

# Potential for Use of Natural Brines in Highway Applications

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## ABSTRACT

Large quantities of strong salt brines are often produced as by-products during extraction of oil and gas. The potential use of waste brines as replacements for conventional sodium and calcium chlorides in highway deicing and in dust control and stabilization was evaluated in laboratory testing. From various geologic formations and depths of the central Appalachian region, 49 samples of brine were collected and analyzed to establish brine quality and variability and to examine potential environmental problems. Analytical testing was carried out for general parameters such as total dissolved solids, pH, and conductivity and for major, minor, and trace constituents. Major constituents of Appalachian brines were chlorides, sodium, calcium, magnesium, and potassium. A variety of minor and trace constituents were noted in the brines, including iron, sulfate, barium, cadmium, chromium, lead, and ammonia. In most cases, concentrations of the minor constituents were not significant; however, certain formations in a given geographical area were found to contain elevated levels of certain components. Brines from different formations had significantly different concentrations of minor and trace constituents. Stability tests showed that brines will not form crystals in closed storage tanks. The constituents of the natural brines were compared with those of conventional deicing agents. The brines were generally higher in iron, zinc, and barium, whereas the conventional chemicals were higher in chrome and cadmium. It was concluded that there are significant quantities of natural brines from the central Appalachian region that are suitable for highway applications.

Sodium and calcium chlorides have been widely used in highway applications because of their low cost, ease of application, and solubility in water. The two principal uses of these salts have been winter deicing and road stabilization and dust control.

The chlorides are useful in winter maintenance because they melt snow as it falls, melt the compacted snow that remains after plowing, weaken the bond between the snow and ice and the road surface, and prevent the formation of ice films. Sodium chloride is more commonly used in deicing applications because of its lower cost (1, pp. 580-612). The primary advantage of calcium chloride is that it melts ice at lower temperatures than does sodium chloride (calcium chloride has a eutectic temperature of  $-58^{\circ}\text{F}$  versus  $-6^{\circ}\text{F}$  for sodium chloride).

Sodium and calcium chlorides are frequently used as surface treatments on unpaved roads. Because they keep unpaved surfaces moist, the chlorides virtually eliminate the nuisances and hazards associated with dust. By controlling dust, the fine materials that provide binding are kept in place and surfaces remain consolidated. Consolidated surfaces drain properly, resist ravelling, and remain hard and smooth. Calcium chloride is particularly attractive as a dust control and stabilization agent because it readily attracts moisture from the air and other sources.

In recent years, the costs of sodium and calcium chlorides have increased dramatically. The impacts of this trend have been most significant in winter maintenance; providing a bare pavement has placed a serious financial strain on many highway agencies. Under the constraints of tight operating budgets, highway agencies are seeking ways to minimize the use of chloride chemicals and alternative materials to substitute for the conventional agents.

One approach is to use liquid chloride chemicals (2). A number of agencies prewet deicing salts with liquids for faster action and reduction of losses due to salt bounce-off. Some agencies apply liquid brine directly to the roadway. A smaller number of agencies mix liquids and abrasives to freezeproof stockpiles and to provide some melting action when air temperatures increase. There are also several examples of agencies that use liquid chemicals for soil stabilization and dust control (3,4). The brines that have been used in all of these applications could be classified as either commercial chemicals or natural brines that are often produced during extraction of oil and gas.

Because natural brines are generated in significant quantities in several regions of the country as an unwanted by-product of oil and gas production, it appears appropriate to examine the use of such brines in highway applications. Brines are often much more concentrated than seawater. Thus, they are difficult to dispose of in an environmentally acceptable manner. The currently preferred method of brine disposal is via injection wells; however, in some parts of the country (for example, the Appalachian region), injection is often not feasible or very expensive because of a lack of sufficiently permeable formations. In addition, increased concern over groundwater contamination may result in legislation that prohibits or curtails deep-well injection. Because there is currently no completely satisfactory and cost-effective method of waste brine disposal, it is often discharged directly into ground or surface waters with potential deterioration of water quality.

Use of natural brine for highway purposes could solve several problems simultaneously. The oil and gas industry would be able to dispose of an unwanted

by-product, and highway agencies could acquire a valuable agent for deicing or stabilization or both at minimal cost. Furthermore, the natural brine that is used would be applied at controlled rates rather than discharged directly to the environment as is now frequently done.

