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Original Research Paper

Studies on Controlled Release of Fertilizer Zinc Sulphate Made with Super Phosphate as Inert Matrix

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Controlled release
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Fertilizer
Inert matrix
Binding agent

ABSTRACT

The paper presents controlled release of zinc sulphate fertilizer made with super phosphate as inert matrix. Pellets were made from the mixture and the release rate of zinc sulphate with time was studied. The parameters covered are fractional zinc sulphate, fractional silicate lime, fractional super phosphate and diameter of the pellet. The parameters also measured with naphthalene coating pellets and compared. The release rate expression was obtained and represented as: $-r_A = 5.85\, f_{ZnSO4}^{1.9}\, f_s^{4.23}\, f_{sl}^{-0.72}\, (d_p/d_s)^{1.2}$. The study is useful to identify the controlled release of zinc sulphate fertilizer and also to predict the release rate at any instant of time.

INTRODUCTION

Development of cost effective controlled release of fertilizers has been felt by farmers, in general, and scientific community in particular. Controlled release of micronutrients is even more important as their requirements to the crops are at very low rates. In pursuance of this task, several strategies have been followed but significant results have not been achieved. Some of them are: 1. Chemically combined form of controlled release fertilizers which has low solubility (Mohd Zobir et al. 2005), 2. Fertilizers embedded in inert matrix (Helaly & Nashar 2002, Yongsong et al. 2005), 3. Fertilizers with permeable coating controlled release fertilizers, 4. Impermeable coatings with small pores, cracks, etc. (Abdekhodaie & Chang 1996), 5. Fertilizers with enzymes which inhibit the release rates such as nitrification inhibitors, 6. Fertilizers with polymer coating, 7. Natural organics that decays slowly due to microbial action and release the fertilizers slowly.

The controlled release fertilizers minimize the loss of fertilizers by leaching, volatilization, rain or water run off of fertilizers. In the present study, superphosphate matrix has been envisaged as it is low cost and is itself fertilizer having controlled release nature, which is further improved by adding the sodium silicate lime binder and further $ZnSO_4$ micronutrient has been added to the fertilizer and pelletized to get suitable size of pellets. The pellets offered long life in aqueous media when compared to unbound super phosphate (Zhongxin et al. 2003, Hudson 1996, Johnson et al. 1999). As time proceeds, $ZnSO_4$ has been released slowly with nearly constant rate. The rate is dependent on the parameters like fractional $ZnSO_4$, fractional matrix, fractional binder content and diameter of pellet.

A detailed study has been conducted to know release of each pellet which contains its own composition and also fractions of various parameters. Several binders were considered in the preparation, but sodium silicate lime was chosen because of its availability at moderate costs. It also has very good capability with superphosphate in the preparation of aggregate. The materials used for the preparation of aggregate are familiar to farmers and the procedure developed can be implemented easily by them. Binder fraction in pellet was maintained in the range from 0.1 to 0.3. However lower binder fractions are favourable on cost consideration. But binder fractions of 0.1, 0.2 and 0.3 are found to be favourable. The results obtained are present in terms of time and cumulative fraction of fertilizer retained in pellet (X_A) and rate ($-r_A$) versus X_A. The results obtained indicated that controlled release fertilizers prepared in the present study last up to 15 days.

The study was also directed to conduct experiments with reduced porosity of the pellet by incorporation of naphthalene coating. Dissolution studies of these coated fertilizers yield slow release fertilizers, thus, producing fertilizers, which lasted from 25 to 28 days. All the pellets were improved their performance in delivering slow release when coated with naphthalene. The improvement is almost double (Lan et al. 2008, Maria & Anna 2004). The study revealed that the release followed zero order and the rate depends exclusively on composition and coating. Individual effects of these parameters are systematically presented here.

MATERIALS AND METHODS

Preparation of zinc sulphate pellets: Controlled release zinc sulphate pellets were prepared with super phosphate and silica gel. Silicate-lime was chosen as binder because of its low cost and availability. The quantity of zinc sulphate in the pellets varied as 5, 10, 15 and 20 percent (Novillo et al. 2001, Devassine et al. 2002, Lamont et al. 1987). The binder and inert materials contribute to remaining percentage. Binder composition varied as 1, 2 and 3 percent, the balance is super phosphate inert.

