Hydrogen Sulphide

– identifying and solving the problem



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Just another day at the sewer office ...

Hydrogen sulphide emissions are a large and well-known problem in the daily transportation of wastewater in sewage network systems. They are particularly well known for the significant risks in connection with work in manholes and at pumping stations, and of course the characteristic odour of rotten eggs.

Grundfos has prepared this booklet as an introduction to the causes of hydrogen sulphide emissions and some of the consequences. It intends to aid sewage workers, managers and other persons working with wastewater transportation on a daily basis. The booklet does not provide complete answers to everything in connection with hydrogen sulphide issues; instead, it is intended as an overview providing insights on the hydrogen sulphide problems you encounter in your daily work.

The booklet was written by Grundfos and includes input from a group of specialist working under the Danish Water and Wastewater Association (DANVA) with hydrogen sulphide problems.

Enjoy your reading.

Kind regards,
Grundfos

Disclaimer
Grundfos has made every reasonable effort to ensure that the information contained in this booklet is accurate and correct.
However, Grundfos assumes no responsibility for direct or indirect losses as a result of the application of the content of this booklet.

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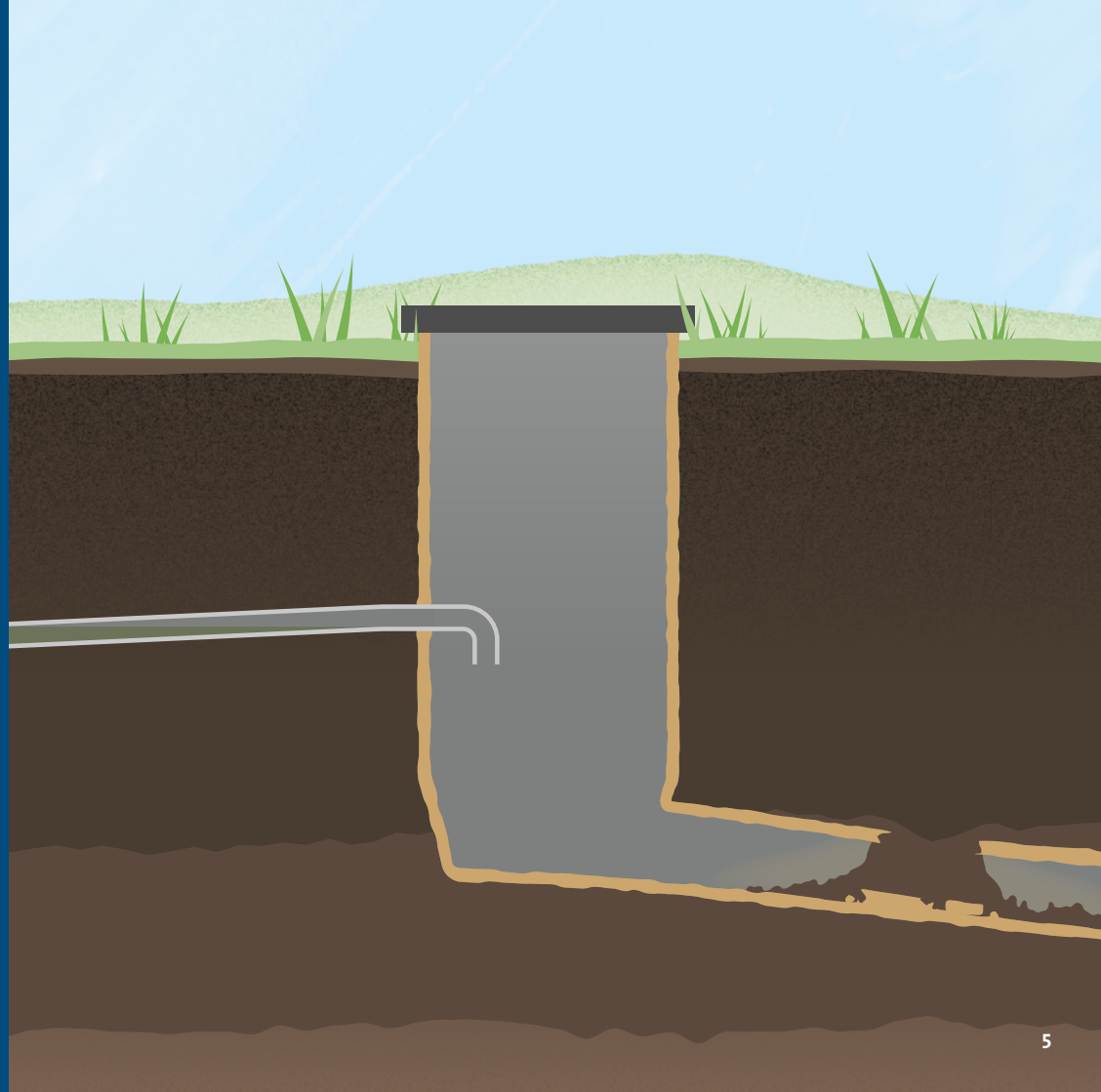
Preface

by Professor Jes Vollertsen
Department of Civil Engineering, Aalborg University, Denmark

Demands for efficiency in the wastewater sector continue to increase, as do requirements on effluent quality. These and other factors have resulted in the centralisation of wastewater treatment and in wastewater transportation over still greater distances. As wastewater needs to be transported over greater distances, interceptor sewers can no longer only consist of gravitational pipes but must increasingly use rising mains.

Centralisation provides clear advantages in wastewater treatment, but the necessity of using pressurised pipes involves a number of disadvantages. One such disadvantage is the development of anaerobic conditions in the pressurised pipes. This leads to the formation of hydrogen sulphide and other odorous gases in volumes that can result in significant problems at the end of the rising mains and for people in the near vicinity.

While it is possible to optimise the rising mains in order to minimise the problems during the planning phase, hydrogen sulphide and other problematic gases are often not taken into account in the planning phase, and the problems subsequently need to be addressed during operation. This is often quite complicated, and finding advice and guidance on how to approach the issue is difficult. This booklet explains some of the basics concerning hydrogen sulphide, odours, and what to do about them. We hope that it can contribute to practical solutions to the many problems in connection with hydrogen sulphide and other odorous gases when pumping wastewater.



