

## Mineral-Based Slow Release Fertilizers: A Review

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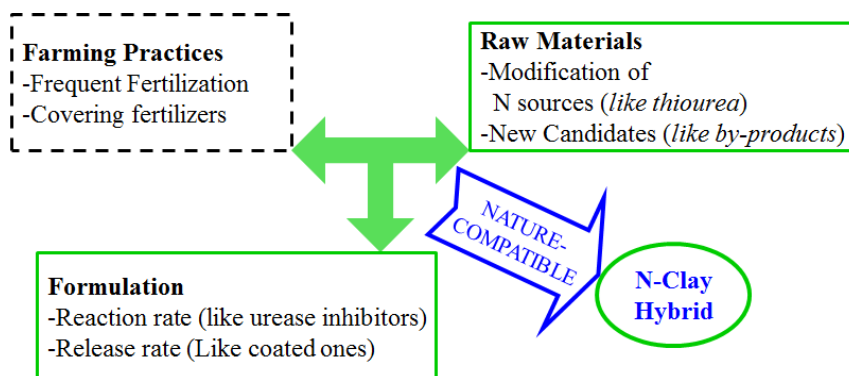
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Global population is expected to reach nine billion in 2050 and the total demand for food is expected to increase approximately by 60 percent by 2050 as compared to 2005. Therefore, it is important to increase crop production in order to meet the global demand for food. Slow release fertilizers have been developed and designed in order to improve the efficiency of fertilizers. Mineral-based slow release fertilizers are useful because the minerals have a crystalline structure and are environmentally friendly in a soil. This review focuses on slow release fertilizers based on montmorillonite, zeolite, and layered double hydroxide phases as a host for nutrients, especially N. Urea was successfully stabilized in the interlayer space of montmorillonite by the formation of urea-Mg or Ca complex, [(Urea)<sub>6</sub>Mg or Ca]<sup>2+</sup> protecting its rapid degradation in soils. Naturally occurring zeolites occluded with ammonium nitrate and potassium nitrate by molten salt treatment could be used as slow release fertilizer because the occlusion process increased the capacity of zeolites to store nutrients in addition to exchangeable cations. Additionally, surface-modified zeolites could also be used as slow release fertilizer because the modified surface showed high affinity for anionic nutrients such as nitrate and phosphate. Moreover, there were attempts to develop and use synthetic layered double hydroxide as a carrier of nitrate because it has positively charged layers which electrostatically bond nitrate anions. Kaolin was also tested by combining with a polymer or through the mechanical-chemical process for slow release of nutrients.

**Key words:** Slow-release fertilizer, Montmorillonite, Zeolite, Layered double hydroxide, Kaolin



Strategic approach to clay-based fertilizers.

## Introduction

Global population keeps constantly increasing and it is expected that it will reach nine billion people in 2050 (UNFPA, 2012). As a result, the world demand for food will continue to increase over the coming years. According to Food and Agriculture Organization of the United Nations (Alexandratos and Bruinsma, 2012), the total food demand in world will increase approximately by 60 percent by 2050 as compared to 2005. Accordingly the increase of crop productivity in agriculture is essential to meet global demand for foods. The proper use of fertilizers in a field can be a solution to increase crop productivity because fertilizers are one of the most effective factors to enhance plant growth. However, the increase in use of fertilizers results in environmental pollution leading to health problems. Environmental pollution is caused by the high solubility of nutrients and their leaching followed by high mobility in soils. The chemical fertilizers have high water solubility, but only a portion can be used by plants. The rest is affected by several processes such as adsorption, degradation, runoff, or leaching when they are applied to a field. In other words, soluble chemical fertilizers are highly inefficient. Therefore excessive application of fertilizers may lead to contamination of surface/subsoils and groundwater by runoff and leaching because inorganic anions such as nitrate and phosphate derived from fertilizers are pollutants (Adetunji, 1994).

