

# Controlled Release of Manganese into Water from Coated Experimental Fertilizers. Laboratory Characterization

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The release of manganese into water from controlled-release formulations containing manganese EDTA or manganese lignosulfonate was studied. These fertilizers were obtained in the laboratory by adhering the source of manganese over urea pellets and by adding a coating. The materials used as adhesives and coatings were mixtures of rosins plus tricalcium phosphate. With regard to the chemical composition, these formulations conformed to national and international standards for commercial fertilizers. The rate of release of manganese was a function of both the source of manganese used and the coating thickness. Under the same conditions the release of manganese was greater for formulations with manganese EDTA than with manganese lignosulfonate. To predict the kinetic behaviors of the two series of formulations, mathematical equations were established. The manganese source plus rosin coatings improved the handling and storage characteristics of the commercial urea pellets. The study of the rosin coatings using scanning electron microscopy showed that they were compact and homogeneous.

**Keywords:** *MnEDTA; Mn lignosulfonate; slow release; rosin*

## INTRODUCTION

For many years fertilizers have been applied in concentrations greatly exceeding those required for the nutrition of plants to ensure an adequate level in the soil solution for a suitable period. This practice led to a loss of the applied product because of leaching and to a risk of surface or ground water pollution, which increases when soluble salts are used as micronutrient fertilizers. In confronting these problems (1), controlled-release (CR) technology can be considered a suitable method to decrease the amounts of micronutrients used while maintaining the benefits of their effectiveness in crops, thereby reducing the risk of environmental damage and the cost of more numerous applications (2, 3).

The following are considered CR fertilizers: (i) nutrient formulations that contain any agent that inhibits microbial activity to avoid the rapid degradation of the fertilizer (4); (ii) slightly soluble organic or inorganic compounds such as urea-formaldehyde (5) or copper polyphosphate (6); (iii) pellets of fertilizers coated with a material that allows for the slow release of the nutrients, which improves their bioavailability (7).

The materials most frequently used as coating are sulfur (8), synthetic polymers (9, 10), and resins (11, 12). In any case, the objective is to obtain a uniform coating layer that is as thin as possible and has the lowest number of pores. This coating helps to enhance those physical properties of the fertilizers that make it possible to handle and store them over long periods of time with no significant deterioration (13). The goal of this paper is to study the possibility of using experimental coated products that contain manganese chelates as fertilizers and to observe how the micronutrient is released into the environment. These products were manufactured by adhering either manganese ethylenediaminetetraacetate (MnEDTA) or manganese lignosulfonate (MnLS) to one source of granular nitrogen

(commercial urea), using a mixture of three rosins (the nonvolatile fraction of pine resin) as an adhesive. One special advantage of this sort of combination of macro- and micronutrients is the relatively even distribution of micronutrients in the soil, coupled with their availability to plants over a longer period of time.

The reasons for having chosen the aforementioned sources of Mn were the high stability of EDTA chelates and the low mobility observed in lignosulfonate complexes (14). Two series of Mn fertilizers were obtained by covering these granulated products with layers of different thicknesses of low solubility materials to obtain the slow release of the micronutrient. The materials used as coatings were a mixture of natural rosin and rosins modified by dismutation and esterification, which improve the stability of natural rosin, as well as tricalcium phosphate.

## EXPERIMENTAL PROCEDURES

**Materials.** The source of nitrogen used was commercial pelleted urea, which was previously sieved to between 2.0 and 2.5 mm. Two commercial sources of Mn were used, CTA-Mn (MnEDTA) of Meristem, S.L. and LIDAUQUEL-Mn (MnLS) of Lida Química, S.L. Used as an adhesive material was a mixture of natural, dismutate (Residis), and esterified (Resi-ester-T) rosins (1:1:1), which were provided by LURESA and dissolved in ethanol. The coating was made with the same mixture of rosins that was used as an adhesive, as well as tricalcium phosphate.

**Fertilizer Preparation.** The pelleted urea was placed into a 14 L coating drum, and the Mn source, finely powdered, was stuck on the pellets by means of the mixture of rosins dissolved in ethanol. This mixture was applied by spraying with a spray gun at regular time intervals, and the excess solvent was evaporated using a flow of air. Once the products reached the required amount of Mn, they were coated with the mixture of rosins plus tricalcium phosphate, according to the methodology proposed by Rico et al. (12).

