Sulfur-coated urea (SCU) is a slow release nitrogen fertilizer manufactured by the Tennessee Valley Authority. Urea granules are sprayed with molten sulfur, then holes in the sulfur coating are sealed with a layer of wax sealant. The sulfur coatings are mixtures of amorphous and crystalline allotropes of sulfur. Coating thickness varies over the surface of each granule. The distribution of coating thickness among granules in a given lot of SCU depends on the conditions under which it is manufactured.

A model was constructed to predict the rate at which urea is released from SCU as a function of time. It was assumed that microorganisms break down coating materials until the urea is exposed to water. The urea dissolves and diffuses out of the granule into the soil. Soil temperature, soil water content, and coating characteristics affect the rate of release.

Diffusion of urea out of open SCU granules was examined theoretically and experimentally. Theoretical equations were
developed which predict that diffusion of urea through small holes in
the coating occurs in two stages. The initial release rate was shown
to be constant. After all the urea has dissolved, the rate of release
decays exponentially.

To test the theory, granules of SCU-31 were immersed in water
and the rate of release of urea from these granules was measured for
70 days. It was found that the cumulative amount of urea released
was an exponential function of time. Urea was released 1.25 times
faster at 35 C than at 5 C, while the theory predicted that release
should be 2.33 times faster at 35 C than at 5 C. The large variability
in hole sizes among open granules may account for the difference
between predicted release rates and those measured experimentally.

Granules of SCU-31 which were alternately wetted and dried at
35 C released more urea than granules which were constantly
immersed. The breakdown of coatings may have been caused by
removal of sealant from holes in the sulfur shell. Alternatively, a
portion of the amorphous sulfur in the coating may have crystallized
as the surface dried, causing cracks to open in the sulfur shell.

Granules in water, the temperature of which was varied between
5 and 35 C each day, released urea at the same rate as samples main-
tained at constant temperature.

Equations were developed to predict the rate at which microbial
populations increase and the rate at which each organism breaks down
the coating materials. The rate of coating breakdown is the product of organism numbers and organism activity.

To establish a relationship between the amount of coating removed and the fraction of granules which have been opened, granules were dipped in benzene for 1 to 10 minutes to remove portions of their coatings. After dipping in benzene, the amount of coating removed was measured and the percentage of open granules was determined. Based on the results of this experiment, it was hypothesized that all SCU granules fall into one of three classes. Class 1: granules are initially open and release urea immediately upon exposure to water. Class 2: sealant must be removed from openings in the sulfur shell before urea is released. Class 3: sulfur must be removed from the coatings before urea is released. The relationship between the amount of coating removed and the number of granules opened was linear for both Class 2 and Class 3 granules.

A computer program was written which predicted the rate at which urea is released from SCU as a function of time. To test the accuracy of these predictions, release of urea from SCU-4, SCU-20, SCU-30, and SCU-23 was measured at the soil temperatures of 25 and 35 C in soil at -0.3 bar soil water potential for 100 days. Release from SCU-4 was also measured at 5 and 15 C and in soil at -15 bars soil water potential. The agreement between predicted and measured release indicated that, for the temperature and soil water conditions studied, the rate of release was accurately predicted using the computer program.
Nitrogen Release from Granules of Sulfur-Coated Urea

by

Wesley Michael Jarrell

A THESIS

submitted to

Oregon State University

in partial fulfillment of the requirements for the degree of

Doctor of Philosophy

June 1977
Approved:

Redacted for Privacy
Professor of Soil Science
in charge of major

Redacted for Privacy
Head of Department of Soil Science

Redacted for Privacy
Dean of Graduate School

Date thesis is presented August 11, 1976
Typed by Glover Redfern for Wesley Michael Jarrell
# TABLE OF CONTENTS

## INTRODUCTION

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
</tr>
</tbody>
</table>

## LITERATURE REVIEW

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Manufacture of Sulfur-Coated Urea</td>
<td>6</td>
</tr>
<tr>
<td>Chemical and Physical Characteristics of SCU</td>
<td>7</td>
</tr>
<tr>
<td>Coating Effectiveness</td>
<td>9</td>
</tr>
<tr>
<td>Mechanisms of Release of Urea from SCU</td>
<td>10</td>
</tr>
<tr>
<td>Factors Affecting SCU Breakdown</td>
<td>13</td>
</tr>
<tr>
<td>Temperature</td>
<td>13</td>
</tr>
<tr>
<td>Soil Water Content and Aeration</td>
<td>14</td>
</tr>
<tr>
<td>Soil Microorganisms</td>
<td>16</td>
</tr>
<tr>
<td>Soil pH and Nutrient Status</td>
<td>17</td>
</tr>
<tr>
<td>Crop Production Studies</td>
<td>18</td>
</tr>
<tr>
<td>Summary</td>
<td>20</td>
</tr>
</tbody>
</table>

## MODEL OF SCU BREAKDOWN AND RELEASE OF UREA

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>21</td>
</tr>
</tbody>
</table>

## RELEASE OF UREA IN AQUEOUS SOLUTION

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Theory</td>
<td>23</td>
</tr>
<tr>
<td></td>
<td>26</td>
</tr>
<tr>
<td></td>
<td>27</td>
</tr>
<tr>
<td></td>
<td>31</td>
</tr>
<tr>
<td></td>
<td>34</td>
</tr>
<tr>
<td></td>
<td>37</td>
</tr>
<tr>
<td></td>
<td>38</td>
</tr>
<tr>
<td>Introduction to Experiments</td>
<td>38</td>
</tr>
<tr>
<td>Materials and Methods</td>
<td>39</td>
</tr>
<tr>
<td>Results and Discussion</td>
<td>43</td>
</tr>
<tr>
<td>Test of Theory</td>
<td>43</td>
</tr>
<tr>
<td>Effects of Wetting and Drying</td>
<td>51</td>
</tr>
<tr>
<td>Effects of Temperature Fluctuation</td>
<td>56</td>
</tr>
</tbody>
</table>

## COATING BREAKDOWN BY MICROBES

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Microbial Population</td>
<td>58</td>
</tr>
<tr>
<td></td>
<td>58</td>
</tr>
<tr>
<td>Model I: Exponential Growth Rate</td>
<td>59</td>
</tr>
<tr>
<td>Model II: Constant Radial Growth Rate</td>
<td>60</td>
</tr>
<tr>
<td>Model III: Constant Growth Rate</td>
<td>61</td>
</tr>
<tr>
<td>Growth Coefficients</td>
<td>62</td>
</tr>
<tr>
<td></td>
<td>62</td>
</tr>
<tr>
<td></td>
<td>64</td>
</tr>
</tbody>
</table>
## LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Cross-section of coating on SCU granule (after McClellan and Scheib, 1973, p. 11).</td>
<td>8</td>
</tr>
<tr>
<td>2. Cross-section of pinhole in wall of SCU granule, showing three portions of diffusion pathway. $\Delta x_1$ is the distance from the solid urea surface to the entrance of the pinhole (cm), $\Delta x_C$ is the length of the pinhole (cm), and $\Delta x_S$ is the distance from the exit of the pinhole to a point in the external solution where concentration of urea in solution is zero (cm).</td>
<td>25</td>
</tr>
<tr>
<td>3. Cross-section of pore in granule coating. $c_{sat}$ is the solubility of urea (g/cm$^3$), $c_1$ is the urea concentration in solution at the entrance of the pinhole (g/cm$^3$), $c_0$ is the urea concentration in solution at the exit of the pinhole (g/cm$^3$), $\Delta x_1$ is the distance from solid urea to the entrance of the pinhole (cm), and $\Delta x_C$ is the length of the pinhole (cm).</td>
<td>28</td>
</tr>
<tr>
<td>4. Relative cumulative release of urea from a single granule of SCU as a function of time.</td>
<td>35</td>
</tr>
<tr>
<td>5. Holder of SCU granules for measuring release in aqueous solution. Cap is held over end of container with a rubber band. Granules are placed between the two screens.</td>
<td>40</td>
</tr>
<tr>
<td>6. Release of urea from SCU-31 as a function of time. 35W means granules were constantly in water at 35 C, and 5W means granules were constantly in water at 5 C.</td>
<td>44</td>
</tr>
<tr>
<td>7. Release of urea from SCU-31 as a function of time. 35D/5W means granules were dried in air at 35 C for 12 hours, then immersed in water at 5 C for 12 hours out of each 24 hour period. 35W/5W means granules spent 12 hours in water at 35 C and 12 hours in water at 5 C during each 24 hour period.</td>
<td>45</td>
</tr>
<tr>
<td>8. Relative cumulative release of urea from SCU-31 granules in 5W treatment as a function of time. Dashed line is curve derived from theory, with $M_a = 0.415$, and solid line is based on assumption of $t_1 = 0$.</td>
<td>47</td>
</tr>
</tbody>
</table>
9. **Release of urea from SCU-31 as a function of time.**
35W/5D means that granules were in water at 35°C for 12 hours, then dried in air for 12 hours during each 24 hour period. Samples were dried for 12 hours at 35°C on the 28th day, then returned to 35W/5D treatments.

10. **Release of urea from SCU-31 as a function of time.**
Granules which spent the first 50 days in water at 5 and 35°C were changed to a different treatment on the 50th day. 35D/35W means granules were dried in air at 35°C for 12 hours and soaked in water at 35°C for the remaining 12 hours during each 24 hour period. 35D/5W means granules were dried in air at 35°C for 12 hours, then soaked in water at 5°C for 12 hours during each 24 hour period.

11. **Effect of temperature on doubling time of an E. coli population (from Johnson, Eyring, and Polissar, 1954).**

12. **Relationship between organism activity or organism growth rate and soil water potential (after Hattori, 1973, p. 307).**

13. **Apparatus for treatment of SCU granules with benzene at constant temperature.** A is an electric motor, B is a pulley which turns at 18 rpm, C is a vial containing granules, D is a sample solution container, E is a controlled temperature water bath, F is a warm water reservoir, G is the temperature controller, H is a water pump, and I is a siphon tube.

14. **Time course of experiments to characterize coating thickness and uniformity of coating thickness for a given SCU material.** Arrows indicate when distilled water solutions were changed. DW indicates dipping in distilled water and B indicates dipping in benzene.

15. **Cumulative release of urea from benzene-treated SCU-10.** The number by each curve indicates the duration of exposure to benzene in seconds during each treatment (Table 4).
<table>
<thead>
<tr>
<th>Figure</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>16. Percentage of granules open as a function of amount of coating removed from SCU-10.</td>
<td>79</td>
</tr>
<tr>
<td>17. Percentage of granules open as a function of amount of coating removed from SCU-23.</td>
<td>80</td>
</tr>
<tr>
<td>18. Percentage of granules open as a function of the amount of coating removed from five SCU products.</td>
<td>81</td>
</tr>
<tr>
<td>19. Release of urea from SCU-4 as a function of time in unlimed soil at 35 C. Soil water potentials were -0.3 and -15 bar.</td>
<td>90</td>
</tr>
<tr>
<td>20. Release of urea from SCU-4 as a function of time at 5, 15, 25, and 35 C. Soil water potential was -0.3 bar.</td>
<td>92</td>
</tr>
<tr>
<td>21. Release of urea from SCU-4 as a function of time on limed soil maintained at 25 and 35 C. Average soil water potential was -0.3 bar.</td>
<td>92</td>
</tr>
<tr>
<td>22. Release of urea from SCU-20 as a function of time on limed soil maintained at 25 and 35 C. Average soil water potential was -0.3 bar.</td>
<td>93</td>
</tr>
<tr>
<td>23. Release of urea from SCU-30 as a function of time on limed soil maintained at 25 and 35 C. Average soil water potential was -0.3 bar.</td>
<td>93</td>
</tr>
<tr>
<td>24. Release of urea from SCU-23 as a function of time on limed soil maintained at 25 and 35 C. Average soil water potential was -0.3 bar.</td>
<td>95</td>
</tr>
<tr>
<td>25. Release of urea from four SCU materials as a function of time at 25 C in limed soil. Average soil water potential was -0.3 bar.</td>
<td>95</td>
</tr>
<tr>
<td>26. Release of urea from four SCU materials as a function of time at 35 C in limed soil. Average soil water potential was -0.3 bar.</td>
<td>96</td>
</tr>
<tr>
<td>27. Release of urea from SCU-4 as a function of time at 35 C on limed and unlimed soil. Average soil water potential was -0.3 bar in both soils.</td>
<td>98</td>
</tr>
</tbody>
</table>
Figure

28. Soil pH as a function of time in limed and unlimed soils. Temperature was 35°C and average soil water potential was -0.3 bar in both soils.  

29. Flowchart of computer program which predicts release of urea from a given SCU product as a function of time. The quantities listed under each subroutine are calculated for each day.

30. Predicted release over time (solid lines) and measured release over time (data points) from SCU-4 on soil at two different soil water potentials. Soil temperature was 35°C.

31. Release of urea from SCU-4 at four temperatures. Soil water potential was -0.3 bar. Predicted release indicated by solid lines.

32. Predicted release (solid lines) and measured release (data points) of urea from SCU-4 at two temperatures on limed soil. Soil water potential was -0.3 bar.
LIST OF TABLES

Table | Page
--- | ---
1. Treatments used to measure effects of temperature and wetting and drying cycles on the release of urea from SCU in aqueous solutions. The designation W indicates that samples were continuously submerged, while D indicates a period during which samples were dry. | 42
2. Equations describing the falling rate period of release for 5W and 35W treatments. The general form of the equation is \( m_r = 1.0 - A - (M_b - M_a) \exp[-k_2(t-t_1)] \). | 50
3. Empirically derived exponential equations describing release from initially open granules of SCU-31. The general form of the equation is \( m_r = 1.0 - B - M \exp(-k_3T) \). | 52
4. Benzene treatments for removal of portions of coatings from five SCU materials. Average exposure time is the period between first contact with benzene and the initiation of rinsing. About 30 seconds elapsed between the last dip in benzene and the initiation of rinsing. | 76
5. Regression equations and correlation coefficients for coating characteristic curves of five SCU products. \( x \) is the amount of coating removed (g/100 g SCU). | 83
6. Soil analysis of Woodburn silt loam soil. Sample was taken from 0-20 cm depth increment. | 85
7. Summary of operations performed by the computer program. All terms in the output column are calculated for each day granules are on the soil. | 101
8. Comparisons of measured release with predicted release of urea from SCU-4 as a function of time. \( K_{g, \text{max}} \) is 0.04 mm/day, \( A_{\text{max}} \) is \( 1.0 \times 10^{-12} \) g/day, and \( A_c / \Delta x_c \) is 0.0005 cm. Soil was not limed. | 104
9. Comparison of measured release with predicted release of urea as a function of time for SCU-4, SCU-20, SCU-30, and SCU-23. Release measured at 25 and 35°C, -0.3 bar soil water potential. $A_c/\Delta x_c = 0.0005$ cm. Soil had received 9.1 metric tons/ha of lime.

10. Comparison of predicted release with measured release from SCU-23, over time. $K_{g,\text{max}} = 0.2$ mm/day. $A_{\text{max}} = 8.0 \times 10^{-13}$ g/day, temperature optimum for growth adjusted to 31°C, $A_c/\Delta x_c = 0.0005$ cm.
NITROGEN RELEASE FROM GRANULES OF SULFUR-COATED UREA

INTRODUCTION

Since John Lawes began the manufacture of superphosphate in 1843, fertilizer research has been aimed at developing materials with soluble nutrients which are more readily available to plants than those from natural sources. Soluble nutrients can enter the soil immediately after application and are available to plants as rapidly as they can reach the root surfaces by diffusion or mass flow. They must be added in sufficient quantity during the growing season to satisfy the needs of the plant for that season.

Ideally, plants should absorb all the nutrients supplied with the fertilizer. In practice this ideal is never reached. Uptake efficiency, which is the amount of fertilizer absorbed by the plant divided by the amount of fertilizer added, is often less than 0.50 for nitrogen (Russell, 1961). Nitrogen (N) is lost from the root zone through volatilization, leaching, denitrification, and uptake by crops. The application of excessive amounts of fertilizer N can pollute soils and surface waters with high nitrate levels, allow plants to accumulate excessive amounts of nitrate in their tissues, and pollute the atmosphere with ammonia and oxides of nitrogen.
Ammonia may volatilize from soils which have received large applications of N, especially when the N is carried in urea (Volk, 1959). A high level of ammonium in the soil inhibits seed germination and is toxic to seedlings (Maynard and Barker, 1969). Denitrification leads to the entry of N into the atmosphere in the form of nitrogen oxides, which may contribute to ozone breakdown in the stratosphere (Johnston, 1972).

High nitrate levels in the soil increase the probability that some nitrate will leach out of the root zone before it can be absorbed by plants. Potentially toxic levels of nitrate can accumulate in ground water supplies (Gentzsch, Runge, and Peck, 1974). Crops can absorb large amounts of nitrate, some of which may remain in the nitrate form in harvested plants (Murphy and Smith, 1967). Animals feeding on this material consequently suffer from nitrate toxicity (Case, 1957).

Fertilizers which release their nutrients slowly into the soil solution have two important advantages over highly soluble forms of fertilizer. They can improve uptake efficiency and decrease the potential for pollution. By maintaining the concentration of nitrogen in the soil solution at an optimum level, plants can absorb enough of the nutrient to produce maximum yields. In addition, the nitrogen is absorbed before it is lost from the root zone by leaching or volatilization.
Fertilizers which release nutrients slowly each fit into one of the following categories: (i) nutrient compounds of low solubility, (ii) materials that require transformation by soil microbes before their nutrients are available to plants, or (iii) soluble fertilizers coated with material which is either permeable to the fertilizer, slowly soluble, or degraded by microbes over a period of time (Lunt, 1968; Hauck, 1972). Combinations of these techniques may also be employed.

Sulfur-coated urea (SCU) falls into the third category. Urea granules are coated with elemental sulfur and the sulfur layers are sealed with a petroleum-derived wax or plastic. After the material has been applied to soil, microbes degrade the coatings, holes are opened in the coatings, and urea diffuses out of the granules through these openings.

The rate at which SCU breaks down and releases its urea depends on soil temperature, soil water content, and characteristics of the coatings. To gain the full advantage from SCU, the rate of breakdown and release of urea must be known. Effects of temperature, water content, and other environmental factors must be considered in predicting release rates. The rate at which a nutrient becomes available from SCU should match the plant requirements for that nutrient during the growing season. When the release pattern is
predictable, maximum advantage can be gained from the use of a

given slow release fertilizer.

Research with SCU has not concentrated on the understanding of
processes which cause the product to release urea or on improving the
ability to predict the rate of release as a function of time. Release
of urea from SCU has been measured in laboratory, greenhouse,
growth chamber, and field experiments. Effects of variables such as
coating weight, soil temperature, and soil water content have been
determined. Unfortunately, no quantitative relationships between
these variables and release patterns have been established. Without
developing these quantitative relationships, the release patterns can-
not be accurately predicted.

This thesis describes research designed to establish quantitative
relationships between release patterns and soil temperature, soil
water content, and coating characteristics of a given material. Using
equations developed to describe these relationships, a model of the
SCU-soil system was constructed. This model allows the prediction
of the availability of nitrogen from SCU as a function of time. The
predicted release patterns for a given material exposed to given sets
of temperature and soil water content conditions were compared to
release measured experimentally under these conditions.

By predicting the performance of a given product in soil, the
model can help the manufacturer to produce materials which will
increase the efficiency of uptake of fertilizer N by plants. Fertilizer dealers and farm managers can select the proper material and management practices so that N availability will match crop requirements in a given cropping situation.
LITERATURE REVIEW

Research with SCU and other slow release fertilizers has been reviewed by Prasad, Rajale, and Lakhide (1971), Hauck and Koshino (1971), Hauck (1972), Allen and Mays (1974), and Davies (1976). These publications thoroughly discuss the manufacture and use of SCU. They also include discussions of release as affected by characteristics of the coatings and by soil temperature, pH, and water content.

