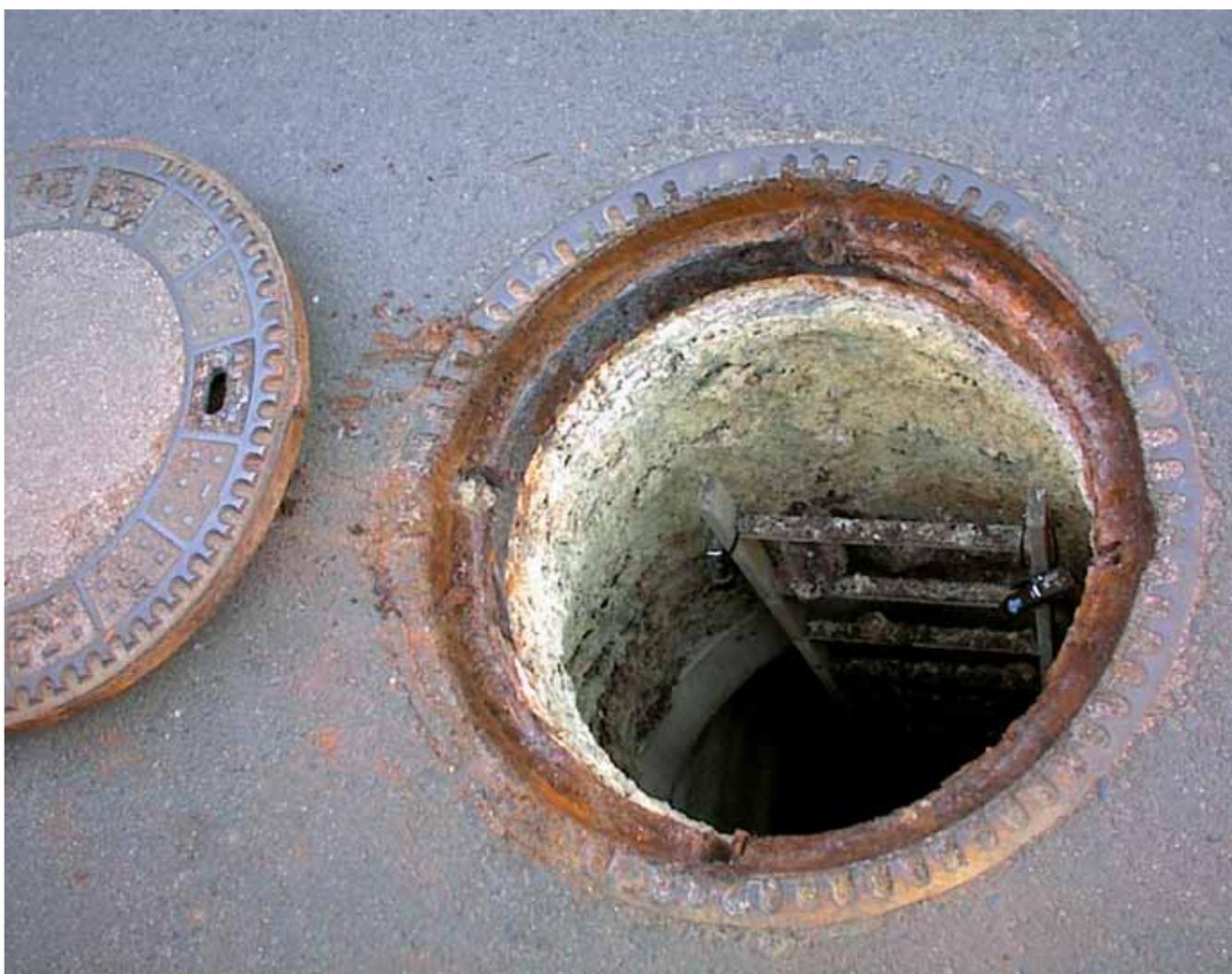




## Elimination of Hydrogen Sulfide from Wastewater Collectors using Iron Salts

The occurrence of hydrogen sulfide (H<sub>2</sub>S) in sewers is a commonly known problem. This foul-smelling, acidic gas is produced by the biogenic decomposition of sulfurous organic and inorganic constituents

under anaerobic conditions. Hydrogen sulfide can particularly be expected to form in combination with long flow times, high temperatures and especially in pressure pipelines.