In spite of the attractiveness of using natural brine in highway applications, there are a number of unanswered questions that must be addressed. The quantity of brine available for highway purposes in a given geographical area must be determined. Although major salts in brines are known, the relative fraction of each is expected to vary with depth and geologic formation and from region to region. Thus, the variation in brine composition as a function of geology and geography must be established, because this will play a key role in determining the utility of brine as a highway material. In addition to the major salts, brines may contain a number of minor or trace constituents, including sulfate, iodide, iron, barium, arsenic, and chromium. Chemical analyses for a number of the minor and trace constituents should be performed to assess potential water pollution problems. It will be necessary to compare the brines used as deicing agents with conventional dry salts with respect to corrosion and pavement deterioration characteristics. Similarly, comparisons are needed of the effects of brines and commercial deicing agents on melting, skid resistance, and refreezing of roadway surfaces. Problems and costs of brine transportation, storage, and handling need to be identified and compared with those for conventional chemicals for both deicing and stabilization applications.

#### OBJECTIVES

A comprehensive research project was conducted at West Virginia University to address the questions raised in the foregoing discussion. The study methodology included both laboratory and field-testing programs. This paper presents the results of laboratory testing conducted to achieve the following objectives:

- \* To test properties and variability of brines from several West Virginia oil and gas fields to establish chemical composition in relation to the feasibility of using brines for highway applications and for potential environmental problems,
- \* To compare the constituents of West Virginia oil and gas field brines with conventional deicing and stabilization chemicals, and
- \* To examine the freezing and stability characteristics of West Virginia brines.

The quantity of brine available for highway purposes in West Virginia is also discussed. The other aspects of the project, addressing related questions about the overall feasibility of natural brines as a highway material, have been described in previous papers (5,6). Although the main focus of the paper is on the quality and quantity of brines in West Virginia, the results are believed to be directly applicable to other eastern brine-producing states such as Pennsylvania, Ohio, and New York (7, pp.294-321). Investigation into the use of eastern brines for dust palliative and stabilization purposes was beyond the scope of this study, but on the basis of recent studies (8,9), this is an area in which additional research appears promising.

#### FIELD-SAMPLING PROGRAM

Brines were sampled from oil and gas fields in the northern and central portion of West Virginia.

Fields were selected so as to obtain brines from a number of different geological formations and depths. The project work plan specified that at least five fields were to be tested; five samples were to be taken from each field over a period of time.

In order to gain information on brine production and availability, contacts were made with several state agencies involved in oil and gas production, various oil and gas companies, and several oil and gas industry trade associations. The oil and gas industry was extremely supportive of the work; five companies provided brine samples or quantities of brine or both. Choice of fields to be sampled was made largely on the basis of recommendations of the oil and gas producers, because they were the most knowledgeable as to where brine production occurs.

Forty-nine samples were collected over a 17-month period from September 1981 to January 1983. Samples were obtained from 12 separate oil and gas fields as designated by Cardwell and Avari (10). Brines were sampled from 13 counties.

Samples were collected from 8 different geological formations, which included more than 12 different oil and gas zones as noted in Table 1. The formations ranged from the Upper Mississippian to the Lower Silurian. Depths of wells from which samples were taken ranged from 1,980 to 11,380 ft.

TABLE 1 Geological Formation, Zone, and Depth of Brines Sampled

Formation	Zone	No. of Samples	Range of Depth (ft)
Mauch Chunk	Maxon	1	1,980
Greenbrier	Big Injun, Big Lime	4	2,050-2,500
Pocono	Weir, Berea	7	2,300-3,000
Hampshire	Gantz, Fourth, Fifth	12	2,380-4,000
Chemung	Benson, Speechley, Riley, Baltown	8	3,825-4,575
Huntersville			
Chert	Not available	7	7,450-7,900
Oriskany	Not available	9	5,110-8,270
Tuscarora	Not available	1	11,380

#### BRINE QUALITY CONSIDERATIONS

In the analysis of the composition of the 49 brines collected in this study, 20 different types of tests were performed. Not all of the tests were carried out for each brine sample because of time and resource constraints.

The range and average value for each test parameter are given in Table 2. Although average values are presented in each case, the average concentration is not believed to be very meaningful for parameters such as barium where variations in levels between brines from different formations are very large. Table 2 also presents a range of values reported for brines in West Virginia, Pennsylvania, and Ohio. Note that the range given is not meant to be comprehensive but represents a sampling of brines with total dissolved solids (TDS) greater than 80 000 mg/L, which was judged to be typical of brines produced in the three states. The constituents determined were divided into four main groups:

1. General parameters: TDS, conductivity, density, pH, acidity;
2. Major constituents: chloride, sodium, calcium, magnesium, and potassium;
3. Minor constituents: iron, sulfate, barium, ammonia, and total organic carbon (TOC); and
4. Trace constituents: zinc, cadmium, arsenic, lead, and chromium.

