



---

## SYNTHESIS OF STRUVITE USING (XRF):X-RAY FLUORESCENT SPECTROMETER: POTENTIAL WASTE-DERIVED FERTILIZER

<sup>1</sup>Ibrahim Yusuf & <sup>2</sup>Saidu Hassan

Department Chemistry

Umar Suleiman College of Education Gashua Yobe State

E-mail: [ibrazuby@yahoo.com](mailto:ibrazuby@yahoo.com)

---

### ABSTRACT

Struvite is a phosphate fertilizer, although it contains a significant amount of nitrogen and magnesium, and it is an effective alternative source of rock phosphate to maintain the agricultural production system. The present review deals with the principles and concept of Struvite formation, crystal growth, elemental contents, pH values. Struvite precipitation occurs in an equimolecular concentration of  $Mg^{2+}$ ,  $NH_4$  and  $PO_4$  at slightly alkaline conditions. Addition of a source of Mg is essential to maintain the favorable condition of  $PO_4$  and Mg. Different factors such as Mg:  $PO_4$ , pH, as well as P and N efficiencies were also discussed. The slower nutrient leaching loss and its fertilizer quality make Struvite an eco-friendly fertilizer. It is possible to overcome the acute shortage of rock phosphate. Struvite can be beneficial, in the sense that it can be used as fertilizer. It provides a good source of phosphorus, Nitrogen and Magnesium for plant growth, Struvite is also economic feasible to be used as fertilizer, due to the anticipated global scarcity of phosphorus reserves. Struvite when used as fertilizer, it does not harm the intake or rooting system of the plants. It can be used in making ornaments, grazing activities, and can be applied on orchards and plants on pots. In addition Struvite when applied once in a growing season it has a low rates of leaching compared to other fertilizers, meanwhile, the rates at which nutrients are released too differs with other conventional fertilizers.

**Key words:** Struvite, Nitrogen, Phosphorous, Fertilizer, Waste water.

## INTRODUCTION

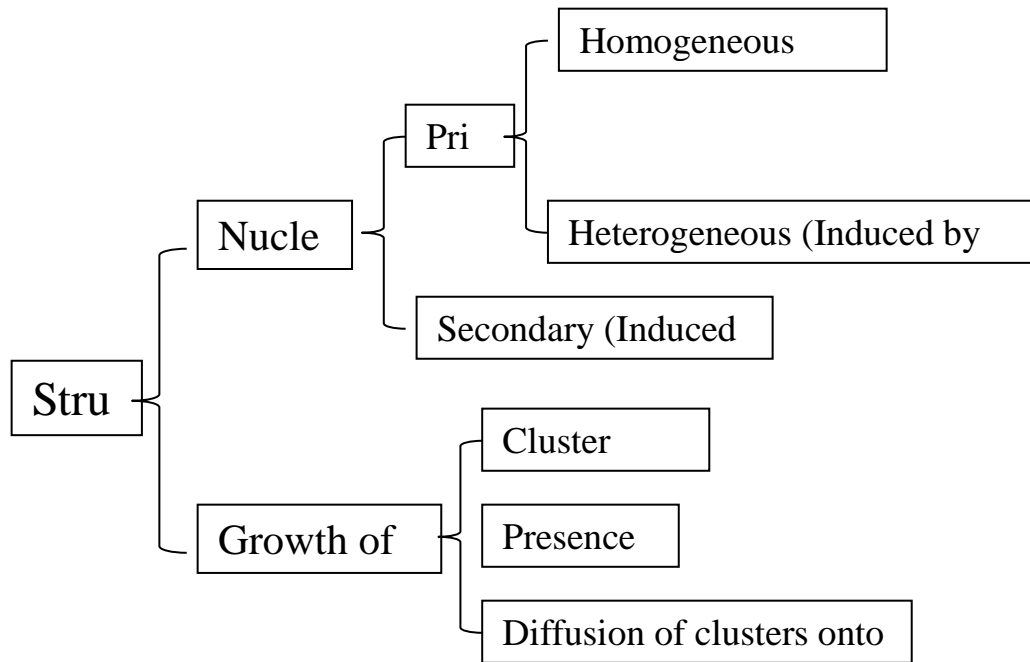
The need to treat wastewater from industrial and domestic sources in order to remove nutrients, organic matter, pathogenic organisms, pollutants and other solids became necessary so as to avoid environmental impacts which also conforms to Urban Waste Water Directive (91/271/EEC) (European Commission, 2012; Lenntech, 2013). The consequences of these substances reaching water bodies include depreciation of amenity value of water, disappearance of important aquatic organisms, difficulty in drinking water treatment, development of anoxic conditions, increase in vegetation that can obstruct navigation and water flow, increase in the rate of sedimentation which shortens the lifespan of the receiving water body, increase in turbidity and more importantly the receiving water body can cause injuries to human health (Nixon, 2009; Lenntech, 2013). But unfortunately, during the wastewater treatment, the wastewater treatment plants are faced with the formation of a white crystalline substance called struvite as shown in figure 1.



