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PROLONGED-ACTION MAGNESIUM-BEARING UREA FROM THERMALLY ACTIVATED DOLOMITE: EFFECT OF ADDITIVE CONTENT AND CALCINATION TEMPERATURE ON GRANULE PROPERTIES

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Abstract:

This study quantifies how the amount of thermally activated dolomite added to a urea melt and the temperature at which that dolomite is calcined jointly govern the properties of the resulting granules. Local dolomite (CaO 27.52 %, MgO 20.24 %, CO_2 43.21 %) was calcined at 400, 500, 600, 700, 800 and 900 °C and introduced into molten urea at ten levels from 0.5 to 5.0 wt %, giving a two-factor full factorial design of 60 compositions plus a dolomite-free control. Dissolution time, melt crystallisation temperature, hygroscopic point, porosity and crushing strength were measured for every composition. Dolomite raised the dissolution time in all 60 cases, from 93.8 s for the control to 94.28–207.62 s, raised the crushing strength to 2.56–3.46 MPa and lowered the porosity below the control value of 5.75 % throughout. Each response was described by an additive linear model in the two factors ($R^2 = 0.891$–0.985; the interaction term was insignificant, $p = 0.37$–0.76). Grouping the model residuals by calcination temperature revealed that three independent responses reach an extremum at exactly 700 °C and change sign between 700 and 800 °C, coinciding with the calculated appearance of free CaO and marking the transition of dolomite from a comparatively inert filler to a reactive additive. Four criteria complete activation of the magnesium component, limitation of free CaO, at least 45.5 % total nitrogen and at least 2.5 MPa crushing strength identify a single regime: 2 g of dolomite calcined at 700 °C per 98 g of urea, a product that dissolves 1.38 times more slowly than unmodified urea, is 12.6 % stronger, 9.9 % less porous and contains 45.72 % N and 0.55 % MgO entirely in the active form, with only 0.10 % free CaO. Compared with a urea–formaldehyde system studied under the same criteria it is 6.7 % stronger, carries 4.5 absolute per cent more nitrogen and requires no imported formalin.

Keywords: urea, dolomite, thermal activation, slow-release fertilizer, prolongation, dissolution time, hygroscopic point, granule strength, free calcium oxide, full factorial design.

I. INTRODUCTION

Urea occupies a position in the nitrogen fertilizer market that no other product approaches, and its share is still rising. That dominance is also the source of the problem addressed here: urea hydrolyses rapidly in the soil, and field measurements place the ammonia released at 2–43 % of the applied nitrogen on arable land and 10–58 % on grassland [1], while what is not volatilised is exposed to leaching and denitrification. The nitrogen that reaches the plant is therefore a fraction of the nitrogen bought, and the obvious remedy is to slow the rate at which the granule gives up its nitrogen.

The routes developed for this purpose fall into two families. The first encapsulates the granule: sulfur, polymers, gypsum, cement and zeolite have all been used as coatings, and the comparative study of Ibrahim et al. [2] shows how differently they perform on the same substrate, while Lawrencia et al. [3] set out the release mechanism each type imposes. A coating, however, is an additional unit operation, it leaves a residue in the soil, and the effect disappears if the film is damaged. The second family modifies the nitrogen chemically, most often by condensing urea with formaldehyde [4], which consumes an imported reagent and lowers the total nitrogen. A third approach leaves the chemistry of urea untouched and changes the structure of the granule with a mineral: Hermida and Agustian [5] recrystallised urea with natural bentonite and extended the release from under 50 min to about 500 min, showing that a cheap clay dispersed through the solid can do what a coating does, without a coating step.

A second, independent deficiency runs alongside the nitrogen problem. Magnesium is the central atom of the chlorophyll molecule and is involved in phosphorus transport and enzyme activation; the meta-analysis of Hauer-Jákli and Tränkner [6] quantifies the penalties that follow when leaf magnesium falls below critical thresholds. On the carbonate-rich alkaline soils of irrigated Central Asia this deficiency is rarely diagnosed because it is rarely measured, and the standard nitrogen fertilizer carries no magnesium at all. The form of supply matters as much as the amount: Härdter et al. [7] found magnesium availability from kieserite to be much greater than from calcined magnesite, a 19.6 % difference in uptake, so oxide- and carbonate-bound magnesium is not agronomically equivalent to soluble magnesium. Lu et al. [8] accordingly fortified phosphate fertilizers with magnesium sulfate together with dolomite and cut magnesium leaching losses from 19.1 % to 3.8 %.

