MINIMIZING THE ENVIRONMENTAL

IMPACT OF UREA DE-ICER FROM AIRPORT RUNWAYS

by

KEITH DONALD FERGUSON

B.A.Sc., University of British Columbia, 1975

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF
THE REQUIREMENTS FOR THE DEGREE OF
MASTER OF APPLIED SCIENCE

in

THE FACULTY OF GRADUATE STUDIES
(Dept. of Civil Engineering)

We accept this thesis as conforming
to the required standard

THE UNIVERSITY OF BRITISH COLUMBIA
August, 1977

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Department of Civil Engineering

The University of British Columbia
2075 Wesbrook Place
Vancouver, Canada
V6T 1W5

Date 7/16/77

Abstract

Urea finds common use at most airports in Canada where it is used as an anti-icer or de-icer. Urea contains up to 46% nitrogen which finds its way to the environment around the airport. Of the potential environmental problems, eutrophication of lakes is of the most concern in British Columbia.

Several methods for minimizing the impact of urea de-icer were considered. Urea can be hydrolyzed to ammonia by the common soil enzyme urease on an airport runway and this ammonia can volatilize to the atmosphere. The natural enzymatic activity on runway test sections was found to cause less than 0.5% of the applied urea to hydrolyze with no volatilization after 90 minutes, at room temperature. Supplemental urease was added to pyrex models to test the effect of various conditions on hydrolysis and volatilization. Thirty-two tests were performed at various temperatures (-4, 0, 4, 12°C), urease additions (100, 200, 500, 750 mg/model), ice thicknesses (3, 5, 8 mm), urea applications (0.45, 0.9, 1.8 kg/70m^2), urea types (Cominco Industrial and Forestry Grade, Sherritt Gordon Mines Industrial Grade) and solar radiations (50 and 100 BTU/h-ft^2). An addition of 500 mg urease to the model cuased hydrolysis of 65% of the applied urea and volatilization of 7% at 12°C. Lower temperatures produced poorer results. Relative to the high costs and low efficiency, control of urea through hydrolysis and volatilization on an airport runway is impractical.

Biological nitrification-dentrification, breakpoint chlorination, selective ion exchange, and air stripping have high nitrogen removal efficiencies under normal conditions, but are not suitable for winter airport operation.

Passage of urea through soil can be an effective method for removal of this de-icing agent if the quantity of nitrate and urea leached to surface waters is low. Published data indicates that soil could be 75-90% efficient in controlling nitrogen loss to surface and ground waters.

A reduction in the quantity of urea used on a runway would decrease the environmental impact. The yellow aura produced by the urea-Ehrlich reagent reaction, was used to monitor the movement of urea in 5 mm thick ice at -4°C. After 90 minutes from placement on the ice, the Cominco Forestry Grade aura covered the largest area. On a weight basis, however, the Sherritt Gordon Mines covered the largest area. This greater aura coverage is due to the smaller particle size of the Sherritt Gordon Mines pellets. If the size of the aura can be correlated with the ease of removal of ice from an airport runway, then the Sherritt Gordon Mines-Industrial Grade urea is more effective as a de-icer than either of the two Cominco grades under the conditions tested.

Further research is recommended in optimizing the use of urea and soil treatment.

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1. Introduction

Ice can be extremely dangerous on an airport runway. Airplanes must have good traction when landing and taking off. Since many of Canada's airports are subjected to cold and icy winters, development of a fast-acting, economical, efficient, and safe means of removing ice was imperative.

Ice usually forms under the following conditions[1]:

a) Super-cooled rain contacting a cold solid.
b) Moisture in air, condensing on a cold surface.
c) Wheeled traffic on wet snow or slush compacting it into ice.
d) A warming condition followed by a return to below freezing, permitting snow melt to refreeze.
e) Insufficient or clogged drains permitting water to overflow onto the pavement, and with decreasing temperature causing ice.
f) Jet engine heat melting snow during low termperatures.

The adhesive strength of ice to pavements can be as high as $8.3 \times 10^5 N/m^2$ (120 lb/in^2), which is approaching the tensile strength of ice[2]. This bond cannot usually be broken without a failure in the ice. Scraping by mechanical means often leaves a thin coat of ice or damages the pavement.

According to the Ministry of Transport (MOT) guidelines, snow and ice control materials must meet two basic criteria[3]:

a) They must provide the required effect in prevention of or removing snow and ice to produce pavement surfaces safe for aircraft operations.

b) They must be compatible with personnel, pavement, equipment, and aircraft depending on their location of use (groundside or airside).

Ice control chemicals can be very efficient in melting

ice. Chemicals, however, must pass a series of aircraft com-
patibility tests, before they are considered for runway
experiments.

From 1962-1972, many chemicals were tested, as shown in
Table 1. Of these 42 chemicals, only four have met the compat-
ibility requirements of MOT for corrosion control. These are,
the liquid chemicals, Monsanto Santomelt 990CR(41), Kaiser Isolv
(39), Union Carbide Ucar (38), and the solid, Urea (42).
Because tests performed by the MOT using the four approved
chemicals indicated that none of the liquid chemicals surpassed
urea in terms of reaction time and rate of application, urea
is the chemical used almost exclusively at all Canadian air-
ports[4].

Chemicals can be applied to a runway surface in two ways,
"de-icing and anti-icing". De-icing involves applying the
chemical after ice has formed. After the chemical has reduced
the ice-pavement bond strength, the ice is removed by mechanical
means. The practice of placing the chemical on a runway to
prevent ice formation is called anti-icing. Anti-icing is
acknowledged to be more effective than de-icing for ice control.
MOT have set the following performance criteria for anti-icing
and de-icing[5].

"For anti-icing -

    The ice control chemical, when applied prior to
or during a freezing rain, or a lowering of temperature,
shall prevent the co-efficient of friction from falling
below half the value of the clean dry pavement; and
will render possible the removal of ice/slush con-
taminant by physical means.

Table 1

Chemical Formulations Considered

for Ice Control

1) Acetamide

2) Ammonium Acetate

3) Formamide

4) Sodium Sulfate

5) Ammonium Nitrate

6) Ammonium Formate

7) Tripotassium Phosphate

8) Acetamide/Ammonium Acetate (90/10)

9) Urea/Acetamide (75/25)

10) Sodium Sulfate/Formamide (75/25)

11) Tripotassium Phosphate/Urea (75/25)

12) Acetamide/Urea (50/50)

13) Acetamide/Ammonium Acetate (75/25)

14) Ammonium Acetate/Acetamide (75/25)

15) Monsanto "A"

16) Monsanto 1D1352B

17) Urea/Ammonium Formate (50/50)

18) Urea/Ammonium Formate (75/25)

19) Ammonium Acetate/Urea (50/50)

20) Ammonium Acetate/Formamide (75/25)

21) Urea/Ammonium Nitrate (75/25)

22) Urea/Formamide/Water (20/75/5)

23) Urea/Formamide/Water (10/85/5)

24) Formamide/Water (85/15)

25) Formamide/Isopropyl Alcohol/Water (62/27/11)

26) Calcium Formate

27) Sanfax IM-149 ($CaCl_2$)

28) Isopropyl Alcohol

29) Hartline Products Company "Instamelt NC" (Urea)

30) Momar Chemicals Company "Ice-go" ($CaCl_2$)

31) Walton-March Incorporated "Ice-Foe"

32) Revere Chemical Incorporated "Ice-Melter" ($CaCl_2$)

33) Monroe Company De-icing "Fluid X-54"

Table I - Continued:

34) Monsanto TKPP (solid pellets)

35) Allied Chemicals ARD-45

36) Dow Chemical Aircraft De-icing Fluid 146/Sand Mixture

37) Glycol/Sand Mixture

38) Union Carbide Ucar Runway De-icer

39) Kaiser Isolv

40) Lyndhurst Runway De-icer

41) Monsanto Santomelt 990CR

42) Urea

<u>For de-icing-</u>

The ice control chemical application shall raise the surface co-efficient of friction of ice to at least half the value of the clean dry pavement within one hour of application and will render possible the removal of ice/slush contaminant by physical means."

Only four materials are regularly used in the control of ice and snow at Canadian airports. Sodium chloride is used only on the groundside (areas not travelled by aircraft) since it causes unacceptable corrosion to aircraft. Calcium chloride is also used only on the groundside. Sand of specific size and quality is used on the groundside and airside. Large aggregates can damage engines and aircraft surfaces. Small sand sizes are less effective in improving the coefficient of friction. Urea is the only chemical used on surfaces where aircraft manoeuvre.

Urea is a commercial synthetic acid amide of carbonic acid with a chemical formula $CO(NH_2)_2$. Nitrogen accounts for about 46% of the total weight (Table 2). It is normally used as an agricultural fertilizer. Airport de-icer urea is granular or pellet in form. Clay, mineral oil, or formaldehyde may be added to prevent the pellets from caking.

Conventional sanding equipment is used to apply the urea pellets. When used as an anti-icer, an application rate of 0.45 kg (1 lb.) of urea per 70 square meters (750 ft.^{2}) of runway is recommended. This is equivalent to 45kg (100 lb) per each 305 meters (1000 ft.) of runway. Only the centre 23m (75 ft.) of the runway is treated during times of low cross-

Table 2

Cominco Urea Product Data

UREA - ANTI-ICING GRADE -(46-0-0)

DESCRIPTION:

A pure grade of urea, NH_2CONH_2, in granular form to which a conditioning agent has been added to maintain a free-flowing characteristic. It is white in color. It is manufactured by reacting ammonia with carbon dioxide at suitably high pressure and elevated temperature.

GUARANTEED
ANALYSIS:

Total nitrogen, N	46%

TYPICAL
ANALYSIS:
(not
guaranteed)

Total nitrogen, N	46.5%
Biuret, $NH_2CONHCONH_2$	1.3%
Additive Combined	.31%
Moisture /	0.05%

SCREEN ANALYSES: (Tyler Standard)

Mesh	+8	+10	+14	+20
%	70	99.5	99.8	99.9

pH OF AQUEOUS SOLUTION: 8

winds. In the presence of strong crosswinds, the spreader vehicle is driven on the windward side of centre.

When urea is used for de-icing, as much snow and ice is removed as possible by mechanical means before the urea is applied. The application rate for de-icing is usually 90 kg./ 305 lineal meters (200 lb./1000 lineal feet).

Urea is effective in anti-icing and de-icing down to -11°C. Urea need not be applied to pavement above 0°C. A hooded thermometer placed on the pavement surface for several minutes is commonly used to measure runway temperatures. Between -7 and -11°C, the urea impregnated ice may become slushy. Under these conditions, immediate removal by sweeping is necessary.

Table 3 lists the quantity of urea used during the winter of 1975-1976 on the airports of B.C.

1.1 Urea Pellet Action

Urea works by lowering the freezing point of water (or the melting point of ice). The relationship between urea, ice, and water is shown in an eutectic diagram (Figure 1) which may be used to explain the action of urea as an anti-icer[6].

> "Consider water to which 10% of urea by weight has been added. Such a solution at 1°C is represented by A in the diagram. The behaviour of the solution on cooling can be deduced by following the vertical line AB. So long as the temperature does not fall below that corresponding to C (about -3°C) on the freezing point curve (WE) no freezing can occur at all. As the temperature falls to that corresponding to C, or to lower temperatures, ice can begin to form; but in contrast to water alone a urea solution does not freeze completely. Initially some water freezes out

Table 3

Quantities of Urea Used at

Airports in B.C. During 1975-76.

Airport Location	Quantity of Urea (tonnes)
MOT airports:	
Abbotsford	10
Kamloops	15
Penticton	6
Pitt Meadows	5
Port Hardy	41
Prince George	102
Prince Rupert	61
Quesnel	20
Sandspit	41
Smithers	10
Terrace*	61
Richmond (VIA)	82
Sidney	26
Williams Lake	16
Municipal airports:	
Campbell River	31
Castlegar	10
Cranbrook	20
Grand Forks	1
Powell River	1
Kelowna	15

* Annual use of Urea at Terrace Airport

year	Tonnes of Urea
72/73	72
73/74	65
74/75	70
75/76	70
76/77	40
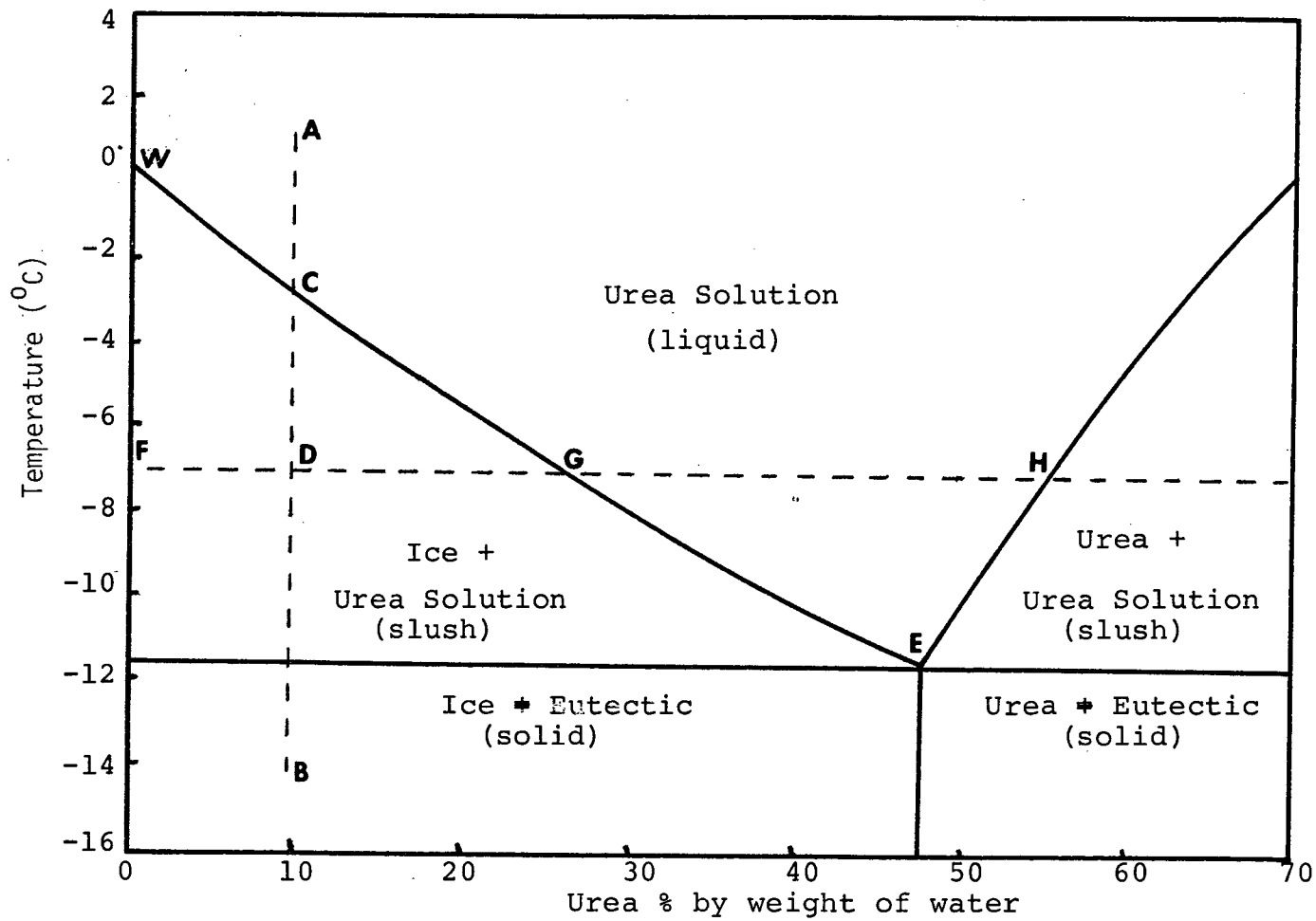
Figure 1

Urea - Ice - Water Eutectic Diagram [7]

leaving a residual solution richer in urea and hence
having a still lower freezing point. If the
temperature is further lowered more ice will form,
leaving a smaller quantity of a yet richer solution
of lower freezing point again. In general, there-
fore, the urea solution originally represented by
A, when cooled to a temperature in the ICE + UREA
solution field, becomes a mixture of ice and a urea
solution - with more ice at increasingly lower temper-
atures. Moreover, the proportion of liquid present
in the mixture is given nearly quantitatively (sic)
by the ratio $\frac{FD}{FG}$ x 100% which gives about 38% at -7°C.

This principle remains valid down to the temperature
of -11.5°C, the minimum freezing point in the urea-
water system (point E). Below the eutectic temper-
ature of -11.5°C urea-water solutions will freeze
completely to give a mixture of ice and the solid
eutectic."

Ice and solid urea cannot exist together for long at
temperatures above -11.5°C. The de-icing action of urea depends
upon the local interaction of ice and urea at the point of
contact and is illustrated by the eutectic diagram[8].

"If for example, starting with ice at -7°C
(point F on the diagram) 10% of urea (by weight of ice)
were added, an ice-urea mixture with the average
composition represented by D would be formed and
the ice would generally loosen and break up. To
secure complete melting, urea in excess of the
quantity represented by G (say 30%) would have to be
added. If, locally perhaps, the concentration of urea
were greater than that represented by the point H
then solid urea would remain with urea solution but
all ice would disappear. Frequently, complete melt-
ing is not required but only sufficient loosening
action to enable mechanical removal to be practic-
able."

Less urea is required to prevent the formation of ice
than to loosen and break up previously formed ice. In de-
icing, heat must be provided to overcome the latent heat of ice
fusion. Anti-icing is, therefore, more efficient at controlling
ice than de-icing.

1.2   The Environmental Impact of Urea

1.2.1 The Problem

Urea is used, among other things, as a fertilizer.
When applied on soil it supplies nitrogen needed by plants.
When applied on an airport runway for de-icing, this urea-
nitrogen reaches the soil-water environment around the airport.
At Vancouver International Airport (VIA) in 1975, for example,
of the 81 tonnes of urea used, 38 tonnes of nitrogen were
released from the de-icer to the environment adjacent to the
runway.

The impact that this nitrogen has on the environment,
depends upon the quantity of urea applied and the conditions
of the receiving system. Each airport has its own pollution
potential.

Ground and surface waters containing excessive nitrogen can
lead to several problems. In 1940, it was found that drinking
waters with high nitrate caused methemoglobinemia in infants[9].
The maximum permissible drinking water standard in Canada is
10.0 mg / 1 Nitrate + Nitrite as N [10].

The discharge of ammonia nitrogen and its subsequent
oxidation can seriously reduce the dissolved oxygen levels
in surface and ground water. This is particularly true in
waters which do not have significant atmospheric re-oxygenation
rates.

Eutrophication is a serious problem posed by excessive
nitrogen release to lakes. It is of particular concern in

some lakes in the Okanagan region of British Columbia. Some
lakes in this area are receiving drainage waters from some
airports where urea is used. Eutrophication is the complex
sequence of changes in aquatic ecosystems caused by an increased
rate of supply of plant nutrients to water. An eutrophic lake
represents the end product of this sequence. It is character-
ized by a high nutrient supply in relation to the volume of water.
The lake may contain dense growths of planktonic green and blue-
green algae, mats of rooted plants and filamentous algae on
the bottom of shallow areas, very low or no dissolved oxygen
in the lower depths in summer, and dominant warmwater fish
species (minnow and bass families) [11]. The process of eutrophica-
tion occurs naturally, but, man's activities can greatly
accelerate it.

1.22 Urea Nitrogen Pathways

Generally, all of the urea-nitrogen which is applied
on an airport runway will not contaminate ground and surface
waters. Nitrogen can assume many forms and follow many re-
action pathways, particularly in soils (Figure 2). These
soil pathways include urea hydrolysis, nitrification, ammonia
volatilization, denitrification, plant up-take and leaching.

Since most of the urea applied to airport runways eventually con-
tacts soil, it is important to examine the soil-nitrogen re-
actions.

The most common way de-icer urea can enter into the soil
system is by percolation. Currently, urea impregnated snow is

PATHWAYS

1 Urea runoff

2 Urea seepage

3 Urea Hydrolysis
  (Urea→NH_3→NH_4^+)

4 NH_3 volatilization

5 NH_4^+ clay fixation

6 NH_4^+ plant uptake

7 Nitrification
  (NH_3→NO_2^-→NO_3^-)

8 NO_3^- plant uptake

9 Denitrification
  (NO_3^-→$N_{2(g)}$)

10 NO_3^- leaching

11 Urea leaching

12 Urea overland flow

NITROGEN FORMS

Urea

NH_3-NH_4^+

NO_3^-

N_2 gas

NH_3 gas
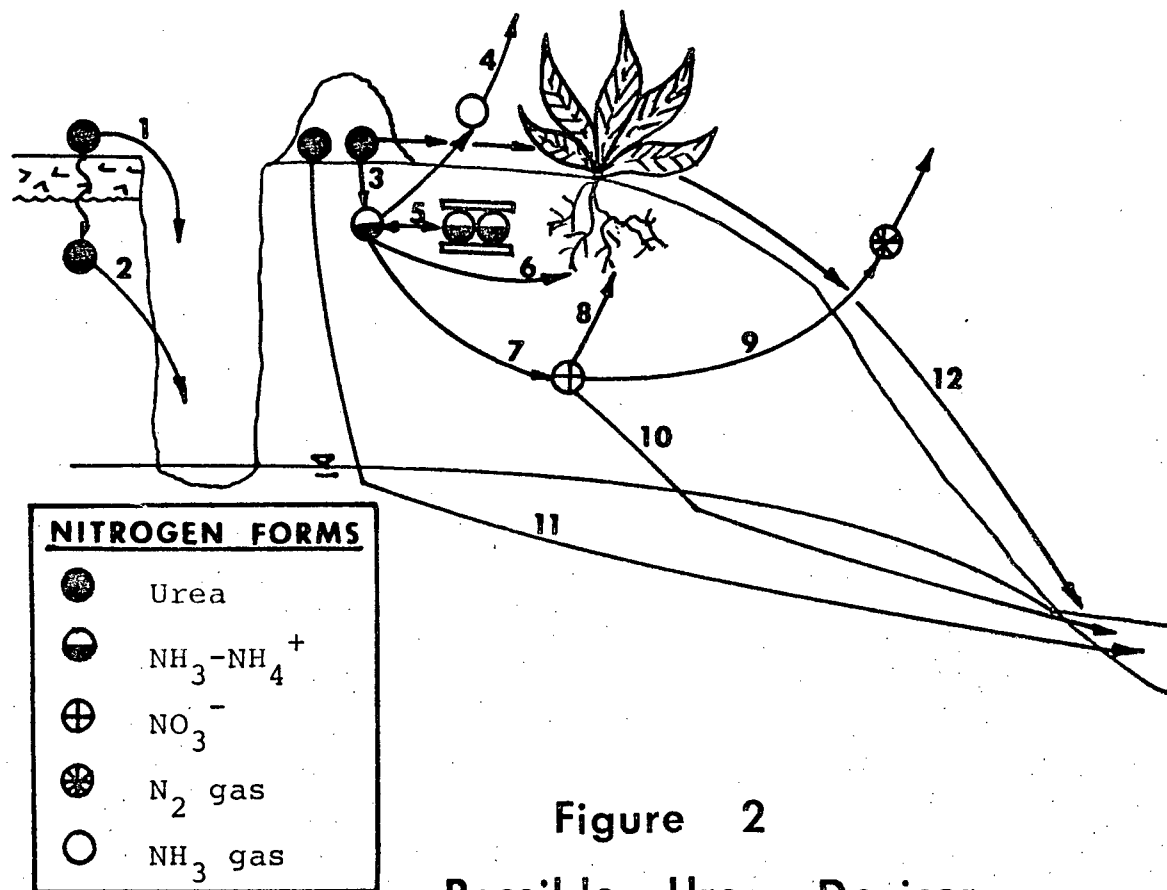
Figure 2

Possible Urea De-icer

Nitrogen Pathways

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blown into windrows parallel to airport runways up to 100 ft from the pavement surface. Once the urea goes into the soil, it enters into a chain of complex reactions which may eventually lead to nitrogen forms being leached to surface waters. The quantity of nitrogen leached is determined by the physical, chemical, and biological properties of the soil and plants which control the nitrogen reactions.

a) Urea Hydrolysis

Urea can be hydrolyzed to ammonia by the soil enzyme urease. Formation of unstable ammonium carbonate is an intermediate step in the reaction.

$$CO(NH_2)_2 + 2H_2O \longrightarrow (NH_4)_2CO_3 \longrightarrow 2NH_3 + H_2CO_3 \qquad (2-1)$$
  Urea   Urease
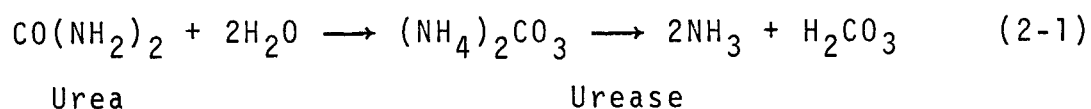
This hydrolysis results in a temporary increase in pH, of which magnitude and duration is dependent upon soil buffering capacity.