*Damage in a manhole caused by biogenic sulfuric acid corrosion (BSC)*

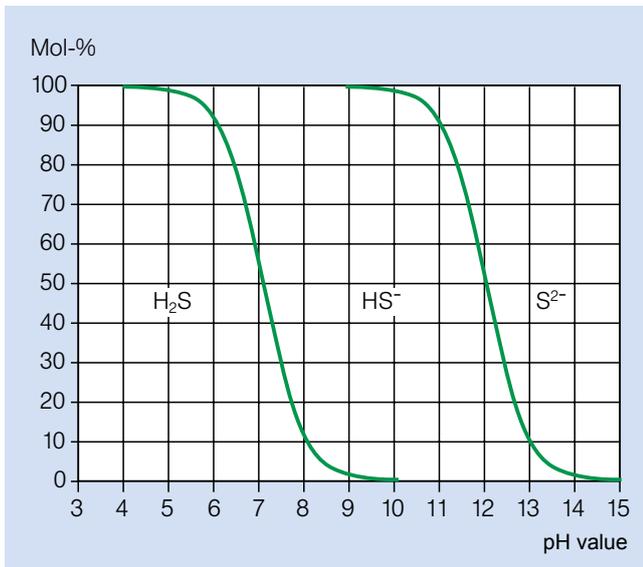


Fig. 1: Hydrogen sulfide – bisulfide – sulfide equilibrium as a function of pH value

## 1. What leads to the formation of hydrogen sulfide?

The hydrogen sulfide and other sulfides initially exist in dissolved – relatively harmless – form as  $H_2S$ ,  $HS^-$  or  $S^{2-}$  depending on the pH value of the wastewater (Fig. 1). The more acidic the environment, the more the equilibrium shifts towards hydrogen sulfide ( $H_2S$ ), which then escapes from the water phase in the form of a gas. In principle, hydrogen sulfide can form in any kind of wastewater. The main source of sulfur in the formation of  $H_2S$  in an anaerobic environment are the sulfate ions that enter the municipal sewage flow in high concentrations from tap water (desulfurication). In addition, wastewater with a high protein content, such as occurs in the food industry, for example, tends towards rapid decomposition and strong  $H_2S$  evolution (desulfuration). Table 1 lists the typical sulfur content of several foods.

## 2. Why is hydrogen sulfide so dangerous?

- Even in very low concentrations (< 0.2 ppm),  $H_2S$  can be detected by its “smell of rotten eggs”, causing severe odour problems.
- At higher concentrations, the gas becomes an increasing threat to health, and at upwards of about 300 ppm has a potentially lethal effect.
- Hydrogen sulfide leads to corrosion in the sewer system and causes high repair costs (cover photo). Its severely corrosive effect – especially on concrete – results from the fact that the hydrogen sulfide oxidises on the surface of the components exposed to the sewer atmosphere to form sulfuric acid.

Beer	160 mg S/kg
Whey	250 mg S/kg
Potatoes	340 mg S/kg
Onions	510 mg S/kg
Coffee, instant	600 mg S/kg
Maize	800 mg S/kg
Rice	1,000 mg S/kg
Fish	2,300 mg S/kg
Yeast	3,000 mg S/kg

Table 1: Sulfur content of several foods

- Hydrogen sulfide or the sulfide ions can have a negative impact on the process of biological wastewater treatment.

## 3. How can the formation of hydrogen sulfide be prevented?

Because hydrogen sulfide only forms under strictly anaerobic conditions, changing the environment by any kind of oxygen supply would, in principle, be a method for preventing sulfide formation. However, it must always be ensured in such cases that an adequate oxygen supply is also guaranteed at the end of the line.

Since the biogenic formation of  $H_2S$  often cannot be prevented – even when using oxidative control measures – it is necessary to apply elimination methods, including targeted precipitation of the sulfides using iron salts.

