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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:

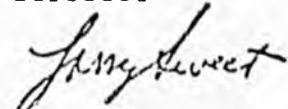
Per your request, the following is some information regarding efforts to find a substitute for the common salt that has attained widespread use in this country for deicing highways. There has been considerable research on the problem of corrosion associated with common salt and Calcium Magnesium Acetate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

MEMORANDUM

State of Alaska
Department of Transportation & Public Facilities

TO: Lynn Harnisch
Staff Engineer
Planning and Programming
Interior Region

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

DATE: October 14, 1982

FILE NO:

TELEPHONE NO: 479-4231

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.

RRV:LLS/bdc

cc: Steve Sisk
John Horn
John Martin
Jon Widdis

STATE OF ALASKA

JAY S. HAMMOND, GOVERNOR

DEPARTMENT OF TRANSPORTATION AND PUBLIC FACILITIES

OFFICE OF THE COMMISSIONER

POUCH Z
JUNEAU, ALASKA 99811
(TELEX 45-3281)
(907) 465-3900

June 4, 1982

Re: Ice Control Methods
and Materials

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

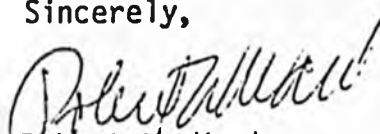
Dear Mr. Bundy:

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,

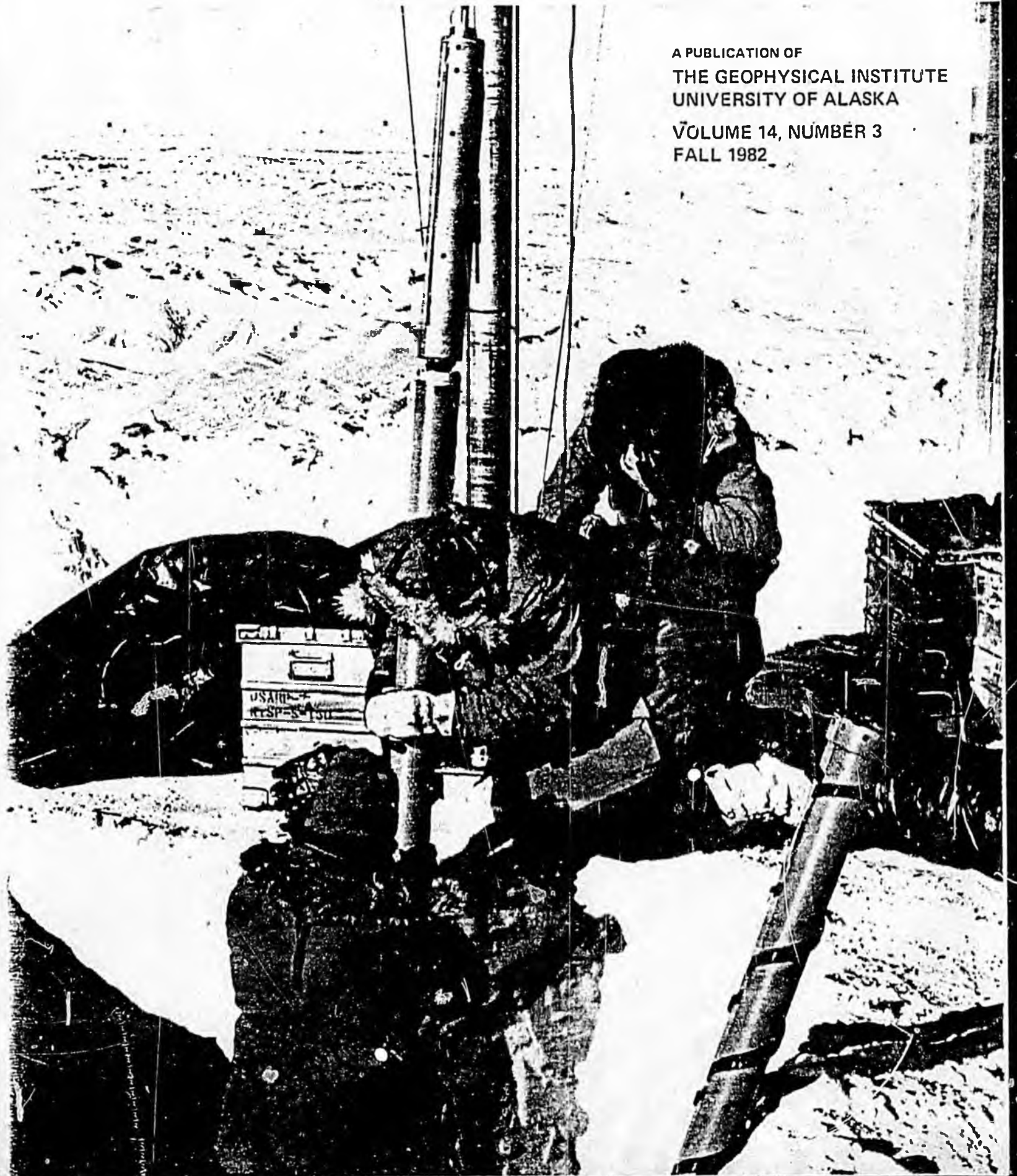

Robert W. Ward
Commissioner

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

THE NORTHERN ENGINEER

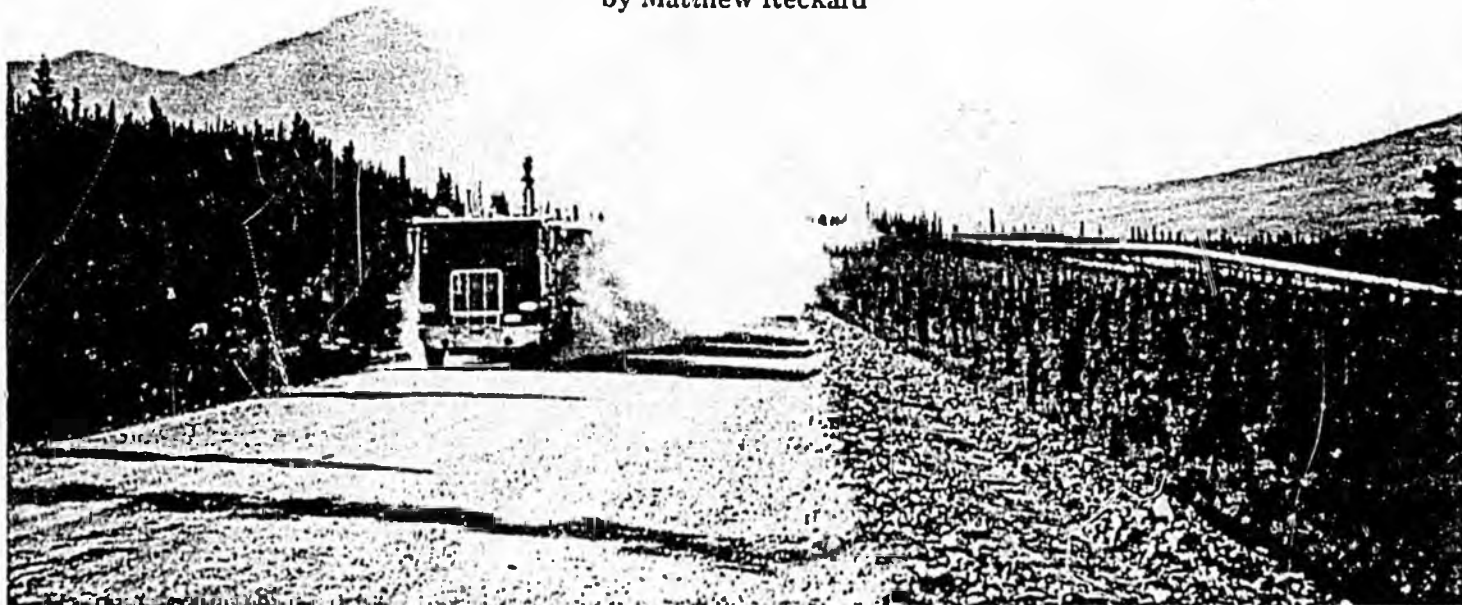
applied science & technology in the north

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UNIVERSITY OF ALASKA
VOLUME 14, NUMBER 3
FALL 1982



HIGH-SPEED GRAVEL ROADS

by Matthew Reckard



The Dalton Highway: not quite a high-speed gravel road — yet.

Alaskans seeking to improve the quality of their rural roads might do well to consider surfacing them with gravel instead of asphalt — especially in areas with extensive permafrost or muskeg. This ironic and seemingly backward idea results from the great difficulties which are encountered in trying to build and maintain a stable road embankment over poor foundation material. Without such stability, asphalt surfaces quickly become distorted, cracked and full of potholes. In severe cases, road crews may not be able to keep roads in a condition for safe high-speed travel, even with a great expenditure of time and money.

Gravel surfaces, of course, suffer from embankment instability too, but the resulting problems are sometimes less severe and are nearly always easier and cheaper to repair. Differential thaw settlement, for example, slowly but continuously creates humps and dips in roads. On a gravel surface, these distortions can be smoothed out as a part of the regular grading plan, sometimes with little or no extra effort. On a paved road there is no alternative but to put up with the humps and dips for as long as can be tolerated, then tear up the entire pavement, recondition the roadbed, and repave.

Technically feasible designs are possible which would provide stable roads over virtually any terrain. Permafrost areas, for example, could be spanned with continuous bridges supported on refrigerated pilings, similar to the above-ground sections of the Alyeska pipeline. Such a design might be practical for spanning small pockets of bad ground, but the cost would be astronomical if it were used for any significant

Matthew Reckard is a research engineer with the Alaska Department of Transportation and Public Facilities, Research Section. A version of this paper was presented at the 33rd AAAS Alaska Science Conference in September 1982.

distance. Over long stretches of unstable ground, then, gravel-surfaced roads are likely to be the most cost-effective means of providing high-speed travel.

Experience has shown that gravel-surfaced roads can provide adequate performance under difficult conditions. Surface roughness measurements made on the Alaska Highway in 1980 by the Research Section of the Department of Transportation and Public Facilities showed a smoother surface on the Canadian (gravel) side of the border than on the Alaska (paved) side. These measurements were made with a Ride Meter over 39 miles of paved road and 62 miles of gravel-surfaced road. Average axle movements were 13% less on the gravel portion than on the paved sections. Perhaps more significantly, the incidence of large (>1") axle movements — which indicates severe dips or potholes — was seven times as great on the gravel sections.

REQUIREMENTS

Many gravel roads are in poor shape, and to make them safe for high-speed travel is not an inexpensive task. The basic needs for location and dimensions

of the road — including alignment, width of surface, and grades — are virtually identical to those for paved roads. Many older roads are narrow, winding and steep, and upgrading these would be expensive no matter what type of surfacing they have.

Gravel-surfaced roads require a greater "crown" (transverse slope) than paved roads to ensure good drainage of water from the surface. This not only reduces muddiness and rutting during rainy weather, but also reduces formation of potholes and "washboarding." A 4% crown is usually recommended for gravel surfaces whereas 2% is typical of paved roads.^{1,2} This requirement has little or no effect on costs, but is sometimes overlooked in building and maintaining gravel roads. A good gravel road also needs a surface layer of hard, crushed gravel with sufficient fine material to act as a binder.³ Such material compacts well and "sets up" into a hard, smooth surface. Many gravel roads have been surfaced with uncrushed material (which is cheaper) and have few silt- and clay-sized particles or "fines" (which is intended to limit frost heaving). The result is loose gravel on the surface, much more dust and poorer overall surface quality.

A major cost in maintaining high quality gravel roads is periodic surface treatment with a dust palliative. This is a wide group of materials which provide a weak cementing action to the gravel, thus promoting a hard, smooth surface with fewer potholes, less washboarding and reduced dust problems. Although this treatment is expensive, it may pay for itself by reducing the need for grading and the loss of surface gravel. The reduction in dust is almost mandatory if high-speed travel is to be made safely. Examples of dust palliatives include waste oil, calcium chloride, emulsified asphalt and lignins. They have been used rarely outside of urban areas in Alaska, although calcium chloride has been used widely in the Yukon (including the Alaska Highway). Calcium magnesium acetate (CMA) might also be an effective dust palliative, since like calcium chloride it is hygroscopic, but it has not been used for this purpose.

CONSTRUCTION COSTS

The most obvious difference between the costs of building gravel and paved roads is the cost of the asphalt pavement. On recent Alaskan rural highway projects, this amounts to roughly \$75,000 per mile of two-lane road, including incidentals such as paint striping and mobilization. In some cases, however, other factors could result in even greater cost differences between gravel and paved roads.

One of these is the limitation on the amount of fines allowed near the surface of the embankment. Current Alaska design policy⁴ places restrictions on fines as deep as 3½ feet below a paved surface in order to reduce frost heaving of the roadway. Thaw weakening of heaved embankments causes severe and permanent damage to asphalt pavements, justifying this policy for paved roads.⁵ Damage to gravel-surfaced roads from thaw weakening, however, is limited to greater muddiness and rutting at breakup — a temporary and relatively inexpensive problem. Greater amounts of fines might therefore be tolerated in gravel-surfaced roads.

"Clean" gravel (free of fines) is often expensive since good sources are rare in many areas. Restrictions of fines content, then, often leads to greater material processing, longer haul distances, and difficulties in securing necessary permits many

Pavement may be no panacea. Asphalt road surfaces in the north, like the cracked one shown here, often break up quickly. (All illustrations courtesy DOTPF.)



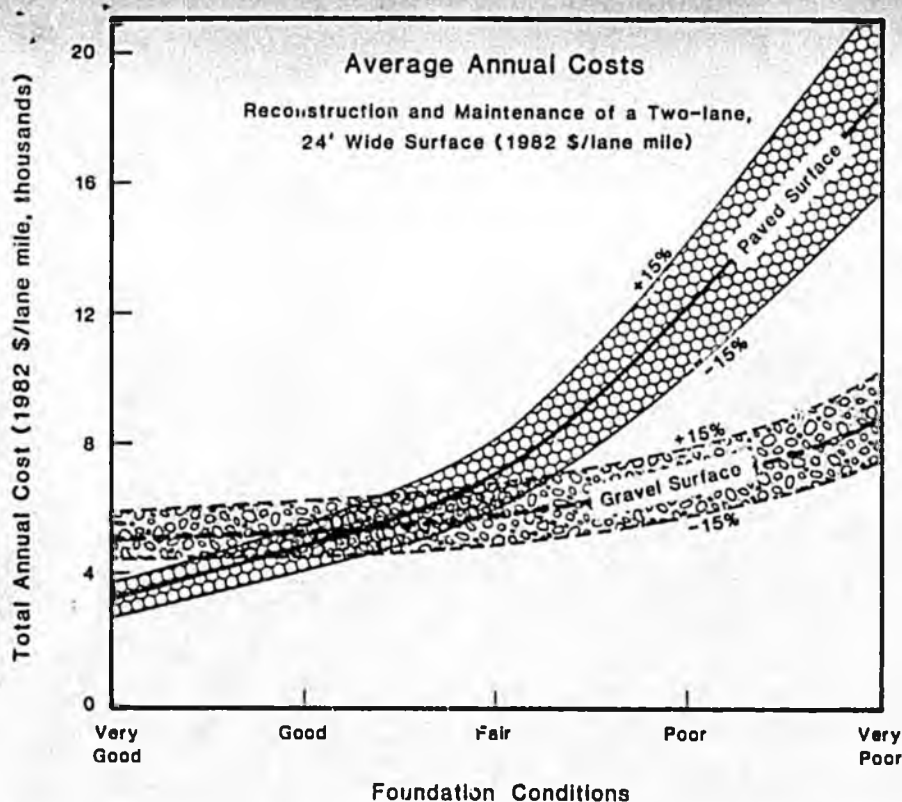


Figure 1. Estimated costs per year for well-maintained roadways.

"clean" gravels are river bottom deposits and mining them can cause environmental damage). Gravel suitable for unpaved roads may be much cheaper than that for paved roads (as much as \$100,000 per mile of two-lane roads, based on some recent contract unit prices).

Similar savings might result where roadways are cut through "dirty" material or even soft, degradable bedrock. For a paved road, excavations must be made to a level well below the final surface to remove these materials. This excavated material must then be replaced with clean gravel hauled from elsewhere. Much of this might be avoided if the road were unpaved, since the original material could be left in place.

Unusually thick road embankments are sometimes built in permafrost areas in order to insulate the original ground and protect it from thawing and settling. In some cases, manufactured insulation board has been placed beneath roadways. In such areas, gravel roads may be much cheaper to build than paved roadways, since there is less need for these measures. This is because gravel surfaces stay cooler in summer than paved ones⁶ (probably due to a combination of greater albedo and the cooling effect of greater evaporation of moisture from gravel surfaces). Since the surface

stays cooler, less insulation is required to prevent thawing the underlying permafrost. The magnitude of the reduction depends upon the local climatic conditions (particularly the thawing index), but calculations utilizing the Modified Berggren Equation suggest that it is approximately equivalent to two feet of gravel in Interior Alaska and one foot on the North Slope. In Interior Alaska, this alone might result in saving \$250,000 per mile for two-lane roadway.

MAINTENANCE COSTS

Maintenance of a high-quality road is not inexpensive even in the best of circumstances. Grading and treatment with dust palliatives must be performed regularly, and the cost of the latter is relatively high. In addition, the surfacing layer of gravel must be renewed every few years as grading and traffic wear it away. These expenses are higher where the foundation soils or the road embankment itself are of poor quality, but they are significant even if a road is built on bedrock.

In contrast, maintenance costs for paved roads are highly variable. If an embankment of material unsusceptible to frost is built on bedrock, it is likely that

an asphalt pavement will have a long life with little need for patching or pothole filling. On poor roadbeds, the situation is drastically different. There have been numerous instances on highway construction projects over permafrost where pavement repairs have been necessary even before the entire project was completed.

Figure 1 illustrates the estimated cost of maintaining a paved road and a gravel-surfaced road in a condition adequate for high-speed (55 mph) travel as a function of the roadbed quality. The estimate assumes maintenance over the alignment for an indefinite period, and the cost of periodic repaving, regravelling and reconditioning are included in the averages. The "foundation quality" is meant to be a combination of both embankment and foundation soil conditions. Costs were estimated based on recent contract prices for various activities, on historical state maintenance costs and work levels, on current prices for asphalt, dust palliatives and other materials, and on interviews with state maintenance, design and construction personnel. Exact predictions of these costs cannot be expected, as is indicated by the range of costs shown in the graph. The estimate indicates that a paved surface is cheaper to maintain than a gravel one if the road foundation is very good and both types of surfaces are kept in good condition. As foundation quality deteriorates, however, this advantage disappears, and where foundation quality is very poor, gravel surfaces appear to be much cheaper.

Many sections of Alaska's highways, paved and unpaved, have not always been kept in a "high-speed" condition, and dust palliatives have rarely been used in rural areas. The cost estimates in Figure 1 therefore necessarily rely to some extent on theoretical instead of empirical data. The accuracy of the estimate — and in particular the exact crossover point between paved and unpaved surface costs — may thus be questioned. That such a crossover exists, however, seems clear.

It also seems clear that high quality gravel surfaces should be given serious consideration when plans for road improvements are formulated. Such surfaces might yield both better performance and lower costs in some areas, and the resulting experience would help to clarify the trade-offs between paved and unpaved roads.

A case in point which is of considerable current interest is the Dalton Highway. Much of this road passes over permafrost which provides a poor foundation. An asphalt pavement may deteriorate rapidly here, and many improvements are possible short of paving the road. Maintenance of a proper crown would by itself improve the road. The only good surfacing gravel ever placed on the road has been put there in the last year and a half; most of the road still has none. Virtually no dust palliatives have ever been used on the Dalton Highway; these could improve the surface further, reduce the need for grading, and reduce the loss of surfacing gravel as well as help to control dust problems.

A program to do all of the above would cost a considerable amount of money, but not nearly as much as a project to pave the road. It might also be more successful than an asphalt pavement on the long stretches of unstable ground the Dalton Highway crosses. On more stable parts of the road, on the other hand, paving may well be the most cost-effective means of improvement.

CONCLUSIONS

High-speed gravel roads merit serious consideration on Alaska's rural highways, particularly where poor foundation conditions — such as permafrost and muskeg — are encountered and in areas where clean gravels unsusceptible to frost are scarce. Asphalt pavements are likely to perform poorly in such areas and to have high construction and maintenance costs. Neither highway users, nor state highway personnel, nor taxpayers will be happy if, a few years after an expensive paving project, a road is as bad as or worse than it was before. Even some parts of Alaska's highways which are now paved might be improved by taking the "backward" step of giving them a high-quality gravel surface — and money could be saved in the process.

This article is adapted from the author's report "Costs and Performance of High Speed Gravel Roads." Requests for the full report should be sent to Barbara Trego, Publications Specialist, Department of Transportation and Public Facilities, Division of Planning and Programming, Research Section, 2301 Peger Road, Fairbanks, Alaska 99707.

REFERENCES

- ¹ Evans, J.H.T. Undated. The Use of Calcium Chloride as a Dustlayer. Yukon Territory Department of Engineering, Whitehorse, Canada. Unpublished paper.
- ² Calcium Chloride in Road Improvement. Technical Data HP1, Allied Chemical Canada, LTD.
- ³ See, for example, AASHTO Specification No. M-147 in "Standard Specifications for Transportation Materials and Methods of Sampling and Testing," July 1970. American Association of State Highway and Transportation Officials, 444 N. Capitol St., N.W., Suite 225, Washington, DC 20001.
- ⁴ Guide for Flexible Pavement: Design and Evaluation. 1982. Alaska DOTPF, Division of Standards and Technical Services, Feb.
- ⁵ McHattie, R., D. Connor and D. Esch. 1980. Pavement Structure Evaluation of Alaska Highways. Alaska DOTPF Research Report No. FHWA-AK-RD-80-1.
- ⁶ Lunardini, V. J. 1981. Heat Transfer in Cold Climates. Van Nostrand-Reinhold Co., NY. ♦

PUBLICATIONS

Note: Building in the North, the collection of classic Eb Rice articles, is being reissued with some minor revisions and updating by the School of Engineering here at the University of Alaska-Fairbanks. In keeping with Eb's wishes, profits — if any — from sales of his book will go toward furthering the cause of northern engineering education.

Important sidelight to the foregoing note: *The Northern Engineer* has very few copies left of the earlier printing of Building in the North. If you need the book, place your order with the *Office of the Dean, School of Engineering, University of Alaska, Fairbanks, AK 99701*. The new copies will be available sometime after the first of the year; price is not yet known, but given inflation over the intervening years, it is sure to be more than the previous \$4.

♦ ♦ ♦ ♦

NOTED

Undergraduates studying civil engineering, geology or geological engineering are eligible to apply for a \$1000 annual scholarship established at the University of Alaska by R&M Consultants. The scholarship is a memorial to the late Ralph Migliaccio, founder of R&M and the firm's president until his death.

Preference will be given to applicants demonstrating high scholastic ability, and financial need may be considered. The University of Alaska Foundation will administer the scholarship fund; scholarships will have a spring semester application deadline and will be awarded for the following fall semester. Forms and further information are available from *Dixie Brown, Executive Director, University Foundation, 113 Bannell Building, University of Alaska, Fairbanks, AK 99701*.

♦ ♦ ♦ ♦

The Alaska Academy of Engineering and Sciences is up and going. A newly released flyer states the academy is open to any individual with a professional interest in Alaska engineering and science. No discipline, group or geographic region within the state will dominate; potential members from academia, industry, government and the private sector are encouraged to join.

The overall purpose of the academy is given as "the advancement of engineering and scientific knowledge, practice, and public service through the encouragement of: (a) scientific research and discovery, (b) technological innovation, (c) discussion of engineering and scientific problems and issues, and (d) publication and discussion of technological and scientific information and knowledge."