In the present study, the pellets of zinc sulphate ($ZnSO_4$) were prepared by mixing zinc sulphate with super phosphate and silicate-lime in the ratios of 5:95, 10:90, 15:85, and 20:80. The inert composition was also varied to obtain various strengths of the pellets. The entire experiment was carried out using 100 µm and 72 µm size super phosphate particles. The mixtures so prepared were taken separately and sufficient amount of water was added to it and made into paste. The paste was then moulded into spherical pellets of diameters 1.2 cm to 1.3 cm. The pellets, thus, prepared were kept in cool and dark place for curing and subsequently used in the experimentation.

Estimation of zinc release: To estimate the release rate of zinc from the zinc sulphate pellets, a pellet was kept in a 500 mL beaker and 200 mL of water is added to it. The beaker was continuously stirred. The zinc sulphate from the pellet releases slowly into the water. The samples of the leachate were collected at various time intervals and analysed for zinc content using EDTA method (Tzika et al. 2003, Maria et al. 2002, Ryusei et al. 2005, Du et al. 2004, Al-Zahrani 1999). The data of time versus concentration of zinc in the leach liquor were obtained for subsequent mathematical analysis.

Porosity measurement: Sample pellet was taken and weighed for its initial weight (W_1). The sample was then placed in a Petri dish and saturated with water. Excess amount of water was wiped out with filter paper. The pellet was again weighed for its final weight (W_2). Difference in weight was noted, which was taken equivalent to weight of water absorbed. Volume of water absorbed was determined by the following equation:

$V = \Delta W/\rho$ (Liu et al. 2006, Pursell et al. 2005, Yan & Zheng-Yin 2007)

Where, ΔW is weight of water absorbed by the pellet (g)

ρ is density of water (g/m^3)

Porosity E = Volume of water absorbed/volume of the pellet.

Volume of the pellet was calculated from measured diameter which was measured using a sensitive micrometer gauge.

RESULTS AND DISCUSSION

The micronutrient controlled release fertilizers were made with matrix of super phosphate using sodium silicate lime as binder. The ingredients were mixed with sufficient amount of water and pelletized. Zinc sulphate was incorporated in the matrix as an active ingredient. Zinc content was varied from 5 to 50% but the pellets with more than 15% of zinc sulphate were disintegrated either due to the force of water hydration or due to lack of sufficient strength to the pellet. Binder fraction was varied from 4 to 9%. To reduce the cost and also to reduce the strength of the pellet, the binder percentage in the pellet was maintained at optimum level (Rui et al. 2007, Oliet et al. 2004). The mechanical strength of the pellet is to be maintained at an appropriate level so that the disintegration of pellet is done with natural forces of the soil. The experiment was carried out with the pellets so prepared. The same experiment was also carried out with the coated pellets (Hamilton & Johnson 1978). The variables covered in the study are fractional zinc sulphate, fractional sodium silicate lime, i.e. binder, and the fractional inert material and diameter of the pellet. Some of the variables have strong influence while others exhibited marginal effect on the release rate. The range of variables covered in the study are presented in Table 1.

Controlled release fertilizer pellets were tested for their release rates. The release of zinc sulphate sustained for 2 to 7 days. In the case of coated pellets period extended up to 14 days. In the present study sparingly soluble naphthalene was envisaged and adopted as coating material. The delayed release of coated pellets is due to the blockage or narrowing of pores in the pellets. The release data in the present study are divided into two sections, viz.., release data of pellets without coating and release data of pellets with coating.

The data are presented in terms of X_A (mole fraction of zinc sulphate retained in the pellet) v_S time

Where $X_A = N_{Ao}\text{-}N_A/ N_{Aox}$

X_A v_S time (t) data for each curve in the present study were fitted into polynomial of type t,

$XA = b_0 + b_1t + b_2t^2 + b_3t^3 + b_4t^4 + b_5t^5$ (Walker 2001). The coefficients $b_0, b_1, b_2, b_3, b_4, b_5$ together with regression coefficients are presented in Table 2. The data are analysed to know the release pattern in terms of release rate v_S X_A (Douglass et al. 2005, Shavit et al. 2003). The release rate equation is expressed as below.

$$-r_A = 5.85\, f_{ZnSO4}^{\,1.9}\, f_s^{\,4.23}\, f_{sl}^{\,-0.72}\, (d_p/d_s)^{1.2}$$

The data are dependent on all the variables like fractional zinc sulphate, fractional sodium silicate lime, fractional super phosphate, diameter of the pellet and diameter of the super phosphate particle.

