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IMPROVEMENT IN PROPERTIES OF UREA BY PHOSPHOGYPSUM COATING

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Abstract: Particle coating is becoming increasingly important in fertilizer, pharmaceutical and food industries. The demand for coating granular fertilizers with minerals is increasing. Urea is coated with PhosphoGypsum, neem oil, polymeric suspensions and micronutrients like sulfer, zinc etc.Coating of PhosphoGypsum on urea fertilizer is a important application of coating process . Coating of urea particles is done to increase nitrogen use efficiency of urea. Nitrogen losses due to leaching, surface volatilization, and denitrification can be minimized by controlling the dissolution rate. Coating also helps to impart strength, increase in bulk density and lowering of caking tendency, thus improving the handling properties.

The objective of present paper is to present the improvement in properties of urea obtained by fluidized bed coating of urea with Phosphogypsum using wet and dry methods.Emulsion of PhosphoGypsum, Neem *(Azadirachta indica* L.) oil, LAB (Linear Alkyl Benzene) and water was prepared in concentrations of 5%, 10% and 15%. Coating experiments were carried out with both PhosphoGypsum, Neem Oil, LAB and water (wet coating) and PhosphoGypsum, Neem Oil and LAB (dry coating) .

PhosphoGypsum coated samples were analyzed for crushing strength, dissolution rate, dustiness factor and phosphogypsum content. Characterization of coated and uncoated urea prills is done to optimize and control the process of coating and also the performance of urea coating process can be checked which is useful for checking feasibility of this process on an industrial scale.

The experimental results showed that wet method is better than dry method and 1.7 mm diameter size particle give better results than 1.4 mm size diameter particle. Dissolution rate, which is directly related to the nitrogen use efficiency is reduced as a result of coating, thus giving coated urea high moisture holding capacity.

Key Words: *Urea, Coating, Phosphogypsum*

Introduction

Urea is widely used as a fertilizer because of its high nitrogen content (46.6%). Unfortunately, urea is very water soluble and in regions with high precipitation the fertilizer may be leached from the soil before plants have an opportunity to assimilate it. Allison [1] and Lundt [2] have reported that as much as 75% of the nitrogen may be lost in areas with high, intermittent rainfalls. Such losses result not only in increased costs, but they also contribute to the contamination of local waters. Although urea losses can be minimized by the repeated application of smaller fertilizer quantities, the costs associated with repeated spreading are often high. One approach to the problem is to encapsulate the fertilizer granules with shells which have low water permeability. Such shells would retard the release of fertilizer and therefore give plants more time for assimilation. Rindt et al.[3], Blouin et al.[4] and McClellan and Scheib [5] were the first to consider, in some detail the agronomic characteristics of slow-release fertilizers made by encapsulating fertilizer granules. Various fertilizer-coat combinations are available, but phosphogypsum coated urea is sufficiently promising to reach large-scale commercialization [6, 7]. It has long been recognized that sulfur is almost, if not equally, as essential for proper plant growth as nitrogen, phosphorus and potassium. However, the importance of the need to fertilize with sulfur was not a matter of concern as long as animal manures and low-analysis fertilizer were in common use. Phosphogypsum is an ideal sulfur source. It is slightly soluble in water and therefore long-lasting in the soil. The sulfur is present in the sulphate form and can be utilized directly by the plant[8] . It is neutral in its soil reactions and does not change the soil pH and as an added bonus, it contains calcium that is also readily available to the growing plant. While there are many other fertilizer sulfur sources, none of them have all the agronomic advantages of phosphogypsum. Elemental sulfur must undergo bacterial conversion to sulphate before the plant can use it. Organic sources of sulfur must be decomposed bacterially before the plant can use the sulfur. While both sulfur and organic sulfur are long-lasting, phosphogypsum demonstrates the same desirable characteristic due to its low solubility. Most of the other sulphate salts that are used for fertilizer are very soluble and the sulphate may be leached from the soil before the plant can use it.

Phosphogypsum does have one major problem as a fertilizer - it is generally available as a wet salt that does not have good handling properties in fertilizer application equipment. If dried, there would be no handling problem but the cost of drying is relatively high.

