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Conference Paper

The Observation of Struvite ($MgNH_4$ PO_4 $.6H_2O$) Precipitation Using Visual MINTEQ

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ABSTRACT

Struvite or Magnesium Ammonium Phosphate Hexahydrate ($MgNH_4$ $PO_4.6H_2O$) is one of the precipitates that generally form in the piping system. The formation of struvite in the piping system is one of the serious problems that can cause blockages, reduced flow volume, and pipe diameter so that it will increase maintenance and production costs. This formation of struvite scale in industrial instruments is detrimental; however, struvite can be used as raw material for slow-release fertilizers. This study will observe the effect of pH in the range of 8, 8.5, 9, 9.5, and 10 on the formation of struvite compositions, consisting of Mg, NH4, PO4, Ca, and K in the surrounding temperature 35°C. The results of this study will be observed using visual MINTEQ software. The result shows that the most suitable pH for struvite formation is 9.5.

Keywords: Precipitation, wastewater, struvite, virtual MINTEQ

Introduction

Struvite (Magnesium Ammonium Phosphate Hexahydrate or MAP) is a material made from crystalization containing magnesium, ammonium, and phosphate (Hao, 2008). In the industry, struvite is often found in pipes which are usually called the crust. The formation of struvite crust on the pipe indicated that it contained magnesium ammonium phosphate compound. One of the industrial tools that are easily scaled by struvite is a boiler, where the tool often flows with hot air. The scale on the pipe can interfere with the running process of an industry. The scale on the pipe can inhibit the flow of air and water in the pipe. Therefore, the scale on this pipe must be removed in industrial processes (Lisanti, 2011). Moreover, struvite can also form in the human body, which is generally formed in the urinating system. The struvite precipitated in our body can cause disease, namely kidney stones. Struvite crust contains magnesium, ammonium, and phosphate, and the general reaction for the formation of struvite can be written as follows:

$$Mg^{2+} + NH_4^{+} + PO_4^{3-} + 6H_2O \rightarrow MgNH_4PO_4.6H_2O \quad (1)$$

Struvite can be used as a fertilizer that can help to cultivate plants (Iswahyudi et al., 2013). There are some studies available in the literature, which observed the method to process a struvite. Generally, some factors affect the formation of struvite, namely, temperature, pH, pressure, and conductivity. However, despite these advantages, the composition of struvite

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eventually can be beneficial. A study conducted by (Rouf, 2013) observed the effect of temperature on the formation of struvite in a mixture of $MgCl_2.6H_2O$ and $(NH_4)2HPO_4$ solution at a temperature of 25-30 ^oC. The results obtained indicate that struvite is formed at a temperature of 25-37 ^oC and other crystals are formed at temperatures above 37 ^oC.

Struvite is formed in two stages, namely nucleation and growth. Nucleation occurs when struvite-forming ions react to form a precipitate core. Furthermore, the crystal nuclei formed will grow until they reach equilibrium conditions (Doyle & Person, 2002). These precipitates can be formed when the concentration of magnesium, ammonium, and phosphate exceeds the solubility of the resulting product, which is expressed by the value of Ks_p (solubility product constant). Doyle and Parsons (2002), reported the results of their review of several researchers that the Ksp value of struvite ranged from $5.5x10^{-14}$ to $4.36x10^{-13}$ (Ksp=13.26-12.6). Meanwhile, The Ksp value of ammonium magnesium phosphate was 3x10-13 (Ksp) = 12.5). Doyle and Parsons (2002) explained that the difference in Ksp of struvite minerals was due to the activity and molarity of the ions contained. The pH of the solution is one of the factors that influence the formation of the struvite scale. The higher the pH used, the solubility of struvite decreases, but the solubility begins to increase when the pH is above pH 9; This condition will cause the ammonium ion concentration to decrease while the phosphate ion concentration increases. Some factors such as pH, ionic strength, and temperature will affect the solubility of struvite (Hanhoun et al., 2010).

The study of wastewater sedimentation has been widely observed experimentally or by simulation. Visual MINTEQ is a chemical software, which can calculate material chemistry properties; moreover, it can be used to predict the formation of struvite scales (Buchanan et al., 1994). Thus, in this study, the effect of pH on the formation of struvite precipitation in artificial wastewater is evaluated. There are 5 pH variations, from 8 to 10 parameters used to predict the chemical properties of the struvite using visual Minteq software. A positive SI is usually necessary to develop struvite and other mineral growth and accumulation.