Effect of fractional zinc sulphate: Zinc sulphate is an active ingredient in the present formulations, its fraction in the fertilizer to be maintained at higher value so as to reduce inert matter to the proposed fertilizer. Zinc sulphate fraction was varied from 1 to 75% and pelletization was done. Fraction above 15% developed cracks after drying indicating poor mechanical strength. Therefore, fractional zinc sulphate in the pellets was maintained in the range of 1 to 15%. Zinc sulphate content in the pellet has strong influence on the

Table 1: Range of variables covered.

S.No.	Variables	Range
1	Fractional zinc sulphate	5 to 20%
2	Fractional inert matrix	77 to 94%
3	Particle size of the inert	100 µm, 75 µm
4	Fractional binder	1 to 3 %
5	Diameter of the pellet	1 to 1.5 cm

Table 2: Values of the regression and other coefficients.

d_p	f_{zn}	f_b	f_I	b_0	b_1	b_2	b_3	b_4	b_5	r^2
With Coating										
1.148	8	8	84	0.9834	-0.0372	7.954e-4	-7.489e-6	3.099e-8	-4.655e-11	0.9721
1.182	10	8	82	0.9702	-0.0390	8.404e-4	-7.899e-6	3.256e-8	-4.873e-11	0.9844
1.157	12	8	80	0.9484	-0.0413	9.210e-4	-8.807e-6	3.680e-8	-5.570e-11	0.97803
1.186	10	6	84	0.9760	-0.0476	1.068e-3	-1.004e-5	4.141e-8	-6.204e-11	0.9730
1.216	12	6	82	0.9717	-0.0486	1.087e-3	-1.026e-5	4.236e-8	-6.356e-11	0.9708
1.294	8	6	86	0.9428	-0.0525	1.186e-3	-1.122e-5	4.652e-8	-7.011e-11	0.9658
1.305	8	7	85	0.9501	-0.0425	9.557e-4	-9.065e-6	3.746e-8	-5.614e-11	0.9764
1.245	10	7	83	0.9747	-0.0406	8.863e-4	-8.358e-6	3.456e-8	-5.190e-11	0.9791
1.163	12	7	81	0.9488	-0.0466	1.060e-3	-1.006e-5	4.170e-8	-6.268e-11	0.9701
1.236	8	9	83	0.9721	-0.0458	1.013e-3	-9.566e-6	3.960e-8	-5.958e-11	0.9744
1.238	10	9	81	0.9751	-0.0547	1.243e-3	-1.184e-5	4.939e-8	-7.479e-11	0.96461
1.196	12	9	79	0.9454	-0.0478	1.090e-3	-1.036e-5	4.303e-8	-6.484e-11	0.9692
1.132	8	5	87	0.9475	-0.0364	7.930e-4	-7.539e-6	3.1417e-8	-4.747e-11	0.9833
1.263	10	5	85	0.8882	-0.0516	1.216e-3	-1.173e-5	4.9107e-8	-7.437e-11	0.9541
1.236	12	5	83	0.9549	-0.0561	1.269e-3	-1.202e-5	4.999e-8	-7.556e-11	0.9631
1.294	8	6	86	0.9752	-0.0428	9.333e-4	-8.777e-6	3.632e-8	-5.466e-11	0.9772
1.182	10	6	84	0.9542	-0.0455	1.006e-3	-9.512e-6	3.9460e-8	-5.949e-11	0.9747
1.117	12	6	82	0.9479	-0.0438	9.692e-4	-9.232e-6	3.8580e-8	-5.848e-11	0.9784
1.241	8	7	85	0.9528	-0.0501	1.124e-3	-1.061e-5	4.388e-8	-6.596e-11	0.9742
1.316	10	7	83	0.9423	-0.0437	9.426e-4	-8.722e-6	3.5634e-8	-5.310e-11	0.9804
1.232	12	7	81	0.9922	-0.0436	8.774e-4	-7.778e-6	3.0864e-8	-4.503e-11	0.9806
1.163	8	8	84	0.9620	-0.04058	8.823e-4	-8.271e-6	3.4030e-8	-5.090e-11	0.9813
1.183	10	8	82	0.9415	-0.0472	1.088e-3	-1.048e-5	4.3887e-8	-6.641e-11	0.9745
1.185	12	8	80	0.9707	-0.0475	1.036e-3	-9.632e-6	3.9453e-8	-5.893e-11	0.9751
Without Coating										
