On-farm trials of practical options for hydrogen sulphide removal from piggery biogas

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ABBREVIATIONS

ANOVA	Analysis of variance
BSP	British standard pipe thread
CAP	Covered anaerobic pond
CH_4	Methane
CO_2	Carbon dioxide
DN	Nominal diameter
FRP	Fibre-reinforced plastic
GHG	Greenhouse Gas
H_2S	Hydrogen sulphide
kWe	Kilowatt (electric)
LSD	Least significant difference
N_2	Nitrogen
NB	Nominal bore
O_2	Oxygen
OD	Outside diameter
pCAP	Partially covered anaerobic pond
ppm	Parts per million
S	Sulphur
SCM	Sugar cane mulch
SWJ	Solvent weld joint
UPVC	Plasticized polyvinyl chloride

ABSTRACT (200 words max)

Manure-derived biogas is increasingly used at Australian piggeries to produce heat and generate electricity. However, high concentrations of hydrogen sulphide (H_2S) in piggery biogas is discouraging further use, because of a lack of practical, cost-effective H_2S removal options. To address this issue, on-farm trials were conducted at two piggeries. One trial tested H_2S oxidation; adding small amounts of air to biogas, upstream of a low-cost enhanced surface treatment vessel which was fabricated on-farm with intrinsic safety measures. Covered anaerobic pond (CAP) effluent provided a convenient, low-cost nutrient source for the biofilm of naturally-occurring microorganisms in the packed column. This treatment was effective, removing over 90% of the H_2S in a single pass and reducing H_2S concentrations from 4,000 ppm to <400 ppm. Another trial tested chemisorption performance of natural, iron-rich red soil, mixed with a ground sugar cane mulch bulking agent, in comparison with cg5 commercial media (iron-oxide pellets). The red soil removed H_2S, but had a substantially lower capacity (~2 g S/kg red soil) than the cg5 (~200 g S/kg media). Accordingly, red soil is unlikely to be feasible as a primary treatment medium, but may be useful for final polishing after an oxidation step has removed most of the H_2S.

1. Introduction

Currently, about 13.5% of total Australian pork production is sourced from farms which capture biogas from piggery effluent. Biogas is used to produce heat and/or generate electricity on-farm and offers considerable potential to reduce greenhouse gas (GHG) emissions from pork production (Wiedemann *et al*., 2016). However, high concentrations of hydrogen sulphide (H_2S) in raw piggery biogas (500-3000 ppm) (Safley and Westerman, 1988; Heubeck and Craggs, 2010; Skerman, 2013) are discouraging further on-farm biogas use in Australia, specifically due to a lack of practical and cost-effective H_2S removal options. Many commercial H_2S removal methods exist (Ryckebosch *et al*., 2011), but have limited applicability on typical Australian farms because of high cost, complexity and associated safety issues. Other options for H_2S removal are still being explored in the literature, such as recent research (Tilahun et al., 2017 and Tilahun et al., 2018) with a hybrid membrane gas absorption and bio-oxidation process at laboratory scale.

Biological oxidation could be a feasible H_2S removal option. With this method, a small amount of air is added to the biogas (2-6 % of total volume, Wellinger and Lindberg, 2005), allowing microorganisms to oxidise H_2S into elemental sulphur and/or sulphuric acid. This can occur inside a digester or in an external treatment vessel (Ryckebosch *et al*., 2011), as long as oxygen, nutrients, moisture and an active inoculum are provided, and conditions are conducive to microbial activity. At the time of writing, most Australian piggery installations were using covered anaerobic ponds (CAPs) rather than heated, mixed tank digesters for biogas production, because of Australia's warm climate, land availability and the low capital cost of these systems. A preliminary trial at an Australian piggery involved the careful addition of air under the cover of a CAP, which showed a decrease in H_2S concentration from

1,300 ppm to less than detectable levels (< 100 ppm). Methane concentration decreased only marginally from 58 volume % to 52 volume % (Tait, 2014). These results were promising, but the distribution of air under a large cover is generally unreliable when not closely monitored. In addition, elemental sulphur is likely to form and may accumulate in a CAP and be converted back into H_2S, thereby exacerbating the H_2S load over time. This result was observed in the preliminary trial above. When the air supply was stopped, the H_2S concentration rapidly increased to a much higher level of around 3,000 ppm before gradually returning to a level around 1,300 ppm over a 1-month period (Tait, 2014). For on-farm CAP installations, oxidation in an external treatment system may be preferable and easier to control. It is of interest to test this approach on-farm, using effluent from a piggery CAP as a cost-effective moisture, nutrient and inoculum source. This would minimise the complexity and operating costs of H_2S removal.

Chemisorption with commercial iron oxide pellets containing iron (III) (Equation 1, Ryckebosch et al., 2011) could be a feasible treatment method (Wellinger and Lindberg, 2005; Skerman, 2017) and some Australian piggeries currently use this method.

$$Fe_2O_3 + 3H_2S \rightarrow Fe_2S_3 + 3H_2O \quad (1)$$

However, there are on-going safety concerns with change-outs of spent commercial media, when large quantities of heat are released as the spent media regenerates following exposure to ambient air (Equation 2, Zicari, 2003).

$$2Fe_2S_3 + O_2 \rightarrow 2Fe_2O_3 + 3S_2 \qquad \Delta H = -198 \text{ kJ/g-mol } H_2S \quad (2)$$

If media are not pre-wetted before a change-out, hazardous sulphur combustion products may be emitted. If pre-wetted, the pellet structure of the media tends to collapse, making it difficult to remove from the chemisorption vessel and affecting the potential to regenerate and reuse the media. To identify cost-effective alternatives to commercial media, a previous

laboratory study (Skerman *et al.*, 2017) compared H_2S removal of commercial iron-oxide pellets with that of a number of alternative media. An iron-rich red soil was identified as a promising candidate (Skerman *et al.*, 2017); however, the performance of the red soil required further testing at on-farm scale. Specifically, scale-up effects may influence on-farm performance, such as the formation of preferential flow paths with sub-optimal gas-solid contact. In addition, on-farm biogas composition and flowrates tend to vary considerably over time, which may affect chemisorption performance.

