The Effect of Mixing Rate on Struvite Recovery from The Fertilizer Industry

Warmadewanthi1,*, A Rodlia1, N Ikhas1, E S Pandebesie1, A Y Bagastyo1, and W Herumurti1

1Department of Environmental Engineering, Faculty of Civil, Environmental and Geo Engineering, Institut Teknologi Sepuluh Nopember Surabaya 60111, Indonesia

*Corresponding author’s e-mail: warma@its.ac.id

Abstract. Fertilizer wastewater contains a high concentration of ammonium and phosphate. One method of reducing the ammonium and phosphate contents is to recover them in the form of magnesium ammonium phosphate (MAP) or struvite (MgNH4PO4.6H2O). The objective of this experiment was to obtain the optimum mixing rate, pH, and molar ratio for struvite precipitation. A mixture of wastewater containing [Mg2+]:[NH4+]:[PO43−] in molar ratios of 1:1:1, 1.5:1:1, and 2:1:1 was added to a 0.5-L beaker glass. Samples were then stirred under G.t values of 0.5 × 10^5, 10^6, and 1.5 × 10^6 for 60 minutes and left for 30 minutes for the sedimentation process. pH was set to 7.5, 8, and 8.5. Subsequently, the experimental results were compared with thermodynamic modelling using PHREEQC v3.0. The results showed that the optimum mixing rate was 158 rpm, which is equal to a G.t of 10^5; the optimum pH was 8.5 ± 0.2; and the optimum molar ratio of [Mg2+]:[NH4+]:[PO43−] was 1:1:1. The removal percentage was 86.14% for ammonium and 98.98% for phosphate. Experimental results displayed a pattern similar to that predicted by the model. Additionally, the morphology of struvite shown by SEM-EDX and XRD analysis also demonstrated that struvite was formed in the precipitate.

Keywords: Ammonium, Phosphate, Precipitation, Recovery, Struvite.

1. Introduction
The fertilizer industry is an important industry, especially in an agricultural country like Indonesia. The industry has different units that produce ammonium fertilizer, phosphoric acid, and various types of fertilizer. Different units generate wastewater of different characteristics. Wastewater from the fertilizer industry typically contains high concentrations of ammonium (NH4+) and phosphate (PO43−) as well as other ions such as Ca2+, Mg2+, F−, Na+, K+, sulfate (SO42−), and Cl− [1]. High concentrations of ammonium and phosphate in water ecosystems cause eutrophication [2], [3].

Currently, many processes for the recycling and recovery of phosphorus (P) have been examined, as it is known that it will be depleted by the year 2100 [4]. This is one of the reasons for the recovery of P, given that there is currently no known substitute [5]. A well-known method of phosphate recovery is chemical precipitation, and in the simultaneous recovery of PO43− and NH4+, struvite (MgNH4PO4.6H2O) is the preferred target. Struvite has several advantages when applied as fertilizer. It can release nutrients more slowly than other fertilizers [6], with a lower metal content compared to...
common commercial fertilizers [7]. Furthermore, struvite is an effective source of N, Mg, and P for plants and can be utilized without destroying plant roots [8].

Struvite precipitation consists of two stages, nucleation and crystal growth, which affect the particle size [9]. Nucleation depends on the rate of initial mixing, while crystal growth depends on the duration of mixing and its velocity [10]. Struvite precipitation depends on several factors, like the precipitation agents, the molar ratio of each component, pH condition, mixing speed, and presence of interfering ions [11]. The precipitation of struvite is conducted by using various sources of Mg as a precipitation agent. Both MgCl₂ and MgSO₄ as soluble salts are regularly used as precipitation agents [12]. Stolzenburg et al. [13] stated that it is vital to prepare MgO suspension when using this material to induce an effective precipitation of struvite. The sequence of the precipitate's excellence in phosphate reduction using different Mg sources is MgCl₂ > MgSO₄ > MgO > Mg(OH)₂ > MgCO₃ [11].

The pH level affects the precipitation of struvite. The purity of struvite reaches 90% within the range of pH 7 to 7.5; however, recovery of the mineral is low [14]. The efficiency of the process of mineral formation increases to 40–80% at a pH level of 8 to 9.5; nevertheless, the purity of the mineral decreases by approximately 30–70% because other minerals are formed as well [15].