Figure 1: Struvite formed in wastewater pipes (Apex Solutions, 2012; Merrill, 2012)

Even though there has been a spontaneous occurrence of struvite in many biological media, for example, rotting organic materials like cow manure and deposits of guano which is an excrement of pinnipeds, bats and seabirds; were found to contain struvite which is produced via the microbiological reaction of phosphorus and magnesium present in the media with the ammonium ions of bacteria metabolisms (Le corre, 2007). And another struvite also found in the field of medicine which affects human kidneys through formation of calculi (frost *et al.*, 2004). Plus the struvite used in the field of soil science to catch nitrogen in compost (Jeong and Hwang (2005). But talking in an industrial scale like the waste water treatment plants and anaerobic digestion facilities, deposition of struvite has been discovered for over 70 years ago and has been causing of pipe blockages and reduction in the rate of discharge flow (Doyle and parsons, 2002).

Struvite crystals occur and develop in two main phases which are birth of crystals (nucleation) and the growth of the crystals as shown in figure 2. The nucleation phase involves the formation of crystal embryos, and it can either be primary or secondary nucleation, the primary nucleation is subdivided into spontaneous homogeneous nucleation which does not exist and foreign particles induced heterogeneous nucleation. On the other hand, the secondary nucleation mainly occurs in the presence of parent crystals which impose a local interaction of impeller and reactor walls with the existing crystals. The parent crystals cause fluctuation on super saturation due to their catalyzing effect on nucleation (Liu *et al.*, 2013).



**Figure 2: Growth and development of struvite crystals (Liu et al., 2013)**

The crystallization of struvite depends on several factors. Nucleation and crystal growth of which their prediction and control is complex as they depend on a range of factors like the initial states of crystals of the compounds, the occurrence and mode of solid-liquid transfer, kinetics and thermodynamics of the reaction plus other physico-chemical parameters like pH, mixing energy, temperature, super saturation level and the presence of foreign ions in the solution. pH is associated with super saturation and notion of solubility, determines the scaling of struvite and it also affects the rate of crystal growth (Neethling and Benisch, 2004; Le Corre, 2007; Ohlinger *et al.*, 1999). Temperature affects the Struvite's crystal morphology and solubility (Jones, 2002; Babić-Ivančić *et al.* (2002). Mixing or turbulence affects the shape and size of the struvite crystals (Durrant *et al.*, 1999), while the presence of foreign ions; the

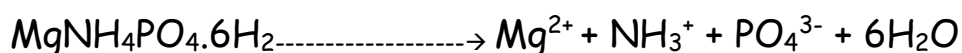
ions can affect the crystal growth because they can block the sites required for crystals formation which will inhibit the crystal size increase (Jones, 2002). Several efforts were put forward which aimed at preventing or controlling the struvite deposition, they include the use of water effluents to dilute the struvite crystals, addition of chemical inhibitors and use of aluminium salts (Le Corre, 2009).

