

## Vivianite Impacts on Solids Processes

By: Bipin Pathak

### Introduction

Vivianite is named in honor of John Henry Vivian (1785 - 1855), an English mineralogist and mine owner who first discovered this mineral in Cornwall. Pure, fresh vivianite is colorless but oxidizes very easily and changes color from deep blue to black. It is an iron-phosphate mineral ( $\text{Fe}_3[\text{PO}_4]_2 \cdot 8\text{H}_2\text{O}$ ), formed in an anaerobic system in the presence of dissolved ferrous ions and phosphorous (P) with relatively low sulfide concentrations. It is different from struvite (magnesium ammonia phosphate precipitate) in terms of chemical composition and appearance. Struvite deposits generally appear as white or off-white crystallizations.

Vivianite is a hard scale build-up that can form on flow meters, valves, pumps, heat exchangers, dewatering equipment and other areas downstream of the anaerobic digestion process (Figure 1). Vivianite formation on mechanical equipment can cause equipment damage or reduction in efficiency. Build-up on instruments makes it very difficult to maintain operations because such instruments are frequently out-of-service or out-of-calibration due to the build-up. Cleaning the scale typically requires manual removal.



Figure 1: Vivianite Scale Formation in (a) Flow Meter Pipe and (b) Centrifuge Dam Plates

### Causes of Formation

In chemical phosphorus removal, orthophosphate ( $\text{PO}_4^{3-}$ ) binds to iron or aluminum and precipitates out of solution. Iron salts are a common choice over other metal salts because of additional benefits in controlling odor and hydrogen sulfide production during anaerobic digestion. Parameters including redox conditions, pH, alkalinity, presence of organic substances, and particle morphology influence the binding and release of phosphorus. The solubility of ferrous and ferric ions varies with pH and oxidation reduction potential (Figure 2a). The reduction of ferric into ferrous iron in anaerobic environments leads to P release from Fe-P minerals. In precipitation reactions, ferrous iron exhibits preference for some chemicals over other chemicals (Figure 2b). This can create conditions that favor formation of vivianite by binding the reduced Fe with P released in the anaerobic environment (Wilfort et. al., 2015).

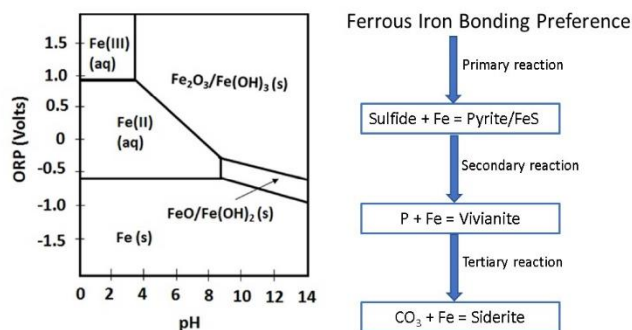


Figure 2 (a) Iron Solubility with pH and ORP (Image from Tilley, 2005), (b) Ferrous Iron Mineral Bonding Preference [Pyrite ( $\text{FeS}_2$ ), Ferrous Sulfide ( $\text{FeS}$ ), Siderite ( $\text{FeCO}_3$ )]

## Identification of Scale Materials

Scale materials can be identified using:

- X-ray Diffraction: To quantify scale materials in percent by weight.
- Elemental Analysis: To characterize the composition of scale materials (Fe, P, O<sub>2</sub>, S, K, etc.)

Once scale materials are identified, it can be determined whether the scale is vivianite, struvite, or some other minerals.

## Vivianite Prevention and Removal

Scale formation can be prevented using one of the following chemical techniques.

- Crystal inhibitor: A proprietary, special polymer that prevents scale crystal nucleation, and disperses the formed scale crystals.
- Scavenger: A proprietary, special polymer that prevents scale crystal nucleation.
- Chelating agent: A substance whose molecules can form several bonds to a single metal ion. An example of a simple chelating agent is ethylenediamine-tetraacetic acid (EDTA).
- Alum: Ortho Phosphate (OP) has more affinity to aluminum than iron. Alum precipitates most of the available OP and leaves soluble iron in solution without bonding.

Chemistry related to scale precipitation and prevention is site specific. Therefore, it is recommended that full scale tests be conducted to fully assess effectiveness of chemicals in vivianite prevention.

## Vivianite Recovery

The occurrence and problems associated with vivianite in municipal solids treatment systems have been reported in literature. However, harvesting of vivianite from sludge for beneficial use is in an embryonic stage. Further work, pilot tests, and full-scale demonstrations are necessary to assess viability of such a process.

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## Further Reading

- Wilfert, et al. (2015). The Relevance of Phosphorus and Iron Chemistry to the Recovery of Phosphorus from Wastewater: A Review. *ES&T (49)* 9400-9414.
- Tilley, R.J.D. (2005). Supplementary Material to Part 3. Reactions and Transformations. *Understanding Solids: The Science of Materials*; John Wiley & Sons, Ltd., pp 531–542.

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