Material and Methods

The study relied on the Visual MINTEQ software packages version 3.0 to forecast solution equilibrium based on the input of the activities of the different ions present in the solution. In the provided solutions, the computer may calculate solid solubility, simulate equilibrium, and speciate inorganic solutes. The effect of pH on some specified minerals was observed by visual minted software which is capable to visualized and demonstrating the precipitated minerals.

Table 1. Details of the experimental parameter

Mineral Species		Experimental Parameter	
		pH (acidity)	**Temperature**
$MgNH_4PO_4.6H_2O$	Struvite	Each minerals tested at pH 8, 8.5, 9, 9.5, 10	Each minerals tested at T = 35^{o}C
MgO	Periclase		
$MgHPO_4:3H_2O$	Newberyite		
$Mg3(PO_4)_2$	Magnesium Fosfat		
$Mg2(OH)3Cl:4H_2O$			
$Mg(OH)_2$	Brucite		

In an oversaturated state equilibrium, the Visual MINTEQ could forecast every precipitated solid phase. MINTEQ was used to determine the minerals in the model by entering total Mg^{+2}, PO_4, O, Cl, NH_4, and hydrogen (H+) value at different pH levels, as shown in table 1. The minerals observed were specified into several variations, which precipitated during experimental

observation. There are 8 minerals as shown in table 1, observed at 5 different pH, in a constant temperature of 35°C.
A saturation index is used to determine the speciation of solid-phase minerals that are precipitated from the wastewater solution. There are some specific parameters, which determine the saturation stage of the precipitation. For instance, when SI<0, precipitation does not occur as the solution is undersaturated. However, the solution is in equilibrium condition when SI=0, where the precipitation might occur. As when SI>0, the precipitation will develop spontaneously as the solution is supersaturated.

Results and Discussions

The various minerals that precipitate from the solution after the dissolution of phosphate minerals are shown below in Table 2, which is observed by visual minteq. The dissolution of these minerals led to the approaching of their maximum at the end of the period. There are some minerals such as struvite ($MgNH_4PO_4.6H_2O$), $MgHPO_4$:$3H_2O$, and Mg3(PO_4)$_2$. It was suggested that struvite could be turned into other minerals by the solution's dissolution.

Table 2. Details of saturation index of each magnesium mineral

Mineral Species	Saturation Index (SI)				
	pH (acidity)				
	8	**8.5**	**9**	**9.5**	**10**
$MgNH_4PO_4.6H_2O$	6	6.5	7	7.5	7.5
MgO	-6	-5.5	-4.95	-4.5	-3
$MgHPO_4$:$3H_2O$	3.4	3.56	3.65	3.7	3.8
Mg3(PO_4)$_2$	8	8.53	9.3	10.2	11
Mg2(OH)3Cl:$4H_2O$	-5.8	-4.5	-2.5	-2	0.4
$Mg(OH)_2$ (active)	-4.8	-4.2	-3.8	-2.2	-1.05
Brucite	-2	-1	-0.8	1.5	2

The comparison result of pH effect on the mineral sedimentation at a constant temperature using visual MINTEQ software is shown in figure 1. As can be seen from the figure, there are shown the saturation index of each mineral with pH variations; moreover, not all minerals have positive SI. Struvite, $MgHPO_4$:$3H_2O$, and Mg3(PO_4)$_2$, are the minerals that have SI>0, which means the precipitation exists and happened spontaneously. As mentioned before, that positive SI is desired to accumulate mineral growth and form mineral deposits. From these three minerals, Struvite and Mg3(PO_4)$_2$ have the highest SI at pH 10, and followed in sequence the lower pH shows lower SI. However, $MgHPO_4$:$3H_2O$ almost has similar SI at entire pH variations, in contrast with the latter two minerals, the lowest SI was shown at pH 10. Based on these results, we can see that at pH 8 to 10, the saturation index value of struvite was positive, which indicates that the conditions were ideal for the formation of mineral deposits.

The other minerals with negative SI are also shown in Figure 1. Periclase, Mg2(OH)3Cl:$4H_2O$, $Mg(OH)_2$, and brucite are mostly having negative SI. As mentioned before SI<0 is undersaturated, which means reaction can not occur in this state. However, Mg2(OH)3Cl:$4H_2O$ and Brucite have some positive SI at pH 10 and 9.5, even with a very low amount. The values for minerals with negative SI are shown a similar trend with positive SI minerals. The SI is higher with the increasing pH. The higher the amount of available phosphate precursors, the more likely it is to cause a higher precipitation reaction.

