Short Communication

Evolution of the Total Sulphur Content in Full-Scale Wastewater Sludge Treatment

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Abstract

The present research studies the evolution of sulphur concentrations during wastewater treatment for various full-scale treatment plants and reveals that a significant amount of S is released as highly soluble sulphates with the sludge water during sludge thickening when sludge is still in aerobic conditions. During digestion, sulphur concentrations in the sludge (expressed as mg S/kg of dry solids) generally increased due to destruction of organic material, and relatively low release of H₂S. During sludge dewatering following anaerobic digestion, only a minor fraction of sulphur is found in sludge water, because sulphates have already been reduced into insoluble sulphides. To limit the sulphur concentration in the waste sludge, it is beneficial to extensively dewater the sludge when still under aerobic conditions, that is, before long-term sludge storage. If anaerobic digestion is used, the formation of sulphides is inevitable, as insoluble sulphides, and to a lesser extent H₂S.

Key words: sewage sludge; sulphur; transformation; anaerobic digestion; dewatering

Introduction

IN A PREVIOUS PAPER (Dewil *et al.*, 2008), the authors studied the origin and transformation of sulphur compounds for a single wastewater treatment plant (WWTP) [Sint-Truiden, Belgium, 80,000 population equivalents (p.e.)] and validated the results using a theoretical speciation of sulphur compounds. The results demonstrated that sulphur occurs mostly as sulphates or sulphides when treatment conditions progress from aerobic to anaerobic, respectively. To further validate these findings, several full-scale WWTPs were additionally assessed, and the findings are reported in this paper.

Sulphur is a major element in waste activated sludge (WAS), both in organic and inorganic form. The dominant inorganic sulphur-containing molecules are either sulphates or (metal-) sulphides, depending on the oxidation-reduction potential (ORP) of the sludge (Dewil *et al.*, 2008). Being a building block of amino acids, and hence proteins, sulphur is also present in the organic material (mostly ester-bonded or carbon bonded). Various studies report a total sulphur concentration in waste

sludge between 0.3 and 2.3% on a dry solid basis (Sommers *et al.*, 1977; Lisk *et al.*, 1992; Gutenmann *et al.*, 1994).

The presence of sulphur has considerable implications for sludge disposal by incineration, as now frequently used for cocombustion with other fuels (coal) in power stations or cement kilns, or for incineration in dedicated sludge combustors (Werther and Ogada, 1999; Van de Velden *et al.*, 2007). During incineration, all sulphur compounds are transformed into gaseous SO₂, which is emitted with the flue gases. To be in compliance with the European emission standards (European Commission, 2000), an efficient but costly SO₂ abatement system is required.

The sulphur concentrations in WAS generally exceed levels encountered with fossil fuels (Leckner *et al.*, 2004). Various studies have observed an increase in sulphur retention when WAS is added as a cofuel because of the high Ca-content of most WAS (Spliethoff and Hein, 1998; Folgueras *et al.*, 2004; Werther, 2007). Although this presence of alkali helps in reducing SO₂ emissions it is recommended to keep the amount of S in the WAS as low as possible.

It is obvious that the total sulphur concentration in WAS plays an important role in sludge disposal, and it is important to know the concentration and behavior of sulphur compounds during sludge treatment. Dewil *et al.* (2008) presented the sulphur transformations during sludge treatment with

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TABLE 1. AVERAGE RESULTS OF SAMPLING CAMPAIGN AROUND THE DIGESTER, WITH S, P, AND Fe IN mg/kg DRY SOLID

		DS (%)		MDS (%)		Total S (mg/kg DS)		Total P (mg/kg DS)		Total Fe (mg/kg DS)	
WWTP		mean	SD	mean	SD	mean	SD	mean	SD	mean	SD
Dendermonde	Digester feed	4.9	1.4	39.5	4.2	9,750	557	25,651	2,641	25,721	7,346
	Digester withdrawal	3.9	0.5	49.1	1.5	11,730	454	31,569	761	32,608	1,746
Antwerpen-Zuid	Digester feed	6.1	0.9	39.4	1.9	9,907	681	27,594	1,022	33,066	6,126
	Digester withdrawal	5.2	0.4	52.6	1.3	11,428	342	29,465	1,709	36,853	1,540
Sint-Truiden	Digester feed	4.2	1.5	41.6	7.2	8,266	685	15,266	1,367	13,810	1,960
	Digester withdrawal	4.8	0.5	55.0	8.5	8,492	628	18,083	942	17,278	2,058
Genk	Digester feed	5.1	0.7	37.7	2.4	8,449	292	22,184	2,324	53,524	3,565
	Digester withdrawal	4.3	3.9	54.3	3.7	13,116	1,334	29,009	2,016	69,289	4,625

WWTP, wastewater treatment plant; DS, dry solid; MDS, mineral dry solid.

accompanying theoretical speciation and validation. As a follow-up study, the sludge treatment lines of various full-scale WWTPs were sampled, and the evolution of the total sulphur content in sludge during the successive treatment steps was measured. Other key- components Fe and P were also measured. Because anaerobic digestion plays an important role in sulphur retention, and because it leads to an increase of total sulphur concentration, special attention was paid to this specific treatment step.