Urea is the most popular nitrogenous fertiliser among the farmers because of its low cost and easy availability.But the major disadvantages of urea are its high solubility in water and it is very much susceptible to nitrogen loss through various pathways like leaching, ammonia volatilisation, nitrification and denitrification.Among these ammonia volatilisation is happened to be the dominant loss mechanism because of conventional method of fertiliser application (wet soil surface broadcasting) followed by the farmers encourage it.Modification of urea has been experimented extensively in for increasing its use efficiency by various crops. Neem*(Azadirachta indica* L.) cake[9] and elemental sulphur[4,5] has been used extensively as coating materials for modifying urea fertiliser.But neem-coated or sulphur-coated urea could not succeed mainly because of inconsistent results and high cost involved particularly in the sulphur coated fertiliser.Therefore, alternative chemical amendments eg, ammonium chloride, zinc sulphate, phosphogypsum, copper sulphate and potassium chloride etc.which are otherwise used as fertilisers by the farmers have been tried for making coated urea.

India is one of the largest consumers of nitrogen fertilizers. Commonly used N fertilizers are anhydrous ammonia (82% N), urea (45- 46% N), ammonium sulfate (21% N) and ammonium nitrate (34% N). But they cause nitrogen losses because of de-nitrification, surface volatilization and leaching. These losses vary from 60% to 75% depending upon crops and conditions. Nitrogen loss potential is also obviously influenced by the fertilizer source of N and the way it is used. Urea manufactured by conventional method using prilling has low strength, low bulk density and it is subjected to caking and lump formation. This results in higher rates of dissolution and difficulty in handling. Also nitrification is faster and urea remains for smaller period time in the soil.

Urea being the main nitrogen fertilizer used by the farmers, development and modification should be made for urea to maximize the efficiency of nitrogen use. This is a major factor for appropriate economics in agriculture and horticulture.

Several agriculture scientists investigated[10,11,12] nitrogen loss inhibitors in the form of chemical to retard nitrification reaction and urease action in the hydrolysis of urea. Following are the nitrification inhibitors that were developed: 2-chloro-6-(trichloromethyl), pyridine (nitrapyrin) manufactured by Dorr Chemical Company under the trade name 'N Serve' ;5-ethixy-3-(trichoromethyl)-1, 2, 4, thiadiazole (terrazole) manufactured by Olin Corporation under the name 'Dwell' ;Molten sulfur Polymeric suspensions, Latex; Neem oil and Phosphogypsum.

Slow-release fertilizers are excellent alternatives to soluble fertilizers because nutrients are released at a slower rate throughout the season and plants are able to take up most of the nutrients without waste by leaching. A slow-release fertilizer is more convenient, since less frequent application is required.

Phosphogypsum coating on urea is a new research and no significant data is published . Phosphogypsum slurry applied on urea, forms fine coating and protects the loss of nitrogen by denitrification and leaching thereby ensuring regulated continuous availability of nitrogen for a longer period, as per the requirement of crops. It also protects crops from soil borne pests.

Experimental procedure

Batch experiments were conducted in a fluidized bed unit [13,14](Figure 1). Urea prills(supplied by Indian farmers fertilizers cooperative, Gujarat) were weighed and feed into the unit through one hopper and mixed thoroughly with phosphogypsum(supplied by Paradeep phosphates Ltd.), Neem oil, linear alkyl benzene(LAB) and water feed through other hopper. Air is forced in the bottom of the fluidized bed by pump. Material enter to the fluidized bed through screw feeder. Steady state was indicated by a constant bed temperature and constant head. Final product samples were collected after 20-30 min of fluidization.By this time urea particles where uniformly coated with the mixture.