Common hydrogen sulphide problems

Hydrogen sulphide is particularly known for creating three problems in the daily work of the utility companies:

1. Health and safety issues because of the smell and hazards associated with hydrogen sulphide.

2. Odour issues for residents near manholes or other sewage constructions.

3. Degradation of installations, components, pipes and constructions.

Health and safety



Hydrogen sulphide is an extremely toxic gas with a characteristic smell reminiscent of rotten eggs. Even at low concentrations, the gas poses a severe health hazard, and at higher concentrations it is lethal. Hydrogen sulphide is treacherous as it paralyses the sense of smell at high concentrations.

As a consequence, "trusting your nose" to warn you is not sufficient.

Standard EN 752, "Drain and sewer systems outside buildings", says: "Appropriate atmospheric monitoring equipment must be used continuously whilst any worker is in the system". This is of vital importance for the people involved.



Odour



As the smell of hydrogen sulphide is very bad even at low concentrations, even a minor problem can result in complex and costly operational procedures, as many utility companies cannot accept odour issues affecting citizens.

Odour issues are governed by standards such as EN 752, which says:
"Sewer systems shall be designed, constructed, maintained and operated to avoid odour nuisance, or toxic, explosive or corrosive gasses".

Corrosion and degradation of installations

Hydrogen sulphide is often perceived as a local problem in manholes or at pumping stations. However, the formation of hydrogen sulphide can also have consequences for the downstream sewage system.



On various surfaces, hydrogen sulphide is converted into sulphuric acid which dissolves the surfaces.

In other words, hydrogen sulphide formation can have major structural, and therefore financial, consequences.

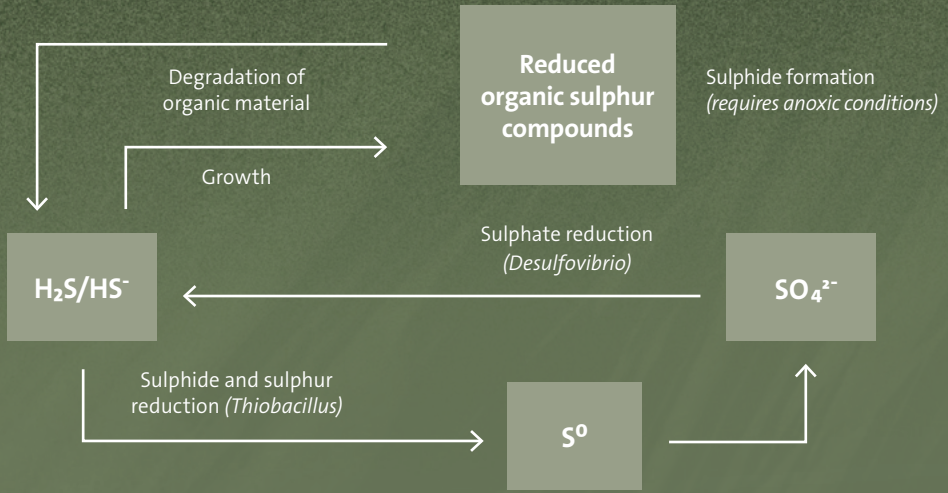
The formation of hydrogen sulphide and the conversion into sulphuric acid is covered in detail later in this booklet.

Effect of gas concentration	Gasphase concentration in air (ppm)
Detection limit, smell	0.0001-0.002
Powerful unpleasant odour	0.5-30
Limit set forth by the Danish Working Environment Authority	5
Damage to eyes and mucous membranes	50-300
Life-threatening	300-500
Immediate death	>700

Process conditions in sewers

Wastewater is often transported over great distances in pressurised systems. In such systems, bacteria can live off the wastewater. They grow in biofilms on the surfaces of pipes, well walls and other submerged surfaces, as they would be flushed away if they were not attached to anything. The biofilm is dominated by the fastest-growing bacteria, and bacteria growth is determined by what the bacteria feed on.

Wastewater contains a great number of chemical compounds that bacteria can live off. In the case of wastewater, bacteria convert organic matter to cell material and CO_2. Much like human beings require oxygen to get energy from the food we eat, bacteria can use various chemical substances such as oxygen (O_2), nitrate (NO_3-) and sulphate ($SO_4$2-). If oxygen or nitrate are present, hydrogen sulphide will not be formed in any significant amounts. This is the case in the first part of the pressurised pipe (see page 10-11) which contains oxygen and nitrate which has been added to or formed (respectively) in the wastewater. When the oxygen and nitrate is depleted, hydrogen sulphide formation commences in the biofilm.



Hydrogen sulphide is formed through biological processes, and the regulating factors are as follows: the amount and type of organic matter, temperature, and pH value. The most important factor for the overall production, however, is how long the bacteria are in contact with stagnant wastewater which is determined by the retention time.

