

4.6. EFFECT OF $\text{Fe}^{2+}/\text{Fe}^{3+}$ ADDITION ON H_2S CONTROL

4.6.1. BACKGROUND

The addition of iron salts to wastewater leads to the precipitation of sulfide as iron sulfide and therefore minimises the transfer of H_2S from the liquid to the gas phase. SWC, like many other wastewater authorities, uses this strategy in some of its H_2S control programs.

Iron ions can be added in the form of either Fe^{3+} or Fe^{2+} , to either rising or gravity mains and at different locations. Fe^{3+} and Fe^{2+} may precipitate not only with sulfide, but also other anions such as phosphate and hydroxide. Fe^{2+} may be oxidised to Fe^{3+} in the presence of O_2 at a suitable pH, while Fe^{3+} may be reduced to Fe^{2+} in the presence of suitable reductants such as sulfide. The complex precipitation and redox reactions involving Fe^{3+} , Fe^{2+} , HS^- , and other anions as well as oxygen makes it difficult to decide on which form of iron salt to use, how much to add and where to add. Over-dosage of iron is common practice today.

Several batch and continuous experiments were conducted to investigate these aspects.

4.6.2. RESULTS OF BATCH EXPERIMENTS

The key results of these experiments are discussed below:

- As expected, iron salts (e.g. ferrous chloride FeCl_2 , ferric chloride FeCl_3) are very effective in precipitating dissolved sulfide. There is evidence that a mixture of FeCl_2 - FeCl_3 is more efficient for sulfide precipitation. The attributable reason is that iron pyrite (FeS_2) is formed, which has a more favourable stoichiometry in terms of Fe:S ratio than FeS (amorphous FeS or mackinawite $\text{FeS}_{(1-x)}$).
- Iron pyrite (FeS_2 or FeS.S^0) is an iron (II) polysulfide and occurs commonly in the Earth's crust under anaerobic or marginally aerobic conditions. It is the most likely form of iron sulfide precipitate in the pH and redox range of raw sewage. Its formation depends on the formation of polysulfide anions (S_2^{2-}) from sulfide ions, which involves oxidation of sulfide ions to elemental sulphur (S^0) and then further reaction with S^{2-} ions to form of the S_2^{2-} -dimers or other polysulfides. (The oxidation of sulfide ions to elemental sulphur or polysulfides in the presence of oxygen is strongly catalysed by metal ions, including iron). The S_2^{2-} -dimers precipitate with Fe^{2+} as FeS_2 in a cubic structure similar to NaCl , with the exact mechanism of its formation still being the subject of some debate.
- The partial oxidation and precipitation of sulfide ions to form pyrite may occur in the presence of oxygen and ferrous (Fe^{2+}) ions. Alternatively, if ferric (Fe^{3+}) ions are present, these may act as the oxidant for sulfide ions (themselves reduced to Fe^{2+}), leading to pyrite precipitation. This explains the above-mentioned greater efficiency of sulfide precipitation using a blend of ferrous-ferric salts. However, other precipitates may also form (e.g. $\text{Fe(II)Fe(III)}_2\text{S}_4$ (greigite) or a mixture between FeS and FeS_2 , which would account for a range of Fe:S precipitation stoichiometry).
- For sewage in the absence of sulfide, addition of dissolved iron (Fe^{2+} or Fe^{3+}) will lead to competing chemical reactions for precipitation of iron hydroxides (e.g. Fe(OH)_2 , Fe(OH)_3 or amorphous FeOOH) as well as iron phosphate (e.g.



$\text{Fe}_3(\text{PO}_4)_2$, FePO_4 or $\text{Fe}_r\text{PO}_4\text{OH}_{(3r-3)}$). Alternatively, phosphate ions (H_2PO_4^- , HPO_4^{2-} , PO_4^{3-}) may be adsorbed to colloidal or solid forms of iron hydroxides. However, it appears that the iron precipitates of sulfide (e.g. FeS or FeS_2) are more stable and insoluble than the hydroxide, phosphate or hydroxyphosphate precipitates. For example, batch tests show that phosphate precipitated in the absence of sulfide is released back into solution when dissolved sulfide is added, while the sulfide disappears from solution. This occurs in the absence of dissolved iron species.