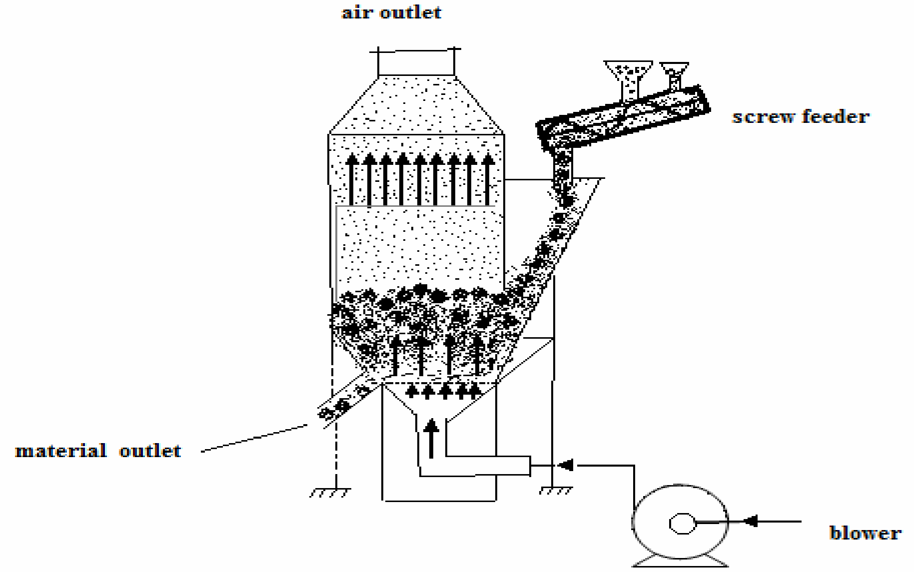

Figure 1: Experimental set up

During the experiments two fluidized bed coating techniques were used: Wet and Dry coating. In Wet coating method Slurry is prepared by mixing of phosphogypsum, Neem oil, linear alkyl benzene (LAB) and water is coated on urea prills. Neem oil acts as an adhesive agent and linear alkyl benzene acts as a surfactant. Phosphogypsum coating of 5%,10% and 15% was done on urea particles of two sizes : 1.4mm and 1.7 mm diameter(this is the general size range in which urea prills are commercially produced so two ends of size range are chosen) ,using wet method. Table 1 shows the amount of material used in wet coating of both sizes.

In Dry coating method a mixture of neem oil, linear alkyl benzene (LAB) and phosphogypsum applied on the urea prills. Water is not used in dry method. Phosphogypsum coating of 5%,10% and 15% was done on urea particles of two sizes : 1.4mm and 1.7 mm diameter in dry method also. Table 2 shows the amount of material used in dry coating of both sizes.

Results and Discussions

The various properties of coated and uncoated urea were studied to highlight the improvement in property due to coating with phosphogypsum and to explore the best coating method dry or wet and the amount of optimum coating which gives best results. These are:

1. Crushing strength: Coated urea fertilizer should have sufficient mechanical strength to withstand normal handling and storage without fracture. The mechanical strength is influenced by its chemical composition, porosity, shape, surface crystal and moisture content[15,16]. Crushing strength is defined as the minimum force required to crushing the individual particle. Crushing strength is measured by applying pressure to individual granules, usually of a specified size range and noting the pressure required to fracture each granule. A compression tester was used for this purpose. Weighted average strength expressed in N/m^2 was determined both before and after coating for particles of size 1.4 mm and 1.7 mm.Figure 2 shows the variation in crushing strength with particle sizes for coated and uncoated urea. When comparing crushing strength data it is important to compare granules of equal size , because crushing strength increases significantly with the increase in the size of the particles.

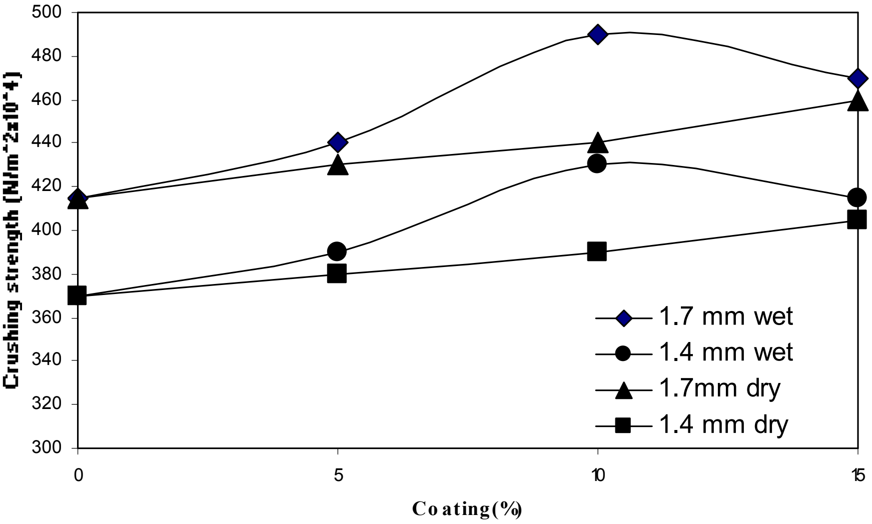

Figure 2: Variation of crushing strength for different percentages of coating and different particle size

