Control of sulfide in sewer systems by dosage of iron salts: Comparison between theoretical and experimental results, and practical implications

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ABSTRACT
Removal of sulfide species from municipal sewage conveyance systems by dosage of iron salts is a relatively common practice. However, the reactions that occur between dissolved iron and sulfide species in municipal sewage media have not yet been fully quantified, and practical application relies heavily on empirical experience, which is often site specific. The aim of this work was to combine theoretical considerations and empirical observations to enable a more reliable prediction of the sulfide removal efficiency for a given dosing strategy. Two main questions were addressed, regarding the dominant sulfur species that results from the oxidation of sulfide by Fe(III) and the dominant precipitation reaction between Fe(II) and sulfide species. Comparison of thermodynamic prediction obtained by an equilibrium chemistry-based computer program (MINEQL+) with experimental results obtained by dosing ferrous salts showed that the product of precipitation is FeS under all operational conditions tested. Regarding the reaction between ferric salts and sulfide species, analysis of thermodynamic data suggested that the dominant product of sulfide oxidation under typical pe/pH conditions prevailing in municipal raw wastewater is SO$_4^{2-}$. However, comparison between sulfide removal in laboratory experiments conducted with multiple samples of raw municipal sewage with a varying composition, and the prediction of MINEQL+ showed the main sulfide oxidation product to be S$_0$. In order to reduce sulfide in sewage to <0.1 mgS/l a minimal molar ratio of around 1.3 Fe to 1 S should be applied when ferrous salts are used, as compared with a minimal ratio of 0.9 Fe to 1 S required when ferric salts or a mixture of ferrous and ferric salts (at a 2 Fe(III) to 1 Fe(II) ratio) are used. It appears that the high Fe to S(-II) ratios often recommended in practice can be reduced considerably by applying tight in-line control.

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1. Introduction

Odorous compounds in sewage systems are usually low molecular weight volatile compounds (30 to 150 g/mol) that originate from oxidation of sulfur and/or nitrogen containing organic material or from the reduction of SO$_4^{2-}$ under anaerobic conditions. The most noticeable odorous gas produced is hydrogen sulfide (H$_2$S), which gives septic sewage its typical rotten-eggs smell. Other compounds (organic and inorganic), present to a lesser extent, include mercaptans (R–CH$_2$–R–SH), volatile organic acids, alcohols, and ammonia (WERF, 2003). The presence of sulfide in wastewater is, by and large, the result of anaerobic reduction of sulfate by sulfate-reducing bacteria such as Desulfovibrio or Desulfotomaculum, which takes place in the submerged portion of combined and sanitary sewers, pumping stations wet wells, and force mains (Elmaleh...
et al., 1998). Reduction of sulfate to sulfide is not favored if dissolved oxygen (DO) or another electron acceptor more thermodynamically favored than sulfate (e.g., nitrate), is present in the aqueous phase (sewage). However, certain sulfate reduction invariably occurs in sewers, even when oxygen is present in the bulk water because of the limited penetrability of O$_{2(aq)}$ into the thick, greasy biofilm that typically develops on the sewer walls (Lahav et al., 2006).

The rate of sulfide generation depends on several factors: pH, temperature, nutrients, hydraulic retention time, presence of biofilm on the pipe surface, and the oxidation-reduction potential (ORP) (Delgado et al., 1999). Following its formation, H$_2$S diffuses from the biofilm into the adjacent wastewater, where it dissociates into three species: hydrogen sulfide (H$_2$S), bisulfide (HS$^-$), and sulfide (S$^{2-}$), according to pH, as described in Eqs. (1) and (2) (Lahav et al., 2006).

$$\text{H}_2\text{S} \rightarrow \text{HS}^- + \text{H}^+ \quad \text{pK}_1 = 7.05 \quad (1)$$

$$\text{HS}^- \rightarrow \text{S}^{2-} + \text{H}^+ \quad \text{pK}_2 = 12.89 \quad (2)$$

At the typical pH values of municipal sewage (6.5<pH<8.5) the dominant species are H$_2$S(aq) and HS$^-$ while S$^{2-}$ is negligible. H$_2$S(aq) has an extremely low odor threshold relative to most other odorous compounds (around 0.5 ppb), along with high toxicity to mammals and aquatic species. A part of the H$_2$S that is generated in the aqueous phase of sewers is invariably emitted to the atmosphere of manholes, head space of gravity sewers and pumping stations wet wells where it poses a risk to maintenance personnel (WERF, 2003). When inhaled, H$_2$S(aq) inhibits an enzyme (cytochrome oxidase) which has an important role in mitochondrial respiration. It also causes eye irritation at concentrations as low as 50–100 ppm, while 300–500 ppm may result in severe poisoning, leading to unconsciousness and death. Since hydrogen sulfide is heavier than air it tends to accumulate at the bottom of manholes and pumping stations. At concentrations higher than 100 ppm, the olfactory system is affected and the human nose cannot sense the typical smell of rotten eggs, thus maintenance personal entering manholes may not be aware of the danger of lethal concentrations. Indeed, between 1983 and 1992, more than 29 H$_2$S-related deaths and over 5500 exposures occurred in the U. S. (Snyder et al., 1995). Release of H$_2$S to the atmosphere can cause a nuisance and health concern to the neighboring population as well (Boon et al., 1998). Dissolved sulfide may also affect biological processes in wastewater treatment plants (e.g. bulking problems, and inhibition of anaerobic digestion), and may be toxic to fish in streams affected by overflow events (Strom and Jenkins, 1984).

