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ICE-MELTING CHARACTERISTICS OF CALCIUM MAGNESIUM ACETATE

Research, Development,
and Technology
Turner-Fairbank Highway
Research Center
6300 Georgetown Pike
McLean, Virginia 22101

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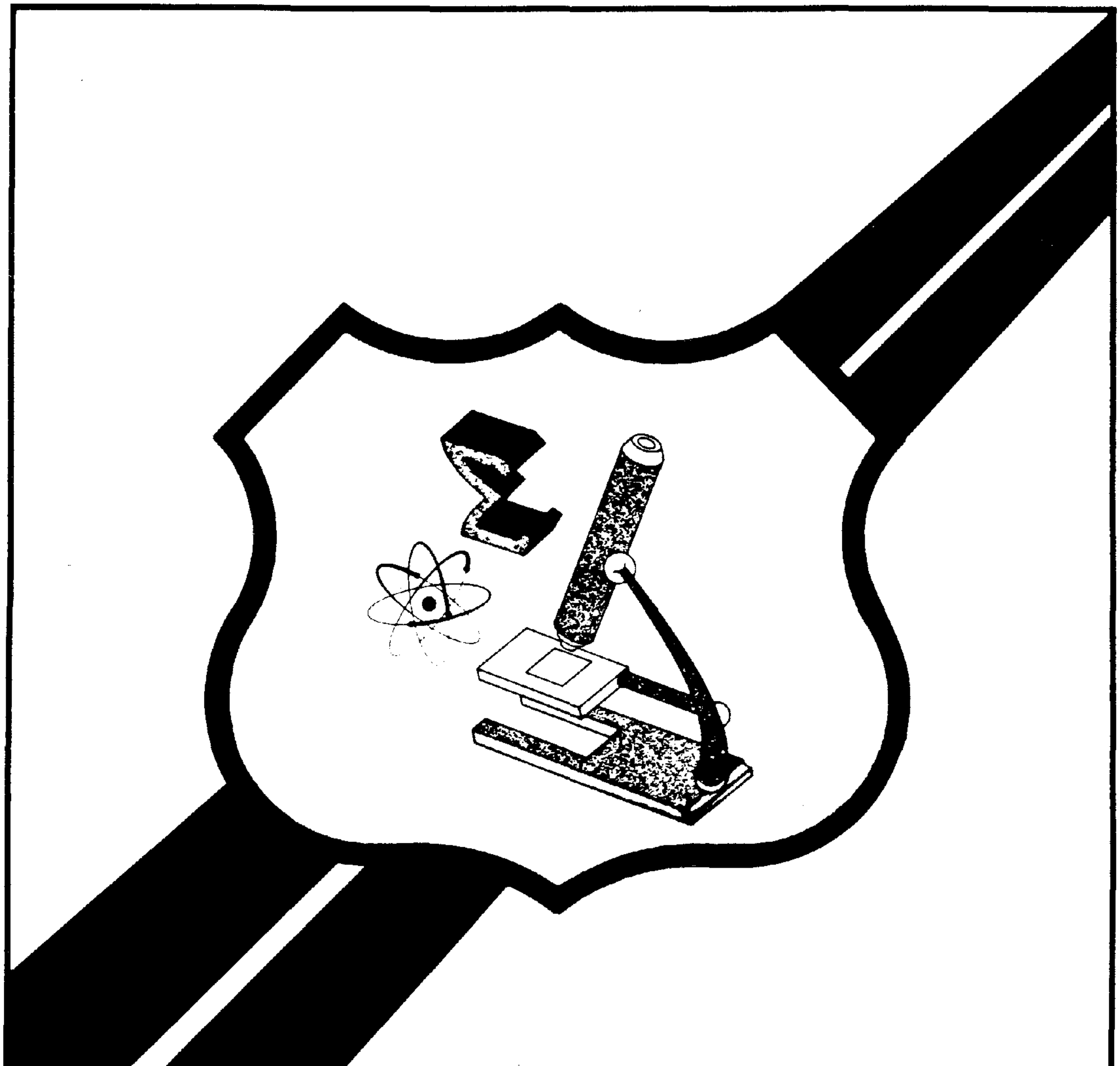
January 1986



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16. Abstract

Pertinent chemical and physical properties of calcium magnesium acetate (CMA) were determined. Included were comparisons of ratios of calcium to magnesium varying from 100% $CaAc_2$ to 100% $MgAc_2$. The objective was to determine the optimum composition of CMA for road deicing.

In a 12-month study involving wetting/drying tests with 11 ratios of Ca/Mg and five pH's, it was found that CMA at pH's above 7.0 and at any Ca/Mg ratio produced no more harm to portland cement concrete than did NaCl. In addition, with compositions containing Mg at levels equal to or greater than Ca, the damage to concrete was significantly reduced.

The lowest eutectic temperature (freezing point) was determined to occur with CMA 3/7 (3 mole fractions Ca to 7 mole fractions Mg). At higher Mg concentrations there is evidence that $MgAc_2 \cdot 8H_2O$ was formed. This apparent hydrated salt has very low solubility at low temperatures.

The anhydrous and minimally hydrated calcium acetate and magnesium acetate have significant heats of solution, with evidently $MgAc_2$ having the higher heat of solution - similar to $CaCl_2$.

The optimum pH for CMA was determined to be at least pH7, with pH9 the likely upper limit due to precipitation of $Mg(OH)_2$. The optimum Ca/Mg ratio was determined to be 3Ca/7Mg ± 1 unit.

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PREFACE

The author wishes to acknowledge the cooperation and helpful interchange that has existed during this contract with various members of the Federal Highway Administration, particularly Dr. Brian Chollar, Contracting Officer's Technical Representative.

Likewise acknowledged are the contributions of Dr. Stanley Dunn and Allen Pomplun, former staff members at these laboratories, who contributed a part of the work reported.

METRIC CONVERSION FACTORS

APPROXIMATE CONVERSIONS FROM METRIC MEASURES

LENGTH

SYMBOL	WHEN YOU KNOW	MULTIPLY BY	TO FIND	SYMBOL
in	inches	2.5	centimeters	cm
ft	feet	30	centimeters	cm
yd	yards	0.9	meters	m
mi	miles	1.6	kilometers	km

AREA

SYMBOL	WHEN YOU KNOW	MULTIPLY BY	TO FIND	SYMBOL
in^2	square inches	6.5	square centimeters	cm^2
ft^2	square feet	0.09	square meters	m^2
yd^2	square yards	0.6	square meters	m^2
mi^2	square miles	2.6	square kilometers	km^2
	acres	0.4	hectares	ha

MASS (weight)

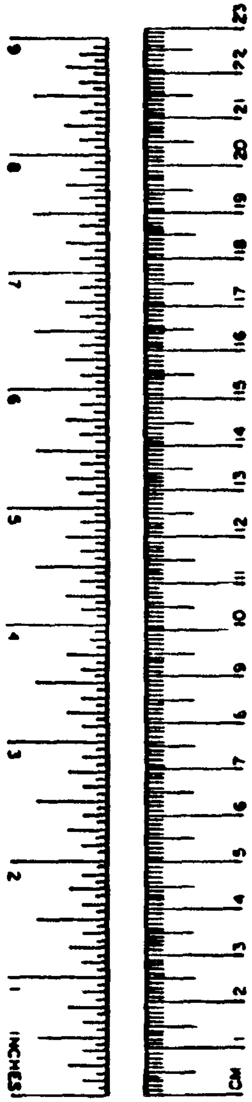
SYMBOL	WHEN YOU KNOW	MULTIPLY BY	TO FIND	SYMBOL
oz	ounces	28	grams	g
lb	pounds	0.45	kilograms	kg
	short tons(2000 lb)	0.9	tonnes	t

VOLUME

SYMBOL	WHEN YOU KNOW	MULTIPLY BY	TO FIND	SYMBOL
tsp	teaspoons	5	milliliters	ml
tbsp	tablespoons	15	milliliters	ml
fl oz	fluid ounces	30	milliliters	ml
c	cups	0.24	liters	l
pt	pints	0.47	liters	l
qt	quarts	0.95	liters	l
gal	gallons	3.8	liters	l
ft^3	cubic feet	0.03	cubic meters	m^3
yd^3	cubic yards	0.76	cubic meters	m^3

TEMPERATURE (exact)

SYMBOL	WHEN YOU KNOW	MULTIPLY BY	TO FIND	SYMBOL
°F	Fahrenheit temperature	5/9 (after subtracting 32)	Celsius temperature	°C



APPROXIMATE CONVERSIONS FROM METRIC MEASURES

LENGTH

SYMBOL	WHEN YOU KNOW	MULTIPLY BY	TO FIND	SYMBOL
mm	millimeters	0.04	inches	in
cm	centimeters	0.4	inches	in
m	meters	3.3	feet	ft
m	meters	1.1	yards	yd
km	kilometers	0.6	miles	mi

AREA

SYMBOL	WHEN YOU KNOW	MULTIPLY BY	TO FIND	SYMBOL
cm^2	square centimeters	0.16	square inches	in^2
m^2	square meters	1.2	square yards	yd^2
km^2	square kilometers	0.4	square miles	mi^2
ha	hectares(10,000 m^2)	2.5	acres	

MASS (weight)

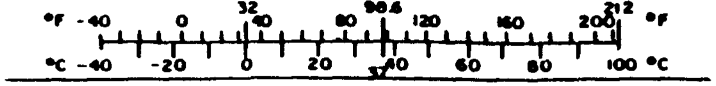
SYMBOL	WHEN YOU KNOW	MULTIPLY BY	TO FIND	SYMBOL
g	grams	0.035	ounces	oz
kg	kilograms	2.2	pounds	lb
t	tonnes (1000 kg)	1.1	short tons	

VOLUME

SYMBOL	WHEN YOU KNOW	MULTIPLY BY	TO FIND	SYMBOL
ml	milliliters	8.03	fluid ounces	fl oz
l	liters	2.1	pints	pt
l	liters	1.06	quarts	qt
l	liters	0.26	gallons	gal
m^3	cubic meters	36	cubic feet	ft^3
m^3	cubic meters	1.3	cubic yards	yd^3

TEMPERATURE (exact)

SYMBOL	WHEN YOU KNOW	MULTIPLY BY	TO FIND	SYMBOL
°C	Celsius temperature	9/5 (then add 32)	Fahrenheit temperature	°F



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INTRODUCTION

In the final report to the U. S. Department of Transportation (DOT), concluding a study (No. FHWA-RD-79-108) titled "Alternative Highway Deicing Chemicals", two candidate deicers were recommended - methanol and calcium-magnesium acetate (CMA). Methanol was found to react more rapidly and to dissipate far more rapidly than does salt (sodium chloride) and therefore is useful only under special conditions. On the other hand, CMA was determined to have road deicing properties very similar to salt.

In addition, under most circumstances CMA has far less corrosion accelerating properties than those of the chloride ion in salt. Also the calcium and magnesium ions have little or no detrimental medical impact in contrast to the sodium ion of salt.

Subseqent to the final report, it also became apparent that CMA can make a significant contribution to the neutralization of acid rain. The decomposition or volatilization of the acetate ion effectively leaves hehind the basic calcium and magnesium ions which neutralize the sulfuric and nitric acids of acid rain. This reaction can occur on the road surfaces producing neutralization of the acids produced in gasoline combustion. It can also significantly affect the streams and lakes into which the CMA is carried by runoff.

In the initial study, preliminary results had been obtained for many of the physical and chemical properties of CMA. The current study had as its objective to obtain further information about these properties. Particular emphasis was put on the evaluation of optimum pH and on the optimum calcium/magnesium (Ca/Mg) ratio for effective road deicing. Included in this evaluation were tests on scaling potential at various pH's and Ca/Mg ratios. The heats of solution, solubilities, liquidus/solidus points, and ice melting rates of several CMA ratios were determined. The stability of CMA in solid and in solution was also evaluated.

The overall objective was to select the optimum pH and Ca/Mg ratio for the deicer.

SCALING POTENTIAL OF CMA

Methods: One hundred and twenty-four (124) cylinders of concrete, 3-in diameter by 6-in height, were prepared in accordance with ASTM C-192 using Wisconsin grade "A" (6 bags per cubic yard) air-entrained concrete from a truck pouring concrete on a major road project in Madison, Wisconsin. The cylinders were poured at the site of the road construction (University Ave. at Randall) and were left on site for 24 hours before being transported back to the laboratory. Single-use cylinder molds (#H-3038 Humboldt Manufacturing, Chicago, IL) were used. Cylinders had been filled earlier at the laboratory with concrete hauled from the road project, but the resultant cylinders contained numerous air pockets and other defects. The problem was apparently due to separation during transportation and to tamping without vibration during filling. In the subsequent preparation, 25 tamping strokes followed by 10 seconds on a 20 cps vibrating platform were applied after each 1/3 filling. Concrete from both truckloads used was approved by the State inspector as meeting Federal standards.

Prior to pouring of the concrete, the screw end of a No. 6 eye-bolt was inserted 1 inch into each cardboard cylinder 3 inches from either end to permit suspension of the cylinders during the drying phase of the treatment cycle.

The molds were stripped off the cylinders 24 hours after preparation. Only 2 cylinders of the 124 prepared were unusable due to air pockets. Due to the high temperatures encountered on the day the cylinders were poured, some of the mold-wax softened and adhered to the concrete. This required scraping to remove the last vestiges of wax on the concrete cylinders. The cylinders were then stored in saturated lime water for 70 days. In preparation for use they were then air dried by suspension on wooden dowels. Four cylinders were attached to a wooden dowel to facilitate insertion into the solution and suspension during the drying phase.

The cylinders were exposed in duplicate to 2% sodium chloride (pH7.0), and to the osmolal equivalent with calcium chloride (pH7), a commercially produced CMA with a 1:1 Ca:Mg ratio (designated PR CMA), and to 11 ratios at 5pH's of calcium and magnesium acetate. The ratios were 10Ca + 0Mg; 9Ca + 1Mg; through 1Ca + 9Mg; and 0Ca + 10Mg.[1] The pH's selected were 6.0, 7.0, 8.0, 8.5, and 9.0. Higher pH's (10 and 11) were initially proposed, but it was found that those pH's could not be achieved without excess hydroxide. Additional controls consisted of deionized water and air. The sodium chloride solution was adjusted to pH7.0 using sodium hydroxide and hydrochloric acid. Calcium chloride was adjusted using calcium hydroxide and hydrochloric acid.

The pH of the calcium and magnesium acetates were adjusted downward with acetic acid, and upward using the appropriate ratio of calcium and magnesium hydroxides. The acidification proved to be simple and rapid; but adjustments to the higher pH's were very slow, due to the low solubility of the hydroxides.

[1] For simplicity in this report a shorthand notation is utilized for CMA of various ratios as follows: CMA 6/4 = CMA with 6 mole fractions of Ca and 4 mole fractions of Mg; CMA 3/7 = CMA with 3 mole fractions of Ca and 7 mole fractions of Mg.

The PR CMA was found to contain approximately 5 percent insolubles. This sample was used without pH adjustment at its initial pH of 10.1.

The sample cylinders were lowered into the specified solutions for a period of 8 hours, and were then removed and suspended in the air for 40 hours except on weekends when the drying phase was extended to 64 hours. Four hundred and fifty milliliters of each solution were placed into rectangular plastic containers, 180 mm by 125 mm by 85 mm (7 in by 5 in by 3¼ in). Upon immersion, approximately a circular half of the cylinder was immersed in the solution.

