

3173

HT

HCR 25

-

HCR 29

3173

THE PRECEDING DOCUMENT(S) MAY NOT FILM
LEGIBLY BECAUSE OF POOR QUALITY OF THE
ORIGINAL.

ACCNR	ACCDTE	TIME	ROUTE	MILE	ACC	NBR	TOT	MAJ	MIN	DAMAGE	TYPE	ROAD	ROAD
	YYMMDD			POINT	DIA-	VEH	FAT	INJ	INJ			CHAR	COND
GRAM													

26.0-26.7

7901166	790218	1645	117600	26.43	9	2				1,300	07	1	04
7903360	790403	0001	117600	26.49	9	1				4,500	40	5	04
7908436	790831	1740	117600	26.44	9	1			2	1,000	05	3	01
8014272	801215	1645	117600	26.44	3	2			2	7,100	08	2	04
8013898	801215	1645	117600	26.44	3	2			1	6,400	08	1	04
8010629	800915	0100	117600	26.44	9	1			1		17	2	02
7819254	781102	1743	117600	26.64	9	2		1	2	4,000	06	6	01
7713066	770909	1640	117600	26.16	9	1			1	2,800	40	1	02
7715266	771024	1355	117600	26.54	4	2				220	08	1	01
7715608	771031	1600	117600	26.50	8	2				1,200	08	1	04
7712153	770821	1730	117600	26.50	9	1				300	14	-	-

RECORD STATS: 13 FOUND; 11 READ; 11 QUALIFIED.

TYPE 'X' BEFORE DEPRESSING 'ENTER' KEY TO STOP READING. > <

MORE

ACCNR	ACCDTE	TIME	ROUTE	MILE	ACC	NBR	TOT	MAJ	MIN	DAMAGE	TYPE	ROAD	ROAD
	YYMMDD			POINT	DIA-	VEH	FAT	INJ	INJ			CHAR	COND
GRAM													

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RECORD STATS: 13 FOUND; 13 READ; 13 QUALIFIED.

25.3-27.4

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	YYMMDD			POINT	DIA-	VEH	FAT	INJ	INJ			CHAR	COND
GRAM													

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8013980	801219	1945	117600	25.39	1	2			2	1,900	07	1	01
7811162	780920	0800	117600	25.69	9	2			4	3,000	07	3	02
7801479	780128	1425	117600	25.69	4	2		2		7,000	08	3	04
7803644	780317	1040	117600	25.42	9	1				5,000	40	1	01
7801979	780207	1745	117600	25.93	9	2		1	2	10,000	05	1	04
7819372	781219	2100	117600	25.69	9	1				100	40	2	04
7814639	781108	0830	117600	25.69	1	2				100	08	1	01
7718820	771224	1250	117600	25.59	9	1				2,550	30	2	04
8107005	810714	1415	117600	25.79	1	2				502	07	1	02
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RECORD STATS: 32 FOUND; 11 READ; 11 QUALIFIED.

TYPE 'X' BEFORE DEPRESSING 'ENTER' KEY TO STOP READING. > <

ACCNR	ACCDTE	TIME	ROUTE	MILE	ACC	NBR	TOT	MAJ	MIN	DAMAGE	TYPE	ROAD	ROAD
	YYMMDD			POINT	DIA-	VEH	FAT	INJ	INJ			CHAR	COND

YYMMDD

POINT DIA-VEH FAT INJ INJ
GRAM

CHAR COND

YYMMDD	ACCID	TIME	ROUTE	MILE	ACC	NBR	TOT	MAJ	MIN	DAMAGE	TYPE	ROAD	ROAD
YYMMDD				POINT	DIA-	VEH	FAT	INJ	INJ			CHAR	COND
					GRAM								
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7903360	790403	0001	117600	26.49	9	1				4,500	40	5	04
7908436	790831	1740	117600	26.44	9	1		2		1,000	05	3	01
8001238	800125	0650	117600	26.80	9	1				3,500	05	1	04
8014272	801215	1645	117600	26.44	3	2		2		7,100	08	2	04
8013898	801215	1645	117600	26.44	3	2		1		6,400	08	1	04
8010629	800915	0100	117600	26.44	9	1		1		1,000	17	2	02
8006878	780515	1400	117600	25.94	9	1		1			40	3	01
8002887	780225	1100	117600	27.12	9	2				700	12	1	05
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RECORD STATS: 32 FOUND; 22 READ; 22 QUALIFIED.

TYPE 'X' BEFORE DEPRESSING 'ENTER' KEY TO STOP READING. > <

ACCID	TIME	ROUTE	MILE	ACC	NBR	TOT	MAJ	MIN	DAMAGE	TYPE	ROAD	ROAD	
YYMMDD			POINT	DIA-	VEH	FAT	INJ	INJ			CHAR	COND	
				GRAM									
7713765	770923	2115	117600	25.94	1	2		2	3	5,000	07	1	01
7711112	770731	2100	117600	27.10	1	2				900	12	1	01
7710832	770725	0016	117600	27.04	9	1		3		6,000	15	3	01
7705050	770329	1718	117600	26.80	4	1		1		1,100	08	6	10
7715256	771024	1355	117600	26.54	4	2				220	08	1	01
7715608	771031	1600	117600	26.50	8	2				1,200	08	1	04
7712153	770821	1730	117600	26.50	9	1				300	14	-	-
7701826	770202	1710	117600	26.34	1	2				3,500	07	1	02
8107400	810725	1500	117600	26.74	9	2				600	08	1	01
8106689	810707	1245	117600	26.57	3	3			5	4,200	08	2	01

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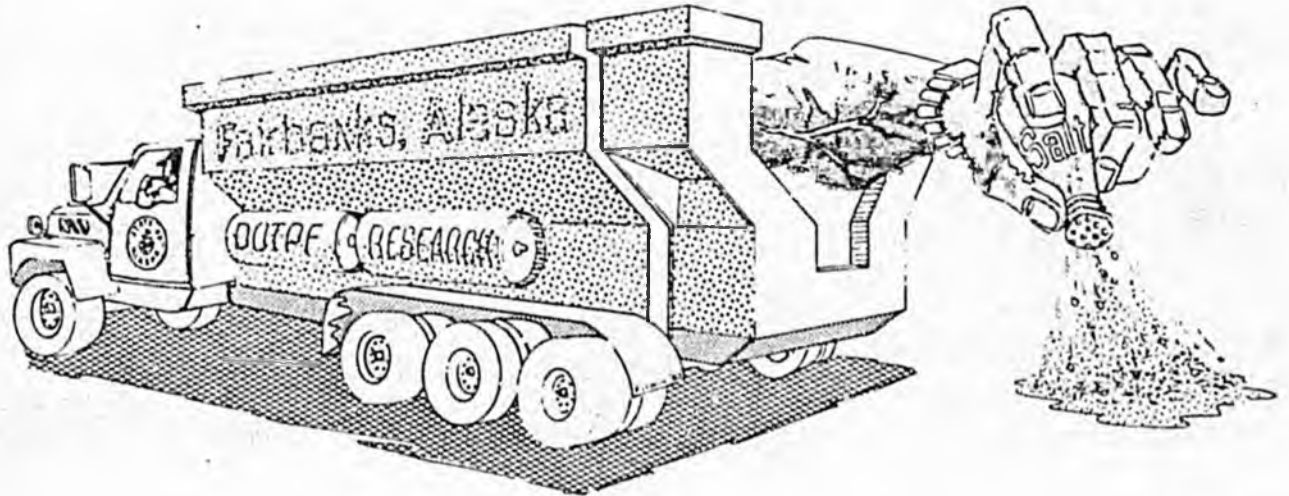
29

RESEARCH NOTES

DIVISION OF PLANNING AND PROGRAMMING
RESEARCH SECTION

January 1983
Vol. 2 No. 7

CMA—An Alternative Road Deicer



The use of sodium chloride (common salt) and calcium chloride has raised controversy both in Alaska and nationwide. These materials can definitely reduce the hazard of wintertime driving but do so at tremendous expense. Pollution and corrosion damage attributable to chloride salts effectively boosts their real cost by a factor 10 to 15 when long term effects are considered. For example, sodium chloride presently selling in Fairbanks for about \$125 per ton would be expected to generate long term damages in excess of \$1,000. The regard for public safety which demands continued use of these readily available materials, has also fueled a search for something better. A safe and economically viable alternative may now be on the horizon.

National research aimed at providing improved road deicing compounds has identified Calcium Magnesium Acetate (CMA) as a potential substitute for calcium and sodium chloride. CMA is essentially made by dissolving crushed limestone into acetic acid. Its composition, $\text{CaMg}(\text{CH}_3\text{CCOO})_4$, is characterized by a varying ratio of calcium (Ca) to magnesium (Mg) which depends upon the type of limestone used. The deicing power of CMA increases with increasing Mg content but is generally within the range of standard chloride salts. The real advantage in its use stems from its low damage potential. It is non-corrosive to most metals, even when compared to tap water. Toxicity is also low and the material decomposes into the three harmless components; carbon dioxide, water and limestone. Limestone residue would actually serve as a soil conditioner for unpaved areas bordering the roadway in sharp contrast to the ground poisoning effect of a chloride salt. Unfortunately, calcium and magnesium acetates can presently be obtained only in the very costly and purified form of laboratory reagents. Availability of CMA in a much less expensive industrial grade must precede its use as a deicing agent.

A DOTPF funded research project was recently completed which examined the possibility of manufacturing low grade CMA within Alaska. A final report outlining this study was authored by M. J. Economides and R. D. Ostermann of the University of Alaska titled "Preliminary Design and Feasibility Study for a Calcium-Magnesium Acetate Unit." The authors discuss production of a "highway grade" saturated CMA solution on a small scale not exceeding 75 tons (dry weight) per day. CMA was shown to be economical at production levels above approximately 17 tons per day with predicted costs running \$290—\$590 per ton depending on production rate and the base price of acetic acid. For comparison calcium chloride costs almost \$650 per ton F.O.B. Fairbanks.

The DOTPF is continuing to sponsor a program of CMA research along two different lines. One study involves a refinement of the manufacturing process and will result in the design of a CMA pilot plant. Another project is attempting to take advantage of CMA's ability to retain moisture in a soil mixture. The possibility exists that it can be used to replace calcium chloride as a dust controller and soil stabilizer for unpaved roads.

Robert L. McHattie, P.E.
Senior Research Engineer

DOTPF RESEARCH

Further information on any of the topics covered in "Research Notes" may be obtained by contacting Larry Sweet, Research Manager. A list of publications produced by the Research Section may be obtained by writing Barbara Trego, Publications Specialist, 2301 Peger Road, Fairbanks, Alaska 99701 or by calling the Research Section at (907)479-2241.

State of Alaska
Dept. of Transportation and Public Facilities
Division of Planning and Programming
2301 Peger Road—Research Section
Fairbanks, Alaska 99701

Bulk Mail U.S. Postage PAID Fairbanks, AK 99701 Permit No. 87
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STATE OF ALASKA
FISCAL NOTE

I. REQUEST

Bill/Resolution No.: HCR 29
 Title: Encourage use of Non-Corrosive
 Sponsor: Miller, Duncan, Grussendorf
 Requestor: House Trans. Committee

II. FISCAL DETAIL

Agency Affected: U of A & DOT&PF
 Program Category Affected: Research
 BRU, Program or Subprogram(s) Affected: Interior Region

EXPENDITURES/REVENUES: (Thousands of Dollars)

	FY 83	FY 84	FY 85	FY 86	FY 87	FY 88
OPERATING						
100 PERSONAL SERVICES		70.0				
200 TRAVEL		5.0				
300 CONTRACTUAL		10.0				
400 COMMODITIES		25.0				
500 EQUIPMENT		40.0				
600 LAND & STRUCTURES						
700 GRANTS, CLAIMS, ETC						
TOTAL OPERATING		200.0				
CAPITAL						
REVENUE						

FUNDING: (Thousands of Dollars)

GENERAL FUND						
FEDERAL FUNDS						
OTHER (Specify Source)						

POSITIONS:

FULL-TIME						
PART-TIME		5				
TEMPORARY						

III. SOURCE OF FUNDS TO OFFSET FISCAL IMPACT OF BILL:

Offsetting of funding not identified in bill.

IV. ANALYSIS: Attach a separate page for any Analysis

Prepared By: Larry Sweet Phone: 479-2241
 Division: Research Section, Planning and Programming Date: 3/18/83
 Approved by Commissioner: H. Glenzer, Jr. Date: 4/13/83
 Department: Transportation & Public Facilities

Distribution:

- Original to Legislative Finance
- Copy to Office of Management and Budget (for Legislature introduced bills)
- Copy to Department (for Governor introduced bills)
- Copy to Sponsor
- Copy to Requestor (if different from Sponsor)

3/8/83

IV. Analysis

Calcium Magnesium Acetate (CMA) is a non-corrosive ice control agent which could replace the corrosive chloride salts currently in use. CMA may also be useful as a dust control agent. CMA can be produced locally from limestone and acetic acid. The objectives of the proposed research are to develop a process design (based on previous work) for the production of CMA, construct and operate a small scale pilot plant based on this design, and demonstrate, through road tests, the effectiveness of CMA as an ice and dust control agent. The evaluation of the process design would entail a complete economic investment analysis. The effectiveness of CMA as an ice and dust control agent would be done by comparison with salt. Work progress will be documented through quarterly progress reports, followed by a comprehensive field report including the process design.

The benefits to the State would be threefold: (1) a new industry employing 20-30 people would be created; (2) the high costs of salt corrosion currently borne by the public and the state and local government would be eliminated; and (3) the "blight" caused by salt poisoning of plants along roadways would be reduced, resulting in a more attractive community.

Specifically the objectives of the demonstration are:

1. The development of a final process design for the production of CMA from acetic acid and native limestone. This design would also include a complete economic analysis of the process.
2. The successful operation of a pilot scale production facility, to demonstrate the validity of the process design.
3. The demonstration of the effectiveness of CMA as a road deicing agent in arctic conditions. This would entail a strip test to be conducted by the State DOT&PF.
4. The evaluation of CMA as a dust control agent for potential use on the Dalton highway.
5. The development of a method of application for CMA as a winterization treatment for sand storage piles.
6. The development of an optimal application method for CMA to insure maximum cost-effective use.

RESEARCH PROPOSAL

Process Plant Design and Test Application Program for Calcium Acetate as a Non-Corrosive De-icing and Dust Control Agent in Interior Alaska

EXECUTIVE SUMMARY

Calcium-Magnesium Acetate (CMA) is a non-corrosive, environmentally benign ice control agent which could be used to replace the corrosive chloride salts currently in use in Alaska. We also believe that CMA can be used to replace calcium chloride as a dust control agent. The adverse effects of salt on automobiles, bridge structures and plant life are well known. We have estimated the damage to automobiles alone in Alaska may exceed \$20,000,000 annually. An obvious incentive exists for the use of non-corrosive chemicals for ice control.

In previous work performed under contract to the Alaska State Department of Transportation, we have demonstrated that CMA can be produced locally through the dissolution of naturally occurring limestones in acetic acid. We have developed a preliminary process design and economic evaluation based on our work. We estimate that CMA could be produced in Alaska for \$300-600/ton (salt equivalent), compared to \$850/ton for calcium chloride delivered to Fairbanks. In view of the "corrosion costs" of chloride salts, CMA at \$600/ton is a bargain.

The results of our previous work, are highly encouraging. We have developed kinetic data on the reaction of acetic acid with limestone, and have constructed a bench scale reactor in our laboratories to gather further design data. What remains to be done, is the completion of a full scale process design and the construction of a pilot plant facility. Furthermore, a road test of CMA as an ice control agent and dust control agent under arctic conditions should be conducted.

Research Objectives

We have identified the following objectives for the proposed project:

1. The development of a final process design for the production of CMA from acetic acid and native limestone. This design would also include a complete economic analysis of the process.
2. The successful operation of a pilot scale production facility, to demonstrate the validity of the process design.
3. The demonstration of the effectiveness of CMA as a road deicing agent in arctic conditions. This would entail a strip test to be conducted by the State D.O.T.
4. The evaluation of CMA as a dust control agent for potential use on the Dalton highway.
5. The development of an optimal application method for CMA to insure maximum cost-effective use.

Project Cost

The total cost of the proposed research would be \$198,000, of which \$67,000 would be salaries and benefits, \$41,000 would be supplies and services (chemicals), and \$36,000 would be equipment. The remaining \$52,000 would be for university overhead.

WORK PLAN

Dr. Ostermann and Dr. Economides will use the results of previous kinetic studies and ongoing bench scale work to develop a process design for a full scale production facility. Both Dr. Ostermann and Dr. Economides have degrees in chemical engineering and experience in the process industry. It is well within their expertise to perform such a design. The design will include the selection of the optimal process scheme, and a complete economic analysis of the process. A flowsheet and equipment list will also be provided.

A pilot plant facility capable of producing 100 gal/day (8 hr. day) will be built based on the process scheme. This pilot plant will be operated to demonstrate the feasibility of the process, develop bulk kinetic data and other design data, and to produce CMA for road tests.

CMA produced in the pilot plant will be applied to a test strip or test intersection in the Fairbanks North Star Borough. This test will be conducted during the winter of 1983-84 by Alaska D.O.T. personnel. A truck equipped with a sand spreader and spray pump will be used since CMA is best applied in saturated solution. The performance of the CMA will be compared with that of salt.

Additional CMA will be used to evaluate its effectiveness as a dust control agent. The primary mechanism of dust control is moisture retention and partial agglomeration. CMA will be compared to calcium chloride using artificially prepared laboratory roadway samples which can be "aged" and observed for weight loss and ease of "dusting".

Sand is stored in large piles. If these piles are not winterized, they will freeze solid in the winter. Currently, salt crystals are added at 5-10 wt % to prevent freezing. It is proposed that CMA solution could be sprayed over the pile with the same effect. This hypothesis will be checked with a series of small scale tests involving several methods of application.

In conjunction with the road tests, several methods of application will be tried to determine the "best" application method.

Russell D. Ostermann
Petroleum Engineering Dept.
University of Alaska, Fairbanks
474 7734

STATE OF ALASKA

JAY S. HAMMOND, GOVERNOR

DEPARTMENT OF TRANSPORTATION AND PUBLIC FACILITIES

OFFICE OF THE COMMISSIONER

POUCH 2
JUNEAU, ALASKA 99811
(TELEX 45-328)
(907) 465-3900

June 4, 1982

Re: Ice Control Methods
and Materials

Mr. R. A. Bundy
P.O. Box 3-5000
Juneau, Alaska 99802

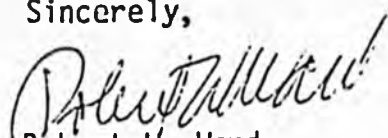
Dear Mr. Bundy:

This refers to your recent letter concerning ice control methods and materials used by this Department.

In Juneau we use three basic materials to control ice on the highways and increase traction when ice is present, namely (1) aggregate consisting of coarse sand and/or small rock chips, (2) sodium chloride crystals, and (3) calcium chloride in pellet form or mixed with water to form a brine solution. We only use the sodium chloride and calcium chloride on the high traffic volume highways, i.e., Egan Expressway and Loop Road where aggregates are ineffective because the high speed and high volume traffic literally blows it off the road. Aggregates, of course, do not melt ice already formed - the chemicals do. They also stop new ice formation through a wide temperature range.

Chemicals are superior to aggregates for ice control. We are, and will continue, to experiment with new materials that, hopefully, will be less corrosive, cost effective and still do the job the public expects. When we find something with those characteristics, I assure you that we will stop using the materials now in use.

Sincerely,


Robert W. Ward
Commissioner

cc: Patrick P. Ryan
Deputy Commissioner, M&O

STATE OF ALASKA

JAY S. HAMMOND, GOVERNOR

DEPARTMENT OF TRANSPORTATION AND PUBLIC FACILITIES
DIVISION OF PLANNING AND PROGRAMMING
RESEARCH SECTION

2301 PECER ROAD
FAIRBANKS, ALASKA 99701-6394
PHONE: (907) 479-2241

March 25, 1982

Re: Calcium Magnesium Acetate (CMA)
Substitute for Salt on Highway
Icing

Mr. Tom Johnson
Senate Resource Committee
Pouch V
Juneau, Alaska 99811

Dear Mr. Johnson:

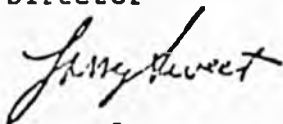
Per your request, the following is some information regarding efforts to find a substitute for the common salt that has attained widespread use in this country for deicing highways. There has been considerable research on the problem of corrosion associated with common salt and Calcium Magnesium Acetate (CMA) has been shown to be an effective substitute.