### **Effect of pH on Struvite Formation**

According to various researches carried out, they indicated that the solubility of struvite depends on pH. Doyle and Parsons (2002) reported that when the pH increases the solubility decreases. And a research by Ohlinger *et al.*, (1998) concluded that the minimum solubility for struvite is at the range of 9 to 11 which coincides with what has been reported by Nelson *et al.* (2003). So, generally, it can be concluded that the solubility of struvite decreases with increase in pH of 9, but at higher pH the solubility increases, this means that there is the possibility of recovery under alkaline conditions, even though researchers like Ichihashi and Hirooka (2012) noted that crystallization may be difficult due to different that may be required for pH adjustment. Hao *et al.*, (2008) carried out a study to find the effect of pH and calcium ions ( $\text{Ca}^{2+}$ ) on the struvite precipitation. The study used ultra-pure water and a tap water, so as to determine the differences the factors may have on both samples. The struvite was formed using  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ ,  $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ , NaOH and  $\text{NH}_4\text{Cl}$  and the control was commercially purchased and it contains 99% of pure crystals of struvite. Pratt *et al.*, (2012) reported that, the precipitation potential of a liquor increased from  $116 \text{ mg L}^{-1}$  to more than  $200 \text{ mg L}^{-1}$  as a result of increase in the pH of the sludge. And there tends to be a competition

when the pH is high. pH can also affect the habit of struvite crystal in synthetic wastewater. Mehta and Batstone (2013) reported that, in a pH greater than 8.0 the struvite forms dendritic crystals, and it forms a tabular structure a pH range between 7.0 and 8.0, but once the pH decreases to less than 6.0 the struvite crystals tends to form needle-like or elongated structure.

Several studies have reported different ranges of pH with which struvite is best formed, even though the type and quality of wastewater determines the optimum pH for struvite. However, initial solution pH has effect on the solubility of the struvite. Ariyanto *et al.*, (2011) carried out an analysis to check the solubility of struvite by dissolving struvite crystals at a temperature of 25°C as follows:



The variation of the solution pH at 25°C was shown in the table 2, it was observed that the activity of phosphate ions influences the changes in the pH as reported by Nelson *et al.*, (2003). And when the initial pH of the solution is changed, and the equilibrium is reached the  $\text{Mg}^{2+}$ ,  $\text{NH}_4$ , and  $\text{PO}_4$  components will form ion complexes like  $\text{NH}_3$ ,  $\text{HPO}_4$ ,  $\text{MgNH}_4\text{PO}_4$ ,  $\text{MgH}_2\text{PO}_4$ ,  $\text{MgHPO}_4$ ,  $\text{H}_3\text{PO}_4$ , and  $\text{NH}_4$  in the system. The solution pH can also affect the morphology of the struvite crystals which has been attribute to phosphorus ions occurring at different solution pH as reported by Musvoto *et al.*, (2000) who concluded that the transformation of different kinds struvite crystals can be attribute to solution pH and the concentration of phosphate and magnesium. Likewise, a study on the morphology of struvite which was conducted at various



solution pH. The struvite crystals were dissolved; three ions were generated on decomposition which is  $\text{NH}_4$ ,  $\text{PO}_4^{3-}$ , and  $\text{Mg}^{2+}$ , and the morphology was later checked. Results indicated an equilibrium pH of 8.4 following a dissolution time of 24 hours at an initial pH of 3 at  $25^\circ\text{C}$ .

## **MATERIALS AND METHODS**

### **Composition Analysis**

The samples were first dissolved by drop wise addition of concentrated nitric acid into distilled water containing our sample, until the crystals were completely dissolved and then diluted for further analysis. Magnesium, ammonium and phosphorus were measured with Hach Lange cuvette tests. Other elements were measured using (XRF): x-ray fluorescent spectrometer: analyses were conducted on samples of Struvite crystals produced in the current work from the supernatant location A and location B as well.