To develop and test promising H_2S removal options, the present study carried out on-farm trials at two separate Australian piggeries. At one piggery, a simple oxidation concept was tested with air added upstream of an enhanced surface treatment vessel, which was supplied with effluent from an onsite CAP to provide the liquid and nutrient source for sustaining the oxidation reactions. At another piggery, field-scale chemisorption was tested for red soil, mixed with ground sugar cane mulch as a bulking agent, to reduce frictional pressure loss through the media.

2. Materials and methods

2.1. H_2S removal at piggery A by oxidation in an external vessel

At piggery A, a new H_2S removal system was designed by the farm owners, with some specialist support, and was constructed and installed using off-the-shelf equipment and local labour. This piggery was a grower-finisher unit (Gopalan *et al.*, 2013) located near Young, New South Wales, Australia, housing 15,000 weaner to finisher pigs (8 – 100 kg live weight). An onsite CAP treated the manure flushed from the pig housing on a regular basis, and

biogas was captured and used for on-farm heat and electricity generation. Prior to the installation of the new H_2S removal system, two 500 L chemisorption vessels (duty/standby) loaded with commercial iron oxide pellets were being used to treat the biogas captured in the CAP. The new H_2S removal system treated biogas supplying two 80 kWe reciprocating generators. Some surplus biogas was exported to a second piggery, resulting in a maximum raw biogas flowrate of 160 m^3/h. The farm owners' primary objectives for installing the new H_2S removal system were to reduce operational costs and to address on-going safety concerns associated with change-outs of a commercial chemisorption medium.

2.1.1. Field set-up – Piggery A

The new H_2S removal system (Fig. 1) consisted of a 10,000 L fibreglass (FRP) tank (Tankworld, 2.56 m OD at mid-height, height 2.2 m), partially filled with 7.7 m^3 of a general purpose plastic packing (Pingxiang Naike Chemical Industry Equipment Packing Co Ltd., China, 25 mm PALL-Rings, specific surface area: 213 m^2. m^{-3}) to a depth of 1.5 m. The packing was supported on 0.4 m high plastic milk crates forming an underdrain to allow uniform distribution of the inlet biogas flow entering the base of the vessel. A layer of plastic mesh (10 mm x 3 mm) was placed over the crates to retain the packing elements. A 1 m diameter bolted flange cover on the sidewall allowed access for removal and cleaning of the packing, using a pressurised water hose, at approximately 10-month intervals. Liquid effluent pumped at a flowrate of 0.17 ± 0.01 L/s from the on-site CAP gravity overflow pit, was sprayed across the packing surface using a nozzle installed in the roof of the vessel. This liquid effluent provided nutrients, moisture and biological inoculum to sustain the H_2S removal. After trickling down through the packing, the liquid effluent was collected at the base of the treatment vessel and pumped to an on-site evaporation bay, completing the single-

pass process. A downstream blower drew biogas through the treatment vessel. The suction provided by the blower drew a small amount of air into the biogas flow, via a T-piece installed in the biogas inlet pipeline, immediately upstream from the treatment vessel. The farm owner used a ball valve on the air inlet line and a gate valve on the biogas inlet line to adjust the venturi suction at the air inlet and thus the proportion of air being drawn into the treatment vessel. When biogas was not flowing, a small positive pressure (up to 50 Pa) in the CAP headspace prevented air entering the biogas pipeline, and a negligible amount of raw biogas was vented to a safe location, above head height. A by-pass pipeline allowed the biogas to be redirected around the treatment vessel (Fig. 1), to enable infrequent offline maintenance.

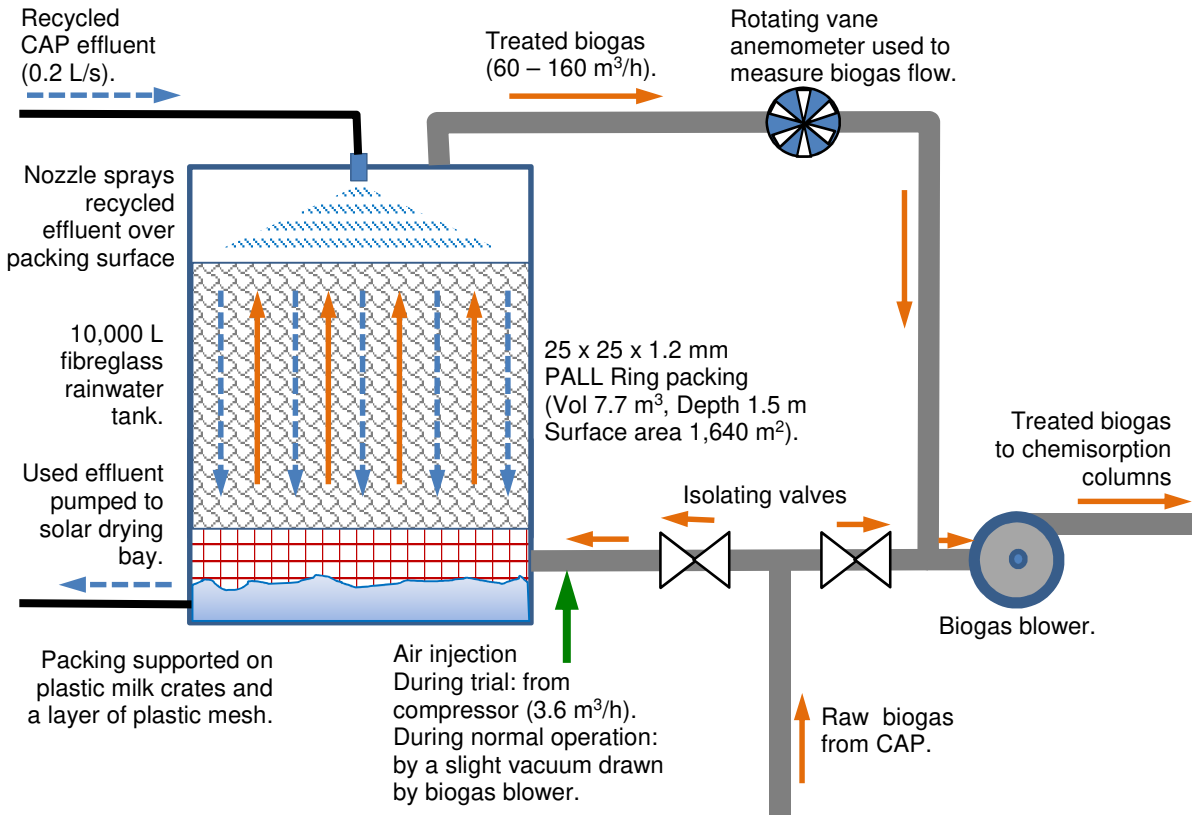


Fig. 1 - Schematic drawing of the H_2S removal system trialled at piggery A, employing oxidation in an external vessel.