Ambitious plans already exist for the group to fulfill its aims. The academy plans to hold a conference each spring; to

CATHODIC PROTECTION OF CONCRETE BRIDGE DECKS IN ALASKA

(Northern Engineer Article)

Matt Reckard

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 section 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

use lower case letter "o"

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conductive layer does not contact any bridge steel, short-circuiting the system. A wearing ^{COURSE} ~~course~~ 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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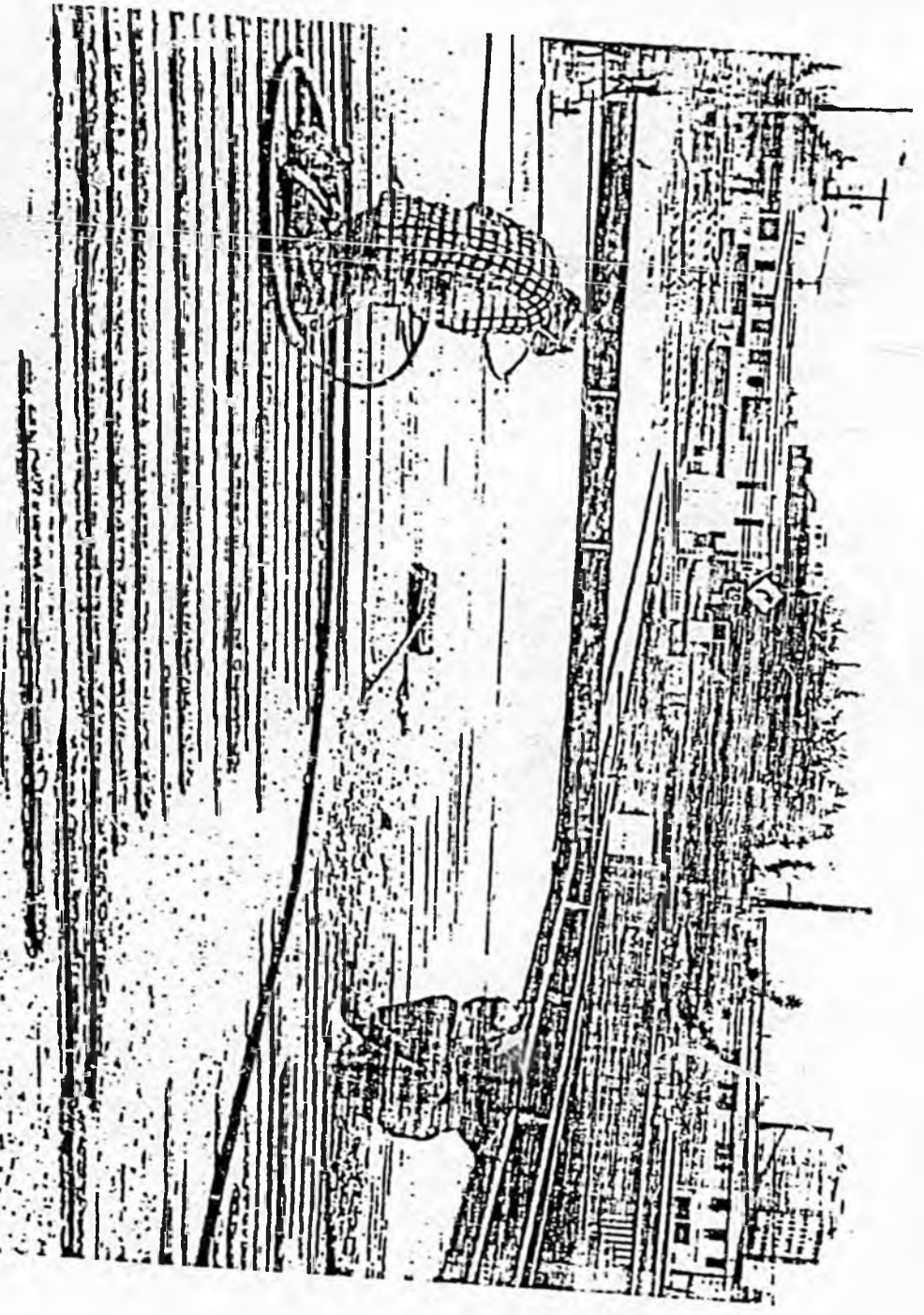


FIGURE 1

Remaining delaminated concrete, Wendell St. Bridge, Fairbanks

photo Steve Reivers

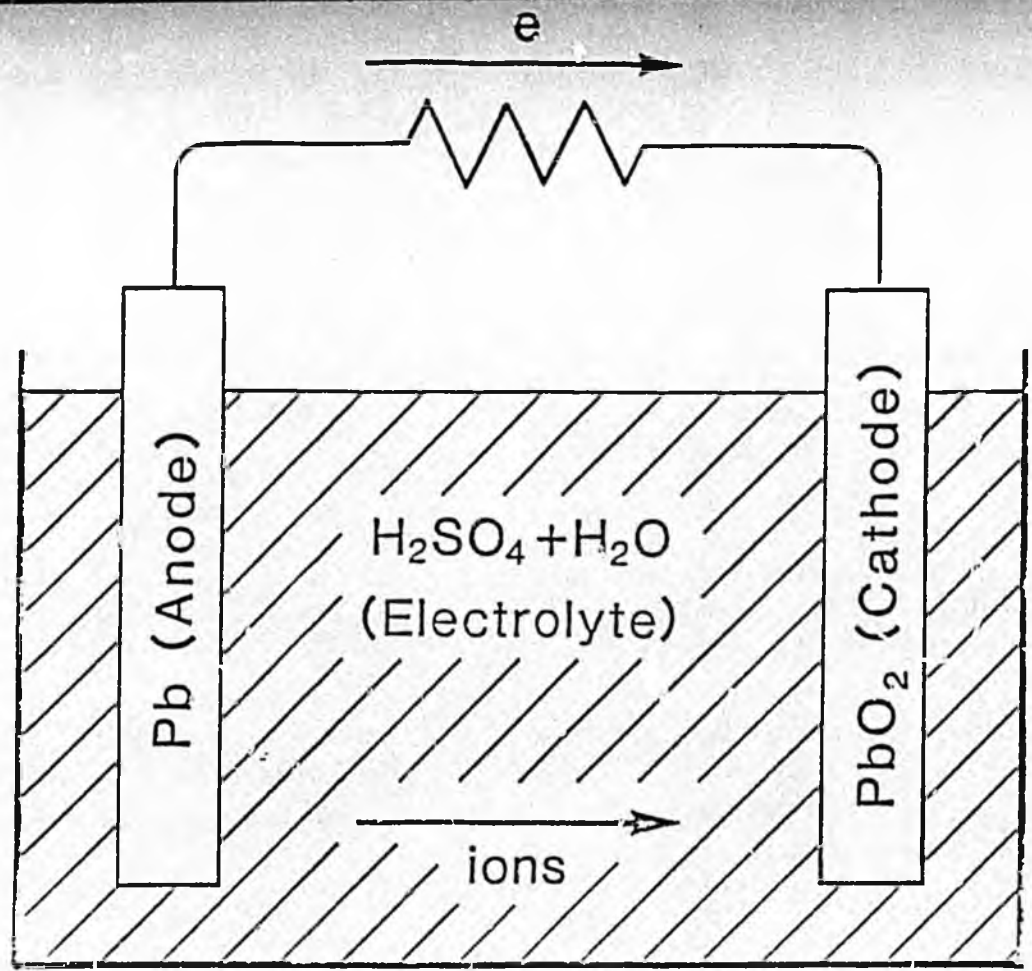


Figure 2: Lead-Acid Corrosion Cell

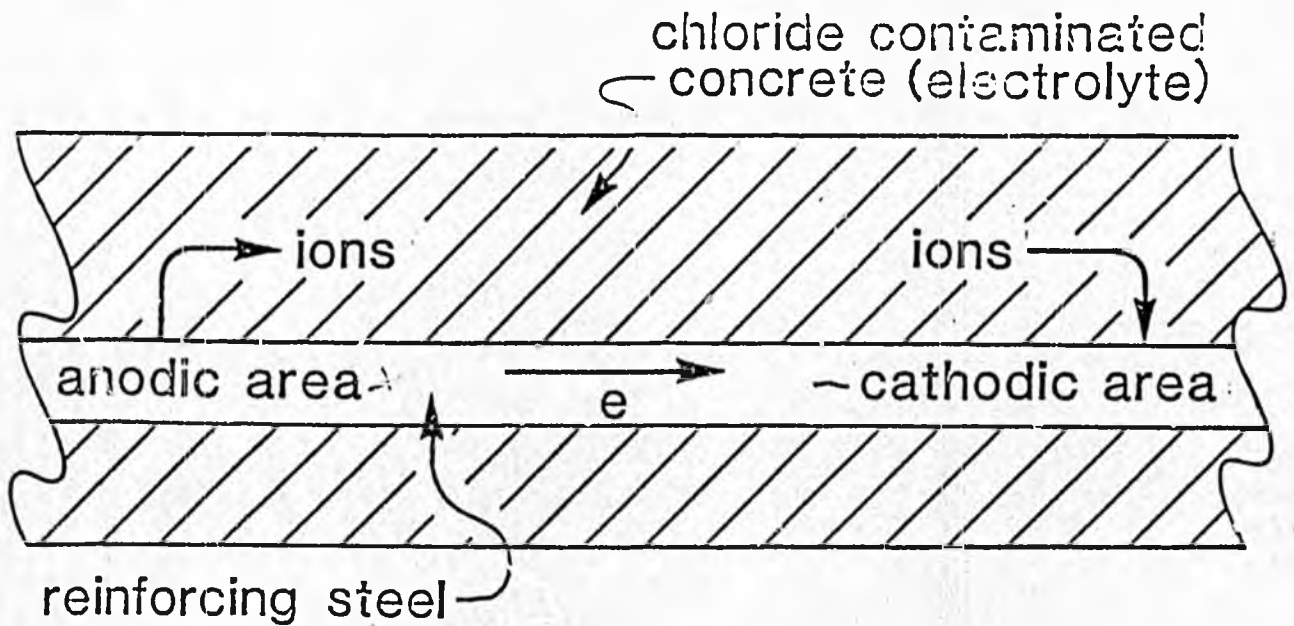


Figure 3: Bridge Deck Corrosion Cell

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):

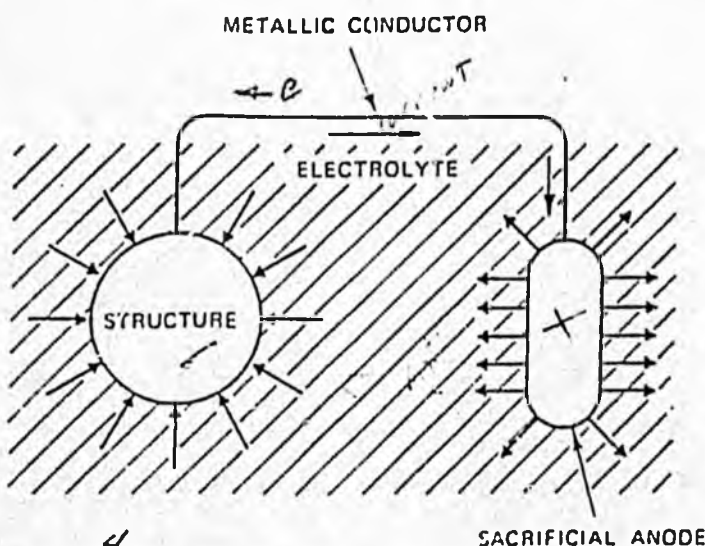
Metal	Typical Potential, volts*
Magnesium alloy (6% Al, 3% Zn, and 0.15% Mn)	-1.60
Zinc	-1.1
Aluminum alloy (5% Zn)	-1.05
Mild steel (rusted)	-0.2 to -0.5
Mild steel in concrete	-0.2
Copper	-0.2

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

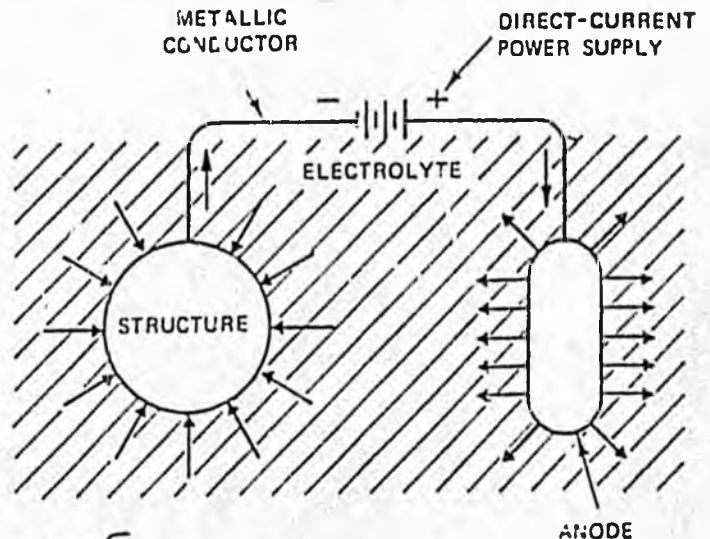
From this listing, it is obvious that the magnesium offers cathodic protection to any of the other metals listed, whereas copper does not. In practice, alloys of magnesium, aluminum, and zinc are used as sacrificial anodes, although only magnesium and zinc are generally used for the cathodic protection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



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

Source: Reference 4

Source: Reference 4

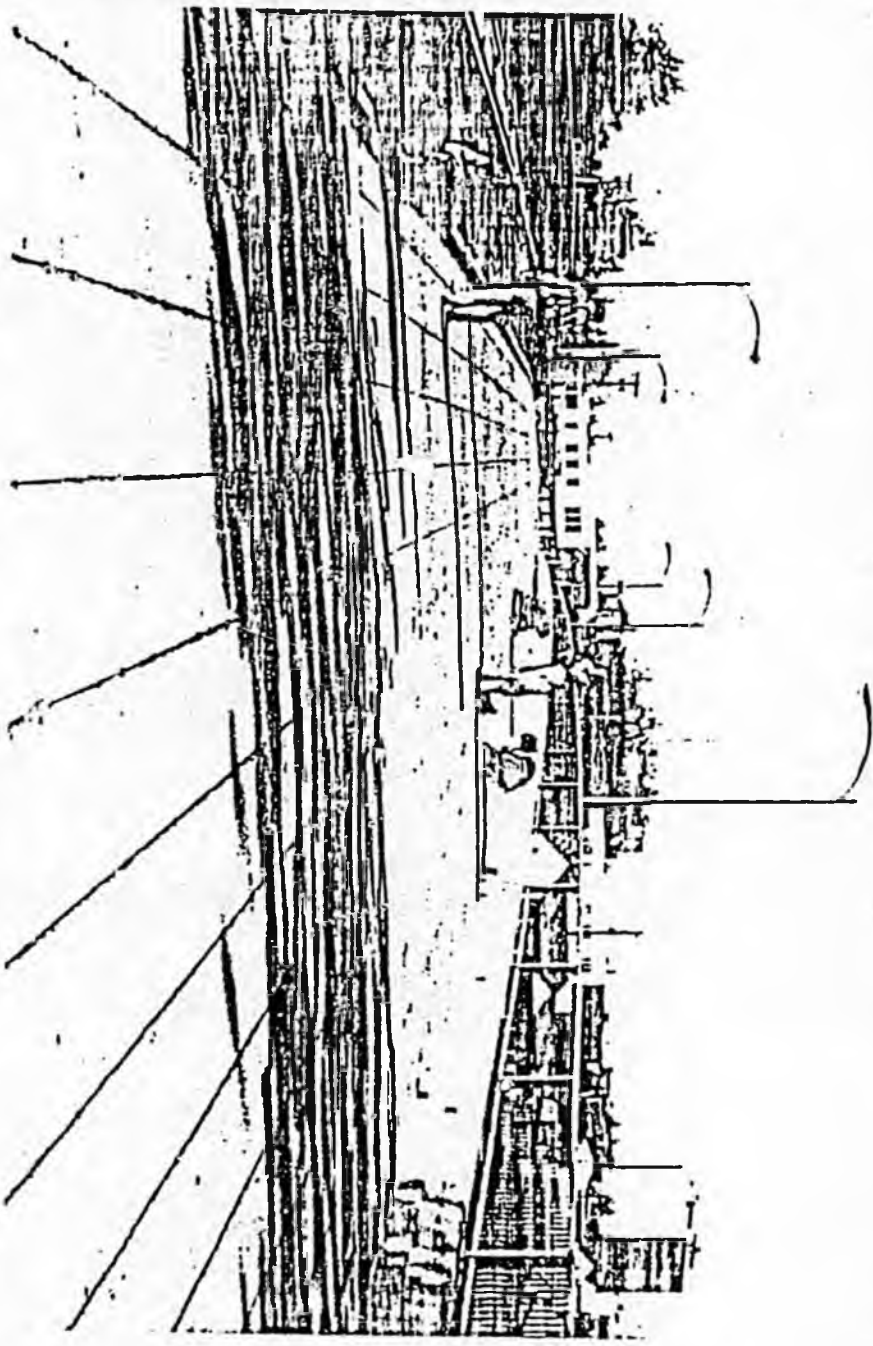
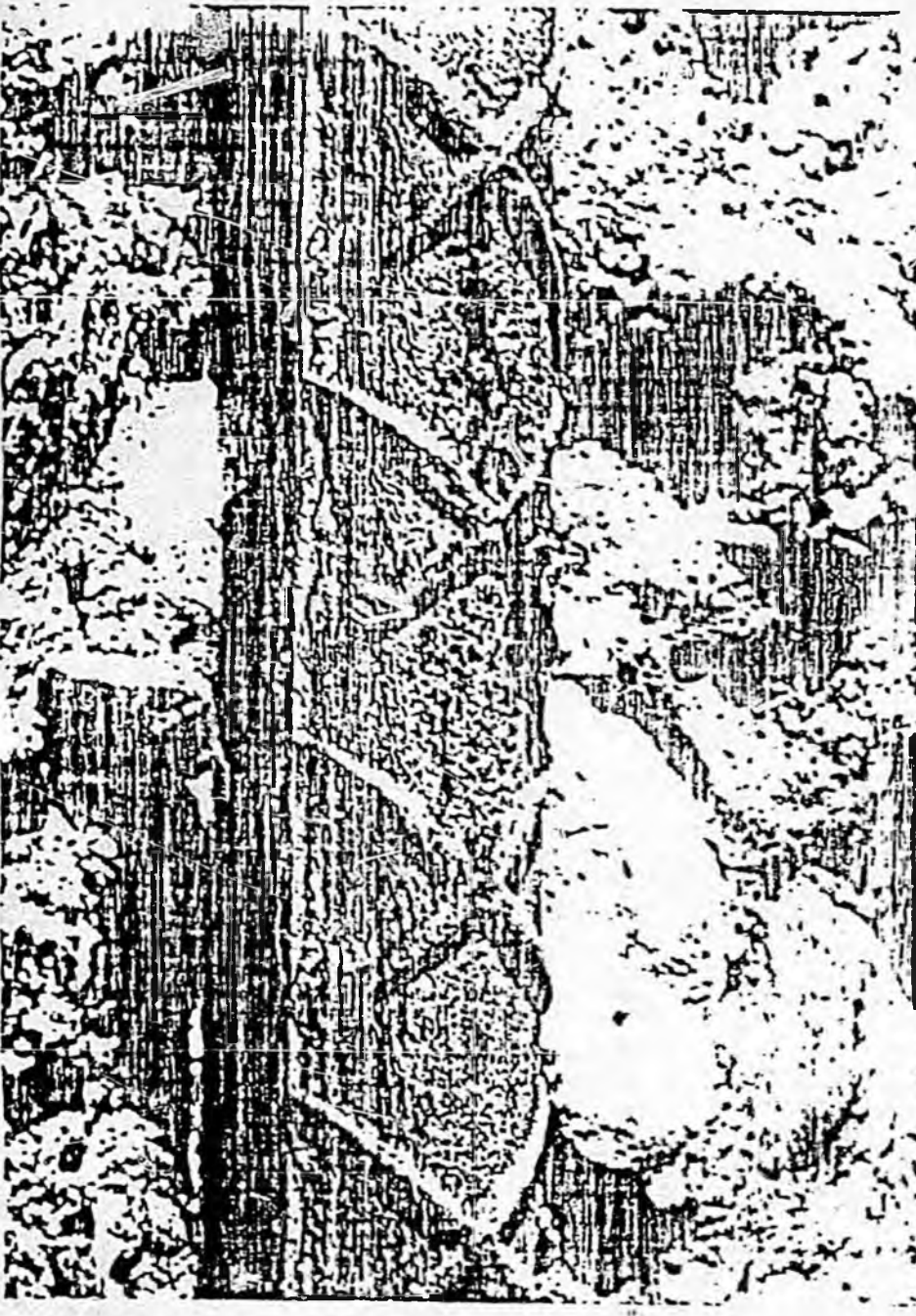


Figure 7: Anodes grouted into deck (Wendell St. Bridge) \rightarrow \leftarrow Plastic anodes
Figure 6: Corrosion pitting on rebar (Wendell St. Bridge) \rightarrow \leftarrow Stirrup bars



The Production of Calcium Acetates As Alternative

INTRODUCTION

Road and airport runway de-icing are serious problems in the north. Sodium and calcium chlorides have been used successfully for many years as de-icing agents. Adverse environmental effects and corrosion problems associated with chloride salts have prompted a search for alternative, cost-effective, de-icing agents.¹⁻⁴

A report entitled "Alternate Highway De-icing Chemicals," from the Bjorksten Research Laboratories, Inc. (1981), reviewed the de-icing characteristics of various compounds. Two candidates were selected which proved economical, and more important, less corrosive than NaCl.

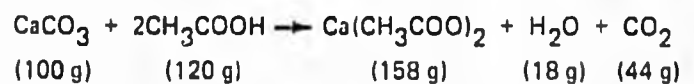
The first, methanol, was found to be "less persistent" due to its low flash point. The second, a mixture of calcium and magnesium acetate (CMA) was found to exhibit superior de-icing characteristics at a competitive price. In contrast to NaCl, CMA is a corrosion inhibitor, is beneficial to most soils, 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 later in this article.

REACTION KINETICS RESULTS

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:



The reaction is slightly exothermic ($\Delta H_r = -4.6$ 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/100 g CaCO₃.

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

The reaction behavior of limestone and acetic acid is reported in Figure 1. Reactions were conducted in a simple stirred tank

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and Magnesium De-Icing Agents

reactor. For a given residence time, as long as enough water was present to provide an unsaturated solution of calcium acetate at the conclusion of the reaction, the water to limestone ratio did not influence the reaction results. However, 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.

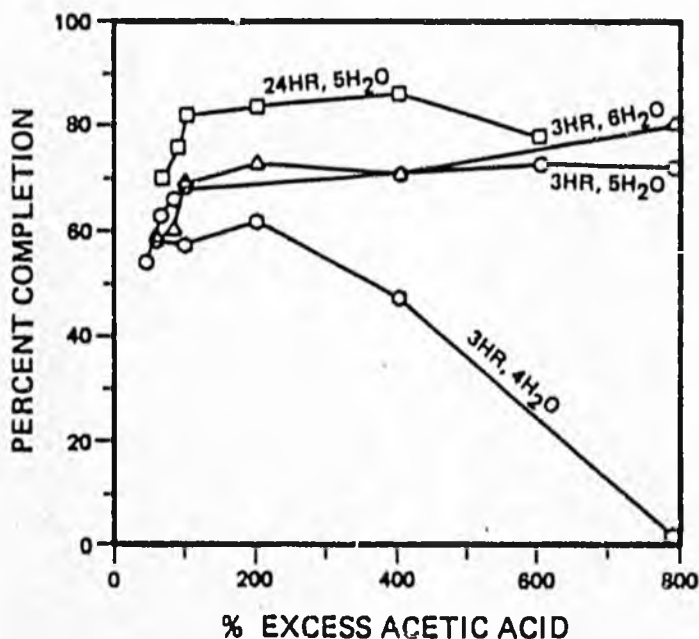


Figure 1. Reaction behavior of limestone and acetic acid: Percent completion vs. excess of acid at various residence times and with varying water content.

Since various water to limestone ratios above 5:1 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 (for brevity, not all results are plotted on Figure 1).

A significant conclusion can be drawn from the above: The acetic acid does not have to be highly refined. Industrial grade acetic acid (95% purity), which is substantially less expensive than reagent grade, can be used since it will have to be diluted to 50% in any event.