Our own research has not been directed toward further investigation of the deicing and environmental qualities of CMA because that information already exists. Rather our effort has been to study methods of producing CMA from industrial grade acetic acid and Alaskan limestone so that an economically feasible process can be developed to produce CMA here in Alaska. Many people feel that some substitute will have to be found to avoid the current widespread damage to vehicles and other equipment.

Dr. Michael Economides of the Petroleum Engineering Department of the University of Alaska is working on our study. A summary report of his work should be available in three months.

I have enclosed a page further describing the use of CMA for highway icing. I hope this information is of use to you. I will see that you get a copy of our report when it becomes available.

Sincerely,
Heinrich Springer
Director


Larry Sweet
Research Manager

LS/emc

Attachment as stated.

cc: John Bures Deputy Commissioner

Road deicing chemical called superior to salt

Iowa Department of Transportation researchers have developed a deicing material that is less corrosive than salt, effective at a lower temperature and is not harmful to the environment. If it proves out in tests this winter, the agency expects to patent the compound and convince a manufacturer in the state to produce it in large quantities.

The material, consisting of sand coated with calcium magnesium acetate, was developed last month by DOT's chief chemist, Wallace Rippie. So far the compound has been tremendously expensive to produce—\$500 a ton compared with \$30 a ton for salt, according to Charles Huisman, a DOT highway engineer who is heading the research. "But we are doing it now with a beaker and a mixer in a laboratory," he says. Huisman expects that commercial production will bring the cost down considerably.

The mixture does not corrode steel in pavements and structures. Huisman says that its use could double the life of bridge decks. In addition, it does not harm plants or pollute water, he says, and in fact is beneficial to soil. Also, indications are that the compound can be formulated to work at temperatures below 20° F, the lowest limit of salt's effectiveness.

One drawback is that it can cause concrete to spall slightly, says Huisman. "But we don't think it would be so detrimental as to preclude its use." □

*From: Engineering
News Record Jan 28
1982*

40 315057

ALTERNATE HIGHWAY DEICING CHEMICALS. EXECUTIVE SUMMARY

A search has been made for road deicing chemicals to replace sodium chloride (NaCl). The impetus for this search stems from the numerous drawbacks associated with the prevalent use of NaCl as a road deicer. All types of chemical compounds were reviewed. Selections were made on the basis of criteria such as water solubility and freezing point lowering, corrosion, toxicity, relative cost or cost potential, effect on soils and plants and water supplies, flammability, concrete compatibility, traction, friction, highway performance, etc. Information was sought first in the literature, then supplemented or verified in the laboratory as needed. Two candidate deicers were found to be as effective as sodium chloride. One, methanol, reacts almost immediately upon contact with snow and ice but is less persistent than NaCl. The other candidate, calcium magnesium acetate (CMA), acts at about the same rate as NaCl in the temperature range of common activity and shows about the same persistence. It gives rise to about the same decreases in coefficients of braking traction and skidding friction as NaCl. In strong contrast to NaCl, CMA is a corrosion inhibitor, is beneficial to most soils and has no potential for harming drinking supplies. The unpurified CMA derived from solid wastes, primarily cellulose, gives improved traction and reduces production costs. The methodology for CMA production, cost evaluated above, is unsophisticated 19th Century technology. Application of modern technology may further lower production costs. (FHWA)

Dunn, SA Dunn, A Schenk, RU

Bjorksten Research Laboratories, Incorporated, Federal Highway Administration Final Rpt. FHWA-RD-79-109, Mar. 1980, 17 p.

Contract DOT-FH-11-9100

ORDER FROM: NTIS

(907) 465-3900

June 4, 1982

Re: Ice Control Methods
and Materials

Honorable Bill Ray
Alaska State Senate
State Capitol
Pouch V
Juneau, Alaska 99811

Dear Senator Ray:

In reply to your April 5 inquiry, attached is a copy of my reply to Mr. R. A. Bundy regarding ice control methods and materials used in the Juneau area.

For your information, I have also attached copies of some recent articles regarding an alternative (Calcium Magnesium Acetate (CMA) for salt. Our own DOT&PF Research Section advises that their efforts are being directed to studying methods of producing CMA from industrial grade acetic acid and Alaska limestone so that an economically feasible process can be developed to produce CMA in Alaska. The Cantwell area is reported to have a large quantity of the raw materials for CMA. The University of Alaska is working on our study and a summary report of the work should be available in about three months.

Sincerely,

Robert W. Ward
Commissioner

Attachments
cc: Patrick P. Ryan
John Bates
Larry Sweet ✓

RWW:PPP:csb

Road deicing chemical called superior to salt

Iowa Department of Transportation researchers have developed a deicing material that is less corrosive than salt, effective at a lower temperature and is not harmful to the environment. If it proves out in tests this winter, the agency expects to patent the compound and convince a manufacturer in the state to produce it in large quantities.

The material, consisting of sand coated with calcium magnesium acetate, was developed last month by DOT's chief chemist, Wallace Rippie. ~~So far, the compound has been tremendously expensive to produce - 500 times more expensive than salt.~~ according to Charles Huisman, a DOT highway engineer who is heading the research. "But we are doing it now with a beaker and a mixer in a laboratory," he says. Huisman ~~is~~

~~is~~ ~~the~~ ~~new~~ ~~material~~ ~~is~~ ~~not~~ ~~as~~ ~~expensive~~ ~~as~~ ~~salt~~ ~~and~~ ~~is~~ ~~not~~ ~~as~~ ~~corrosive~~ ~~as~~ ~~salt~~ ~~and~~ ~~is~~ ~~not~~ ~~as~~ ~~harmful~~ ~~to~~ ~~the~~ ~~environment~~ ~~as~~ ~~salt~~. Huisman says that it ~~is~~ ~~so~~ ~~could~~ ~~double~~ ~~the~~ ~~life~~ ~~of~~ ~~bridge~~ ~~decks~~. In addition, it does not harm plants or pollute water, he says, and in fact is beneficial to soil. Also, indications are ~~that~~ ~~the~~ ~~compound~~ ~~can~~ ~~be~~ ~~formulated~~ ~~to~~ ~~work~~ ~~at~~ ~~temperatures~~ ~~below~~ ~~20~~ ~~degrees~~ ~~Fahrenheit~~, ~~the~~ ~~lowest~~ ~~limit~~ ~~of~~ ~~salt's~~ ~~effectiveness~~.

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*File: Engineering
News Record Jan 28
1982*

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Dunn, SA Dunn, A Schenk, RU
Bjorksten Research Laboratories, Incorporated, Federal Highway
Administration Final Rpt. FHWA-RD-79-109, Mar. 1980, 17 p.
Contract DOT-FH-11-9100
ORDER FROM NTIS

Snow great for skiing but it's war for these crews

By SCOTT YATES
Staff Writer

With nearly 400 miles of road to plow in the Fairbanks area, the state Department of Transportation and the city's Public Works Garage shuddered under the load of snow dumped here Monday and Tuesday.

In addition to the DOT's 12 pieces of snow removal equipment, four private graders were hired for anywhere from \$50 to \$80 an hour to help punch open the roads. The city, which hasn't hired outside help since the winter of 1970-71, was on the verge of employing private help itself when the snow stopped.

This week's heavy, wet snow presented special difficulties in a city accustomed to dry, light flakes that blow away in the backwash of passing vehicles.

"The wet snow we had the other day is the absolute worst," said John Horn, regional director of the DOT's Maintenance and Operations. He said it's heavier to push and it does not cast as well. When wheels move, it's more likely to damage objects such as mailboxes along the road.

Speed is of the essence after a wet snowfall. Unless it is plowed early, Horn said, traffic can beat the snow down into an almost impenetrable snowpack.

Which roads get attention first are decided by DOT highway superintendents. Mostly, Horn said, it has to do with which roads have the most traffic.

Airport Way heads the priority list for the DOT, partly because it's a major city thoroughfare and partly because it's right outside the department's door. Other roads within that first category include the Richardson Highway to Etelson, the Steese to Fox and the Parks Highway halfway to Nenana.

College Road, Cushman Street, Illinois, University Avenue, Geist Road, Farmers Loop, the Davis Road area and Chena Hot Springs Road are included within the second priority listing.

Horn is quick to point out that Birch Hill Road, where he has a house, is among the 54 roads with the lowest priorities. "I can tell you I receive no special treatment," he said.

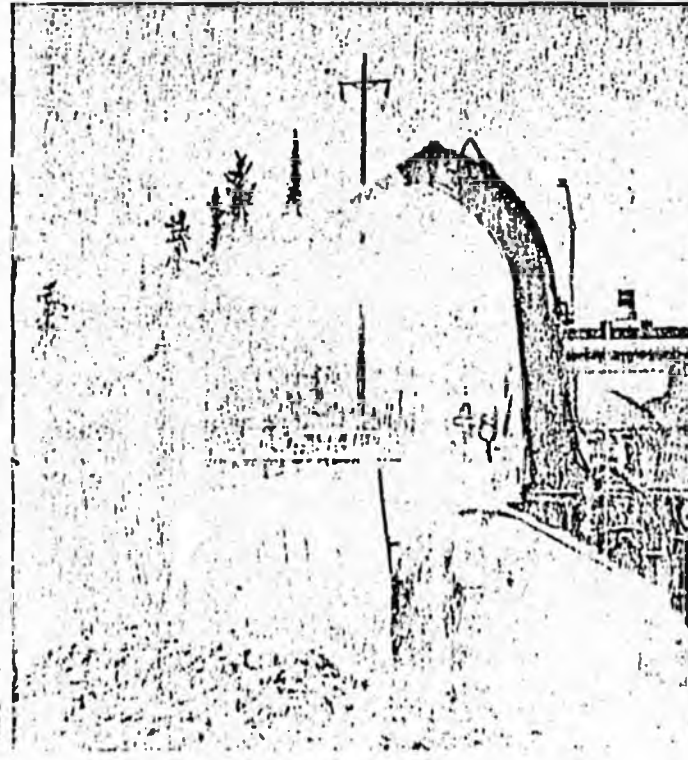
Dud Weber, assistant superintendent of the Public Works Garage, said after a snowfall, the first city roads to be plowed are the one-way streets downtown: Barnett, Lacey, Noble and Gaffney.

Upon completion, the graders are split into two teams, one on each side of the river. South Cushman, Cowles, Lathrop, 23rd and 17th avenues are among the secondary priorities for the city. The hospital entrance, the fire department stations and streets around local schools are all areas which are cleared early.

Some areas like Slaterville, Arctic Park or Island Homes are normally not plowed at all, Weber said. Plowing on the such narrow streets narrows them even more, Weber explained. "It's a question of putting up with a big windrow or fighting the snow on the street." Given the amount of snow that fell in the last storm, Weber decided on the latter.

Although the DOT has more miles to plow than the city (250 miles to 132 miles), Weber said the state agency has the advantage he

(See SNOW, page 2)



FALL CLEANUP—A snowblower followed by a road scraper works on Trainor Gate Road Thursday afternoon, still cleaning up the snow dumped on the Fairbanks area earlier this week. Snowfall was as much as a foot in outlying hills. City and state road crews worked frantically to first open the roads, then to clear the snow.

SNOW . . .

(Continued from page 1)
cause of it has a night crew on duty. Weber is alerted to heavy snows by the police or other city employees who call him at home.

Monday morning he was awakened at 3 a.m. and went into the office to call out more crews.

Once the roads are punched open, "the first lick," Horn said, the real work begins. That includes smoothing off the snowpack and winging back the windrows.

Providing traction for vehicles on hills and at intersections usually begins after the snow has been plowed.

The state uses both salt and sand on the roads. Horn explained that salt is only effective at plus 21 degrees, so it is not used the majority of the winter.

He acknowledged the corrosive effects of salt, and said that DOT researchers are working on an alternative to the tender eating salt.

The city is also experimenting with non-toxic chemicals which act as an anti freeze on the roadway. Those are only experiments, however, and Weber said the city mostly relies on spreading different sizes of gravel.

A checklist of icy spots are compiled each day for dispatching the city's two sanding trucks.

(Staff photo by Joe Curran)

MEMORANDUM

State of Alaska
Department of Transportation & Public Facilities

TO: Lynn Harnisch
Staff Engineer
Planning and Programming
Interior Region

DATE: October 14, 1982

FILE NO:

TELEPHONE NO: 479-4231

FROM: Robert R. Venusti
Director
Planning and Programming
Interior Region

SUBJECT: Dalton Highway
Evaluation

The current version of the region's FY-84 through FY-89 Transportation Improvement Program contains a fairly substantial annual allocation of State funds for improvements to the Dalton Highway. To maintain as much flexibility as possible in where and how the funds can be expended, the scope of work for each allocation in the TIP is for rehabilitation and resurfacing, with specific project termini to be identified as the funds become available.

Due to the continued high level of community and legislative interest in the Dalton Highway, and in keeping with our goal of incorporating the planning of capital improvements for the highway into our ongoing regional planning process, we should begin to evaluate a number of different options for programming something besides annual "maintenance" type projects for the highway. Hopefully the results of this effort will be an eventual shifting away from the tendency to treat the Dalton Highway as a politically unique entity, and an increased capability on our part to identify the need for and program specific categories of projects (i.e. reconstruction, rehabilitation, surfacing, etc.) along the length of the facility.

I suggest the following as a starting point for options to be considered:

- a) Rehabilitate the existing road to its original design standards - gravel surface.
- b) Upgrade the road to current AASHTO standards - gravel surface.
- c) Either a) or b), with:
 - 1) Crushed aggregate gravel surface
 - 2) Paved surface.
- d) Either a) or b) with:
 - 1) Asphalt surface treatment
 - 2) Calcium chloride surface treatment.

All of the above options (or appropriate combinations thereof) should be compared on the basis of life-cycle costs. They should also be evaluated in the context of recommendations and information coming out of the

Western Arctic Alaska Transportation Study and the Interior Transportation Study, as well as whatever information is available pertinent to the proposed construction of the Northwest Alaska Gas Pipeline project. Updated traffic forecasts for the highway should consider expanded North Slope oil development, mineral and other resource development in or adjacent to the highway corridor, and increased tourist traffic.

Once we have attached cost figures to option a) through d) we should be in a position to make some basic policy decisions regarding investment strategies for capital improvements on the Dalton Highway. For purposes of this analysis we should include the unpaved portion of the Elliott Highway between Wickersham Dome and Livengood.

Please prepare a draft outline for this effort, including a proposed time schedule and budget, for my review by November 15. I would like to have the cost estimates for all options to be evaluated available by mid-February of 1983. The overall evaluations should be completed in time to be incorporated into the FY-85 CIP development (June of 1983). If you have any questions, please contact myself or Larry Soden.

RPV:LLS/bdc

cc: Steve Sisk
John Horn
John Martin
Jon Widdis

STATE OF ALASKA

Bill Sheffield, Governor

DEPARTMENT OF TRANSPORTATION AND PUBLIC FACILITIES

MAINTENANCE AND OPERATIONS, INTERIOR REGION

2301 PEGER ROAD
FAIRBANKS, ALASKA 99701
PHONE: (907) 452-1911

March 25, 1983

Ms. Denise Zachery
c/o Representative Mike Miller
House Democrats Office
Pouch V
Juneau, AK 99811

Dear Ms. Zachery:

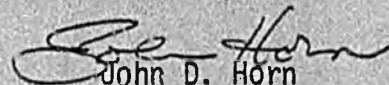
Enclosed for your information is a draft copy of the interim report on the second phase of this Department's study into the possible production of Calcium Magnesium Acetate (CMA) for use as a deicing agent on Alaskan roads.

We feel that it is an appropriate time to perform a demonstration project to test both the economics of commercial production of this chemical and its effectiveness in comparison with the salts commonly used to deice roads. The results of the research conducted to date by the Petroleum Engineering Department of the University of Alaska and our own lab tests have been encouraging.

Potential suppliers of both acetic acid and limestone, the two ingredients necessary to make CMA, have contacted the Department to indicate their interest in participating in a CMA demonstration.

A demonstration could be performed by the private sector in cooperation with DOT/PF personnel.

Sincerely,



John D. Horn
Acting Deputy Commissioner
Interior Region

cc: Daniel A. Casey, Commissioner

attachment

A PROCESS DESIGN, BENCH SCALE PILOT PLANT AND
WIDE FIELD APPLICATIONS OF CALCIUM ACETATE

AN INTERIM REPORT

by

Michael J. Economides
Russeli D. Ostermann
Bertrand Theuveny
Andrew H. Thomas

Department of Petroleum Engineering
University of Alaska
Fairbanks, Alaska 99701

MARCH, 1983

Prepared for:

STATE OF ALASKA
DEPARTMENT OF TRANSPORTATION AND PUBLIC FACILITIES
DIVISION OF PLANNING AND PROGRAMMING
RESEARCH SECTION
2301 Peger Road
Fairbanks, Alaska 99701

The contents of this report reflect the views of the authors who are responsible for the facts and the accuracy of the data presented herein. The contents do not necessarily reflect the official views or policies of the Alaska Department of Transportation and Public Facilities. This report does not constitute a standard, specification or regulation.

INTRODUCTION

This project is a continuation of the previously funded "Preliminary Design and Feasibility Study for a Calcium-Magnesium Acetate Unit" (Reference Project F15631-CMA).

Calcium-Magnesium Acetate (CMA) exhibits excellent de-icing characteristics, yet is non-corrosive, and not harmful to plants. In our previous work, a process concept was developed for the production of CMA from native Alaskan limestone and acetic acid, based on laboratory scale reaction experiments. The next logical step in the development process was the construction and operation of a small scale pilot plant to gather specific process data necessary for a full-scale process design. That is the subject of the current project.

In addition to our design work, we undertook to produce about 500 gallons of CMA solution from a batch process based on our limited laboratory studies. This interim report gives a brief summary of our progress.

The next step in the development process will be the design, construction and operation of a demonstration plant to serve the dual purpose of proving the viability of the process, and to provide enough CMA for field tests. It should be noted that nowhere is CMA manufactured in bulk and, therefore, is unavailable in the amounts necessary for wide-scale testing. A

proposal has been submitted to the State of Alaska through the Fairbanks North Star Borough. Approval is pending.

It has recently been suggested that CMA may be useful as a dust-control agent as well as a de-icing agent, however, this has not presently been verified. We have designed a set of experiments to test the utility of CMA in dust control, but expect that a road test will be required for positive determination. Funds are currently being sought for this research.

BACKGROUND

Road and runway de-icing are serious problems in the northern latitudes. The problem is most pronounced in the coastal regions of Alaska where freeze-thaw cycles occur several times during the winter. Sodium chloride (salt) and calcium chloride have been used for many years as de-icing agents, however, these materials are highly corrosive to automobiles, airplanes and roadway bridge structures.

Recently, several salt-damaged bridge structures were replaced in Fairbanks at a cost of over \$600,000. The cost of

salt-related damage to bridges in the Anchorage and Juneau areas where salt is used more frequently are correspondingly higher.

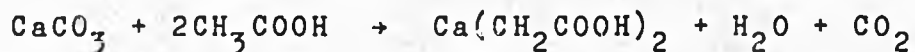
Furthermore, road salts are injurious to most forms of plant life. In the spring, a drive along heavily salted roadways in Anchorage reveals a virtual moonscape with dead or stunted plants. The success of ongoing roadway beautification projects in Anchorage and Fairbanks will be questionable with the continued use of road salts.

In a report entitled "Alternate Highway De-Icing Chemicals" published by the Bjorksten Research Laboratories, a mixture of calcium and magnesium acetate (CMA) was identified as an effective, non-corrosive, de-icing compound. In the solid form, CMA is a white powder resembling powdered sugar. It can be applied as a solid or in a saturated solution. The effective temperature range is about the same as common road salt. In contrast to salts, however, CMA is non-corrosive, not harmful to plant life, and has no potential to harm drinking water supplies.

In previous work at the University of Alaska, funded by the State Department of Transportation (DOT), we have demonstrated that CMA can be produced from limestone, water, and acetic acid. The preliminary report of our reaction studies has been presented in a previous report to the State DOT. This funding is of significance, since limestone is readily available in Alaska. Acetic acid must currently be "imported" from the "lower

48", but could be produced locally from refinery by-products if a market were available.

In simple terms, CMA is the reaction product of the dissolution of limestone in acetic acid and water.



The dissolution process is slightly exothermic (gives off heat) and produces considerable amounts of CO_2 . The resulting solution remains acidic, and must be neutralized with sodium or calcium hydroxide.

Limestone is composed of calcium and magnesium carbonates in varying amounts. Pure magnesium acetate, which could be produced from pure magnesium carbonate, is superior to calcium acetate. Dolomites contain relatively larger amounts of magnesium carbonate and can approach 50% in composition. Unfortunately, the benefits of a 50-50 mixture over pure calcium acetate are not very significant. Therefore, it is most appropriate to use readily available limestone regardless of the magnesium carbonate content.