The molar ratio of each component of struvite precipitation also has a specific effect on the precipitation process. Based on stoichiometry, the molar ratio of [Mg²⁺]:[NH₄⁺]:[PO₄³⁻] is equal to 1:1:1. However, Mg level higher than the stoichiometric ratio is required to enhance the precipitation of struvite [16,17]. An additional controlling factor related to struvite precipitation is the excess concentration of NH₄⁺. Optimum struvite precipitation from semiconductor wastewater can be reached at a molar ratio of [NH₄⁺]:[PO₄³⁻] of 15:1 [16]. Capdeville et al. [18] demonstrated that a high molar ratio of [N]:[P] increased the induction time of struvite formation and decreased the effect of the Ca²⁺ ions that existed in the solution.

The presence of competitor ions, such as Ca²⁺, Fe⁺, F, and SO₄²⁻, also affects struvite precipitation. Le Corre et al. [19] ascertained that an amorphous calcium phosphate precipitate is formed at high concentrations of Ca²⁺ in wastewater. The presence of Ca²⁺ significantly retards precipitation of struvite when the [Ca²⁺]:[Mg²⁺] ratio is more than 1:1 [20]. This research also revealed that a limited dose of Fe³⁺ was a more competitive inhibitor of struvite precipitation than Ca²⁺. Ryu et al. [21] mentioned that high concentrations of F have an impact on the precipitation of struvite. On the other hand, Sulfate ions increase the induction time of struvite formation [22].

Additionally, the mixing intensity affects the recovery of struvite [23]. For the crystallization of struvite by means of MgO suspension, mixing speeds in the range of 10 to 90 rpm and a reaction time of 50 to 100 min are favourable [24].

This research was conducted to investigate struvite precipitation from fertilizer wastewater that contains high concentrations of PO₄³⁻ and NH₄⁺. The optimum mixing rate, optimum pH, and optimum molar ratio in the struvite precipitation process were determined. The morphology and content of the precipitate were analysed to identify the presence of struvite and other minerals that might be formed in the precipitate. The results were compared with those of a thermodynamic model simulated using PHREEQC version 3.0 software.

2. Materials and Method
Wastewater used in this research was taken from representative fertilizer plants, namely an ammonium fertilizer plant (Unit 1) and a phosphoric acid unit (Unit 2). The characteristics of the wastewater from each unit are shown in Table S1.

Wastewater from Unit 1 was low in turbidity (8.3 NTU) and slightly alkaline (pH of 9.7) and mainly contained 5,234 mg/L of NH₄⁺ and 417.01 mg/L of chemical oxygen demand (COD). On the other hand, Unit 2 produced highly turbid (1,736 NTU) and acidic (pH of 1.5) wastewater that contained 30,875 mg/L of PO₄³⁻, 601.19 mg/l of Ca, 105.33 mg/L of Mg, 676 mg/L of F, and 3,600 mg/L of COD. In the current study, wastewater from Units 1 and 2 was firstly mixed to attain the
molar ratio of $[\text{NH}_4^+]:[\text{PO}_4^{3-}]$ of 1:1 for the experiments. The mixed wastewater was stirred continuously for one day and then sedimentation was continued for 2 hours. After the sedimentation process, the supernatant of mixed wastewater from Units 1 and 2 was found to be high in $\text{PO}_4^{3-}$ (14,656 mg/L), $\text{NH}_4^+$ (2,864 mg/L), and COD (3,675 mg/L), as shown in Table S2. It was noted that the molar ratio of $[\text{NH}_4^+]:[\text{PO}_4^{3-}]$ was equal to 1:1.03.

A total of 20 L of wastewater was used to conduct each set of experiments. $\text{MgCl}_2\cdot6\text{H}_2\text{O}$ (Merck, Germany) was added as a source of Mg in the solution and NaOH (Merck, Germany) was used to adjust the pH. In the precipitation experiments, a jar test apparatus consisting of six 1-L glass beakers (Iwaki) was used. Firstly, 500 mL of wastewater was put into the beaker and the pH was adjusted by using NaOH. Different molar ratios of $[\text{Mg}^{2+}]:[\text{NH}_4^+]:[\text{PO}_4^{3-}]$ were applied in this process, namely 1:1:1.03, 1.5:1:1.03, and 2:1:1.03, with different total multiplication products of the velocity gradient and detention time (G.t) of $0.5 \times 10^6$, $10^6$, and $1.5 \times 10^6$. The mixing process was done for 60 minutes and was followed by sedimentation for 30 minutes. The pH was monitored during the mixing process by using a pH meter. The supernatant was taken to measure the residual concentrations of ammonium, phosphate, fluoride, and sulfate by spectrophotometer (Genesys 20). Residual Ca and Mg concentrations were measured by atomic absorption spectrophotometer (Shimadzu AA 7000). The filtered precipitate was subsequently dried at room temperature for 48 hours for further analysis [16]. The morphology and elemental composition of the precipitate were measured by scanning electron microscope (SEM, Carl Zeiss, EVO MA 10) equipped with an energy dispersive X-ray spectroscopy (EDX, Bruker), while the crystal phases were identified by X-ray diffractometry (XRD, Philips X’Pert powder diffractometer).

