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Technical Information 5.01

Hydrogen sulfide elimination from biogas

The sulfide-binding properties of iron salts have been put to technical use in waste water and sewage sludge treatment for a long time. The use of iron salts for sulfide precipitation in the field of digester gas desulfurization and for hydrogen sulfide removal from waste water collectors has proven to be particularly effective in this context [1, 2]. This technology has likewise been used successfully for many years in the elimination of hydrogen sulfide in biogas facilities.

Fig. 1: Green gas facility in Rathenow, Brandenburg [3]

1. The hydrogen sulfide problem in biogas facilities

Anaerobic microbial degradation of organic substances in biogas facilities produces not only the principal components methane (CH_4) and carbon dioxide (CO_2), but also hydrogen sulfide (H_2S). Among other things, the hydrogen sulfide concentration in the biogas is dependent on the substrates used, and can range from a few ppm in facilities processing renewable resources to several thousand ppm when fermenting liquid manure, biological waste and food remains [4].

While most of the secondary components in the biogas cause no trouble, the hydrogen sulfide it contains gives rise to a variety of problems.

Hydrogen sulfide imposes particular demands as regards occupational health and safety. Hydrogen sulfide is an extremely toxic gas. The inhalation of relatively large quantities leads to "internal suffocation", as with hydrogen cyanide. Air containing just 350 ppm H_2S has a life-threatening effect following lengthy exposure, and hydrogen sulfide can no longer be perceived as an odour at concentrations > 500 ppm. The effect of concentrations $> 1{,}000$ ppm is lethal within just a few seconds.

In the same way as **hydrogen sulfide has a cytotoxic effect** on the human nervous system, concentrations upwards of 50 mg/l dissolved hydrogen sulfide in the fermentation substrate have a toxic effect and inhibit the methane-forming bacteria [5]. In addition, high hydrogen sulfide concentrations can lead to a situation where certain microorganisms reduce sulfur energetically more efficiently than methane-forming bacteria can reduce CO_2 to CH_4. Upwards of a content of approximately 2% dissolved hydrogen sulfide, this results in a decline in the methane concentration in the biogas [6].

Moreover, **hydrogen sulfide combines with trace elements to form poorly soluble metal sulfides** that are hardly available to the methane-forming bacteria and thus lead to a trace element deficiency and a reduced degradation rate.

Hydrogen sulfide is the main cause of corrosion of the structures and materials of a biogas facility. The hydrogen sulfide component is oxidised during combustion, leading to the formation of acidic sulfur dioxide (SO_2):

$$2\,H_2S + 3\,O_2 \longrightarrow 2\,SO_2 + 2\,H_2O$$

This is a highly corrosive gas. Sulfur dioxide causes rapid overacidification of the engine oils during combustion in the gas engine. This results in increased wear, frequent bearing damage, higher consumable costs and longer plant downtimes.

Moreover, being a catalyst poison, hydrogen sulfide leads to the **inactivation of oxidation catalysts** used to comply with the formaldehyde limit specified by the German Technical Instructions on Air Quality Control (TA Luft). Instead of the formaldehyde, the sulfur contained in the combustion offgas is bound in the catalyst, thus blocking the reactions that should actually take place.

If biogas is to be upgraded for **feeding into the natural gas grid**, not only must the methane concentration be increased and the carbon dioxide eliminated, but also, and in particular, the hydrogen sulfide has to be removed from the gas.

According to DVGW* Code of Practice 260, the hydrogen sulfide concentration must be limited to values < 5 mg/Nm^3 gas.

For the technical and microbiological reasons described above, biogas must be desulfurized – preferably in the fermenter by binding sulfides.

2. Biogas desulfurization

2.1 Rough desulfurization

2.1.1 Internal biological desulfurization by addition of air

One common method for desulfurizing biogas is biological oxidation by atmospheric oxygen. To this end, air is injected into the gas space of the fermenter above the surface of the liquid, or into the secondary fermenter. A quantity of generally 8 to 12% by volume fresh air is added to the generated biogas stream by means of a pump [7]. As a result of the atmospheric oxygen, hydrogen sulfide is oxidised into elemental sulfur by microorganisms that grow on the surfaces in the gas space. This sulfur accumulates on the surfaces and ultimately passes back into the substrate, where it is partly converted into hydrogen sulfide again [8], the remainder being discharged from the fermenter with the fermentation residue.

$$2\,H_2S + O_2 \longrightarrow 2\,S + 2\,H_2O$$

The efficiency of this process is limited, however, because the air supply cannot be exactly adapted to the quantity of gas produced and the prevailing hydrogen sulfide concentration.

One serious drawback of this method is the possibility of sulfuric acid being formed. In the presence of atmospheric oxygen, sulfur bacteria can colonise all the surfaces in the gas space, oxidising the hydrogen sulfide produced into sulfuric acid. This biogenic sulfuric acid likewise leads to massive corrosion damage on all concrete and metallic materials.

In addition, the following points have to be taken into account in connection with this method:

- The method is not suitable for plants for upgrading biogas to natural-gas quality, since excessive quantities of oxygen and inert gas are introduced into the biogas, and these accompanying substances have to be removed from the biogas again.
- The methane content of the biogas is significantly reduced, resulting in declining performance of the units.
- The demands of CHP (combined heat and power) station manufacturers for generally 100 to 500 ppm H_2S can not reliably be complied with, and warranty claims are voided.
- The gas quality is neither reliable, nor constant.