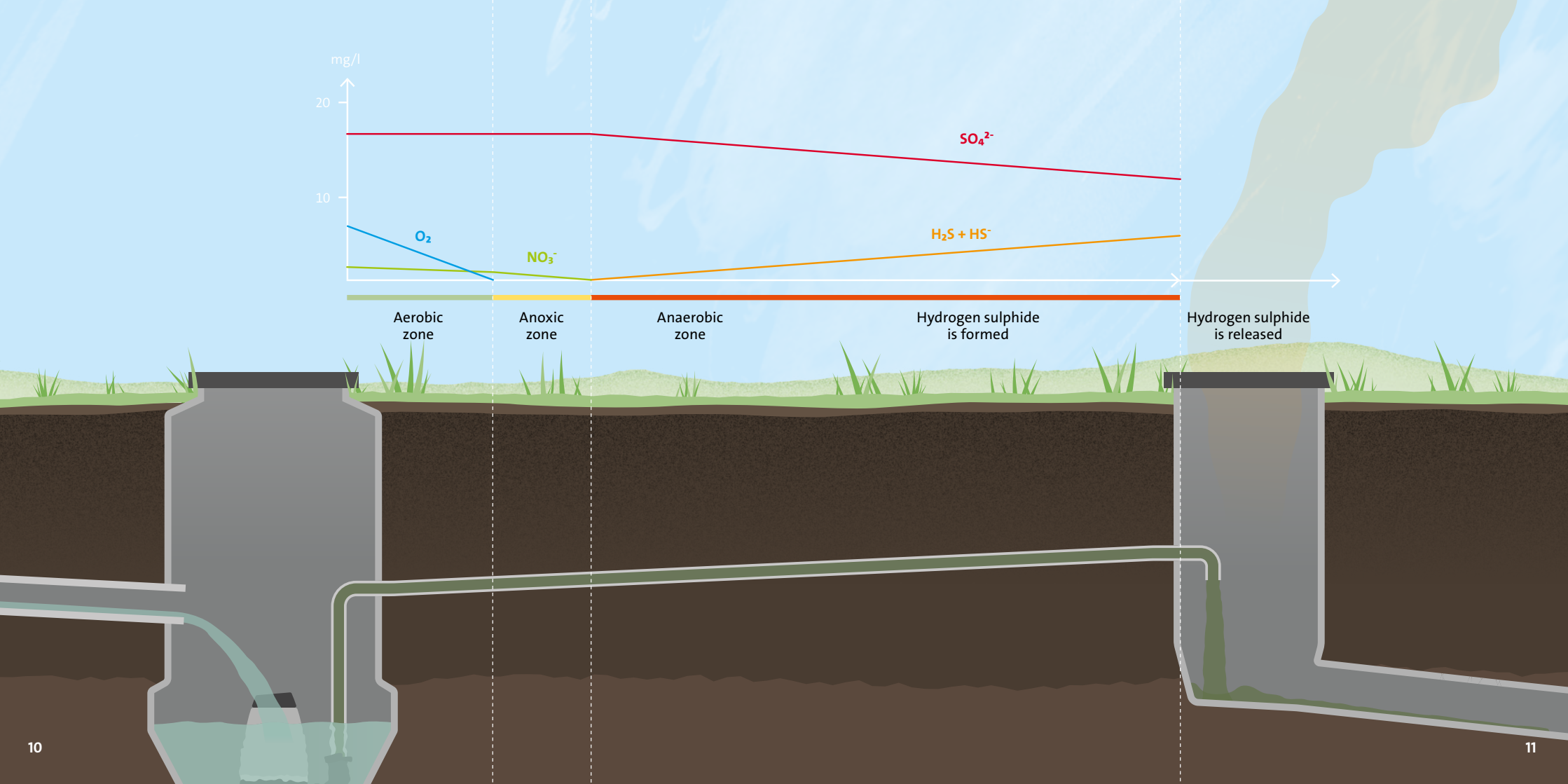
In this connection, it should be remembered that infiltrating water, surface water or rainwater in common systems shortens the retention time.

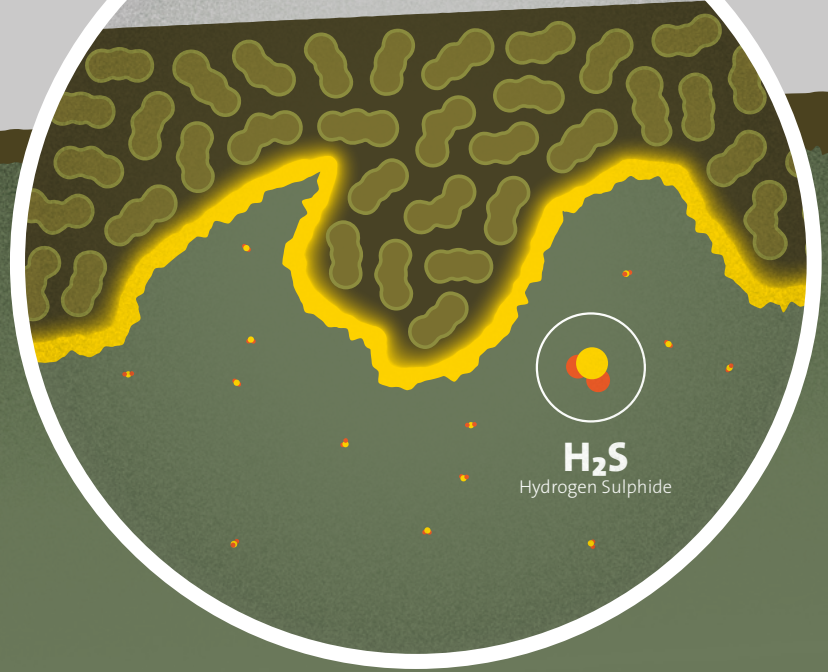
Temperature influences production. The production of hydrogen sulphide increases by approximately 3-5% per degree Celsius. However, growth is influenced more by retention time than by temperature.

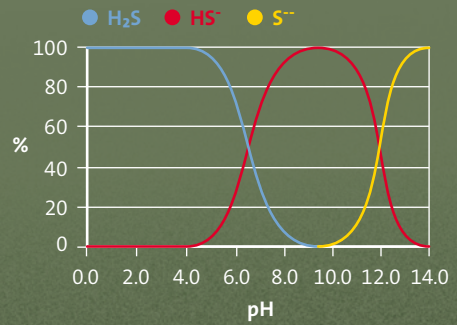
Factors that influence sulphide formation

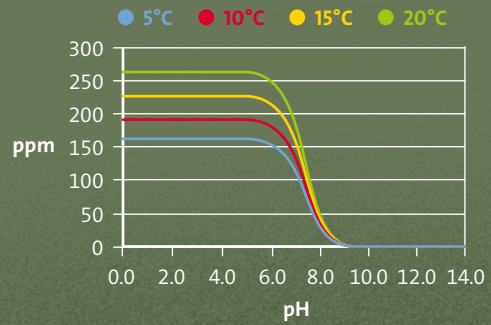
Parameter	Effect
Area/volume ratio	Large A/V ratio results in increased sulphide production. Large pipe diameters result in a low A/V ratio*
Anaerobic retention time	Increases sulphide concentration. Large pipes in pumping mains result in anaerobic retention time*
Flow	High flow (> 1 m/s) reduces biofilm thickness and sulphide production
Wastewater sulphate content	Not a limiting factor at more than 5-15 gS m^{-3}
Quality of organic substrate	Easily degradable substrates such as VFAs and alcohols increase the growth rate
Temperature	The temperature coefficient is low (approx. 3-5% growth rate increase per degree Celsius)
pH value	Optimal between pH 5.5 and 9 (not limiting in normal wastewater)

* Overall, however, sulphide formation will be smallest in large pipes


mg/l
20
10
SO_4^{2-}
O_2
NO_3^-
$H_2S + HS^-$
Aerobic zone
Anoxic zone
Anaerobic zone
Hydrogen sulphide is formed
Hydrogen sulphide is released







Once the hydrogen sulphide has been formed in the biofilm, part of it will enter the waterphase directly in the wastewater as dissolved gas. A significant part of the gas produced can remain dissolved in the wastewater as long as it remains under pressure in the pressurised part of the system. When the wastewater reaches a manhole or another open well with atmospheric pressure, the hydrogen sulphide gas is released into the air. This is the source of the previously mentioned problems.