Dolomite is the obvious raw material for such a dual role in a country that holds large deposits of it, but it is agronomically inert until decarbonated, and the extent of decarbonation is set by the calcination temperature. Decomposition proceeds in stages, the magnesium component first; Rodriguez-Navarro et al. [9] resolved the mechanism by two-dimensional X-ray diffraction and electron microscopy, and Resio [10] showed that the number of stages observed depends on the furnace configuration. Temperature also controls the quality of the oxide: Huang et al. [11] showed that higher calcination increases the crystallinity and grain size of MgO while reducing its surface area and hydration reactivity. At the other end of the range the same temperature carries a penalty, because free CaO appears once the calcium carbonate begins to decompose, and it hydrates in storage with a volume increase that can crack a granule.

The urea melt imposes its own limits. Urea decomposes above its melting point, and Schaber et al. [12] identified cyanic acid formation above 152 °C and its subsequent reaction with intact urea to give biuret, a species restricted by fertilizer specifications; any additive that raises the alkalinity of the melt risks accelerating that reaction. Mechanical quality is a second constraint: Rahmanian et al. [13]

measured apparent crushing strengths of 2.0 MPa for urea prills and 2.47–2.87 MPa for fluidised-bed granules. Storage behaviour is a third; caking has been reviewed by Benzaouia et al. [14], and internal transformations continue in granules long after they leave the plant [15]–[16].

What the literature does not provide is a quantitative description of the urea–dolomite system in which both variables are varied together over a range wide enough to locate the point at which the additive changes its role. A two-factor full factorial experiment over 60 compositions is used here to fit additive linear models to five granule properties; the systematic residuals of those models locate the transition, and four independent criteria select a single operating regime.

II. MATERIALS AND METHODS

Industrial granulated urea of grade B conforming to GOST 2081-2010 [20], containing 46.65 % N, was used as the base material. The dolomite was a local natural mineral containing 27.52 % CaO, 20.24 % MgO, 43.21 % CO_2, 2.14 % SiO_2 and 2.33 % physically bound moisture, with a $CaO{:}\,MgO$ mass ratio of 1.360 against 1.39 for stoichiometric dolomite; it is therefore close to true dolomite stoichiometry and not significantly diluted by calcite or magnesite.

The dolomite was ground and spread as a thin layer in a muffle furnace at 400, 500, 600, 700, 800 and 900 °C. After calcination each sample was cooled in a desiccator, transferred immediately to a sealed vessel and analysed as soon as possible, because highly reactive CaO recarbonates on contact with atmospheric CO_2. The chemical composition and the loss on ignition were determined for every regime, and from them the degree of decarbonation α and the contents of active (free) MgO and free CaO were calculated on a basis of 100 g of original raw material. Internal consistency was checked through the concentration coefficient of the six non-volatile oxides, which must be identical for all of them within analytical error if no oxide is formed or lost.

III. RESULTS AND DISCUSSION

The calculated indicators are shown in Fig. 1. The loss on ignition rises from 8.16 % at 400 °C to 36.79 % at 900 °C and the degree of decarbonation from 13.5 to 79.8 %. Because 50.6 % of the carbon dioxide of stoichiometric dolomite belongs to the magnesium carbonate, these figures separate into two processes: $MgCO_3$ decomposition reaches 26.7 % at 400 °C, 82.0 % at 600 °C and is complete at 700 °C, whereas $CaCO_3$ is untouched up to 600 °C and then decomposes to 13.5, 40.1 and 59.0 % at 700, 800 and 900 °C. The two oxides therefore diverge (Fig. 1b): active MgO rises steeply to 27.42 % at 700 °C and then almost stops, gaining only 4.0 percentage points over the next 200 °C, whereas free CaO is absent below 700 °C, appears at 5.08 % there and multiplies to 16.46 and 25.68 %. The material balance closes to better than 0.01 % at every temperature and the concentration coefficients of the six non-volatile oxides agree to within a coefficient of variation of 0.4–1.4 %.