PHREEQC version 3.0 software was used to assess the equilibrium chemical species in the solution [25]. This model allows the user to add a thermodynamic database of possible solid phases that could form in the solution, such as struvite, bobbierrite, calcium phosphate precipitate, and so forth. The solid phases included in this prediction model can be seen in Table S3. Modification of the thermodynamic database included the stoichiometric reaction of the precipitate, enthalpy, and solubility product of the precipitate (Ksp).

3. Results and Discussion

3.1 Effects of Mixing Rate

Struvite precipitation consists of two stages, nucleation and crystal growth, which affect the particle size [9]. Nucleation depends on the rate of initial mixing, while crystal growth depends on the duration of mixing and its velocity [10]. The results for the effects of velocity gradient (G) and G.t value on $\text{NH}_4^+$ and $\text{PO}_4^{3-}$ removal are shown in Table 1. From Table 1, it can be seen that higher mixing rate resulted in an increase in removal efficiency of ammonium and phosphate. Previous research has also found that at a small G.t value, the removal efficiency of phosphate is relatively low, while at greater G.t values, it is higher [9]. The G.t value did not have a significant effect on the recovery of ammonium and phosphate, although the experiment results showed that the recovery increased when the mixing energy increased.

The improvement in removal in this study is in line with other research that reported that the removal efficiency of struvite decreased at lower G.t values [23]. The higher the mixing rate, the faster the induction time, and thus nucleation happens more rapidly [28]. It was found that at a G.t value of $1.5 \times 10^6$, equal to 207 rpm, the removal efficiencies of ammonium and phosphate decreased. This was due to the instability of struvite crystals, which led to the breakage of the crystals and decrease of the removal efficiencies of ammonium and phosphate [10]. Based on the result, the G.t value used for subsequent experiments was $10^6$, which was equivalent to a mixing speed of 158 rpm and a reaction time of 60 minutes.
It can be concluded that greater molar ratio required higher mixing energy due to the driving force required for the process. It was also found that the amount of precipitate increased with the increasing mixing energy as it affected the sedimentation rate. High mixing velocities may have caused the formation of more precipitates, causing larger crystals to form, allowing more ammonium to bind. This can be proved by the increase in turbidity after the mixing process, as shown in Figure 1.

Table 1. Effect of mixing rate on ammonium and phosphate removal

| Removal (%) at a Molar Ratio of $[\text{Mg}^{2+}]:[\text{NH}_4^+:][\text{PO}_4^{3-}]$ of 1:1:1 | pH 7.5 | pH 8  | pH 8.5 |
|-----------------------------------------------|-------|-------|--------|
| G.t                                           |       |       |        |
| $0.5 \times 10^6$                              | 80.39 | 95.25 | 81.67  |
| $1 \times 10^6$                                | 81.06 | 95.28 | 83.60  |
| $1.5 \times 10^6$                              | 79.01 | 95.13 | 80.42  |

| Removal (%) at a Molar Ratio of $[\text{Mg}^{2+}]:[\text{NH}_4^+:][\text{PO}_4^{3-}]$ of 1.5:1:1 |
|-------------------------------------------------|-------|-------|--------|
| G.t                                           |       |       |        |
| $0.5 \times 10^6$                              | 66.62 | 99.48 | 67.20  |
| $1 \times 10^6$                                | 68.34 | 99.85 | 69.80  |
| $1.5 \times 10^6$                              | 66.14 | 99.77 | 68.35  |

| Removal (%) at a Molar Ratio of $[\text{Mg}^{2+}]:[\text{NH}_4^+:][\text{PO}_4^{3-}]$ of 2:1:1 |
|-------------------------------------------------|-------|-------|--------|
| G.t                                           |       |       |        |
| $0.5 \times 10^6$                              | 50.76 | 99.86 | 57.96  |
| $1 \times 10^6$                                | 56.99 | 99.90 | 58.29  |
| $1.5 \times 10^6$                              | 52.10 | 99.85 | 55.02  |