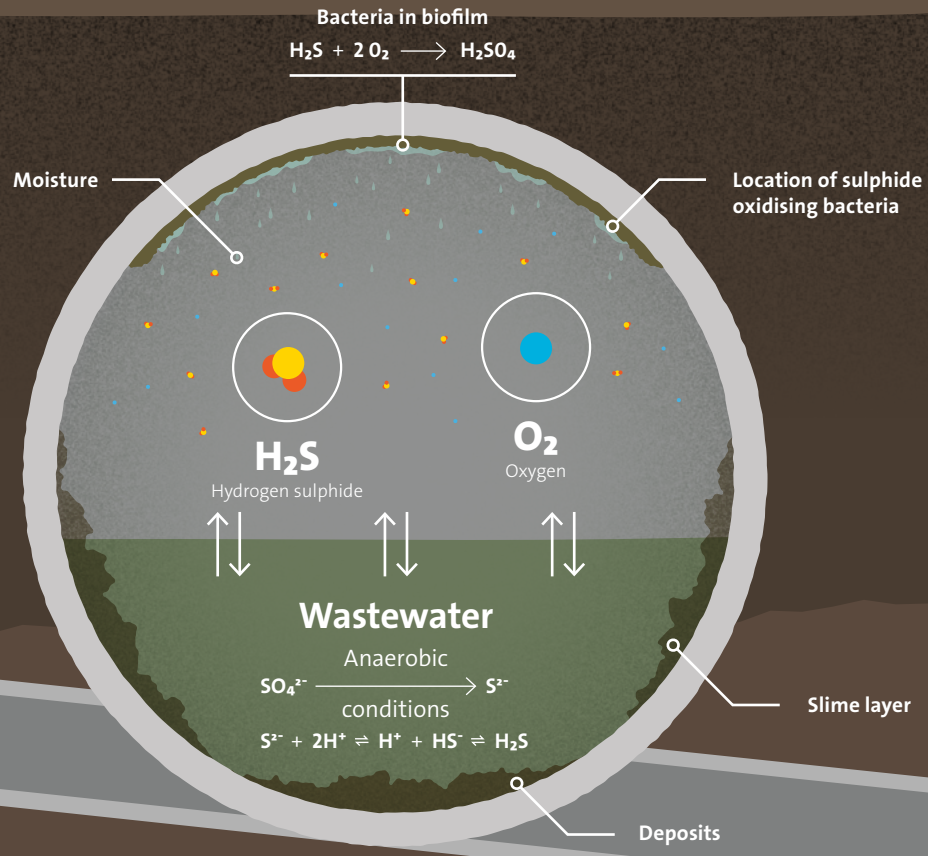
How much of the produced gas that is degassed depends on wastewater pH value and temperature, and on the degree of turbulence in the transition from the pressurised system to the gravitational system. The figures on the opposite page show the correlation between distribution in the water and gasphase, and pH and temperature. pH value is a major factor in the magnitude of a hydrogen sulphide problem.

At pH values below approx. pH 6, almost all hydrogen sulphide will be in gaseous form and evaporate in the wells so that even a minor production creates major problems. Above pH 8.5, all hydrogen sulphide is dissolved in the waterphase so that no evaporation occurs. As wastewater is acidified in case of long retention times, this can significantly increase the problems.

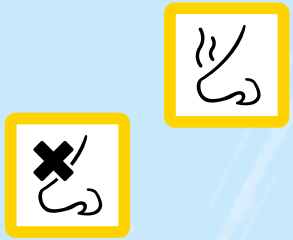
Wastewater temperature deviations are often quite small in systems in temperate parts of the world. In case of industrial wastewater, however, the deviations can be more pronounced, which can contribute to increasing hydrogen sulphide issues. In wastewater at higher temperatures, bacteria production by time will be higher, and more hydrogen sulphide will therefore be produced. Also, a larger part of the produced hydrogen sulphide will evaporate.

Turbulence is the physical force that drives hydrogen sulphide out of the wastewater. High turbulence results in the biggest issues; the more splash, the more gas!

The design of the well therefore plays an important role for the size of the problems.



Odour issues



Odour problems are usually located at one single site such as a pumping station that receives water from several pipes, or a manhole. In serious cases, odour issues can occur along an entire sewage pipe. Passers-by or residents near the source of the issues may complain. In order to act on citizen enquiries, utility company staff often visit the site, only to find no apparent odour issue.

The scope of the problem often varies greatly, and there are a number of reasons for this. Hydrogen sulphide issues are often linked to high retention times. Dry weather often results in the highest retention times. In older, separated systems, infiltrating water after precipitation and surface water and rainwater in the common system shorten the retention time, thereby often decreasing the problems.