The immersion/drying test was conducted for a total of 12 months. At the end of the study the cylinders were evaluated on the basis of the degree of scaling of the concrete, using a refinement of the ASTM rating system (ASTM C672). A secondary rating was made of the cylinder color.

RESULTS

None of the rated cylinders had scaling greater than a rating of 1 by the ASTM Method. The region from 0 to 1 was therefore subdivided as shown in table 1A.

The results of this rating and the color ratings are shown in table 1B.

Summations of the ratings, presented in table 2, show that pH6, and to a lessor extent pH7, was detrimental to the concrete. In addition, a Ca/Mg ratio of 5/5 or lower appeared to have less effect on the concrete. None of the CMA ratios appeared more detrimental to concrete than was NaCl when the CMA solution alkalinity was greater than pH7.

TABLE 1A.
Rating System for Concrete Scaling.

ASTM Scaling (C672)	
0	No scaling visible.
0.2	Slight surface roughness, possibly minute area of shallow scaling.
0.4	Modest surface roughness, or small areas of shallow scaling.
0.6	Moderate surface roughness, or modest areas of shallow scaling.
0.8	Substantial surface roughness or moderate areas of shallow scaling.
1.0	Shallow surface scaling and roughness not exceeding 1/8 inch in depth.
2.0	Slight to moderate scaling.
3.0	Moderate scaling (coarse aggregate exposed).
4.0	Moderate to severe scaling.
5.0	Severe scaling (coarse aggregate exposed over entire surface).

Color	
A	Darker or no color change.
B	Slightly lighter in color.
C	Moderately lighter in color.
D	Substantially lighter in color.
E	Almost white in color.

TABLE 1B.

Ratings of Concrete Cylinders After 12 Months of Treatment with Calcium and Magnesium Acetates.

	REP 1		REP 2	
Treatment	ASTM Scale Rating	Color	ASTM Scale Rating	Color
$Ca_{10}Mg_{0}$ pH6	1.0	D	0.6	D
$Ca_{10}Mg_{0}$ pH7	0.4	E	0.3	D
$Ca_{10}Mg_{0}$ pH8	0.1	A	0.2	A
$Ca_{10}Mg_{0}$ pH8.5	0.6	A	0.3	A
$Ca_{10}Mg_{0}$ pH9	0.2	A	0.1	A
$Ca_{9}Mg_{1}$ pH6	0.8	D	0.8	E
$Ca_{9}Mg_{1}$ pH7	0.1	E	0.3	E
$Ca_{9}Mg_{1}$ pH8	0.1	A	0.1	A
$Ca_{9}Mg_{1}$ pH8.5	0.4	A	0.1	A
$Ca_{9}Mg_{1}$ pH9	0.3	A	0.3	A
$Ca_{8}Mg_{2}$pH6	1.0	D	1.0	D
$Ca_{8}Mg_{2}$ pH7	0.3	E	0.5	E
$Ca_{8}Mg_{2}$ pH8	0.2	A	0.2	A

TABLE 1B.

Ratings of Concrete Cylinders After 12 Months of Treatment with Calcium and Magnesium Acetates (continued).

	REP 1		REP 2	
Treatment	ASTM Scale Rating	Color	ASTM Scale Rating	Color
$Ca_8 Mg_2$ pH8.5	0.3	A	0.1	A
$Ca_8 Mg_2$ pH9	0.3	A	0.2	A
$Ca_7 Mg_3$ pH6	0.6	D	0.5	D
$Ca_7 Mg_3$ pH7	0.4	E	0.3	E
$Ca_7 Mg_3$ pH8	0.4	A	0.3	A
$Ca_7 Mg_3$ pH8.5	0.4	A	0.4	A
$Ca_7 Mg_3$ pH9	0.4	A	0.3	A
$Ca_6 Mg_4$ pH6	0.7	D	0.7	D
$Ca_6 Mg_4$ pH7	0.3	E	0.2	E
$Ca_6 Mg_4$ pH8	0.4	A	0.2	A
$Ca_6 Mg_4$ pH8.5	0.3	A	0.4	A
$Ca_6 Mg_4$ pH9	0.1	A	0.2	A
$Ca_5 Mg_5$ pH6	0.8	D	0.9	D
$Ca_5 Mg_5$ pH7	0.8	E	0.3	E

TABLE 1B.

Ratings of Concrete Cylinders After 12 Months of Treatment with Calcium and Magnesium Acetates (continued).

	REP 1		REP 2	
Treatment	ASTM Scale Rating	Color	ASTM Scale Rating	Color
Ca_5 Mg_5 pH8	0.0	A	0.1	A
Ca_5 Mg_5 pH8.5	0.3	A	0.1	A
Ca_5 Mg_5 pH9	0.3	A	0.4	A
Ca_4 Mg_6 pH6	0.8	D	0.7	D
Ca_4 Mg_6 pH7	0.3	E	0.2	E
Ca_4 Mg_6 pH8	0.2	A	0.1	B
Ca_4 Mg_6 pH8.5	0.2	A	0.1	A
Ca_4 Mg_6 pH9	0.2	A	0.2	A
Ca_3 Mg_7 pH6	1.0	E	0.8	E
Ca_3 Mg_7 pH7	0.3	E	0.2	E
Ca_3 Mg_7 pH8	0.2	A	0.2	B
Ca_3 Mg_7 pH8.5	0.3	B	0.2	B
Ca_3 Mg_7 pH9	0.1	B	0.1	B

TABLE 1B.

Ratings of Concrete Cylinders After 12 Months of Treatment with Calcium and Magnesium Acetates (continued).

	REP 1		REP 2	
Treatment	ASTM Scale Rating	Color	ASTM Scale Rating	Color
$Ca_2 Mg_8$ pH6	0.7	E	0.6	E
$Ca_2 Mg_8$ pH7	0.1	E	0.3	E
$Ca_2 Mg_8$ pH8	0.1	A	0.2	B
$Ca_2 Mg_8$ pH8.5	0.1	B	0.1	A
$Ca_2 Mg_8$ pH9	0.1	B	0.1	B
$Ca_1 Mg_9$ pH6	0.7	E	0.8	E
$Ca_1 Mg_9$ pH7	0.2	D	0.2	D
$Ca_1 Mg_9$ pH8	0.1	B	0.1	C
$Ca_1 Mg_9$ pH8.5	0.0	B	0.1	B
$Ca_1 Mg_9$ pH9	0.1	B	0.1	B
$Ca_0 Mg_{10}$ pH6	0.8	D	0.7	D
$Ca_0 Mg_{10}$ pH7	0.2	C	0.2	C

TABLE 1B.

Ratings of Concrete Cylinders After 12 Months of Treatment with Calcium and Magnesium Acetates (continued).

	REP 1		REP 2	
Treatment	ASTM Scale Rating	Color	ASTM Scale Rating	Color
Ca_0 Mg_{10} pH8	0.1	C	0.1	C
Ca_0 Mg_{10} pH8.5	0.1	C	0.1	C
Ca_0 Mg_{10} pH9	0.1	C	0.1	C
Air	0.0	C	0.1	C
Calcium Chloride	0.1	C	0.1	D
Sodium Chloride	.3	C	.4	C
PR CMA	.4	C	.4	C
Deionized water	0.2	C	0.2	C

TABLE 1C.

Rerating to Assure Consistency.

	Reratings				Original Ratings			
$Ca_{10}Mg_0$pH7	0.4	E	0.2	E	0.4	E	0.3	D
CMA	0.3	C	0.4	D	0.4	C	0.4	C
Ca_9Mg_1pH8	0.2	A	0.2	A	0.1	A	0.1	A
Ca_8Mg_2pH8	0.3	A	0.3	A	0.3	A	0.5	A

TABLE 2.

Summation of Immersion/Drying Ratings.

	Average Ratings
PH6, CMA	0.77
pH7, CMA	0.29
pH8, CMA	0.17
pH8.5, CMA	0.23
pH9, CMA	0.20

Ratio Ca	Ratio Mg	Average Ratings pH7-9	Average Ratings pH6
10	0	0.28	0.80
9	1	0.21	0.80
8	2	0.26	1.00
7	3	0.36	0.55
6	4	0.26	0.79
5	5	0.29	0.85
4	6	0.19	0.75
3	7	0.20	0.90
2	8	0.14	0.65
1	9	0.11	0.75
0	10	0.13	0.75
NaCl		0.35	
$CaCl_2$		0.10	
PRCMA		0.40	
H_2O		0.20	

Compositional Changes

Solid Residue: Within 1 month after the immersion scaling tests were initiated, a white solid residue was visible above the water line on many of the concrete cylinders. Although the total weight of solid was under 0.1 g on any cylinder, an analysis of the cation content seemed warranted. Some of this solid was scraped off of three cylinders and dissolved in dilute hydrochloric acid with slight gas evolution. The calcium and magnesium compositions were determined. Table 3 shows that the solid contained substantially increased calcium over the original solution for the CMA 5/5 and CMA 0/10 samples. This suggests the extraction of some calcium ion out of the concrete.

Solutions: Samples of the solution in the immersion containers were also analyzed for calcium, magnesium, and acetate after 1 month. Table 4 shows that the solutions were also somewhat enriched in calcium over the initial solution composition. Acetate recovery varied from 78 to 100 percent. The greatest variability occurred with the CMA 5/5 samples. There was substantial mold growth on some samples, and this may have accounted for much of the acetate loss.

pH Adjustments

The pH's of the CMA solutions were tested after 1 month of immersion testing. The results in table 5 show that there was a substantial shift in pH which was influenced strongly by the Ca/Mg ratio. At CMA 10/0, the pH of the solutions were all close to 7.7. The pH gradually increased as the amount of Mg increased until CMA 0/10 solutions had pH's significantly over pH8.0.

TABLE 3.
White Solid on Sides of Cylinders - pH8.5.

	CMA (10/0) [$CaAc_2$]	CMA (5/5) [CMA (1/1)]	CMA (0/10) [$MgAc_2$]
Concentration ratio of Mg/Ca ions	0.00/100	33.3/66.7	37.1/63.9

TABLE 4A.

Mole % of Magnesium of Total Ca + Mg in Scaling Test Solutions.

pH	CMA (10/0) [CaAc$_2$]	CMA (5/5) [CMA (1/1)]	CMA (0/10) [MgAc$_2$]
6	0.05%	47.6	95.9
7	(Average of combined solutions)	48.1	90.3
8	"	48.6	97.0
8.5	"	45.5	96.8
9	"	44.0	94.8
Average	0.05%	46.8	94.8

TABLE 4B.

Acetate Recovery in Scaling Test Solutions.

pH	CMA (10/0)	CMA (5/5)	CMA (0/10)
6	95	79	85
7	89	78	90
8	89	100	87
8.5	91	100	85
9	87	92	89

TABLE 5.

Final pH of CMA Immersion Solutions After One Month (13 Immersion Cycles).

Other	CaMg ratio orig pH	100Ca 0Mg 10/0	90Ca 10Mg 9/1	80Ca 20Mg 8/2	70Ca 30Mg 7/3	60Ca 40Mg 6/4
Deionized H_2O 8.95 8.90	6.0	7.69 7.71	7.66 7.67	7.69 7.69	7.72 7.74	7.76 7.75
Prod. CMA 8.26 8.24	7.0	7.69 7.68	7.70 7.71	7.70 7.72	7.72 7.81	7.61 7.74
NaCl 9.84 8.87	8.0	7.76 7.77	7.74 7.71	7.72 7.71	7.74 7.75	7.76 7.77
$CaCl_2$ 7.20 7.24	8.5	7.71 7.73	7.72 7.72	7.72 7.71	7.70 7.69	7.70 7.72
Control	9.0	7.74 7.70	7.72 7.71	7.72 7.71	7.70 7.69	7.73 7.74

TABLE 5.

Final pH of CMA Immersion Solutions After One Month (13 Immersion Cycles).

continued.

CaMg ratio / orig pH	50Ca 50Mg 5/5	40Ca 60Mg 4/6	30Ca 70Mg 3/7	20Ca 80Mg 2/8	10Ca 90Mg 1/9	0Ca 100Mg 0/10
6.0	7.79 7.79	7.83 7.81	7.90 7.89	7.94 7.94	8.03 8.04	8.27 8.33
7.0	7.54 7.57	7.81 7.83	7.86 7.90	7.88 7.90	8.06 8.08	8.22 8.26
8.0	7.79 7.80	7.82 7.83	7.86 7.88	7.94 7.92	8.02 8.00	8.31 8.69
8.5	7.75 7.73	7.78 7.75	7.83 7.81	7.89 7.86	8.07 8.03	8.70 8.20
9.0	7.71 7.73	7.74 7.71	7.78 7.82	7.77 7.75	7.85 7.89	8.08 8.24

This substantial and rapid pH shift indicated the need to modify the procedure. Beginning after 3 months, the solutions were replaced every 2 months. The total solution volume was adjusted by the addition of deionized water every 3-weeks. More frequent water additions were unnecessary because the containers were covered with tight-fitting lids except when the concrete cylinders were immersed in the solutions. After the end of the seventh month, the solutions were replaced weekly because it was found that substantial pH changes occurred within a 1-week period involving three immersions. This is shown in table 6 which shows the pH change of the pH6 solutions over a 3-week period.

TABLE 6.

Change of pH 6.0 Solutions During Nine Immersions.

	Start	1 EXP.	2 EXP.	3 EXP.	6 EXP.	9 EXP.
Deionized	5.2	7.5	8.7	8.4	8.7	8.4
CMA (10/0)	6.0	6.3	6.8	7.1	7.6	7.6
CMA (9/1)	6.0	6.4	6.8	7.2	7.7	7.7
CMA (8/2)	6.0	6.4	6.8	7.3	7.7	7.7
CMA (7/3)	6.0	6.4	6.9	7.4	7.7	7.7
CMA (6/4)	6.0	6.5	7.1	7.5	7.8	7.7
CMA (5/5)	6.0	6.5	7.2	7.6	7.8	7.8
CMA (4/6)	6.0	6.6	7.2	7.6	7.8	7.8
CMA (3/7)	6.0	6.7	7.4	7.7	7.9	7.9
CMA (2/8)	6.0	6.8	7.9	7.9	8.0	7.9
CMA (1/9)	6.0	7.0	8.2	8.1	8.1	8.0
CMA (0/10)	6.0	7.1	8.3	8.3	8.3	8.3

PHYSICAL PROPERTIES OF CMA

Heats of Solution

Methods: A 265-ml Dewar flask was further insulated with styrofoam inside a cardboard box. A Beckman differential thermometer was suspended approximately 1 mm above the inside bottom of the flask, and a precision, fractional-degree thermometer was suspended beside it. The Beckman thermometer was adjusted to the desired temperature range, and the apparatus was placed in a Gilson Chromotography Chamber glass-fronted refrigerator adjusted to the desired temperature. Temperatures selected were 8, 12, 16, 20, and 25, ± 1 °C.

Approximately 100 g of water were placed into the Dewar flask, and a tightly sealed bottle containing the experimental acetate salt was weighed and suspended from the mouth of the flask by a copper wire. Sufficient salt was used to produce a diacetate salt-to-water mole ratio of 1 to 420 ± 20. The flask was covered with a styrofoam cap slotted for the thermometers and for the handle of the glass, ring-shaped stirrer. The apparatus was then held for 16 to 40 hours to attain thermal equilibrium.