Figure 1. The Turbidity of the Supernatant after Mixing. 3.2 Effects of pH
The degree of acidity or pH was a factor that affected formation of struvite. The pH value affected the solubility of struvite and its thermodynamic properties [29]. The change in pH was caused by the induction time. Induction time was 7–14 minutes [30]. The first change in pH occurred because of the mixing and dissolution of magnesium [13]. The addition of MgCl₂ decreased the pH as well [31]. The experimental results for recovery of PO₄³⁻ and NH₄⁺ fitted the model predictions well (Table 2).

Table 2. The effect of pH on the recovery of NH₄ and PO₄

| pH    | [NH₄⁺] Model Prediction | [NH₄⁺] Experimental Results | [PO₄³⁻] Model Prediction | [PO₄³⁻] Experimental Results |
|-------|-------------------------|------------------------------|--------------------------|-------------------------------|
| 7.5   | 89.90                   | 81.06                        | 95.67                    | 95.28                         |
| 8     | 91.45                   | 83.60                        | 97.16                    | 97.56                         |
| 8.5   | 92.59                   | 86.14                        | 98.34                    | 98.98                         |

| pH    | [NH₄⁺] Model Prediction | [NH₄⁺] Experimental Results | [PO₄³⁻] Model Prediction | [PO₄³⁻] Experimental Results |
|-------|-------------------------|------------------------------|--------------------------|-------------------------------|
| 7.5   | 67.68                   | 68.34                        | 99.90                    | 99.85                         |
| 8     | 67.16                   | 69.80                        | 99.97                    | 99.94                         |
| 8.5   | 65.25                   | 70.09                        | 99.99                    | 99.97                         |

| pH    | [NH₄⁺] Model Prediction | [NH₄⁺] Experimental Results | [PO₄³⁻] Model Prediction | [PO₄³⁻] Experimental Results |
|-------|-------------------------|------------------------------|--------------------------|-------------------------------|
| 7.5   | 48.87                   | 56.99                        | 99.94                    | 99.90                         |
| 8     | 48.01                   | 58.29                        | 99.98                    | 99.98                         |
| 8.5   | 48.21                   | 58.64                        | 99.99                    | 99.97                         |

The results of the experiment showed that the optimum pH for struvite formation at a mixing rate of 158 rpm (G.t value of 1 × 10⁶) was 8.5 ± 0.2. However, at pH 8.5 and the higher molar ratio of [Mg²⁺]:[NH₄⁺]:[PO₄³⁻] of 1.5:1:1, the NH₄⁺ removal decreased. Based on modelling using PHREEQC, it was found that other precipitates could have formed during precipitation, namely bobierrite (Mg₃(PO₄)₂.8H₂O), MgF₂, and fluorapatite (Ca₅(PO₄)₃F) (Fig. 2). When pH range was within 8 to 9, it could make the solubility of struvite decline [10]. Additionally, Mg₃(PO₄)₂.8H₂O might have slowed reaction kinetics as it formed with a reaction time of 5–480 minutes at pH 9 in the treatment of anodizing wastewater [32]. In line with that study, since the reaction rate was slower for Mg₃(PO₄)₂.8H₂O, it was unlikely to form under these experimental conditions. It was also predicted that MgF₂ and Ca₅(PO₄)₃F would affect the recovery of struvite [22].
3.2 Effects of Molar Ratio

The molar ratio had a significant impact on the composition of struvite precipitate (Figure 3). Adding an excess of magnesium would be beneficial in increasing the removal efficiency of phosphate but would reduce the purity of the struvite product [10]. The molar ratio of \([\text{NH}_4^+]:[\text{PO}_4^{3-}]\) in this wastewater was 1:1.03, with additions of the stoichiometric amount of Mg. Moreover, struvite was dominant in the precipitate. The excess concentration of Mg was not necessary because it might alter the purity of struvite. Another precipitate of magnesium phosphate, which was preferable, would be formed at a molar ratio of \([\text{Mg}^{2+}]:[\text{PO}_4^{3-}]\) higher than 1.5:1.