Urease is a common soil enzyme and often exists as "free urease" absorbed on clay minerals. Paulson and Kurtz[12] showed that free urease complexed by soil colloids was primarily responsible for the hydrolytic breakdown of urea.

Alexander[13] found that urease was significantly active from 2°C to 37°C. Bremner[14] showed that urease induced urea hydrolysis can occur at below freezing temperatures as low as -10°C to -20°C. Beaton[15] concluded: "This evidence of urease activity at low temperatures along with

the knowledge of urea's ability to melt ice at temperatures down to 11°F(-12°C) suggestes that urea applied late in the fall or even under winter conditions will be converted to ammonium."

Simpson and Melsted[16] found urea hydrolysis rates to be 2 to 6 times greater at 25°C than at 1°C. Gasser[17] found that, at 5°C, hydrolysis was slow and was complete after 16 days in soil which had been previously manured; and only about 40% was hydrolyzed after 18 days in unmanured soil. Complete hydrolysis required 6-7 weeks at 5°C and about 3 weeks at 25°C for unmanured soils. He concluded that urea may remain unchanged for considerable periods when applied to old arable soils containing small amounts of organic matter, especially in the spring when the soil is cool.

Simpson and Melsted[16] found temperature to be the most important soil factor affecting urea hydrolysis rates, followed by pH and soil type. Soil moisture and urea concentration were found to be of much less importance. After an 8 week period at 1°C, up to 100% of the nitrogen added as urea was recovered as exchangeable ammonium. The minimum hydrolysis rate in higher pH soil (6.2pH) at 1°C was found to be 30 pounds of urea-N per acre per day hydrolyzed, and in lower pH soils (5.1pH) 10 pounds of urea-N per acre hydrolyzed per day.

Gasser[17] found that at 5°C, hydrolysis of urea was slow and was complete after 18 days in the manured soil;

only about 40 per cent was hydrolyzed after 18 days in the unmanured soil as shown in Table 4.

Table 4

Nitrogen Recovered from Clay Soils

Days	NH_4^+-N*	NO_3^--N*	Urea-N*	Total*
		- Unmanured -		
0	1	0	91	92
		@ 5°C		
4	6	0	86	92
8	14	1	84	99
12	23	1	67	91
18	35	1	62	98
		@ 25°C		
3	15	1	78	94
6	33	3	52	88
10	52	10	26	88
14	58	24	10	92
		- Farmyard manure -		
0	3	0	89	92
		@ 5°C		
4	22	1	70	93
8	50	3	40	93
12	64	4	21	89
18	82	7	0	89
3	57	7	26	90
6	69	21	0	90
10	52	39	0	91
14	43	48	3	94

*(Nitrogen recovered, as per cent of N applied during decomposition of urea supplying 100 lb. of N/acre to two clay soils).

Soil urease activity is generally related to

the number of ureolitic micro-organisms present[18].

b)   Nitrification

Ammonia produced by the hydrolysis of urea is converted to nitrate (NO_3^-) by a group of soil organisms called nitrifiers. The Nitrosomonas group of bacteria convert the ammonia under aerobic conditions to nitrite (NO_2^-) as shown in equation 2-2.

$$2NH_3 + 3O_2 \longrightarrow 2NO_2^- + 2H^+ + 2H_2O \quad (2-2)$$
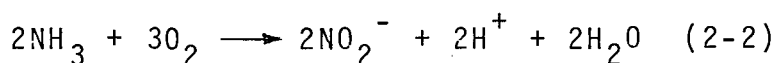
The Nitrobacter group convert the nitrite to nitrate shown in equation 2-3.

$$2NO_2^- + O_2 \longrightarrow 2NO_3^- \quad (2-3)$$
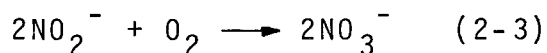
In most soils, the second step of the reaction involving the Nitrobacter group is more rapid then the first step, therefore NO_2^- is usually found in limited quantities. Generally speaking environmental factors favouring crop growth favour nitrification. These soil environmental factors include: nitrifying organism population, reaction, aeration, moisture content, and temperature[15]. The optimum soil pH favouring nitrification is between 6.5 and 7.8.Negligible nitrification occurs in soils with a pH below 5.0.

Nitrification proceeds at a measureable rate at any temperature above freezing, although the rate varies considerably. Nitrification proceeds only one-half as

rapidly at 10°C as at 15°C and only one-tenth as rapidly at 5°C. The optimum range is 32 to 35°C[18].

Simpson and Melsted [16] working with their Illinois soils at 1°C, found no measureable quantities of nitrates in any of the soils after an 8 week period. At 25°C, they found that complete nitrification had occurred in 3 out of 4 high pH (6.1) soils. Nitrification after 8 weeks ranged from 25 to 50% of the applied urea-N at 25°C for the 4 low pH soils.

Well aerated soils are required to support nitrification since oxygen is needed in the process. Coarse textured soils with good structure are conducive to nitrification, whereas, poorly drained soils are not.

Urea applied nitrogen can be lost in two ways to the atmosphere, through ammonia volatilization and denitrification.

c) Ammonia Volatilization

For ammonia volatilization to occur, the urea must first be hydrolyzed (Eq'n 2-1), and the rate of volatilization, therefore, is governed by the rate of urea hydrolysis. Volatilization is represented by Equation 2-4.

$$NH_{3(l)} \longrightarrow NH_{3(g)} \qquad (2-4)$$
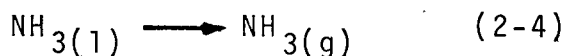
Ammonia volatilization occurs when the absorption capacity of the soil is insufficient to hold the ammonia. Ammomia volatilization increases with: high

soil pH, calcium carbonate in soil, low organic matter and
clay content, high urease activity, low nitrification
capacity, air movement over soil surface, high urea
application rates, high soil temperatures, and rapid dry-
ing of the soils due to evaporation.

Volatilization losses from surface applied
urea have been reported to occur even on acid soils.
This occurs because of localized areas of alkalinity
around the urea pellets caused by the hydrolysis of urea [15].

Ammonia losses from forest soils have ranged
from less than 5 percent to 20-40 percent of the applied
urea[19].

Mahendrappa[20] working with some forest floor
materials following urea fertilization found that,
depending upon the source of organic matter, the maximum
rate of ammonia volatilization occurred on the second or
third day. The quantity of ammonia volatilized within a
week of urea application constituted the major proportion
of the total quantity of ammonia given off in 42 to 56 days.
The rate of ammonia volatilization from fertilized forest
floors was found to be dependent on the concentration
gradient of the urea in solution around the sites where
the enzyme urease hydrolyzes urea to ammonia. Large urea
particles would cause greater gaseous loss of ammonia
since larger concentration gradients would develop. How-
ever, the larger particle, with lower surface area (by

weight), may contact less urease.

Previous urea applications have been found to increase ammonia volatilization of subsequent urea additions[21]. This may have occurred because previous nutrient application increased the number and activity of ureolytic and other soil micro-organisms, which in turn caused an increased hydrolysis of urea to ammonia. A shift in the NH_4^+/NH_3 equilibrium in the direction of increased NH_3 concentration and subsequent volatilization could also have occurred. Prior fertilization (4 years before) was found to nearly double ammonia volatilization losses. Glacial outwash soil had the lowest ammonia volatilization of all soils tested (9.8%) possibly because of its low pH (4.6) and low microbial activity.

As shown in Table 5, volatilization loss of ammonia has been shown to be minimal at low temperatures[22].

Table 5

Volatilization of Ammonia in Soils

Soil Type	Soil pH	Temperature		
		7°C	16°C	22°C
Lakeland f.s.1	5.6	1.1*	7.1	41.1
Lakeland f.s.III	5.4	1.1	9.2	15.7
Lakeland f.s.V	6.3	5.1	32.9	36.9
Leon f.s.I	4.4	0.4	16.3	26.7
Leon f.s.II	5.9	8.3	27.2	36.0

(100 pounds of urea-nitrogen to bare moist soils).
* % loss in 7 days.

In these experiments, Volk[22] noted that slowing the rate of conversion of urea to ammonia would increase the period during which precipitation could reduce volatile loss of ammonia by washing any residual urea into the soil.

Gasser[23] experimented with 4 soils at 5°C and 25°C as shown in Table 6.

Table 6

Volatilization of Ammonia in Loams

Temp	Soil*			
	1	2	3	4
@ 5°C (after 18 days)	0.4**	2.2	19.6	7.3
@ 25°C (after 14 days)	2.2	2.2	10.3	5.4

*(soils 1 and 2 were clay loams, 3 and 4 were sandy loams).

**NH_3 lost as % N applied (100 lb of Urea-N/Acre)

Sandy loams exhibited higher volatilization rates than clay loams.

d)   Denitrification

The second way in which urea nitrogen may be lost to the atmosphere is through denitrification. This is a microbial process which converts nitrate or nitrite to nitrogen gas as shown in Equation 2-5.

$$NO_3^- + H^+ \longrightarrow 1/2\ N_2 + 5/4\ O_2 + 1/2\ H_2O \quad (2\text{-}5)$$
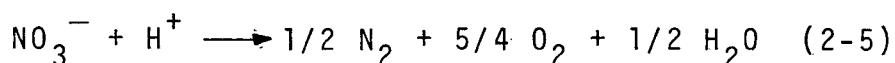
For denitrification to take place, there must be no oxygen in the microenvironment of the bacteria, and available organic matter for energy. For this reason, denitrification is most likely to occur in waterlogged soils with large quantities of fresh or readily decomposable crop residues. High temperatures and neutral to alkaline soil conditions also favour denitrification. All of these conditions exist in many soils of western Canada, and as a result, there could be substantial losses of soil and fertilizer nitrogen, especially during warm spells in May and June[15].

The Department of Soil Science at the University of Saskatchewan estimated that denitrification accounts for losses of 10-30 percent of the available soil nitrogen. Other studies have shown that 10 to 20 percent of the applied fertilizer nitrogen could be lost through denitrification[24]. DeBell (et al.)[25] found gaseous losses of nitrogen oxides from three forest soils to be of low magnitude (less than 1%).

e)   Plant Uptake

Plants can utilize nitrogen in various forms, however, nitrate and ammonium are the forms most commonly used. Most agricultural crops prefer nitrate. Nitrate is more likely to be free in the root zone as it is highly mobile. Optimal plant yield requires an excess of nitrate nitrogen in the soil. Care must be taken since excessive

quantities of nitrogen can extend growing periods and delay crop maturity.

Nitrate is not accumulated uniformly by the various tissues and organs of plants. There are many environmental factors which influence nitrate accumulation and, therefore, extreme variations are found in nitrate content in the same tissue from plant to plant[26].

On the average, about 50% of the applied fertilizer nitrogen is recovered by upland crops[24]. The plant families: Amaranthaceae, Chemopodiaceae, Cruciferae, Compositae, Gramineae, and Solanaceae have been shown to accumulate high levels of nitrate.

Nitrate does not accumulate uniformily through the growing period of a plant.[27]

"In summary, experiments with several cereal plant species under 'normal conditions' indicate that in the early vegetative stages, the leaf tissue can accumulate nitrate in relatively high concentrations (400 to 1500 μg NO_3^--N g. fresh weight^{-1}). This initial accumulation, under normal conditions, is at-tributable to available water and nitrate in the soil that favours high rates of absorption. Thus, in the early stages of development, absorption and trans-location exceeds the capacity for nitrate reduction and assimilation. As the plant develops the con-centration of nitrate decreases in both leafy and non-leafy tissue, with the more rapid decrease occurring in the leaf tissue. The decrease in nitrate content is attributable to the following several factors: a) Rapid growth tends to dilute the nitrate con-centration; b) the capacity of the leaf tissue to reduce and assimilate nitrate is increased not only from having a greater amount of the proper enzymes but having an adequate supply of energy for the reductive steps; and c) a reduction in available water and nitrate in the soil. In mature plants nitrate accumulates primarily in tissue that exhibits a low capacity for reduction and assimilation

(monchlorophyllus stem and stalk structures).
From studies with weeds and soybeans (Wells un-
published work), it appears that other plants
exhibit a similar pattern of nitrate accumula-
tion."

The nitrogen content of most crop plants is
from 1 to 3% of the dry weight[15]. Vigorous growth and a
deep green colour are normally related to an adequate
supply of nitrogen.

Data on plant-uptake of nitrogen has been publish-
ed by various authors, as shown in Table 7.

Table 7

Plant Uptake of Nitrogen

lbN/Acre*	Source	lbN/Acre in Harvested Crop	Crop
480	Urea	223	Pensacola Bahiagross
480	Urea	261	Pangola grass
480	Urea	137	Carpet grass
480	Urea	280	Coastal Bermudagrass

* (Urea applied monthly in six portions and watered-in
immediately.)[28]

Table 7 - Continued:

Crop	Yield (BU/A)	Nitrogen Grain or Seed	Removed by Cropping-lb./Acre All of the above ground growth (grain or seed plus straw, stover, etc.)
Wheat	40	58	76
Barley	60	57	90
Oats	80	49	81
Rapeseed	35	70	115
Grass (Hay)	3		120
Corn (Grain)	100	90	157
Corn(Silage)	15		136
Alfalfa (Hay)*	4		240*

*Most of the nitrogen removed by effectively nodulated alfalfa is fixed from the atmosphere[15].

Crop[26]	Yield cwt/Acre	Pounds Nitrogen in Total Plant
Wheat	24	85
Barley	28.8	90
Oats	27.2	100
Flax	11.2	54
Rapeseed	15	119
Grass	60	86
Alfalfa	80	248
Peas	18	118
Corn	120	139
Potatoes	300	225
Sugar Beets	300	160

An increase in temperature from 5°C to 35°C
has been noted to cause an increase in the rate of nitrate
absorption of perennial ryegrass roots, with the greatest
increase occurring between 15°C and 25°C [26].

Broadbent[29] concluded that uptake of nitrogen
by plants is retarded at low temperatures and winter losses
of nitrogen are higher than in summer, even on permanent
pastures. In Ontario, 40 lb. of nitrogen top dressed
on fall wheat in early spring gave a yield increase over
non-fertilized wheat equivalent to 80 lb. of nitrogen top
dressed in the late fall[30].

A practical factor which will influence urea
nitrogen - soil interaction is the MOT regulations re-
garding crops near airports. MOT regulations restrict
crops which may be grown adjacent to airport runways.
This is done to minimize the possibility of birds acting
as a hazard to aircraft. Infield grass areas are required
to be free of weeds and have a height between 5 and 8 inches
to restrict accessibility of birds to worms, beetles, insects,
etc. in the cover crop. Cereal grains and market garden crops
are not permitted within 1200 feet of runways. Where
present, these crops should be replaced with hay, alfalfa,
or flax which require little or no plowing or cultivating
and attract few birds. Corn, oats, and sunflowers are
prohibited on airport property. Areas further than
1200 feet from the runways may be leased for agricultural

uses in the following order of preference:

a)   Hay
b)   Alfalfa
c)   Flax
d)   Soybeans
e)   Pasture, Golf Courses)
      Driving Ranges,   ) Only if fully secure
      Archery Ranges   ) fencing is provided.
      Other human recreation)
f)   Fall rye
g)   Fall wheat
h)   Spring Wheat
i)   Barley
j)   Other cereal grains and crops except corn and oats.

f)   Leaching

The mobility of ammonium and nitrate ions
in soil differs markedly. Ammonium ion may be retained
in an exchangeable form on or near the soil surface. Expanding
lattice clay minerals such as montmorillonite, illite,
and vermiculite permit NH_4^+ to enter the clay structure
and become fixed. A large proportion of fixed ammonium
can be held within the lattice of these clays and will be
unavailable to crops and for transformation by nitrifiers.
In this case, ammonium is only freely mobile when a soil
system is temporarily overloaded or in a soil with low
cation-exchange capacity. Various workers have shown that
at neutral or slightly acid soil conditions, organic
matter fixes little or no ammonia, but, at pH levels 9
or 10, fixation increases rapidly.

"The available evidence indicates that in
the zone of high concentration, the amount of
ammonium fixed by clays and organic matter is gen-
erally low in relation to the amount applied. In-
creased mineralization of soil nitrogen resulting

from the increase in pH apparently compensates
for reduced crop uptake of NH_3 nitrogen caused
by fixation"[31].

Nitrate, on the other hand, is highly mobile
in soil. Nitrate diffuses very slowly without appreciable
water movement. Water in soil is a storage medium for
nitrate. Nitrate may move faster, slower, or at the same
rate as the average total water in the soil. If the water
moves upward because of lack of rain and high evaporation,
nitrate can accumulate at the soil surface as an evaporite
crust.

Nitrate in the upper part of the soil is
utilized more by plants than deeper nitrate because of
greater plant root activity. Nitrate concentrations in the
root zone are extremely variable depending on the timing
of sampling in relation to the last fertilization, crop
growth, and rainfall or irrigation. Little nitrate appears
to be leached in the presence of a growing crop. This
occurs because of rapid uptake of nitrate ions by plants
and reduced movement of free water due to the removal of
water by plants. For nitrate to move below the root zone,
there must be nitrate present and downward water movement.
Nitrate may reach the water table in a few hours and be
lost from the plant rooting zone. Nitrate below the root
zone and above an aquifer is generally chemically stable
because of an insufficient supply of oxidizable carbon for
the denitrifiers and no significant source of ammonium
for the nitrifiers.

Thomas[32] reports that in very dry soils, to which water has been added, nitrate may lag behind the water front. In moist soils, heavy rains cause the nitrate and water front to move at the same rate.

Leaching losses of up to 10 percent of the available nitrogen Prairie soils is commonly assumed[18]. Percolation water can account for 5-25% of the nitrogen removal from humid region soils subject to rotation cropping[24]. Most leaching occurs in late fall and winter if the soil is not frozen, and in the early spring.

Leaching in winter may be significant if heavy rains occur. Thomas concludes[33]:

"Not only does drainage proceed more slowly from cold soils (Penman and Schofield, 1941) but frozen soils do not drain at all. When the frozen soil is thawed, some downward movement of nitrate will occur, but it will not be deep unless this is followed by spring rains. This suggests that in areas with cold winter climates, late fall application of nitrogen may be just as effective as spring application, but that neither will be very good if followed by heavy spring rains."

Volk[34] and others have published data of nitrogen losses through leaching as shown in Table 8.

Thomlinson[35] found that urea moves about as readily as nitrate and more easily than ammonium in soils. Soils high in organic matter seem to restrict the movement of urea[36].

Little is known of the fate of nitrate once it reaches an aquifer. The safest assumption is that nitrate will remain in the water table until flushed through or pumped out[26]. The residence time of water in an aquifer

may be a few days or more than a hundred years. While the concentration of nitrate is subject to fluctuations caused by dilution, stratification, and mixing, the potential for it to enter water wells and surface waters exists.

Table 8

Soil Nitrogen Leaching Losses

lb N/A[34]	Source	lb N/A drainage	Crop
480	Urea	0.5	Pensacola Behiagrass
480	"	7.2	Pengola grass
480	"	81.1	Carpet grass
480	"	5.8	Coastal Bermudagrass

Cropping[24]	N applied	N loss	
		Unfertilized ----- kg/ha/yr	Fertilized --------
Corn	129	5.6	15.1
Oats,Alfalfa	17	4.3	5.7
Alfalfa	0	4.8	3.9
Alfalfa	0	4.7	8.6
Cont. Corn	129	6.6	14.0
Cont.Bluegrass	17	0.3	0.7

2.   Minimizing the Environmental Impact

The Federal Government of Canada through the Ministry
of Transport (MOT) developed the procedure of using urea as a
de-icer. Recognizing the potential for adverse effects, MOT
with Environment Canada has been sponsoring a program to evaluate
urea's environmental impact. This study forms a part of the
program. The objectives were:

    a)   To carry out a literature review on urea in-
          cluding an up-date on findings available from
          the joint Air Canada (Cominco) MOT studies.

    b)   To determine the rate of hydrolysis and
          volatilization of urea during winter conditions.

    c)   To discuss additional means of minimizing
          nitrogen release to ground and surface waters.

    d)   To suggest possible urea additives and other in-
          fluencing factors, giving consideration to b)
          and c) above.

Methods for minimizing the environmental impact of
urea include: nitrification-denitrification, breakpoint chlorina-
tion, selective ion exchange, air stripping, soil and plants,
volatilization of ammonia on airport runways, and reduction of
urea usage. Since there is no published literature concerning
volatilization of ammonia on airport runways and reduction of
 urea usage, a laboratory research program was devised to test
these urea control methods for airport application. The re-
maining methods for minimizing the environmental impact of urea
were examined in a literature review. Section 1.2.2 "Urea
Nitrogen Pathways", constitutes an important part of this review.
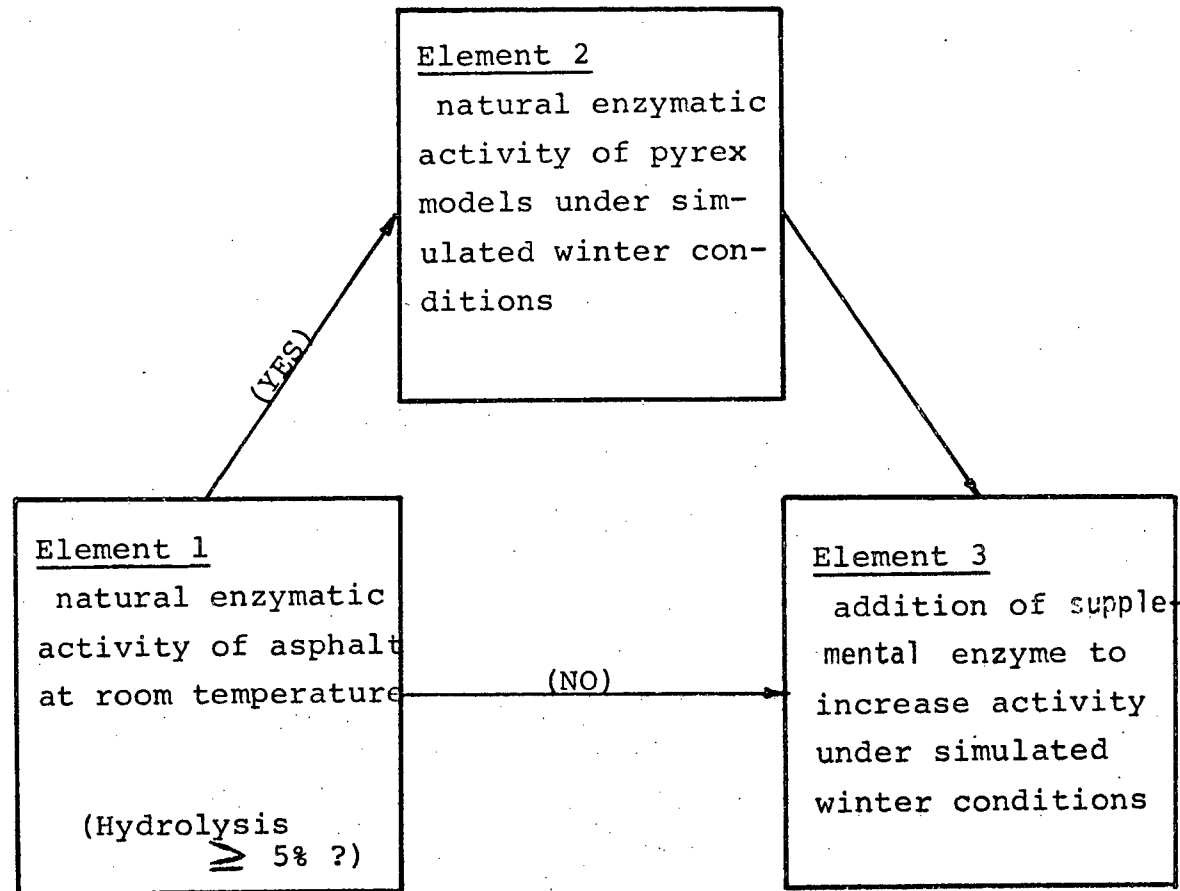
Experimental Research

2.1   Volatilization of Ammonia by Urease on Airport
        Runways.

The control of urea de-icer may be accomplished on
the airport runway itself. Urea can be hydrolyzed to ammonia
by the soil enzyme urease, and this ammonia can volatilize to
the atmosphere. Since urease is an abundant soil enzyme, it
may be found on the surface of the airport runway. It is
associated with clay and other soil particles which could find
their way onto the runway by wind. Urease from the soil exhibits
what could be called, "a natural enzymatic activity". At winter
temperatures, urease is the only agent which can induce urea
hydrolysis.