PILOT PLANT STUDIES

Unfortunately, we have met with several delays in the construction and operation of our pilot plant unit. The reaction assembly is in place, but the necessary fume vents have not yet been installed. This delay is due to local construction backlogs and was beyond our control. However, it would appear that the fume hoods will be installed shortly and we can begin operation.

BATCH STUDIES

Due to the lack of availability of the pilot plant, we concentrated our efforts on the batch production of CMA for road tests. Numerous difficulties were encountered in the conduction of the reactions; many more than anticipated. However, after much experimentation, we have arrived at an acceptable process scheme. In this manner, the batch studies have fulfilled (at least qualitatively) part of the goal of the pilot plant studies.

BATCH PRODUCTION OF CMA

The procedure we settled on for CMA production is outlined below. It should be emphasized that this is by no means finalized; it is merely a procedure that works.

Our reactor for use in these experiments was a 55 gallon plastic drum equipped with a large agitator. In our initial studies, the agitator was replaced by a small circulating pump. This was found to be totally inadequate. A high degree of agitation is required to keep the carbonate particles suspended in the reacting liquid.

Foaming was another problem of critical severity. Unless the reaction was conducted at a moderately controlled rate, a very stable foam forms, necessitating removal.

MATERIALS: 20% (wt) acetic acid (pure)
 20% limestone (crushed)
 60% water

PROCEED

1. Mix the water and acid in the drum;
2. Introduce the limestone slowly to avoid foaming;
3. Stir for about 1 day;
4. Let stand (to settle) for several days;
5. Remove the liquid and place in a second drum;
6. Recycle the solid material settled from the drums;
7. Add NaOH solution (about 50-50% NaOH/water);
8. Continue to add NaOH solution until pH = 7 (It may be necessary to add water if a precipitate forms. This merely means that the solution is oversaturated with CMA);
9. CMA is ready to use..

DISCUSSION:

The neutralization reaction is difficult to control since NaAc forms a buffer solution. In practice, it may not be possible to obtain a pH of 7. A typical neutralization is plotted in Figure 1.

As can be seen in Figure 1, it was necessary to add water at points (1) and (2) to redissolve CMA which had precipitated out

of solution. With practice, the correct amount of water could initially be added to avoid this problem.

In general, it is undesirable to allow CMA to precipitate because it tends to form a gel-like solution which is difficult to stir and to redissolve. Selecting the right amount of water to add with the NaOH will depend on the limestone purity. Hence, it is possible to determine only an approximate range for application.

Figure 2 shows a plot of pH versus volume NaOH solution added. In this format, the added water correction does not appear and a more "normal" neutralization curve is obtained.

To further complicate neutralization, the reaction is not instantaneous. Figure 3 shows the response of pH with time following the addition of NaOH. About 5 minutes will elapse between the time of the NaOH addition and the final pH.

The reaction rate for this process can be monitored by measuring the CO_2 evolution. In general, the dissolution of 1 mole of CaCO_3 releases 1 mole of CO_2 . Figure 4 shows a plot of reaction rate versus time measured in this manner. As is evident, the reaction rate declines rapidly, dropping over 3 orders of magnitude in the first several hours. Figure 5 shows a plot of cumulative CO_2 production versus time. It is evident that long reaction times on the order of several days are

required. This behavior is typical of batch reactions. The reaction time can be shortened by using continuous reaction equipment, which maintains concentrations in the first reaction range.

FIGURE 1

Neutralization of CMA Solution

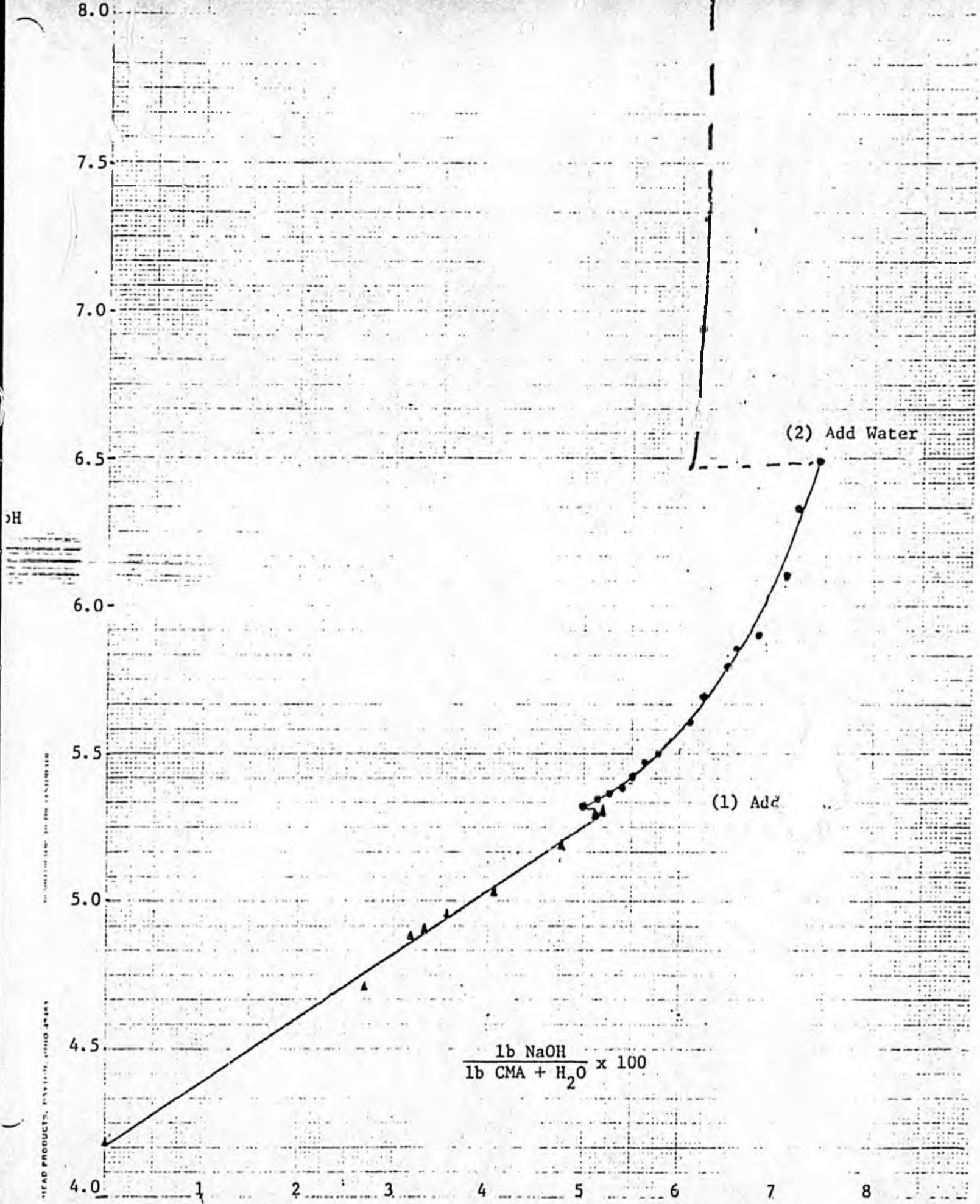


FIGURE 2

Titration of an Unknown Solution of CMA

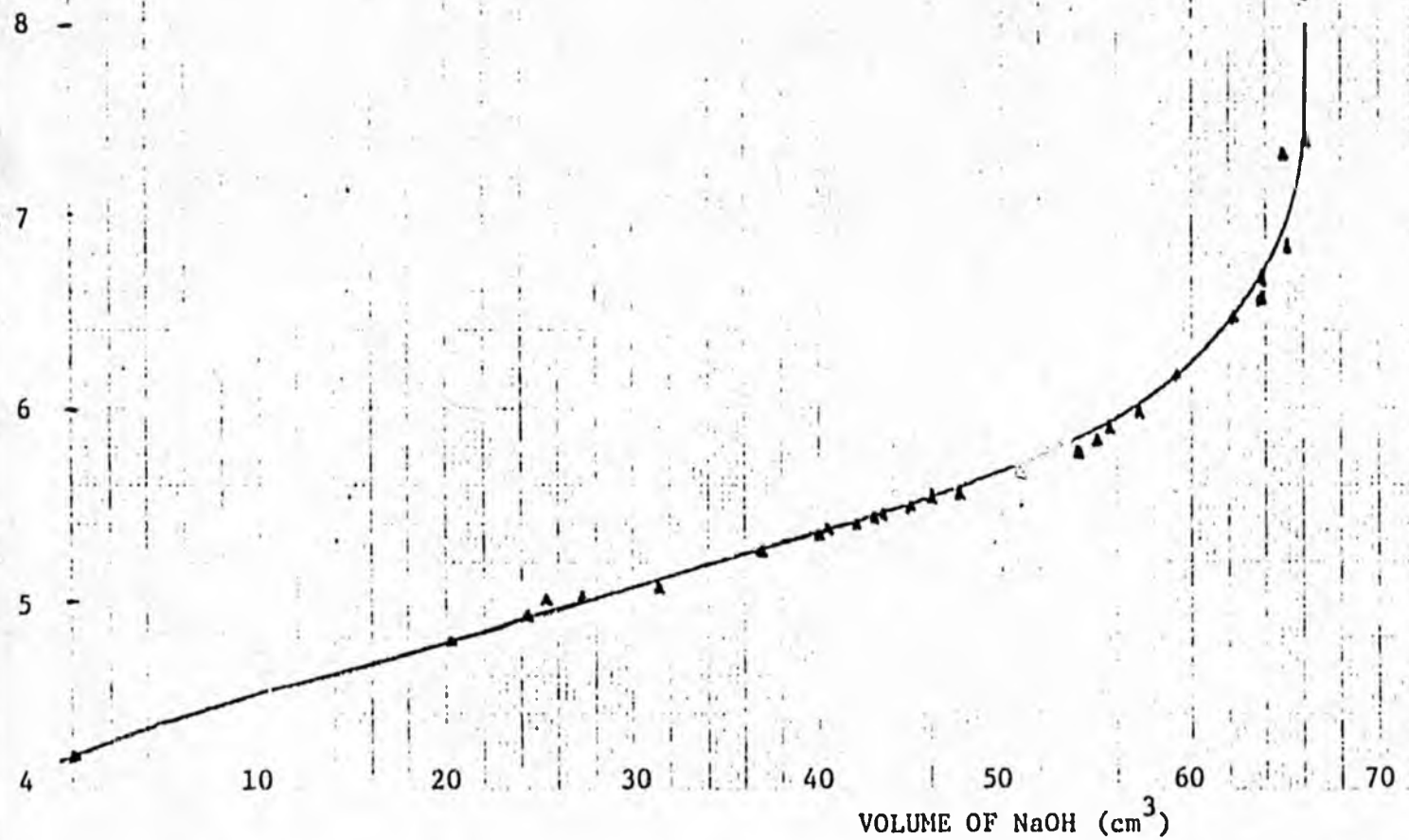


FIGURE 3

Evolution of pH versus time after adding some NaOH to the solution near equivalence point.

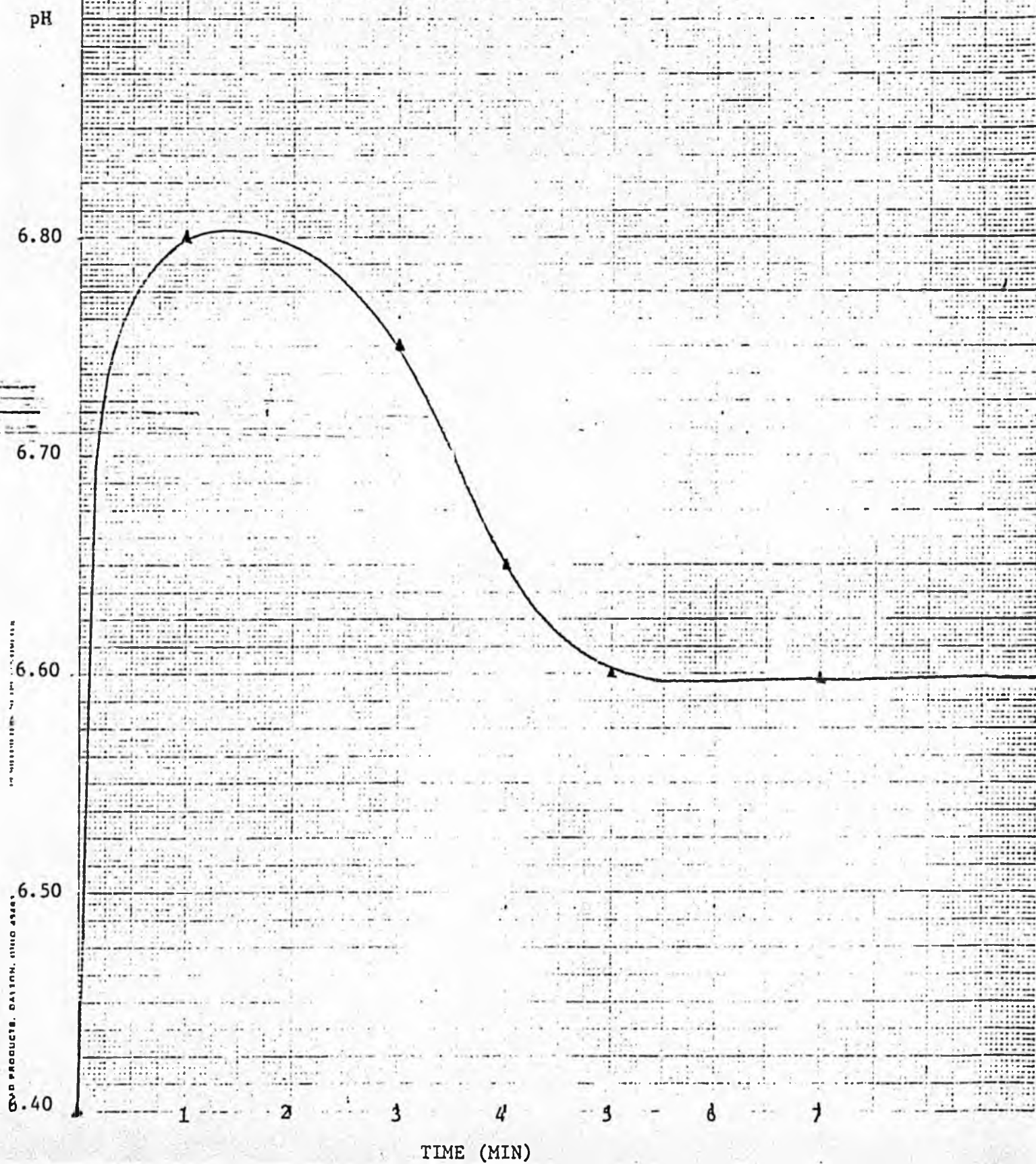
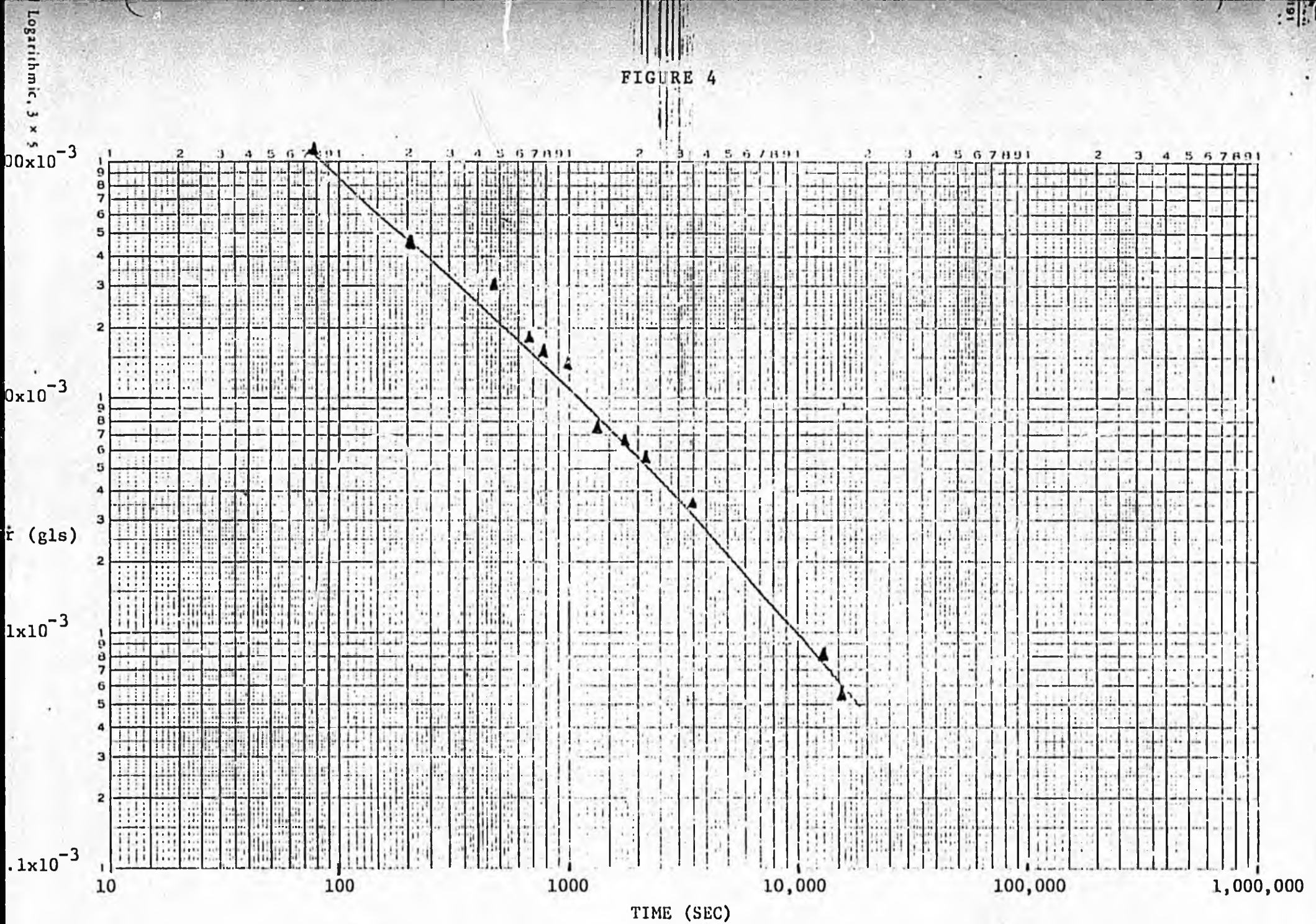
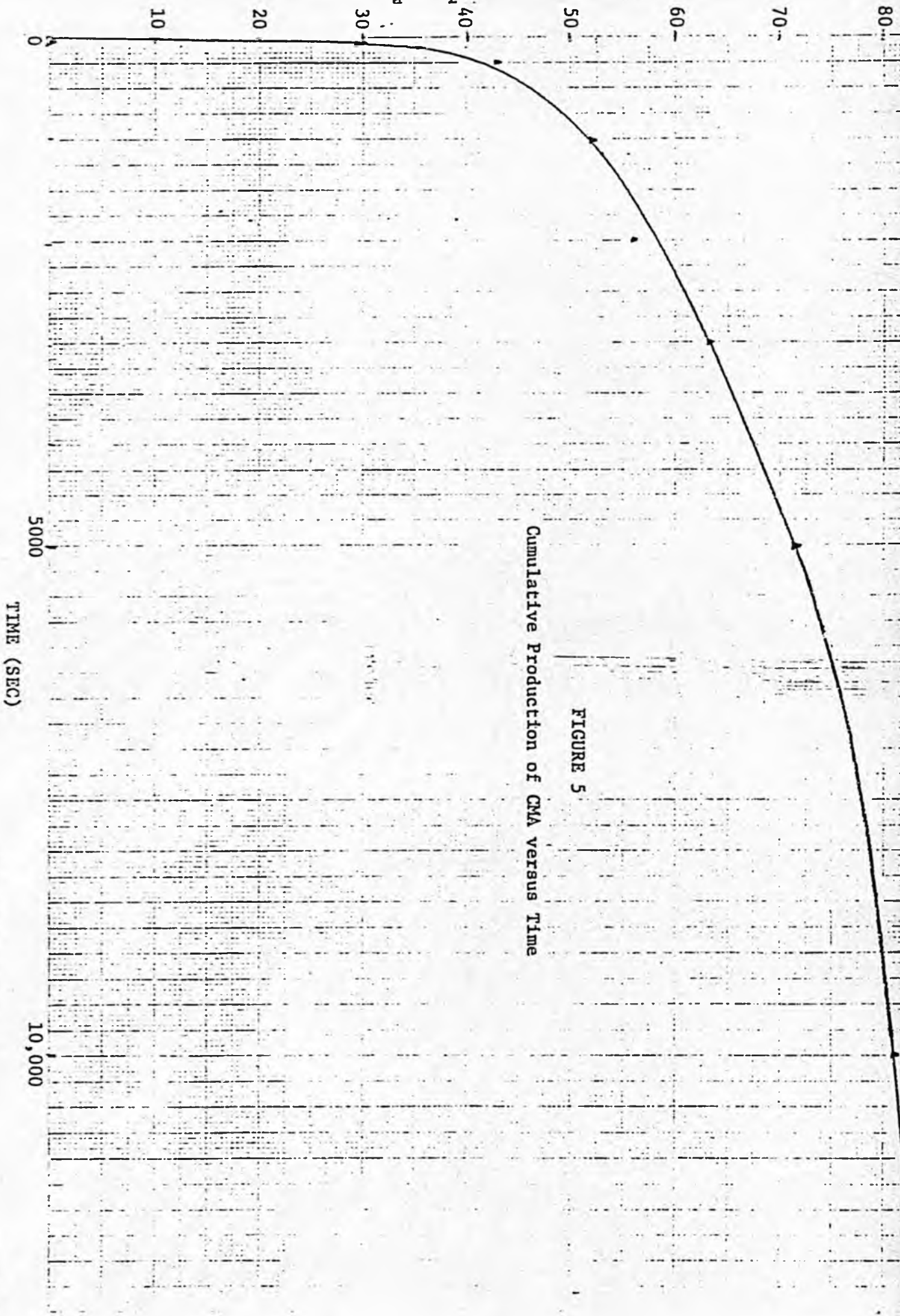


FIGURE 4



Production Rate of CMA (Limestone 14.5%, H₂O 58.6%, HAc 26.9%)

Mass of $C_a(Ac)_2$ Produced (gr)



Cumulative Production of CMA versus Time

FIGURE 5

Preliminary Design and Feasibility Study
for a Calcium-Magnesium Acetate Unit

FINAL REPORT

by

M. J. Economides

Assistant Professor of Petroleum Engineering

and

R. D. Ostermann

Assistant Professor of Petroleum Engineering

PRELIMINARY DESIGN AND FEASIBILITY STUDY
FOR A CALCIUM-MAGNESIUM ACETATE UNIT

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Fairbanks, Alaska 99701

July, 1982

Prepared for:

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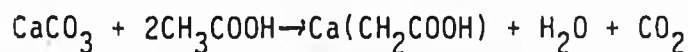
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FOREWORD

Fundamental regard for winter time driving safety has resulted in an extensive and continuing application of NaCl and CaCl₂ de-icing salts to the road surface. The de-icing benefit of these materials is however, negatively offset by secondary costs due to metal corrosion and pollution effects. Literature sources place the total cost of salt usage at approximately 10-15 times that of the salt product itself. The public's objection to secondary costs such as rusty automobile fenders often provides a pungent criticism of roadway salting practices. In addition, corrosion of bridge reinforcing steel is a problem of great magnitude to the highway engineer.