Materials and Methods

Selected WWTPs

WWTPs of Genk, Dendermonde, and Antwerpen-Zuid were selected for this study. Additionally, the WWTP of Sint-Truiden was also sampled around the digester: results have already been reported (Dewil *et al.*, 2008). All WWTPs are located in Flanders (Belgium), and are based on the activated sludge process. Their sludge treatment line consists of a sludge thickening step (gravitational or gravity belt thickeners), followed by an anaerobic digestion and ultimately a mechanical dewatering (consisting of a dewatering centrifuge or a recessed plate filter press). A full description of each WWTP is presented below.

The procedure presented in a previous paper (Dewil *et al.*, 2008) is summarized as follows: all WWTPs were sampled periodically, eight times within a 1 month's period. Due to the high residence time and the broad residence time distribution in the digester, the crosscorrelation of samples taken at the entrance and exit of the digester is not guaranteed. However, this is inherent to the sampling of a full-scale continuous digester. Multiple sampling and the transformation of the data into average values, however, improves the crosscorrelation of the results, thus providing a representative average view of the sulphur balance throughout the plant.

Analysis of the sludge samples

The dry solid content (%DS), mineral dry solid content (%MDS), pH, and ORP were measured for all samples according to APHA (2005). As shown by Dewil *et al.* (2008), the distribution of S among its different compounds is influenced by the concentration of Fe, which is added as Fe^{3+} for phosphate precipitation: the total concentrations of the key components under scrutiny, that is, S, P and Fe, were therefore determined by ICP-OES analysis (Dewil *et al.*, 2006). Prior to the analysis, the sludge samples were subjected to a high-

pressure microwave digestion method, as described in Dewil *et al.* (2006).

Based on the measured concentrations, mass balances were conducted. For the ease of calculation and comparison, the balances consider a standard amount of excess sludge of 1,000 kg.

Results and Discussion

Influence of anaerobic sludge digestion

To determine the influence of sludge digestion on the total sulphur content of waste sludge, all five WWTPs were studied by sampling both the feed and the discharge of the sludge digester. The time-averaged results for the measured concentrations in the sludge are presented in Table 1 and expressed in mg S/kg DS. Figure 1 shows the changes in S-concentration during digestion for all selected WWTPs.

For three of the four WWTPs, the sulphur concentration in the sludge increases significantly with digestion. In these three plants Fe^{3+} is added for phosphate removal, but not so in Sint-Truiden (see Fig. 1). The increasing concentration, measured as mg S/kg DS, is explained by the significant destruction of organic material during digestion and associated release of biogas. If sulphur is not proportionally released (as H_2S) in the biogas, its concentration (as measured on a DS basis) increases. The retention of H_2S in these WWTPs is enhanced by the presence of Fe, which binds the sulphides; hence, forming an insoluble black precipitate FeS or Fe_2S_3 (both compounds

FIG. 1. S-concentration in sludge before and after digestion.

FIG. 2. Concentration measurements WWTP Genk.

were not separately measured). The WWTP of Sint-Truiden shows no increase in sulphur concentration (Fig. 1). This difference with the other three WWTPs results from both the very low Fe concentrations in the sludge (measured by ICP-OES as mentioned before) and the fact that no Fe^{3+} was added in this particular WWTP for phosphate precipitation during the sampling period. Fe and P concentrations are almost equal, and all Fe are expected to be bound as FePO_4 (the Fe salt with lowest solubility product value). No residual Fe ions are therefore present to bind the formed sulphides and they are released with the biogas, as demonstrated in Dewil *et al.* (2008).

WWTP Genk

The concentration measurements for the WWTP Genk are presented in Fig. 2. The sludge treatment process in this WWTP consists of a gravitational thickening, followed by a

digestion and a mechanical dewatering using centrifuges. The sludge digestion consists of two steps. The first step is a mesophilic digestion at a temperature of approximately 37°C. This step is followed by a cold digestion, where the sludge is introduced in a second reactor, which is neither heated nor stirred. In the second reactor, the sludge is moreover thickened and the supernatant is evacuated. A separate sampling of this supernatant was not possible.

It is interesting to note the very efficient digestion in this station with an MDS fraction in the sludge increasing from about 30% before to about 50% after digestion. This means that large amounts of organic dry solids (ODS) are transformed into biogas. It is, hence, not surprising that the sulphur content is concentrated in the DS from 9,708 mg/kg DS to 15,220 mg/kg DS.

