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Powdery ferric compounds for biogas process desulphurisation

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Desulphurisation strategies are essential for biogas plants, since high hydrogen sulphide concentrations significantly reduce the biogas quality. Internal chemical desulphurisation using ferric compounds provides advantages regarding substrate-dependent dosage as well as prevention of process imbalance and corrosive damages within gas-transporting components of the biogas plant. Up to now, the usage of ferric compounds is based only on the iron content, whereas chemical and physical properties are not taken into consideration. To cope with this problem, powdery ferric compounds of different chemical composition and grain size were compared by studying their influence in dependence of process parameters like hydrodynamics or hydraulic retention time using laboratory scale biogas reactors. The presented results enable specific recommendations regarding which type of ferric compound is advantageous to provide an optimal desulphurisation effect depending on the plant specific process parameters. The desulphurisation of iron(III) hydroxide compounds, for example, was significantly better in comparison to pure iron(III) oxide at a low retention time of 8 days. Furthermore, effects on process stability and methane content were observed.

Keywords
desulphurisation, biogas, ferric hydroxide, ferric oxide, hydrogen sulphide

Biogas, which is produced during anaerobic digestion of organic compounds in biogas reactors, contains up to 2 % hydrogen sulphide besides the required methane (FNR 2013). Hydrogen sulphide sources occurring within biogas process are organic bound sulphur (sulfanyl-groups of proteins) and inorganic sulphur represented by sulphate (Wagner 1979). A high amount of hydrogen sulphide does not only lead to corrosion of gas-bearing plant components, cogeneration units and central heating boilers (FNR 2013, Mollekopf et al. 2006), it directly inhibits the biogas process due to its toxic effect on process relevant microorganisms (Kroiss und Wabnegg 1982, Verink 1988). Furthermore, the precipitation of essential trace elements caused by either sulphanide (HS^-) or sulphide (S^{2-}) leads to an indirect process inhibition (Kroiss und Wabnegg 1982). Since high amounts of hydrogen sulphide significantly impact the biogas quality, desulphurisation strategies are essential for every biogas plant.

The most common desulphurisation treatment in agricultural biogas plants is the introduction of oxygen either via internal dosage utilizing the fermenter cover or externally via separate fermenter components. Oxygen supply leads to oxidation of hydrogen sulphide bound sulphur into elemental sulphur by chemo- and photoautotrophic bacteria. Possible disadvantages of this treatment are process inhibition, less gas quality and the formation of explosive gas mixtures due to the introduction of oxygen, as well as the low regulation capacity (Mollekopf et al. 2006). Desulphurisation via introduction of oxygen is often supported by an internal chemical desulphurisation (Otto and Güssbacher

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2013). In contrast to desulphurisation via oxygen supply, this treatment allows a substrate dependent dosage. Moreover, oxygen-caused process inhibition and corrosion of gas-bearing plant components can be avoided (Mollekopf et al. 2006).

Beside iron salts like ferrous chloride, which are applied to biogas plants in form of a strongly acidic, aqueous solution (Mollekopf et al. 2006), iron(III) hydroxide and iron(III) oxide are applied as powder. Currently an iron content based dosage without any regard to chemical and physical properties of the ferric compounds is used. The results presented in this article, however, show that especially these parameters strongly influence the desulphurisation. Furthermore, effects on process stability and methane content were observed. The specific application of ferric compounds finally aims for an optimum desulphurisation under the existing process parameters using the appropriate ferric compound and the appropriate dosage. Thereby, a costly downstream desulphurisation of biogas caused by underdosage or additional costs caused by overdosage of ferric compounds could be avoided. In this context, several powdery ferric compounds of different chemical composition and grain size were compared in the presented work regarding their desulphurisation effect in dependence of process parameters like hydrodynamics or hydraulic retention time in laboratory scale biogas reactors.