National research into alternative de-icing compounds has led to recognition of Calcium Magnesium Acetate (CMA) as the most viable substitute for NaCl and CaCl₂. CMA provides an ice melting capability similar to chloride salts while raising little or no corrosion potential for most steel or aluminum vehicle components. Furthermore, CMA has been shown to be a safe, non-toxic substance with respect to animal and plant life.

CMA is fairly easily produced by the action of acetic acid on calcium carbonate (limestone) as indicated below:



Details of critical reaction parameters and a chemical process design are presented within this report.

The extremely high cost of CMA has prevented its use in all but limited testing situations. CMA is commercially available only in laboratory reagent grade as either the pure calcium or pure magnesium acetate. These products are intended for laboratory usage and are priced at many dollars per pound. This study was initiated to investigate production methods and economics associated with making a low grade of CMA from raw materials readily available to a potential Alaskan producer.

This report evaluates the small scale production (14 - 72 tons per day dry

weight equivalent) of a "highway grade" CMA solution. Findings indicate that CMA becomes economical at production levels of more than 17 tons per day. It was calculated that the cost of CMA would range between \$290 and \$590 per ton depending on rate of manufacture and the base price of acetic acid. These figures compare very favorably with the current cost of CaCl_2 used by the Alaska DOTPF of almost \$650 per ton (F.O.B. Fairbanks), especially in view of secondary damage attributable to the chloride salt.

An interesting point is emphasized by the authors regarding potential economic ramifications of Alaskan CMA. It is reasonable to expect that petroleum derived, low grade, low cost acetic acid can be made available within Alaska as a result of oil related industry. Under this circumstance, with acetic acid costs possibly below \$1.00 per gallon, larger scale production of CMA could become a significant Alaskan enterprise. It is further conceivable that Alaska could eventually become a major producer and exporter of low grade CMA to a national or international market.

As project manager I would recommend a course of action leading to manufacture and use of CMA as a de-icing agent in Alaska. In view of the promising nature of this report's findings, work is continuing with construction of a small "bench scale" pilot plant, a refining of the process design and field trials of experimentally produced CMA. An important first-trial of CMA will involve treatment of a roadway sand stock pile to prevent freezing.

Robert McHattie, P. E.
Senior Research Engineer
Alaska Department of Transportation
and Public Facilities

ABSTRACT

The adverse environmental effects and corrosion problems associated with the use of chloride salts as de-icing agents have prompted a search for alternative de-icing compounds. Calcium and Magnesium Acetates (CMA) exhibit excellent de-icing characteristics yet are not corrosive or harmful to the environment.

A viable process design for the production of CMA has been developed based on the results of a series of kinetic reaction experiments conducted at the University of Alaska. Acetic acid and native Alaskan limestones were used as the raw materials. An economic evaluation of the process indicates a selling price of less than \$600/ton of solid CMA, based on the production of a saturated, aqueous CMA solution in small scale facilities (10,000 - 50,000 gallons/day). At the upper range of production rates studied (50,000 GPD) and for an acetic acid cost of \$1.25/gallon, the calculated CMA price was \$290/ton of solid. This represents a minimum price and is attractive when compared with the cost of other de-icing compounds.

The results of this cooperative project between the Petroleum Engineering Department at the University of Alaska, Fairbanks and the State D.C.T. are highly encouraging. With the use of native Alaskan limestone and acetic acid, the process economics point toward a high quality, competitively priced product. The environmental advantages of CMA over chloride salts and reduced secondary costs due to lower corrosion rates for vehicles and bridges indicate that CMA may become the premier de-icing agent.

INTRODUCTION

Road and airport runway de-icing are serious problems in the northern latitudes. Sodium and calcium chlorides have been used successfully for many years as de-icing agents. However, adverse environmental effects and corrosion problems associated with chloride salts have prompted a search for alternative, cost-effective, de-icing agents. (1,2,3,4)

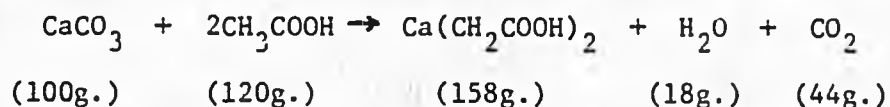
A report entitled "Alternate Highway De-icing Chemicals" from the Bjorksten Research Laboratories, Inc. presented a review of the de-icing characteristics of various compounds. Two candidates were selected which proved economical, and more importantly, less corrosive than NaCl.

The first, methanol, was found to be "less persistent" due to its low flash point. The second, a mixture of calcium and magnesium acetate (CMA) was found to exhibit superior de-icing characteristics at a competitive price. In contrast to NaCl, CMA is a corrosion inhibitor, is beneficial to most soils, and has no potential for harming drinking supplies. Hence, CMA does not exhibit many of the "extended costs" associated with the application of NaCl.

CMA can be produced by the simple dissolution of naturally occurring carbonates in acetic acid. These carbonates are readily available in the form of native limestones and dolomite. We have discovered that, for economic and technical reasons, the production of calcium acetate (CA) alone is preferred. This subject is dealt with in a later section of this report.

REACTION EXPERIMENTS

Calcium acetate is formed by the dissolution of calcium carbonate in an acetic acid solution. Water and carbon dioxide are byproducts. The stoichiometric equation is given below:



The reaction is slightly exothermic ($\Delta H_r^0 = -4.6\text{kcal/gmol.}$). The solubility limit of CaAc (calcium acetate) is 28% by weight. Hence, if a saturated solution of CaAc is desired, a simple material balance indicates a water requirement of 338 g. H₂O/100g CaCO₃.

A series of experiments was undertaken to define the process kinetics and ultimate degree of completion functions of the reaction temperature, reactant concentrations, and extent of particle size reduction for the calcium carbonate. Alaskan limestone delivered from a quarry near Livengood, Alaska, and laboratory acetic acid were used as reactants.

The reaction behavior of limestone and acetic acid is reported in Figure 1. The reactions were conducted in a simple stirred tank reactor. At a given residence time, there was no discernible difference between the various water to limestone ratios, as long as enough water was present to provide an unsaturated solution of calcium acetate at the conclusion of the reaction. This minimum ratio of 4 to 1 on a mass basis proved inhibiting at high acetic acid excess. This result is to be expected since the reaction is based on the dissociation of acetic acid. An insufficient amount of water results in inadequate dissociation of acetic acid.

Since various water to limestone ratios above 5:1 (for brevity not all results are plotted on Figure 1.) did not exhibit any discernible difference in the reaction completion rate, the entire subsequent set of experiments was done at a 5:1 weight ratio of water to limestone.

A significant conclusion can be drawn from the above. The quality of the acetic acid does not have to be highly refined. Industrial grade acetic acid (95% purity) which is significantly less expensive than reagent grade, can be

(5)

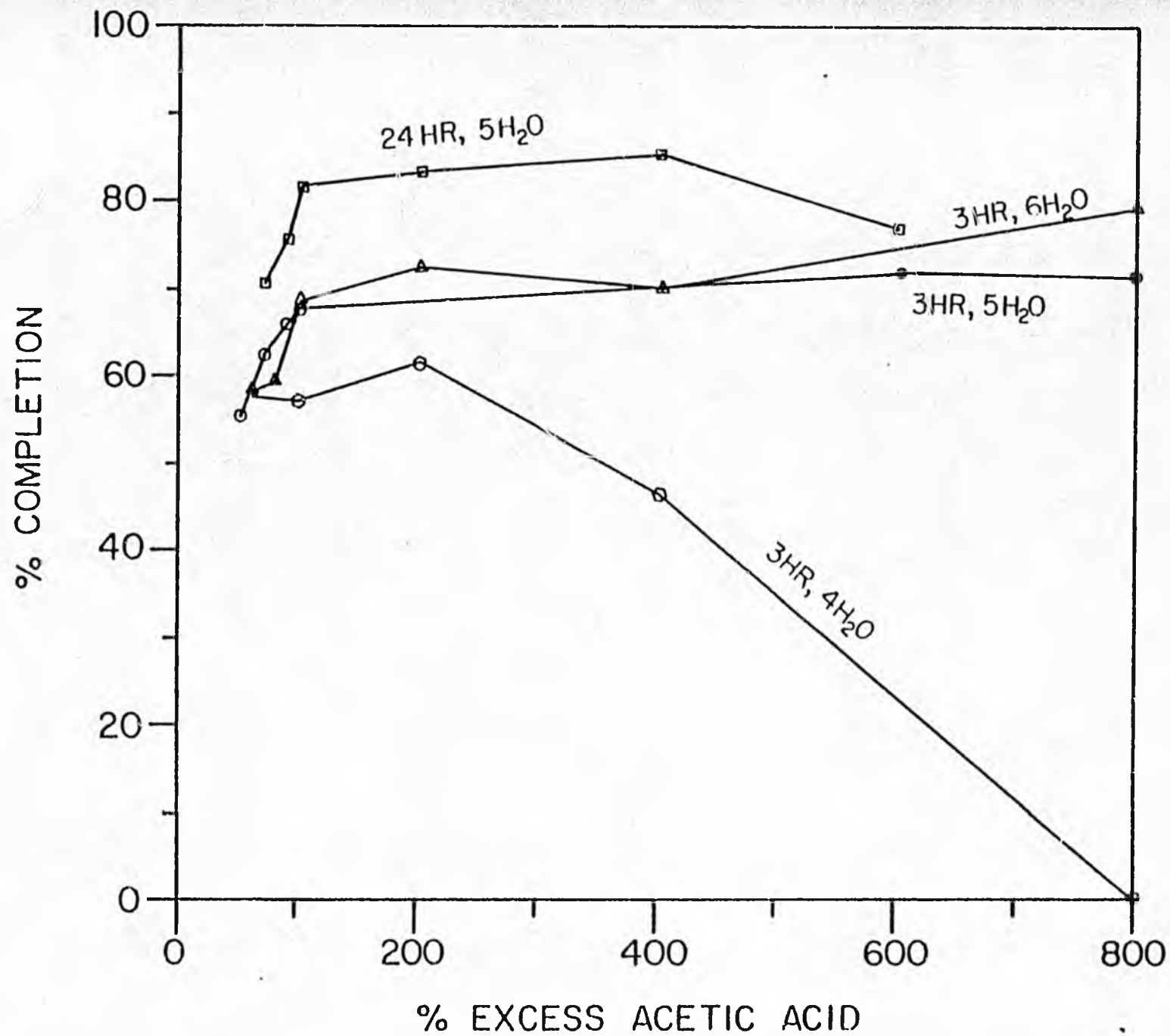


Figure 1. Reaction Behavior of Limestone and Acetic Acid: Percent Completion vs. Excess of Acid at Various Residence Times and Water Content.

used since it will have to be diluted to 50% in any event.

There is another major benefit out of the findings. Liquid phase oxidation (LPO) of waste cellulose (or methanol carbonylation) produce acid at about the optimal 50% concentration. Both methods of production could be implemented in Alaska. Especially attractive is the methanol carbonylation since several industrial concerns are contemplating methanol production in the state. The supply of carbonate for the acetate process seems assured. The state houses large deposits of limestone and dolomite.

Figures 2 through 5 present a comprehensive picture of the reaction results. The series of experiments were intended to gauge the effects of excess acid, reaction temperature and limestone particle sizes on the completion of the reaction. The results are for batch reactions with a three hour residence time.

The amount of excess acetic acid did not appear to affect the reaction completion significantly. Hence, acid consumption can be held at a manageable level.

Neutralization of acetic acid by NaOH can be considered. However, a further economic evaluation may point toward an associated acid recovery unit. An extraction step using an appropriate solvent, followed by a distillation step may be indicated.

The effect of the temperature is significant. An increase in the reaction temperature from room level of 20°C to 60°C results in an increase in the rate of completion of over 20%. A similar effect was observed in using more finely ground limestone. The "first" and "second" crushing that appear in Figures 2 through 5 refer to two consecutive outputs of a commercially available rock crusher. Both of the last two findings will have an effect on the economic optimization of the process. The beneficial effect on the completion rate must be balanced against the operating and energy costs. Finally, the residence time in the reactor appears significant. A 20% difference in the reaction completion was observed if a reaction time of 24 hours was used instead of 3 hours.

(7)

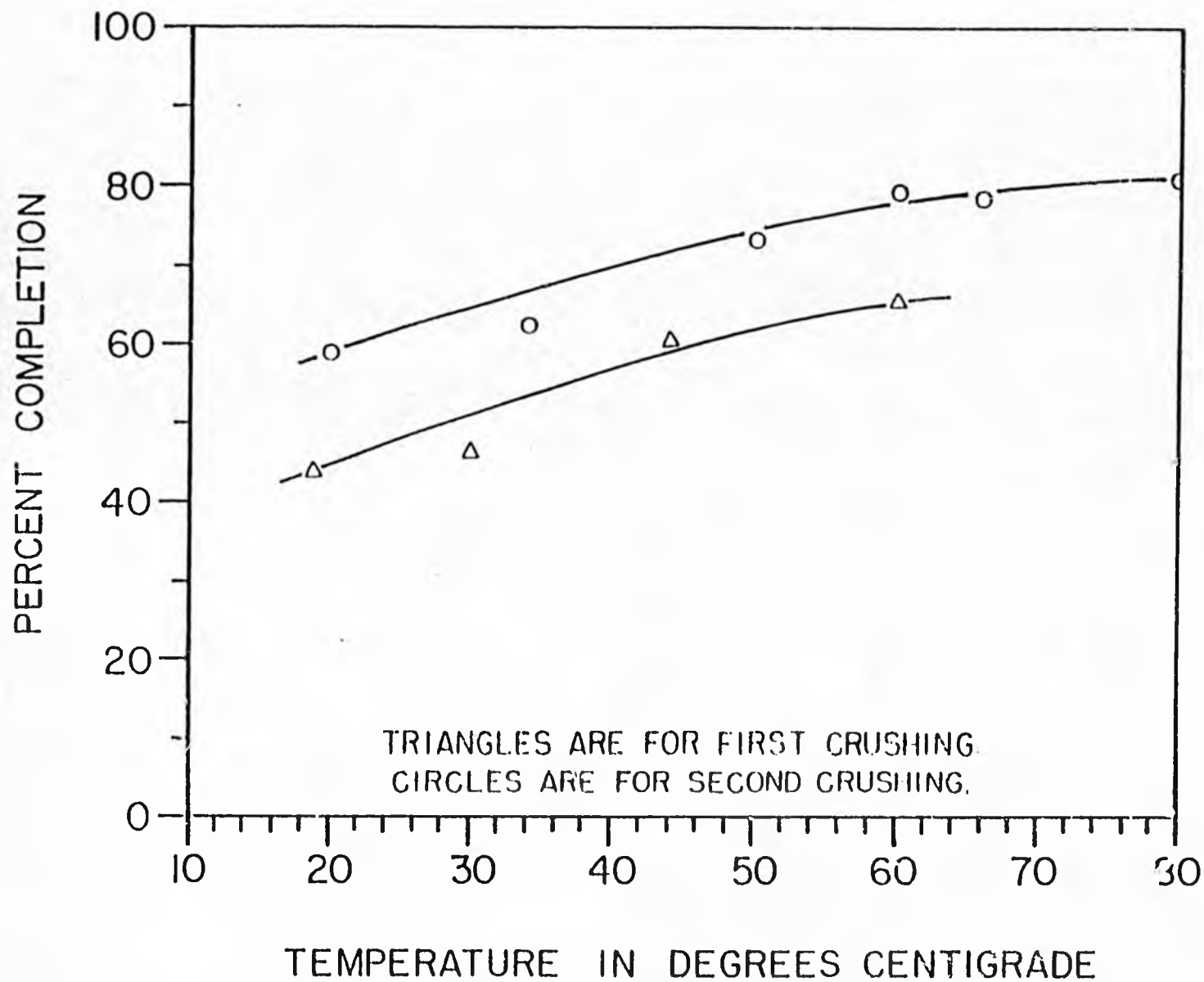


Figure 2. Reaction Performance for Limestone and 0% Excess Acetic Acid

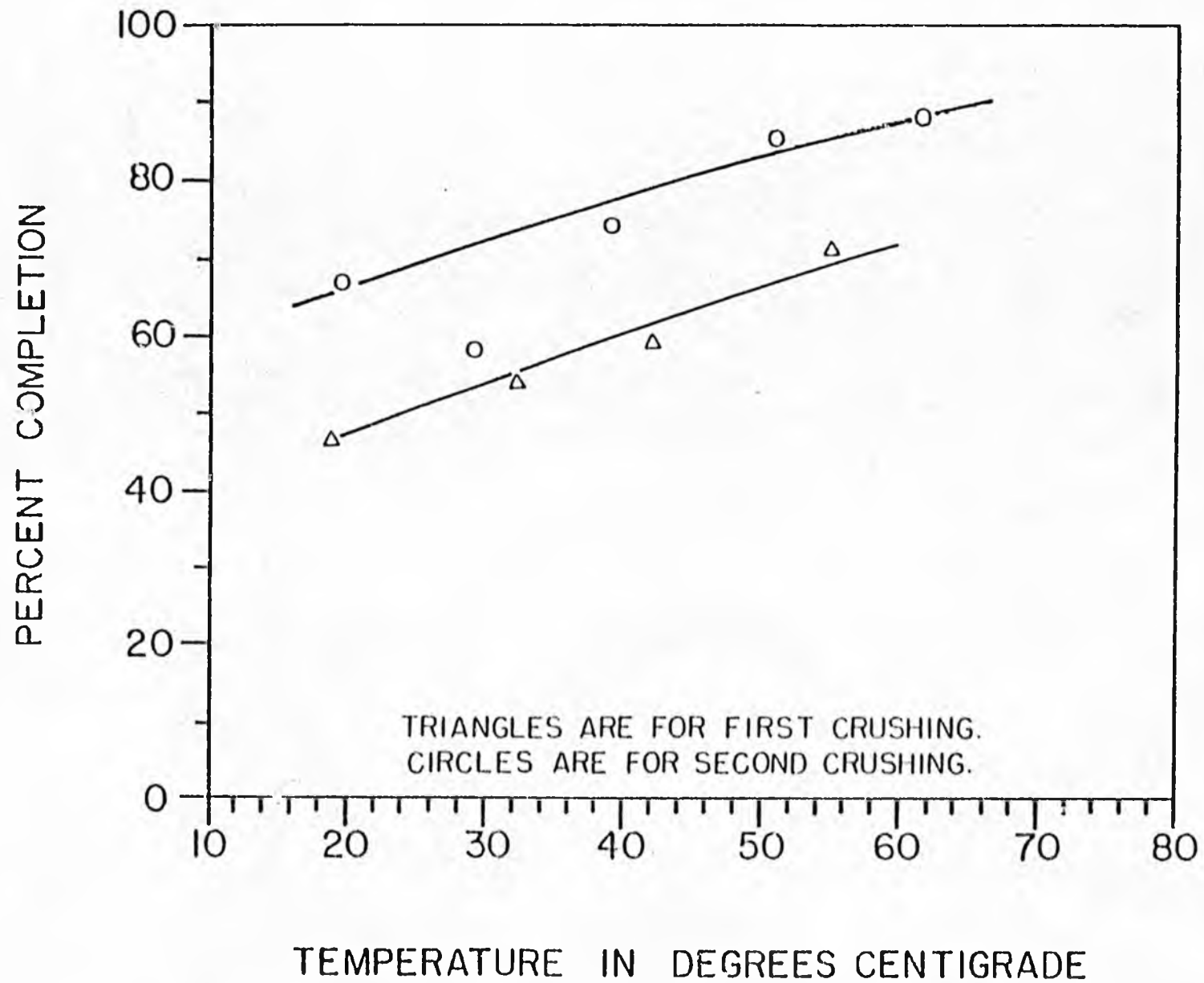


Figure 4. Reaction Performance for Limestone and 50% Excess Acetic Acid.