**Table 1. Products Prepared with Mn-EDTA or Mn-LS on Urea, Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>, and Rosins<sup>a</sup>**

product	Mn <sup>b</sup> (%)	N (%)	conditioner	coating (%)		
				mixture of rosins	tricalcium phosphate	total
MnEDTA0	1.58 (1.94)	38.63 (1.71)	4.21			
MnEDTA1	1.43 (2.96)	35.67 (1.99)	3.88	5.82	2.06	7.88 (5.63)
MnEDTA2	1.27 (2.49)	32.24 (1.82)	3.51	11.61	5.30	16.91 (4.75)
MnEDTA3	1.23 (2.18)	29.77 (1.76)	3.24	15.17	7.65	22.82 (4.17)
MnLS0	2.11 (2.02)	33.29 (1.68)	6.73			
MnLS1	1.98 (2.73)	30.67 (1.86)	6.20	6.28	3.16	9.45 (4.87)
MnLS2	1.93 (2.86)	29.78 (1.64)	6.02	8.37	3.65	12.02 (5.32)
MnLS3	1.81 (2.19)	28.22 (1.56)	5.70	11.88	4.85	16.73 (4.01)

<sup>a</sup> Average of five replications. <sup>b</sup> Values in parentheses represent the coefficients of variation.

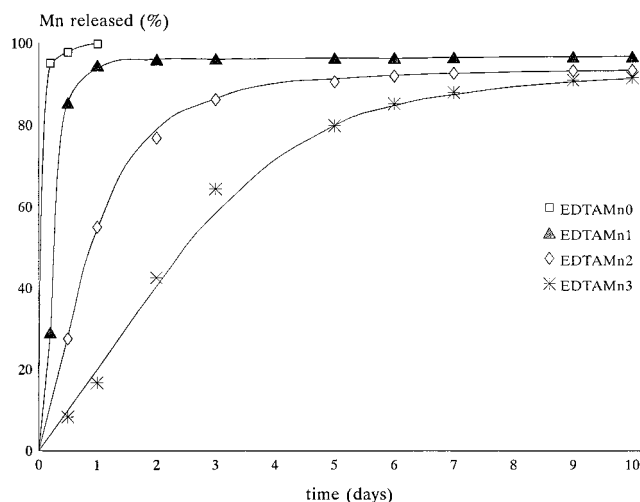
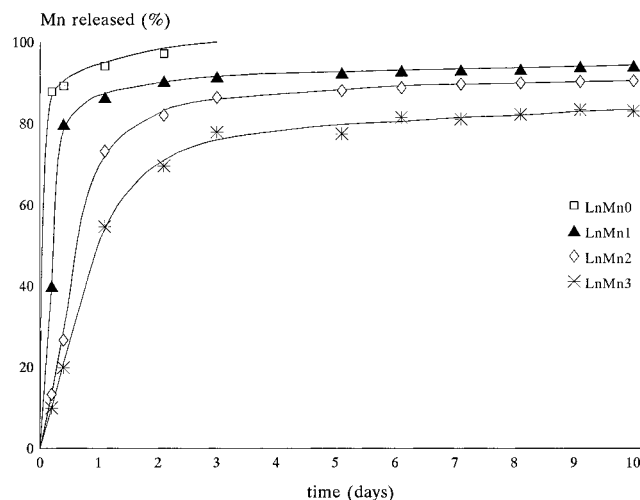
**Prepared Fertilizers Series.** One series corresponded with MnEDTA and the other with MnLS adherence over urea pellets. The uncoated products MnEDTA0 and MnLS0 were obtained, and these products were later coated. The compositions of all prepared products are shown in Table 1. As can be observed, Mn content ranges from 1.23 to 1.58% and from 1.81 to 2.11% in the MnEDTA and MnLS series, respectively, with coefficients of variation ranges from 2 to 3%. The percent weight of the coating ranges from 7.88 to 22.8 and from 9.45 to 16.7 in the MnEDTA and MnLS series, respectively, with coefficients of variation ranges from 4 to 6%. All products complied with national (15) and international regulations (16) on the permitted concentrations of micronutrient.

**Release of Manganese into Water.** Samples of 0.5 ± 0.001 g of Mn formulations were placed in triplicate in double-stoppered polyethylene bottles, and 10 mL of deionized water was added to each one. The small bottles were kept at a constant temperature in a thermostatically controlled compartment (21 ± 1 °C). A 5 mL aliquot of the floating solution was periodically separated out and filtered, and the Mn content in the filtrates was determined. Deionized water was added into the small bottles to replace the initial water volume. The influence of temperature on the release of Mn with the thickest coating was studied for the products of each series by keeping the bottles at 4 and 40 °C.