1.243	8	9	83	0.8654	-0.0765	2.797e-3	-4.414e-5	3.069e-7	-7.752e-10	0.9819
1.281	10	9	81	0.8346	-0.0840	3.051e-3	-4.756e-5	3.284e-7	-8.271e-10	0.9814
1.387	12	9	79	0.6013	-0.0703	2.798e-3	-4.556e-5	3.222e-7	-8.235e-10	0.8677
1.126	8	8	84	0.8574	-0.0850	3.353e-3	-5.445e-5	3.848e-7	-9.831e-10	0.9628
1.165	10	8	82	0.8261	-0.0860	3.308e-3	-5.289e-5	3.707e-7	-9.429e-10	0.9625
1.287	12	8	80	0.8745	-0.0832	3.109e-3	-4.890e-5	3.386e-7	-8.533e-10	0.9766
1.092	8	6	86	0.8883	-0.0804	2.906e-3	-4.507e-5	3.100e-7	-7.788e-10	0.9818
1.263	10	6	84	0.8668	-0.0862	3.196e-3	-5.005e-5	3.459e-7	-8.716e-10	0.9769
1.268	12	6	82	0.8815	-0.0800	2.935e-3	-4.571e-5	3.144e-7	-7.881e-10	0.9773
1.204	8	7	85	0.8732	-0.0783	2.853e-3	-4.447e-5	3.066e-7	-7.704e-10	0.9816
1.406	10	7	83	0.8796	-0.0793	2.828e-3	-4.338e-5	2.961e-7	-7.396e-10	0.9736
1.462	12	7	81	0.8634	-0.0837	3.148e-3	-5.002e-5	3.490e-7	-8.846e-10	0.9770
1.162	8	5	87	0.8334	-0.0864	3.305e-3	-5.256e-5	3.667e-7	-9.297e-10	0.9726
1.206	10	5	85	0.8783	-0.0765	2.740e-3	-4.206e-5	2.871e-7	-7.169e-10	0.9794
1.236	12	5	83	0.7360	-0.0696	2.653e-3	-4.239e-5	2.967e-7	-7.539e-10	0.9336
1.128	8	6	86	0.8726	-0.0644	2.277e-3	-3.508e-5	2.398e-7	-5.988e-10	0.9808
1.172	10	6	84	0.8790	-0.0825	2.942e-3	-4.552e-5	3.137e-7	-7.906e-10	0.9788
1.242	12	6	82	0.8338	-0.0955	3.619e-3	-5.732e-5	3.995e-7	-1.012e-9	0.9586
1.126	8	7	85	0.9209	-0.0811	2.900e-3	-4.441e-5	3.020e-7	-7.516e-10	0.9825
1.139	10	7	83	0.8816	-0.0907	3.493e-3	-5.593e-5	3.919e-7	-9.958e-10	0.9765
1.234	12	7	81	0.8512	-0.0895	3.565e-3	-5.646e-5	3.894e-7	-9.561e-10	0.9554
1.184	8	8	84	0.8729	-0.0836	3.031e-3	-4.689e-5	3.216e-7	-8.055e-10	0.9792

release rates. A graph is drawn for X_A v_S time as shown in Fig. 1 (Man Park et al. 2005). The figure reveals that there is continuous release of zinc sulphate with time. There are two distinct regions observed from the graph. The first region is the region A where nearly 60-80% of zinc sulphate in the pellet is released in the first 12 hrs of the experimentation. The remaining 40% was released over the period of up to 6.5 days. This region is observed as second region. The release mechanisms are different for each region (Walworth et al. 2003). In the first region the availability of zinc sulphate in the pellet to release is abundant, which may be due to availability of zinc sulphate in macropores and diffuses with less resistance. In the region B, zinc sulphate present in the micropores has to diffuse to macropores where the resistance to diffusion is very high. It may be due to small size of the pore and due to further reduction of micropore size because of the destruction caused by coating material. Initial lag region has not been found significant in the present case but seen in Shavit et al. (2003).