Grain stillage, a by-product of the bioethanol production, was used as substrate for the biogas reactors. This substrate is rich in proteins and sulphate residues from starch-hydrolysis via sulphuric acid addition, which is typically used during bioethanol production (Gustavsson et al. 2013). Therefore high concentrations of hydrogen sulphide are expected to evolve during fermentation of grain stillage, which makes it a useful substrate to study desulphurisation. Because bioethanol production generates high amounts of the by-product grain stillage in a relatively short period of time (5–10 L stillage per L bioethanol, Murphy and Power 2008), fermentation techniques using high organic loading rates (up to 10 g L^{-1} d^{-1}) at low hydraulic retention times (< 10 d) are required. Schmidt et al. (2014) showed a stable fermentation of grain stillage in continuous stirred tank reactors at hydraulic retention times of 6 days. The high-performance bacterial strains adapted during these experiments were used as inoculum for fermentation of stillage within the presented study, which enables a performance at low hydraulic retention times.

Material and Methods

The ferric compounds listed in Table 1 were compared regarding their desulphurisation efficiency in biogas reactors. Therefore, 5 semi-continuously fed 10 L reactors were operated with ferric compounds differing in their chemical composition and grain size. The reactors were stirred continuously at 80 min^{-1}. Substrate addition was performed every 30 min via peristaltic pumps. The lack of an automatic level drain required the daily removal of an inflow equivalent volume of effluent. The following process analyses were performed twice a week: dry matter (DM) and organic dry matter (ODM) (Strach 2013a), total amount of volatile fatty acids (VFA) according to Kapp and VFA/TAC according to FAL (Strach and Dittrich-Zechendorf 2013), composition of VFA via gas chromatography (GC) (Apelt 2013) and the total ammonia nitrogen (Strach 2013b). PH value and biogas production rate were measured daily. Biogas composition was analysed three times a day using an AwiFLEX measuring system (Awite Bioenergie GmbH, Langenbach, Germany).

Table 1: Ferric compounds used for experiments

Product	Chemical composition	Grain size in µm < 63	63–250	250–500	> 500	Iron content[2)] in g kg DM^{-1}	Calcium content[2)] in g kg DM^{-1}
Type 1	ferric hydroxide	99.61%	0.10%	0.09%	0.20%	338	127
Type 2	ferric hydroxide	13%	62%	21%	3%	352	113
Type 3	ferric hydroxide	1%	6%	69%	24%	362	105
Type 4	ferric hydroxide, ferric oxide	13%	62%	21%	3%	450	88
Type 5[1)]	ferric oxide	13%	62%	21%	3%	629	0.4

[1)] Type 5 was used only within the first experiment (Figure 1, Table 2).

[2)] Measured via ICP-OES (iCAP 6200 ThermoFisher) after nitric acid digestion.

The reactors were run at an organic loading rate of 8 kg_{ODM} m^{-3} d^{-1} and a hydraulic retention time of 8 d. The temperature was set at 38–41 °C via thermostat. Proceeding from an organic loading rate of 5 kg_{ODM} m^{-3} d^{-1} during start-up a daily increase of 0,2 was carried out using 1–2 g $NaHCO_3$. Simulated thin stillage (liquid phase of resuspended dried stillage pellets; Protigrain, Crop Energies, Zeitz) was used as substrate. The stillage pellets were dissolved in water at a weight ratio of 1 : 3.75 and separated using an oscillating sieve (0.4 mm mesh size) after mixing for 24 h. Depending on the substrate batch, the following values were determined: DM = 10–16 %, ODM = 89–98 $\%_{DM}$ and, per kg of DM, 56 g crude ash, 341 g crude protein, 86 g crude lipids, 100 g crude fiber, 418 g nitrogen free extractives for the first substrate batch (day 1 to 443 of the experiment), 60 g crude ash, 315 g crude protein, 76 g crude lipids, 107 g crude fiber, 441 g nitrogen free extractives for the second substrate batch (day 444 to 598 of the experiment). The substrate was supplemented with a trace element solution: 140 mg $NiCl_2 \cdot 6\ H_2O$, 35 mg $CoCl_2 \cdot 6\ H_2O$, 22 mg $Na_2MoO_4 \cdot 2\ H_2O$, 13 mg $(NH_4)_6H_2W_{12}O_{40} \cdot H_2O$ per kg DM.