H$_2$S released from the liquid phase to the confined sewer atmosphere is readily absorbed on the thin moisture layer on the sewer crown, walls and surfaces above the water line. There, it can be oxidized to sulfate by autotrophic aerobic bacteria (Acidithiobacillus thioxidans) residing in this moisturized layer (Okabe et al., 2007). Corrosion, induced by this acidic reaction can substantially reduce the life of concrete components of wastewater conveyance systems (WWCS), e.g., pipes, manholes, wet wells, thereby having profound economic effects (Witherspoon et al., 2004; Hvitved-Jacobsen, 2002). USEPA (1985) estimated that replacement or repair of corroded sewers cost around US$ 3.2 billion in one decade alone.

In the past three decades, many technologies have been studied with the aim of minimizing odor release from WWCS. These methods can be roughly divided into preventive methods (i.e. minimization of odorous compounds formation) and removal methods (treating the gas after it has formed). Treatment methods can be further subdivided into aqueous-phase and gas-phase treatments. The methods most often described in the literature are summarized in Table 1, which also shows a preliminary assessment of the advantages and disadvantages of each of the WWCS odor control methods.

Out of the methods listed in Table 1, dosage of iron salts is the most common technique implemented worldwide for the abatement of sulfide-associated problems in gravity sewers. Being specific to H$_2$S, and the relatively low cost of iron salts are the main advantages of this method. The first advantage can also be considered a disadvantage, as iron salts are not effective in removing any other odorous compounds. However, despite the fact that this method has been implemented for many years and in different parts of the world, the reactions that occur between dissolved iron species and sulfide in gravity sewers have not yet been fully characterized and quantified and thus the practical application of the method relies heavily on empirical experience, which is often site specific. There is also a large inconsistency between the recommendations that appear in various sources regarding the required ratio between iron salts and sulfide, which often suggests a very high dosage of iron salts, much higher than the stoichiometric requirements. For example, in the Los Angeles sanitation district where FeCl$_2$ was added in the early 1990’s to large diameter gravity sewers, a ratio of 7:1 was found necessary for 90% sulfide removal for dissolved sulfide concentrations higher than 4 mg S/l, and 15:1 and 100:1 for dissolved sulfide of between 1 and 4 mg S/l, and less than 1 mg S/l respectively (all ratios based on anhydrous FeCl$_2$ to dissolved sulfide on a weight basis) (Padival et al., 1995). All these ratios are much higher than the stoichiometric requirement. Likewise, in the city of Mesa, Arizona, FeCl$_2$ was dosed to interceptor sewers in a ratio that exceeded the stoichiometric ratio by at least 50% (Jameel, 1989).

The problem of dosage control is exacerbated by the fact that the vague definition “municipal sewage” describes a heterogeneous medium that often changes considerably within the course of a single hour, let alone between seasons. As a result, a major control problem exists when attempting to minimize sulfide concentrations in the sewage via the addition of iron salts if the effect of various components in the sewage (pH for example, but also other parameters) has to be monitored in real time to decide on the dosing strategy. The aim of the current work was thus to combine theoretical and experimental considerations in order to quantify the phenomena that occur in raw municipal wastewater following the addition of iron salts. Identification of the controlling reactions would, hopefully, allow developing a reliable recommendation on dosing strategy, which would aid in reducing the excessive addition of iron salts that is currently recommended, and thus make the method more cost effective. The wastewater used in the work was collected from a main gravity collector in an arbitrary fashion and its composition (apart from the sulfide concentration and EC) was neither
Table 1 - Advantages and disadvantages of current methods for odor and corrosion control in collection systems and pumping stations