The research samples were collected at Damaturu water treatment plant (Yobe State), at two (2) different locations. Super saturation ratio (SSR) was used as an indication of the possibility of Struvite formation at the sampling locations in the water treatment plant. Wastewater samples were tested in the treatment plant laboratory, for parameter and the resulting data were used to evaluate the Struvite formation potential by running a Struvite formation program. The analysis takes a period of two months. The parameters that are used to calculate SSR were measured every 2 weeks over a period of two months regularly to investigate the difference in the readings at two different locations of the treatment stream. The sampling locations were, namely, (a) the centrate formed after centrifuging of the sludge and (b) the centrate

sump. The reason for sampling at the sump was to investigate the possible Struvite precipitation at this location due to prevalent lower temperatures. Each of the samples was centrifuged at 4000 RPM for 10 min to reduce the solids content. The resulting supernatant was then filtered using 0.45  $\mu\text{m}$  filter paper prior to analytical measurements. All parameters and conditions would be measured according to APHA et al. (2005). pH conditions will be tested and find out most favorable pH for the formation of Struvite.

Table 1: Supernatant features of the water samples used in this study

Parameters	Values
PH	8.0
Temperature	31 <sup>0C</sup>
N-NH <sub>4</sub> <sup>+</sup>	700mg/l
P-PO <sub>4</sub> <sup>-3</sup>	49mg//
Mg <sup>+2</sup>	34mg/l

From the results, it was formed that by the addition of magnesium chloride ( $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ), ammonium chloride ( $\text{NH}_4\text{Cl}$ ) and potassium dihydrogen phosphate ( $\text{KH}_2\text{PO}_4$ ) to distilled water in a beaker containing the water samples and stirred using a magnetic stirrer. Since ideally struvite forms in a Mg:N:P molar ratio of 1:1:1, here also the same molar ratio was maintained. This concentration was chosen in order to maintain the same conditions for Struvite formation.



**Table 2. Buffer and acid or base added to control the pH values in the water samples**

Buffer	Concentration (mm)	pH Correction	pH
MES	40	1100 $\mu$ l of 2ml HCl	5.9
EPPS	20	160 $\mu$ l 2ml HCl	7.5
CHES	50	1200 $\mu$ l of 2ml NaOH	8.0

MES, N-(morpholino)-ethane-sulfonic acid; EPPS, N-2-hydroxy ethylpiperazine-N9-propane-sulfonic acid; CHES, cyclohexylamino-ethane-sulfonic acid.

**TABLE 3: Comparison of heavy metals content in Struvite from the two sample location (A&B) and NPK fertilizer**

ELEMENTS	LOCATION A	LOCATION B
NPK FERTILIZER		
AS	0.5	0.6
0.8		
Ca	1800	6300
44.700		
Cd	0.3	0.01
4.98		
Cr	0.51	10.00
31.56		
Cu	6.20	4. 40
20.80		
Fe	360	7541
920		
Hg	Nil	Nil
Nil		
Pb	0.31	0.14
0.90		

Unit mg/kg sample

The table 3 shows the concentration of elemental content on the Struvite collected from the sample in the locations of the water treatment plant and compared with the concentration

of NPK fertilizer. From the result obtained the major concern is regarding  $Cd^{2+}$  when applying P-fertilizer, mainly due to easy uptake by plants and their apparent relative effect on human health. It can be seen that with Struvite there is no concern regarding metal contamination, including  $Cd^{2+}$ . Similarly, the low heavy metal content of Struvite was observed by Uysal *et al.* This low heavy metal content of Struvite can be explained by its specific structure, which prevents the placement of impurities, such as heavy metals, into the well-defined structure of crystal. It should be taken into account that these release rates are calculated on the basis of the solubility of Struvite in distilled water. Yet, in field conditions more complex reactions are involved that affect the availability of nutrients to plants.