* *German Association of the Gas and Water Trade*

Fig. 2: Possible points of addition for iron salts – mixing tank (left) and straight into the fermenter (right)

2.1.2 External biological desulfurization

Another possibility for biological desulfurization is the use of desulfurization columns outside the fermenter. This method offers greater operational reliability than internal biological desulfurization, because the air supply for desulfurization can be adjusted more accurately.

For external biological desulfurization to operate optimally, the microorganisms have to be supplied with nutrients and trace elements, and a washing solution temperature of 28 °C to 32 °C has to be maintained. This can lead to problems, especially in winter when the outside temperatures are low. There is moreover a risk of the desulfurization column being congested by the oxidation product sulfur.

As a result of atmospheric oxygen being added, this method is again unsuitable for use in plants for upgrading biogas to natural-gas quality.

2.1.3 Iron salts

In this process, the iron salts are added to the fermentation substrate via the feed slurry reservoir, the solids feeder, or directly into the fermenter.

In contrast to downstream gas purification, the hydrogen sulfide is already retained in the fermenter when iron salts are added.

The hydrogen sulfide formed is directly bound in the form of poorly soluble iron sulfide while still in the liquid phase of the fermenter, and removed from the system with the discharged solids.

$$Fe^{2+} + S^{2-} \longrightarrow FeS\downarrow$$
$$2\,Fe^{3+} + 3\,S^{2-} \longrightarrow 2\,FeS\downarrow + S$$

When the fermentation substrate is spread, the iron sulfide it contains is readily oxidised by atmospheric oxygen, forming soluble sulfate that is directly available to plants.

Both divalent and trivalent iron salts are essentially suitable for precipitating sulfides. Addition of ferrous chloride solution and of iron hydroxide have emerged as the two most common processes.

The use of KRONOFLOC ferrous chloride solution has proven to be a straightforward, effective and inexpensive method in practice.

The following procedure has demonstrated its worth in practice for determining the added quantities necessary for reliable desulfurization of a biogas facility.

1. The added quantities can be roughly estimated on the basis of the following factors:

- Initial hydrogen sulfide concentration in the raw biogas
- Target hydrogen sulfide concentration
- Daily biogas production volume.

2. Precise determination and optimization of the added quantities is then performed specifically for each biogas facility in an on-site plant trial.

The added quantity is usually 100 to 220 $g_{Iron}/t_{Substrate}$, although it is very much dependent on the substrate used.

The method described permits selective hydrogen sulfide removal with good elimination rates and can easily be integrated in the existing process without requiring additional desulfurization units.

2.2 Fine desulfurization with activated carbon

Very low hydrogen sulfide concentrations in the raw gas are required in view of the upgrading of biogas to biomethane and the feeding of the latter into the natural-gas grid, and also to protect oxidation catalysts for offgas purification. These H_2S concentrations can usually only be achieved by fine desulfurization. The most commonly practised method for fine desulfurization is the use of activated carbon filters, where the hydrogen sulfide is bound to the activated carbon surface by adsorption and subsequently oxidized catalytically.

The activated carbon is constantly fed with biogas during operation, meaning that its loading capacity is eventually reached and the activated carbon filter needs to be replaced. The loaded activated carbon has to be either disposed of or regenerated in a complex process.

In many cases, a combination where rough desulfurization by means of iron salts is followed by fine desulfurization can be economical for **increasing the service life of activated carbon filters** and significantly **reducing the** high **operating costs**.

3. All the benefits at a glance

Just as the problems caused by hydrogen sulfide are numerous, so are the applications for iron salts in biogas generation.

The following applications have established themselves to date:

- Desulfurization to **protect the engines**, in order to comply with specified hydrogen sulfide limits. The service life of the engine oils can also be prolonged.
- **Protection of the oxidation catalysts** for offgas purification.
- **Support of internal and external biological desulfurization** by base-load dosing in winter or in the event of load peaks.
- The use of iron salts is the only method permitting the **binding of H_2S directly in the fermenter**. This has a positive effect on the microbiological processes taking place and can lead to an increase in the methane concentration.
- Thanks to the high reactivity of iron salts with sulfides (smallest solubility product), trace elements remain available in the liquid phase, as long as free Fe ions are present. The **trace elements** thus continue to be **available to methane-forming bacteria** and are not extracted from the system by the formation of metal sulfides.
- The **combination of activated carbon and iron salts** prolongs the service life of the activated carbon and reduces the operating costs.
- If biogas is to be upgraded to natural-gas quality, iron salts are a simple and reliable solution for rough desulfurization in terms of process engineering. No additional oxygen or inert gas is added, meaning that this method can be seen as an optimum complement to fine desulfurization.

4. Concluding remark

Hydrogen sulfide is a dangerous and destructive component of biogas that has an equally negative impact on man, the environment, structures and materials. The use of renewable energies and of sulfur-containing residues in biogas facilities gives rise to serious problems, meaning that measures for eliminating hydrogen sulfide are of great importance. In this respect, iron salts make a decisive contribution to the optimum operation of a biogas facility

References

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