2.1.2. Intensive field trial

The new H_2S removal system was commissioned and operated for about 6 months before an intensive field trial was carried out. The packing was new when the system was commissioned and had not been cleaned before or during the intensive field trial. On the day before the intensive trial began, upstream and downstream biogas composition was measured to determine the normal operational performance of the new H_2S removal system. After this, a positive displacement compressor was connected to the air inlet port to pump air into the flowing biogas, at a controlled air flowrate of 3.6 ± 0.1 m^3/h. Over the range of biogas flowrates observed during the trials (60-160 m^3/h), this air flowrate corresponded to 2.3 – 6.0% air (by volume) in the biogas mixture, which was within the recommended range for biological oxidation (Wellinger and Lindberg, 2005). The biogas composition was closely monitored during the trial, to prevent unsafe conditions.

During the trial, biogas composition was measured at sampling taps installed upstream and downstream of the treatment vessel, using a Geotech Biogas 5000 portable analyser (Geotech, Leamington Spa, Warwickshire CV31 3JR, UK). The upstream sampling point was located upstream of the air inlet so that we could measure the composition of the raw biogas coming from the CAP, before the addition of air. The downstream sampling point was located directly downstream of the treatment vessel outlet port. The analyser measured methane (CH_4), carbon dioxide (CO_2), oxygen (O_2), H_2S and balance gases [likely to be nitrogen (N_2) and water vapour] with typical accuracies of ± 0.5%, ± 0.5%, ± 1.0% and ± 100 ppm for 0 – 5000 ppm H_2S range, respectively. The instrument was pre-calibrated using two standard gas mixtures (GasTech Australia Pty Ltd, Wangara WA 6065), containing 60% CH_4 / 40% CO_2 and 2000 ppm H_2S in N_2. During the trial, a rotating vane anemometer

(TSI VelociCalc Plus, Model 8324-M-GB, Rev 2.3, USA) was temporarily installed to measure the flowrate in the biogas pipeline downstream of the treatment vessel.

Biogas composition was measured over a series of five tests (Tests 1 to 4 and Post test) carried out over a 2-day period. During these tests, biogas flowrates through the treatment vessel were varied by running various combinations of generator units and/or by diverting some of the biogas around the treatment vessel. Throughout Day 1, the air compressor was used to supply air to the inlet biogas stream. Test 1 was conducted at the normal biogas flow range from 140 – 160 ± 2 m^3/h, which is typical for running two 80 kWe generators plus some transfer of biogas to a second piggery. For Test 2, the biogas flowrate was reduced to 62 ± 2 m^3/h, which is typical for running one 80 kWe generator. On Day 2, the air compressor was initially turned off and the biogas flowrate was similar to Test 1 (145 ± 2 m^3/h). The air compressor was then turned on for Test 3 which was run at an unaltered biogas flowrate. For test 4, the air compressor remained on, but the biogas flowrate was reduced to 100 ± 2 m^3/h which is typical for running two 80 kWe generators with no export of biogas to the other piggery.

Three to five replicate biogas measurements were taken at 30-60 minute intervals for each test, commencing at least 30 minutes after changing the biogas flowrate, to allow conditions to stabilise.

At the completion of the intensive trial, the treatment system was returned to normal operating conditions, with air again being drawn into flowing biogas by the suction of the downstream biogas blower (Section 2.1.1). Measurements of biogas composition were then used to adjust the air inlet valve, so that the amount of air being drawn in was similar to that

supplied by the air compressor during the intensive trial. The treatment system was left overnight in this normal operating state, and upstream and downstream biogas composition measurements were taken on the following day to assess the extent of H_2S removal. These measurements were termed "post-test" (Table S1).

2.2. Chemisorption tests

2.2.1. Materials

Red soil was excavated from just below the soil surface (A horizon) at 203 Tor Street, Toowoomba Qld (S 27° 32' 05", E 151° 55" 46"). This soil was classified as a krasnozem (Great Soil Group, Stace *et al*., 1968) or red ferrosol (Australian Soil Classification, Isbell, 1996). To reduce frictional pressure drop across the red soil media bed in the field trials, the red soil was mixed with ground sugar cane mulch as a bulking agent (SCM, Rocky Point Mulching, Woongoolba Qld 4207) in the proportion 40% SCM by volume. Two batches of red soil and SCM mixtures were prepared for separate testing in the trial, named red soil+SCM 1 and red soil+SCM 2. These separate tests were performed to examine reproducibility, especially because of the expected natural variability in the red soil and sugar cane mulch ingredients. cg5 commercial iron-oxide pellet medium was sourced from Shanxi Clean Company of Catalysis and Purification Technologies Development. The physico-chemical properties of the red soil and cg5 were previously reported by Skerman *et al.* (2017).