TABLE 2 Comparison of Project Brine Concentration with Reported Values (11,13,15)

Item	Project Brines		
	Range	Mean	Reported Range <sup>a</sup>
Conductivity (μmhos/cm)	200 000-605 000	413 800	140 000-598 000
Density (lb/gal)	9.191-10.129	9.774	8.985-10.235
pH	2.72-6.14	4.3	4.4-6.5
Acidity (mg/L)	80-227	144	2-560
Concentration (mg/L)			
TDS	90 420-323 700	218 600	80 000-373 000
Cl	57 510-192 420	128 600	52 500-190 840
Na	29 130-82 240	52 740	37 150-75 000
Ca	5470-57 900	31 310	8790-49 000
Mg	645-4950	3200	1900-10 000
K	30-3310	590	122-8200
Fe	28-750	276	2-560
SO <sub>4</sub>	<5-547	163	0-1100
Ba	1.3-2500	545	0-1150
NH <sub>3</sub> -N	11-386	51	7-450
TOC	6-45	29	NA
Cd	<0.01-1.627	0.365	<0.1-6.0
Cr	<0.06	<0.06	<0.1-0.7
As	0.138-0.457	0.263	NA
Pb	1.583-6.100	3.360	<0.1-6.0
Zn	0.212-1.739	0.619	0-13

Note: NA = not available; TDS = total dissolved solids; TOC = total organic carbon.

<sup>a</sup>West Virginia, Ohio, and Pennsylvania.

#### General Parameters and Major Constituents

The TDS of the samples collected ranged from 90 420 to 323 700 mg/L with a mean value of 218 600 mg/L (Table 2). This TDS range is typical of that found in surrounding states. Brine strength generally increased with depth. This relationship has also been reported by others, including Waite et al. (11), Hoskins (12), and Poth (13). Exceptions to this general observation are probably due to dilution by fresh water as noted by Poth (13).

The levels of the so-called major constituents (Cl, Na, Ca, Mg, and K) are noted in Table 2. It may be seen that the average calcium concentration was more than 31 000 mg/L. This is significant in that the presence of calcium salts is known to allow the use of deicing agents at lower temperatures than is feasible with sodium salts alone. A high calcium level is also desirable for use in dust palliative applications. As shown in Table 2, concentrations of the major constituents in the brines sampled fall within the ranges reported by others.

The data were analyzed to examine the potential relationship between TDS and the major constituents, including conductivity. A statistical package was used to plot the data, perform a linear regression, calculate the correlation coefficient, and determine coefficients for the equation of the line of best fit. Correlation coefficients were found to be .989 and .966 for chloride and sodium, respectively, which indicated relatively good correlation between TDS and these two parameters. Good correlation was noted between TDS and conductivity; the correlation coefficient was .933. However, the respective correlation coefficients for calcium, magnesium, and potassium were .754, .365, and .613, which indicated data scatter and poor correlation. Similar results were found by Poth (13) for Pennsylvania brines.

#### Minor and Trace Constituents

Iron, sulfate, barium, ammonia, and TOC are categorized in this paper as minor constituents, although the classification is admittedly somewhat arbitrary. Iron ranged from 28 to 750 mg/L with an average value of 276 mg/L, as noted in Table 2. The high

variability of iron in brines is probably mainly attributable to sample handling during collection and analysis. On exposure to air, ferrous iron will slowly oxidize to ferric iron at the pH values normally prevailing in brines. The ferric iron may settle as an insoluble precipitate in the bottom of brine storage tanks or pits or even in a sample bottle and therefore escape analysis.

Sulfate levels, which varied from 5 to 547 mg/L (average 163 mg/L), are of interest with respect to attack of concrete. Pierce (14) concluded that sulfate levels of 150 mg/L or less would result in negligible attack on concrete, whereas levels of 150 to 1500 mg/L would show a positive degree of attack and above 1500 mg/L, the degree of attack would be severe. Also to be considered is that brine applied to the roadway would be diluted by snow or ice almost immediately and would run off as melting occurred. Based on the foregoing considerations, the sulfate level in West Virginia brines would not be expected to contribute significantly to concrete deterioration. Sulfate would be expected to be low in brines containing elevated concentrations of barium because barium sulfate (barite) has a solubility of only around 3 mg/L at 64.4° F. This was borne out in project samples that had high barium levels in that low sulfates were typically found there. It may be seen that barium levels varied widely in the brines sampled; the range was from 1.3 to 2500 mg/L. Barium levels over 25 mg/L occurred in 22 of the 48 samples analyzed for barium. However, almost all of the high-barium samples were taken from one field where brine was produced from the Huntersville Chert and Oriskany formations. Other investigators have also reported the presence of elevated barium levels in Huntersville Chert and Big Injun brines (15).