The mass balances are presented in Fig. 3. During thickening about 10% of DS and MDS is released into the sludge

FIG. 3. Mass balances WWTP Genk.

FIG. 4. Concentration measurements WWTP Dendermonde.

water. Over the thickening step, the balances are 90% consistent for all three analyzed components. The error of 10% is due to measurement errors, and is acceptable for a full-scale sampling process. During digestion, a (relatively) large fraction of the ODS is decomposed (about 30%). It should, however, be noted that part of this decrease is due to the release of DS into the supernatant during the cold digestion step. Looking at the digestion as a whole, the total amount of S in the sludge remains constant, meaning that no significant amount is released into biogas or supernatant. The balances for Fe and P are consistent within about 10%, corresponding to the measurement accuracy.

It is seen that during thickening a significant fraction of S (20%) is removed with the filtrate. In the dewatering step, after anaerobic digestion, only a limited fraction of S is released (2%). The difference is explained by the ORP of the sludge (Dewil *et al.*, 2008). During thickening, the sludge is in near-aerobic conditions; hence, the major fraction of sulphur

is present as soluble sulphates, which are released in the sludge water. During anaerobic digestion, these sulphates are transformed into metal sulphides (mostly FeS and Fe₂S₃), which are insoluble and remain in the sludge during dewatering. As a result, the sulphur concentration decreases significantly during thickening and remains constant during dewatering (Fig. 2).

WWTP dendermonde

The results for the various sludge types at successive steps in the WWTP Dendermonde are presented in Fig. 4. The sludge treatment of this WWTP consists of a gravitational thickening followed by a mesophilic digestion and a subsequent dewatering using a recessed plate filter press for solids concentration. The sludge water released from thickening and dewatering is mixed, and jointly recycled to the secondary treatment, thus making a sampling of the separate flows im-

FIG. 5. Mass balances WWTP Dendermonde.

FIG. 6. Concentration measurements WWTP Antwerpen-Zuid.

possible. Only a mixed sample could be collected. For construction of the partial mass balances, the assumption was made that the DS content of both sludge waters is approximately the same. During thickening the sulphur concentration in the sludge decreases significantly to a nearly constant concentration. The sulphur found in the mixed flow of filtrate and centrate is primarily originating from the thickening step. An increase in sulphur concentration is again observed during anaerobic digestion.

Balances are presented in Fig. 5. The balances are consistent for P, but a significant increase of Fe during the subsequent sludge handling steps is observed. This could not be accounted for, but is probably due to an erroneous peak addition of Fe^{3+} for phosphate removal during the sampling period. For S, the mass balances are correct within 10%, with only 36.68 g remaining after dewatering of the total inflow of 61.38 g. For this station, a decrease of the total S concentration over the complete treatment line was observed. This is attributed to a higher S release during total treatment than decrease by DS decomposed (mainly during digestion) or loss.

Antwerpen-Zuid

The concentration measurements for the WWTP Antwerpen-Zuid are presented in Fig. 6. The sludge treatment consists of a

gravitational thickening and subsequent digestion and dewatering by means of centrifuges. As observed previously, the S-concentrations decrease significantly during the thickening step and increase again during digestion, hereby confirming the previous observations.

The mass balances are presented in Fig. 7. They are conclusive for S. The balance over the thickener illustrates the large release of S into the filtrate. During the dewatering step after digestion, only a limited amount of S is released as biogas.

Sint-Truiden

The results of the Sint-Truiden measurement campaign are not reported in the paper, as they are already published in detail (Dewil *et al.*, 2008).

Conclusions

The evolution of sulphur concentrations during sludge treatment was studied for various full-scale treatment plants.

When sludge is still in aerobic conditions, a significant amount of S is released to the sludge water during sludge thickening. This release is attributed to the presence of highly soluble sulphates (following a speciation in Dewil *et al.*, 2008). During the digestion step, the sulphur concentration in the sludge generally increases due to the destruction of organic

FIG. 7. Mass balances WWTP Antwerpen-Zuid.

matter and associated release of biogas. During the successive sludge dewatering step, only a minor fraction of sulphur is found in the sludge water. Here, the sulphates have already been reduced to insoluble sulphides.

Although it appears beneficial to extensively dewater the sludge when still in aerobic conditions (to considerably limit the sulphur concentration in the waste sludge), this has drawbacks because the aerobic sludge quantity will still be larger and more difficult to dewater.

If anaerobic digestion is applied, the formation of sulphides is inevitable, mostly as insoluble sulphides and to a minor extent as H_2S .

Author Disclosure Statement

The authors declare that no competing financial interests exist.

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