If this natural enzymatic activity does not cause a
significant quantity of urea to be hydrolyzed, then it is pos-
sible to increase the activity by the addition of a supplemental
urease to the runway surface. This supplemental urease may be a
Jackbean meal.

A laboratory research program was proposed to deter-
mine the natural enzymatic activity on an airport runway and to
investigate the possibility of enzyme addition to increase the
activity. The program was divided into 3 elements as shown in
Figure 3.

To determine the natural enzymatic activity, tests
were to be done on runway samples at room temperature (in order
to assess the maximum likely hydrolysis rate (Element 1)). If

Element 2
 natural enzymatic
activity of pyrex
models under sim-
ulated winter con-
ditions

Element 1
 natural enzymatic
activity of asphalt
at room temperature

(Hydrolysis
$\geq$ 5% ?)

Element 3
 addition of supple-
mental enzyme to
increase activity
under simulated
winter conditions

(YES)

(NO)

Figure 3

Volatilization of Ammonia Study Flow

Diagram

less than 5% of the applied urea were found to be hydrolyzed, after 90 minutes from urea application (the maximum length of time MOT officials felt the urea pellets would be allowed to sit on the runway before sweeping), then the research would proceed to Element 3.

If the hydrolysis rate was found to be greater than 5%, then Element 2 would be initiated. Tests, under varying conditions of temperature, ice thickness, urea application rate, urea type, and solar radiation would be performed. The natural enzymatic activity found in Element 1 of the research would be duplicated using laboratory grade urease and Pyrex models. Pyrex surfaces would be used, rather than pavement, to afford greater experimental control, as it is extremely important to know the concentration of urease and urea on the model surface. Neither of these concentrations could be measured if a pavement surface was used because it is impossible to thoroughly clean the surface between tests. Also, permeability of asphalt makes total retrieval of liquid impossible.

Element 3 of the research would involve using the pyrex models, and laboratory grade urease to investigate the possibility of increasing ammonia volatilization through the addition of urease to an airport runway under winter conditions. In Element 3, the experimental conditions used in Element 2, as well as different enzyme concentrations would be used.

Analytical Methods

After a review of the published literature, the method chosen for the determination of ammonia was the "Phenate Method" as outlined in Standard Methods[37]. Advantages of this method over other ammonia analysis methods for this application are:

  a) It is a "standard method" and therefore generally accepted.

  b) It does not require the sample temperature to be raised (important because temperature affects both chemical and biological hydrolysis rates).

  c) There is little delay between adding the reagents and analysis.

  d) It is a simple method involving neither complicated equipment nor expensive reagents.

The method chosen for the determination of urea utilizes the Phenate Method for ammonia and an "urease incubation"[38]. The incubation involves the addition of a concentrated, buffered, urease solution to the urea sample. This converts all the urea to ammonia. The process follows the urea hydrolysis reaction as shown in equation 2-1. The ammonia formed from the hydrolysis of urea is then measured using the Phenate Method.

The intensity of the blue colour formed in the Phenate Method is, within certain limits, proportional to the ammonia concentration. Unhydrolyzed urea does not react with the Phenate Method chemicals and urease is inactive once the chemicals are added.

In a sample containing ammonia and urea (with or without urease) the Phenate Method applied to a freshly collected sample yields the ammonia concentration, and applied after a urease incubation, yields the sum of the ammonia plus urea

concentration.

Ammonia and urea standards were used to establish a calibration curve. The absorbance of the solution was measured with a Bausch and Lombe Spectronic 88 spectrophotometer.

2.1.1 Natural Enzymatic Activity of Airport Runway

Four pieces of airport runway were tested in order to measure their natural enzymatic activity. Two pieces were obtained from Abbotsford Airport, one asphalt (Model 1) and one concrete (Model 2). Two asphaltic surfaces were from Vancouver International Airport (VIA) (Model 4 and 5). Areas of runway were isolated by placing tin foil containers, from which the bottom was cut, on the surfaces and sealing them with silicone. The two Abbotsford pieces had isolated model areas of 450 square centimetres (25 cm. x 18 cm.). Model 4 had a test area of 314 $cm.^2$ (20 cm. diameter) and Model 5 had 160 $cm.^2$ (10 cm. x 16 cm.). Both of the VIA models were rougher and more weathered than the Abbotsford models. Model 4 had some clay, grass clippings, and soil on its surface.

All models, except Model 2, received Cominco Industrial Grade (C-IG) urea equivalent to 0.90 kg urea/70$m.^2$ (2 lb./750 $ft.^2$) and sufficient distilled water to produce an initial depth of 5 mm. Due to the permeability of the asphalt surfaces, some of the urea solution was lost from the surface. This was particularly evident in Model 4 which had a visible crack. Table 9 summarizes the results.

Table 9

Natural Enzymatic Activity

of Airport Runway

Model No.	Percent Urea Hydrolyzed after 90 minutes	Comments
1	0.5	Abbotsford asphalt
3	0.4	Abbotsford concrete
4	0.2	VIA asphalt
5	0.4	VIA asphalt

All the airport surfaces had experienced previous urea applications indicating that some residual urea and ammonia were expected to be on the surface. To test this theory, only distilled water was added to the surface of Model 2. After 90 minutes, a sample of liquid was removed and analyzed. A residual urea concentration was found, equivalent to 0.79 μg /cm^2 (13 μg/in^2), and a residual ammonia concentration of 0.30 μg/cm^2(5 μg/in^2). The urea concentration is only 0.023% of a 0.90 kg /70m^2 application. Since this piece probably experienced many urea applications, it is clear that virtually none of the applied urea remained on the runway surface. At an airport, most urea is removed by sweepers and plows during winter operations. Any urea remaining on the runway after winter, is removed by spring rains.

Based on the residual found on Model 2, residual urea could account for up to 28% of the ammonia concentration, after 90 minutes, for Model 1. Therefore, the actual percent of urea hydrolyzed would be less than 0.5% - shown in Table 9.

Since the natural hydrolysis rate at room temperature was less than 0.5%, the rate under winter conditions must be insignificant. The second experiment of the laboratory program ("low temperature activity of enzyme") was therefore deleted.

2.1.2. Addition of Enzyme to Increase Activity

In order to study the possibility of increasing hydrolysis and volatilization of urea by the addition of the enzyme urease, a series of 32 tests were performed under various environmental conditions. These conditions included:

a) ice thickness - 3mm , 5mm , 8mm

b) temperature - -4°C, 0°C , +4°C, +12°C

c) urea application rate - 0.45 kg/70m^2, 0.90 kg/70m^2, 1.80 kg/70m^2

d) urea type - Cominco-Industrial grade (C-IG), Cominco-Forestry Grade (C-FG), Sherritt Gordon Mines - Industrial Grade (SGM-IG)

e) urease additions - 100 mg, 200mg, 500mg, 750mg (per model)

f) solar radiation - 50 BTU/h-ft^2, 100 BTU/h-ft^2

g) solar radiation - buffer addition.

Solar radiation was modelled by a QF 500 A, 500 watt, quartz, General Electric lamp. This lamp produced more infra-

red and less ultra-violet than the sun. About 20% of the lamp's output was light and 80% was heat. The input electrical energy was assumed to be completely converted to light or heat energy. The output energy was assumed to be evenly distributed over the light coverage area. Neither of these assumptions are true. The actual solar insolation is lower than that calculated because of the energy conversion assumption, and greater than the calculated value because of the energy distribution assumption. The net error should not be too great. Light meters and thermometers could have been used to determine the exact accuracy of this model, but, this was considered beyond the needs of this experiment.

The height of the lamp was adjusted to achieve two representative solar insolation rates. Solar radiation #1 represented an insolation rate of 50 BTU/h-ft ^{2} which approximates a noon sun in late December at 56° North Latitude(Fig.4).

Solar radiation #2 represented an insolation rate of 100 BTU/h-ft ^{2} which approximates a noon sun in late December at 48° North Latitude (Figure 5) (or mid-February and November at 56° North Latitude).

To begin a test, MCB Manufacturing Chemists' 'Double Strength' (U x 80 L817) urease was mixed with distilled water and poured into 33.5 cm x 21.5 cm (720 cm ^{2}) pyrex containers.

The models were placed in a controlled environment room, at the desired temperature for about 12 hrs. After this cooling period, urea was added.
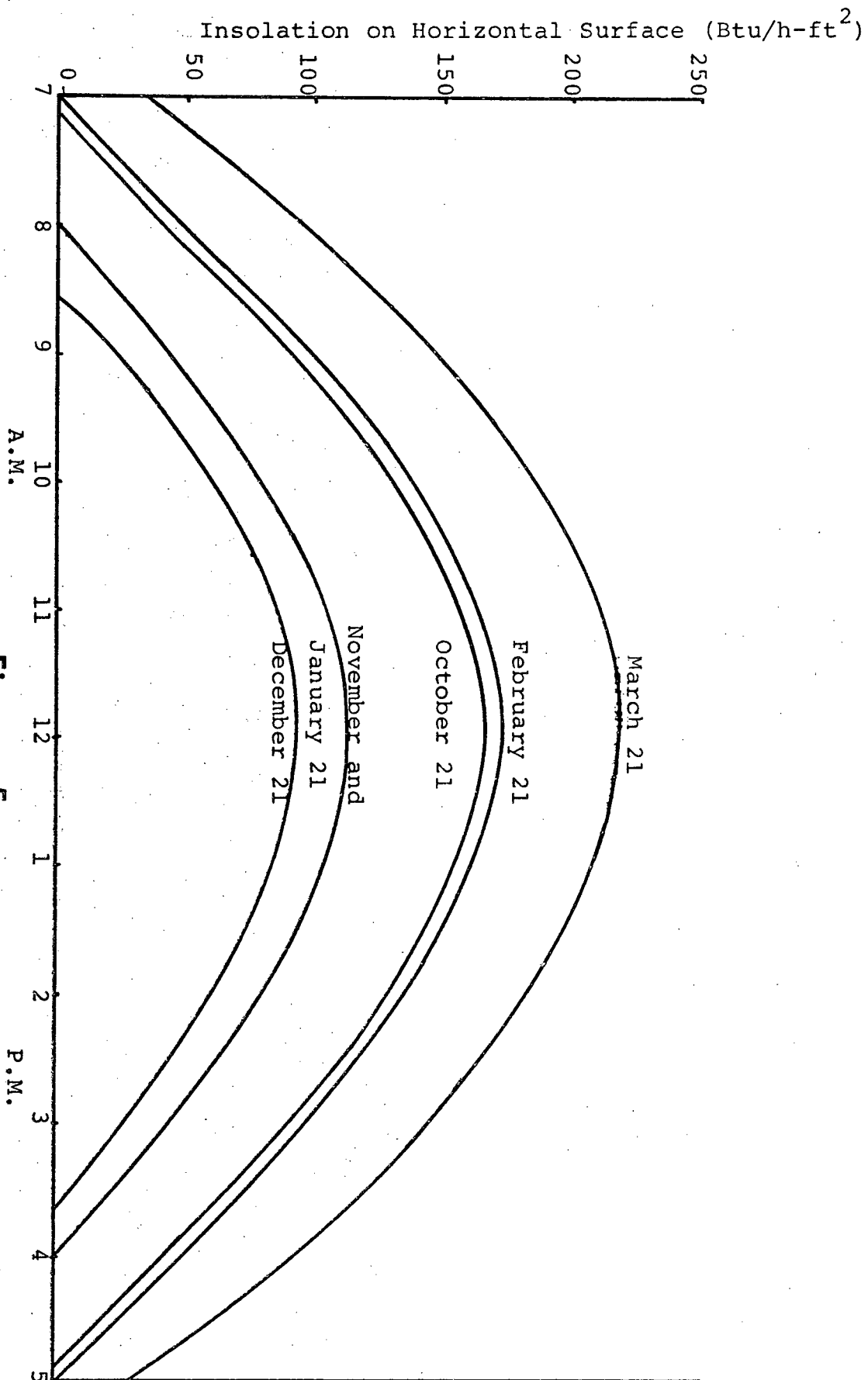
Figure 4

Monthly Variation of Insolation at 56° N.L.

Insolation on Horizontal Surface (Btu/h-ft²)

March 21

February 21

October 21

November and
January 21

December 21
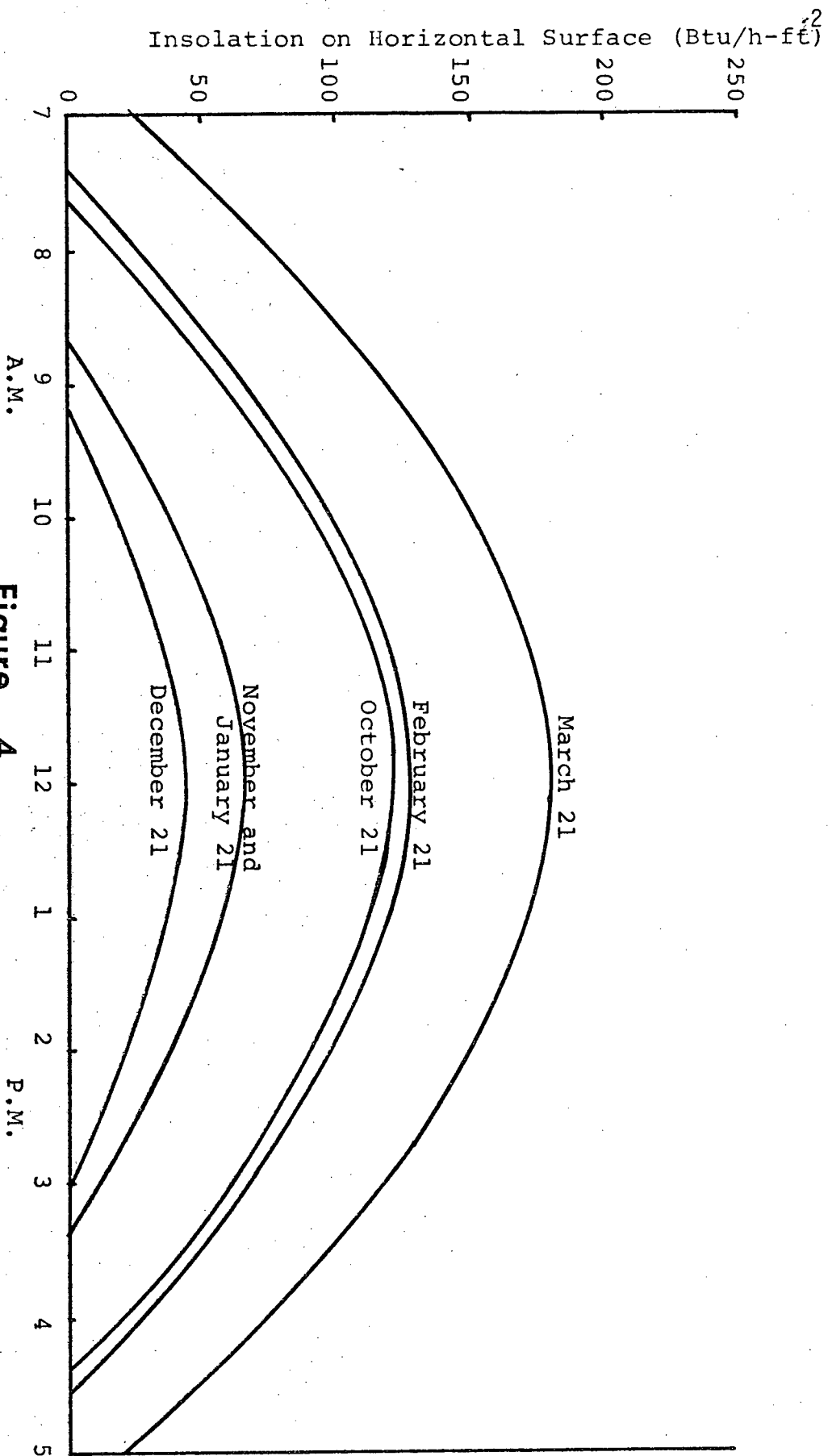
Figure 5

Monthly Variation of Insolation at 48° N.L.

Insolation on Horizontal Surface (Btu/h-ft^2)

March 21

February 21

October 21

November and
January 21

December 21

After 90 minutes, samples were taken from the melt-water and ice fractions. Meltwater is the liquid formed by the action of urea on ice. Samples were obtained by tipping the pyrex model and collecting the liquid in a beaker. The ice was melted to liquid by placing the pyrex model in a warm water bath and samples were taken from the resulting liquid. Ammonia concentration, urea concentration, and volume of liquid, were determined for the ice and meltwater fractions.

At any time, the urea content in the system obeys the equations:

$$U_t = U_h + U_u \qquad (2\text{-}6)$$

where: U_t = total weight of applied urea

U_h = weight of urea hydrolyzed

U_u = weight of urea unaltered

but, $U_h = U_{hl} + U_v \qquad (2\text{-}7)$

where: U_{hl} = weight of urea hydrolyzed which remains in liquid phase.

U_v = weight of urea hydrolyzed which goes to gas phase (volatilization of ammonia).

therefore, $U_t = U_{hl} + U_v + U_u \qquad (2\text{-}8)$

and, $U_v = U_t - U_{hl} - U_u \qquad (2\text{-}9)$

The percent urea hydrolyzed is given by:

$$\frac{U_h}{U_t} \times 100\% = \frac{U_{hl} + U_v}{U_t} \times 100\% \qquad (2\text{-}10)$$

The percent urea volatilized is given by:

$$\frac{U_v}{U_t} \times 100\% = \frac{U_t - U_{hl} - U_u}{U_t} \times 100\% \qquad (2\text{-}11)$$

The parameter U_t is known, and U_{hl} and U_u can be calculated

$$U_u = B_m \times V_m + B_i \times V_i \qquad (2\text{-}12)$$

where: B_m = urea concentration in meltwater

V_m = volume of meltwater

B_i = urea concentration in ice

V_i = volume of liquid from ice

$$U_{hl} = \frac{1}{2} (A_m \times V_m + A_i \times V_i) \frac{60}{17} \quad (2\text{-}13)$$

where: A_m = ammonia concentration in melt water

A_i = ammonia concentration in ice

and, 60 is the molecular weight of urea

17 is the molecular weight of ammonia

1/2 is the number of moles of urea which produces one mole of ammonia (from equation 2-1)

Table 10 summarizes the tests and results. The effects of different environmental conditions may be deduced from the results. The comparison is made with the aid of line graphs and "pie diagrams". In these pie diagrams the entire circle represents the applied urea, U_t, as depicted in Figure 6.

Temperature (Figure 7 and 8)

When the temperature was increased the quantity of urea hydrolyzed increased dramatically, from 7% at -4°C to 49% at 12°C (of the applied urea) for an addition of 200 mg. urease to the model, and from 17% at -4°C to 65% at 12°C for 500 mg. urease. At -4°C, the meltwater contained no ammonia and only 9% of the applied urea for the 200 mg. urease test and only

Table 10
Hydrolysis Resulting from Urease Addition

TEST NO.	TEMPERATURE °C −4	0	4	12	UREASE X100 mg 1	2	5	7½	Ice Th. mm 3	5	8	Ur. App. kg/70m² 45	.9	18	Ur. Ty. Ci	Cf	SGM	Other S1	S2	B	% Ur. Hyd.
A-1		•				•				•			•		•						20 %
A-2		•					•			•			•		•						38
B-1		•				•				•		•			•						38
B-2		•				•				•				•		•					9
C-1			•			•			•				•		•						11
C-2		•				•					•		•		•						22
D-1	•					•				•			•		•						7
D-2	•						•			•			•		•						17
E-1			•			•				•			•		•						30
E-2			•				•			•			•			•					63
F-1				•		•				•			•			•					49
F-2				•		•				•			•		•						65
G-1		•				•				•			•				•				12
G-2		•				•				•			•				•				18
H-1		•			•					•			•		•						18
H-2		•					•			•			•			•					58
I-1		•			•					•		•			•						7
I-2		•					•			•			•		•						26
J-1		•				•				•				•	•						9
J-2		•				•				•				•			•				6
K-1	•					•			•			•					•				11
K-2	•					•			•			•					•				4
L-1	•					•			•			•					•				13
L-2	•					•			•					•			•				4
M-1	•					•			•			•			•						10
M-2	•					•			•					•	•						4
N-1	•					•				•			•		•			•			26
N-2	•						•			•			•		•			•			30
O-1	•					•				•			•		•				•		51
O-2	•						•			•			•		•				•		67
P-1		•				•				•			•		•				•	•	22
P-2		•					•			•			•		•				•	•	28

U_t = weight of applied urea

U_h = weight of urea hydrolyzed to ammonia

U_u = weight of urea unaltered (chemically)

U_{hl} = weight of hydrolyzed urea in liquid

U_v = weight of volatilized urea

meltwater

gas

ice fraction

Figure 6

Key to "Pie Diagrams"

4% urea for the 500 mg. test. At 0°C , ammonia was found in the meltwater.

Figure 8 shows that the percentage of the applied urea hydrolyzed after 90 minutes increases linearly when plotted against temperature for a 200 mg. urease addition. Other than the point at 4°C , the 500 mg urease curve is approximately parallel to the 200 mg. curve.

Ammonia volatilization occurred only at +12°C with a 500 mg. urease addition (7% of the applied urea).

Urease (Figure 9 and 10)

At 0°C and 8 mm. ice thickness, an addition of 100 mg urease caused 7% of the applied urea to be hydrolyzed, whereas 500 mg. urease caused 26% to be hydrolyzed. No ammonia was volatilized.

The percentage of urea and hydrolyzed urea (ammonia) in the meltwater and ice fractions, does not follow any pattern for this experiment. In some cases, the attempted retrieval of meltwater by tipping the model did not yield all the liquid. Some was trapped under the ice surface. For this reason, data comparing urea and hydrolyzed urea in the meltwater or ice fraction is not very accurate. The calculations of overall percent urea hydrolyzed and remaining urea in the system are of greater accuracy (perhaps ± 20%).

The percent urea hydrolyzed is proportional to the concentration of urease as shown in Figure 10.