## 4. Why are iron salts so well-suited to eliminating hydrogen sulfide?

Bonding  $H_2S$  with iron salts is based on the high affinity of iron for sulfides. Regardless of the compound form or valence of the iron, iron sulfide always forms in the presence of sulfides ( $FeS$ ; Table 2). On account of the extremely low solubility of  $FeS$ , competitive reactions with other constituents in the water can be ruled out.

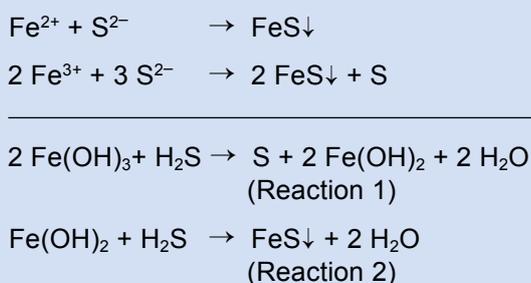


Table 2: Reaction equations for sulfide precipitation

## 5. Which KRONOS products are most suitable for this purpose?

In principle, all KRONOS iron salts are suitable for hydrogen sulfide elimination. The question as to which product should be given preference is primarily governed by local conditions with regard to logistics and handling.

The primary candidates are:

### 1. KRONOFLOC ferrous chloride solution as a ready-to-use liquid precipitant with 8.7% $\text{Fe}^{2+}$ .

The product is delivered in 60 l canisters, 200 l drums, 1 m<sup>3</sup> containers or in bulk in road tankers. If only small quantities are required, the product can be metered directly from its original container. TI 2.03 provides information on the transport, storage and metering of KRONOFLOC delivered in bulk.

### 2. FERRIFLOC ferric chloride sulfate solution with 12.3% $\text{Fe}^{3+}$ .

Delivery and storage are the same as for KRONOFLOC.

### 3. QUICKFLOC ferrous sulfate as a solid precipitant with 17.8% $\text{Fe}^{2+}$ .

The product is delivered in 25 kg bags on 1 t pallets. The QUICKSOLV metering station is available for storing, dissolving and metering. This system is described in detail in TI 2.01.1.

It occasionally is claimed that it is impossible to eliminate hydrogen sulfide using iron salts containing sulfate. This argument seems plausible at first, but naturally is false. The reason is that the sulfate concentration in the wastewater is not the minimizing factor in the biogenic formation of  $\text{H}_2\text{S}$ .

This means that a major surplus of sulfates is present in virtually all types of wastewater, enabling the formation of hydrogen sulfide, and that any additional contribution from the precipitant is irrelevant. The question of how much sulfide can be formed in a given type of wastewater is essentially governed by the temperature, the volume of wastewater, the hydraulic and design-related parameters, as well as the concentration of simple organic compounds, such as organic acids and alcohols (similar to denitrification).

## 6. Where should the precipitant be added?

The effect of the iron salts is based on the precipitation of the dissolved sulfides in the water phase. This must occur at an early stage, before the hydrogen sulfide enters the gas phase and becomes perceptible. Points where the following requirements can be met are suitable as metering points in the sewer system:

- Delivery by road tanker
- Safe storage
- Safe handling of chemicals



Fig. 2: Underground tank at a pumping station with catch basin



Fig. 3: Metering station in a manhole

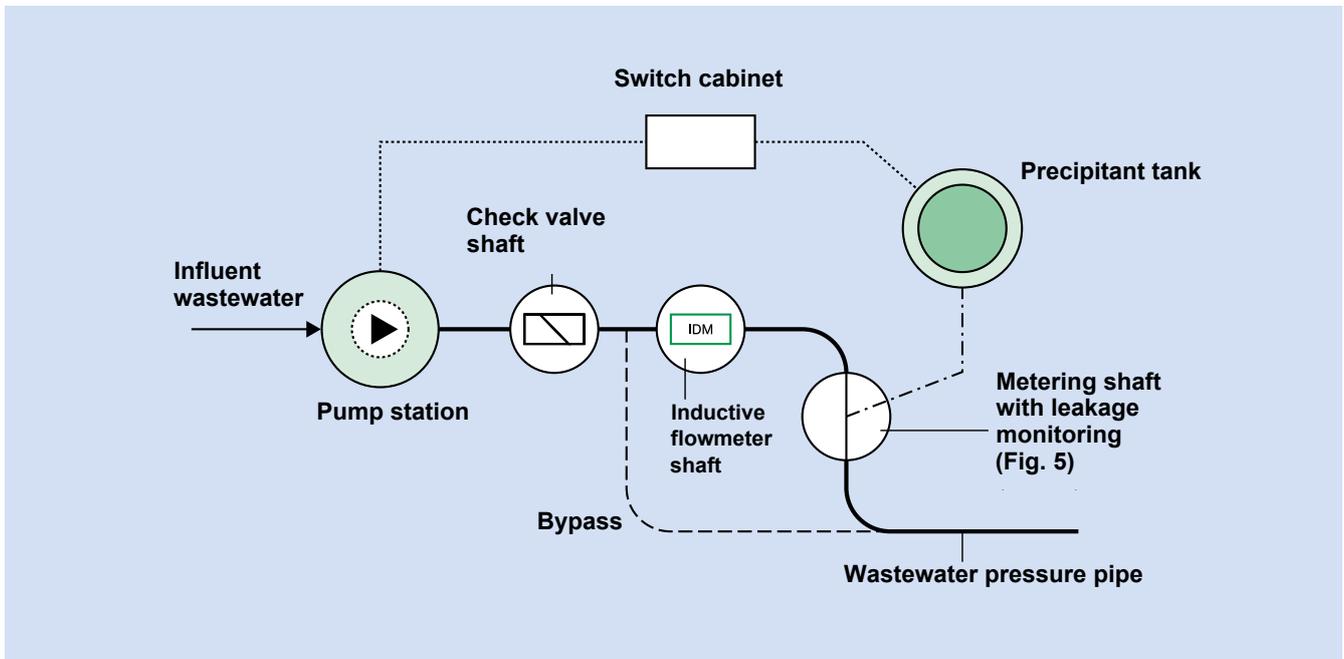


Fig. 4: Arrangement for preventive metering

The high speed of reaction of sulfate precipitation with iron salts supports two metering options:

**a) Preventive metering (Fig. 4):**

The iron salt is added at the start of a problematic section, i.e. at a point where no degradation processes have yet begun. It has proven effective in the case of wastewater pressure lines to add the iron salt directly to the pressure line via a seeding point (e.g. tapping sleeve, Fig. 5).

Acid-proof diaphragm pumps are used to meter the product (TI 2.3). To adapt the added quantities to the rate of sulfide generation, we recommend using the pipeline dimensions and the wastewater volume generated to calculate the dwell time of the wastewater between inflow and outflow. The quantity of iron salt added is preferably adapted to the expected sulfide

concentration by a measurement curve controller (e.g. PLC). If necessary, the system should also account for rain events.

Premature addition need not be feared, since the products of hydrolysis (hydroxides) of the iron can also bond the hydrogen sulfide (Table 2).

**b) Addition upstream of the emission point:**

The spontaneous reaction between the dissolved iron and the dissolved sulfides takes only a few seconds, but can be observed by watching the wastewater rapidly turn black. For this reason, it is also effective to add the iron salts a short distance upstream of the emission point – i.e. into wastewater that has already begun to degrade. Basically, any turbulent outflow of anaerobic wastewater at the end point of pressure lines, for example, should be avoided. In practice, this can be achieved by shifting the pressure line outlet to below the water level while at the same time adding iron salt just upstream from the end of the wastewater line or into the wastewater pumping station.

An arrangement of this kind makes it possible to establish a controlled section for sulfide precipitation, similar to online phosphate precipitation. Continuously monitoring H<sub>2</sub>S emissions by connecting an online H<sub>2</sub>S sensor to the metering pump can help to reliably maintain target values, e.g. a maximum allowed workplace concentration (MAC) of 10 ppm in the coarse and fine screening building (Fig. 6).