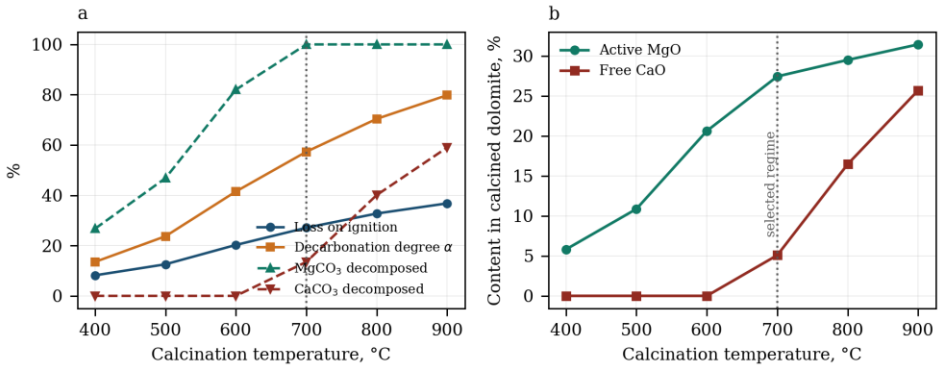

Fig. 1. Calculated indicators of dolomite calcination: (a) loss on ignition, overall degree of decarbonation and the separate decomposition of the magnesium and calcium carbonates; (b) active MgO and free CaO in the calcined dolomite. Basis: 100 g of original raw material.

The longer a granule takes to dissolve, the more slowly nitrogen is released into the soil solution, so the dissolution time is the primary response of this work. Unmodified industrial urea granules dissolve completely in 93.8 s on average. Dolomite lengthened the dissolution time in every one of the 60 compositions, without exception (Fig. 2a). With dolomite calcined at 400 °C, 0.5 % raises the figure to 116.07 s, 2 % to 158.43 s (1.69 times the control) and 5 % to 207.62 s (2.21 times). The increment per unit of additive is largest at low loadings each 0.5 % adds 10–15 s between 0.5 and 3.5 % and falls to 2–6 s above 4 %, so the curve flattens as the granule approaches the limit of what a dispersed filler can do to the dissolution front.

Calcination temperature acts in the opposite direction and much more weakly: every 100 °C between 400 and 700 °C shortens the dissolution time by 6–9 s on average, but between 700 and 900 °C the same step costs only about 2 s. The extremes of the matrix are 207.62 s (5 % of dolomite calcined at 400 °C) and 94.28 s (0.5 % at 900 °C), the latter indistinguishable from the control.

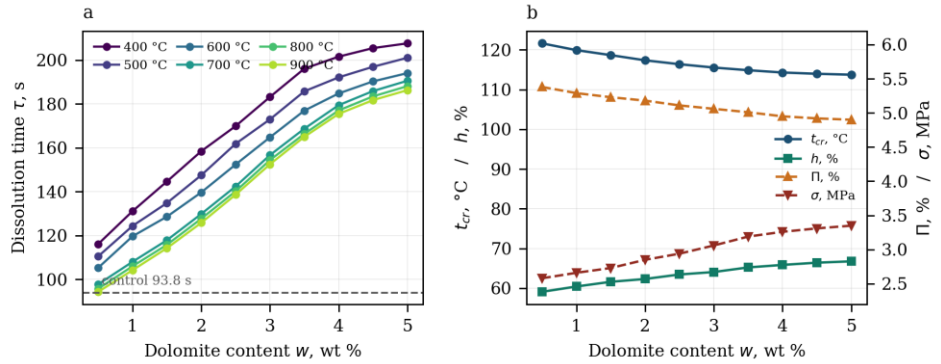

Fig. 2. (a) Dissolution time of the granules against dolomite content for the six calcination temperatures; (b) crystallisation temperature, hygroscopic point, porosity and crushing strength against dolomite content for dolomite calcined at 700 °C.

