

**PILOT PLANT STUDIES AND PROCESS DESIGN FOR THE
PRODUCTION OF CALCIUM-MAGNESIUM ACETATE**

FINAL REPORT

BY

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IMPLEMENTATION

The search for non-corrosive deicing chemicals for highway applications has taken on a national emphasis as a part of the Strategic Highway Research Program. Calcium-Magnesium-Acetate (CMA) has been identified as the most promising alternative to the corrosive salts commonly in use for deicing.

Because of high transportation costs for shipping deicing chemicals to Alaska and because we felt that it may be economically feasible to produce CMA in Alaska, the Alaska Department of Transportation and Public Facilities has been investigating this product for use in Alaska.

This report describes research sponsored by the Alaska Department of Transportation and Public Facilities which has studied the manufacture of this non-corrosive deicing chemical and its application to Alaskan roads. Other reports concerning CMA studies are "Preliminary Design and Feasibility Study for Calcium-Magnesium-Acetate Unit", Report 83-16, "Corrosion of Steel in Calcium-Magnesium-Acetate (CMA) Deicer", Report 85-27, and a report on the environmental effects of the CMA produced in Alaska. The latter report is scheduled for completion in the spring of 1986 and is being coordinated with other federally sponsored environmental assessments of CMA.

In our studies University researchers and Department personnel have made and tested CMA in the laboratory and produced and field tested some 10,000 gallons of liquid CMA. Our field tests using a standard water truck and maintenance crews for application went smoothly and produced effective results.

As noted in the Conclusion, using the criteria discussed by the researchers, the cost to manufacture CMA in Alaska is between \$415 and \$442 per ton. This cost is highly dependent upon the cost of the acetic acid used in the manufacturing process; the costs above assume an acetic acid cost of \$0.20 per pound.

If a decision is made to stop using the present corrosive chemicals and switch to CMA, the initial costs to the Department will increase. However, as summarized in this report, the total costs including corrosion and environmental effects from our present practices are 10-15 times the first cost of purchasing sodium chloride, our most commonly used deicing chemical. If the Department decides to pursue implementation of CMA the next steps are to file an environmental impact statement using the results of the environmental study nearing completion and to conduct a full scale winter-long demonstration of CMA at a designated maintenance station.

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A B S T R A C T

Chloride salts are commonly used as deicing chemicals in many northern states. These chemicals are corrosive to automobiles, bridge decks and other public structures, and cause considerable damage to plants found near salted roadways.

Calcium Magnesium Acetate (CMA) offers potential as an alternate deicing chemical. CMA is a generic term applied to the reaction product of acetic acid and limestone. It is non-corrosive and has no known potential to cause environmental damage.

During 1982-1984, over 12,000 gallons of saturated CMA solution were produced by researchers in the Petroleum Engineering Department of the University of Alaska - Fairbanks. The raw materials were acetic acid, hydrated lime and native limestone. The product CMA solution was used in road tests in Fairbanks as well as for environmental studies. The results of these pilot plant studies is presented in this report.

A process design for the production of 12,000 GPD of CMA from native limestone based on the results of the pilot plant studies is presented. For a grass-roots operation located in Fairbanks, the total capital cost is estimated at \$215,000, including site and structure costs. Using current prices for acetic acid, limestone and hydrated lime, a product price of \$413 per ton (dry CMA equivalent) is required for a 15% annual rate of return. It should be noted that raw materials costs amount to over 85% of the annual operating costs with capital cost amortization amounting to only 2% of the product cost. The process economics are thus relatively insensitive to changes in capital costs due to process design changes. Moreover, acetic acid cost alone accounts for 70% of the product price. The key to reducing the price of CMA lies in obtaining inexpensive acetic acid.

1.0 INTRODUCTION

Winter driving safety on icy roads is an issue of major concern to people living in most of the northern tier states and Canada. Currently, sodium chloride (common road salt) and calcium chloride are used extensively as deicing compounds throughout the country. The use of these chemicals has a definite positive value which must be measured in terms of human lives saved, as well as reduction in vehicular damages and lost productivity which may occur in ice related accidents.

There are also negative effects offsetting these benefits. With the use of salts, in addition to the costs of acquisition and application, secondary costs are incurred by associated corrosion and environmental damages. A commonly used estimate is that the total cost associated with salt usage, including damage costs, is roughly 10 to 15 times the cost of the applied salt itself.

A significant portion of these costs may be attributed to bridge deck corrosion, utility system corrosion, and in general, corrosion of susceptible public structures and equipment. However, the brunt of the damage costs are borne by the private sector, through the corrosion of personal automobiles. Additionally, salt is harmful to most plants found near the roadways. While it is difficult to estimate a dollar amount for this damage, it is very visible, and aggravating to the public. In response to "rusted out" automobiles and damaged lawns and landscaping, the public often offers potent criticism concerning salting practices, making the responsibility of the local DOT to assure the safety of the roadways doubly difficult.

The above concerns have triggered an earnest search for alternative methods of deicing roadways. Thermal, physical, and alternative chemical methods have been considered. F. Wood⁽¹⁾ in a paper dealing with salt damages to motor vehicles, presents a convenient summary of some of the physical and thermal deicing methods attempted. Zenewitz⁽²⁾, has published a more extensive survey. While many different methods are technically feasible, he reports that the general feeling among highway personnel is that none of these methods are cost effective. However, it should be stressed that any economic assessment not taking into account the full spectrum of salt related damages should be questioned.

Several chemicals have been proposed as substitutes for road salt. Under the sponsorship of the Federal Highway Administration, researchers at the Bjorksten Research Laboratories in Madison, Wisconsin, conducted a major study assessing alternative deicing chemicals. In the final report on this study, Dunn and Schenk⁽³⁾

report that only two chemicals, methanol and calcium magnesium acetate (CMA), have deicing properties similar to sodium chloride, are non-corrosive, and have the potential to be produced at reasonable costs. (CMA is in the simplest sense a salt, the reaction product of acetic acid and limestone.)

Salt can be obtained in most areas in the "lower 48" states at less than \$20 per ton. If the damage costs are estimated at \$200 per ton, it would appear that CMA may be a feasible substitute if it can be produced in the "lower 48" for less than \$220/ton.

Considerable interest has been generated surrounding the properties and production of CMA in Alaska. The research section of the Alaska State Department of Transportation and Public Facilities (DOTPF), and the Petroleum Engineering Department at the University of Alaska - Fairbanks (UAF) have been investigating the production and use of CMA in Alaska. In the "lower 48" states, salt typically costs \$10 to \$20 per ton with damage costs of about \$200/ton. In Alaska, since salt must be shipped by barge from the West Coast, the price is increased to over \$100 per ton. It would be reasonable to assume that the damage costs in Alaska are also about \$200/ton, adjusted for Alaskan prices. Repair and replacement costs are also high in Alaska. If damage repair costs were estimated at 25% greater than in the "lower 48", or \$250 per ton, it would appear that the true "cost" for the use of road salt in Alaska could be nearly \$350 per ton. Thus the benefits of using non-corrosive CMA, and hence the economically allowable price for CMA are higher in Alaska than in the "lower 48" states.

The obvious difficulty with the economic analysis of switching from salt to CMA lies in determining the "actual" cost of salt damage. While it is clear that the costs are substantial, and real, they are distributed over several sectors of the economy. Without a reasonably reliable estimate of the cost of salt damage, it will be difficult to evaluate what price the State could afford to pay for CMA and still achieve an economic benefit. Considerable damage to bridge decks and public structures is attributable to salt, but a large proportion of the damage is also borne by the private sector. Thus it may not be possible for the State DOTPF to show a "cost savings" through the use of CMA. Any price for CMA substantially above the current cost of salt, will result in increased operating costs for the DOTPF, even after deducting the potential repair costs and savings associated with decreased bridge deck corrosion and other damage to public structures.

It is anticipated that an election to use CMA will be more a policy decision (i.e. not to use corrosive salts) spurred on by adverse public opinion regarding salt usage, than an economic decision. Thus, the technical question may well be "How do we make CMA

for the lowest possible cost?" as opposed to "Is that cost economic?".

For the last two years, researchers at UAF have been studying the production of CMA. Over 10,000 gallons of saturated CMA solution has been produced in a pilot plant operated at the local DOTPF facility in Fairbanks. This is the equivalent of roughly 12 tons of dry CMA product. The CMA has been used for limited road tests, and for environmental studies. In the current report, the results of our pilot plant and process design studies are presented.

2.0 BACKGROUND

2.1 Costs and Benefits of Deicing

Chloride salts have been used for many years for the control of ice and snow on the nation's streets, roads, and highways. Usage has risen to over 12 million tons annually. Even in Alaska, with relatively few miles of roadways, current usage is over 8,000 tons annually. As the public encounters "rusted out" automobiles, damaged lawns, and landscaping and the appearance of salt residue on shoes and carpets, controversy is raised regarding the use of these salts. The immediate question is, "Do the benefits outweigh the costs of salt usage?". If not, it may be appropriate to discontinue their use.

While the actual cost of salt and its application is easily obtained estimates of the benefits and damage costs are more elusive. The economic benefits of road deicing are primarily realized through the reductions in the number and severity of ice related accidents on treated roads as opposed to untreated roads. The cost of an accident is estimated in terms of productivity losses as well as actual structural damage.

One major benefit expected from deicing would be a reduction in deaths and injuries associated with ice related accidents. It is of course difficult to assign a dollar figure to this benefit.

Costs associated with the use of salts include vehicular and bridge deck corrosion, damages to structures and utility systems, and environmental damages. It is difficult to obtain reliable estimates of the magnitude of these damages since they are so pervasive and occur over extended periods of time.

The costs and benefits of deicing have been analyzed in some detail by Brenner and Moshman⁽⁴⁾ and Murray and Ernest⁽⁵⁾. The results of the studies are summarized in Table 2-1:

Table 2-1
Annual Costs of Road Salting
(In millions of dollars)

	<u>Brenner and Moshman (4)</u>	<u>Murray and Ernst (5)</u>
Utilities	2	10
Vehicle Corrosion	643	2000
Highway Bridge Decks	160	500
Trees and vegetation	0	50
Water Supplies	10	150
Salt and Application	200	200
	<u>1015</u>	<u>2910</u>

Murray and Ernst⁽⁵⁾ have estimated a total U.S. cost for salt use, including damages, at about \$2.9 billion annually. Given an annual cost of \$200 million for salt purchase and application, the total cost of salt would appear to be fifteen times greater than the cost of purchase and application alone. While the relationship may be used for the purposes of cost estimation in the "lower 48", the relationship would not apply for Alaska.

In Alaska, salt costs nearly \$100 per ton, or ten times as much as in the "lower 48". Using the ratio calculated above, damage costs for Alaska would be estimated at \$1500 per ton. This figure is probably unrealistic.

If we assume that repair costs are roughly 25% higher in Alaska and that salt costs ten times as much as in Alaska as opposed to the "lower 48", the appropriate ratio would be only 3 to 1. That is, the total cost for salt usage is three times the cost of purchase and application, or \$200-300 per ton. Considering the unique nature of Alaska, many other variables may be involved, making comparison to "lower 48" figures difficult. The above figures should be used with caution. However, in the absence of more accurate data, it may be used for the purpose of rough estimation.

The estimates of Brenner and Mosham⁽⁴⁾ give a factor of three lower than Murray and Ernst⁽⁵⁾. The reason for this difference is unclear. However, the larger question as to whether the benefits of deicing outweigh the costs would appear to be clear in either case. Brenner and Mosham⁽⁴⁾ (See Table 2-2) have estimated the total benefit from deicing to be \$18.4 billion annually. Thus in the case of Brenner and Mosham the benefit cost ratio is roughly 18:1 while the ratio is 6:1 for Murray and Ernst⁽⁵⁾. Both studies indicate a substantial economic benefit to be derived from deicing. Moreover, the savings in human lives alone should be sufficient to justify the expense.

TABLE 2-2
Annual Economic Benefits of Deicing
(Brenner and Mosham⁽¹⁾)

	Annual Economic Savings In Millions of Dollars
Reduced Fuel Usage	200
Reduced Wage Losses	10,600
Reduced Production Losses	7,000
Reduced Losses in Goods Shipments	600
	<u>18,400</u>

2.2 Salt Use in Alaska

Over 8,000 tons of road salts, including calcium and sodium salts are used annually in Alaska. In addition to deicing, calcium chloride is also used as a dust palliative. The vast majority of the salt used in Alaska is sodium chloride used in the Central region (Anchorage area). The current distribution of salt use in Alaska is presented in Table 2-3. (Data supplied by the State of Alaska DOTPF). About 90% of the salt is applied in the Central area with smaller amounts in Interior and Southeast.

TABLE 2-3
Current Salt Usage in Alaska

Region	Tons per year	
	NaCl	CaCl ₂
Interior	500	0
Central	6950	440
Southeast	140	250
Total	7590	690

2.3 Alternate Deicing Chemicals

Dunn and Schenk⁽³⁾ have compared alternate highway deicing chemicals. The primary requirements for a chemical to be a viable deicer substitute are: a) solubility of chemical in water, b) low rate of volatilization, c) minimal pollution effects, d) minimal corrosion effects, e) a non-hazardous nature, and f) low cost.

In the preliminary evaluation of the alternative chemicals, transuranium elements, actinide series, rare earth metals, noble gas, etc., are eliminated. Sodium salts are not considered because of the potential damage of sodium ions on plants, soils, and ground water contamination. All chlorides, nitrates, and sulphates are considered to be unsuitable. Dunn and Schenk⁽³⁾ suggested that potassium salts of carbonic acid (freezing point - 36°C) might work. They also studied the possibility of using a eutectic mixture of potassium salt of phosphoric acid, tetra potassium pyrophosphate, ammonium salts of phosphoric acid, ammonium salts of carbonic acid, and organic salts of Na, K, Mg, Ca and ammonium ions, glycine, methanol, ethanol, isopropanol, acetone, urea formamide, dimethyl sulphoxide, and urethane.

Dunn and Schenk⁽³⁾ have reported that two chemical compounds, methanol and CMA showed the most promise as deicing compounds. These chemicals were evaluated on the basis of criteria such as: traction, skidding, friction, field performance, compatibility with cement, asphalt and road paint, and corrosion of the commonly used metals associated with vehicular and roadway construction.

Dunn and Schenk⁽³⁾ suggested that methanol should not pose any significant environmental or corrosion problems. However, care should be taken in the storage and use of methanol because of its flammability. CMA is essentially nonflammable, nontoxic, and retards corrosion of most metals.

Both deicing agents can be produced from cellulosic and other organic wastes by high pressure, high temperature technology with producer gas or natural gas as an intermediate. Also, large deposits of dolomite are available in many areas for the manufacture of CMA.

Methanol was found to be "less persistent" than CMA due to its high volatility. CMA was selected as the preferred deicing substitute for sodium and calcium chlorides. A detailed analysis is presented in the Dunn and Schenk report⁽³⁾.

2.4 Properties of CMA

The effective evaluation of CMA as a deicing compound will require detailed knowledge of its physical and chemical properties. The primary test of a chemical compound as an effective deicer is its ability to depress the freezing point of water.

Figure 2-1 illustrates the freezing points of a solution of various salts as a function of composition. Calcium acetate and magnesium acetate are not quite as effective as the chloride salts in reducing the freezing point of water. However, at higher concentrations, the acetates are effective down to about 0°F.

However, the effectiveness of a deicing chemical depends on more than just freezing point depression. There does not appear to be any firm, quantitative measures of deicing effectiveness, although parameters such as pounds of ice melted per pound of salt applied, and rate of melting are indicators.

Moreover, factors such as traction improvement and increased braking efficiency are important in determining the effectiveness of a deicer. Dunn and Schenk⁽³⁾ have reported laboratory tests of braking traction and skidding friction for NaCl and CMA. The tests indicate that CMA should function well as a deicer.

In practice, however, the utility of CMA can best be assessed through large scale field tests. By the end of 1984 over 200 tons of CMA were field tested in Washington and Michigan. Within Alaska, about 5,000 gallons of saturated solution have been used on Fairbanks streets. The preliminary results of these tests indicate that CMA performs well as a deicer. In Fairbanks, a 50% increase in braking efficiency was reported within 5 minutes of CMA application. While these tests are encouraging, larger tests will have to be made before widespread application is prudent.

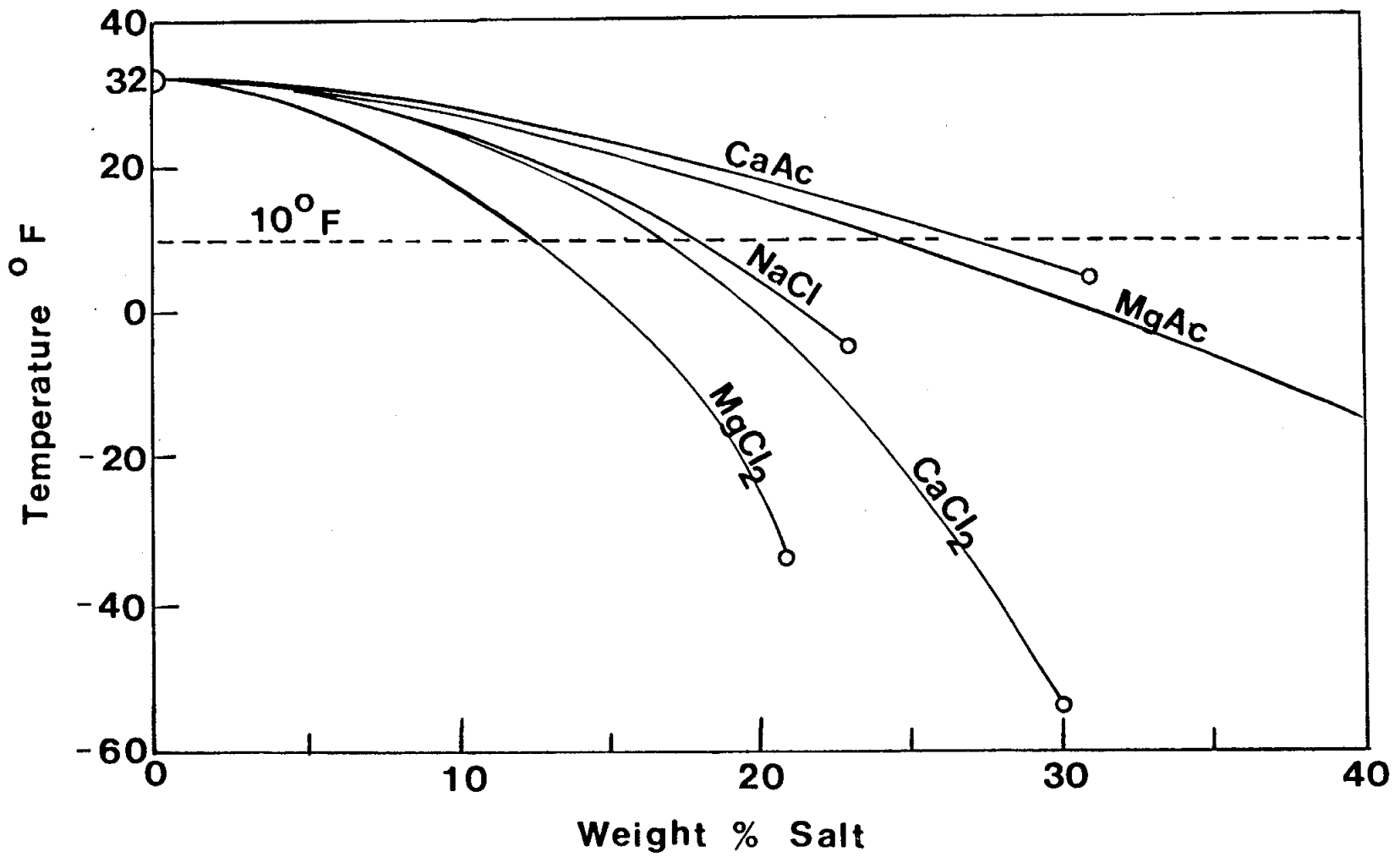


Figure 2-1: Phase Relationships for Various Salts

Repeated laboratory tests have indicated that CMA is not corrosive to steel, zinc or aluminum. Dunn and Schenk⁽³⁾ present an extensive treatment of this topic. Additional tests are underway at the national level.