Manufacture of Sulfur-Coated Urea

Sulfur-coated urea (SCU) is produced by the Tennessee Valley Authority with a continuous-flow process (Sulphur Institute Journal, 1974; Shirley and Meline, 1975). Urea pellets are preheated in a revolving drum to prepare the granule surfaces for sulfur application. The material moves to a second drum where it is sprayed with molten sulfur. Granules receive several overlapping, thin coats of sulfur before they move to a third chamber, where a petroleum-based sealant is applied over the layer of sulfur on the granule surface. Finally a conditioner, consisting of diatomaceous earth or vermiculite, is added to reduce the stickiness of the sealant and to make the surface hydrophilic. Aggregates of granules cemented together are screened out. The final product contains 13 to 20 percent sulfur (w/w), 2 to 3 percent sealant (w/w/), and about 2 percent conditioner (w/w).
Coating techniques and materials in use now have evolved over time to increase production rates and decrease costs. Sulfur was originally atomized pneumatically. Production rates were doubled by converting to hydraulic pressure atomization. A microcrystalline wax was used as the sealant on early products. Decreased availability of the wax forced the TVA to switch to a sealant consisting of Brightstock oil and low molecular weight polyethylene.

To understand the release mechanisms of SCU, the chemical composition of sulfur and sealant materials must be known. Differences in materials and manufacturing processes result in differences in release characteristics (Shirley and Meline, 1975).

Chemical and Physical Characteristics of SCU

SCU granules have diameters ranging from 1 to 5 \text{mm}, although for a given lot of SCU, the range in diameters only spans about 1 \text{mm}. Sulfur shells range from 30 to 300 \text{\mu m} in thickness and the sealant layers range from 20 to 150 \text{\mu m} in thickness (McClellan and Scheib, 1975, 1975). Sulfur and sealant coating thicknesses vary considerably over the surface of individual granules (Figure 1), but no quantitative description of this variability is available.

Electron microscopy has shown that sulfur coatings are a mosaic of two sulfur allotrops (McClellan and Scheib, 1975). Crystals of rhombic sulfur ($S_\alpha$) are set in a matrix of polymeric sulfur ($S_\infty$).
Figure 1. Cross-section of coating on SCU granule (after McClellan and Scheib, 1973, p. 11).
Cooling rates determine the proportion of each allotrope in the coating. Rapid cooling of SCU after the sulfur coating stage results in coatings with up to 5 percent $S_\infty$. Maximum tensile strength occurs with about 7 percent of the sulfur in the amorphous form (Ludwig and Dale, 1973). The $S_\infty$ slowly crystallizes to the thermodynamically stable $S_a$. The resulting decrease in volume may strain the coating sufficiently to cause cracking.

Pinholes and cracks develop in sulfur coatings as they cool (McClellan and Scheib, 1973). Numbers and sizes of these openings have not been quantified for any SCU product. The sealant is used to plug these defects and fill depressions, strengthen the shell, and decrease the initial rate of release of urea. Without sealant, a thicker layer of sulfur must be added to produce low initial release rates (Blouin, Rindt, and Moore, 1971; Shirley and Meline, 1975).

**Coating Effectiveness**

TVA has developed a standard test to measure the effectiveness of the coating process, that is, the percentage of granules which are completely coated in the manufacturing process (Rindt, Blouin, and Getsinger, 1968). Fifty grams of SCU are immersed in 250 ml of water at 38°C. The coating effectiveness of each lot of granules is designated by the amount of urea which has entered the unstirred solution after seven days, expressed as a percentage of its total urea.
content. For example, SCU-30 is a product from which 30 percent of the urea is released under these conditions.

Occasionally the amount of release between the 7th and 30th day is measured. Steady release rates ranging from 0.1 to 0.5 percent per day have been found for this period (Rindt, Blouin, and Getsinger, 1968). The proportion of granules involved in this release is not known.

Hauck and Koshino (1971) and Allen and Mays (1974) have emphasized the need for improved product characterization which would allow release over time to be predicted more accurately.

**Mechanisms of Release of Urea from SCU**

A certain percentage of any lot of SCU granules contain major defects. These defects allow the granules to empty rapidly when placed in water (Lunt, 1968; McClellan and Scheib, 1975). It is this percentage which is measured by the TVA test described in the previous section. Remaining granules release urea either slowly or not at all.

The release of urea from intact granules can be conveniently divided into two stages. In the first stage the coating material is removed or broken down, so that eventually the urea is exposed to water. During the second stage urea diffuses out of the granule into solution. Nearly all studies of SCU have failed to consider these two
stages separately. Instead, only the end result of these two processes—the amount of urea leaving the granule as a function of time—is measured.

The mechanism by which coatings are broken down has not been determined, yet this process is critical in determining release rates (Hauck, 1972; Scheib and McClellan, 1976). Several mechanisms have been suggested.

Microbial activity increases release rates. Oertli (1973, 1974) discovered that intact SCU granules in sterile solution released almost no urea over a 12 week period. After a lag period, during which little urea was released, granules in nonsterile solutions began to release urea rapidly. Inoculation with *Thiobacillus thiooxidans* increased the rate of release and decreased the solution pH compared with nonsterile, uninoculated solutions.

Organisms were isolated from glass slides coated with sealant, which had been buried in soil. Introduction of these organisms into mineral nutrient solutions containing SCU did not accelerate release rates over those measured in nonsterile, uninoculated solutions. Oertli concluded that organisms other than *Thiobacillus thiooxidans* can break down SCU coatings, but his isolates were not as effective as organisms present in nonsterile solutions. He apparently did not consider that growth conditions in solution may have been unfavorable for his soil isolates.
The importance of microorganisms in effecting the breakdown of SCU applied to soils is not known, although Allen, Hunt, and Terman (1971) found that breakdown of soil-applied SCU was slightly slower when the sealant contained a coal-tar derivative microbiocide. More recently, the effectiveness of the microbiocide in delaying release has been questioned, and its use has been discontinued.

Once a granule has been opened, urea diffuses through the opening into the surrounding medium. McClellan and Scheib (1975) speculated that one well-developed pinhole was sufficient to allow diffusion of all urea from the granule. Hashimoto and Mullins (1974) reported that release from some granules could be explained by using a diffusion model composed of two stages. During the first stage granules release urea at a constant rate. During the second stage the rate of release decreases as a logarithmic function of time. Their complete results have not been published or confirmed.

Lunt (1968) observed that granules release urea more rapidly in soil than in solution. He suggested that the organic sealant may be adsorbed by soil colloids and removed from the coatings. No evidence was offered in support of this hypothesis.

A third mechanism of coating breakdown may be the conversion of polymeric $S_\infty$ to crystalline orthorhombic $S_a$. If freshly coated material is cooled rapidly to temperatures below 90 C, crystals remain small and little strain develops in the coating. Slow cooling
produces large crystals with a massive, brittle structure containing numerous strain cracks (McClellan and Scheib, 1975). The crystallization process in SCU coatings has not been studied under typical soil conditions, although at least one worker has speculated about its importance over the long term (Hashimoto, 1976). The crystallization rate of polymeric $S_\infty$ is accelerated by increasing temperature (Tobolsky and MacKnight, 1965), adding ammonium (Das and Ghosh, 1939), exposing sulfur to light (Schenk, 1955), and raising solution pH (Carson, 1907).

Factors Affecting SCU Breakdown

Temperature

Temperature affects the rate of coating degradation as well as the rate at which urea diffuses out of granules. Oertli (1973) measured the rate of urea release from SCU granules in mineral salt solutions at three temperatures. Mineral salts were included to encourage growth of microbes. Release rates increased with increasing temperature from 14 to 34 C. Almost no release was observed from initially intact granules at 14 C over the 12 week course of the experiment. At 34 C, granules in nonsterile environments released all of their urea within 75 days. Oertli calculated a $Q_{10}$ value of 5 for the release process. A $Q_{10}$ value of this magnitude indicates that
the activation energy for release is nearly 30 kcal/mole. He did not explain how the $Q_{10}$ value was calculated or its significance in terms of the mechanism of release.

Allen, Hunt, and Terman (1971) measured rates of urea release from two SCU materials incorporated into soil. Soil temperatures were maintained at 10, 20, or 30 C for 16 weeks. Release rates were very sensitive to temperature. At 30 C both materials released 100 percent of their urea within 2 to 5 weeks, while only 60 to 75 percent was released from the granules at 10 C in 16 weeks.

Dawson and Akratanukul (1973) incorporated SCU into soil and measured release of urea from granules at 16, 24, and 32 C. After 21 days the 32 C treatment had released the most urea. Snyder and Gascho (1976) measured release of urea from two SCU materials over time in field studies. One set of studies was initiated in July and a second in January. They found that the initial rate of release was faster from granules applied in July but six months after application the January applied materials had released more urea. They concluded that intact granules were stable for at least three months under cool conditions, but opened readily in warm soils.

**Soil Water Content and Aeration**

Soil water content and aeration influence release rates, although Lunt (1968) felt that the effect should be small within the range of soil
water contents suitable for plant growth. Dawson and Akratanakul (1973) measured nitrogen release and plant uptake of nitrogen from SCU at soil water potentials of -0.10, -0.35, and -2.5 bars, and at temperatures of 16, 24, and 32 C. Nitrogen release was most rapid at the soil water potential of -0.10 bar and soil temperature of 32 C. At lower soil water content and lower temperatures, less urea was released.

Ferrous sulfide (FeS) has been observed on granule surfaces in flooded soils (Giordano and Mortvedt, 1970). The FeS coating apparently decreases the rate of release far below rates in moist soil. The authors also suggested that inadequate soil aeration may inhibit the activity of wax degrading organisms, which are primarily aerobic.

Prasad (1976) determined the effects of soil water content on the rate of release of urea from two materials. He measured release in soils at three water contents equivalent to potentials of -0.01, -0.25, and -3.0 bars. Two soils were used. In one soil release increased with increasing soil water content. This was true in the other soil during the first three weeks, after which the -0.25 bar treatment released its urea most rapidly. The author was unable to explain his results with a consistent model.

Liegel and Walsh (1976) concluded that intermittent wetting and drying of SCU granules in an irrigated cornfield reduced release rates below the level required for optimum yield. When the soil was
kept moist, release proceeded more rapidly than under wetting and drying conditions.

**Soil Microorganisms**

Soils harbor organisms capable of growing on hydrocarbons similar to the sealant materials, although their growth is usually slow (Foster, 1962; Johnson, 1967). Some fungi can utilize unbranched hydrocarbons. Actinomycetes (*Nocardia* and *Streptomyces*) can break down branched as well as normal hydrocarbons. Several genera of bacteria (*Corynebacter*, *Pseudomonas*) are capable of oxidizing most components of petroleum, including aromatic compounds. Because fungi and actinomycetes are drought tolerant they are more active in dry soils or intermittently dry soils than are the bacteria.

Elemental sulfur is oxidized by both autotrophic and heterotrophic organisms (Burns, 1967). *Thiobacillus* is the dominant genus of autotrophic sulfur oxidizers, with members active over a wide range of soil conditions. A few genera of heterotrophic bacteria (e.g., *Pseudomonas*), fungi (e.g., *Penicillium*), and actinomycetes can oxidize elemental sulfur, although they do not derive energy from this reaction (Vitolins and Swaby, 1965).

Early formulations of SCU included a coal-tar derivative microbiocide in the sealant. Its use has been discontinued (Tennessee Valley Authority, 1976; Shirley and Meline, 1975), although Allen,
Hunt, and Terman (1971) concluded that the microbiocide was effective in decreasing the rate of urea release from SCU granules incorporated into soil. The microbiocide was less effective when the granules were applied to the soil surface. Its effectiveness decreased with increasing temperature. Subsequent agronomic research has produced conflicting reports on the effectiveness of microbiocides in delaying breakdown (Tennessee Valley Authority, 1976). New sealant materials may be inherently more resistant to microbial attack, eliminating the need for a microbiocide to delay the breakdown of coating materials.

**Soil pH and Nutrient Status**

Liming accelerates the rate of release of urea from SCU granules in moist soil (Giordano and Mortvedt, 1970). Adverse effects of low pH on microbial activity may be responsible for slower breakdown in acid soils. Although thiobacilli are most active at soil pH values between 5 and 7, sulfur oxidation occurs slowly at pH values as low as 2 or 3 (Gray and Williams, 1971). Carbon dioxide, released as calcium carbonate, dissolves and neutralized soil acidity and stimulates the growth of autotrophic sulfur-oxidizing bacteria (Burns, 1967).

Lack of an essential element occasionally limits the rate of microbial activity in soils. Burns (1967) suggests that liming may
stimulate microbial activity by increasing the availability of calcium. Giordano and Mortvedt (1970) observed accelerated breakdown of SCU on soil which had received phosphorus (P). Low P levels apparently limited the rates of microbial activity on untreated soil and hence limited the rate of coating breakdown.

**Crop Production Studies**

SCU has frequently been compared to readily-available nitrogen sources in field studies. Crop responses have been studied with potatoes and corn (Leigel and Walsh, 1976), melons (Locascio and Fiskell, 1970), tomatoes (Shelton, 1976), rice (Prasad and Rajale, 1972; Sanchez et al., 1973), forages (reviewed by Allen and Mays, 1974), sugar cane (Gascho and Snyder, 1976), and ornamentals (Furuta, Sciaroni, and Breece, 1967).

Allen and Mays (1974) surveyed results of field experiments and concluded that the major agronomic benefit of SCU application was a decrease in excessive uptake of N by plants immediately after fertilizer application. For crops such as corn or wheat this is not an advantage, unless either nitrogen toxicity or leaching is a problem. Crops that are harvested several times during the growing season, such as forages and tomatoes, may lose much nitrogen with the first harvest if excessive (luxury) N uptake occurs. By releasing its urea at adequate but not excessive rates, SCU encourages more efficient
plant utilization of fertilizer nitrogen.

Along with decreasing the excessive uptake of N by plants, SCU may increase the efficiency of N use in a different manner. Rice paddies which are only intermittently flooded provide ideal situations for denitrification. During the drained portion of the cycle, ammonium is oxidized to nitrate. After flooding the soil becomes aerobic and nitrates are reduced to gaseous nitrogen oxides and molecular nitrogen, forms which plants cannot utilize. Sanchez et al. (1973) found that under these conditions rice fertilized with SCU produced up to 59 percent more grain than rice which received regular urea. SCU released its nitrogen steadily during the growing season. Smaller amounts of nitrogen were denitrified and soil nitrogen supplies were constantly renewed. The authors, assuming a 32 percent higher cost per unit N for SCU compared with regular urea, concluded that use of SCU was economically advantageous in this cropping situation.

The use of SCU can have several economic advantages: (i) it may decrease the amount of N fertilizer required for economically optimal yields by increasing N uptake efficiencies, (ii) it may decrease the number of fertilizer applications required to obtain optimum yields, (iii) in soils low in plant-available sulfur, the sulfur coating serves as a source of this nutrient, (iv) SCU has better handling characteristics than regular urea. Balanced against these potential benefits are added costs of sulfur, wax, and the
manufacturing process. Freight rates per unit N are higher for SCU than for regular urea because SCU contains less N per unit weight than does urea.

Costs of materials and manufacturing may decrease as the coating process is made more efficient. Furthermore, as the release of urea from SCU becomes better characterized, SCU may be used more effectively by matching the proper material with the cropping situation in which it performs most economically.

Summary

SCU consists of urea granules coated with a layer of sulfur. Holes in the sulfur are sealed with a petroleum-derived wax. Urea is released through openings in the coatings. These openings may be present initially or may appear after the product has been in the soil for some period of time. The mechanism which causes holes to open in coatings is not known, but appears to be sensitive to temperature, soil water content, microbial activity, soil pH, and soil nutrient status.
MODEL OF SCU BREAKDOWN AND RELEASE OF UREA

Past studies with SCU have measured release of urea in soils and in solutions under a variety of conditions. However, few of the results of these studies are analyzed in the terms that Scheib and McClellan (1976) proposed, that is,

The slow release of nitrogen from SCU may result from differences in the time periods required for individual granules to begin releasing urea through pores. The mechanism of slow release apparently has both diffusion-controlled and nondiffusion-controlled (defect initiated) components operating simultaneously.

The observed release of urea from SCU over time thus depends on the rate at which holes open in intact coatings, and the rate at which urea diffuses through these pores into the external solution. The series of events occurring after SCU is applied to moist soil may be summarized as follows: (i) some fraction of the granules have pores or cracks in their coatings which allow water to enter the granule and dissolve urea; urea diffuses out through these openings into the soil. (ii) remaining granules have coatings which break down and eventually open to allow water to enter the granule. The time required for the pore to open in a given soil depends on the nature and the thickness of the coating, soil temperature, and soil water content.

The above description will serve as a model of SCU breakdown and the subsequent release of urea in soil. To quantify these
components of release, equations will be developed for the following steps of the process,

(i) the rate at which urea diffuses out of an open granule through a pore in its coating,

(ii) the rate at which coatings are broken down, assuming that soil microbes break down the coating materials and eventually open holes through the coatings.

(iii) the rate at which holes appear in coatings as coating material is broken down, with the nature and thickness of the coating dictating the time required for a hole to open in the coating of a given granule, and

(iv) effects of soil temperature and soil water content on all processes which control the rate at which urea enters the soil from a given SCU product.

Equations describing these components of the model are developed below. These equations are incorporated into a computer program which predicts the amount of urea which is released from SCU granules over time. The accuracy of the model is tested by comparing predicted release rates with release measured in soils.
RELEASE OF UREA IN AQUEOUS SOLUTION

Theory

Urea diffuses out of SCU granules through openings in the coatings. Openings range in size from tiny pinholes, to cracks, to large areas of coating failure. Large failures result in rapid emptying of the granules, while small openings allow only a very slow rate of diffusion out of the granules.

For SCU granules with small openings in their coatings, the release of urea as a function of time consists of a constant rate period and a falling rate period. During the constant rate period water enters the granule and dissolves the urea, which then diffuses out into the surroundings. The internal solution remains saturated with urea until all solid urea has dissolved, at which time release enters the falling rate period. This occurs at time \( t = t_1 \), when all the urea inside the granule is in saturated urea solution. During the falling rate period, the urea concentration inside the granule decreases as the urea diffuses out of the granule.

Diffusion of urea out of an open granule should obey Fick's First Law of Diffusion,

\[
\frac{dm}{dt} = -DA \frac{dc}{dx},
\]

where
$m = \text{mass of urea which has diffused out of the open granule (g)},$

$t = \text{time since diffusion began (sec)},$

$D = \text{diffusion coefficient for urea in water (cm}^2/\text{sec}),$

$A = \text{cross-sectional area through which diffusion occurs (cm}^2),$

$c = \text{concentration of urea in solution (g/cm}^3),$

$x = \text{distance through which diffusion occurs (cm)}.$

In considering release from a single open granule or from a number of open granules, it is convenient to express diffusion in terms of the relative mass of urea, $m_r$, which diffuses out of the open granule,

$$\frac{dm_r}{dt} = -kDA \frac{dc}{dx}, \quad (1)$$

where

$$m_r = \frac{m}{M_0}, \text{ where } M_0 \text{ is the mass of urea originally present in the open granule in grams, and}$$

$$k = \frac{1}{M_0} \quad (l/g).$$

Assume that urea diffuses through a pore in the coating with cross-sectional area $A_c$ and length $\Delta x_c$ (Figure 2). If the concentration in solution at the entrance of the opening is $c_1 \text{ g/cm}^3$, and the urea concentration at the exit is $c_2 \text{ g/cm}^3$, the concentration gradient term $\frac{dc}{dx}$ may be replaced with $(c_2 - c_1) / \Delta x_c$. Diffusion always occurs from a region of high concentration to a region of low concentration. Thus $(c_2 - c_1)$ is always negative.
Figure 2. Cross-section of pinhole in wall of SCU granule, showing three portions of diffusion pathway. \( \Delta x_1 \) is the distance from the solid urea surface to the entrance of the pinhole (cm), \( \Delta x_c \) is the length of the pinhole (cm), and \( \Delta x_s \) is the distance from the exit of the pinhole to a point in the external solution where concentration of urea in solution is zero (cm).
Substituting \((c_2 - c_1)/\Delta x_c\) for \(dc/dx\) in Equation 1 and rearranging terms gives

\[
\frac{dm_r}{dt} = -kD\left(\frac{A_c}{\Delta x_c}\right)(c_2 - c_1) .
\] (2)

The ratio \(A_c/\Delta x_c\) is a characteristic of the geometry of the diffusion pathway. Figure 2 shows the three major portions of the diffusion pathway in an open granule. Urea dissolves, diffuses through the internal solution to the opening, through the opening, and into the surrounding solution. Each portion of the pathway has a different geometry. Rather than derive the general solution to this problem, a simplified analysis will be presented based on the assumption that certain special conditions are met.

