



**STUDIES ON POTASSIUM CHLORIDE BASED –CONTROLLED RELEASE FERTILIZER  
MADE FROM SAND– CEMENT MATRIX COATED WITH NAPHTHALENE**

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**ABSTRACT:** Sand matrix based KCl controlled release fertilizer is made and tested. The parameters of the study are initial fraction of KCl, fractional binder, Fractional inert, Diameter of the pellet and Particle size of the sand. The release of fertilizer from the pellet depended on the compositional parameters of the study. Based on Fick's second law, a model was developed for the sand matrix fertilizers with naphthalene coating. Simulated data from the model was agreeing well with experimental values.

The developed equations are as follows:

$$X_A = g_t = \frac{3}{\rho_s r} \left[ \frac{Dt}{(l_c m_l)} (c_s) \right] \quad 0 < t < Y$$

**Keywords:** Plant nutrients, fertilizer, controlled release, modeling, naphthalene, KCl

## INTRODUCTION

Application of fertilizers is inevitable in the modern farm practice to get better yields. Fertilizers add nutrients to the plants those are not adequately supplied by the soil. Fertilizers are classified into two broad groups namely organic and inorganic. Organic fertilizers are derived from living resources like plant or animal. For example: manure, sewage sludge, blood meal, cotton seed meal and bone meal etc. Chemical fertilizers are manufactured synthetically and have many advantages like it could be manufactured at a very fast rate and also at low cost. The fertilizer could be supplied to the plant at a very faster rate but some times the release is too fast need to be controlled for several reasons as discussed below.

Since the solubility of chemical fertilizers is very high leads to the condition of abundant supply of nutrient to the plant which in turn causes root burn and finally damage the plant. Increased intake of fertilizers is highly susceptible for the attack of pest. In addition to the problems mentioned above, cost of the produce is high with the increased use of fertilizer. The other unwanted conditions are loss of fertilizer by way of leaching leads to the ground water pollution. To overcome the above problems the use of controlled release fertilizers are recommended. Controlled release fertilizers are broadly defined as products that release nutrients to the soil for plant uptake at a pre-determined time and rate.

The application of controlled release fertilizers have following objectives

1. To improve the yield and reduce the cost of production.
2. To increase the nutrient efficiency and quality of the produce.
3. Reduction of plant toxicity and stress.
4. Substantial reduction in ground water pollution and water bodies.
5. Reduction of the labor cost for the application of fertilizer.

Application of controlled release fertilizer could achieve the following advantages

1. Root burn can be avoided with the application of controlled release fertilizers even at the increased quantities of fertilizers supplied.
2. Fertilizers are released at a slower rate throughout the season; so that plants could take up most of the nutrients without much waste by way of leaching.
3. Reduced seed or seedling damage from high local concentrations of salts
4. Reduced leaf burn from heavy rates of surface application.

Application of controlled release fertilizers has several advantages. Despite the several advantages of controlled release fertilizers, only about 0.15% (Dr. Sunil K. Jain reviewed the controlled release fertilizer with coating<sup>65</sup>) of the total fertilizers consumption is controlled release fertilizers. This is mainly due to the very high cost of Controlled release fertilizers and lack of proper legislation in many parts of the world.

Hence, the development of cost effective controlled release fertilizers have been a never ending quest for scientific community and a delight to the farmers as it offers several advantages over conventional fertilizers.

Several methodologies have been visualized and adopted for the preparation of controlled release fertilizers. But works on cost effective methods are meager. In pursuance of the task, several strategies have been followed. They are

- ❖ Chemically combined form of controlled release fertilizers (1-11).
- ❖ Fertilizers embedded in inert matrix. (12-23).
- ❖ Fertilizers with permeable coating (24-53).
- ❖ Fertilizers with enzymes which inhibit the release rates such as nitrification inhibitors and other release retarding agents (54-58).
- ❖ Use of Natural organics that decays slowly due to microbial action and release the fertilizers slowly (59-63).

Apart from the techniques mentioned above there are several other methods reported in literature given in chapter 2. The methods mentioned in the literature are not cost effective. In view of this, present work is proposed so as to produce reasonably cheaper fertilizer.

In India, the farming community made several attempts to develop the controlled release fertilizers and practiced. The methods they adopted were tar coated urea; neem cake mixed with urea and urea coated with neem seed extract and were practiced. The farmers found difficulty in the preparation of tar coated urea and urea coated with neem extract as it resulted uneven and uncoated urea. For the case where urea mixed with neem cake has very low retention capacity because of its high porosity. The practice of neem extract coated urea was failed because of tedious procedure required for it. The methods available so far failed due to one or other reasons. Due to the above reasons an attempt is made in the present study to develop a controlled release fertilizer.

Sixteen nutrient elements are essential for the growth and reproduction of plants. Plants obtain the most abundant nutrients – carbon, hydrogen and oxygen – from water and the air. The other 13 elements are divided into three categories: primary, secondary and micronutrients. Nitrogen (N), phosphorus (P) and potassium (K) are primary nutrients which are required in fairly large quantities compared to the other nutrients. Calcium (Ca), magnesium (Mg) and sulfur (S) are secondary nutrients needed for the plant in lesser quantities than the primary nutrients. Zinc (Zn), manganese (Mn), iron (Fe), boron (B), copper (Cu), molybdenum (Mo) and chlorine (Cl) are micro- nutrients which are required by plants in very small quantity. The primary and secondary nutrients are required in large amount. These are said to be as macro nutrients, Among them KCl is an important fertilizer applied to water logged rice fields which is liable to loose through run of water because of its instantaneous nature of dissociation and high mobility.

Some of the KCl fertilizer also lost through seepage. To retain the KCl fertilizer for longer time in the field, it is necessary to develop a controlled release fertilizer. Hence an attempt is made in the present study to develop controlled release potassium chloride fertilizer.

The aim of the study is to develop cost effective controlled release potassium chloride fertilizer and evaluate its release rate and release fraction with time. It is further proposed to develop a model and compare the results with the model developed. Potassium chloride, sand and cement system was envisaged, with which controlled release fertilizer pellets are made with sand matrix and cement as a binder. The sand is present everywhere on the earth and is available to the farmers at free or negligible cost, so that the controlled release fertilizers could be prepared at less cost.

Among the several binders considered for the pellets preparation, cement was chosen because of its availability at moderate costs. It also has very good binding capacity with sand in the preparation of aggregate. As the materials used for the preparation of the aggregate are familiar to the farmers, the procedure developed can be easily implemented. The pellets prepared are of various composition of KCl, sand and cement.

The binder fraction in pellet was maintained in the range from 0.05 to 0.3. However lower binder fractions were favored on cost consideration. The binder fractions beyond 0.3 were found to be unsuitable as the pellets so made were unable to release the KCl. The data are analyzed and the results obtained are presented in terms of time Vs fraction of fertilizer retained in pellet ( $X_A$ ) and release rate ( $-r_A$ ). The results revealed that the pellets prepared in the present study could last up to 18 days. The study was also directed to conduct experiments with pellets of reduced release by incorporating pore blocking agents like benzoic acid. Dissolution studies of these pellets resulted slow release fertilizers. Benzoic acid based fertilizer lasted for 38 days. Thus the controlled release fertilizers produced are highly useful for the farming community.

Based on Fick's second law, a model was developed for the above controlled release fertilizers. The data simulated from the model is in good agreement with experimental values. The developed model constituted with correction factor ( $m_f$ ) parameter together with other parameters is highly useful for predicting the release rate data. The controlled release fertilizers can be prepared using the above knowledge.

The developed equations are as follows:

$$\text{With Coating: } X_A = g_t = \frac{3}{\rho_s r} \left[ \frac{Dt}{(l_c \cdot m_f)} (c_s) \right] \quad 0 < t < Y$$

$$X_A = g_t = 1 - \frac{c_s}{\rho_s} \exp\left(-\frac{3D}{r l_c} (t - Y)\right) \quad t > Y$$

Where  $l_c$  depends on system of the study and its parameters.