Calcium and Magnesium Acetates are generally regarded as environmentally benign. The Merck Index⁽⁶⁾ lists the following lethal dose (LD) levels for mice and rats:

Calcium Acetate:	LD ₅₀ orally in rats	4.28 g/kg
Magnesium Acetate:	LD ₅₀ intravenous in mice	18 mg/kg

By comparison, sodium chloride has a lethal level of LD₅₀ (orally in rats) of 3.75 g/kg. In fact, calcium acetate is used commercially as a food stabilizer. Tests are currently underway in Alaska to assess the effects of CMA contamination on plant and animal life in ponds. At the present time, there are no indications of major problems.

3.0 PRODUCTION OF CMA

3.1 Basic Chemistry

CMA is a generic term applied to the reaction products of limestone or dolomite and acetic acid. Limestone is composed of calcium and magnesium carbonates (CaCO_3 , MgCO_3) and varying amounts of impurities. Typical compositions of limestone and dolomite are presented in Table 3-1. The data were taken from a master's thesis by Sanusi⁽⁷⁾. The relative amounts of calcium and magnesium acetates found in the final product CMA will depend on the composition of the limestone or dolomite used.

TABLE 3-1
Typical Compositions from Dolomite and Limestone (After 7)

	<u>Limestone^a</u>	<u>Dolomite^b</u>
CaO	55.28	31.20
MgO	0.46	20.45
CO ₂	43.73	47.87
SiO ₂	.42	.11
Fe ₂ O ₃	.05	.19
Other	.06	.18

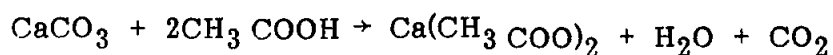
- a. Virginia High Calcium Limestone
b. Illinois Niagran Dolomite

Magnesium acetate is actually a "better" deicing chemical than calcium acetate, showing a greater freezing point depression (See Figure 2-1). Most limestones are predominately composed of calcium carbonate, some having a purity of over 95%. Dolomites can have magnesium carbonate contents approaching 50%. Most of the potential limestone sources in Alaska are high in calcium content. Moreover, the chemistry for the production is largely the same in either case. However, limestone composition varies considerably, even among limestones having little magnesium content. For these reasons, this study focuses on the production of calcium acetate (CA) from pure calcium carbonate.

Calcium acetate can be produced from limestone or hydrated lime.

3.1.1 Production From Limestone

Calcium acetate is produced from the reaction of acetic acid (CH_3COOH or HAc) and calcium carbonate as follows:



The reaction is slightly exothermic ($\Delta H_r^0 = -4.6$ Kcal/mol), and produces a considerable amount of carbon dioxide gas. Acetic acid will not react with calcium carbonate in the anhydrous state. It must be mixed with water to allow ionization. The solubility limit of CaAc in water is about 28% at 25°C. Hence, if a saturated solution of CA is desired, a simple material balance would indicate a water requirement of 388 g.H₂O/100 g.CaCO₃. However, the reaction does not go to completion under these conditions, making the reaction somewhat more complicated.

The solubility of calcium carbonate in water is very low. Experiments have shown that if stoichiometric quantities of water, acetic acid, and calcium carbonate necessary to produce a saturated solution, are mixed, the reaction will not go to completion, but will stop at a pH of about 5.6 with only 86% of the acid reacted. Perhaps the easiest way to view the reaction is as a titration of an acetic acid solution with calcium carbonate. Ideally, calcium carbonate would continue to be dissolved in the solution until neutrality was achieved. However, the solubility limit for calcium carbonate is reached before neutrality in all but solutions too dilute to be of value. Thus the normal product is a acidic solution containing unreacted acetic acid.

A series of experiments was conducted to determine the degree of completion achieved as a function of the composition of the original acid solution, and time. In general, the more dilute the solution, the greater the amount of carbonate which would react, and hence the more acid which would be neutralized. The results of these experiments are presented in Figure 3-1. The degree of completion is measured as percent of original acid consumed. In all reactions, an excess of calcium carbonate was used.

A cursory analysis of Figure 3-1 indicates that the rate of reaction and to a minor extent, the ultimate degree of completion depends on the original ratio of water to acetic acid. It should be noted that essentially no reaction continued beyond four hours. Figure 3-2 shows the relationship between reaction completion and initial water/acid ratio at various reaction times. In Figure 3-3, the time required to achieve 95% of maximum completion is plotted versus original water/acid ratio.

In general, CA can be produced by reacting acetic acid and calcium carbonate in any proportion in aqueous solution. While it may seem appropriate to aim at 100% acid utilization as a goal, it should be noted that this is not feasible. The maximum conversion obtained at a water/acid ratio of 4 is only 85%.

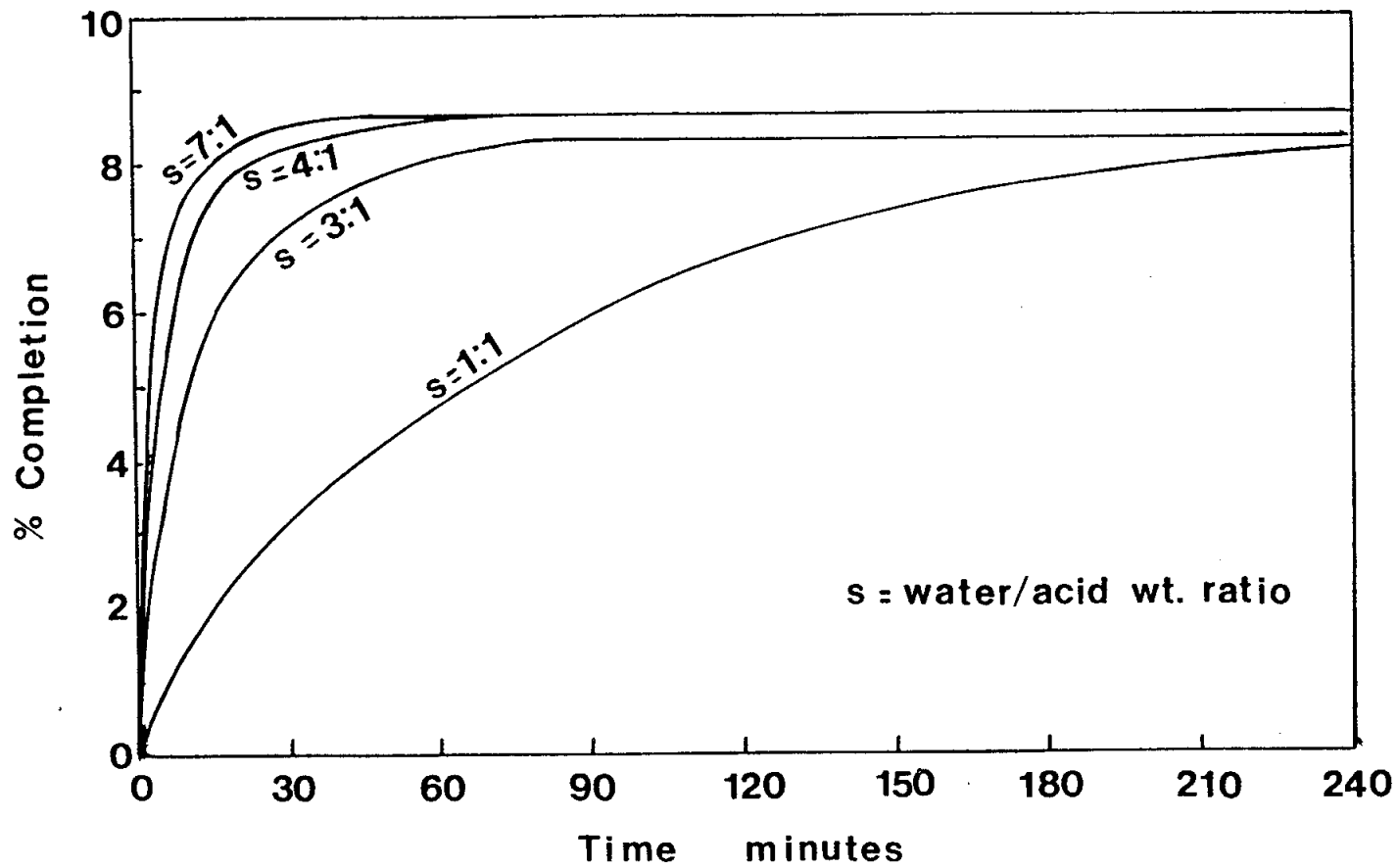


Figure 3-1: Reaction Rates for CMA Production

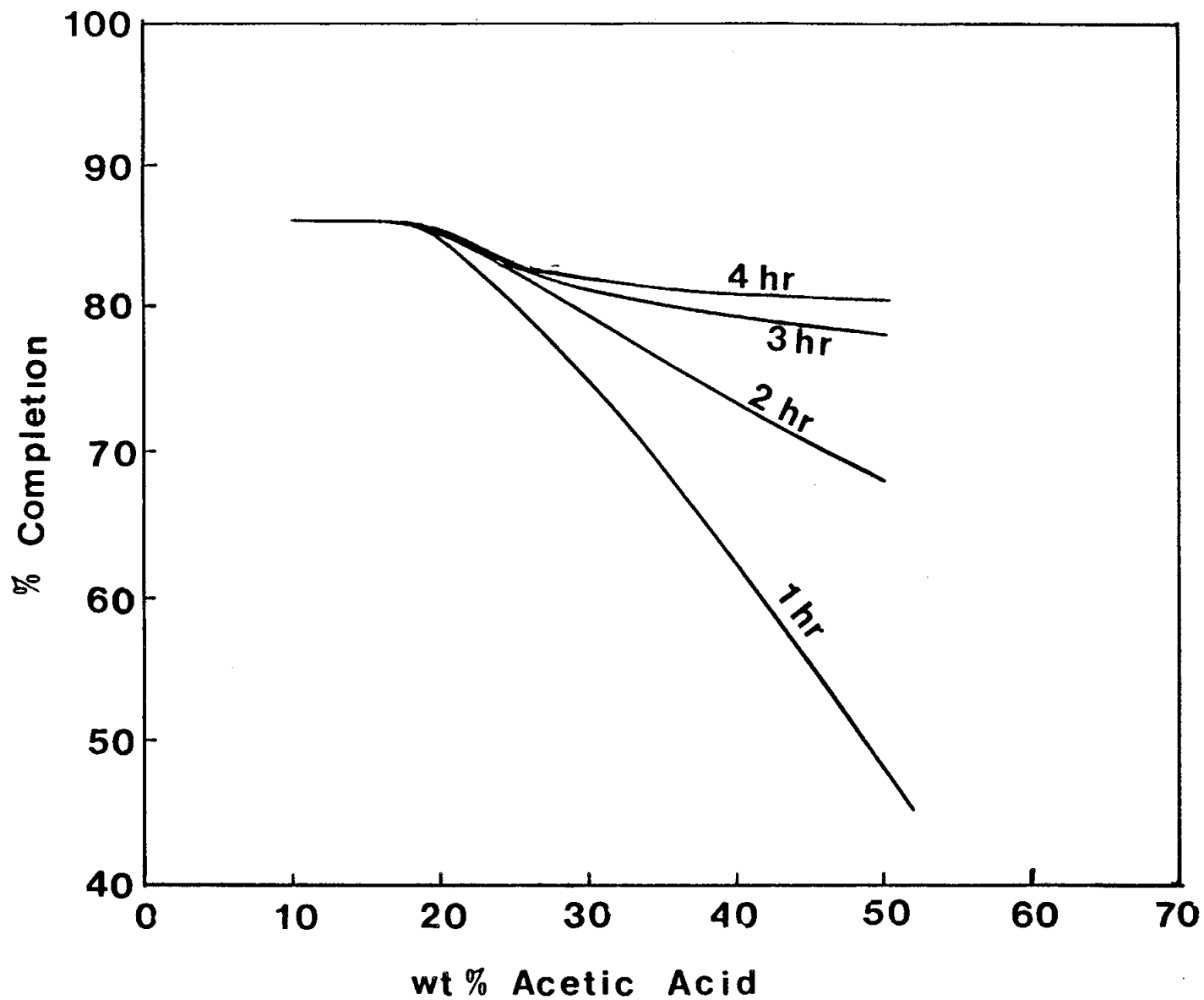


Figure 3-2: Reaction Completion Versus Acid Concentration

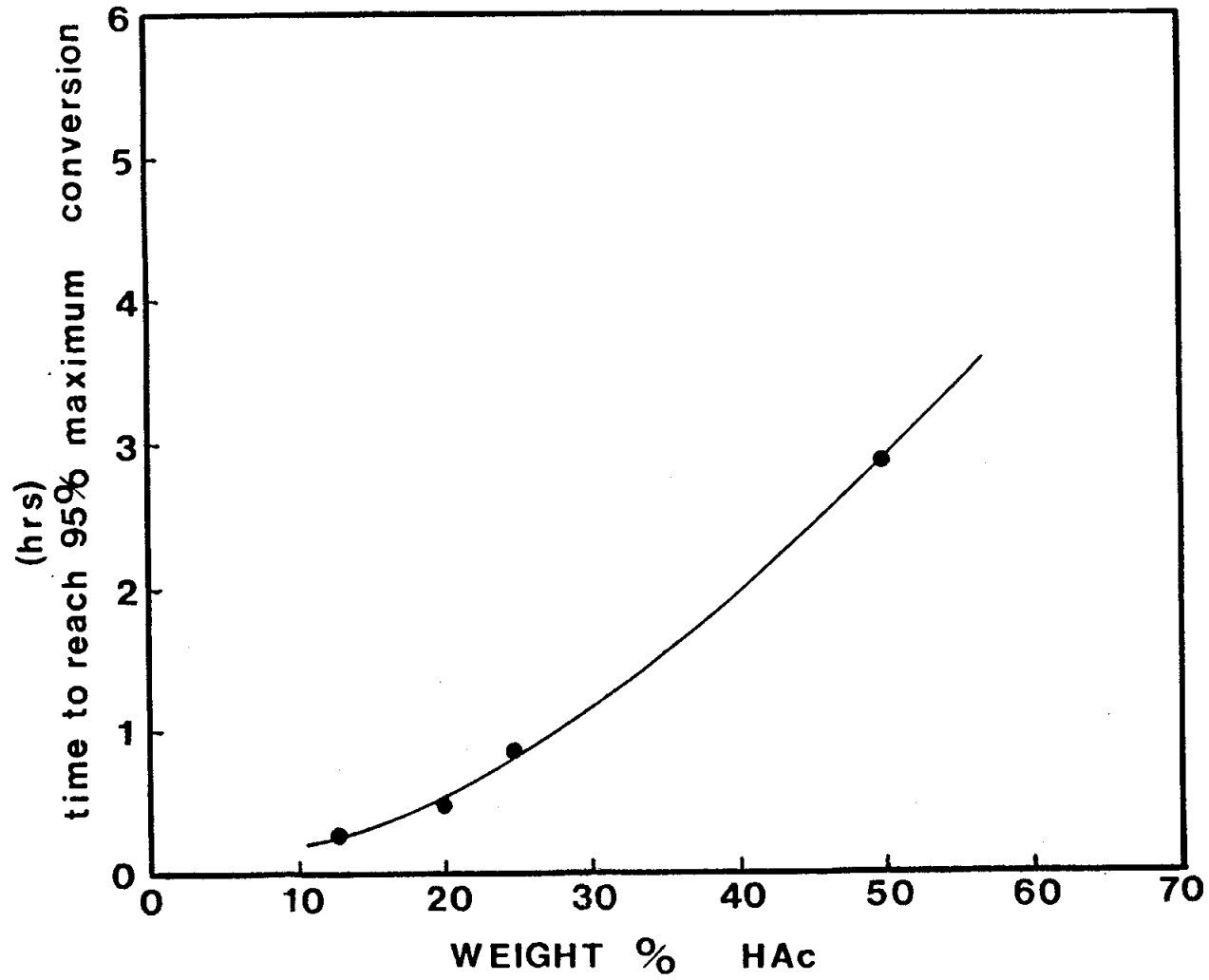
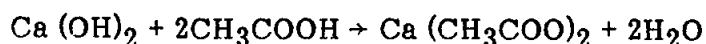


Figure 3-3: Reaction Time Versus Acid Concentration

The goal of this study is to define a process for the production of saturated CA solution. At 25°C, a saturated solution of CA is 28% CA by weight. The stoichiometric proportions of water, acetic acid and calcium carbonate assuming 100% completion required are 388 g. H₂O, 120 g. HAc and 100 g. calcium carbonate. However, at a water/acid ratio of 3.88:1.20, the conversion is only 86%.

A material balance for the reaction starting with stoichiometric proportions is given in Figure 3-4. The final product is a concentrated, but not saturated CA solution, with an excess of unreacted acetic acid. In a large scale plant, it may be feasible to recover the acid through any of a number of stock process. However, in a small or moderate scale plant, it will be more cost effective to use a neutralizing agent such as sodium or calcium hydroxide. In particular, the use of calcium hydroxide (hydrated lime) is recommended since the neutralization product is CA. The stoichiometric equation for this reaction is presented below.



The amount of calcium hydroxide required for neutralization is dictated by the amount of unreacted acid remaining in solution, which in turn is directly related to the original acid concentration. This relationship is presented in Figure 3-5. The final solution CA concentration after neutralization may also be calculated from the original acid concentration. This relationship is presented in Figure 3-6.

Thus, a two step process is envisioned, wherein a solution of acetic acid and water is reacted with an excess of calcium carbonate. The resulting solution is decanted and neutralized with calcium hydroxide. A representative material balance is presented in Figure 3-7. This material balance is for the production of a 26 wt. % solution of CA, slightly less than saturated.