The use of 50% acetic acid may allow an additional cost savings. Liquid phase oxidation (LPO) and methanol carbonylation are common methods of acetic acid production which could be implemented in Alaska. Both of these processes produce acid at approximately a 50% concentration. One of the major factors in the cost of high-purity acetic acid is the cost of purification. Since the CMA process could make use of 50% acetic acid, the purification process and its cost could be eliminated.

Methanol carbonylation is especially attractive 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 experiments were designed to gauge the effects of excess acid, reaction temperature and limestone particle sizes on the degree of completion of the reaction. The results are for batch reactions with a three hour residence time.

The amount of excess acetic acid did not augment 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

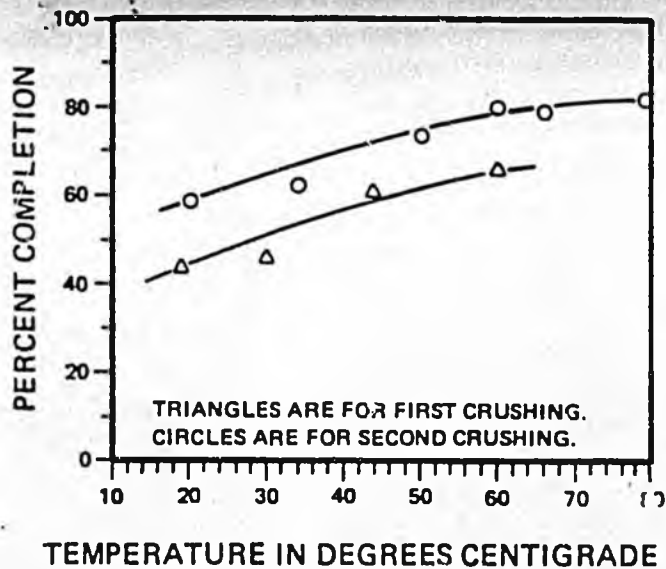


Figure 2. Reaction performance for limestone and no excess acetic acid.

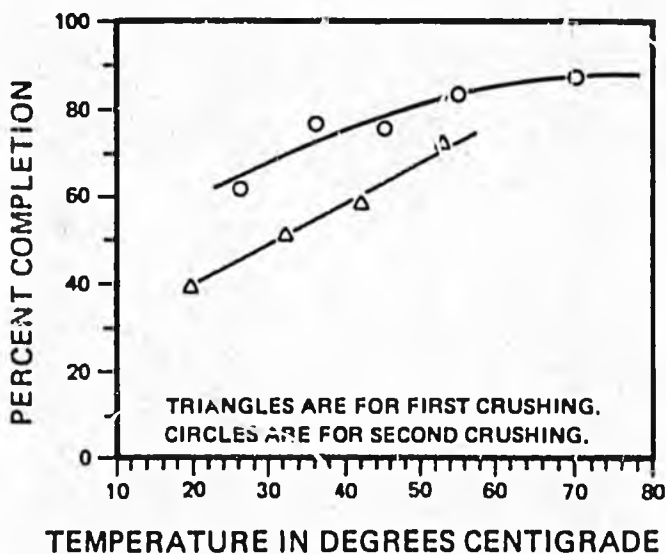


Figure 3. Reaction performance for limestone and 20% excess acetic acid.

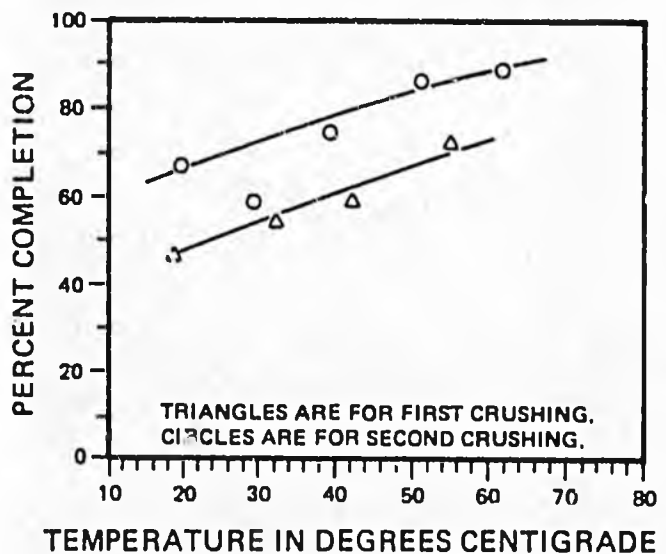


Figure 4. Reaction performance for limestone and 50% excess acetic acid.

associated acid recovery unit. An extraction step using an appropriate solvent, followed by a distillation step, would suffice.

The effect of temperature is significant. An increase in reaction temperature from 20°C to 60°C results in an increase in the completion of over 20%. A similar effect was observed with the use of 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 plant design. The beneficial effect on the completion must be balanced against operating and energy costs. Finally, the residence time in the reactor is significant. A 20% increase in the reaction completion was observed when a reaction time of 24 hours was used instead of three hours.

PROCESS DESIGN AND ECONOMICS

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

Figure 6 shows a block diagram of the preliminary process design envisioned for CMA production. Raw limestone is first crushed in two stages to particles of 1/8" to 1" diameter. The crushed limestone is then mixed with acetic acid and water in a continuously 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 a mixture of unspent acetic acid, unreacted limestone and inert materials, is then passed through a filtration unit. In the

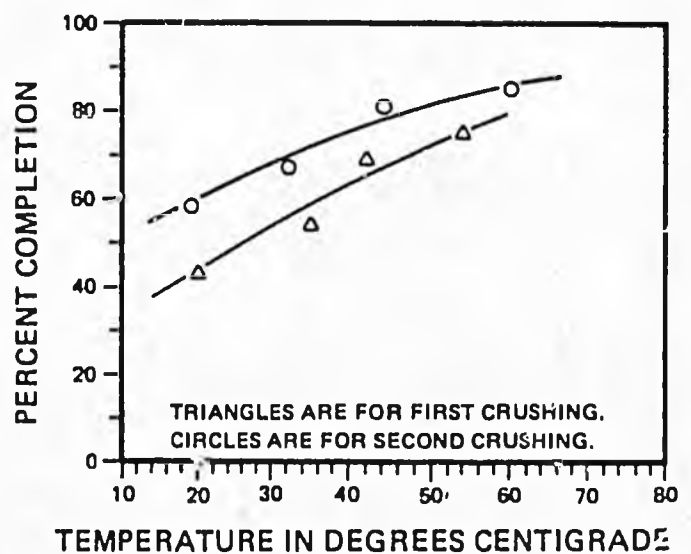


Figure 5. Reaction performance for limestone and 100% excess acetic acid.

filtration unit unreacted solids are removed and sent to a settling pond where they are neutralized by adding 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 checked for appropriate pH value and sent to a liquid product storage tank. With an optional process addition, it would be possible to evaporate the liquid product to produce a solid calcium or magnesium acetate product.

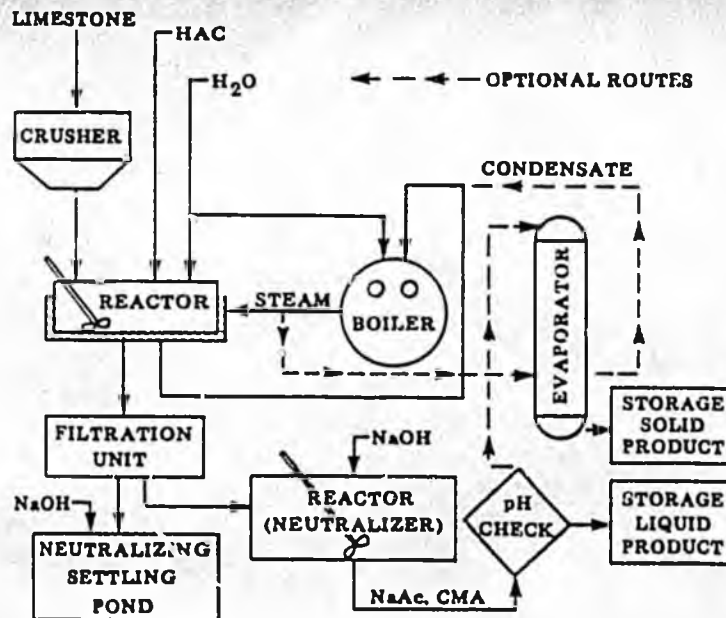


Figure 6. Block diagram of conceptual process design.

On the basis of this design, we have completed an economic analysis of the proposed CMA plant. It should be emphasized that this analysis represents a best-case scenario, with continuous plant operation and minimal storage facilities.

Figure 7 shows the required selling price as a function of acetic acid cost for a 10,000 gallon per day (GPD) plant and a 50,000 GPD plant. It is apparent that there is some economy of scale, but 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 with a fixed cost for acetic acid (\$1.25/gallon). It is obvious that a minimum plant capacity of about 12,000 GPD is dictated by the economics. Little additional economy

of scale is indicated above the production rate of 30,000 GPD. In these two figures, 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.

Figures 7 and 8 indicate that the cost of acetic acid is the single most important factor in the selling price of CMA. If acetic acid must be shipped to Alaska from Texas, for example, at a cost of over \$2.50 per gallon, the price of CMA will be more than \$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 the purification stage taking the acid from 50% to purities of more than 90%. Hence, if a 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 at a cost as low as \$1 per gallon.

Even if imported acetic acid is used, the price of \$500 per ton of solid CMA may not be excessive. CMA is not corrosive as are calcium and sodium chlorides, so 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, it may save a great deal in maintenance costs. In

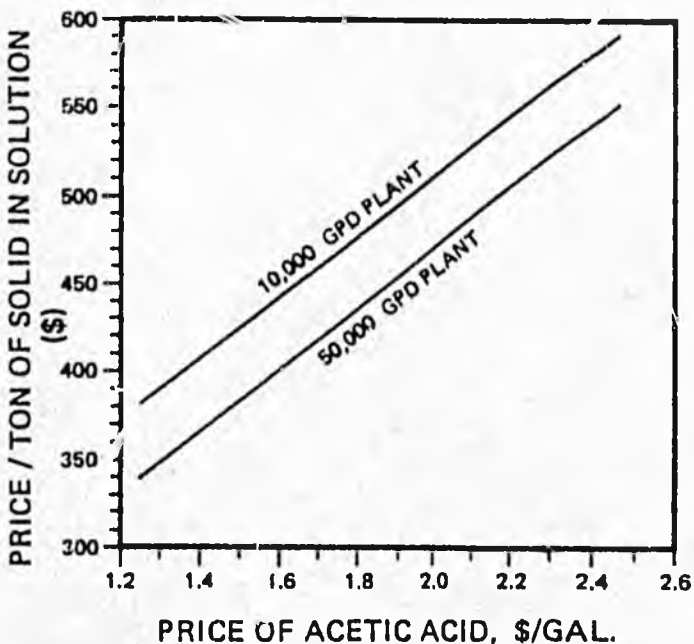


Figure 7. Required selling price of CMA for various acetic acid prices.

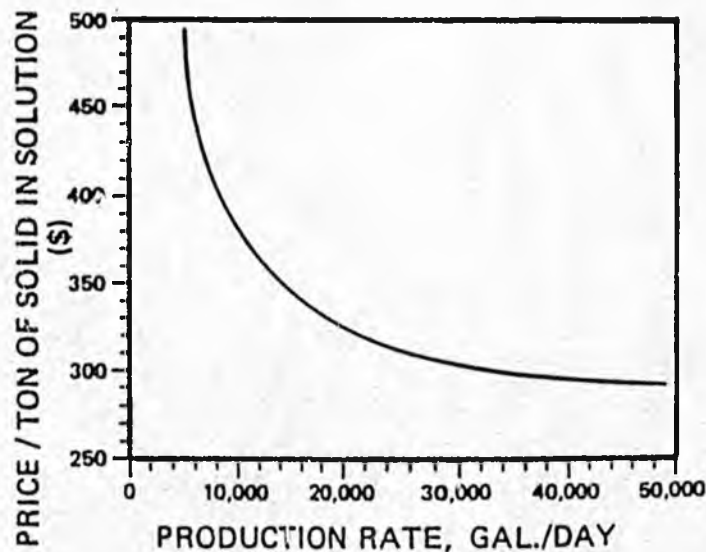


Figure 8. The effect of plant size on the CMA price (\$1.25/gallon acid).

addition, since airports cannot use chloride salts for runway de-icing, but must now rely on more expensive methanol or urea, CMA may have a particular cost advantage.

FREEZING AND EUTECTIC EXPERIMENTS

There are two objectives in this series of experiments: (1) determination of eutectic relationships 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 range 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 several concentrations. The results seen in the accompanying figures represent the average readings gathered over three test runs. The best de-icing agent is a concentrated solution (27% by weight) of MgAc. At the lowest temperature tested (-75°C), the solution gelled, but did not freeze.

Figure 9 shows the eutectic behavior of sodium chloride solutions. The saturation point for NaCl is 26% by weight. Figures 10 and 11 show the eutectic characteristics of CaAc and MgAc respectively. The upper limit (saturation point) for CaAc was 28%, while that for MgAc was somewhat lower. 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 is shown in Figure 12.

The findings of our freezing experiments, in addition to corroborating the de-icing performance of the acetate com-

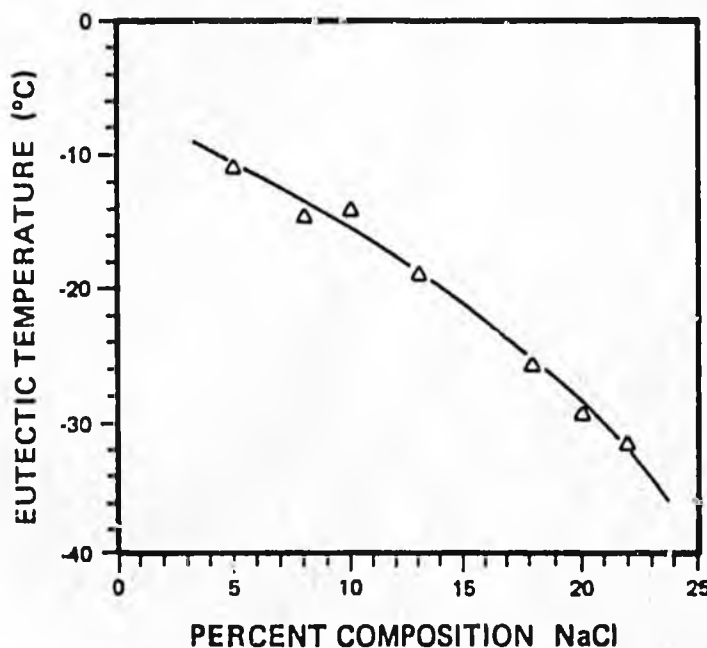


Figure 9. The freezing temperature of NaCl solutions as determined by experiment.

pounds, have also pointed out a major conclusion. Since the best dolomite deposits in the state 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/50% CaAc 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 (Fig. 12) while a pure solution of CaAc has a freezing point of -26°C (Fig. 10).

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

A FUNDAMENTAL STUDY OF FREEZING POINT DEPRESSION IN AQUEOUS $\text{Ca}(\text{O}_2\text{CCH}_3)_2$ AND $\text{Mg}(\text{O}_2\text{CCH}_3)_2$ SOLUTION

The Debye-Hückel theory provides a satisfactory interpretation of freezing point depression in dilute aqueous solution. Brown and Prue⁵, Christoffersen and Prue⁶ and Prue *et al.*⁷ have demonstrated the applicability of the Debye-Hückel theory in dilute solutions of sodium, potassium, magnesium and calcium ions with a variety of anions. While the thermodynamic properties of dilute aqueous solutions are well established, there is little in the literature for concentrated solutions. The above studies dealt with molarities of less than 0.1, far below the saturations contemplated in this work.

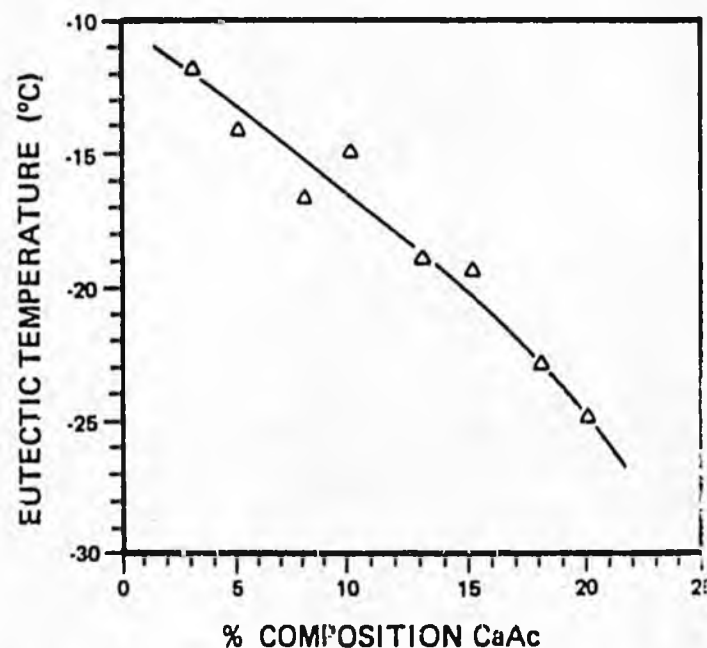


Figure 10. Eutectic diagram of CaAc solutions.

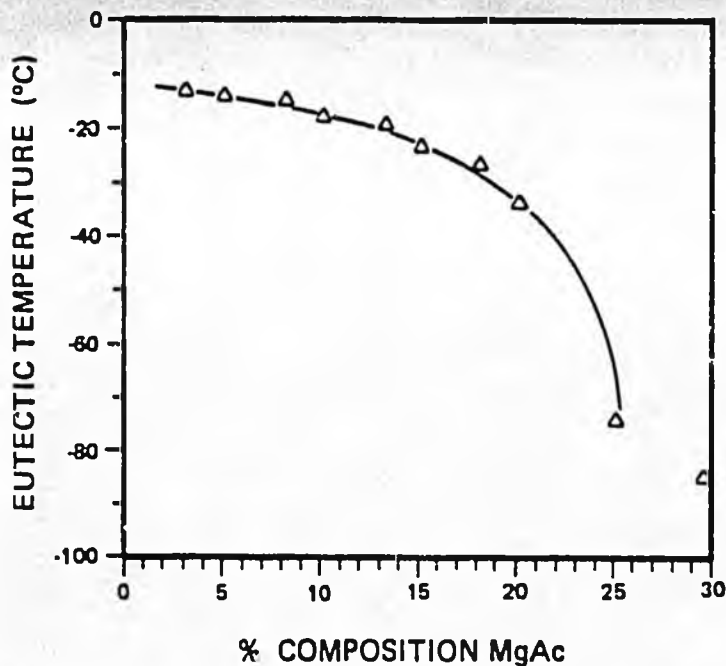


Figure 11. Eutectic diagram of MgAc solutions.

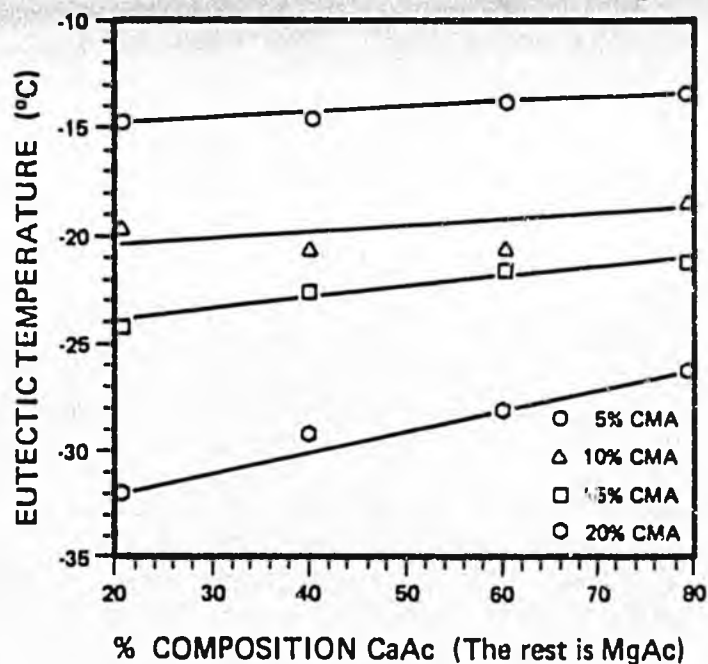


Figure 12. Eutectic characteristics of various compositions of CMA solutions.

At sufficiently high dilutions, the interactions between ions in solution are purely coulombic, and the osmotic and activity coefficients are determined by the charge type alone. At higher molalities, specific effects become marked and eventually become dominant. Various explanations of these phenomena have been offered in the context of activity coefficients.^{8,9}

The freezing point depression ΔT_f can be obtained from the relationship:

$$\Delta T_f (1 + b\Delta T_f) = \Sigma m \lambda \phi \quad (1)$$

first introduced by Guggenheim and Prue,¹⁰ where, for aqueous solutions, $b = 4.8 \times 10^{-4} \text{ } ^\circ\text{K}^{-1}$ and λ is the cryoscopic constant, equal to $1.860 \text{ } ^\circ\text{K/mole}\cdot\text{kg}$. Σm is equal to $2m$ for symmetrical electrolytes (such as NaCl, CuSO₄ and NaO₂CCH₃) and $3m$ for asymmetrical electrolytes, such as CaCl₂, Ca(O₂CCH₃)₂ and Mg(O₂CCH₃)₂. The molality, m , is defined as the number of moles per 1000 g of solvent.

The osmotic coefficient, ϕ , is given by the equation:

$$\phi = 1 - \frac{1}{3} A [z_+ z_-] I^{1/2} \sigma(I^{1/2}) \quad (2)$$

where A is the Debye-Hückel constant ($1.124 \text{ kg}^{1/2} \text{ mole}^{-1/2}$), z_+ and z_- are the charge numbers of the ions, I is the ionic strength, and σ is a function describing the ionic interaction within a solution. Values of the function σ can be obtained from:

$$\sigma(y) = \frac{3}{y^3} (1 + y - \frac{1}{1+y} - 2 \ln(1+y)) \quad (3)$$

The ionic strength I is related to the ionic activity coefficient by:

$$-\log f_i = \frac{az_i^2 \sqrt{I}}{1 + \beta \gamma \sqrt{I}} \quad (4)$$

where f_i is the activity coefficient, α and β are parameters varying with temperature and the dielectric constant, and γ is the ion-size parameter, or effective ionic radius.

The ionic strength can be estimated from the summation of the product molarity times ionic charge squared for all ionic species present in the solution, i.e.:

$$I = 0.5 (c_1 z_1^2 + c_2 z_2^2 + \dots + c_i z_i^2) \quad (5)$$

We have taken this relationship one step further. Since c is the molarity, defined as number of moles per 1000 cc of solution, a simple relationship between molality and molarity can be written:

$$m_i \rho_{\text{solution}} = c_i \quad (6)$$

Further, for a single electrolyte, we can write:

$$m_1 z_1 = m_2 z_2 \quad (7)$$

as a necessary condition of neutrality, or

$$m_2 = \frac{m_1 z_1}{z_2} \quad (8)$$

Introduction of equations (6) and (8) in (5) for a single electrolyte yields:

$$I = m_1 \rho_{\text{solution}} \left(\frac{z_1^2}{2} + \frac{z_1 z_2}{2} \right) \quad (9)$$

We label the expression within the parentheses the *Ionic Strength Indicator (ISI)* which is a characteristic parameter of single-electrolyte aqueous solutions. For two monovalent ions,

the value is equal to 1, for a monovalent/bivalent combination it is 3, and for two bivalent ions the ISI is equal to 4.

Example Calculation

Calculate the freezing point depression of a 28% (by weight) aqueous solution of NaCl.