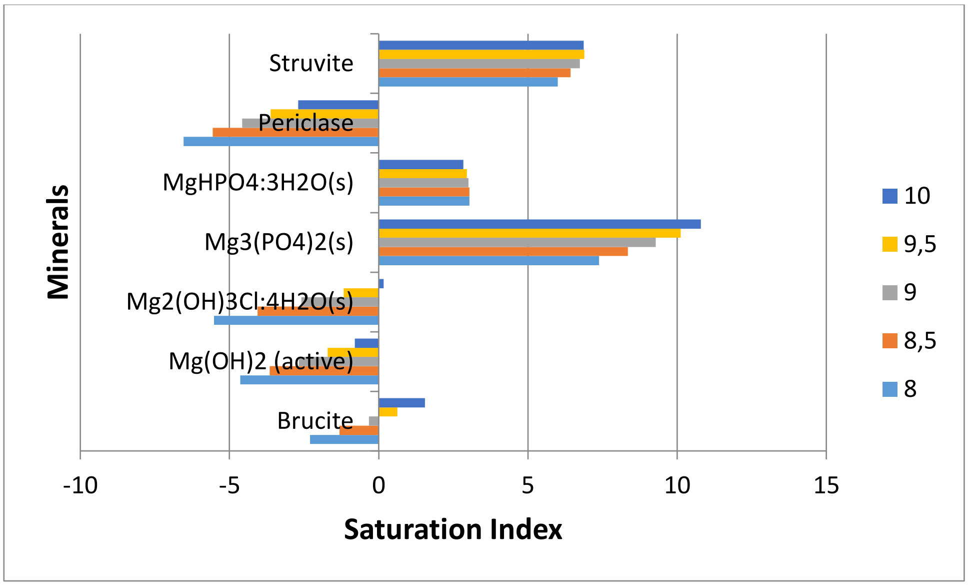

Figure. 1. Modeling results of minerals from MINTEQ calculation

In the precipitation analysis, the struvite formation potential can also be used as a major indicator. This is a relative value that is determined by a system's SI value. The amount of the formation potential may be determined by changes in the concentrations of struvite constituent ions (ammonium, magnesium, and phosphate) and circumstances (pH, temperature, and conductivity) in the solution. Minerals of struvite-(K), struvite, and $Mg3(PO_4)_2$ should be precipitated, according to the Visual MINTEQ algorithms. Sylvite minerals, on the other hand, were undersaturated.

Conclusions

The conclusions of this study are summarized as follows:

- The optimum pH to develop sedimentation is at 9.5 to 10, as it shows the highest SI compare to others. Struvite, $MgHPO_4.3H_2O$, and $Mg3(PO_4)_2$ are the main minerals controlling the recovery of MAP ions out of solution at 35 °C and range Ph from 8 to 10. Struvite crystals deposited from solution at various pH show the same morphology as a function of pH variation.
- The computer model developed using Visual MINTEQ in the investigation accurately predicts dissolved mineral concentrations. This software proven to be useful for engineering and operating plant practices interested in preventing Struvite damage to infrastructure and in the removal of nitrogen and phosphorus nutrients from wastewater streams.

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References

Buchanan, J. R. (1994). Thermodynamic of struvite precipitation. *T. ASAE.*, 37, 617-621
Buchanan, J. R. et al. (1994), *Thermodynamic of struvite precipitation. T. ASAE*, 37, 617-621.
Doyle, J. D., & Parsons, S. A. (2002). *Struvite formation, control and recovery. Water Research, 36*(16), 3925-3940. doi: 10.1016/s0043-1354(02)00126-4.

Hanhoun, M., Montastruc, L., Azzaro-Pantel, C., Biscans, B., Freche, M., & Pibouleau, L. (2010). Temperature impact assessment on struvite solubility product: A thermodynamic modeling approach. *Chem. Eng., 167,* 50-58. doi:10.1016/j.cej.2010.12.001

Hao, X. D., Wang, C-C., Lan, L., & Van Loosdrecht, M. C. M. (2008). Struvite formation, analytical methods and effect of ph and Ca^{2+}. *Water Sci, Technol., 58*(8), 1687-92. doi: 10.2166/wst.2008.557.

Iswahyudi. (2013). Pengolahan limbah garam (bittern) menjadi struvite dengan pengontrol pH. *Jurnal Teknologi Industri Pertanian, 1*(2), 1-5.

Lisanti. (2011). *Steam and boiler*. (online) (http://methanefermentation.blogspot.co.id/2011/03/steam-n-boiler.html) diakses pada tanggal 06 Mei 202

Rouff A. A. (2013). Temperature-dependent phosphorus precipitation and chromium removal from struvite-saturated solution. *J Colloid Interface Sci., 5,* 392, 343-348. doi: 10.1016/j.jcis.2012.10.013