2.2.2. Field trial at Piggery B

255 Chemisorption trials of red soil mixtures were carried out at piggery B, a breeder piggery in
256 south-east Queensland with a 700 sow capacity, previously described by Skerman and
257 Collman (2012). At this farm, biogas was produced by a partially covered (~50% of the
258 liquid surface) anaerobic pond (pCAP) treating the liquid manure flushed from the pig sheds.
259 During the trial, the whole biogas flow captured from the pCAP was directed through a
260 chemisorption test column for treatment, before being burnt in an onsite hot water system.
261 The biogas was pumped through the chemisorption test column under a maximum positive
262 pressure of 3.5 kPa using a biogas blower installed upstream of the test column. Water heated
263 by the biogas-fired hot water system was circulated through underfloor heating pads in the
264 farrowing sheds, to provide heat for piglets up to weaning age (28 days). The trials measured
265 and compared the farm-scale H_2S removal performance of the red soil+SCM mixtures and
266 the cg5 commercial iron-oxide pellets.
267
268 Fig. 2 is a schematic of the test apparatus at piggery B. The chemisorption test column was
269 constructed with DN 300 mm UPVC pipe (ID 305 mm) and solvent weld fittings (Fabfit,
270 Stapylton Qld). The chemisorption media was suspended on a stainless steel mesh base plate,
271 supported on a 250 mm deep plenum formed by randomly placing 40 mm lengths of
272 DN 20 mm Class 12 UPVC pressure pipe in the base of the column. A sheet of geotextile
273 fabric was placed on top of the stainless steel mesh to retain fine media particles. The upper
274 and lower sections of the column were connected with a UPVC flanged joint, sealed with an
275 insertion rubber gasket secured with stainless steel bolts, to provide a gas-tight seal. The
276 flanged joint provided access for insertion and removal of the media. The chemisorption
277 column was connected to upstream and downstream 2 inch (NB 50 mm) stainless steel
278 pipelines, using polyethylene pipe (NB 25 mm) and fittings. The raw biogas entered the top
279 of the column, passed through the packed media in a downward direction (as recommended

to maintain bed moisture, Zicari, 2003), and flowed out from the plenum in the base of the column. To prevent water from blocking the outlet pipeline, condensate was periodically drained via a manually operated tap installed in the base of the plenum. A Landis+Gyr Model 750 gas meter, fitted with an Elster IN-Z61 pulse output kit, measured biogas flow through the chemisorption test column. The pulse output from this meter was logged at 5 minute intervals, using a HOBO UX120 4-channel data logger installed on an adjacent piggery shed wall.

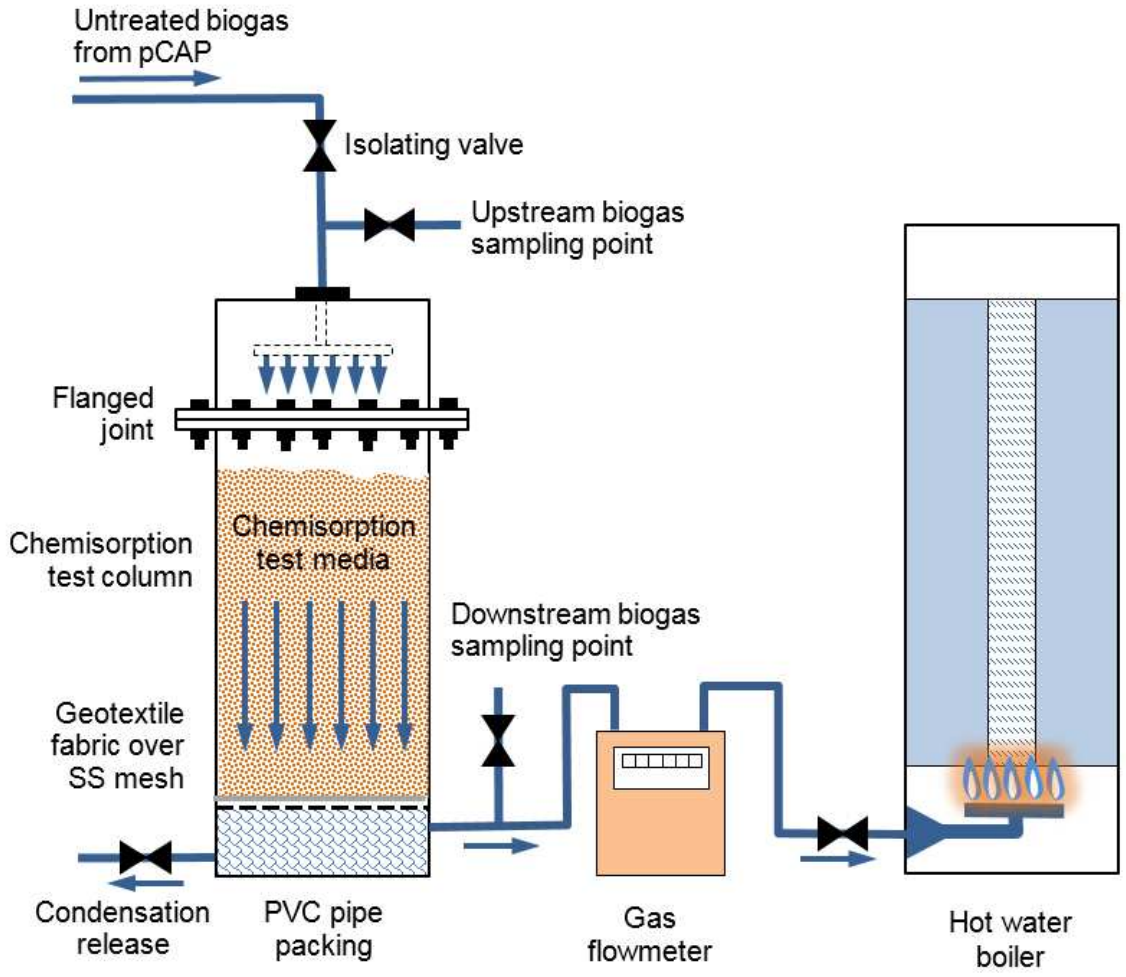


Fig. 2 - Schematic drawing of the chemisorption test column and hot water system installed at piggery B.

Three chemisorption media (red soil+SCM 1, red soil+SCM 2 and cg5) were tested separately over three discrete test periods. To perform a test, the medium was loaded into the chemisorption column with the upstream biogas line isolated and biogas blower turned off. The biogas blower was then switched on, the isolation valve upstream of the chemisorption test column opened, and the biogas pipeline purged of air via the condensate drain line. A leak check was performed using soapy water, and the isolation valve downstream of the chemisorption test column was opened before starting the hot water system. The hot water system operated continuously throughout the red soil+SCM trials, but operation was interrupted during the cg5 trial for a period of about one month while the pCAP was being desludged. During this desludging period, the chemisorption test column was isolated to prevent air ingress into the cg5 medium. Piggery manure continued to discharge into the pCAP during the desludging period and the cover remained floating on the lagoon liquid surface, but the pipeline connecting the cover to the biogas extraction system was disconnected and the cover was moved around on the pond surface to allow machinery access for desludging. After the desludging was completed, the pCAP was topped-up with a mixture of bore water and recycled secondary treatment pond effluent. The biogas pipeline was reconnected to the floating pond cover and biogas was diverted to an upstream flare for two days to purge any oxygen in the pipeline. The biogas composition was then measured to confirm successful purging of oxygen before the hot water system and chemisorption vessel were recommissioned. No pond desludging was carried out during the red soil+SCM 1 and red soil+SCM 2 trials, which were conducted following the cg5 trial.