Fig. 5: Addition directly into the pressure pipeline via a seeding point.

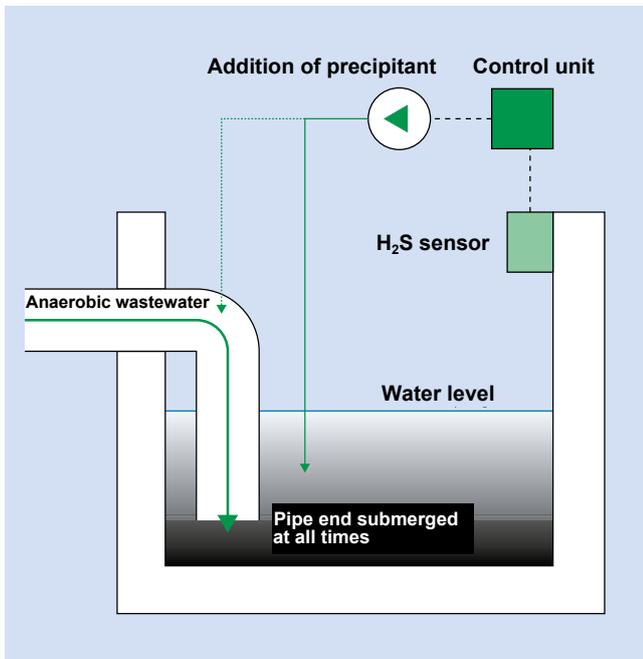


Fig. 6: Online addition upstream of the emission point

## 7. How much has to be added?

### a) Theory:

The dissolved sulfides in the wastewater can be determined analytically as  $S^{2-}$  e.g. according to DIN EN 38 405.

If data on the concentration of dissolved sulfides in the wastewater are available, and the wastewater flow rate is known, a simple calculation can be used to determine the quantity to be added (Table 3).

### b) Practice:

In practice, however, data are usually only available for the hydrogen sulfide concentration in the gas phase. But even these values support a fairly good estimation of the required quantities. The actual quantities required can then be determined empirically.

The following, pragmatic procedure has proven successful in practice:

1. The  $H_2S$  content in the collector air is measured at neuralgic problem points over several days.
2. The iron salt solution is added at suitable dosing points upstream of the measurement points, using a typical standard quantity of 15 g Fe/m<sup>3</sup> wastewater.
3. The quantity added is adapted in accordance with the results of gas analysis, based on the residual  $H_2S$  content in the collector air. In this context, the added quantities may have to be adapted to the flow and dwell times in the sewer system.
4. When adding quantities online, the times at which the metering pumps are switched on and off, and the steepness of the metering curve, must be adapted to the target value.

Existing or expected sulfide concentration	4 mg $S^{2-}$ /l
in the problematic area of the collector	$\triangleq$ 4 g $S^{2-}$ /m <sup>3</sup>
Wastewater inflow (e.g. wastewater pump capacity)	50 m <sup>3</sup> /h
Iron concentration in the precipitant (KRONOFLOC)	8.7 % $Fe^{2+}$
Density of KRONOFLOC	1.37 g/cm <sup>3</sup>
Molar mass sulfur	32.06
Molar mass iron	55.85

$$\frac{0.004 \cdot 55.85 \cdot 50}{32.06 \cdot 0.087 \cdot 1.37} = 3.0 \text{ l KRONOFLOC/h}$$

Table 3: Sample calculation for determining quantities to be added

## 8. What happens to the precipitated sulfides??

The virtually insoluble iron sulfide is a very fine solid with poor sedimentation properties. In other words, iron sulfide does not settle in the sewer, but passes into the treatment plant with the wastewater flow. As a rule, this dark-black wastewater also passes through the primary sedimentation stage; only in the biological stage of the treatment plant is it oxidised, thus being made available for simultaneous phosphate precipitation. This double precipitation effect is illustrated schematically in Fig. 7.

The black discoloration of the treated wastewater inflow provides clear, visual proof that  $H_2S$  elimination has taken place. The iron method is not well accepted by receiving treatment plants that have no biological stage, i.e. no oxidative decolouration.