**External Concentration**

It will be assumed that the concentration of the external solution is zero. In a dilute solution which is well-stirred, this condition is met. In moist soils it is also generally valid. Water is continually being redistributed throughout the soil in response to potential gradients. As water moves past the granule it sweeps away urea from the mouth of the opening. Hydrolysis of urea in the soil also contributes to maintaining low urea concentrations. In dry soils where water films are thin and discontinuous, high concentrations of urea can
accumulate, causing the external concentration to become significantly greater than zero.

**Constant Rate Period**

Figure 3 shows the two portions of the diffusion pathway which control the rate of diffusion. Under steady state conditions, the rate at which urea diffuses from the solid boundary to the entrance of the opening equals the rate at which urea diffuses through the opening. This equality is expressed by the following equations,

\[
\frac{dm}{dt} = -kD\left(\frac{A_i}{\Delta x_i}\right)(c_i - c_{sat}) = -kD\left(\frac{A_c}{\Delta x_c}\right)(c_0 - c_i),
\]

where

\[A_i/\Delta x_i = \text{term which describes the diffusion geometry inside the granule (cm}^2/\text{cm}),\]

\[A_c/\Delta x_c = \text{term which describes the diffusion geometry of the opening in the coating (cm}^2/\text{cm}),\]

\[c_i = \text{concentration of urea at the entrance of the opening (g/cm}^3),\]

\[c_{sat} = \text{solubility of urea (g/cm}^3),\] and

\[c_0 = \text{concentration of urea at the exit of the opening (g/cm}^3).\]

Since \(c_0 = 0,\)
Figure 3. Cross-section of pore in granule coating. $c_{sat}$ is the solubility of urea (g/cm$^3$), $c_i$ is the urea concentration in solution at the entrance of the pinhole (g/cm$^3$), $c_0$ is the urea concentration in solution at the exit of the pinhole (g/cm$^3$), $\Delta x_i$ is the distance from solid urea to the entrance of the pinhole (cm), and $\Delta x_c$ is the length of the pinhole (cm).
Rearranging terms,

\[
\frac{A_i}{\Delta x_i} (c_{\text{sat}} - c_i) = \frac{A_c}{\Delta x_c}c_i .
\]

Imagine a spherical granule of radius \( r \), with a pore \( \Delta x_c \) cm long passing through the coating. As urea dissolves and diffuses out of the granule, the solid urea surface retreats away from the opening. The value of \( A_i/\Delta x_i \) is constantly changing as the granule empties. An "average" value of \( A_i/\Delta x_i \) is assumed to describe the geometry of the diffusion pathway inside the granule. Because the length of the pore, \( \Delta x_c \), is constant, \( A_c \) determines the value of \( A_c/\Delta x_c \). If \( A_c \) is sufficiently small, then

\[
\frac{A_c}{\Delta x_c} \ll \frac{A_i}{\Delta x_i} .
\]

The remainder of the theoretical section will only discuss the release of urea from granules where \( A_c/\Delta x_c \) is small relative to \( \Delta A_i/\Delta x_i \). Urea in granules which are initially open is released rapidly and does not contribute to slow release over a long term. Granules which are closed are eventually opened by soil microorganisms. The size of the cracks or holes produced by soil microorganisms are expected to be
small, although the range in size has not been determined. From Equations 4 and 5, then,

\[
\frac{A_i}{c_i(\Delta x_i)} \approx \frac{c_{\text{sat}}}{c_{\text{sat}}} \Delta x_i
\]

and

\[
c_i \approx c_{\text{sat}}.
\]

Thus the rate of diffusion out of the granule is

\[
\frac{dm_r}{dt} = -kD \frac{A_c}{\Delta x_c} c_i \approx -kD \frac{A_c}{\Delta x_c} c_{\text{sat}}.
\]

At constant temperature, \(kD(A_c/\Delta x_c)\) is constant. Defining

\[
k_l = kD \frac{A_c}{\Delta x_c},
\]

\[
\frac{dm_r}{dt} = k_l c_{\text{sat}} dt.
\]  

To solve for the relative mass of urea, \(m_r\), which has diffused out of the granule during time \(t\), both sides of Equation 7 are integrated between appropriate limits:

\[
\int_0^{m_r} \frac{dm_r}{dt} = k_l c_{\text{sat}} \int_0^t dt,
\]

and
Equation 8 indicates that, for small values of $\frac{A_c}{\Delta x_c}$ and low external urea concentrations, urea is initially released from the granule at a constant rate.

**Falling Rate Period**

The constant rate period continues until time $t = t_1$ when all the solid urea has been dissolved. The relative mass of urea which has been released during the constant rate period is designated as $M_c$. The remainder of the urea, $1.0 - M_c$, is released during the falling rate period.

Release after time $t = t_1$ may be described by the following considerations:

Let

$$c_i = \frac{m_i}{V}, \quad (9)$$

where

$c_i =$ concentration of urea inside granule at some time $t = t_1$ (g/cm$^3$),

$m_i =$ grams of urea inside granule at time $t$, and

$V =$ volume of granule (cm$^3$).

In terms of the relative mass,
\[ m_i = (1.0 - m_r) \rho_u V \]  

where \[ \rho_u = \text{density of solid urea, } 1.32 \text{ g/cm}^3. \]

Substituting this term for \( m_i \) in Equation 9,

\[ c_i = \frac{(1.0 - m_r) \rho_u V}{V}. \]  

Substituting this term for \( c_i \) in the right hand side of Equation 3,

\[ \frac{dm_r}{dt} = -k \frac{DA_c}{\Delta x_c} \left[ c_0 - \frac{(1-m_r) \rho_u V}{V} \right]. \]

Since the external concentration \( c_0 \) is equal to zero,

\[ \frac{dm_r}{dt} = -k \frac{DA_c}{\Delta x_c} \left[ - \frac{(1-m_r) \rho_u V}{V} \right], \]

and

\[ \frac{dm_r}{dt} = -k \frac{DA_c}{V \Delta x_c} (m_r - 1) \rho_u V. \]  

Rearranging Equation 12,

\[ \frac{dm_r}{(m_r - 1)} = -k \frac{DA_c}{V \Delta x_c} \rho_u V dt. \]  

According to Equation 1, \( k \) is the reciprocal of the mass of urea.
initially inside the granule, therefore

\[ k = \frac{1}{\rho \cdot V} \]

When this expression for \( k \) is substituted into Equation 13,

\[ \frac{dm_r}{(m_r - 1)} = -\frac{DA_c}{V \Delta x_c} \; dt \]

Defining

\[ k_2 = \frac{DA_c}{V \Delta x_c} \]

and integrating both sides of the equation between appropriate limits as follows,

\[ \int_{M_c}^{m_r} \frac{dm_r}{(m_r - 1)} = -k_2 \int_{t_1}^{t} dt \]

results in

\[ \ln\left(\frac{m_r - 1}{M_c - 1}\right) = -k_2(t - t_1) \]

Taking the exponential of both sides of the equation and rearranging,

\[ \frac{m_r - 1}{M_c - 1} = \exp[-k_2(t - t_1)] \]
\[ m_r - 1 = (M_c - 1) \exp[-k_2(t - t_1)], \]
\[ m_r = 1 + (M_c - 1) \exp[-k_2(t - t_1)]. \] (16)

For convenience, the equation is put in the form
\[ m_r = 1 - (1 - M_c) \exp[-k_2(t - t_1)], \] (17)

where \( (1 - M_c) \) = relative mass of urea in the granule released during the falling rate period. The pattern of release from a granule with a small opening consists of a constant rate period, described by Equation 8, and a falling rate period, described by Equation 17. Cumulative release as a function of time was calculated for a granule containing 0.015 g of urea with an opening such that \( A_c / \Delta x_c \) is 0.003 cm. The temperature is constant at 25 C. Granule volume is 0.015 g/\( \rho_u \) or 0.0114 cm\(^3\), where \( \rho_u \) is the density of solid urea, 1.32 g/cm\(^3\). The constant \( k \) is equal to \( 1/0.015 \) g or 66.7/g.

**Diffusion Coefficient as Function of Temperature**

The diffusion coefficient and the solubility of urea are temperature-dependent quantities. To calculate expected diffusion rates, these terms must be corrected for temperature.

The temperature dependence of the diffusion coefficient is described by the Einstein equation
Figure 4. Relative cumulative release of urea from a single granule of SCU as a function of time.

The equation for the relative cumulative release, $m_r$, is given by:

$$m_r = 1.0 - (1.0 - M_C) \exp \left[ -\frac{DAC}{V\Delta x_c} (t - t_1) \right]$$

Parameters used in the equation:

- $\frac{A_C}{\Delta x_c} = 0.003 \text{ cm}$
- $T = 25 \text{ C}$
- $V = 0.0114 \text{ cm}^3$
- $k_l = 66.7 \text{ g}$
D = \frac{RT}{Nf}, \quad (20)

where

\[ R = \text{universal gas constant (0.082 l-atm/mole-deg)}, \]
\[ T = \text{absolute temperature (°K)}, \]
\[ N = \text{Avagadro's number (6.02 x 10^{23} molecules/mole)}, \]
\[ f = \text{frictional coefficient (g/sec)}. \]

For a given molecule, the frictional coefficient is proportional to viscosity, \( \eta \), as follows:

\[ f' = k\eta, \quad (21) \]

where \( k = \text{constant}. \)

Substituting for \( f \) in Equation 20 yields

\[ D = \frac{RT}{Nk\eta}. \quad (22) \]

The viscosity of water is also a function of temperature, as expressed by the equation (Moore, 1972)

\[ \eta = A \exp(\Delta E_{vis}/RT), \quad (23) \]

where

\[ A = \text{constant (g/cm-sec)}, \]
\[ \Delta E_{vis} = \text{activation energy for viscous flow (cal/mole)}, \]
\[ R = \text{universal gas constant (1.98 cal/mole-deg K)}, \]
\[ T = \text{absolute temperature (degrees Kelvin)}. \]
The constants \( A \) and \( \Delta E_{\text{vis}} \) for water were evaluated by first substituting appropriate values of \( \eta, T, \) and \( k \) at 5 and 35 C into Equation 23, taking the logarithm of both sides, and solving the simultaneous equations. It was found that

\[
\eta = (7.02 \times 10^{-6}) \exp(2135/T).
\]  

(24)

Substituting this expression for \( \eta \) in Equation 22,

\[
D = \frac{RT}{Nk(7.02 \times 10^6)} \exp(-2135/t).
\]  

(25)

To solve for \( k \), Equation 25 is rearranged and values of \( D, R, T, \) and \( N \) at 20 C are entered in the equation. It is found that

\[
k = 3.54 \times 10^{-13} \text{ cm}^3.
\]

Substituting this value of \( k \) back into Equation 25,

\[
D = (5.36 \times 10^{-5})T \exp(-2135/T) \text{ cm}^2/\text{sec},
\]

or

\[
D = (4.63)T \exp(-2135/T) \text{ cm}^2/\text{day}.
\]  

(26)

**Urea Solubility as Function of Temperature**

Data on the solubility of urea over the temperature range of 5 C to 40 C were used to calculate a linear equation relating solubility to
temperature. The relationship as determined by calculating a least-squares fit of these points is

\[ c_{\text{sat}} = (6.96 \times 10^{-3})T_c + 0.45, \]  

(27)

where \( c_{\text{sat}} \) = solubility of urea (g/cm\(^3\)) at temperature \( T_c \) (°C).

Summary

Based on the assumption of small opening size, the following quantities must be supplied to calculate the release pattern from a given granule: (i) the size of the opening in the coating \( (A_c/\Delta x_c) \), (ii) the amount of urea remaining in the granule, and (iii) the temperature of the granule. The amount of urea inside the granule determines which stage of release the granule is in. If all remaining urea is in solution, release has entered the second, exponential stage. The temperature of the granule is substituted into Equations 26 and 27 to calculate the diffusion coefficient and the solubility of urea.

After a hole has opened in the coating of a granule, release can be predicted. Equations are developed in later sections which allow the prediction of the number of open granules on the soil at any time.

**Introduction to Experiments**

This thesis is primarily concerned with predicting the release of urea as a function of time from granules which are initially closed.
However, because it is difficult to recover open granules from soil without damaging them, it is convenient to determine whether the diffusion theory applies to a sample of granules, some of which are initially open. Openings in these granules range in size from large areas of coating failure to minute cracks and pinholes (McClellan and Scheib, 1973). Thus the value of $A_c/\Delta x_c$ may vary greatly among granules. Average values of $A_c/\Delta x_c$ and of granule volumes will be assumed to apply so that data can be analyzed in terms of the diffusion theory developed earlier to describe release from a single granule.

Release of urea from SCU granules which were initially open was measured in sterile, aqueous solutions. Temperature was held constant or allowed to fluctuate within established limits. Granules were either constantly immersed or alternately wetted and dried.

**Materials and Methods**

About 100 granules of SCU-31 (Appendix 1) weighing 1.25 g were placed between two 20-mesh nylon screens secured into a polyvinyl chloride cylinder with a diameter of 2.6 cm (Figure 5). These holders, with the granules in place, were suspended in 500 ml distilled water contained in 900 ml glass jars. The screen on the upper side was required because the wax surface of these granules is hydrophobic, causing them to float unless held down by a second screen.
Figure 5. Holder of SCU granules for measuring release in aqueous solution. Cap is held over end of container with a rubber band. Granules are placed between the two screens.
The water contained 5 µg/ml of phenylmercuric acetate (PMA) to inhibit the growth of microorganisms and urease activity. Each treatment had three replications.

The temperature and wetting and drying treatments that were used are shown in Table 1. The duration of the "Day" and "Night" treatment periods was 12 hours for each, so that a complete cycle was 24 hours long. At each sampling the holders were raised above the solution and water was squirted through the glass tube, over the granules, and into the sample jar. Full sample jars were then weighed and the total amount of solution in each sample was determined by subtracting jar tare weights from total weights. Aliquots of each sample were stored in polyethylene bottles until analyzed. Jars were refilled with 500 ml of water containing 5 µg/ml PMA. Solutions were changed frequently to assure that external urea concentrations remained low to meet the assumptions on which the theoretical equations were based. Replacement PMA solutions were maintained at the required temperature prior to their use. Samples from the 35W, 35W/5D, 35D/5W, and 5W treatments were initially taken every morning for 20 days. Samples from the 35W/5W treatment were taken after each temperature change. As the release rate decreased, samples were taken at intervals of two days, although the temperature and water conditions were still cycled daily.
Table 1. Treatments used to measure effects of temperature and wetting and drying cycles on the release of urea from SCU in aqueous solutions. The designation W indicates that samples were continuously submerged, while D indicates a period during which samples were dry.

<table>
<thead>
<tr>
<th>Treatment Designation</th>
<th>Day (12 hrs)</th>
<th>Night (12 hrs)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Temperature</td>
<td>Moisture</td>
</tr>
<tr>
<td></td>
<td>°C</td>
<td></td>
</tr>
<tr>
<td>35W</td>
<td>35</td>
<td>Wet</td>
</tr>
<tr>
<td>35W/5W</td>
<td>35</td>
<td>Wet</td>
</tr>
<tr>
<td>35D/5W</td>
<td>35</td>
<td>Dry</td>
</tr>
<tr>
<td>35W/5D</td>
<td>35</td>
<td>Wet</td>
</tr>
<tr>
<td>5W</td>
<td>5</td>
<td>Wet</td>
</tr>
</tbody>
</table>

Samples containing more than 20 μg urea-N/ml were analyzed colorimetrically with the method of Watt and Chrisp (1953). Those samples with less than 20 μg urea-N/ml were analyzed with a diacetylmonoxime procedure. Aliquots up to 10 ml in volume containing 1 to 10 μg urea-N were mixed with 2.5 ml of 20 percent NaCl solution, 2.0 ml of 12.5 percent KH₂PO₄ in concentrated H₂SO₄, and 0.5 ml of a solution of manganese chloride, diacetylmonoxime and semicarbazide hydrochloride in water. Samples were heated in a water bath maintained at 60 °C for two hours and then allowed to cool at room temperature. Transmittance was obtained at 520 nm on a Bausch and Lomb Spectronic 20.
Results and Discussion

Initially some granules released their urea very rapidly (Figures 6 and 7). After 20 days granules maintained in water at 5 or 35 °C (Figure 6) had ceased to release urea. Granules subjected to wetting and drying cycles continued to release urea at an average rate of about 0.15 percent per day (Figure 7).

Test of Theory

The theoretical model derived earlier describes release from a single open granule. This model was applied to the release curves obtained experimentally to test its validity for a sample of granules. The falling rate period of release, as described with Equation 17, was fitted to the release data. For convenience, \( m_r \) was set equal to the cumulative relative mass of urea released from all granules, both open and closed, in the sample. To account for the presence of closed granules, a constant \( A \), representing the relative mass of urea in closed granules, had to be included in the equation. Also, the term for the relative mass of urea released during the falling rate period, which is \( 1 - M_c \) in Equation 17, had to be expressed as \( M_b - M_a \), where \( M_b \) is the relative mass of urea in open granules and \( M_a \) is the relative mass of urea released during the constant rate period.

The equation which results from these modifications of Equation 17 is
Figure 6. Release of urea from SCU-31 as a function of time. 35W means granules were constantly in water at 35 C, and 5W means granules were constantly in water at 5 C.
Figure 7. Release of urea from SCU-31 as a function of time. 35D/5W means granules were dried in air at 35 C for 12 hours, then immersed in water at 5 C for 12 hours out of each 24 hour period. 35W/5W means granules spent 12 hours in water at 35 C and 12 hours in water at 5 C during each 24 hour period.
\[ m_r = 1.0 - A - (M_b - M_a) \exp[-k_2(t-t_1)] , \] (28)

where

\[ m_r = m/M_0 , \] where \( M_0 \) is the mass of urea in open and in closed granules, and \( m \) is the mass of urea which has diffused out of open granules in time \( t \),

\[ A = \text{relative mass of urea in granules which are not open}, \]

\[ M_b = \text{relative mass of urea in open granules}, \]

\[ M_a = \text{relative mass of urea released during constant rate period}, \]

\[ k_2 = \text{rate constant} \ (1/\text{days}), \]

\[ t = \text{time measured from the beginning of the experiment (days)}, \]

\[ t_1 = \text{time at which falling rate period begins (days)}. \]

The fraction of urea in intact granules, \( A \), was assumed to be that fraction of urea which was not released after 20 days in water. For the 35W treatment, \( A \) was 0.333, and for the 5W treatment, \( A \) was 0.344. Results of the 5W treatment are shown in Figure 8. The value of \( M_b \) for the 35W treatment was therefore 0.667, and for the 5W treatment, \( M_b \) was 0.656.