Phosphate originated from fertilizers may contribute to eutrophication of lakes and rivers increasing algal biomass which leads to depletion of oxygen once it is incorporated into an aquatic system (Charette et al., 2013). In addition, P fertilizers containing trace contaminants such as Cd, Cr, Pb, Ur and Ra can be a serious long-term problem (Mortvedt JJ, 1987; Sharpley and Menzel, 1987). In a soil, nitrogen from fertilizers is likely to be transformed to nitrate which is highly mobile via runoff or leaching. The high concentration of nitrate in groundwater or drinking water may cause the “Blue Baby Syndrome” mainly in infants preventing red blood cells from carrying sufficient oxygen (Powlson et al., 2008). Therefore, the efficient use of fertilizers to meet the demand for macronutrients (nitrogen, phosphorus, and potassium) is of great importance and a key in the productivity of agriculture and protection of environment and health.

The difference between the rate of nutrient release from fertilizers and the rate of nutrient uptake by plant roots results in low efficiency of fertilizers. In order to increase their efficiency, the fertilizers from which nutrients are more slowly released than usual have been developed and tested, which are the so called “slow release fertilizers”. There are many advantages for use of slow release fertilizers compared to normal fertilizers. They: (1) reduce damage to seeds or seedlings of crops by high local concentration of salts; (2) prevent rapid nitrification and nitrogen loss; (3) supply nutrients sustainably; (4) decrease

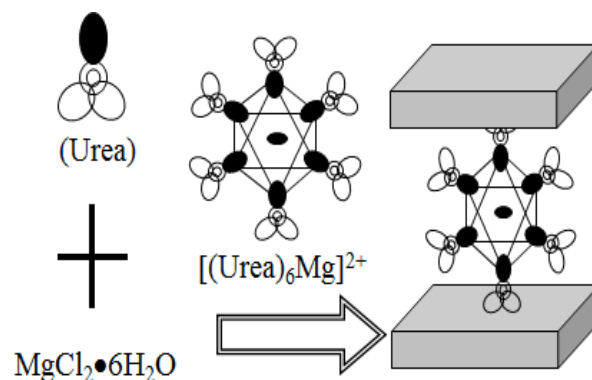
chemical and biological immobilization in soils which blocks uptake of nutrients by plant roots; (5) lower a fertilizer application frequency consequently reducing a detrimental effect on environment (Govind, 1979; Ni et al., 2010; Guo et al., 2006; Shaviv and Mikkelsen, 1993).

Several types of slow release fertilizers have been prepared based on a wide range of materials including various minerals (Bansiwali et al., 2006; Bortolin et al., 2013; Kim et al., 2011; Park et al., 1997; Pereira et al., 2012). Mineral-based slow release fertilizers has attracted special attention because they are not only environment-friendly but also contribute to long term fertility in a soil. In fact, typical minerals have both framework charge and crystal structure to protect nutrients from rapid degradation. Therefore, the objective of this review is to summarize the research on preparation of mineral-based slow release fertilizers using montmorillonite, zeolite, layered double hydroxide, and kaolinite minerals. The main part of the review is divided into four sections that deal with montmorillonite, zeolite, layered double hydroxide, and kaolin as slow release fertilizers.

## Mineral-based Slow Release Fertilizers

**Use of montmorillonite for urea-type fertilizers** Montmorillonite is a swelling type of 2:1 layered clay mineral of the smectite group. Each layer consists of an octahedral sheet sandwiched by two tetrahedral sheets. Nanosized interlayer space is hardly accessible to macromolecules and microbes. Exchangeable cations are located in the interlayer space of montmorillonite due to negative charges of the layer resulting from isomorphous substitution. Since montmorillonite has a low layer charge density, it swells well and interlayer cations participate in ion exchange process in a soil. These properties of montmorillonite are favorable for the preparation of a slow release fertilizer.