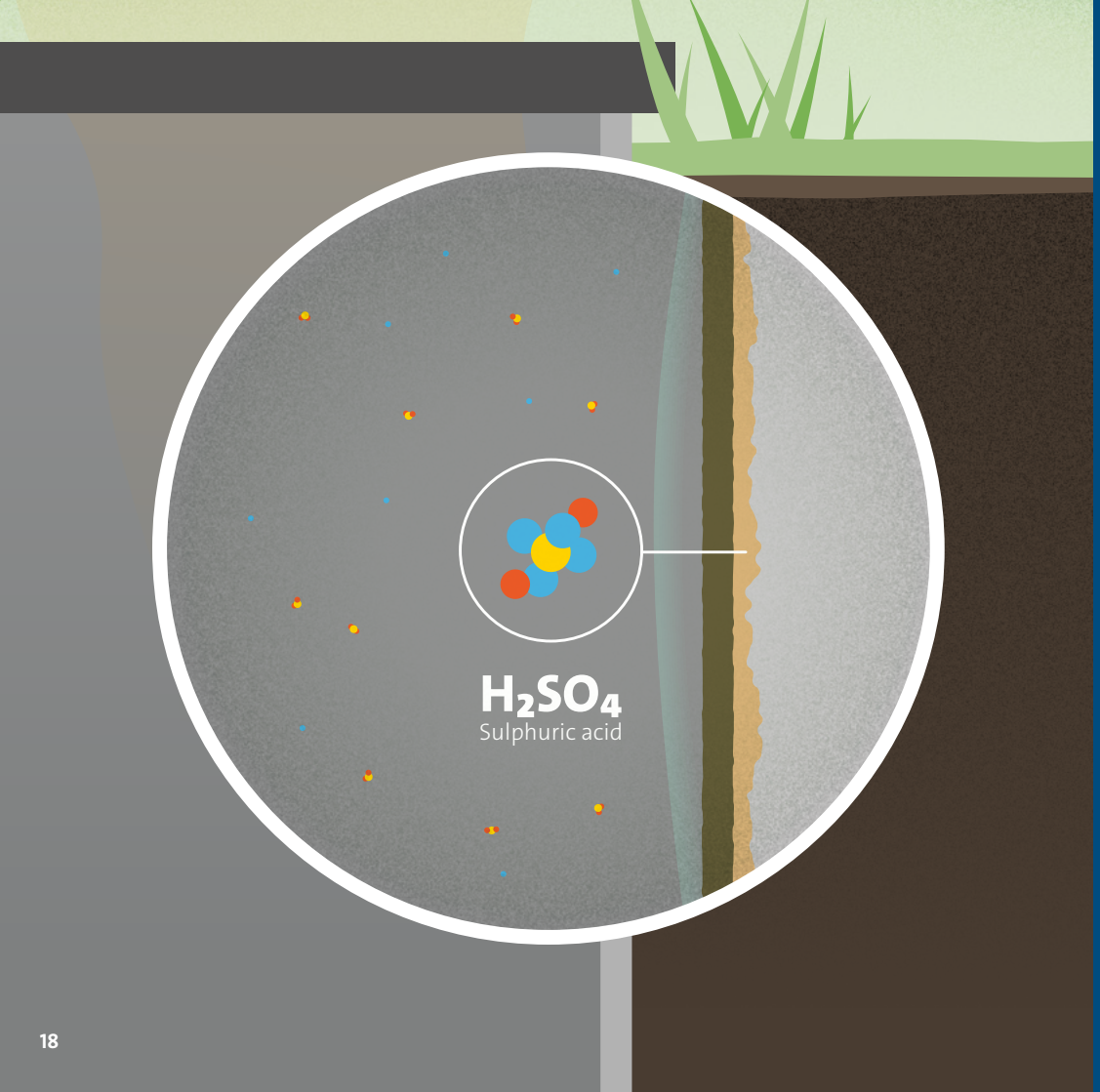
Variations in wastewater amounts over a 24-hour period are also an important factor. In any given system, the profile is decided by human activity with a morning peak, an afternoon peak and so on. Industry effluents to some degree can even out these patterns, but often the varying loads have a great impact on odour issues, as the varying retention times result in varying gas volumes in the manhole.

In pressurised systems, the odour will primarily occur when pumping to the manhole. Such operations, however, are brief and last only a matter of seconds or minutes.

During the first pumping phase, an immediate occurrence of evaporated gas is seen which gives off a powerful odour. When the pumped wastewater subsequently runs on into a gravitational system, a draught of air containing gas continues into the gravitational pipe, removing the odour from the manhole and reducing the evaporation of hydrogen sulphide.

With some pipelines, retention time is not the deciding factor for odour issues; instead, the presence of industrial wastewater in the system is important. Certain types of industrial wastewater (from food production, processing of organic material etc.) have a high potential for hydrogen sulphide production because of organic matter, high temperature, or increased evaporation at the source because of low pH value.

In short, odour issues vary over time and depend on the weather and other factors such as industrial effluents. Finding the source of hydrogen sulphide issues therefore requires closer examination of systems, retention times, and the types of wastewater received.



Corrosion



When the hydrogen sulphide has been released to the air, it can only disappear through chemical or biological oxidisation. This involves conversion into sulphur (a yellowish-white substance) or sulphate (dissolved in water).

On metal or electrically charged surfaces, sulphur is often converted into yellowish-white sulphur or black sulphur compounds. These deposits can short-circuit electrical components. Black or red ventilation grates, corroded padlocks and rusty lids on manholes are often seen in connection with hydrogen sulphide problems; these issues can lead to operational disruptions and other problems.

A thick biofilm is often seen in the well and on sewer pipe walls. This film contains special bacteria that live on converting hydrogen sulphide to sulphate. This is a major problem, as sulphate becomes sulphuric acid when mixed with water. The sulphuric acid is precipitated on the pipe surface.

If the surface is made of concrete, it is corroded to crumbling plaster. Damage can often be seen as a soft layer of plaster or exposed structural stones in the concrete. A shoulder is often formed at the passage between the wastewater and the air phase; this is a sign of hydrogen sulphide corrosion. The process described here can significantly shorten concrete pipe life. In some cases, wells and pipes can crumble in a very short time. In documented cases from Denmark, in just 18 months concrete pipes had corroded to such a degree that they had to be replaced.

It is important to remember that the biological process that produces sulphuric acid removes hydrogen sulphide from the sewer atmosphere. In many systems, corrosion is thus not only a process that breaks down the infrastructure; it also removes odour issues. The utility company may therefore encounter new issues at locations which have been renovated using sliplining, as the hydrogen sulphide is removed through corrosion to a smaller extent.

Gasphase logger

To know the extent of any given hydrogen sulphide issue, it is necessary to do measurements of gas levels using an approved logger.

Grundfos recommends handling complaints by installing gas loggers in order to uncover and document any problems.

Operating a logger for a period of time provides valuable information on the scale of the problem, and in fact on the source of the issue.

There are several sources of errors when logging hydrogen sulphide in the gasphase. However, they can be eliminated through careful logger installation.

Gasphase logger installation check list

- Hang the logger on a chain so that it can easily be retrieved for service.
- Hang the logger as close to the wastewater surface in the well as possible, taking care that the logger is not flooded at high levels of wastewater. This ensures correct measurements as it minimises the impact from absorption to surfaces and evaporation from the pumping well.
- Check that the signal from the logger gets through. If needed, install an antenna extension, and be careful when installing the antenna.
- Set the logging interval as low as possible (every 15 seconds) as all pump operations in the pumping well, which are typically very brief, must be included.