During the start-up of the experiment 0.06 g ferric compound Type 1 per g DM of substrate were added to all reactors. Afterwards the reactors were shifted to one of the five examined ferric compounds applying a dosage according to their iron content (1.86 g Fe per day). The dosage of the ferric compound and several process parameters, for instance stirring performance and hydraulic retention time, were varied within the experiments. Occurring process instabilities were balanced via addition of $NaHCO_3$ in order to stabilise the pH value above 7.

Results and Discussion

The influence of the chemical composition

Comparing the different ferric compounds (Table 1), it was observed that especially the chemical composition had an influence on desulphurisation (Figure 1). The desulphurisation effect of the ferric hydroxide compounds (Type 1–3) turned out to be 50-fold better at a hydraulic retention time of 8 days compared to Type 5. Type 5, the pure ferric oxide compound, showed the lowest desulphurisation effect. The lower desulphurisation performance of ferric oxide containing compounds probably resulted from a lower chemical reactivity of ferric oxides in comparison to ferric hydroxides.

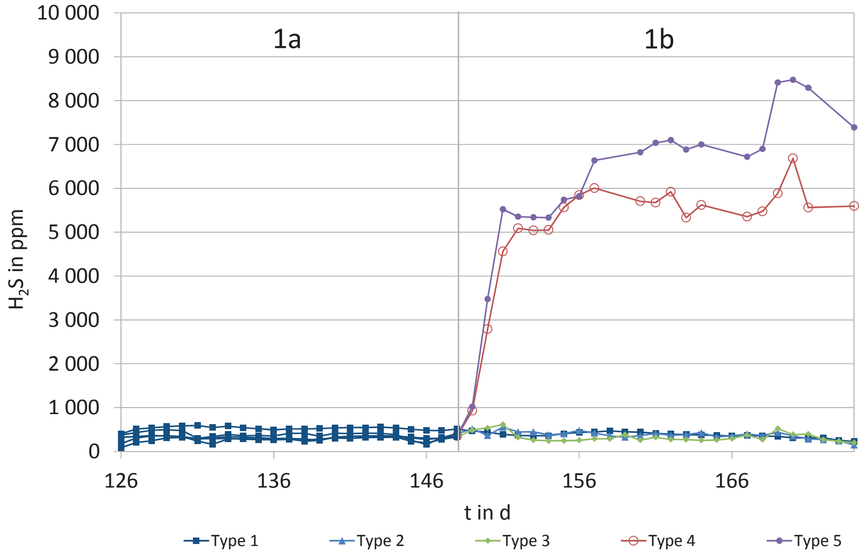

Figure 1: Hydrogen sulphide (H_2S) concentration of the reactors during start-up under addition of Type 1 (1a) and after change to different types of ferric additives (1b)

A higher chemical reactivity of ferric hydroxide compared to pure ferric oxide compounds was previously shown by Rahn et al. based on batch experiments using an experimental set-up for simulating anaerobic fermentation processes (Rahn et al. 2015a). Thereby the desulphurisation performance in anaerobic waste water samples was determined by photometrical measurement of the black staining caused by iron sulphide formation. In addition, the laboratory scale biogas reactors used within the presented study provided the modification of process parameters like the hydraulic retention time due to their quasi-continuous experimental set-up. By extending the hydraulic retention time of the substrate within the reactor from 8 to 11 d, the chemical reaction time was extended accordingly. This caused an improvement of the ferric oxide containing compounds regarding their desulphurisation efficiency, whereas no further improvement was detected for the ferric hydroxide compounds. Experiments with lower hydraulic retention times in turn showed a better desulphurisation performance of the more chemically reactive ferric hydroxide compared to ferric oxide containing compounds (Figure 2).