However, in order to use montmorillonite as a framework for the slow release fertilizer, a main problem is how a nutrient



**Fig. 1.** Illustration of urea-Mg cation complex intercalated in montmorillonite.

like neutral urea can be effectively protected or held in the negative interlayer space of montmorillonite. Mortland (1966) suggested that urea may coordinate through its carbonyl group to the metal ion in Cu (II), Mn(II), and Ni (II) montmorillonites and may be bonded to the metal ion in Mg-, Ca-, Li-, Na-, and K-montmorillonites by coordination. Park et al. (2004) reported that urea was successfully stabilized in the interlayer space of montmorillonite by the formation of positive urea-Mg complex,  $[(\text{Urea})_6\text{Mg}]^{2+}$  which acts like cations to be easily intercalated into the interlayer space, so that montmorillonite can protect rapid degradation of urea in a soil. Fig. 1 shows illustration of urea-Mg cation complex intercalated in montmorillonite. They prepared the urea-Mg complex in the solid state by mixing Mg-salt and urea at 105°C for 4h through ligand interaction between Mg cations and urea molecules. Urea was easily released out from montmorillonite through washing with water because of weak ligating power between magnesium cation and urea but it was evident that the urea-complex in montmorillonite showed less loss of nitrogen and fast effectiveness as a nitrogen fertilizer (Park et al., 2004).

As a further research of metal-urea complex montmorillonite, Kim et al. (2011a) focused on the optimization of massive urea intercalation into montmorillonite using anhydrous calcium or magnesium salts to minimize water and the characterization of urea-intercalated montmorillonite. In their research the coordination of Ca-urea complex was found to be much stronger than that of Mg-urea complex. It was shown that montmorillonite could accommodate urea molecules up to 52.7% (w/w) in the form of either cationic or neutral metal-urea complexes (Kim et al., 2011a). Moreover, the application of metal urea complex-intercalated montmorillonite to soils could suppress  $\text{NH}_3$  and  $\text{N}_2\text{O}$  emissions from the soils (Kim et al., 2011b). They reported a noticeable decrease in ammonia emission rate from  $38.5 \text{ N mg m}^{-2}\text{h}^{-1}$  of urea by itself applied to soils to  $28.3 \text{ N mg m}^{-2}\text{h}^{-1}$  from soils where the Ca/Mg-urea intercalated montmorillonite was applied. The decrease in ammonia emission in the latter was postulated to be because of delayed urea hydrolysis, dissolution of ammonia into water adsorbed in montmorillonite, adsorption of ammonia by montmorillonite, and diffusion of urea molecules into inner soils (Kim et al., 2011b).

There was another approach to prepare a slow release fertilizer in the form of montmorillonite nanocomposite. Pereira et al. (2012) prepared slow-release urea nanocomposite based on urea intercalation into montmorillonite by an extrusion process at room temperature. The extrusion process needs minimal amounts of water, could be carried out at very low temperatures, and the size of nanocomposite granules could be easily adjusted. Urea intercalates in the interlayer spaces of montmorillonite during the extrusion process and the extrusion process leads to composites in the form of pellets using a twin-screw extruder (Pereira et al., 2012). Urea contents of

the prepared nanocomposites were in the range of 50 to 80 wt%. This nanocomposite showed a slow release behavior for urea dissolution, even in low montmorillonite amounts, which is related to exfoliation of montmorillonite caused by the extrusion process (Pereira et al., 2012).

**Use of zeolite for slow release fertilizers** Zeolites are naturally occurring microporous crystalline aluminosilicates. They have an open three-dimensional structure containing exchangeable cations to satisfy the electrostatic charge of the framework of silica and alumina tetrahedral units. The framework contains open cavities like pores in the form of channels and cages. Exchangeable cations and water molecules occupy these interconnected cages and channels, so that the charge resulting from alumina tetrahedra in the framework determines the ion-exchange property of zeolites. The size of clinoptilolite channels controls the size of the molecules or ions that can pass through them and therefore a zeolite like clinoptilolite can act as a chemical molecular sieve allowing some ions to pass through while blocking others (Munpton, 1999). Those structural and chemical properties of zeolites are appropriate for agricultural uses like fertilizers and soil amendments.

