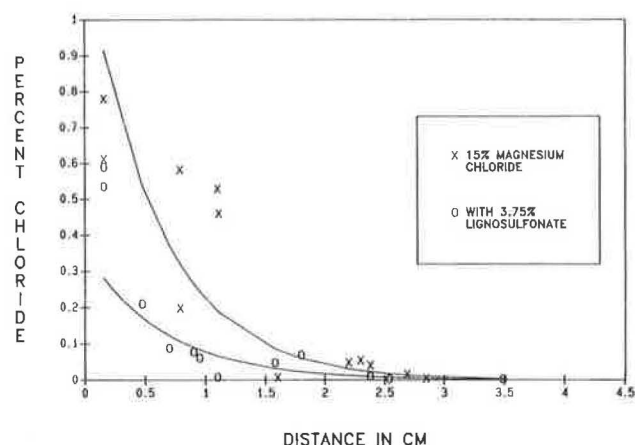| Sample	Time Weeks	Corr. Current microamps/cm^2
15% MgCl$_2$	2	3.3
w/3.75% lignosulfonate	2	1
15% MgCl$_2$	6	100
w/3.75% lignosulfonate	6	30
15% NaCl	6	60
w/3.75% lignosulfonate	6	15

FIGURE 2   Chloride penetration into Wiss-Janey test blocks using 15 percent magnesium chloride solutions.

cylinders were placed in 100 percent humidity at 20°C to 25°C for 15 days.

Only the sides of the cylinders were painted with epoxy paint 52 days later. A dam was attached to the top to hold the salt solutions. Fifty milliliters of 3 percent salt solutions, with and without 0.75 percent calcium lignosulfonate, were ponded weekly on the upper flat surface for 9 months and kept at 30°C. Solutions were put on each Monday and removed each Friday with the surface rinsed with 25 ml of fresh water.

The test cylinders were then analyzed for chloride content at different depths by cutting about 0.3-cm slices perpendicular to the cylinder axis with a rock saw having a 1.5-mm-thick diamond blade. The slices were then ground to a powder. A weighed amount of the powder, about 0.5 g, was put into 40 ml of deionized water and allowed to soak overnight. A portion of the solution was filtered, acidified, and then titrated with standard silver nitrate solution to determine the chloride content. Background chloride content of the mortar blocks was around 0.004 percent.

The chloride content of each slice was determined as percent of mortar and represented the average value of each slice. The mean distance the chloride ion traveled was from the top of the block to the middle of the slice.
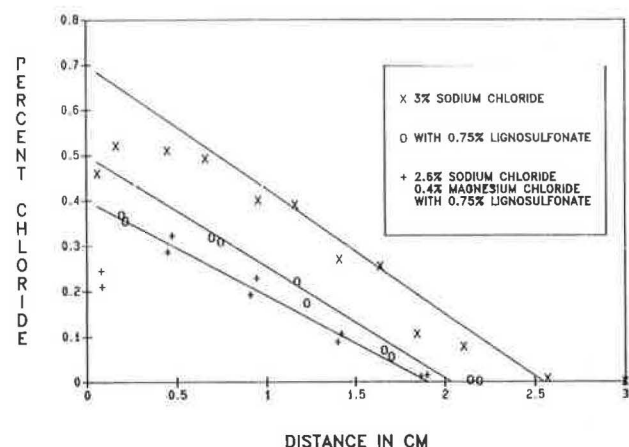
The data for the 3 percent sodium chloride, 3 percent chloride with 0.75 percent calcium lignosulfonate, and 2.6 percent sodium chloride with 0.4 percent magnesium chloride and 0.75 percent calcium lignosulfonate are shown in Figure 3. The data for 3 percent calcium chloride with and without 0.75 percent calcium lignosulfonate are shown in Figure 4. In Figures 3 and 4, even though chloride concentrations of the test solutions are the same, the cylinders treated with lignosulfonate have lower chloride concentrations in the first slice of the blocks.

The data for the 3 percent magnesium chloride with and without 0.75 percent calcium lignosulfonate are shown in Figure 5. The solution with lignosulfonate did not perform as well in this experiment as indicated in the previous Wiss-Janey test. A partial explanation will be given later in the discussion of the mechanism of action.