For example, the availability of phosphorous is affected by phosphorous fixation, which is due to its binding capacity to organic and mineral compounds in soil. In the case of nitrogen, the availability is affected by ammonia volatilization and denitrification. If a faster release is requested, it is always possible to see Struvite formation as a capturing step for phosphate, which later can be reformulated into a more suitable fertilizer.

## CONCLUSION

Struvite can be beneficial, in the sense that it can be used as fertilizer. Struvite provides a good source of phosphorus, Nitrogen and Magnesium for plant growth (Li and Zhao, 2003). Bhuiyan *et al.* (2008) reported that struvite when used as fertilizer, it has a slow releasing rate when applied in a higher rates and it does not harm the intake or rooting system of the plants. He went further to say that it can be used in

making ornaments, grazing activities, and can be applied on orchards and plants on pots. In addition struvite when applied once in a growing season it has a low rates of leaching compared to other fertilizers, meanwhile, the rates at which nutrients are released too differs with other conventional fertilizers. Struvite is also a natural resource to cement and phosphate industries which they use as a cement binder and fire-resistant panels respectively (Zhou and Wu, 2012). Japan has commercialized struvite as a fertilizer used in growing vegetables and rice, but the other parts of the world were left behind due to lack of awareness on its use as a fertilizer and its insufficient availability to the farmers (Ueno and Fujii, 2001; Shu et al., 2006). Potassium salts can be used to adjust the concentrations of nitrogen phosphorus and potassium to achieve a good NPK fertilizer, or the potassium ion can be used instead of the ammonium ion thereby transforming the salt  $MgKPO_4 \cdot 6H_2O$ . The cost of the fertilizer is therefore raised through the adjustment so that crops that require large amount of magnesium for can be supplemented (Pastor, 2006). Struvite is also economic feasible to be used as fertilizer, due to the anticipated global scarcity of phosphorus reserves. The economic viability of phosphorus reserves was predicted to be consumed in the next 6-7 decades, annual consumption of  $P_2O_5$  in 2050 was anticipated to be over 60 million tons, therefore there is need to pay attention into recycling of waste like struvite in order to cater for the need of the population and for better sustainable development (Molinos-Senante, et al., 2011).

## REFERENCES

- Apex Solutions (2012) Hard Facts: Struvite [online]. [Accessed 8 June 2013] Available at: <http://theapexsolution.wordpress.com/2012/09/06/struvit/>
- Babić-Ivančić, V., Kontrec, J., Kralj, D. and Brečević, L. (2002) Precipitation diagrams of struvite dissolution kinetics of different struvite morphologies. *Croatica Chemica Acta* 75, pp: 89-106.
- Doyle, J.D. and Parsons, S.A. (2002) Struvite formation, control and recovery. *Journal of Water research*, 36(16), pp. 3925-3940.
- Durrant, A.E., Scrimshaw, M.D., Stratful, I. and Lester, J.N. (1999) Review of the feasibility of recovering phosphate from wastewater for use as a raw material by the phosphate industry., *Environmental Technology* 20, pp: 749-758.
- Frost, R.L., Weier, M.L. and Erickson, K.L. (2004) Thermal decomposition of struvite. *Journal of Thermal Analysis and Calorimetry*, 76(3), pp. 1025-1033.
- Hao, X., Wang, C., Lan, L. and Van Loosdrecht, M.C.M. (2008) Struvite formation, analytical methods and effects of pH and Ca<sup>2+</sup>. *Journal of Water science and technology: Journal of the International Association on Water Pollution Research*, 58(8), pp. 168.
- Ichihashi, O. and Hirooka, K. (2012) Removal and recovery of phosphorus as struvite from swine wastewater using microbial fuel cell. *Bioresource technology*, 114pp. 303.
- Jeong, Y. and Hwang, S. (2005) Optimum doses of Mg and P salts for precipitating ammonia into struvite crystals in aerobic composting. *Bioresource technology*, 96(1), pp. 1-6.