<table>
<thead>
<tr>
<th>Method</th>
<th>References</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Increasing DO concentration by air (or pure oxygen) injection to prevent anaerobic conditions and expedite oxidation of the sulfide in the bulk sewage</td>
<td>Takatosti et al. (1998); Derek (1995); USEPA (1985); Holder and Leow (1994); Tanaka and Takenaka (1995)</td>
<td>Air is readily available — no need for transportation; no addition of chemicals; no negative byproduct formation; may improve quality of sewage arriving at treatment plant.</td>
<td>Low solubility of oxygen in water makes for a local effect and thus multiple injection points are required; high energy and maintenance requirements.</td>
</tr>
<tr>
<td>Dosage of nitrate salts (KNO₃, Ca(NO₃)₂) to elevate redox potential — encouraging anoxic activity rather than anaerobic</td>
<td>Bentzen et al. (1995); Derek (1995); Tomar and Abdullah (1994)</td>
<td>Nitrate salts are highly soluble thus high concentration may be attained in the water, allowing for full penetration into sewer biofilm, with effective prevention of anaerobic conditions; relatively inexpensive chemical.</td>
<td>A preventative measure rather than a sulfide removal method. Sulfide generated before point of injection will not be treated; unwanted addition of counter cations to sewage (e.g. Na⁺, K⁺, Ca²⁺); need for frequent transport of chemicals to injection point; possible negative effects on wastewater treatment plant because of nitrate load; need for a control system in the sewer to optimize dosages.</td>
</tr>
<tr>
<td>Chemical oxidation of odorous compounds by ozone, hydrogen peroxide, chlorine compounds, potassium permanganate etc.</td>
<td>Tomar and Abdullah (1994); Boon (1995); Sercombe (1995); Charron et al. (2004)</td>
<td>O₃ — no salts addition; harmless byproducts; adds oxygen to water. H₂O₂ — fairly specific to sulfide, no salts and byproducts addition; adds oxygen to water. Cr⁶⁺ and Cr₂O₇²⁻ strong oxidizers, high removal efficiency for H₂S and other organic substances.</td>
<td>General disadvantages for all agents: toxic to transportation and maintenance personnel, expensive to purchase and handle, non-specific oxidizers thus above stoichiometric amounts are required. Cl₂ and Cr₂O₇²⁻ addition releases unwanted salts to the water.</td>
</tr>
<tr>
<td>Addition of iron salts — either ferric or ferrous or combination of both (FeCl₃, Fe(Cl)₂, Fe(NO₃)₃, Fe₂(SO₄)₃).</td>
<td>Poulton et al. (2002); Jameel (1989); Padival et al. (1995)</td>
<td>Specific and effective oxidation of sulfide by Fe⁶⁺, followed by FeS precipitation (double effect); not toxic; no harmful byproducts; relatively inexpensive; may help in reducing soluble phosphorous compounds concentration.</td>
<td>Does not oxidize or precipitate any other odorous compounds apart from sulfides. May add undesirable anions to the water; may cause unsolicited flocculation and settling in the sewer; may precipitate with P compounds thus demand will increase beyond stoichiometry.</td>
</tr>
<tr>
<td>Treatment of malodorous gases by adsorption (activated carbon) or biofiltration reactors.</td>
<td>Jensen (1990); Wang et al. (2002); LeBeau and Milligan (1994); Vaith et al. (1996); Brennan et al. (1996)</td>
<td>Effective in places where sulfides are generated locally (like pumping stations). No chemicals addition to the water; no transportation requirements; much experience has been gathered with these systems in recent years.</td>
<td>Treats only the odor problem — does not prevent corrosion. Beds tend to degrade with time; requires close maintenance.</td>
</tr>
<tr>
<td>Elevation of pH to above 8.5 by addition of strong base which shifts the equilibrium of the dissolved sulfide towards the non-volatile species (S²⁻; HS⁻).</td>
<td>Jensen (1990)</td>
<td>May be effective in cases where local odor abatement is required.</td>
<td>Effective only locally, since the pH is bound to decrease down stream; addition of unwanted salts. High requirement due to high buffering capacity of the sewage. Requires tight control.</td>
</tr>
<tr>
<td>Microbial supplementation to out-compete sulfate-reducing bacteria</td>
<td>Richman (1997)</td>
<td>May also reduce BOD and solids in WWCS.</td>
<td>Uncertainty in potential impacts on downstream treatment systems.</td>
</tr>
<tr>
<td>Control of headspace ventilation rates; construction of tall vents – higher than the neighboring buildings – in order to emit the odorous compounds above the dwelling level.</td>
<td>Olson et al. (1997a,b); Boon (1995); Boon et al. (1998)</td>
<td>Relatively simple solution; does not require maintenance; no operating expenses.</td>
<td>Treats only the odor problem — does not prevent corrosion; local effect; many vents are required — expensive construction; not aesthetic; ineffective in certain wind patterns.</td>
</tr>
</tbody>
</table>
monitored nor altered. The objective was to understand the main reactions and consequently to establish an appropriate dosing strategy for iron salts for usage in the case of a typical, though ever changing, municipal sewage.

The two dissolved iron species (ferric iron and ferrous iron) that have been typically used for sulfidation elimination react with sulfide species in two different ways: ferrous iron (Fe(II)) tends to precipitate with sulfide species to form (according to the literature) a variety of precipitants, while ferric iron (Fe(III)) oxidizes sulfide species (to either sulfate or elemental sulfur) while being reduced itself into ferrous iron.

The most common way to describe the reaction between ferrous iron and sulfide is the following simple precipitation reaction:

\[
Fe^{2+} + S^{2-} \rightarrow FeS(s).
\] (3)

However, apart from Eq. (1) one can find in the literature other possible reactions between Fe(II) and sulfide species. For example, Wei and Osseo-Asare (1995) reported that in the first few minutes of the reaction between S(-II) and Fe(II) the reaction proceeds via the formation of intermediate species before FeS precipitates:

\[
Fe^{2+} + nHS^{-} \rightarrow Fe(HS)_{n}^{2-n} \quad \text{(rapid reaction)}
\] (4)

\[
Fe(HS)_{n}^{2-n} \rightarrow FeS(s) + (n-1)HS^{-} + H^{+} \quad \text{(slow reaction)}
\] (5)

This is an interesting observation since Drobner et al. (1990) hypothesized that one of these possible intermediates may be involved in the precipitation of solid pyrite (FeS2) as described in Eqs. (6) and (7):

\[
FeS + H_{2}S \rightarrow Fe(HS)_{2}.
\] (6)

\[
Fe(HS)_{2} \rightarrow FeS_{2}(s) + H_{2}.
\] (7)

Drobner et al. (1990) managed to generate FeS2(s) in the lab by mixing S(-II) and Fe(II) under strict anaerobic conditions at 100 °C for 2 weeks. However, it is unclear from their work whether FeS2 precipitation is also possible under the typical conditions prevailing in gravity sewers (25–35 °C).

Two other possible mechanisms for the precipitation of pyrite were suggested by Padival et al. (1995):

\[
Fe^{2+} + 2HS^{-} + 0.5SO_{2} \rightarrow FeS_{2}(s) + H_{2}O + H^{+}
\] (8)

\[
FeS + S_{2}^{2-}(s) \rightarrow FeS_{2}(s).
\] (9)

The actual occurrence of the reactions described in Eqs. (8) and (9) in sewers may also be considered questionable because under the typical pH range encountered in municipal sewage dissolved oxygen, if exists, is more likely to oxidize sulfide rather than to take part in a precipitation reaction. Moreover, typically, elemental sulfur is not found in sewage at a high concentration.