Readings were taken from both thermometers. The acetate salt sample was then dumped into the water as the timer was activated. The flask was immediately covered, and stirring was initiated. Stirring was continued throughout the test period, and the differential thermometer was read at 1-minute intervals for 10 minutes. A final reading was then made on the precision thermometer.

The temperature readings were plotted on graph paper, and the curve was extrapolated back to 0 minutes to determine the ΔT_0 of the salt. The emptied bottle was reweighed to get the exact weight of salt used. Finally, the Dewar flask and solution were weighed to accurately measure the water content in the flask.

The heat capacity of the system was determined utilizing a 55-g cylinder of copper heated in boiling water. The heated cylinder was dropped into 100-g of H_2O and the temperature increase of the water was measured. From this, the formula for the heat capacity was determined to be: Calories/1 ^{o}C = grams of water + 21.2.

The heat of solution and the mole ratio were then calculated according to the following quotations:

Formula for Evaluation of Heats of Solution

$$\frac{\text{Heats of Solution}}{\text{(calories/mole)}} = \frac{\Delta T_e\ (^{o}C)}{\text{wt. of CMA (g)}} \times \frac{(\text{g of } H_2O + 21.2)\ \text{calories}}{1\ ^{o}C} \times \frac{\text{wt. of CMA (g)}}{\text{mole}}$$

Formula for Calculation of Mole Ratios

$$\frac{\text{Moles of } H_2O}{\text{Mole of CMA}} = \frac{\text{wt. of } H_2O\ \text{(g)}}{\text{wt. of CMA (g)}} \times \frac{\text{g CMA/mole}}{18\ \text{g } H_2O\text{/mole}}$$

Except for $MgAc_2 \cdot 4H_2O$, the salts tested were dried overnight in a vacuum oven at 100 ^{o}C. A slow bleed of air was permitted to sweep out the moisture by adjusting the vacuum to 710 mm mercury. Calcium acetate was dried from the monohydrate, whereas, the CMA 6.7/3.3 and CMA 3.3/6.7 were dried from concentrated aqueous solutions. Titration for calcium, magnesium, and alkalinity showed that the dried salts were not totally anhydrous as was expected. The salts had the following hydration levels: $CaAc_2 \cdot 1/3H_2O$; $Ca_2MgAc_6 \cdot 1/3H_2O$; $CaMg_2Ac_6 \cdot 1/6H_2O$. "PR" CMA was tested without drying. This material had a hydration level of 1 - i.e., $CaMgAc_4 \cdot 1H_2O$ or CMA $5/5 \cdot H_2O$.

Results: The calculated heats of solution of the salts are shown in table 7 and figure 1. Literature values for $CaAc_2$, for NaCl, and for $CaCl_2$ and its hydrates are shown in table 8.

There appears to be a slightly higher heat of solution at 16 $^{\circ}C$ than at other temperatures for $CaAc_2$ and CMA. However, the differences may well be within experimental error. It is evident that both of the anhydrous acetate salts have strongly positive heats of solution. The data indicate that the anhydrous $MgAc_2$ has a higher heat of solution than does $CaAc_2$. By extrapolation anhydrous $MgAc_2$ would appear to have a heat of solution of 17 to 18 Kcal/mole. This is comparable to anhydrous $CaCl_2$ (18 Kcal/mole).

Total dehydration of $MgAc_2$ was not attempted because earlier drying attempts at 140 $^{\circ}C$ had produced substantial decomposition with the loss of substantial acetate. Adding calcium acetate appeared to stabilize the magnesium acetate. Table 9 shows that a calcium acetate level greater than 50 percent was needed to prevent significant acetate loss from the powdered mixed salts dried at 140 $^{\circ}C$.

The vacuum drying results indicate that vacuum drying at 100 $^{\circ}C$ may attain essentially anhydrous CMA, and probably $MgAc_2$ also, without significant decomposition since the $CaMg_2Ac_6$ sample was dried to a very low water level with no evident decomposition. Furthermore, the hydration remaining in the CMA salts appeared to be associated primarily with the calcium acetate, since the amount of hydration halved as the calcium concentration halved in the two mixed salts which were vacuum dried.

TABLE 7.
Heats of Solution of CMA Deicers.

Substance	Temp. °C	Mole Ratio (H_2O:1 Solute)	Kcal/mole
$CaAc\cdot 1/3H_2O$ or CMA 10/0·$1/3H_2O$	8.2	419	6.40
	12.1	416	6.07
	16.7	435	6.67
	19.9	421	6.38
	25.3	407	6.29
$1/3Ca_2Mg_1Ac_6\cdot 1/3H_2O$ or CMA 6.7/3.3·$1/9H_2O$	8.0	419	9.13
	12.4	424	8.97
	16.5	408	9.28
	19.2	440	9.40
	25.2	427	9.18
PR CMA or PR CMA 5/5·$1H_2O$	8.4	431	9.43
	13.8	408	9.52
	16.4	430	9.83
	19/0	415	9.57
	24.7	401	9.43
$1/3CaMg_2Ac_6\cdot 1/6H_2O$ or CMA 3.3/6.7·$1/8H_2O$	7.6	422	13.70
	12.4	414	13.91
	15.6	422	14.33
	20.4	407	13.95
	25.2	425	13.78

TABLE 7.

Heats of Solution of CMA Deicers (continued).

Substance	Temp. °C	Mole Ratio (H$_2$O:1 Solute	Kcal/mole
MgAc$_2$·4H$_2$O	8.0	424	3.38
or	12.1	403	3.31
CMA 0/10·4H$_2$O	15.9	428	3.23
	19.9	623	3.01
	24.7	442	2.99
Other Measured Values			
MgAc·4H$_2$O	20.0	43.8	1.64
or			
CMA 0/10·4H$_2$O	20.5	56.4	2.01
PR CMA	20.0	63	7.58
or	20.0	142	8.98
PR CMA 5/5·1H$_2$O	26.0	1116	9.97

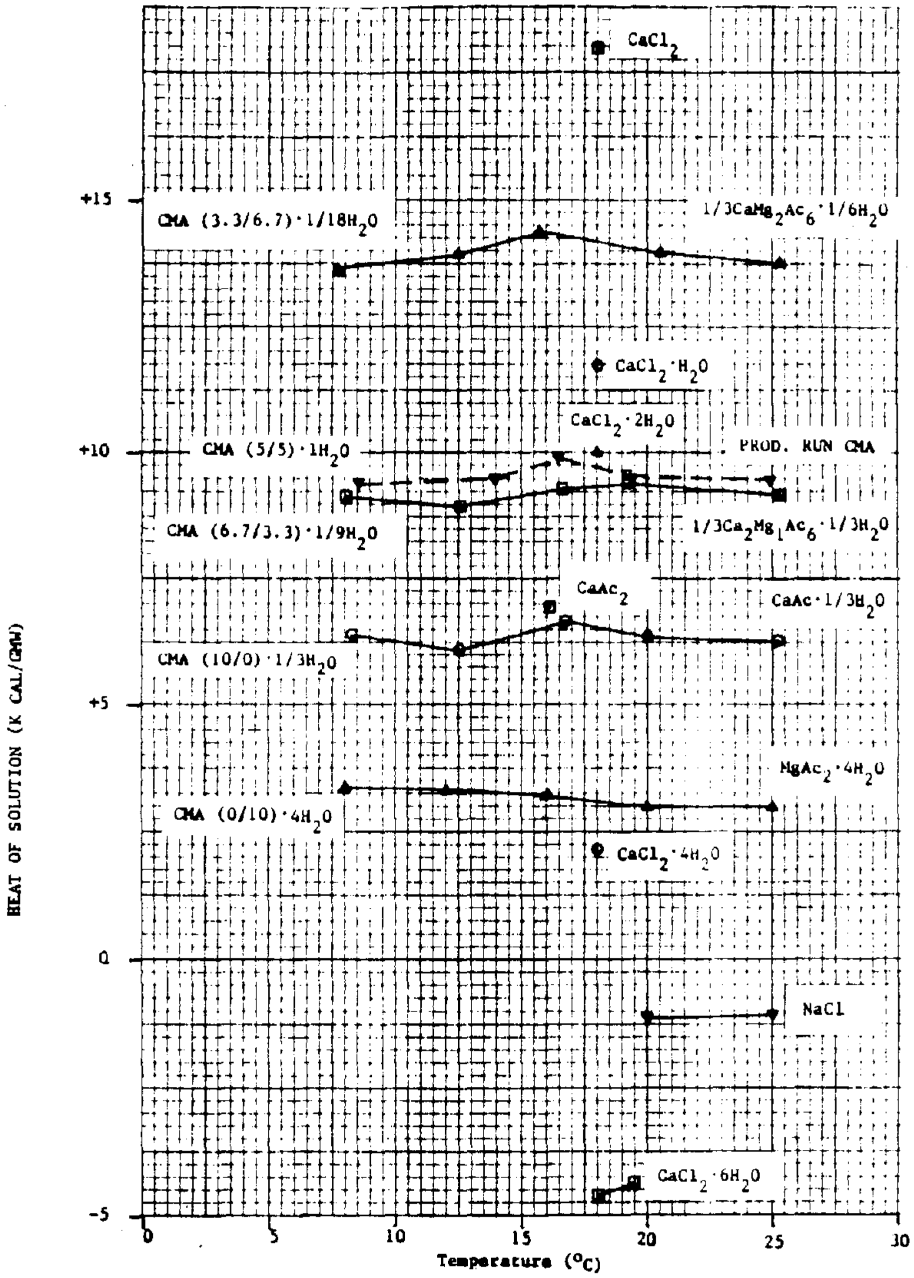

FIGURE 1. Heats of Solution of Deicers.
Nominally 420:1 Ratio Water:Solute

TABLE 8.
Literature Data - Heats of Solution.

Substance	Temp. °C	Mole Ratio (H_2O:1 mole solute)	Heat of Solution (Kcal/mole)
(A) $CaAc_2$	16	440	+6.93
(A) $CaAc_2 \cdot H_2O$	17	600	+5.85
(C) NaCl	25	400	-1.020
(C)	18	200	-1.281
(C)	20	315	-1.083
(D) $CaCl_2$	18	300	+17.41
(B)	18	400	+17.99
(D)	25	555	+19.82
(B) $CaCl_2 \cdot H_2O$	18	300	+11.71
(B) $CaCl_2 \cdot 2H_2O$	18	400	+10.04
(B) $Cacl_2 \cdot 4H_2O$	18	400	+2.2
(B) $CaCl_2 \cdot 6H_2O$	18	400	-4.56

A. Handbook of Chem. & Physics, 39th Edition, 1957.

B. Intl. Critical Tables, Vol. 5., 1929.

C. Calculated from Kaufman, "Sodium Chloride: The Production and Properties of Salt and Brine", ACS Monographic 145, 1960.

D. Lange, Handbook of Chemistry, 1952.

TABLE 9.

Extent of Acetate Loss From CMA Dried at 140 °C for 18 Hours.

CMA Composition	% Acetate Loss
CMA 10/0	0
CMA 6.7/3.3	0
CMA 5/5	2.8
CMA 0/10	20.2%

Solubility

Methods: Weighed quantities of various ratios of $CaAc_2 \cdot H_2O$, $MgAc_2 \cdot 4H_2O$ and water were placed into screw cap vials, sealed, and placed into cooling equipment at 20, 0, and -18 ^oC. The samples were shaken several times daily to achieve equilibrium. Water or additional salts were added as needed to produce a solution with a small excess of solid. Weighed samples of the solution were then analyzed for Ca and Mg and the CMA solubility was calculated on the basis of weight and of molality. An additional solubility test was conducted with CMA 10/0 and CMA 0/10 at approximately the eutectic temperature for $CaAc_2$, -14.7 ^oC.

Results: At 0 ^oC, as the concentration of magnesium vs. calcium increased in the CMA, a gradually accelerating increase in molality was observed (table 10). The maximum osmolality was at approximately 95% $MgAc_2$ (figure 2). A similar increase in osmolality was observed at -18 ^oC with the actual solubility being only slightly less than at 0 ^oC.

The solubility at 20 ^oC of approximately CMA 2/8 was essentially identical to that at 0 ^oC. It therefore appears that there is only a very slow change in solubility with changes of temperature for high magnesium CMA.

The saturation molality increased with increased magnesium until the maximum molality was attained at a magnesium concentration greater than nine times as great as the calcium concentration.

The solubilities of pure $CaAc_2$ and pure $MgAc_2$ were obtained from the literature and additional data were collected to extend the results.(1,2) These results are shown in figures 3 and 4. $CaAc_2$ increases in solubility substantially as its temperature is lowered below about 40 °C until it reaches its eutectic at -14.7 °C.

$MgAc_2$ solubility declines slowly below 0 °C. Rivett extrapolated his data to project an eutectic of -29 °C for $MgAc_2$. However, in the current study, supercooling was observed in the satrated solutions. This was followed by heat evolution and solidification at temperatures as high as -8.5 °C. Analysis of the solid showed a composition of $MgAc_2 \cdot 8H_2O$. This solid dissolved in its own water of hydration when placed on the finger - i.e., at 34 °C.

TABLE 10.

Solubility and Molalities of Various Ratios of CMA at 20, 0, and -18 °C.

Nominal Mole Ratio Ca	10	9	5	3	2	1	0
Nominal Mole Ratio Mg	0	1	5	7	8	9	10
Solubility	0 °C						
g $CaAc_2/KgH_2O$	377.3	332.3	199.4	138.7	106.0	34.1	0
g $MgAc_2/KgH_2O$	0.3	43.8	192.2	283.7	359.8	541.6	547.6
Total Weight	377	376.1	391.6	422.4	465.8	575.7	547.6
Mole $CaAc_2/KgH_2O$	2.385	2.101	1.261	0.877	0.670	0.216	0.000
Mole $MgAc_2/KgH_2O$	0.000	.308	1.350	1.992	2.527	3.804	3.846
Total Molality	2.385	2.409	2.6111	2.869	3.198	4.020	3.846
Calculated Ca/Mg Ratio	$\frac{10}{0}$	$\frac{8.7}{1.3}$	$\frac{4.8}{5.2}$	$\frac{3.1}{6.9}$	$\frac{2.1}{7.9}$	$\frac{0.5}{9.5}$	$\frac{0}{10}$

TABLE 10.
Solubility and Molalities of Various Ratios of
CMA at 20, 0, and -18 °C
(continued).