(D-1)	(A-1)	(E-1)	(F-1)
9 7	6 14	30	51 49
84	25	70	200 mg Urease
	55		

$-4^{\circ}C$ $0^{\circ}C$ $+4^{\circ}C$ $+12^{\circ}C$

(D-2)	(A-2)	(E-2)	(F-2)
4 17	9 4 34	37 63	35 58
79	53		500 mg Urease
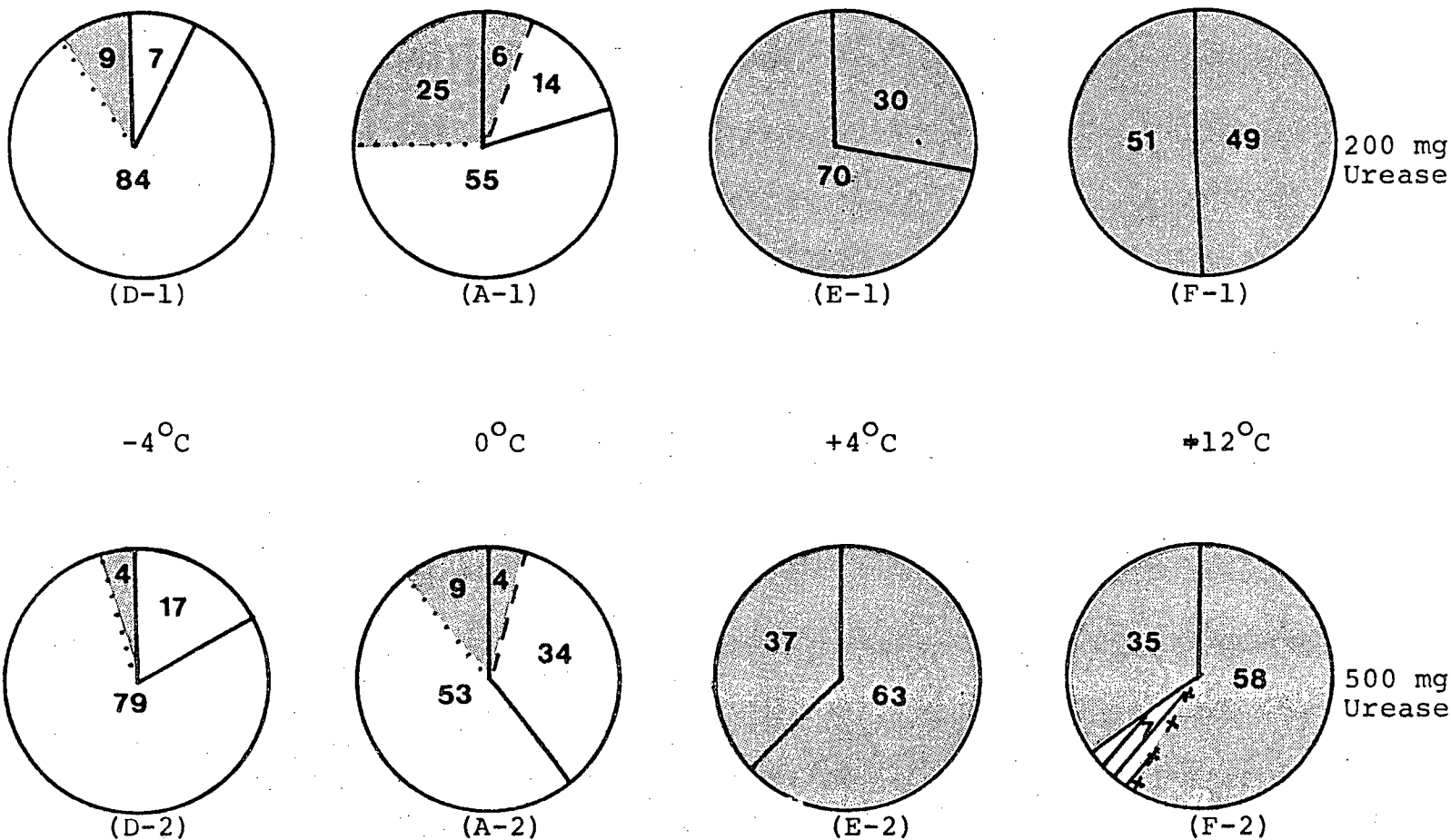
Figure 7

Effect of Temperature

at 5 mm Ice and 0.9 kg/70 m^2 Urea
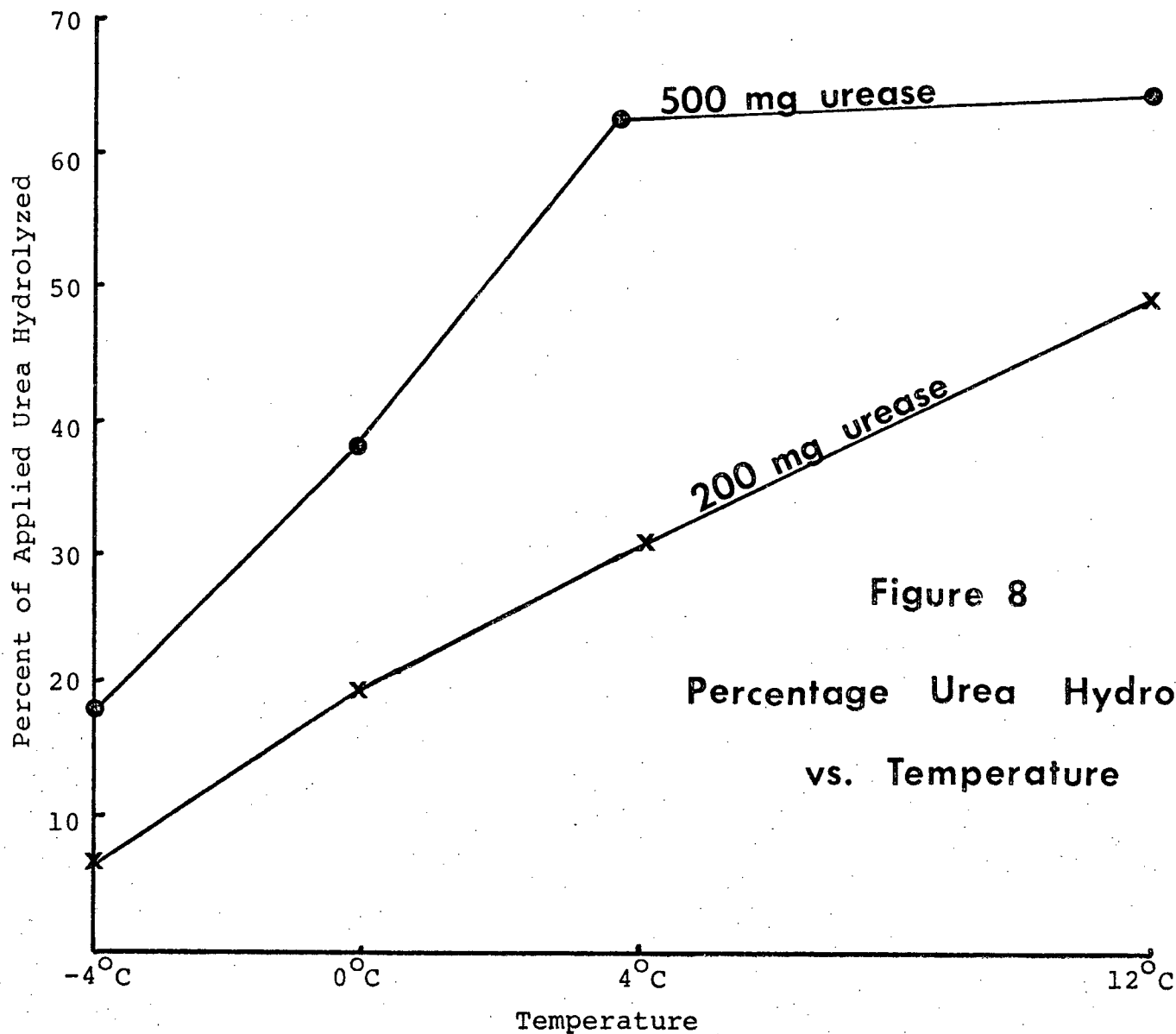
Figure 8

Percentage Urea Hydrolyzed

vs. Temperature
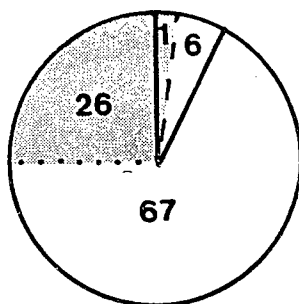
(I-1)
100 mg

(C-2)
200 mg

(I-1)
500 mg

(H-1)
100 mg
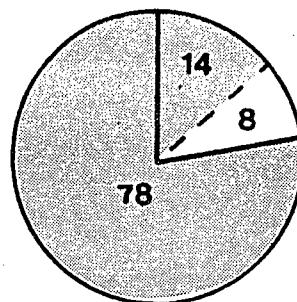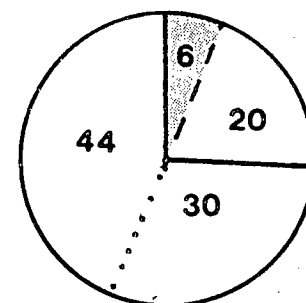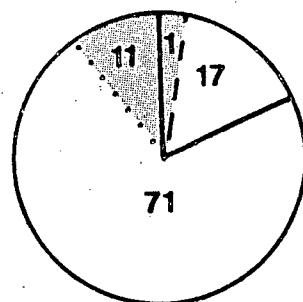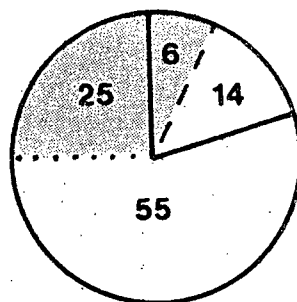
(A-1) **Figure 9**
200 mg

(A-2)
500 mg

(H-2)
750 mg
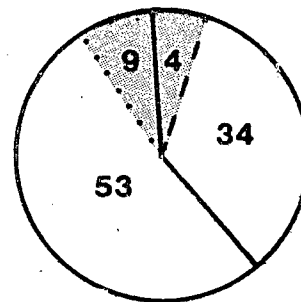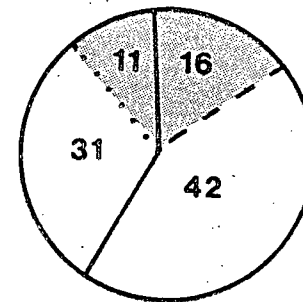
Effect of Urease

at 0°C and 0.90 kg/70 m^2 Urea
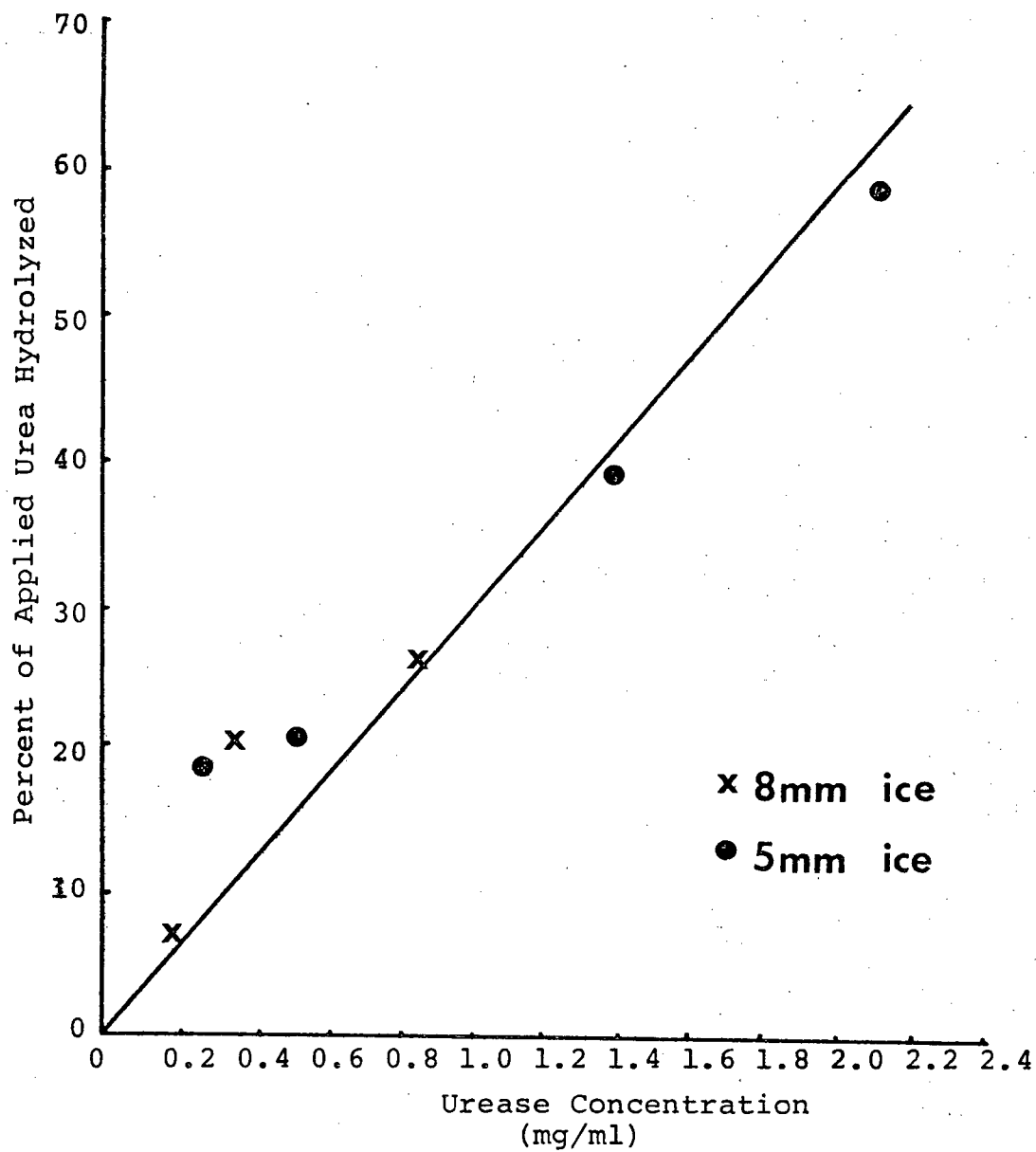
Figure 10

Percent Urea Hydrolyzed vs.

Urease Concentration

Ice Thickness

While the actual quantity of meltwater would be the same for different ice thicknesses, the amount retrieved was not, in these experiments. The 5 mm thick ice test yielded the least meltwater (12 ml from 5 mm ice versus 20 ml and 88 ml for the 3 mm and 8 mm tests respectively). Different quantities of meltwater were retrieved because of incomplete ice formation prior to the test, trapped air bubbles under the ice, and different meltwater lens configurations around the drophole. This incomplete meltwater retrieval affected the results.

The thinner ice models with a greater urease concentration, would have been expected to produce a greater percentage of hydrolyzed urea than the thicker ice. However, this did not occur as shown in Figure 11.

Urea application

While, as shown in Figure 12, an increase in urea application decreases the percentage of urea hydrolyzed, the actual quantity is roughly equal (128 mg. -0.45 $kg/70m^2$; 185 mg - 0.90 $kg/70m^2$; 165 mg - 1.80 $kg/70m^2$).

Urea type (Figure 13 and 14).

The three types of urea tested exhibited similar percent urea hydrolyzed under similar conditions.

Solar radiation (Figure 15)

Solar radiation influenced greatly the quantity of urea hydrolyzed after 90 minutes. In one case, 500 mg urease, and
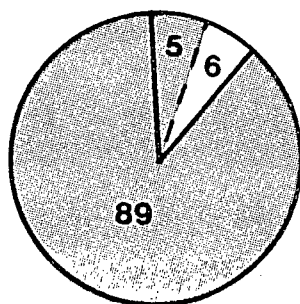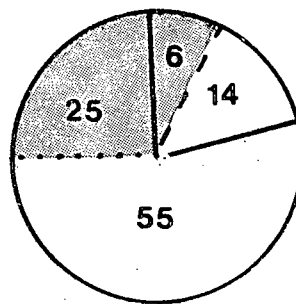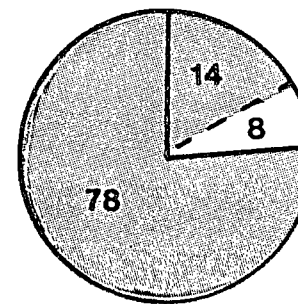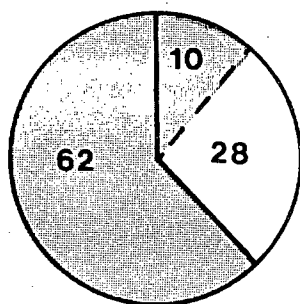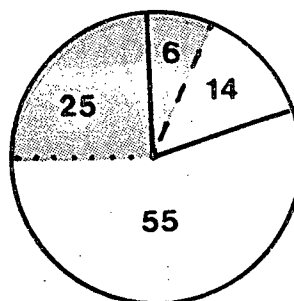
Figure 11

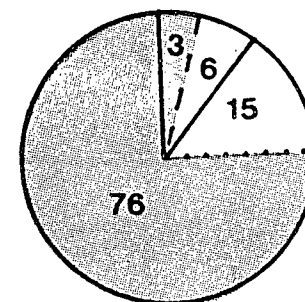**Effect of Ice Thickness**

at $0^{O}C$ and 200 mg Urease Addition
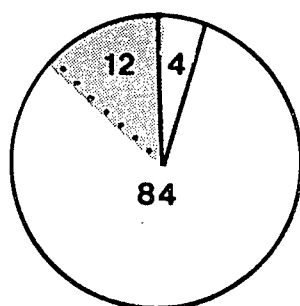
(B-1)
0.45 kg/70 m^2
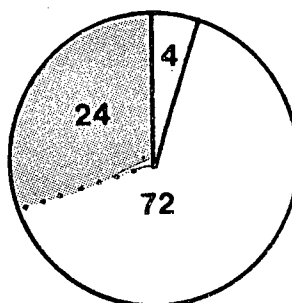
(A-1)
0.90 kg/70 m^2

(B-2)
1.8 kg/70 m^2

Figure 12

Effect of Urea Application Rate
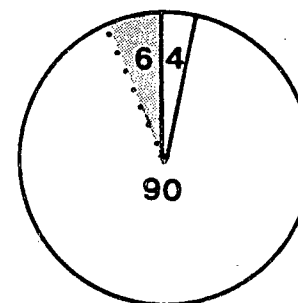
at 0°C, 200 mg Urease, and 5 mm Ice Thickness

(M-2)   (K-2)   (L-2)

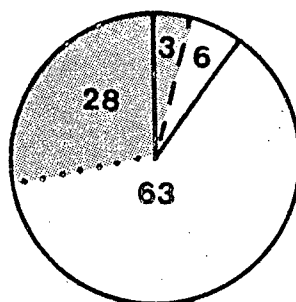C-IG   C-FG   SGM-IG

5 mm ice
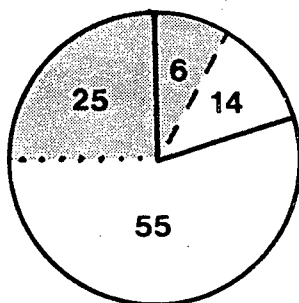$-4^{\circ}C$

(J-1)   (J-2)
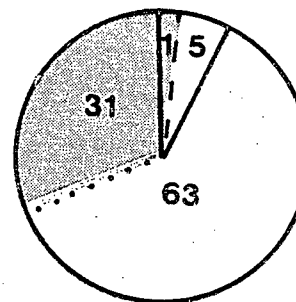
C-IG   C-FG

8 mm ice
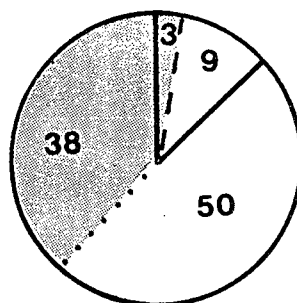$0^{\circ}C$

Figure 13

Effect of Urea Type

at 200 mg urease and 1.8 kg/70 m^2 urea

(A-1)

C-IG

(G-1)

C-FG
Urea Type
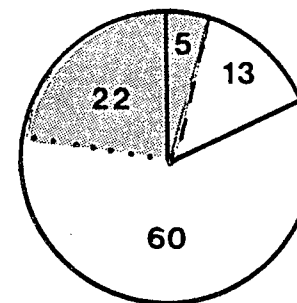
(G-2)

SGM-IG

$0^{\circ}C$

0.9 kg/
$70m^2$ ur.
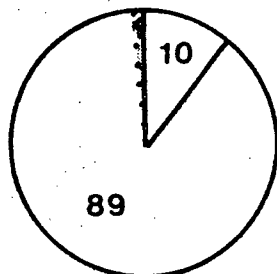
(M-1)
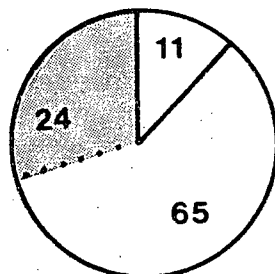
(K-1)

(L-1)

$-4^{\circ}C$

0.45 kg/
$70\ m^2$ ur.

Figure 14

Effect of Urea Type
at 200 mg Urease and 5mm Ice Thickness

(D-1) (N-1) (O-1) (P-1)

Solar Rad. #1   Solar Rad. #2   Solar Rad. #2
                                    + Buffer

200 mg
Urease
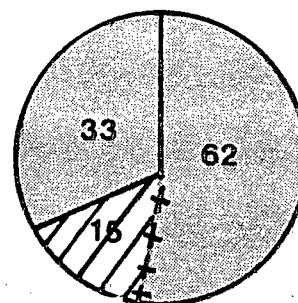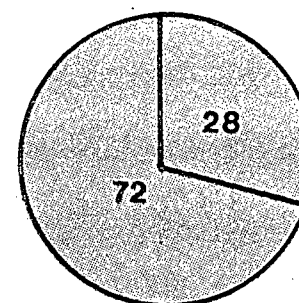
(D-2) (N-2) (O-2) (P-2)

500 mg
Urease

Figure 15

Effect of Solar Radiation

at -4°C, 5mm Ice, and 0.90 kg/70m^2 Urea

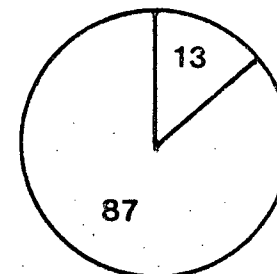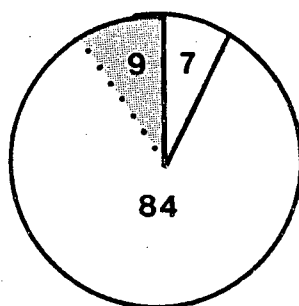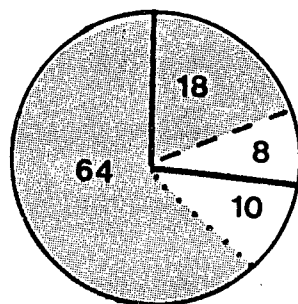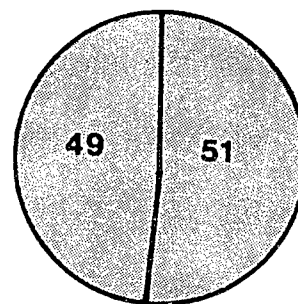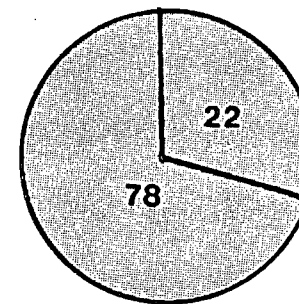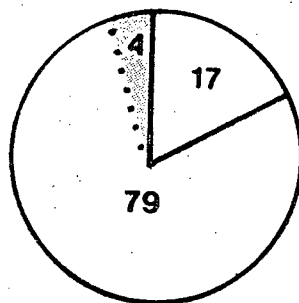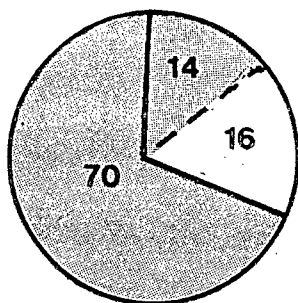solar radiation #2 caused 15% of the applied urea to be volatilized. With no solar radiation, very little meltwater formed, whereas, with only solar radiation #2 added, all the ice was converted to meltwater. As no thermometer was placed in the model, it is not known how much the temperature was raised by solar radiation.

2.2 Reduction of Urea Use

The environmental impact of urea may be reduced by decreasing the quantity of urea used on an airport runway. This can be done by optimizing the application rate and the urea type, for best de-icing.

In order to gain a better understanding of the de-icing action of urea pellets, experiments using an urea indicator, and photography equipment were done. Several indicators were tested including: Ehrlich's reagent, Tollen's reagent, phenolphthalein, and litmus paper. Ehrlich's reagent produced the best results.

Ehrlich's reagent was developed as a method for the determination of urea in blood and urine, based on the urea-p-di-methylaminobenzaldehyde reaction. An immediate, clear, stable yellow complex forms from the reaction. The absorbance of the coloured solution may be determined with a spectrophometer set at 425 nm wavelength. Levine (et al.)[41] noted that the calibration curve is linear up to 100 mg urea/ 100 ml. Ammonia was not found to interfere with the reaction.