The Values of  $m_f$  for each system is presented under

$$m_f = 0.52488 f_{\text{kcl}}^{0.8} f_c^{-0.32} f_s^{1.75} f_d^{-0.19} \dots \text{Benzoic acid coating}$$

## MATERIALS AND METHODS

### Materials

Materials used in the present study are classified into two groups. The first group is those principally used for the preparation of pellet either in making pellet matrix or coating material. The second groups of materials are utilized in analysis of the leachant.

The first group or pellet forming materials are as follows.

1. Potassium Chloride (fertilizer)  
Sand (inert material)
2. Cement (binding agent)
3. Naphthalene coating material

Potassium chloride utilized in the present study is an analytical reagent whereas sand is of river bed origin washed number of times followed by drying in oven at 110 °C for four hours. Cement utilized in the preparation of pellet is Portland cement. The chemicals used for the pellets of coatings are wood polish and naphthalene is of commercial grade. The other chemical employed as coating material is analytical grade Benzoic acid.

Chemicals used for the analysis of the leachant are presented here under.

1. Silver Nitrate AR
2. Potassium chromate AR
3. Sodium chloride. AR

Properties and uses of various other materials utilized in the present study are presented hereunder.

### Potassium Chloride

Potassium Chloride is fertilizer or active ingredient in the present study. Analytical grade Potassium Chloride was incorporated in the pellet. It is a primary nutrient and is necessary for the healthy growth of the plant. Potassium chloride (KCl) is a fertilizer which is most conveniently expressed as  $K_2O$ . It is made by the reaction of hydrochloric (muriate) acid on potassium containing materials. It contains about 63.17%  $K_2O$  and K content of about 52.44%. It is also known as the muriate of potash.

Potassium is readily absorbed and may accumulate in plant tissue greater amount than actual crop requirement. Potassium is relatively mobile in acidic sands under high rainfall conditions. Particularly it is mobile where the application of ammonium salts is more. In some cases, soluble potassium salts may be toxic if ionic concentration is high enough to interfere with water uptake by the crop. Under these conditions, controlled release potassium is beneficial. KCl is highly soluble in water as it readily dissociate in water, is liable for loss with water either by seepage or by drainage. Hence KCl has been selected for the development of controlled release fertilizer. Controlled release fertilizer pellets were prepared with varying proportions KCl, inert and binder proportions.

**Sand:** Sand is selected as inert matrix or barrier material for the release since it is cheap and shows a tendency to form aggregate with cement, makes it suitable for the matrix material in the present study. It is cheap and easily available for farmers as it may be procured from neighboring streams. It is generally a part of soil, so that no unwanted residue is left in the field unlike controlled release fertilizers made with polymer coating. Sand matrix has the advantage of negligible cost as it can be procured from neighboring streams at meager cost.

**Cement:** Several binding agents were visualized for the study. Among them sodium silicate, tar, cement, lime and plaster of paris are prominent. But Cement binder was selected for the study as it is available abundantly to farmers at fairly cheaper price. Hence cement sand system was selected for the study.

### Coating Materials Used

#### Naphthalene

Naphthalene, also known as naphthalene, bicyclo[4.4.0]deca-1,3,5,7,9-pentene or antimite, is a crystalline, aromatic, white, solid hydrocarbon with formula  $C_{10}H_8$  and the structure of two fused benzene rings. It is best known as the traditional, primary ingredient of mothballs. It is volatile, forming a flammable vapor, and readily sublimates at room temperature, producing a characteristic odor that is detectable at concentrations as low as 0.08(gm mole/lit).

A naphthalene molecule is derived by the fusion of a pair of benzene rings. (In organic chemistry, rings are fused if they share two or more atoms.) Accordingly, naphthalene is classified as a benzenoid, polycyclic aromatic hydrocarbon (PAH). There are two sets of equivalent hydrogen atoms: the alpha positions are 1, 4, 5, and 8 on the drawing below, and the beta positions are 2, 3, 6, and 7. Unlike benzene, the carbon-carbon bonds in naphthalene are not of the same length. The bonds C<sub>1</sub>-C<sub>2</sub>, C<sub>3</sub>-C<sub>4</sub>, C<sub>5</sub>-C<sub>6</sub> and C<sub>7</sub>-C<sub>8</sub> are about 1.36 Å (136 pm) in length, whereas the other carbon-carbon bonds are about 1.42 Å (142 pm) long. This difference, which was established by x-ray diffraction is consistent with the valence bond model of bonding in naphthalene that involves three resonance structures (as shown below); whereas the bonds C<sub>1</sub>-C<sub>2</sub>, C<sub>3</sub>-C<sub>4</sub>, C<sub>5</sub>-C<sub>6</sub> and C<sub>7</sub>-C<sub>8</sub> are double in two of the three structures, the others are double in only one. Like benzene, naphthalene can undergo electrophilic aromatic substitution. For many electrophilic aromatic substitution reactions, naphthalene reacts under mild conditions than does benzene. For example, both benzene and naphthalene react with chlorine in the presence of a ferric chloride or aluminum chloride catalyst. Naphthalene and chlorine can react to form 1-chloronaphthalene even without a catalyst. Similarly, whereas both benzene and naphthalene can be alkylated using Friedel-Crafts reactions. Naphthalene can also be alkylated by reaction with alkenes or alcohols, with sulfuric or phosphoric acid as the catalyst. It is normally used as a chemical intermediate, wetting agent/surfactant and also as a fumigant.

#### **Preparation of Potassium chloride pellets**

Controlled release Potassium Chloride fertilizer pellets were made with sand-cement composite as an inert matrix. Cement was chosen as binder because of its availability and low cost. The initial fraction of Potassium Chloride in the pellets was varied as 5, 10, 15, 20, 25 and 30 percent. Cement composition was varied as 5, 10, 15, 20, 25 and 30 percent. The sand composition was varied as the binder and inert materials together contribute to inert matrix. The particle size of sand was also varied as it alters the porosity of the pellet which affects the diffusion rate. The sand particle sizes of 250µm, 212µm and 106µm were used for the preparation of pellets. The ranges of variables covered in the present study are presented as table 5.1.

In the present study, the pellets of Potassium Chloride (KCl, sand & cement system) were prepared by mixing Potassium Chloride with sand and cement in the ratios of 5:95, 10:90, 15:85, 20:80, 25:75, 30:70. The inert composition was also varied to obtain varied strength to the pellets. The proportions of the sand-cement-fertilizer ratios are maintained as 70:30, 75:25, 80:20, 85:15, and 90:10, 95:5. The ingredients of the pellet were mixed with minimum amount of water in a ceramic crucible and moulded into spherical pellets. The mould sizes were varied as 1cm, 0.75cm, and 0.5cm. Larger particle sand sizes are made as they are not suitable for fertilizer applications. Small size pellets were not attempted as they are limited to shorter time of release. The size of the pellet was also limited by the size of the constituent sand particles. The pellets were cured and dried in shade for 10 days. The procedure was repeated to prepare pellets with different sizes sand particle.

#### **Procedure for Pellet Coating**

Phase inversion technique was used for pellets coating with benzoic acid and naphthalene. The coating chemicals were dissolved separately in kerosene till the saturation condition was attained. The pellets were dipped in saturated solution followed by drying at 60°C for one hour. All the kerosene was evaporated leaving behind the coating materials inside the pores of the pellets. For the wood polish coated pellets were dipped in polish followed by drying at room temperature.

#### **Dissolution Procedure**

Pellets of known composition were taken in separate 500ml beakers to which 200ml of water was added. The leaching takes place as the time progresses. The solution was stirred gently and 1ml of the leachant sample was taken and transferred into a conical flask to which 10ml of distilled water was added. One ml of distilled water was added soon after the leachant sample was taken out of the beaker. The beaker was closed with a lid to avoid loss of water by evaporation. Similar procedure was repeated for the pellets in other beakers also. The samples were tested for KCl content by volumetric analysis by titrating against silver nitrate solution. Samples of leachant were collected from time to time and tested for its KCl concentration. The time versus concentration of potassium chloride in the leach liquor was obtained for the pellets with and without coating. The concentration data was taken for 20 days for the pellets without coating. The release data was extended for a maximum period 40 days in the case of pellets with coating.