For original acid concentrations of less than 24 weight percent, the resulting product will be an undersaturated solution. At 24 weight percent acetic acid, a saturated solution results. For concentrations greater than 24 weight percent a saturated solution and solid CMA are produced. This relationship is a direct result of the stoichiometry of the reaction and the fact that a saturated solution contains 28 weight percent of CA. Solubility limits are influenced by temperature. The figures used here are at 25°C. It should be noted, however, that any solid product will be "soaked" with solution and would require considerable dewatering and drying to be marketable or useful as a "solid" product. The decision as to whether a saturated solution or solid product is more

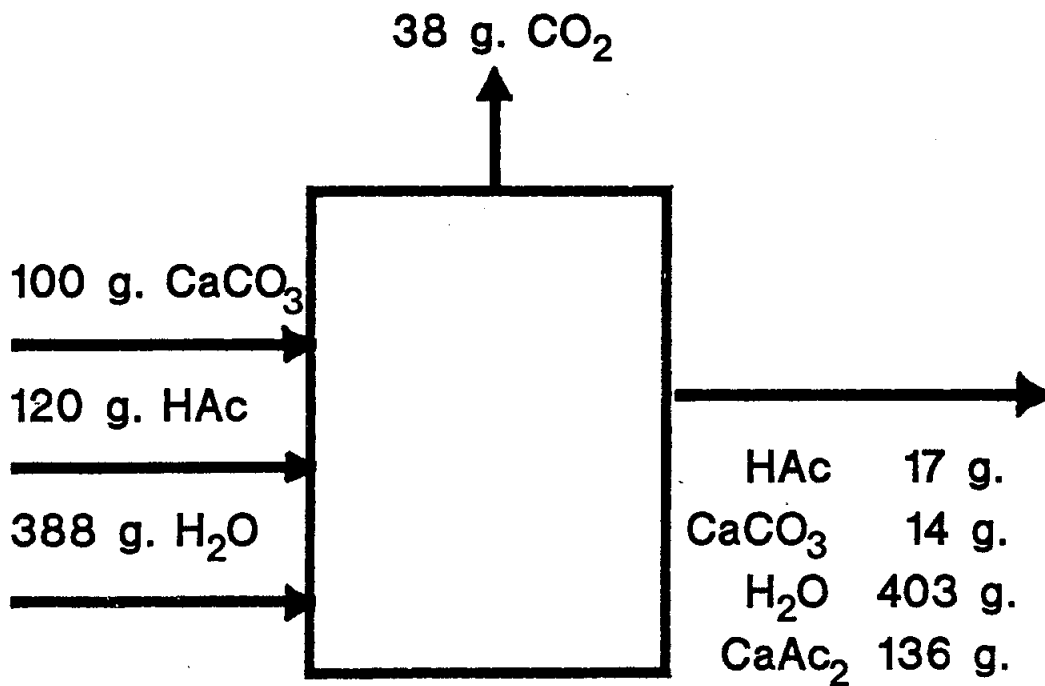


Fig. 3-4 Material Balance with Stoichiometric Feed

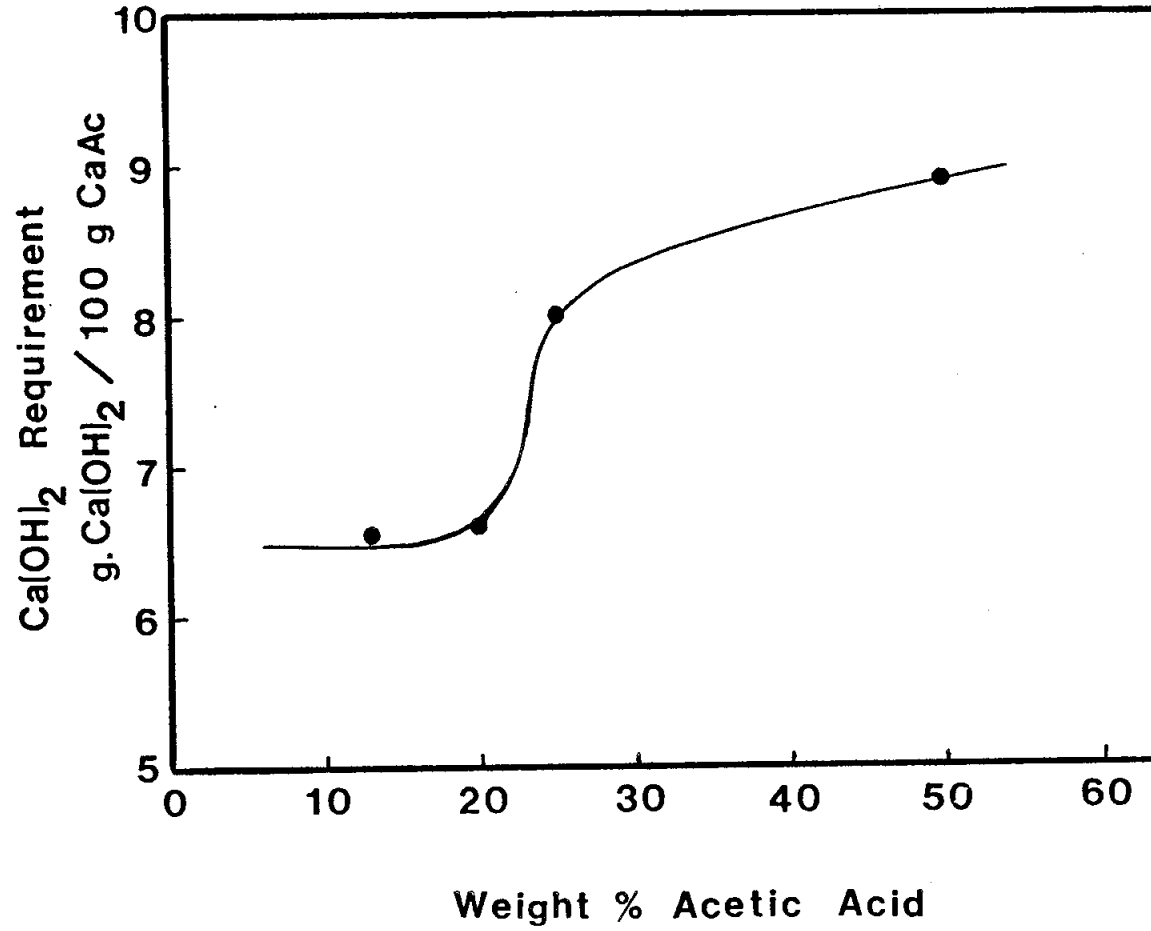


Figure 3-5: Calcium Hydroxide Required Versus Acid Concentration

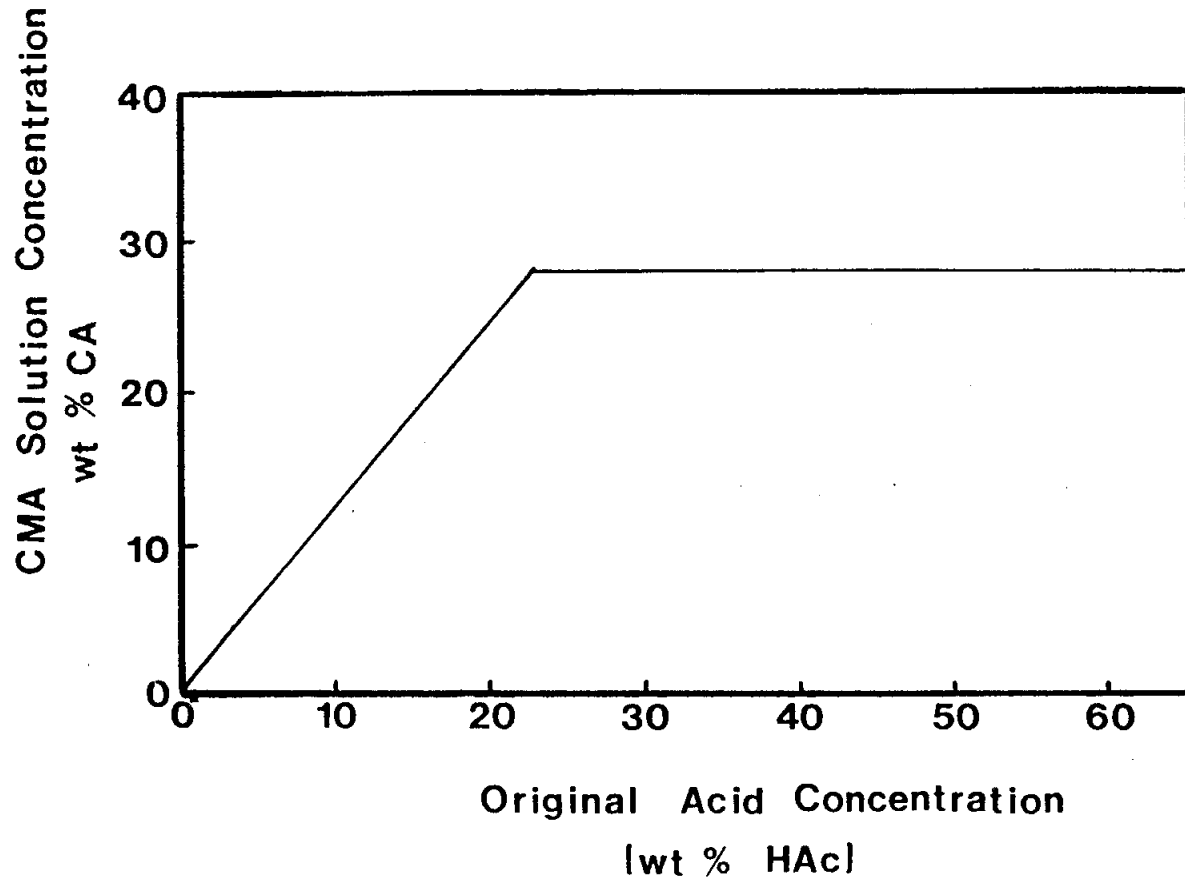


Figure 3-6: Final Solution Strength Versus Acid Concentration

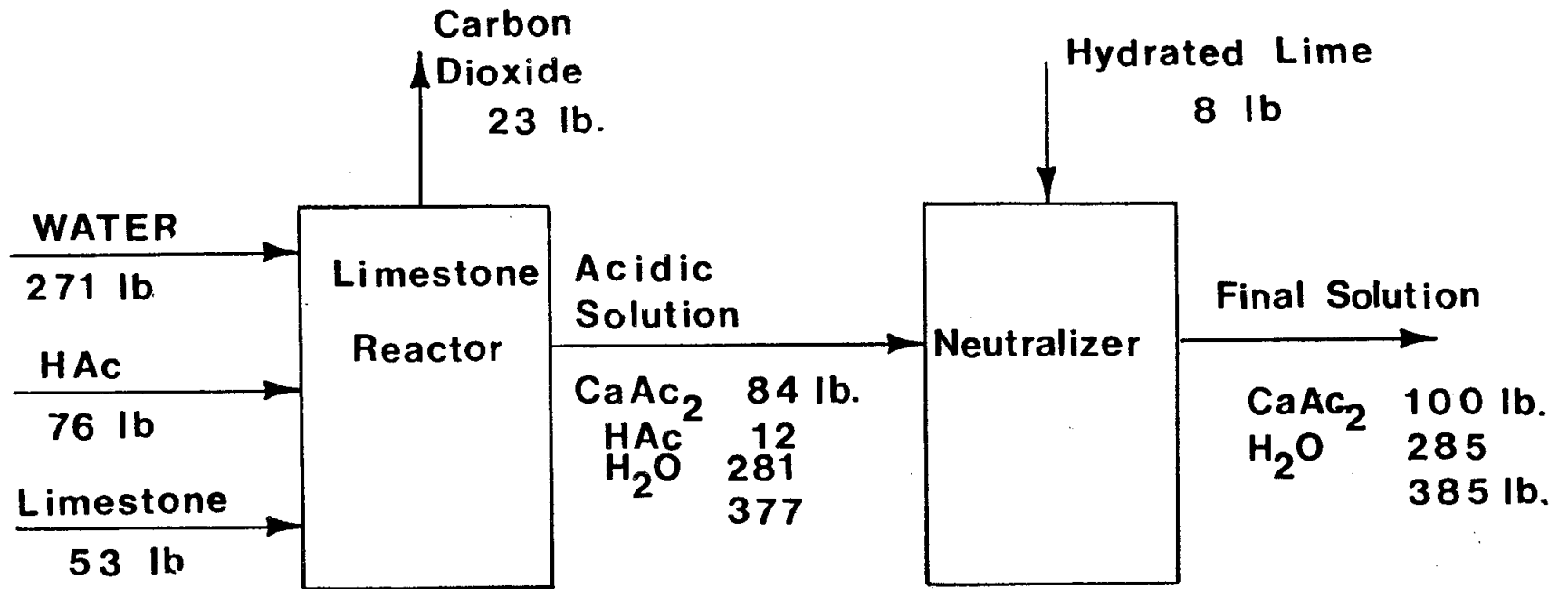


Fig. 3-7 Material Balance for Two-Step Process

desirable will depend on the relative costs of lime (calcium hydroxide) and the preferred form of the product for application purposes. In this study, it is presumed that the desired product is a saturated or nearly saturated solution.

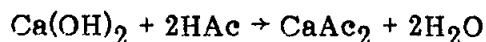
Finally, it should be noted that the above discussion is based upon reaction with pure calcium carbonate. If limestone is used, the reaction kinetics and ultimate degree of completion will vary with the nature of the limestone. The behavior of a representative dolomite is indicated on Figures 3-1 along with the data for pure calcium carbonate.

In general, it can be seen that the reaction with limestone is somewhat slower, and does not proceed to a great degree of completion as with pure calcium carbonate.

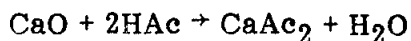
3.1.2 Production From Lime

Calcium Acetate (CA) can also be produced from the reaction of lime or hydrated lime with acetic acid as follows:

Hydrated Lime:



Lime:



This reaction is somewhat simpler than the reaction with limestone. No carbon dioxide is produced and no solubility barriers prevent the reaction from going to completion. As a result, the reaction may be conducted on a stoichiometric basis. A material balance for a representative reaction is presented in Figure 3-8.

3.2 Sources of Raw Materials

3.2.1 Acetic Acid

There are currently no manufacturers of acetic acid in Alaska. Thus, all acetic acid must be obtained from outside Alaska. The current delivered cost of glacial acetic acid in small quantities in Alaska is about 48¢ per pound including shipping and handling. The current world market price for acetic acid is 25¢/lb. (f.o.b Los Angeles). Shipping costs vary from 5-9¢/lb (Anchorage). This makes for a delivered price of about 30¢/lb or \$600/ton. Since .76 lb of HAc are required per pound of CA product, the cost contribution of HAc is about \$456/ton. Clearly, the key to economic CMA production is to control the HAc cost.

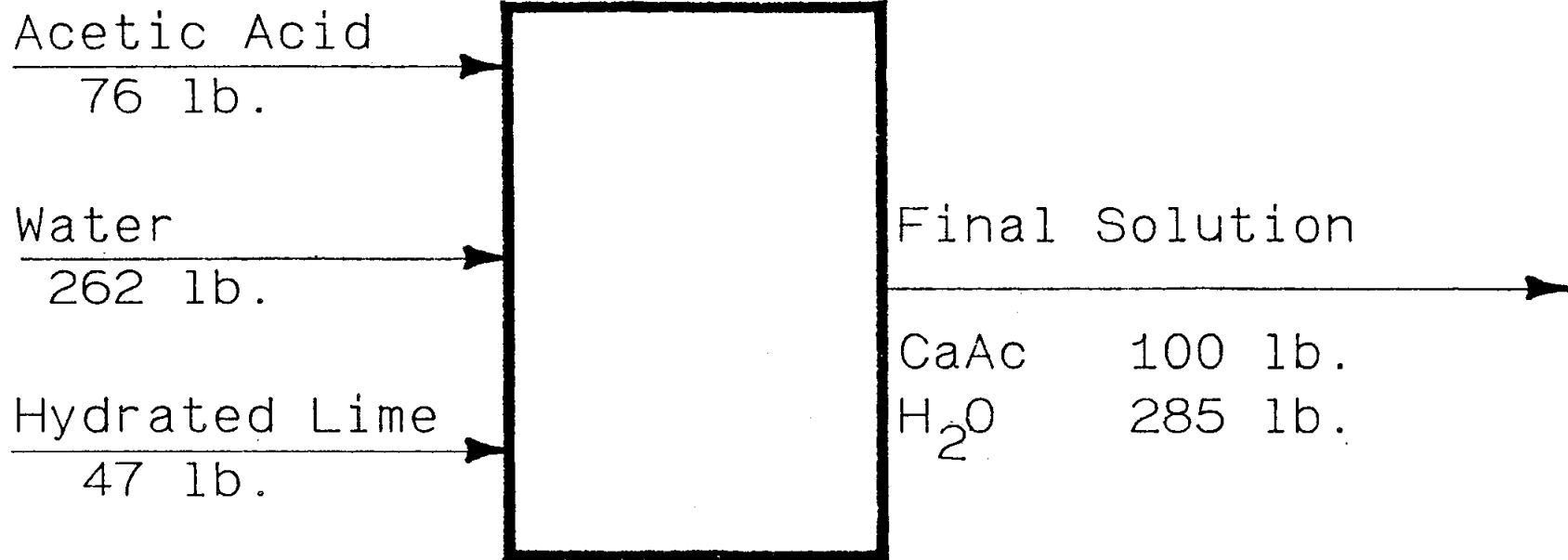


Figure 3-8. Material Balance Production from Hydrated Lime

For CMA production, large quantities of acetic acid will be needed. Earlier calculations have shown that the cost of production of CMA can be significantly reduced if the cost of acetic acid is decreased. Moreover, it is not necessary to use glacial acetic acid. A 50-50 mixture (volume basis) of acetic acid-water will suffice. Since a large portion of the cost of glacial acetic acid manufacture is associated with purification of reaction products, it is reasonable to expect that a petroleum derived, low grade, low cost acetic acid could be made available within Alaska.

We have completed a literature search for various processes for the manufacture of acetic acid. Although acetic acid can be produced from various chemicals, the three major routes are as follows:

1. The liquid phase oxidation of hydrocarbons.
2. Carbonylation of methanol.
3. Conversion of feedstocks derived from Biomass.

Of these three processes, the first is the most suitable for Alaska since light hydrocarbon fractions could be available from refineries within the State.

3.2.1.1 Liquid Phase Oxidation of Hydrocarbons

Process Description:

Liquid-phase catalytic oxidation (LPO) of n-butane was introduced by Celanese in 1952 at a large plant located near Pampa, Texas. Butane is dissolved in acetic acid along with a suitable homogeneous catalyst (e.g. cobalt, chromium, vanadium or manganese acetate) and sparged with air under high pressure. Pressures near the critical value are used. Temperatures from 95-100°C and pressures from 10-54 atm are usually required. Tubular reactors with a length to diameter ratio of 16-60 are required to obtain acceptable yields and conversions. The reaction products contain methylethylketone, ethylacetate, methylvinylketone, acetic acid, butyric acid, formic acid, propionic acid, and water. Figure 3-9 shows the process schematic. The acid-water product out of the light ends column typically contains 70% HAc, 3% HBU, 4% HF, 2.5% HPr, with the rest water. For CMA use, it may not be necessary to further purify this mixture, as there is no reason to assume that formates, propionates, and butyrates would not be similar to acetate as a deicer.