- Jones, A.G. (2002) *Crystallization process system*. Butterworth/ Heinemann, London (UK).
- Le Corre, K.S., Valsami-Jones, E., Hobbs, P. and Parsons, S.A. (2009) Phosphorus Recovery from Wastewater by Struvite Crystallization: A Review. *Critical Reviews in Environmental Science and Technology*, 39(6), pp. 433-477.
- Le Corre, K.S., Valsami-Jones, E., Hobbs, P. and Parsons, S.A. (2006) Impact of reactor operation on success of struvite precipitation from synthetic liquors. Submitted to: *Environmental Technology*.
- Le Corre, K.S., Valsami-Jones, E., Hobbs, P., Jefferson, B. and Parsons, S.A. (2007) Struvite crystallisation and recovery using a stainless steel structure as a seed material. *Journal of Water research*, 41(11), pp. 2449-2456
- Le Corre, K.S., Valsami-Jones, E., Hobbs, P. and Parsons, S.A. (2005) Impact of calcium on struvite crystal size, shape and purity. *Journal of Crystal Growth* 283, pp: 514-522.
- Le Corre, K.S., Valsami-Jones, E., Hobbs, P., Jefferson, B. and Parsons, S.A. (2009) Agglomeration of struvite crystals. *Journal of Water research*, 41(2), pp. 419-425.
- Le Corre, K.S., Valsami-Jones, E., Hobbs, P., Jefferson, B. and Parsons, S.A. (2007) Agglomeration of struvite crystals. *Journal of Water research*, 41(2), pp. 419-425.
- Lenntech (2013) *Venturi* [Online] [Accessed 03 September 2013] Available at: <http://www.lenntech.com/venturi.htm>.
- Lenntech, (2013). *General effects of eutrophication* [Online][Accessed 07 September 2013] available at: <http://www.lenntech.com/eutrophication-water-bodies/eutrophication-effects.htm>.

- Li, X.Z. and Zhao, Q.L. (2003) Recovery of ammonium-nitrogen from landfill leachate as a multi-nutrient fertilizer, *Journal of Ecological Engineering*, 20, pp. 171-181.
- Liu, Y., Kumar, S., Kwag, J. and Ra, C. (2013) Magnesium ammonium phosphate formation, recovery and its application as valuable resources: a review. *Journal of Chemical Technology & Biotechnology*, 88(2), pp. 181-189.
- Mehta, C.M. and Batstone, D.J. (2013) Nucleation and growth kinetics of struvite crystallization. *Journal of Water research*, 47(8), pp. 2890.
- Merrill G. T. (2012) Control of struvite scaling [Online]. [Accessed 8 June 2013] Available at: <http://home.comcast.net/~merrilldoug/index.html>.
- Molinos-Senante, M., Hernández-Sancho, F., Sala-Garrido, R. and Garrido-Baserba, M. (2011) Economic Feasibility Study for Phosphorus Recovery Processes. *Ambio*, 40(4), pp. 408-416.
- Neethling, J.B. and Benisch, M. (2004) Struvite control through process and facility design as well as operation strategy. *Water Science and Technology* 49, pp: 191-199.
- Nixon, S.W. (2009) Eutrophication and the microscope. *Hydrobiologia*, 629(1), pp. 5-19
- Ohlinger, K.N., Young, T.M. and Schroeder, E.D. (1999) Kinetics effects on preferential struvite accumulation in wastewater. *Journal of Environmental Engineering* 125, pp: 730-737.
- Pratt, C., Parsons, S.A., Soares, A. and Martin, B.D. (2012) Biologically and chemically mediated adsorption and precipitation of phosphorus from wastewater. *Current opinion in biotechnology*, 23(6), pp. 890.
- Xu, H., He, P., Gu, W., Wang, G. and Shao, L. (2012) Recovery of phosphorus as struvite from sewage sludge ash.



Synthesis of Struvite Using (Xrf): X-Ray Fluorescent Spectrometer: Potential Waste-Derived Fertilizer

*Journal of Environmental Sciences (China)*, 24(8), pp. 1533.