DIFFUSION COEFFICIENTS

Fick's first law of diffusion was used to calculate the diffusion of chloride ion into the mortar blocks as expressed in the following equation:
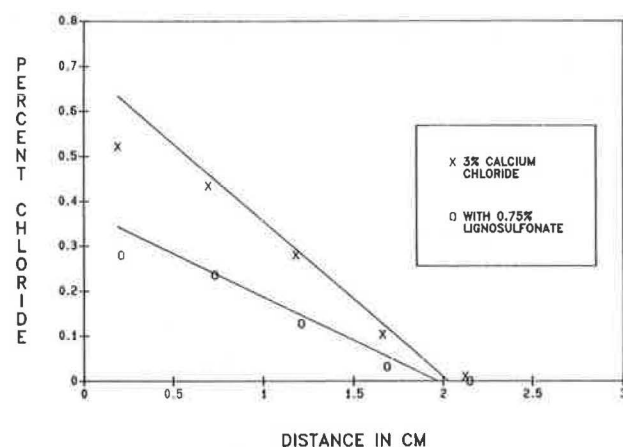
$$J = -D * dc/dx \tag{1}$$

FIGURE 4   Chloride penetration into mortar test blocks using 3 percent calcium chloride solutions.

FIGURE 3   Chloride penetration into mortar test blocks using 3 percent sodium chloride solutions.
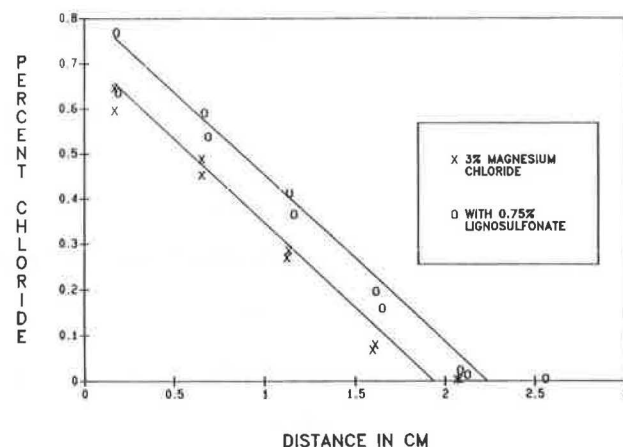

FIGURE 5   Chloride penetration into mortar test blocks using 3 percent magnesium chloride solutions.

where

J = flux of chloride ion,
c = concentration term,
x = distance traveled, and
D = diffusion coefficient.

Equation 2, which is a linear solution of Equation 1, shows the relationship of concentration of chloride c at depth x in time t with diffusion coefficient D and chloride apparent surface concentration c_0 (12).

$$c = c_0 * \left[1 - \frac{x}{2(D * t)^{1/2}} \right] \qquad (2)$$

Plotting c/c_0 versus x yields a straight line with intercept of 1. The slope of the line is then equal to the expression $-\frac{1}{2}(D * t)^{1/2}$. For each salt treatment, the diffusion coefficient D (in units of cm²/sec) was calculated from Equation 2 using the experimentally determined slopes. For these experiments, the ratio c/c_0 was the ratio of the percent chloride ion in each slice divided by the percent apparent surface concentration, and where the distance x from the top of each cylinder to the middle of each slice was in centimeters, and time t in seconds. The total time for these experiments was 9 months. The apparent surface concentration c_0 was obtained from Figures 3 through 5, by linearly extrapolating the percent chloride plots back to zero distance, which is the surface of the block.

The diffusion coefficients for the present experiments, calculated using Equation 2, are presented in Table 2. The values range from 3.2 to $6.0 * 10^{-8}$ cm²/sec. Typical values for high quality concrete are about $0.1 * 10^{-8}$ cm²/sec for high-quality concrete to $5 * 10^{-8}$ cm²/sec for low-quality concrete (12). The ability of chloride to penetrate to any depth in the concrete is a function not only of the diffusion coefficient, which is dependent on the quality of the concrete, but also the apparent surface concentration, which is a function of the interface between the bulk liquid and the concrete surface. For the cylinders treated with sodium chloride solution, the addition of lignosulfonate not only resulted in lowering the diffusion coefficient but also lower apparent chloride surface concentration, as presented in Table 2. When judged on the ability to give lower chloride concentrations at any depth, sodium chloride with lignosulfonate, and magnesium chloride and calcium chloride with and without lignosulfonate, all are better to use as a deicing salt than sodium chloride.