3.3. Crystallisation temperature, hygroscopic point, porosity and strength. The four remaining responses are shown for the selected calcination temperature in Fig. 2b and in Table 1. Pure urea melt crystallises at 128.0 °C; dolomite lowers this in every composition, by 5.2–14.6 °C at the lowest loading and by 11.1–22.1 °C at the highest, and at the selected regime the melt crystallises at 117.36 °C, a shift of 10.6 °C that the granulation tower can absorb without re-tuning. The differences between the 400 and 700 °C series for this response (0.3–1.3 °C) are smaller than the thermal-effect

measurement error of ±5 °C and are not significant individually; the temperature effect is established below from the residuals over all 60 points.

Table 1

Measured properties and calculated composition of the granules obtained with dolomite calcined at 700 °C

w, wt %	τ, s	t_{cr}, °C	h, %	Π, %	σ, MPa	N, %	MgO, %	free CaO, %
0 (control)	93.80	128.00	58.40	5.75	2.53	46.65	0	0
1	107.99	119.92	60.43	5.29	2.66	46.18	0.274	0.051
2	129.80	117.36	62.33	5.18	2.85	45.72	0.548	0.102
3	156.66	115.54	64.08	5.06	3.06	45.25	0.823	0.152
4	179.43	114.29	65.87	4.95	3.26	44.78	1.097	0.203
5	190.56	113.74	66.77	4.90	3.35	44.32	1.371	0.254

Note: N, MgO and free CaO are calculated from the composition of the raw materials; at this calcination temperature the MgO is entirely in the active form.

3.4. Quantitative description. Fitting the additive model of Section 2.5 to all 60 points gives

$$\tau = 132.15 + 21.476\,w - 0.05654\,T \qquad (2)$$

$$t_{cr} = 133.01 - 1.5446\,w - 0.02024\,T \qquad (3)$$

$$h = 49.88 + 1.770\,w + 0.01509\,T \qquad (4)$$

$$\Pi = 4.184 - 0.1045\,w + 0.001640\,T \qquad (5)$$

$$\sigma = 2.689 + 0.1878\,w - 0.000287\,T \qquad (6)$$

The coefficients of determination are 0.977, 0.891, 0.899, 0.956 and 0.985 respectively, the residual standard deviations 5.08 s, 1.48 °C, 1.25 %, 0.07 % and 0.03 MPa, and the Fisher criteria 1212, 232, 253, 622 and 1909 hundreds of times the tabulated value $F_{0.05}(2;57) \approx 3.16$ ($n = 60$, $f_1 = 2$, $f_2 = 57$). The signs match the physical picture: more dolomite lengthens the dissolution and strengthens the granule while reducing the porosity and the crystallisation temperature, whereas higher calcination shortens the dissolution and lowers the crystallisation temperature while raising the hygroscopic point and the porosity. The coefficients quantify the asymmetry already visible in Fig. 2a: one additional per cent of dolomite adds 21.5 s to the dissolution time, whereas 100 °C of additional calcination removes only 5.7 s.

3.5. The transition at 700 °C. Because the temperature effect is small relative to the scatter of individual rows, it was analysed through the mean residuals of the linear models, grouped by calcination temperature and normalised to the largest residual of each response (Fig. 3). For the dissolution time, the crystallisation temperature and the hygroscopic point the mean residual moves monotonically from 400 to 700 °C, reaches an extremum at exactly 700 °C and changes sign between 700 and 800 °C. That three mutually independent responses place the extremum at the same temperature cannot reasonably be a coincidence. Porosity shows the same tendency more weakly, and for crushing strength the residuals are practically constant with temperature (±0.01 MPa), consistent with that response being

controlled by the amount of additive rather than by its state.

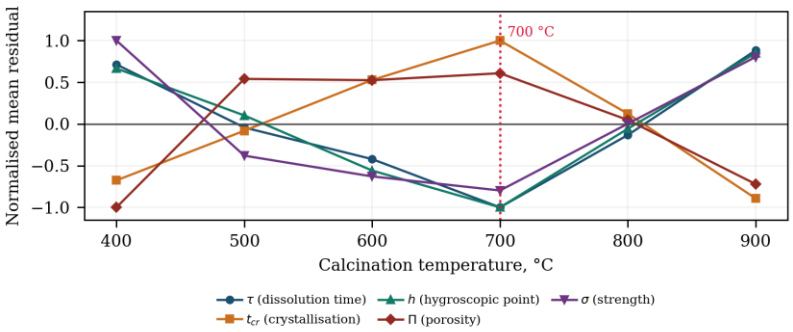

Fig. 3. Mean residuals of the additive linear models grouped by calcination temperature, each response normalised to its own largest residual. For crushing strength the absolute residuals do not exceed ±0.01 MPa.