However, the option that the reactions described in Eqs. (3)–(9) may occur in gravity sewers should not be overlooked because if they do occur, they may significantly affect the Fe(II) dosage required for dissolved sulfide elimination.

Possible reactions between ferric iron (Fe(III)) and sulfide species are also not entirely straightforward. Under the most common description, Fe(III) may oxidize sulfide species to either solid elemental sulfur or to sulfate:

\[
2Fe^{3+} + HS^{-} \rightarrow 2Fe^{2+} + S_{2}^{2-}(s)\downarrow
\] (10)

\[
8Fe^{3+} + HS^{-} + 4H_{2}O \rightarrow 8Fe^{2+} + SO_{4}^{2-} + 9H^{+}.
\] (11)

The ferrous iron produced in the above reactions may further react with surplus sulfide via precipitation (if pH is sufficiently high), thus contributing to the overall removal efficiency of ferric salts. From practical and economic perspectives, the knowledge of whether the product of the oxidation reaction is sulfate or elemental sulfur is important since the amount of ferric ions required to fully oxidize sulfide to sulfate is four times higher than the amount required for fully oxidizing sulfide to elemental sulfur. Furthermore, elemental sulfur is an end product that is far less problematic from the environmental perspective (although in many cases the sulfate background concentration is much higher than the concentration possibly generated from sulfide oxidation). As shown later in the paper an analysis based on equilibrium considerations suggests that the favorable thermodynamic oxidation product is sulfate under the pH and redox conditions typically encountered in municipal sewage. Despite this, it has been widely reported that the main product of sulfide oxidation (at least in tap water) is elemental sulfur.

Apart from Eqs. (10) and (11) the literature cites other possible reactions between ferric iron and sulfide species. Under the typical pH of municipal sewage Fe(III) hydrolyzes rapidly to form amorphous Fe(OH)3(s). Davydov et al. (1998) suggested that Fe(OH)3 reacts with S(-II) to form a variety of species:

\[
2Fe(OH)_{3}(s) + 3H_{2}S \rightarrow 2FeS_{3}(s)↓ + S_{2}^{2-}(s)↓ + 6H_{2}O
\] (12)

\[
2Fe(OH)_{3}(s) + 3H_{2}S \rightarrow Fe_{2}S_{3}(s)↓ + 6H_{2}O.
\] (13)

According to Davydov et al. (1998), Fe2S3 further transforms to produce the more stable species, FeS2(s) and FeS4(s-):

\[
2Fe_{2}S_{3}(s)↓ + FeS_{2}(s)↓ + FeS_{4}(s-)
\] (14)

Padival et al. (1995) observed that a mixture of ferric and ferrous iron salts (at a ratio of 2 to 1) exhibited better sulfide removal efficiency than that of either salt by itself. These authors suggested the following reaction to explain this observation:

\[
Fe^{2+} + 2Fe^{3+} + 4HS^{-} \rightarrow FeS_{2}(s)↓ + 4H^{+}
\] (15)

However, Padival et al. (1995) did not show a direct evidence for the formation of either Fe2S3(s) or FeS4(s-), and consequently the reaction proposed in Eqs. (12)–(15) cannot be considered to be more than a hypothesis. Furthermore, when dosing a mixture of iron species with a molar ratio of 2 to 1 (Fe(III) to Fe(II)) to a solution that contains sulfide in excess, 2/3 mol of Fe(III) will oxidize one third mole of sulfide (assuming that S0 is the final oxidation product as shown in Eq. (8)). The 2/3 mol of ferrous iron generated in this reaction (plus the 1/3 mol that was initially dosed as Fe2+) will then precipitate with a further 1 mol of S2- as FeS↓. Thus, the reaction proposed by Padival et al. (1995) cannot unequivocally explain the observation that a 2 to 1 ferric/ferrous mixture is
The examples given above demonstrate the incomplete nature of the information provided in the literature regarding sulfide removal by iron salts in a municipal sewer environment. The aim of the current work was thus to combine theoretical considerations and experimental observations in order to attain a more reliable picture that would enable prediction of the sulfide removal efficiency for a given dosing strategy of ferric and ferrous iron salts. The two main questions that were addressed in the work were: (1) which is the dominant sulfur species that results from the oxidation of sulfide by Fe(III) in a municipal sewage environment, and (2) what is the dominant precipitation reaction between ferrous iron and sulfide species in a municipal sewage environment. Another question that was addressed empirically was related to the sulfide removal efficiency of a combination of ferric and ferrous salts as compared with that of either salt alone. First a theoretical analysis was carried out, based on equilibrium chemistry, using the MINEQL+ computer program (Environmental Research Software, 2001). Following this, a set of laboratory experiments were conducted to determine the minimal dosage of Fe(II) and Fe(III) salts required to attain >95% sulfide removal efficiency. Following this, the experimental results were compared with the theoretical ones and conclusions were drawn with respect to dosing strategy.

2. Materials and methods

2.1. Analyses

Ferrous iron concentration was determined by the modified o-phenanthroline method proposed by Herrera et al. (1989). Absorbance was measured with a Genesys 10 spectrophotometer, Spectronics. Ferric iron concentration was determined by the sulfosalicylic acid technique (Karamanev et al., 2002). Sulfide in "clean" water was analyzed using the Iodimetric method and in sewage using the Methylene Blue method (Methods 4500-S2− F and 4500-S2− D; Standard Methods, 2005).