Nominal Mole Ratio Ca	10	9	5	3	2	1	0
Nominal Mole Ratio Mg	0	1	5	7	8	9	10
Temperature					+20 °C	-18 °C	-18 °C
g $CaAc_2/KgH_2O$					106.9	43.7	0.00
g $MgAc_2/KgH_2O$					351.3	519.1	531.4
Total Weight, g/KgH_2O					458.2	562.8	531.4
Mole $CaAc_2/KgH_2O$					0.676	.276	0.000
Mole $MgAc_2/KgH_2O$					2.467	3.646	3.732
Total Molality					3.143	3.922	3.732
Calculated Ca/Mg Ratio					$\frac{2.2}{7.8}$	$\frac{0.7}{9.3}$	$\frac{0}{10}$

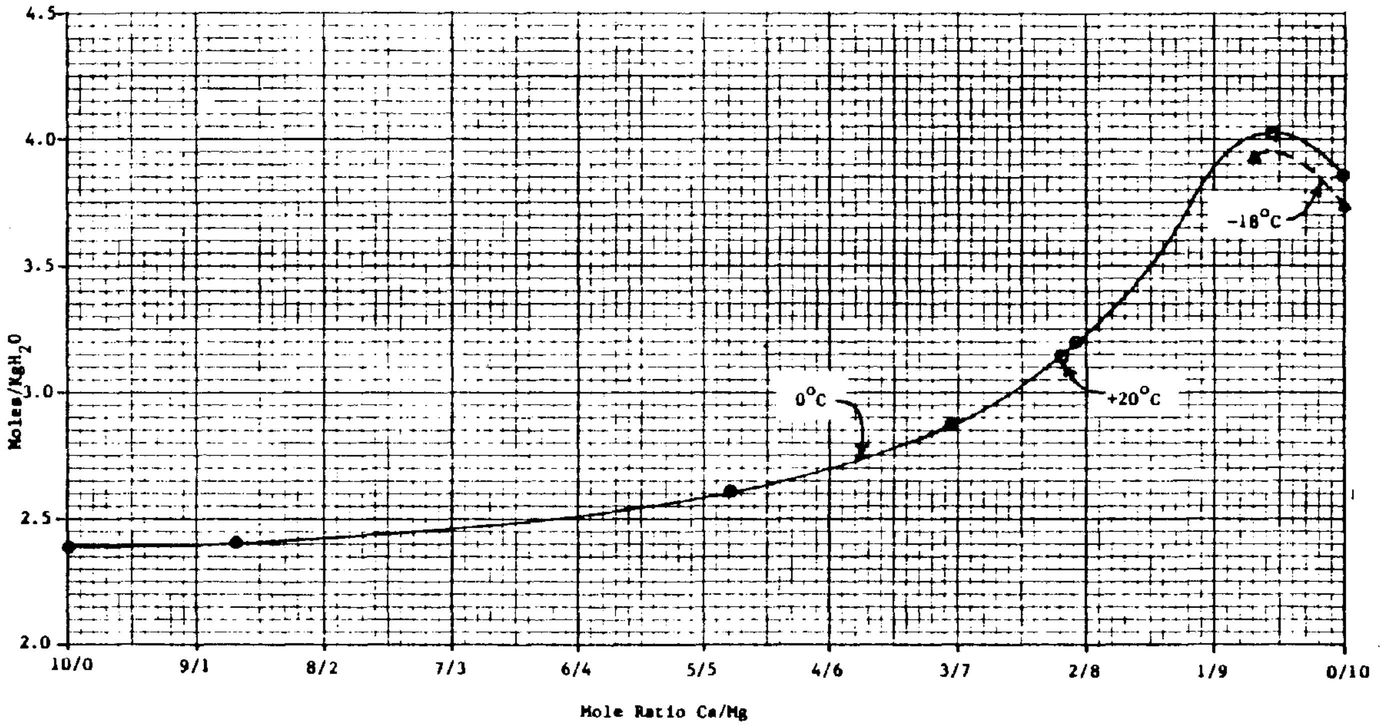

FIGURE 2.
Solubility vs. Temperature of CMA (Moles/kg Water).

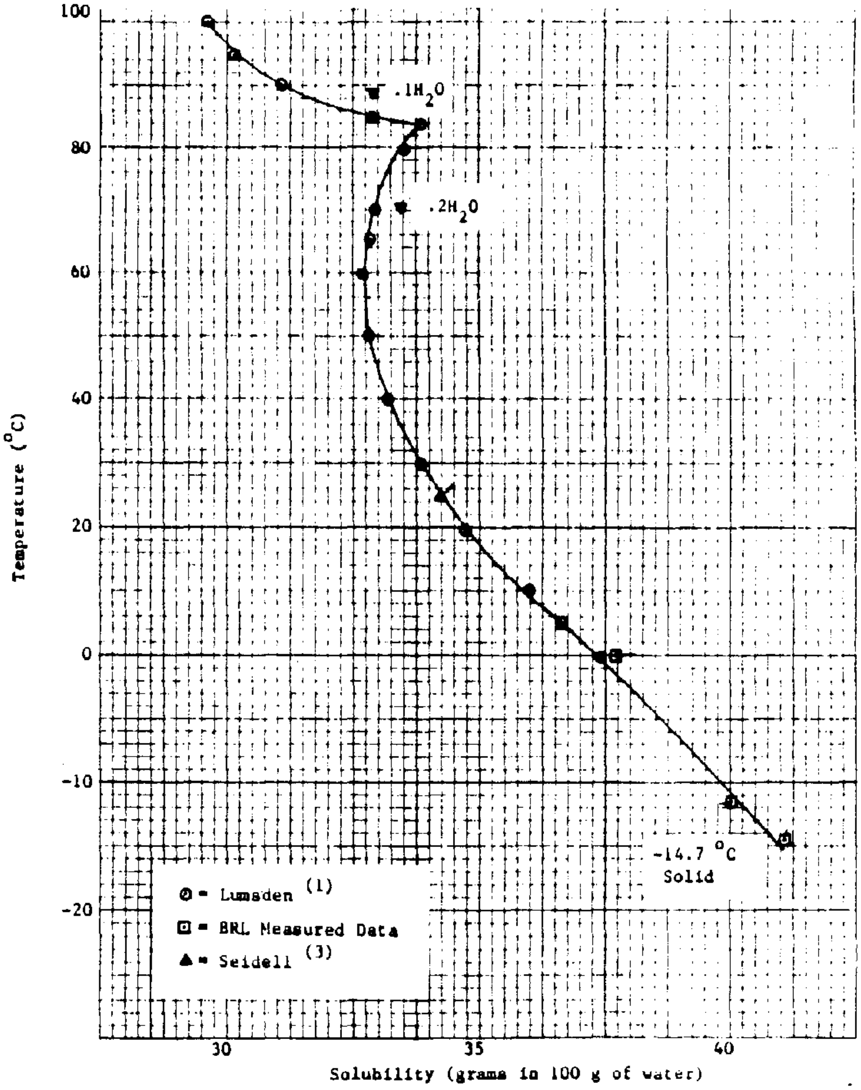

FIGURE 3.

Solubility vs. Temperature of Calcium Acetate $Ca(OAc)_2$.

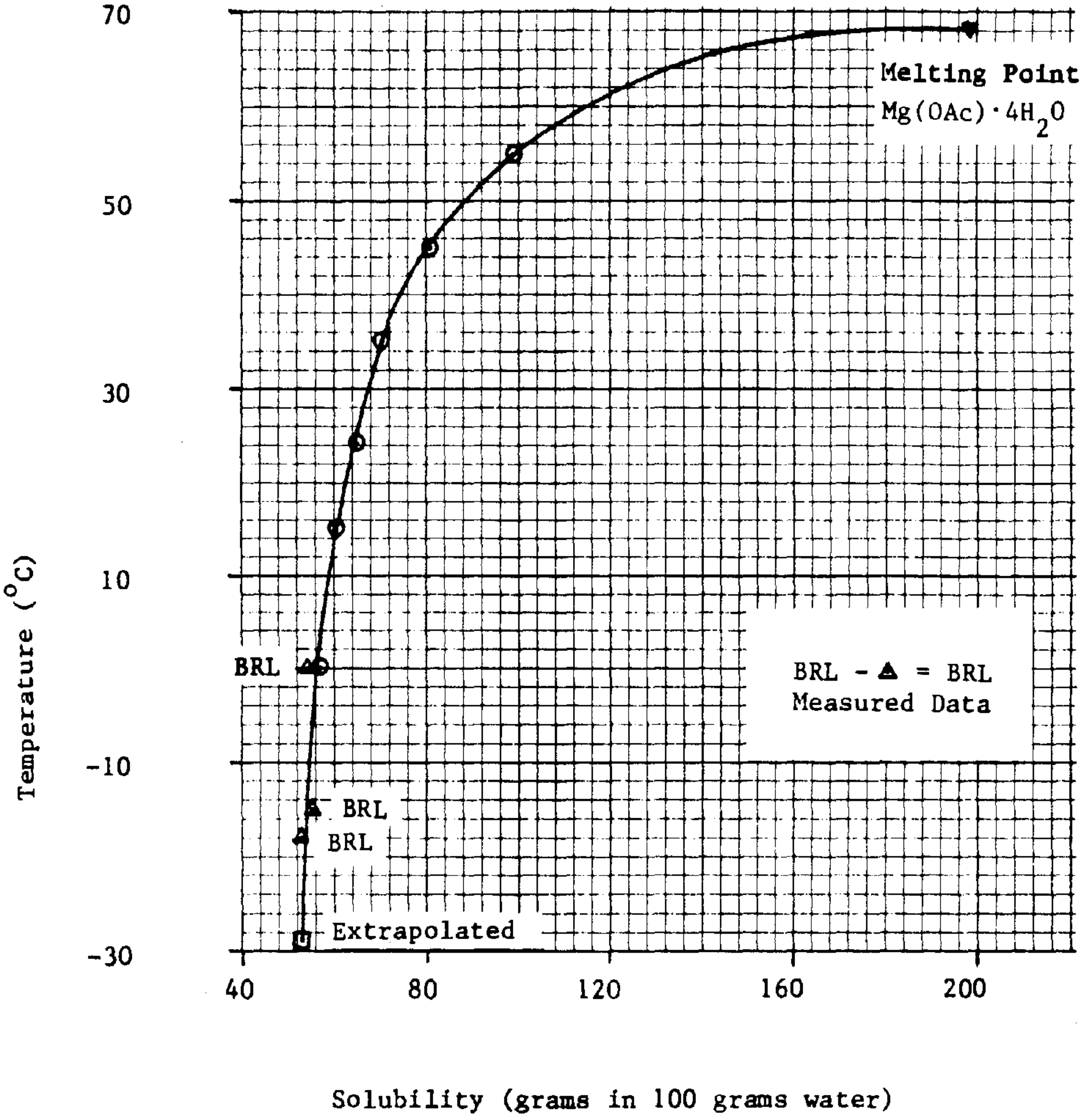

FIGURE 4.
Solubility vs. Temperature of Magnesium Acetate.(2)

LIQUIDUS-SOLIDUS

Methods: Calcium and magnesium acetates were dissolved in water to produce concentrations of 0.23 molal (equivalent to 2.0% NaCl), 0.5, 1.0, and 1.5 molal solutions with 11 Ca/Mg ratios ranging from 10/0, 9/1 to 1/9, and 0/10. In addition, solutions with these ratios were prepared at concentrations close to saturated.

Approximately 10 ml of each solution were placed in a test tube (25 mm D X 200 mm H), together with a metallic loop stirrer and the detector for a digital electronic thermometer reading to 0.1 °C.

The sample tube was lowered into an ethylene glycol antifreeze bath and chilled sufficiently to freeze the sample. When the solution was frozen, the tube was removed from the bath, and was clamped inside a larger glass tube to slow the rate of heat absorption. The sample was then permitted to warm slowly. The solidus was considered to be the temperature at which the metallic thermometer probe was released from firm retention in the sample. The liquidus was determined as the temperature at which all of the solid (usually ice) dissolved. These values were reproducible to ± 0.1 °C for liquidus; about 1 °C for solidus.

Liquidus Results

Figure 5 shows the liquidus data. At low concentrations, the liquidus changed very little with changes in the Ca/Mg ratio. However, except for the 0.23 molal solutions, there was a small but consistent trend toward a lower liquidus temperature as the proportion of magnesium cation increased. As the solution concentration increased, the decrease in liquidus temperature was greater than proportional to the increase in concentration down through 1.5 molal. In the near saturated solutions the liquidus decreased substantially with the increased proportion of magnesium cation up to the 2/8 ratio, due to increasing solubility as the magnesium content increased. Beyond that point the liquidus rapidly increased to higher than 0 ^{o}C due to the formation of a solid that was insoluble at 0 ^{o}C. Analysis of the insoluble solid from the $MgAc_2$ (CMA 0/10) sample indicated that its composition was $MgAc_2 \cdot 8H_2O$.

Solidus Results

Table 11 and figure 6 show the solidus data. The solidus temperature increased slowly with increasing magnesium composition at the lowest concentration tested, 0.23 molal. With the more concentrated solutions, the solidus temperature declined as the magnesium content increased, particularly above the CMA 5/5 composition. In the 1.0 and 1.5 molal solutions the solidus temperature continued to decline. In the 0.5 molal and saturated solutions, the CMA 3/7 composition represented a minimum solidus temperature. Very likely this is dependent on whether the octahydrate of $MgAc_2$ formed. When this occurred, the solidus temperature evidently increased appreciably.

In the near saturated solutions with ratios between CMA 2/8 and CMA 0/10, supercooling occurred regularly. When crystalization finally occurred, a substantial heat evolution was observed with the solution temperature increasing as much as 20 ^{o}C. When this occurred, the solidus temperature also increased.

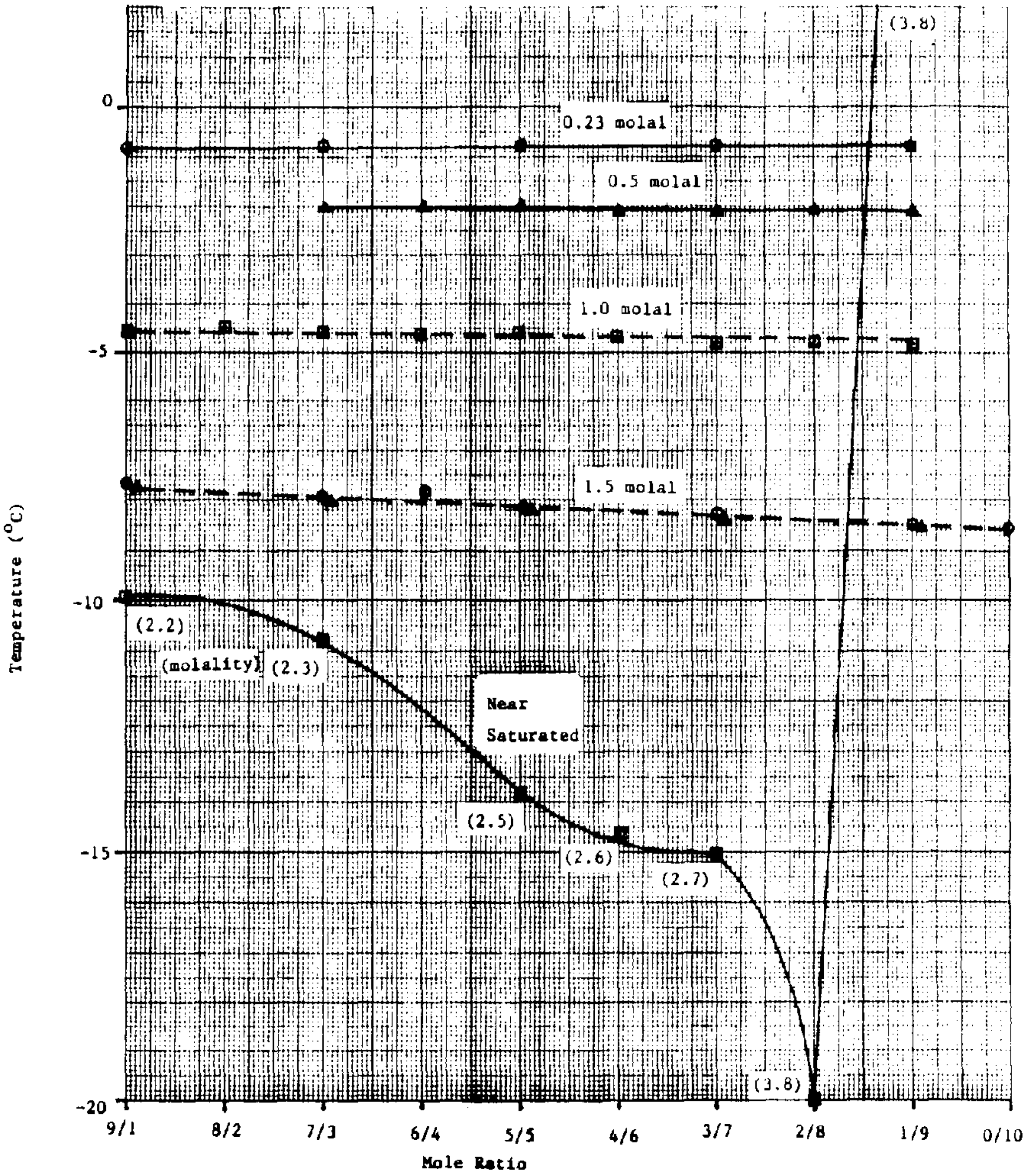

FIGURE 5.
Liquidous vs. Mole Ratio.