Strategies for handling hydrogen sulphide

Prevention

- **P** Prevention through addition of nitrate/ferric iron (oxidised).
- **P** Prevention of hydrogen sulphide formation by emptying the pipe using a compressor.
- **P** Removal of biofilm from the inner surface of the pipe using a cleaning pig.

Removal

- **R** Precipitation of produced hydrogen sulphide using iron (or a different metal).
- **R** Increase of pH value to more than 8.5 so that hydrogen sulphide is not released to the gasphase.
- **R** Oxidation of produced hydrogen sulphide using strong oxidants such as hydrogen peroxide, hypochlorite, ozone or pure oxygen.
- **R** Filter solutions at wells and ventilations which removes odours but not corrosion.
- **R** Sacrificial pipe.

The choice of solutions depends on system layout, implementation options, and what the utility company is used to. It is also important whether the objective is to remove odour or corrosion.

The next pages show a brief overview of how the various solutions work and a brief description of pros and cons.

It is important to consider the consequences of dosing when adding any type of chemical!

Consider the following:

- pH value
- Changes in wastewater composition
- Consequences for treatment plants
- Is the problem moved to somewhere else?

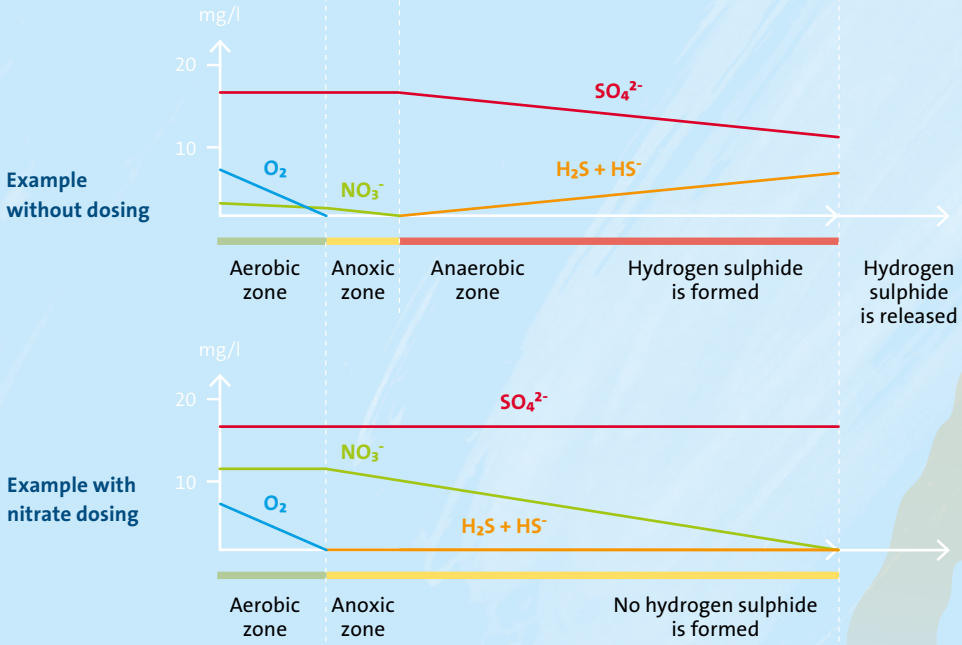


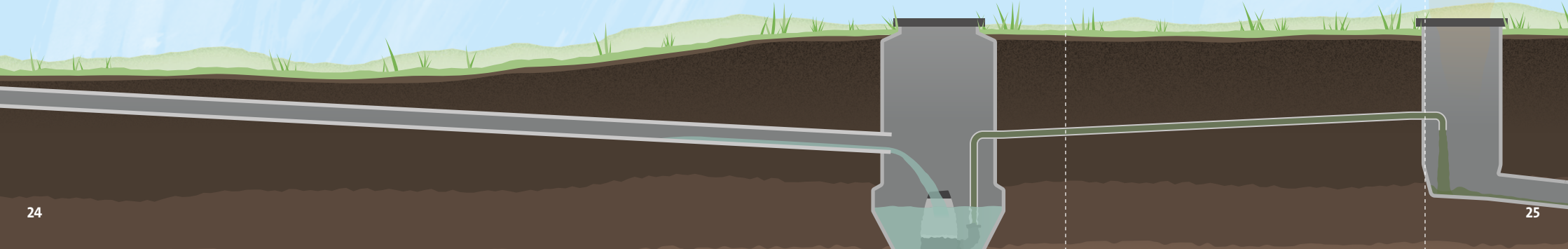
Prevention of hydrogen sulphide formation using nitrate or iron(III)

It is possible to prevent formation of hydrogen sulphide by dosing nitrate or oxidised iron.

The illustration on the opposite page shows various sewer process conditions. When dosing nitrate or iron(III), bacteria along the entire pipe up to the pumping well will feed off nitrate or iron(III) as well as organic matter, and no significant volumes of hydrogen sulphide will be formed.

Nitrate has one other great additional advantage: it prevents formation of other odorous substances such as sulphur compounds, fatty acids etc. One downside is that the processes that prevent hydrogen sulphide formation also remove some of the organic matter that is needed for biological nitrogen removal at the wastewater treatment plant at the end of the system.