The molality, m , can be obtained by dividing the weight of sodium chloride in 1000 g of solvent by the MW of NaCl.

$$m = \left(\frac{280 \times 1000}{120} \right) / 58.5 = 6.6$$

The ionic strength, I , can be calculated using $\rho = 1.323$ g/cc (the measured density of 28% NaCl solution) and $ISI = 1$.

$$I = 6.6 \times 1.323 \times 1 = 8.73 \text{ and } I^{1/2} = 2.95$$

Then, $\phi(I^{1/2}) = .179$

The osmotic coefficient may then be evaluated:

$$\phi = 1 - \frac{1}{3} \times 1.124 \times (1 \times 1) \times 2.95 \times .179 = .802$$

and finally (ignoring $b\Delta T_f$)

$$\Delta T_f = 2 \times 6.6 \times 1.860 \times .802 = 21^\circ\text{K or } ^\circ\text{C}$$

The predicted freezing point depression for a 28% NaCl solution is 21°C below the freezing point of water.

The Debye-Huckel theory has been applied to CMA solutions. Table 1 presents the predicted results. The theoretical freezing points lag behind the experimental by approximately 10°C . Apparently, certain special activity coefficients are in effect here. However, the slight differences observed among the experimental results of the freezing points of the three compounds were observed in the fundamental prediction as well, i.e., the order of de-icing effectiveness was MgAc, NaCl and CaAc. A combination of the Debye-Huckel theory and our experimental results can be extended to other similar salts in like concentration ranges to provide a good prediction of their de-icing characteristics.

CONCLUSIONS

This work resulted in a number of original findings. A reaction scheme involving acetic acid and native limestone has resulted in a good yield of calcium acetate. While dolomites were equally effective, the calcium-magnesium acetate mixture that was produced did not exhibit a better de-icing performance than that of calcium acetate. Hence, in view of the scope of this work, only the reaction of limestone (CaCO_3) with acetic acid can be considered as a viable means to produce an acetate de-icing agent.

A process design and economic evaluation was presented. The price of CMA varied from \$590/ton for a 10,000 gallon per day plant at \$2.50 per gallon of acetic acid, to \$290/ton for a 50,000 gallon per day plant at \$1.25 per gallon of acetic acid. These prices are within the ranges of prices for present de-icing compounds. The immense secondary costs associated with the use of chloride salts make the acetates even more attractive.

TABLE 1
Predicted Freezing Point Depression
Using the Debye-Huckel Theory

NaCl		CaAc		MgAc	
% w	$\Delta T_f (^\circ\text{C})$	% w	$\Delta T_f (^\circ\text{C})$	% w	$\Delta T_f (^\circ\text{C})$
0	0	0	0	0	0
5	2.9	5	2.8	5	3.1
10	6.1	10	5.8	10	6.4
15	9.7	15	9.2	15	10.2
20	13.8	20	13.2	20	14.7
25	18.5	25	17.3	25	19.9

Finally, the de-icing and eutectic characteristics of the acetates have been experimentally determined and fundamentally justified using the Debye-Huckel theory.

ACKNOWLEDGMENT

This work was done under a research grant from the Alaska Department of Transportation and Public Facilities Division of Planning and Programming, Research Section.

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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

transported to the Materials & Research Division in Bangor.

Slides 22 and 23

The pH of the above mixtures was further adjusted to 9 - 10 by the addition of acetic acid. The wet material was then dried in the oven to yield powdered CMA which contained a certain amount of unreacted limestone and some quick lime. The powdered material had a total weight of 1180 pounds.

During December the relative slipperiness of saturated solutions of CMA, Sodium Chloride, Calcium Chloride and Urea, and also with water were composed on both asphalt and concrete surfaces. This testing was conducted using a British Portable Pendulum Tester in accordance with ASTM E-303. When tested on Bituminous Pavement, Sodium Chloride, CMA and Urea all gave comparable values, being about 90% of the frictional resistance shown by plain water on the pavement surface. On concrete however, the CMA frictional value was only 76% of the value for plain water, compared with the sodium chloride value of 87%, calcium chloride value of 66% and the Urea value of 93%.

Slide 24

On December 29, 500 lb. of the material was mixed with 3 yd.³ of sand.

On January 6, 1983, we had a snowy day. We spread 45 lbs. of salt on one part of the driveway (50 ft. long) in the parking lot, and 45 lbs. of CMA mixture on another side (50 ft.),

with a 30 ft. stretch at the middle, without any deicing agent.

Photographs were taken, but not developed yet.

The impression we had so far is:

- 1) Without tracking, CMA started to deice slower than NaCl. But after about an hour, it worked fairly well.
- 2) CMA is more persistent. Evidence: Next day when another layer of snow fell on the pavement, we could see that CMA is still effective.
- 3) Bad feature of CMA - Tracking into the building. When it dried, white residue appeared. This probably was due to extra lime in the mixture.

Future Plan

- 1) Corrosion test on various metals.
- 2) Ponding test on concrete slabs with rebars inside.
- 3) More field test.

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 \$650/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.

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

FINAL REPORT

by

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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

FINAL REPORT

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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.

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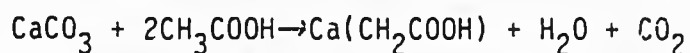
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FOREWORD

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.

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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.O.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)

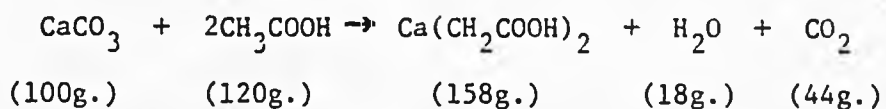
A report entitled "Alternate Highway De-icing Chemicals" from the Bjorksten Research Laboratories, Inc. presented a review of the de-icing characteristics of various compounds. Two candidates were selected which proved economical, and more importantly, less corrosive than NaCl .

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. $\text{H}_2\text{O}/100\text{g CaCO}_3$.

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)

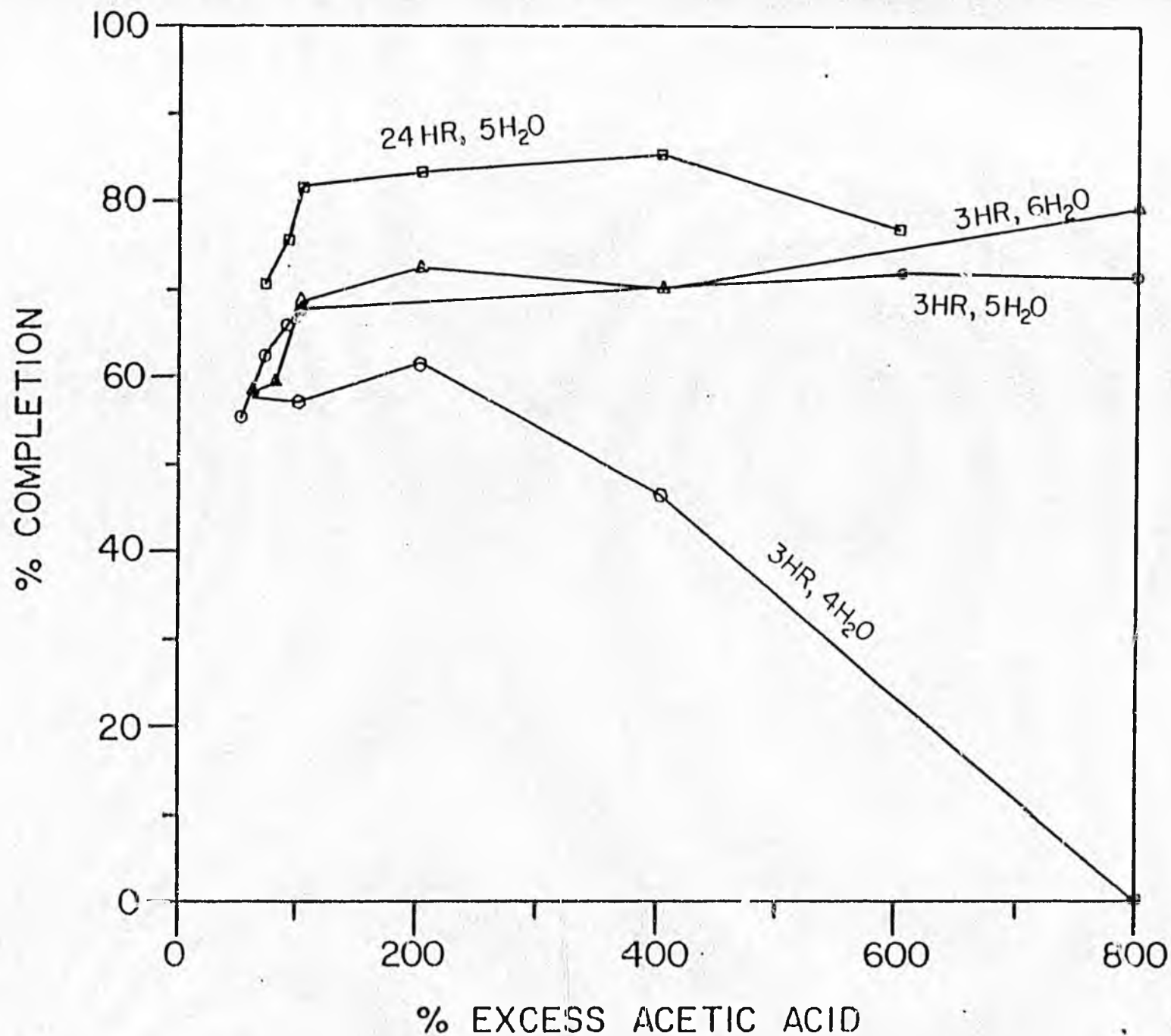


Figure 1. Reaction Behavior of Limestone and Acetic Acid: Percent Completion vs. Excess of Acid at Various Residence Times and Water Content.

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 plant. 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)

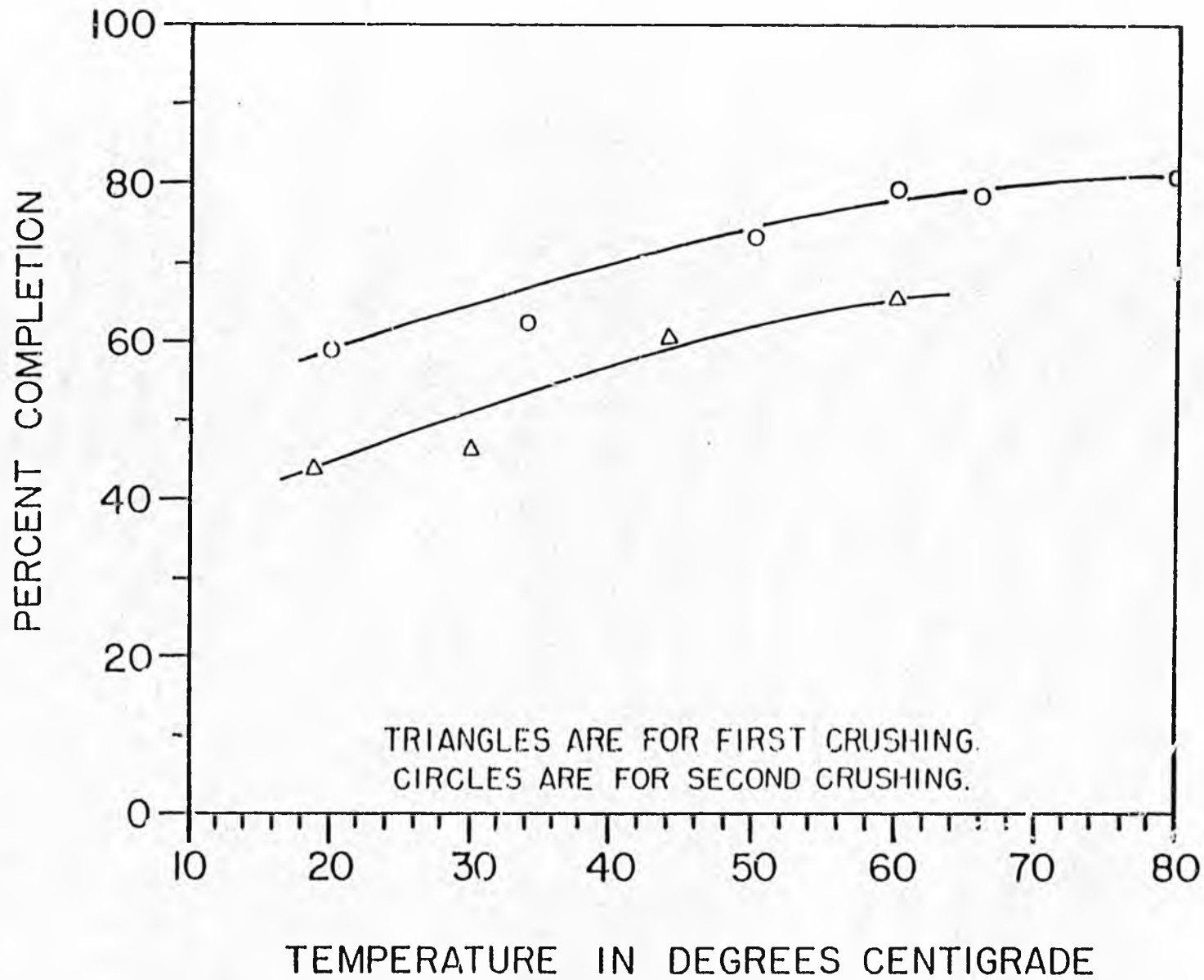


Figure 2. Reaction Performance for Limestone and 0% Excess Acetic Acid

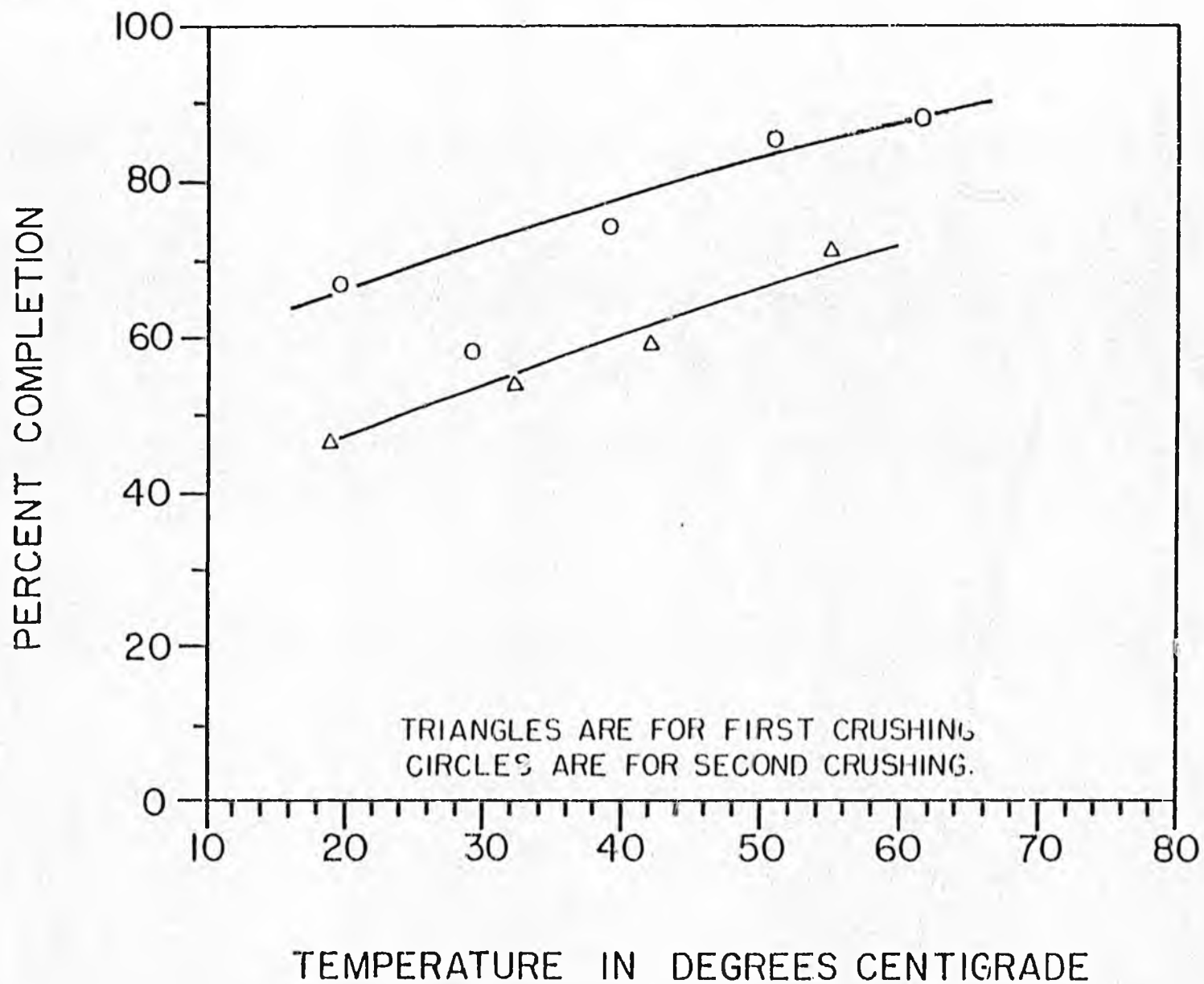


Figure 4. Reaction Performance for Limestone and 50% Excess Acetic Acid.

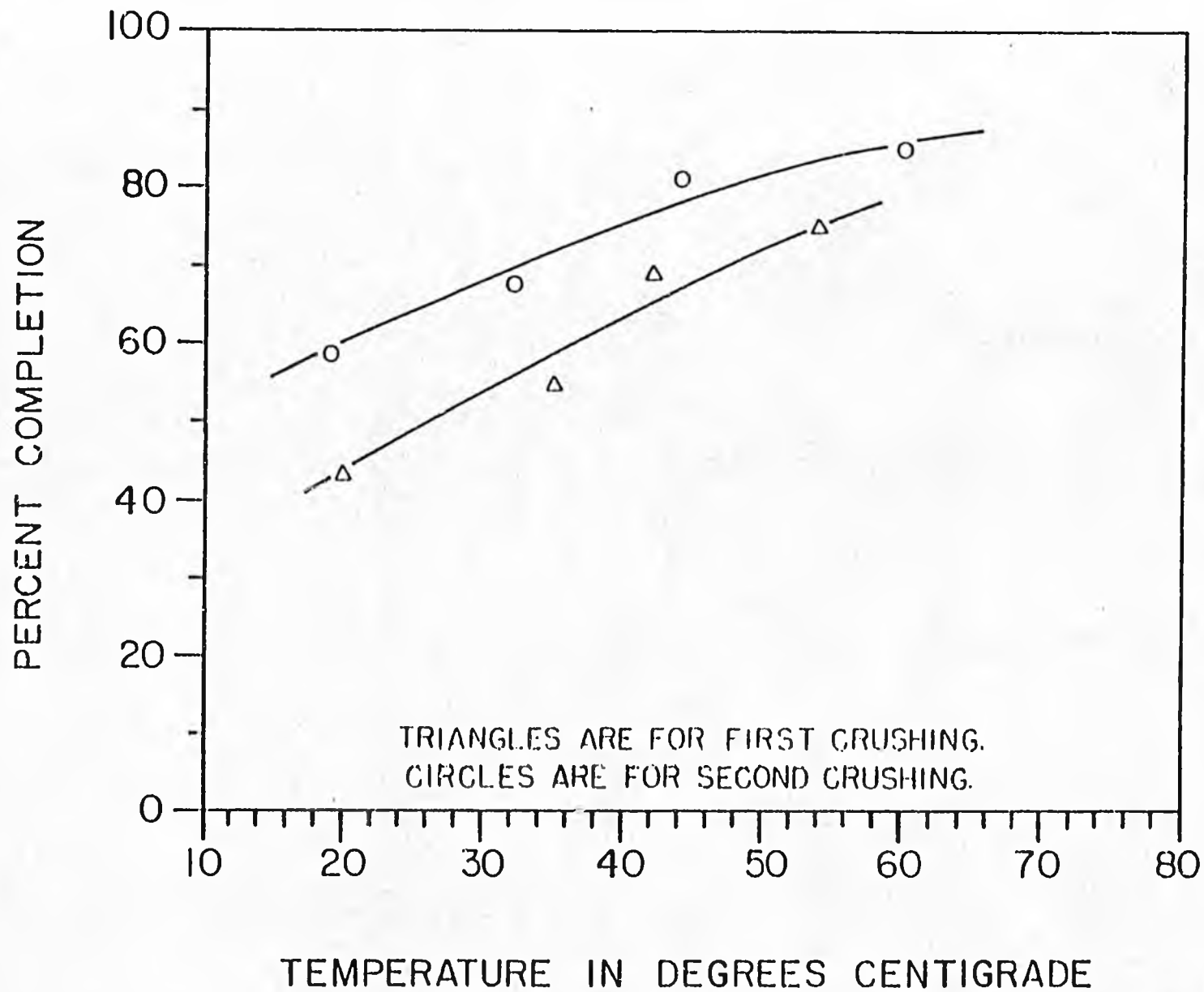


Figure 5. Reaction Performance for Limestone and 100% Excess Acetic Acid.

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

(12)

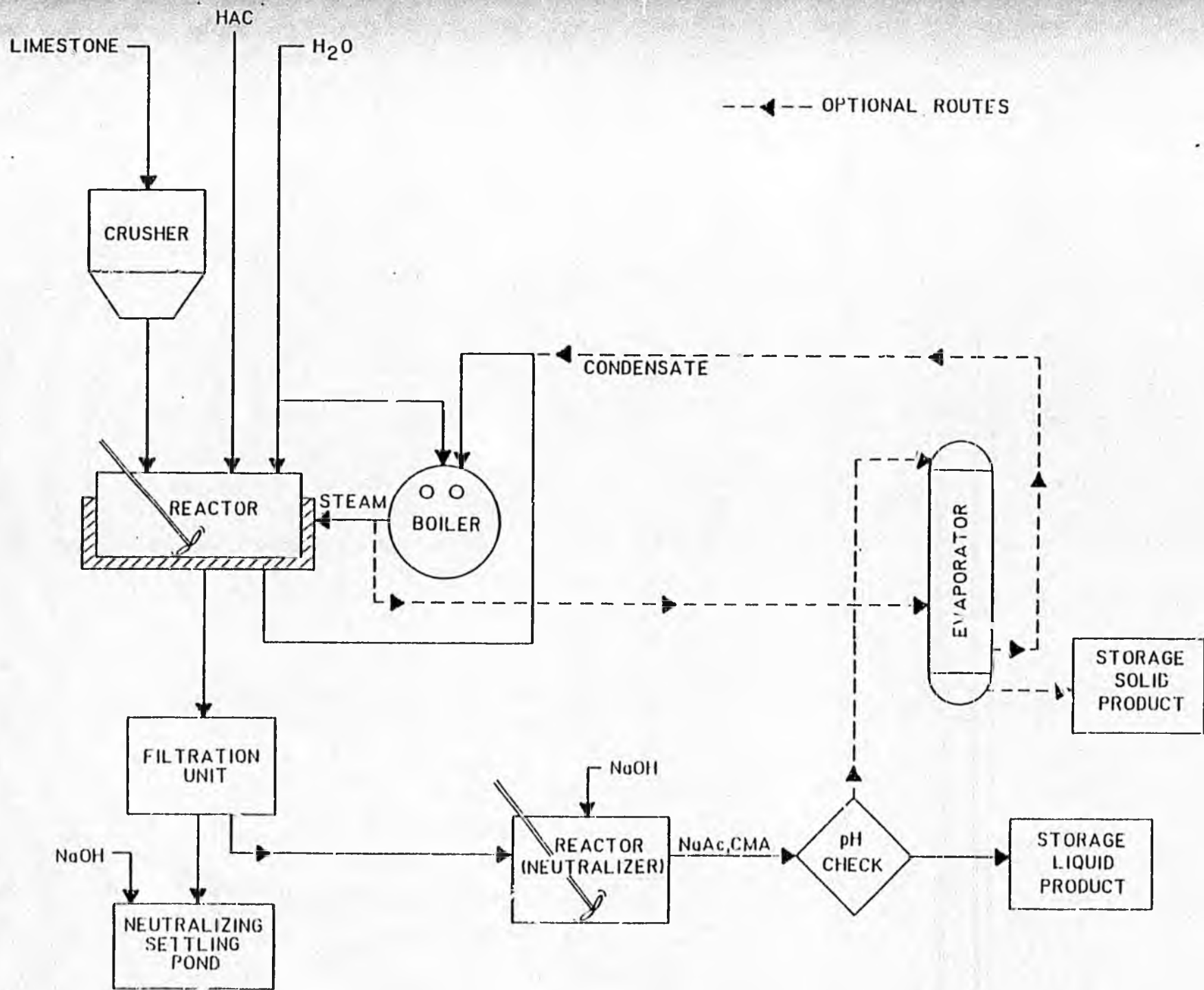


Figure 6. Block Diagram of Conceptual Process Design.