![Figure 2. Prediction of Precipitate based on PHREEQC Modelling](image)

![Figure 3. Effects of molar ratio on residual concentrations of phosphate and ammonium](image)

Table 3 shows the residual concentrations of various ions that were present in the supernatant. The presence of Ca and F had an effect on struvite formation at a molar ratio of \([\text{Mg}^{2+}]:[\text{NH}_4^+]:[\text{PO}_4^{3-}]\) of
1.5:1:1, and the concentration of residual Ca and F decreased significantly because of the formation of fluorapatite (Ca$_5$(PO$_4$)$_3$F) and MgF$_2$ at pH 8.5, as shown by the model prediction.

**Table 3. Residual concentration of interfering ions**

| Molar ratio of [Mg$^{2+}$]:[NH$_4^+$]:[PO$_4^{3-}$] | Residual [F$^-$] Experimental Results (mg/L) | Residual [F$^-$] Model Prediction (mg/L) | Residual [Ca$^{2+}$] Experimental Results (mg/L) | Residual [Ca$^{2+}$] Model Prediction (mg/L) | Residual [SO$_4^{2-}$] Experimental Results (mg/L) | Residual [SO$_4^{2-}$] Model Prediction (mg/L) |
|--------------------------------------------------|---------------------------------------------|------------------------------------------|-----------------------------------------------|-----------------------------------------------|-----------------------------------------------|-----------------------------------------------|
| 1:1:1                                            | 250                                         | 280.06                                   | 1.86                                          | 0.007                                         | 447                                           | 454                                           |
| 1.5:1:1                                          | 39                                          | 37.22                                    | 3.06                                          | 0.681                                         | 443                                           | 454                                           |
| 2:1:1                                            | 44                                          | 42.81                                    | 6.3                                           | 1.717                                         | 441                                           | 454                                           |

Calcium would effect struvite formation at a molar ratio of [Mg$^{2+}$]:[Ca$^{2+}$] of 1:1 at a higher pH [20]. However, the molar ratio of [Mg$^{2+}$]:[Ca$^{2+}$] in this solution was 19:1. The residual concentration of fluoride increased slightly as the molar ratio of [Mg$^{2+}$]:[NH$_4^+$]:[PO$_4^{3-}$] increased to 2:1:1, given that Mg would dominate the reaction with PO$_4$ to form magnesium phosphate precipitate. Again, the presence of SO$_4^{2-}$ did not have a significant effect on struvite precipitation under all conditions. A higher concentration of SO$_4^{2-}$ in a solution would extend the induction time of struvite precipitation [33]. The residual concentration of Ca in this experiment was higher than that predicted by the model because Ca$_5$(PO$_4$)$_3$F as a small particle with a size of around 1 μm was difficult to separate by way of the normal filtration process [34]. In this treatment, the separation of precipitate was only undertaken by sedimentation. As a result, the precipitate was not properly separated from the supernatant. Hence, this could be the reason why the residual concentration of Ca was higher in the experimental results than in the model prediction.

### 3.3 Identification of Precipitates

The analysis of dry precipitate was conducted using SEM-EDX and XRD. The morphology of the precipitate seen in this study was rod-shaped with several impurities on the surface, as can be observed from the SEM image in Figure 4. Pure struvite crystals are rod-shaped and have a clean surface [35]. The crystals produced in this research contained a few impurities, as revealed by the elemental composition of EDX. A high atomic percentage of fluoride was found. Once again, this verified that fluoride precipitate was discovered in the solid phase. Other impurities were also found, such as S, Si, and Ca, although at lower atomic percentages. The crystals in this experiment were rod-shaped with sharp edges and small agglomerates on the surface. It was predicted that the agglomerates were mineral impurities formed during precipitation. Those minerals were predicted to be Ca$_5$(PO$_4$)$_3$F and MgF$_2$. Fluoride ions can cause precipitates to become defective and small. The impurity ions can inhibit the growth rate because they block the active growth part, so the crystal is small [36]. The presence of calcium will also disturb struvite crystallization, reducing the size of crystals and inhibiting struvite growth [37].

Minerals formed in the precipitate were analysed by XRD (Figure 5). Yet again, it revealed some impurities, such as the peaks of fluorapatite and MgF$_2$.