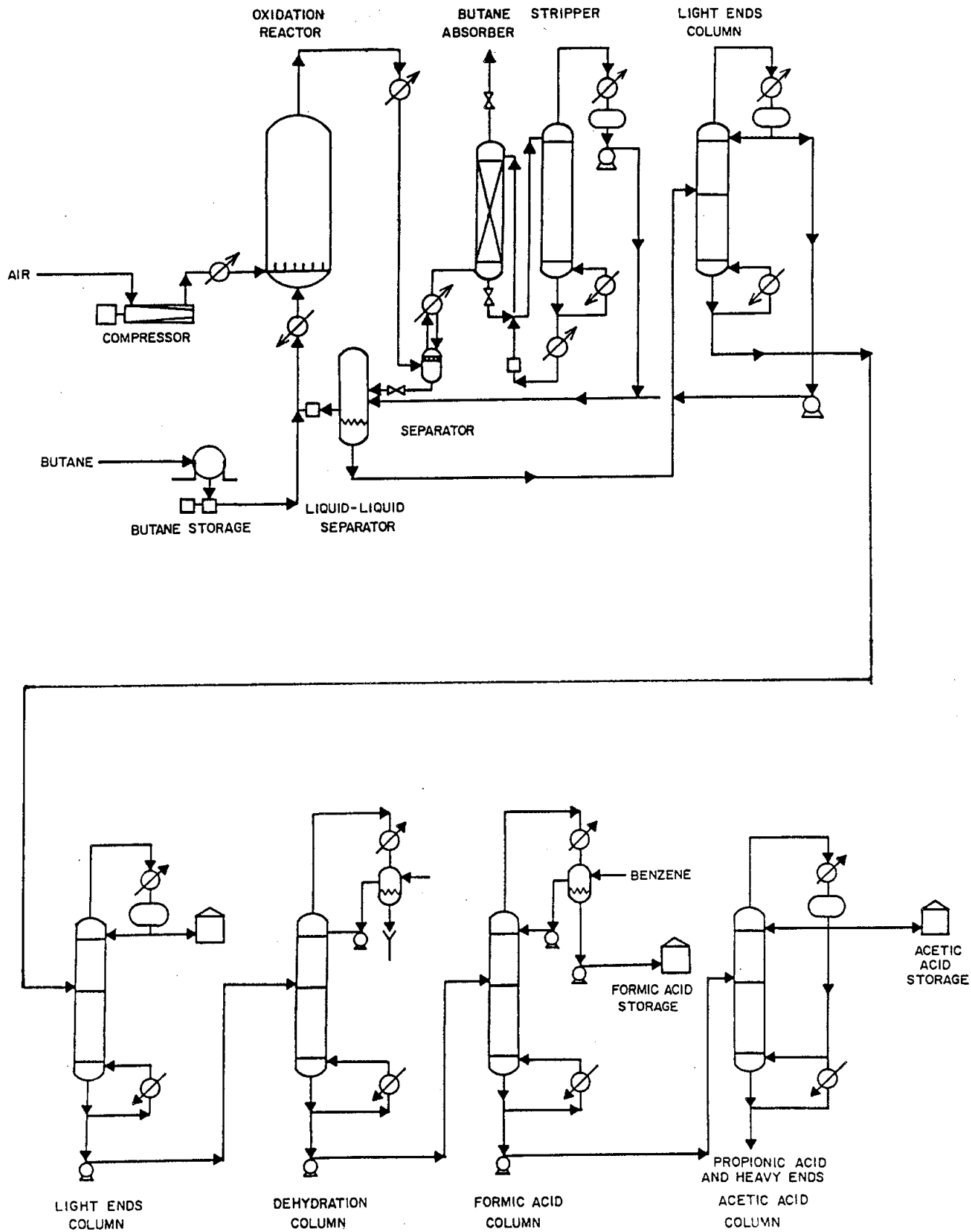


Figure 3-9: Process Schematic for the Producing of Acetic Acid

Laboratory Study:

In our laboratories we are concentrating our efforts on the process conditions for the manufacture of acetic acid from liquid phase oxidation of propane and butane. Since propane can be made available at the North Pole Refinery, it is desirable to ascertain whether propane can be converted to acetic acid through LPO. The scope of this study will be limited to determine process conditions such as pressure, temperature, conversion, flow rate, etc., and no attempts will be made to purify acetic acid. If and when need arises this aspect can be studied further.

3.2.2 Limestone

To maximize the deicing characteristics of a CMA solution, the ratio of magnesium to calcium ions should be as high as possible. Dolomite is a form of limestone having a high percentage of magnesium ions. The chemical formula for dolomite is $\text{CaMg}(\text{CO}_3)_2$. Typical compositions for dolomite and limestone are given in Table 3-1.

A study was conducted to locate the Alaskan deposits of dolomitic limestone most suitable for CMA production. The evaluation was accomplished in three stages. The first stage was a thorough literature search. The second stage was field work in which promising sites were examined in detail. The third stage was analysis and evaluation of the data collected, culminating in our recommendation of the most suitable sites for dolomitic limestone recovery. The quantity and composition of the material, accessibility and ease of transportation were considered.

3.2.2.1 Literature Search

The available literature concerning location, size, accessibility, and composition of limestone deposits within Alaska was examined. In addition, the Alaska Department of Geological and Geophysical Surveys and Mineral Industry Research Laboratory personnel at the University of Alaska provided up-to-date information and unpublished data. Dr. Gil Eakins, James Clough, and Dr. Florence Weber of the USGS, and Dr. P.D. Rao and Dr. Paul Metz of MIRL all made significant contributions.

A Master's Thesis by Sanusi⁽⁷⁾ was the starting point for this study. The reader should consult this thesis for more detailed information, and an excellent treatment of limestone resources. A number of other references were obtained by cross referencing. The majority of the published data are related to either pure limestone (CaCO_3) for cement manufacture or marble for use as a building material. Many of the reports dealt with the marble deposits on the Southeastern panhandle. A map of carbonate deposits in Alaska excerpted from this study is given in Figure 3-10.

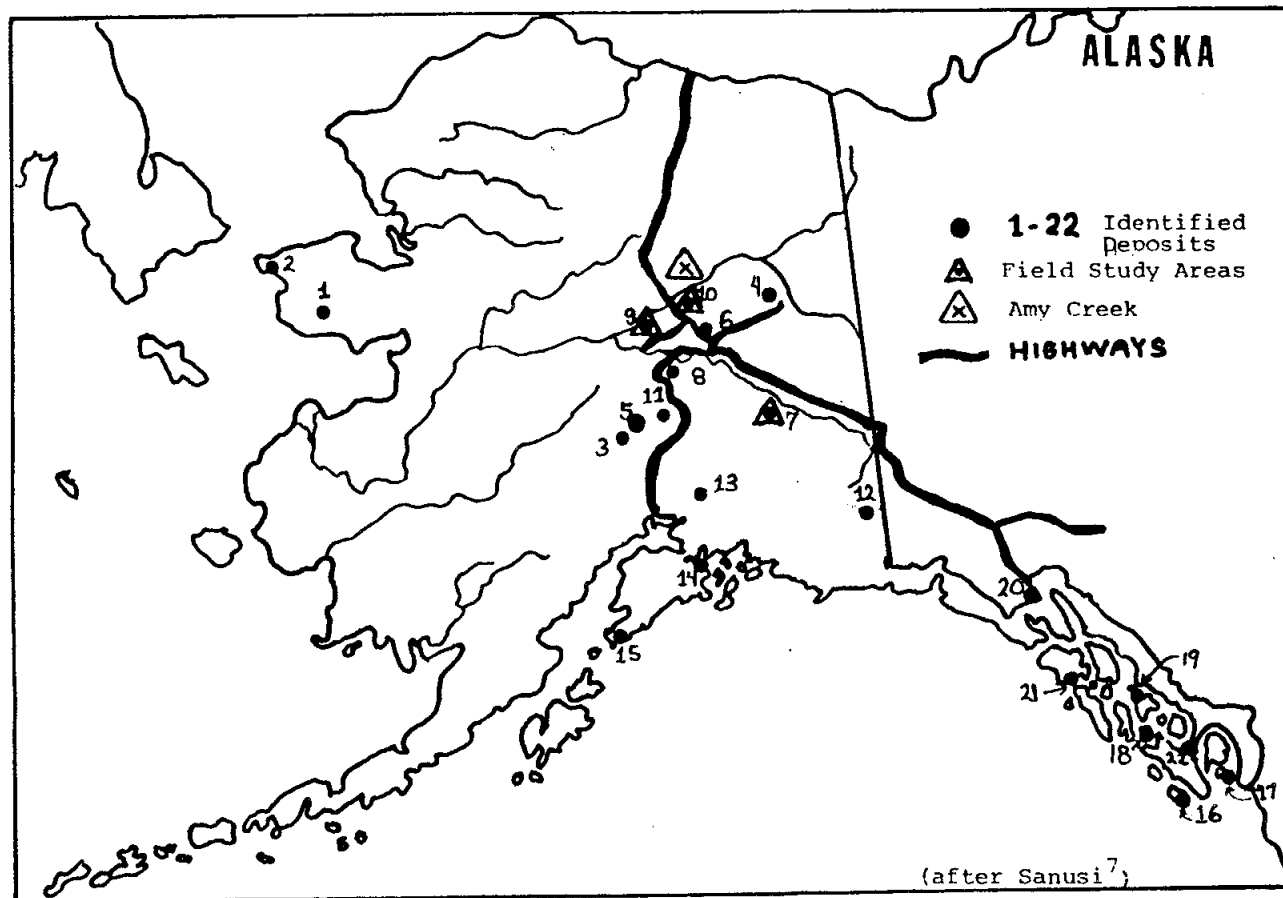


Figure 3-10: Location of Carbonate Deposits in Alaska

Figure 3-10 cont'd.

Summary of identified limestone deposits in Alaska (after Sanusi⁷)

Name	Location	Mean & CaCO ₃	Estimated Reserves (mil. tons)	Comments
<u>Western Region</u>				
1) Mount Distin	Nome Area	N.A.	N.A.	Thickness ranges from 2,200 ft. to 3,200 ft. and of high purity. Further field work required.
2) Port Clarence	Lost River area Seward Peninsula	N.A.	N.A.	Several thousand feet thick with sequences of black limestone 500 to 1,000 thick exposed east of Lost River.
<u>Interior Region</u>				
3) Chulitna River	West and southwest of Golden Zone mine	88.0	103	Two deposits at the heads of Long and Copeland Creeks. Easily accessible.
4) Crazy Mountains	Crazy Mts., 20 miles from Steese Highway	N.A.	N.A.	Easily accessible but further field work required.
5) Foggy Pass	15 miles northwest of Cantwell at the entrance of Foggy Pass	89.0	100	Very close to McKinley Park. Consists of grey crystallized, folded and contorted limestone.
6) Fox	3/4 mile southwest of Fox	53.0	N.A.	Easily accessible. Too small for commercial development.
7) Hoo Doos	East of Isabel Pass	94.0	300	Highly fractured. Easily accessible.

Figure 3-10 cont'd

Summary of identified limestone deposits in Alaska (continued)

Name	Location	Mean & CaCO ₃	Estimated Reserves (mil. tons)	Comments
8) Nenana	Birch Creek Schist	95.0	N.A.	A blue-grey lens, 1 to 4 ft. thick and 400 ft. long. Too small for commercial development.
9) Rampart	15 miles north of Manley Hot Springs, North Fork of Baker Creek	90.0	N.A.	Easily accessible. Further exploration work needed.
10) Tolovana	40 miles northwest of Fairbanks, Minto Flats-Dugan Hills	99.0	N.A.	A very large deposit which needs evaluation.
11) Windy Creek	Windy Creek	92.0	180	Easily accessible and approximately 4 miles from Cantwell.
<u>Southcentral Region</u>				
12) Chitistone & Nizina	Wrangell Mtns.	N.A.	N.A.	Sporadically distributed along the southern flank of the Wrangell Mountains. Very little is known.
13) Kings River	Matanuska Valley, Kings River drainage. North of Glenn Highway	97.0	33	Consists of several large steeply dipping masses.
14) Potter	1/2 mile northeast of Potter	96.0	N.A.	Consists of several lenses. Needs further exploration work.

Figure 3-10 cont'd.

Summary of identified limestone deposits in Alaska (continued)

Name	Location	Mean & CaCO ₃	Estimated Reserves (mil. tons)	Comments
15) Seldovia	Seldovia, Kenai Peninsula	89.0	0.2	Transportation limited to barge.
<u>Southeast Region</u>				
16) Dall & Long Island	Waterfall Bay and Gleva Bay	95.0	200	Massive and extensively folded. Accessibility almost impossible.
17) Glacier Bay	Willoughby, north & south Marble Islands	97.0	N.A.	Accessible with difficulties.
18) Heceta-Tuxekan	Heceta and Tuxekan Islands	94	N.A.	High purity, massive and thickness extremely variable.
19) Mud Bay	Northwest Shrubby Island	N.A.	15	Exposed as a 1500 foot beach outcrop.
20) Pleasant Camp	Haines cut-off international boundary	N.A.	N.A.	Further field work required.
21) Saginaw Bay	Kuiu Island	N.A.	N.A.	Needs further exploration.
22) San Alberto Bay	Wadleigh Island	N.A.	40	Accessible by waterway.

NOTE: N.A. - not available

3.2.2.2 Field Study

From the list of limestone deposits, several locations were chosen for field study using the following criteria:

- Composition: The deposit should approach the ideal composition of dolomite.
Accessibility: The deposit must be easily reached, also, it should not be in or close to Federally operated parks or preserves.
Location: The deposit should be relatively close to a major processing and distribution center.
Quantity: The deposit should be large enough for commercial use.

The Hoodoos deposit near Isabel Pass and several deposits along the Elliot Highway were examined in detail and samples of limestone were collected. The location of the field study sites are highlighted in Figure 3-10.

3.2.2.3 Data Analysis and Evaluation

The collected samples were analyzed for calcium and magnesium contents using a Direct Current Plasma Emission Spectrograph. Table 3-2 shows the results of the samples studied.

TABLE 3-2
CALCIUM AND MAGNESIUM CONTENT OF SELECTED SAMPLES
(Percentage of whole rock)

<u>Location</u>	<u>Calcium</u>	<u>Magnesium</u>	<u>Mg/Ca</u>
Hoodoos 1	38.45	0.168	0.0044
Hoodoos 2	33.47	1.490	0.0445
Hoodoos 3	37.95	0.317	0.0083
Hoodoos 4	33.93	0.389	0.0114
Amy Creek 1	22.27	12.020	0.5393
Amy Creek 2	22.98	13.000	0.5657
Livengood 1	22.75	0.280	0.0123
Livengood 2	21.20	12.186	0.5748
Livengood 3	36.29	0.303	0.0083
Livengood 4	22.39	12.490	0.5578

3.2.2.4 Conclusions

The Livengood #4 location was selected as the most promising site for future study and utilization. This deposit is part of a major outcropping. High grade dolomite is present in quantities far beyond that necessary for CMA production. The current projected CMA requirements is about 9,000 T/yr. This would require about 9,000 T of limestone, or about 4,500 yards of limestone/year. Although the extent of this deposit is not clearly defined, the deposit is several hundred feet wide, at least 40 feet in height

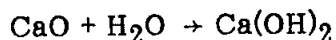
and extends (judging from outcroppings), for several miles. This deposit is located approximately 40 miles north of Fox, Alaska on the Elliot Highway. The dolomite is exposed behind a roadcut on the east side of the road.

The dolomite is medium gray in color on a fresh surface and weathers to light brown on exposed areas. It is finely crystalline, and highly fractured. No fossils were found as it has been recrystallized. A number of the fractures contain calcite.

The site was chosen because of its relatively high percentage of magnesium, proximity to Fairbanks along a major roadway, and the large volume of material present. Another important aspect is the fact that the deposit has already been used by the Department of Transportation for roadwork. Therefore, the state already has rights to the deposit and no environmental impacts are apparent.

3.2.3 Lime

Hydrated lime or calcium hydroxide is a common compound often used as a soil conditioner. It is produced from limestone in the form of calcium oxide (CaO). The addition of water converts CaO to calcium hydroxide through the following reaction:



Lime is a by-product of the production of acetylene gas from calcium carbide and water, and is used in the manufacture of cement. There are currently no cement plants in Alaska, but there are at least two acetylene plants, one in Palmer (Big-Three Lincoln) and one in Anchorage (Liquid Air Corporation).

The plant in Palmer produces about 200 tons/year of dry calcium hydroxide. Table 3-3 presents the analysis of the calcium hydroxide produced at Big Three Lincoln in Palmer, Alaska. This product is currently classified as a "waste" and poses a disposal problem for the manufacturer. The product is in the form of a white powder. Roughly 5,000 cubic yards have accumulated at the plant site. The facility in Anchorage produces a smaller amount (exact production not known). To produce 8,000 ton/year of CA (current projected demand), roughly 3,700 ton/year of calcium hydroxide would be required. Current calcium hydroxide production rates are not sufficient to serve as the raw material for CA production. However, if limestone is the base calcium source, the amount of calcium hydroxide required for neutralization is only 800 ton/year.

Thus one quarter to one half of the required lime could be obtained in Alaska. The lime is currently a disposal problem, and could probably be obtained at a relatively low cost.

TABLE 3-3
Hydrated Lime Analyses
(Dry Basis)

	Acetylene Generator By-Product Hydrate		Commercial Hydrate
	From Generator	From Settling Pond	Sample 1
Ca(OH) ₂	96.50	95.00	96.44
Available CaO	(73.00)	(69.80)	(72.50)
CaCO ₃	1.25	2.00	1.76
SiO ₂	1.10	0.83	0.38
R ₂ O ₃ (Al ₂ O ₃ ,Fe ₂ O ₃)	0.50	0.20	0.57
Mg(OH) ₂	0.25	0.20	0.57
S	0.15	0.16	0.03
P	—	0.01	0.01
Free Carbon	—	0.40	—

4.0 PILOT PLANT STUDIES

In the past three years, we have produced CMA successfully from lime and limestone, in lab scale, bench scale and pilot plant scale processes. In this section of the report, our experiences are summarized.

4.1 Bulk Production of CMA From Hydrated Lime (Calcium Hydroxide)

As discussed above, the reaction of acetic acid with hydrated lime is much easier to conduct than that with limestone. In many areas, hydrated lime is readily available for purchase as a common agricultural soil conditioner. In Alaska, significant quantities are available as a by-product of acetylene manufacture. At the present time, this material is a nuisance, posing a disposal problem. As a result, it may be available as a raw material for CA manufacture at little or no cost. However, the current level of lime production from this source is far less than would be required if all salt usage in the state were replaced by CA. Thus, it is envisioned that if CA is produced in Alaska, it would be produced from limestone, and not from lime. However, as mentioned above, there is a need in the limestone process for a neutralizing agent such as hydrated lime (calcium hydroxide).

In the summers of 1983 and 1984, 5,000 and 7,000 gallons respectively of saturated CA solution were produced. At this juncture, we were in need of a significant quantity of CMA for road and environmental tests. Since hydrated lime was available at no cost in sufficient quantity for our purposes, this reaction route was chosen. A pilot plant was constructed at Alaska State DOTPF facilities in Fairbanks by personnel of the Petroleum Engineering Department at UAF. In the sections that follow, this plant, and our experiences in operating it are detailed.

4.1.1 Equipment

A schematic diagram of the pilot plant is presented in Figure 4-1. The plant consisted essentially of two 500 gallon stainless steel reactors, associated feed tanks, product tanks, and transfer pumps and hoses. The key elements are described below:

1. Reactors (2) - 500 gallon stainless steel tank with a loosely fitted top closure, and a bottom drain (1.5" pipe). A mounting bracket for an agitator was attached in the top center of the reactor (see Figure 4-1).
2. Agitators (2) - 1.5 hp electrically driven, single shaft, twin propeller agitator.
3. Acid Pump - Wilden air operated Teflon diaphragm pump, 5-20 gpm capacity.
4. Air Compressor - 1.5 hp air compressor to drive acid pump.