The effectiveness of these solutions to reduce chloride penetration can better be seen by calculating the time to corrosion onset. Corrosion of rebar in concrete usually starts when the chloride content at the rebar exceeds a given amount. The critical chloride concentration c_c at the rebar for corrosion to start is generally considered to be about 0.4 percent for cement or about 0.07 percent for concrete (12,13). By assuming the same linear relationship as in Equation 2, Equation 3 can be used to calculate the time for corrosion onset t_c, which is the time for the chloride concentration to reach the critical value.

$$t_c = \frac{1}{4D} \times \left(\frac{L}{1 - c_c/c_0} \right)^2 \qquad (3)$$

where

L = depth of the concrete cover over the rebar,

c_c = critical chloride content taken as 0.07 percent, and
c_0 = apparent surface concentration.

Using the apparent surface concentrations and diffusion coefficients in Table 2, the time t_c to reach a critical chloride concentration c_c of 0.07 percent at different covers over the rebar was calculated. Because the mortar for these tests was designed to be of low quality, the time t_c for sodium chloride treatment was only 1.0 year for 2.54-cm (1-in.) cover and 9.5 years for a 7.62-cm (3-in.) cover. In comparison, using the same apparent surface chloride concentration, a good-quality concrete with a diffusion coefficient of about $1 * 10^{-8}$ cm²/sec (12) and a 2.54-cm (1-in.) cover would have a life of about 6 to 7 years before corrosion onset.

The calculated times to corrosion onset t_c for all the test samples are presented in Table 3. Adding 25 percent lignosulfonate to the salt has the potential of increasing bridge life 70 percent over using plain salt. The use of a small amount of magnesium chloride with sodium chloride and lignosulfonate would slightly more than double the life of the bridge. The data clearly demonstrate the potential benefit of significant increased bridge life by adding lignosulfonate to deicing salts.

PROPOSED MECHANISM FOR LIGNOSULFONATE INHIBITION OF CHLORIDE DIFFUSION

The basic mechanism appears to be the same as what is commonly known as the Howard process for the precipitation of lignosulfonates (14). In this process, lime is used to precipitate lignosulfonates from solution. Lignosulfonates are adsorbed on the hydrated lime forming a bulky insoluble precipitate network. Calcium lignosulfonate is soluble at acid pH, but as the pH increases, a calcium lignosulfonate precipitate is formed. This process does not appear to occur to the same extent with magnesium ion.

If the presence of lignosulfonate in the deicing salt resulted only in an insoluble layer on the surface, then only the apparent surface concentration of chloride ion seen by the mortar would be affected. The interior of the mortar should remain the same in terms of pore solution concentration and composition, and the diffusion coefficient of the mortar towards chloride would not be affected. This result was not found to be the case, as demonstrated by significant changes in the calculated diffusion coefficient (see Table 2).

When sodium chloride solution is ponded on the surface of the mortar cylinder, hydroxide ion in the pore solution can diffuse, increasing the pH of the ponded salt solution. As pore solution diffuses out, the ionic strength of the pores decreases, which could result in increased diffusion of chloride ion. Also, some of the more soluble components could dissolve, increasing the pore size. When calcium lignosulfonate is present, it moves into the surface pores and adsorbs onto the hydrated lime in the alkaline environment, eventually sealing off the pores significantly. At the same time, hydroxide ion from the pores trying to diffuse would also react with calcium ion in solution, and an insoluble calcium hydroxide-lignosulfonate matrix could be deposited in the surface pores. With the weekly changes of the ponding solution containing

TABLE 2 SURFACE CONCENTRATIONS AND DIFFUSION COEFFICIENTS OF
CHLORIDE IONS IN TEST MORTAR CYLINDERS

Sample	Solution Concentration % Chloride	Surface[a] Concentration % on Mortar	Diffusion[b] Coefficient $*10^{-8}$ cm^2/sec
3% NaCl	1.82	0.70	6.0
3% NaCl + 0.75% Lig	1.82	0.50	4.0
2.6% NaCl + 0.75% Lig + 0.4% $MgCl_2$	1.89	0.40	3.2
3% $MgCl_2$	2.26	0.72	3.6
3% $MgCl_2$ + 0.75% Lig	2.26	0.82	4.7
3% $CaCl_2$	1.91	0.70	4.1
3% $CaCl_2$ + 0.75% Lig	1.91	0.38	3.6

a. Extrapolated value from Figures 3, 4, and 5.

b. Calculated using equation (2) in the text. Estimated
maximum variation 5%.

lignosulfonate, the pH of the salt solution would gradually decrease as the diffusion of alkaline pore water is retarded. The diffusion of chloride ion into the mortar is similarly retarded. The pH of the salt solution was measured at the end of each week and decreased when lignosulfonate was present, as indicated in Table 4.