To fit Equation 28 to the data, it was converted to the form

\[ \ln(1.0-A-m_r) = \ln(M_b - M_a) - k_2(t-t_1) . \] (29)

In order to use Equation 29, the value of \( t_1 \) must be known. The
Figure 8. Relative cumulative release of urea from SCU-31 granules in 5W treatment as a function of time. Dashed line is curve derived from theory, with \( M_a = 0.415 \), and solid line is based on assumption of \( t_1 = 0 \).
method by which $t_1$ was calculated is discussed below. Since the same series of calculations to determine $t_1$ were performed for the 35W treatment as for the 5W treatment, only the calculations for the 5W treatment are discussed.

Time $t_1$ is the time required for completion of the constant rate period. The relative mass of urea which is released during this period, $M_a$, is the difference between the relative amount of urea in open granules at the beginning of the experiment, $M_b$, and the relative mass of urea remaining inside the granule at the beginning of the falling rate period. The mass of urea inside the open granules at time $t_1$ is the mass which can be dissolved in solution inside open granules, or $c_{sat}V$, where $c_{sat}$ is the solubility of urea, g/cm$^3$, and $V$ is the volume of open granules, cm$^3$. The mass of urea inside open granules at the beginning of the experiment is $\rho_uV$, where $\rho_u$ is the density of solid urea, 1.32 g/cm$^3$. Therefore, the relative mass of urea inside the open granules at the beginning of the falling rate period is

$$\frac{c_{sat}V}{\rho_uV}M_b = \frac{c_{sat}}{1.32}M_b.$$  

Because $M_b - M_a$ is also equal to the relative mass of urea released during the falling rate period, we have
\[ M_b - M_a = \frac{c_{sat}}{1.32} M_b. \]

Solving for \( M_a \),

\[ M_a = M_b - \frac{c_{sat}}{\rho_u} M_b. \]

At 5°C, \( c_{sat} \) is 0.484 g/cm\(^3\) and \( M_b \) is 0.656, so that

\[ M_a = 0.656 - \left( \frac{0.484}{1.32} \right)(0.656), \]

and

\[ M_a = 0.415. \]

The average rate of release at 5°C during the first two days is 0.187/day, so that

\[ m_r = 0.187t. \]

At time \( t_1 \), \( m_r \) is equal to \( M_a \), and

\[ M_a = 0.187t_1. \]

Solving for \( t_1 \),

\[ t_1 = \frac{0.415}{0.187} = 2.22 \text{ days}. \]

For the 35W treatment, \( t_1 \) is found to be 0.76 day.
The proper value of \( t_1 \) is then substituted into Equation 29 and 
\( \ln(1.0-A-m_r) \) is regressed against \((t-t_1)\) to give the equations for 
the 5W and 35W treatments (Table 2).

Table 2. Equations describing the falling rate period of release for 
5W and 35W treatments. The general form of the equation 
is \( m_r = 1.0 - A - (M_b - M_a) \exp[-k_2(t-t_1)] \).

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Equation</th>
<th>( R )</th>
</tr>
</thead>
<tbody>
<tr>
<td>5W</td>
<td>( m_r = 1.0 - 0.344 - 0.26 \exp[-0.24(t-2.22)] )</td>
<td>0.999</td>
</tr>
<tr>
<td>35W</td>
<td>( m_r = 1.0 - 0.333 - 0.20 \exp[-0.30(t-0.76)] )</td>
<td>0.987</td>
</tr>
</tbody>
</table>

The theoretical release curve which results from this analysis 
is shown in Figure 8 (dashed line). Unlike the curve which describes 
release from a single granule (Figure 4), an abrupt change in slope 
occurrs at time \( t_1 \). This indicates that the data cannot be analyzed 
strictly in terms of the theoretical predictions for release from a 
single granule. It appears that a larger amount of urea is released 
initially from the granules than is predicted from theory. This may 
be attributed to granules which contain large openings and consequently 
high values for \( A_c / \Delta x_c \).

\[
m_r = 1.0 - B - M \exp(-k_3 t), \tag{30}
\]

where
\[ B = \text{fraction of urea in closed granules}, \]
\[ M = \text{constant}, \]
\[ k_3 = \text{constant (l/days)}, \text{ and} \]
\[ t = \text{time measured from the beginning of the experiment (days)}. \]

This equation was converted to the form

\[ \ln(1.0 - B - r_m) = \ln M - k_3 t. \]  \hspace{2cm} (31)

**Effects of Wetting and Drying**

A value of \( B \) was chosen by trial and error which gave the maximum correlation coefficient for the data. The terms in Equation 30 are given in Table 3 for all five treatments. This exponential equation accurately describes release during the first 20 days. It also provides a means for determining the value of \( B \), the fraction of urea which is in closed granules, for short-term measurements of release as a function of time. The amount of urea remaining in intact granules ranged from 33 percent to 35 percent except for treatment 35D/5W. In this case about 12 percent more urea was released during the first 20 days than in the other treatments (Figure 7).

As stated earlier, the objective of this thesis is the prediction of the release of urea as a function of time from granules which are
initially closed. These granules are eventually opened by soil microorganisms after SCU is placed in the soil. Although the sizes of the fresh openings have not been measured, they are expected to be small. When other factors are equal, granules with similar coating thicknesses will be open after similar lengths of time on the soil. Thus it is expected that the values of $A_c/\Delta x_c$ for granules which are opened on a given day will fall within a narrow range.

Table 3. Empirically derived exponential equations describing release from initially open granules of SCU-31. The general form of the equation is $m_r = 1.0 - B - M \exp(-k \Delta t)$.

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Equation</th>
<th>R</th>
</tr>
</thead>
<tbody>
<tr>
<td>35W</td>
<td>$m_r = 1.0 - 0.33 - 0.20 \exp(-0.23t)$</td>
<td>-0.97</td>
</tr>
<tr>
<td>35W/5D</td>
<td>$m_r = 1.0 - 0.35 - 0.26 \exp(-0.21t)$</td>
<td>-0.98</td>
</tr>
<tr>
<td>35W/5W</td>
<td>$m_r = 1.0 - 0.33 - 0.21 \exp(-0.18t)$</td>
<td>-0.98</td>
</tr>
<tr>
<td>35D/5W</td>
<td>$m_r = 1.0 - 0.21 - 0.35 \exp(-0.21t)$</td>
<td>-0.97</td>
</tr>
<tr>
<td>5W</td>
<td>$m_r = 1.0 - 0.33 - 0.48 \exp(-0.25t)$</td>
<td>-0.99</td>
</tr>
</tbody>
</table>

Future experiments to test the validity of the theoretical model should be done using granules with small values of $A_c/\Delta x_c$.

Separate experiments should be performed to determine the size range of openings which form in coatings of initially closed granules after they are applied to the soil.
It appears from Figure 8 that the value of \( t_1 \) may be less than 2.22 days. As a limiting case, data from all five treatments were fit to a simple exponential equation (Equation 30) based on the assumption that \( t_1 \) was zero. The data fit well with Equation 30 as shown by data in Table 3.

Granules from 35W/5D, 35W, and 5W treatments were also dried at 35 C at some point during the experiment to determine the effects of drying on initially intact granules (Figures 9 and 10). The 35W/5W granules were dried once for 12 hours at 35 C on the 28th day (Figure 9), then returned to the 35W/5W treatment. Over the next 8 days, the granules released 10 percent of their urea.

The 35W and 5W treatments were changed to 35D/35W and 35D/5W treatments after 50 days (Figure 10). These new 35D/35W and 35D/5W treatments released 10 to 12 percent of their urea within 12 days after the first drying.

Granules dried rapidly in the air with low relative humidity (40 percent) inside the 35 C growth chamber. The cause of high release rates after drying at 35 C is not clear (Figures 7, 9, and 10). Some volatile components of the sealant may have evaporated, removing coverings from holes in the coatings. Evaporation of water droplets from the granule surface may have cooled wet regions relative to dry regions. Sufficient strain may have developed from temperature differentials to rupture weak regions of the shell. Finally, the rate
Figure 9. Release of urea from SCU-31 as a function of time.  
35W/5D means that granules were in water at 35 C for 12 hours, then dried in air for 12 hours during each 24 hour period. Samples were dried for 12 hours at 35 C on the 28th day, then returned to 35W/5D treatments.
Figure 10. Release of urea from SCU-31 as a function of time. Granules which spent the first 50 days in water at 5 and 35 C were changed to a different treatment on the 50th day. 35D/35W means granules were dried in air at 35 C for 12 hours and soaked in water at 35 C for the remaining 12 hours during each 24 hour period. 35D/5W means granules were dried in air at 35 C for 12 hours, then soaked in water at 5 C for 12 hours during each 24 hour period.
of crystallization of polymeric sulfur, $S_\infty$, to $S_\alpha$ may have been accelerated by the rapid drying. The resulting decrease in volume may have ruptured the coatings.

**Effects of Temperature Fluctuation.**

Release from the granules subjected to the 35W/5D treatment was nearly as rapid as those of the 35W/5W treatment although samples were out of solution for 12 hours out of each 24 hour period. Locascio, Fiskell, and Martin (1974) reported that SCU granules which were merely kept moist released urea as rapidly as granules continually immersed in water. The film of water over the granule surface allows urea to diffuse rapidly away from the opening, which implies that this portion of the diffusion pathway is not a limiting factor as long as granules are kept moist.
COATING BREAKDOWN BY MICROBES

Microorganisms colonize the surface and degrade the coatings of SCU granules at a rate which depends on the growth rate of the colony and the activity of each organism. Microbial growth rates and activities in turn are functions of type of organism, nature of the sealant or sulfur coating, soil temperature, soil water content, and soil chemical properties. As organisms degrade the sealant and sulfur, holes are eventually opened through the coating, exposing the urea to water. The urea then dissolves and diffuses out of the granule through openings into the soil.

To predict the rate at which granules are opened in soil, the rate of coating breakdown in the soil must be known. The number of organisms, $N$, present on the surface of a granule, and the average activity per organism, $A$, ($g$ substrate utilized/day/organism), determine the rate of coating breakdown according to

$$A_{tot} = NA,$$

where $A_{tot}$ is the total activity/gramule, the amount of the coating broken down on a single granule per day (g/day). Equations developed in this section allow the total activity to be calculated from soil temperature and water content data.
Microbial Population

It is assumed that a single type of organism, or several organisms with similar growth and activity characteristics, are responsible for the breakdown of both sealant and sulfur. Three models for microbial growth rate—exponential, constant radial, and simple constant—will be considered.

Model I: Exponential Growth Rate

The exponential model predicts number of organisms present at time \( t \) according to the equation

\[
N = N_0 \exp(kt), 
\]

(33)

where

\[
N = \text{number of organisms at time } t, \\
N_0 = \text{number of organisms at time } t = 0, \\
k = \text{growth rate constant (1/day),} \\
t = \text{time (days)}. 
\]

This growth function is most frequently observed for microbes growing in solution with no factors limiting growth. The period of exponential growth is usually short for colonies growing on surfaces such as nutrient agar media (Pirt, 1967).
Model II: Constant Radial Growth Rate

The linear model for colony growth is as follows:

\[ r = \frac{K}{g} t + r_0, \]  \hspace{1cm} (34)

where

- \( r \) = radius of colony at time \( t \) (mm),
- \( r_0 \) = radius of colony at time \( t = 0 \) (mm),
- \( K \) = growth constant (mm/day), and
- \( t \) = time (days).

This equation can be changed to predict the number of organisms by assuming a constant number of organisms \( D_0 \) per unit area \( A \), or

\[ N = D_0 A. \]  \hspace{1cm} (35)

To obtain an expression for \( N \) in terms of time, we first set

\[ A = \pi r^2, \]  \hspace{1cm} (36)

and then calculate \( A \) as a function of time. Substituting the expression given by Equation 34 for \( r \) yields

\[ A = \pi \left( \frac{K}{g} t + r_0 \right)^2. \]  \hspace{1cm} (37)

Finally, substituting for \( A \) in Equation 35 yields
When the initial number of organisms is assumed negligible compared to the number of time \( t \), \( r_0 \) is very small, and the equation reduces to

\[
N = \pi D_0 (K^2 t^2 + K t r_0 + r_0^2) .
\]  

Substituting the constant \( K' \) for \( \pi D_0 K_0^2 \), we obtain

\[
N = \pi D_0 K' t^2 .
\]  

Model III: Constant Growth Rate

One may imagine that growth of organisms on the granule surface may be limited by a mineral nutrient required for growth. In this instance the maximum growth rate is set by the rate at which the nutrient can diffuse to the granule surface. For example, Giordano and Mortvedt (1970) found that release of urea from SCU was accelerated by adding phosphorus to the soil. The phosphorus may diffuse to the granule surface at a constant rate, and this would result in a constant rate of growth of the microbial colony. This rate is expressed by the relationship:

\[
N = K_c t + N_0 ,
\]  

\[
N = \pi D_0 (K^2 t^2 + K t r_0 + r_0^2) .
\]
where $K_c$ is a constant (organism/day) and the other terms are defined above.

Growth Coefficients

The coefficients $k$, $K$, and $K_c$ are functions of temperature, water content, nutrient status, organism type, and substrate type. Their numerical values may be obtained by first choosing a maximum value for a given organism and substrate which is only attained at optimum temperature and water content conditions. This maximum, e.g., $K_{g,\text{max}}$, is corrected for temperature and water content as follows

$$K_g = K_{g,\text{max}} f(T) g(\psi), \quad (42)$$

where

$f(T) = \text{correction function for effects of temperature on growth},$

$g(\psi) = \text{correction function for effects of water content on growth}.$

As an example, the growth constant $K_g$ will be determined and the correction function for sub-optimal soil temperature and water content will be derived. It will be assumed that $K_g$ will have its maximum value, $K_{g,\text{max}}$, at the temperature of 35 C and the soil water potential of -0.3 bar. Assume that with water content constant,
$K_{g,25 \, C}$ is equal in value to $0.5 \, K_{g, \, \text{max}}$. Also assume that at constant temperature, $K_{g, -10 \, \text{b}}$ is equal to $0.25 \, K_{g, \, \text{max}}$. So $f(T)$ at $25 \, \text{C}$ is $0.5$, and $g\,(\psi)$ at $-10 \, \text{bars}$ is $0.25$. The growth rate constant observed under these conditions is

$$K_{g, \, 25 \, \text{C}, -10\, \text{b}} = (0.50)(0.25)K_{g, \, \text{max}} = 0.125 \, K_{g, \, \text{max}}.$$ 

**Maximum Growth Rate.** Values of $K_{g, \, \text{max}}$ used in the model will be based on literature data and experimental data reported in the thesis.

**Soil Temperature.** Johnson, Eyring and Polissar (1954) derived Equation 43 for the relative doubling time $t_d \ (0 < t_d < 1)$ as a function of temperature for *Escherichia coli*. The doubling time is the period of time required for a population of organisms to double in numbers. Their derivation was based on thermodynamic considerations.

$$t_d = \frac{0.003612T \exp(24.04-7500/T)}{1 + \exp(238-75000/T)}, \quad (43)$$

where $T$ is Kelvin temperature. Figure 11 shows the relationship between $t_d$ and temperature. As temperature increases the relative doubling time $t_d$ reaches a maximum value of $1.00$ at $39 \, \text{C}$, then decreases abruptly. An equation of this type is generally applicable to most organisms. The equation will be used to calculate the
Figure 11. Effect of temperature on doubling time of an *E. coli* population (from Johnson, Eyring, and Polissar, 1954).
temperature proportionality constant for growth. The optimum temperature can be adjusted depending upon the organism considered. For purposes of this discussion the correction function for temperature, \( f(T) \), will be assumed to be given by Equation 43, so that

\[
K_g = K_{g, \text{max}} \left( \frac{0.003612 T \exp(24.04 - 7500/T)}{1 + \exp(238 - 75000/T)} \right) g(\psi). \tag{44}
\]

**Soil Water Content.** Relations between soil water content and microbial growth are difficult to analyze theoretically. Hattori (1973) derived relative rates of sulfur oxidation by soil microorganisms as a function of soil water potential (Figure 12), using data from Moser and Olsen (1953). Analysis of this relationship yields the following equations:

\[
-0.10 < \psi \leq -0.001 \quad g(\psi) = 0.435 \ln(-\psi) + 2.00, \tag{45}
\]

\[
-1.0 \leq \psi \leq -0.10 \quad g(\psi) = 1.00, \tag{46}
\]

\[
-30. \leq \psi \leq -1.0 \quad g(\psi) = -0.294 \ln(-\psi) + 1.00, \tag{47}
\]

where \( \psi = \) soil water potential.

No distinction was made between effects of soil water content on growth as opposed to activity. These equations are assumed to apply to both growth and activity correction coefficients.

Organism numbers may decrease as conditions for growth become unfavorable. Starvation, water content, and temperature...
Figure 12. Relationship between organism activity or organism growth rate and soil water potential (after Hattori, 1973, p. 307).
extremes can kill organisms. Chen and Alexander (1973) measured survival of organisms in media at various water activities \( (a_w) \). The minimal \( a_w \) which allow organisms to grow ranged from 0.880 (analogous to -170 bars) to 0.985 (-20 bars). Organisms in soil over CaCl2 died at different rates, but most had decreased in numbers by 60 to 70 percent in the course of five days. The shape of these dying curves is roughly that of exponential decay. Death rates may be calculated by assuming that growth ceases at -30 bars and death begins at this potential. The rate at which organisms die will be assumed to be proportional to \( \ln(a_w) \) and to the number of organisms present, \( N \), so that

\[
\frac{dN}{dt} = -K_d \ln(a_w)N ,
\]

where

\[
\frac{dN}{dt} = \text{rate at which organism numbers decrease} \quad \text{(organisms/day)},
\]

\( K_d \) = death rate constant (1/day), and

\( a_w \) = activity of water.

The potential of water in the soil, \( \psi \), is related to the activity of water as follows (Nobel, 1974),

\[
\psi = \frac{RT}{V_w} \ln a_w ,
\]

or
where

\[ \frac{\psi V_w}{RT} = \ln a_w , \]  \hspace{1cm} (49) \]

where

\( R = \) universal gas constant (0.082 l-atm/mole-degs),

\( T = \) absolute temperature (degrees Kelvin), and

\( V_w = \) molar volume of water (18 cm\(^3\)/mole).

When the expression for \( \ln(a_w) \) from Equation 49 is substituted into Equation 48 it becomes

\[ \frac{dN}{dt} = -K_d \left( \frac{\psi V_w}{RT} \right) N . \]  \hspace{1cm} (50) \]

To calculate the decrease in organism numbers during time \( t \), Equation 50 is rearranged and integrated between appropriate limits,

\[ \int_{N_0}^{N_1} \frac{dN}{N} = -K_d \left( \frac{\psi V_w}{RT} \right) \int_0^{t_1} dt , \]

\[ \ln(N_1/N_0) = -K_d \left( \frac{\psi V_w}{RT} \right) t_1 , \]  \hspace{1cm} (51) \]

where

\( N_0 = \) number of organisms alive at time \( t = 0 \),

\( N_1 = \) number of organisms alive at time \( t = t_1 \),

\( t_1 = \) time (days).
The exponentials of both sides of Equation 51 are taken to put it in a more convenient form,

\[ \frac{N_1}{N_0} = \exp(K_d \frac{w}{RT} t_1) , \]

or

\[ N_1 = N_0 \exp(K_d \frac{w}{RT} t_1) . \]  

(52)

**Microbial Activity**

The rate of microbial activity in grams of substrate consumed per day is calculated like the growth rate constant. The activity \( A \) of a single organism on a given day is found by correcting the maximum activity rate \( A_{\text{max}} \) for temperature and soil water content, as follows:

\[ A = A_{\text{max}} f_a(T) g_a(\psi) . \]  

(53)

**Maximum Activity Rate.** Rates of SCU coating breakdown by microorganisms have not been measured as a function of soil temperature and soil water content. Values for later use were selected from a range of activities of organisms utilizing similar substrates.