TABLE 11.
Liquidus/Solidus Measurements of Calcium and Magnesium Acetate Solutions.

CMA Composition	Solution Molality	Solidus	Liquidus
9/1	2.20, pH9	-15.4	-9.9
7/3	2.34, pH9	-23	-10.8
5/5	2.50, pH9	-23	-13.8
4/6	2.50, pH9	-32	-14.7
3/7	2.68, pH9	-37	-15
2/8	3.77, pH7	-34	-20
1/9	3.77, pH9	-21	+11
0/10	3.77, pH8.7	-15 to -9	+14 to +28
9/1	1.5, pH7	-16.2	-7.7
7/3	1.5, pH7	-20.1	-8.0
6/4	1.5, pH7	-19.8	-7.9
5/5	1.5, pH7	-28	-8.2
3/7	1.5, pH7	-30	-8.3
1/9	1.5, pH7	-31	-8.5
0/10	1.5, pH7	---	-8.6
9/1	1.5, pH9	-15.8	-7.8
7/3	1.5, pH9	-20.5	-8.0
5/5	1.5, pH9	-28	-8.2
3/7	1.5, pH9	-30	-8.4
1/9	1.5, pH9	-32	-8.5
9/1	1.0, pH7	-11.9	-4.6
8/2	1.0, pH7	-13.8	-4.5
7/3	1.0, pH7	-16.4	-4.6
6/4	1.0, pH7	-18.4	-4.6

TABLE 11.
Liquidus/Solidus Measurements of Calcium and Magnesium Acetate Solutions (continued).

CMA Composition	Solution Molality	Solidus	Liquidus
5/5	1.0, pH7	-20.1	-4.6
4/6	1.0, pH7	-27	-4.7
3/7	1.0, pH7	-28	-4.8
2/8	1.0, pH7	-29	-4.8
1/9	1.0, pH7	-30	-4.8
7/3	0.5, pH7	-11.6	-2.0
6/4	0.5, pH7	-11.0	-2.0
5/5	0.5, pH7	-12.6	-2.0
4/6	0.5, pH7	-15.4	-2.1
3/7	0.5, pH7	-16.5	-2.1
2/8	0.5, pH7	-14.4	-2.1
1/9	0.5, pH7	-13.8	-2.1
9/1	0.23, pH7	-7.3	-0.9
7/3	0.23, pH7	-6.3	-0.8
5/5	0.23, pH7	-5.7	-0.8
3/7	0.23, pH7	-5.5	-0.8
1/9	0.23, pH7	-5.9	-0.8
H_2O		0.0	0.0
NaCl (2%, 0.34 molal)	0.34	-7.6	-1.0
$CaCl_2$ (0.23 molal)	0.23	-6.8	-0.7

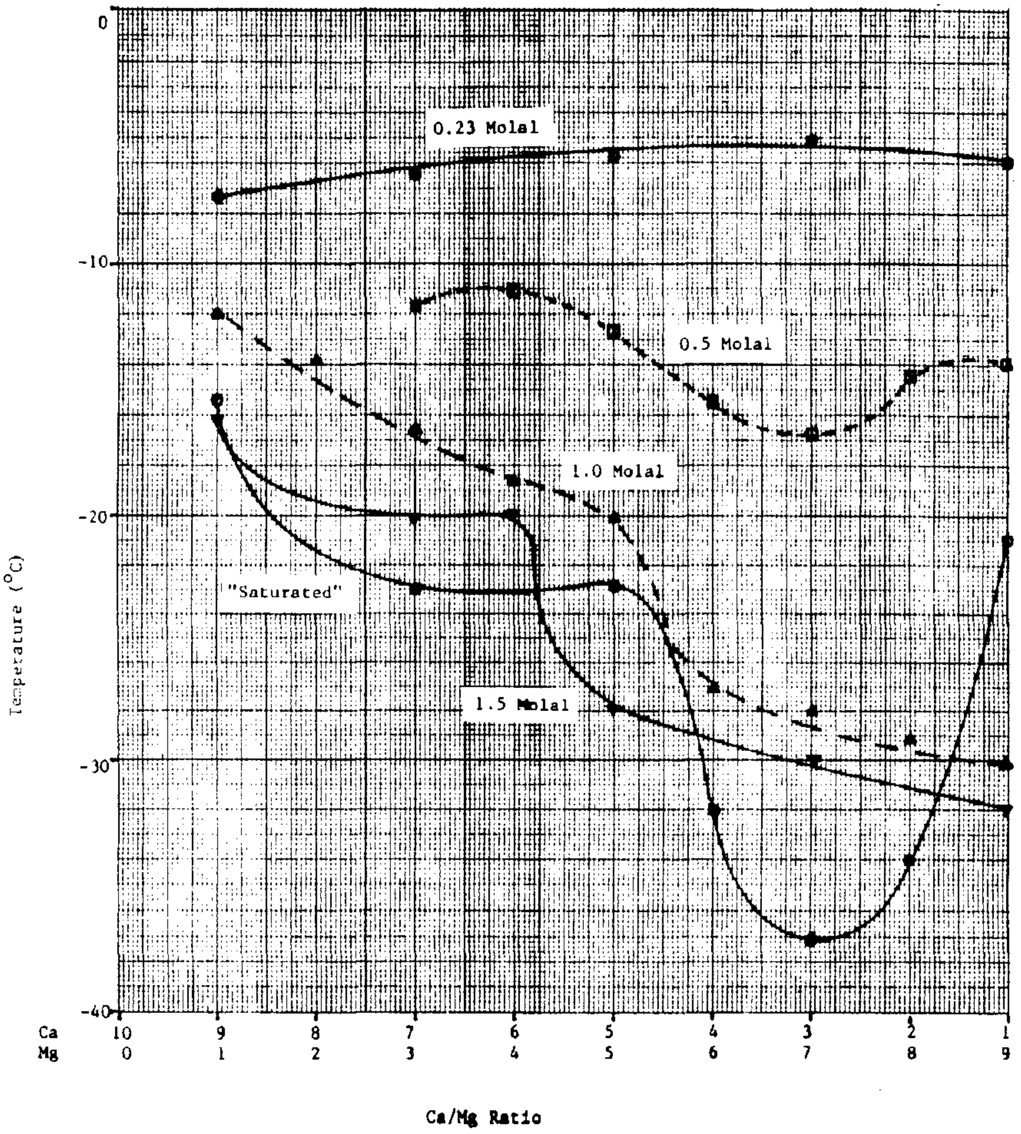

FIGURE 6.
Solidus vs. Mole Ratio.

COMPOSITION AND STABILITY OF CMA

Methods: Aqueous solutions and solid PR CMA were stored for 9 months to evaluate the chemical stability of the material. Samples were placed in half-liter plastic bowls with tight fitting plastic lids. Samples tested included 1% CMA, 5% CMA, 10% CMA, 30% CMA, and solid CMA. Four samples at each composition were prepared. Two of the four samples had five 15-mm-deep triangular notches cut into the top of the bowls to provide open air exposure. A 5-mm slit was put into the lid of each "closed" bowl to assure the minimum air exchange needed for aerobic microbial growth.

One each of the open and closed containers at each CMA composition was stored at ambient temperature (20 to 25 ^{o}C) and the other sample containers were stored at -18 ^{o}C (0 ^{o}F). Samples were weighed and visually inspected several times during the first month and at less frequent intervals thereafter for 285 days (9.4 months).

Several crystal types appeared in the ambient open samples, and several of them were tested to determine the calcium and magnesium compositions.

Calcium and magnesium were determined by colorimetric titration. (4) Magnesium was found to interfere with calcium in high magnesium samples. Therefore total calcium and magnesium was determined for these samples before and after precipitation of calcium by ammonium oxalate solution. The difference in titer was considered to be calcium.

At the end of the test, the test samples were dissolved into 500 ml of aqueous solution. Substantial hydrochloric acid was needed to dissolve the insoluble suspensions, which released an odorless gas, presumed to be carbon dioxide, on addition of the acid. Total calcium and magnesium were measured on these samples. Acetate was determined using the Boehringer-Mannheim enzymatic method. (5) Acetate retention was then calculated in comparison to the total calcium and magnesium ions.

Powdered X-ray crystalography was applied to a PR CMA and to pure calcium, magnesium, and mixed acetate salts by Dr. S.W. Bailey of the University of Wisconsin Geology Dept.

Results

The closed samples experienced little change in weight during the 9 months of storage (table 12). Except for the 30 percent composition sample, the ambient temperature samples developed considerable mold growth. The black color of the mold growth is suggestive of Aspergillus niger or common bread mold. In spite of this extensive mold growth the samples all retained over 89 percent of the original acetate composition (table 13).

Surprisingly, the ambient open samples, except for the 30% solution, lost more acetate than did the equivalent closed samples. These samples dried to the point where their compositions resembled a $CaAc_2 \cdot H_2O + MgAc_2 \cdot 4H_2O$ analysis. The pH of the samples declined from pH10 to approximately pH7.5, apparently due to the absorption of CO_2.

The -18 °C open solutions also had only very small weight losses. The acetate losses were modest and comparable to those of the closed samples.

The solid open samples appeared to gain moisture at higher relative humidities and to lose moisture at low relative humidities. A simple hygrometer indicated a relative humidity of 95 to

100 percent in the -18 °C freezer; whereas, the ambient temperature conditions fluctuated from about 70% RH in the first month down to about 40% RH during most of the rest of the test period. The -18 °C sample absorbed moisture from the original $CaMgAc_4 \cdot 1H_2O$ composition to approximately $CaMgAc_4 \cdot 3.5H_2O$. The CMA particles at the surface became somewhat caked. This suggests that this layer had a higher water content - likely $CaMgAc_4 \cdot 5H_2O$ as occurred with the ambient open, liquid solutions. If that is so, it seems likely the balance of the sample attained approximately a $CaMgAc_4 \cdot 3H_2O$ level of hydration.

Chemical analysis of the crystals from the dry, ambient open samples revealed some very nearly pure calcium acetate and magnesium acetate crystals (table 14). Other crystals had calcium to magnesium ratios suggestive of 1:1, 2:1, and 3:1 salts. The 10% CMA, -18 °C open sample was permitted to dry to crystalization, and its crystals also resembled the pure calcium or magnesium acetates. This evidence for complex crystals from chemical analysis of the crystals is therefore mixed and inconclusive.

X-ray crystalography of the dried samples of pure calcium acetate proved to be $CaAc_2 \cdot 1.0H_2O$. Magnesium acetate dried to alpha $MgAc_2 \cdot 4H_2O$. The slowly dried pure crystals of CMA (1:1) were found to contain $MgAc_2 \cdot 4H_2O$, $CaAc_2 \cdot 1.0H_2O$ and $CaAc_2 \cdot 0.5H_2O$.

X-ray crystalography of the PR CMA 1/1 gave a mixture of at least two phases. $CaAc_2 \cdot 0.5H_2O$ was present as a major component, accounting for about 20 lines of the pattern. An additional eight or more lines, including the two most intense lines of the pattern, were unidentified. The extra lines do not fit the patterns of any calcium or magnesium acetate or acetate hydrate in the Powder Diffraction File (PDF). However, the PDF does not contain any intermediate compositions between the Ca and Mg end members.

These results suggest that complex salts may be a reality but they offer little information as to their actual compositions. The presence of calcium acetate salts suggests that the unknown salts may be mixed calcium magnesium salts with a magnesium content over 50 percent of the total.

TABLE 12.

Percentage Weight Changes During Storage of CMA Solutions and Solid CMA.

Treatment	1 month	2.7 months	6.2 months	9.4 months
Ambient, Open				
1%, RT Open	-26.4	-92.5	-98.9	-98.9
5%	-17.5	-55.8	-94.0	-94.2
10%	-16.7	-52.7	-87.6	-87.6
30%	-13.2	-42.7	-68.8	-68.9
Solid	+1.6	-0.8	-1.3	-0.5
Ambient, Closed				
1%	-0.6	-2.2	-5.9*	-8.2
5%	-0.3	-1.5	-4.0*	-6.2
10%	-0.4	-1.6	-4.4	-7.1*
30%	-0.3	-1.0	-2.8	-4.4
Solid	+0.2	+0.1	-0.6	-0.1
-18 °C Open				
1%	+0.3	+0.3		-2.9
5%	-0.1	-0.6		-3.0
10%	-0.1	-1.0		-2.4
30%	-0.1	-0.3		-4.4
Solid	+6.8	+13.3		+14.7
-18 °C Closed				
1%	+0.1	+0.1		0.0
5%	-0.1	-0.1		-0.2
10%	+0.1	+0.1		-0.1
30%	-0.1	0.0		-0.1
Solid	+0.3	+0.4		+0.9

* Visible Mold Growth

TABLE 13.

Final Percent of Acetate Present in Comparison
to Combined Mg and Ca.

Temperature	Ambient		-18 °C		Average
Treatment	Open	Closed	Open	Closed	
Sample Description					
1% CMA in Water	82.9	91.2	90.1	91.6	89.0
5% CMA in Water	85.9	95.8	88.9	92.5	90.8
10% CMA in Water	90.6	95.2	95.4	90.0	92.8
30% CMA in Water	99.4	92.0	100.1	95.6	96.9
Solid CMA	89.5	92.2	86.2	90.0	89.5
Average	89.7	93.3	92.3	91.9	91.8
Original Solid CMA	96.1				

TABLE 14.

Cation Composition of Crystals.

Sample Source	Crystal Description	Mole Percent	
		Ca	Mg
30% CMA RT, Open	Blocky crystals on top	5.2	94.8
	Bluish blocky crystals	73.4	26.6
	Colorless needles	94.3	5.7
5% CMA RT, Open	Bluish Blocky crystals	50.3	49.7
	Colorless needles	67.6	32.4
10% CMA RT, Open	Colorless needles	68.0	32.0
	Bluish blocky crystals	57.1	42.9
	Bottom crust	44.0	56.0
1% CMA RT, Open	Bluish blocky crystals on top	43.9	56.1
	Colorless needles	51.8	48.2
10% CMA 0 °F, Open	Colorless needles	91.0	9.0
	Colorless blocky crystals	6.3	93.7
	Bluish blocky crystals	6.9	93.1

RATES OF ICE MELTING

Methods: Deionized water, boiled for 45 minutes, was placed in molds made of square acrylic tubing (7/8 in ID, 1/16 in wall). Three-inch pieces of the tubing were cut and glued to 1 in by 1 by 1/4 in thick aluminum plates with RTV silicone rubber. The filled molds were covered with parafilm and placed in a freezer at -15 ^{o}C to freeze the water.