When 3 percent calcium chloride solution is added to the surface of the mortar, the product of the concentration of the calcium ion, 0.27 M, and the concentration of hydroxide (pH 13+) in the pore water exceeds the solubility product for calcium hydroxide, which is 4.7×10^{-6} (*15*). Calcium hydroxide is precipitated in the surface pores, reducing the permeability to chloride ion. Because calcium hydroxide is reasonably soluble at 0.19 g per 100 ml, the pH of the solution remains high, as indicated in Table 4.

When lignosulfonate is present, the precipitating calcium hydroxide and lignosulfonate react as in the Howard process, forming an insoluble material that appears to be much more

efficient at sealing the surface than calcium hydroxide alone. This effect is confirmed by the low apparent surface concentration of chloride ion. As the insoluble material builds up, it results in slower diffusion of pore solution from the mortar block into the salt solution, decreasing pH (see Table 4).

When 3 percent magnesium chloride is added to the cylinder, the product of the concentration of magnesium ion, 0.32 M, and that of the hydroxide ion from the pore solution exceeds the solubility product of magnesium hydroxide of 5.6 $\times 10^{-12}$ (*15*) and precipitated magnesium hydroxide forms in the pores.

When lignosulfonate is present, the Howard process cannot occur. The magnesium ion ties up almost all the hydroxide from the pore solution and probably covers any of the calcium hydroxide surfaces in the mortar matrix. Only a small amount of calcium ion from the calcium lignosulfonate is available, which is 6 percent of the 0.75 percent lignosulfonate, yielding about 0.011 M calcium ion. From the calcium hydroxide

TABLE 3   CALCULATED TIMES TO CORROSION ONSET FOR DEICING
SALTS WITH AND WITHOUT LIGNOSULFONATE

		t_c, Time in Years[a]		
Sample	Cover	2.54 cm	5.08 cm	7.62 cm
3% NaCl		1.0	4.2	9.5
3% NaCl + 0.75% Lig		1.7	7.0	15.6
2.6% NaCl + 0.75% Lig + 0.4% $MgCl_2$		2.4	9.4	21.2
3% $MgCl_2$		1.7	7.0	15.7
3% $MgCl_2$ + 0.75% Lig		1.3	5.2	11.7
3% $CaCl_2$		1.5	6.1	13.5
3% $CaCl_2$ + 0.75% Lig		2.1	8.5	18.9

a. Calculated using D and C_0 from Table 2 and equation 3.

TABLE 4   pH OF SALT SOLUTIONS AT THE END OF EACH WEEK

Week	NaCl	NaCl + Lig	NaCl + Lig + $MgCl_2$	$CaCl_2$	$CaCl_2$ + Lig	$MgCl_2$	$MgCl_2$ + Lig
1	11.82	11.54	11.64	11.82	11.54	9.32	9.78
3	11.68	10.04	11.73	11.46	10.06	9.51	9.46
5	11.34	9.18	10.20	11.28	9.48	9.39	9.40
7	11.26	8.54	9.45	11.03	8.81	9.41	8.81
9	11.52	9.18	9.94	10.44	8.16	9.57	9.72
11	11.13	8.68	8.71	11.08	7.78	9.58	9.27
13	10.91	8.57	8.20	11.08	8.00	9.40	9.11
15	11.15	8.64	8.16	11.05	7.86	9.54	8.88

a. All solutions were 3% salt with 0.75% calcium lignosulfonate
with the exception that one was 2.6% sodium chloride with
0.4% magnesium chloride and 0.75% calcium lignosulfonate.

solubility product of 4.7×10^{-6}, the hydroxide concentration needed for precipitation is 4.3×10^{-4} M. As indicated in Table 4, the pH of the magnesium chloride solution is about 9.3, which is 2×10^{-5} M hydroxide, and is not high enough for precipitation.

In the previous Wiss-Janey experiment, the addition of lignosulfonate to magnesium chloride reduced chloride penetration (see Figure 2). These experiments were run at 15 percent salt and 3.75 percent calcium lignosulfonate. In this solution, the concentration of calcium from the lignosulfonate is five times greater at 0.066 M. Using the solubility product for calcium chloride, the hydroxide concentration needed for precipitation is 7.1×10^{-5} M, which is probably high enough at the mortar block surface to cause the Howard process to occur.