CMA PILOT PLANT

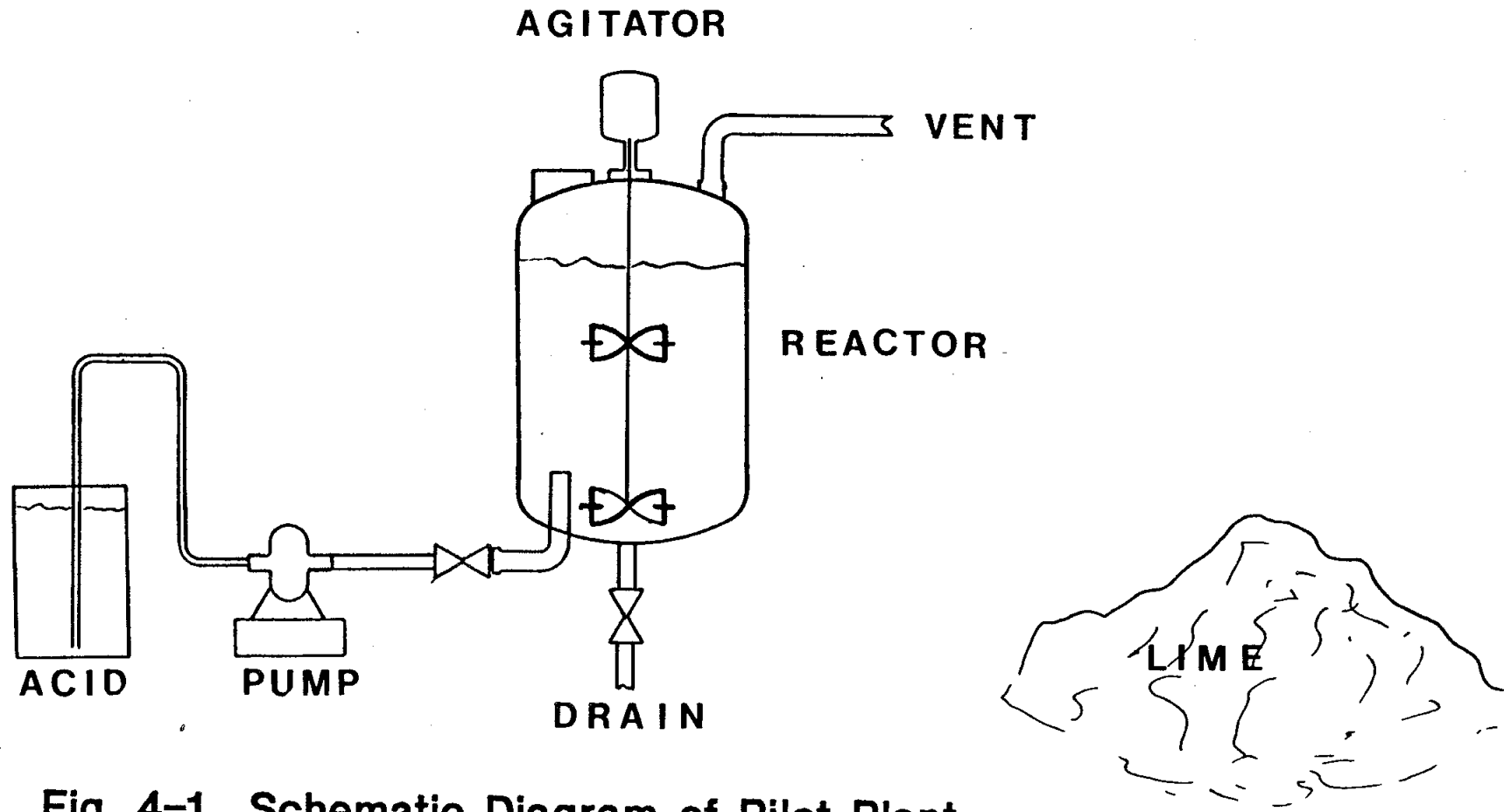


Fig. 4-1 Schematic Diagram of Pilot Plant

5. Generator - 6kW generator to power the air compressor and agitators.
6. Miscellaneous Tubing and Piping - Two 25 foot sections of Teflon hose (1" ID) were used for transfer of acid and products.

Many modifications to the above equipment would be acceptable. The important factor to consider, is that the reactor and any pumps or tubing coming in contact directly with the acid should be of a corrosion resistant material. As described below, it is possible to conduct the reaction so that the reactor itself never encounters an acidic solution. In this event, all that is required is an agitated vessel capable of withstanding exposure to caustic lime. The only equipment coming into contact with the acid would be the transfer lines and pump.

4.1.2 Raw Materials

Glacial acetic acid was shipped in 55 gallon drums from bulk chemical suppliers in the "lower 48" states. It was of research purity, although this is certainly not required. Virtually any grade of acid would suffice. As the pilot plant was set up in a "remote" location without water, electricity, or sewer facilities, water was hauled in and stored in a 1000 gallon tank. Hydrated lime was donated by Big Three - Lincoln in Palmer, Alaska. An analysis of the lime is presented in Table 3-3. The lime had been exposed to the elements for several years, and had "acquired" some impurities, mostly inerts. The most significant problem with the lime was a varying water content throughout the stockpile, and over the course of the summer. This uncertainty made quality control measurements a necessity.

4.1.3 Operating Procedures

The reactions were conducted in the batch mode. Little attempt was made to minimize the reaction and turnaround times. In 1983, the plan called for the production of 5,000 gallons of saturated solution. Ten batches were prepared. In 1984, an additional 7,000 gallons were produced in fourteen batches. The procedure was the same for each batch, although the final adjustment of pH and density for each batch was unique. The following procedure was followed:

1. Reactor was filled with 300 gallons of fresh water.
2. Roughly 22 cubic feet, or 1200 lbs. of lime were added to the tank, while agitating. The lime was added manually using 2.5 gallon buckets, which were filled by hand from the storage pile. Initially, the buckets were weighed, in an attempt to more accurately control the amount of lime added. However, the variation in water content of the lime was significant enough to make exact knowledge of the

appropriate amount of lime to add unknown. Thus, the amount of lime added varied from one batch to the next. The quality control procedure described below assured a constant product quality.

3. While agitating, two barrels of acetic acid were pumped into the bottom of the tank. The acid was added slowly to avoid contacting the tanks directly with undiluted acid. The reaction is exothermic, and the solution temperature rose to nearly 180°F during the mixing process. If all of the acid were added suddenly, it may be possible to approach the boiling point of the solution.
4. The tank was agitated for up to 8 hours, or until the pH became stable. The solution was then allowed to settle for several hours.
5. A sample of clear liquid was withdrawn from the tank and the gravity and pH were measured. Typically, the solution was less than saturated with CA. The CA concentration was estimated from the specific gravity of the solution. A computation was made to determine the amount of lime required to bring the density up to the desired mark. This amount of lime was then added to the solution.
6. The density having been adjusted, acetic acid was added to bring the pH to approximately eight. The amount of additional acetic acid was determined by scaling up a simple titration of the solution liquid. It was also possible to monitor the tank pH directly while adding acid.
7. The tanks were allowed to settle for several more hours. The clear solution was then pumped to storage facilities. In 1983, the solution was pumped directly into a 3000 gallon tank truck for storage and application. In 1984, the solution was stored in a variety of drums and tanks.

4.1.4 Quality Control

The desired product for the pilot plant was saturated CMA solution. The inherent uncertainty in the water content and composition of the lime made it impossible to assure product quality through metering of the reactants. It was necessary to adjust both the pH and the gravity of the product solution to the desired values. The desired specifications for the product were:

Specific Gravity = 1.14

Weight Percent = 25

pH = 8.0

Density was determined by weighing a known volume of fluid. Using published data on density of CA solutions versus weight fraction CA, the CA concentration can be determined from density. Care was required to see that the fluid sample did not contain

appreciable amounts of suspended solids. Filtration is recommended.

The concentration of the solution can be increased to the desired value (25 weight percent) by adding calcium hydroxide and acid. A simple material balance calculation yields the following relationship for calculating the pounds of calcium hydroxide required to increase the concentration to 25 weight percent:

$$S = (W + A + L)/1.48 * (.25 - X)$$

where W = original amount of water used lb., L = original amount of lime used (lb), A = original acid used (lb), and X = actual weight fraction CA.

The adjustment of pH is somewhat easier. A small sample (200 cc.) of clear solution is titrated to a pH of eight with acetic acid. The amount of acid required is then divided by 200 to obtain a ratio of volume acid required per volume of solution. The volume of solution in the tank is roughly 400 gallons at this point. The ratio is simply multiplied by 400 to obtain the estimate of the gallons of acid required to neutralize the tank. In the final adjustment, the pH of the tank is monitored directly, and acid or lime is added manually to bring the pH to eight.

4.1.5 Material Balances

A material balance representing a typical batch is presented in Figure 4-2. It should be recognized that in reality, some water and inert material will be present, in the "lime", necessitating the use of slightly more "lime" (by weight) than indicated in the Figure. In general, the correct amount of lime required can be determined by dividing the pure lime requirement by the weight fraction of pure lime in the actual lime used. If the lime is particularly wet, the amount of water added with the lime should be subtracted from the total water required.

4.1.6 Observations

Little difficulty was encountered with the pilot plant operations. Once operating procedures were established, the process worked quite well. It was possible to complete the production of a 500 gallon batch in under six hours. Two people could produce two parallel batches in an eight hour shift (2000 gallons).

This particular pilot plant design was one of expediency. The process was labor intensive, and could certainly be improved upon. The purpose of this pilot plant was two-fold. First, a supply of CA was necessary for environmental studies and field tests. Second, it was demonstrated that CA can be produced simply and efficiently with a minimal amount of equipment.

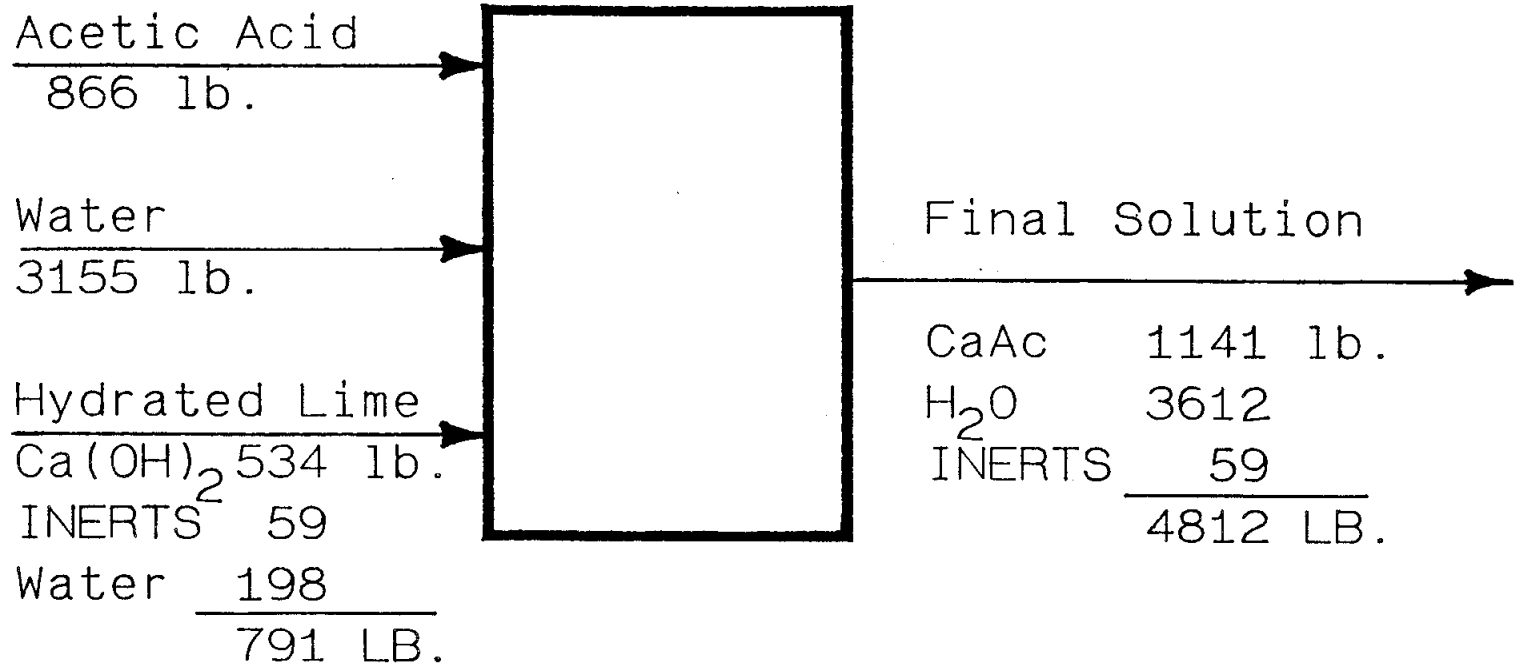


Fig. 4-2. Material Balance For Pilot Plant Production

4.1.7 Problems

Acetic acid in pure form freezes at about 60°F. We encountered difficulty with the acid freezing routinely. It will be necessary to provide heated storage facilities for the acid. The problem can be alleviated somewhat by mixing water in with the acid. The heat of mixing upon contact with water tends to warm the mixture, and the freezing point of aqueous acetic acid solutions is much lower than pure acetic acid.

The reaction of acetic acid with lime is exothermic. Although no gas is produced, there is a tendency for the mixture to foam at high temperature. Care must be taken regarding the speed with which the acid is added to avoid overheating the solution.

Acetic acid vapor is a health hazard as well as being flammable. In general, any personnel involved in this process should be instructed on proper safety procedures regarding the use of acetic acid. More importantly, the reaction area should be adequately ventilated. While the fumes given off from the tanks themselves are minimal, some small amounts of acid may escape during transfer operations. Extreme caution should be exercised at all times in handling the acid.

It is possible to use too little water in the reactors and to produce more CA than can be held in solution. On two occasions this occurred, once by accident, and once intentionally. When CA precipitates, it forms a hydrated crystal, thus pulling additional water from the solution. As a result, the solution in effect "gels" suddenly, to a consistency not unlike thick oatmeal. With the proper equipment, this paste could be collected and further dried to a powdered form. However, for the purposes of this study, and with the equipment at hand, the paste was unmanageable. However, the addition of a small amount of water was sufficient to redissolve the entire mixture. In one case, as little as five gallons of water added to the 400 gallons of paste was sufficient to redissolve the entire mixture. Care should be taken to see that this precipitation does not occur, as it may damage the agitators.

4.2 The Production of CMA From Limestone

The production of CMA from limestone was somewhat more complicated than described above. A two step process is required. First, calcium carbonate is dissolved in a solution with an excess of acetic acid. In the second step, the excess acid is neutralized with calcium hydroxide. The evolution of carbon dioxide is a further complication.

Numerous lab scale studies were undertaken to determine the stoichiometry and kinetics of the reaction of acetic acid with limestone. A limited number of bench scale

studies were also performed. In the previous section of this report dealing with CMA chemistry, the basics of the reaction and results of these studies are summarized. A detailed report covering the results of these experiments will be released at a later date. However, the information essential for a process design is presented here.

5.0 PROCESS DESIGN

Process designs are presented below for the production of CMA from limestone and lime. These designs are based on the results of our experiences with the pilot plant, and numerous lab scale studies of the reactions involved. The designs have been verified in our laboratories, and should provide a valid basis for specific equipment design and cost analysis. The design basis is 12,000 GPD production with a stream factor of .95, for an annual production of 5140 TPY of dry CA equivalent. The economics of CMA production will be site specific, and will depend heavily on the costs and properties of the raw materials. The final desired form for the product i.e., solid or saturated solution, may also influence the final design.

5.1 Production of CMA From Limestone

5.1.1 Material Balance

The production of CMA from limestone requires a two step process. In the initial step, a solution of acetic acid is allowed to react with excess calcium carbonate (or limestone). The liquid product is then separated from the solid, unreacted carbonate, and neutralized with calcium hydroxide. The concentration of the original acetic acid solution will determine to some extent the concentration of the final product. In general, if the acid concentration exceeds 24 weight percent, the product will be a saturated solution with a solid precipitate. As described in the discussion of the pilot plant above, this precipitation will result in a thick paste-like product, which would require special handling. If the concentration of the acid is exactly 24 weight percent, a saturated solution will result after neutralization. If the acid concentration is less than 24 weight percent, an undersaturated solution will result. The relationship between original acid concentration and product concentration is presented graphically in Figure 3-6.

While it may appear that the best course of action is to use a high original acid concentration, it should be noted that the amount of calcium hydroxide required per pound of CA increases with increasing acid concentration (See Figure 3-5). Since calcium hydroxide is normally more expensive than limestone, it may be best to minimize calcium hydroxide consumption. However, if calcium hydroxide consumption is eliminated through the use of a dilute solution of the acid, the resulting product would be too dilute to be useful directly, and would require expensive concentration. The final decision as to how to proceed will be an optimization question involving the prices of limestone and lime, and the expense of concentrating the solution.

A material balance for the production of saturated solution is presented in Figure 3-7. A similar material balance for the production of saturated solution and solid CMA is presented in Figure 5-1.

The reaction represented in Figure 5-1 is valid, but would result in the production of solid CMA along with a saturated solution. While it may be desirable to produce a solid product the resulting mixture is too thick to be handled in a stirred tank reactor, and contains unreacted HAc and solid limestone in addition to the CA product.

The process design specified in this report is for the production of a nearly saturated solution of CA. The material balance presented in Figure 5-2 is the basis for this design.

The first reactor, in which the acetic acid and limestone react, may be operated either in the batch or continuous mode. A residence time of about four hours is required. If the reaction is to be conducted in the continuous mode, more detailed information regarding the kinetics of the reaction will be required for proper sizing. The degree of agitation and particle size will also be important parameters.

Operation in the batch mode is more forgiving of incomplete kinetics characterization. Moreover, in the continuous mode any impurities in the limestone would build up in the reactor. The continuous mode would require continuous cleaning, or the availability of a duplicate reactor for operation during the cleaning cycle for the first reactor.

The process design presented in this report is based on the material balance given in Figure 5-2. For the purpose of standardization, the design is based on the reaction of pure calcium carbonate. If limestone is used, slight changes are experienced due to the presence of varying amounts of inert materials, and somewhat decreased conversion versus that obtained with pure carbonate. These factors have very little effect on the process design, but do affect the material balance, and hence the process economics.

The major effect of inerts is to require correspondingly more "limestone" to obtain the proper amount of carbonate. If the limestone contains X (weight fraction) calcium carbonate, then based on the material balance presented in Figure 5-2, $53.1/X$ pounds of limestone would be required per 100 lbs. of CaAc_2 as opposed to 53.1 lbs. If an excess of limestone, Y, is used (Y = weight fraction excess calcium carbonate). The total limestone feed would be $53.1(1 + Y)/X$. The resulting waste stream of inerts would be $(1 + Y)(53.1)(1-X)/X$ and the amount of unreacted limestone would be $53.1 Y$.