2.2. Experimental procedure

Sulfide stock solution was prepared using crystalline Na2S·xH2O which was standardized using the Iodometric method (Method 4500-S2− F in Standard Methods, 2005). Raw municipal sewage was taken in the morning before each experiment directly from an 80 cm gravity sewer. The sample was rigorously mixed in the lab for 45 min in order to reduce the sulfide concentration in the sample via oxidation/stripping. The sulfide concentration that remained in the sample after 45 min was analyzed using the Methylene Blue method (Standard Methods, 2005).

Sixteen 63 ml bottles were dried, sealed and weighed and sewage was poured into each of the bottles which were then sealed again with rubber caps and left for 30–40 min until all dissolved oxygen was consumed. A volume of between 0.30 and 0.315 ml sulfide solution was then injected through the rubber caps directly into the sewage in order to attain a concentration of 5 mg S/l. Strict measures were exercised to avoid sulfide oxidation or volatilization during injection. Ferrous, ferric, or 2:1 ferric to ferrous mixture salts were then injected into the bottles. Four iron salt dosages were injected to the 12 bottles (3 repetitions per dosage), two more bottles were injected with sulfide only and to two more bottles only iron salts were added (control). The experimental procedure is described schematically in Fig. 1.

Following the dosage the bottles were mixed thoroughly and left to stand for 30–40 min. Subsequently, 0.11 ml of 100 g/l AlCl3 was injected to all bottles in order to allow for better separation between the solid and liquid phases. Following AlCl3 addition the bottles were mixed thoroughly, weighed, and centrifuged at 2800 rpm for 10 min until two distinct phases were visible. The bottles were then, one at a time, emptied slowly through the rubber cap with a 60 ml syringe without disturbing the layer that contained the solids. In order

Fig. 1–Schematic describing the laboratory experimental procedure.
to maintain a neutral pressure inside the bottle and minimize sulfide and ferrous oxidation \(N_{\text{Fe}}\) was simultaneously injected into the bottle through the rubber cap. At the end of this step, only the solid phase remained in the bottle. 2.3 ml of the supernatant from each bottle was then put into two test tubes and analyzed for sulfide. The rest was injected into a 60 ml test tube that contained 1 ml of 1 N HCl for ferric and ferrous analysis. The acid was added \textit{a priori} to prevent Fe(II) oxidation which takes place rapidly at high pH.

The now almost empty bottle with the solid phase sediment was reweighed, uncapped and connected to a zinc sulfide trap. The trap consisted of two bottles in a row, each containing 30 ml of a mixture of zinc acetate and NaOH (pH>11). The bottles were capped and \(N_{\text{Zn}}\) was injected into the empty bottle for 1 min to remove oxygen that entered the bottle while it was uncapped. Then, 5 ml of 6 N HCl solution was injected into the bottle in order to dissolve the solid phase. \(N_{\text{Zn}}\) was injected into the bottle for 2 min right after the acid injection in order to strip \(H_2S(g)\) into the sulfide trap, in which it precipitated to form ZnS. The two sulfide traps were then recombined, mixed thoroughly and analyzed for sulfide which now contained dissolved iron species) were weighed then recombined, mixed thoroughly and analyzed for sulfide.

The two individual parameters found to mostly affect FeS precipitation were pH and alkalinity. Changing the temperature resulted in only a slight difference in results as did a change in ionic strength at the low pH range (pH<7.5). At higher pH values, high ionic strength resulted in a lower fraction of total S(-II) that precipitated as FeS.

As described above, FeS precipitation is pH dependant. Out of the three soluble sulfide species, only the most basic species (i.e. \(S^{2-}\)) reacts directly with \(Fe^{2+}\) to form FeS, thus at a higher pH more FeS is expected to form.

The effect of pH on FeS precipitation as calculated by the MINEQL+ model is shown in Fig. 2. When the pH is increased from 6.5 to 7.5, the remaining sulfide concentration in solution decreases from 0.9 mg S/l to 0.2 mg S/l, or in other words sulfide removal efficiency increases from 55% to 90% (initial S(-II) concentration\(=2\) mg/l). Furthermore it is shown that in order to reach an equilibrium concentration of 0.1 mg S/l the required Fe(II) to S(-II) molar ratio at pH 6.5 is in 3.5:1, at pH 7 it is 1.6:1 and at pH 7.5 and pH 8.1 it is 1.1:1 and 1:1 respectively. Under these conditions the minimum attainable sulfide concentration decreases by 50% (from 0.09 mg/l to 0.04 mg/l) when pH increases from 7.0 to 7.5.

The total inorganic carbon concentration (\(C_C\)) has two contradicting effects on the equilibrium sulfide concentration following the addition of Fe(II) salts. On the one hand it provides buffering capacity, i.e. it is instrumental in minimizing a decrease in pH as a result of sulfide oxidation. On the other hand, when ferrous salts are added at a high Fe(II) to S(-II) molar ratio, precipitation of \(FeCO_3\) (siderite) may compete with the formation of FeS, resulting in a much higher residual sulfide concentration than at the same Fe(II) to S(-II) ratio but with a lower inorganic carbon concentration. The effect of the inorganic carbonate concentration is shown in Fig. 3, using two \(C_C\) concentrations: 500 and 1200 mg/l as \(CaCO_3\). Fig. 3 shows that under all three pH values tested (pH 6.5, 7.0 and 7.5) the precipitation of \(FeCO_3\) at the higher \(C_C\) value results in a higher residual sulfide concentration, but the effect is more pronounced at low pH values.