This effect can be demonstrated by adjusting the pH of 3 percent magnesium chloride with and without 0.75 percent calcium lignosulfonate and 15 percent magnesium chloride containing 3.75 percent calcium lignosulfonate to pH 9.5 with dilute caustic. The 3 percent magnesium chloride forms a fluffy gelatinous precipitate. The solution with lignosulfonate forms a smaller amount of precipitate, which did not appear as gelatinous. This result explains why the magnesium chloride solution with lignosulfonate was less effective at reducing chloride penetration at the 3 percent concentration. The supernatant has most of the lignosulfonate still in solution. The 15 percent solution has lots of precipitate with little lignosulfonate left in solution.

The reason, then, that the 3 percent magnesium chloride with 0.75 percent calcium lignosulfonate did not reduce chloride diffusion is that the Howard process could not occur because the concentration of calcium ion and hydroxide ion did not exceed the solubility product as it did in the original 15 percent salt experiments.

In actual practice, the magnesium chloride with lignosulfonate is generally added to roads as a solid or in a 28 percent solution. These are condensed sufficiently to produce high enough concentrations of calcium for precipitation by the Howard process to occur.

CONCLUSION

Calcium lignosulfonates, which are added to deicing salts as corrosion inhibitors toward exposed mild steel, have been shown to have additional advantages:

1. Lignosulfonates yield a substantial reduction in corrosion when fractures in concrete lead to the reinforcing bar—up to 70 percent reduction for a 3 percent salt solution with 0.75 percent lignosulfonate;

2. Lignosulfonates form insoluble precipitates in the surface pores that reduce the apparent surface chloride concentration; and

3. Lignosulfonates produce conditions that reduce the diffusion coefficient of chloride ion into the concrete and of alkalinity out of the concrete.

Reinforced concrete structures with exposed rebar, with cracks leading to the rebar, and with areas of undamaged concrete would benefit from calcium lignosulfonates in the deicing salts through the reduction in corrosion rates and reduced chloride penetration.

REFERENCES

1. J. Neal. A Lignosulfonate-Based Corrosion Inhibitor for Use with Deicing Salts. Presented at the Winter Maintenance Committee Meeting, TRB, National Research Council, Washington, D.C., 1985.
2. QWIKSALT® + PCI®. *Technical Bulletin*, Great Salt Lake Minerals and Chemicals Corporation, Ogden, Utah, undated.
3. FREEZGARD® + PCI®. *Technical Bulletin*, Great Salt Lake Minerals and Chemicals Corporation, Ogden, Utah, undated.
4. PCI® Corrosion Control Polymer. *Technical Bulletin*, Georgia-Pacific Corporation, Tacoma, Wash., undated.
5. The Great Salt Debate. *Better Roads*, June 1987, pp. 30–35.
6. D. Wheat. New Defense Against Winter Assault. *The Wenatchee World*, Jan. 15, 1988.
7. R. McCrum. CMA and Salt Mix Cuts Corrosion. *Better Roads*, June 1988, p. 32.
8. D. A. Komac. *Statewide Experiments with Chemical Deicers*. Washington State Department of Transportation, Olympia, 1989.
9. T. Wieman. *QWIKSALT® Plus PCI®, A Safer Deicer*. Washington State Department of Transportation, Olympia, undated.
10. M. Callahan. *Deicing Salts With and Without Corrosion Inhibitors*. Iowa Department of Transportation, 1988.
11. D. W. Pfeifer and M. J. Scali. *NCHRP Report 244: Concrete Sealers for Protection of Bridge Structures*. TRB, National Research Council, Washington, D.C., 1981.
12. E. Vesikari. *Service Life of Concrete Structures with Regard to Corrosion of Reinforcement*. Research Reports 553.53, Technical Research Center of Finland, Espoo, 1988.
13. O. A. Kayyali and M. N. Hague. Chloride Penetration and the Ratio of Cl^-/OH^- in the Pores of Cement Paste. *Cement and Concrete Research*, Vol. 18, 1988, pp. 895–900.
14. K. Sarkanen and C. Ludwig. *Lignins, Occurrence, Formation, Structure and Reactions*. Wiley, New York, 1971, p. 802.
15. *CRC Handbook of Chemistry and Physics, 68th Edition*. Chemical Rubber Publishing Co., Cleveland, Ohio, 1987, p. b-207.