The hydrogen sulfide bound in the iron sulfide is released again if the pH of the wastewater drops significantly below pH 6.

On account of the high buffer capacity in the untreated wastewater, this condition is never reached as a rule when using common added quantities.

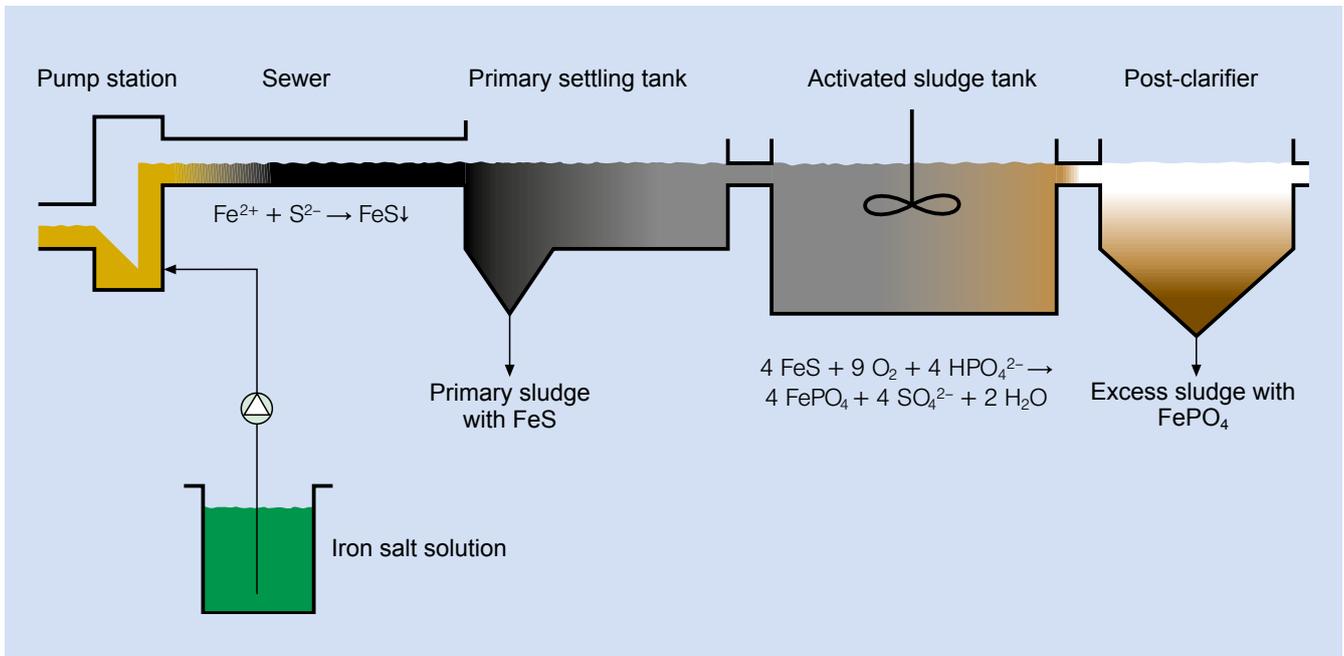


Fig. 7: Hydrogen sulfide elimination with sulfide and phosphate precipitation

## 9. What else needs to be considered for the successful implementation of hydrogen sulfide elimination?

Using iron salts to precipitate the sulfides dissolved in wastewater is a very reliable elimination process. The special feature of this method is that the iron salt must be added at a point where no hydrogen sulfide is yet present. Therefore, selecting a suitable dosing point is of fundamental importance for the applicability and success of the method.

In addition to being located upstream of the problem area, the dosing point must also offer the technical means for safe storage and handling of the precipitants. Several metering points are often required, depending on the design of the collector system and the affected sewer sections.

The efficiency of the process ultimately depends on how successfully the quantity of iron salt added can be adapted to the various sulfide loads.

## 10. What results are available??

The effectiveness of H<sub>2</sub>S elimination with iron salts is illustrated below on the basis of two practical examples.