### Porosity Measurement

Sample pellet was taken and weighed for its initial weight ( $w_1$ ). The sample was then placed in a petre dish and was saturated with water. Excess amount was wiped out with filter paper. The weight of the pellets was again taken ( $w_2$ ). Difference in weight is the weight of water adsorbed. The porosity of the pellet was measured as given below.

Porosity  $\varepsilon = (w_2 - w_1) / w_1$ .

$$\varepsilon = \text{porosity} = w_2 - w_1 / w_1 = \Delta w / w_1$$

### Measurement of Coating Thickness

Film thickness of benzoic acid was measured by weight difference method.

Thickness of pellets Coating: ( $l_c$ )

Initial weight of the of the pellet =  $w_{1c}$

Radius of the pellet (initial) =  $r_1$

Initial volume of the pellet = ( $V_1$ )

Weight of the pellet after coating =  $w_{2c}$

Change in weight =  $w_{2c} - w_{1c} = \Delta w_c$

Where  $\rho$  is the density of the coating material

Volume of Coating =  $V_2 = \Delta w_c / \rho$

Total pellet Volume =  $V_1 + V_2 = V_T$

Increase in radius is obtained from the following expression

$$V_T = \frac{4}{3} \pi r_2^3$$

Where  $r_2$  is radius after coating

The total volume of the pellet multiplied with porosity of the pellet will get pore volume

Porosity =  $\varepsilon$

$$V_T = (4/3) \times \pi r_2^3 \times \varepsilon$$

From above equation will get  $r_2$

$$r_2 - r_1 = l_c$$

From equation will get thickness of the coating.

## RESULTS AND DISCUSSION

Application of synthetic fertilizer is highly useful in increasing the productivity of any crop. It has been in practice for some time and their benefits have been derived by the farming community. Application of fertilizer in excess quantities has several disadvantages such as increased cost of product, root burn, loss of fertilizer by running water or by seepage. Over dosage might also lead to the condition of excess absorption that may attract pest and cause severe damage to crop and loss to the farmers. Therefore it is customary to use organic fertilizer to avoid this type of damage. Limited availability of organic fertilizer forces the farmer to go for synthetic fertilizer. But in practice it is not possible to deliver the nutrient at a desired level by synthetic fertilizer. Therefore, an urge is felt for slow or controlled release fertilizer. The other aspect of excess usage of synthetic fertilizer is environmental pollution. The lost fertilizer may find its way to drainage system or reach the water table. The drained water contaminates the down stream water bodies and ground water in those localities. Nitrate contamination is one such example. Application of nitrate and urea lead to the increase in nitrate pollution in the ground water. The continued and increased usage of fertilizer may pollute ground water making the water not fit for consumption. The other contaminants originated from fertilizers are heavy metals such as Copper, Manganese, Molybdenum, Zinc, Iron, Aluminum, Cobalt, Cadmium, Chromium and Nickel. All the micronutrients may cause environmental degradation when applied in excess amount. All these factors demand the use of controlled release fertilizers.

### Classification of Controlled release fertilizer

Controlled release fertilizers are classified as follows:

**Natural Organics:** Fertilizers like compost contain nutrient values like nitrogen, phosphorus, potassium and other nutrients in combined state and when decomposed it is released as the fertilizer.

**Natural Inorganic:** Some minerals like fluorapatite are the source of phosphate. As it is, these rocky aggregates are insoluble in water but in course of time the rock will disintegrate the minerals will liberate slowly and makes the phosphate available to plant but the release is very slow. The rock is made to react with sulfuric acid to form super phosphate which can be considered as a controlled release fertilizer.

**Synthetic Fertilizers:** Synthetic fertilizers are highly soluble in water and release nutrients at high rate. These fertilizers are sometimes modified to retard the release.

- A. Fertilizer without any modification
- B. Controlled Release Fertilizer
  1. Coated controlled release fertilizer
  2. Chemically modified controlled release fertilizer
  3. Matrix base controlled release fertilizer.
  4. Controlled release fertilizers using enzymatic inhibition.

The term controlled release fertilizer refers to the fertilizer that release nutrient to an extended period. The main objective of the study is to minimize the cost of fertilizer and to extend the period of release. Sometimes aspirations are cast to produce a fertilizer to release at a predetermined time and rate. The controlled release fertilizers could be made with several strategies but the following two are in practice.

1. **Coated controlled release fertilizers:** Several types of materials have been used for coating and tested for their release rates, Sulfur coated urea, neem oil coated urea and polymer coated urea are few among them. Polymers of several types as coating materials have been under study.

2. **Chemically modified controlled release fertilizers:** In this type release rate of fertilizer is decreased by altering the molecular structure to form a new compound. Ex: Urea formaldehyde, Isobutylidene di urea (IBDU), Crotonylidene di urea (CDU), trimethylene tetra urea oxamide, glycouril, and ammelide are some nitrogen based controlled release fertilizers. Magnesium ammonium phosphate ( $MgNH_4PO_4$ ) is a slowly soluble source of nitrogen and phosphorous. Guanyl urea sulfate (GUS) and Guanyl urea phosphate (GUP) are readily soluble in water but are absorbed in soil colloids transforming it into mineralization and have slow release character. Among all these fertilizers sulfur coated urea is improved and favored to go for commercial production by some companies but due to the high cost its use is limited to very low percent of total production.

**TABLE-1 : RANGE OF VARIABLES COVERED IN THE STUDY**

Content	MAXIMUM	MINIMUM
Sand,%	85	55
Cement, %	30	5
KCl, %	30	5
Particle Of The Sand, $\mu m$	250	106
Pellet size, mm	0.5	1
Benzoic acid	Saturated solution	Saturated solution
Wood polish	Saturated solution	Saturated solution
Naphthalene	Saturated solution	Saturated solution

Application of synthetic fertilizer is highly useful in increasing the productivity. It has been in practice for some time and their benefits have been derived by the farming community. Application fertilizer in luxurious quantities has several disadvantages such as increased cost of product, root burn, loss natural resource. Loss of fertilizer may either by running water or by seepage. Excess fertilization may either cause stress to the plant or root burn. Over dosage might also lead to the condition of excess absorption and may in turn attract pest cause severe damage to crop and loss to the farmers. Therefore it is customary to use organic fertilizer to avoid this type of damage which is inherently possess slow release character. But in practice it is not possible to deliver the nutrient at a desired level by synthetic nutrients.

Therefore, a constant need/urge is felt for slow or controlled release fertilizer. The other aspects of excess usage of synthetic fertilizer are environmental degradation. The lost fertilizer may find its way either to drainage system or to underground water table. The drained water contaminates the down stream water bodies and ground water in those localities. Nitrate contamination is one such example. Application of urea or ammonia may lead to the increase in nitrate pollution in the ground water. The continued and increased usage of fertilizer may pollute ground water making the water not fit for biological consumption. The other contaminations originated from fertilizers are heavy metals such as Copper, Manganese, Molybdenum, Zinc, Iron, Aluminum, Cobalt, Cadmium, Chromium and Nickel. All the micronutrients may cause environmental degradation when applied in uncontrolled manner. All these factor demand the use of controlled release fertilizers.

### **IMPORTANCE OF KCL BASED CONTROLLED RELEASE AS FERTILIZER**

Plant nutrient potash is normally applied as potassium chloride or muriate of potash. As potassium chloride is ionic and dissociate completely and is easily liable to loose through drainage. It is envisaged to develop potassic control release fertilizer by fixing in an inert matrix. Several inert matrixes were envisaged among them sand, fly ash, organic compost etc. In the present study sand is selected as matrix material as it is easily available to formers at no cost. The binder compatible to sand in making aggregate is cement. Though the cement is a manufactured product, it is available at low cost when compared to any other type of binders. CRF of potassium chloride is made with the procedure outlined in materials and methods. The sand matrix CRF is made and tested in the procedure outlined in chapter materials and methods. The release data are obtained in terms of concentration versus time and shown as Figure1. The figure reveals concentration of fertilizer or the leach ant increases with time. Observation of fig1 reveals three regions. The first region is initial region, where the release of fertilizer is large in short interval. It can be attributed to the fact certain quantity of fertilizer reside in large pores are transported out of the pellet. The next region which is due to increased resistance to mass transfer may be micro pore diffusion and hence decreasing mass transport conditions prevail. The third region is the one where the concentration of the fertilizer in the pore sap falls below its saturation concentration. The calculated data consisted of fraction of KCl released from the pellet ( $X_A$ ), rate of release of KCl and other factors.