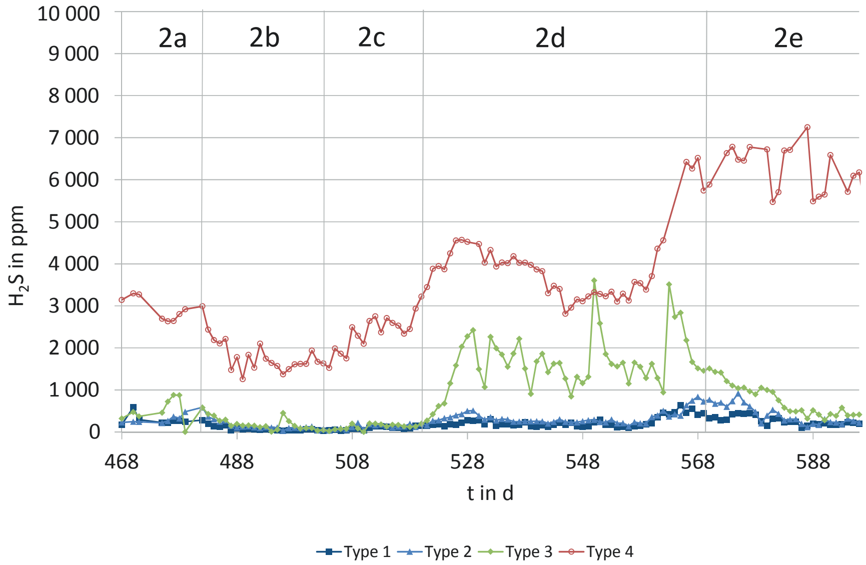

Figure 2: Hydrogen sulphide (H_2S) concentration of the reactors at a hydraulic retention time of: 8 days (2a), 6.5 days (2b), 5 days (2c), 3.5 days (2d) and 2 days (2e)

The influence of the grain size

While the tested ferric hydroxide compounds showed no differences in their desulphurisation performance when applied in high dosages (Figure 1), a grain size dependent difference was detected at lower dosages. A 3-fold reduction of the ferric iron dosage resulted in a better desulphurisation efficiency of the fine-grained ferric hydroxide compounds, Type 1 and Type 2, compared to the coarse-grained Type 3 (Figure 3). The higher chemical reactivity of fine-grained compounds could be explained by an increasing particle surface with decreasing grain size.

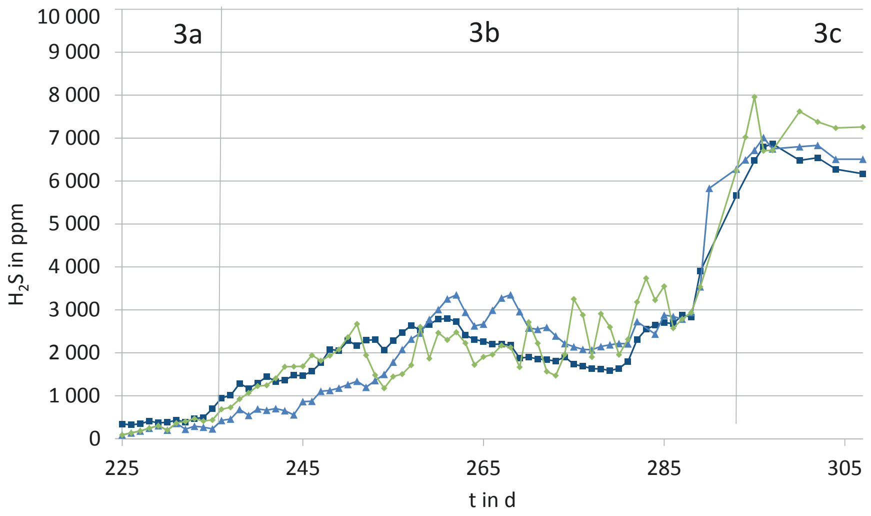

Figure 3: Hydrogen sulphide (H_2S) concentration of the reactors at different dosages of ferric compound (per g dry matter: 1.86 g iron (3a), 1.24 g iron (3c) and 0.62 g iron (3c))