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 -----	\$182,000
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

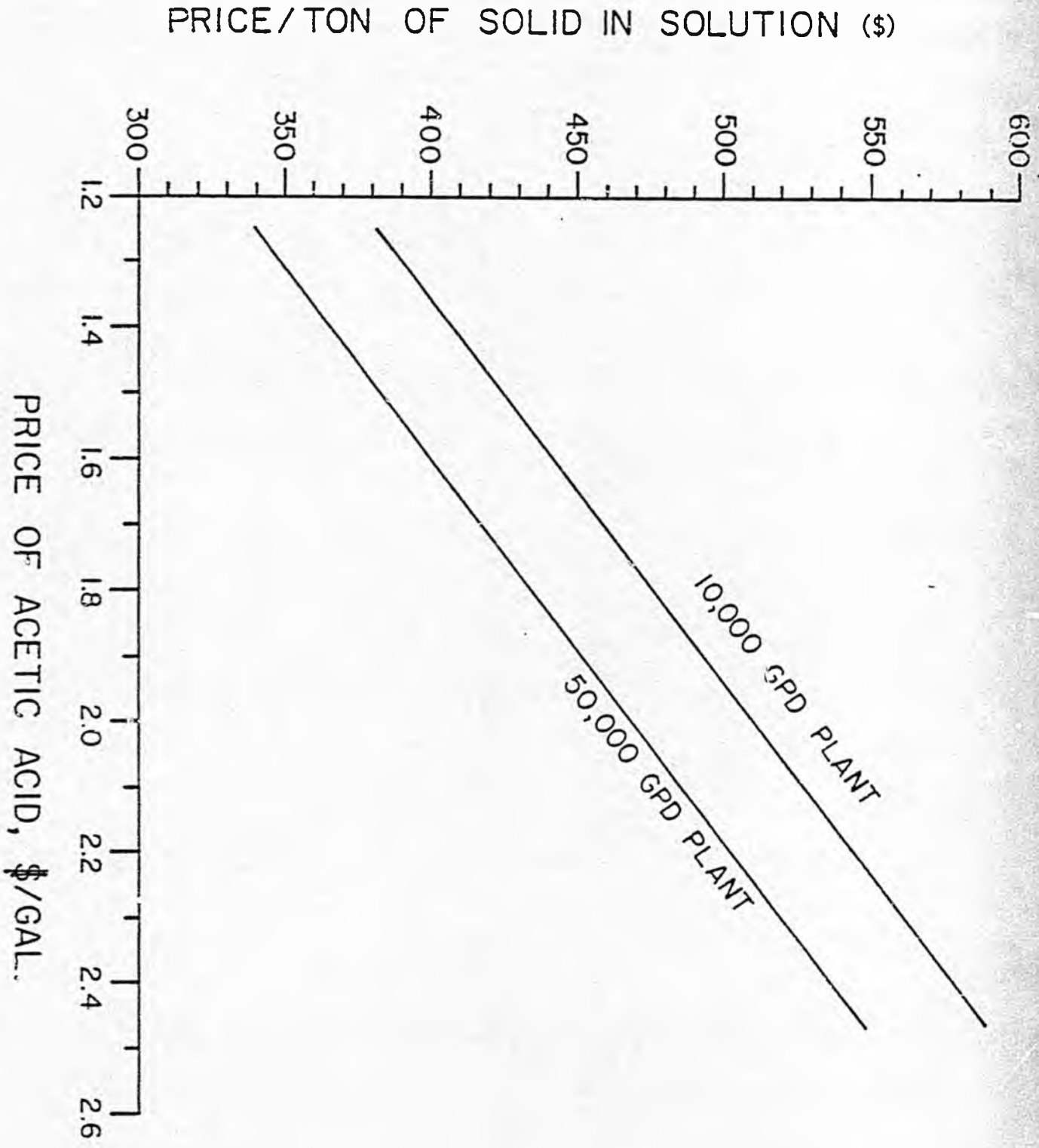


Figure 7. Required Selling Price of CMA for Various Acetic Acid Prices.

(17)
PRICE / TON OF SOLID IN SOLUTION (\$)

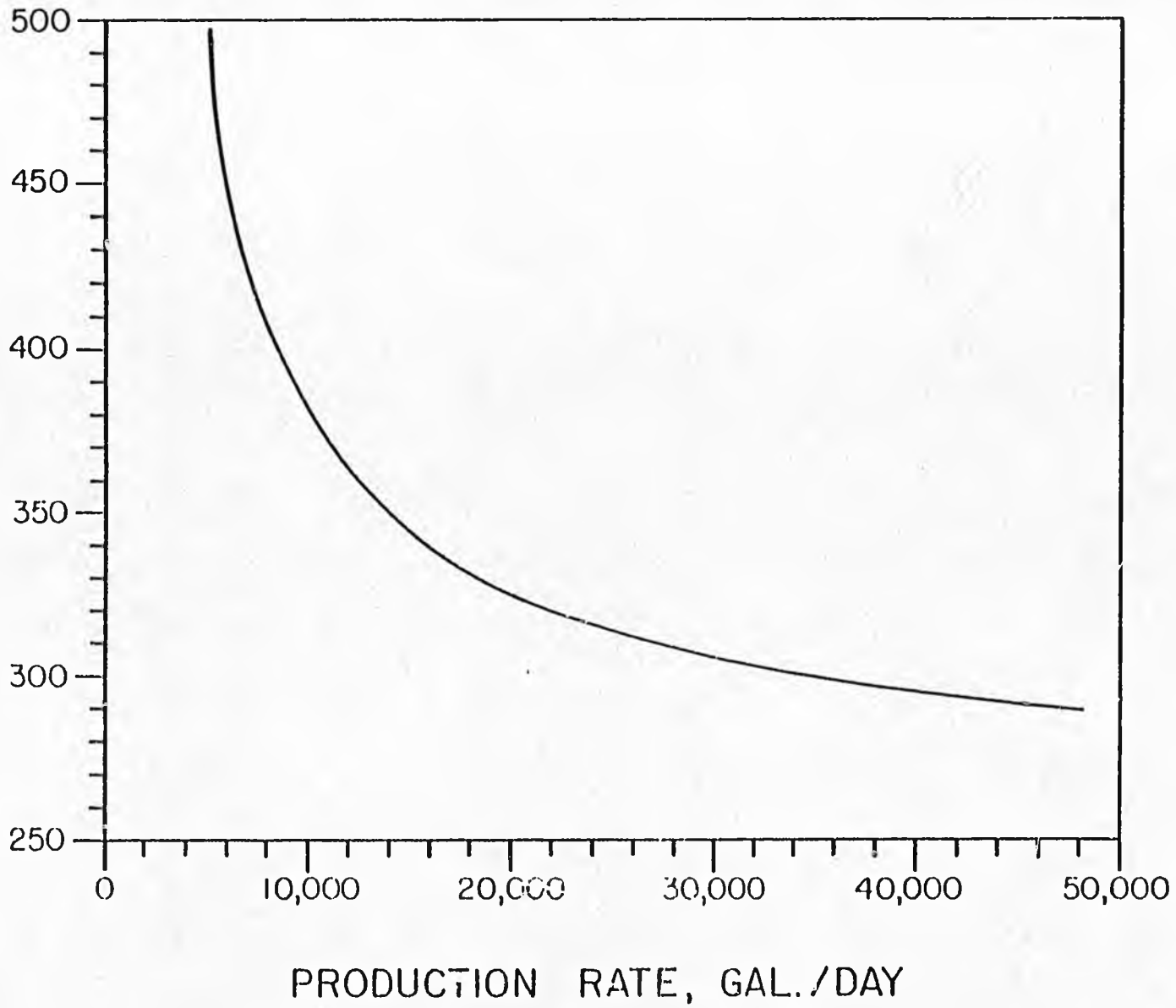


Figure 8. The Effect of Plant Size on the CMA Price. (\$ 1.25/ gallon acid)

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

(20)

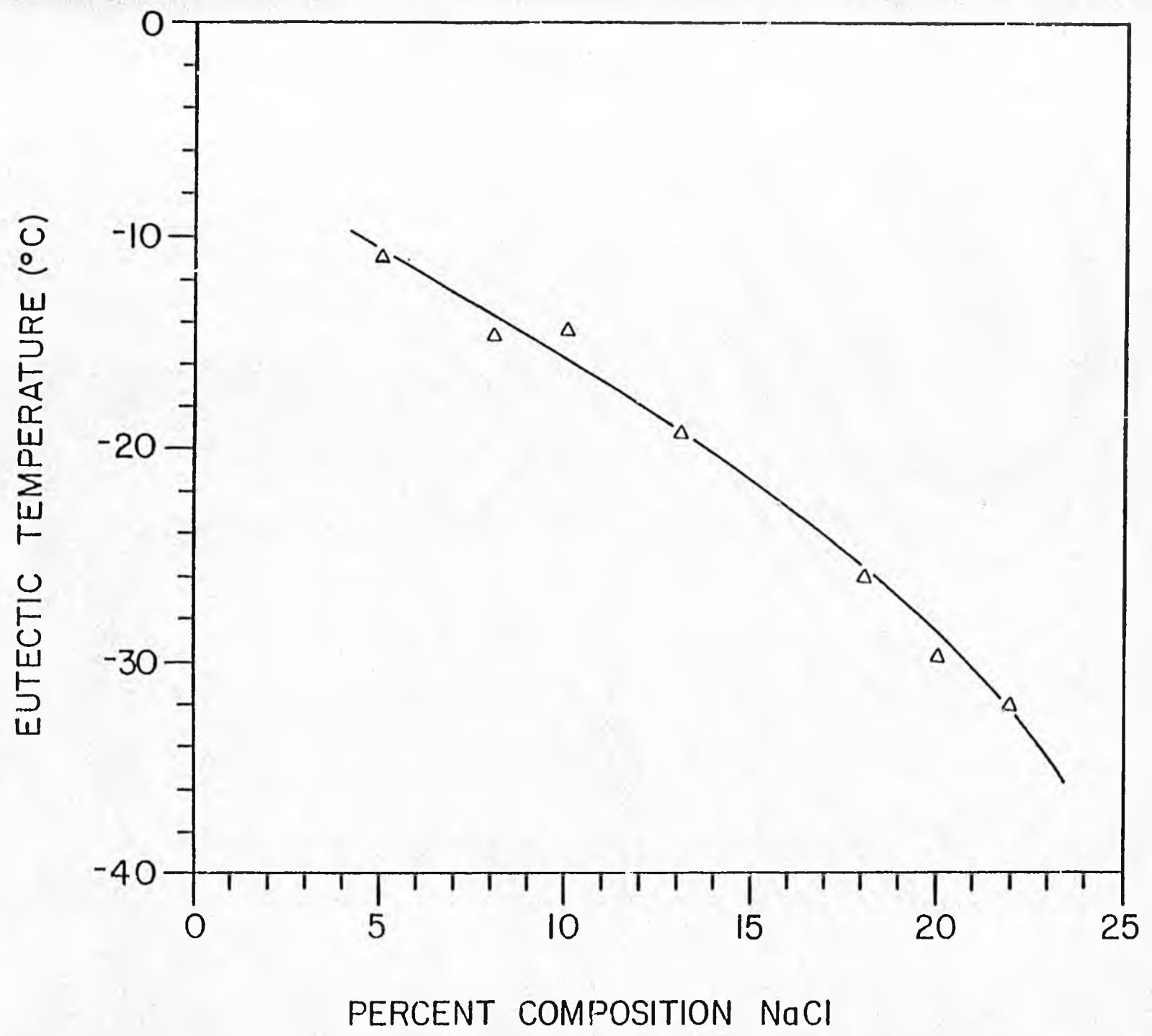


Figure 9. Experimental Determination of the Freezing Temperature of NaCl Solutions.

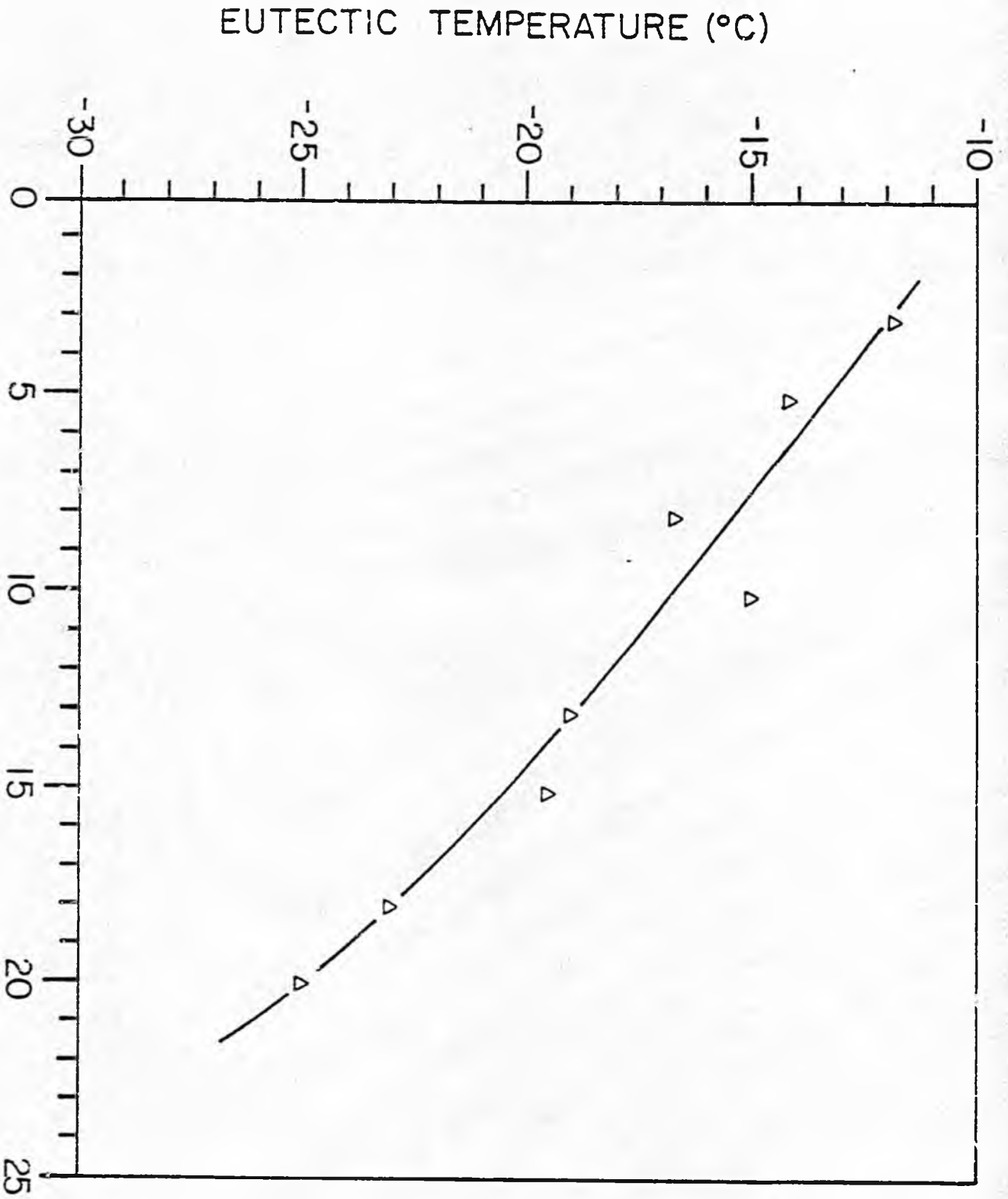
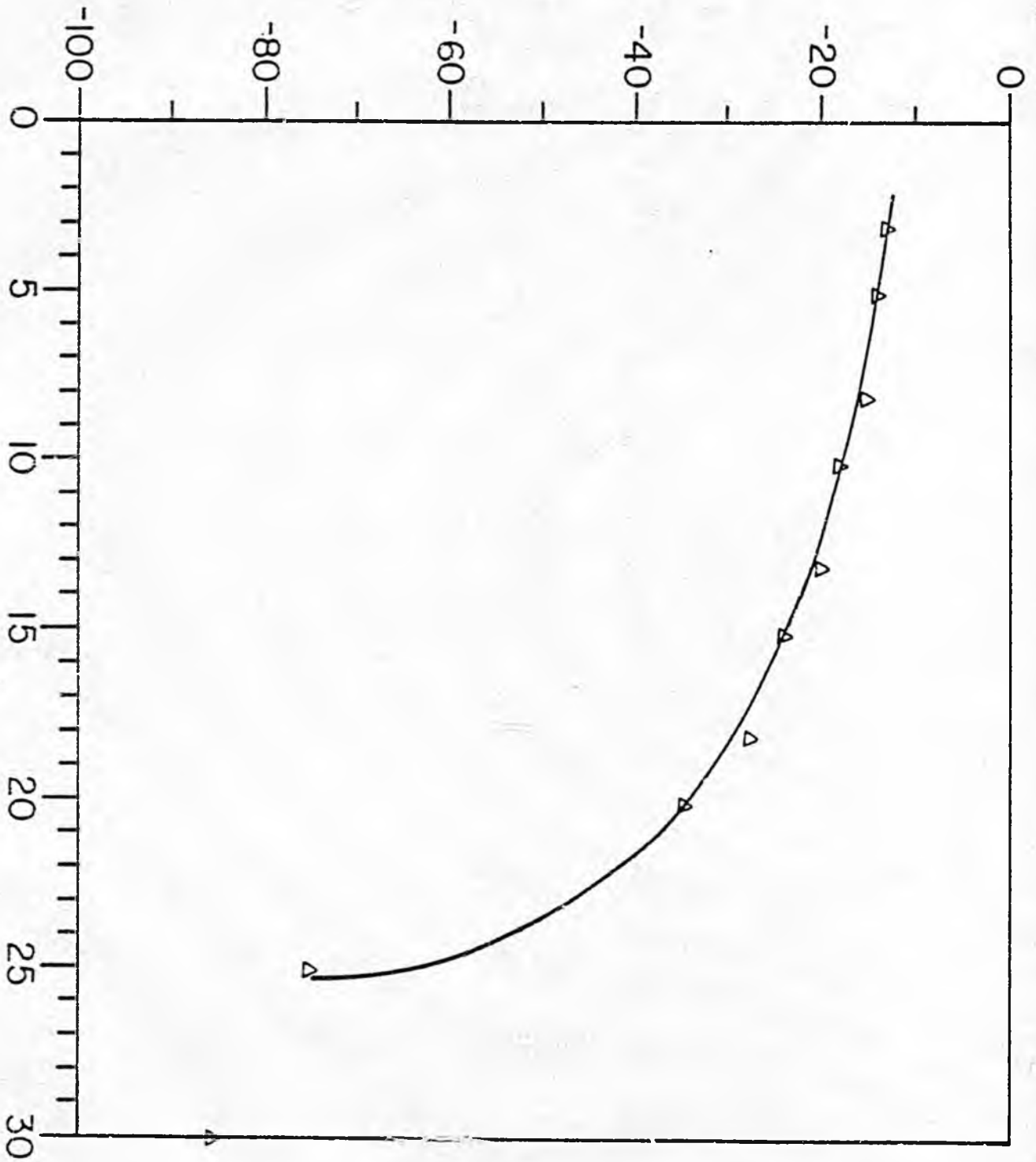


Figure 10. Eutectic Diagram of CdAc Solutions.

EUTECTIC TEMPERATURE (°C)



% COMPOSITION MgAc

Figure 11. Eutectic Diagram of MgAc Solutions

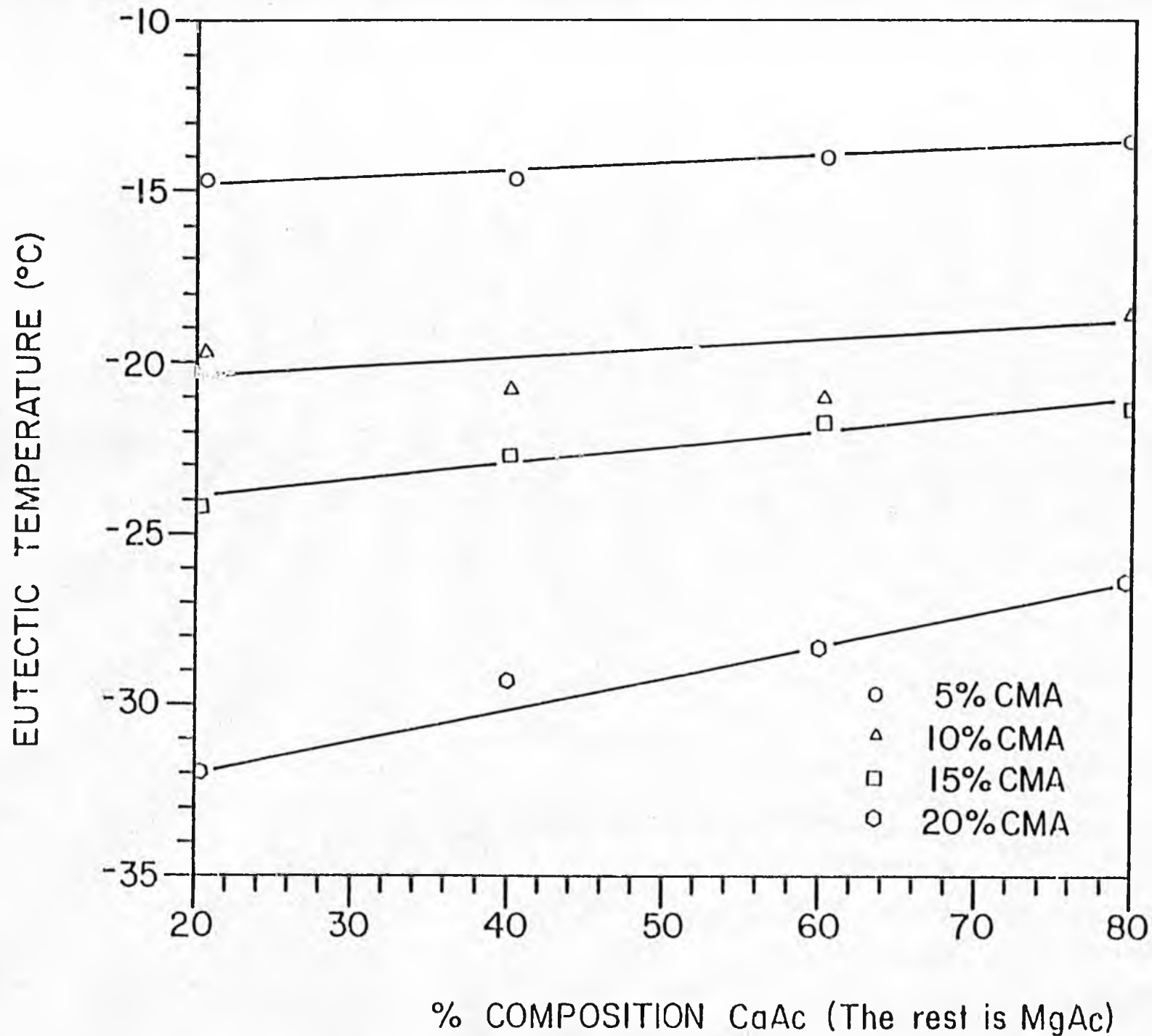


Figure 12. Eutectic Characteristics of Various Compositions of CMA Solutions.

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.

REFERENCES

1. Terry, Robert C., Road Salt, Drinking Water, and Safety, Ballinger Co., Cambridge, Mass., 1974.
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3. Hermann, William and A. Mantes, "Corrosive Effects of De-Icing Salts", Journal ANNA, Nov., 1966, pp 1457-1461.
4. Welch, B., et al., "Economic Impact of Highway Snow and Ice Control - State of the Art", FHWA-RD-77-20, Interim Report, Sept., 1976.
5. Peters, M. and K. Timmerhaus, Plant Design and Economics for Chemical Engineers, McGraw Hill, New York, 1968.

