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Environmentally acceptable synthesis of magnesium bearing fertilizers.
2. Mechanochemical preparation

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Mechanochemical synthesis of magnesium bearing fertilizer by using magnesium sulphate and magnesium sulphate hydrates is reported. The use of mechanochemical synthesis methods has a number of advantages. Solvent-free synthesis, low-temperature operation, high yields, and the absence of by-products make these methods the most environmentally acceptable. Based on widely used fertilizer compounds, magnesium salts and urea, a new compound with chemical formula $MgSO_4{\bullet}6OC(NH_2)_2{\bullet}0.5H_2O$ is obtained. The high ratio of urea to magnesium sulphate corresponds to the use of nitrogen as a major bioelement, and sulphur and magnesium as trace elements, which meets the requirements for the fertilizer products and mixtures. The new product implies smaller losses of nitrogen and its low hygroscopicity supposes good storage stability.

Keywords: mechanochemistry, fertilizers.

INTRODUCTION

Magnesium is the eighth most common element in the Earth's crust. Its content in the crust is about 2.4% (Patnaik, 2003) [1] and is mainly associated with the carbonate minerals magnesite and dolomite. The richest source of bioavailable magnesium, is the hydrosphere. In seawater, the concentration of magnesium is about 55 mmol/L, and smaller, but also significant, amounts of magnesium are found in river environments and surface waters [2]. Magnesium is one of the main bioelements and performs important functions for the development of living organisms – animals and plants. Maintaining effective intensive agriculture requires suitable soils and the application of large amounts of fertilizers that provide the bioelements needed by plants [3–4]. Magnesium is part of the chlorophyll structure and it is most commonly associated with plant growth, which is why magnesium salts find wide application in agrochemistry. Natural (kieserite, epsomite) and synthetic crystal hydrates of magnesium sulphate are used as stand-alone preparations or in the composition of microfertilizers, because in addition to magnesium, they contain another important bioelement – sulphur. Urea, on the other hand, is a commonly used nitrogen fertilizer. Approximately 60% of the bound nitrogen used for fertilization is applied as urea [5]. This is determined both by its high bound nitrogen content of the order of 46% and by its convenient use. There are two main problems facing the use of urea as fertilizer. The concomitant production of biuret which is toxic to plants and the loss of bound nitrogen after application to the soil. While the former is being addressed by controlling the production process and introducing an additional purification stage, the latter still lacks an effective solution. The loss of fixed nitrogen depends on many factors: soil type and moisture, temperature, pH, type of crop sown, rate of fertilizer applied, etc. In practice, it is very difficult to estimate what the losses will be for a particular application. However, there are published models concerning specific cases [6]. The most significant losses are related to volatilization of nitrogen derivatives, the majority in the form of NH_3. Published data on nitrogen losses under different application conditions are contradictory, but it is accepted that losses when urea is used are relatively high and between 10 and 40% of the nitrogen applied as urea is lost, mainly as ammonia [7].

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Various methods have been developed to reduce the losses of bound nitrogen when fertilizing with nitrogen fertilizers, such as coating the urea particles with a polymer shell [8]. More sophisticated techniques such as mixing urea with rice husk ash with or without the addition of magnesium sulphate, produces also a slow-release urea product [9–11]. Other additives to urea have been investigated in search of ammonia emission reduction – phosphogypsum, $(NH_4)_2HPO_4$, $ZnSO_4$, NH_4Cl or KCl [12]. Wang and co-authors [13] in 2022 reported on the effect of magnesium sulphate, borax and zeolite additions to urea as fertilizer and showed that although there was a slight increase in losses of bound nitrogen as N_2O from 0.7 to 1.7%, losses as ammonia decreased from 39 to18%.

There are a considerable number of studies devoted to the interaction of magnesium sulphate with urea [14–15]. The presence of urea in the aqueous solutions of magnesium sulphate results of magnesium sulphate complexes where the magnesium ion coordinates urea molecules and depending on the synthetic conditions, compounds of different compositions and physicochemical characteristics are obtained – $MgSO_4 \cdot 5OC(NH_2)_2 \cdot 2H_2O$ and $MgSO_4 \cdot 6OC(NH_2)_2 \cdot 2H_2O$, $MgSO_4 \cdot OC(NH_2)_2 \cdot 3H_2O$ and $MgSO_4 \cdot OC(NH_2)_2 \cdot 2H_2O$. The studies of the crystallohydrates of magnesium salts revealed that urea molecule effectively replaces water molecules, which in turn, leads to an increase of the resistance and thermal stability of the new compounds thus suggests slower release properties (Georgieva et al., 2022; Kossev et al., 2021; Rusev et al., 2018) [16–18]. Later research on the interaction of magnesium sulfate and urea has been presented mainly in patent developments, which is conditioned by the interest they represent for use as agrochemical preparations (Patents WO 098367, 2013; WO 036494A1, 2021 and US20200189987A1, 2020). The characteristic feature of all these patents is that they describe the preparation of mixtures of urea complexes of magnesium sulphate and/or their mixtures with urea and crystal hydrates of magnesium sulphate, rather than individual defined chemical compounds. In our laboratory we have obtained two new complexes $MgSO_4 \cdot 4OC(NH_2)_2 \cdot 2H_2O$ and $MgSO_4 \cdot 6OC(NH_2)_2 \cdot 0.5H_2O$ the latter one of particular interest for agrochemistry because with its high urea to magnesium ratio, low hygroscopicity and good storage stability [19].