A correlation between grain size and desulphurisation capacity was also detected by reducing the stirring performance from 80 to 40 rpm. A less mixed digestate led to an increased deposition of bigger particles and consequently to both a decreased availability of the ferric compound and a decreased desulphurisation efficiency within the reactor. The coarse-grained ferric hydroxide compound, Type 3, showed the lowest desulphurisation performance, which turned out to be 10-fold decreased (Figure 4). An increasing hydrogen sulphide content in Type 1 and 2 treated reactors, observed after reducing the stirring performance, may be interpreted as response to the disturbance of the process. After a short time of adapting the microbial community, the process stability was restored within these reactors. The hydrogen sulphide content decreased to its initial value after just one hydraulic retention time (8 d). The same effect occurred at lower hydraulic retention times. The viscosity of the digestate might be reduced by water addition in course of lowering the hydraulic retention time. Hence, an increased deposition of bigger particles reduced their availability within the reactor. Thus, the desulphurisation efficiency decreased with increasing grain size under these experimental conditions. Reducing the hydraulic retention time to 3.5 d resulted in a 10-fold decreased desulphurisation efficiency within the reactor treated with Type 3, the coarse-grained ferric hydroxide.

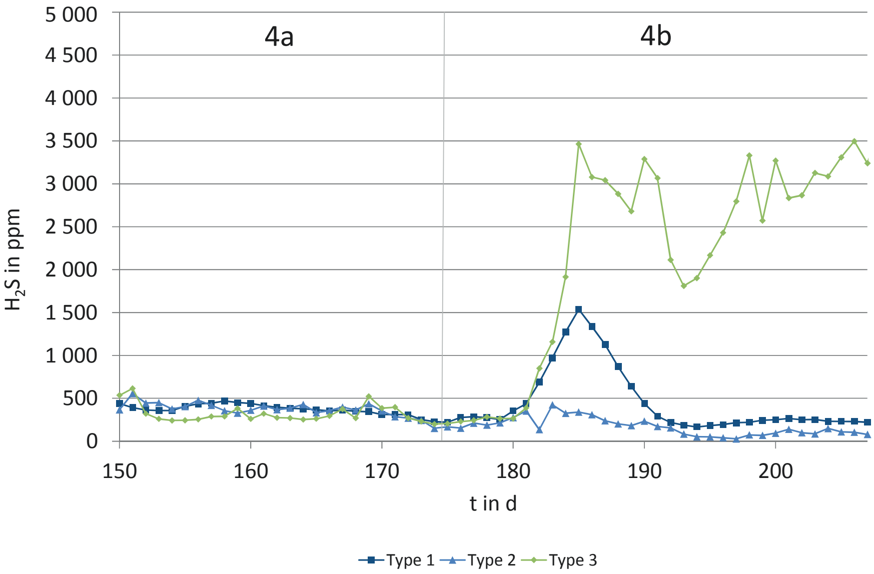

Figure 4: Hydrogen sulphide (H_2S) concentration of the reactors while stirring at 80 rpm (4a) and 40 rpm (4b)

The influence of ferric compounds on process stability and biogas composition

Besides the ferric compound mediated desulphurisation of the biogas reactors, an influence on the methane content was observed at constant levels of specific biogas production. Biogas from the ferric oxide (Type 5) treated reactor contained in average 1 % less methane (Table 2). This might be caused by inhibiting effects of a higher hydrogen sulphide content within this reactor. Although a direct toxic effect on process involved microorganisms is only expected at hydrogen sulphide concentrations of 13,000 ppm and higher (Kroiss and Wabnegg 1982), an indirect inhibition due to precipitation of trace elements appears already at lower concentrations. Hence, process inhibition might occur due to limitation of trace elements which are essential for enzymes and thus for microbial activity (Gustavsson et al. 2013, Schmidt et al. 2014).