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)

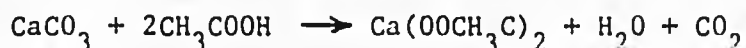
The variables in equation (1) can be evaluated:

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.

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

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

STATE OF ALASKA

DEPARTMENT OF TRANSPORTATION AND PUBLIC FACILITIES

MAINTENANCE AND OPERATIONS, INTERIOR REGION

Bill Sheffield, Governor

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:

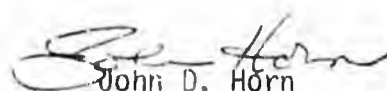
Enclosed for your information is a draft copy of the interim report on the second phase of this Department's study into the possible production of Calcium Magnesium Acetate (CMA) for use as a deicing agent on Alaskan roads.

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
Russell 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.

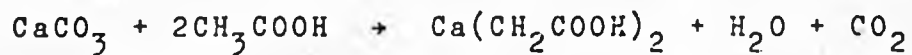
Furthermore, road salts are injurious to most forms of plant life. In the spring, a drive along heavily salted roadways in Anchorage reveals a virtual moonscape with dead or stunted plants. The success of ongoing roadway beautification projects in Anchorage and Fairbanks will be questionable with the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

PROCEDURE:

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.

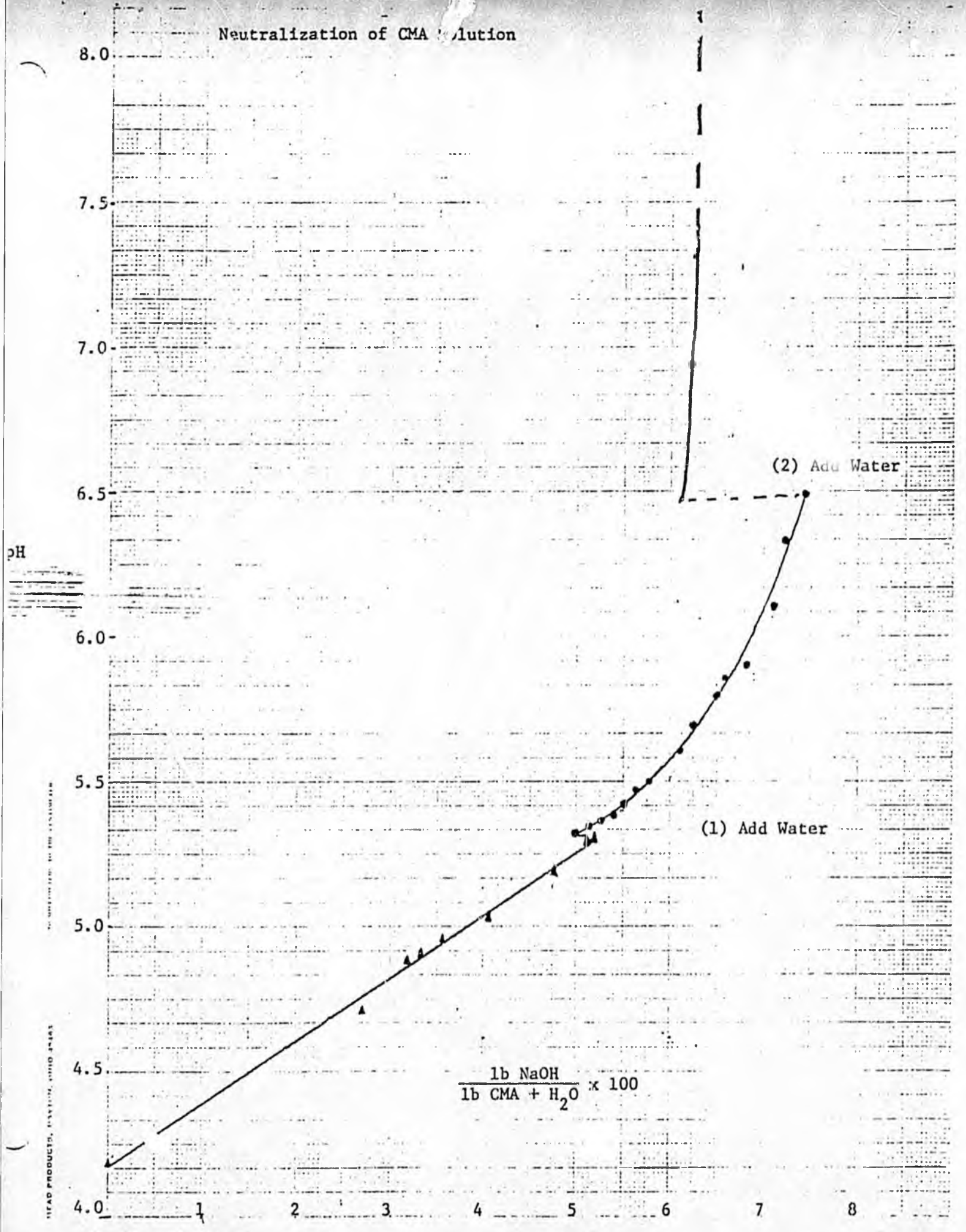
To further complicate neutralization, the reaction is not instantaneous. Figure 3 shows the response of pH with time following the addition of NaOH. About 5 minutes will elapse between the time of the NaOH addition and the final pH.

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



$$\frac{1b \text{ NaOH}}{1b \text{ CMA} + \text{H}_2\text{O}} \times 100$$

(1) Add Water

(2) Add Water

HEAD PRODUCTS, EASTON, OHIO 45121

pH

FIGURE 2

Titration of an Unknown Solution of CMA

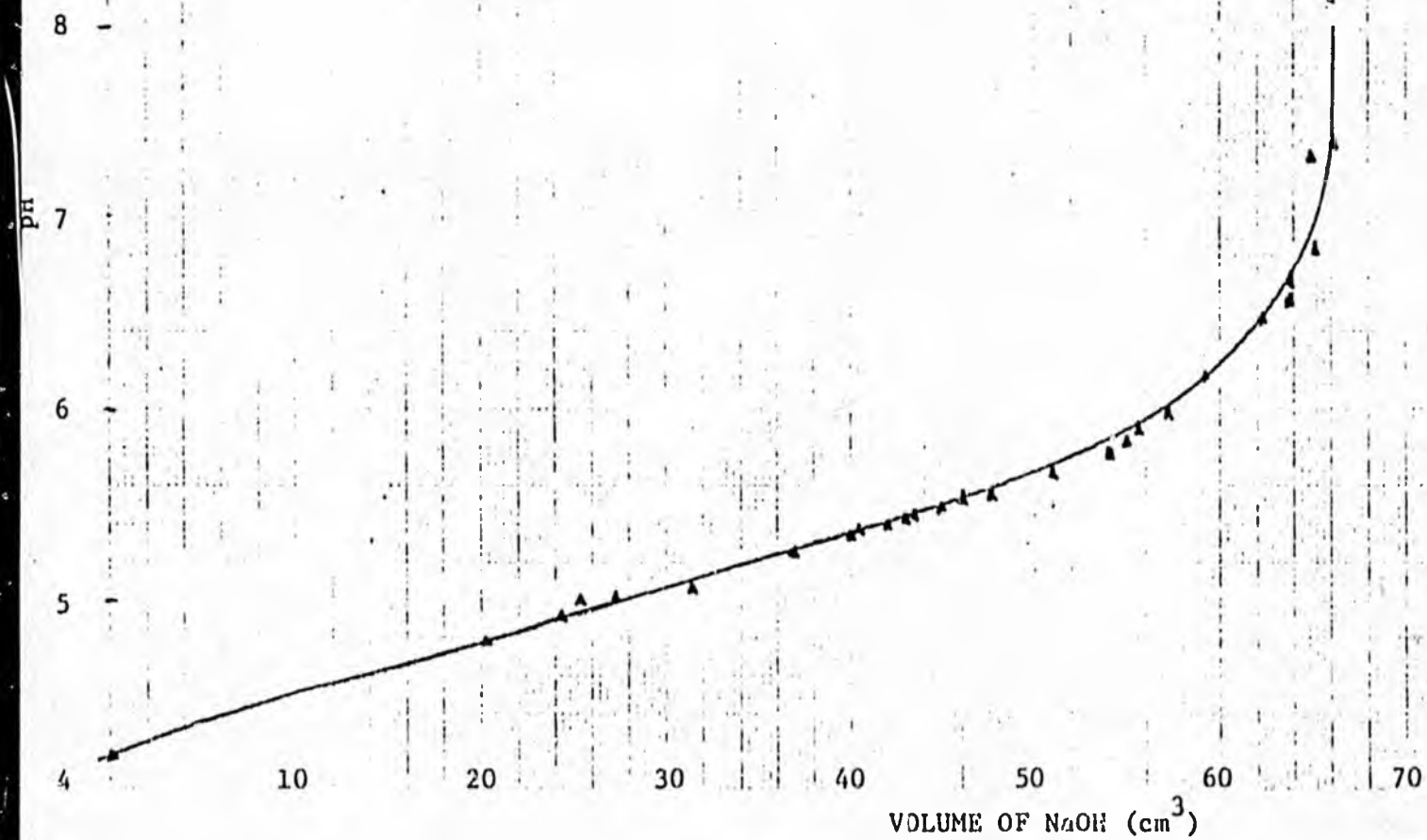


FIGURE 3

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

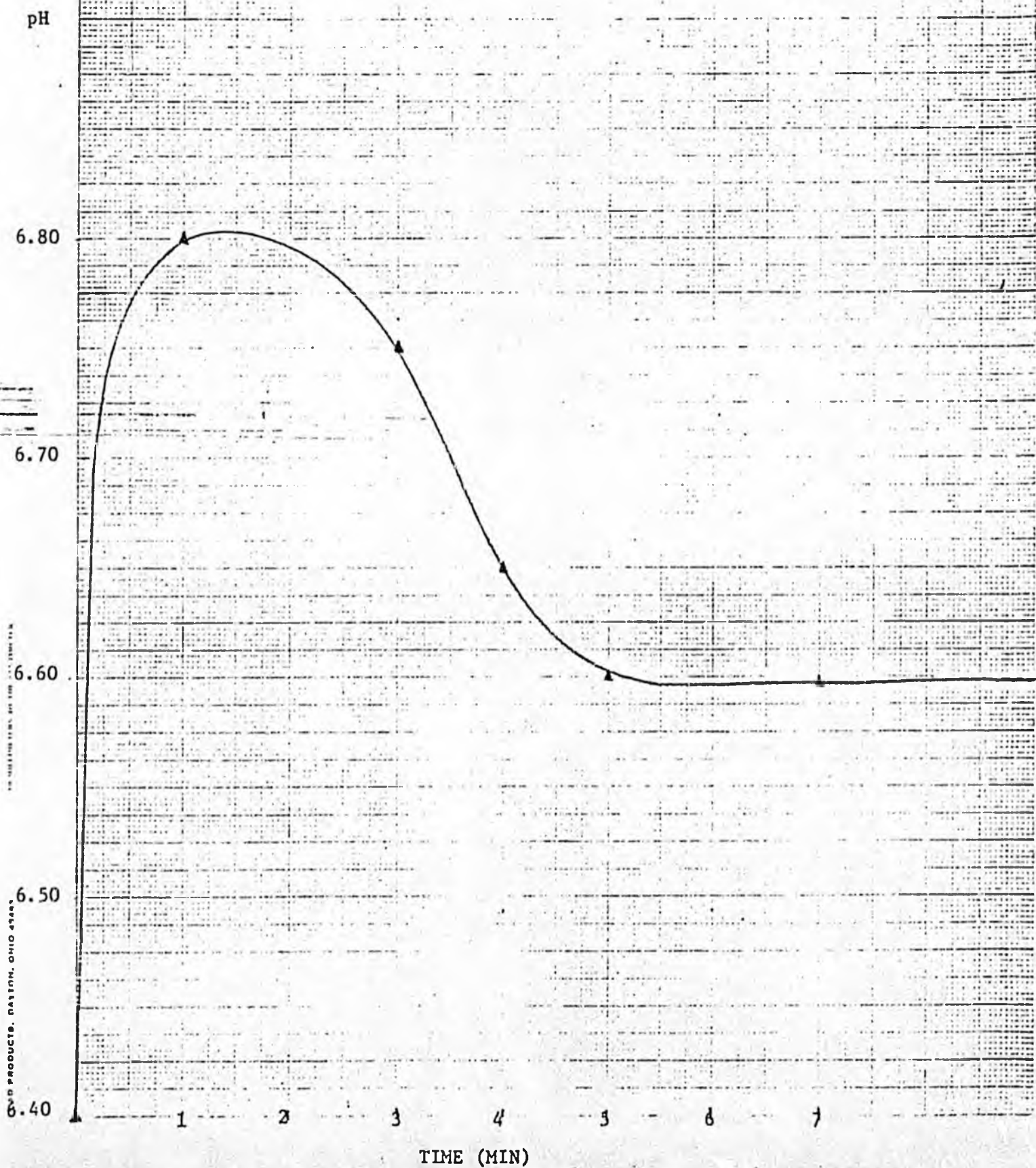
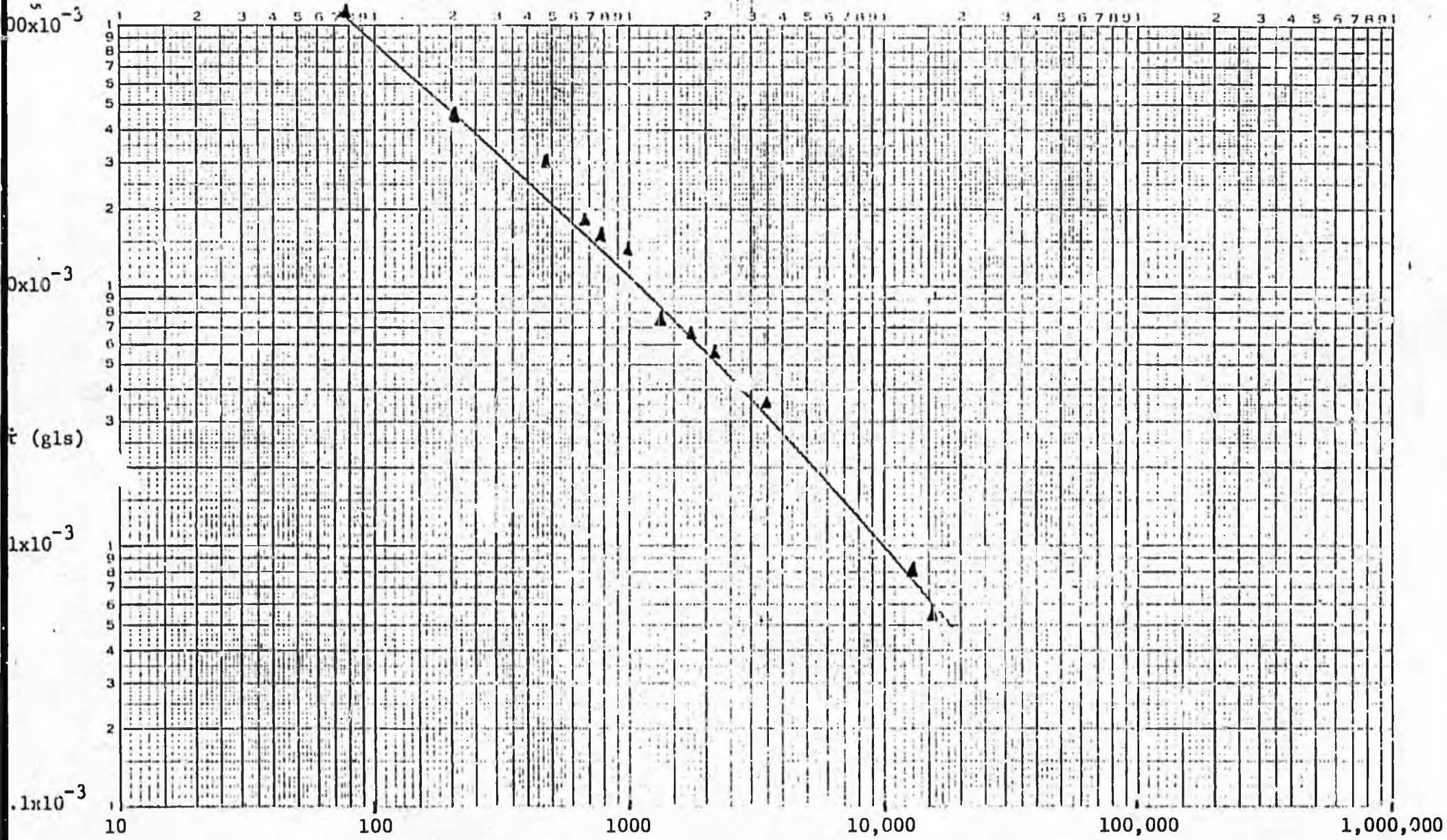


FIGURE 4



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

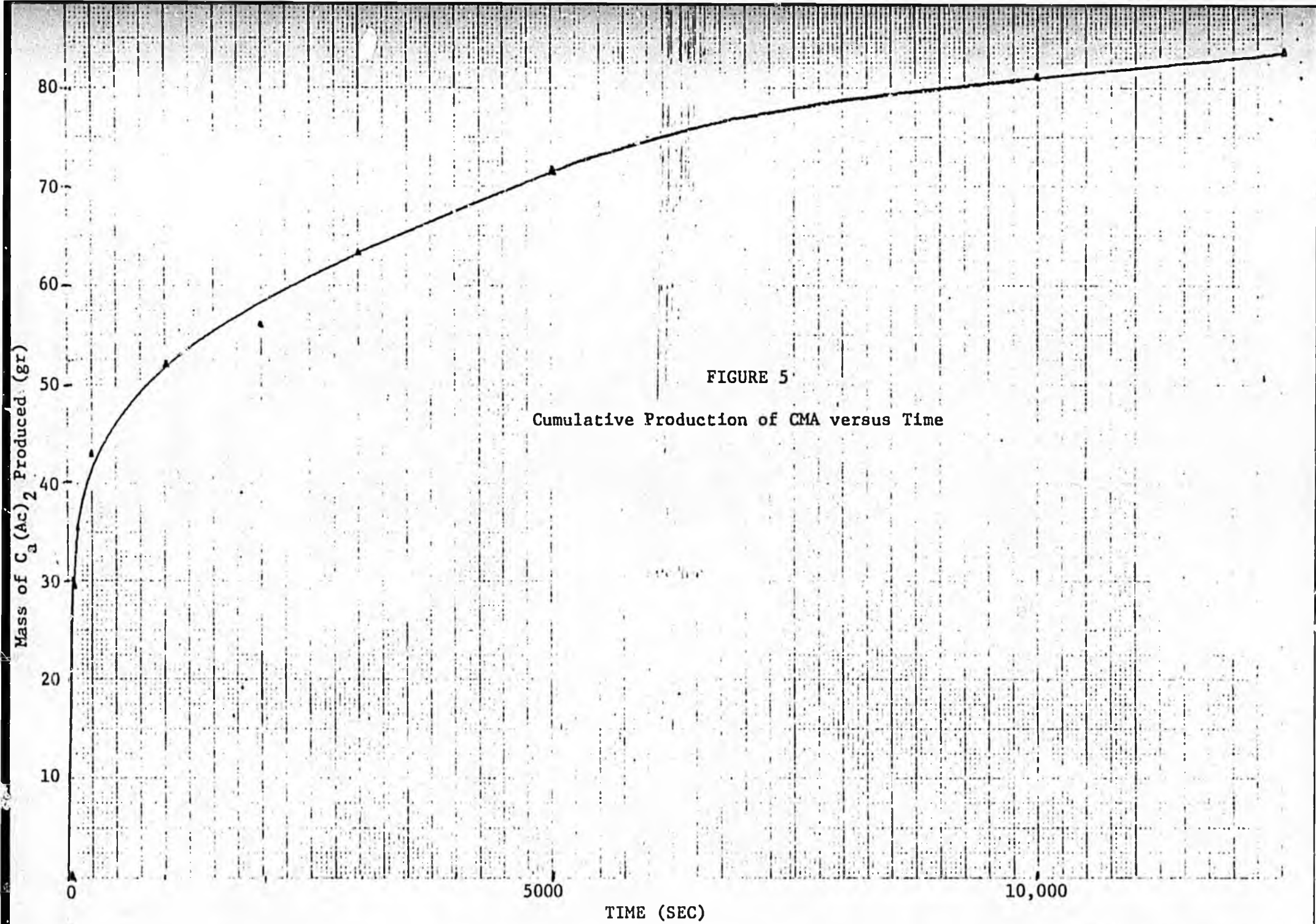


FIGURE 5

Cumulative Production of CMA versus Time

TO: MM
FROM: dz
DATE: 13/April 1983
RE: HCR 29/Calcium Magnesium Acetate

Complaints regarding rusting automobiles in Juneau prompted introduction of this resolution.

When trying to find statewide statistics on salt damage to automobiles, it was also found that salt has corrosive effects on bridge structures. Four bridge structures were replaced in Fairbanks at a cost of \$641,000.00. It is estimated that damage to bridges in Anchorage and the Southeast, where salt is used more frequently, is significantly higher. Unfortunately, there are no statewide Dept. of Transportation statistics regarding corrosive damage. Estimates on corrosion costs to automobiles alone in Alaska are approximately \$40 million annually. Attached are federal statistics.

Sodium Chloride (common salt) and Calcium Chloride are compounds that are presently used for de-icing.

Previous studies with Calcium Magnesium Acetate (CMA) have shown that it exhibits excellent de-icing characteristics. CMA is also non-corrosive, does not harm plants and does not pollute water. It has in fact been shown to be beneficial to soil. CMA also can work as a de-icing agent at temperatures below 20° F whereas salt can't.

Nowhere is CMA manufactured in bulk so that wide-scale testing can be done. The University of Alaska does have a bench scale pilot plant ready to produce this material. (U of A requested \$196. to complete the pilot plant. Bettisworth has put \$158.4 into his capital supplemental to fund this project.)

CMA can be produced from limestone, water, and acetic acid. Limestone is readily available in Alaska (Cantwell area is reported to have large quantities of this material). Currently, acetic acid must be imported from the Lower 48, but could be produced locally from refinery by-products if a market were shown available. This may open the doors for the state to become a major producer and exporter of CMA to a national or international market.

This resolution, if passed, will encourage the Dept. of Transportation to use CMA as a non-corrosive ice control agent and continue research on this material. By D. O. T. working with the University of Fairbanks and completion of the pilot plant, the effectiveness of CMA as a de-icing and dust control agent could be done in comparison with salt. Read fiscal note analysis.

Attached is a technical report from Massachusetts regarding salt damage. Finding indicate that the level of salt use should be reduced because of the harmful effects that it has on pollution of water supplies. I don't know if we want to get into the technical end of this. . . but encourage continued research.

(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
bcc: Patrick P. Ryan
John Bates
Larry Sweet ✓

RW:PPP:cst

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

By SCOTT YATES
Staff Writer

With nearly 100 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 it does 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 Eielson, 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 51 roads with the lowest priorities. "I can tell you I receive no special treatment," he said.

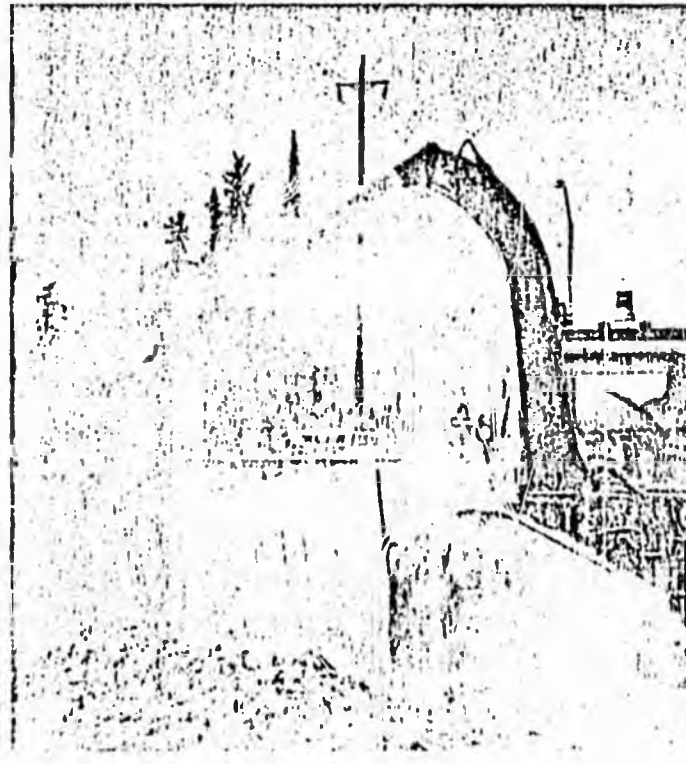
Bud Weber, assistant superintendent of the Public Works Garage, said after a snowfall, the first city roads to be plowed are the one-way streets downtown: Barnette, Lacey, Noble and Gaffney.