Gas bubbles occurred near the top of the ice so the samples were warmed sufficiently to permit inversion of the ice columns. The ice samples were then quickly returned to the freezer.

Cube-shaped pellets of the deicers were prepared or selected with a size of 0.25 in or 0.125 in on a side. Eleven CMA ratio samples were prepared from $MgAc_2 \cdot 4H_2O$ and $CaAc_2 \cdot H_2O$ in the appropriate Ca/Mg ratios. The Ca/Mg ratios used were 10/0, 9/1, 8/2, 7/3, 6/4, 5/5, 4/6, 3/7, 2/8, 1/9, and 0/10. In addition, $CaCl_2$, NaCl, and PR CMA were tested. Except for NaCl, the pellets were prepared by adding a small amount of water to make a stiff paste which was immediately compressed in a mold. The pellets were then air dried before use. Individual NaCl crystals of the desired size were selected from a package of rock salt.

The 14 individual molds of ice were lined up side by side in a 3¼ in by 14 in rectangular opening in a styrofoam freezer box which was adjusted to the appropriate temperature. A 4 in by 16 in piece of glass covered the opening on the outside. The pellets of deicers were weighed and placed in the freezer box for 1 hour to attain the appropriate temperature. The pellets were then quickly placed on the surface of the ice columns and the rate of penetration into the ice was measured using a cathetometer. Rates of penetration of the pellets into the ice columns was measured over a 2-hour period. Melting rates were tested at five different temperatures; 0, -2, -5, -10, and -20 °C. The deicer pellets varied substantially in weight. Therefore, the results were calculated on the basis of rate of penetration per gram of deicer on the assumption that the rate of penetration would increase linearly with weight.

Results: The rates of penetration of the deicer pellets into the ice are shown in figures 7A to 7E for the 0.25-in pellets and in figures 8A to 8E for the 0.125-in pellets.

In both series the penetration by the NaCl and $CaCl_2$ pellets was more rapid than was the penetration by any of the CMA pellets. With a few exceptions $CaCl_2$ penetrated more rapidly than did NaCl.

There was no clear pattern visible in the CMA ratio studies, except at very low temperatures when the high calcium pellets often did not begin to melt the ice.

The slower melting rate by CMA in comparison to NaCl and $CaCl_2$ appears to be a result of the lower density of the pellets and of the high level of hydration of the salts. The high hydration reduced any heat of solution effects, as also occurred with the $CaCl_2$. The low density caused the pellets to float higher above the ice surface, thus reducing the effective ionic concentration at the salt surface.

It appears probable that an improved deicing rate can be attained by increasing the density of the CMA and also by reducing its level of hydration.

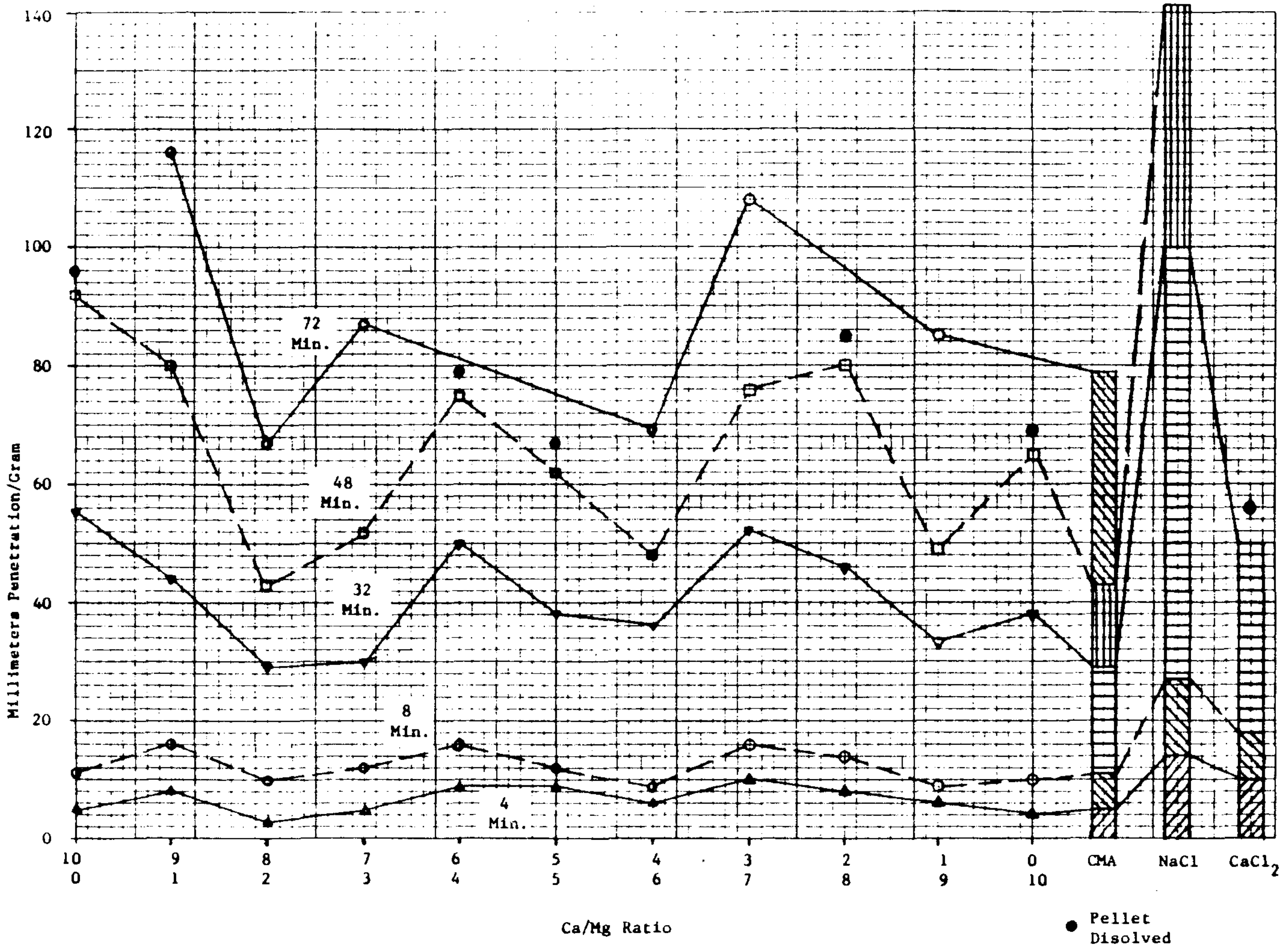

FIGURE 7A.
Rate of Ice Melting (0 °C), 0.25-in Pellets.

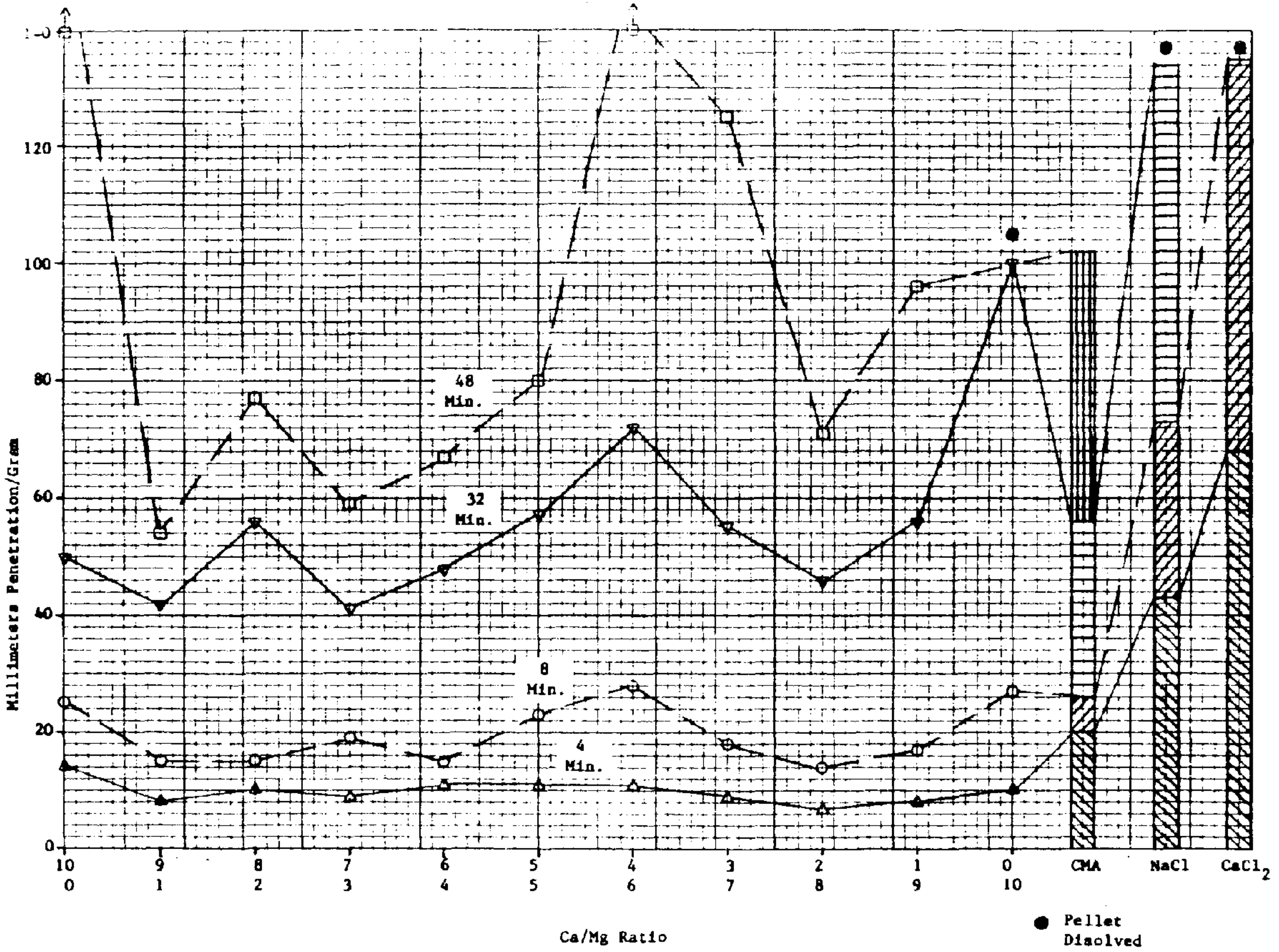

FIGURE 7B.
Rate of Ice Melting (-2 ^{O}C), 0.25-in Pellets.

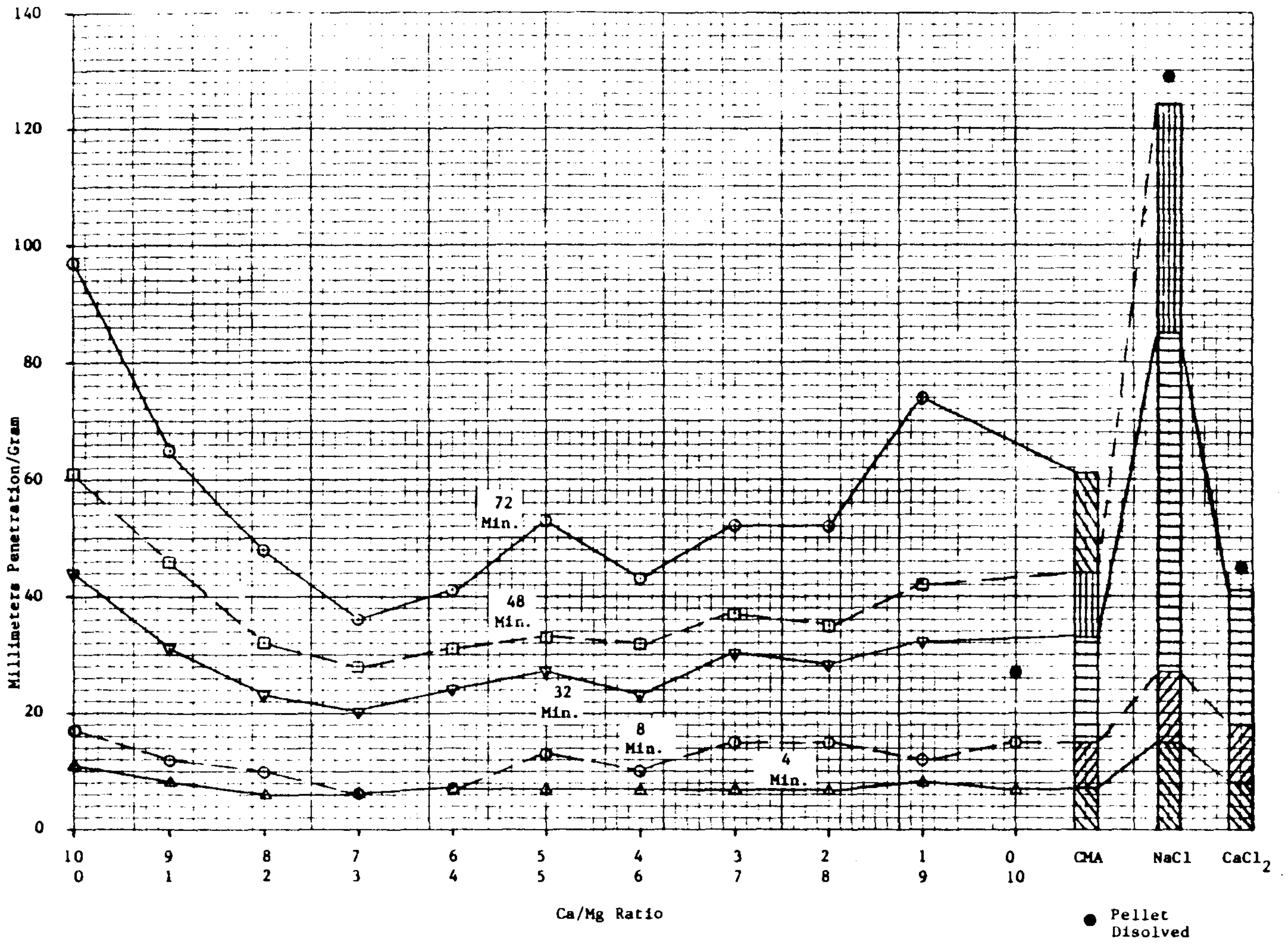

FIGURE 7C.
Rate of Ice Melting (-5 ^{O}C), 0.25-in Pellets.