The figure shows that for urea of same size coated by wet method ,has better crushing strength as evident by higher values ,then that produced by dry method because more uniform and strong coating is formed in wet method. Also in case of urea produced by wet coating maximum crushing strength is shown by 1.7mm particle at 10 % coating, further increase in coating does not increase the crushing strength. So 1.7 mm urea particles coated with 10 % poshpogypsum show the best crushing strength behaviour.

2. Dissolution rate: The coated and uncoated urea samples were analyzed for dissolution rate[17]. 5 gm of urea particles were put in a beaker containing 50 ml of double distilled water maintained at room temperature. Magnetic stirrer was used at constant speed. The time required for complete dissolution of urea was noted down. This gives the dissolution rate . Figure 3 shows the variation in dissolution rates with particle sizes for coated and uncoated urea.

The figure shows that rate of dissolution decrease with the increase in coating percentage so coated urea dissolves slowly as compared to uncoated(shown by zero percent coating in graph). The rate of dissolution is least for 1.7 mm size particles having coated by wet method by phosphogypsum. So 1.7 mm wet coated particle is best in terms of slow dissolution and is thus suitable for slow release of nitrogen a property highly desirable of a nitrogenous fertilizer. The phosphogysum forms a protective coating on the urea thereby providing a physical barrier for fast dissolution of urea which is highly undesirable.

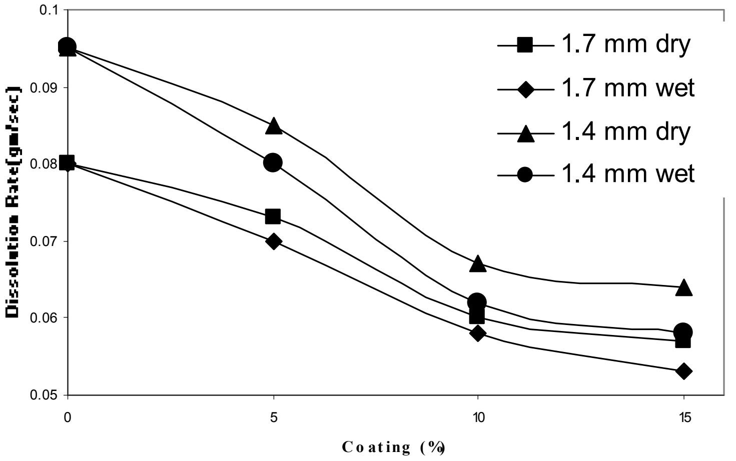

Figure 3: Variation in dissolution rates with particle sizes for coated and uncoated urea

3. Dustiness: Due to the large quantities of fertilizer produced and raw materials handled in bulk, their dustiness is of particular concern and can cause problems like, a significant quantities of material can be lost during processing, handling and application resulting in lost revenues.Also, environmental pollution and exposure of employees to hazardous levels of dust is not indicative of a responsible organization. So dustiness of fertilizer is very undesirable property. The dustiness was measured by taking known amount of phosphogypsum coated urea in a bunker funnel. After taking 10 grams of coated urea in a bunker funnel compressed air is passed from the bottom of the funnel with 10 Psi of pressure. After 5 min sample is removed from the bunker funnel and then weighed . The weight loss is calculated. The amount of weight loss is called dust. Figure 4 shows the percentage of phosphogypsum lost as dust with particle sizes for coated and uncoated urea.

The figure shows clearly that amount of dust generated is higher for dry coated urea particles than wet coated ones. The least amount of dust generation is observed for 1.7 mm urea particles produced by wet fluidization. The dust generation is more in dry coated particle since coated material do not bind strongly with the urea surface, so wet methods is better to control dust problem.

4. Phosphogypsum content: The total phosphogypsum deposited on the urea particles was determined by a crush test. A weighted sample (approximately 10 g) of phosphogypsum coated urea was crushed in a crucible containing 10 ml of water to obtain a fine slurry. The slurry was washed onto a filter paper with excess water. The residue is washed with benzene for removal of Neem oil .The filtered phosphogypsum was left overnight in the oven at 80^0 C to dry and weighed the following day. Figure 5 shows the percentage of phosphogypsum content with particle sizes for coated urea.