Table 1 below, summarises test conditions for the three trials. During each trial, biogas composition was measured in triplicate, upstream of the chemisorption test column and, without delay, downstream of the column, using the same Geotech Biogas 5000 portable

316 analyser used in the trials at piggery A (Section 2.1.1). Biogas flow meter readings were
317 recorded manually from the Landis+Gyr gas meter (Section 2.2.2) during regular site visits
318 (generally hourly for the red soil+SCM trials and daily for the cg5 trial). To augment the
319 manual recordings, five-minute flow volume data was also downloaded from the logger
320 described above, at the end of each media trial.
321

Table 1 - Basic physical characteristics and test conditions for the on-farm trials at piggery B carried out using the two red soil+sugar cane mulch (SCM) mixtures and cg5 commercial media.

Parameter	Units	Red soil+SCM 1	Red soil+SCM 2	cg5
Mass	kg	22.34	36.14	34.22
Volume	L	29.96	48.36	48.95
Depth	m	0.41	0.66	0.67
Bulk density	kg/m^3	750	750	700
Bed void fraction	%	69	69	76
Pore volume	L	20.55	33.08	37.11
Depth / diameter		1.3	2.2	2.2
Mean biogas flowrate	L/min	40.8	44.1	37.2
Mean superficial flow velocity	m/min	0.58	0.60	0.51
Mean biogas residence time	s	42	66	79

322

323 At the end of the cg5 trial, the media bed was first thoroughly wetted before opening the
324 chemisorption vessel, to prevent possible melting of the vessel due to the highly exothermic
325 regeneration reaction following exposure of the spent cg5 media to air (Equation 2). This
326 wetting caused a notable collapse in the pellet structure, affecting the regeneration and reuse
327 potential of the media. No follow-on tests were conducted with regenerated media in the
328 present study.
329

330 Pressure drop was also measured across all the tested media beds, using a TSI Model 8705
331 DP-CALC^{TM} micro-manometer, connected to gas sampling ports immediately upstream and
332 downstream of the chemisorption test column. These measurements were performed at the

start and end of each chemisorption test, and at various times during each test, to examine whether the properties of the media bed had notably changed with the progressive accumulation of sulphide minerals.

2.2.3. Laboratory experiments

Additional laboratory experiments were performed to test the chemisorption of a red soil+SCM mixture. The methodology used in these laboratory experiments was identical to that described in Skerman *et al.* (2017). In short, the laboratory experiments measured the single-pass chemisorption of H_2S on a bed of red soil+SCM, held in a cylindrical PVC test column (internal diameter 29.8 mm). The test gas, fed into the column at a controlled flowrate of 360 mL/min, contained 2000 ppm H_2S in high purity nitrogen, and was pre-humidified by bubbling the gas through a 150 mm depth of deionised water. The resulting relative humidity was confirmed to be >95%. The composition of the treated gas exiting the test column was measured with the H_2S sensors. After data processing, as described by Skerman *et al.* (2017), the results provided a breakthrough curve of measured H_2S concentrations in the treated gas exiting the test column over time.

2.2.4. Data analysis

ANOVA and LSD (Genstat software, Version 16.1, Payne *et al.*, 2011) were used to test for significant difference (at a 5% significance level) between mean CH_4, CO_2 and balance gas concentrations upstream and downstream of the chemisorption column in the field trials. Chemisorption capacities of each medium were calculated using mass balance, comparing instantaneous mass flow of H_2S into the chemisorption column, versus corresponding

instantaneous mass flow of H_2S out of the chemisorption column. H_2S was assumed to behave as an ideal gas, justified by the low H_2S concentrations relative to other gaseous constituents. The calculated sorption capacities were further analysed by fitting two-phase exponential curves (Equations 3 and 4), using Genstat and the solver function in Microsoft Excel® to minimise the sum of the squares of the differences between measured and modelled values:

$$D = A1 + B1.K1^{x} \quad \text{when } x < C \tag{3}$$

$$D = A2 + B2.K2^{(x-C)} \quad \text{when } x > C \tag{4}$$

where D is the downstream H_2S concentration (in the treated biogas); *A1, A2, B1, B2, K1, K2* and C are empirical fitted parameters, and x = S chemisorption capacity of the media (g S/kg medium).

3. Results and discussion

3.1. H_2S removal with in-line air addition and oxidation in an external vessel

Fig. S1 and Table S1 in the supplementary materials present measured biogas composition upstream (raw) and downstream (treated) of the treatment vessel during the intensive trial at piggery A. H_2S in the raw biogas was typically between 4,000 and 4,200 ppm. The day before the intensive trial, when air was being drawn into the biogas stream by the suction provided by a downstream biogas blower, H_2S in the treated biogas remained high at around 3,678 – 3,860 ppm. This indicated that the amount of air being drawn in before the intensive trial started, was inadequate for effective treatment. When an air compressor was used to

supply air into the flowing biogas, H_2S in the treated biogas rapidly decreased to 2,285 ppm and then to 321 ppm over an 8 h period. H_2S removal extent was subsequently high at 87-95% whilst the air compressor was operating. This high H_2S removal extent was consistent with typical performance of biological oxidation (Wellinger and Lindberg, 2005). The progressive improvement in H_2S removal at the start of the intensive trial, when the air compressor was first switched on, indicated that activity was being stimulated by the addition of air. At times during the trial when the air compressor was intermittently switched off, the H_2S concentration in the treated biogas again increased to high levels (3,895-4,001 ppm), but as soon as the compressor was switched on again, the H_2S concentration rapidly decreased to 680 ppm or less. The lowest outlet H_2S concentration measured during the trial was 231 ppm. At the completion of the trial, the treatment system was returned to normal operation, with air being drawn in by the suction of the downstream blower. Measurements on the subsequent day showed that H_2S removal was also high at about 90% (post-test, Table S1). Thus, it was concluded that adequate amounts of air could be drawn in by the passive suction of a downstream blower, but also that the valve settings controlling the venturi suction appear to require semi-regular adjustment to ensure an adequate air supply for effective H_2S removal.