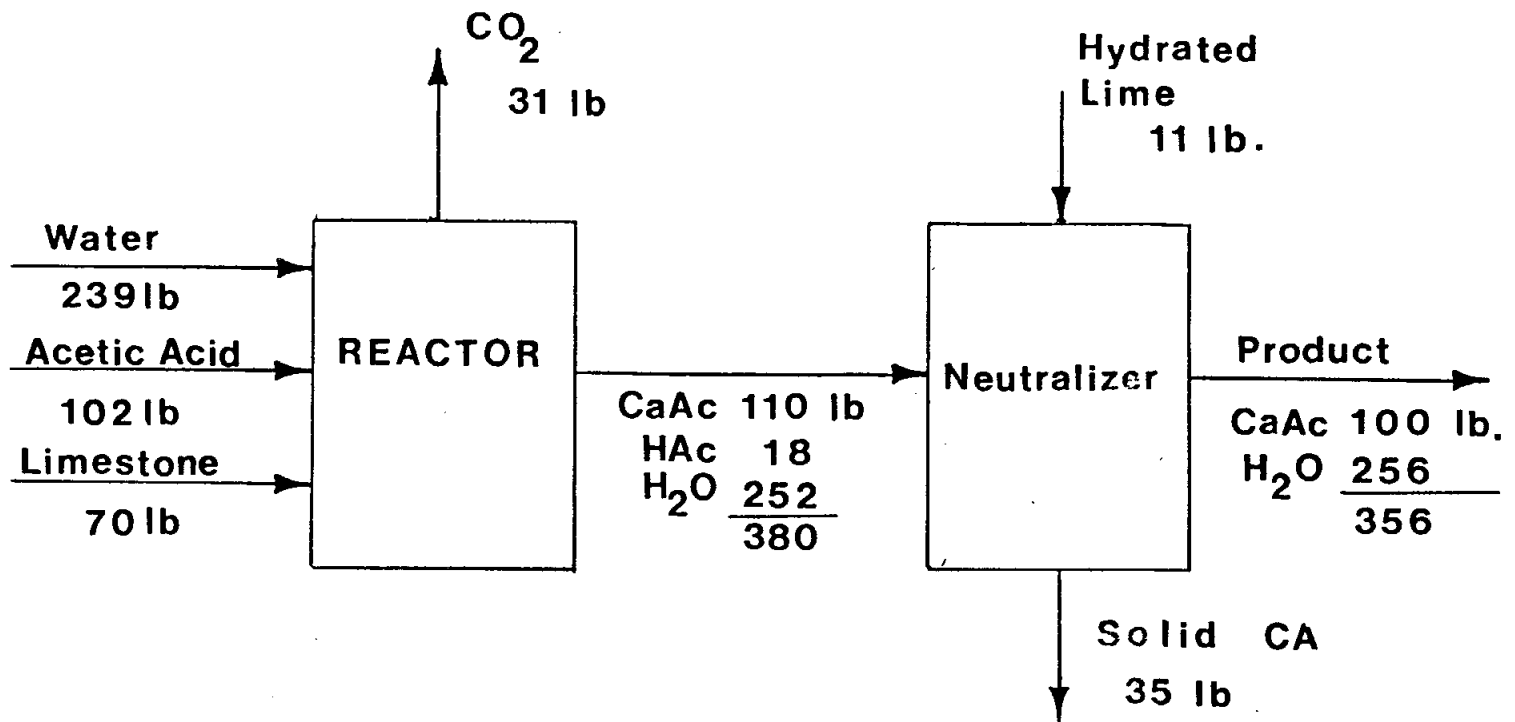
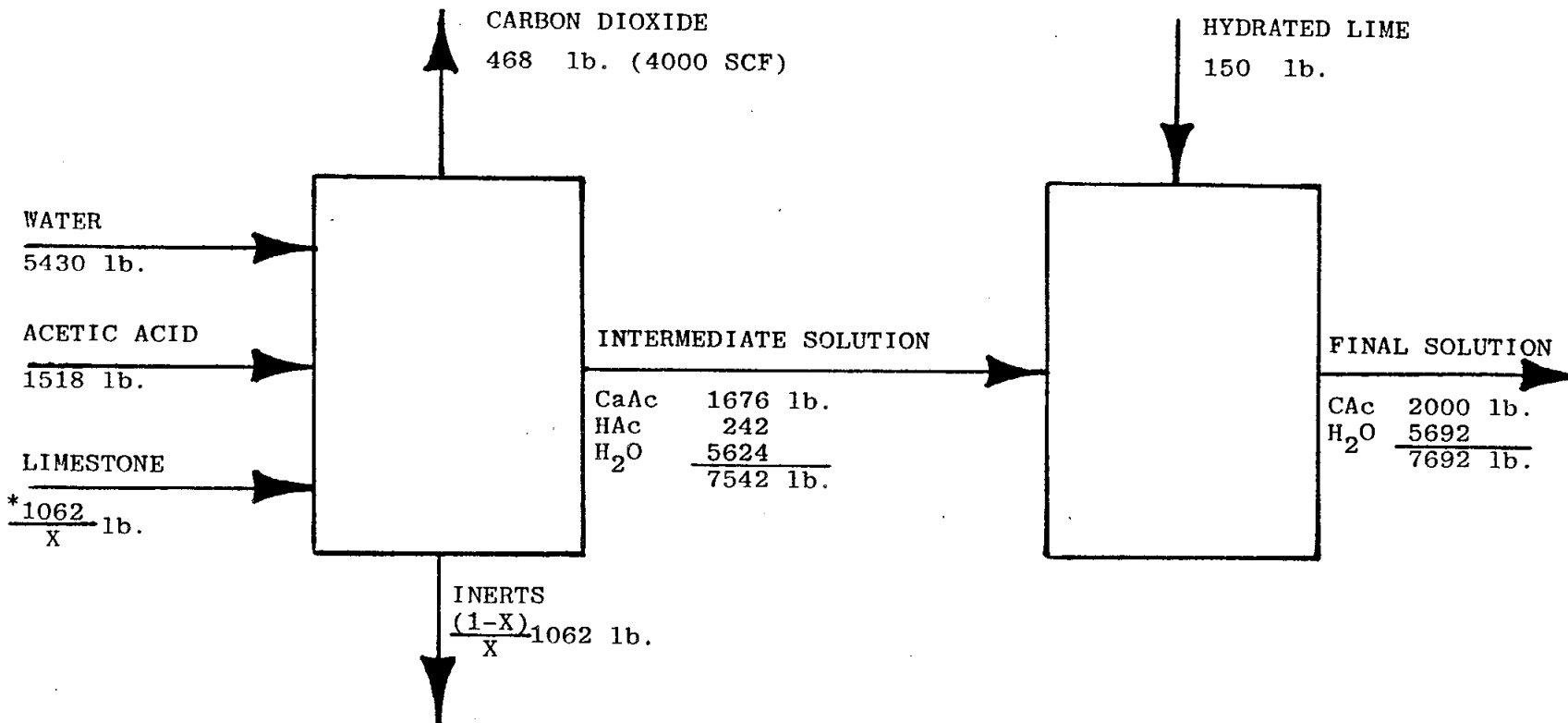


Figure 5-1: Material Balance for Production of Saturated Solution and Solid CA



* If the limestone purity is X (wt. fraction $\text{Ca}(\text{CO})_3$), the limestone requirement is $1062/X$.

Fig. 5-2 Material Balance for Process Design - Production from Limestone (Based on a production of 1 ton of dry CA in a 26 wt% solution)

The effect of changes in conversion is a change in the amount of Ca(OH)_2 required for neutralization. This effect is shown in Figure 5-3. The equipment design and operation procedures would be unaffected.

5.1.2 Process Description

The process could be operated in either a batch or continuous mode. Continuous mode operation is normally more economical for large scale operations. However, a large investment in real time control equipment is required. This equipment would include flow controllers, level controllers, pH controllers, density measurement equipment, solid metering systems, etc. The presence of this equipment would require a highly trained staff of at least two.

The same process can be conducted in the batch mode by a two-man crew, using manual controls. In this case, the extra expenditure necessary to "automate" the process cannot be justified. If a design were contemplated for a much larger plant, (greater than 100,000 GPD) a continuous process might be justified.

While the reaction must be conducted in two steps, reaction and then neutralization, the same reactor can be used for both reactions. The basic process design in this case consists of three 4,000 gallon reactors and the associated transfer equipment. A detailed equipment list is given below. A process schematic is presented in Figure 5-4.

A complete batch can be produced in one 8-hour shift. Thus it is possible to achieve a 12,000 GPD production rate with a single reactor and three shift operation. However, as is demonstrated below, the reactor cost is a small factor in determining the overall process cost. Thus it is more desirable to install parallel reactors and conduct the entire daily production in one shift. This approach greatly simplifies the logistics of operation, and allows the flexibility to increase production to 36,000 GPD if desired. In particular, the production could be performed seasonally if desired, requiring four months to produce the annual equivalent of 12,000 GPD production. In this case, however, large storage capacity (over 4 million gallons) would be required.

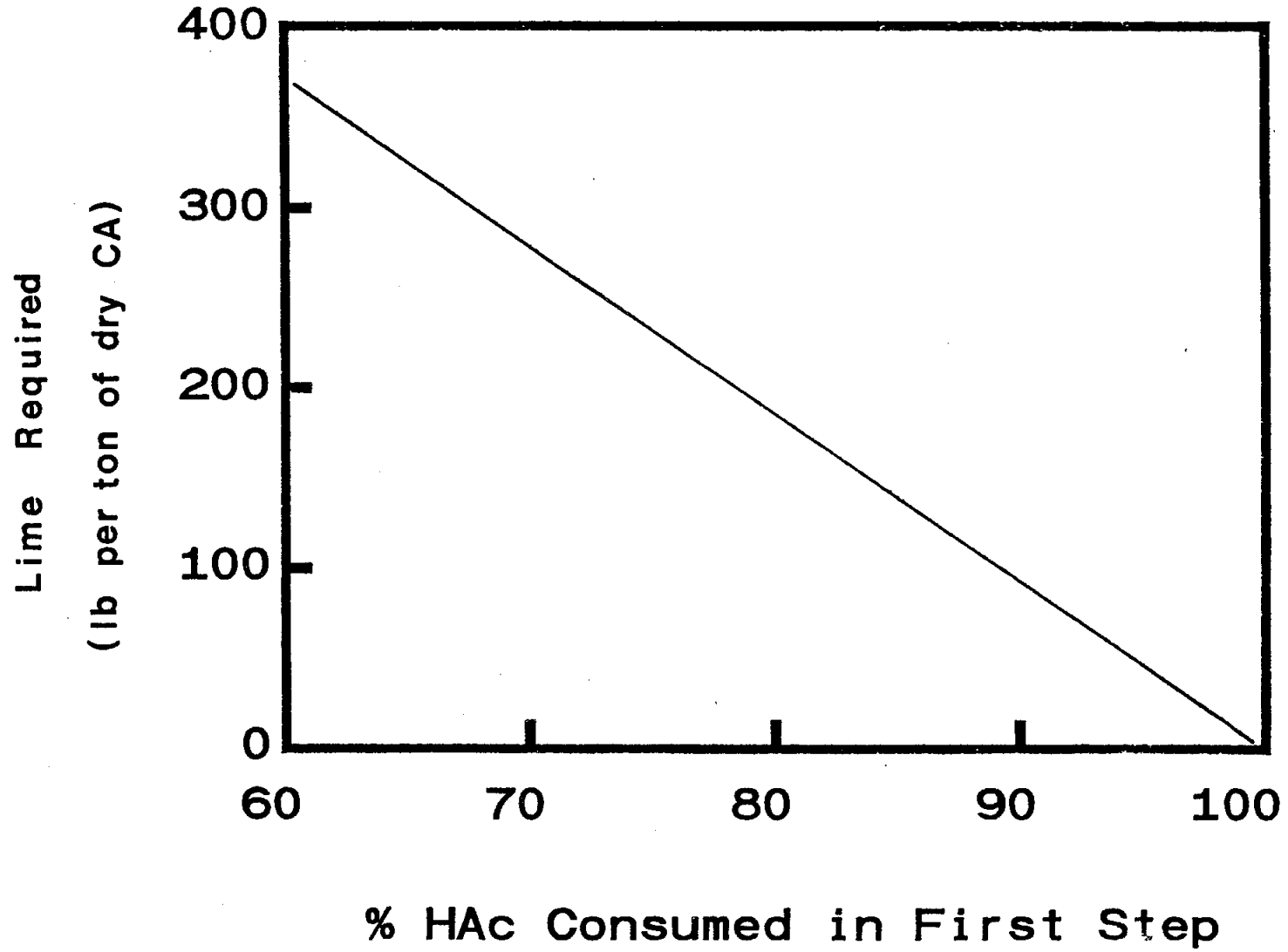


Figure 5-3: Effect of Conversion on Ca(OH)_2 Consumption

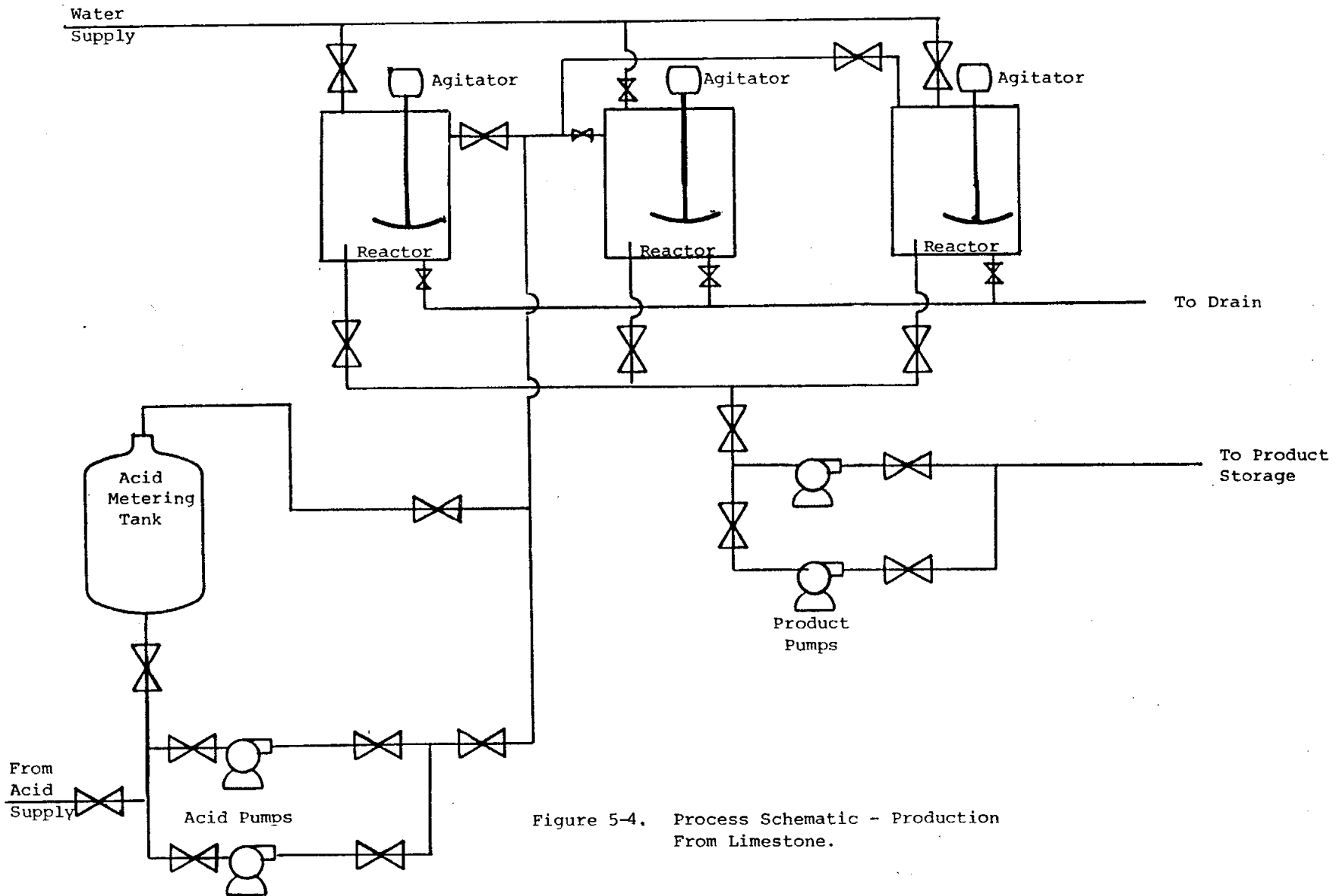


Figure 5-4. Process Schematic - Production From Limestone.

Equipment List

- Reactors (3) - 4,000 gallon stainless steel (316) (any other material resistant to acetic acid would suffice). Reactor should be fitted with top closure to accommodate CO₂ venting. Since foaming can occur, at least 20% freeboard should be allowed. Approximate dimensions 8' diameter - 9' height. Unit should be equipped for top entering turbine agitator (20 hp).
Unit Cost - \$5,200
- Acid Pump (2) - 100 GPM pump rated for acetic acid (316 ss).
Unit Cost - \$2,000
- Solids Conveyor (2) Small conveyor system capable of moving limestone and lime from storage to tank. Must be moveable to service all tanks.
Unit Cost - \$8,100
- Product Pump (3) - 300 GPM pump rated for mild slurry service.
Unit Cost - \$3,300
- Agitator (3) - 20 hp top entering, turbine agitator. All immersed parts - 316 ss.
Unit Cost - \$7,000
- Acid Storage/Metering Tank - 1,000 gallon stainless steel tank with top closure for venting. Tank is used to measure acid quantity before addition to reactors.
Unit Cost - \$7,000
- Piping and Vent Lines - Miscellaneous transfer lines.
Unit Cost - \$4,000

Front End Loader -	For moving limestone.	Unit Cost - \$13,000
Analytical Equipment -	pH meters (3), one ton scales for weighing lime and limestone, laboratory balances, glassware, furniture, etc.	\$8,000
Building -	50 x 60 metal building with 20' ceiling clearance, heated with office and laboratory (500 feet) space.	\$70,000
Land -	Suitably zoned site which can accommodate excavation to bury 50,000 gallon storage tanks. (Extremely Variable - \$20,000 (est.))	

5.1.3 Utilities

Electricity and water are required for the process. Heating oil is required for the building. For the building described above, fuel distributors in the Fairbanks area estimate the total annual fuel requirement at 6,000 gallons of No. 2 Diesel Heating Oil. Current prices in Fairbanks are about \$1.00 per gallon, for an annual requirement of about \$6,000.

About 7,000 kwh/month of electricity is required. Most of the power is for the operation of the agitators (3-20 hp motors). Current rates in Fairbanks are about \$.11 per kwh, for a total annual cost of about \$9,230. Rates may vary around the state.

About 15,000 GPD, or 5.5 million gallons of water on an annual basis are required. It may be possible to use river or well water at a very low cost. However, the current cost in Fairbanks for city water service would amount to about \$13,570 per year.

5.1.4 Labor

The manufacturing operation can be handled easily by two laborers. The major operations involved are loading the reactors with limestone, water and acetic acid. Additional time will also be required for quality control measurements and adjustments. A supervisory position with responsibility for the entire operation is also advised. With added experience and training, it should be possible to reduce the staff to two, however, the design is based on a three man operation.

Labor costs will vary widely depending on location and other factors. For the purposes of this study, it was assumed that manual labor would cost \$30,000 per year plus benefits, and that the supervisory position could be filled for about \$40,000 plus benefits. The total benefit rate was estimated at 50%.

5.1.5 Raw Materials

The basic raw materials for this process are acetic acid, limestone, and calcium hydroxide. The base prices assumed for these materials delivered to Fairbanks were \$.20/lb., \$75/ton, and \$200/ton respectively. The raw materials are required in the following amounts relative to tons of CA produced:

acetic acid	0.760 ton/ton CA
limestone	0.530 ton/ton CA
calcium hydroxide	0.075 ton/ton CA

5.1.6 Economic Analysis

With a very small operation such as this, many economies may be realized through integration of the process with some existing facilities. As detailed below, for a stand alone facility, the building cost alone amounts to over half of the total capital expense. If a building were already in use with 2-3000 square feet of extra space, considerable savings could be realized.

This analysis is based on a stand-alone grass-roots operation.

Capital Cost

	#	Unit Cost	Source	Total
Conveyor/Elevator	1	\$8,100	Goodman, Inc.	\$ 8,100
Reactors	3	5,100	Greer Tanks	15,300
Acid Tank	1	3,000	Greer Tanks	3,000
Acid Pump	2	2,000	Durco	4,000
Product Pump	2	3,300	Gallagher	6,600
Agitator	3	7,000	Chemineer	21,000
Piping & Valves	-	4,000	misc. (est.)	4,000
Storage Tanks	4	8,000	Greer Tanks	42,000
Front End Loader	1	13,000	Yukon Equipment	13,000
Analytical Equip.	-	8,000	misc. (est.)	8,000
				<u>\$125,000</u>
Building (50x60 metal on slab)				70,000
Land (will vary greatly)				<u>20,000</u>
				<u>\$215,000</u>

The total capital cost of \$215,000 could be amortized over a 20 year period at 15% for \$34,349/year. If a building is available, and if storage facilities for the product liquid are available (or unnecessary . . . as for an on demand production basis), the total capital cost would drop to \$73,000.