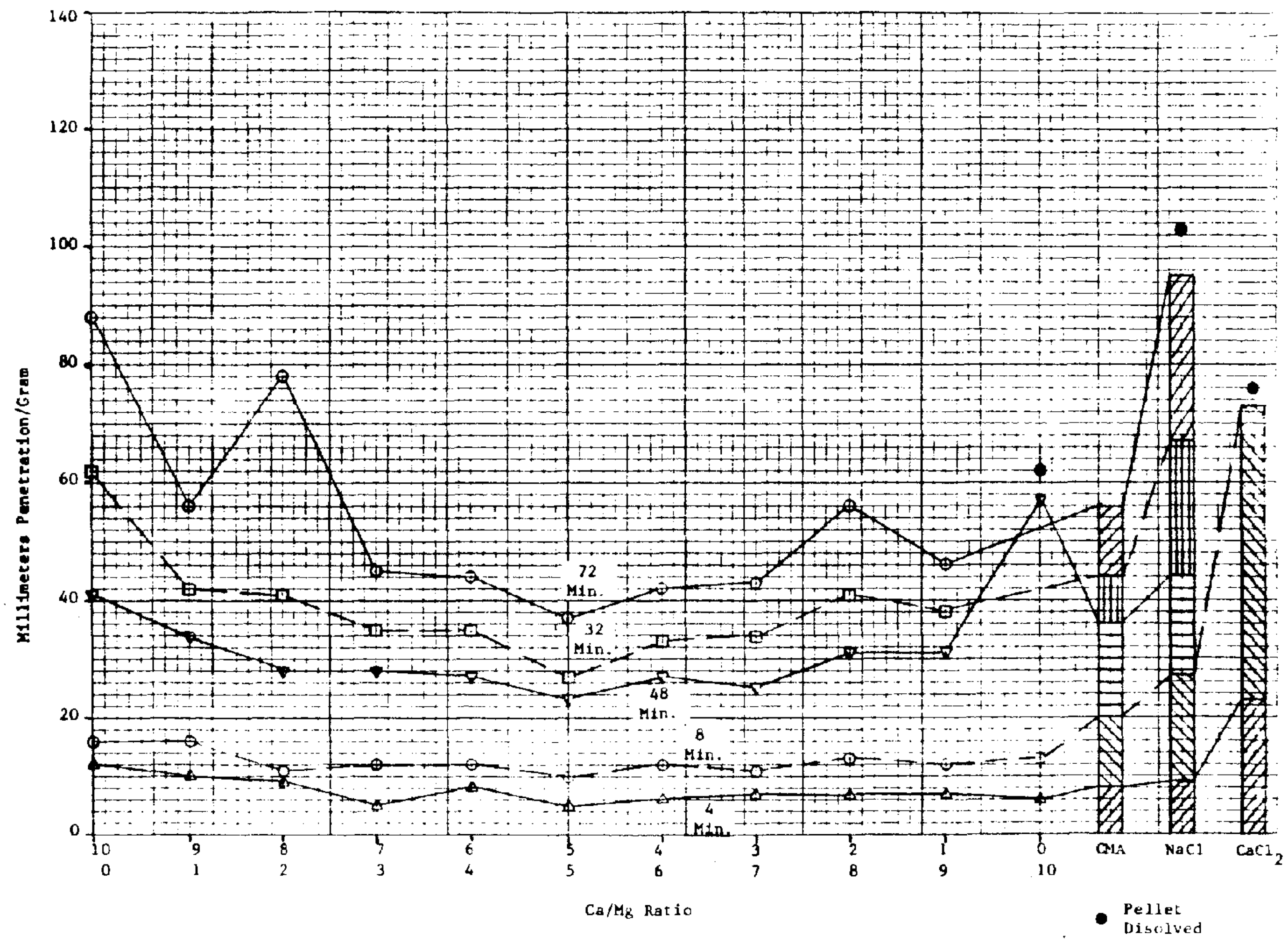

FIGURE 7D.
Rate of Ice Melting (-10 ^{o}C), 0.25-in Pellets.

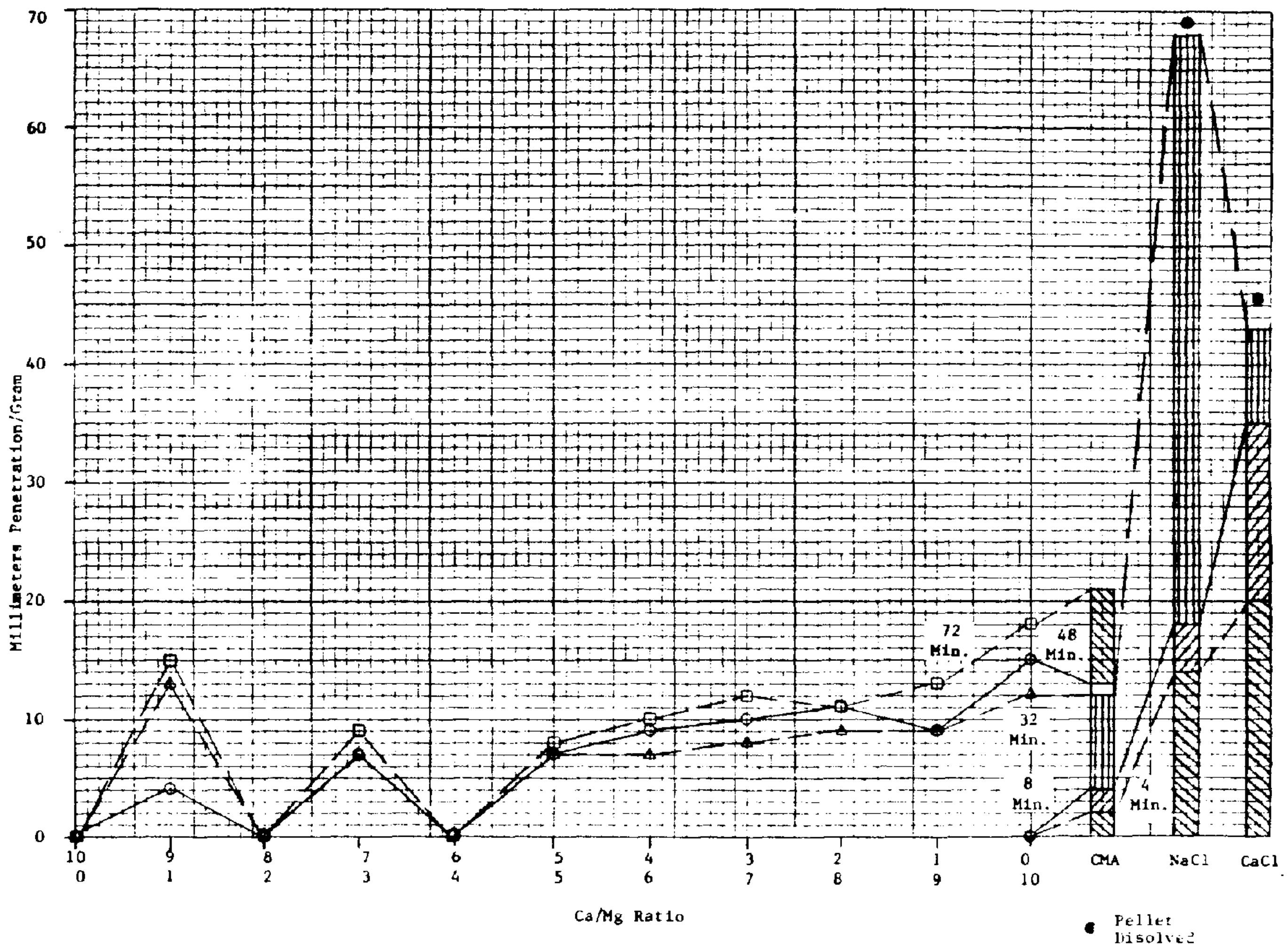

FIGURE 7E.
Rate of Ice Melting (-20 °C), 0.25-in Pellets.

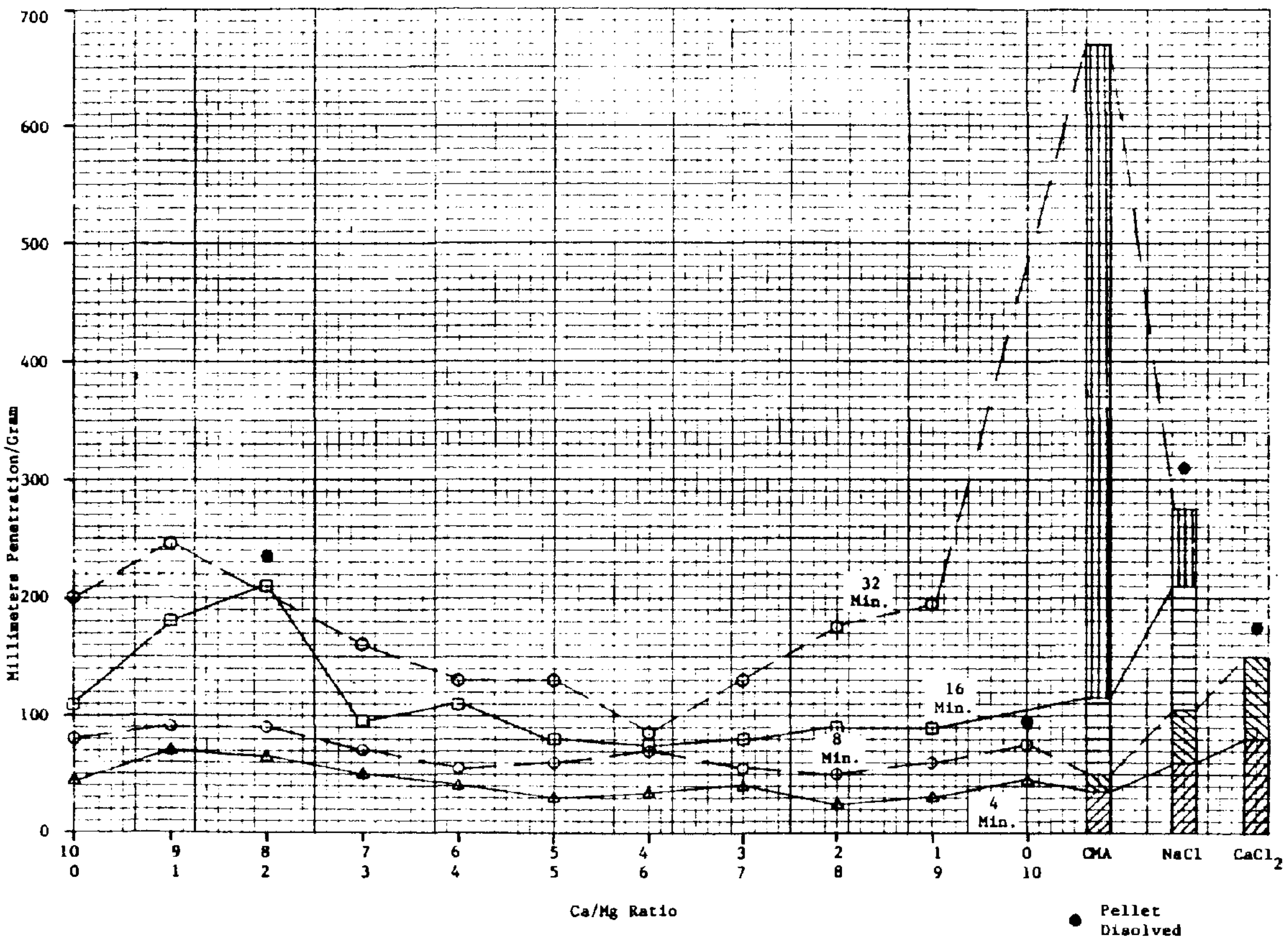

FIGURE 8A.
Rate of Ice Melting (0 ^{O}C), 0.125-in Pellets.

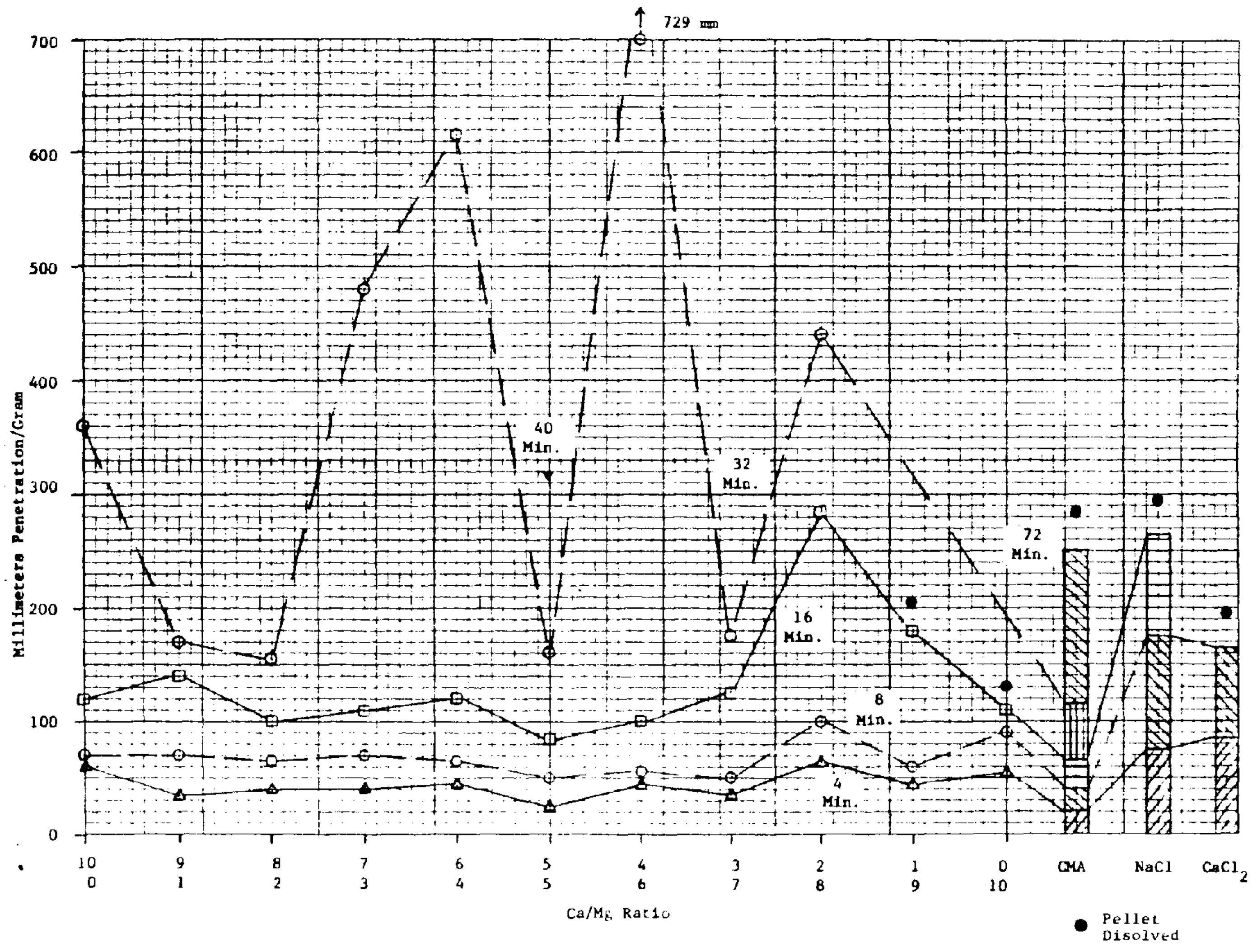

FIGURE 8B.
Rate of Ice Melting (-2 °C), 0.125-in Pellets.