### Table 2 - Range of concentrations of parameters used in the MINEQL+ simulations

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Units (mg/l)</th>
<th>Parameter</th>
<th>Units (mg/l)</th>
<th>Parameter</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>([Cl^-])</td>
<td>250–350</td>
<td>([Ca^{2+}])</td>
<td>40–220</td>
<td>pH</td>
<td>6–9</td>
</tr>
<tr>
<td>([SO_4^{2-}])</td>
<td>37–210</td>
<td>([Mg^{2+}])</td>
<td>26.40</td>
<td>Ionic strength (M)</td>
<td>0.027–0.19</td>
</tr>
<tr>
<td>([Na^+])</td>
<td>100–230</td>
<td>([Zn^{2+}])</td>
<td>0.5</td>
<td>Alkalinity (mg/l as (CaCO_3))</td>
<td>500–600</td>
</tr>
<tr>
<td>([K^+])</td>
<td>20–40</td>
<td>Sulfide (mg/l as S)</td>
<td>0.72–8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>([NH_4^-]N)</td>
<td>20–100</td>
<td></td>
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</tr>
</tbody>
</table>
3.2. Investigation of the reactions between Fe(III) and S(-II)

Based on thermodynamic analysis, sulfide oxidation by Fe(III) is expected to result in sulfate (SO$_4^{2-}$) as the dominant product for most pH and redox conditions. The thermodynamic reactions that link the species SO$_4^{2-}$, S$^0$, and H$_2$S in the aqueous phase are listed in Table 3. Manipulating these equations allows plotting lines on a $p_e$–pH diagram that represent an equal concentration of each two species in the system. With respect to redox reactions, in the area above the line the oxidized species can be considered dominant while below the line the reduced species are dominant. By plotting all the redox and acid-base equilibrium equations it is possible to generate a Pourbaix diagram which depicts the domains of dominance of the various sulfur species for all $p_e$ and pH conditions (Fig. 4).

Fig. 4 shows, based on thermodynamic considerations, that the $p_e$–pH domain in which S$^0$ is expected to form is very narrow. Above pH 7.0 it is hardly expected to form at all, and SO$_4^{2-}$ is the favorable thermodynamic product. The results of this analysis also suggest that in order to end up with S$^0$ under the conditions prevailing in municipal sewage (i.e. pH between 6 and 8) the aqueous phase should be in a reducing state ($p_e$=−3 or below). When ferric salts are dosed in excess...
the wastewater shifts to the oxidative state. According to Fig. 4 $SO_4^{2-}$ should then become the dominant specie. Yet, it has been often reported (e.g. Padival et al., 1989; Lahav et al., 2004) that $S^0$ rather than $SO_4^{2-}$ is formed as the main product of the reaction between Fe$^{2+}$ species and sulfides. Thermodynamic data, therefore, appears not to give a good prediction of the reactions between ferric salts and sulfides. As stated before, knowledge of the expected sulfur product is of considerable importance with respect to the dose of ferric salts required for oxidation of a given sulfide concentration.

### 3.3. Results of laboratory experiments

The results of the experiments in which ferrous salts were added to raw municipal sewage are shown in Fig. 5. Generally it can be stated that the removal of sulfide with ferrous salts showed a pattern that was parallel to that calculated by the MINEQL+ program. The simulation lines (representing pH 7.0 and pH 7.5) were attained from MINEQL+ by using the following conditions ($EC=1.6$ dS/m, temperature 27 °C and $CT=500$ mg/l as CaCO$_3$). These conditions were also applied for simulating the plots shown in Figs. 6 and 7. The measured range of conditions of the raw sewage samples used in the research was $EC: 1.5–8.0$ dS/m; pH: 7.0–7.5; $CT=380–485$ mg/l as CaCO$_3$; $[NH_4-N]=20–43$ mg/l; and COD: 700–1900 mg/l. In the low Fe(II) to S(-II) molar ratios (0.5:1 to 0.7:1) sulfide removal in the laboratory was slightly better than that anticipated by MINEQL+ (i.e. lower residual sulfide concentrations). This observation can be attributed to one of the two following reasons: (1) in real sewage sulfide undergoes further reactions, apart from FeS precipitation (e.g. precipitation with heavy metals that may be present at low concentrations); (2) certain spontaneous oxidation of sulfide by oxygen might have occurred despite the effort to create oxygen free environment in the experiments; (3) uncontrolled volatilization of H$_2$S, due to the fact that the system was not completely sealed at all times; and (4) natural analytical errors. The third reason is less likely to have occurred because no sulfide odor was sensed. When the Fe(II) to S(-II) molar ratio that was applied was higher than 0.9 to 1 at times the experimental results showed a slightly lower sulfide removal (i.e. higher residual sulfide concentration) than that predicted by MINEQL+. This may perhaps be attributed to uptake of Fe$^{3+}$ by other species in the sewage (e.g. larger than expected FeCO$_3$ precipitation due to $CT$ higher than the 500 mg/l as CaCO$_3$ used in the simulation) or to the possible presence of substances in the sewage which may retard FeS precipitation. The reader is reminded that the aim was to test the practical average sulfide removal in typical, heterogeneous municipal sewage, and thus the wastewater samples were not subjected to comprehensive characterization. Since the constituents in the sewage varied considerably between samples it was expected that the experimental results will not precisely match the theoretical prediction which was calculated based on a constant set of data (constant $EC$, $CT$, etc.). Taking this into account, the experimental results were very close to the theoretical prediction, as much as can be expected from a heterogeneous varying medium such as municipal sewage.