### 1. Use of KRONOFLOC in a 5 km pressure pipeline.

To avoid H<sub>2</sub>S emissions, KRONOFLOC is added at the inlet of a pressure pipeline as a preventive measure (Fig. 9).

### 2. Use of KRONOFLOC to maintain the MAC in a grit chamber.

The signal from an H<sub>2</sub>S sensor supports the establishment of a controlled section and activates the dosing pumps as needed (Fig. 8). The steepness of the rise or fall in H<sub>2</sub>S concentration determines the added quantity.

Phases with low H<sub>2</sub>S loads (e.g. rainy weather) are detected and the required quantity of precipitant automatically reduced (Fig. 10).



Fig. 8: An H<sub>2</sub>S sensor takes continuous readings in the grit chamber. The signal is processed and the KRONOFLOC metering pumps activated. The results are illustrated in Fig. 10.

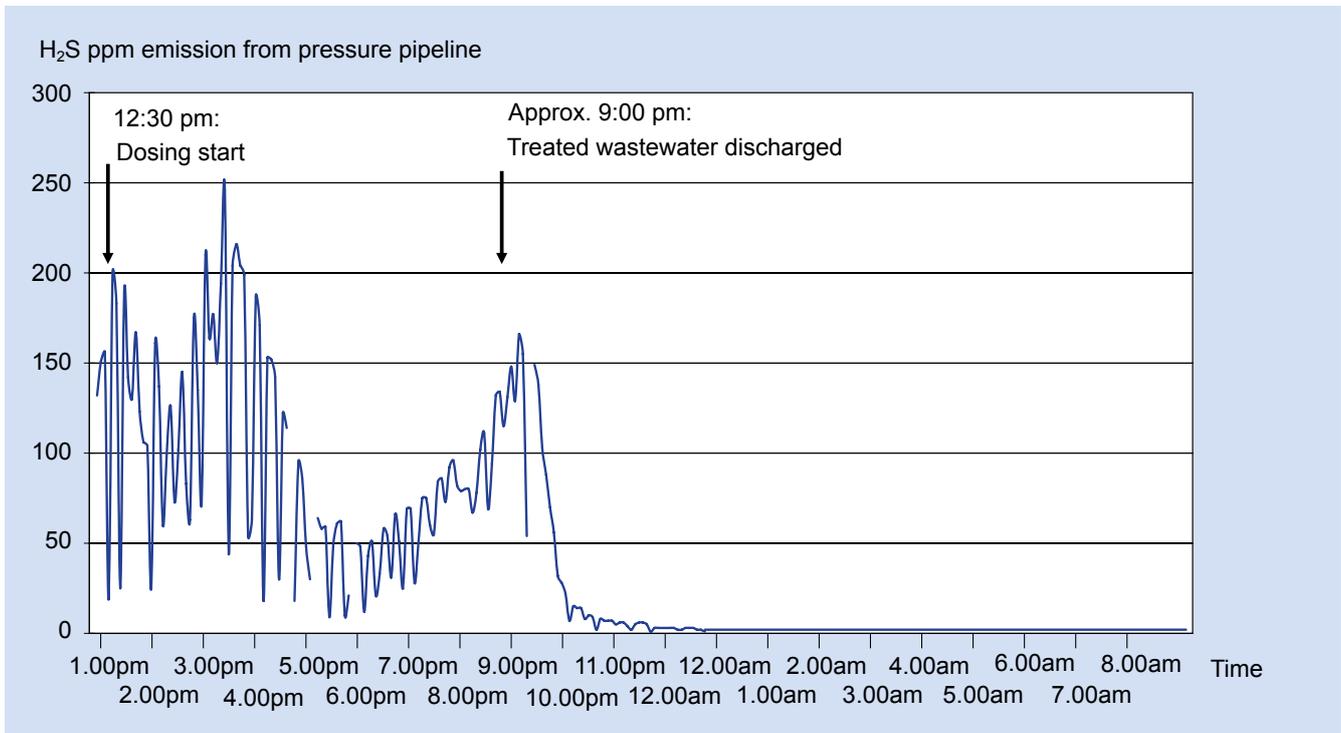


Fig. 9: Effect of KRONOFLOC addition as a preventive measure

Pressure pipeline data (Fig. 9)	
Dimensions	DN 250
Volume	Approx. 245 m <sup>3</sup>
Wastewater volume, Q <sub>TW</sub>	Approx. 570 m <sup>3</sup> /day
Wastewater dwell time in the pressure pipeline	9 –14 hours
Average added quantity	30 g Fe <sup>II</sup> /m <sup>3</sup>