The transition point from region A to region B is called $X_{critical}$, where sharp change in the mode of diffusional transport takes place. $X_{critical}$ depends upon the system of pellet and is different for coated and uncoated pellets. The $X_{critical}$ for coated pellet is 60%, and for uncoated pellet 70-80% (Li 2003, Sharma 1979).

The fractional zinc sulphate in the pellet increases the release of zinc sulphate as observed in Figs. 2, 3, 4, 5 and Figs. 6, 7, 8, 9, 10 for the zinc sulphate pellets with and without naphthalene coating. It is also clear that for the pellets with coating, the zinc sulphate release extended up to 14 days whereas for the pellets without coating the release was only up to 7 days.

Effect of binder: Binder has marginal influence on the release pattern. Binder fraction is varied from 4 to 9%. If binder fraction is less than 4%, the pellet mechanical strength is too poor to with stand handling while its fraction above 9% the pellets are strong, impervious and non destructive in nature. As all these qualities are undesirable, the pellets made with binder fraction above 9% were discarded. Graphs drawn between X_A v_S time with fraction binder as parameter are shown in Figs. 11 and 12) (Lamont et al. 1988, Jarosiewicz & Tomaszewska 2003). The figures reveal that X_A decreases with time. As fraction binder increases marginal decrease in release is recorded. Therefore, pellets with 4% binder are selected, used in the present study and recommended for use.

Effect of inert material: Fractional inert material has little effect on X_A, for it fraction is maintained nearly constant at about 80 to 85%. The effect is shown in Figs. 13 and 14 (Prasanthi et al. 2003). The figure reveal that X_A decreases with time.

Effect of pellet diameter: The effect can be seen for the pellets without coating (Fig. 15) and with coating (Fig. 16). The figures reveal that X_A decreases with time. The two regions can be seen in both the figures. As the diameter of the pellet increases, zinc sulphate retention in the pellet increases at any time. This is in general agreement with the earlier observations (Vaka et al. 2005).

Effect of particle size of the inert super phosphate: Particle size of super phosphate has marginal effect (Figs. 17 and 18). As size of the particle increases porosity of the pellet also increases, hence the release rate. $X_{critical}$ values were also found varying.

CONCLUSIONS

1. The controlled release fertilizer made of zinc sulphate, sodium silicate lime and super phosphate is readily available at low cost.
2. The release rate increased with increase in fractional zinc sulphate.
3. The rate of release decreased with increase in inert percentage.

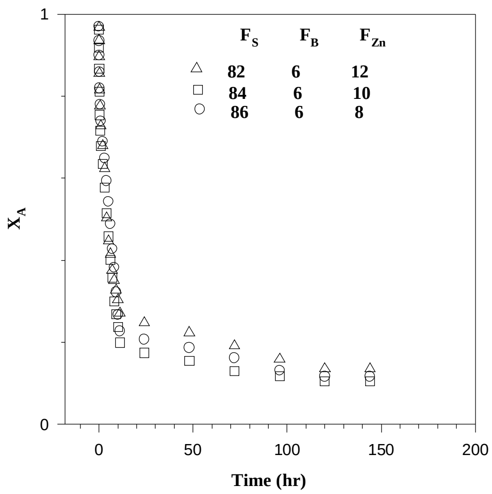

Fig. 1: Variation of X_A with time (without coating).

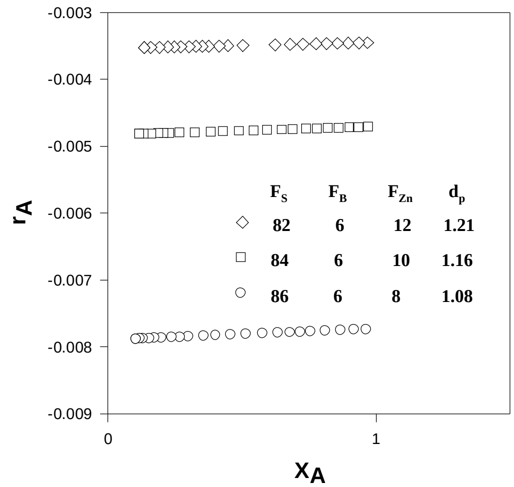

Fig. 2: Variation of r_A V_e X_A (without coating).