- The available data indicates that iron salts can be dosed ahead of sulfide formation and will react to form hydroxyl-phosphate complexes and/or precipitates. These will act as “carriers”, suppressing the appearance of dissolved sulfide (and hence dissolved or gaseous H_2S) where sulfate reduction occurs downstream.
- Bacterially-mediated formation of iron sulfides (e.g. FeS or FeS_2) appears to be the same in composition and structure to those formed by purely inorganic (or abiogenic) processes. The iron sulfides may be precipitated on the cell wall, with a capsule or slime layer surrounding the cell itself.
- Exposure of pyrite (or other iron sulfide precipitates) to oxygen will likely result in the formation of iron oxides, such as Fe_3O_4 (magnetite) or Fe_2O_3 (hematite), and elemental sulphur (S^0). The sulphur may then be further oxidised, eventually to sulfate (e.g. by acid-producing sulphur oxidising bacteria).

A diagram showing some of the likely interactions between iron, phosphate and hydroxide ions is shown in

Figure 27. Currently, laboratory work is being carried to test the reactions presented and to determine the stoichiometry. From this, model precipitation reactions can be developed with greater confidence.

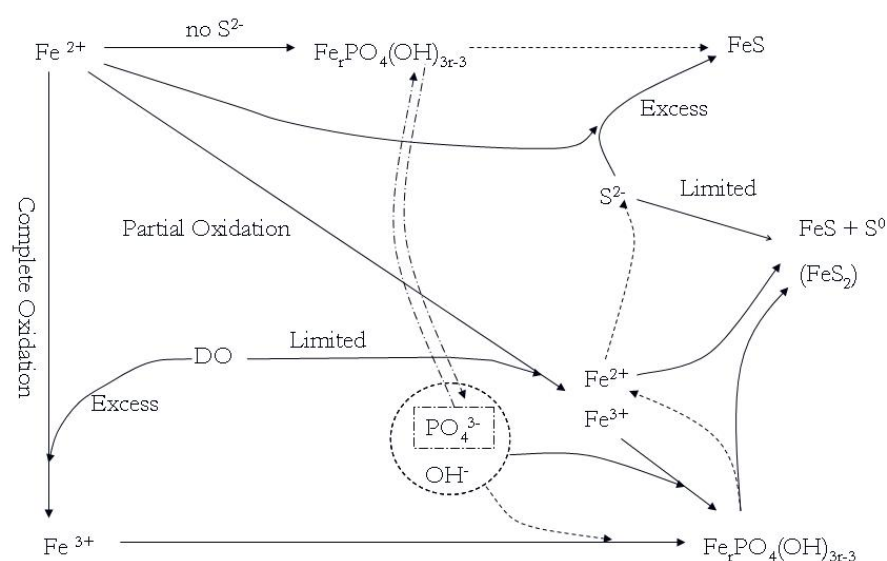


Figure 27. Hypothetical chemical precipitation interactions between phosphate, hydroxide and sulfide and iron species.

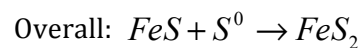
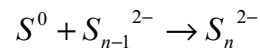
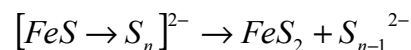
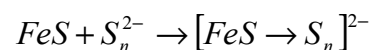
4.6.3. RESULTS OF CONTINUOUS EXPERIMENTS

Fe²⁺ was dosed to the laboratory experimental setup of the rising main described previously, and measurements were done to investigate the fate of added Fe²⁺, and its effect on sulfide production and phosphate precipitation. The results of Fe²⁺ dosing to the first reactor are shown in Figure 28.