A calibration curve was plotted from data using

urea standards and Ehrlich reagent at 0°C (Figure 16). The
calibration curve levels off abruptly above 50 mg. urea/10 ml.
As a quantitative method for urea, Ehrlich reagent is unsuitable
above this concentration (at 425 nm wavelength).

Three types of urea were photographed - Sherritt
Gordon Mines - Industrial Grade (SGM-IG), Cominco-Industrial
Grade (C-IG), and Cominco-Forestry Grade (C-FG). The two
Cominco grades of urea contain Formaldehyde as an anti-caking
additive, while the Sherritt Gordon Mines' pellets contain white
mineral oil. The three types of urea pellets vary in size as
shown in Table 11 and Figure 17. On a weight basis, the
Sherritt Gordon Mines pellets cover a larger surface area than
the two Cominco grades.

Close-up photographs were taken of single urea
pellets, and urea applied at 0.90 kg/70m^2 for each urea type.
Photographs at 0 (no pellet), 0 (pellet) 2,5,10,15,30,60, and
90 minutes after pellet placement on the ice surface were taken.
The ice was 5 mm thick and contained 3% Ehrlich reagent. Tests
were conducted at -4°C.

The reaction between Ehrlich's reagent and urea,
produces a yellow "aura" which indicates the movement of urea
through ice. The first attempt to photograph a single C-FG
pellet involved a small 12.5 cm x 12.5 cm plastic grid taped
onto the pyrex model. The 3% Ehrlich reagent was added, frozen,
and photographs of the urea pellet taken. The aura, after 90
minutes, is characterized by a 1 cm wide channel which fans out
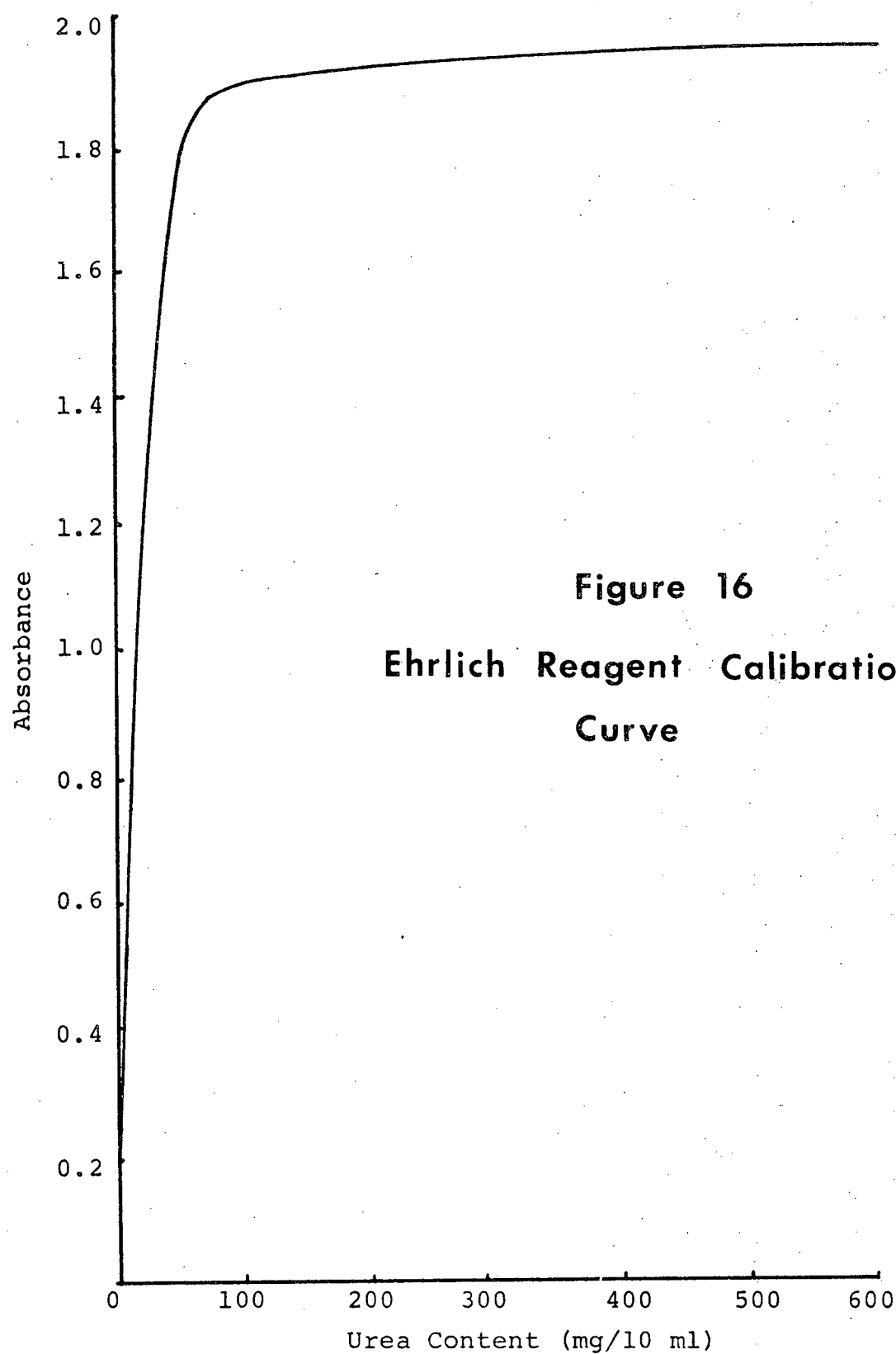
Figure 16

Ehrlich Reagent Calibration Curve

Table 11

Screen Analysis for Urea Types

- Sherritt Gordon Mines-Industrial Grade (white Mineral Oil conditioning agent)

Sieve	(mm)	Cumulative Wt. %
+8 (U.S. stnd.)	(2.38)	3.4
+10	(2.00)	14.5
+12	(1.68)	51.7
+14	(1.44)	79.0
+16	(1.19)	88.1
+20	(0.95)	95.1
Passing +20	(<0.95)	100.0

- Cominco-Industrial Grade (Formaldehyde conditioning agent)

Sieve		Cumulative Wt. %
+8(Tyler Mesh)	(2.06)	70.0
+10	(1.65)	99.5
+14	(1.18)	99.9
+20	(0.80)	99.9

- Cominco-Forestry Grade (Formaldehyde conditioning agent)

Sieve		Cumulative Wt. %
+4 (Tyler Mesh)	(4.12)	40
+6	(2.75)	99.5

cominco forestry grade
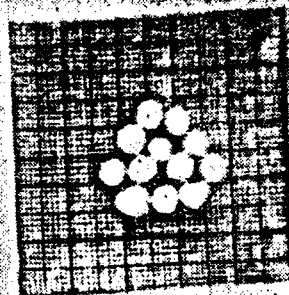
cominco industrial grade
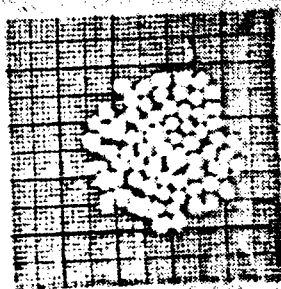
sherritt gordon mines-industrial grade
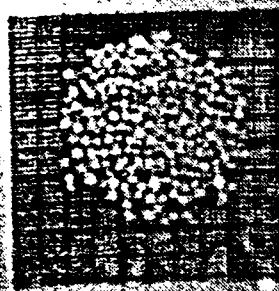
Figure 17
1 Gram of the Three Types of Urea

at the edge of the grid (Figure 18). At the conclusion of the experiment, the ice was removed from the model, and a dome shaped ice lens was found under the grid. The plastic grid prevented the urea pellet from penetrating this ice lens. The yellow aura indicated where the urea-rich liquid front had travelled down the side of the dome and fanned out at the edge of the grid. This behaviour resembles the action of a liquid, rather than molecular diffusion of urea through solid ice, as molecular diffusion would have been expected to produce a concentric aura about the pellet drophole. The aura seems to indicate the movement of urea at the ice-solid interface.

In subsequent experiments, ice could not form under the grid, which was glued to the model's glass surface. Photographs of the three types of, single, urea pellets showed that the urea-Ehrlich reagent aura grew with time (Figures 19, 20, and 21). The urea pellets do not remain stationary, even when they sit on smooth surfaces at the bottom of the drophole. Differential solution of the sides of the pellet, and, or, ice crystal orientation caused the pellet to wander up to 2 cm. Due to their "longer life", the larger C-FG pellets travelled the furthest (Figures 22 and 23). The C-FG pellet completely dissolved in 30 minutes, the C-IG in 10 minutes, and the SGM-IG in 5 minutes.

The rate of yellow aura growth is not equal for the three urea types (Figure 24). After 90 minutes, the C-FG aura covered 3.6 times as much area as the C-IG aura, and 6.0 times as much as the SGM-IG. The average rate of aura growth is greatest almost immediately after pellet application (Figure 25).
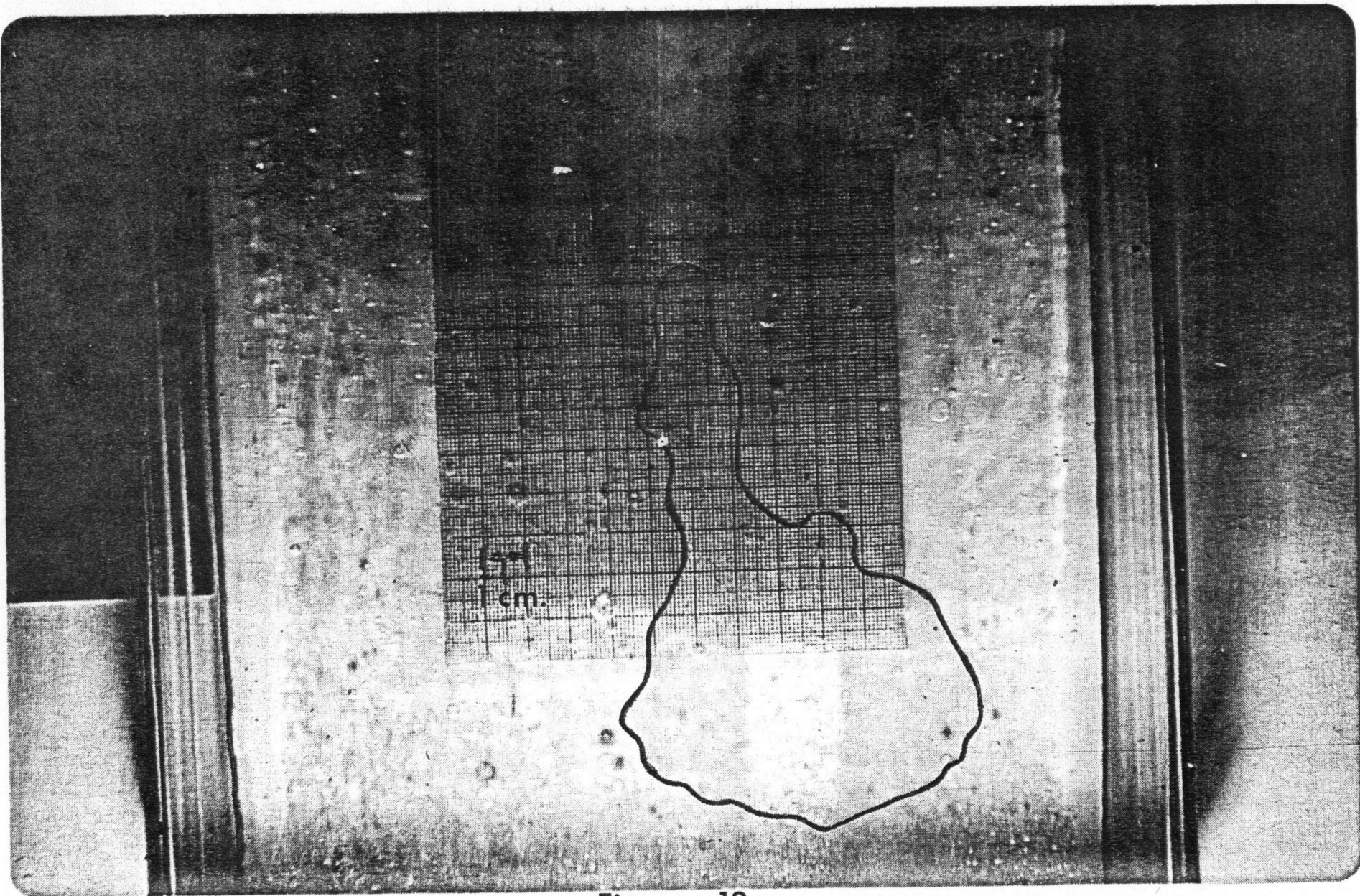
Figure 18

Aura (at 90 min.) for "Domed Grid Experiment"

2 min.

5 min.

10 min.

15 min.

30 min.

Composite
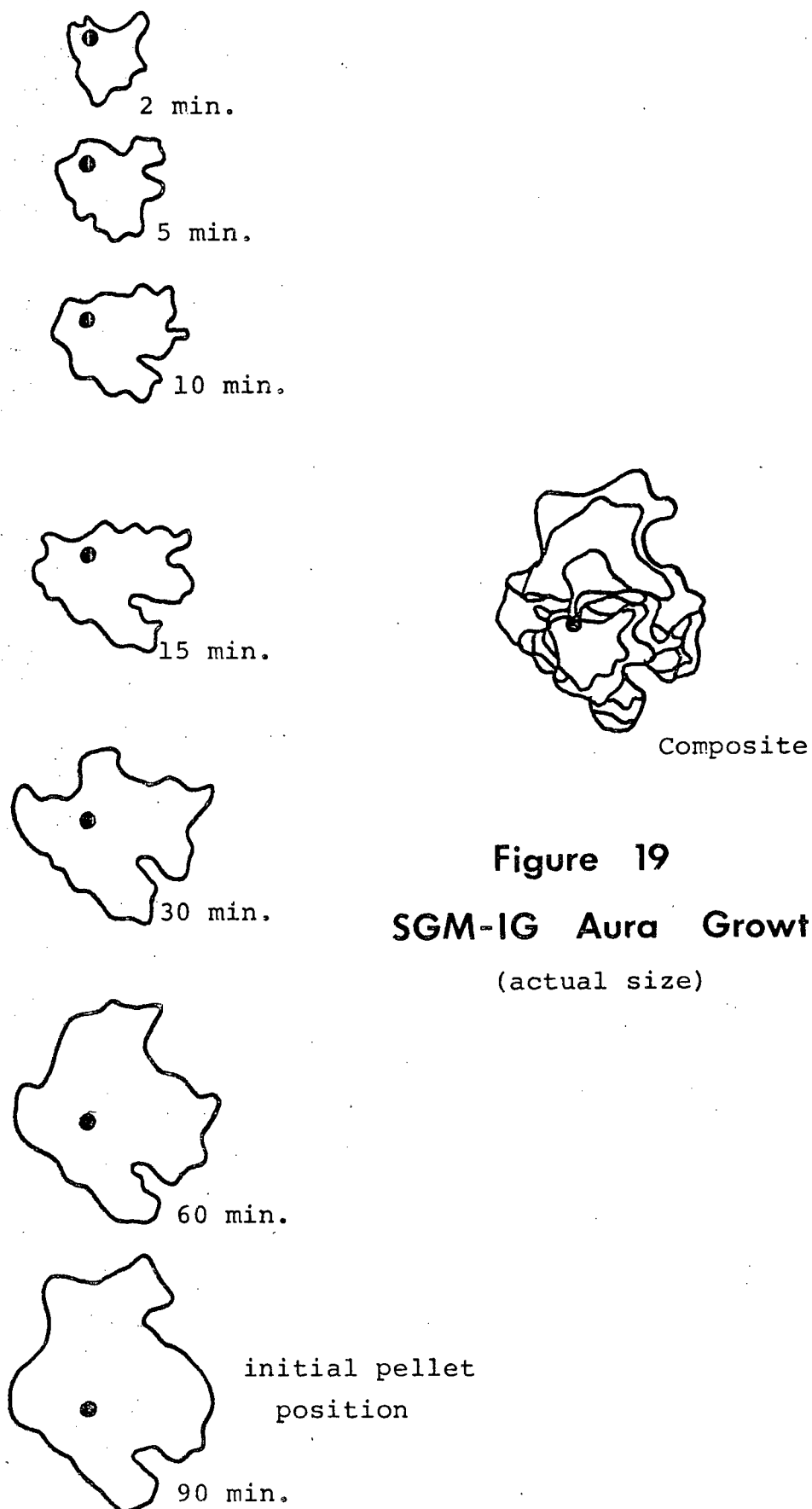
Figure 19

SGM-IG Aura Growth

(actual size)

60 min.

initial pellet
position

90 min.

2 min.

5 min.

10 min.

15 min.

30 min.

60 min.

90 min.

Composite
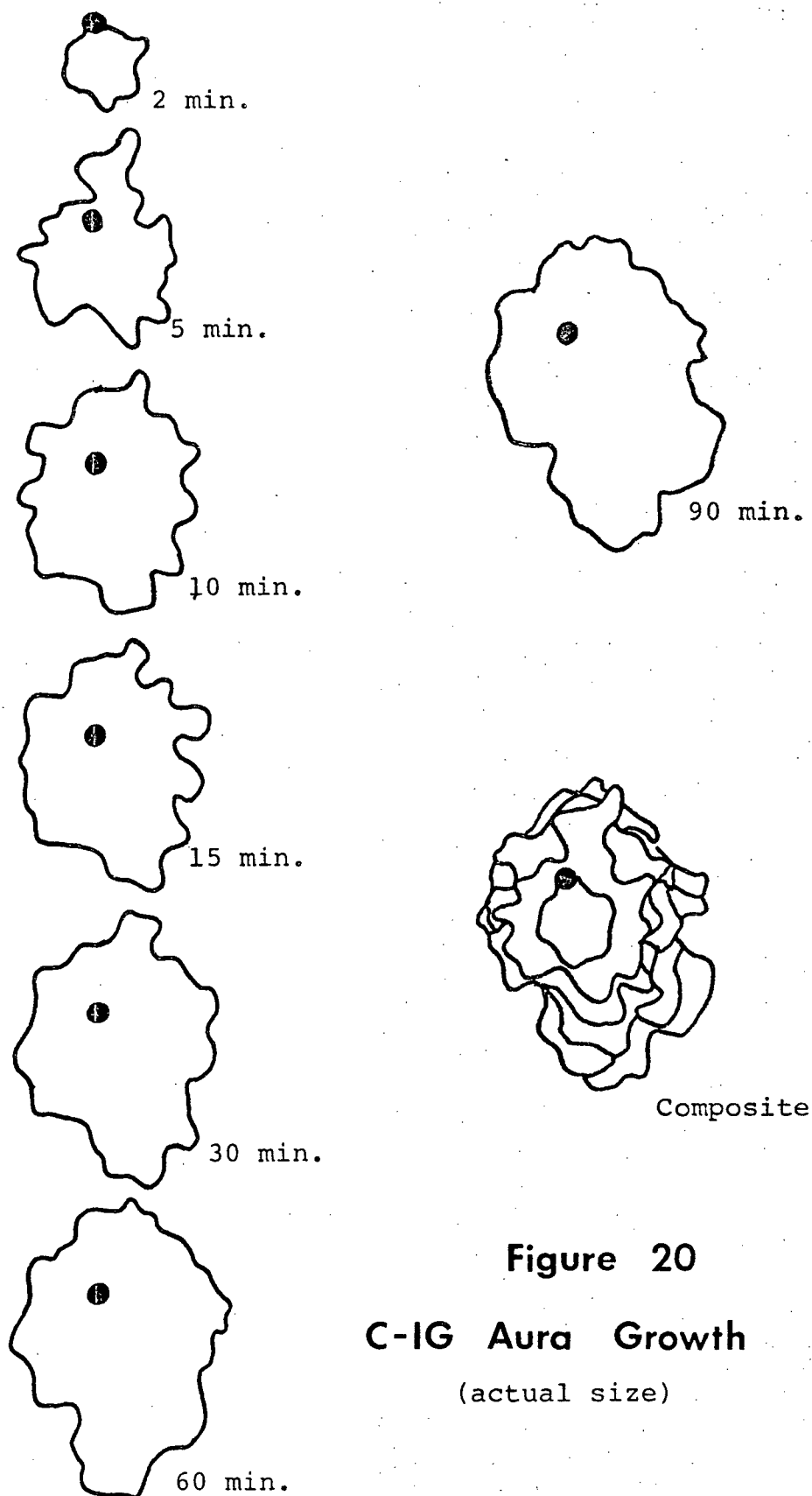
Figure 20

C-IG Aura Growth

(actual size)

2 min.

5 min.

10 min.

15 min.

30 min.

60 min.

90 min.