### **CONTROLLED RELEASE POTASSIUM CHLORIDE FERTILIZER MADE FROM SAND-CEMENT MATRIX AND COATED WITH NAPHTHALENE**

Naphthalene is a petrochemical and is sparingly soluble in water. It is an organic chemical and has no affinity to water. Fertilizer pellets were dipped in the kerosene solution of naphthalene and the samples were subsequently dried in air. A thin coating of naphthalene was obtained by phase inversion technique. The coating on the pellet narrows down the pore diameter making the diffusion slower. Thus the coated pellets were experimented for their release in terms of various parameters of the pellets as discussed earlier.

#### **Effect of initial fraction of potassium chloride**

Potassium chloride fertilizer is the principal component of the pellet and its composition is to be maximized in the pellet. In view of this pellets were made with KCl fraction varying from 0.05 to 0.5, but those with KCl fraction above 0.3, were physically unstable. A graph is drawn as  $X_A$  versus time with initial fraction of KCl in pellet as parameter and shown as fig.1. The figure reveals three regions namely initial release region, slow release region and final or fast release region. The initial fractional release is found to be minimum for pellets with KCl fraction of 0.3. For pellets with less KCl composition the initial release is relatively high and would range from 0.05 to 0.025. The negative slope of the first order region is decreasing with increase in initial fraction of KCl indicating slow release rate. For pellets with lower initial KCl fraction the slope is uniform and the release is faster. The release sustained from 10 to 15 days. The higher initial fraction of KCl in the pellet offered longer release period.



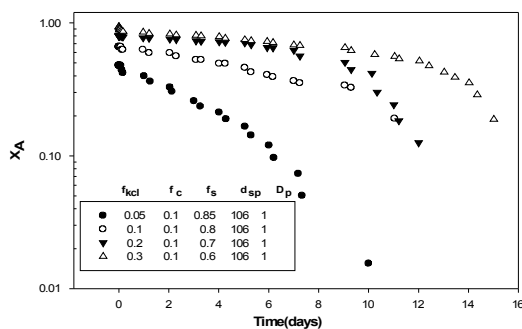


Fig. 1. Variation of  $X_A$  with time(days)- Effect of initial fractional KCl.

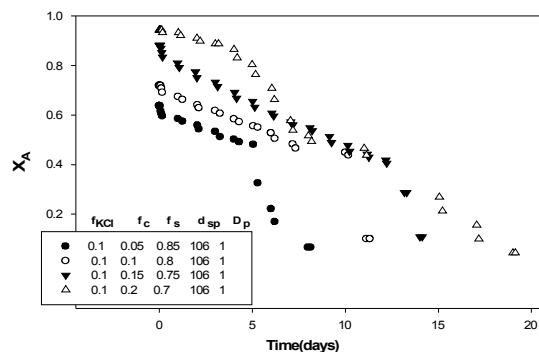


fig.2. Variation of  $X_A$  with time(days) - Effect of fractional binder.

### Effect of fractional binder

The binder composition in the pellet has significant influence on release pattern. The release sustained for longer period as the binder fraction increases. Increased binder fraction offers strong and impervious pellet makes the release slow. The graph shown as fig. 2 indicates the effect of binder. The region B is decreasing with decreasing binder fraction. The release sustained for 11 to 19 days as the binder fraction increases from 0.1 to 0.2. Either for economy or for lower residue in the field on the long run lower binder fraction is preferable. The binder fractions 0.15 and 0.2 have shown a marginal influence and hence 0.1 binder fractions are suggested for practical applications.

### Effect of pellet diameter

Effect of pellet diameter is shown in fig.3. Large diameter pellets offer more resistance for mass transfer and thereby slow release was observed. Plots are drawn for  $X_A$  versus time with pellet diameter as parameter and shown as fig.3. The figure reveals large diameter pellets offer slow release. The negative slope of the plots is decreasing with increase in diameter indicating slower rate of release. Smaller diameter pellets show more uniform release rate when compared to pellets. Therefore, smaller diameter pellets are preferred. The release lasted for 9 to 15 days.

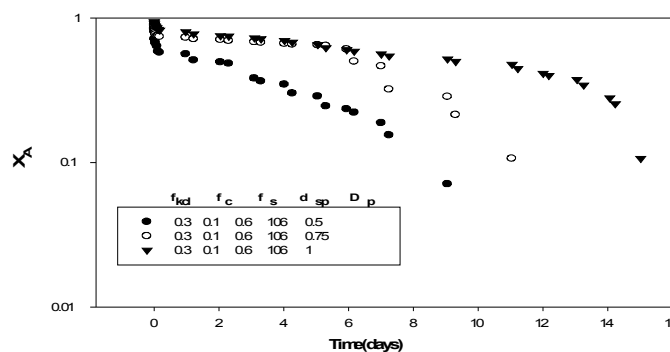


Fig.3. Variation of  $X_A$  with time(days)-Effect of pellet diameter.

### Effect of particle size of the sand

The sand particle sizes were varied from 106  $\mu$ m to 250  $\mu$ m in the present study. Pellets with the smaller size sand particle offered the longer release period. Fig.4 shows the effect of particle size of sand. The fig.4 reveals that the release period extended from 11 to 15 days as the particle size varied from 250  $\mu$ m to 106  $\mu$ m. For the smallest size particle (106  $\mu$ m) the release is not yet complete during the period covered in the present study. Smaller particle sizes are always effective but the availability of such particles is a limitation.

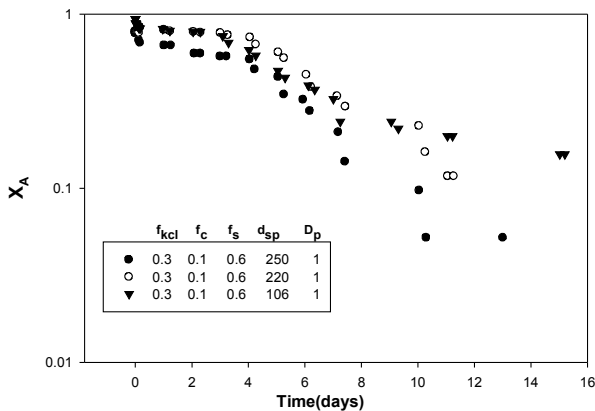


Fig.4. Variation of  $X_A$  with time(days)-Effect of sand particle size

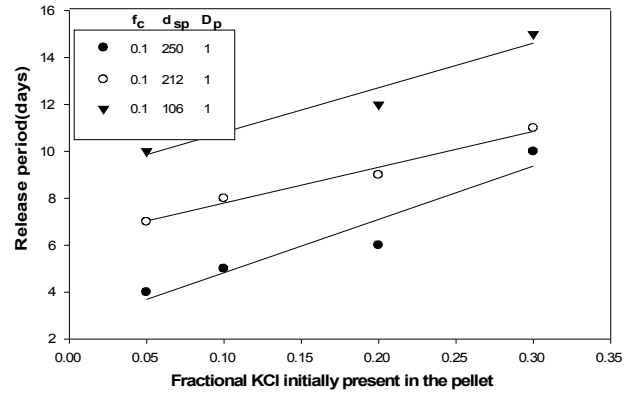


Fig.5. Variation of release period with fractional KCl initially present in the pellet - Effect of sand particle size

A graph is drawn as fractional KCl against release period and the fig.5 reveals that the release period is increasing with the increase in initial KCl fraction. KCl release period was also extended as the sand particle size is decreased, it is maintained throughout experiment.

Fig.6. is a graph shows the effect of binder fraction on release period. The figure reveals as the binder fraction increases the release period is extended. Smaller the sand particle size gives the extended release period. Therefore it is recommended to use smallest possible size particle for the preparation of the controlled release fertilizer.