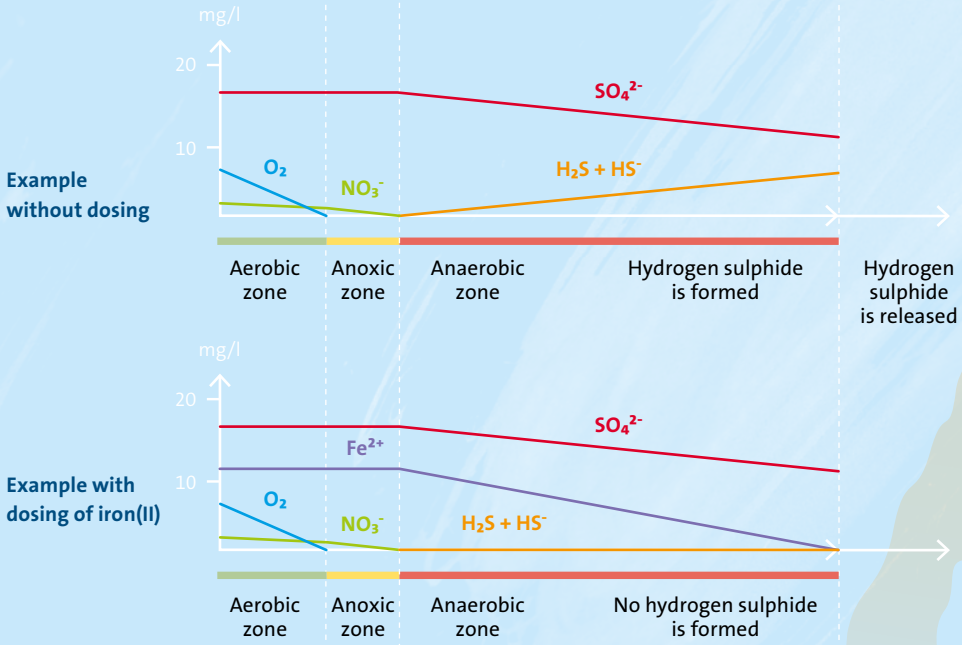
R Removal of hydrogen sulphide through chemical precipitation

Once hydrogen sulphide has been formed, there are different ways of removing it. If the hydrogen sulphide must be neutralised in the water-phase, one option is chemical precipitation. This can be achieved using iron(II), which may often be the most economical alternative.

In its liquid form, HS-, hydrogen sulphide binds to iron(II) and is precipitated as heavily soluble complexes. The result is less hydrogen sulphide in gaseous form, or none at all, when the pumped wastewater arrives at the manhole. The reason is that hydrogen sulphide in gaseous form is driven into liquid form because of the equilibrium between the two forms.

At low pH values (below 7), when most of the hydrogen sulphide is in gaseous form, the effect of the dosed iron(II) is reduced. The reasons for this are complex and not fully understood.

It is therefore very important that when dosing iron to abate hydrogen sulphide, the dosed amount and/or system pH is controlled effectively. The iron is delivered as an acidic solution and will therefore contribute to lowering wastewater pH value when dosing.



Hydrogen sulphide regulation through pH changes

The scale of a hydrogen sulphide problem in any given location is governed by several different factors.

As described earlier, the amount of hydrogen sulphide in the gasphase is determined by turbulence, temperature and pH value. It is possible to manage turbulence and particularly pH value to control degassing so that it only happens in selected locations.

Dosing a base raises the pH value which means that the hydrogen sulphide remains in the waterphase. For the utility company, it can be desirable to "move the problem" elsewhere where odour issues are acceptable, or a solution is possible.

If the pH value is raised to above 8.5, all of the hydrogen sulphide will be in the waterphase. Part of the hydrogen sulphide dissolved in water can be oxidised downstream in the system by adding oxygen in the gravitational part of the sewer network. However, the utility company must be aware that at the entry to the wastewater treatment plant, it will be necessary to lower the pH to achieve correct treatment processes. There is thus a significant potential for major hydrogen sulphide issues here.

In connection with biological treatment of formed hydrogen sulphide, chimney solutions or sacrificial pipes, another option could be to add small amounts of acid to ensure sufficient evaporation to achieve the optimal effect from the chosen solution.

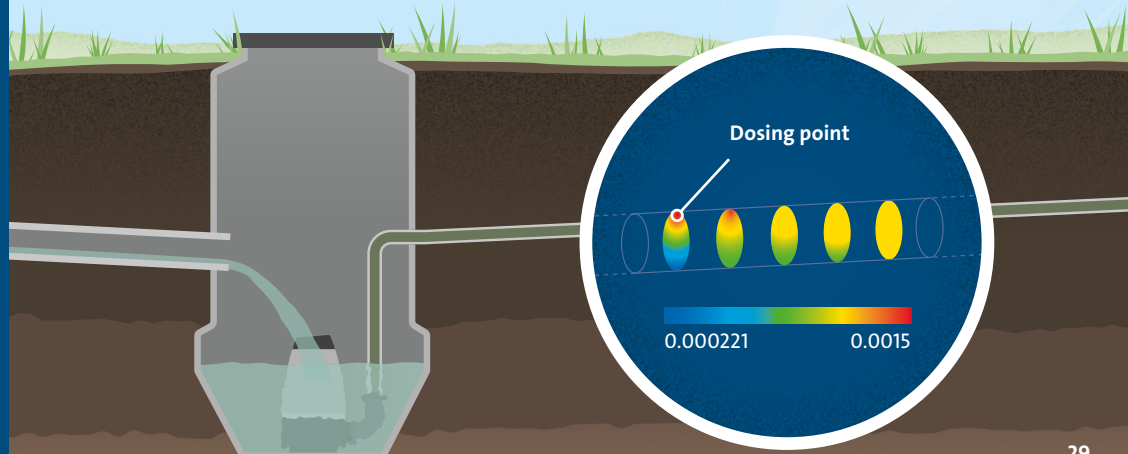
It should be added that shock dosing of lye can also prevent the formation of hydrogen sulphide. A sudden increase in pH value will kill the biofilm on the inner pipe walls, preventing the formation of hydrogen sulphide. This method will not be covered further in this booklet.

Correct dosing of chemicals

Correct dosing is vital in order to achieve optimum effect from chemicals, no matter which chemical is used for removal or prevention. Grundfos recommends dosing directly into the pressurised pipe downstream of the pump while it is running. This demands strict requirements on the dosing pump and may require protecting the pipe itself from the effects of the dosed chemicals.

The method described ensures that the chemical is completely mixed into the wastewater, achieving the optimum effect.

Using a CFD model, Grundfos has calculated that full mixing of the dosed chemical is ensured at a distance of approximately twice the pipe diameter from the dosing point when the pump is running.



Other methods

There are a number of other solutions for managing the formed hydrogen sulphide.

(R) Oxidation using strong oxidants

A number of strong oxidants, including hydrogen peroxide, hypochlorite, ozone or pure oxygen, make it possible to convert hydrogen sulphide to sulphur or sulphuric acid in the waterphase.

It is cumbersome and costly to produce ozone and pure oxygen onsite, as it requires large installations and considerable energy costs. By contrast, using hydrogen peroxide and hypochlorite is relatively economical. These methods are particularly suitable when major problems need to be solved with great process speed, typically in connection with industrial effluents. The solution removes odour issues as well as corrosion.