The figure shows that maximum percentage of phosphogypsum is deposited on 1.7 mm diameter urea particles coated with 10 % phosphogypsum by wet method. The higher amount that is 15 % coated urea has less percentage of phosphogypsum because excess amount of phosphogypsum deposited is not retained on the surface and is lost in handling. The coated urea prepared by dry method has less amount of phosphogypsum content than that prepared by wet method due to poor adherence of coating material in dry method.

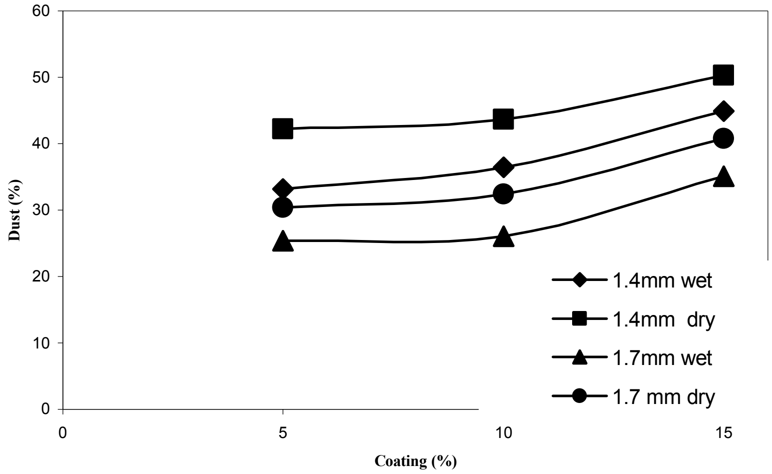

Figure 4: Percentage of phosphogypsum lost as dust for coated urea

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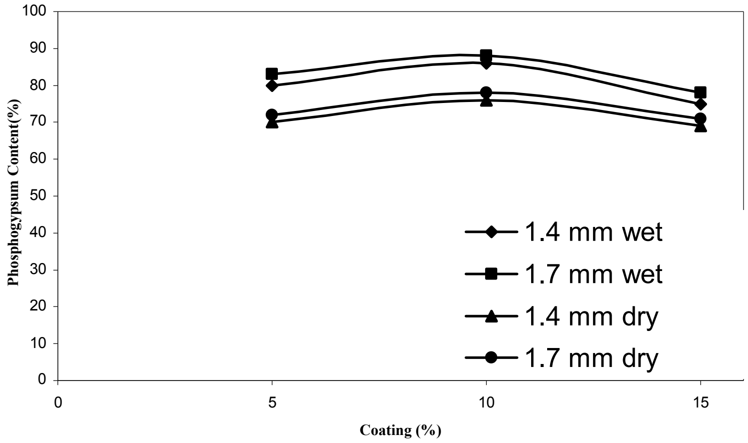

Figure 5: Percentage of phosphogypsum content for coated urea

Microscopic analysis

Among visible methods, Optical microscopy and Scanning Electron Microscopy (SEM) are the two techniques that are used to study the morphology of the particles. The particle surface was observed to check for layering and agglomeration. Layering is desired for the particle coating. Surface irregularities and shape of particles before and after coating was observed.

Several particles were selected randomly and observed under optical microscope at magnifications of 5X, 20X and 50X. Images were taken at these magnifications and analysis of these images for changes in surface properties was done. Few sample images (Figure 6) are shown for coated and uncoated urea particle for both dry and wet coating with different percent of phosphogypsum coating using optical microscope.