**Physical Tests.** The set of methods used to determine the characteristics of the products was based on those proposed by the Tennessee Valley Authority (17) and the International Fertilizer Development Center (18). These tests evaluate the fertilizers in relation with the possibility of damage during their handling and storage. The tests measure the following: grain size, bulk density, crushing strength, abrasion resistance, critical relative humidity, and absorption moisture rate under conditions of 88% relative humidity for 72 h. In every test, the uncoated urea was used as a control.

**Electron Microscopy Micrographs.** The pellets of the experimental fertilizers were also subjected to a scanning electron microscopy (SEM) study. They were split into two halves, and the fractions obtained were adhered to sample holders with carbon LIT-C glue. The samples were metal coated with a 60 nm layer of platinum using an SEM coating unit PS-3 metal coater and were examined by SEM Hitachi model S-2500. Micrographs were taken at different magnifications.

**Analysis Methods.** Nitrogen was determined according to a Kjeldhal method (19) using a Tecator Kjeltec 1026. Rosin percentages were usually determined by the difference between the total and the sum of the other components. These calculations were validated by determining the total rosins through UV-visible spectrophotometry. The three rosins were determined together due to their similar solubilities in organic solvents and absorption bands. The three-rosin mixture dissolved in benzene gave a maximum at 279 nm, and the other components of the fertilizer did not interfere in the measurement under these conditions. Manganese and calcium were determined by atomic absorption spectrophotometry (Perkin-Elmer model 3300).

**Figure 1.** Cumulative release of manganese from MnEDTA prepared fertilizers into static water.**Figure 2.** Cumulative release of manganese from MnLS prepared fertilizers into static water.

## RESULTS AND DISCUSSION

**Rate of Release of Mn into Water.** With the uncoated products (MnEDTA0 and MnLS0), total solubilization of Mn was reached in 1 day, whereas it was slowly released for the coated products. Figures 1 and 2 show the percentage of Mn solubilized in water at 21 °C as a function of time for the first 10 days of the test. The curves of both series showed analogous trends over the following days, the solubilized Mn being nearly 100 and 95% for MnEDTA and MnLS, respectively, by the end of 1 month of the experiment. The micronutrient solubilization rate decreased as coating thickness in-

**Table 2. Simple Linear Correlation for the Coated Products between  $\ln I$  and the Time  $t$  in days**

product	coating (%)	$\ln I_0^a$	$k^b$ (days <sup>-1</sup> )	$R^2$ (%)
MnEDTA1	7.88	3.03	0.6525	92.19
MnEDTA2	16.91	4.01	0.2650	84.29
MnEDTA3	22.82	4.54	0.1982	96.04
MnLS1	9.45	3.68	0.2869	56.63
MnLS2	12.02	3.96	0.1929	67.62
MnLS3	16.73	4.24	0.1381	86.20

<sup>a</sup> Intercept of the regression equations obtained with the ordinate axis. <sup>b</sup> Solubility rate constant.

creased in both cases, but the source of Mn also influenced this rate, which was lower for MnLS than for MnEDTA.

The release of Mn behaves in two different stages, the first of which is faster and the second is slower. However, the differences between them become smaller as the percentage of coating increases. This can be explained by the fact that the layer around the pellets became more even and had fewer pores and defects, which are the cause of release in the first stage. In the second stage, the micronutrient was emitted more gradually due to diffusive phenomena through the protective coating of the products.

The solubilization rate diminished as time elapsed, and in most of the products, this rate was proportional to the amount of Mn not solubilized. Thus, the Mn released could be represented by a first-order kinetics equation (20). In our case, the percentage of nonsolubilized Mn ( $I$ ) can be calculated as a function of time ( $t$ ) using the equation

$$\ln I = \ln I_0 - kt \quad (1)$$

where  $k$  is the solubility rate constant and ( $I_0$ ) is the initial content of Mn. It should be pointed out that, instead of the value of  $I_0$  having to be 100 ( $\ln I_0 = 4.6$ ), when  $\ln I_0$  is calculated, lower values can be found due to the initial rapid solubilization of a part of the Mn present in the pellets, and those values are nearer to 4.6 as the thickness of the coating increases. The values calculated ( $\ln I_0'$ ) have been defined as the intercept of the regression equations obtained with the ordinate axis considering that  $I_0'$  indicates the percentage of each product with an effective coating.