In this work, we present a mechanochemical synthesis of $MgSO_4 \cdot 6OC(NH_2)_2 \cdot 0.5H_2O$ from magnesium hydrates, commonly used as a fertilizes. The use of mechanochemical synthesis methods has a number of advantages, such as solvent-free processes, low-temperature operation, high yields, absence of by-products est.

MATERIALS AND METHODS

The substances used in the experiments were the commercial products magnesium $MgSO_4 \cdot 7H_2O$ and $CO(NH_2)_2$ with correspondingly 99.0 and 99.5% purity. The other magnesium salts were obtained after thermal treatment of $MgSO_4 \cdot 7H_2O$ at 110 °C for 24 h for $MgSO_4 \cdot H_2O$, and at 340 °C for 2 h for $MgSO_4$.

For the mixing of the reagents, a planetary ball mill "Pulverisette 7 Premium line" was used. The operating conditions for all of the experiments were as follows: capacity of one mortar 45 ml – loading 5 g; size and number of agate balls – Ø10 mm, 18 pcs. The ratios 1:1; 1:2; 1:3; 1:4; 1:5; 1:6; 1:7; 2:1 between $MgSO_4 \cdot xH_2O$ (x = 0, 1, 7) and $CO(NH_2)_2$ were applied respectively. Additional syntheses, with time and speed variations, were performed for the systems with reagents rations 1:6 and 1:1. The time and speed for those experiments were in the range of 3–120 min and 100–750 rpm.

Powder diffraction analyses were used to verify the purity of reagents and the resulting products. The powder diffraction patterns were obtained by X-ray diffractometer "D2 Phaser", Cu-Kα radiation

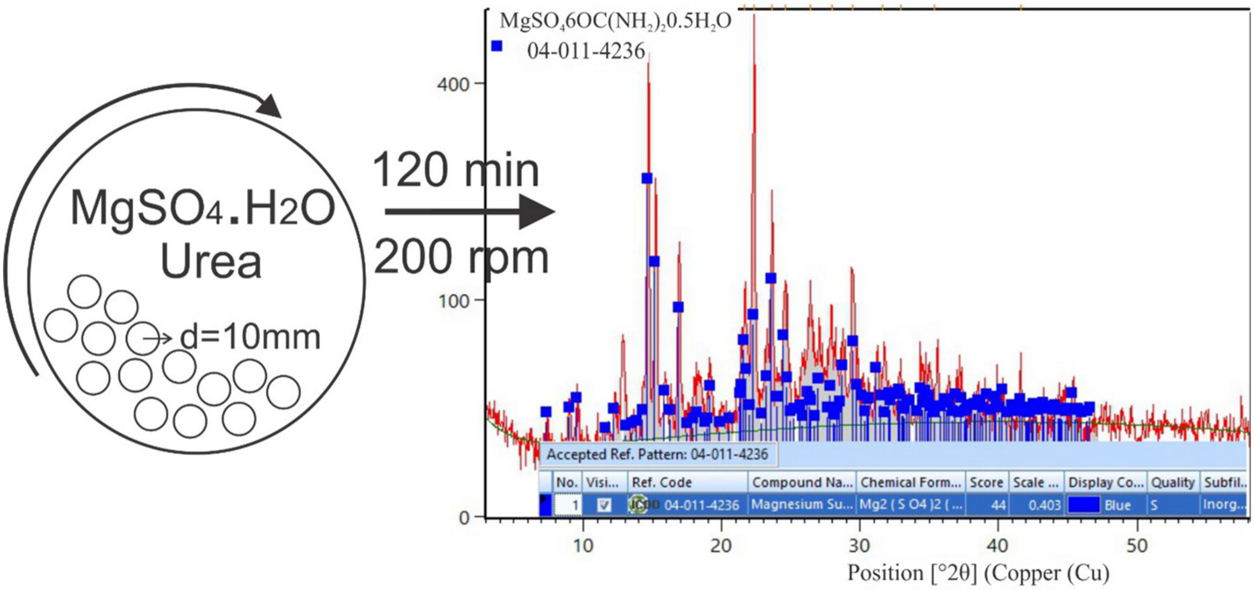
Fig. 1. Measurement system.

(1.54 Å), 2θ range from 3° at 70°, 0.05 step size and measuring time 1 s per step.