Table 2: Specific gas production, methane and hydrogen sulphide content of the reactors

	Type 1–3 (day 150–174)	**Type 5 (day150–174)**	**Without addition of iron (day 234–258)**
Specific gas production [1)] in mL g ODM^{-1}	620 ± 46	630 ± 46	600 ± 40
Methane content [1)] in %	57 ± 0.3	56 ± 0.3	55 ± 0.2
Hydrogen sulphide content in ppm	380 ± 84	6,000 ± 1,047	10,270 ± 682

[1)] A nested ANOVA under a significance level of 5 % was performed using SPSS Statistics (IBM Germany GmbH, Ehningen). Resulting from that, the methane content showed a significant difference ($p = 0.007 < 0.05$), while the specific gas production did not show such difference ($p = 0.781 > 0.05$).

Without supplementation of ferric compounds the hydrogen sulphide content rose up to a maximum of 11,000 to 12,000 ppm due to the relatively high sulphate content of the stillage which was used as substrate. In that case methane production was reduced by 2 % (Table 2). Increased competition for hydrogen between sulphate reducing bacteria and methanogenic archaea at higher hydrogen sulphide concentrations might lead to limitations of methane production (Braun 1982).

Furthermore, experiments with reduced hydraulic retention times showed an influence of the ferric compounds on process stability. Reducing the hydraulic retention time to 3.5 d resulted in a decrease of the pH value and in an increase of the VFA content. This effect was comparatively low within Type 1 and 2 treated reactors. In both cases the amount of VFA remained below 1 g L^{-1}. The reactor treated with the coarse-grained ferric hydroxide, Type 3, rose up to a VFA content of about 1.5 g L^{-1}. The largest increase showed the reactor treated with ferric oxide containing compound, Type 4. In this case VFA values up to 6 g L^{-1} were measured (Figure 5).

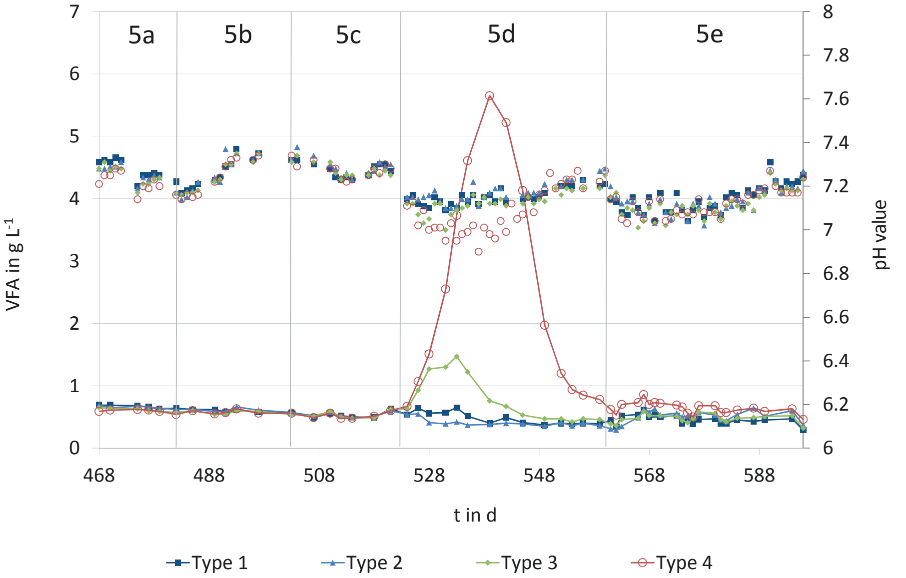

Figure 5: The total amount of volatile fatty acids (VFA) and pH value of the reactors at 8 days (5a), 6.5 days (5b), 5 days (5c), 3.5 days (5d) and 2 days (5e) hydraulic retention time