Through the use of a linear regression analysis to the  $\ln I$  values as a function of time  $t$ , the values of the slopes and ordinates at origin were estimated with acceptable correlation coefficients and probability levels (Table 2). In this table, it can be observed that the increase in coating made the kinetic model fit the experimental values more closely.

The behavior of these fertilizers can also be estimated by a potential equation

$$y = at^b \quad (2)$$

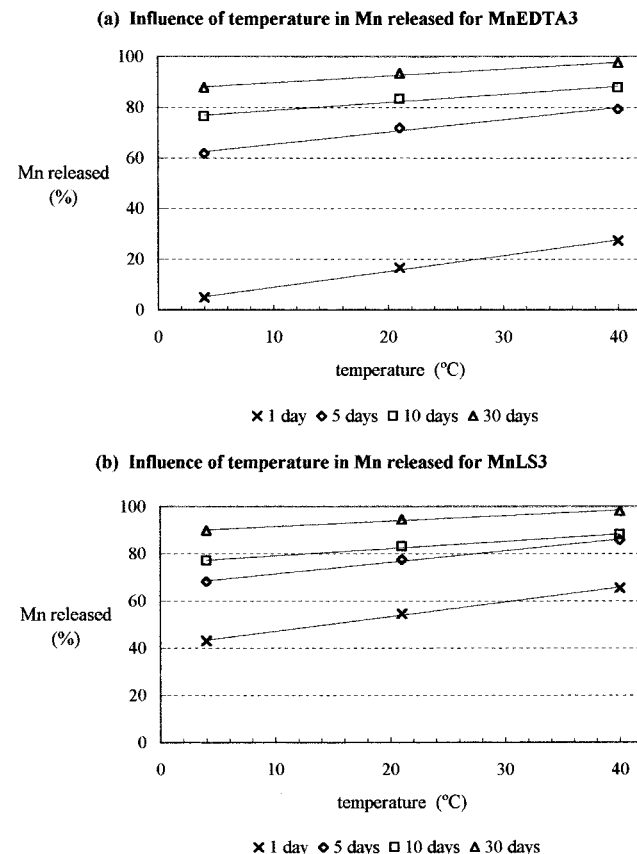
where  $y$  is the percentage of Mn solubilized,  $t$  is the time,  $a$  represents the percentage of Mn solubilized in the first day, and  $b$  is the order of the equation with respect to time. For this mathematical model, acceptable correlation coefficients and probability levels were also found (Table 3).

When the coating thickness of the products increased, the initial release rate of the micronutrient decreased. Similarly, the Mn source also had an influence over the release rate. The release of Mn for the MnLS series was

**Table 3. Constants from Fitting the Empirical Equation  $y = at^b$  to Release Data of Manganese into Static Water**

product	coating (%)	$a^a$	$b^b$	$R^2$ (%)
MnEDTA1	7.88	89.71	0.0579	80.20
MnEDTA2	16.91	47.04	0.3646	84.63
MnEDTA3	22.82	17.36	0.7818	96.13
MnLS1	9.45	67.08	0.1886	86.18
MnLS2	12.02	52.95	0.2682	88.59
MnLS3	16.73	34.69	0.4112	89.51

<sup>a</sup> Percentage of manganese solubilized at 1 day. <sup>b</sup> Order of the equation with respect to time.

**Figure 3.** Cumulative release of manganese into static water as a function of temperature from (a) MnEDTA3 and (b) MnLS3.

lower than for the MnEDTA series when the percentages of coating were similar. This kinetic of micronutrient applied as lignosulfonate was reported by Rico et al. (12). Thus, the Mn release of one MnLS series fertilizer could be similar to that of another MnEDTA series fertilizer with a thicker coating. The two mathematical models could predict the Mn release into water by fertilizers made under these conditions.