The measurement of ammonia volatilization after the application of urea and the newly obtained urea complex ($MgSO_4 \cdot H_2O \cdot 6[OC(NH_2))]$ on a commercial organic substrate was carried out by GT-903 Series Gas Detector. The used organic substrate has the following characteristics (NH_4+NO_3) 25–50 mg/100 g; P (P_4O_5) 30–50 mg/100 g; pH 5.5–6.5; EC (mS/cm) 0.6–1.0; bulk density (kg/L) 0.45–0.55; moisture (%) 40–50). Two samples containing organic substrate and pure urea or newly obtained urea compound were prepared. Amounts of 100 g organic substrate, 10 ml of water and 0.17 mol Urea were applied for both systems. The samples were placed in a desiccator and measurements were performed ones per day. The measurement system is presented on the Fig. 1.

RESULTS AND DISCUSSION

The XRD analyses show that within the parameters used for the mechanochemical synthesis, a single-phase product was not obtained when $MgSO_4$ or $MgSO_4 \cdot 7H_2O$ were applied as reagents. In the case of $MgSO_4$ no reaction between the reagents was observed, unless some water was added to the vessel which allows the magnesium sulphate to be dissolved and consequently urea adducts to be formed. A mixture of urea complex and reactants in all of the studied rations. In difference when $MgSO_4 \cdot 7H_2O$ was used, a very dense mass is formed. It adheres to the walls of the vessel and was difficult to separate. The results reveal formation of $MgSO_4 \cdot 6OC(NH_2)_2 \cdot 0.5H_2O$, but within the used grinding parameters (temperature, revolutions, size of the balls) a single phase product was not obtained. For all ratios of the reagents, the final product was a mixture of two or three phases, and relatively the highest yield of the desired product was obtained at a ratio $MgSO_4 \cdot 7H_2O$: $1OC(NH_2)_2$. It should also be noted that even for a short time (2–3 min) of tribochemical treatment a liquefied product was formed and that's why it was applied a secondary heat treatment. The trials of a series of short grinding, drying, and regrinding did not lead to a significantly different result. The best results were obtained in the system $MgSO_4 \cdot H_2O$ – Urea. The received products were with high degree of crystallinity and easily removable from the vessel. All of them contain $MgSO_4 \cdot 6OC(NH_2)_2 \cdot 0.5H_2O$ confirming that this is the most stable urea complex of magnesium sulphate. Using of magnesium sulphate monohydrate as a reagent allowed obtaining of single phase product of $MgSO_4 \cdot 6OC(NH_2)_2 \cdot 0.5H_2O$ and almost 100% yield is achieved for the ratio of $MgSO_4 \cdot H_2O:6OC(NH_2)$ and 120 minutes grinding time (Fig. 2). The precise parameters of the synthesis are patent pending.



Accepted Ref. Pattern: 04-011-4236

No.	Visi...	Ref. Code	Compound Na...	Chemical Form...	Score	Scale ...	Display Co...	Quality	Subfil...
1	☑	04-011-4236	Magnesium Su...	Mg2 (S O4)2 (...	44	0.403	Blue	S	Inorg...

Fig. 2. Schematic presentation of machanochemical synthesis of $MgSO_4 \cdot 6OC(NH_2)_2 \cdot 0.5H_2O$.

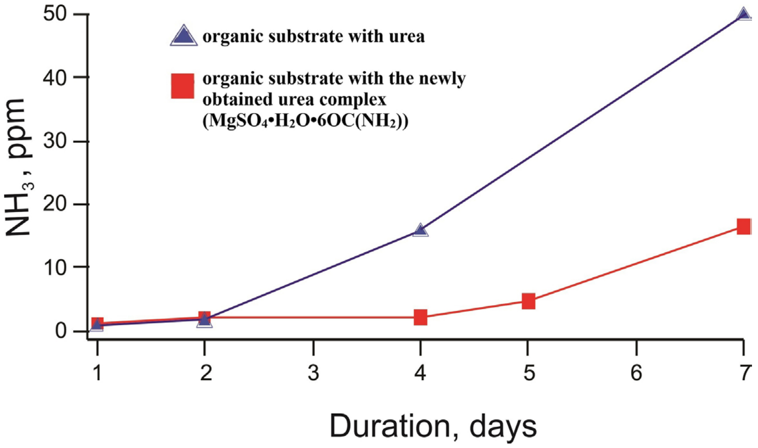


Fig. 3. Ammonia volatilisations for the studied systems.

The ammonia volatilizations for the studied systems are presented in Fig. 3. The results show different tendencies for the urea and the newly obtained urea complex ($MgSO_4•H_2O•6OC(NH_2)$), proving that the nitrogen release is slower in the case of the urea complex and that it stays in the soil for a longer time.

CONCLUSIONS

The tribochemical method is suitable for obtaining of $MgSO_4•6OC(NH_2)_2•0.5H_2O$. The method allows this product to be obtained systematically, simply, selectively and without obtaining secondary products. Being single-phase, the discussed product is easy to be characterized and has strictly defined properties. The high ratio of urea to magnesium sulphate corresponds to the use of nitrogen as a major bioelement, and sulfur and magnesium as trace elements. This meet the requirements for the fertilizer products and mixtures. Longer-term measurements in the presence of plants should be performed.

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