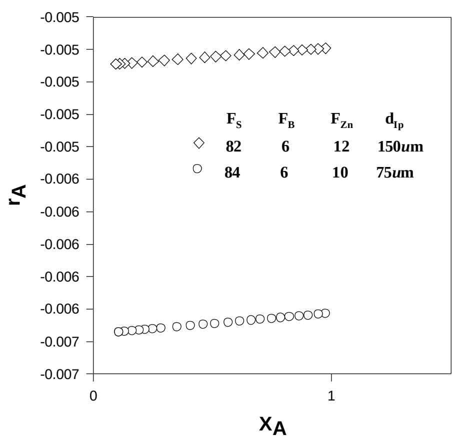

Fig. 3: Variation of r_A V_e X_A (without coating).

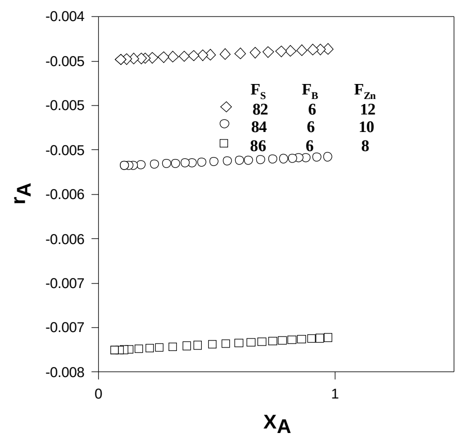

Fig. 4: Variation of r_A V_e X_A (without coating).

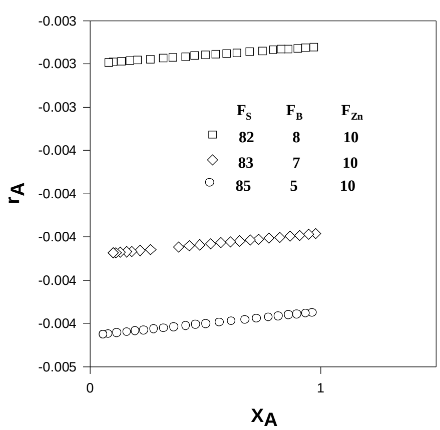

Fig. 5: A variation of r_A V_e X_A (without coating).

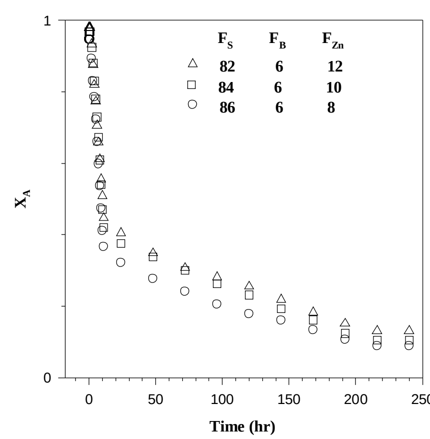

Fig. 6: A variation of X_A with time (with napthalene coating).

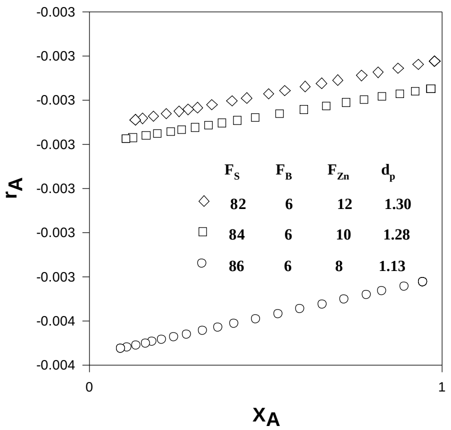

Fig. 7: Variation of $r_A V_e X_A$ (without coating).

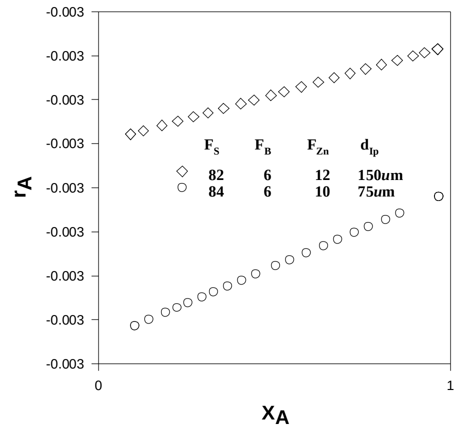

Fig. 8: Variation of $r_A V_e X_A$ (without coating).