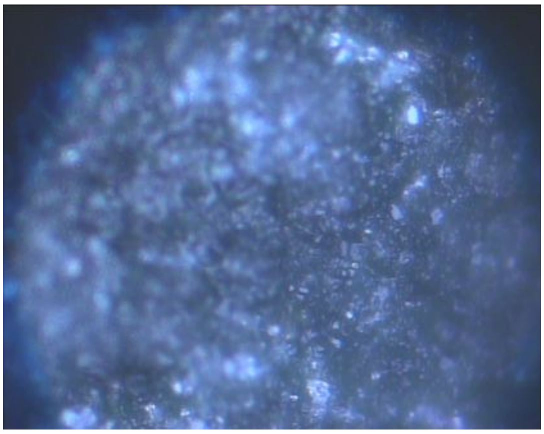

Figure 6(a): Uncoated urea 1.7mm dia (20X)

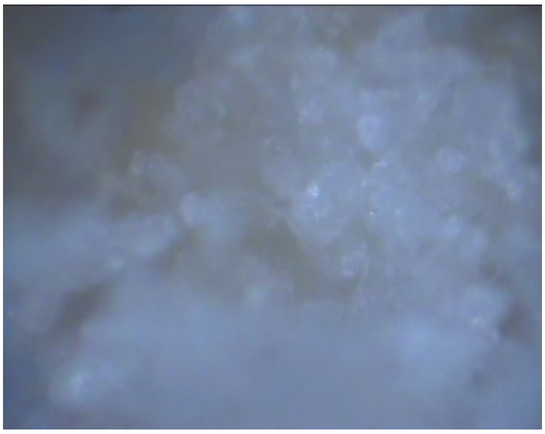

Figure 6(b): 15% wet coated urea 1.7mm dia (20X)

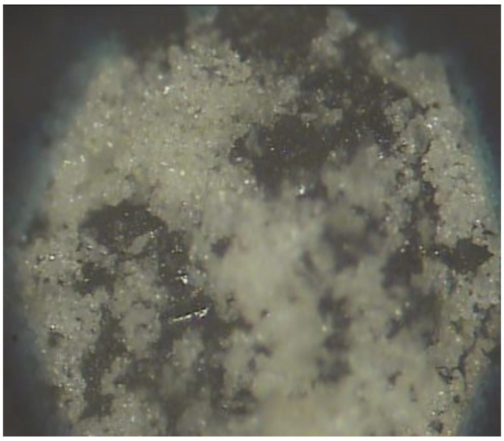

Figure6(c):5% drycoating 1.7mm dia (5X)

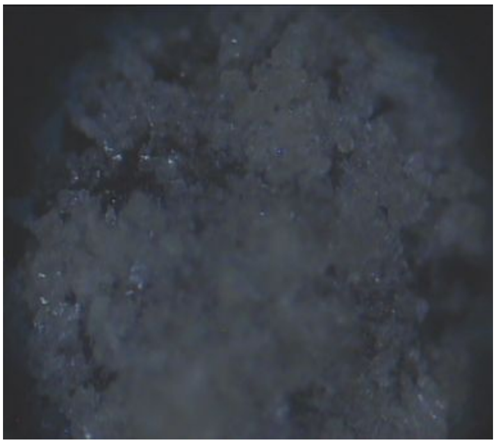

Figure6(d):15% drycoating 1.7mm dia (50X)

The scanning electron microscopy images shown in figure 7 also revels clearly the change in morphology due to coating of urea with different percentages of phosphogypsum using wet and dry method. The urea obtained by wet coating gives more uniform coating as compared to that obtained by dry coating.