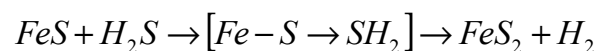
The results show that the Fe²⁺ dosing at 21 mg/l could completely prevent sulfide accumulation (concentration <1.0 mg S/L) in all reactors. Based on sulfate balance, the dosing ratio of Fe(II) to dissolved sulfide was found to be 0.76:1 (molar ratio). It is interesting to note that this strategy could keep dissolved sulfide concentrations below 1 mg/L in the four rising main reactors. In addition, ferrous phosphate precipitation was not significant in rising main reactors. Although the stoichiometric ratio of Fe(II) to S(-II) seems to be lower than the theoretical ratio based on the assumption that FeS is the product of precipitation, the value of about 0.7 was consistently obtained with repeated experiments. With a lower amount of Fe(II) dosing, this ratio further decreased to 0.5-0.6.

Based upon these results, it can be postulated that pyrite (FeS₂) may be formed during the precipitation and iron precipitates may consist of FeS and FeS₂. The process of pyrite formation at ambient temperature is determined by two alternative mechanisms.

- a. The polysulfide mechanism



- b. The H₂S mechanism



Since there was no significant accumulation of elemental sulfur in the reactor, the second mechanism is thought to be prevalent in the system. The hydrogen generated in this reaction could be further used in other anaerobic reactions such as sulfate reduction or methane production.