Physico-chemical dissolution and removal of H_2S in the sprayed liquid were likely to have been insignificant, as confirmed by Henry's law equilibrium calculations. Such calculations showed that if H_2S gas transfer achieved equilibrium with a H_2S partial pressure of 2,000 ppm (conservative average of inlet versus outlet concentrations) and under the best-case scenario of a biogas pressure of 50 Pa (gauge), then the 0.2 L/s effluent flow would have removed less than 1% of the total H_2S by direct dissolution and transport. This is not surprising because commercial biogas purification systems based on water scrubbing typically require gas pressures of 4–8 bar (400–800 kPa) and often also cool raw biogas to 5–

10°C to further increase gas solubility and enhance performance (Wellinger *et al*., 2013). The present system operated at low pressures and ambient temperature (>15°C). Also, air addition was a definite requirement to observe notable H_2S removal (Fig. S1). These findings indicated that biological or chemical oxidation was by far the dominant H_2S removal process.

A number of operational factors such as temperature, reaction time and air placement can influence biological oxidation (Wellinger and Lindberg, 2005). Biogas flowrate was varied during the present trial, but appeared to be only weakly related to H_2S removal. Instead, H_2S removal progressively improved during the course of the trial, because of the addition of air by an air compressor. The treated biogas however contained traces of oxygen (0.5 – 1.1% by volume), indicating that O_2 was supplied in excess. Stoichiometrically, a 0.5% concentration of air in biogas is required to convert 2000 ppm H_2S (20°C and 1 atm) into elemental sulphur and water. A prolonged exposure to excess O_2 can encourage acid-forming conditions, further favouring complete oxidation into sulphate (Pokorna and Zabranska, 2015). The measured pH of the liquid pumped from the CAP overflow into the treatment vessel was 7.3 and the pH of the liquid discharged from the base of the treatment vessel was 7.4. This minimal change in the measured pH was expected, due to the typically high alkalinity of pig effluent (Staunton *et al*., 2015; Sell *et al*., 2011) buffering any production of sulphuric acid. It may be possible to optimise air addition to further improve system performance, but this would require longer term monitoring. From a maintenance perspective, the production of sulphuric acid (neutralised to sulphate) may be more desirable than elemental sulphur, so that the plastic packing requires less frequent clean outs. At this piggery, the liquid effluent discharged from the single-pass scrubbing vessel is pumped into an uncovered evaporation basin. Consequently, any further H_2S produced by sulphate reducing microorganisms (under subsequent anaerobic conditions) is not captured in the CAP.

The trial results showed that the treatment system was effective for the maximum 160 m^3/h biogas flow at the piggery A. H_2S concentrations in the treated biogas were very encouraging, being as low as 231 – 680 ppm. Biogas of this quality is suitable for most boilers and some internal combustion engines (Wellinger and Lindberg, 2005) without further treatment. The tabulated concentrations of CH_4, CO_2, O_2 and balance gases (mainly N_2) in the raw and treated biogas (Table S1) suggest that the dilution of the biogas by the added air would be unlikely to have a major adverse effect on the operation of boilers and electrical generators commonly used at piggeries.

The results further indicated that CAP effluent is an effective source of moisture and nutrients for H_2S oxidation, providing a very practical and cost-effective biogas treatment option for piggeries. One concern is the potential for minerals such as struvite and other solids to clog the plastic packing. In this regard, a slightly depressed pH could discourage the formation of struvite (Webb and Ho, 1992), and this could be enabled by adding more air to promote sulfuric acid production. At piggery A, the plastic packing was removed about 4 months after the intensive trial. By then (10 months after initial commissioning), the packing had accumulated substantial amounts of a cream-coloured solid. The solid was successfully removed from the packing using a high-pressure water hose, before the packing was returned to the treatment vessel which was then recommissioned. As outlined in Table S2, it was estimated that it would take approximately 2 years for the packing to be completely filled with elemental sulphur, assuming that the biogas H_2S is sequestered and then oxidised to elemental sulphur with no formation of sulphate (worst case scenario). This estimate was based on the normal biogas flowrate of 160 m^3/h, an average biogas H_2S concentration of 4049 ppm, a H_2S removal rate of 90% and a packing volume of 7.7 m3, with 91% void space.

458 This result suggests that the packing may have been substantially clogged with elemental
459 sulphur when it was cleaned out after 10 months of operation, and that mostly elemental
460 sulphur formed, with minimal sulphate (sulphuric acid) formation.
461
462 **3.2. Chemisorption**
463
464 Fig. S2 presents a laboratory breakthrough curve measured for red soil+SCM (Section 2.2.3),
465 showing that breakthrough was occurring after approximately two hours of exposure to the
466 test gas. The resulting S sorption capacities at various downstream H_2S concentrations are
467 consistently lower than the laboratory results for pure red soil and cg5 (Table 2). Fig. 4
468 presents measured biogas composition and cumulative biogas flow for chemisorption field
469 trials at piggery B. Average O_2 concentrations during the trials were less than 0.05 %, which
470 is not significantly different from zero within the measurement precision of the instrument.
471 This indicated that the biogas pipeline and impermeable cover on the pCAP were gastight
472 and had minimal air ingress. Operation of the chemisorption column did not result in
473 significant differences between the mean CH_4, CO_2 and balance gas concentrations in the raw
474 and treated biogas ($P>0.05$). In comparison to data of Skerman (2013) for the same pCAP
475 recorded over an earlier 14-month monitoring period, CH_4 and CO_2 concentrations were
476 similar, but the mean H_2S concentration in the raw biogas was lower in the present study
477 (Fig. 4). This variation in H_2S could be due to different ambient temperatures affecting the
478 pond temperature and H_2S solubility, variations in pig diets, or sludge accumulation and
479 desludging. For example, the cg5 trial was temporarily interrupted by desludging at about
480 2,700 m^3 cumulative biogas treated (Fig. 4c). After the desludging event, the CH_4
481 concentration was higher and the CO_2 and H_2S concentrations were lower (Figs. 4c).