Ammonia and TOC levels were also examined for a limited number of samples. The level of ammonia ranged from 11 to 386 mg/L and TOC varied from 6 to 45 mg/L. These levels are not likely to result in environmental problems when brine is used for deicing. A thin layer of oil was observed floating on the brine in some storage tanks. If the oil is collected along with the brine, elevated TOC values and possible slippery pavement conditions could result. When the brines are removed from storage tanks, at the wellhead it is relatively easy to avoid oil contamination simply by leaving the last foot of liquid in the brine storage tank.

Five trace constituents were analyzed: arsenic, cadmium, lead, zinc, and chromium as noted in Table 2. The values are generally in the range found by others for brines in this area. All of the trace constituents except zinc have maximum limits based on toxicity under the Resource Conservation and Recovery Act (RCRA) of 1976. It is important to note that production brines are excluded from regulation under RCRA and that the following comparison with RCRA-regulated wastes is made simply to gain a perspective on the trace constituent levels. Table 3 presents the RCRA limits and range of sample values obtained for the trace constituents and for barium, which is also covered by RCRA. Also shown in Table 3 is the number of times the RCRA limits were exceeded by the 49 project brine samples. It may be noted that barium is probably the only element of concern and, as noted earlier, most of the high-barium samples originated from one oil and gas field. Brines from formations with high barium levels would require pretreatment for reduction of the element before highway application.

#### Brine Variability

One of the objectives of the brine-sampling program was to evaluate variability in quality from dif-

TABLE 3 Comparison of Trace Constituent Values with RCRA Limits

Constituent	Maximum Limit Under RCRA (mg/L)	Range of Project Brines (mg/L)	No. of Samples Exceeding Limit
Arsenic	5	0.138-0.457	0
Barium	100	1.3-2500	22
Cadmium	1	<0.01-1.627	2
Chromium	5	<0.06	0
Lead	5	1.583-6.100	2

ferent formations and zones as well as changes in brine quality over a period of time for a given formation. Another aspect of brine variability of interest is the change in brine quality from location to location for a given formation or zone.

Nine different sample groupings were made in order to evaluate variability. Groupings were established based on the number of formations, zones, counties, or wells from which the samples were taken. Sampling extended over a time span of approximately 17 months. For each grouping of samples, variation was determined for each of the sample parameters by using the coefficient of variation (standard deviation divided by mean).

Table 4 presents the percent coefficient of variation (percent CV) for all groups for 10 sample constituents. The average percent CV for each group is also listed. Examination of Table 4 reveals that the largest variation occurs in Group 2A, which includes samples from two formations, four zones, and two counties. Sampling from different counties does not necessarily produce large variability, however, as may be noted from groups 1A (four counties) and 3A (six counties). Therefore, major variations in brine quality were not due to areal differences but to formation and zone-quality differences. The CV for the TDS of samples from Group 1A was only 5.6 percent even though 13 different wells were sampled, which indicates relatively uniform strength of the brines from four counties and two deep-lying formations. Samples taken from single wells (1C, 2C, 2D, 3B) generally exhibited the lowest variation, as would be expected. For example, the percent CV for TDS was only 3 percent for Group 2C. The seven samples in this group were taken over a period of 13 months and analysis of the data showed no trend in increasing or decreasing concentration with time.

The variation of brine quality between four different formations is demonstrated by the data in Table 5, where mean values are shown for a variety of brine quality parameters. Comparison of values clearly illustrates that brines from different formations have markedly different concentrations of major and trace constituents, as would be expected. Brines sampled from the deeper-lying Huntersville Chert and Oriskany formations were almost twice as strong as those from the Chemung and Pocono formations. It is interesting to note that the Chemung and Pocono samples are weaker than those from the Hampshire formation, which actually lies between them.

#### Comparison of Constituents in Dry Deicing Agents and Brines

It would be expected that the dry agents (NaCl and CaCl<sub>2</sub>) used for deicing or road stabilization would also contain a variety of minor and trace constituents, although little published information is available in this regard. Seven dry agents were analyzed for six minor and trace substances, as shown in Table 6. The samples, both sodium chlorides, were randomly collected over a 2-year period from three sources: West Virginia Department of Highways (WVDOT) Sabraton maintenance facility, West Virginia University (WVU) physical plant, and the city of Morgantown. In order to compare the dry agents with the brines, the dry salts were first dissolved in distilled water to approximately 200 000 mg/L and the TDS of each sample was determined. Results were then expressed as milligrams of constituent per kilogram TDS, which allows direct comparison of the dry agents and the brines. Also shown in Table 6 are results adapted from an analysis (11) of dry NaCl used in Pennsylvania. The brine group values presented are group average values for each constituent. The samples in the groups shown represent every major formation sampled.