Many studies in the literature reported that even the addition of zeolite to the source of N could improve the nitrogen use efficiency in a soil (Gruener et al., 2003; McGilloway et al., 2003; Rehakova et al., 2004) because it could improve retention of nutrients like ammonium and potassium ions (Eturki et al., 2012). In addition, zeolite reduces nitrification (Ippolito et al., 2011) consequently decreasing nitrate leaching (Perrin et al., 1998). The small internal tunnels of clinoptilolite have been found to physically protect ammonium ions from intense nitrification by microorganisms (Ferguson and Pepper, 1987) because water-occupying channels in the clinoptilolite framework are probably enough for small cations like ammonium and potassium to enter, but too small for nitrifying bacteria to access the ammonium ions (Ramesh and Reddy, 2011). Therefore, ammonium occupying the channels of zeolite would not be released easily as compared to nitrogen chemical fertilizers, suggesting  $\text{NH}_4$ -zeolites have a good potential for the slow release of N fertilizer.

Park and Komarneni (1997) prepared zeolites to occlude ammonium nitrate and potassium nitrate by molten salt treatment

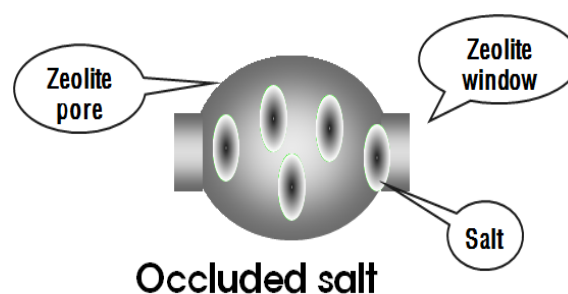


Fig. 2. Illustration of occluded salt in zeolite pore.

not only because the salt occlusion provides an additional capacity for nutrients but also because the occluded nutrients are more slowly released than the free ionic one. Fig. 2 illustrates salt occlusion in zeolite pores. The occluded form of nitrate in natural zeolites increased in the following order: erionite > clinoptilolite > chabazite > phillipsite with molten potassium nitrate treatment, and phillipsite > erionite > chabazite > clinoptilolite with molten ammonium nitrate treatment (Park and Komarneni, 1997). Park and Komarneni (1998) demonstrated that the occluded  $\text{NH}_4^+$  and  $\text{NO}_3^-$  forms were released slowly and steadily, as compared to exchangeable  $\text{NH}_4^+$  in zeolites during 30d treatment in a simulated soil solution. It suggested that the salt-occluded zeolites would be useful as slow release fertilizers.

Surfactant modified-zeolites are also potential slow release N fertilizers. Li (2003) determined the feasibility of a surfactant-modified zeolite prepared by hexadecyltrimethylammonium, a cationic surfactant as a fertilizer carrier to control nitrate release. He concluded that by batch and greenhouse tests, the surfactant-modified zeolite was a good sorbent for nitrate, while slow release of nitrate was achievable. These properties suggest that the surfactant-modified zeolite is a potential candidate as the slow release fertilizer to control the release of nitrate and other anions (Li, 2003) but that the capacity may be too low.

In addition to nitrogen, there have been attempts to control phosphorus release using zeolites (Allen et al., 1993; Pickering et al., 2002; Bansiwali et al., 2006). Allen et al. (1993) showed that mixtures of zeolite and phosphate rock could provide slow release fertilization by dissolution and ion exchange reactions. By mixing  $\text{NH}_4^-$  and K-clinoptilolite with phosphate rock, the dissolution and cation-exchange reactions increased the solubility of the phosphate rock and simultaneously released ammonium and potassium into solution due to an exchange-induced dissolution (Allen et al., 1993). The mechanism of the exchange-induced dissolution is that the plant uptake of  $\text{NH}_4^+$  or  $\text{K}^+$  frees exchange sites which are occupied by  $\text{Ca}^{2+}$ , lowering the soil solution  $\text{Ca}^{2+}$  concentration and inducing further dissolution of phosphate rock (Pickering et al., 2002). Moreover, Bansiwali et al. (2006) reported the possibility of surfactant-modified zeolite for the slow release fertilizer of phosphorus. Zeolite-A was modified using hexadecyltrimethylammonium bromide, a cationic surfactant leading to the increase of its surface capacity to retain anion, phosphate ( $\text{PO}_4^-$ ) and P loading increased by a factor of 4.9 as compared to the unmodified zeolite-A (Bansiwali et al., 2006). And in the constant flow percolation experiment, phosphate from the surfactant-modified zeolite-A was supplied after 1,080 hours, whereas phosphate from chemical P fertilizer ( $\text{KH}_2\text{PO}_4$ ) was done within 264 hours (Bansiwali et al. 2006), suggesting its potential application as slow P release-fertilizer.