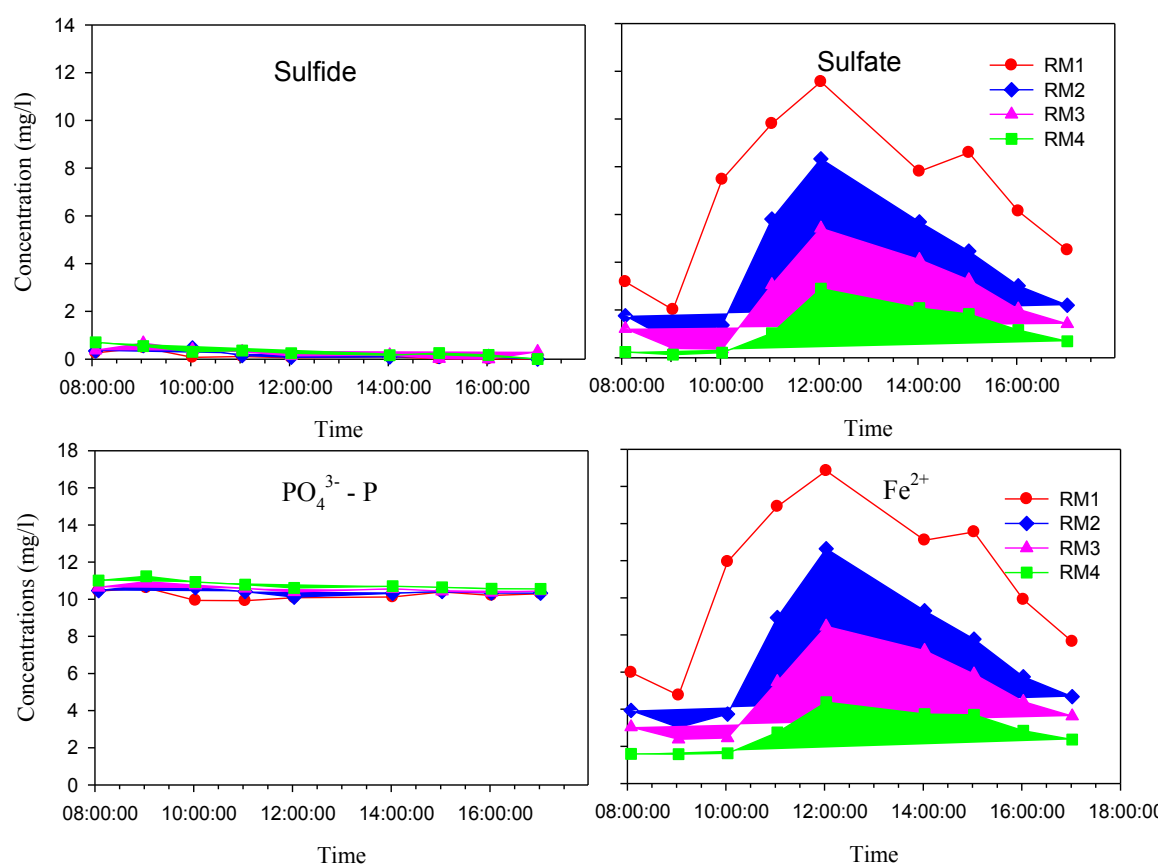


Figure 28: Sulfide control by ferrous addition – 1 week after ferrous dosing

4.7. SPATIAL VARIATIONS OF BIOFILM ACTIVITIES ALONG A SEWER LINE

In all existing sewer models, the biofilm activities are assumed identical along a sewer pipe. This is questionable as the biofilm at different locations of a sewer pipe is expected to be exposed to depleting substrate levels leading to reduced bacterial activity. If proven untrue, this could significantly compromise the quality of sewer models.

Both the lab-reactor and the in-situ Robbin's Device systems clearly show that both the actual and maximum H₂S production rates of sewer biofilms at different locations are considerably different. As an example, Table 2 shows that the sulfate reducing capacity of the sewer biofilm (represented as the maximum sulfate reduction rate) decreases with increase in biofilm location. The lab-reactor as well as field data (not given here) show that the biofilm further downstream has less opportunities to be exposed to sulfate so that less sulfate reducing bacteria will develop at these locations. The results presented in Table 2 also show that mixing has a major impact on the activity of biofilms. This aspect is also being incorporated into the sewer model.

Table 2: Comparison of sulfate reduction rates among the 4 rising main reactors in the lab-system. Fresh wastewater was added to each reactor at the beginning of each test. Samples were taken hourly for sulfur measurement. Sulfate reduction rates were determined from the slope of the sulfate profiles with time. In Experiment #1, the reactors were stirred continuously. In Experiment #2, reactors were mixed prior to sampling. RM denotes rising main.

Experimental Conditions	Sulfate reduction rate (mg S/L-h)			
	RM#1	RM#2	RM#3	RM#4
Experiment #1: Continuous stirring	4.20	3.46	2.61	2.29
Experiment #2: Stirred while sampling	3.15	2.51	2.39	2.10

4.8. METHANE FORMATION IN RISING MAIN SEWERS

4.8.1. BACKGROUND

The interaction between sulfate reducing bacteria (SRB) and methanogenic bacteria (MB) in sewer systems is a recent focus of interest. Sewer systems are sulfate-fed anaerobic environments where, according to the previous works, SRB should easily outcompete MB. However, the fact that the biomass is clustered in biofilms and that sulfate may become limiting enables MB to grow, probably in the inner part of the biofilm near the wall. MB would grow on the excess VFA and hydrogen produced by fermentation that is not taken up by SRB.

Methane formation in sewer systems is very important not only from the point of view of modelling sulfide production, but also for correctly predicting soluble COD transformations. The methane itself is likely to be supersaturated in the sewage as it is pumped through a rising main at pressures exceeding atmospheric pressure. Gaseous methane may come out of solution at points in the system where there is a pressure drop (e.g. high points in the rising main hydraulic profile) and is then likely to be vented to atmosphere where air vents are located at such points. Similarly, the dissolved methane will most likely be stripped from the sewage when it is discharged to the wastewater treatment plant. This may occur partly at the inlet works as the raw sewage passes through the screens and grit removal system, or in downstream processes such as the weirs of primary sedimentation tanks (if present) or via aeration devices (e.g. in an activated sludge treatment process).

Methane released to the atmosphere contributes is a significant greenhouse gas with a lifespan of about 12 years and a global warming potential of roughly 21-23 times higher than carbon dioxide. In practical terms, the release of 1 kg of CH₄ is roughly equivalent to the CO₂ emissions associated with the generation of roughly 20kWh of electricity. For a system such as the Tugun-Elanora rising main network, assuming the sewage enters the WWTP with an average dissolved methane concentration of 10 mg/L, the release of that methane to the atmosphere will be equivalent to the global warming potential arising from power generation emissions equivalent to about 30% of the Elanora WWTP power consumption on the SE QLD power generation grid.

Methane concentrations were measured during several batch experiments as well as the continuous operation of laboratory reactor system.