**Soil Temperature.** The temperature correction coefficient can be derived from the Arrhenius equation,

\[ f_a(T) = A \exp(\Delta E_A / RT) , \]  

(54)
where

\[ f_a(T) = \text{relative rate constant}, \quad 0 \leq f_a(T) \leq 1, \]

\[ A = \text{constant}, \]

\[ \Delta E_A = \text{activation energy for rate-limiting reaction in organisms} \]

\[ \text{(cal/mole)}, \]

\[ R = \text{gas constant (1.98 cal/mole-deg)}, \] and

\[ T = \text{absolute temperature (degrees Kelvin)}. \]

The temperature correction coefficient \( f_a(T) \) is the relative activity rate, with a maximum value of 1.0 at the optimum temperature for optimum activity. Most biological processes double in rate with each temperature increase of 10 C over the temperature range of 5 to 35 C. By assigning \( f_a(T) \) a value of 1.0 at 35 C and 0.125 at 5 C, the constant terms \( A \) and \( \Delta E_A/R \) can be evaluated. This analysis gives

\[ A = 2.34 \times 10^8, \]

and

\[ \Delta E_A/R = 5.94 \times 10^3 \quad \text{degrees Kelvin}. \]

Equation 54 then becomes

\[ f_a(T) = (2.34 \times 10^8) \exp\left(\frac{5.94 \times 10^3}{T}\right). \]
Soil Water Content. The relationships shown in Figure 12 and Equations 45, 46, and 47 will be used to calculate the water content correction coefficient.

Summary

When values are chosen for $K_{g, \text{max}}$ and $A_{\text{max}}$, rates of microbial growth and activity may be calculated for any temperature or soil water content. The rate of coating breakdown can thus be calculated. It is then necessary to know the relationship between the amount of coating removed and the percentage of granules opened. This relationship is expected to be different for different SCU products. The next section describes a test which provides a means of predicting the percentage of granules which are opened as the coating is broken down.
COATING THICKNESS AND UNIFORMITY

Introduction

As noted earlier, current laboratory methods for characterizing SCU only measure release of urea from broken and poorly formed granules (Lunt, 1968). Results of experiments in which the release in solution was measured indicate that a large fraction of the urea is retained indefinitely in intact granules. Short term release can be predicted, but long term breakdown remains difficult to predict. The distribution of coating thicknesses and uniformity among intact granules must be known.

A procedure was developed to characterize the coatings of SCU materials. In this procedure portions of the coating are removed with an organic solvent. Coating thickness varies over the surface of the granule. As the coating is gradually removed, regions where the coating is thinnest are opened first. The minimum amount of coating material which must be removed to expose the urea of a granule to solution will serve as a measure of that granule's resistance to breakdown. The relationship between the amount of coating removed and the number of granules opened will be expressed by an equation derived from experimental data. This equation has the general form

$$G_o = f(C_{BD})$$

(56)
where
\[ G_o = \text{fraction of granules which have opened, and} \]
\[ C_{BD} = \text{amount of coating material which has been removed from granules.} \]

**Materials and Methods**

Experiments were designed to characterize coating uniformity and thicknesses of five SCU materials, SCU-4, SCU-10, SCU-20, SCU-30, and SCU-23. These products had a range of coating characteristics described in Appendix 1.

A non-polar solvent was required to dissolve sealant materials as well as the sulfur. Reagent grade benzene was chosen because coating materials are sparingly soluble in it, and the dissolution rate is slow enough to allow gradual removal of the coating.

Samples were exposed to benzene for periods of time which varied in length to remove different portions of the granule coatings. After exposure to benzene, the rate of urea release from the exposed granules was measured in distilled water.

The samples were contained in polyethylene cylinders. These were prepared by removing the bottoms from vials and placing nylon screens on both ends. Twenty gram samples of SCU were placed in each vial thus prepared. Twenty-one vials were attached to the apparatus shown in Figure 13. Using this instrument, samples could
Figure 13. Apparatus for treatment of SCU granules with benzene at constant temperature. A is an electric motor, B is a pulley which turns at 18 rpm, C is a vial containing granules, D is a sample solution container, E is a controlled temperature water bath, F is a warm water reservoir, G is the temperature controller, H is a water pump, and I is a siphon tube.
be dipped into benzene or into distilled water at the rate of 18 times per minute. Samples were dipped to be sure that high urea concentrations did not build up around the granules. Dipping guaranteed that urea concentrations at the surface of each open granule stayed low relative to urea concentrations within the granule.

The time course of the experiment is illustrated in Figure 14. Treatments were replicated three times. All samples were first dipped in 100 ml of distilled water for 24 hours to remove most of the urea from broken and open granules. Then all samples were dipped in 100 ml benzene for periods of time as shown in Table 4, with the exception of three control samples. Control samples were never exposed to benzene, but received the same distilled water treatments as the benzene-treated granules. After exposure to benzene, samples were dipped in distilled water. Solutions were changed after 3, 27, 39, 51, and 63 hours. At this point, each sample was again exposed to benzene for the same period of time as it was during the first exposure. Following the second exposure to benzene, samples were again dipped in distilled water. Solutions were changed 3, 27, 39, 51, and 63 hours after the second dipping.

The amount of coating removed was determined by evaporating 20 ml of the original 100 ml of benzene to dryness and weighing the residue. Urea concentrations in the rinse water were determined using the method of Watt and Chrisp (1953).
Figure 14. Time course of experiments to characterize coating thickness and uniformity of coating thickness for a given SCU material. Arrows indicate when distilled water solutions were changed. DW indicates dipping in distilled water and B indicates dipping in benzene.
Table 4. Benzene treatments for removal of portions of coatings from five SCU materials. Average exposure time is the period between first contact with benzene and the initiation of rinsing. About 30 seconds elapsed between the last dip in benzene and the initiation of rinsing.

<table>
<thead>
<tr>
<th>Treatment Number</th>
<th>Number of Dips</th>
<th>Average Time of Exposure</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>3</td>
<td>40</td>
</tr>
<tr>
<td>3</td>
<td>6</td>
<td>55</td>
</tr>
<tr>
<td>4</td>
<td>16</td>
<td>75</td>
</tr>
<tr>
<td>5</td>
<td>30</td>
<td>135</td>
</tr>
<tr>
<td>6</td>
<td>60</td>
<td>240</td>
</tr>
<tr>
<td>7</td>
<td>90</td>
<td>315</td>
</tr>
</tbody>
</table>

Results and Discussion

This study was designed to determine the relationship between the amount of coating removed and the fraction of granules which subsequently released its urea. Cumulative release of urea from all materials tested approached a maximum value with time as shown in Figure 15 for SCU-10. Equation 30 was fitted to the data using the method discussed in the section describing release in aqueous solutions,

$$m_r = 1.0 - B - M \exp(-k_2t).$$  \hspace{1cm} (30)

A computer program was written to select the value of \( B \) for each treatment which gave the largest correlation coefficient. The value of \((1.0-B)\) for a given treatment was then designated as the fraction of
Figure 15. Cumulative release of urea from benzene-treated SCU-10. The number by each curve indicates the duration of exposure to benzene in seconds during each treatment (Table 4).
granules opened following that treatment.

For each benzene treatment, the fraction of granules open after treatment was plotted as a function of the amount of coating material removed by the benzene. Untreated samples each produced only one point, namely the amount of urea released in distilled water. Treated samples each produced two points, one from the first and one from the second treatment. The sum of the amounts of coating removed from granules in the first and second benzene treatments was used to calculate total coating loss after the second treatment. Figure 16 is a graph of these points for a material containing a sealant (SCU-10), and Figure 17 is the graph for a product coated only with sulfur (SCU-23).

The relationship between the amount of coating removed and number of open granules, as shown in Figure 16 for SCU-10, was also obtained for SCU-4, SCU-20, and SCU-30, all of which were coated with sealant (Figure 18). Data from SCU-23 did not fit this relationship (Figure 17). This suggests that SCU products which have a sealant applied over the sulfur coating are composed of three classes of granules. Percentages of granules in each class will be given for SCU-10 (Figure 16).

Class 1: Granules with openings through their coatings which are initially open and release urea immediately. The rate of release
Figure 16. Percentage of granules as a function of amount of coating removed from SCU-10.
Figure 17. Percentage of granules open as a function of amount of coating removed from SCU-23.
Figure 18. Percentage of granules open as a function of the amount of coating removed from five SCU products.
is governed by diffusion conditions. For SCU-10, about 21 percent of the granules were initially open.

**Class 2:** Granules with openings through their sulfur coatings which are closed by sealant. Portions of the sealant coatings on granules must be removed to expose openings in the sulfur shell. Water then enters the granule, dissolves the urea, and urea diffuses out of the granule. For SCU-10, about 60 percent of the granules were in this class.

**Class 3:** Granules which have no holes in the sulfur coatings. A portion of the sulfur must be removed before holes open in the thinnest part of the shell and urea is exposed to water. Because the sulfur coating is generally thicker than the sealant coating, the rate at which the contents of new granules becomes exposed is slow. Nineteen percent of the SCU-10 granules were in this class.

A linear equation was fitted to each part of the coating characteristic curves (Figure 18). Equations for these lines and correlation coefficients are given in Table 5.

SCU-23 contains no sealant and thus is expected to have only Class 1 and Class 3 granules. From Table 5 it is apparent that the slope of the coating characteristic equation for SCU-23 is similar to the slopes of curves for Class 3 granules from the other SCU products.
If the rate at which coating is removed by microorganisms is known, the rate at which granules are opened can be calculated from the coating characteristic equations.

Table 5. Regression equations and correlation coefficients for coating characteristic curves of five SCU products. x is the amount of coating removed (g/100 g SCU).

<table>
<thead>
<tr>
<th>Material</th>
<th>Sulfur</th>
<th>Class 2</th>
<th>R</th>
<th>Class 3</th>
<th>R</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>%</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SCU-4</td>
<td>18.5</td>
<td>17.7 + 12.5x</td>
<td>0.96*</td>
<td>47.0 + 5.6x</td>
<td>0.98*</td>
</tr>
<tr>
<td>SCU-10</td>
<td>15.5</td>
<td>21.7 + 19.7x</td>
<td>0.92*</td>
<td>76.4 + 2.5x</td>
<td>0.82*</td>
</tr>
<tr>
<td>SCU-20</td>
<td>19.5</td>
<td>31.6 + 27.0x</td>
<td>0.87*</td>
<td>58.0 + 5.4x</td>
<td>0.90*</td>
</tr>
<tr>
<td>SCU-30</td>
<td>15.0</td>
<td>39.5 + 21.3x</td>
<td>0.89*</td>
<td>60.3 + 7.2x</td>
<td>0.91*</td>
</tr>
<tr>
<td>SCU-23</td>
<td>25.0</td>
<td></td>
<td></td>
<td>29.0 + 5.8x</td>
<td>0.97*</td>
</tr>
</tbody>
</table>
RELEASE OF UREA FROM SCU GRANULES IN SOIL

The effects of temperature and soil water content on the release of urea from SCU have been reported in the literature (e.g., Oertli, 1973; Prasad, 1976). However, these studies contain little information about the coating characteristics of the materials used. Data are needed which quantify effects of soil temperature and soil water content on the release of urea from SCU granules as a function of time after coating thicknesses have been characterized.

Release of urea from SCU granules as a function of time was measured in two experiments, labelled A and B. In Experiment A, SCU granules were applied to the soil surface in low density. Soil temperature and water content were constant. In Experiment B, soil was limed and the granules were sprayed regularly with distilled water. Granules were rinsed to keep urea concentrations low at the granule surfaces. The temperature of the soil was maintained constant.

Materials and Methods

Experiment A

A ring of polyvinyl chloride (PVC) pipe, with an inside diameter of 25 cm and a height of 4 cm, was glued to a plywood square 30 cm x 30 cm to form the soil container. A circle of black
polyethylene plastic was sealed to the plywood inside the ring to make the container water-tight.

For temperature and water content experiments, 500 g of air-dried Woodburn silt loam soil, ground to pass a 2 mm screen, were placed in the container. The Woodburn soil is classified as an Aquultic Argixeroll. Chemical characteristics of the Woodburn silt loam are listed in Table 6.

Table 6. Soil analysis of Woodburn silt loam soil. Sample was taken from 0-20 cm depth increment.

<table>
<thead>
<tr>
<th>pH</th>
<th>Exchangeable Cations (meq/100 g)</th>
<th>Cation Exchange Capacity (meq/100 g)</th>
<th>Organic Matter (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.0</td>
<td>Ca 8.7 Mg 1.2 K 0.63</td>
<td>15.2</td>
<td>2.7</td>
</tr>
</tbody>
</table>

The samples were maintained at temperatures of 5, 15, 25, and 35 C by placing them in a growth chamber. Water content treatments for SCU-4 corresponded to soil water potentials of -0.3 and -15 bars. The -0.3 bar treatments were brought to a water content of 32 percent (w/w) by adding water to the soil surface. The -15 bar soils were brought to a water content of 14 percent (w/w) by first wetting the soil until it contained about 30 percent water, then allowing the soil to dry to the desired water content, determined by weighing the samples. The soil was reground, sieved, and returned to the columns. Water
content was checked regularly in all treatments by weighing the columns, and water was added where losses were greater than 15 ml per column.

SCU-4 granules were evenly distributed over the moist soil surface at a rate equivalent to 100 kg N/ha. The number of granules added per column was determined during application. Containers were covered with aluminum foil and placed in large polyethylene bags to minimize water loss. The plastic was more permeable to oxygen than to water vapor, allowing the internal atmosphere to remain aerobic while keeping evaporation losses low.

Three columns were sacrificed for each treatment after incubation periods ranging in length from 2 to 126 days. Intervals between samplings were chosen to best describe the time course of release. At sampling time, granules were removed by hand and intact granules were counted. Granules which were easily crushed with forceps and found to be only partially filled with solid urea were counted separately from those which were completely intact. All recovered granules were crushed in a solution containing 50 µg PMA and allowed to dissolve overnight. Coatings were spun down in centrifuge tubes and the supernatant was decanted into 100 ml volumetric flasks. The extraction was repeated twice with distilled water. Urea concentration in the extract was measured using the method of Watt and Chrisp (1953). The amount of urea released to the soil was
calculated as the difference between the amount of urea added in the SCU and the amount recovered from the granules. The number of granules open on the soil surface was obtained as a percentage of the number originally added. It was found that amounts of release as calculated by the two methods agreed well. Therefore, only granule counts were taken in later samplings.

The pH of about 25 g of soil from sacrificed treatments was measured after granules were removed. Soil was saturated with distilled water and stirred thoroughly. Soil pH was determined 30 minutes later using a pH meter with a glass electrode.

Experiment B

Air-dried Woodburn silt loam soil (Table 6), ground to pass a 2 mm sieve, was mixed with reagent grade \( \text{CaCO}_3 \) at a rate equivalent to 9.1 metric tons/ha. Two hundred grams of limed soil were spread over a square sponge 10 cm x 10 cm x 2 cm, placed in the bottom of a square plastic pot 10 cm x 10 cm x 15 cm. The soil formed a layer about 1 cm deep over the sponge. The sponge allowed water to evaporate slowly through drainage holes in the pot, bringing some of the nitrogen products out of the soil. Oxygen could diffuse through large air spaces in the sponge, maintaining good aeration throughout the soil.
The equivalent of 300 kg N/ha (0.432 g N/pot) as SCU was distributed over the soil surface in each pot. Four materials, described in Appendix I, namely, SCU-4, SCU-20, SCU-30, and SCU-23, were applied in separate experiments. A light mist of distilled water was sprayed over the granules every 48 hours to rinse away urea from granule surfaces and to replace soil water lost by evaporation. Although soil water content varied, it remained within the range equivalent to -0.1 to -1.0 bar soil water potential, with an average of -0.3 bar. This range was assumed to be optimal for microbial growth and activity (Equation 46). Openings of pots were covered with plastic to reduce evaporation from the soil surface. Fresh air circulated through the air space in the pot when plastic coverings were removed for water applications.

Four replicate samples were taken after different time intervals to determine the amount of urea remaining inside the granules. Granule recovery and urea analysis techniques were the same as those used in Experiment A. The urea released as a function of time was assessed by urea analysis only. Granules were not counted. Soil pH was determined as in Experiment A.
Results and Discussion

Soil Water Content

Release of urea from SCU-4 was the same at both soil water contents tested during the first 30 to 40 days in Experiment A (Figure 19). The amounts released in soil at -0.3 and -15 bar were nearly identical up to 30 days after application. Since the initial release consists mostly of diffusion out of granules which are initially open, these results indicate that soil water potential had little effect on the rate at which urea diffuses out of these open granules. SCU-4 on soil at -0.3 bar soil water potential began to release urea after about 40 days, indicating that granules were beginning to open. No urea was released from SCU-4 on soil at -15 bars soil water potential between the 10th and 100th days. Rates of microbial growth and activity in the soil at -15 bars were too low to open holes in granule coating during the first 100 days.

Soil Temperature

Experiment A. Soil temperature affected both the amount of urea released during the first ten days, and the rate of release over longer periods of time (Figure 20). At 35 C, release reached a temporary maximum at about 14 percent released. Between the 30th and 45th days, SCU-4 at 35 C began to release urea, indicating that
Figure 19. Release of urea from SCU-4 as a function of time in unlimed soil at 35 C. Soil water potentials were -0.3 and -15 bar.
holes were being opened in the coatings. At 25 C, coatings were not opened until after the 70th day. Coatings of intact granules at 5 and 15 C were not opened during the course of the experiment.

Microbial activity at 5 and 15 C was too low to open coatings of intact granules during the first 100 days.

Experiment B. The rate of release of urea from SCU-4, SCU-20, and SCU-30 was affected by soil temperature (Figures 21, 22, and 23 respectively). The sulfur coatings of these three materials were all coated with sealant. The sealant appears to break down more rapidly at 35 C than at 25 C, so granules are opened more rapidly at the higher temperature.

In contrast, the release of urea as a function of time from SCU-23, which had no sealant coating, was no affected by temperature (Figure 24). Organisms which oxidize sulfur may have a lower temperature optimum for growth and activity than organisms which attack the sealant. If the temperature optimum for sulfur oxidation by organisms were 30 C, for example, rates of oxidation at 25 and 35 C may be nearly equal. Alternatively, the sulfur shell may be broken down by chemical or physical mechanisms which are only slightly sensitive to temperature.
Figure 20. Release of urea from SCU-4 as a function of time at 5, 15, 25, and 35°C. Soil water potential was -0.3 bar.

Figure 21. Release of urea from SCU-4 as a function of time on limed soil maintained at 25 and 35°C. Average soil water potential was -0.3 bar.
Figure 22. Release of urea from SCU-20 as a function of time on limed soil maintained at 25 and 35 C. Average soil water potential was -0.3 bar.

Figure 23. Release of urea from SCU-30 as a function of time on limed soil maintained at 25 and 35 C. Average soil water potential was -0.3 bar.
Coating Characteristics

The test of coating effectiveness developed by TVA is generally used to predict rates of release from different SCU products as a function of time. Coating characteristics had a marked effect on amounts of urea released over time (Figures 25 and 26). At 25 °C, the TVA test accurately predicted the relative amounts of urea released from the four products after 15 days (Figure 25). Between the 15th and 71st days, average rates of release from SCU-4, SCU-20, and SCU-30 were 0.57, 0.45, and 0.41 percent per day respectively. Results of the TVA test did not accurately predict relative release rates after the 15th day at 25 °C.