Examination of the data in Table 6 shows that the dry agents as well as the brines contain a variety of trace constituents. The brines are generally higher in iron, zinc, and barium, whereas the dry agents are higher in chrome and cadmium. The dry calcium chloride samples also had elevated lead levels when compared with the brines. However, because relatively little calcium salt is used at present for deicing, the higher lead values do not appear significant.

TABLE 4 Variability of Brine Samples Within Groups

Item	Group							
	1A	1B	1C	2A	2B	2C	2D	3A
No. of samples	16	8	3	18	10	7	3	10
No. of formations	2	2	1	2	1	1	1	1
No. of counties	4	1	1	2	2	1	1	6
No. of zones	1	1	1	4	3	1	1	3
No. of wells	13	6	1	8	7	1	1	6
Percent CV								
TDS	5.6	2.8	0.5	9.5	5.4	3.0	1.0	22.2
Cl	3.4	1.7	1.0	10.7	5.3	1.1	1.0	18.9
Na	6.8	5.3	2.8	13.5	4.5	1.7	1.7	22.5
Ca	24.1	20.1	24.4	25.0	14.0	1.8	3.0	40.1
Mg	21.8	16.3	10.5	15.5	16.7	1.7	6.4	28.5
K	85.6	75.9	5.1	77.6	96.5	65.8	49.7	99.8
Ba	45.2	14.6	11.6	258.0	178.9	26.9	7.8	123.4
As	11.6	11.6	1.8	10.3	13.4	1.9	15.9	24.3
Pb	14.2	16.3	5.7	28.9	27.7	15.7	26.8	24.1
Zn	43.3	44.1	5.4	18.7	11.4	6.4	9.3	17.5
Avg	26.2	20.9	6.9	46.8	37.4	12.6	12.3	42.1

Note: CV = coefficient of variation; TDS = total dissolved solids. Groups are defined as follows: 1A, two formations; 1B, two formations; 1C, single well; 2A, two formations; 2B, single formation; 2C, single well; 2D, single well; 3A, single formation; 3B, single well.



TABLE 5 Variation of Brine Samples Between Formations

Item	Group			
	1A	2B	3A	2C
Formation	Huntersville Chert, Oriskany	Chemung	Pocono	Hampshire
Concentration (mg/L)				
TDS	303 640	185 820	167 340	217 020
Sodium	74 570	45 700	40 260	58 450
Chloride	185 390	112 360	100 790	134 650
Calcium	44 580	35 310	23 840	22 940
Lead	4.429	2.887	2.610	4.055
Arsenic	0.388	0.232	0.212	0.231
Cadmium	0.328	0.117	0.296	1.033

Note: Concentrations given are mean values. Groups are defined as follows: 1A, two formations, four counties; 2B, single formation, two counties; 3A, single formation, six counties; 2C, single formation, single well.

TABLE 6 Comparison of Constituents in Dry Deicing Agents and Brines

Agent	Constituent (mg/kg TDS)					
	Cr	Pb	Fe	Cd	Zn	Ba
Dry salts						
NaCl-WVDOH-1982	2.4	5.8	9.1	8.3	0.7	- <sup>a</sup>
NaCl-Mgtn-1982	1.9	5.4	10.6	8.9	0.6	-
NaCl-Mgtn-1983	-	-	-	10.4	-	132
NaCl WVDOH-1983	-	-	-	9.1	-	96
NaCl WVU-PP-1982	2.7	6.2	17.3	6.1	0.3	-
CaCl <sub>2</sub> WVDOH-1982	6.2	53.9	24.4	16.6	2.0	-
CaCl <sub>2</sub> WVU-PP-1982	8.5	46.0	27.6	18.4	2.3	-
NaCl-Penna.	0.7	8.8	12.3	1.7	0.8	0.1
Brines						
Group 1A <sup>b</sup>	<0.2	14.6	1350	1.1	3.4	4838
Group 2A	<0.3	17.3	1122	2.5	3.0	454
Group 2C	<0.2	18.7	783	4.8	3.2	21.7
Group 2D	<0.3	12.2	315	<0.05	2.9	50.8
Group 3B	<0.3	14.4	631	2.5	2.0	65.5

Note: WVDOH = West Virginia Department of Highways; Mgtn = Morgantown; WVU = West Virginia University; PP = physical plant.

<sup>a</sup>Data unavailable.

<sup>b</sup>See Table 4 for definition of groups.

### Freezing Tests

Freezing tests were carried out on brines and dry salt solutions at temperatures of from 5 to 15.8° F. Testing was done in an environmental chamber where a fan provided continuous air circulation to maintain the constant temperature desired. Samples were covered to avoid evaporation.