These observations support the following qualitative model. Finely dispersed dolomite particles act in the crystallising melt as a structure-forming filler, giving a denser, stronger and more slowly dissolving granule, the size of the effect being set first of all by how much of it is present. Dolomite calcined at 400–600 °C consists mainly of $CaCO_3$ and MgO ($\alpha \leq 41.5$ %) and behaves as a comparatively inert filler; above 700 °C free CaO appears and interacts with the melt and with atmospheric moisture, lowering the crystallisation temperature, raising the hygroscopic point and the porosity and reducing the prolongation. The 700–800 °C interval therefore marks the transition from inert filler to reactive additive. The first part of this model is supported directly by the evidence below; the third rests on the calculated free CaO content and the systematic residuals, and its confirmation would require differential thermal analysis of the melt and determination of NH_3 in the gas phase, which were not carried out here.

The diffraction pattern of the sample containing 2 g of dolomite calcined at 700 °C per 98 g of urea contains 35 lines between $2\theta = 18.85$ and 78.26°. The urea lines at $d = 3.99$; 3.61; 3.04 and 2.53 Å coincide with the reference pattern to better than 0.003 Å, so the urea lattice is unchanged; the lines at 2.78; 2.41; 1.70 and 1.45 Å belong to CaO and those at 2.43; 2.11 and 1.49 Å to MgO. The strongest calcite line ($d = 3.035$ Å) is superimposed on a urea line ($d = 3.046$ Å) and cannot be separated from it, while the other characteristic calcite lines and the portlandite lines are absent. Because the additive amounts to only 2 % of the product, no quantitative phase analysis of residual carbonate was attempted.

Four criteria were applied. The first requires complete decomposition of $MgCO_3$, which is first satisfied at 700 °C. The second limits the free CaO content, because its hydration during storage causes volume expansion and cracking of the granule and raises the alkalinity of the melt: free CaO is 5.08 % at 700 °C against 16.46 and 25.68 % at 800 and 900 °C 3.2 and 5.1 times more while the active MgO gains only 7.5 and 14.6 % relative. The first criterion therefore demands a temperature no lower than 700 °C and the second no higher, fixing the calcination temperature at a single value. The third sets a total nitrogen content of at least 45.5 %, restricting the additive to $w \leq 2$ % (45.72 % N at 2 %, 45.48 % at 2.5 %); the fourth, a crushing strength of at least 2.5 MPa, is satisfied by every composition. Since dissolution time, strength and MgO content all increase monotonically with w within the permitted range, the optimum lies at its boundary: 2 g of dolomite calcined at 700 °C per 98 g of urea.

The measured properties of this product are a dissolution time of 129.80 s (1.38 times the control), a

crushing strength of 2.85 MPa (12.6 % above the control and more than twice the specification), a porosity of 5.18 % (9.9 % below the control), a hygroscopic point of 62.33 % and a crystallisation temperature of 117.36 °C; its calculated composition is 45.72 % N, 0.55 % MgO entirely in the active form and 0.75 % CaO of which 0.10 % is free.

IV. CONCLUSION

Introducing thermally activated dolomite into a urea melt yields a slow-dissolving, magnesium-bearing modified urea. In all 60 compositions the dissolution time rose (94.28–207.62 s against 93.8 s) and the crushing strength increased (2.56–3.46 against 2.53 MPa), while the porosity fell below the control (4.26–5.56 against 5.75 %) and the hygroscopic point improved. The dependence of all five responses on the dolomite content and the calcination temperature is described by additive linear models with coefficients of determination of 0.891–0.985 and Fisher criteria of 232–1909, the interaction term being insignificant in every case. The dolomite content dominates: 1 % of additive adds 21.5 s to the dissolution time, whereas 100 °C of calcination removes only 5.7 s. The systematic residuals of these models reach an extremum at exactly 700 °C for three mutually independent responses and change sign between 700 and 800 °C. This coincides with the calculated appearance of free CaO and identifies the 700–800 °C interval as the transition of dolomite from a comparatively inert filler to a reactive additive.

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