Similar results were found for release over time at 35 °C (Figure 26). Between the 7th and 64th days at 35 °C, SCU-4 released urea at an average rate of 1.03 percent per day (Figure 26). During this same period, release from SCU-20 averaged 0.93 percent per day and from SCU-30, 0.83 percent per day. At the end of 64 days, similar amounts of urea had been released from SCU-4, SCU-20, and SCU-30. Apparently the coatings on SCU-4 granules were broken down more rapidly than coatings on SCU-20 granules. Microbes which attack the microcrystalline wax on SCU-4 may break down the wax more rapidly than other organisms can oxidize the polyethylene-oil sealant.
Figure 24. Release of urea from SCU-23 as a function of time on limed soil maintained at 25 and 35 C. Average soil water potential was -0.3 bar.

Figure 25. Release of urea from four SCU materials as a function of time at 25 C in limed soil. Average soil water potential was -0.3 bar.
Figure 26. Release of urea from four SCU materials as a function of time at 35 C in limed soil. Average soil water potential was -0.3 bar.
Between the first and last sampling dates, SCU-23 released less urea than any of the other materials (Figures 25 and 26).

Organisms which utilize sulfur may be growing more slowly than those which utilize sealant. Also, the sulfur coating was thicker than the sealant coating, so that even at equal rates of activity, a greater period of time would be required to open SCU-23 granules than would be required to open sealant-coated granules.

Soil pH

Application of lime accelerated the rate of release of urea from SCU-4 (Figure 27). As Figure 28 indicates, soil pH remained higher in limed soil than in unlimed soil. Apparently the higher pH stimulated the activity of microorganisms and accelerated the rate of coating breakdown.

Summary

SCU-4 released urea at a faster rate in soil at -0.3 bar soil water potential than in soil at -15 bar soil water potential. SCU-4, SCU-20, and SCU-30 released more urea at 35 C than at 25 C, while SCU-23 did not. The sealant coating appears to be more sensitive to temperature than the sulfur coating. Mixing lime with the soil caused SCU-4 to release urea more rapidly than it did on unlimed soil.
Figure 27. Release of urea from SCU-4 as a function of time at 35 °C on limed and unlimed soil. Average soil water potential was -0.3 bar in both soils.

Figure 28. Soil pH as a function of time in limed and unlimed soils. Temperature was 35 °C and average soil water potential was -0.3 bar in both soils.
These data are quantitative measurements of the effects of temperature, soil water content, and coating characteristics. The following section uses this information to construct and test a model which predicts the release of urea from SCU as a function of time.


Computations have been developed in previous sections which will be used to construct a mathematical model. This model predicts the release of urea as a function of time from a given SCU product.

To manipulate the equations in the model, a computer program was written which uses the equations to calculate release of urea over time. Figure 29 is a flowchart of the computer program. The program was written in FORTRAN IV to be run on a CDC 3300 computer. For each day the material is on the soil, values of coefficients in the equations are corrected for soil temperature and soil water content. Then the amount of coating which will break down each day is calculated. Using the coating characteristic curves, the percentage of the granules which will open each day is then calculated. Finally, the amount of urea which will diffuse out of open granules into the soil is predicted for each day. Table 7 summarizes these calculations.

The percentage of granules which are initially open (Class 1 granules) for a given product is given by the value of the y-intercept of the coating characteristic curve for that material (Table 5). To calculate predicted release in the following discussion, this value has been slightly adjusted so that predicted and measured amounts of initial release are approximately equal. The magnitude of these changes is generally within the error of the measured points (±3
Figure 29. Flowchart of computer program which predicts release of urea from a given SCU product as a function of time. The quantities listed under each subroutine are calculated for each day.
Table 7. Summary of operations performed by the computer program. All terms in the output column are calculated for each day granules are on the soil.

<table>
<thead>
<tr>
<th>Input</th>
<th>Equation Number</th>
<th>Output</th>
</tr>
</thead>
<tbody>
<tr>
<td>MAINLINE</td>
<td>26</td>
<td>Diffusion coefficient</td>
</tr>
<tr>
<td></td>
<td>27</td>
<td>Urea solubility</td>
</tr>
<tr>
<td></td>
<td>43</td>
<td>Growth rate correction coefficient</td>
</tr>
<tr>
<td></td>
<td>55</td>
<td>Activity rate correction coefficient</td>
</tr>
<tr>
<td></td>
<td>26</td>
<td>Daily temperature maxima and minima</td>
</tr>
<tr>
<td></td>
<td>27</td>
<td>Daily soil water content and water potential</td>
</tr>
<tr>
<td></td>
<td>43</td>
<td>Maximum rates of growth and activity</td>
</tr>
<tr>
<td></td>
<td>55</td>
<td>Geometry term for openings</td>
</tr>
<tr>
<td></td>
<td>45, 46</td>
<td>Characteristics of specific SCU product</td>
</tr>
<tr>
<td>TEMPER</td>
<td>42</td>
<td>Growth and activity maximum rates</td>
</tr>
<tr>
<td></td>
<td>42</td>
<td>Temperature and water content correction</td>
</tr>
<tr>
<td>SOLH2O</td>
<td>45, 46</td>
<td>Growth rate correction coefficient</td>
</tr>
<tr>
<td></td>
<td>47</td>
<td>Temperature and water content correction</td>
</tr>
<tr>
<td></td>
<td>47</td>
<td>Growth rate correction coefficient</td>
</tr>
<tr>
<td>BDCOAT</td>
<td>42</td>
<td>Activity rate correction coefficient</td>
</tr>
<tr>
<td></td>
<td>53</td>
<td>Organism numbers</td>
</tr>
<tr>
<td></td>
<td>32</td>
<td>Organism activity</td>
</tr>
<tr>
<td>RELEASE</td>
<td>32</td>
<td>Coating loss</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>Number of granules opened</td>
</tr>
<tr>
<td></td>
<td>17</td>
<td>Urea loss from granules still in linear release stage</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Urea loss from granules in exponential release stage</td>
</tr>
</tbody>
</table>
percentage points). These small changes have no practical significance in terms of SCU performance in the field. By making these minor initial adjustments, predicted amounts of cumulative release as a function of time are more easily compared with measured cumulative release over time.

The values of $K_{g, \text{max}}$ and $A_{\text{max}}$ have not been determined experimentally. Various combinations of $K_{g, \text{max}}$ and $A_{\text{max}}$ were used to fit predicted release to release measured in soil as a function of time. The values of $K_{g, \text{max}}$ and $A_{\text{max}}$ which give the best fit at 35 C and -0.3 bar were used to predict release at other temperatures and soil water contents. Amounts of release predicted by the model as a function of time were compared with amounts of release from SCU granules on soil as described in the previous section (Tables 8, 9, and 10). The agreement between predicted and measured release was a test of the ability of the model to respond to changes in soil temperature and soil water content.

**Soil Water Content**

The values of $K_{g, \text{max}}$ and $A_{\text{max}}$ derived for SCU-4 in Experiment A predict that little release will occur in soil at a temperature of 35 C and a soil water potential of -0.3 bar over a period of 100 days (Figure 30 and Table 8). Eventually, as the population of microbes on the granule surface increases, enough material may be
Figure 30. Predicted release over time (solid lines) and measured release over time (data points) from SCU-4 on soil at two different soil water potentials. Soil temperature was 35 C.
Table 8. Comparison of measured release with predicted release of urea from SCU-4 as a function of time. $K_{g, \text{max}}$ is 0.04 mm/day, $A_{\text{max}}$ is $1.0 \times 10^{-12}$ g/day, and $A_c/\Delta x_c$ is 0.0005 cm. Soil was not limed.

<table>
<thead>
<tr>
<th>Soil Temperature</th>
<th>Soil Water Potential</th>
<th>Length of Time on Soil</th>
<th>Average Release and Standard Deviation</th>
<th>Predicted Release</th>
</tr>
</thead>
<tbody>
<tr>
<td>°C</td>
<td>bars</td>
<td>days</td>
<td>%</td>
<td>%</td>
</tr>
<tr>
<td>35</td>
<td>- 0.3</td>
<td>2</td>
<td>4.2 ± 0.1</td>
<td>14.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10</td>
<td>14.2 ± 0.9</td>
<td>14.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>25</td>
<td>13.1 ± 4.1</td>
<td>15.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>45</td>
<td>21.2 ± 5.8</td>
<td>19.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>90</td>
<td>35.2 ± 7.6</td>
<td>38.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>100</td>
<td>57.8 ± 8.0</td>
<td>63.9</td>
</tr>
<tr>
<td>35</td>
<td>-15.0</td>
<td>2</td>
<td>5.9 ± 1.0</td>
<td>14.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10</td>
<td>12.5 ± 2.7</td>
<td>14.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>25</td>
<td>14.8 ± 2.1</td>
<td>14.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>45</td>
<td>18.2 ± 6.4</td>
<td>15.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>70</td>
<td>17.6 ± 3.6</td>
<td>16.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>100</td>
<td>19.1 ± 6.4</td>
<td>21.3</td>
</tr>
<tr>
<td>25</td>
<td>- 0.3</td>
<td>9</td>
<td>9.2 ± 2.0</td>
<td>14.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>21</td>
<td>16.7 ± 1.2</td>
<td>14.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>49</td>
<td>13.7 ± 3.2</td>
<td>15.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>70</td>
<td>11.3 ± 4.5</td>
<td>17.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>91</td>
<td>24.3 ± 6.4</td>
<td>21.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>126</td>
<td>40.7 ± 1.2</td>
<td>37.7</td>
</tr>
<tr>
<td>15</td>
<td>- 0.3</td>
<td>20</td>
<td>8.0 ± 1.0</td>
<td>14.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>41</td>
<td>10.2 ± 3.8</td>
<td>14.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>60</td>
<td>7.0 ± 4.0</td>
<td>14.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>82</td>
<td>11.8 ± 1.0</td>
<td>14.7</td>
</tr>
<tr>
<td>5</td>
<td>- 0.3</td>
<td>5</td>
<td>6.7 ± 1.2</td>
<td>14.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>42</td>
<td>10.7 ± 2.2</td>
<td>14.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>60</td>
<td>10.1 ± 1.0</td>
<td>14.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>90</td>
<td>8.8 ± 2.6</td>
<td>14.7</td>
</tr>
</tbody>
</table>
removed so that holes are opened in the coatings on the drier soil.
Release of urea from SCU should be studied over a greater variety of soil water contents to more accurately determine the functions which relate the rate of coating breakdown to soil water content.

**Soil Temperature**

**Experiment A**

Table 8 and Figure 31 contain measured and predicted amounts of release over time. Between the 70th and 100th days, granules at 25 C began to open and the release rate increased, as predicted by the model. At 5 and 15 C, no urea was released after the first ten days, again as predicted by the model. These data indicate that equations which adjust the values of $K_{g,\text{max}}$, $A_{\text{max}}$, and D for temperature are sufficiently accurate to predict release at different temperatures.

**Experiment B**

Table 9 compares predicted to measured release for SCU-4, SCU-20, SCU-30, and SCU-23 at 25 and 35 C. Figure 32 contains the predicted release as a function of time curves for SCU-4 at 25 and 35 C, along with the amounts of release measured in experiments. The values of $K_{g,\text{max}}$ and $A_{\text{max}}$ derived at 35 C accurately
Figure 31. Release of urea from SCU-4 at four temperatures. Soil water potential was -0.3 bar. Predicted release indicated by solid lines.
Table 9. Comparison of measured release with predicted release of urea as a function of time for SCU-4, SCU-20, SCU-30, and SCU-23. Release measured at 25 and 35°C, -0.3 bar soil water potential. $A_c/\Delta x_c = 0.0005$ cm. Soil had received 9.1 metric tons/ha of lime.

<table>
<thead>
<tr>
<th>Material</th>
<th>Soil Temperature</th>
<th>Length of Time on Soil</th>
<th>Average Release and Standard Deviation</th>
<th>Predicted Release</th>
<th>$K_g, \text{max}$</th>
<th>$A_{\text{max}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>°C</td>
<td>days</td>
<td>%</td>
<td>%</td>
<td>mm/day</td>
<td>g/day $\times 10^{12}$</td>
</tr>
<tr>
<td>SCU-4</td>
<td>25</td>
<td>15</td>
<td>10.6 ± 4.1</td>
<td>14.7</td>
<td>0.2</td>
<td>4.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>36</td>
<td>16.0 ± 2.2</td>
<td>18.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>56</td>
<td>32.5 ± 6.0</td>
<td>32.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>71</td>
<td>43.4 ± 5.3</td>
<td>48.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>35</td>
<td>7</td>
<td>17.0 ± 3.6</td>
<td>14.8</td>
<td>0.2</td>
<td>4.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>36</td>
<td>53.3 ± 2.1</td>
<td>42.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>50</td>
<td>66.0 ± 5.1</td>
<td>66.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>64</td>
<td>75.6 ± 5.4</td>
<td>82.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SCU-20</td>
<td>25</td>
<td>15</td>
<td>26.2 ± 8.3</td>
<td>28.7</td>
<td>0.1</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>36</td>
<td>42.5 ± 8.7</td>
<td>30.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>56</td>
<td>42.9 ± 7.5</td>
<td>40.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>71</td>
<td>50.6 ± 6.2</td>
<td>52.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>35</td>
<td>7</td>
<td>27.5 ± 6.5</td>
<td>29.6</td>
<td>0.1</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>36</td>
<td>56.6 ± 2.0</td>
<td>50.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>50</td>
<td>63.2 ± 9.7</td>
<td>60.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>64</td>
<td>75.5 ± 4.6</td>
<td>68.7</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 9. Continued.

<table>
<thead>
<tr>
<th>Material</th>
<th>Soil Temperature</th>
<th>Length of Time on Soil</th>
<th>Average Release and Standard Deviation</th>
<th>Predicted Release Kg, max</th>
<th>A_max g/day x 10^12</th>
</tr>
</thead>
<tbody>
<tr>
<td>SCU-30</td>
<td>25°C</td>
<td>15 days</td>
<td>42.9 ± 3.8 45.8 0.1 1.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>36 days</td>
<td>54.6 ± 4.7 47.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>56 days</td>
<td>61.6 ± 10.2 54.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>71 days</td>
<td>65.5 ± 3.1 65.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>35°C</td>
<td>7 days</td>
<td>45.7 ± 6.5 45.7 0.1 1.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>36 days</td>
<td>73.5 ± 7.6 63.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>50 days</td>
<td>85.5 ± 1.4 74.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>64 days</td>
<td>79.4 ± 3.0 83.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SCU-23</td>
<td>25°C</td>
<td>15 days</td>
<td>28.1 ± 2.6 26.4 0.2 2.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>36 days</td>
<td>27.5 ± 2.1 27.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>56 days</td>
<td>36.2 ± 6.3 35.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>71 days</td>
<td>43.9 ± 7.4 46.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>35°C</td>
<td>7 days</td>
<td>25.2 ± 2.8 26.4 0.1 1.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>36 days</td>
<td>27.3 ± 4.7 29.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>50 days</td>
<td>42.0 ± 2.4 36.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>64 days</td>
<td>46.5 ± 3.0 49.6</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 32. Predicted release (solid lines) and measured release (data points) of urea from SCU-4 at two temperatures on limed soil. Soil water potential was -0.3 bar.
predicted the pattern of release at 25 C.

The rate of urea release over time from SCU-23 at 25 C was about equal to the rate of release at 35 C. As suggested above, this similarity may be due to a temperature optimum for growth which is between 25 and 35 C. By decreasing the temperature optimum for growth from 40 to 31 C, the agreement between predicted and measured release was improved (Table 10).

Table 10. Comparison of predicted release with measured release from SCU-23, over time. $K_{g,\text{max}} = 0.2$ mm/day, $A_{\text{max}} = 8.0 \times 10^{-13}$ g/day, temperature optimum for growth adjusted to 31 C, $A_c/\Delta x_c = 0.0005$ cm.

<table>
<thead>
<tr>
<th>Soil Temperature</th>
<th>Length of Time on Soil</th>
<th>Average Release and Standard Deviation</th>
<th>Predicted Release</th>
</tr>
</thead>
<tbody>
<tr>
<td>°C</td>
<td>days</td>
<td>%</td>
<td>%</td>
</tr>
<tr>
<td>25</td>
<td>15</td>
<td>28.1 ± 2.6</td>
<td>26.4</td>
</tr>
<tr>
<td></td>
<td>36</td>
<td>27.5 ± 2.1</td>
<td>27.9</td>
</tr>
<tr>
<td></td>
<td>56</td>
<td>36.2 ± 6.3</td>
<td>35.1</td>
</tr>
<tr>
<td></td>
<td>71</td>
<td>43.9 ± 7.3</td>
<td>46.6</td>
</tr>
<tr>
<td>35</td>
<td>7</td>
<td>25.2 ± 2.8</td>
<td>26.4</td>
</tr>
<tr>
<td></td>
<td>36</td>
<td>27.3 ± 4.7</td>
<td>29.2</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>42.0 ± 2.4</td>
<td>36.6</td>
</tr>
<tr>
<td></td>
<td>64</td>
<td>46.5 ± 3.0</td>
<td>49.6</td>
</tr>
</tbody>
</table>

Coating Characteristics

The values of $K_{g,\text{max}}$ and $A_{\text{max}}$ depend on the nature of the organism and the type of substrate which is being broken down.
Release from materials coated with the same sealant, such as SCU-20 and SCU-30, should be accurately predicted using the same values of $K_{g,\text{max}}$ and $A_{\text{max}}$ for both products. As seen from Table 9, agreement between predicted and measured amounts of release was generally good when values of $K_{g,\text{max}}$ and $A_{\text{max}}$ for SCU-20 and SCU-30 were assumed to be equal.

SCU-4 had higher values of $K_{g,\text{max}}$ and $A_{\text{max}}$ than did SCU-20 or SCU-30. This indicates that the sealant coating on SCU-4 must be broken down more rapidly than the coatings on SCU-20 and SCU-30. The greater resistance of the sealant on SCU-20 and SCU-30 to microbial attack may be the reason that microbiocides are apparently ineffective in the polyethylene-oil sealants (Tennessee Valley Authority, 1976). The sealants themselves are so resistant to attack that a microbiocide is not required to slow release.

The values of $K_{g,\text{max}}$ and $A_{\text{max}}$ which best predicted release from SCU-23 were comparable in value to values of $K_{g,\text{max}}$ and $A_{\text{max}}$ for other materials (Tables 9 and 10). Sulfur-oxidizing organisms may break down sulfur as rapidly as the sealant is broken down on other materials. But, because the sulfur is thicker than the sealant, a longer period of time elapses before SCU-23 granules begin to open.
Summary

The model of SCU breakdown and release of urea discussed above predicts the rate at which urea is released from SCU as a function of time. Growth and activity constants were determined by trial and error so that the pattern of release as predicted by the model matched measured release in soil at -0.3 bar and 35 C. Use of these constants in the model accurately predicted release at other temperatures and a different soil water content.
SUMMARY AND RECOMMENDATIONS

A mathematical model has been constructed which predicts the rate of release of urea from SCU as a function of time. Some SCU granules have openings in their coatings and release their urea shortly after application to soil, while the remainder are closed. The model assumes that coatings on the closed SCU granules are broken down by soil microorganisms until urea is exposed to water. The urea dissolves and diffuses out of the granule into the soil solution.

Quantitative relationships were derived to calculate the number of organisms on the granule surface at any time, the rate at which each organism breaks down the coating material, the thickness of the coatings on granules, and the rate at which urea diffuses out of the open granules. Soil temperature, soil water content, and coating characteristics of a given lot of SCU granules were the main variables considered in making these calculations.

Diffusion of urea out of open SCU granules was examined theoretically and experimentally. The release of urea from any single granule with a small opening in the coating consists of a constant rate period and a falling rate period. For the constant rate period, the relative fraction, \( m_t \), of urea which is released in time \( t \) days is
where \( k \) is the reciprocal of the mass of urea inside the granule (1/g), \( D \) is the diffusion coefficient (cm\(^2\)/day), \( A_c \) is the cross-sectional area of the opening in the coating (cm\(^2\)), \( \Delta x_c \) is the length of the opening (cm), and \( c_{sat} \) is the solubility of urea (g/cm\(^3\)).