In summary, higher process stability was detected for reactors with better desulphurisation performance resulting from the ferric compounds applied. Reduced process stability is probably caused by increased hydrogen sulphide concentrations (Figure 2) and the related direct and indirect effects on the biogas process. A further reason might be the ferric compound composition. The ferric hydroxide compounds analysed within this study contained a higher proportion of calcium carbonate compared to ferric oxide components. That might improve the buffer capacity of the concerned reactors (Otto and Güssbacher 2013). Reduction of the hydraulic retention time caused a decrease of specific gas production within all reactors, as expected from a process technological point of few. The reactor treated with the ferric oxide containing compound, Type 4, showed the strongest decrease in specific gas production associated with an increased VFA concentration (Figure 6). The experimental set-up did not allow for an explicit statement regarding the process stabilising effect of ferric oxide containing compounds, since these compounds were not or less effective at low hydraulic retention times as shown in Figure 2. For this purpose, experiments with increased hydraulic retention times are required. Ferric oxide compounds probably exhibits process stabilizing properties when applied at higher retention times. Due to their chemical properties they are dissolved much more slowly within the reactor compared to ferric hydroxide compounds and thus take effect more sustainably (Rahn et al. 2015a, Rahn et al. 2015b).

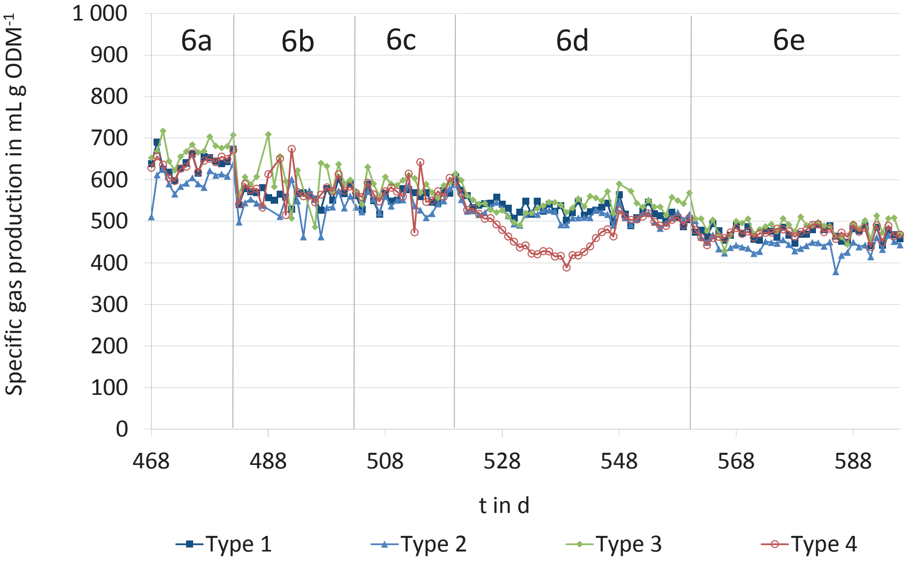

Figure 6: Specific gas production of the reactors at 8 days (6a), 6.5 days (6b), 5 days (6c), 3.5 days (6d) and 2 days (6e) hydraulic retention time

Conclusion

The results showed that chemical and physical properties of the ferric compounds strongly affected their desulphurisation performance within biogas processes. Thus, ferric hydroxide compounds showed a better desulphurisation performance compared to ferric oxide containing compounds especially at low hydraulic retention times. Thereby, an up to 50-fold improvement of the desulphurisation performance was measured when applying ferric hydroxide compounds. Without addition of ferric compounds the hydrogen sulphide content was 80-fold higher compared to ferric hydroxide supplementation. When comparing three types of ferric hydroxide compounds, the dependence between desulphurisation performance and grain size became obvious. The higher the proportion of fine grained components, the better the desulphurisation performance. This effect was enhanced at reduced dosage of ferric compounds, reduced stirring performance or low digestate viscosities.

Furthermore the results indicated not only an influence of ferric compounds on desulphurisation performance, but also influences on process stability and gas quality. The biogas process of ferric hydroxide treated reactors was more stable regarding process disturbances caused by the reduction of hydraulic retention time.

Further studies using various substrates in laboratory and industrial scale would advance the method and enable predictions about the desulphurisation performance of ferric oxide containing compounds at longer hydraulic retention times. This raises the question if either chemically slower reacting ferric oxide containing compounds remain as storage for desulphurisation or get removed from the system by gradual deposition of the particles within the reactor.

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