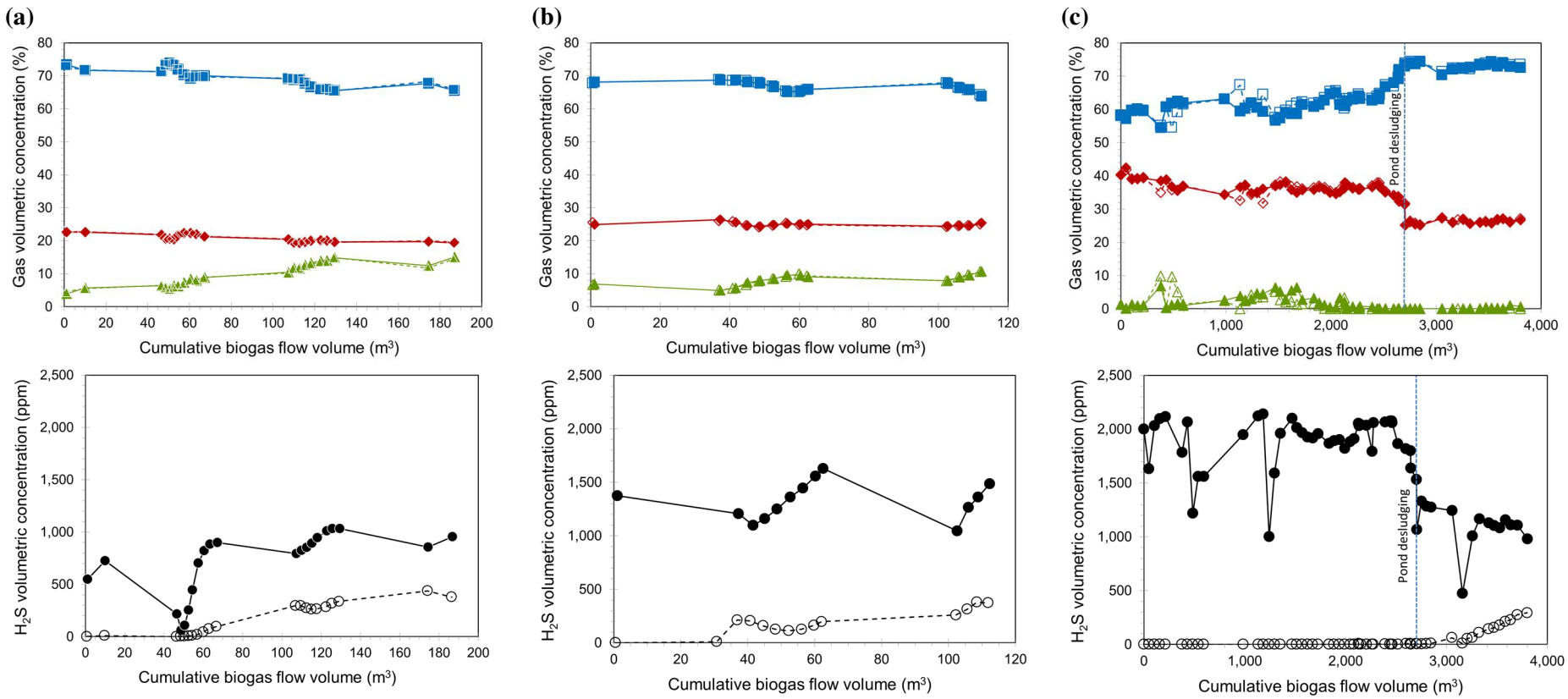
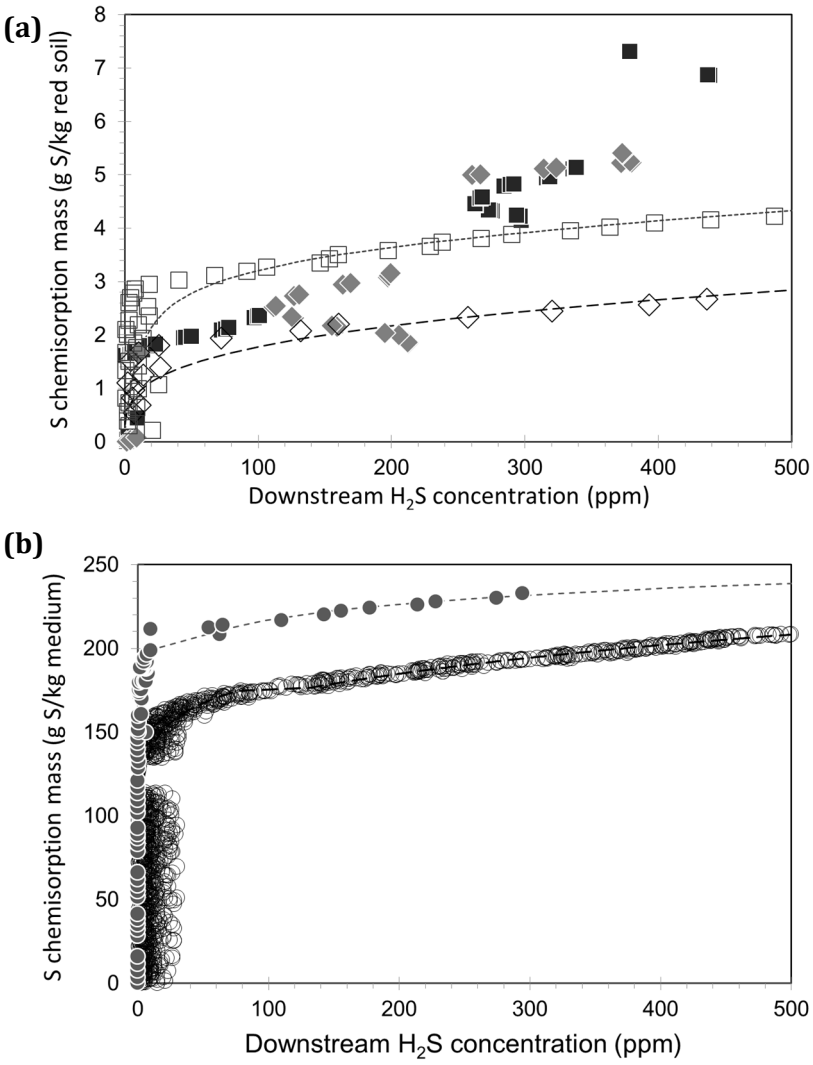


Fig. 4 - Measured concentrations of CH_4 (■), CO_2 (◆), balance gas (▲) and H_2S (●) during the field chemisorption trials at piggery B. The data are for measurements recorded upstream (raw biogas, closed symbols) and downstream (treated biogas, open symbols) of the chemisorption vessel, and for (a) the red soil+SCM 1 trial, (b) the red soil+SCM 2 trial, and (c) the cg5 trial.