Composite

Figure 21

C-FG Aura Growth

(actual size)
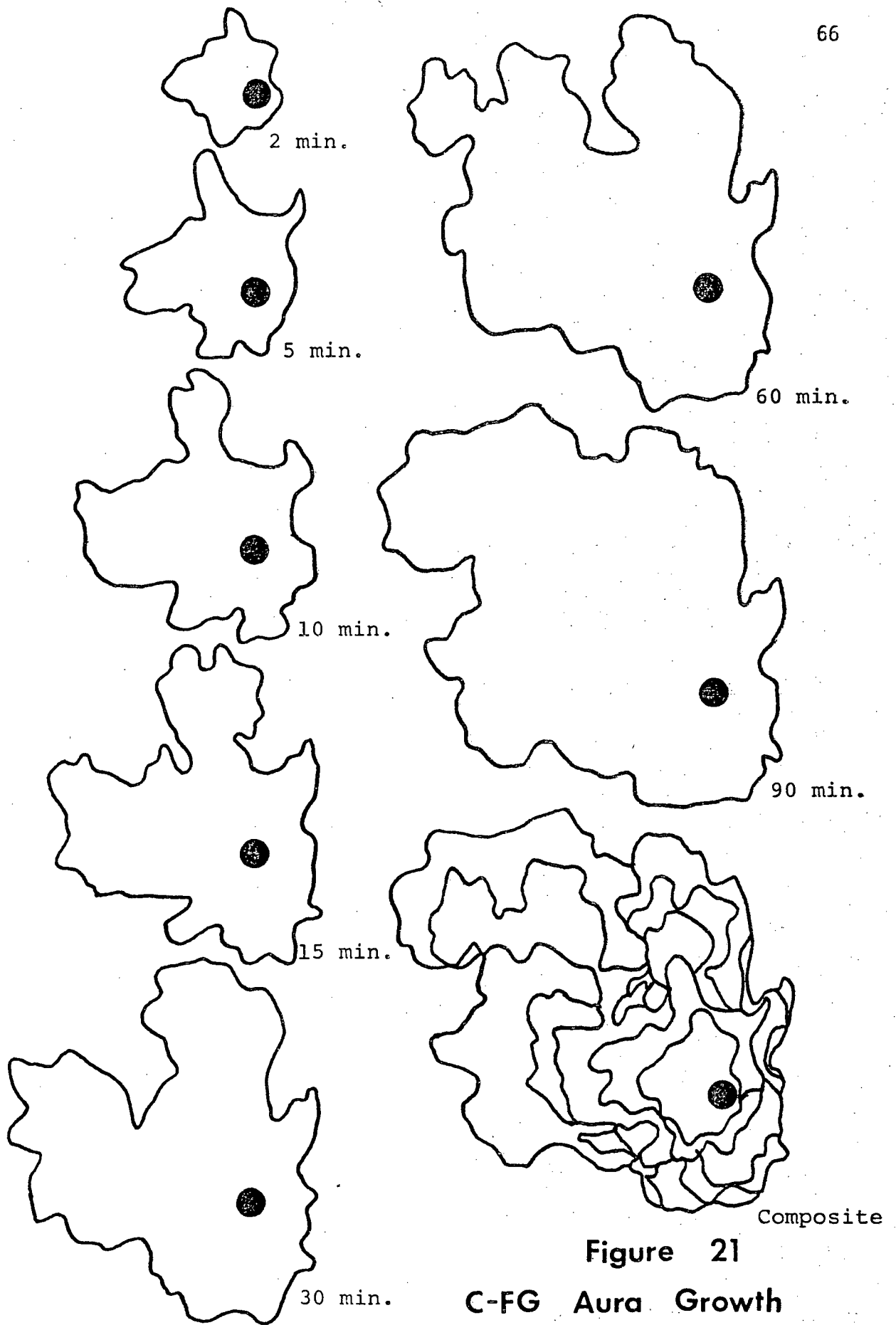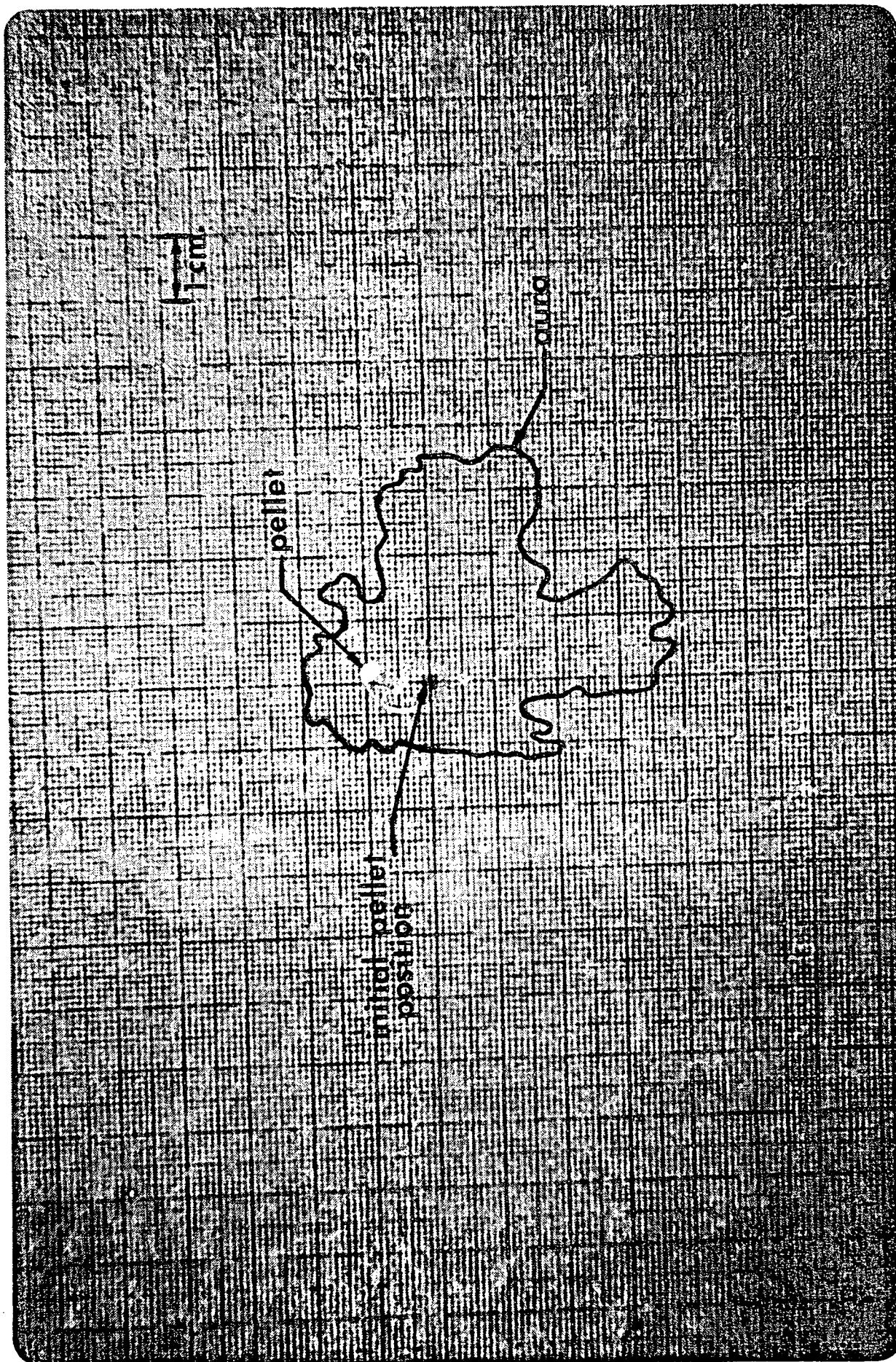
Figure 22

C-FG Pellet and Aura at 15 min.

final pellet
position

first pellet
position
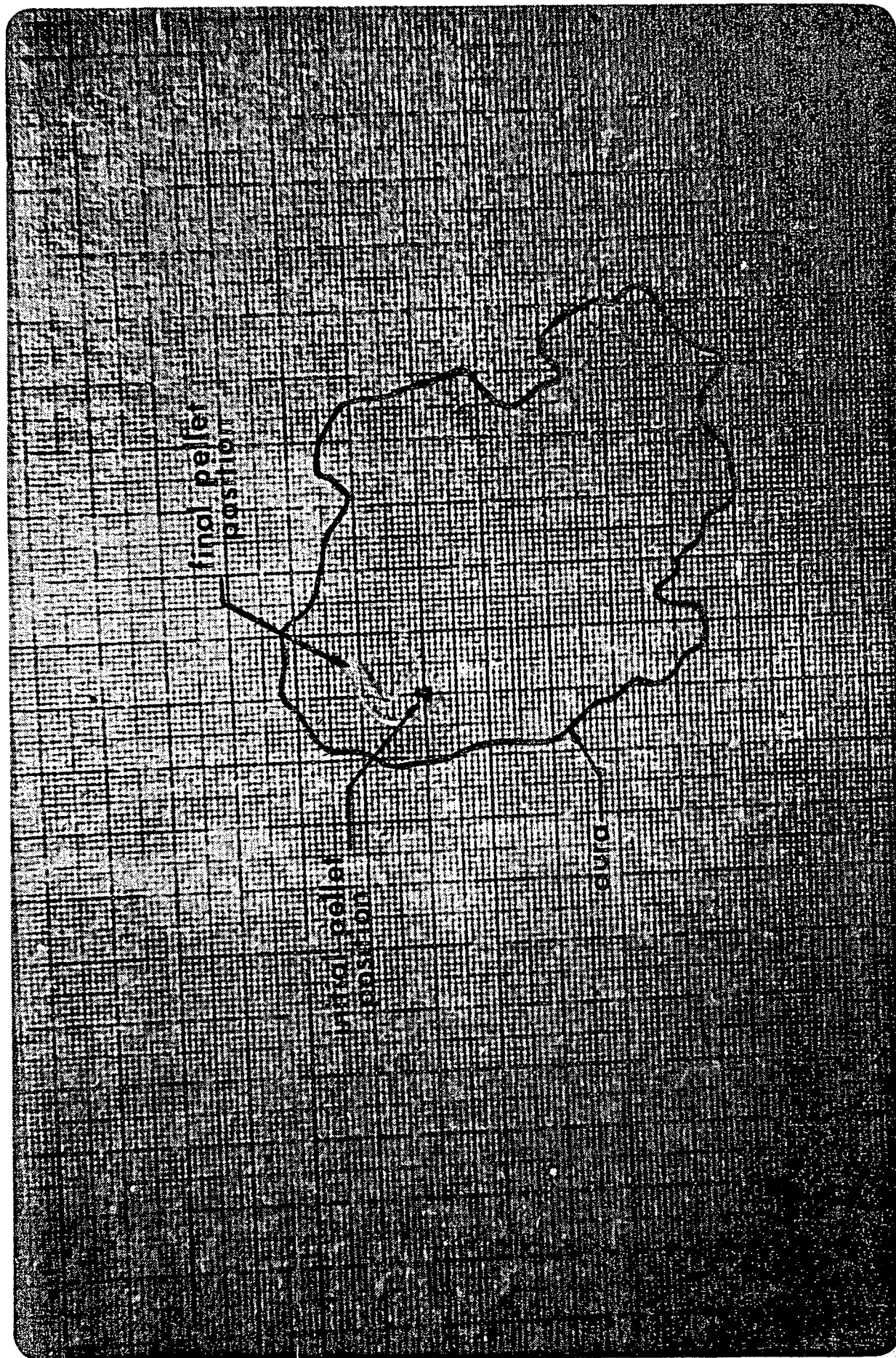
aura

Figure 23

C-FG Aura at 90 min.
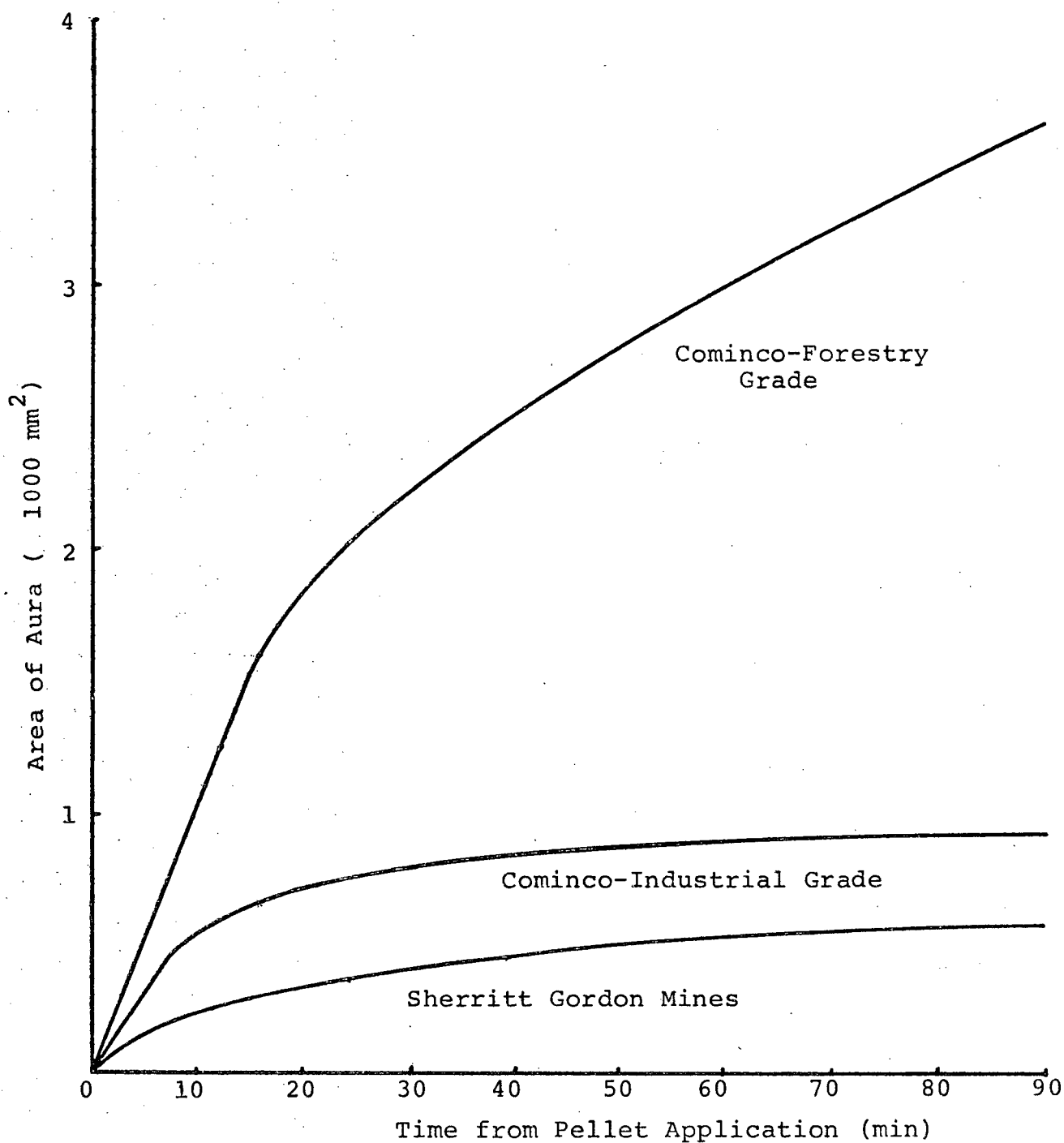
Figure 24

Aura Coverage Area vs. Time
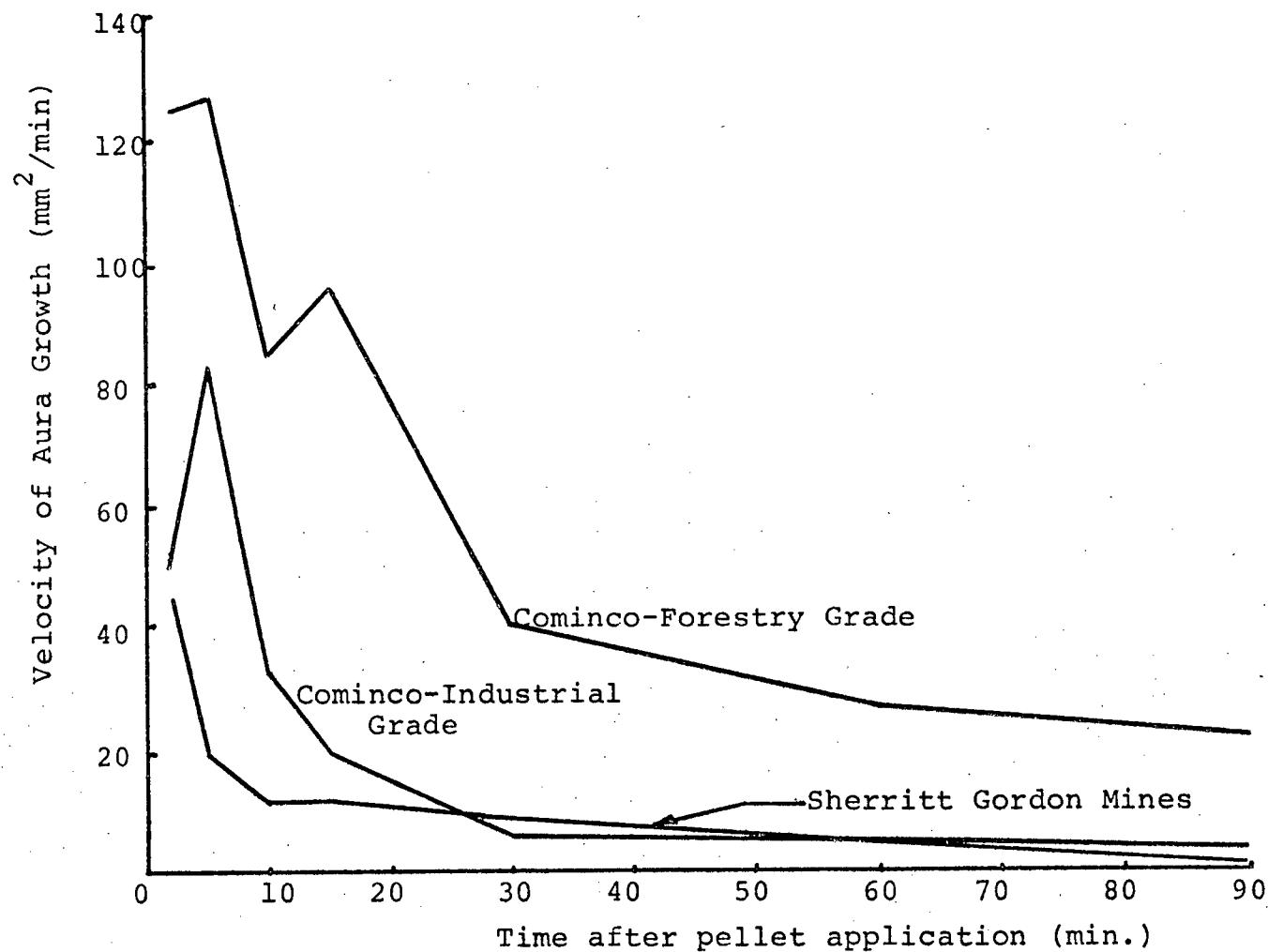
Figure 25

Average Rate of Aura Growth

After 90 minutes, both the C-IG and SGM-IG urea pellets had very low aura growth rates. The Cominco-Forestry Grade aura was growing at an average rate of 22 mm^2/min. after 90 minutes. At that time the SGM-IG and C-IG auras had approached their largest size, while the C-FG aura would be expected to grow significantly for some time.

The yellow aura growth follows two processes - the disintegration of the solid urea pellet to produce a urea rich liquid, and the movement of the liquid front away from the pellet produced drophole. As this front moves, the urea concentration of the liquid decreases and its ability to melt ice also decreases - explaining the decreasing rate of aura growth.

In spite of a larger aura growth rate, the C-FG pellet did not produce the largest aura on a weight basis. For the three types of urea, Figure 26 illustrates the aura area by urea weight versus time. After 90 minutes, the SGM-IG pellet aura covered 1.9 times the area, per mg. of urea, of the C-IG pellet; and 3.0 times of C-FG urea. For a given weight of urea, therefore, the SGM-IG produces a larger aura.

Tracings of photographs in Figure 27, 28, and 29, at the 0.90 kg/70m^2 urea application rate, show that, by weight, the SGM-IG urea produced the largest aura. After 90 minutes, the C-FG aura was about half the size of SGM-IG aura.

The auras associated with each of the 205 SGM-IG pellets overlapped such that, after 90 minutes, the total aura area was only 34% of the theoretical area. The overlap of auras
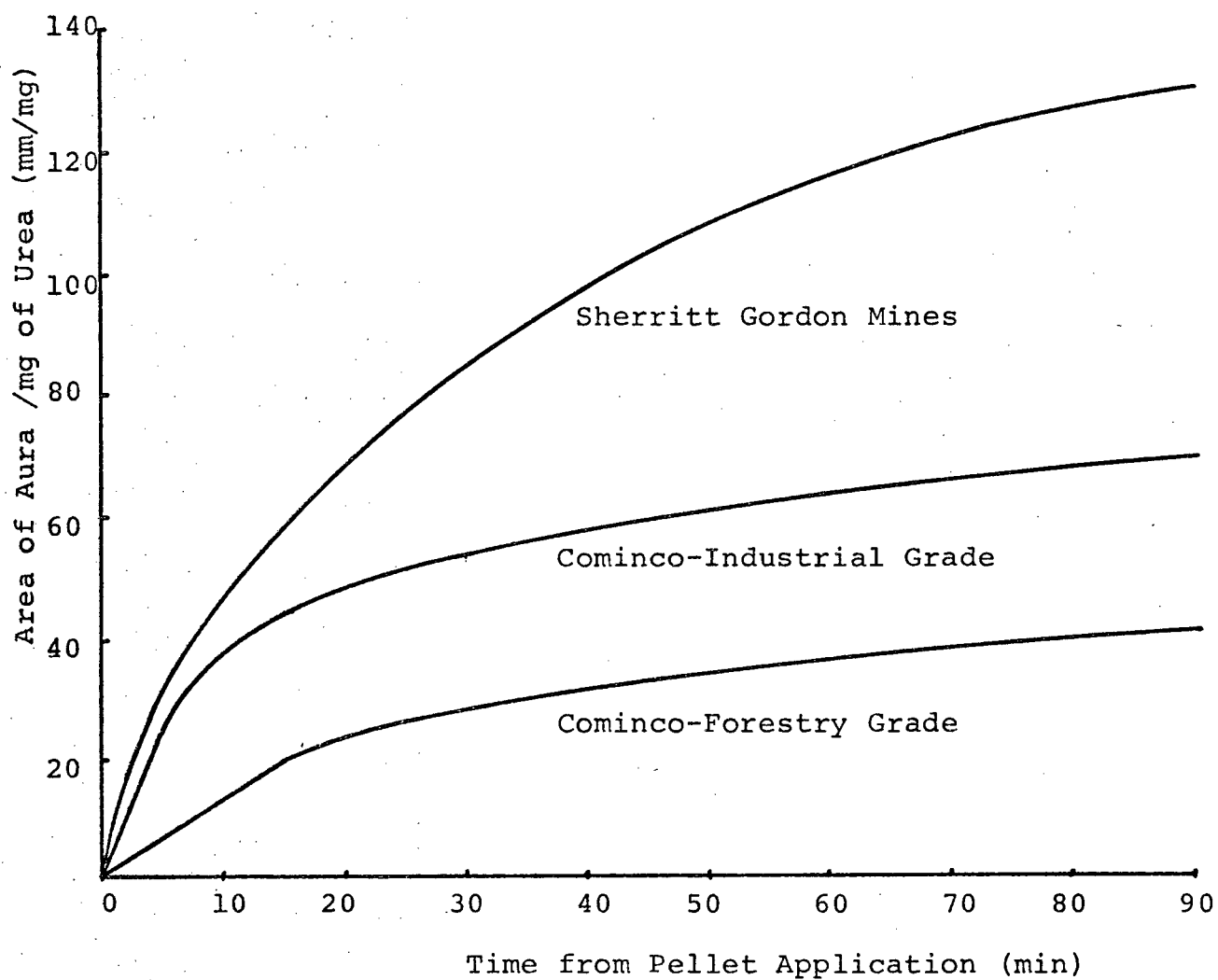
Figure 26