Struvite still displayed a higher peak in this precipitate and it was proved that struvite was dominant in this solution under optimal conditions. This showed that selective separation of NH$_4^+$ and PO$_4^{3-}$ can be conducted for the treatment of fertilizer wastewater. The greatest advantage of this process is that the fertilizer industry would obtain other sources of fertilizer, which would be
incredibly interesting from an economic point of view. However, the challenge in this process is to increase the purity of struvite and to remove several impurities that might form in the precipitate.

| EL | AN | Series | unn.C (%) | norm. C (%) |
|----|----|--------|-----------|-------------|
| C  | 6  | K-series | 25,76     | 25,76       |
| O  | 8  | K-series | 42,24     | 42,24       |
| F  | 9  | K-series | 13,7      | 13,7        |
| Na | 11 | K-series | 1,22      | 1,22        |
| Mg | 12 | K-series | 6,47      | 6,47        |
| Si | 14 | K-series | 0,45      | 0,45        |
| P  | 15 | K-series | 8,84      | 8,84        |
| S  | 16 | K-series | 0,65      | 0,65        |
| Ca | 20 | K-series | 0,67      | 0,67        |

Figure 4. SEM and EDX Results (a) SEM Results (b) EDX Results

Figure 5. XRD Pattern Analysis of Precipitate

4. Conclusions
From this research, it can be concluded that the optimum mixing energy for struvite precipitation was a G_t value of 10^6 or equal to 158 rpm. The optimum pH was 8.5 ± 0.2 with a molar ratio of [Mg^{2+}]:[NH_4^+]:[PO_4^{3-}] of 1:1:1. The removal efficiencies of ammonium and phosphate were 83.60 and 99.91%, respectively. Under these conditions, model prediction by PHREEQC version 3.0 showed that the trend of the model prediction fitted the experimental results. The presence of interfering ions, such as Ca, SO_4, and F did not have a significant effect on struvite precipitation when the molar ratio
of \([\text{Mg}^{2+}] : [\text{NH}_4^+] : [\text{PO}_4^{3-}]\) was 1:1:1. Model prediction by PHREEQC v 3.0 showed that the trend of the model prediction fitted the experimental results.

**Supplementary Data**

**Table S1.** The characteristics of wastewater from each unit

| Parameter     | Unit | Wastewater               |
|---------------|------|--------------------------|
|               |      | Unit 1       | Unit 2       |
| Turbidity     | NTU  | 8.3          | 1,736        |
| pH            | –    | 9.7          | 1.5          |
| \(\text{NH}_4^+\) | mg/L | 5.234      | –            |
| \(\text{PO}_4^{3-}\) | mg/L | –          | 30875        |
| \(\text{Ca}^{2+}\) | mg/L | 0.29       | 601.19       |
| \(\text{Mg}^{2+}\) | mg/L | 10.64       | 105.33       |
| F             | mg/L | –            | 676          |
| \(\text{SO}_4^{2-}\) | mg/L | –          | 577          |
| COD           | mg/L | 417.01      | 3,600        |

**Table S2.** The characteristics of mixed wastewater

| Parameter     | Unit | Value          |
|---------------|------|----------------|
| pH            | –    | 2.5            |
| \(\text{PO}_4^{3-}\) | mg/L | 14,656        |
| \(\text{NH}_4^+\) | mg/L | 2,864         |
| \(\text{Ca}^{2+}\) | mg/L | 3.17          |
| \(\text{Mg}^{2+}\) | mg/L | 54.76         |
| F             | mg/L | 493            |
| \(\text{SO}_4^{2-}\) | mg/L | 454           |
| COD           | mg/L | 3,675          |

**Table S3.** Values of solubility products of minerals that were considered in the modelling

| Minerals                           | pKsp at 25 ºC |
|-----------------------------------|---------------|
| Struvite (\(\text{MgNH}_4\text{PO}_4\cdot 6\text{H}_2\text{O}\)) | 13.15 [26]    |
| Bobierrite (\(\text{Mg}_3(\text{PO}_4)_2\cdot 8\text{H}_2\text{O}\)) | 25.20 [27]    |
| Trimagnesium phosphate (\(\text{Mg}_6(\text{PO}_4)_2\cdot 8\text{H}_2\text{O}\)) | 23.10 [27]    |
| Hydroxyapatite (\(\text{Ca}_9(\text{PO}_4)_3\cdot \text{OH}\)) | 3.421 [25]    |
| Fluorite (\(\text{CaF}_2\)) | 10.60 [25]    |
| Fluoroapatite (\(\text{Ca}_9\text{F}(\text{PO}_4)_3\)) | 59.00 [26]    |
| \(\text{MgF}_2\) | 8.10 [26]      |
| Calcium sulphate (\(\text{CaSO}_4\)) | 4.36 [25]    |
| Gypsum (\(\text{CaSO}_4\cdot 2\text{H}_2\text{O}\)) | 4.50 [25]    |

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