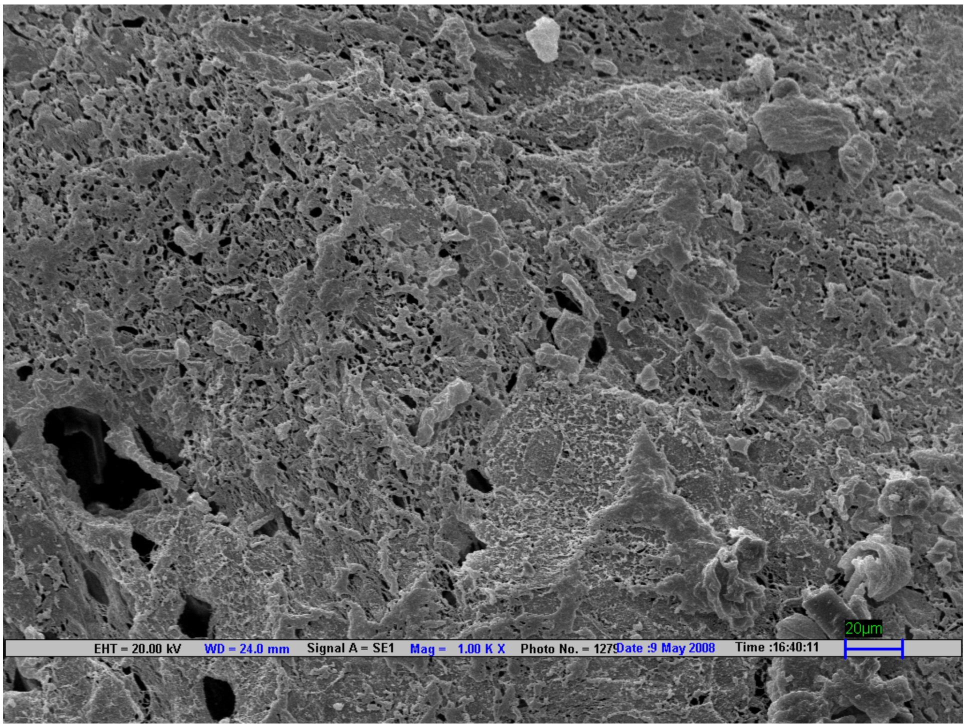

Figure 7(a): SEM image of uncoated urea size 1.7mm

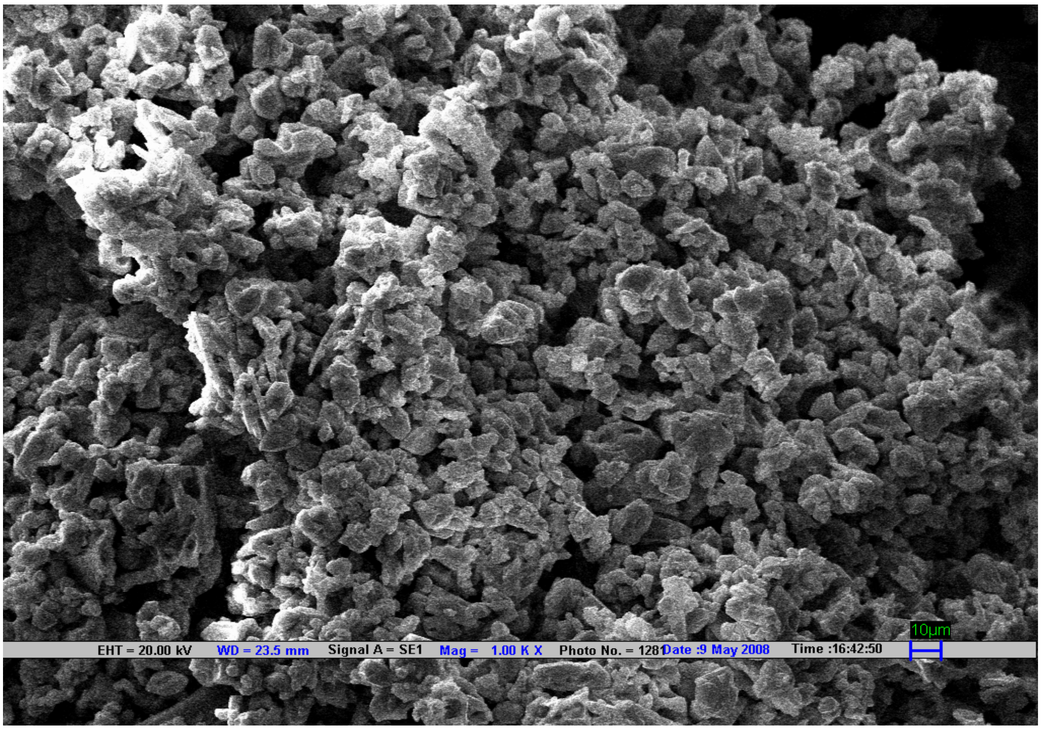

Figure 7(b) : SEM image of coated urea size 1.7mm (15% dry coating with phosphogypsum)