Table 7 presents the test results, showing that eight different brine samples were used in four different concentration ranges. In addition, the sodium

chloride deicing agents from two different sources were tested for comparison in two different concentration ranges. Temperatures of 5.0, 8.6, 10.4, 12.2, 14.0, and 15.8° F were used. The four strongest brines showed no indication of freezing even at 5° F, although some salt crystals dropped out of solution in the strongest brine because of insolubility at the lowest temperature. This would not be expected to cause a problem during storage because the crystals would redissolve as temperatures rose. The stronger NaCl solutions both had some ice crystals at 5° F even though brines 12 and 17, which were relatively lower in TDS, did not. The superior performance of the brines at 5° F was probably due to their CaCl<sub>2</sub> content. The concentration of NaCl that would just freeze at 5° F is about 214 500 mg/L (16), whereas that of CaCl<sub>2</sub> at 5° F is estimated as 196 800 mg/L (17).

At 10.4° F, none of the brines were completely frozen, although the weakest brines (10 and 16) still had ice crystals floating on top of the brine. At 14.0° F, the weakest brines and the weakest salt solutions still had some ice crystals. At 15.8° F, no ice crystals were noted even in the weakest brines.

### Brine Stability

Because brines contain high concentrations of a variety of salts, there is concern that, with time, salts may precipitate or form crystals, which may interfere with brine storage and handling. Potential brine stability problems were investigated in both covered and uncovered containers. The effect of temperature and type of container (glass and unpro-

TABLE 7 Freezing-Test Results

Sample	TDS (mg/L)	Condition of Sample by Temperature (° F)					
		5.0	8.6	10.4	12.2	14.0	15.8
B-10	164 380	X	IC-80%	IC-30%	IC-25%	IC-25%	NF
B-16	161 460	X	IC-80%	IC-25%	IC-20%	IC-20%	NF
B-20	188 760	X	IC-50%	NF	NF	- <sup>a</sup>	-
B-37	190 230	X	IC-30%	NF	NF	-	-
B-12	215 420	NF	NF	NF	NF	-	-
B-17	212 160	NF	NF	NF	NF	-	-
B-32	323 700	NF	NF	NF	NF	-	-
B-14	305 180	NF	NF	NF	NF	-	-
Dry NaCl							
Morgantown	222 780	IC-10%	NF	NF	NF	-	-
WVDOH	220 950	IC-15%	NF	NF	NF	-	-
WVDOH	163 690	-	-	-	-	IC-25%	-
WVDOH	161 700	-	-	-	-	IC-30%	-

Note: X = frozen; IC = ice crystals; NF = not frozen; SC = salt crystals; B = brine.

<sup>a</sup>Dash indicates not tested.

tected steel) was also examined. Initial volumes of brine in the glass and steel containers were 800 and 100 ml, respectively.

Six different brines were used during the testing in closed containers. All tests were run in duplicate except those in the glass bottles. No major change (salt precipitation or crystallization) in any sample was noted either at room temperature or at 40° F for as long as 20 months of observation. In some samples, there was a small amount of iron oxide floc on the bottom in the first 1 to 5 weeks as iron in the sample oxidized and precipitated. However, the small amount of floc formed would have no impact on storage or handling of the brine. Potential concrete pavement discoloration due to the iron floc has been discussed in a previous paper (6).

Uncovered stability tests were carried out in duplicate with two different brines. Samples were allowed to evaporate until salt crystallization and precipitation occurred in all cases. Stability was examined both at room temperature and under conditions of alternating warm and cold temperatures to simulate year-round storage of brine. Estimates of the amount of evaporation were made by observing changes in sample depth for the steel containers and by observation of both depth and weight changes for the glass containers. The final TDS was estimated from the initial TDS based on the change in sample volume. Observations were made approximately every 2 days to record the onset of crystal formation or precipitation. For one brine, the sample began to form crystals after 36 percent evaporation in glass beakers and after about 55 percent evaporation in the steel containers. The stronger brine tested exhibited crystal formation after about 9.5 percent evaporation in glass and 14 percent in steel containers. It is not known why crystals were formed earlier in glass than in steel containers, but the latter would be expected to give results closer to those expected during field storage of brines if uncovered steel tanks were used. For the steel containers, it may be noted that brine became unstable over about 375 000 mg/L. This was to be expected because the maximum concentration of brine typically noted in formations (presumably near saturation) is around 350 000 mg/L.

After crystal formation was noted, distilled water was added to bring the brines back to their original test volume in order to observe whether the crystals would redissolve. In all cases, it was noted that the crystals went back into solution, which showed that the crystallization was reversible.