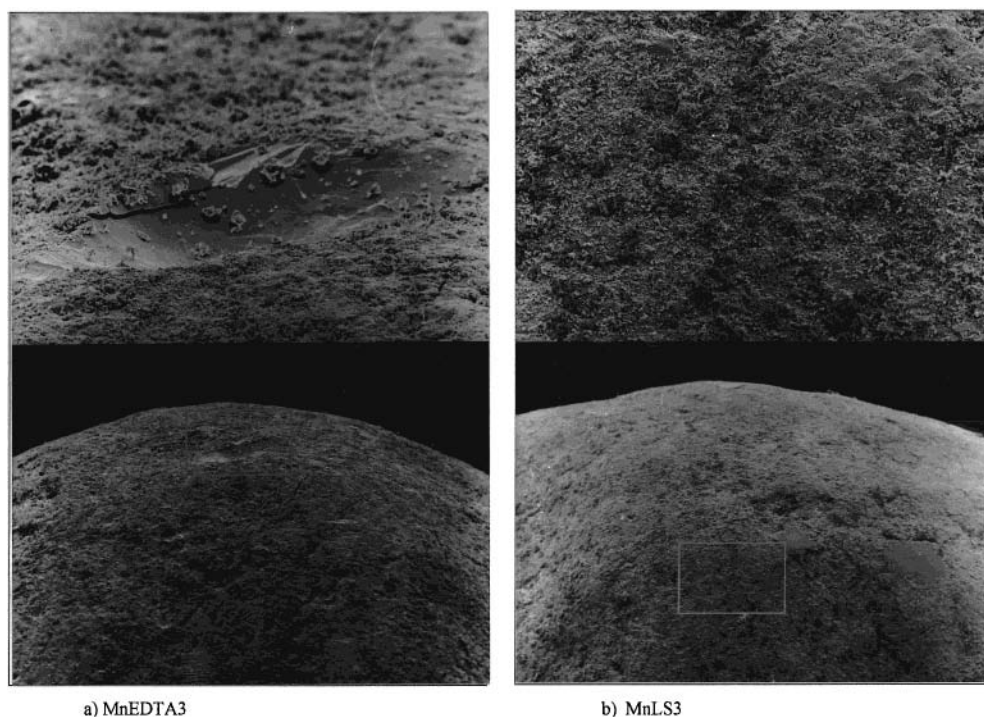
The influence of temperature in the kinetics of Mn solubilization was studied in the most coated fertilizer of the two series. Figure 3 shows the Mn released as a function of temperature and time. The increase in temperature led to an increase in the Mn released for the same elapsed time, as could be expected. What is more interesting to observe is that analogous slopes were obtained for the two fertilizers, which indicates that the coating is affected by temperature in the same way, regardless of the Mn source. The influence of temperature was similar for the two series until the coating began to deteriorate. Initially, the release of Mn was lower for the MnEDTA fertilizer because its coating



**Table 4. Grain Size, Bulk Density, Crushing Strength, Abrasion Resistance, and Moisture Absorption of the Prepared Fertilizers**

product	% of fraction size		crushing strength (kg·grain <sup>-1</sup> )	bulk density (g·cm <sup>-3</sup> )	abrasion resistance % of degradations	moisture absorbed (%) at 21 °C, 88% RH		
	2.5–3.2 mm	2.0–2.5 mm				24 h	48 h	72 h
control <sup>a</sup>	1.1	90.2	0.97	0.70	0.16	13.0	16.6	20.2
MnEDTA0	13.0	81.8	1.22	0.70	0.51	8.6	14.3	19.1
MnEDTA2	16.6	82.4	1.51	0.74	0.05	3.4	4.8	6.4
MnEDTA3	36.4	62.8	1.66	0.75	0.02	2.2	2.9	3.8
MnLS0	6.7	87.8	1.29	0.73	0.62	7.6	13.7	18.6
MnLS2	14.4	84.9	1.55	0.74	0.09	5.1	7.5	8.8
MnLS3	15.9	83.5	1.72	0.75	0.05	3.4	5.0	6.5

<sup>a</sup> Commercial granular urea.



**Figure 4.** Micrographs of the surface of coated pellets: (a) MnEDTA3 (800× and 150×); (b) MnLS3 (800× and 150×). (The figure is reproduced here at 50% of its original size.)

was the thicker, but the behaviors of both fertilizers became similar as time went by.

**Physical Properties.** The properties tested in the pellets of the experimental fertilizers are related to the characteristics that allow for their suitable storage and handling and can be affected by the addition of the layer that contains the Mn source and by the coating. The tests were performed only with the uncoated product and with the two products that have the thickest coatings in each series because the others release the Mn too quickly to be considered slow-release fertilizers. The physical properties are summarized in Table 4.

**Grain Size.** The grain size values are expressed as percentages of the product that is retained in each sieve. The size became larger than for the control due to adhesion of the micronutrient source and the coating, but the percentage of coating had only a slight influence on the size of the coated products. The required specifications are that at least 85% of the granules have sizes between 1.0 and 4.0 mm. In the prepared products percentages of the granules from 94.8 to 99.4 have a size between 2 and 3.2, and most of the granules included measured from 2.0 and 2.5 mm. This meant that the specifications were well adhered to and that there was very little risk of fractures which could result in smaller particles.