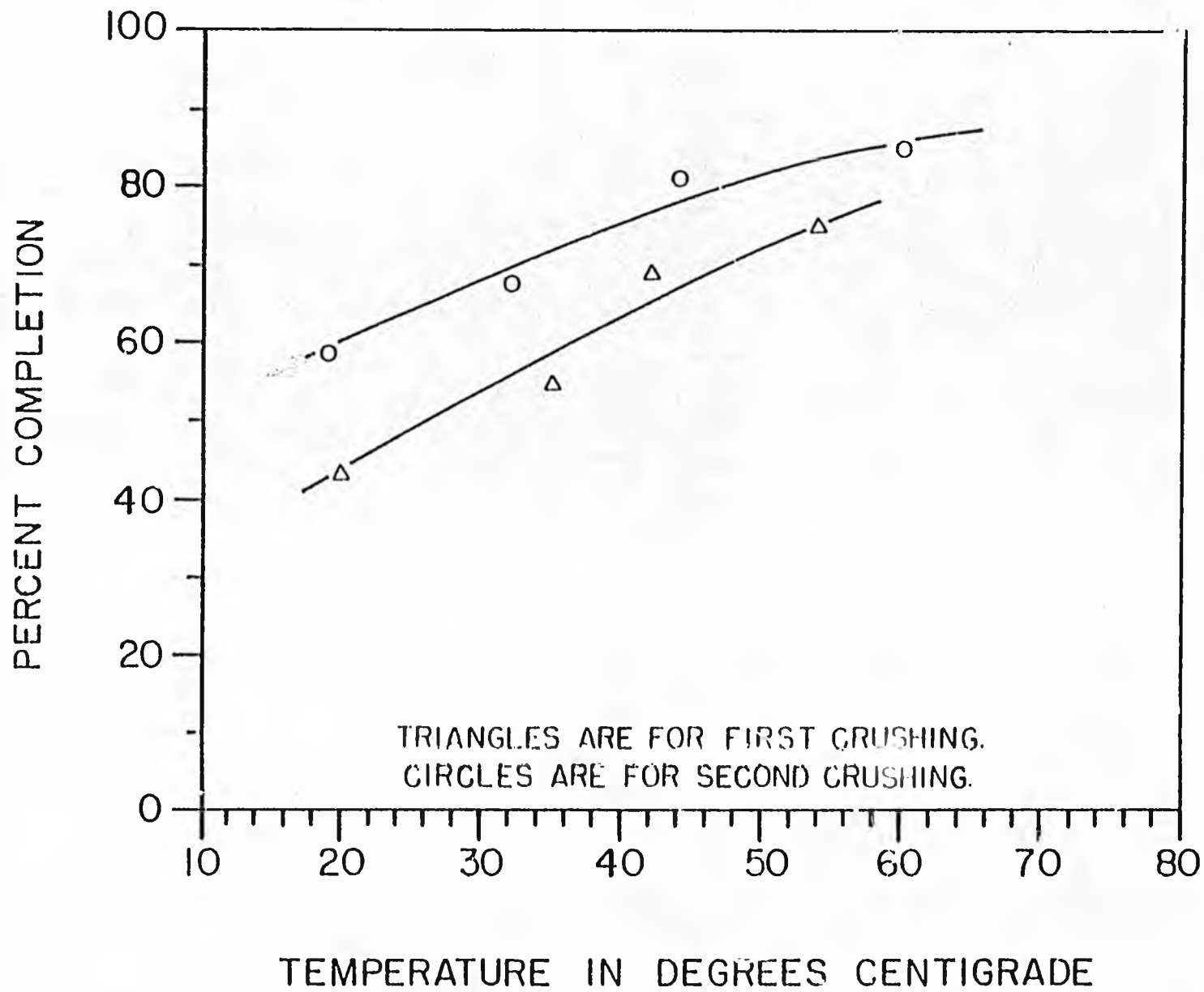


Figure 5. Reaction Performance for Limestone and 100% Excess Acetic Acid.

PROCESS DESIGN AND ECONOMICS

A rigorous economic analysis for a proposed process requires a detailed process design. However, an approximate analysis can be completed on the basis of a preliminary design. This is common practice in the industry.

For a simple reaction process such as that of production of CMA, capital costs do not contribute a very large proportion of the required selling price of the product. Rather, it is the operating cost and more specifically the raw materials costs which are controlling. At moderate capacities any errors or omissions in the plant capital cost estimation do not alter the selling price significantly. Thus, it is possible to obtain a reasonably reliable estimate of selling price with only a process design.

Figure 6 shows a block diagram of the preliminary process design envisioned for the CMA production. Raw limestone is first crushed in two stages to 1/8" to 1" diameter aggregate particles. The crushed limestone is then mixed with acetic acid and water in a continuous stirred tank reactor. The reactor is sized for a three hour mean residence time and is heated to 70°C by an external steam heating jacket. The reaction product, consisting of the mixture of unspent acetic acid and unreacted limestone and extraneous inert material is then passed through a filtration unit. In the filtration unit unreacted solids are removed and sent to a neutralizing settling pond where they are neutralized by addition of sodium hydroxide. The filtrate containing the product acetates is then sent to a neutralizer reactor where excess acetic acid is neutralized by the addition of sodium hydroxide. The resulting acetate solution is then checked for appropriate pH value and sent to liquid product storage tank. In an optional process addition, it would be possible to evaporate the liquid product to produce a solid calcium or magnesium acetate product.

The major process components are described below:

1. Crusher: Particle size was found to be a significant variable in the reaction efficiency. A two-stage crusher will be utilized to reduce the limestone to 1/8" to 1" diameter aggregate particles.

Crusher Price --- \$14,000.00

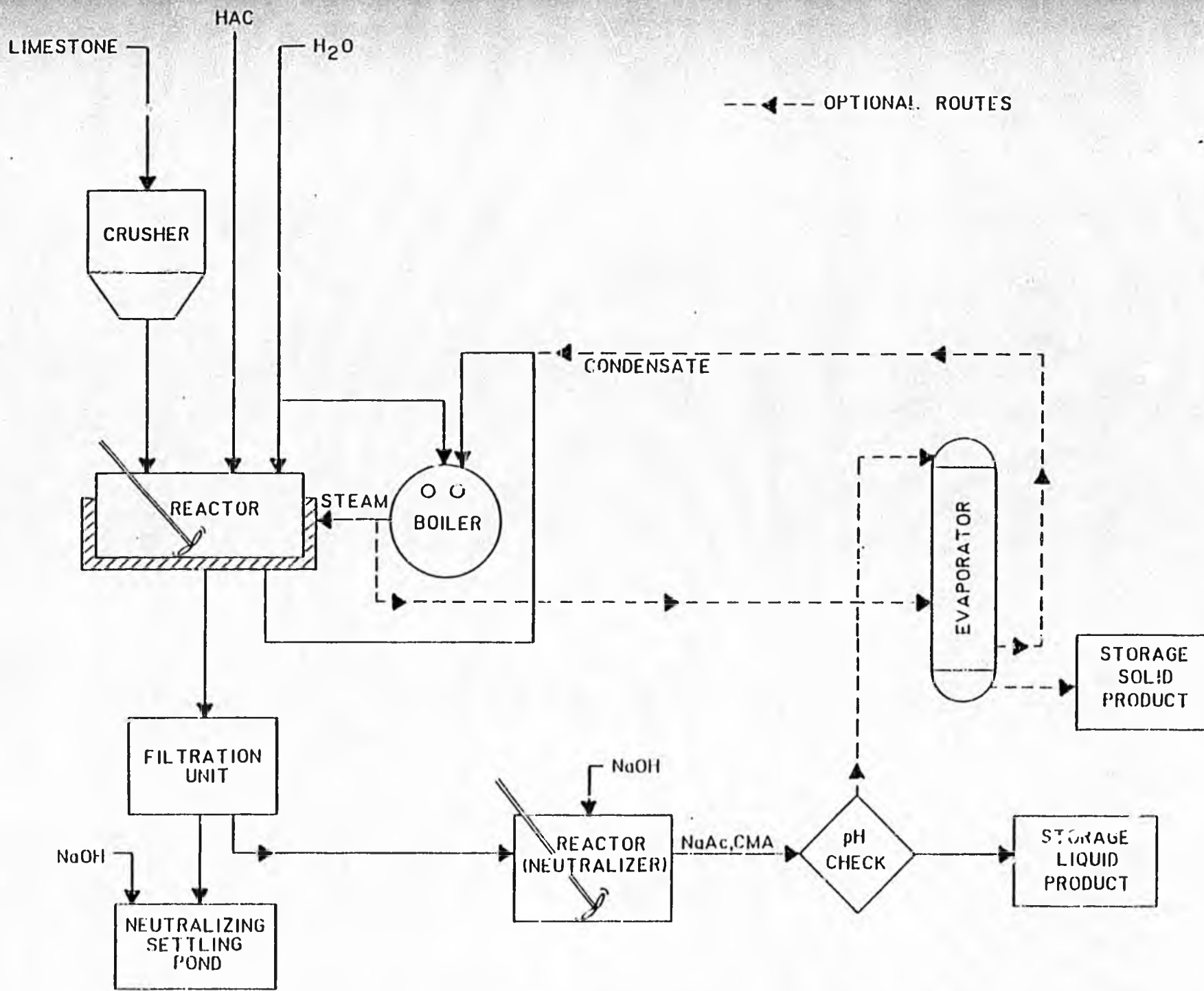


Figure 6. Block Diagram of Conceptual Process Design.

2. Reactors: Two 8,000 gallon reactors are required. The first reactor must be equipped with an external steam heating jacket. Since acetic acid is corrosive to mild carbon steel, the reactors must be constructed of 316 stainless steel.

Reactor Price --- \$110,000.00

3. Boiler: A turnkey boiler package capable of producing 4,000 pounds per hour of 250 psig steam will be required for the reactor jacket heating and space heating. The packaged unit will include a boiler, feed water de-aerator, boiler feed pumps, chemical injection pumps, stack and shop assembly.

Boiler Cost --- \$24,000.00

4. Vessel: A carbon steel storage tank capable of handling three days production (150,000 gallons) is included.

Vessel Cost --- \$70,000.00

5. Filter Press: A 304 stainless steel horizontal-plate filter press is also included.

Filter Press Cost --- \$28,000.00

6. Front End Loader: A front end loader with an 18 cu.ft. capacity is required.

Front End Loader Cost --- \$27,000.00

A summary of the major capital equipment costs for the plant is listed in Table 1. In addition, a 10% contingency has been added on giving a total major capital cost of \$300,000.00 for the CMA plant. It is common practice in capital cost estimating to use multipliers to estimate instrumentation, installation, piping, electrical, and indirect costs for the construction of chemical process plants. (5) Table 2 presents a summary of these additional costs for the CMA plant. This gives a total of \$185,000.00 for the additional costs associated with

TABLE 1

MAJOR CAPITAL EQUIPMENT COSTS

CRUSHER -----	\$ 14,000
REACTORS (2) -----	110,000
PACKAGED BOILER -----	24,000
STORAGE TANKS -----	70,000
FILTER PRESS -----	28,000
FRONT END LOADER -----	27,000
	<hr/>
Subtotal -----	\$273,000
10% Contingency -----	27,000
	<hr/>
TOTAL MAJOR CAPITAL EQUIPMENT -----	\$300,000

TABLE 2

ADDITIONAL PLANT COSTS

INSTRUMENTATION (6% of Major Capital Equipment (MCE)) -----	\$ 18,000
INSTALLATION (30% of MCE) -----	90,000
PIPING (7% of MCE) -----	21,000
ELECTRICAL (5% of MCE) -----	15,000
INDIRECT COSTS (15% of MCE) -----	45,000
	<hr/>
Subtotal -----	\$189,000
MCE -----	300,000
	<hr/>
TOTAL CAPITAL INVESTMENT -----	\$489,000
WORKING CAPITAL (10% of Capital Investment) -----	49,000
	<hr/>
TOTAL INVESTMENT -----	\$538,000

the CMA plant. When combined with the capital equipment estimate, this yields a capital cost estimate of \$489,000.00. Working capital can be estimated roughly as 10% of the total investment. Inclusion of working capital results in a total plant cost of \$538,000.00. This figure represents the total investment which must be recovered through the selling of the CMA product.

On the basis of the preceding design, we have completed an economic analysis of the proposed CMA plant. It should be emphasized that this analysis represents a best case scenario, allowing for continuous operation, and minimal storage facilities. The required selling price of the CMA product can be calculated by the following equation:

$$P = \frac{CF - TD + A(1-T)}{G(1-T)}$$

where;

P = price of solution (\$/gallon)

G = annual production rate (gallons)

D = annual depreciation (straight line method)

A = annual operating cost

T = tax rate (50%)

CF = cash flow using uniform series present worth value with ROR = 20% (rate of return)

This equation has been used to calculate the required selling price (dollars per gallon of solution) required as a function of the price of acetic acid and the production capacity of the plant. A detailed example of the derivation and use of this equation is presented in Appendix 1. Figure 7 shows the required selling price as a function of acetic acid cost for a 10,000 gallon per day plant and a 50,000 gallon per day plant. It is apparent that there is some economy of scale. However, the final plant size will most likely be dictated by market considerations. Finally, Figure 8 presents the selling price for CMA as a function of production rate alone given a fixed cost for acetic acid (\$1.25/gallon). It is apparent that a minimum plant capacity of about 12,000 gallons per day is dictated by the economics. Little additional economy of scale is indicated above the production rate of 30,000 gallons per day. In Figures 7 and 8 the price of CMA has been reported in dollars per ton of solid in solution to allow comparison with current prices of sodium chloride and calcium chloride.

From an analysis of Figures 7 and 8 it is apparent that the cost of acetic

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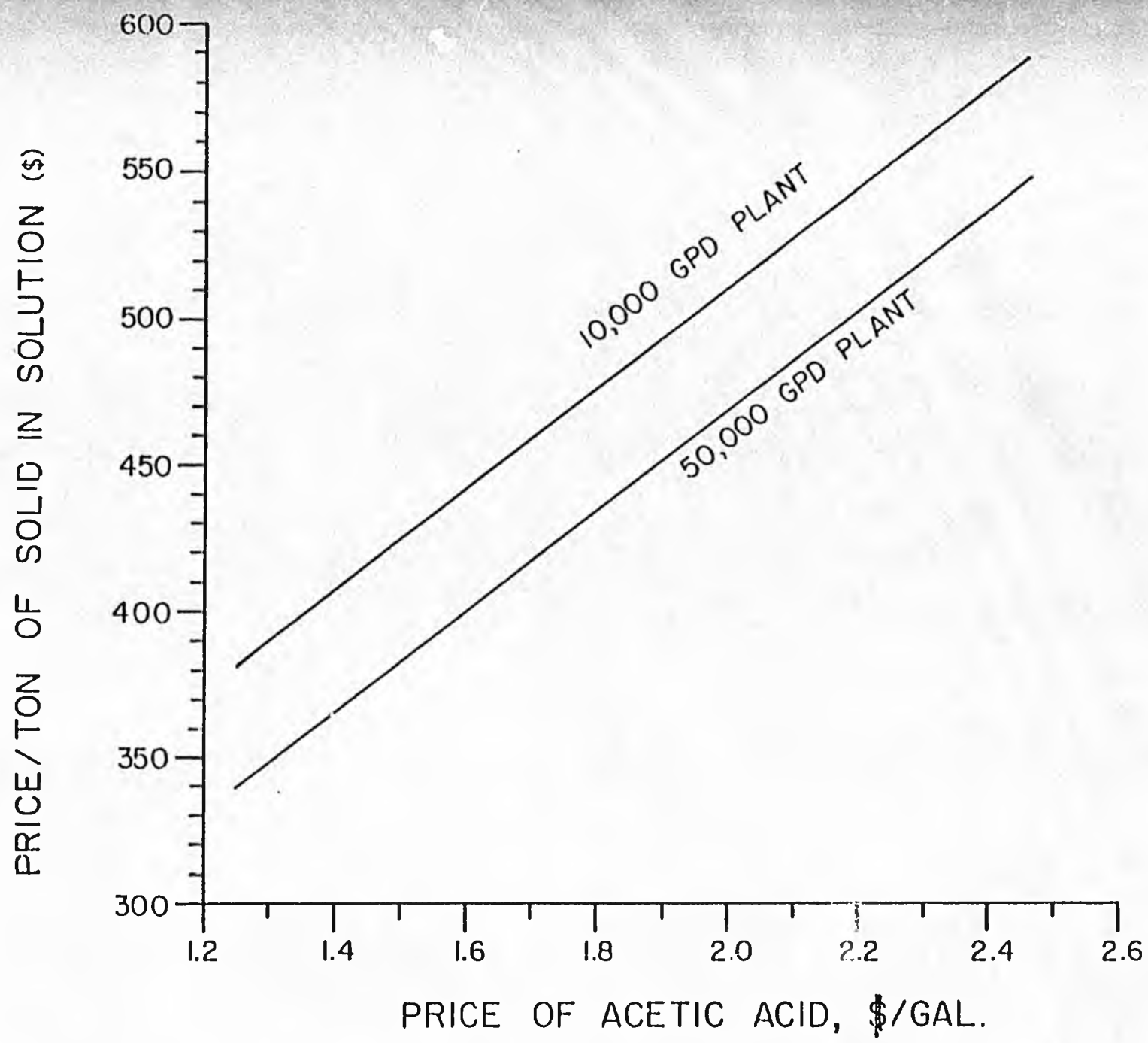


Figure 7. Required Selling Price of CMA for Various Acetic Acid Prices.