Aura Growth per Weight of Urea

initial pellet position

0 [scale] 5 cm
scale
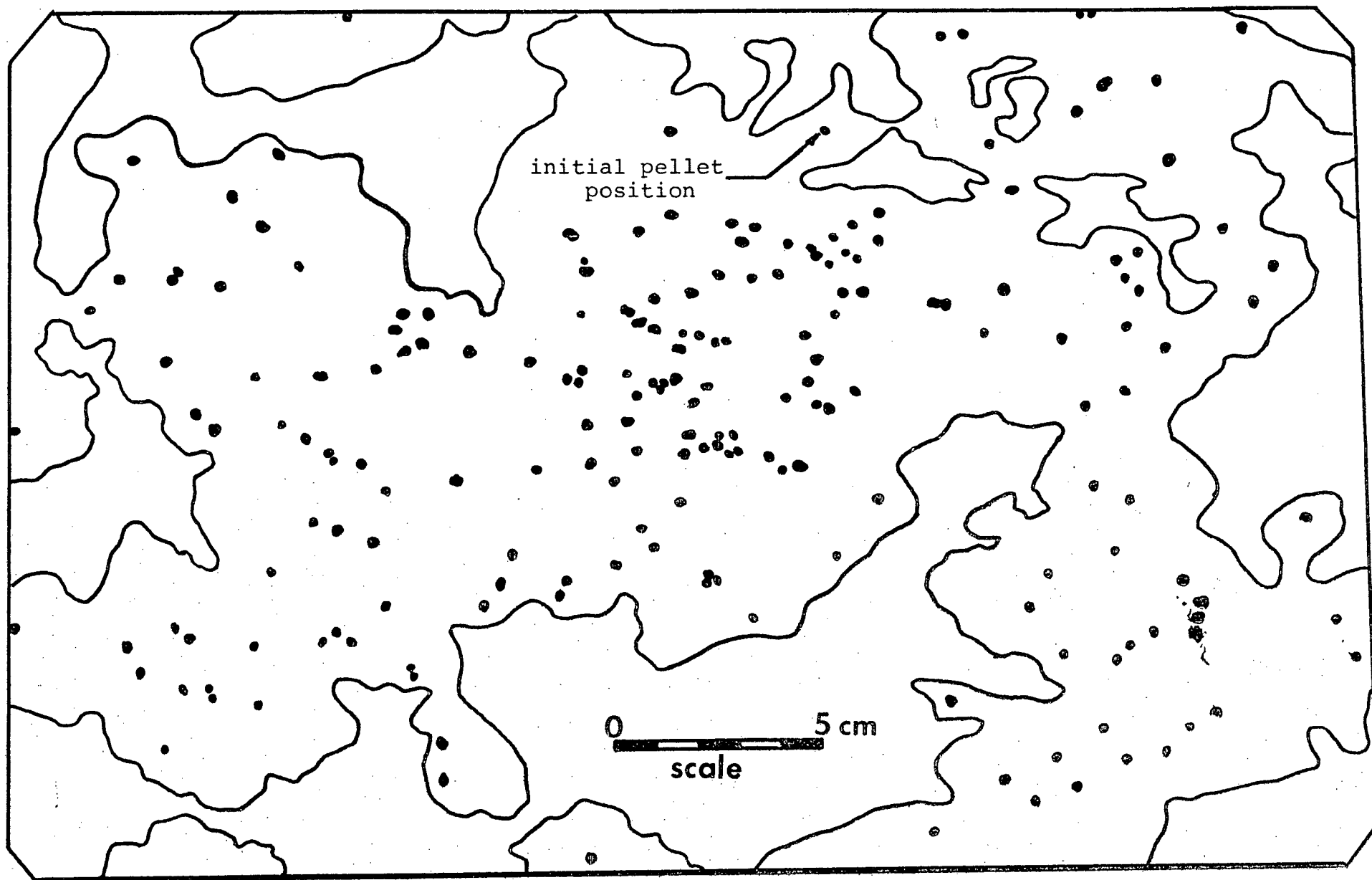
Figure 27
SGM-IG Aura for Urea at 0.9 kg/70 m^2
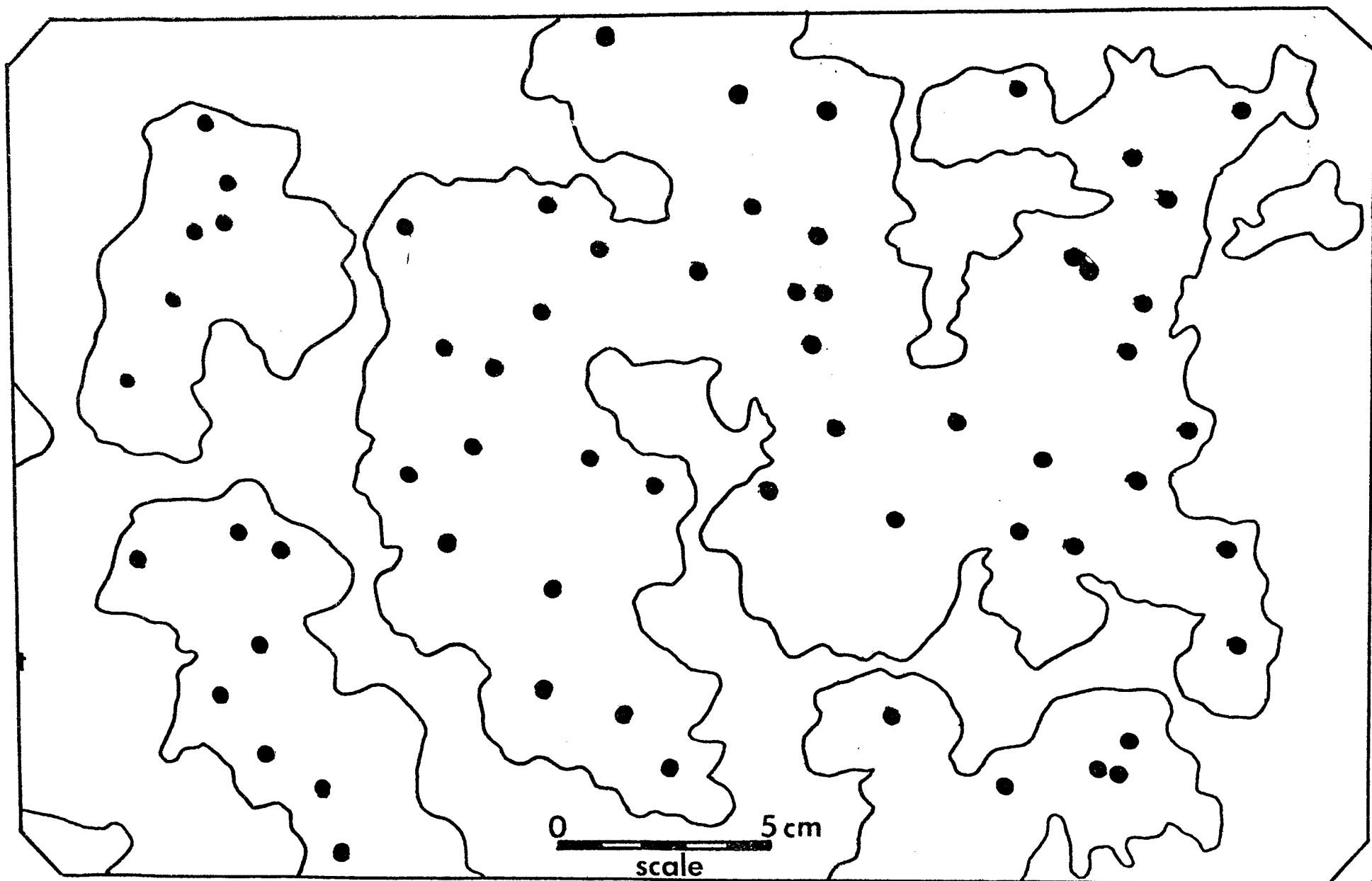
Figure 28
C-IG Aura for Urea at 0.9 kg/70 m^2
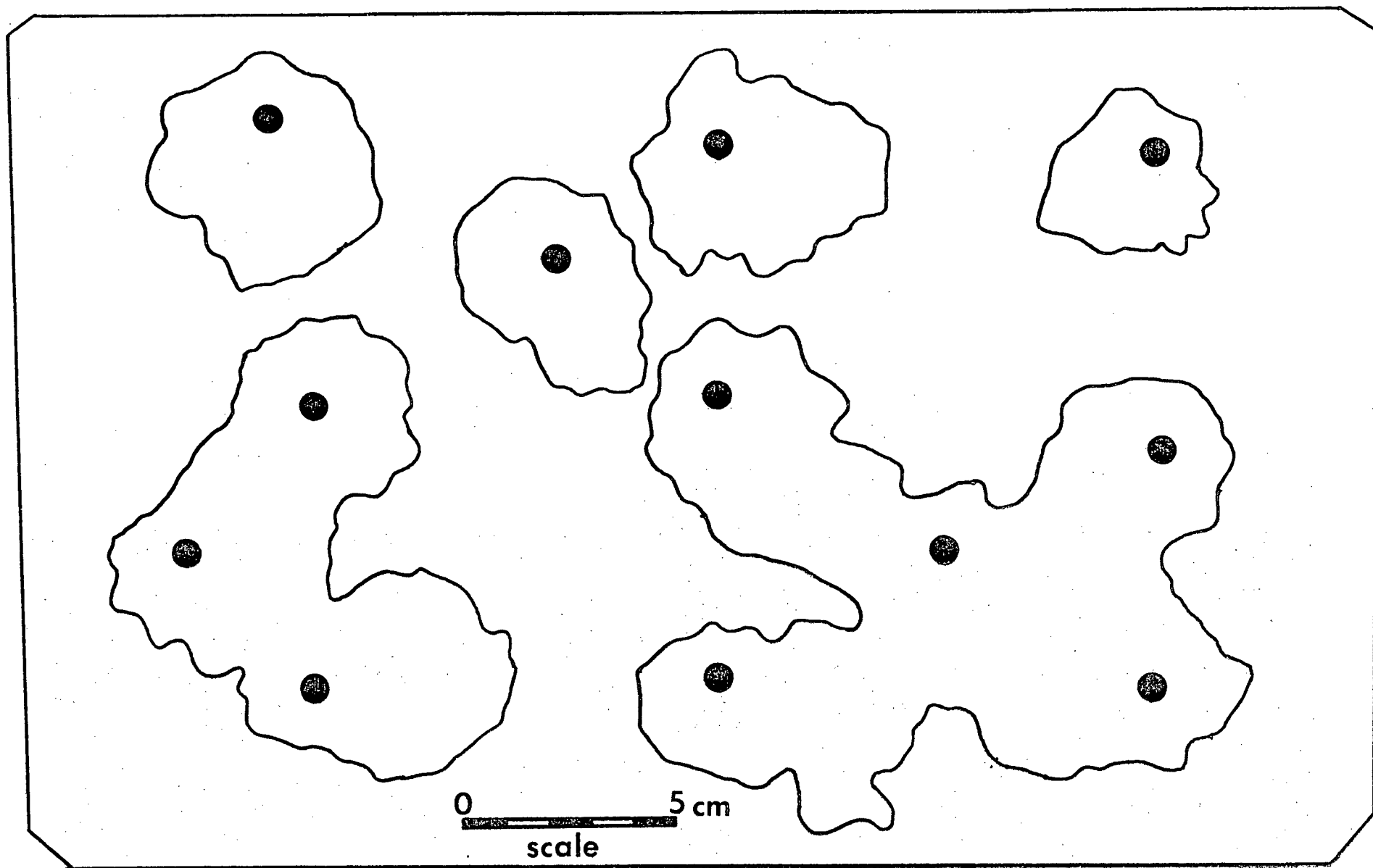
Figure 29
C-FG Aura for Urea at 0.9kg/70m^2

for the two Cominco grades was the same (Table 12).

Pellets were randomly placed on the ice surface. Had these pellets been evenly distributed, the aura size would have been greater in each.

Literature Review of Nitrogen
Removal Treatment Systems

2.3   Biological Nitrification - Denitrification

This treatment method utilizes Nitrosomonas and Nitrobacter bacteria for nitrification; Pseudomonas, Micrococcus, Achromobacter, and Bacillus for denitrification. Nitrosomonas oxidize ammonium to nitrite, as shown in equation 2-2. Nitrobacter oxidize nitrite to nitrate, as shown in equation 2-3. The net reaction is:

$$NH_4^+ + 2O_2 \longrightarrow NO_3^- + 2H^+ + H_2O \qquad (2-14)$$
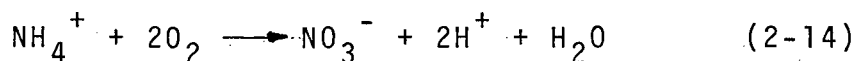
The energy released by these reactions is required by the organisms for growth. Major environmental factors which control the rate of nitrification include: temperature, pH, ammonia concentration, and dissolved oxygen concentration.

Denitrification is the conversion of nitrate nitrogen to gases such as nitrogen, nitrous oxide, or nitric oxide. This process occurs in the absence of oxygen. Dentrification is a two step process involving conversion of nitrate to nitrite, followed by conversion of nitrite to nitrogen gas.

When methanol is used as the electron donor, denitrification is represented by:

Table 12

Aura Area at 90 min. for 0.9 kg/70m^2 Urea

Urea Type	Number of Pellets Applied	Area of Aura (mm^2)	% Area of Aura of Total Model Area	Theoretical Area of Aura (based on single pellet)(mm^2)	Actual Area / Theoretical Area %
C-FG	12	22700	36	43200	53
C-IG	67	35500	56	66700	53
SGM-IG	205	41800	67	122200	34

Energy reaction:

$$6NO_3^- + 5CH_3OH \longrightarrow 5CO_2 + 3N_2 + 7H_2O + 6OH^- \qquad (2-15)$$

Synthesis reaction:

$$3NO_3^- + 14CH_3OH + CO_2 + 3H^+ \longrightarrow 3C_5H_7O_2N + 19H_2O \qquad (2-16)$$
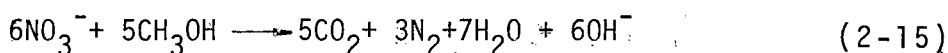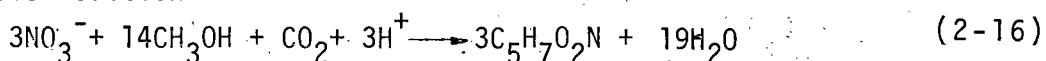
In general, an M/N ratio (mg. of methanol per mg of initial nitrate nitrogen) of 3.0 will enable 95% denitrification[42]. Brewery wastes, volatile acids, and molasses may also be used as electron donors.

Major environmental factors which control the rate of denitrification include: temperature, pH, carbon concentration, and nitrate concentration.

Figure 30 is the flow diagram of the nitrification-denitrification process.

2.4   Breakpoint Chlorination

Breakpoint chlorination is a process in which dilute aqueous solutions containing ammonia are oxidized to nitrogen gas by the addition of chlorine. When chlorine gas is dissolved in water, hydrolysis of the chlorine molecule occurs:

$$Cl_2 + H_2O \longrightarrow HOCl + H^+ + Cl^- \qquad (2-17)$$
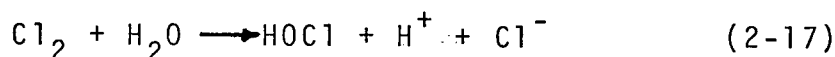
After sufficient chlorine has been added, Hypochlorous acid (HOCl) causes the oxidation of ammonium ion by:

$$NH_4^+ + 1.5HOCl \longrightarrow 0.5N_2 + 1.5H_2O + 2.5H^+ + 1.5Cl^- \quad (2-18)$$
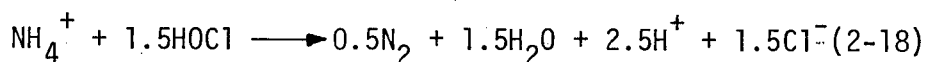
In practice, the actual weight ratio of chlorine to ammonia nitrogen at breakpoint ranges from 8:1 to 10:1[43].

The optimum range of pH for breakpoint chlorination is pH 6 to 7. Tests conducted outside this range show an appreciably higher chlorine requirement for breakpoint and slower reaction rates.

Influent

NITRIFICATION

(conventional Activated Sludge Plant)

Aeration
Tank

Nitrification
Clarifier

Return Sludge

Excess
Sludge

methanol

DENITRIFICATION

Denitrification
Clarifier

Aerated Nitrogen
Stripping
Channel

Anoxic Mixed
Denitrification
Reactor

Return Sludge
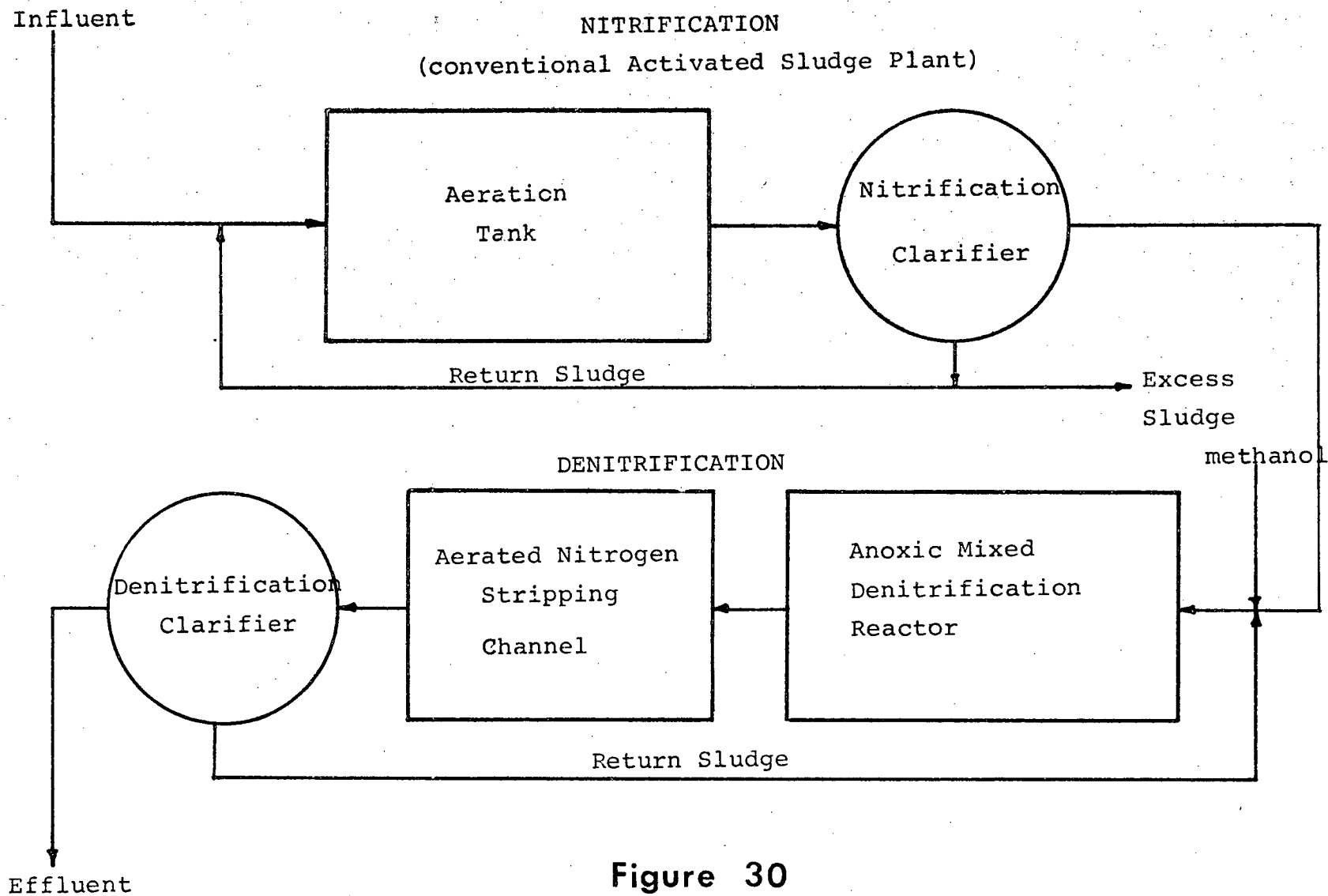
Effluent

Figure 30

Nitrification - Denitrification   Flow   Diagram

Nitrate and odorous nitrogen trichloride (NCl_3) are occasionally found in the effluent, depending upon the degree of pretreatment and pH in the reaction zone. The total concentration of these residuals rarely exceeds 10% of the influent ammonia concentration[44].

For breakpoint chlorination to work, the urea deicer must first have been hydrolyzed to ammonia. Hydrolysis can occur chemically or biologically. Chemical hydrolysis proceeds very slowly at temperatures around 25°C and would be insignificant at temperatures below freezing[45].

Atkinson[46] found that the bacteria Proteus vulgaris exhibited urease activity in water as low as 0°C. Soil bacteria such as Bacillus pasteurii, Klebsiella, Eschericha, and Citrobacter also exhibit urease activity, but not at very low temperatures. It may be possible to nurture a bacteria culture to supply the urease activity for hydrolysis. In a biological reactor, the urease bacteria sludge would be recycled, similar to a conventional activated sludge system.

There are three major problems with this system. Due to icing problems, the reactor may not operate at freezing temperatures. Moreover, at low temperatures above freezing, the hydrolysis efficiency would be low. In times of low deicer waste flow, to prevent bacteria starvation (particularly in summer months), urea would have to be added directly to the reactor.

2.5   Selective Ion Exchange

Selective ion exchange also requires prior hydrolysis of the urea waste stream.

Conventional ion exchange resins have not worked well in practice for removal of ammonium or nitrate ions from wastewaters because of resin preference for other ions. An exchanger which is selective for ammonium is more effective than conventional resins. Clinoptilolite zeolite, is the currently favoured exchanger.

Selective ion exchange is a simple process. While the wastewater passes downward through the clinoptilolite bed, the ammonia is removed. When the ammonia concentration in the effluent exceeds a specified critical level, the bed is re-generated by passing a concentrated salt solution through it. Ammonia may be removed from the regenerant by release of nitrogen gas or recovery of an ammonia solution, thus avoiding the problem of disposal of a concentrated brine solution (Figure 31).

The factors which significantly affect the ion ex-change process are: pH, hydraulic loading rate, clinoptilolite size, pretreatment, wastewater composition and bed depth. The optimum pH for ammonia exchange is between pH 4 and 8. Typical hydraulic loading rates for 20 x 50 mesh clinoptilolite are 7.5 to 20 Bed Volumes/hour (BV/hr.) or 0.95 - 2.6 gpm/ft ^{3}. Data indicates that 20 x 50 mesh clinoptilolite efficiency decreases above 20 - 30 BV/hr , whereas 50 x 80 mesh loses efficiency above 40 BV/hr. Excessive head losses can occur if the suspended solids concentration of the influent is greater than 35 mg/l.

Influent

Clinoptilolite

Bed

Regenerant

Recovery

Ammonia,
Nitrogen Gas,
or
Ammonia Sol-
ution

Effluent

Figure 31

Selective   Ion   Exchange   Flow   Diagram [47]
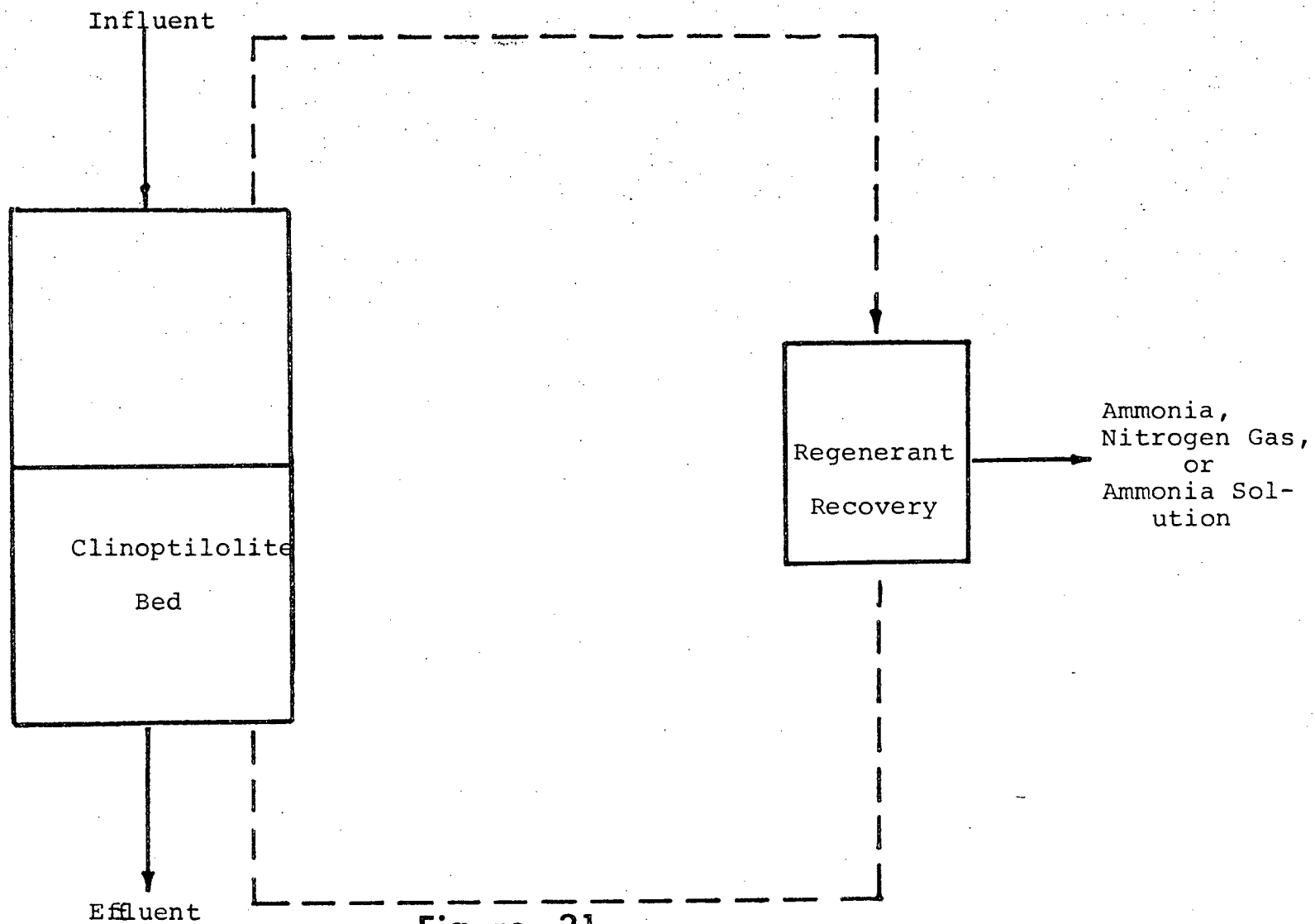
Suspended solids are removed by pretreatment. When a high
degree of pretreatment is used, the bed depth is usually about
4 feet[48].

2.6   Air Stripping

In air stripping, ammonium ion is converted by pH
adjustment, to ammonia, which is released to the atmosphere by
stripping (Equation 2-19).

$$NH_4^+ \longrightarrow NH_3 + H^+ \tag{2-19}$$
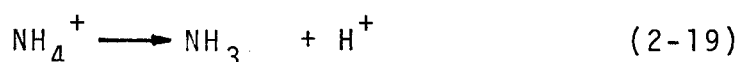
At pH 10.5 to 11.5 virtually all of the ammonium can be con-
verted to NH_3 gas. Lime is used to increase the pH.