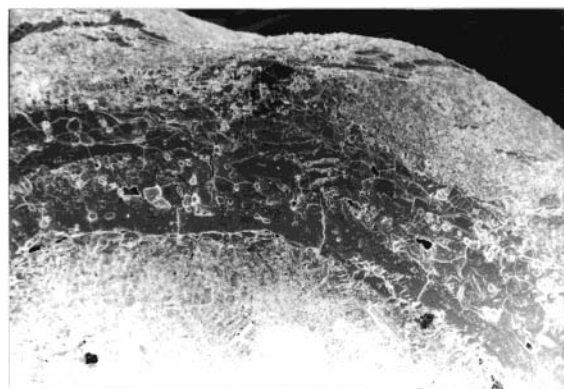
**Bulk Density.** This test is required for bag sizing, storage, and transport. It shows that only the value obtained for the uncoated product of the MnEDTA series was the same as for the control and that the rest of the results were larger. However, in every case, the increase was <7.1%. With respect to the series, the bulk density for the MnLS series was greater than for the MnEDTA series for products with similar coating percentages. In all cases, the bulk densities were within the usual range for pelleted fertilizers, which range from 0.72 to 1.20 g/cm<sup>3</sup> (2).

**Crushing Strength.** This test is a measure of the resistance of granules to deformation or fracture under pressure. High values are better for avoiding breakage and pellet strain during handling and bag storage. For uncoated products, the values of crushing strength were 20% greater than for the control, and for coated products the increase of the value with respect to the control ranged from 54 to 76%. Thus, the rosin–tricalcium phosphate coating increased the hardness of granules.

**Abrasion Resistance.** This is a test of the resistance to the formation of dust as a result of grain–grain and grain–equipment contact. The percentage of degradation values for uncoated products was higher than for the control, whereas the percentages for coated products



(a) MnEDTA2



(b) MnLS3

**Figure 5.** Cross-sectional micrographs of coated pellets: (a) MnEDTA2 (150 $\times$ ); (b) MnLS3 (200 $\times$ ). (The figure is reproduced here at 50% of its original size.)

**Table 5. Average Coating Thickness from SEM Micrographs**

product	av thick-ness ( $\mu\text{m}$ )	standard error	confidence intervals (95%)
MnEDTA2	97	1.64	95–100
MnEDTA3	122	1.12	120–123
MnLS2	73	1.81	70–75
MnLS3	87	0.95	85–88

were far lower than for the control. Therefore, the coating also improved this physical property.

**Moisture Absorption.** This test made it possible to estimate the minimum relative humidity that could cause damage to the structural stability of the products during their handling and storage, as well as the moisture absorption rate. The moisture absorption started at 80.5% relative humidity (RH) (21) for the control, at 70.4% RH for uncoated products, and at 88.0% RH for coated products. Thus, the relative humidity must be kept at 88.0% during the moisture absorption rate test in order for the coated products to absorb significant amounts of water. The amounts of water absorbed by the coated products were far lower than for the other products, and they decreased as the coating thickness increased. Similarly, the moisture absorption rate decreased with the increase in percentage coating.

**Electron Microscopy Micrographs.** SEM micrographs of uncoated fertilizers were of little interest because only a thin layer formed by the micronutrient source was observed. To examine the surface and the coat profile of the coated fertilizers, SEM micrographs were obtained at different magnifications. The surface

of the coating pellets (Figure 4) for the most coated products of two series looked compact and uniform enough, but a greater number of pores were found in the pellets with a less thick coating. The roughness observed is due to the tricalcium phosphate applied on the surface of the coat, but when a little part of the rosin layer is not completely covered by the salt, the surface appears smooth, compact, and homogeneous. In the cross-section micrographs (Figure 5) two zones can be observed: the outer resin coating, with the micronutrient source, uniformly adhered to the pellets, and the inner region, made up of urea. Some small cracks and pores can be seen, but no large pores that permit a free circulation of the solution between the interior of grains and the exterior have been found.

The study of the SEM micrographs made it possible to establish the mean thickness of coating (Table 5). These results demonstrated that the increase of coating percentage led to a proportional increase of thickness similar for both series of fertilizers. In any case, the standard error values obtained for the thickness of the layer show that the coating is well distributed around the pellets.

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