(17)

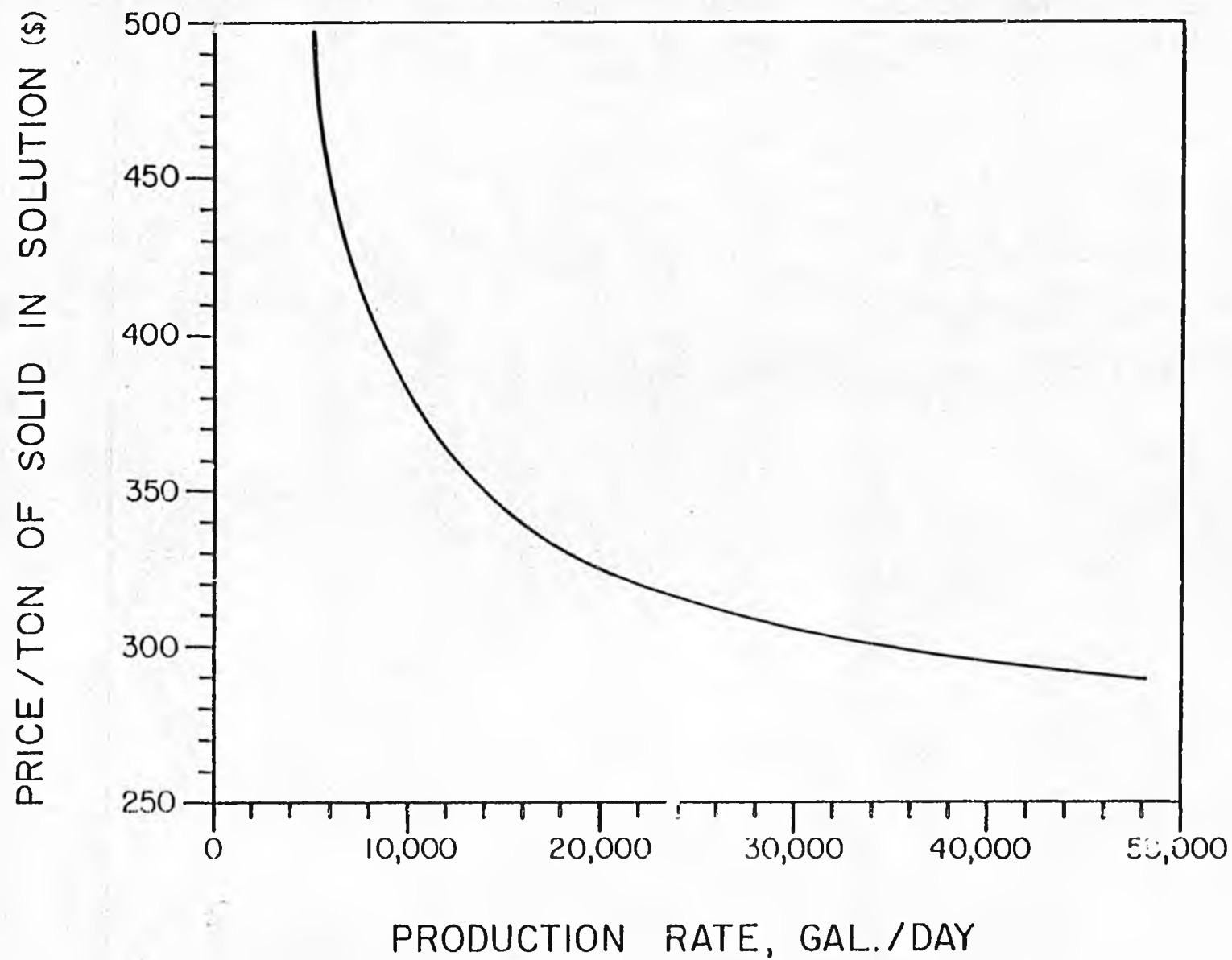


Figure 8. The Effect of Plant Size on the CMA Price. (\$ 1.25/ gallon acid)

acid is the single most important factor in determining the selling price of the CMA product. If acetic acid must be shipped to Alaska from Texas, for example, at a cost of over \$2.5 per gallon, the price of CMA will be in excess of \$500 per ton of solid in solution. However, acetic acid is normally shipped and delivered in purities in excess of 90%. Since in our process acetic acid is diluted with water to roughly 50%, it does not make sense to pay an additional premium for high purity acetic acid. In fact, one of the major costs of producing acetic acid is in the purification stage taking the acid from 50% to purities in excess of 90%. Hence, if a local production facility for acetic acid were located in or near Alaska, it should be possible to purchase dilute acetic acid at a considerable savings, perhaps as low as \$1 per gallon.

Even utilizing imported acetic acid, the price of \$500 per ton of solid CMA may not be excessive. CMA is not corrosive as is calcium chloride and sodium chloride. Hence, there is an inherent cost advantage in using CMA as opposed to chloride salts. Therefore, while CMA may cost more in the initial stage of application, significant cost savings may be realized in the area of maintenance. In addition, since airports cannot use chloride salts, but rely on more expensive methanol or urea, CMA may have a particular advantage.

FREEZING AND EUTECTIC EXPERIMENTS

There were two objectives in this series of experiments: (1) Determination of eutectic diagrams for various solutions of salts; and (2) evaluation of the de-icing performance of the salts under varying atmospheric conditions.

The eutectic diagrams are the result of measurements gathered in the laboratory. A cold testing chamber was used to evaluate freezing properties over a wide spectrum of ambient temperatures (0°C to -75°C). A comprehensive laboratory study involved the use of different de-icing salts (CaAc, MgAc, NaCl and CMA) at different percentage solutions. The results seen in the accompanying figures represent the average readings gathered over three test runs. The ideal de-icing salt is obviously a concentrated solution (27% by wt.) of MgAc. At the lowest temperature tested (-75°C), the solution merely gelled.

Figure 9 contains the eutectic behavior of sodium chloride solutions. Our data agrees with published data. In the case of the acetates, a 28% solution of CaAc was the upper limit (saturation point) while a slightly lower concentration was the saturation limit for MgAc. Figures 10 and 11 contain the eutectic characteristics of CaAc and MgAc respectively. While CaAc did not prove more effective than NaCl, MgAc was decidedly more effective with a eutectic point depression of 75°C. Hence, a mixture of Calcium-Magnesium Acetate (CMA) with a high concentration of MgAc should be the most effective de-icer. A 25% solution of CMA with 70-80% MgAc would be sufficient for the most severe climatic conditions, as it is shown in Figure 12.

The findings of our freezing experiments, in addition to corroborating the de-icing performance of the acetate compounds, have also pointed out a major conclusion. Since the best dolomite deposits contain less than 50% magnesium carbonate, the limit of the CaAc/MgAc ratio is de facto determined.

A re-examination of the findings shown in Figure 12 lead to the observation that a 50% MgAc contribution in a CMA solution is not any more effective than a "pure" calcium acetate solution. For example, a 20% CMA solution containing 50% MgAc has a freezing point of -29°C (Figure 12) while a similar solution of CaAc has a freezing point of -26°C (Figure 10).

Dolomite with magnesium carbonate concentration of greater than 50% is not found in appreciable quantity in Alaska. Since the use of dolomite containing lower concentrations of magnesium carbonate results in a solution which is no more effective than calcium acetate derived from abundant limestones, and since

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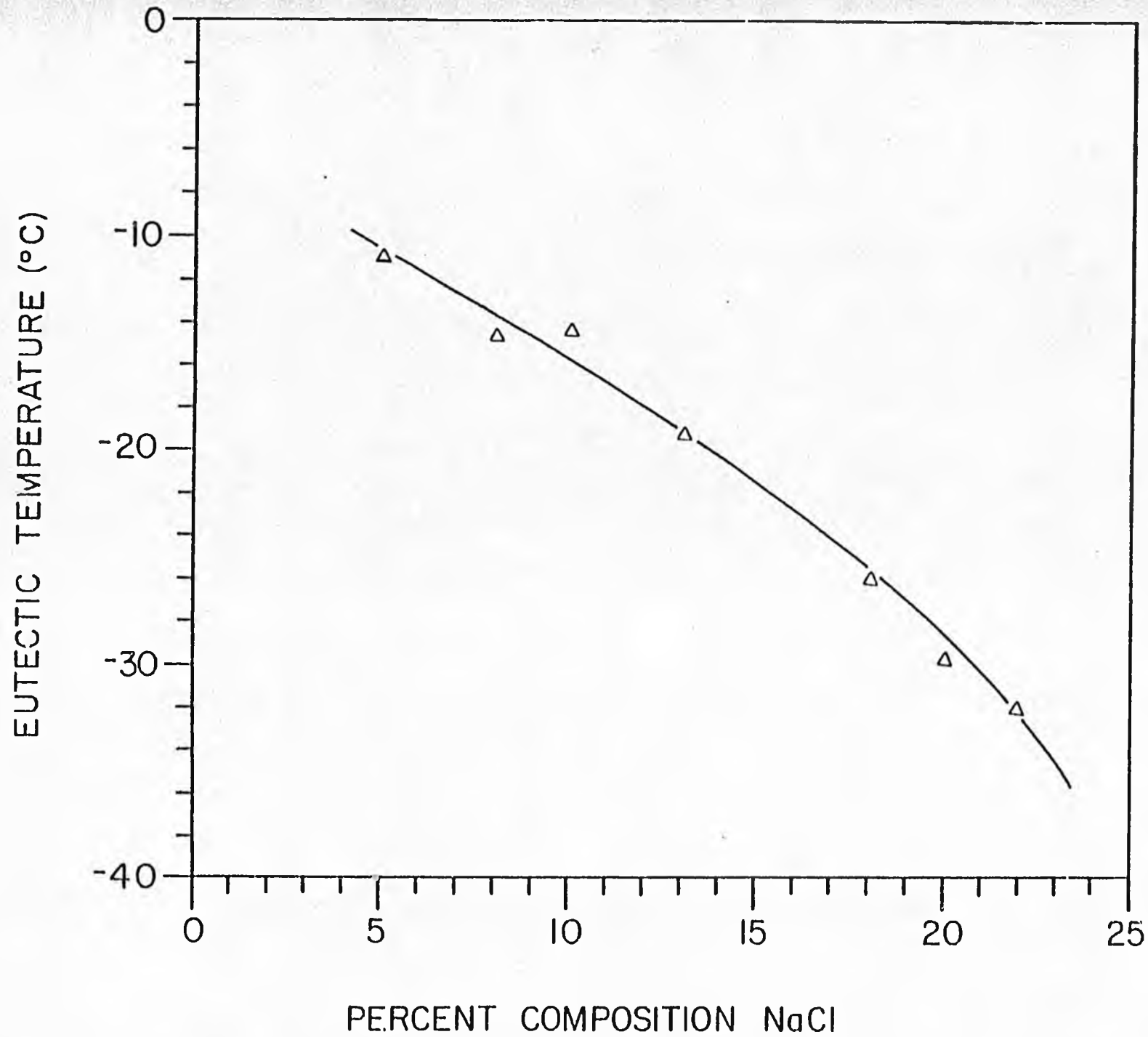


Figure 9. Experimental Determination of the Freezing Temperature of NaCl Solutions.

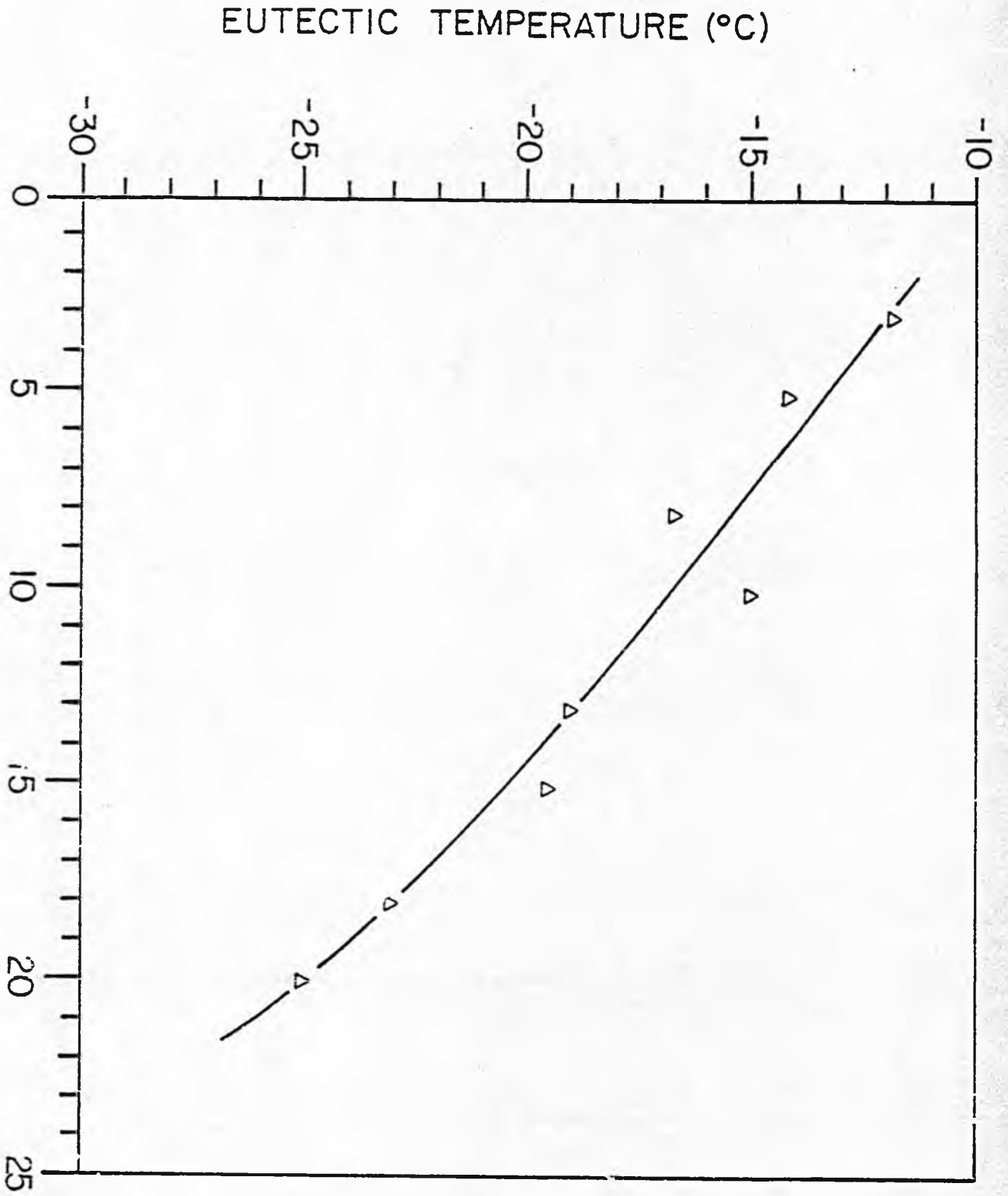


Figure 10. Eutectic γ gram of CaAc Solutions.
% COMPOSITION CaAc

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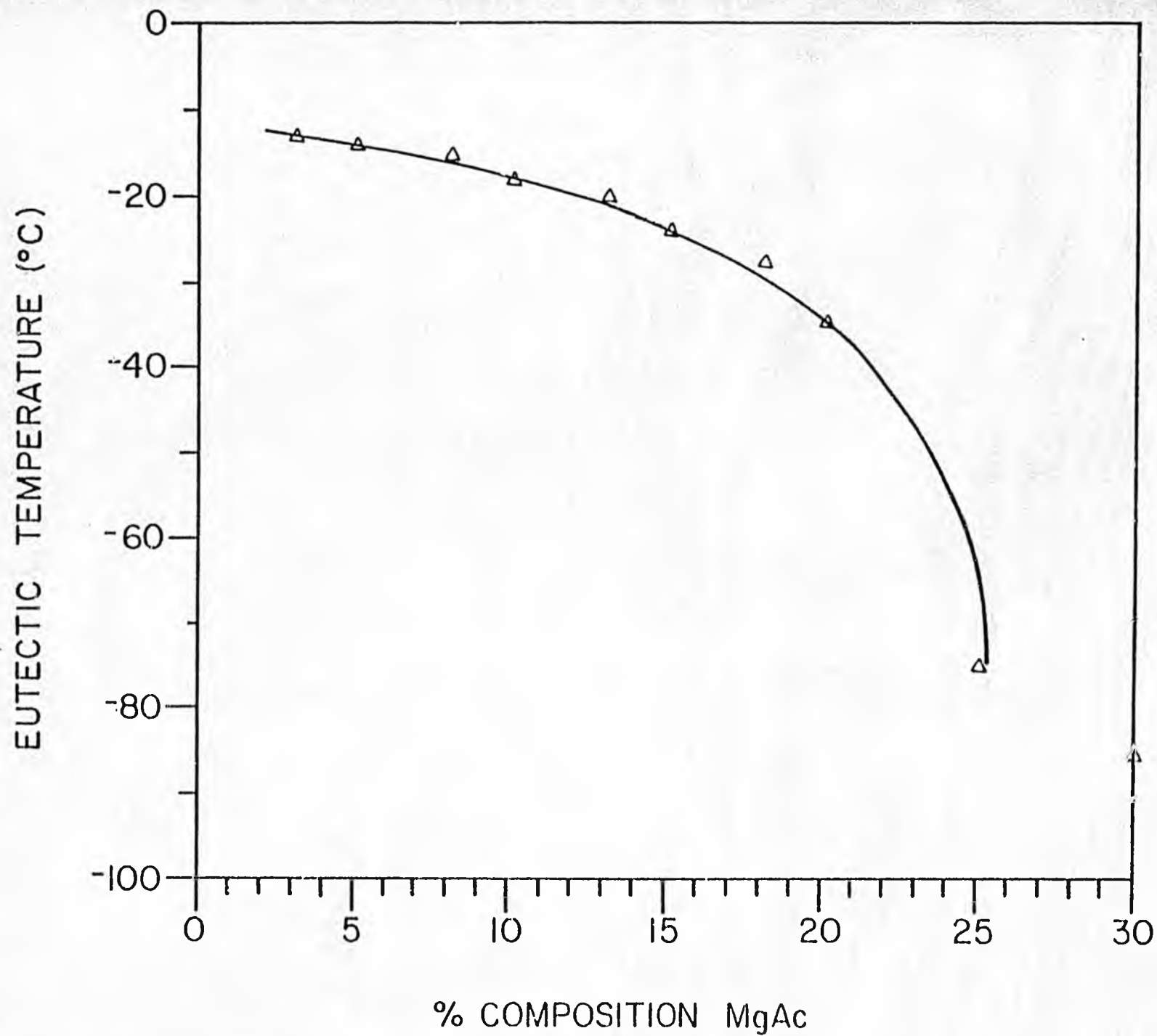


Figure 11. Eutectic Diagram of MgAc Solutions

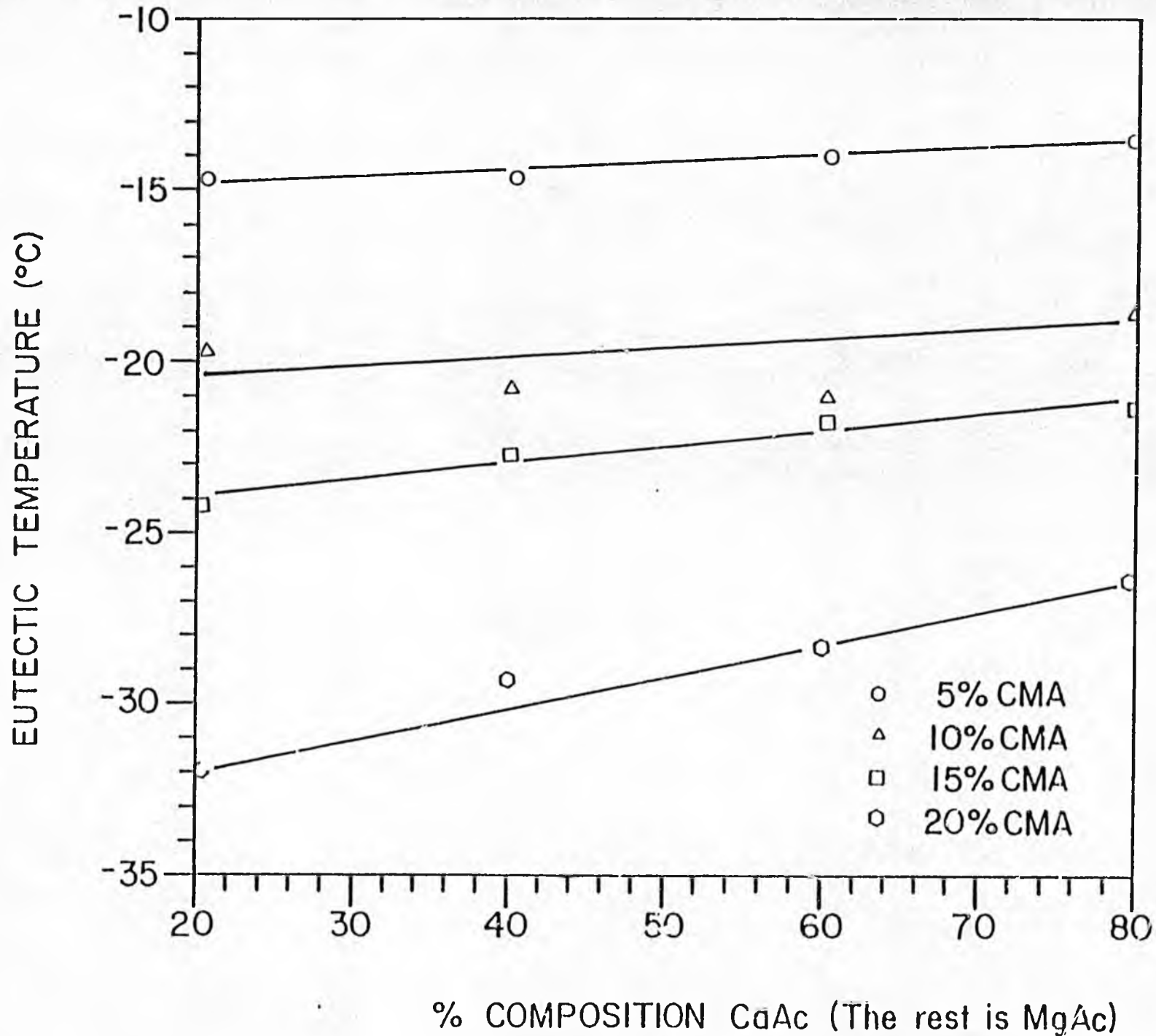


Figure 12. Eutectic Characteristics of Various Compositions of CMA Solutions.

dolomite is more expensive than limestone, it can be concluded that calcium acetate would be the most economic route for the process. To avoid confusion, we continue to use the nomenclature CMA throughout this report. However, it should be realized that we refer to a calcium acetate solution containing only small amounts of magnesium acetate.