Annual Operating Cost:

As is to be expected, the operating costs are totally controlled by the raw material costs. A breakdown is give below.

	<u>Annual Cost</u>
Utilities:	
Heating (6,000 gal. @ \$1/gal.)	\$6,000.
Electricity (7,000 kwh/mo. @ \$.11)	9,230.
Water (5.5 mil. gal. @ \$2.25/1000 gal. + \$100/mo.)	13,570.
	<u>\$28,800</u>
Labor:	
Supervisor (1 @ \$40,000)	\$40,000.
Laborers (3 @ \$30,000)	90,000.
	<u>\$130,000.</u>
Benefits at 50%	65,000.
	<u>\$195,000.</u>
	Total
Raw Materials:	
Acetic Acid (3,900 ton @ \$400/ton)	\$1,560,000.
Limestone (2,730 ton @ \$75/ton)	204,750.
Calcium Hydroxide (380 ton @ \$200/ton)	76,000.
	<u>\$1,840,750.</u>
Subtotal - Operating Costs	<u>\$2,064,550.</u>
Contingency (10% of Capital)	\$22,000.
	<u>\$2,086,550.</u>

The process is fairly easy to analyze, consisting of a cash flow and one initial investment of \$215,000. The gross cash flow (before tax) can be computed as:

$$I = 5,140 S - 2,086,550$$

where S is the selling price in dollars per ton of dry CA equivalent and I is annual before tax net income. Based on an initial investment of \$215,000, the required selling price for several rates of return on investment (ROI) is listed in Table 5-1, and plotted in Figure 5-5.

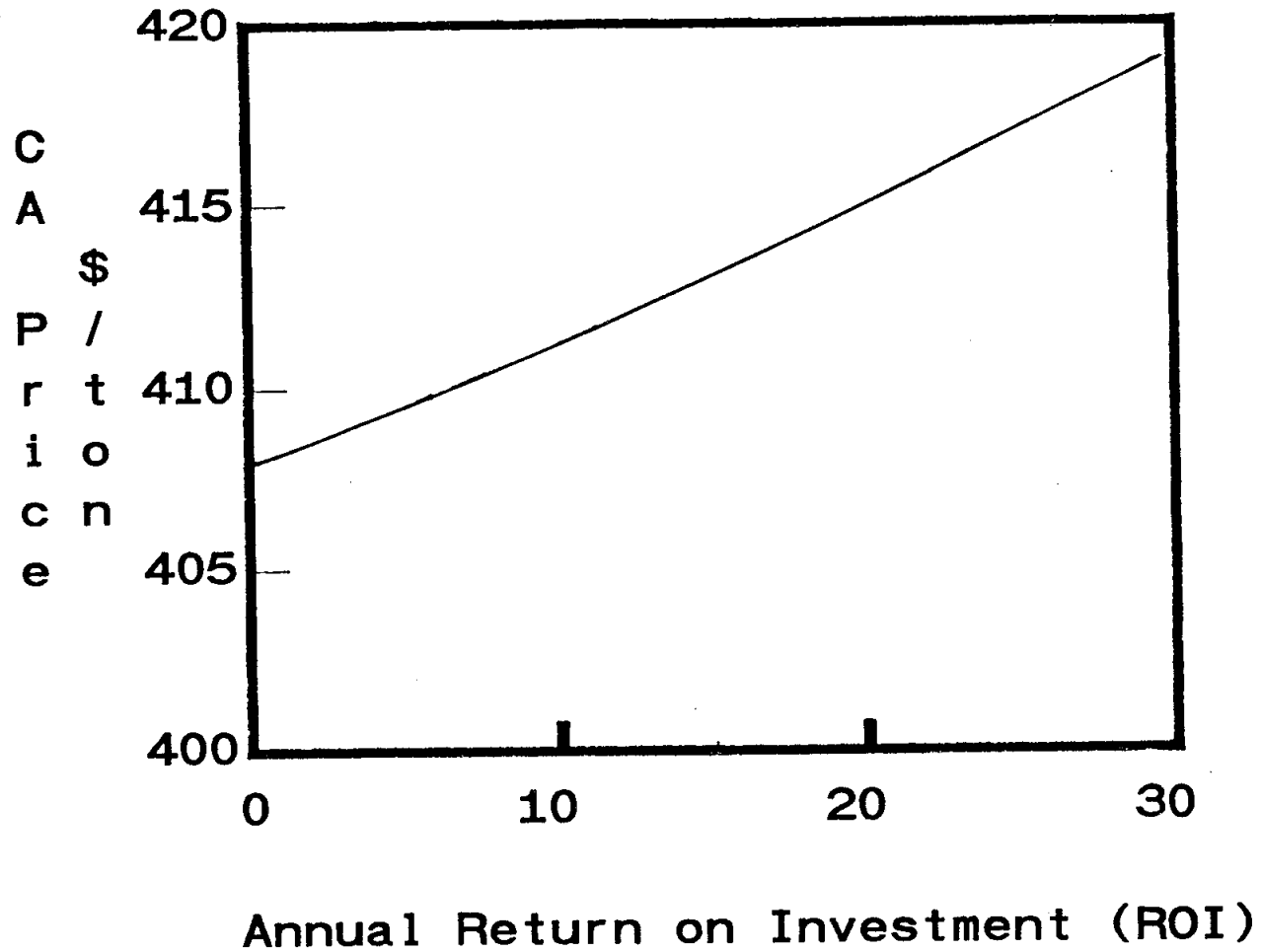


Figure 5-5: Effect of ROI on Selling Price for Production from Limestone

TABLE 5-1
CA Price Required for Specific ROI
(Limestone - 20 year life)

Annual ROI	Net Cash Flow	CA Price
0 %	10,750	408 \$/ton
10	25,253	411
15	34,349	413
20	44,152	415
25	54,377	417
30	64,841	419

It is useful to examine the effects of raw material prices on the required selling price for a 15% ROI. The total annual operation cost exclusive of raw materials is \$245,800 giving a per ton cost (based on 5,140 ton/year CA) of \$48/ton CA. The total cash flow required for 15% ROI is \$34,349, or \$6.40/ton. It is clear that capital cost ammortization is a minor part of the required selling price of CA. Furthermore, labor and utility costs represent less than 12% of the selling price.

The total annual acetic acid requirement is 7,800,000 pounds. The total limestone requirement is 2,730 tons (based on 100% purity). The total lime requirement is 380 tons/year. These figures are based on an annual production rate of 5,140 ton/year of CA. The total required revenues from CA at 15% ROI can then be calculated as:

$$\begin{aligned} \text{Annual Revenue} = & 245,800 (\text{op. cost}) + 34,349 (\text{ROI}) + 7,800,000 C (\text{acid cost}) \\ & + 2,730 \text{ PL (limestone)} + 380 \text{ PC (Calcium hydroxide)} \end{aligned}$$

where C is the per pound cost of acetic acid delivered to Fairbanks, PL is the cost of ground (1-1.5 mm) limestone delivered to Fairbanks, and PD is the cost of powdered or pelletized calcium hydroxide delivered to Fairbanks. (If the limestone and lime are less than 100% pure, the PL and PC terms should be divided by the weight fraction of limestone and lime.)

For an annual production rate of 5,400 tons, the above equation can be reduced to:

$$P = 54.5 + 1,518 C + .53 \text{ PL} + .074 \text{ PC}$$

where P is the required selling price for CA on a dollar per dry ton equivalent basis, for an annual ROI of 15%. For the design case where C = \$.20/lb, PL = \$75/ton, and PC =

\$200/ton, the required price is \$415/ton. The relationship between required selling price and raw material costs are plotted in Figures 5-6 and 5-7.

5.2 Production of CA From Hydrated Lime

CA can be produced more easily from hydrated lime (calcium hydroxide). The chemistry of the reaction is discussed in section 3.1.2 and a material balance is given in Figure 3-8.

Pilot plant studies indicate that the reaction with lime requires only about 1 hour to go to completion, with about an hour of settling time and one hour for pH adjustment required. Thus it should be possible to complete two batches in an eight hour shift. Hence two - three thousand gallon reactors should be sufficient.

5.2.1 Material Balance

The material balance for this process design is presented in Figure 5-8. The reaction proceeds stoichiometrically with no surprises. It should be noted however, that the material balance is based on pure Ca(OH)_2 .

Thus for the production of one ton of CA, 940 lb of lime is required. For a lime purity of X (wt fraction Ca(OH)_2), $940/X$ lbs of impure lime would be required.

5.2.2 Process Description

The process consists of a simple acid-base titration. The reactor is first filled with the appropriate amount of lime and water. Then sufficient acetic acid is added to bring the pH to about 8. After about one hour of agitation, the pH and density are adjusted through the addition of additional lime and acid as described in section 4.1.4. A schematic of the process is presented in Figure 5-9.

Equipment List:

The equipment descriptions for this process are exactly the same as those presented in section 5.1.2 for the design for production from limestone, with the following changes:

- reactors - two 3,000 gal. reactors of the same type described in 5.1.2;
- agitators - two of the same type described in 5.1.2.

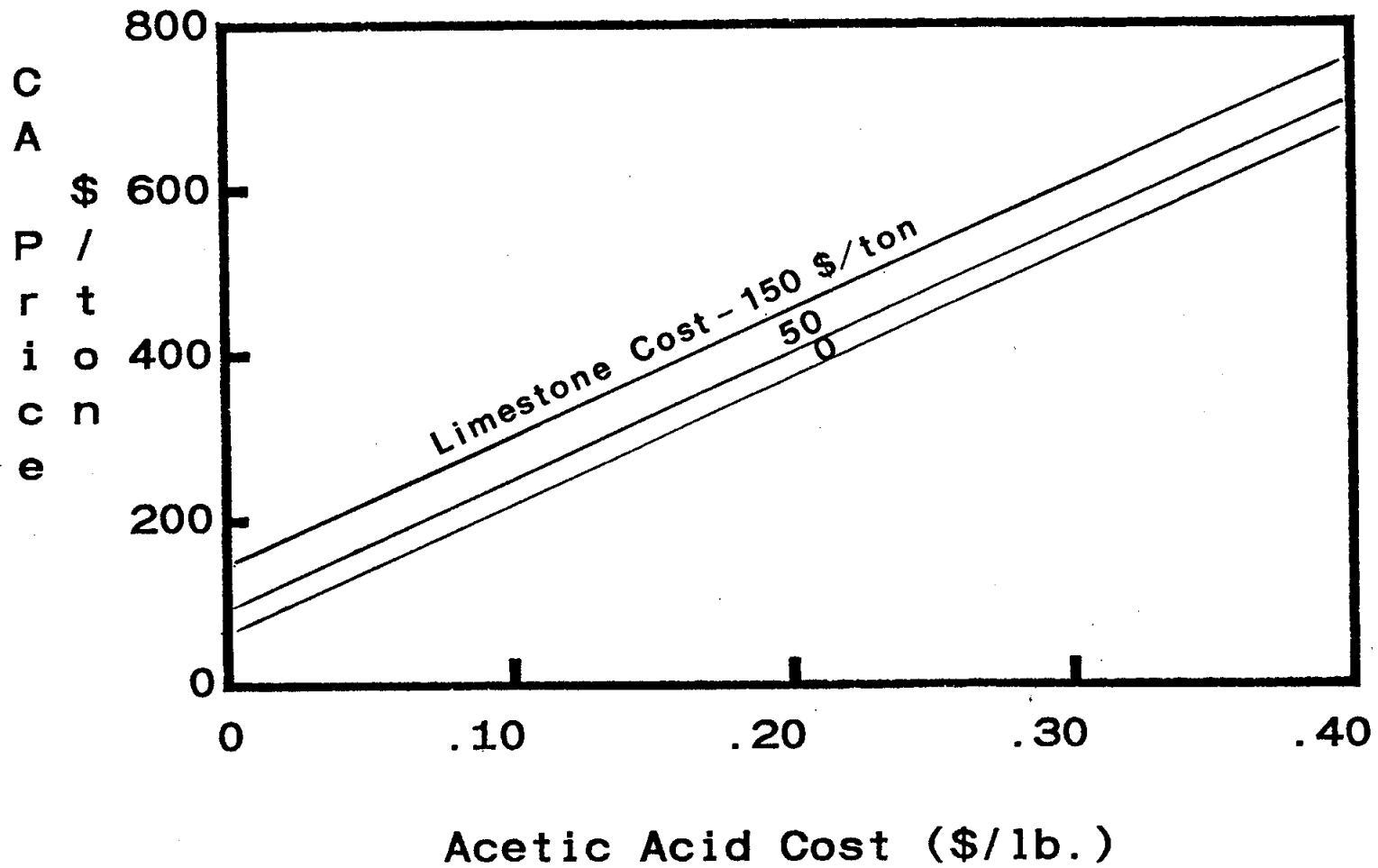


Figure 5-6: Effect of Acid and Limestone Cost on Selling Price of CA for Production for Limestone

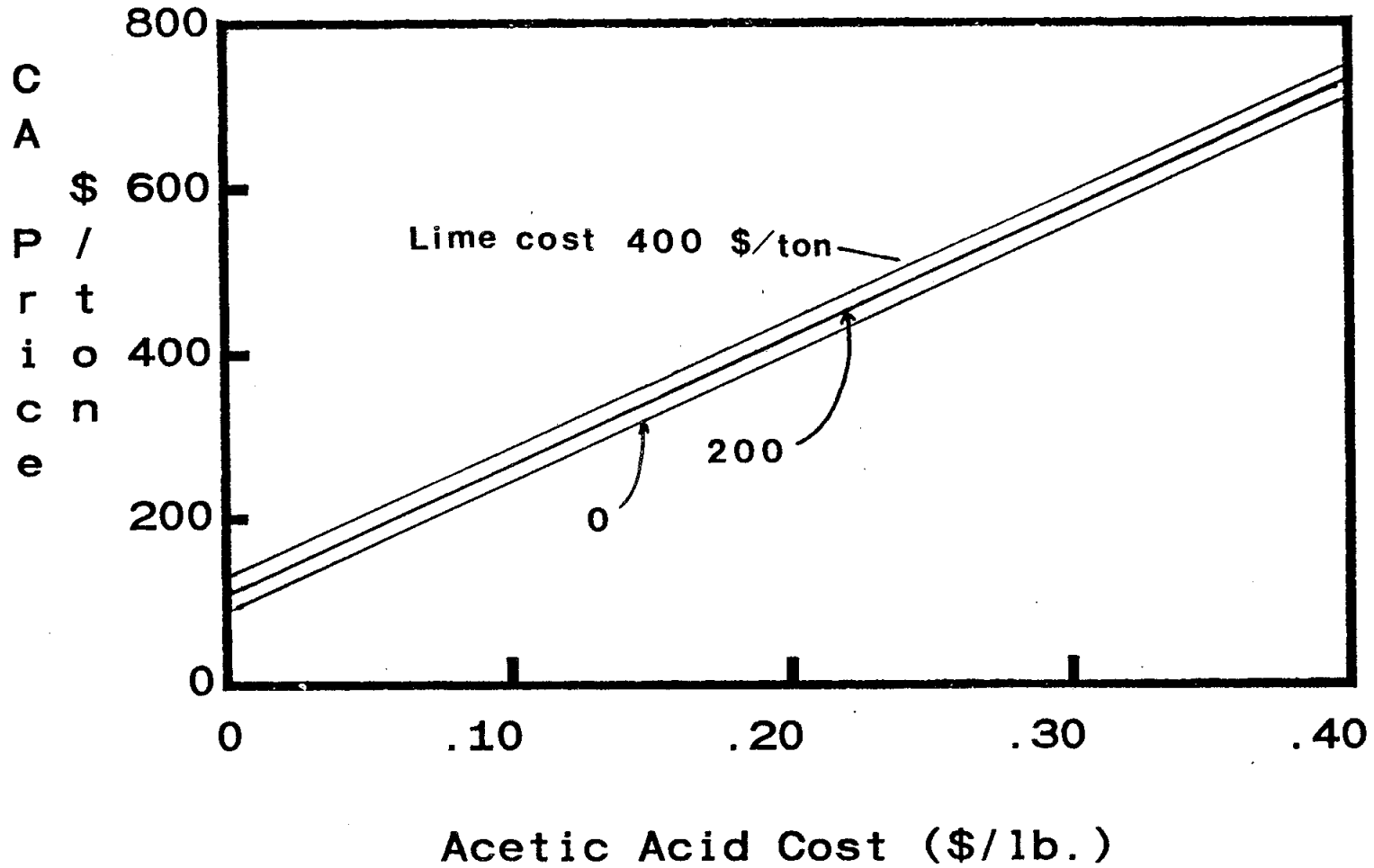


Figure 5-7: Effect of Hydrated Lime Costs on CA Selling Price for Production from Limestone