During the falling rate period, release is an exponential function of time,

\[
m_r = 1.0 - (1.0 - M_c) \exp\left(\frac{DA_c}{V\Delta x_c} (t-t_1)\right),
\]

where \( M_c \) is the relative mass of urea released during the falling rate period, \( V \) is the volume of the granule (cm\(^3\)), and \( t_1 \) is the time in days at which the constant rate period ends. Release of urea into water from SCU-31 granules which were initially open obeyed the simple exponential equation

\[
m_r = 1.0 - B - M \exp(-k_3 t),
\]

where \( B \) is the relative mass of urea in closed granules, and \( M \) and \( k_3 \) are constants.

Organism numbers were calculated by assuming that the radius of the colony of organisms on the surface of the granule increases at a
constant rate. The relationship between organism numbers and time is

\[ N = \pi D_0 K_g t^2, \]  

where \( N \) is the number of organisms on the granule at time \( t \) (days), \( D_0 \) is the density of organisms in the colony (organisms/mm\(^2\)), and \( K_g \) is the growth rate of the colony (mm/day). The value of \( K_g \) is calculated from the equation

\[ K_g = K_{g,\text{max}} f_g(T) g_g(\psi), \]  

where \( K_{g,\text{max}} \) is the maximum growth rate which occurs at optimum temperature and soil water potential, \( f_g(T) \) is a correction term for soil temperature \( T \), and \( g_g(\psi) \) is a correction term for soil water potential \( \psi \). Both \( f_g(T) \) and \( g_g(\psi) \) range in value from 0 to 1. For \( f_g(T) \), the equation used was

\[ f_g(T) = \frac{0.003612 T \exp(24.04-75000/T)}{1 - \exp(238-75000/T)}, \]  

where \( T \) is the absolute temperature in degrees Kelvin. To calculate \( g_g(\psi) \), three equations were used:

\[ g_g(\psi) = 0.435 \ln(-\psi) + 2.00, \quad -0.10 \leq \psi \leq -0.001, \]  
\[ g_g(\psi) = 1.0, \quad -1.0 < \psi \leq -0.10, \]  
\[ g_g(\psi) = -0.294 \ln(-\psi) + 1.00, \quad -30 < \psi \leq -1.0. \]
The rate at which each organism breaks down the coating material is calculated from the equation

\[ A = A_{\text{max}} f_a(T) g_a(\psi) \]  \hspace{1cm} (53)

where \( A \) is the rate at which the coating is broken down (\( \text{g/organism/day} \)), \( A_{\text{max}} \) is the maximum value of \( A \) reached at optimum temperature and soil water potential, \( f_a(T) \) is a correction term for the soil temperature \( T \), and \( g_a(\psi) \) is a correction term for the soil water potential \( \psi \). A \( Q_{10} \) of 2 was assumed, so that a form of the Arrhenius equation was used to calculate \( f_a(T) \),

\[ f_a(T) = 2.34 \times 10^8 \exp\left(\frac{5.94 \times 10^3}{T}\right) \]  \hspace{1cm} (55)

where \( T \) is the absolute temperature in degrees Kelvin. The term \( g_a(\psi) \) has the same value as \( g_g(\psi) \) at a given soil water potential.

The rate at which closed granules were opened depends on the rate at which coating is removed, which is given by the product of organism numbers and organism activity, and the thickness of the coatings. To characterize the distribution of coating thicknesses in a given lot of SCU granules, portions of the coatings were removed by dipping granules in benzene. After each benzene treatment, the amount of coating which had been removed was determined by evaporating an aliquot of benzene to dryness and weighing the residue. The
amount of urea released from granules after treatment was measured to determine the fraction of the granules which were open.

The results of this experiment indicated that three classes of granules are present in a given lot of SCU. Class 1 granules are initially open and release urea with no coating removed. Class 2 granules have holes through their sulfur shells but the holes are plugged with sealant. Class 3 granules have no holes through their sulfur coatings. The relationship between the fraction of granules opened and the amount of coating removed was linear for both Class 2 and Class 3 granules. The curve for Class 2 granules intercepts the y-axis at the percentage of urea in Class 1 granules.

A computer program was written which used the mathematical relationships developed above to predict release from a given SCU material under given soil temperature and water conditions. The predictions made by this model were verified by comparing the rate at which urea was released from SCU-4, SCU-20, SCU-30, and SCU-23 in soil with release as predicted by the model. The constants \( K_{g,\text{max}} \) and \( A_{\text{max}} \) were estimated by fitting the predicted release in soil at a temperature of 35°C and a soil water potential of -0.3 bar to the release measured in soil under these conditions. When release was predicted at 5, 15, and 25°C, and in soil at -0.03 and -15 bars soil water potential, good agreement was found between predicted release and release measured as a function of time under these temperature
and water potential conditions.

The results presented above indicate that the TVA test, which measures the percentage of granules initially open in a given lot of SCU, is not an accurate indicator of the rate of release of urea from SCU as a function of time. To predict the pattern of release from all granules, coating characteristics of unopened granules must also be considered. The coating characteristic equations derived here provide a means of predicting the rate at which granules will be opened. The model provides a theoretical framework in which the factors affecting release may be placed. For example, processes other than microbial activity may also be important in determining rates of coating breakdown. Equations which relate rates of these physical or chemical processes to the stability of SCU granules in soil can be incorporated into the model to increase the accuracy of predictions.

The model may be further developed and refined through studies such as the following:

(i) Mechanisms of coating breakdown other than microbial activity should be investigated. Physical and chemical processes may also play a role in opening holes in granule coatings. The relative importance of biological, chemical, or physical processes in breaking down coatings may vary depending on soil temperature, soil water
content, soil chemical characteristics, and the nature of coating materials.

The stability of $S_\infty$, the polymeric form of elemental sulfur, in the soil system may be important in determining how long granules remain unopened in the soil.

(ii) More measurements of release as a function of time under a wider variety of temperature, water, and soil chemical conditions are required to test the model more thoroughly. Coating characteristics of the SCU products must be known accurately and must be considered in all tests. Fluctuating temperature and fluctuating water content should be imposed upon samples of SCU in soil.

(iii) Effects of temperature and water content on sealant and sulfur oxidation rates should be accurately measured to obtain more accurate values of growth rate and activity maxima. These maxima may be determined in soil or on artificial media. Soil pH, nutrient status, and aeration are other important variables whose effects on coating breakdown rates must be carefully measured.

(iv) Stochastic equations may describe the relationships which determine release patterns better than the equations used in this model. The times required for granules with identical coating characteristics to open may be normally distributed about some mean value. The deterministic approach followed in this thesis only considers the average time requires for a granule to open, and may thus
produce inaccurate predictions.

(v) Once release under given conditions can be accurately predicted, rates of urea hydrolysis, nitrification, and solute movement may be considered in the model. Concentration and distribution of different nitrogen forms throughout the soil profile could be accurately calculated for each day of the growing season.

The above studies would all improve the ability to predict how well a given SCU product can supply nitrogen to a crop during the growing season. Until the predictions can be made with accuracy and confidence, the advantages of SCU over other fertilizer materials cannot be fully realized.
BIBLIOGRAPHY


Hashimoto, Isao. 1976. Personal communication.


APPENDIX 1

Description of SCU Materials Used in Experiments

Lot numbers, composition, and release percentages according to TVA standard test, for six SCU materials used in laboratory and growth chamber experiments.

<table>
<thead>
<tr>
<th>Lot Number</th>
<th>Fe</th>
<th>N</th>
<th>Sealant Type</th>
<th>Sealant Content</th>
<th>Conditioner Type</th>
<th>Conditioner Content</th>
<th>Factory Designation</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-11-72B</td>
<td>18.5</td>
<td>35.2</td>
<td>Wax</td>
<td>3.2</td>
<td>DE</td>
<td>2.0</td>
<td>SCU-4</td>
</tr>
<tr>
<td>7-20-72B</td>
<td>14.2</td>
<td>38.2</td>
<td>Wax</td>
<td>2.0</td>
<td>DE</td>
<td>2.0</td>
<td>SCU-31</td>
</tr>
<tr>
<td>3-3-75A</td>
<td>15.5</td>
<td>36.8</td>
<td>PO</td>
<td>2.0</td>
<td>DE</td>
<td>2.5</td>
<td>SCU-10</td>
</tr>
<tr>
<td>3-4-75B</td>
<td>19.5</td>
<td>35.4</td>
<td>PO</td>
<td>2.0</td>
<td>DE</td>
<td>2.5</td>
<td>SCU-20</td>
</tr>
<tr>
<td>3-4-75A</td>
<td>15.0</td>
<td>37.1</td>
<td>PO</td>
<td>2.0</td>
<td>DE</td>
<td>2.5</td>
<td>SCU-30</td>
</tr>
<tr>
<td>11-02-73C</td>
<td>25.0</td>
<td>34.5</td>
<td>None</td>
<td>None</td>
<td>None</td>
<td>None</td>
<td>SCU-23</td>
</tr>
</tbody>
</table>

1. Shellmax 800, microcrystalline wax containing 0.25 percent coal tar microbiocide.
2. Diatomaceous earth.
3. 30 percent low molecular weight polyethylene plus 70 percent Brightstock oil.
MEANINGS OF VARIABLE NAMES

ADJEXP = RECIPROCAL OF VOLUME OF INDIVIDUAL GRANULE, 1/CC.

ADJAGE = XYAGE ADJUSTED FOR SOIL TEMPERATURE AND SOIL WATER CONTENT, CM/DAY.

ADJLUS = AMOUNT OF COATING LOST FORM 100G OF SCU.

ASHALU = SLOPE OF CURVE DESCRIBING CLASS 3 GRANULES.

ASTEEP = SLOPE OF CURVE DESCRIBING CLASS 2 GRANULES.

AVGWT = AVERAGE WEIGHT OF THE GRANULES.

BSHALU = INTERCEPT OF CURVE DESCRIBING CLASS 3 GRANULES.

BSSTEIL = INTERCEPT OF CURVE DESCRIBING CLASS 2 GRANULES.

CONST = VALUE OF THE GEOMETRY TERM FOR DIFFUSION THROUGH THE OPENING IN THE COATING, CM.

CUMDAY(J) = CUMULATIVE PERCENT OF UREA RELEASED FROM ALL OPEN GRANULES ON DAY J.

CUMLOS(J) = CUMULATIVE LOSS OF COATING LOST FROM A SINGLE GRANULE UP TO AND INCLUDING DAY J.

CUMREL(J) = CUMULATIVE AMOUNT OF UREA RELEASED FROM GRANULES INITIALLY OPENED ON DAY J.

DIFFCO = DIFFUSION COEFFICIENT CORRECTED FOR TEMPERATURE, CM X CM/DAY.

EXPUNE = EXPONENT FOR DIFFUSION OUT OF GRANULES WHICH NO LONGER CONTAIN SOLID UREA.

GRANREL = GRAMS OF SCU GRANULES OPENED EACH DAY PER 100G OF SCU.

GRANREL(J) = NUMBER OF GRANULES OPENED ON DAY J, PER 100 GRAMS OF SCU.

HPJACF(J) = SOIL WATER POTENTIAL CORRECTION FOR BOTH GROWTH AND ACTIVITY ON DAY J.

NYKAYG = THE NUMBER OF TIMES THE PROGRAM WILL CALCULATE RELEASE.

OPTADJ = ADJUSTMENT FOR OPTIMUM TEMPERATURE: OPTIMUM TEMPERATURE FOR GROWTH IS (39-OPTADJ).

OPTACT = ACTIVITY OF SINGLE ORGANISM CORRECTED FOR TEMPERATURE AND SOIL WATER POTENTIAL.

ORMGM = NUMBER OF ORGANISMS ON A SINGLE GRANULE.

PICTOR = FRACTION OF GRANULE WEIGHT WHICH IS UREA.

PERORU = RATE OF COATING BREAKDOWN FOR A SINGLE ORGANISM, G/DAY.

R = RADIUS OF COLONY ON GRANULE SURFACE, CM.

REL(J) = AMOUNT OF UREA RELEASED FROM GRANULES OPENED ON DAY J.

REXURE = AMOUNT OF UREA REMAINING INSIDE GRANULES, G/100 G OF SCU.

SAITOR(J) = TOTAL AMOUNT OF UREA WHICH MAY BE CONTAINED IN SOLUTION INSIDE GRANULES OPENED ON DAY J.

SCU = IVA DESIGNATION OF FERTILIZER PRODUCT.

SOLJAR(J) = SOLUBILITY OF UREA ON DAY J, G/CC.

SOLSAFE(I) = SUIT WATER POTENTIAL EACH DAY I.
**SULACT** = RATIO OF ACTIVITY RATE OF SULFUR ORGANISMS TO ACTIVITY RATE OF SEALANT ORGANISMS.

**SULGRO** = RATIO OF GROWTH RATE OF SULFUR ORGANISMS TO GROWTH RATE OF SEALANT ORGANISMS.

**TEMACT(1)** = TEMPERATURE CORRECTION FOR ACTIVITY.

**TEMGRO(1)** = TEMPERATURE CORRECTION FOR GROWTH.

**TEMPHI(1)** = MAXIMUM TEMPERATURE ON DAY 1.

**TEMPLU(1)** = MINIMUM TEMPERATURE ON DAY 1.

**VOL(1)** = VOLUME OF GRANULES OPENED EACH DAY IN 100G OF SEALANT.

**VOLAT(1)** = VOLUMETRIC WATER CONTENT ON DAY 1.

**XINTER** = INTERCEPT OF CURVES FOR CLASS 2 AND CLASS 3 GRANULES, G COAT REMOVED/100G SCU.

**XKAYGE** = VALUE OF GROWTH CONSTANT K, CM/DAY, FOR THE SEALANT.

**XMAXLs** = MINIMUM AMOUNT OF COATING WHICH MUST BE REMOVED TO OPEN ALL GRANULES, G/100G SCU.

**YKAYGE** = VALUES OF XKAYGE TO BE RUN THROUGH THE PROGRAM.

**XMAXLs** = MINIMUM AMOUNT OF COATING WHICH MUST BE REMOVED TO OPEN ALL GRANULES, G/100G SCU.

**YKAYGE** = VALUES OF XKAYGE TO BE RUN THROUGH THE PROGRAM.

**DIMENSION SATTOF(200), GRAMREL(200), REL(200), VOL(200)**

**DIMENSION ADJLOS(200)**

**DIMENSION Vol(10), REL(200), CUMREL(200), SOLUBY(200)**

**DIMENSION FEMS/FEMPHI(200), TEMPHI(200), TEMPLU(200)**

**DIMENSION VARS/DIFFUS(200), COMREL(200), DIFF(200)**

**DIMENSION WATER/SOLWAT(200), VOLWAT(200)**

**DATA (FEMPHI=200(30.)), (FEMPLU=200(20.))**

**DATA (SOLWAT=200(.35)), (VOLWAT=200(.35))**

**FORMAT(F10.2)**

**FORMAT(F10.6)**

**FORMAT(F10.5)**

**FORMAT(2F10.5)**

**FORMAT(F12.6)**

**FORMAT(2F12.6)**

**FORMAT(F12.5)**

**FORMAT(2F10.5)**

**FORMAT(1S15,F12.6)**

**FORMAT(5X,5F12.6)**

**FORMAT(1S15,5F12.6)**

**FORMAT(1S15,F12.6)**

**FORMAT('I' CUMULATIVE RELEAS AT DAY 200)'10X,**
FOR EACH LOT OF GRANULES 

CONSTANT XAYGE /4X,FR*6

PER ORG PICTURE AVG+W CNST SULACT

1 ISULGRU /2Y,9*2,6*4,F9*7,2FR*4

THIS PROGRAM PREDICTS RELEASE OF SCU /',F4*1)

READ IN NUMBER OF RELEASE CURVES TO BE CALCULATED*
READ(60,6004) NXAYGE

READ IN VALUES OF XAYGE FOR EACH CURVE.
READ(60,6005)(XAYGE(I),I=1,NXAYG)

READ IN DESIGNATION OF SCU PRODUCT.
READ(60,6007) SCU

READ IN MAXIMUM AMOUNT OF COATING LOST/100G SCU.
READ(60,6007) XMAXLS

READ IN PERCENT OREA IN LOT OF SCU.
READ(60,6003) PICTURE

READ IN AVERAGE WEIGHT OF GRANULES.
READ(60,6007) AVG+W

READ IN COATING CHARACTERISTIC CURVES AND INTERCEPT.
READ(60,6008) ASTEEP,BSLEEP,ASHALU,BSHALU,XINTER
* * * * * *
READ IN RATIO OF CROSS SECTONAL AREA TO LENGTH OF PORE.
READ(60,6009) CONST
* * *

* * * * * *
READ IN SULACT AND SULGRO.
READ(60,6010) SULGRO,SULACT
* * *

WRITE(61,6117) SULC

DO 100 JK=1,NXKAYE
N=JK*10
XKAYE=YKAYE(JK)
WRITE(61,6115) XKAYE

* * * * * *
READ IN RATE AT WHICH SINGLE ORGANISM BREAKS DOWN COATING, U/DAY.
READ(60,6209) PERORG
* * *

WRITE(61,6116) PERORG,PICURE,AVGWTG,CONST,SULACT,
ISULGRO

* * * * * *
CALCULATE NUMBER OF GRANULES IN 100G OF SCU.
GRANUM=100./AVGWTG
* * *

CALL TEMPER(SULUBY)
CALL SOLH2OCDIFFUS,DIFTEM)
CALL BDCMAT(CUMLOS,XKAYE,PERORG,SULGRO,SULACT,GRANUM,
1XINTER)
CALL RELEASE(CUMLOS,ASTEEL,ASTEP,ASHALU,BSHALU,XINTER,
1DIFTEM,TOTREL,CURL,SULUBY,CGDAY,CONST,GRANUM,
2PCTURE,XXAXLS)
WRITE(61,6112)(1,CUMLOS(I),I=1,200)
WRITE(61,6113) ASTEM,PSTEP,ASHALU,BSHALU,XINTER
WRITE(61,6114)(1,CUMREL(I),I=1,200,5)
100 CONTINUE
STOP
END
SUBROUTINE TEMPER(SULURY)

DIMENSION SULURY(200)
COMMON/EMPS/TEMPHI(200),TEMPLO(200)
COMMON/VARY/TEMGRU(200),TEMACT(200),DIFTEM(200)
OPTADJ=5.

DO 10 I=1,200

* * * * * *
CALCULATE AVERAGE TEMPERATURE.
* * *
* * * * * *
* * * * * *
CALCULATE ABSOLUTE TEMPERATURE.
* * *
*TABS=TEMPT*273.

* * * * * *
ADJUST ABSOLUTE TEMPERATURE FOR GROWTH OPTIMUM.
*IPLUS=TABS+OPTADJ

* * * * * *
CALCULATE GROWTH CORRECTION COEFFICIENT FOR TEMPERATURE.
*TEMGRU(I)=-.003612*IPLUS*EXP(24.027/500./IPLUS)/
1(1+EXP(234-75000/IPLUS))

* * * * * *
CALCULATE ACTIVITY CORRECTION COEFFICIENT FOR TEMPERATURE.
*TEMACT(I)=2.34E0F*EYPC-5940.11ABS

* * * * * *
CALCULATE DIFFUSION COEFFICIENT.
*DIFTEM(I)=4.03*FABS/EXPC2135./FABS)

* * * * * *
CALCULATE SOLUBILITY OF UREA
*SULURY(I)=.00696*TEmpf+.45

10 CONTINUE

RETURN
END
SUBROUTINE SOLH2O(DIFFUS, DIFTEM)
DIMENSION DIFFUS(200), DIFTEM(200)
COMMON/WATER/SOLWAT(200), VOLWAT(200)
COMMON/RETWAT/H2OACT(200), DIFH2O(200)

* * * * * * * * *
CALCULATE ACTIVITY CORRECTION COEFFICIENT FOR SOIL WATER.