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APPENDIX 1

SAMPLE ECONOMIC CALCULATION

The working equation is:

$$P = \frac{CF - TD + A(1-T)}{G(1-T)} \quad (1)$$

where:

P = price of solution (\$/gallon)

G = annual production rate (gallons)

D = annual depreciation (straight line method)

A = annual operating cost

T = tax rate (50%)

CF = cash flow using uniform series present worth value with ROR = 20% (rate of return)

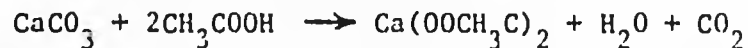
The variables in equation (1) can be evaluated:

G: 365 days x 50,000 GPD = 18.25×10^6 gallons

D: The depreciation is 1/10 of the capital investment (i.e., \$53,800).

A: The operating costs can be divided into the costs of raw materials and the fixed costs such as labor, instrumentation and maintenance.

To calculate the costs of raw materials a stoichiometric balance of the general reaction is indicated:



In order to produce 50,000 gallons of solution per day there is a need for:

48 tons of CaCO_3 (at \$60/ton)

12,700 gallons of Acetic Acid (at e.g. \$2.00/gal.)

53,000 gallons of water (at \$2.25/1000 gal)*

Then A = \$10,800,000 which includes \$10,400,000 for materials and \$400,000 for fixed operating costs, instrumentation, labor and maintenance.

T: The tax rate taken at 50%

* Calculated using density of solution of 87.4 lbm/ft^3 , 80% reaction completion, 97.14% pure Alaskan limestone, and a saturated acetate solution (25% calcium acetate, 75% water).

CF: Is the amount of money required to recover a capital investment using a certain rate of return. In this case a 20% ROR would require a uniform series present worth factor of .235.

$$\text{Hence, } CF = \$538,000 \times .235 = \$129,000$$

Using equation (1) the price of solution is \$0.60/gal which can be converted to \$420/ton of solid in a saturated CMA solution (25%).

Derivation of Equation (1)

Equation (1) is essentially a simple rearrangement of the cash flow equation:

$$CF = \text{Net Income} - \text{Tax} \quad (2)$$

Where:

$$\text{Net Income} = PG - A \quad (3)$$

and

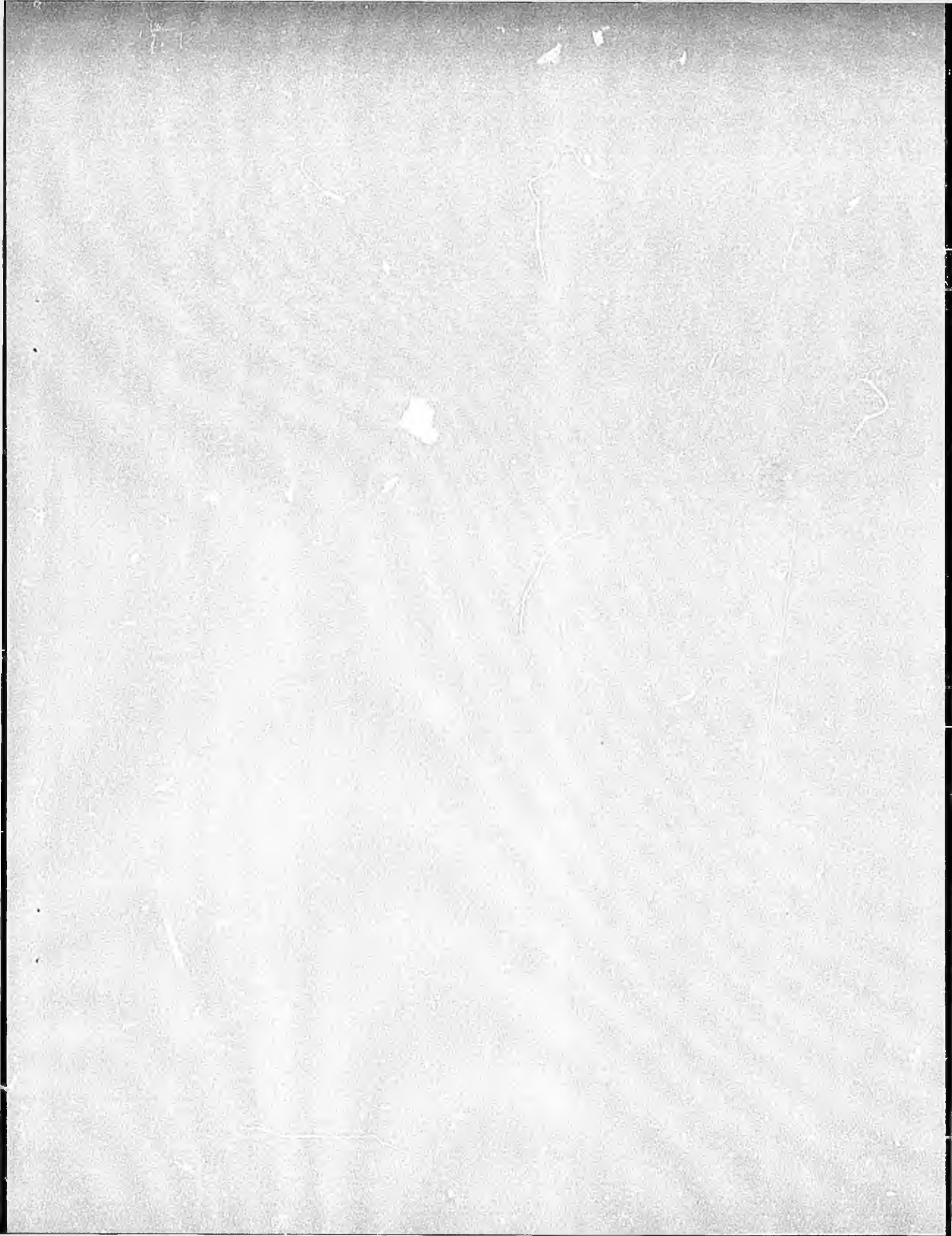
$$\text{Tax} = (PG - A - D)T \quad (4)$$

Combining Terms:

$$CF = (PG - A) - (PG - A - D)T \quad (5)$$

Rearranging

$$P = \frac{CF - TD + A(1-T)}{G(1-T)} \quad (6)$$



CATHODIC PROTECTION OF CONCRETE BRIDGE DECKS IN ALASKA

(Northern Engineer Article)

Matt Reeland

TO BE PUBLISHED IN THE NORTHERN ENGINEER
SPRING 03

Reinforced concrete is commonly used for bridge decks. In recent years an alarming increase in delamination and spalling of the concrete cover of these decks has been observed (see figure 1). This deterioration not only makes travel over these bridges rougher, but can eventually lead to structural damage to the bridge. A great deal of effort has been made to understand the causes of this damage and prevent it, since deck repairs or replacement is expensive.

The principal cause of the delamination and spalling of bridge deck concrete is galvanic corrosion of the reinforcing steel, although this was not widely recognized for many years.¹ One means of preventing this damage is to install cathodic protection systems on the bridge, which can stop this corrosion. (Move last sentence of previous up to here)

Two of these systems have been recently installed in Alaska. The first was placed on the upper vehicle ramp at the Anchorage International Airport domestic terminal building; it began operating in December 1981. The second was installed on the Wendell Street Bridge in Fairbanks and began operating in October 1982. A third system is planned for the Cushman Street Bridge in Fairbanks; it is scheduled to be installed next summer.

The corrosion of rebar in bridge decks is similar to what occurs in many types of galvanic cells, such as the lead-acid automobile battery shown schematically in Figure 2. In a bridge deck, different parts of the reinforcing steel become anodic or cathodic (see Figure 3) due to differences in residual stresses and impurities in the steel, cracks, moisture content, and aeration of the concrete, and other factors.^{2,3}

The concrete cover, which normally would protect steel from corrosion due to its alkalinity, becomes an effective electrolyte when contaminated by chloride ions from de-icing salts used on the bridge. Corrosion products (principally rust) build up at the anodic areas of the rebars, and because they occupy a greater volume than the original steel, they exert pressure on the concrete, which eventually cracks. Thermal expansion, water freezing in the cracks, and other factors can then extend the cracking, separating the cover layer of concrete from the rest of the deck (delamination). The delaminated concrete can eventually spall off, leaving

the top mat of the reinforcing steel exposed.

This problem has grown worse in recent years due to the increased use of de-icing salts on highways and bridges. One means of preventing this damage would be to avoid the use of salts by substituting other materials such as sand, fly ash, or calcium magnesium acetate (CMA). Another means is to place an impermeable layer between the surface of the bridge deck and the reinforcing steel. In this way chloride penetration to the level of the steel is prevented or at least retarded, and the corrosion will not occur (or will progress much more slowly). Several methods have been used to retard or halt chloride penetration to the level of the rebars, such as the specification of dense, low-slump concrete, greater cover depth of concrete, polymer-modified concrete, or the application of waterproof membranes. Galvanized and epoxy-coated rebar has also been used. Some form of protection is required on all new concrete bridge decks built by the state of Alaska.

None of these methods will stop corrosion on existing chloride-contaminated decks, however. The removal and replacement of all contaminated concrete or the entire deck is possible, but very expensive. Short of this, the only method known that can completely halt ongoing corrosion is cathodic protection.

Cathodic protection has long been used for corrosion protection of buried and submerged structures such as pipelines, docks, and ships, and for the protection of elevated water and fuel tanks. Cathodic protection of bridge decks, however, is relatively new, and designs are still somewhat experimental.

The principle behind cathodic protection is to make all of the steel (or other material) to be protected cathodic with respect to another material placed in the electrolyte to which it is electrically connected. This can be done by connecting the steel to a less noble metal, such as zinc or magnesium. The less noble metal ^{thus} has becomes the anode in a galvanic cell, and it, rather than the steel, corrodes (see Figure 4). This is known as "sacrificial-anode" cathodic protection. The anode material eventually corrodes completely and must be replaced.

Another method is to connect the steel to be protected to another material

placed in the electrolyte and force the steel to become cathodic by using an external power source. This is known as "impressed-current" cathodic protection (see Figure 5). Corrosion of the anode in such a system will be negligible if the correct choice of material is made, thus eliminating the need for anode replacement.

Impressed-current systems have usually been chosen for use on bridge decks for two principal reasons. The first is that the amount of protection can be easily varied by altering the voltage and current from the power source. In a sacrificial-anode system, the voltage is determined by the relative oxidation potentials of the anode and cathode materials, and the current is determined by the amount and location of the anodic material; once such a system is built, neither can be changed. The second advantage of impressed-current systems is that the anodes do not need replacement. Since the anodes must be placed in the electrolyte (i.e. the bridge deck concrete) replacing them would be difficult and expensive.

Current flow between an anode and a cathode will be greatest where the electrical resistance between them is the least. Thus if an anode is placed very close to any one part of the steel to be protected, nearly all the current will flow to that part of the steel, rather than take longer, less conductive paths to more remote locations on the structure. The more remote parts may then receive insufficient current to protect them from corrosion. Moreover, the areas receiving large currents may be "over protected" which has been observed to weaken the bond between rebar and concrete. This may be due to an increase of sodium and potassium ions near the cathode (rebar) or because of the release of hydrogen there.^{2,4} By moving the anode farther away from the structure, the distances between the anode and different parts of the structure will become more nearly equal and, if the electrolyte is homogeneous, so will the electrical resistance and current density.

On buried structures where the soil is the electrolyte, anodes can easily be placed at a location relatively far from the structure. It may be possible, for example, to completely protect a buried cylindrical tank by installing three anodes, 120° away from each other, around the tank and perhaps half the tank's diameter away from it. On a bridge deck, however, the concrete is the electrolyte, and the distance between the anodes and the cathodes (rebars) can never be more than a few inches.

One means of achieving even current densities over bridge decks is to place anodes in a highly conductive layer of coke breeze and asphalt placed over the entire deck. Care must be taken to ensure that the

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conductive layer does not contact any bridge steel, short-circuiting the system. A wearing ^{course} ~~cause~~ of conventional paving material is needed since the coke breeze mixture is relatively weak.² Relatively even protection can be given to the top layers of rebar this way, although there is little protection of lower rebar. Chloride concentrations decrease with depth, however, so the lower rebar rarely if ever requires protection.

A disadvantage of this system is that the two overlay layers (typically 5" thick) greatly increase the dead load on the bridge. Another method of anode placement has been developed which requires less overlay thickness. In this method, a series of parallel grooves are cut in the bridge deck, and anodic wires are grouted into them. The anodes themselves are thus widely distributed over the deck, and the conductive layer is eliminated, although a wearing course is still required. The cathodic protection systems recently installed in Alaska have been of this type.

Repairs to these bridges were needed before the systems were installed; this work is shown in Figure 1, which illustrates the seriousness of the problem. Pitting found on corroded rebar is shown in Figure 6. All unsound concrete was removed, the remaining concrete was chipped away from any partially exposed rebar, and the concrete and exposed rebar were cleaned. The decks were then patched with latex-modified concrete.

After the deck repair, the cathodic protection systems could be installed. Anode wires for the systems are made of platinum coated niobium with copper cores. These were grouted in grooves cut in the deck with a mixture of coke breeze and polyvinyl ester resin. Figure 7 shows the Wendell Street Bridge after this was completed and before the final wearing course of concrete was placed.

Electric power to energize the system comes from a control box where AC line power is first transformed to the desired voltage and then rectified to DC. The positive terminal is connected to the anode wires via header cables imbedded in the deck; the negative terminal is connected to the reinforcing steel itself.

The amount of polarization (voltage) impressed on the reinforcing steel must be kept within a certain range. A minimum negative voltage of about 850 mV, compared to a copper-copper sulfate half cell, is desired to ensure protection of the steel; a maximum of (negative) 1100 mV is desired to avoid "overprotection".⁴ Reference cells were imbedded in the decks in order to monitor the steel polarization; in the Wendell Street system these are made of molybdenum/molybdenum oxide while at the Anchorage Airport they are zinc. Automatic voltage control is provided by a microprocessor in the control box, which monitors the voltage readings on the reference cells and adjusts the current flow as needed. The amount of power required by the systems is quite small; the larger (Wendell Street Bridge) system is expected to stabilize at about 60 watts.⁵

These systems should stop corrosion of the reinforcing steel in these bridge decks, avoiding the need for further expensive deck repairs. Corrosion probes have been installed in the decks to enable detection of any further corrosion, should it occur. The performance of these systems is being monitored by the vendor, Norton Corrosion Ltd., Inc. of Woodinville, Washington. The data gathered should result in a better understanding of both the physical and economic effectiveness of these systems, and may lead to improved designs in the future. The Federal Highway Administration has estimated that the use of these systems may be able to save billions of dollars nationwide.⁶

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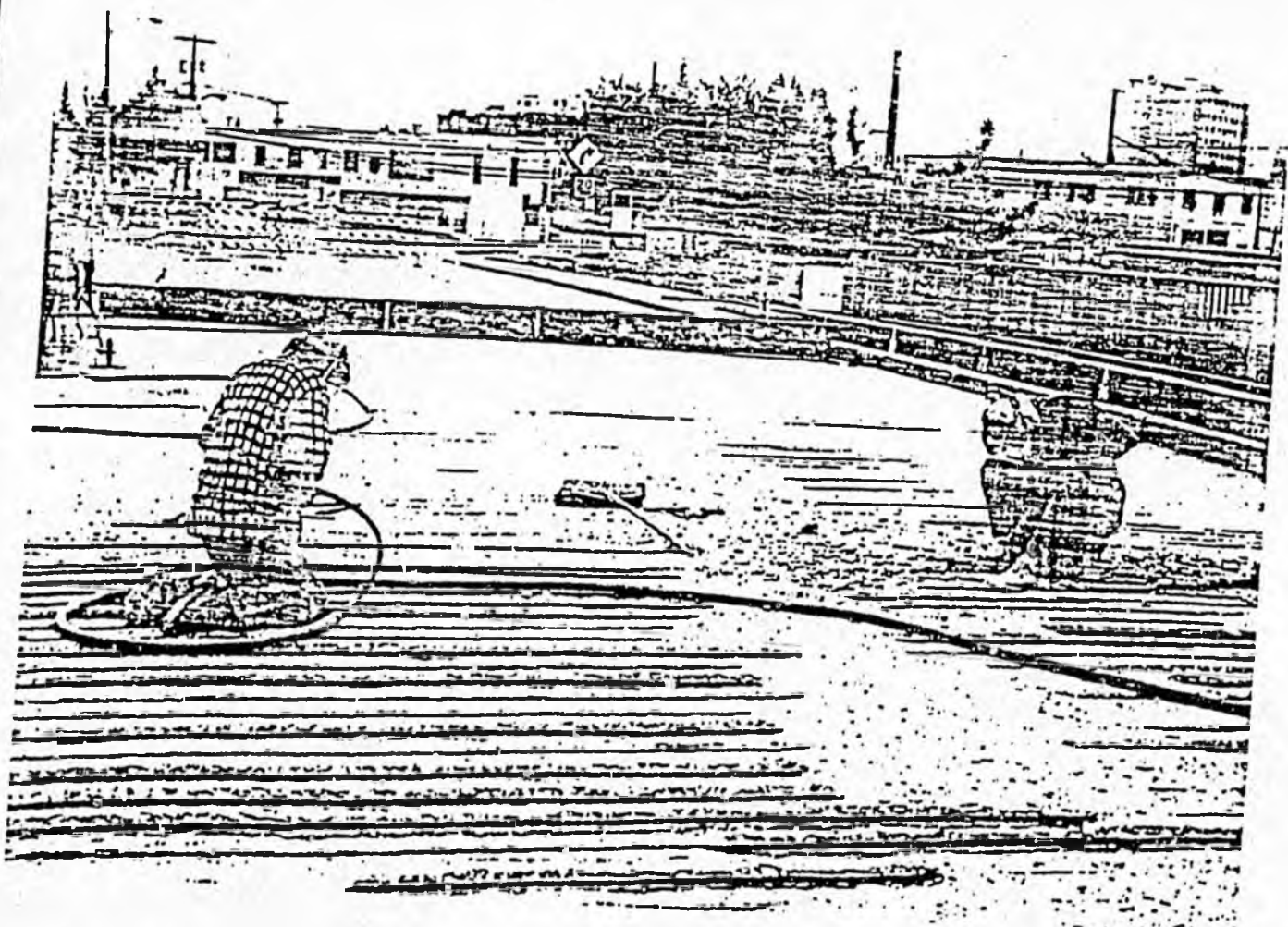