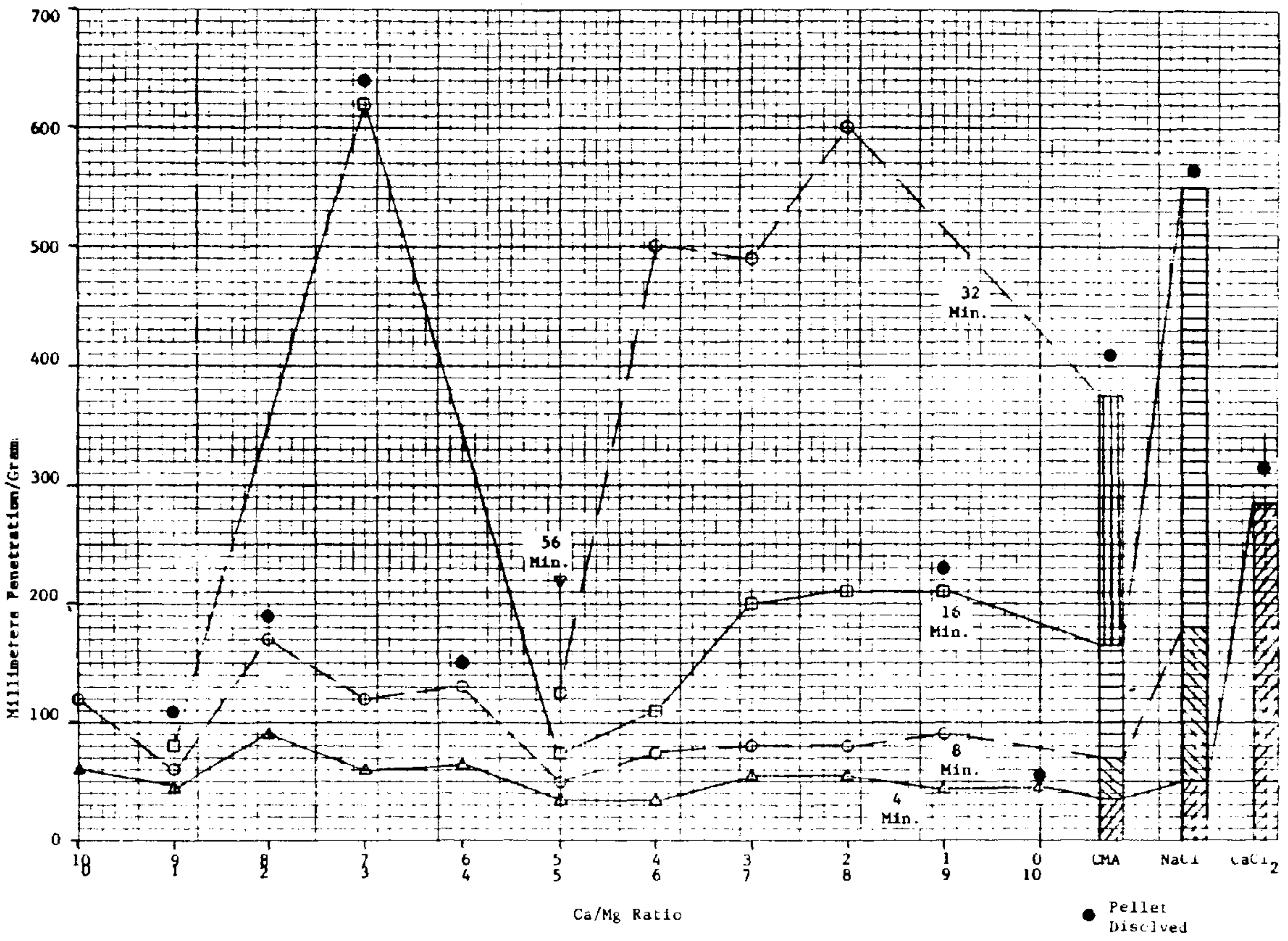

FIGURE 8C.

Rate of Ice Melting (-5 °C), 0.125-in Pellets.

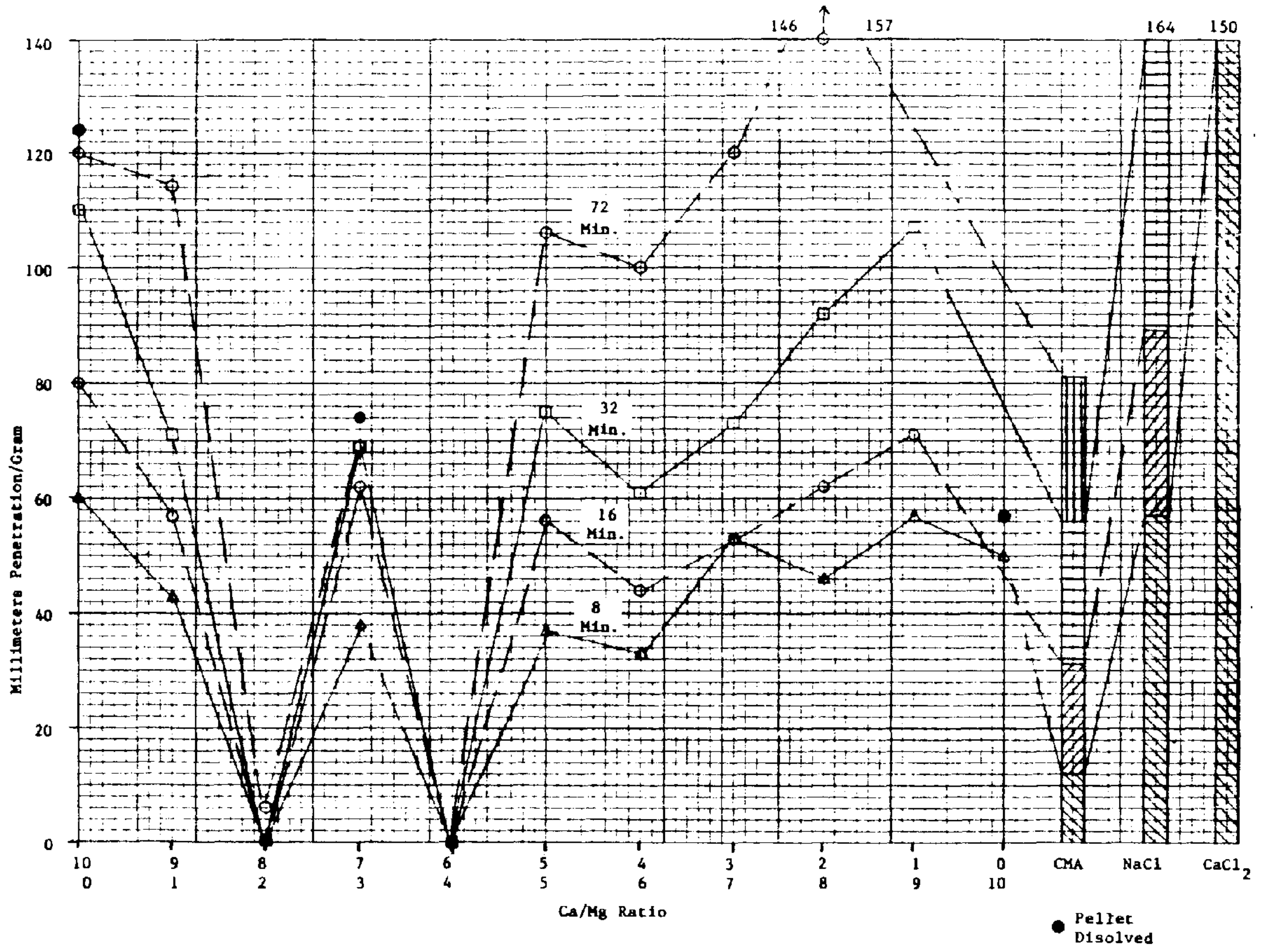

FIGURE 8D.
Rate of Ice Melting (-10 ^{O}C), 0.125-in Pellets.

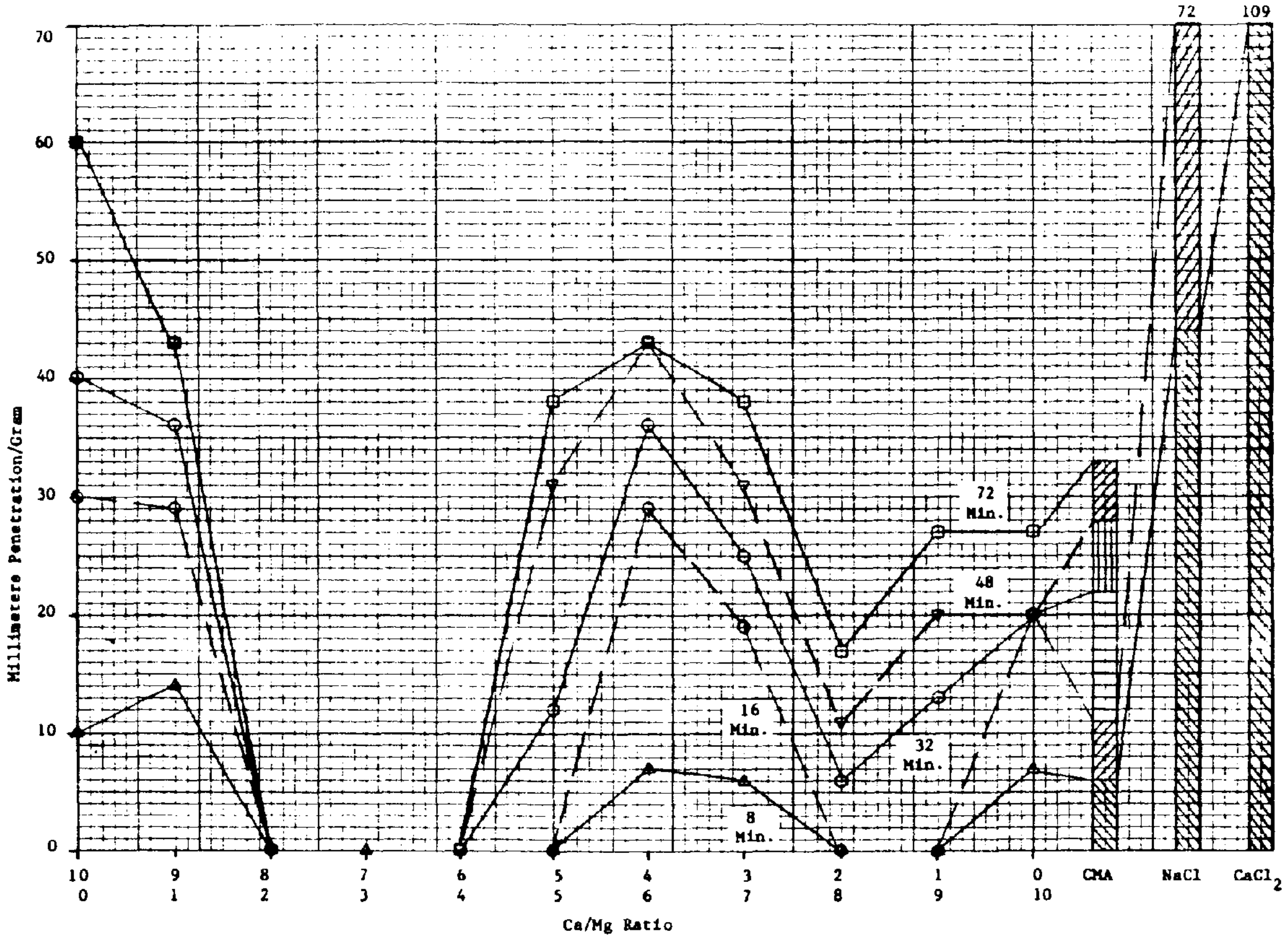

FIGURE 8E.
Rate of Ice Melting (-20 °C), 0.125-in Pellets.

RECOMMENDED pH AND Ca/Mg RATIOS FOR OPTIMUM DEICING

pH

Concrete scaling studies with various Ca/Mg ratios demonstrated clearly that a pH of 7.0 or less is seriously harmful to concrete. On the other extreme, magnesium ion precipitates in the form of the hydroxide above pH9.0 at the concentration used. The limits of acceptable pH for CMA, therefore, appear to be pH8.0 ± 1.0, with the optimum pH likely being pH8 or somewhat higher.

Ca/Mg Ratio

The higher solubility of the $MgAc_2$ appears to favor a Ca/Mg ratio with a high proportion of magnesium. For example, the greatest solubility (molality) is achieved at a magnesium concentration over ten times as great as the calcium concentration. This is tempered by the tendency of the magnesium acetate to form the insoluble octahydrate as its concentration approaches or exceeds three times the concentration of $CaAc_2$.

The concrete scaling tendencies of CMA appear to be minimized at concentrations of magnesium greater than the concentration of calcium. The anhydrous forms of calcium and those of calcium magnesium acetates of differing Mg/Ca ratios have substantial heats of solution. Extrapolation of the data from nearly anhydrous CMA samples indicates that anhydrous $MgAc_2$ will have a heat of solution similar to that of anhydrous $CaCl_2$.

The rates of ice melting showed no clear cut benefit at different Ca/Mg ratios except at very low temperatures below the eutectic temperatures for $CaAc_2$. The slow rate of ice melting for CMA appeared to be due primarily to the tendency of the CMA crystals to be buoyed up in their own concentrated solution. This indicates a need for a more dense form of CMA. The tendency of $CaAc_2$ to form needle-like crystals interferes with this goal. At higher magnesium concentrations a more dense, blocky crystal appears to predominate.

As a result of all of these factors it appears that a Ca/Mg ratio of 5/5 or less is optimum. Indeed, the bulk of the evidence supports a ratio of 3/7. Some data suggest that an even lower ratio would be desirable. The only serious risk evident to preclude a ratio as low as 1/9 is the insolubilization of the $MgAc_2$ at low temperatures due to apparent formation of the octahydrate. This is, however, a serious enough risk that it seems warranted to keep the ratio no lower than 2/8.

Recommendations

1. Density: Maximization of the density and bulk density of CMA for road application appears to be an important goal. Although the lower rate of ice melting by CMA vs. NaCl appears to be less of a problem under the dynamic conditions of highway useage, nonetheless, reduced bulk density does mean that fewer pounds of CMA can be carried on a spreader truck as well as in other hauling vehicles. We therefore recommend studies whose objective will be to produce CMA with the maximum density and bulk density feasible.

2. Acid rain neutralization: The potential for CMA to neutralize the combustion acids which constitute acid rain is a phenomenon worthy of serious study. Not only can this material neutralize the nitrogen and sulfur acids produced in automobile propulsion, but also CMA flowing into rivers and lakes can serve to neutralize the acids brought into these bodies of water by

acid rain. In addition, the highway surfaces coated with CMA may also contribute significantly to cleansing the air of these acids as the air simply blows across these surfaces. This is likely to be the least significant contribution, but it nonetheless seems worthy of evaluation. Overall, total replacement of rock salt by CMA for road deicing offers the potential to dramatically reduce the damage from acid rain since most of the road deicer is spread in the north-east quarter of the U.S. where acid rain poses the most serious problem. We therefore recommend studies to assess the overall impact that CMA can provide if utilized as a total replacement for rock salt for deicing roads.

3. Enhancing melting characteristics and cost: High magnesium CMA promises to offer road deicing qualities in many ways superior to those of rock salt. Included in these qualities are ice melting at lower temperatures, high heat of solution to facilitate ice melting, corrosion inhibition under most environmental conditions, and the potential to neutralize acid rain. A further enhancement of ice melting characteristics may additionally be achieved by introduction of additional organic acid species. The calcium and magnesium salts of various species may provide an added level of solubility which may further lower the effective ice melting temperatures. In addition, if other species can be produced more cheaply than can acetate, total cost of the combined deicer could be lower. We therefore recommend an additional evaluation of other Ca and Mg salts of low molecular weight organic acids to CMA for their potential to further enhance the properties of CMA and/or to reduce the total cost of the deicer.

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