According to Eqs. (10) and (11) it transpires that in order to fully oxidize sulfide to either elemental sulfur or sulfate a 2:1 and 8:1 Fe(II):S(-II) molar ratio is required, respectively. In the process of oxidizing sulfide Fe(III) is reduced to Fe(II) that, at

### Table 3 – Reactions used for plotting the Pourbaix diagram

(source of equilibrium constants: Benjamin, 2002)

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Equilibrium constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>$SO_4^{2-} + 8H^+ + 6e^- \rightarrow S^0 + 4H_2O$</td>
<td>$pe^0=6.03$ Oxidation reduction</td>
</tr>
<tr>
<td>$HSO_4^- + 7H^+ + 6e^- \rightarrow S^0 + 4H_2O$</td>
<td>$pe^0=5.66$ half reactions</td>
</tr>
<tr>
<td>$SO_4^{2-} + 9H^+ + 8e^- \rightarrow HS^- + 4H_2O$</td>
<td>$pe^0=4.21$</td>
</tr>
<tr>
<td>$S + 2H^+ + 2e^- \rightarrow H_2S$</td>
<td>$pe^0=2.89$</td>
</tr>
<tr>
<td>$S + H^+ + 2e^- \rightarrow HS^-$</td>
<td>$pe^0=-1.04$</td>
</tr>
<tr>
<td>$H_2S \leftrightarrow HS^- + H^+$</td>
<td>$pK_1=7.05$ Weak acid reactions</td>
</tr>
<tr>
<td>$HSO_4^- \leftrightarrow SO_4^{2-} + H^+$</td>
<td>$pK_1=2.25$</td>
</tr>
</tbody>
</table>

![Fig. 4 – Pourbaix diagram of the $SO_4^{2-}/S/H_2S$ system.](image-url)
the typical pH of municipal sewage, may precipitate with the remaining sulfate as FeS. Thus, 1 mol of ferric salts can theoretically remove an overall amount of 1.5 (0.5 oxidized plus 1 precipitated) and 1.125 (0.125 oxidized plus 1 precipitated) mol of sulfide when the oxidation product is elemental sulfur or sulfate, respectively. In both cases, the overall sulfide removal efficiency of ferric salts is higher than that expected by the addition of an iron-equivalent amount of ferrous salts. Since the cost of ferrous and ferric salts (normalized per g Fe) is almost identical this suggests that the use of ferric salts should be preferred.

The results of the thermodynamic analysis presented in Fig. 6 suggest that the main product of sulfide oxidation under the conditions prevalent in municipal sewage is sulfate. Direct
analysis of the end product of sulfide oxidation by ferric salts requires the measurement of either elemental sulfur or sulfate and since the sulfate background is high in Israeli sewage (25–40 mg S/l) and solid elemental sulfur is a problematic compound to measure accurately in a heterogeneous medium such as raw sewage. Thus an indirect approach (i.e. comparison of laboratory results with theoretical results predicted by MINEQL+) was adopted for the aim of determining the dominant end product of sulfide oxidation by ferric salts.

The MINEQL+ program can be used to predict the results of precipitation reactions, but it does not cover redox reactions. In order to predict the sulfide concentration following its oxidation by Fe(III), it was assumed that the oxidation continued until all Fe(III) was reduced to Fe(II) (i.e. sulfide concentration was assumed to be in considerable excess). The method for calculating the residual sulfide concentration following this reaction was: For each Fe(III) to S(-II) ratio investigated, the oxidized sulfide concentration was calculated according to either end product possible (i.e. 2:1 or 8:1 Fe(III):S(-II) molar ratio for oxidation to elemental sulfur or sulfate respectively). For example: for an initial sulfide concentration of 5.0 mg S/l and the addition of ferric iron at a molar ratio of 0.4:1 Fe(III):S(-II) (i.e. 3.48 mg Fe³⁺/l for 5 mg S/l), 20% of the initial sulfide would be oxidized to elemental sulfur or, alternatively, 5% of the initial sulfide would be oxidized to sulfate. Thus, the remaining sulfide concentration after the oxidation step would be either 4 mg S/l or 4.75 mg S/l, respectively. At the conditions tested in the lab it was reasonable to assume that Fe(II) would be reduced completely to Fe(II) and the remaining Fe(II) would precipitate with sulfide. At this point Fe(II):S(-II) molar ratio is either 0.5:1 assuming oxidation to elemental sulfur or 0.42:1 assuming oxidation to sulfate. These two new molar ratios were now inserted as inputs into the MINEQL+ program and the results were compared with the laboratory results obtained from experiments with raw wastewater to which sulfide and ferric salts were added at varying concentration ratios, as shown in Fig. 6. Since the empirical results were much closer to the theoretical line that simulated the case in which S(-II) is oxidized to elemental sulfur it was concluded that, in all likelihood, under all Fe(III):S(-II) molar ratios tested, that sulfide is in fact oxidized to elemental sulfur rather than to sulfate.

A similar procedure was carried out to analyze the results of sulfide removal with a mixture of iron salts (at a ratio of 2:1 between Fe(III) and Fe(II)). The effect of the mixed dosages was tested following a report in the literature that mixtures were observed to result in more efficient sulfide removal (Padival et al., 1995) than the equivalent dosage of each of the individual species alone. Again, the experimental laboratory results were compared with MINEQL+ prediction. In this case it was assumed that given an initial 1:1 molar ratio between iron species and sulfide, 33.33% of the initial sulfide would be oxidized if the oxidation product was elemental sulfur and only 8.33% if the oxidation product was sulfate. Here again the residual sulfide concentration (that remains following the reaction with all the ferric dosed) was assumed to precipitate with Fe(II).