#### Use of layered double hydroxide for slow release

**fertilizers** Layered double hydroxide (LDH), which is known as anionic clay, is a mineral with a permanent positive charge in a layer. It has a layer structure consisting of positively charged brucite-like sheets. Exchangeable anions are held in interlayer spaces to compensate its positive charges which are generated by isomorphic substitution of original divalent cations by trivalent cations in a structure. Its chemical composition is generally shown by the following formula,  $[\text{M}^{2+}_{1-x}\text{M}^{3+}_x(\text{OH})_2]^{x+} [\text{A}^{m-}]_{x/m} \cdot n\text{H}_2\text{O}$  where  $\text{M}^{2+}$  is usually a divalent cation ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Co}^{2+}$  or  $\text{Fe}^{2+}$ ),  $\text{M}^{3+}$  a trivalent cation ( $\text{Al}^{3+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Mn}^{3+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Co}^{3+}$  or  $\text{Ni}^{3+}$ ) and  $\text{A}^{m-}$  a  $m$ -valent anion (e.g.  $\text{CO}_3^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{PO}_4^{3-}$ ,  $\text{SO}_4^{2-}$  or  $\text{Cl}^-$ ). The  $\text{M}^{3+} / (\text{M}^{2+} + \text{M}^{3+})$  ratio,  $x$ , is basically in the range  $0.1 \leq x \leq 0.5$  (Khan and O'Hare, 2002; Trave et al., 2002). Hydrotalcite  $[\text{Mg}_6^{2+}\text{Al}_2^{3+}(\text{OH})_{16}]^{2+} \text{CO}_3^{2-} \cdot 4\text{H}_2\text{O}$  is one of the naturally occurring LDH accommodating carbonate as an interlayer anion. A wide variety of LDHs, however, can be easily synthesized at both laboratory and industrial scales (Komarneni et al., 1996; De Roy et al., 2001; Khan and O'Hare, 2002) even at room temperature.

Since LDH has positive charges on a layer surface and thus could be used as a nitrate carrier or for controlled nitrate release for agricultural uses, several studies have been conducted for nitrate ion release characteristics to check the feasibility of LDH as the slow release fertilizer (Komarneni et al., 2003; Gillman and Noble, 2005; Halajnia et al., 2013; Urena-Amate et al., 2011; Torres-Dorante et al., 2009). Komarneni et al. (2003) carried out the experiment of nitrate release from several LDHs in simulated soil solutions and investigated the influences of the type of anions present in the soil solution, their concentration, and crystal size and charge density of LDHs. According to their results, a small particle size of LDH was more effective in the nitrate release than a large particle size. In the LDH with higher layer charge density (Mg:Al=2:1),  $\text{Cl}^-$  anion present in the simulated soil solution facilitated more  $\text{NO}_3^-$  to be released than did  $\text{CO}_3^{2-}$  from this anionic clay, while divalent anions like  $\text{SO}_4^{2-}$  and  $\text{CO}_3^{2-}$  led to more  $\text{NO}_3^-$  release in the LDH with lower layer charge density (Mg:Al=3:1) (Komarneni et al., 2003). Gillman and Noble (2005) examined affinity of hydrotalcite for a range of anions in multi-anion solutions containing  $\text{NO}_3^-$ ,  $\text{PO}_4^{3-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{CO}_3^{2-}$ , and  $\text{Cl}^-$  showing its high affinity for  $\text{PO}_4^{3-}$  and  $\text{CO}_3^{2-}$ , with lower affinity for  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$  and  $\text{Cl}^-$ . They suggested that  $\text{NO}_3^-$ -hydrotalcite applied to soils as a fertilizer would be almost irreversibly converted to either  $\text{PO}_4$  or  $\text{CO}_3$ -hydrotalcite over time by exchange with nitrate. However, according to other research (Halajnia et al., 2013), Mg-Al-LDH (4:1) with the low layer charge density showed high  $\text{NO}_3^-$  adsorption rate and adsorption capacity compared with phosphate and sulfate. Halajnia et al. (2013) revealed that the adsorption process was endothermic for phosphate and sulfate and exothermic for nitrate. Thus they suggested that the synthesized LDH