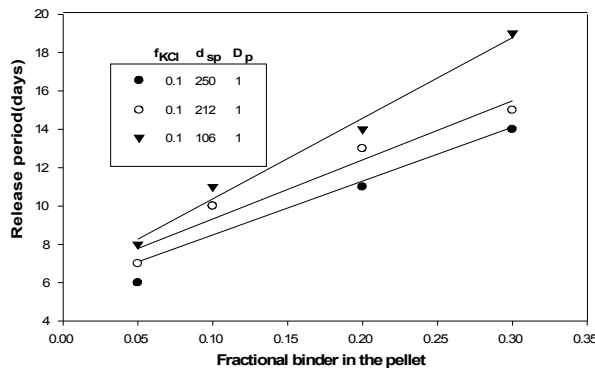


Fig.6. Variation of release period with binder fraction - Effect of sand particle size

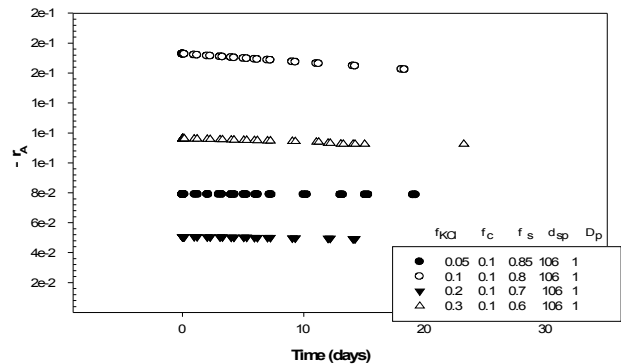


Fig.7. Variation of  $-r_A$  with Time(days)-Effect of initial fractional KCl

A graph is drawn as release rate of  $-r_A$  with time and shown as Fig.7 with initial fractional KCl as parameter. The figure reveals that the rate is nearly constant with in and increase in release rate could be observed as the  $f_{KCl}$  is increased in the pellet.

### CONCLUSIONS

1. Sand matrix based controlled release potassium chloride fertilizer is prepared.
2. Spherical fertilizer pellets were made and diameters of the pellets were varied from 0.5cm to 1cm. The release was extended from 11 to 18 days as the pellet diameter increased from 0.5 to 1 cm. Small diameter pellets are generally favored as they spread into more area. But in release point of view larger diameter pellets are advantageous.
3. Sand as inert matrix was selected because of its availability to the farmers and its meager cost to the farmers. Sand leaves no residue unlike polymer coatings.

4. Cement was selected as binder and its fraction in the pellet was varied from 0.05 to 0.20. It is considered to be a cheap binding material and it is easily available in the market. Pellets with binder fraction above 0.05 are found to be stable. The pellets with 0.15 to 0.2 binder fraction offered longer release period. Pellets with 0.1 to 0.15 binder fractions are recommended as they release sufficiently for longer period and also economical. These fertilizers disintegrate and mix with soil without altering soil characteristics.
5. KCl fraction in the fertilizer was varied from 0.05 to 0.3. Pellets having KCl fraction beyond 0.3 are unstable hence not suitable for the preparation of pellet. Pellets with 0.3 KCl fraction released the fertilizer fairly longer period up to 18 days and it also provides low initial release fraction. Higher the fraction initial fractional KCl in the pellet longer the release period.
6. Sand particle size in the pellet was varied from 106  $\mu\text{m}$  to 250 $\mu\text{m}$ . The pellet prepared with 106  $\mu\text{m}$  size sand particles offered longer release period i.e up to 18 days.
7. Studies were also carried out with the coated pellets: naphthalene was used for coating the pellets.
8. For naphthalene coated pellets the release was extended to a maximum of 19 days.
9. The methods developed in the present study could be adopted by the farmers for the preparation of controlled release fertilizer as they are simple to practice. The preparation costs of these fertilizers are marginal hence cost effective.
10. The release studies are evaluated in stagnant liquids but the actual release period in the field conditions may be high. The actual release period may last for several months.
11. Further study is required in the field level. Agronomic evaluation of the fertilizer is another necessity.
12. The model equation developed for the pellets with coating is presented hereunder.

For the region B:

$$g_t = \frac{3}{\rho_s r} \left[ \frac{Dt}{l_c m_l} (c_s) - \frac{l_c}{6} \right] \quad t^1 < t < Y$$

Model equation for each coating the correction factor  $m_l$  is varying:

System	Equation	A.D	S.D
Naphthalene coating	$m_l = 0.9874 f_{\text{KCl}}^{0.21} f_c^{-0.78} f_s^{-1.32} f_d^{0.46}$	19.355	22.498

A.D = Average deviation ; S.D = Standard deviation

For the region C:

The region for  $t > Y$ , in the present study, for most of sets the fractional KCl in the pellet falls below 0.01 which is insignificant but can be expressed by the following equation.

$$g_t = \left( 1 - \frac{c_s}{\rho_s} \exp\left(-\frac{3D}{rl_c} t\right) \right) \quad t > Y$$

### MATHEMATICAL MODELLING

Baker<sup>93</sup> developed a model for dissolution of spherical drug. The model equation is as follows.

$$\frac{M_t}{M_0} = 4 \left( \frac{Dt}{\pi l^2} \right)^{0.5} \quad \text{for } 0 \leq \frac{M_t}{M_0} \leq 0.4$$

$$\frac{M_t}{M_0} = 1 - \left( \frac{8}{\pi^2} \right) \exp\left(-\frac{\pi^2 Dt}{l^2}\right) \quad \text{for } 0.4 \leq \frac{M_t}{M_0} \leq 1.0$$

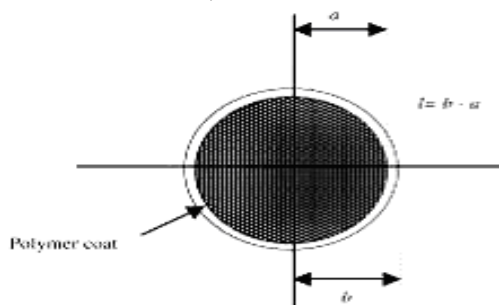
Alzaharni<sup>39</sup> developed a mathematical model for polymer coated controlled release fertilizer

$$\frac{M_t}{M_0} = 6(1 + \alpha) \frac{tD^{0.5}}{(\pi b)^{0.5}}$$

The developed model equations for fertilizer granule coated with polymeric materials. Model for matrix type of controlled release fertilizer has not been reported therefore the following model is developed on the lines of C.Du, J. Zhou and A.Shaviv, H.Wang<sup>37</sup>

$$g_r = \begin{cases} 0 & t < t' \\ \frac{3}{\rho_s r} \left[ \frac{D(t-t')}{l} (c_2 - c_1) - \frac{l}{6} \right] & t' < t < Y \\ 1 - \frac{c_s}{\rho_s} \exp \left( -\frac{3D}{r l} (t - Y) \right) & t > Y \end{cases}$$

**MATHEMATICAL MODEL FOR THE RELEASE OF POTASSIUM CHLORIDE FROM PELLETS COATED WITH BENZOICACID, NAPHTHALENE AND WOOD POLISH.**



Crystalline KCl particles are mixed with sand and cement mixture with little amount of water and made into pellets. The potassium chloride crystals dissolved in water and distributed through out the body of the spherical pellets. When these pellets are kept for drying the moisture either evaporates or takes part in the reaction in the formation of sand cement aggregate. In the course of drying, water gets evaporated to form super saturated solution and re- crystallization begins. As the time progresses the water in the pellet completely evaporates resulting in the formation of tiny crystals. These crystals are embedded in the sand cement matrix. At the instance, when the pellet is placed in water, the pellet gets saturated with water forming a super saturated solution. As the time progresses, the KCl crystals present in the pore sap dissolve slowly with the onset of diffusion through pores followed by the passage through the liquid boundary layer surroundings the pellet. The core material is considered to be super saturated solution of KCl. As the time lapses the core shrinks in size and paving a way to form concentration gradient. The release of dissolved KCl from the core diffuses through the void spaces. The mass balance of dissolved core material is described by a continuity equation in thin spherical shells. From the total volume of pellet only a fractional volume (i.e. void volume) is useful for diffusion. Hence the diffusion rate alters and can be accounted for by a correction factor  $m_l$  and it depends on the composition of the pellet such as  $f_{KCl}$ ,  $f_s$ ,  $f_c$ ,  $d_p$ ,  $D_{sp}$ .