DO 70 I=1, 200
   TEMWAT=SOLWAT(I)
   IF(TEMWAT.LT.1.) GO TO 50
   IF(TEMWAT.GT.1.) GO TO 60
   H2OACT(I)=1.
50 H2OACT(I)=0.435*ALOG(TEMWAT)+2.
60 H2OACT(I)=-29*ALOG(TEMWAT)+1.
70 CONTINUE
* * *
RETURN
END
SUBROUTINE BDCOAT(CUMLOS, XKAYGE, PERORG, SULGRU, SULACT, GRANUM, XINTER)

DIMENSION CUMLOS(200)
COMMON/VARY/TEMGRU(200), TEMACT(200), DIFTEM(200)
COMMON/RETWAT/H2OACT(200), DIFH2O(200)
R=0.

CALCULATE AMOUNT OF SEALANT REMOVED ON FIRST DAY FROM A SINGLE GRANULE.

ORGNUM=3140000. *XKAYGE*XKAYGE*TEMGRU(1)*TEMGRU(1)*
H2OACT(1)
ORGACT=PERORG*(TEMACT(1)*H2OACT(1))
CUMLOS(I)=ORGNUM*ORGACT

CALCULATE AMOUNT OF SEALANT REMOVED ON REMAINING DAYS FROM A SINGLE GRANULE.

DO 10 I=2,200
URUACT=PERORG*(TEMACT(I)*H2OACT(I))
ADJKGE=XKAYGE*TEMGRU(I)*H2OACT(I)
R=ADJKGE+R
ORGNUM=3140000.*R*R

DETERMINE WHETHER ORGANISM NUMBERS ARE MORE THAN MAXIMUM ALLOWABLE ON THE SURFACE.
IF (ORGNUM.GT.33400000) ORGNUM=33400000.
CUMLOS(I)=ORGNUM*ORGACT+CUMLOS(I-1)

DETERMINE WHETHER ALL SEALANT HAS BEEN REMOVED.
IF (CUMLOS(I)*GRANUM.GT.XINTER) GO TO 100
10 CONTINUE

CONVERT CONSTANTS FOR SEALANT ORGANISMS TO CONSTANTS FOR SULFUR ORGANISMS.
XXAYGE=SULGRU*XXAYGE
PERORG=SULACT*PERORG
R=0.
K=I+1
* * * * *

CALCULATE AMOUNT OF SULFUR REMOVED EACH DAY FROM A SINGLE GRANULE.

DO 20 J=K,200

ORGACT=PERURG*(TEMACT(J)*H2UACT(J))

ADJKGE=YMAYGE*TEMGRO(J)*H2UGACT(J)

R=ADJKGE+R

ORGNUM=3140000**R*R

IF(ORGNUM.GT.33400000.) ORGNUM=33400000.

CUMLOU(J)=ORGNUM*ORGACT+CUMLOU(J-1)

20 CONTINUE

* * *

RETURN

END
SURROUTINE  RELE5E(CUMLOS,ASTEEL,ASTEEP,ASHALO,BSHALO,
INTER,DIFTEM,TUREL,CUMREL,SOLUBY,CUMDAY,CONSI,GRANUM,
2PCTURE,XMAXLS)
DIMENSION GRANREL(200)
DIMENSION DIFTEM(200)
DIMENSION CUMLOS(200),DIFFUS(200),CUMDAY(200)
DIMENSION TUREL(200),CUMREL(200),SOLUBY(200)
DIMENSION SATTOT(200),GRAMREL(200),REL(200),VUL(200)
DIMENSION ADJLOS(200)
DIMENSION URANREL(200)
DIMENSION DIFFEM(200)
DIMENSION CJMLOS(200),DIFFUS(200),CUMDAY(200)
DIMENSION TOFREL(200),CUMREL(200),SUlURY(200)
DIMENSION SACII0f(200),GRAMREL(200),REL(200),VUL(200)
DIMENSION ADJLOS(200)

WRITE(61,6134)
6134 FORMAT('HAVE JUST ENTERED RELE5E')
AVGWIG=.0169

DO 70 JKL=1,200
CUMDAY(JKL)=0.
70 CUMREL(JKL)=0.

* * * * * *
CALCULATE RECIPROCAL OF AVERAGE GRANULE VOLUME,
TO BE INSERTED INTO EXPONENT.
ADJEXP=1/(AVGWIG*0.75*PCTURE)
* * *
A=ASTEEL

* * * * *
CALCULATE AMOUNT OF COATING REMOVED FROM 100G SCO ON
FIRST DAY
ADJLOS(1)=CUMLOS(1)*GRANUM

* * * * *
CALCULATE AMOUNT OF CHEMICAL, VOLUME OF UREMA, AND AMOUNT
RELEASED FROM GRANULES WHICH OPEN ON THE FIRST DAY
GRAMREL(1)=A*ADJLOS(1)
VOL(1)=0.75*N*GRAMREL(1)*PCTURE
REL(1)=DIFTEM(1)*CONSI*SOLUBY(1)*GRAMREL(1)
CUmREL(1)=REL(1)
CUMDAY(1)=CUmREL(1)

* * * * *
CALCULATE PERCENTAGE OF OPEN GRANULES FOR REMAINING
DAYS
DO 10 IDAY=2,200
* * * * * *  
CALCULATE EXPONENT FOR DAY IDAY.
EXPNUM=DIFFEM(IDAY)*CONST*ADJEXP  
* * *  

* * * * * *  
CALCULATE D*C(SAT) FOR DAY 'IDAY'
DIFSUL=DIFFEM(IDAY)*SOLUBY(IDAY)  
* * *  
ADJLOS(IDAY)=CUMLOS(IDAY)*GRANUM  

* * * * * *  
DETERMINE WHETHER OR NOT ALL GRANULES HAVE OPENED.
IF(ADJLOS(IDAY)*GT.XMAXLS) ADJLOS(IDAY)=XMAXLS  
* * *  

* * * * * *  
DETERMINE WHETHER CLASS 2 OR CLASS 3 GRANULES ARE BEING OPENED.
IF(ADJLOS(IDAY)*GT.XINTER) A=ASHALO  
* * *  

* * * * * *  
CALCULATE AMOUNT OF UREA, NUMBER OF GRANULES, AND VOLUME OF GRANULES OPENED ON DAY IDAY.
DADOLS=ADJLOS(IDAY)-ADJLOS(IDAY-1)
GRAMREL(IDAY)=A*DADOLS
GRANREL(IDAY)=GRAMREL(IDAY)/AVGWFG  
VOL(IDAY)=0.758*GRANREL(IDAY)*PICTURE  
* * *  
IDAYPL=IDAY+1

* * * * * *  
CALCULATE AMOUNT OF UREA RELEASED FROM GRANULES WHICH ARE STILL IN LINEAR PHASE OF RELEASE
DO 20 IRUN=2,IDAYPL
IBACK=IDAY-IRUN+2
REL(IBACK)=DIFSUL*CONST*GRANREL(IBACK)/PICTURE
CUMREL(IBACK)=CUMREL(IBACK)+REL(IBACK)
TEMPREM=PICTURE*(GRANREL(IBACK)-CUMREL(IBACK))
SATTUR(IBACK)=VOL(IBACK)*SOLUBY(IDAY)
IF(TEMPREM.LT.SATTUR(IBACK)) GO TO 100
20 CONTINUE  
* * *

DO 60 IRUN=IRUN+1  
GO TO 60
100 IRUNPL=IRUN+1
CALCULATE AMOUNT OF UREA RELEASED FROM GRANULES WHICH HAS ENTERED EXPONENTIAL RELEASE PHASE

\[
\text{DO 30 JRUN=IRUNPL, IDAYPL}
\]

\[
\text{JAACK=IDAY-JRUN+2}
\]

\[
\text{REMORE=LIRAMEL(JBACK)-CUMREL(J3ACK)}
\]

\[
\text{REL(JBACK)=REMORE*(1.-EXP(-EXPONE))}
\]

\[
\text{CUMREL(JBACK)=CUMREL(JBACK)+REL(JBACK)}
\]

\[
\text{30 CONTINUE}
\]

CALCULATE AMOUNT OF UREA RELEASED FROM ALL GRANULES ON DAY 'IDAY'.

\[
\text{DO 40 I=1,IDAY}
\]

\[
\text{CUMDAY(IDAY)=CUMDAY(IDAY)+COMREL(I)}
\]

\[
\text{10 CONTINUE}
\]

ADD PERCENTAGE OF GRANULES IN CLASS 1 TO CALCULATED RELEASE FOR EACH DAY

\[
\text{DO 50 I=1,200}
\]

\[
\text{CUMDAY(I)=CUMDAY(I)+BSTEPP-3.}
\]

WRITE OUT CALCULATED RELEASE AS A FUNCTION OF TIME.

\[
\text{WRITE(61,6100)(I,CUMDAY(I),GRAMREL(I), I=1,200)}
\]

\[
\text{6100 FORMAT('DAY CUMDAY GRAMREL'/(5(I5,2F7.2)))}
\]

RETURN

END
APPENDIX 3

Sample Calculation of Release for a Single Day

The example below summarizes calculations made for a specific product under specific soil temperature and water content conditions.

All required input data is entered in the mainline, and transferred to subroutines as needed. Release is calculated for the first 200 days after SCU-4 is applied to soil. Comments on each subroutine follow.

**TEMPER**

Temperature-dependent terms are calculated for all 200 days.

**SOLH2O**

Corrections are made for effects of soil water content on growth and activity coefficients.

**BDCOAT**

The amount of coating broken down each day is calculated from organism numbers and organism activity. The number of organisms on each granule is calculated from the radius of the microbial colony on the surface. This radius in turn is calculated from the corrected growth coefficient $K_g$ for sealant organisms. Organism activity is calculated by correcting $A_{\text{max}}$ of sealant organisms for temperature and water content.
After all sealant-limited granules are opened, sulfur organisms open remaining intact coatings. Growth and activity coefficients are converted from those characteristic of sealant organisms to those for sulfur oxidizers. The proportionality constants SULACT and SULGRO relate activity and growth respectively of sealant organisms to activity and growth of sulfur organisms.

The average density of organisms is $10^6$ organisms/mm$^3$. The maximum number of organisms the surface can support is the product of average density and the surface area of the average granule.

**RELEASE**

The amount of coating removed on Day I is multiplied by the slope of the coating characteristic curve (initially 12.5 for SCU-4), giving the fraction of granules opened on Day I. These are termed Group I granules. After all sealant-limited granules are opened, sulfur must be removed for further breakdown to occur. The slope of the coating characteristic curve decreases (to 5.6 for SCU-4).

Diffusion of urea out of granules on Day I is calculated as follows: Release from granules in the first, linear stage of release is calculated for Group I, Group (I-1), Group (I-2), ... , Group (J+1), using Equation 8. Group J granules are the first granules encountered in which all urea inside the granule is in solution. Urea release from granules in Group J through Group 1 is calculated using the exponential diffusion equation (Equation 17). Then amounts of urea released
on Day I from all granules which have opened is summed to give the
total release on Day I.

**Inputs: Description, Variable Name, Value**

SCU designation = SCU-4.0.

Activity of sulfur organisms relative to sealant organisms
= SULACT = 2.0.

Growth rate of sulfur organisms relative to sealant organisms
= SULGRO = 2.0.

\[ K_{g,\text{max}} = X_{\text{KAYGE}} = 0.3 \text{ mm/day}. \]

\[ G_{\text{max}} = \text{PERORG} = 4.0 \times 10^{-12} \text{ g/day}. \]

\[ A_c / \Delta x_c = \text{CONST} = 0.0005 \text{ cm}. \]

Fraction urea = PCTURE = 0.765.

Average granule weight = AVGWTG = 0.020 g.

Coating characteristics:
ASTEEP = 12.5
BSTEESP = 17.7
ASHALO = 5.6
BSHALO = 47.0
Intercept = XINTER = 4.25 g/100 g SCU.

Temperature maximum = TEMPHI(I) = 30 C.

Temperature minimum = TEMPLO(I) = 20 C.

Soil water potential = SOLWAT(I) = 0.35 bar.

Volumetric water content = VOLWAT(I) = 0.35.
<table>
<thead>
<tr>
<th>Calculation</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Mainline</strong></td>
<td></td>
</tr>
</tbody>
</table>
| Number of granules in 100 g SCU, GRANUM | \[
\frac{100}{\text{AVGWTG}} = 5000.0
\]
| **TEMPER** |        |
| Average temperature for each day, TEMPT | \[
\frac{\text{TEPHI}(45)+\text{TEPLO}(45)}{2} = 25.0
\]
| Absolute temperature, TABS | TEMPT + 273. = 298.0 |
| Adjustment for optimum temperature, TPLUS | TABS + OPTADJ = 298.0 |
| Solubility of urea, SOLUBY(I) | \[
0.00696 \times \text{TEMPT} + 0.45 = 0.624
\]
| Temperature correction for K, TEMGRO(I) | \[
0.003612 \times \text{TPLUS} \times \exp(24.02 - \frac{7500}{\text{TPLUS}})
\]
| Temperature coefficient for activity, TEMA CT(45) | \[
1 + \exp(238 - \frac{7500}{\text{TPLUS}})
\]
| Diffusion coefficient, DIFTEM(45) | \[
(2.34 \times 10^{8}) \times \exp(-\frac{5940}{\text{TABS}})
\]
| SOLH2O |        |
| Activity and growth coefficient corrections for soil water content, H2OACT(45) | \[
\frac{4.03 \times \text{TABS}}{\exp(\frac{2135}{\text{TABS}})} = 0.929
\]
<p>|   | 1.00  |
|   | 1.00  |</p>
<table>
<thead>
<tr>
<th>Output</th>
<th>Calculation</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>BDCOAT</strong></td>
<td>G<strong>rowth</strong> coefficient <strong>K</strong> <em>g</em> correction, <strong>ADJKGE</strong></td>
<td></td>
</tr>
<tr>
<td>Colony radius, <strong>R</strong></td>
<td><strong>R(44)+ADJKGE</strong></td>
<td>2.25 mm</td>
</tr>
<tr>
<td>Number of organisms on surface, <strong>ORGNUM</strong></td>
<td><strong>3140000. <em>R</em>R</strong></td>
<td>1.59 x 10^7</td>
</tr>
<tr>
<td><strong>ORGACT</strong></td>
<td>**PERORG<em>TEMACT(45)<em>H2OACT(45)</em></em></td>
<td>2.06 x 10^-12 g/day</td>
</tr>
<tr>
<td>Cumulative amount of coating removed by Day 45, <strong>CUMLOS(45)</strong></td>
<td><strong>CUMLOS(44)+ORGACT*ORGNUM</strong></td>
<td>1.13 x 10^-3 g</td>
</tr>
<tr>
<td><strong>ADJKGE</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Colony radius, <strong>R</strong></td>
<td><strong>R(44)+ADJKGE</strong></td>
<td>2.25 mm</td>
</tr>
<tr>
<td>Number of organisms on surface, <strong>ORGNUM</strong></td>
<td><strong>3140000. <em>R</em>R</strong></td>
<td>1.59 x 10^7</td>
</tr>
<tr>
<td><strong>ORGACT</strong></td>
<td>**PERORG<em>TEMACT(45)<em>H2OACT(45)</em></em></td>
<td>2.06 x 10^-12 g/day</td>
</tr>
<tr>
<td>Cumulative amount of coating removed by Day 45, <strong>CUMLOS(45)</strong></td>
<td><strong>CUMLOS(44)+ORGACT*ORGNUM</strong></td>
<td>1.13 x 10^-3 g</td>
</tr>
<tr>
<td><strong>ADJKGE</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Colony radius, <strong>R</strong></td>
<td><strong>R(44)+ADJKGE</strong></td>
<td>2.25 mm</td>
</tr>
<tr>
<td>Number of organisms on surface, <strong>ORGNUM</strong></td>
<td><strong>3140000. <em>R</em>R</strong></td>
<td>1.59 x 10^7</td>
</tr>
<tr>
<td><strong>ORGACT</strong></td>
<td>**PERORG<em>TEMACT(45)<em>H2OACT(45)</em></em></td>
<td>2.06 x 10^-12 g/day</td>
</tr>
<tr>
<td>Cumulative amount of coating removed by Day 45, <strong>CUMLOS(45)</strong></td>
<td><strong>CUMLOS(44)+ORGACT*ORGNUM</strong></td>
<td>1.13 x 10^-3 g</td>
</tr>
<tr>
<td><strong>RELESE</strong></td>
<td><strong>Reciprocal</strong> of volume of urea in a single granule, <strong>ADJEXP</strong></td>
<td></td>
</tr>
<tr>
<td>Exponent of exponential release equation, <strong>EXPONE</strong></td>
<td><strong>DIFTEM(45)<em>CONST</em>ADJEXP</strong></td>
<td>0.057 day^-1</td>
</tr>
<tr>
<td>Product of diffusion coefficient and urea solubility, <strong>DIFSOL</strong></td>
<td>*<em>DIFTEM(45)<em>SOLUBY(45)</em></em></td>
<td>0.579 g/cm-sec</td>
</tr>
<tr>
<td>Cumulative amount of coating lost from 100 g SCU, <strong>ADJLOS(45)</strong></td>
<td>*<em>CUMLOS(45)<em>GRANUM</em></em></td>
<td>8.055 g</td>
</tr>
<tr>
<td>Amount of coating lost on Day 45, <strong>ADJLOS</strong></td>
<td><strong>ADJLOS(45)-ADJLOS(44)</strong></td>
<td>0.234 g/100 gSCU</td>
</tr>
<tr>
<td>Weight of SCU granules opened on Day 45, <strong>GRAMREL(45)</strong></td>
<td><strong>A*DADJLOS</strong></td>
<td>1.31 g</td>
</tr>
<tr>
<td>Number of granules opened on Day 45, <strong>GRAMREL(45)</strong></td>
<td><strong>GRAMREL(45)/AVGWTG</strong></td>
<td>65.5</td>
</tr>
<tr>
<td>Output</td>
<td>Calculation</td>
<td>Result</td>
</tr>
<tr>
<td>----------------------------------------------------------</td>
<td>---------------------------------------------------------------</td>
<td>--------</td>
</tr>
<tr>
<td>Volume of granules opened on Day 45, VOL(45)</td>
<td>0.758*GRAMREL(45)*PCTURE</td>
<td>1.32 cm³</td>
</tr>
<tr>
<td>Amount of SCU diffused out of granules opened on Day 45, REL(45)</td>
<td>DIFSOL<em>CONST</em>GRANREL(45)/PCTURE</td>
<td>0.025 g</td>
</tr>
<tr>
<td>Total amount of SCU per 100 g SCU granules opened on Day 45, CUMREL(45)</td>
<td>CUMREL(44)+REL(45)</td>
<td>0.025 g</td>
</tr>
<tr>
<td>Amount of urea which can be contained inside granules in saturated solution, SATTOT(45)</td>
<td>VOL(45)*SOLUBY(45)</td>
<td>0.822 g</td>
</tr>
<tr>
<td>Amounts of urea released from Groups 1,1-1,1-2,...,J+1 are calculated. Granules in Group J are the first encountered with all their urea in solution</td>
<td>GRAMREL(J)-CUMREL(J)</td>
<td></td>
</tr>
<tr>
<td>Amount of urea remaining inside Group J granules on Day I, REMURE</td>
<td>REMURE*(1-EXP(-EXPONE))</td>
<td></td>
</tr>
<tr>
<td>Amount of urea released in exponential stage from granules opened on Day I, REL(J)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Percentage of total added urea which has diffused out of open granules by Day 45, CUMDAY(45)</td>
<td>[ \sum_{i=1}^{45} \text{CUMREL}(i) ]</td>
<td>30.0 percent</td>
</tr>
</tbody>
</table>