In summary, the stability tests showed that the brines will be stable in covered storage tanks. If uncovered tanks are used, crystals will form if brine strength is allowed to increase to around 375 000 mg/L TDS. It should be noted that very little net evaporation would occur much of the year (especially in winter) in West Virginia, even with uncovered tanks, because of normal rain and snowfall.

#### BRINE QUANTITY CONSIDERATIONS

The quantity of brine produced from a given well depends on a variety of factors, including the geological formation tapped and its depth and the well's location, construction, age, and operation (7). Many wells produce little brine when first put into production but produce more with time; others yield large quantities of brine initially.

The actual quantity of brine produced nationally is difficult to determine reliably because many states do not keep detailed records. A study made by the Interstate Oil Compact Commission (IOCC) (18) estimated that 23.7 million barrels of brine per day

were being produced nationwide from oil production in 1963; 115,068 barrels were produced in West Virginia. It is not clear in the report whether the West Virginia figure also included brine from gas wells, but it appears that it did.

No comprehensive figures were available from West Virginia state agencies on the quantities of brine produced in the state. However, recent studies regarding brine production had been made for Ohio and Pennsylvania that may be used to estimate brine production in West Virginia. In a report prepared by Templeton and Associates (19) for the Ohio Water Development Authority, it was noted that 35,000 active oil and gas wells in Ohio produced approximately 40,000 barrels of salt water per day in 1979. As part of a study for the Pennsylvania Department of Natural Resources, Waite et al. (11) estimated typical ranges in waste fluid volume in Pennsylvania produced per well. Their results are presented in Table 8 for shallow and deep gas and oil wells.

In order to make comparisons of brine production in West Virginia based on the data from Ohio and Pennsylvania, the number of active gas and oil wells and the production for each state as reported by the IOCC (20) is presented in Table 9. It may be seen that West Virginia has somewhat greater total gas production than the other two states but that the gas production per well is similar in all three states. Ohio leads by far in total oil production and in production per well, whereas Pennsylvania and West Virginia show fairly similar oil production per well. Based on the similar oil and gas production statistics in West Virginia and Pennsylvania and on the fact that many of the same producing formations are in use in the two states, the Pennsylvania brine production values were used to estimate brine quantities for West Virginia.

Examination of Table 8 shows that, as expected, brine production is greater for deep wells than for shallow wells. In West Virginia, wells are classed as deep if they are more than 6,000 ft or are below the top of the Huntersville Chert or Onondaga Limestone formations. Based on this classification, approximately 90 percent of the gas wells and 100 percent of the oil wells in West Virginia may be designated as shallow. Using average values from Table 8 and the number of wells as given in Table 9, it was estimated that 480 million gal of brine are produced annually in West Virginia. A second estimate based on the adjusted data from the IOCC (20) noted earlier gave 1,100 million gal per year. The

TABLE 8 Estimated Waste Fluid Volumes (11)

Development Area	Waste Fluid Type	Typical Ranges in Waste Fluid Volumes per Well
Shallow oil Venango District	Fluid produced during drilling <sup>a</sup>	0-2,000 gal
	Stimulation fluid	26,000 gal
	Production fluid (after 6 months of pumping)	1-2 bbl/day (42-84 gal/day)
Bradford District	Fluid produced during drilling <sup>a</sup>	0-2,000 gal
	Stimulation fluid	30,000 gal
	Production fluid (after 6 months of pumping)	1-2 bbl/day (42-84 gal/day)
Shallow gas (Upper Devonian)	Fluid produced during drilling <sup>a</sup>	0-5,000 gal
	Stimulation fluid	40,000 gal
	Production fluid	0-1 bbl/day (0-42 gal/day)
Deep gas (Medina formation)	Fluid produced during drilling <sup>a</sup>	0-25,200 gal
	Stimulation fluid	58,800 gal
	Production fluid	2-4 bbl/day (84-168 gal/day)

Note: Estimated volumes of fluids produced during drilling, does not include top hole water or ground water encountered before surface pipe is set. All ranges are considered typical for the type of well indicated. Individual wells or groups of wells in selected locations may differ significantly from the ranges indicated here.

<sup>a</sup>These estimates apply only to air-rotary-drilled holes.