Temperature is a critical factor in stripping tower
design. At 20°C a 90 - 95% ammonia removal is possible, whereas,
at 10°C the practical efficiency is only 75%. Data over a wide
range of air to water flows, indicates a 30% drop in efficiency
at 5°C compared to 22.2°C [49]. Due to ice formation, a stripping
tower must be shut down in freezing weather. Heating the
stripping air is usually impractical.

Ammonia can be released from stripping ponds operated
at high pH with surface agitation. At Lake Tahoe, the pond con-
tents are recycled 4-13 times by pumping through vertical spray
nozzles into the air above the ponds. A minimum of 37% of the
ammonia was found to be removed in cold weather. Breakpoint
chlorination could be added to increase ammonia removal efficiency.

Prior hydrolysis of urea is required for air stripping.
An hydrolysis pond may be more effective than a biological re-
actor system. The urea waste would be added to the dirt pond
and mixed such that soil would contact the urea. Very large

amounts of power would be required to keep the soil in suspension. Urease in the soil would induce hydrolysis. This pond would also act as an air stripping pond, releasing ammonia to the atmosphere.

Three environmental problems must be considered in an ammonia stripping process. These are: air pollution, washout of ammonia from the atmosphere, and noise. The odor threshold of ammonia is $35mg/m^3$, while eye, nose, and throat irritation occurs at $280-490$ mg/m^3. Plants can be affected at concentrations of 700 mg/m^3 and human or animal toxicity may occur at $1700-4500$ mg/m^3. Typical concentrations of air discharged from an ammonia stripping tower is around 6 mg/m^3 [50].

Data from Orange County California indicates that the concentration of ammonia in rainfall would approach the natural background levels within 16,000 ft of the tower[51]. Generally, only a stripping tower in proximity to a lake or reservoir could significantly affect the aquatic environment.

Noise can occur from three sources: motors, fans, and water. Noise levels can be reduced by adequate control measures.

2.7   Collection - Disposal

Urea applied to airport runways can follow many paths. It may, run off the runway and be caught in subsurface drains; percolate through the runway asphalt and seep into the soil; travel to surface water by overland flow; or, seep into the soil directly, as a liquid, or, indirectly from snow. Urea

found in subsurface drains, ditches adjacent to the runway, and snow, may be collected and disposed of.

It is possible to collect urea rich waste streams in ponds or tanks. Snow, impregnated with urea, could be placed in tanks or in an area such that the liquid snow melt would collect in them. Tanks or ponds would be pumped out and their contents disposed of or treated.

Estimation of the volume of liquid and its' urea concentration is difficult, as these parameters are related to precipitation, quantity of urea de-icer used, and urea lost to the soil, among others.

Three things can be done with a collected urea-rich liquid, it can be: used as a fertilizer (possibly in a greenhouse); discharged to a secondary treatment plant; or, combined with other foods for consumption by ruminants.

The possibility of feeding urea to animals has been a subject of much interest. The National Academy of Sciences has considered this as a urea waste stream disposal method[52].

Ammonia is the common denominator in the utilization of non-protein nitrogen (NPN), of which urea is a type, by ruminants. Most rumen bacteria prefer ammonia nitrogen over that supplied by peptides and amino acids.

Data have been gathered for NPN fed to various types of animals. For beef cattle, past evidence indicates that a unit of urea nitrogen most often has not been equivalent in

feeding value to a unit of supplemental protein nitrogen. In dairy cattle studies, where urea provided all the dietary nitrogen, rates of growth and milk production were only 65% of optimum. Two major factors are related to urea usage by ruminants:

1)   acceptance of urea-containing diets

2)   effective utilization of the consumed diets.

Urea can serve as a useful source of nitrogen in practical sheep diets. The beneficial use of NPN for chicks and laying hens has not been demonstrated. NPN cannot be given to swine to any appreciable extent. Horses have a greater capacity to utilize NPN than chickens or swine, but, the efficiency of nitrogen utilization from NPN is considerably less than that of nitrogen from intact protein.

"To answer the question 'How much NPN can be added to the diet of a ruminant?', it will be necessary to ask:

a)   What is the level of protein in the basal diet relative to the animal's requirement?

b)   What is the energy level (soluble or available carbohydrate) in the basal diet?

c)   What level of soluble nitrogen is in the basal diet?

d)   Is the level of other dietary components (especially required mineral elements) high enough to sustain maximum rumen microbial growth?

e)   What feeding system will be used?

f)   What is the expected level of intake?

g)   Does the growth or production requirement for amino acids exceed the capacity of rumen microbial synthesis so that some rumen bypass of natural protein is needed?"[53]

3.   Conclusions

         The effectiveness of urea for ice removal from
airport runways has been well documented, but, its environ-
mental impact has not. Of the potential environmental prob-
lems, eutrophication of lakes is of the most concern in
British Columbia.

Urea Nitrogen Soil Pathways

         Most of the applied urea de-icer contacts soil
at some time. Urea which percolates into soil would be
chemically altered.

1.   Soil urease would be active at airport winter tempera-
tures, but complete hydrolysis of the applied urea could take
several months at these low temperatures. Urea which perco-
lates into soil would not be expected to reach ground or surface
waters in an unaltered form.

2.   Ammonia volatilization and ammonium plant uptake rates
would not be expected to be significant at low temperatures.
However, urea applied in the winter on a runway may volatilize
as ammonia or be available for crops as ammonium ion (or nitrate)
in spring.

3.   Hydrolysis of urea causes a localized increase in soil
pH, which favours ammonium fixation on clays. However, the
ratio of ammonia to ammonium is governed by pH, with high pH
favouring ammonia. The hydrolysis of urea would result in a
large proportion of ammonia (a small amount of which would
volatilize), and a small proportion of ammonium ion which,

in soils with a large clay content, would be held, permanently or temporarily, by the clay particles (and organic matter). Ammonia moving away from the area of hydrolysis would encounter lower pH soil and, therefore some ammonia would be converted to ammonium ion, which could be retained in available exchangeable form or fixed in less available positions.

4. Nitrification would not occur at freezing temperatures, but since hydrolysis may take several months, the ammonia may be available for the nitrifier organisms in spring. Nitrification of this ammonia could occur.

5. Rates of denitrification would not be expected to be significant at low temperatures. Loss of nitrogen from soil by this pathway, would not be expected.

6. Urea in subsurface drains and drainage ditches may flow unaltered to surface waters, if there is little soil contact. On frozen soils, urea in the overland flow could reach surface waters unaltered.

An increase in urea concentration of surface waters could occur soon after urea application. An increase in nitrate of ground water could take several months, depending upon climatic and soil conditions.

Nitrate is the nitrogen form, from urea de-icer, of most concern as a pollutant of ground waters. It can also reach surface waters. As such, nitrate concentrations of environmentally sensitive waters around airports should be monitored. The urea concentration of surface waters should also be monitored.

Minimizing the Environmental Impact

A)   Soil and Plant Treatment

For soil and plants to act as a urea control process, the quantity of nitrate leached to surface waters must be low. This can be achieved, by increasing:

a) NH_3 volatilization
b) NH_4^+ clay fixation
c) NH_4^+ plant uptake
d) NO_3^- plant uptake
e)   denitrification

Or, by decreasing:

f)   nitrification

1.   Practically, little can be done to increase denitrification and volatilization, or decrease nitrification at an airport.*

2.   Ammonium clay fixation can be increased by the addition of clay to soils adjacent to the runways. As the hydrolysis of urea makes more ammonium available, less would be fixed, as the soil has a limited capacity for fixation. Also, not all the ammonium is held permanently, and some may be released at a later date. Excavation of natural soil and replacement with high clay content soils would be expensive. Excavation would be necessary to at least the 30 meter distance from the runway in which urea impregnated snow is thrown by the airport snow removal equipment.

_____
*Apparently, nitrification inhibitors are commercially available. Before use, the environmental impact of these must be considered.

The addition of clay to soils causes some serious problems. Soils with a high clay content have greater overland flow, and, therefore, urea would reach surface waters. Also, clayey soils restrict the growth of crops, hampering this pathway for removal of nitrogen from soil. The disadvantages for nitrogen control by the addition of clay to soils, exceed the advantages.

3.   Replacement of natural crops adjacent to the runway, with high nitrogen uptake crops, is the best means of utilizing soil and plants to prevent nitrogen release to waters. Grass is possibly the most suitable crop which is permitted by MOT guidelines adjacent to the runway. Its capacity to absorb nitrogen from soil is moderately high (to 120 lb N/acre[16]). There is no net removal of nitrogen from the system if the crop is cut and allowed to decompose on the soil surface. The crop must therefore be removed from the airport. The yield of grass, relative to other crops permitted by MOT, is low (about 3 BU/A), and harvested as hay, it is readily marketable.

Pensacola Bahiagrass seem to be of special merit since fields of this grass afford lower quantities of leached nitrogen than some other grass types. (0.5 lb N/A in drainage). However, this grass type will not survive in northern temperate climates.

Approximately 10-25% of the applied nitrogen can
be assumed to be leached from growing crop fields;
soil and plants could be 75-90% efficient in reducing
nitrogen loss to ground and surface waters. Management
of the plants adjacent to the runway is a very im-
portant component in the treatment process. To ensure
maximum crop uptake of nitrogen:

    a)   There must be an actively growing crop.

    b)   The urea impregnated snow and slush should be
          distributed over a large soil surface area.

    c)   The crops must be clipped and the cuttings
          removed from the airport property in the
          summer.

B)   Volatilization of Ammonia by Urease on Airport
       Runways

1.   The natural enzymatic activity of an airport
runway at room temperature caused less than 1% of the
applied urea to be hydrolyzed after 90 minutes, as
measured in the lab. Because there was residual
ammonia on the runway samples, the actual percentage
of urea hydrolyzed is lower than 0.5%. The natural
hydrolysis rate on a runway surface, therefore, must
be insignificant under winter airport conditions.

2.   Hydrolysis was found to be linearly proportional to temperature and urease concentration. Tests with different rates of urea application confirmed this.

3.   Using 3 types of urea, it was found that, changing the type of urea or pellet size, does not affect the quantity of urea hydrolyzed.

4.   Just increasing solar radiation increased the rate of hydrolysis. Solar radiation provides the activation energy and melts the ice to water - both are needed for hydrolysis.

5.   Attempted recovery of the meltwater by tipping the pyrex model is not satisfactory. Pipettes placed in the pellet drophole, and holes bored through the ice, could give better results.

6.   From a practical and economic viewpoint, the addition of urease to an airport runway in order to induce ammonia volatilization is impractical. Laboratory grade urease costs about $1 per gram. A 500 mg. urease per $720 cm^2$ application corresponds to a cost of $170,000. for the average airport runway.

Even with high solar radiation, less than 20% of the applied urea would be expected to volatilize to ammonia gas. Additional urease coatings would also be necessary throughout the winter, as the enzyme would be removed by rain, wind, vehicle wheels, and ice removal.

The odor caused by a high ammonia concentration in air may be unacceptable at an airport.

C)   Reduction of Urea Use

Reducing the quantity of urea used at an airport would not only reduce the environmental impact, but, also reduce the cost of ice control.

1.   If the urea-Erlich reagent aura size can be positively correlated with the ease of ice removal, then the Sherritt Gordon Mines-Industrial Grade pellets are more effective as a de-icer, by weight, than either of the two Cominco grades under the test conditions.

The greater aura size of the Sherritt Gordon Mines urea is felt to be due to its pellet size and not its anti-caking additive. Comparing the aura size, on a weight basis, for the two Cominco Grades, shows that larger pellets are less effective than smaller pellets for de-icing.

2.   A hollow on an airport runway would accumulate urea, whereas, a dome would transfer the solution to lower areas. The ice pavement bond would be broken in the low areas, but, may not be in the domed areas. A smooth runway surface would be more desirable than a rough surface from a ice control point of view.

3.   Neither the SGM-IG nor the C-IG pellets have significant de-icing capability after 20 minutes from application. From an airport operational standpoint,

if after 20 minutes an application of SGM-IG or
C-IG pellets has not achieved sufficient de-icing,
a second application of urea would be required. The
C-FG pellets have significant de-icing capability
after 90 minutes. In spite of this, the C-FG pellets
are not more suitable for de-icing, since the area of
melt after 90 minutes (as shown by the aura), is small
compared to that of the other two types of urea. The
SGM-IG pellets are the most suitable.

D)   Biological Nitrification-Denitrification

Biological nitrification can treat limited
quantities of urea directly, without the hydrolysis
pretreatment. In order to treat the resulting NO_3^-,
de-nitrification must follow. The overall process
is impractical because of cost and the necessity for
urea feed in summer, and, at times, in the winter.
At low liquid temperatures, the tankage requirements
for biological processes are large. The liquid could
be heated, but, this would be an additional cost.

E)   Breakpoint Chlorination

Breakpoint chlorination is applicable to
the NH_3-NH_4^+ forms only. Hydrolysis of urea by
chemical means is insignificant below 25°C, and there-
fore, is not suitable for winter airport conditions.
Biological hydrolysis in a reactor is an unproven
process-development and implementation would be ex-

pensive. Sporadic feed is also a major problem with an hydrolysis biological reactor.

F)   Selective Ion Exchange

Selective ion exchange systems can be operated sporadically and temperature does not have a major effect on process efficiency. Disposal or treatment of the contaminated brine solutions may be costly. The efficiency of selective ion exchange removal of urea nitrogen is low, and therefore, the urea must be converted to ammonia prior to treatment. A hydrolysis reactor would also be used in this system.

G)   Air Stripping

Air stripping would probably be cost prohibitive if not for the possibility of using ponds. These would perform both urea hydrolysis and ammonia volatilization. The efficiency of nitrogen removal would be low at near freezing temperatures. Any nitrogen forms lost through seepage may be prevented from leaching to ground water by soil reactions. The odor caused by ammonia in the air could be a serious problem.

H)   Collection-Disposal

Collection of urea-rich liquid and disposal as fertilizer, or as food for ruminants, is applicable to only small waste volumes because of the cost of collection tanks and transportation of liquid. Since

large volumes of dilute solutions would have to be disposed of, these disposal methods are not satisfactory.

Treatment of urea solutions by secondary treatment plants may be possible under special circumstances. Most airports do have sewer connections, but, not all cities have secondary sewage treatment plants. Large volumes of dilute solutions can also adversely affect secondary treatment plant's performance.

I)   Rating

Before any other method for minimizing the environmental impact of urea, the possibility of reducing the quantity of urea used, should be considered. The other methods may be rated, from a cost, efficient, and practical point of view, from most effective to least, as follows:

1.   Soil and Plant Treatment
2.   Air Stripping
3.   Collection-Disposal
4.   Selective Ion Exchange
5.   Breakpoint Chlorination
6.   Biological Nitrification-Denitrification
7.   Volatilization of Ammonia by Urease on an Airport Runway.

4.   Further Research

On the basis of this study, further research is indicated. Since control of urea de-icer through volatilization of ammonia on an airport runway is both inefficient and costly, further study in this area is not recommended.

Urea waste stream treatment methods such as, nitrification-denitrification, breakpoint chlorination, selective ion exchange, air stripping, collection and disposal, are probably too expensive and subject to too many operational problems to be effective. Of these treatment methods, probably only air stripping and collection-disposal warrant further research. Before a detailed cost and efficiency study can be done, data concerning liquid volumes and urea concentrations of the waste stream must first be gained.

Soil seems to be the least costly and one of the most efficient treatment mediums for a urea waste stream. Future study is required to delineate the quantity of urea that can go into the various soil reaction pathways. Test plots, using N^{15} isotope could be an excellent way of following urea de-icer. The quantity of urea and nitrate which reaches surface waters are the most important parameters to identify.

The possibility of selecting a crop to control urea de-icer, that is, to maximize nitrogen uptake, seems quite feasible. Test plots using different crops could be planted adjacent to airport runways. Since soil types, precipitation levels, length of growing season, and temperature determine plant types, one crop may not be suitable for urea control at all Canadian airports. It may be necessary to amend soils with lime, potassium, phosphorus, and perhaps other plant nutrients to improve and encourage growth of crops for fall utilization of nitrogen from urea used for de-icing purposes.

Reduction of Urea Use

Laboratory Research

Ideally, charts could be developed such that airport managers could select the urea application rate knowing: the pavement temperature, ambient air temperature, rate of solar insolation, and ice thickness. Study of the following topics would aid in the preparation of these charts.

An urea indicator would be used to investigate each topic. Ehrlich reagent was found to be satisfactory, however, a different indicator may produce a more visible aura.

1. Determination of the urea concentration gradient around the pellet drophole would provide information about the urea-rich liquid. Samples of solution could be obtained from the urea pellet drophole. Samples away from the hole would be obtained by boring through a thin ice layer. The indicator solution may be used to determine the urea concentrations in some cases.

2. The size of the urea solution lens under the ice may be determined with the aid of a cast. Attempts to make casts of the under-surface of the ice using wax and plaster of paris failed because the heat given off by the hardening wax and plaster, melted the ice. A cool clay or Plasticine may work.

Of particular interest, would be slow release pellets. These coated pellets would be expected to produce larger auras since they would probably deliver more urea   (indicated by the aura)

to the bottom of the drophole than conventional pellets.
In this case, the area of broken ice-pavement bond would be
larger. Casts could be made of ice subjected to this urea.

3.   The greater aura growth per pound of urea for the
Sherritt Gordon Mines-Industrial Grade pellet is believed
to be due to its particle size and not to the white mineral
oil conditioning agent used. A test of this hypothesis using
an indicator reagent and two pellets of the same diameter -
one with mineral oil, and one without, could be done.

4.   This optimization of urea study used only one set of
environmental conditions - -4°C, 0.90 kg/70 m^2 urea, 5mm ice
and no solar radiation. Work should be done under different
conditions, such as, the ones used in the volatilization of
urea on an airport runway research.

5.   Runway surfaces could be used - painted white and a
grid added for photographic purposes. The effect of airport
runway irregularities on aura growth and urea effectiveness
should be investigated.

6.   The correlation, if any, between aura size and ease
of ice removal is very important to determine. If a positive
correlation exists valid conclusions based on the Ehrlich
aura may be drawn.

        A spring mounted scraping bar may be used (Figure 32).
The unit should be bolted to a piece of runway asphalt rather
than a glass or metal surface, so that the ice-asphalt bond
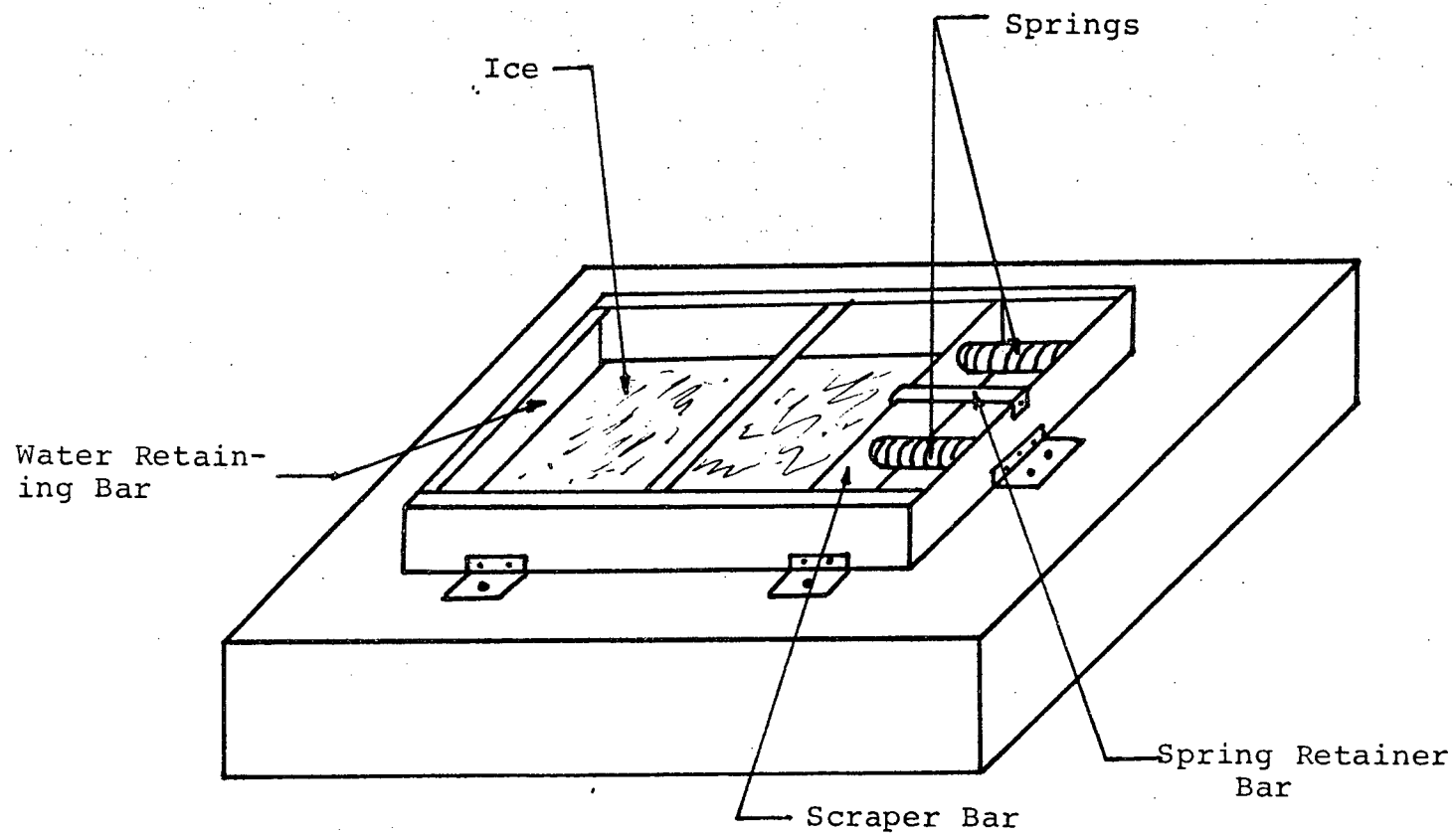would be duplicated exactly.

Springs

Ice

Water Retain-
ing Bar

Spring Retainer
Bar

Scraper Bar

Figure 32

Ice Scraper Mechanism

To begin the test, the scraping bar springs would be
compressed and the bar held in place. The water retaining
bar would also be installed and the test area should be
checked to see that it is watertight. The water-indicator
solution would be poured onto the frozen surface. After ice
formation, the water retaining bar would be removed, the urea
applied, and the scraping bar released. Photographs of the
aura would be taken until the scraping bar removed the ice.
Removal of the ice would indicate that the ice-asphalt bond
strength was less than the scraping bar force. The relation-
ship between aura size and ease of ice removal would then be
determined.

7.   Previous research conducted by MOT indicates that dye
coated urea pellets are more effective de-icers than white
pellets. The energy absorbing ability of black surfaces
is believed to be responsible for this. To test the theory
a solar lamp and dye coated pellets could be used. However,
care should be taken since the dye may interfere with the
urea indicator.

The mechanical scraping mechanism could be used to
test the dye coated pellets' effectiveness.

Airport Runway Research

1.   Anti-icing is difficult to model in the laboratory,
whereas, de-icing is relatively simple. The important de-
icing conditions to consider are: urea application rate,
ice thickness, and temperature. In addition to these con-

ditions, a model of anti-icing requires that other factors be considered: the condition of the asphaltic surface prior to pellet addition (a thin layer of water will dissolve the pellet); the rate, type, and temperature of precipitation; the movement of the pellets between the time it is applied and dissolves (movement may be caused by wind); and the elapsed time between urea application and action.

Since anti-icing is the method of urea application recommended by MOT, the possibility of optimizing the urea type and rate of application should be investigated. The residual effect of urea is the most important parameter to quantify. A test plot on a section of pavement may be the best way to model anti-icing. The three types of urea could be applied in strips and the relative ability to prevent ice formation be tested.

2. It may be possible to optimize the urea distribution. Pellets may be placed more evenly with fertilizer spreaders than sand spreaders. Tests could be conducted at airports using each spreading method.

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