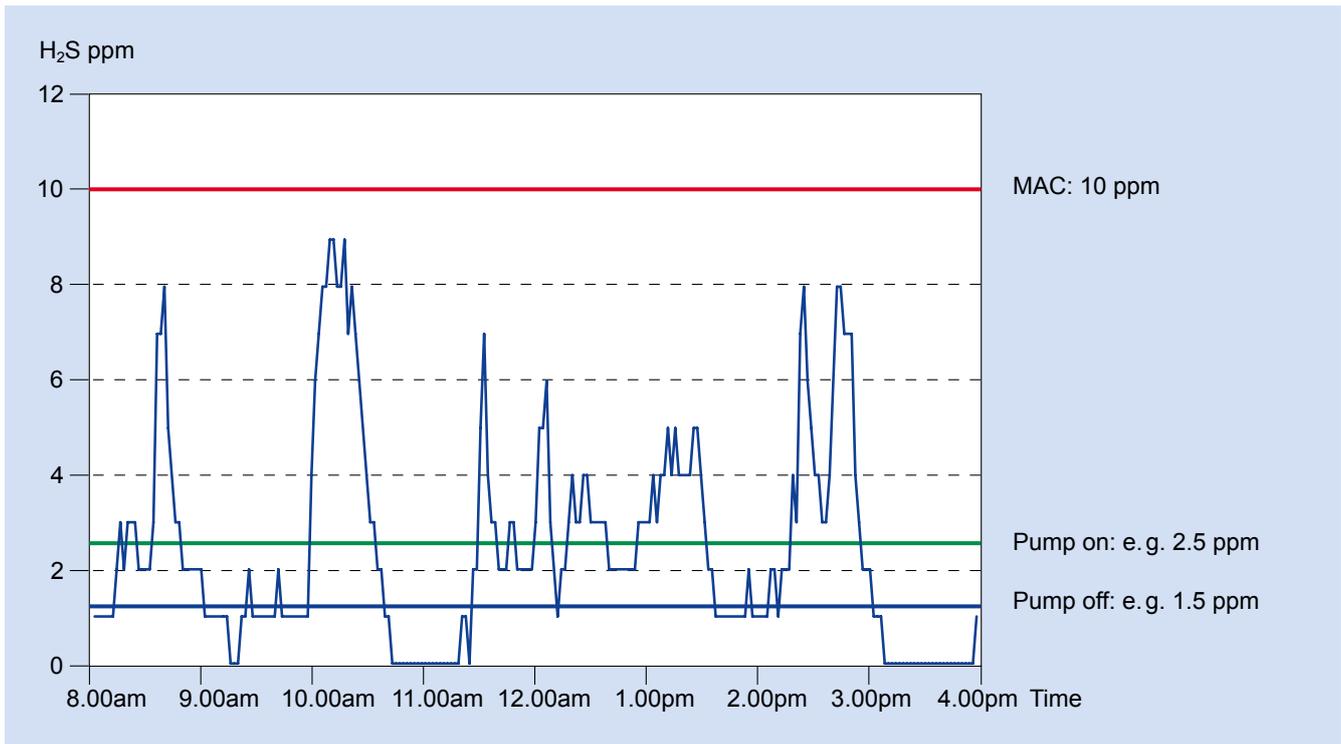


Fig. 10: Typical curve of H<sub>2</sub>S concentration with controlled, online addition of iron salts to maintain the MAC value in a grit chamber

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Consult our Safety Data Sheets before using any of our products.

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