TABLE 9 Oil and Gas Production Statistics for Ohio, Pennsylvania, and West Virginia, 1981 (20)

State	Gas			Oil		
	No. of Wells	Yield		No. of Wells	Yield	
		Annual (ft <sup>3</sup> 000,000s)	Per Well (ft <sup>3</sup> 000s/day)		Annual (bbl x 10 <sup>3</sup> )	Per Well (bbl/day)
West Virginia	26,925	161,251	16	14,700	2,433	0.4
Ohio	18,619	141,134	18	22,441	13,551	1.6
Pennsylvania	20,526	122,456	16	26,138	3,229	0.3

lower estimate is felt to be more reliable because it is based on more recent data. The 480 million gal of brine translates to a unit production of 1.3 gal of brine per 1,000 ft<sup>3</sup> of gas produced and 2.6 bbl brine per barrel of oil produced. It is important to bear in mind that brine production varies widely from well to well depending on factors discussed earlier. Thus, although an average value of 0.52 bbl of brine per day was used in estimating brine production from an average West Virginia gas well, actual values reported by oil and gas producers vary from zero to 25 bbl per day.

It is recognized that even if the previous estimate of 480 million gal of brine production per year is reasonable, only a portion of the brine would be available or suitable for highway applications. Brines unsuitable for use include those that are too weak or that contain undesirable levels of contaminants. It is also likely that the use of brine from a number of wells would not be cost-effective because of their remote location or low production or both, which would result in unacceptably high transportation costs. If only 10 percent of the estimated 480 million gal per year was available for use on roadways, the dry salt equivalent would amount to approximately 34,000 tons (assuming a TDS of 170 000 mg/L). This amount is about 35 percent of the salt used for deicing in the 1981 winter season by WVDOT.

The supply of brine available over a period of years will be an important factor in evaluating the feasibility of brine use. In this regard, it may be noted that during the past 5 years of available record (1977 to 1981), gas production in West Virginia increased approximately 6 percent and oil production remained approximately constant (20). Thus, it would appear that the quantity of brine available increased slightly in the same period.

#### CONCLUSIONS AND RECOMMENDATIONS

On the basis of the results of the study described here, it was concluded that there are significant quantities of natural brines from the central Appalachian region (including West Virginia, Ohio, Pennsylvania, and New York) that are suitable for highway applications. Brines from this region have relatively high calcium concentrations. This is an asset both in deicing and in stabilization and dust control. Of the minor and trace constituents in these brines, barium was the only element of concern.

Major variations in brine quality are not due to areal differences but to differences in formation and zone. Brines from different formations have significantly different concentrations of major and trace constituents. Brine strength tends to increase with depth. Over a period of 13 months, there was no change in brine concentration from a given formation. It is recommended that brines continue to be monitored over time to determine any long-term changes in composition.

Stability tests showed that the brines will be stable in covered storage tanks. If uncovered tanks

are used, crystals will form if brine strength is allowed to increase to around 375 000 mg/L TDS. Under the relatively humid conditions found in the Appalachian region, little net evaporation would be expected to occur, even with uncovered tanks.

The constituents of the natural brines examined were compared with those of conventional chloride chemicals. The brines were generally higher in iron, zinc, and barium, whereas the conventional chemicals were higher in chrome and cadmium. Dry calcium chloride samples had elevated lead levels when compared with the brines.

Because of the apparent attractiveness of using natural brines in highway applications, it is recommended that studies similar to the one described here be conducted in other geographic regions that produce significant quantities of brine. Analysis of brines could identify those formations or zones that are suitable sources of brines for highway applications. Formations producing brines that are too weak for highway applications or that create environmental problems could be delineated and avoided. The analysis might also suggest instances where pretreatment of brines, if they are attainable at low cost, could produce a suitable material for highway applications.

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## Calcium Magnesium Acetate Research in Washington State

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### ABSTRACT

As part of a pooled-fund research project, the Washington State Department of Transportation was selected to field test approximately 100 tons of calcium magnesium acetate (CMA) to evaluate its potential as a deicing chemical in direct comparison with salt (sodium chloride) and urea. Evaluation included all aspects of storage, handling, use, and performance. CMA was applied whenever necessary at each test site; the same application rates were used as those now used for salt. Typical equipment consisted of front dump trucks with the spinner ahead of the rear axle and rear-discharge hopper trucks. All equipment was used without modification. The use of CMA at the beginning of a storm reduced the amount of bonding of snow to the roadway surface. This effect of keeping the roadway surface bare for longer periods of time reduced the cost of snow fighting. This was accomplished with a chemical application rate of 125 lb per lane mile. The addition of sand to CMA reduced the problems of dust, caking, and uneven distribution. The sand provided moisture and weight to the application, which resulted in a smoother, more even distribution. CMA spread above the ice and snow was excessively dusty, which created problems in the spreading and distribution. CMA is slower to react on compact snow and ice than is salt or urea. This delay in reaction time was not considered a handicap in the overall snow-fighting procedure. The conclusion was that CMA shows promise as a deicing-melting chemical. The problems of dust, light weight, and brittleness need further research and may be significantly alleviated by development of a hydrated compound.