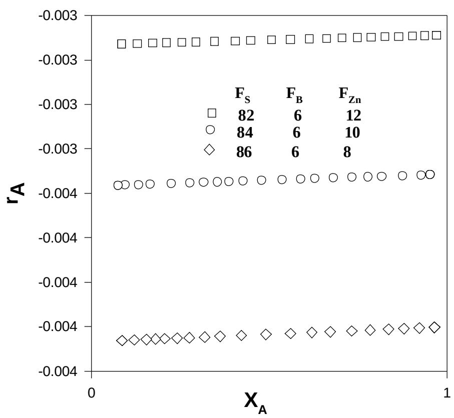

Fig. 9: Variation of $r_A V_e X_A$ (without coating).

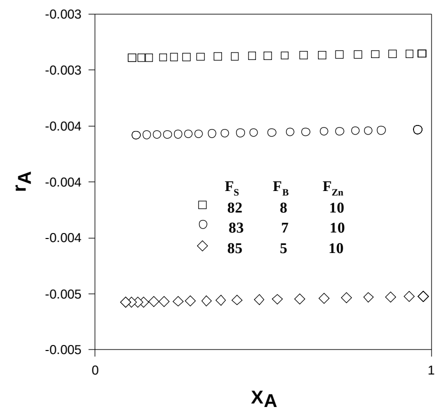

Fig. 10: Variation of $r_A V_e X_A$ (without coating).

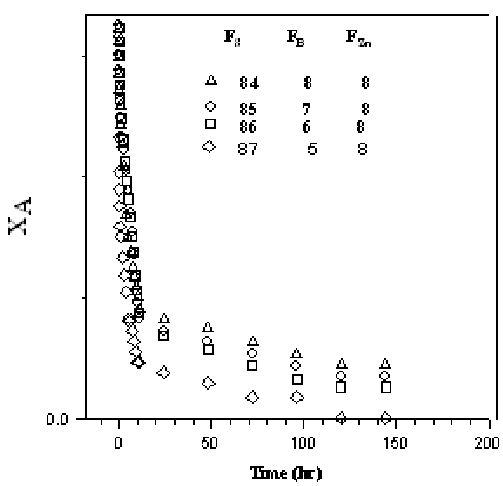

Fig. 11: Variation of X_A with time (without coating).

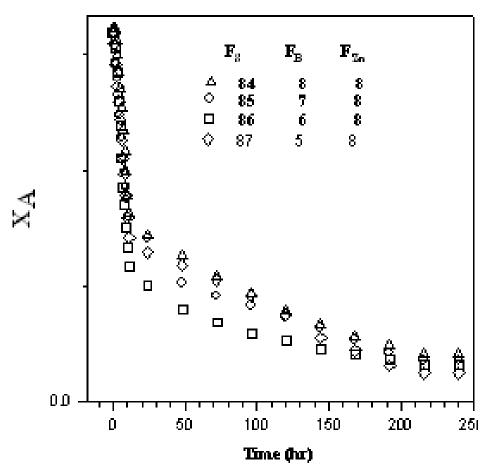

Fig. 12: Variation of X_A with time (with napthalene coating).

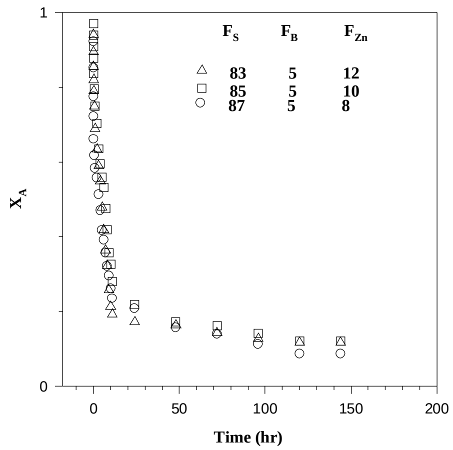

Fig. 13: Variation of X_A with time (without coating).