In the results presented in Fig. 7 it can be seen that the residual sulfide concentrations obtained in the experiments were indeed lower than the results predicted by the MINEQL+ program for both sulfide oxidation to elemental sulfur and to sulfate (for Fe:S molar ratios of between 0.5:1 and 0.7:1). Nevertheless, the predicted line that was generated under the assumption that sulfide is oxidized to elemental sulfur is much closer to the experimental observations. These results strengthen the conclusion derived from the previous observa-
ions (Fig. 6) that sulfide oxidation with Fe(III) produces elemental sulfur rather than sulfate as the dominant end product under the conditions prevailing in municipal wastewater.

The experimental results presented in Fig. 7 suggest, as hypothesized in the literature (Padival et al., 1995), that a combination of ferrous and ferric salts is more effective for sulfide removal in comparison with either salt alone. In order to understand the theoretical basis behind this observation two possible reactions, involving iron species and sulfide, that are capable of removing sulfide from solution at a ratio higher than 1:3.3:1 (Fe to S\(^{2-}\)) were considered in addition to the reactions presented in Eqs. (12) and (13) (Davydov et al., 1998), and which result in a 2 (Fe) to 3 (S) theoretical ratio. The former reactions, that involve precipitation of FeS\(_2\), are shown in Eqs. (16) and (17) (Drobner et al., 1990; Padival et al., 1995):

\[
\text{Fe}^{2+} + 2\text{HS}^- + 0.5\text{O}_2 \rightarrow \text{FeS}_2(s) ↓ + \text{H}_2\text{O} + \text{H}^+
\]

\[
\text{FeS} + \text{H}_2\text{S} \rightarrow \text{Fe}^{2+}(\text{S}^-) \rightarrow \text{FeS}_2(s) ↓ + \text{H}_2.
\]

Eq. (16) is unlikely to occur in raw sewage since it requires the presence of dissolved oxygen and, furthermore, FeS\(_2(s)\) is a mineral that has been reported to be formed only under conditions that are not encountered in municipal sewage (high temperature and/or pressure). The same reasoning applies for discounting the reaction depicted in Eq. (17).

Theoretically, Eq. (13) results in sulfide removal at a Fe:S(-II) ratio of 1:1.5 and can thus be used to explain the better sulfide removal observed. However, since Eq. (13) involves only Fe(III) ions, Fe(II) was not oxidized to Fe(III) under the experimental conditions, and a mixture of 2:1 Fe\(^{2+}:\text{Fe}^{3+}\) was added, the conditions of the mixture under the assumption that the reaction depicted in Eq. (13) takes place allow only for a theoretical removal ratio of 1 (Fe) to 1.33 (S) i.e. the same removal ratio that is achieved under the assumption that sulfide is oxidized to elemental sulfur by ferric salts alone. Therefore, Eq. (13) cannot be used to explain the slightly better sulfide removal observed both in our study and in Padival et al. (1995). However, it should be noted that this slightly “better” removal efficiency may also be a result of natural experimental deviation not unlike the deviation observed in Fig. 6 (addition of ferric salts alone) and Fig. 5 (addition of ferrous salts alone).

4. Summary and conclusions

Interactions between iron and sulfide species in sewage media are complex and despite the fact that the subject of dosage of iron salts for the purpose of minimizing sulfide concentration in wastewater has been investigated for many years, the data that appears in the literature is incomplete, and at times even contradicting. In particular, the main precipitation product of ferrous iron and sulfide, as well as the main oxidation product of sulfide oxidation by ferric iron in wastewater medium, has not been unequivocally ascertained. Comparison of thermodynamic prediction obtained by the MINEQL+ program with experimental results obtained by using ferrous salts to remove sulfide showed that the product of precipitation is very likely to be FeS under all the operational conditions tested. With respect to the reaction between ferric salts and sulfide, analysis of thermodynamic data (Pourbaix diagram) suggests that the dominant product of sulfide oxidation under typical pH/pe conditions prevailing in municipal raw wastewater is SO\(_4\). However, comparison between sulfide removal efficiency in laboratory experiments conducted with multiple (different) samples of raw municipal sewage (with both ferric salts and a mixture of ferric and ferrous salts) and the prediction of the MINEQL+ program showed that the main sulfide oxidation product is in fact elemental sulfur.

No evidence was found for the existence of other iron and sulfide precipitation products (apart from FeS) that were suggested in literature.

The results obtained in this study are significant from the practical and economic standpoints since it was demonstrated that when sulfide containing wastewater is dosed with ferric salts the main product is elemental sulfur and not sulfate, therefore the amount of ferric salts required for achieving a desired sulfide target in the aqueous phase is much lower than in the case that the main oxidation product had been sulfate.

The results show that in order to reduce sulfide to concentrations lower than around 0.1 mg S/l with a safety factor a molar ratio higher than around 1.3 (Fe) to 1 (S\(^{2-}\)) should be applied when ferrous salts are used, and >0.9 to 1 when ferric salts and a mixture of salts (at a 2 Fe(III) to 1 Fe(II) ratio) are applied. The decision between the alternatives should be taken based on local cost of chemicals, however, in many places this cost (per Fe unit mass) is almost identical and therefore the use of ferric salts seems to be more cost effective. The results also suggest that the very high ratio between Fe and S(-II) that appears in certain recommendations in the literature may not be justified from a chemical standpoint. It would appear that a better control on the in-line sulfide concentrations in the wastewater and sewage discharge would allow minimizing the iron salts dosage and would enable high sulfide removal efficiency at a cost effective fashion. Such control can be attained, for example, by using sulfide-specific electrodes available on the market or by applying polarographic H\(_2\)S gas sensors to which samples are pumped from the sewer at predetermined time intervals (see for example http://www.analyticaltechnology.com).

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