$$4 \Pi r^2 \Delta r \frac{\partial c(r,t)}{\partial t} = 4 \Pi r^2 N_r|_{r=r} - 4 \Pi r^2 N_r|_{r=r+\Delta r} \text{-----}1$$

- $C_{core}$  = molar concentration of dissolved core material inside the void spaces per unit volume of solution
- $r$  = radial coordinate
- $\Delta r$  = thickness of the shell
- $t$  = diffusion time

Where molar flux of fertilizer in the radial direction is approximated by Fick's law per unit area.

$$N_r = -\frac{D}{m_i} \frac{\delta c}{\delta r} \quad \text{-----2}$$

By combining equations (1) & (2) the following equation results.

$$\frac{\delta c}{\delta t} = \frac{D}{m_i} \left[ \frac{\delta^2 c}{\delta r^2} + \frac{2}{r} \frac{\delta c}{\delta r} \right] \quad \text{-----3}$$

The concentration with respect to r, t

$$m_i \frac{\delta c(r,t)}{\delta t} = D_{eff} \left[ \frac{\delta^2 c(r,t)}{\delta r^2} + \frac{2}{r} \frac{\delta c(r,t)}{\delta r} \right] \quad \text{-----4}$$

By substituting u for C (r, t) Eqn (3) becomes

$$\frac{\delta u}{\delta t} = \frac{D}{m_i} \frac{\delta^2 u}{\delta r^2} \quad \text{-----5}$$

Hence consider  $\left( \frac{D}{m_i} = D^1 \right)$

The above equation represents the distribution of concentration of dissolved core material.

Boundary conditions

$$u(0, t) = C_1 a \quad t > 0 \quad \text{-----6}$$

$$u(r, t) = C_2 a \quad t > 0 \quad \text{-----7}$$

$$\text{Initial condition } u(x,0) = 0 \quad t = 0 \quad \text{-----8}$$

Where x is any radial distance from the surface of the pellet.

The method of separation of variables is applied to solve Eqn(5) ,

For simplicity, u(x,t) is represented by X(x).T(t)

$$u(x,t) = X(x) T(t) \quad \text{-----9}$$

Where X(x) is function of x, and T (t) is function of t, by substituting X(x).T (t)

For u(x, t) and by rearrangement

$$\frac{1}{D^1 T} \frac{dT}{dt} = \frac{1}{X} \frac{d^2 X}{dx^2} = -\lambda^2 \quad \text{-----10}$$

Where λ is a constant.

From Equation (9)

$$\frac{dT}{dt} = -\lambda^2 D^1 T \quad \text{-----11}$$

$$\frac{d^2 X}{dx^2} = -\lambda^2 X \quad \text{-----12}$$

Solving Eqns (11) & (12) gives, following solutions result

$$X: \left\{ \begin{array}{l} A_1 x + A_2 \quad \text{for } |r|=0 \\ B_1 \sin \lambda x + B_2 \cos \lambda x \quad \text{for } |r| \neq 0 \end{array} \right\} \quad \text{-----1}$$

$$T: \left\{ \begin{array}{l} \text{constant} \quad \text{for } |r|=0 \\ B_3 e^{-\lambda^2 D^1 t} \quad \text{for } |r| \neq 0 \end{array} \right\} \quad \text{-----1}$$

Where  $A_1, A_2, B_1, B_2, B_3$  are constants.

Therefore the solution to the differential equation is as follows

$u(x,t)=$

$$\left\{ \begin{array}{l} a_1x + a_2 \\ (A_3 \sin \lambda x + B_4 \cos \lambda x) \exp(-\lambda^2 D^1 t) \end{array} \right\} \begin{array}{l} \text{for } \lambda = 0 \\ \text{for } \lambda \neq 0 \end{array} \quad \text{-----15}$$

We know that

for  $\lambda = 0$

$$u(x,t) = a_1x + a_2 \quad u(l,t) = c_2b$$

by boundary condition

$$c_1a = a_2 \quad u(l,t) = a_1l + a_2$$

$$a_1l = c_2b - c_1a \quad c_2b = a_1l + c_1a$$

$$a_1 = \frac{c_2b - c_1a}{l}$$

Where  $a_1, a_2, A_3, B_4$  are constants.

Applying the boundary conditions from equations (6) and (7), to the solution for  $\lambda = 0$ , and using the principal of superposition:

$$u(x,t) = c_1a + \frac{(c_2b - c_1a)}{l}x + (A_3 \sin \lambda x + B_4 \cos \lambda x) \exp(-\lambda^2 D^1 t) \quad \text{-----16}$$

Applying the boundary conditions to the above expression implied that the value for  $B_4$  is zero, and that

$$\lambda = \lambda_n = \frac{n\pi}{l} \quad n = 1, 2, 3, \dots \quad \text{-----17}$$

Therefore

$$u(x,t) = c_1a + \frac{(c_2b - c_1a)}{l}x + \sum_{n=1}^{\infty} A_n \sin \lambda_n x \exp(-\lambda^2 D^1 t) \quad \text{-----18}$$

The initial condition, equation (11), requires that

$$-c_1a - \frac{(c_2b - c_1a)}{l}x = \sum_{n=1}^{\infty} A_n \sin \lambda_n x \quad \text{-----19}$$

Using Fourier series expansion yields

$$A_n = \frac{2}{l} \int_0^l \left[ -c_1a - \frac{(c_2b - c_1a)}{l}x \right] \sin \frac{n\pi x}{l} dx$$

$$= \frac{2}{n\pi} [(-1)^n c_2b - c_1a], \quad n = 1, 2, 3, \dots \quad \text{-----20}$$

Thus the final solution is

$$u(x,t) = c_1a + \frac{(c_2b - c_1a)}{l}x + \frac{2}{\pi} \sum_{n=1}^{\infty} \frac{1}{n} ((-1)^n c_2b - c_1a) \sin \frac{n\pi x}{l} \times \exp[-n^2 \pi D^1 t / l] \quad \text{-----21}$$

When  $l$  is thickness of hypothetical membrane formula to be added

$$\left( \frac{4\pi}{3} [r^3 - (r-l)^3] = \frac{\text{mass}}{\text{density}} \right)$$

Hence the diffusion distance  $x$  in mm in the membrane is defined as

$$x = r - a \quad \text{-----22}$$

From Eqns (21) & (22) we get that

$$c(r,t) = \frac{ac_1}{r} + \frac{(c_2b - c_1a)}{rl}(r-a) + \frac{2}{\pi r} \sum_{n=1}^{\infty} \frac{1}{n} ((-1)^n c_2b - c_1a) \sin \frac{n\pi(r-a)}{l} \times \exp \left[ -n^2 \pi D^1 t / l \right] \quad \text{---23}$$

From this expression  $D (\delta c / \delta r)_{l=r-a}$  which is the current volume flux  $J_0$  in  $\text{kg h}^{-1}$  rate at which the diffusing substances emerges at the interface) is readily calculated.

$$J_0 = \frac{D^1}{lr} (c_2b - c_1a) + \frac{2D^1}{\pi r} \sum_{n=1}^{\infty} \frac{1}{n} ((-1)^n c_2b - c_1a) \times \exp (-n^2 \pi D^1 t / l^2) \quad \text{----- 24}$$

Quantity of fertilizer released,  $Q_t$  can be obtained as

$$Q_t = J_0 4\pi abt \quad \text{-----25}$$

From Eqns (24) and (25)

$$Q_t = 4\pi ab \left[ \frac{D^1 t}{lr} (c_2b - c_1a) + \frac{2D^1 t}{\pi r} \sum_{n=1}^{\infty} \frac{1}{n} ((-1)^n c_2b - c_1a) \exp \left[ -n^2 \pi D^1 t / l \right] \right] \quad \text{-----26}$$

As the exponential coefficient appearing in the Eqn (26) is proportional to  $n^2$ , the term in the series with a large value for  $n$  or larger value for  $Dt/l^2$  decay very quickly with time. Thus, as a good approximation, only the first and the second terms may be retained. The nutrient concentration  $c_1$  is very small when the water volume outside the granule is large enough, and it can be regarded as zero,  $c_1 = 0$ . When the release is complete,

As  $t = \alpha$  equation (26) becomes

$$Q_t = 4\pi ab \left[ \frac{D^1 t}{lr} (c_2b - c_1a) - \frac{l}{6} \right] \quad t^1 < t < Y \quad \text{27A Region A}$$

$$Q_t = \frac{4\pi D^1 ab^2 c_2}{lr} \left[ t - \frac{l^2}{6D^1} \right] \quad t > Y \quad \text{27B Region B}$$

This has an intercept on the  $t$  axis given by  $t_1$

$$t_1 = \frac{l^2}{6D^1} \quad \text{-----27}$$

Where  $t_1$  in days was defined as the lag period.