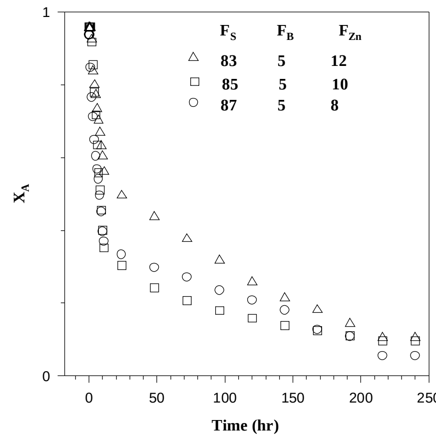

Fig. 14: Variation of X_A with time (with napthalene coating).

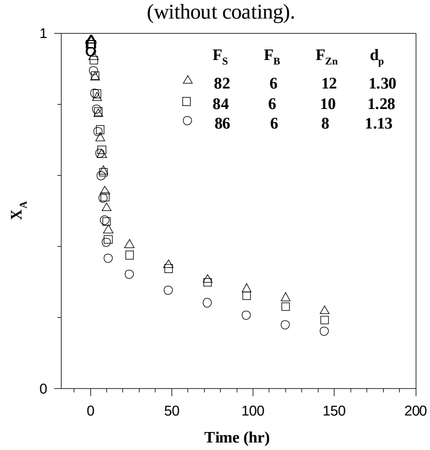

Fig. 15: Variation of X_A with time (without coating).

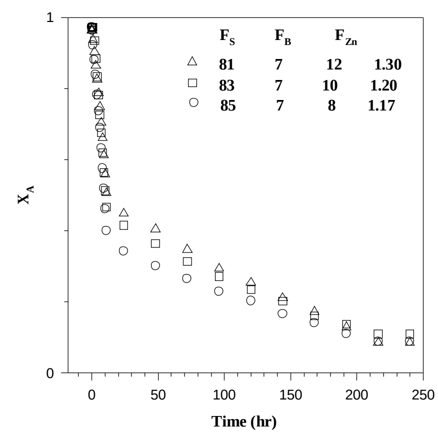

Fig. 16: Variation of X_A with time (with napthalene coating).

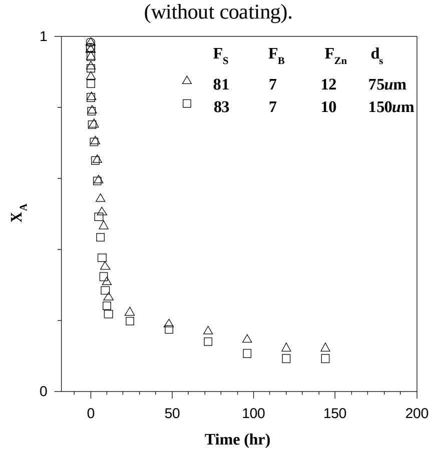

Fig. 17: Variation of X_A with time (without coating).

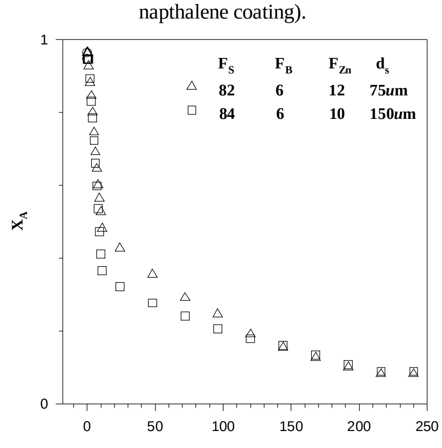

Fig. 18: Variation of X_A with time (with napthalene coating).

4. The increase in diameter of the pellet decreased the fractional release rates.
5. The rate of release decreased with increase in binder percentage.
6. As the inert particle size increased the porosity also increased, thus, increasing release of zinc sulphate.
7. For the pellet without coating the zinc sulphate release was up to a period of seven days. Initially the release rate was high and after 12 hrs the release rate decreased.
8. The Naphthalene coated pellets extended the release of zinc sulphate from 7 days to 14 days with a slow release in the initial period followed by gradual increase.
9. The rate of release of fertilizer is related to fractional zinc sulphate at any instant of time in following format.

$$-r_A = 5.85\, f_{ZnSO4}^{1.9}\, fs^{4.23}\, f_{sl}^{-0.72}\, (d_p/d_s)^{1.2}$$

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