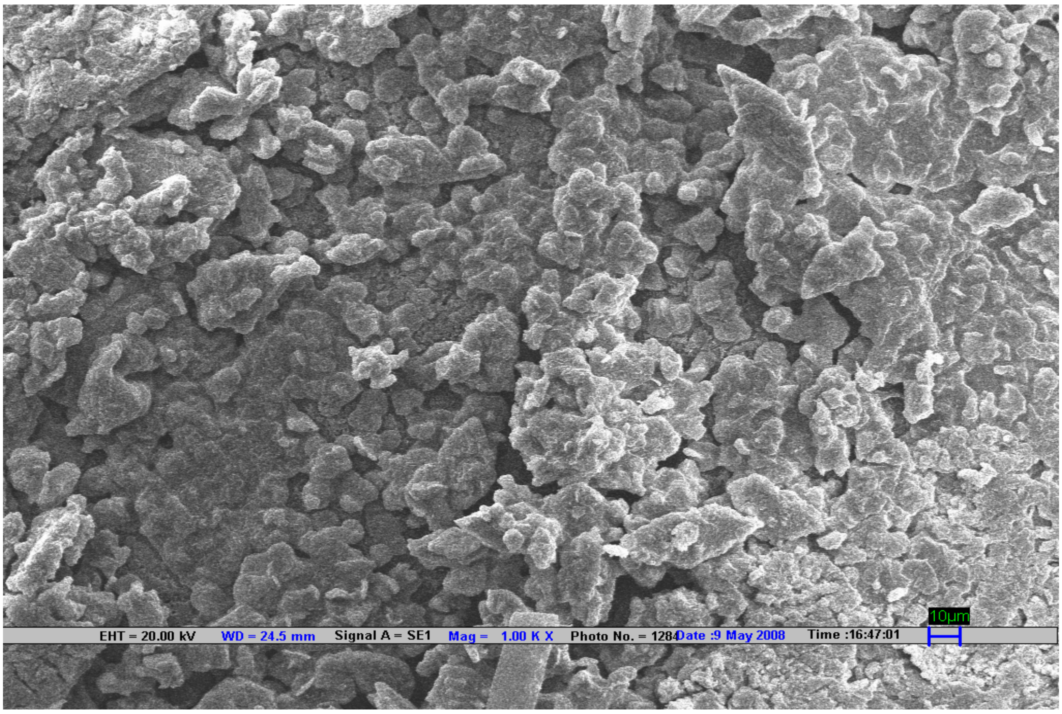

Figure 7(c) : SEM image of coated urea size 1.7mm (15% of wet coating with phoshpogypsum)

Table.1 Materials used in Phosphogypsum coating(expressed in percentage) on urea particle size 1.4mm and 1.7 mm diameter using wet method

S.No.	Material	5%	10%	15%
1	Urea prills (grams)	89	83	76
2	Phosphogypsum(grams)	5	10	15
3	Water (grams)	5	6	8
4	Neem oil(grams)	1	1	1
5	LAB in drops	4	4	4

Table.2 Materials used in Phosphogypsum coating(expressed in percentage) on urea particle size 1.4mm and 1.7 mm diameter using dry method

S.No	Material	5%	10%	15%
1	Urea prills (grams)	94	89	83
2	Phosphogypsum(grams)	5	10	15
3	Neem oil(grams)	1	1	2
4	LAB in drops	4	4	4

Conclusion

Slow-release fertilizers are excellent alternatives to soluble fertilizers. Because nutrients are released at a slower rate throughout the season, plants are able to take up most of the nutrients without waste by leaching. A slow-release fertilizer is more convenient, since less frequent application is required. Fertilizer burn is not a problem with slow-release fertilizers even at high rates of application; however, it is still important to follow application recommendations. Slow-release fertilizers may be more expensive than soluble types, but their benefits outweigh their disadvantages.

Phosphogypsum slurry applied on urea, forms fine coating and protects the loss of nitrogen by denitrification ensuring regulated continuous availability of nitrogen for a longer period, as per the requirement of crops.

The present study has shown that the possibility of using phosphogypsum as a coating material for urea in the form of phosphogypsum, Neemoil and water emulsion. This emulsion when used in 10% concentration on 1.7 mm urea particles showed reduction in dissolution rate, better crushing strength and improved handling properties due to low dustiness. The experimental results showed wet method is better than the dry method and particle size 1.7mm diameter size showed better results than 1.4mm diameter size.

The surface morphology of coated urea observed in the optical microscope and scanning electron microscope (SEM) showed that the surface roughness was influenced by the type of coating technique and percentage of phosphogypsum coating.Wet coating gives more uniform and even coating then dry one.

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