In the present case  $l$  is very small, so  $t_1$  is also small, and the total lag period is still decided by  $t$ . Where  $l$  is very small,  $a=b=r$ , therefore

$$Q_t = 4\pi r^2 \left[ \frac{D^1 t}{l} (c_2 - c_1) - \frac{l}{6} \right] \quad \text{-----28}$$

Cumulative release of nutrient in moles is  $g_t$

$$X_A = g_t = \frac{Q_t}{M_o} \quad \text{-----29}$$

$X_A$  = Cumulative fraction released.

Where  $M_o$  is the total mass of nutrient, nutrient density  $\rho$ , in  $\text{kg m}^{-3}$

$$M_o = \frac{4}{3} \pi r^3 \rho_s \quad \text{-----30}$$

From Eqns (30) & (31)

$$g_t = \frac{3}{\rho_s r} \left[ \frac{D^1(t-t^1)}{l} (c_2 - c_1) - \frac{l}{6} \right] \text{-----31}$$

Where  $c_1=c_s$  and  $c_2=0$  and by neglecting  $t^1$

$$g_t = \frac{3}{\rho_s r} \left[ \frac{D^1(t-t^1)}{l} c_s - \frac{l}{6} \right] \text{-----32}$$

By differentiating equation (33)

$$\frac{dg_t}{dt} = \frac{3D^1c_s}{\rho_s r l} \text{-----33}$$

Where  $c_s$  is the saturated concentration of nutrients in  $\text{kg m}^{-3}$

When there is no solid fertilizer in the granule ( $t > Y$ ), the concentration in the granule is no longer saturated: Where  $Y$  is the time when the fertilizer in the pellet reaches its saturation concentration.

$$c_t = \frac{(1 - g_t)M_0}{V} = \rho_s (1 - g_t) \text{-----34}$$

Where  $c_t$  is the nutrient concentration in the granule in  $\text{kg m}^{-3}$ ,  $Y$  is the time when all the solid nutrients dissolved in  $d$ , and  $V$  is the granular volume in  $\text{m}^3$ .

By substituting Equation (35) in (34)

$$\frac{dg_t}{dt} = \frac{3D^1}{\rho_s r l} \rho_s (1 - g_t) = \frac{3D^1}{r l} (1 - g_t) \text{-----35}$$

When  $t=Y$ , the boundary value for the cumulative percentage of nutrient release  $g_y$  is

$$g_Y = \frac{M_0 - c_s V}{M_0} = 1 - \frac{c_s}{\rho_s} \text{-----36}$$

From Eqns (36) & (37)

$$g_t = 1 - \frac{c_s}{\rho_s} \exp\left(-\frac{3D}{r l} t\right) \text{-----37}$$

Initial lag period for release was not significant in the present work and it can be seen from fig. 1 - 8.

For the present case  $1-X_A$  or  $g_t$  is very small and  $Y$  is large hence can be neglected.

However and can be computed from the following expression

$$g_t = \left( 1 - \frac{c_s}{\rho_s} \exp\left(-\frac{3D}{r l} (t - Y)\right) \right) \quad t > Y$$

$g_t$  = fractional fertilizer released is exactly equal to  $1-X_A$

$X_A$  = fractional fertilizer released

Therefore,

$$1 - X_A = \frac{C_s}{\rho_s} \exp\left(-\frac{3D}{r l} (t - Y)\right) \quad t > Y \text{---38}$$

Where  $Y$  is time taken to reach the saturation point.

Where  $l=l_c$  is the thickness of the coating material and computed with the procedure outline below.

**Film thickness of benzoic acid, wood polish and naphthalene were measured by weight difference method and the method followed is presented hereunder.**

Thickness of pellets Coating: ( $l_c$ )

Initial weight of the of the pellet before coating =  $w_{1c}$



Radius of the pellet (initial) before coating =  $r_1$   
 Initial volume of the pellet before coating = ( $v_1$ )  
 Weight of the pellet after coating =  $w_{2c}$   
 Change in weight =  $w_{2c} - w_{1c} = \Delta w_c$   
 Where  $\rho$  is the density of the coating material  
 Volume of Coating =  $V_2 = \Delta w_c / \rho$   
 Total pellet Volume =  $v_1 + v_2 = V_T$   
 Increase in radius is obtained from the following expression

$$V = \frac{4}{3} \pi r_2^3$$

Where  $r_2$  is radius after coating  
 The total volume of the pellet multiplied with porosity of the pellet will get pore volume  
 Porosity =  $\epsilon$   
 $V = (4/3) \times \pi r_2^3 \times \epsilon$   
 From above equation will get  $r_2$   
 $r_2 - r_1 = l_c$   
 From equation will get thickness of the coating.

**Model for Region B:**

Therefore, the nutrient release from naphthalene-coated pellet is as follows:

$$g_t = \frac{3}{\rho_s r} \left[ \frac{D^1 t}{l_c} (c_s) - \frac{l_c}{6} \right] \quad t^1 < t < Y$$

The value  $l/6$  is negligible when compared to the term  $\frac{D^1 t}{l_c} (c_s)$ .

$$\frac{D}{m_t} = D^1$$

As the system is highly porous initial time lag for release is also negligible, i. e hence  $t^1$  in the expression is neglected.

$$g_t = \frac{3}{\rho_s r} \left[ \frac{D^1 t}{l_c} (c_s) \right] \quad 0 < t < Y \quad \dots\dots\dots 39$$

$$1 - X_A = g_t = \frac{3}{\rho_s r} \left[ \frac{D^1 t}{l_c} (c_s) \right] \quad 0 < t < Y \quad \dots\dots\dots 40$$

Above expression is more general but it is suitable for the present case with some modification which depends on the material and property of the pellet. The most influential property is the pore diffusivity and it is related with the pellet composition.

Hence  $D^1$  is considered to be function of  $m_t$ .

The value of  $m_t$  is again depends on  $f_{KCl}$ ,  $f_c$ ,  $f_s$ .

Therefore  $m_t \propto (f_{KCl})^{n1} (f_c)^{n2} (f_s)^{n3}$

$$m_t = m_1 (f_{KCl})^{n1} (f_c)^{n2} (f_s)^{n3}$$

On regression analysis, empirical relationships were obtained for each coating and presented hereunder.

System	Equation	A.D	S.D
Naphthalene coating	$m_t = 0.9874 f_{kcl}^{0.21} f_c^{-0.78} f_s^{-1.32} f_d^{0.46}$	19.355	22.498

A.D = Average déviation; S.D = Standard déviation

The model equation can be represented by the following equation for region B.

$$g_t = \frac{3}{\rho_s r} \left[ \frac{D t}{(l_c m_l)} (c_s) \right] \quad 0 < t < Y$$

Where  $g_t = 1 - X_A$ .