(P) Compressor solutions using atmospheric air

In case of very long retention times in a pipe, another option is to use a compressor to pump atmospheric air into the pressurised pipe along with the wastewater, possibly controlled by a timer. This adds atmospheric air containing oxygen to the biofilm, and retention time is shortened because of the increased volume of added air. Both of these factors can minimise hydrogen sulphide formation. One drawback is the formation of air pockets in the system which disturb pump operation and overall hydraulics.

(R) Biological removal using air filters

During air purification using biological filters, air containing hydrogen sulphide passes through a biological filter with bacteria growing on a moist medium (bark chips, Leca® pellets or similar) that convert the odorous substances to odourless substances. These filters are relatively costly to install but are very economical and robust in operation. One important challenge is that a major part of the formed hydrogen sulphide must be in gaseous form to be removable by the biological component of such a solution.

(R) Sacrificial pipe

A sacrificial pipe is a concrete pipe intended to corrode. In this solution, the conversion of hydrogen sulphide to sulphuric acid happens in a preselected pipeline. The odorous hydrogen sulphide is removed from the air, and corrosion occurs in a controlled location. If there is sufficient oxygen in the air in the pipe, sulphur will also be formed. The hydrogen sulphide must be in gaseous form in order to be converted into sulphuric acid in the biofilm on the walls of the sacrificial pipe. The pipe must also be placed in a location where periodical odour issues are acceptable.

(R) Encapsulation of formed gas

Encapsulation refers to any solution where the manhole is sealed using rubber flanges, or where a carbon filter is installed in order to remove hydrogen sulphide from the exit air. These can be easy and quick solutions to a problem. They solve odour issues quite effectively during the initial period, but the utility company must be prepared to frequently service and/or replace the filters. This solution does not prevent corrosion.

An overview of the pros and cons of each method is shown on the following page.

Overview of various methods for the prevention or removal of hydrogen sulphide

The table below shows suggested pros and cons of various methods of preventing and removing hydrogen sulphide. The table does not provide exhaustive information on all cases, as utility companies vary greatly in their approach to daily tasks, the prices of chemicals, etc. The table should be regarded as a starting point for a peer discussion when choosing a solution.

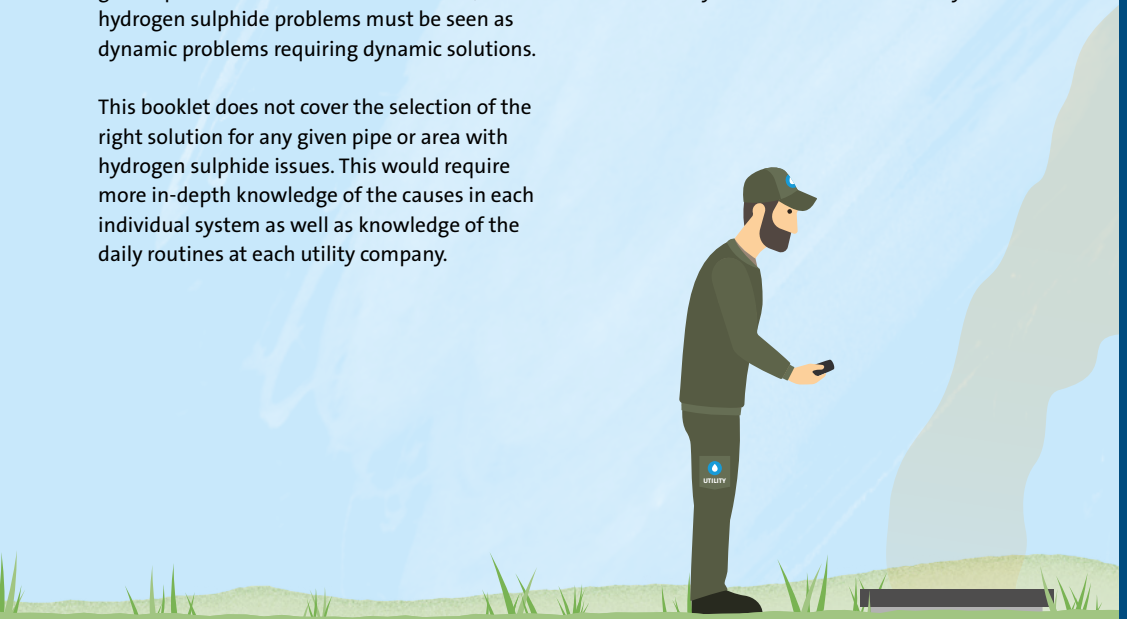
	Prevention through pH regulation	Prevention using a cleaning pig	Prevention through adding air	Prevention using nitrate	Removal through chemical precipitation	Removal through biological air cleaning
Pros	• Effective	• Effective • Removes other pipe deposits as well	• Simple to implement • No chemicals at pumping stations	• Simple to implement • Prevents formation of H_2S • Effective towards other odorous substances than H_2S	• Simple to implement • Adding iron can improve phosphorus precipitation at the WWTP	• Effective towards other odorous substances than H_2S
Cons	• May result in moving the problem in the system if pH value drops later • As biofilm rebuilds, dosing must be repeated • May be problematic in relation to the WWTP processes • Health and safety issues	• Involves risk of blocking • Must be repeated often, sometimes weekly	• Hydraulic problems because of air pockets • Easily degradable organic matter is degraded • May result in growth of other bacteria and increase biofilm thickness/pipe roughness	• Easily degradable organic matter is degraded • May result in growth of other bacteria and increase biofilm thickness/pipe roughness	• Not effective at low pH values • Lowers wastewater pH value • Produces chemical sludge	• Does not prevent corrosion • Often requires a large installation footprint

Do you need help?

As indicated by several explanations and illustrations in the presentation of hydrogen sulphide issues found in this booklet, all hydrogen sulphide problems must be seen as dynamic problems requiring dynamic solutions.

This booklet does not cover the selection of the right solution for any given pipe or area with hydrogen sulphide issues. This would require more in-depth knowledge of the causes in each individual system as well as knowledge of the daily routines at each utility company.

At Grundfos, we look forward to discussing your hydrogen sulphide issue. Contact Grundfos, and we will assist you to the best of our ability.



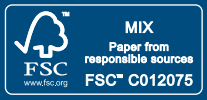
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