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 be-

(See SNOW, page 2)



FALL CLEANUP—A snowblower followed by a road sweeper 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 Curcio)

COMM = ST
DATE = 052483
TIME = 1330
YEAR = 83
DOC ID st 0524831330
HEADING

SENATE TRANSPORTATION
STANDING COMMITTEE
May 24, 1983
1:30 p.m.

Members Present: Senator Pappy Moss, Chairman
Senator Don Gilman
Senator Jan Faiks

Members Absent: Senator Bettye Fahrenkamp
Senator Jalmar Kerttula

CALENDAR HCR 29 Amended Title: Encouraging the Department of
Transportation and Public Facilities to use
calcium-magnesium acetate as an ice and dust
control agent.

WITNESS REGISTER
WITNESS:

Representative M. Mike Miller, Prime Sponsor
Alaska State Legislature
Pouch V
Juneau, Alaska 99811
Position Statement: Testified on HCR 29.

WITNESS:
Dick Hamilton, Acting Director
Maintenance and Operations, Southeast Region
Department of Transportation and Public Facilities
P.O. Box 3-1000
Juneau, Alaska 99801
Position Statement: Testified and answered questions.

PREVIOUS ACTION
HCR 29 No previous action to record on HCR 29.

ACTION NARRATIVE
TAPE#18, SIDE A.
Recording
Number 000
Chairman Moss brought the meeting of the Senate
Transportation Committee to order at 1:36 p.m.
Senator Faiks announced that SCR 27 had

Number 048

favorably impressed the Rules Committee which was going to calendar that resolution as soon as possible. Chairman Moss announced that HB 321 and HB 322 would go to a Subcommittee, the chairman of which would be Senator Kerttula who would select other members if necessary, and work in whatever time-frame is necessary to study the merits of those two bills. Moss then brought HCR 29 to the floor and introduced Representative M.M. Miller as the prime sponsor. Representative Miller noted that currently in the Southeast and Interior Regions chloride salts were being used for both ice and dust control, but that these were responsible for at least \$20 million in damage to cars through rust. Senator Faiks asked about the use of salt on the road in Juneau as compared to its use in Anchorage.

Number 101

Representative Miller stated that a representative from the Department of

Number 164

Transportation and Public Facilities was available to answer that, but that chloride salts were used all over the state. Miller explained that there had been developed a substance called calcium-magnesium acetate (CMA) which is not currently on the market but the ingredients of which are available in Alaska; limestone and petroleum by-products. Miller stated that the University was successfully mixing the CMA on an experimental basis, but on a small scale. Miller noted that Representative Bettisworth had money in the University budget now for research on a larger scale, and he stated that if the CMA worked out as expected, the state would probably want to hand it over to private industry. Miller stated that CMA had the potential to become an exported product and that the resolution simply encouraged the Department to continue as they are.

Representative Miller described CMA further as a

non-corrosive non-polluting substance, an effective de-icer, the ingredients of which were readily available, and he pointed out that the acetic acid could be produced as a refinery by-product.

Number 189

Senator Gilman asked if CMA had the same dust-controlling capability as calcium chloride. Representative Miller replied that CMA had the same effect as a dust-controlling substance.

Number 230

Dick Hamilton, Acting Director for Maintenance and Operations for the Southeast Region of the Department of Transportation and Public Facilities, introduced himself and noted that CMA acted in the same way as calcium chloride in that it sucked moisture from the atmosphere, and was being studied at this time as a dust-controlling agent. Hamilton added that in comparing de-icing in Juneau and Anchorage, a greater quantity of liquid calcium chloride was used because of the warmer temperatures in

Juneau which were responsible for a greater amount of black ice. Hamilton pointed out that at colder temperatures sand and other methods could be used. Hamilton noted that liquid calcium chloride was used over dry chemical because it cut the consumption by 50 percent, and it had an almost instant de-icing capability. Hamilton stated that if CMA were available it would be used in the same manner as the calcium chloride and that calcium chloride was used rather than sodium chloride because it was less corrosive.

Number 300

Senator Gilman asked the cost of a ton of calcium chloride. Mr. Hamilton replied that it was \$400 per ton, and that sodium chloride was about \$150 per ton, adding that preliminary reports indicate that CMA would be equivalent in cost to calcium chloride. Gilman asked how many tons were used each year statewide. Representative Miller noted that Alaska used

Number 350

830,000 tons of a mix including sand and gravel and 688 tons of calcium chloride and 76,000 tons of sodium chloride.

Chairman Moss noted that cost of the material was not the primary concern, but the dollars spent on automobiles, concrete, and bridges. Moss quoted from a report on cathodic protection of concrete bridge decks in Alaska, "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...In a bridge deck, different parts of the reinforcing steel become anodic or cathodic due to differences in residual stresses and impurities in the steel, cracks, moisture content, and aeration of the concrete, and other factors," and mentioned that the article pointed out that reinforced concrete was commonly used for bridge decks, and that there was an alarming increase in delamination and spalling.

st 0524831 DOCUMENT=
Number 374

7 OF 8 PAGE = 8 OF 10

Chairman Moss asked whether CMA could be used in the same manner as urea at airports but without the detrimental effects. Representative Miller pointed out that the urea could probably be replaced with CMA which was much less expensive. Mr. Hamilton commented that the Department used urea extensively as the FAA required that they not use a chloride de-icer. Senator Faiks explained that the high temperatures caused by jet takeoffs reacted with the substance used on the runways and created a blue smoke of pollutants. Moss asked whether CMA would cause that type of problem and was told by Hamilton that it would not.

Number 435

Mr. Hamilton stated that the Department of Transportation was in favor of HCR 29, and informed the Committee that DOT had put in \$42,000 along with Senator Bettisworth's \$158,000 to do the pilot plant study. Hamilton noted that the pilot plant was finished and they

expected to have 5,000 gallons of CMA ready for the coming winter, but that product was not yet available commercially although a North Pole refinery had expressed interest as far as contracting their own engineering study on how they could produce acetic acid. Hamilton explained that the industry didn't want to make the capital investments required before they were satisfied that everything would work, but he suspected that if DOT put out a request for bid proposals they'd find out whether or not there was interest in producing CMA.

Number 488

Chairman Moss noted that Limestone would be available locally in areas where it was needed. Mr. Hamilton restated that the production of CMA was a simple process. Senator Faiks asked about the white residue left by CMA. Representative Miller pointed out that the white residue left by chlorides was corrosive whereas that left by CMA was not. Moss noted that the Committee had

seen a series of bills recently that addressed the future, including the one addressing the High Float Emulsion asphalt and the one before the Committee, and he stated that it represented great strides forward in the maintenance and construction of the highways of the State.

Number 520

Chairman Moss asked for a motion to move HCR 29 out of the Transportation Committee. Senator Faiks moved HCR 29 out of Committee with individual recommendations. As there were no objections it was so ordered by Chairman Moss. Chairman Moss adjourned the Senate Transportation Committee meeting to a close at 2:00 p.m.

Number 525

END OF DOCUMENT

COMMITTEE REPORT

HOUSE

FURTHER:

(9)

3/30/83

Date: 4/14/83

Mr. Speaker:

The Committee on TRANSPORTATION has had HCR 29

Encouraging the Department of Transportation and Public Facilities to use calcium-magnesium acetate as an ice and dust control agent.

under consideration and reports it back as follows:

- do pass do not pass
- do pass with attached amendments(s)
- replace with CS for _____ same title
 new title
- and recommends _____
- AND attaches a "Letter of Intent" New Fiscal Note
- reports it back without recommendation Zero Fiscal Note Attached
- referred to the _____ Committee

**MEMBERS SIGNING
DO PASS**

**MEMBERS HAVING
OTHER RECOMMENDATIONS:**

[Signature]
[Signature]
Mike Parks Do Pass
M.W. Miller Do Pass

[Signature]
[Signature]

M.W. Miller Vice-Chairman
CHAIRMAN

TO: MM
FPCM: dz
DATE: 13/April 1983
RE: HCR 29/Calcium Magnesium Acetate

Complaints regarding rusting automobiles in Juneau prompted introduction of this resolution.

When trying to find statewide statistics on salt damage to automobiles, it was also found that salt has corrosive effects on bridge structures. Four bridge structures were replaced in Fairbanks at a cost of \$641,000.00. It is estimated that damage to bridges in Anchorage and the Southeast, where salt is used more frequently, is significantly higher. Unfortunately, there are no statewide Dept. of Transportation statistics regarding corrosive damage. Estimates on corrosion costs to automobiles alone in Alaska are approximately \$40 million annually. Attached are federal statistics.

Sodium Chloride (common salt) and Calcium Chloride are compounds that are presently used for de-icing.

Previous studies with Calcium Magnesium Acetate (CMA) have shown that it exhibits excellent de-icing characteristics. CMA is also non-corrosive, does not harm plants and does not pollute water. It has in fact been shown to be beneficial to soil. CMA also can work as a de-icing agent at temperatures below 20°F whereas salt can't.

Nowhere is CMA manufactured in bulk so that wide-scale testing can be done. The University of Alaska does have a bench scale pilot plant ready to produce this material. (U of A requested \$196. to complete the pilot plant. Bettisworth has put \$158.4 into his capital supplemental to fund this project.)

CMA can be produced from limestone, water, and acetic acid. Limestone is readily available in Alaska (Cantwell area is reported to have large quantities of this material). Currently, acetic acid must be imported from the Lower 48, but could be produced locally from refinery by-products if a market were shown available. This may open the doors for the state to become a major producer and exporter of CMA to a national or international market.

This resolution, if passed, will encourage the Dept. of Transportation to use CMA as a non-corrosive ice control agent and continue research on this material. By D. O. T. working with the University of Fairbanks and completion of the pilot plant, the effectiveness of CMA as a de-icing and dust control agent could be done in comparison with salt. Read fiscal note analysis.

Attached is a technical report from Massachusetts regarding salt damage. Finding indicate that the level of salt use should be reduced because of the harmful effects that it has on pollution of water supplies.

SUMMARY

Economic Analysis -- Environmental Impact Highway De-Icing

320 references provided this data:

- * Total annual national cost of salt related damages =
\$3 billion
(about 15 times the annual cost for salt & application)
(6 times the entire annual national budget for snow & ice removal)
- * largest cost from vehicle damage
- * most serious damage seems to be water pollution & degradation of health which may result
(can't put a dollar figure on this)

Findings DO indicate that salt use should be reduced. Amount of reduction should be determined on basis of local conditions. Damages are very large but not uniform across all locations.

There is a huge dollar figure on annual cost to the states from road salt use. (SEE attached - pg. 1)

Heavy salt use can upset the natural ecological balance -- this cannot be assigned a dollar figure.

Several states have found increases of salt in groundwater and surface drinking water -- this has been directly linked to de-icing salts.

EPA/600/2-76/105
May 1976

PB 253 268
Environmental Protection Technology Series

*An Economic Analysis of the
Environmental Impact of
Highway Deicing*



PRODUCED BY
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INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA 22161

Municipal Environmental Research Laboratory
Office of Research and Development
U.S. Environmental Protection Agency

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA-600/2-76-105	2.	3. RECIPIENT'S ACCESSION NO. PB-253 268
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	6. PERFORMING ORGANIZATION CODE	
7. AUTHOR(S) Donald M. Murray Ulrich F. W. Ernst	8. PERFORMING ORGANIZATION REPORT NO.	
9. PERFORMING ORGANIZATION NAME AND ADDRESS Abt Associates Inc. 55 Wheeler Street Cambridge, Massachusetts 02138	10. PROGRAM ELEMENT NO. 13C611	
	11. CONTRACT/ NO. 68-03-0442	
12. SPONSORING AGENCY NAME AND ADDRESS Municipal Environmental Research Laboratory Office of Research and Development U.S. Environmental Protection Agency Cincinnati, Ohio 45268	13. TYPE OF REPORT AND PERIOD COVERED Final 8/74 to 7/75	
	14. SPONSORING AGENCY CODE EPA-ORD	

15. SUPPLEMENTARY NOTES
Hugh Masters, Project Officer, FTS 342-7541

16. ABSTRACT

This study involves an analysis of the cost of damages that result from the use of salt (sodium chloride and calcium chloride) on highways to melt snow and ice. A large literature search and several surveys were carried out in order to determine the types and extent of damages that have occurred. The report contains over 320 references.

An in-depth analysis was performed on all of the data obtained. The major cost sectors examined were: Water supplies and health, vegetation, highway structures, vehicles, and utilities. For each of the sectors a cost estimate was developed. ~~The total annual national cost of salt related damage approaches \$3 billion dollars or about 15 times the annual national cost for salt purchase and application. While the largest costs result from damage to vehicles, the most serious damage seems to be the pollution of water supplies and the degradation of health which may result.~~ It is particularly difficult to assign costs in this latter area and therefore the estimate may substantially understate the actual indirect costs to society.

These findings indicate that the level of salt use should be reduced. The amount of the reduction should be determined on the basis of local conditions.

PRICES SUBJECT TO CHANGE

17. KEY WORDS AND DOCUMENT ANALYSIS		
a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Deicers Snowstorms Ice Control Economic Analysis Sodium Chlorides Water Pollution	Salt Stormwater Runoff Environmental Impact Snow Control	13E
18. DISTRIBUTION STATEMENT Release to Public	19. SECURITY CLASS (This Report) Unclassified	21. NO. OF PAGES
	20. SECURITY CLASS (This Paper) Unclassified	

10

SECTION 1

FINDINGS AND CONCLUSIONS

1.1 SUMMARY OF FINDINGS

There have been a substantial number of reports of salt related damage in the literature. Most of the reports are deficient in hard cost data. Consequently, by examining different small subsets of the data, various individuals have arrived at opposite conclusions: in some cases that salt damage is insignificant and in other cases, that road salting must be discontinued completely. Examination of all of the literature and contact with hundreds of persons and agencies who are aware of salt related damage has led to the finding that, in general, the damages are very large although not uniform across all localities. Through analysis of all of the available data, the best estimate (in many cases the lower bound) of the annual cost to the snowbelt states that results from the use of road salt is as follows:

	<u>Total (in millions)</u>
Water Supplies and Health	\$ 150
Vegetation	50
Highway Structures	500
Vehicles	2,000
Utilities	10
Salt Purchase and Application	200
Total	\$ 2.91 Billion

damage to vehicles alone is 210 x the salt purchase & application cost \$4,000,000 in Alaska

(500,000 / 2,500,000) (2,000,000) \$4,000,000

Furthermore, heavy salt use in many instances upsets the natural ecological balance, resulting in damages which cannot be assigned a dollar figure. This is one of the many reasons that the above dollar amounts must be considered as lower bounds. The most potentially serious of all these damages are the irreversible ones, such as the risk of increased hypertension that results from the heightened levels of sodium in water supplies. For example, groundwater supplies have been most severely affected. Over 90 communities in Massachusetts have one or more supplies

with a sodium content greater than 20 mg/liter, the maximum allowed for persons on low sodium diets. Over 30 water supplies in Connecticut contain more than 20 mg/l sodium and the number is increasing. As much as 5% of the population consuming water contaminated by road salt may be adversely affected.

The use of salt for winter maintenance generally results in better traction on the highways, but because of a number of confounding factors, especially driver behavior, the link between salt and safety has not been proved. While several studies have reported that salt reduces accidents, the methods of data collection and analysis have been found to be mathematically unsound.

Finally, carefully designed reduced salting policies seem to have gained public acceptance as a result of public information programs. The most notable case is the State of Connecticut where state salt use was reduced by 33% because of rising sodium content in water supplies. There is every reason to believe that the residents of individual cities and towns or other states would accept a salt reduction if the salt related damages were made known to them.

1.2 CONCLUSIONS

In the past a number of claims have attempted to downgrade the seriousness of road salt related damage by placing emphasis on the comparisons of the effectiveness of salt and sand, or by concentrating on the lack of importance of vegetation in comparison to human lives (i.e., safety on the roads). Because these claims do not address the whole problem, they are superficial, misleading, and in a few cases, irresponsible. The facts are:

- Several states have experienced significant increases of salt in groundwater and surface drinking water supplies that have been directly linked to the use of deicing salts.
- In particular cases, the levels exceed Public Health Service safety standards set in 1962 and in most cases the levels exceed the standards set by leading researchers, heart specialists and the American Heart Association.
- The cost in terms of permanent health degradation is extremely difficult to measure, but is likely to be very high.
- The cost of actual damage to vehicles, highways and structures, utilities, and vegetation are immense. ~~The annual damage costs at a very lower bound, approach \$3 billion.~~ This "hidden" cost is almost 15 times the annual national budget for the purchase and application of road salt, and out 6 times the entire annual national budget for snow and ice removal.

The implications of these facts are clear. Without a doubt the most serious problem is our water supplies. While the cost of damage to bridge decks and vehicles is high, but reversible, the damage to health may not be reversed. We can no longer afford to ignore the fact that we are depositing large quantities of salt into the water that nature provides us and upon which are dependent every moment of our lives. The most advanced medical research indicates that water with more than 20 mg/l sodium is unhealthy and detrimental to a substantial fraction of the population. The American Heart Association supports this fact. Disregard for the quality of drinking water in this and any instance is extreme negligence and we must face the issue squarely. Road salt may be only one of the many serious pollutants in our environment, but that is no excuse to allow the present situation to exist any longer. In order to avoid further damage and high costs, salt use for winter maintenance must be reduced in many areas.

Na 22.99

NaCl gram molecule

= 58.44 grams

35.45

.051 gram salt/lit.

20 ppm

.393 gm Na/gm of NaCl

.051 gm NaCl //



PETROLEUM ENGINEERING

(907) 474-7734

April 11, 1983

Representative Mike Miller
Democrat, Juneau
Pcuch V
Mailstop 3100
Juneau, AK 99811

Dear Representative Miller:

I am quite pleased with your demonstrated interest on the problems of deicing and our work to develop effective alternative deicing agents. The Research Section of the Alaska D.O.T. has already exercised a significant amount of effort on the subject and they have been most supportive and cooperative with us. Your resolution will certainly help our combined efforts.

I would like to take this opportunity to supply you with certain facts on the benefits and costs of road deicing.

A report by the Institute for Safety Analysis (Brenner and Moshman, 1976) indicates the following benefits associated with road deicing.

TABLE 1

ANNUAL ECONOMIC BENEFITS FROM ROAD DEICING

<u>Category</u>	<u>Amount (In \$ Millions)</u>
Reduced Wage Losses	
(i) Lateness to work	12,200
(ii) Work Absenteeism	4,800
Reduced Production Losses	11,300
Reduced Losses in Goods Shipments	970
Reduced Fuel Costs	330
	<hr/>
TOTAL	29,600

The numbers in Table 1 are inflated figures from Brenner and Moshman (1976) including 61% inflation to date.

While the annual economic benefits to the "national good" are unassailable, there are certain major costs associated with using the present deicing agents.

Sodium chloride (the common salt) and calcium chloride are the presently used compounds. By depressing the freezing temperature of water, they allow the melting of ice and, therefore, its removal either by natural runoff or by the movement of vehicles. Murray and Ernst (1976) have estimated the costs of road deicing.

TABLE 2

ANNUAL COST OF ROAD-SALTING

<u>Category</u>	<u>Amount (In \$ Millions)</u>
Water Supplies and Health	242
Vegetation	81
Highway Bridge Decks	805
Vehicles	3,220
Utilities	16
Salt Purchase and Application	332
<i>NO AUTO REPAIR!</i> TOTAL	4,686

The numbers in Table 2, also inflated since the 1976 figures, offer several interesting conclusions. The ratio between the annual benefits (Table 1) and the annual costs is 6.3 offering substantial reasons why road deicing, when viewed on the national scale, is a desirable undertaking.

However, a comparison between the cost of salt purchase to the damages that are associated with its use (1/15) leads to the obvious conclusion that alternative, noncorrosive and environmentally benign deicers are extremely attractive.

Rep. Miller
Page Three (3)
April 11, 1983

My estimates are that in Alaska, the corrosion costs to automobiles alone are approximately \$40 million annually. This figure was derived by assuming 400,000 vehicles in Alaska sustaining an average of \$100 corrosion damage annually. Considering that no salts are used for deicing in the Interior, the bulk of the damage must be assessed to southeast and south central Alaska. Bridge deck replacement in Fairbanks cost several hundred thousand dollars, recently.

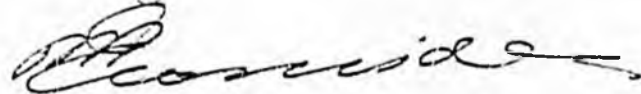
Furthermore, as Murray and Ernst (1970) point out, "heavy salt use...upsets the natural ecological balance" causing irreversible damages which cannot be assigned an actual dollar cost. These include the risk of increased hypertension. This item cannot be underestimated. Groundwater supplies have been severely affected. In the east of the country, several potable water sources have a salt content of more than 20 mg/liter, the maximum allowable for persons on low sodium diets. This has been directly linked to the use of salt as a deicing agent. Hence, while the cost on the permanent health degradation may be difficult to assess, it is likely to be very high.

Our research on calcium-magnesium acetate (CMA) has resulted in a compound that may be produced by using native Alaskan raw materials and at prices in the region of the acquisition costs of chloride salts. The environmentally benign and noncorrosive nature of CMA offer a compelling rationale in its favor.

We would like to explore with you the logistics of undertaking a controlled test in Juneau and elsewhere in the southeast. Sometime next winter, we could coordinate our efforts with the D.O.T. people. We have a limited supply of CMA on stock and we could have a significantly larger quantity by then.

Let us know how we could be of help

Sincerely,



Michael J. Economides
Assistant Professor
Petroleum Engineering Department

P.S. A copy of the Northern Engineer with one of our papers on CMA is enclosed.

References:

Brenner, R. and Moshman, J.: "Benefits and Costs in the Use of Salt to Deice Highways", Institute of Safety Analysis, Washington, DC, Nov. 1976.

Murray, D.M. and Ernst, V.F.W.: "An Economic Analysis of the Environmental Impact of Highway Deicing", U.S. E.P.A. Rept., EPA-600/2-76-105. May, 1976.

cc: Larry Sweet
MJE:bb

STATE OF ALASKA

Bill Sheffield, Governor

DEPARTMENT OF TRANSPORTATION AND PUBLIC FACILITIES

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

MAINTENANCE AND OPERATIONS, INTERIOR REGION

March 25, 1983

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

Dear Ms. Zachery:

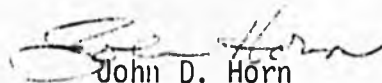
Enclosed for your information is a draft copy of the interim report on the second phase of this Department's study into the possible production of Calcium Magnesium Acetate (CMA) for use as a deicing agent on Alaskan roads.

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
Russell 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.