photo Steve Powers

FIGURE 1
Removing delaminated concrete, Wendell St. Bridge, Fairbanks

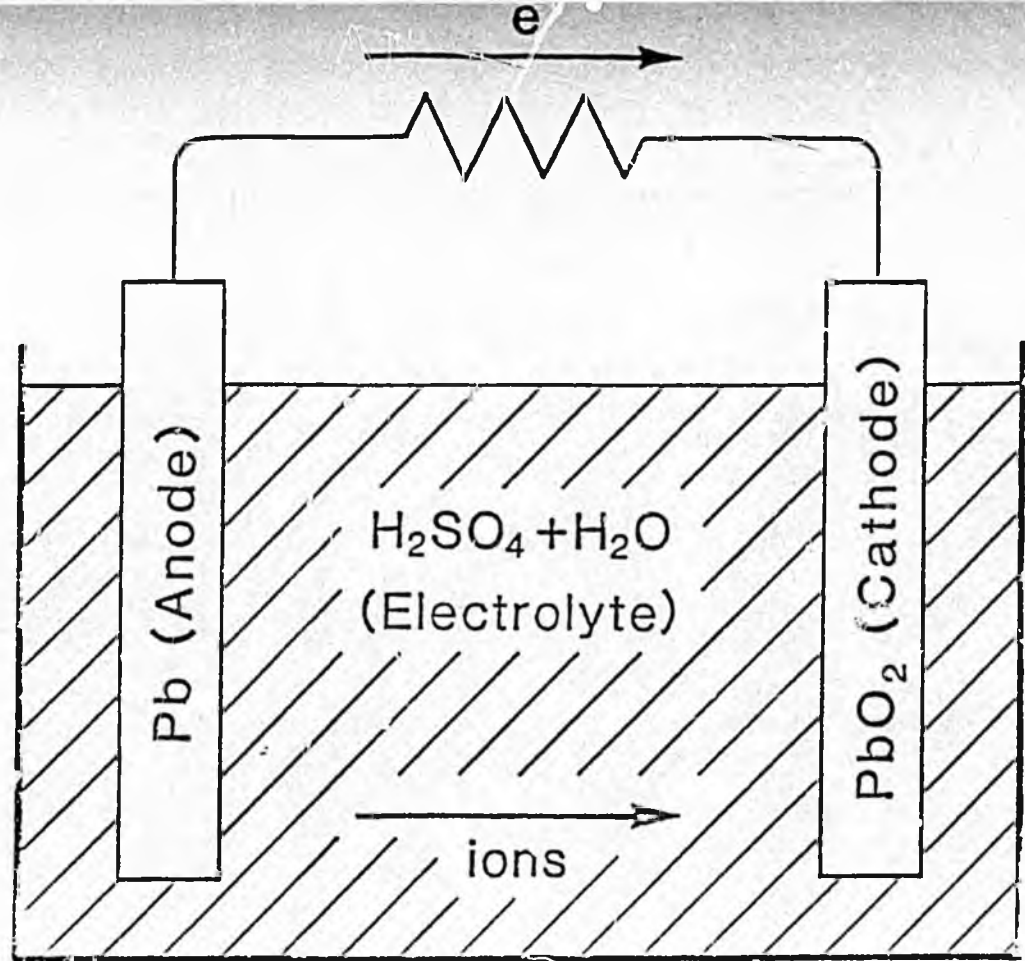


Figure 2: Lead-Acid Corrosion Cell

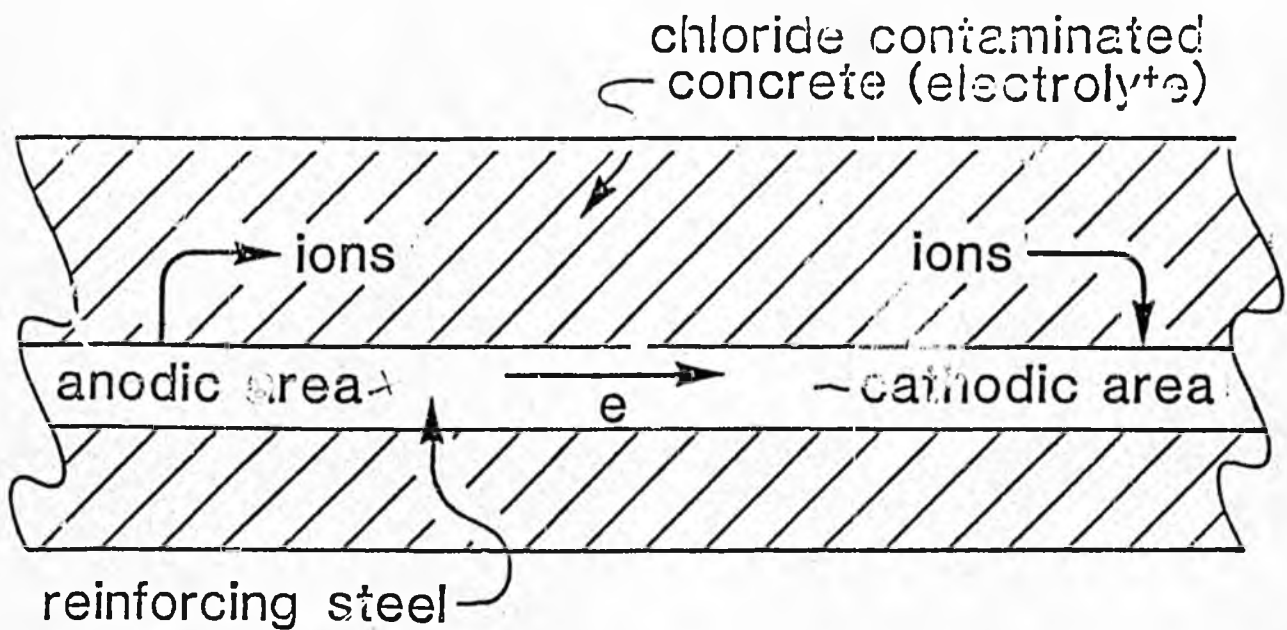


Figure 3: Bridge Deck Corrosion Cell

The use of cathodic protection grew rapidly with the development, in the mid-1930's, of a new source of direct current, known as the copper oxide rectifier. These earliest cathodic-protection applications were very successful; and it was apparent that the cathodic-protection method of corrosion control gave the following advantages:

1. When properly applied, corrosion is completely stopped.
2. The effectiveness of cathodic protection in arresting corrosion can be measured by a simple, nondestructive electrical measurement.
3. The cost of applying cathodic protection is a fraction of the replacement cost of the threatened structure, and cathodic protection is clearly the least expensive means of providing long-term, maintenance-free service life for metal structures in corrosive environments.

Shortly after the end of World War II, corrosion problems developed with large-diameter, prestressed-reinforced-concrete water pipelines in Europe, Israel, and North Africa (13, 14, 15, 16). During the 10-year period between 1945 and 1955, the use of cathodic protection to prevent such corrosion became widespread. Other cathodic-protection applications for steel in concrete include underground portions of concrete water-storage tanks, steel reinforcement and liner plate of concrete nuclear-reactor containment vessels, and concrete-coated piling; however, the use of cathodic protection in these applications has not reached major proportions.

How Cathodic Protection is Applied

The cathodic protection of metal is applied by causing a flow of current from any source to the metal (5). Two methods are generally used to transmit the protective current (17, 18, 19). In one, the threatened structure is made the cathode of an electrolytic corrosion cell with a more active metal as an anode. In the second, the threatened structure is made to react as a cathode by using an external power source.

Electrolytic-Cell Method (Sacrificial-Anode Systems)

To obtain cathodic protection by the electrolytic-cell method, a metal electrode that is anodic to the metal of the structure is connected to the structure by a metallic conductor and is placed in the electrolyte with the structure, as shown in Figure A-2. In this arrangement, the structure and the anode operate as a bimetallic corrosion cell. The anode electrode is sacrificed; thus, the name "sacrificial-anode system." In effect, the corrosion is transferred from the structure to the anode, which is expendable and may be easily replaced. The driving potential for the current is the natural potential difference between the metal of the structure and the anode. Some typical potential relationships are shown in the limited tabulation of the practical galvanic series of metals given as follows (19):

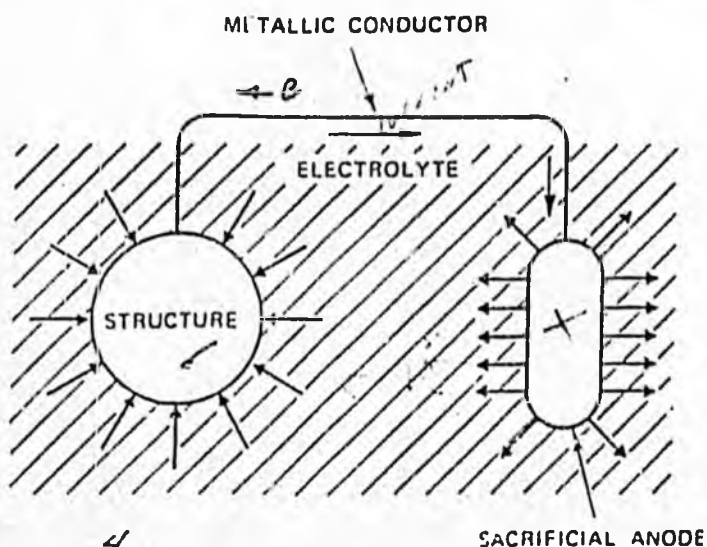
Metal	Typical Potential, volts*
Magnesium alloy (6% Al, 3% Zn, and 0.15% Mn)	-1.60
Zinc	-1.1
Aluminum alloy (5% Zn)	-1.05
Mild steel (rusted)	-0.2 to -0.5
Mild steel in concrete	-0.2
Copper	-0.2

* Typical potential normally observed in neutral soils and water, measured to the copper sulfate reference.

From this listing, it is obvious that the magnesium offers cathodic protection to any of the other metals listed whereas copper does not. In practice, alloys of magnesium, aluminum, and zinc are used as sacrificial anodes, although only magnesium and zinc are generally used for the cathodic protection of steel reinforcement in concrete.

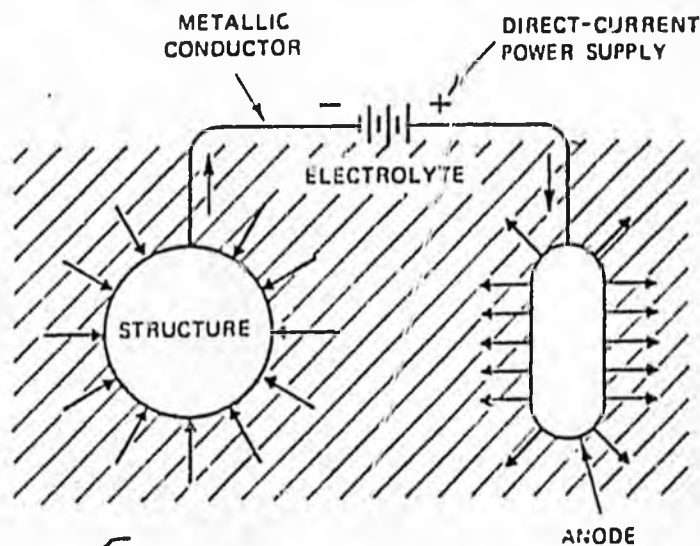
External-Power Approach (Impressed-Current Systems)

The external-power approach to cathodic protection is shown in Figure A-3. This system operates in the same



4
Figure A-2. Sacrificial-anode cathodic protection.

Source: Reference 1



5
Figure A-3. Impressed-current cathodic protection.

Source: Reference 4

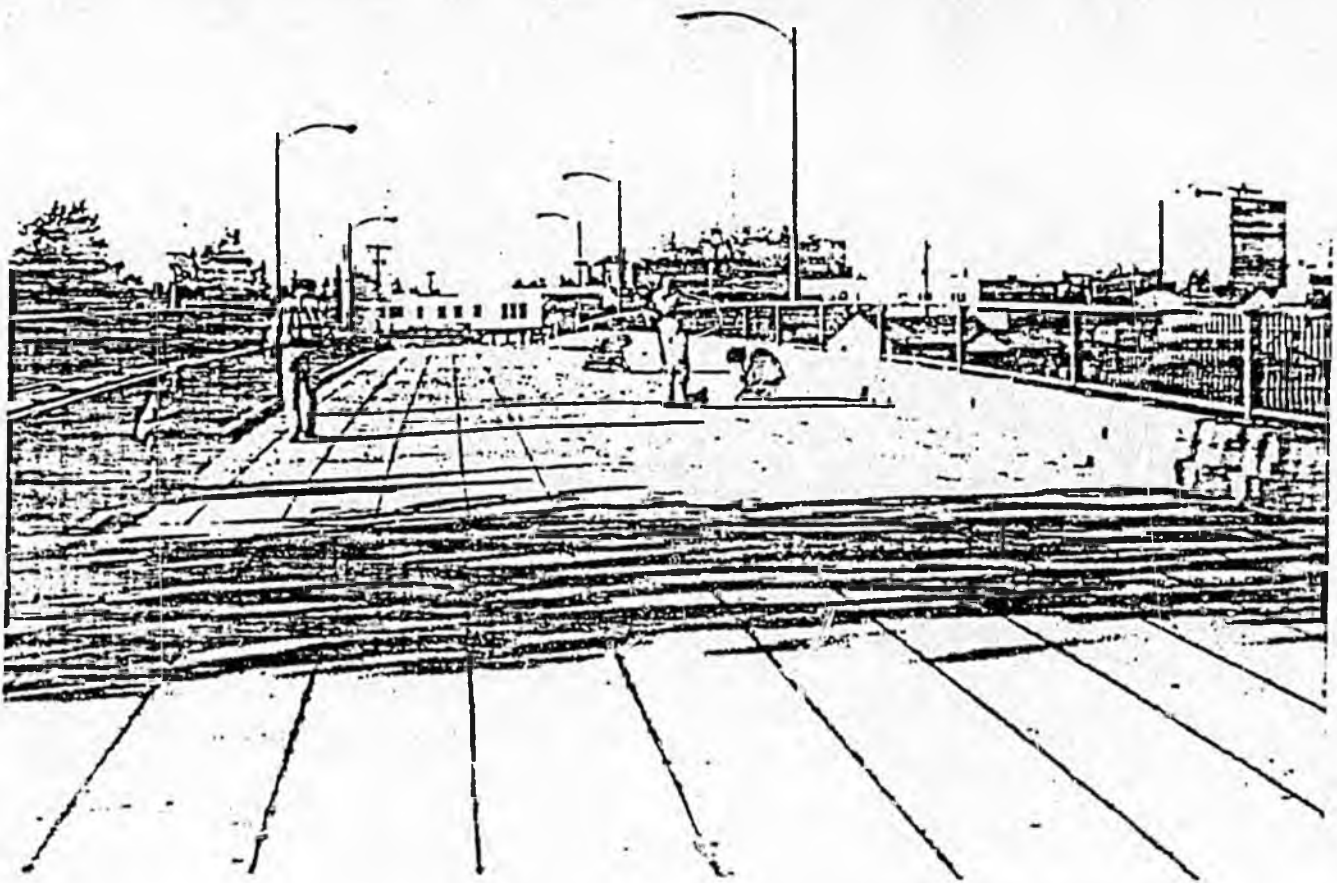
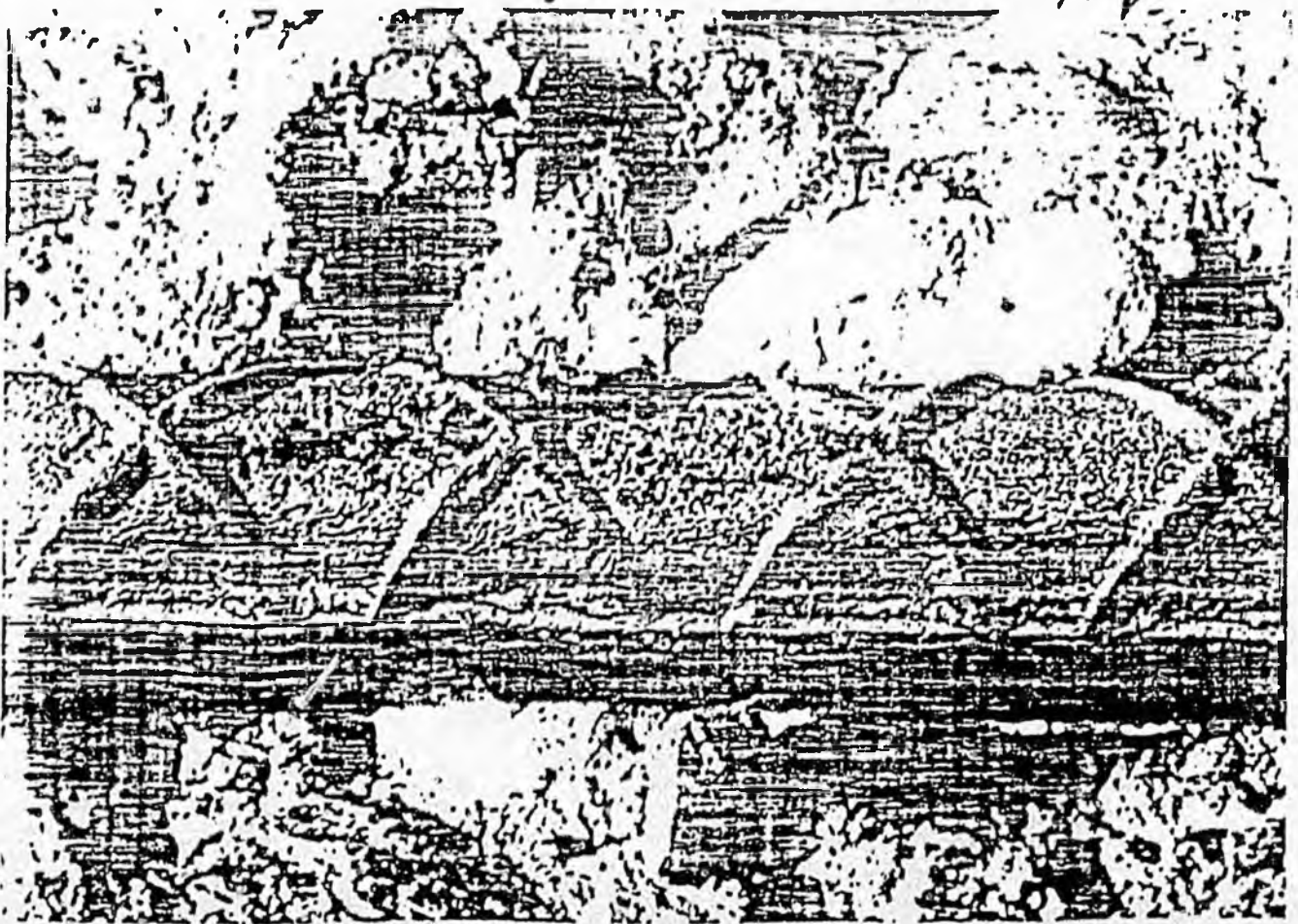


Figure 7: Anodes grouted into deck (Wendell St. Bridge) ↗

Figure 6: Corrosion pitting on rebar (Wendell St. Bridge) ↘

photo credit
Steve Hines



1/13/83

I. INTRODUCTION

We first learned about the CMA project at the TRB meeting in January 1980. We heard the presentation of the work by Dr. Dunn, Dr. Stanley and Dr. Scheck. Due to budgetary restraints we only started actively pursuing the idea at the beginning of 1982 when our proposal for a CMA research project was approved.

It has been known that there are three processes to produce CMA.

- (1) Quick lime reacting with acetic acid.
- (2) Hydrated lime (Calcium Hydroxide and Magnesium Hydroxide) reacting with acetic acid.
- (3) Limestone $\text{CaCO}_3 + \text{MgCO}_3$ (Calcium Carbonate and Magnesium Carbonate) reacting with acetic acid.

Theoretically all three will do, but in reality (1) is better than (2) which is better than (3).

Since the beginning of our project, our emphasis has been:

- (1) Use local resources and waste products.
- (2) Use a method that requires a small amount of energy.
- (3) Use the method that is most cost effective.

In our search for sources of resources and waste products, we found that Lime Products Corp. in Union, Maine had an interest in this project. They produce high magnesium limestone. They don't have the capability of producing either quick

lime or hydrated lime from limestone, since that production requires high temperatures. The limestone, coarse and fine are shown in Slides 1 and 2.

We also located some waste acetic acid from W. H. Shurtleff Co. The acetic acid had to be diluted before it can react with limestone. From the lab experiment we knew that the reaction will not be complete. That is, some limestone will be left over. But the leftover limestone can be used as abrasive agent, therefore we decided to use a coarse grade limestone.

Acetic acid is used at a 10% solution - another source is vinegar, and Maine is rich with apple orchards which could provide the juice to make vinegar.

II. SMALL SCALE TRIAL BATCH

June 24, 1982 mixed 10 lbs. of coarse dolomitic limestone with 10 gal. of 10% acetic acid in a small concrete mixer for 10 minutes.

This was repeated five times, the residue and liquid poured into a container for evaporation.

July 16, 1982 obtained 40 lb. of stone - CMA mixture.

Slides 3 to 5

The final product is shown on Slide 6.

When this mixture is dissolved in water, the solids filtered out, the filtrate dried, a white powder as shown in Slide 7 remains.

III. LARGE SCALE TRIAL BATCHES

Slides 8 to 12

On July 30, 1982 the contractor mixed 100 gal. HAC (diluted due to false meter indication to 2%) with 4000 lbs. coarse limestone in a concrete mixer. The liquid and limestone residue were placed in a basin (40' x 10').

By the end of October, 1982, this "coarse" batch only contained few "puddles" of liquid pH = 6.5. The liquid was transferred to a drum, the "wet" solid was transferred to other drums (five-55 gal. drums) and stored. These will be dried and analyzed in the near future. The total weight of wet material is 3320 lbs.

Slides 13 to 17

On August 11, 1982, another mixture was made. It consisted of 200 gal. HAC (diluted to 10%, 2000 gal.) and 8000 lbs. fine limestone mixed in a concrete mixer, placed in a drying basin (20' x 10').

By the end of October, 1982, the solution began to congeal (Slide 18).

Slides 19 to 21

On November 30, 1982 the solution in the "fine" batch was transferred into four-55 gal. drums. At the same time quick lime was added and the mixture was stirred. The pH of the mixtures were between 11.5 and 12. The drums were then