Y is the time when the concentration of KCl in pore sap reaches its saturated concentration which is very small and is in negligible proportion. The simulated data are representing fairly well with the present study and can be observed from the figures 8 to 11

#### Model for Region C:

The region for  $t > Y$ , in the present study, for most of sets fractional KCl in the pellet falls below 0.01 which is insignificant but can be expressed by the following equation.

$$g_t = \left( 1 - \frac{c_s}{\rho_s} \exp\left(-\frac{3D}{rl_c} t\right) \right) \quad t > Y$$

Experimental data for the region C is fairly close to the simulated data without any correction factor  $m_l$  and can be observed from the fig. 12 to 15

$$1 - g_t = \frac{c_s}{\rho_s} \exp\left(-\frac{3D}{rl_c} t\right)$$

$$\text{Or } X_A = \frac{c_s}{\rho_s} \exp\left(-\frac{3D}{rl_c} t\right)$$

#### Region A

The mechanism of release may be due to the transport of KCl during the drying along with the water and remain at the surface. The KCl present at the surface dissociates instantaneously and released soon after the introduction of the pellet into the water. It is varying with the composition of the pellet. It is observed that greater the sand fraction greater the initial region. It is also increasing with decrease in the KCl fraction but decreased with the binder fraction and could be observed from the fig. 8 to 10. The initial fraction greatly reduces with the imposition of coating to the pellet. But this region is not governed by the model equation. Since the time taken for the release in this initial region/region A is very low. Therefore it is felt that it is no necessity for the development of a model for this particular region.

#### Comparison:

##### Region B:

$X_A$  versus time data is simulated from the model equations for different pellets and tabulated along with experimental values. Graphs are drawn for  $X_A$  versus time together with simulated data and shown in figures for each coating type in the following graphs.

**Naphthalene coating:** Comparison of plots in figures 8-11 are for model developed and experimental data for the region 'B' respectively.

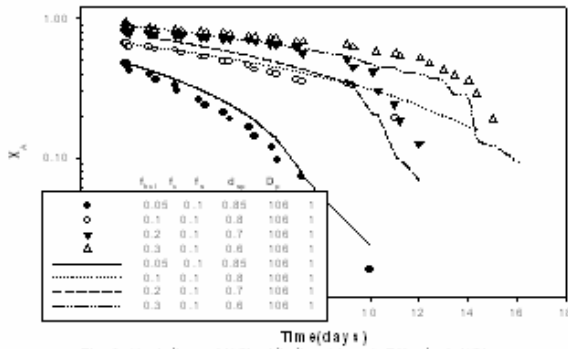


Fig. 8 Variation of  $X_A$  with time(days) -Effect of KCl Compare with Model.

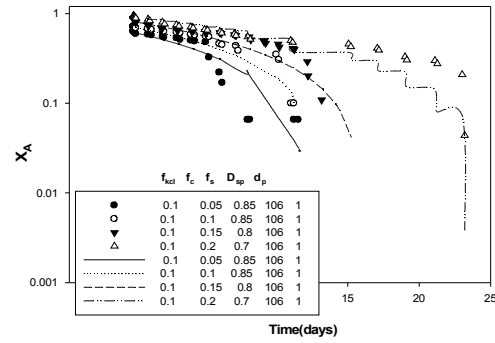


Fig.9.Variation of  $X_A$  with time(days) -Effect of binder Compare with Model.

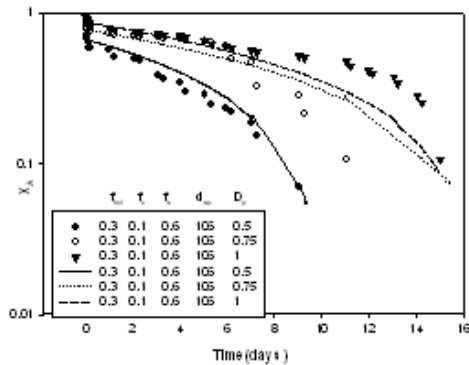


Fig. 10. Variation of  $X_A$  with time(days) -Effect of pellet size compare with Model.

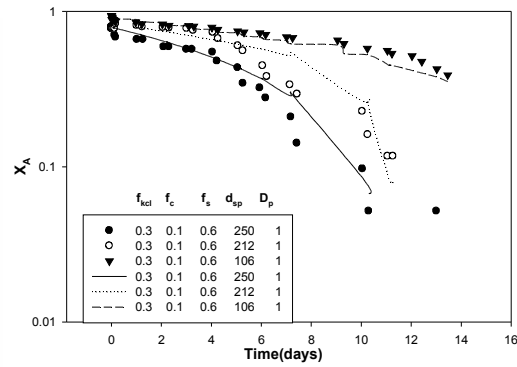


Fig.11.Variation of  $X_A$  with Time(days) -Effect of sand particle size compare with Model.

**Region 'C':** Experimental  $X_A$  versus time (days) together with simulated data from the model equation are compared for region 'C' for different coatings namely for Benzoic acid, Wood polish, Naphthalene coating in the figures.

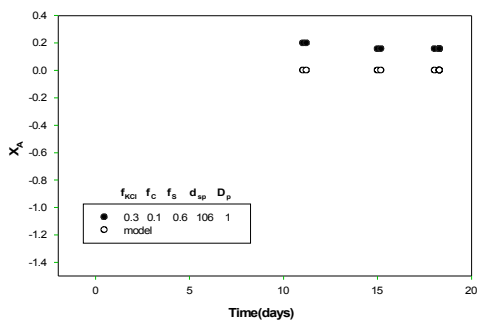


Fig.12.Variation of  $X_A$  with Time(days)compare with model for Region'c' of Naphthalene coating.

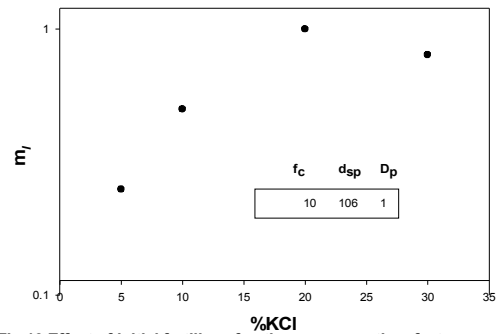


Fig.13.Effect of initial fertilizer fraction on correction factor  $m_1$  - Naphthalene coating.

Correction factor  $m_f$  for pore diffusion resistance for different pellet compositions is functions of compositional parameters are presented in the following figures.

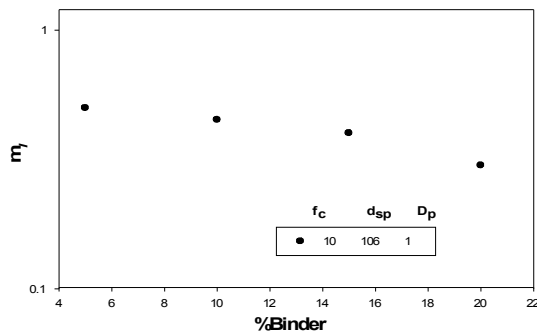


Fig. 14. Effect of binder fraction on correction factor  $m_f$  - Naphthalene coated pellets.

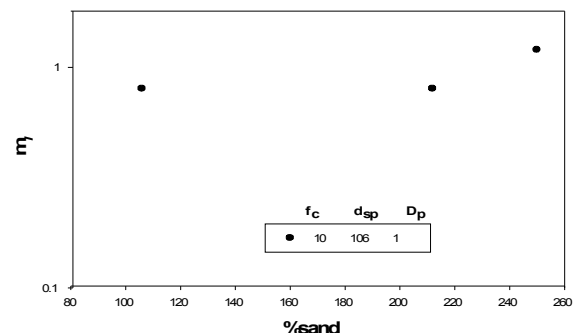


Fig. 15. Effect of sand particle size on correction factor  $m_f$  - Naphthalene coated pellets.

**Table – 2** Naphthalene coating: Composition and diameter of various naphthalene coated pellets in the present study with correction factor.

S.No	KCl	Cement	Sand	Multification factor	Sand Particle Size $\mu\text{m}$	Diameter of the pellet (c.m)
1	5	10	85	0.45	250	1
2	10	5	85	0.5	250	1
3	10	10	80	0.3	250	1
4	20	10	70	0.5	212	1
5	30	10	60	0.8	212	1
6	5	5	90	0.5	212	1
7	5	10	85	0.3	212	1
8	20	10	70	1	106	1
9	30	10	60	0.8	106	1
10	10	10	80	0.5	106	1
11	20	5	75	1.5	106	1
12	10	10	80	0.45	106	1
13	5	5	90	0.8	106	1
14	5	10	85	0.35	106	1
15	10	5	85	0.7	106	1
16	10	10	80	0.7	106	1
17	20	10	70	0.8	106	1
18	20	5	75	0.9	106	1

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