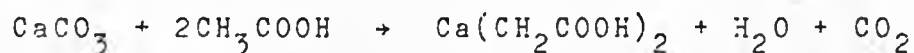
Furthermore, road salts are injurious to most forms of plant life. In the spring, a drive along heavily salted roadways in Anchorage reveals a virtual moonscape with dead or stunted plants. The success of ongoing roadway beautification projects in Anchorage and Fairbanks will be questionable with the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

PROCEDURE:

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

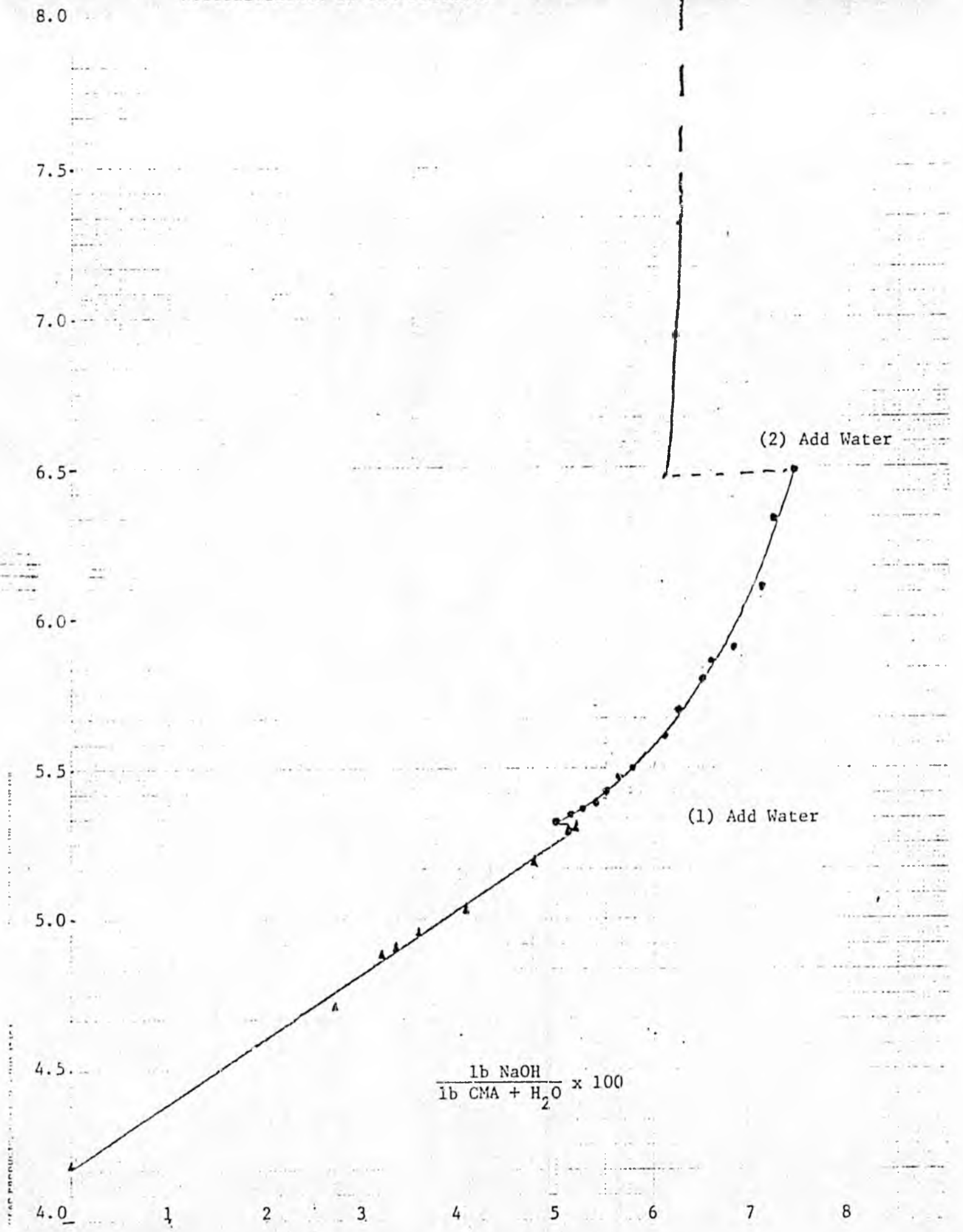


FIGURE 2

Titration of an Unknown Solution of CMA

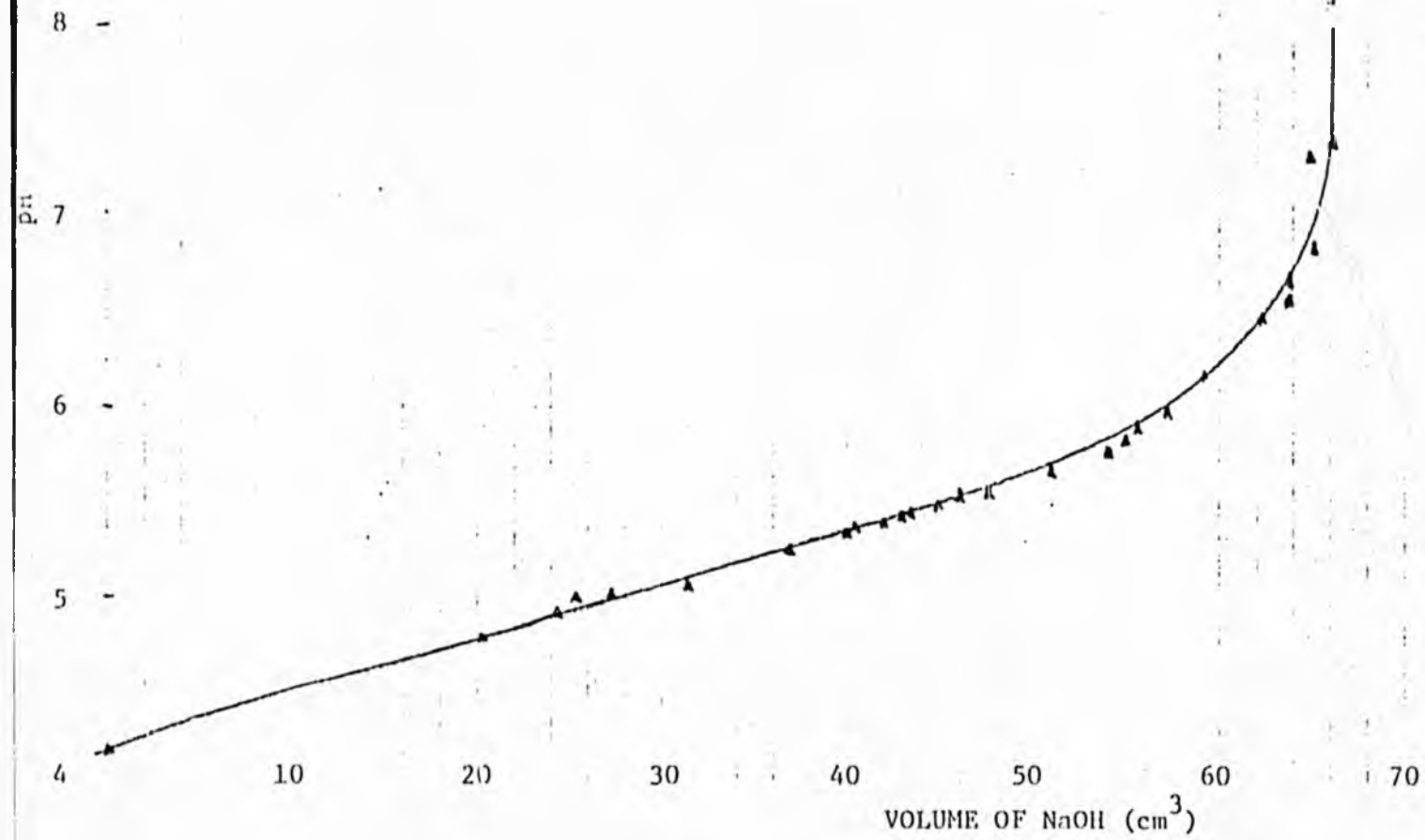


FIGURE 3

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

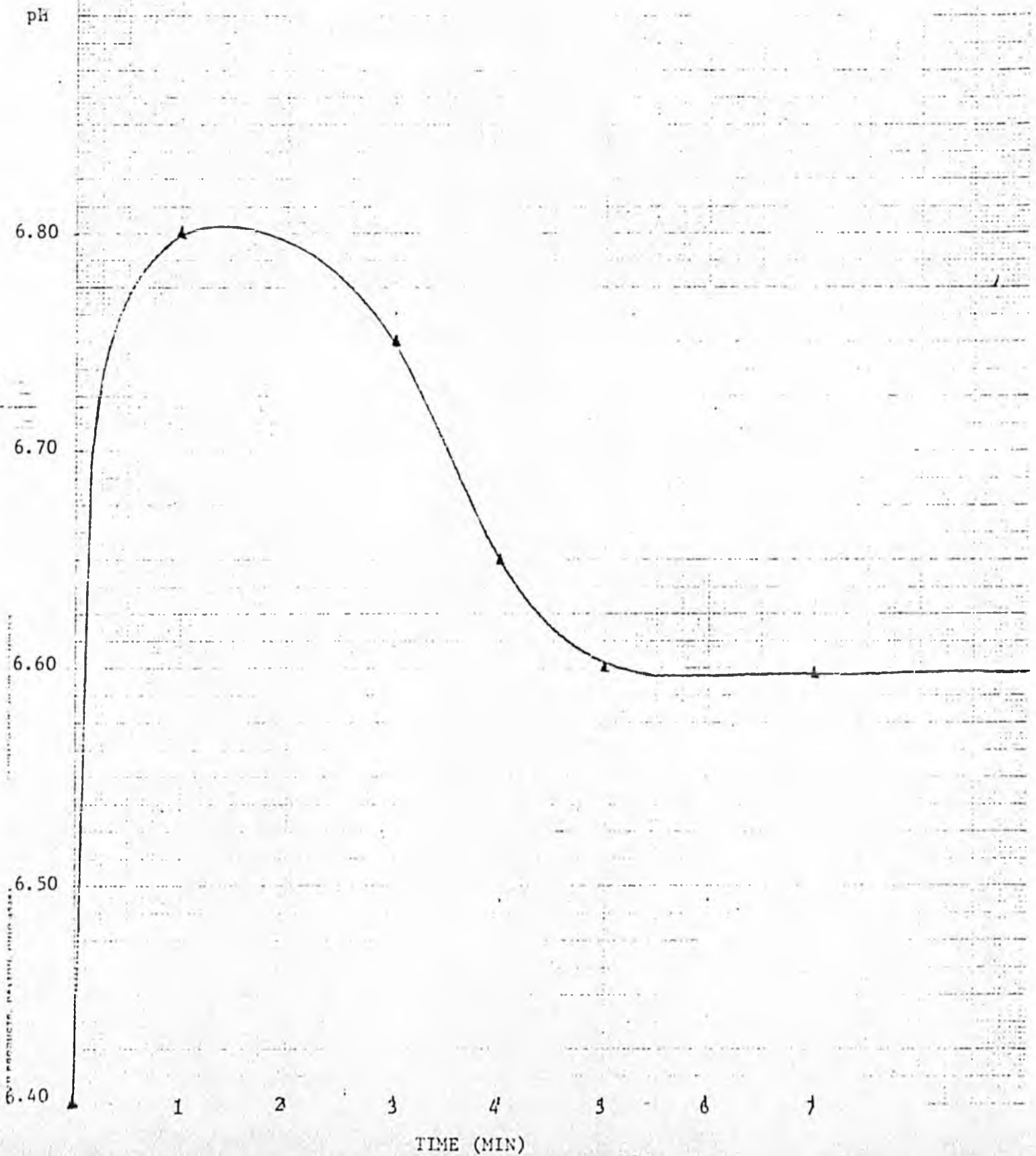
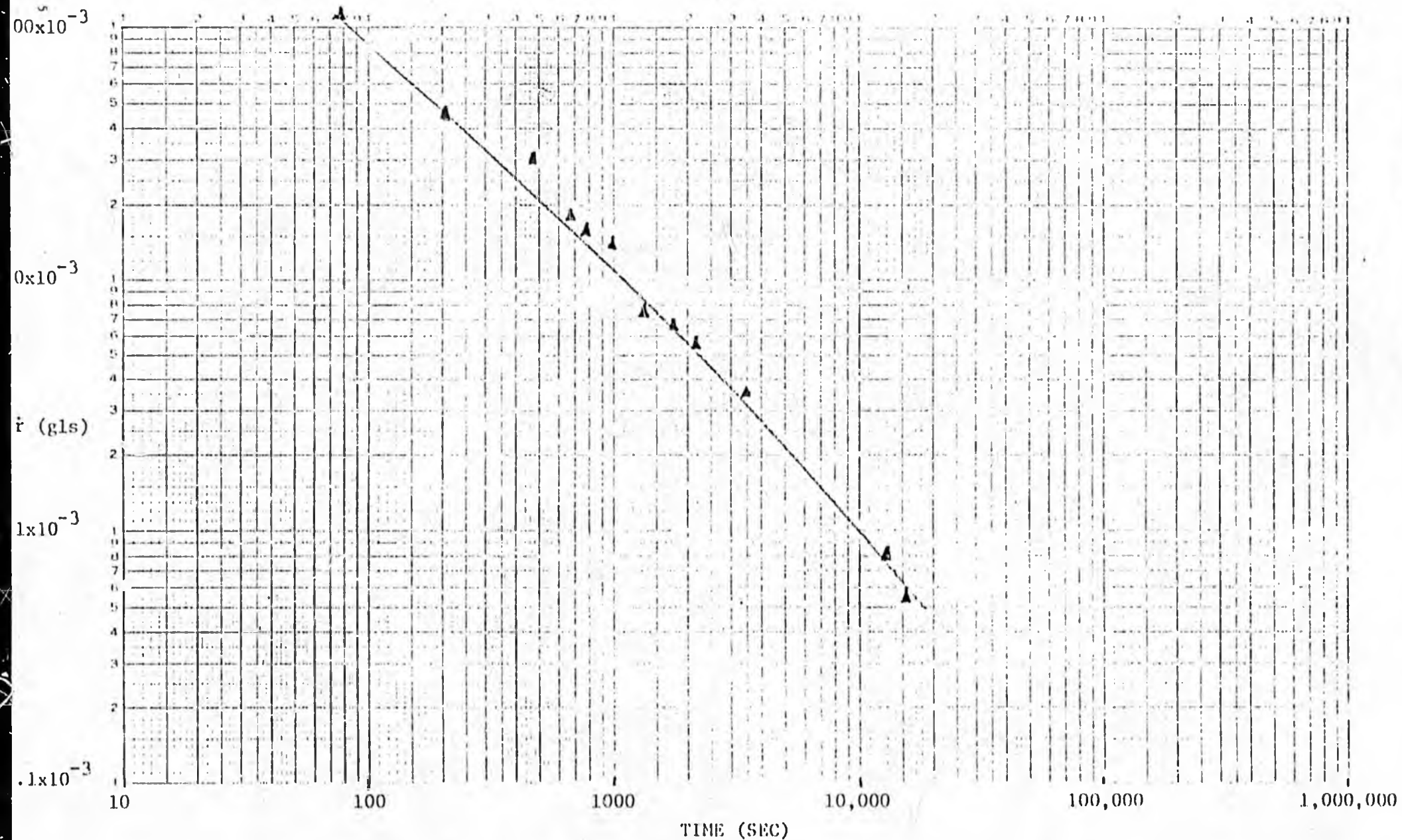


FIGURE 4



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

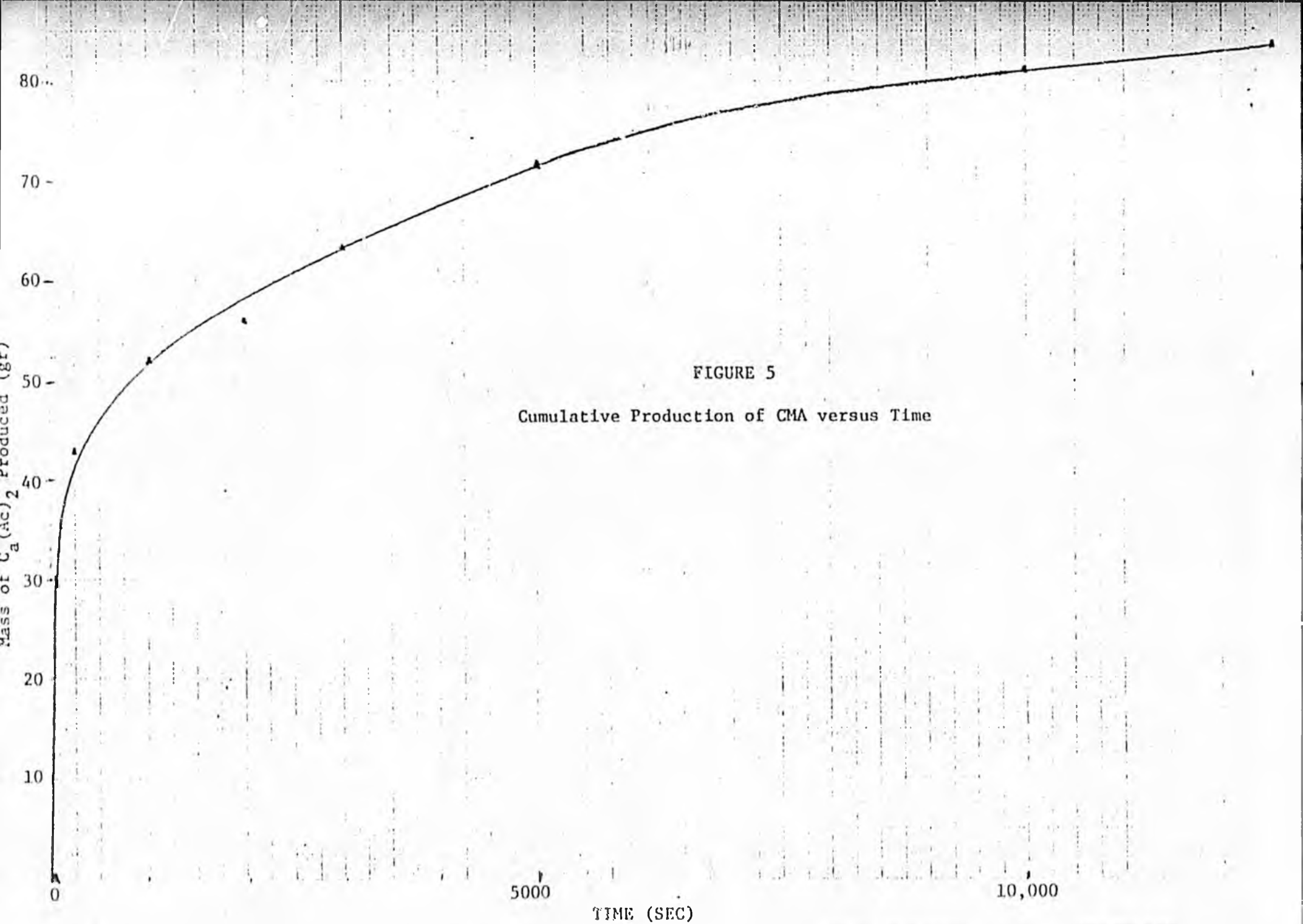


FIGURE 5

Cumulative Production of CMA versus Time

STATE OF ALASKA

BILL SHEFFIELD, GOVERNOR

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

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

December 9, 1982

Re: CMA Pilot Plant
Design, F21551

Dr. Michael Economides
Dr. Russell Ostermann
Petroleum Engineering Department
University of Alaska, Fairbanks

Dear Drs. Economides and Ostermann.

The results of your research project entitled "Preliminary Design and Feasibility Study for a Calcium-Magnesium Acetate Unit" and the current Phase II project "CMA Pilot Plant Design" have generated a great deal of interest for the use of this non-corrosive substitute for the salt that is presently being used for snow and ice control on Alaskan highways.

The possible use of CMA as a dust control agent and soil stabilizer for highway surfaces in the summer, which was not envisioned in the original proposals, has increased the interest in making full scale operational tests.

This morning I learned that the Transportation Committee of the Fairbanks Chamber of Commerce intends to endorse your proposal to the Borough for the demonstration of the effectiveness of CMA on a Borough road. I also learned that officials of the North Pole Refinery are not waiting for the results of your current pilot plant project but are doing design studies of their own to investigate the factors involved in production of acetic acid on a large volume scale.

I have been repeatedly asked about the status of the pilot plant project because of the new found potential use of this product on the Dalton Highway.

I know that there have been many delays in assembling your pilot plant. It appears that it may now be almost ready for operation. However, the types of demonstration projects that are being discussed could involve thousands of gallons of CMA where your pilot plant is only capable of producing 15-20 gallons per day.

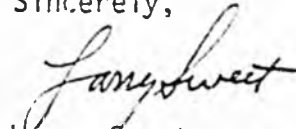
Dr. Economides
Dr. Ostermann

- 2 -

December 9, 1982

If there is anything that I can do to expedite getting your plant in operation, please let me know. For sometime now this project has been of extreme interest and the questions your project is seeking to answer are vital. Please keep me informed.

Sincerely,



Larry Sweet
Research Manager

LS/emc

cc: Bel Frol
Staples Brown

VOLUME 10-82

DATE: 10/8/82

CALCIUM MAGNESIUM ACETATE - CMA

M & R's research effort has continued on calcium magnesium acetate, better known as CMA. This is a substitute for salt. We have been working very closely with industry and have produced in our M & R backyard a 40 lb. batch of CMA utilizing our concrete mixer for 10 minutes of agitating. The ingredients were a 10% solution of acetic acid provided by W. R. Shurtleff (at no cost) and 50 lbs. of coarse dolomitic limestone, courtesy of Lime Products Corp. The 10 minutes of agitation allowed the acid to extract the calcium and magnesium to form in a solution. This was then evaporated by solar means during the period 6/24 - 7/16.

With the small test batch behind us, staff undertook a more ambitious project by mixing the same ingredients but in a large concrete mixer at the Union plant of Lime Products Corp. On August 11, 8,000 lbs. of fine dolomitic limestone, 1800 gal. water and 200 gal. of glacial acetic acid were mixed and placed in evaporation chambers. This may be one of the earliest and probably largest produced batches of CMA to date.

Recognizing the process is now a valid method, Lime Products Corp. is proceeding to evaluate the economics of producing CMA in a continuous flow-evaporation cycle.

DEER MIRRORS

FHWA's Technical Report RD-82/061 is entitled "Evaluation of Deer Mirrors for Reducing Deer-Vehicle Collisions". In the transmittal from the Director of the Office of Research, FHWA, dated August 4, it was noted "During the past 10 years numerous methods have been tried to reduce the more than 200,000 deer-vehicle collisions which occur each year on the nation's highways. Some techniques, such as properly maintained deer fencing and under-passes, have been successful. Others, such as fixed signing, have not. Reflective devices (deer mirrors) are supposed to create a visual barrier when car headlights strike them to arrest deer movement. In recent years, at least eight states have employed reflective devices along the roadside; however, because of a lack of an organized data collection program, results were either inconclusive or misleading.

This memorandum distributes the subject report which concludes that "deer mirrors" are not effective in reducing deer-vehicle collisions. The cost of their installation and maintenance is not justified. The report (1) documents the results of a four year study in south-central Maine and (2) reviews the literature concerning the effectiveness of reflective devices in reducing deer-vehicle collisions. The report will be of interest to wildlife researchers, wildlife biologists, environmental specialists, traffic and maintenance engineers, and state wildlife agencies."

This effort was undertaken thru a cooperative effort by many Maine DOT staff. Particular appreciation is extended to the individual snowplow operators who for four years maneuvered their plow blades around 30" posts, recognizing in the seat of the cab these plow operators have difficulty in seeing objects within the first 40 feet of their front tire; also to the maintenance supervisor who reported deer-vehicle impacts plus the State Police who patrol the area. The Department of Inland Fish & Wildlife was instrumental in documenting the deer-vehicle collisions. The mirrors were installed under construction contract (federal-state) change order. The project was designed by Dr. James Gilbert, Wildlife Unit at the UMO Campus. He was funded for the study directly by the Federal Highway's Office of Research. This was the first project which directly evaluated the effectiveness of the deer-vehicle mirrors. It is regrettable that after 16 months the impact-vehicle rate ceased although the study was carried for three more years. Hunters have always said the deer are smart animals and perhaps this study indicates the degree of their intelligence!

DOTFF RESEARCH DIVISION

AASHTO ROAD TEST

The AASHTO Road Test was conceived, designed, constructed and tested to measure the actual destruction effect of various wheel loadings on numerous test sections of different thicknesses.

X
 BSB
 Chuck
 Matt

RECEIVED
 NOV 11 1982