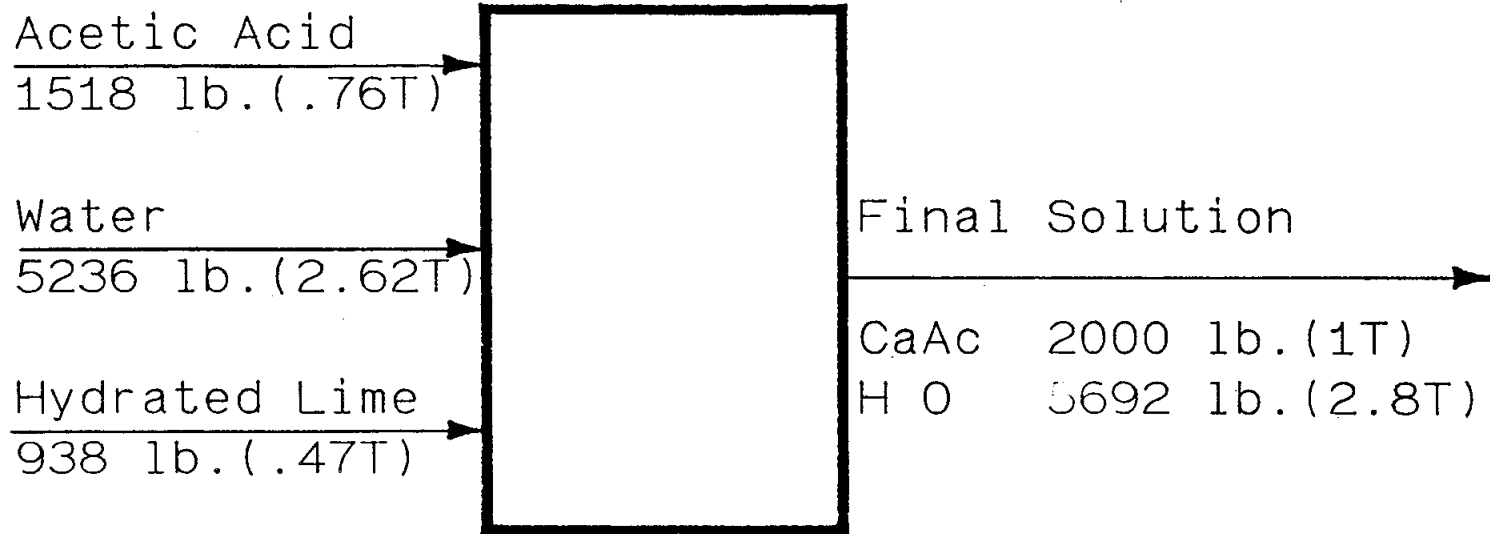


Figure 5-8. Material Balance for Process Design
Production from Hydrated Lime

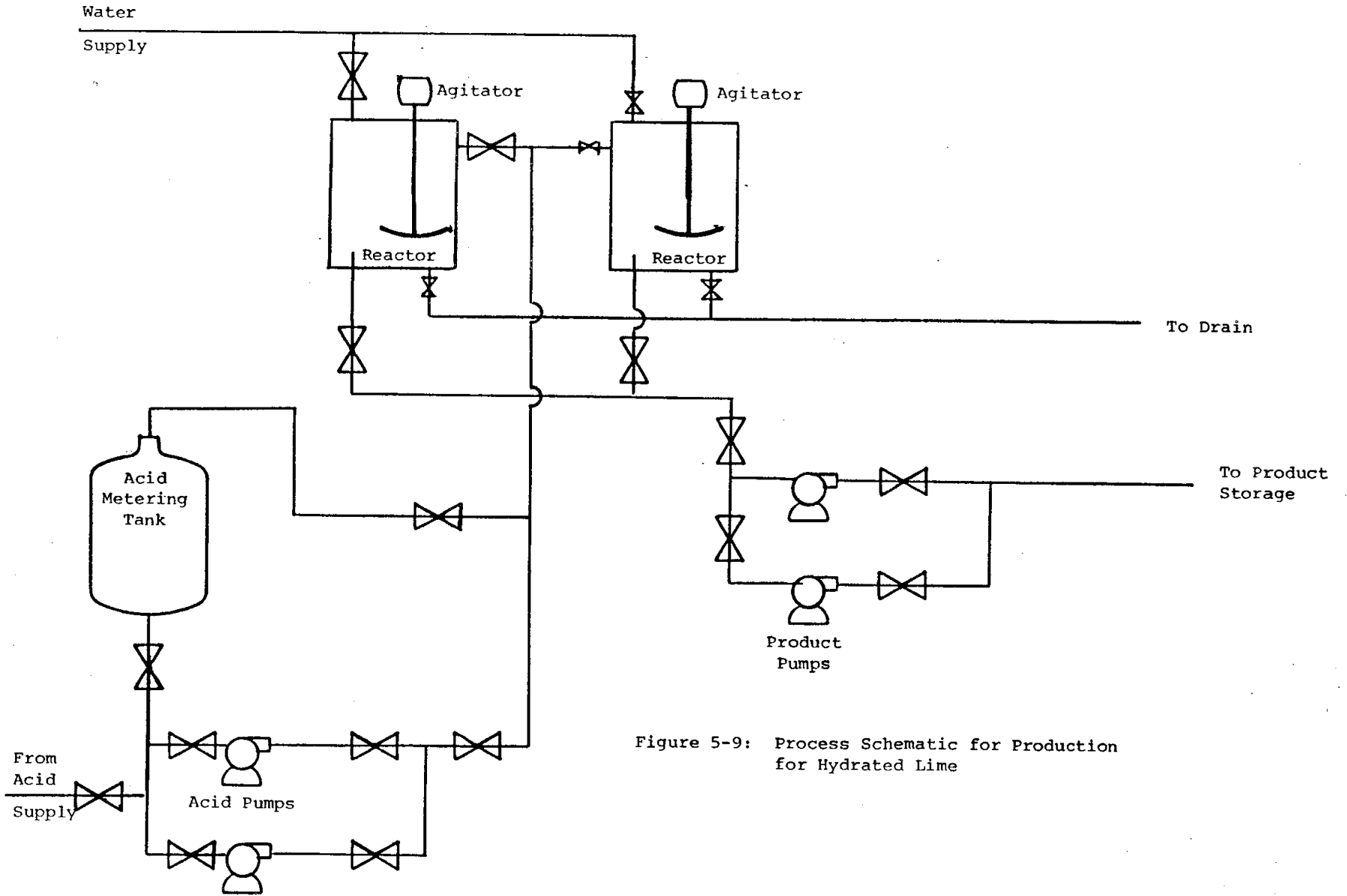


Figure 5-9: Process Schematic for Production for Hydrated Lime

5.2.3 Utilities

The utility requirements for this process are essentially the same as for the limestone process. About 6,000 gal/year of No. 2 heating oil is required for building heat, at a cost of about \$6,000.

About 15,000 GPD, or 5.5 million gallons per year of water are required for the process and cleanup. It may be possible to use well or river water at a very low cost. However, the cost for "city" water would be about \$13,570/year.

Since this process only requires two agitators instead of three, the electrical usage would be correspondingly lower than for production from limestone. The total electrical requirement is estimated at \$6,153/year (4660 kwh/month at \$.11 per).

5.2.4 Labor

Since this is a one step reaction, a single laborer should be able to handle loading and operating the reactors. A supervisory manager could handle the quality control measurements and oversee the operation.

Labor costs will vary widely. For this analysis, it was assumed that manual labor would cost about \$30,000/year plus benefits, and that the supervisory position could be filled for \$40,000/year plus benefits. The benefit rate was estimated at 50%.

5.2.5 Raw Materials

The base raw materials for this process are hydrated lime (calcium hydroxide), acetic acid, and water. The hydrated lime would be shipped in bags or by bulk shipment from the lower 40 states. Acetic acid was assumed to be pure (100%). The estimated costs of lime and acid delivered to Fairbanks, were \$200/ton and \$.20/lb respectively.

The raw materials are required in the following amounts relative to tons of CA produced:

acetic acid -	0.76 ton/ton CA;
hydrated lime -	0.47 ton/ton CA.

5.2.6 Economic Analysis

The economics of production from hydrated lime is very similar to that for production from limestone. Capital costs represent a very small portion of the annual cash flow. Over 80% of the operating costs are direct raw materials costs.

The economic analysis presented below is for a 12,000 GPD (5,400 ton/year) grass-roots facility.

Capital Costs:

	#	Unit Cost	Source	Total
Reactors	2	\$ 5,100	Greer Tanks	\$ 10,200
Acid Tank	1	3,000	Greer Tanks	3,000
Acid Pumps	2	2,000	Durco	4,000
Product Pumper	2	3,300	Gallgher	6,600
Conveyor/Elevator	1	8,100	Goodman, Inc.	8,100
Agitators	2	7,000	Chemineer	14,000
Analytical Equipment	-	8,000	---	8,000
Piping	-	4,000	---	4,100
Storage Tanks	4	8,000	---	42,000
Front End Loader	1	13,000	---	13,000
				<u>\$113,000</u>
Building (50x60 metal on slab)				70,000
Land (will vary)				20,000
			Total	<u>\$203,000</u>

The total capital cost of \$203,000 could be amortized over a 20 year period at 15% for \$32,432/year. If a building and storage facilities are available, the total capital cost drops to \$71,000, which could be amortized at \$11,343/year.

Annual Operating Cost:

Operating costs are almost totally controlled by raw material costs. Over 90% of the operating costs are attributed to direct raw material costs. A breakdown is give below:

	Annual Cost
Utilities:	
Heating Oil (6,000 gal. @ 1 \$/gal)	\$ 6,000
Electricity (4,670 kwh/mo @ 11¢ per kwh)	6,150
Water (5.5 mil gal @ \$2.25/1,000 gal + 100 \$/mo)	13,570
	<u>\$25,720</u>
Labor:	
Supervisor (1 @ \$40,000)	\$ 40,000
Laborer (1 @ \$30,000)	60,000
	<u>Subtotal \$100,000</u>
Benefits	50,000
	<u>\$150,000</u>

Raw Materials:	
Acetic Acid (3,900 ton @ \$400/ton)	\$1,560,000
Hydrated Lime (2,410 ton at \$200/ton)	482,000
	<u>\$2,042,600</u>
Subtotal - Operating Costs	<u>2,217,720</u>
Contingency	<u>20,000</u>
Total Operating Costs	\$2,237,720

The process is fairly easy to analyze, consisting of a cash flow and single initial investment of \$203,000. (It should be noted that the total operating cost is almost identical with the limestone case at \$2,086,550.) Gross (before tax) cash flow can be computed as:

$$I = 5,140 S - 2,237,720$$

where S is the selling price for CA in dollars per dry ton equivalent, and I is annual before tax, net income. Based on an initial investment of \$203,000, the required selling price for several rates of return are listed in Table 5-2 and plotted in Figure 5-10.

TABLE 5-2
CA Price Required for Specific ROI
(Hydrated Lime - 20 year life)

Annual ROI	Net Cash Flow	CA Price
0%	10,203 \$/yr	437
10	23,844	440
15	32,431	442
20	41,687	443
25	51,342	445
30	61,222	447

The effects of raw material costs on required selling price at 15% ROI has been investigated. The total operating cost, exclusive of raw materials is \$195,720 for a per ton cost (based on 5,140 ton/year production) of \$38/ton. For a 15% ROI, the capital cost contribution is only \$6/ton of CMA. Clearly, the economics of the process depends mostly on raw material costs.

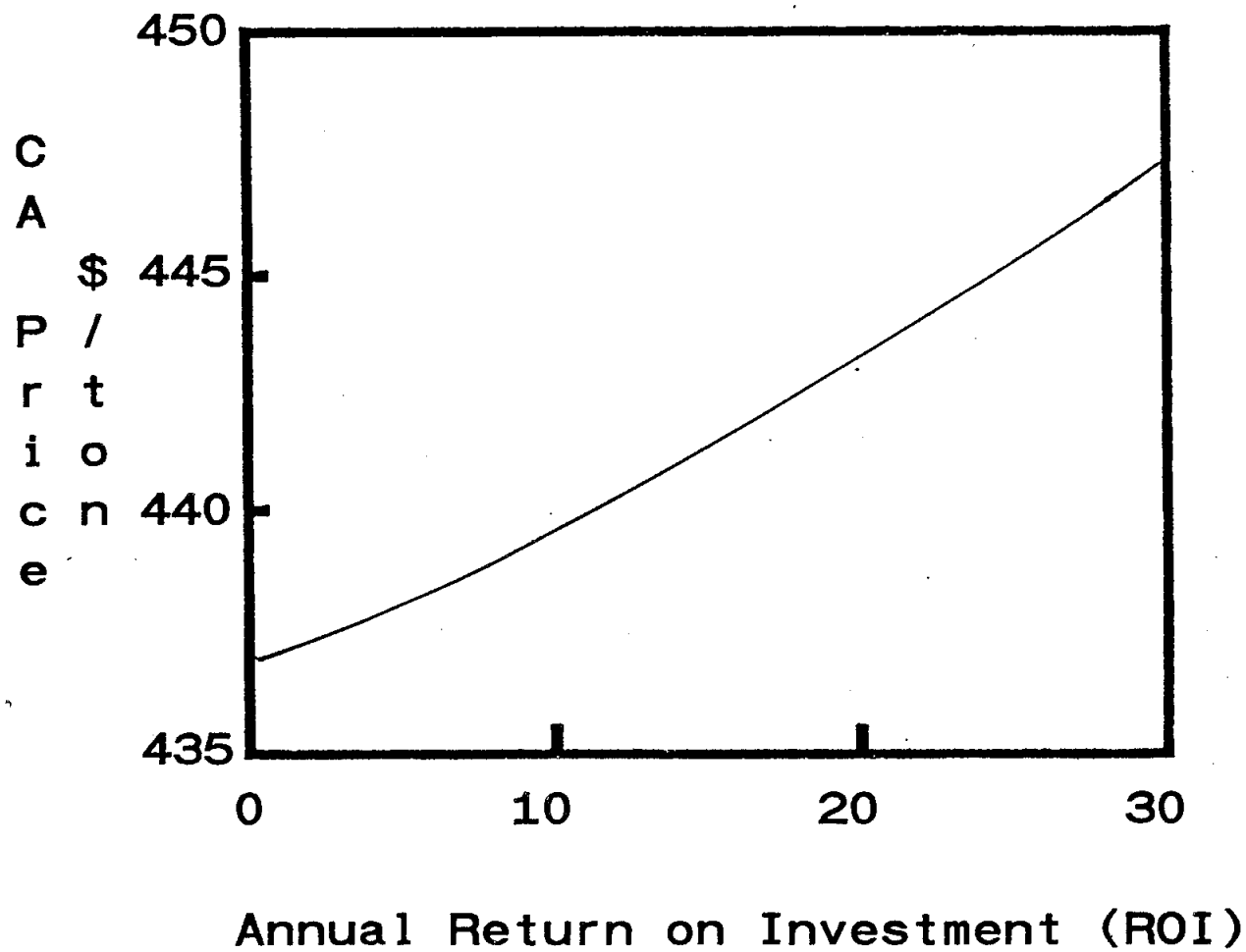


Figure 5-10: Effect of ROI on Selling Price

The total acetic acid requirement is 7,800,000 pounds. The total hydrated lime requirement is 2,410 tons (based on 100% purity). The total annual revenue required from CA sales can be computed as a function of acid and hydrated lime price as:

$$\begin{aligned} & \text{Annual Revenue} + \$195,720 \text{ (Op. Cost)} + 32,431 \text{ (ROI)} \\ & + 7,800,000 C \text{ (Acid Cost)} + 2,410 PC \text{ (Hydrated Lime)} \end{aligned}$$

where C is the per pound cost of acetic acid delivered to Fairbanks, and PC is the delivered cost of hydrated lime (calcium hydroxide). If the lime purity is less than 100%, PC should be divided by the weight fraction calcium hydroxide.

For an annual rate of production of 5,140 tons, the above equation can be reduced to:

$$P = 44.4 + 1,518 C + .47 PC$$

where P is the required CA selling price per ton of dry CA equivalent for an annual ROI of 15%.

For the design case where C = 0.20 \$/ton and PC = 200 \$/ton, the required selling price is 4342 \$/ton. The relationship between required selling price and raw material costs are presented in Figure 5-11.

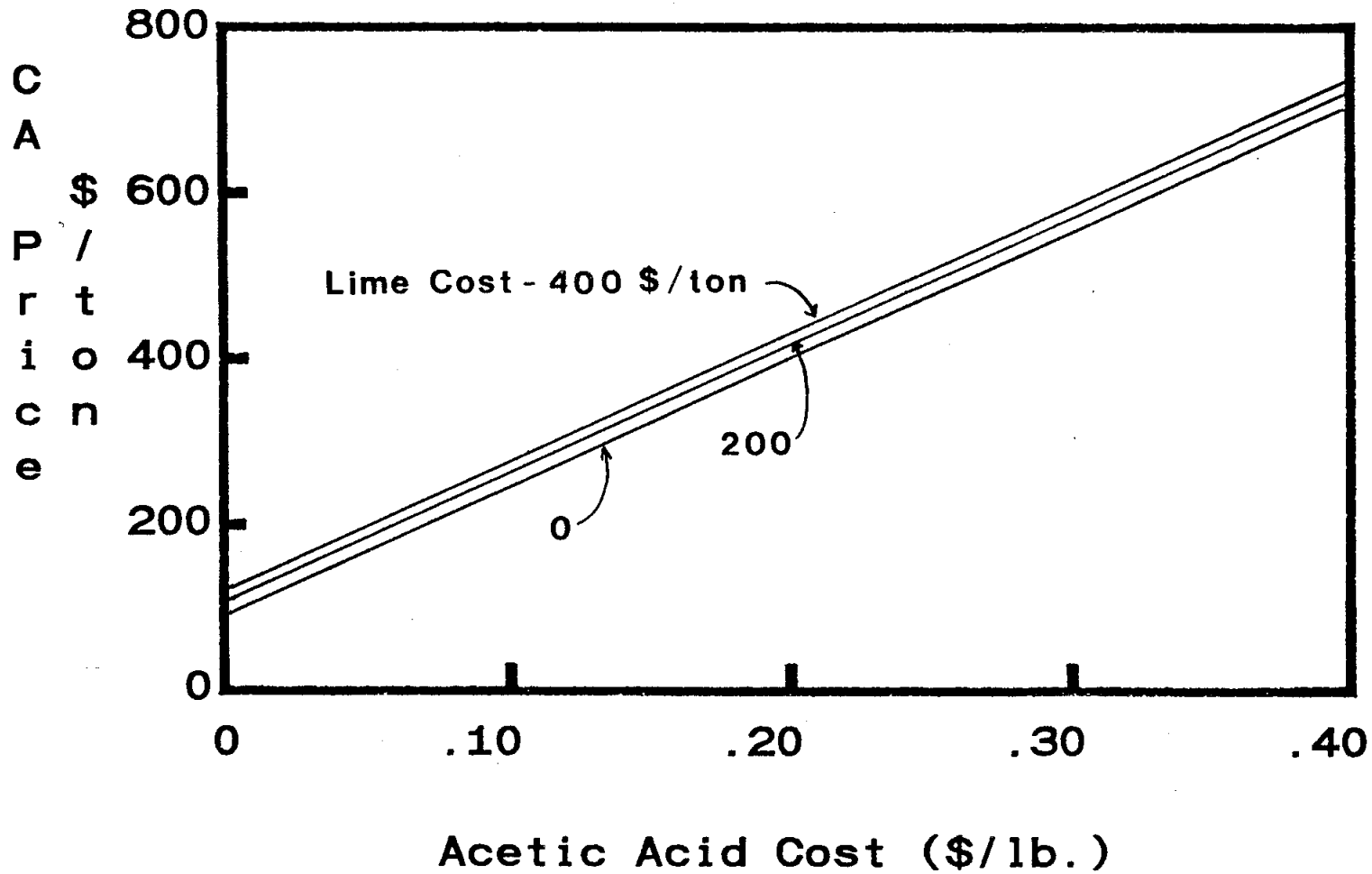


Figure 5-11: Effect of Acid and Hydrated Lime Cost for Production for Hydrated Lime

CONCLUSIONS

CMA can be produced in a fairly simple process from either limestone or hydrated lime. The capital cost are roughly the same in either case, and operating costs are comparable. For production from limestone, raw material costs are somewhat lower while capital costs are higher. The required selling price for 15% ROI is \$415/ton. For production from lime, capital costs are slightly lower (\$12,200 less), and operating costs are slightly lower, but raw materials costs are higher. The required selling price for production from lime at 15% ROI is \$442/ton.

In either case, the controlling factor in the economics is the price of acetic acid. About .76 tons of acetic acid are required per ton of dry CA. Since acetic acid costs about \$.2/lb or \$400/ton, the contribution of acid to total cost is \$304/ton. A substantial discount in acetic acid price to say \$.10/lb would bring the acetic acid contribution down to \$152/ton, or a total cost of 250 \$/ton.

With current prices, acetic acid is available on the West Coast at a delivered price of \$.25/lb. Shipping costs are roughly \$.05/lb. Therefore, the current contribution of acetic acid would be \$456/ton. However, with a long term purchase agreement and the possibility of using "off-spec" acetic acid, it may be possible for the price to be reduced to the neighborhood of \$.20/lb delivered in Anchorage.

For production from limestone, the capital cost contributes only \$6/ton to the selling price of CA. Hence considerable latitude in equipment design is possible. The operating costs for utilities and labor amounts to about \$48/ton of CA produced. The total non-raw material cost is then only \$54/ton. Furthermore, the contribution of limestone costs to the selling price is only about \$40/ton. Thus variations in limestone cost have a small effect (less than 10%) on the total cost.

In general, capital cost, operating cost and limestone and hydrated lime costs are minor factors in the total CA price. The major factor is acid cost. While the product may be attractive at \$400/ton, the key to reducing this cost significantly lies in the reduction of acid cost.

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