(Mg:Al=4:1) can efficiently reduce nitrate leaching during the cold and nongrowing seasons because nitrate adsorption would increase with decreasing temperature. Urena-Amate et al. (2011) attempted to control nitrate release using modified LDH by hydroxypropyl methylcellulose (HPMC) in its different shape. They reported that the addition of HPMC led to slower nitrate release compared with unmodified LDH, and that the shape of tablet in the modified LDH was more effective in retarding nitrate release than that of granule. Moreover, in a long-term research under greenhouse conditions, LDH showed a potential to be used as a long-term nitrate exchanger to control nitrate movement in a soil (Torres-Dorante et al., 2009).

**Use of kaolin for slow release fertilizers** Kaolin is a type of clay minerals consisting mainly of hydrated aluminosilicate or kaolinite formed through hydrothermal alteration of feldspar and muscovite, usually containing quartz (Prasad et al., 1991). Kaolin was used as a nutrient-carrier through a mechanochemical process like milling to reduce the crystallinity of kaolin and to simultaneously allow incorporation of nutrients into its structure. Nutrients such as  $\text{KH}_2\text{PO}_4$  and  $\text{NH}_4\text{H}_2\text{PO}_4$  were incorporated into an amorphous kaolin structure through a milling process at least at 400 rpm rotational speed and these systems of either kaolin-  $\text{KH}_2\text{PO}_4$  or kaolin-  $\text{NH}_4\text{H}_2\text{PO}_4$  showed slow release of nutrients when dispersed in water (Solihin et al., 2011). In other way kaolin was used as one of the constituents to prepare a superabsorbent polymer which can slowly release nutrients. Liang et al. (2006) prepared controlled release nitrogen, phosphorus and potassium compound fertilizer consisting of the core/shell structure with the function of water retention. Its core was formaldehyde and polyphosphate potassium fertilizer, and the shell was P(acrylic acid-co-acrylamide)/kaolin superabsorbent composite. Various inorganic clays including kaolin were added to this type of fertilizers in order to improve swelling property, hydrogel strengths, and production costs (Wu et al., 2003; Zhang et al., 2006; Lee et al., 2005; Liang et al., 2006). The fertilizers not only showed good slow release of nutrients but also high water retention capacity.

## Conclusions

It is clear that global food demand will continuously increase as the world population keeps increasing. In order to provide sufficient food, the increase in crop productivity is necessary, which could be achieved through use of fertilizers. However, excessive use of fertilizers can cause several problems to environments and human health. Therefore, much attention has been paid to slow release fertilizers for improving the efficiency of fertilizers. This review dealt with slow release fertilizers using minerals such as montmorillonite, zeolite, layered double hydroxide, and kaolin. It is evident from the

published literature that these minerals, especially the first three have a great potential for slow release fertilizers. Montmorillonite could be used to stabilize urea in the form of urea-Ca or Mg complex as well as to form nanocomposites with urea. The potential of zeolites for slow release fertilizers has been confirmed by their increased capacity through the occlusion. Additionally layered double hydroxide or modified one has shown the slow release of nutrients under a variety of conditions. Kaolin also has been tested by combining with a polymer or through the mechanical-chemical process with nutrients to check its capacity for slowly releasing nutrients. However, in terms of slow release of nutrients from the mineral-base fertilizers, most studies have been conducted in a laboratory for a short-term under limited conditions, but only a few studies were conducted in a soil. Therefore, more studies are needed for not only examining the behavior of the mineral-based fertilizers in a pot or a field but also for checking their long-term effects in a soil.

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