



Review

Struvite formation and decomposition characteristics for ammonia and phosphorus recovery: A review of magnesium-ammonia-phosphate interactions

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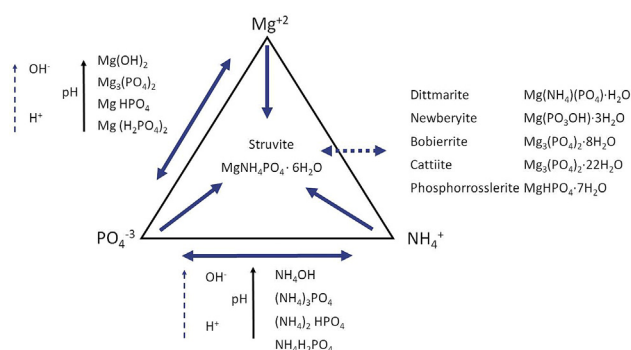
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HIGHLIGHTS

- Struvite ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$) has a complex and highly variable crystallization process.
- Ammonia, phosphate, and magnesium can form crystals with different structures.
- Struvite decomposition also has complex sequence of reactions and mechanisms.
- Struvite crystals forming in wastewater and urine contain impurities.
- Struvite formation is very sensitive to solution pH and ammonia concentration.

GRAPHICAL ABSTRACT



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ABSTRACT

Struvite ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$) forms in aqueous systems with high ammonia and phosphate concentrations. However, conditions that result into struvite formation are highly dependent on the ionic compositions, temperature, pH, and ion speciation characteristics. The primary ions involved in struvite formation have complex interactions and can form different crystals depending on the ionic levels, pH and temperature. Struvite as well as struvite analogues (with substitution of monovalent cations for NH_4^+ or divalent cations for Mg^{2+}) as well as other crystals can form simultaneously and result in changes in crystal morphology during crystal growth. This review provides the results from experimental and theoretical studies on struvite formation and decomposition studies. Characteristics of NH_4^+ or divalent cations for Mg^{2+} were evaluated in comparison to monovalent and divalent ions for formation of struvite and its analogues. Struvite crystals forming in wastewater systems are likely to contain crystals other than struvite due to ionic interactions, pH changes, temperature effects and clustering of ions during nucleation and crystal growth. Decomposition of struvite occurs following a series of reactions depending on the rate of heating, temperature and availability of water during heating.

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1 Introduction

Struvite ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$) forms in aqueous systems with high ammonia and phosphate levels (wastewater and kidneys) often as orthorhombic crystals. In natural environments, its occurrence have been associated with newberyite $\text{Mg}(\text{PO}_3\text{OH}) \cdot 3(\text{H}_2\text{O})$, hanayite $(\text{NH}_4)_2\text{Mg}_3\text{H}_4(\text{PO}_4)_4 \cdot 8(\text{H}_2\text{O})$, brushite $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$, and stercorite $\text{NaNH}_4\text{HPO}_4 \cdot 4\text{H}_2\text{O}$ (Mineral Data, 2005). Struvite consists of PO_4^{3-} (tetrahedral), $\text{Mg}(\text{H}_2\text{O})_6^{2+}$ (octahedral), and NH_4^+ (tetrahedral) groups which are held together by hydrogen bonds (Whitaker and Jeffery, 1970) (Fig. 1). The orthorhombic struvite crystals exhibit cell dimensions of $a = 6.941 \pm 0.002 \text{ \AA}$, $b = 6.137 \pm 0.002 \text{ \AA}$, $c = 11.199 \pm 0.004 \text{ \AA}$ (Whitaker and Jeffery, 1970; Ferraris et al., 1986). Table 1 presents selected chemical characteristics of the struvite crystals.

The PO_4^{3-} tetrahedron is regular with mean P–O bond length of 1.543 Å. The $\text{Mg} \cdot 6\text{H}_2\text{O}$ octahedron is distorted with mean Mg– H_2O length of 2.0810 Å, and $\text{H}_2\text{O} \cdot \text{H}$ length of 0.792 Å. The water O–H bond length is significantly smaller than the intermolecular separation which may be due to H atom taking part in bond formation (Whitaker and Jeffery, 1970). The water molecules form six short hydrogen bonds that are among the shortest ever found in crystalline hydrates (Chiari and Ferraris, 1982; Ferraris et al., 1986) with distances ranging from 263.0 to 269.5 pm while the seventh, which is in contact with another water molecule, is longer (314.1 pm). The ammonium ion forms one strong hydrogen bond (N–O with bond distance 280 pm), and the other hydrogen bonds are weaker (Stefov et al., 2005). Bond strength is inversely related to bond length (i.e.,

shorter bond distance indicates stronger bond). A stronger bond also has a high bond dissociation enthalpy (BDE) (i.e., energy required to break it). Clustering effects around charged ions, ionic sizes, and change in the size of the atomic arrangements by electron and hydrogen interactions affects the bond distances and stability of the crystals forming.

Formation (and growth of struvite) crystals may be initially caused by salt bridges (a combination of two noncovalent interactions, i.e., hydrogen bonding and electrostatic interactions). Presence of ions (e.g., NH_4^+ , PO_4^{3-}) in water increases the strength of hydrogen bonds (Urbic, 2014), which may be due to salt bridges. The salt bridge effect also explains the formation of struvite through biomineralization mechanisms (Li et al., 2015). Hydrogen bonds have a controlling influence on the crystallization of large complex salts during initiation and growth of crystals and ionic

Table 1
Chemical characteristics of struvite crystals (National Center for Biotechnology Information, 2015).

Property	Value
Molecular weight	247.42 g/mol
Hydrogen bond donor count	10
Hydrogen bond acceptor count	11
Exact mass	247.05 g/mol
Topological polar surface area	84.8 Å ²
Heavy atom count	13 (not counting H)
Complexity	49.8
Covalently bonded unit count	9

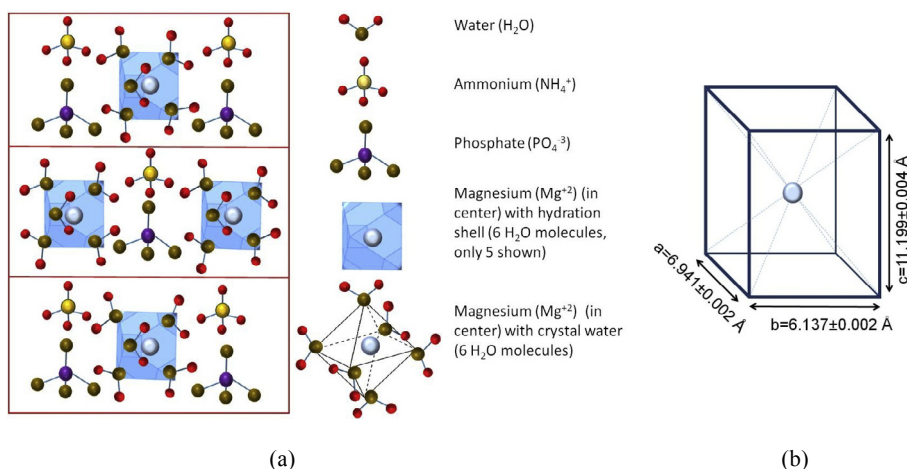


Fig. 1. Struvite crystal structure: (a) arrangement of ionic groups, (b) dimensions orthorhombic struvite crystal (Whitaker and Jeffery, 1970).

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