Fig. 5 and Table 2 present estimated sorption capacities (Section 2.2.4) corresponding to downstream H_2S concentrations in treated biogas. A breakthrough threshold of 20 ppm was used in the present work, to account for substantial measurement variability in field data for red soil+SCM. A concentration of 200 ppm H_2S was also of interest, being a common upper limit for internal combustion engine generators (Wellinger and Lindberg, 2005). To protect the hot water system at piggery B, the field trials were only run for H_2S concentrations up to about 400 ppm. Equations 3 and 4 were used to estimate sorption capacities for cg5 data, pure red soil lab data and red soil+SCM lab data. However, sorption capacities for the red soil+SCM field trials had to instead be determined by linear interpolation of the measured data in Fig. 5a, because of observed erratic behaviour. For the two red soil+SCM media, the on-farm sorption capacity at breakthrough (20ppm) (1.8 and 1.7 g S/kg red soil) were between those of pure red soil (Skerman *et al.*, 2017) and red soil+SCM measured in the lab. This is somewhat expected, because the heterogeneity in red soil+SCM is likely to have caused short-circuiting along preferential flow paths. This heterogeneity of the red soil+SCM is also evident in the erratic field data in Fig. 5a, suggesting that H_2S removal intermittently recovered at higher downstream H_2S concentrations.

512



513

514 **Fig. 5 - Masses of S removed by chemisorption plotted against downstream H_2S concentrations.**
515 **The data are normalised (a) per unit mass of red soil in on-farm red soil + SCM1 (■), on-farm**
516 **red soil + SCM2 (◆), laboratory pure red soil (□) or laboratory red soil + SCM (◇), or (b) per**
517 **unit mass of on-farm cg5 media (●) or laboratory cg5 media (○). The dotted lines show the**
518 **exponential curves fitted to the data (Section 2.2.4). The laboratory cg5 data were from**
519 **Skerman *et al*. (2017).**

520

521 Similar to the lab observations of Skerman *et al*. (2017), cg5 had substantially greater
522 sorption capacities than red soil+SCM in the field trials. The sorption capacity of cg5 at
523 breakthrough (20 ppm) was two orders of magnitude greater than that of red soil+SCM. The
524 high sorption capacity of cg5 is likely a result of its engineered nature, with a high porosity

525 providing rapid access to a highly reactive iron content (Skerman *et al*., 2017). For reference,
526 the binding capacity stated in the cg5 manufacturer's product brochure is 250 g S/kg medium
527 (ACP Technologies Inc, 2012). It is not known whether this supplier-claimed capacity is for
528 breakthrough or for complete saturation (Skerman *et al*., 2017). Interestingly, the on-farm
529 breakthrough capacity of cg5 (186 g S/kg cg5) was considerably higher than measured in the
530 lab (147 g S/kg cg5, Skerman *et al*., 2017). The optimum vessel height to vessel diameter
531 ratio for cg5 is suggested to be 3:1 to 6:1 (ACP Technologies Inc, 2012), and this was met in
532 the laboratory tests of Skerman *et al*. (2017) (approximately 5), but not in the field trials
533 (ratio of 2.2). Therefore, height to diameter ratio is not likely to be the cause for the better
534 cg5 performance in the field trials. However, Nemec and Levec (2005) suggested wall effects
535 could be significant at column diameter/particle diameter ratios less than 10. The column
536 diameter/particle diameter ratios in the present cg5 field trials and in the lab trials of Skerman
537 *et al.* (2017) were 65.6 and 6.4, respectively. Accordingly, wall effects could have impeded
538 the lab performance. Finally, whilst every effort was made to exclude O_2 from the cg5 field
539 trials, particularly during the desludging interruption, it is possible that some O_2 entered the
540 biogas resulting in partial in-situ regeneration of the cg5, thereby increasing the sorption
541 capacity in the field trials.
542

Table 2 – S sorption capacities (g S/kg red soil or cg5) of red soil+SCM, pure red soil and cg5 media for on-farm and laboratory trials (Skerman, 2017), recalculated from the data presented in Fig. 5.

Downstream H_2S concentrations (ppm)	On-farm			Laboratory		
	Red soil +SCM 1	Red soil +SCM 2	cg5	Red soil +SCM	Pure red soil	cg5
10	1.68	1.17	186	0.92	2.88	147
20 (breakthrough)	1.80	1.68	195	1.12	2.95	156
50	1.97	1.70	208	1.45	3.06	167
100	2.35	1.75	217	1.78	3.23	176
150	2.80	1.79 / 2.87[1]	222	2.00	3.40	181
200	3.25	1.83 / 3.18[1]	226	2.17	3.60	185
250	3.71	4.69	229	2.44	3.78	187
300	4.86	5.09	232	2.66	3.91	193
400	6.19		236	2.84	4.11	201

[1] There were two ordinate (S chemisorption mass) values at these downstream H_2S concentrations (Fig. 5a).

Mixing red soil with ground SCM greatly reduced pressure drop across the column in the field trials, compared with red soil alone, so that the blower supply pressure was adequate. Similarly to the laboratory study of Skerman *et al.* (2017), measured pressure drop was about 60 times greater for the red soil+SCM than for the cg5 commercial media. Pressure drop for red soil+SCM ranged from 1.0 to 1.4 kPa/m media depth at a biogas down-flow velocity range from 0.48 to 0.64 m/min. Pressure drop for the cg5 media ranged from 0.020 to 0.023 kPa/m media depth for a biogas down-flow velocity range of 0.47 to 0.55 m/min. This substantially lower pressure drop is an additional benefit of the engineered nature of the cg5 commercial media. Pressure losses did not clearly correlate with mass of H_2S chemisorbed over time (Fig. S3 of the Supplementary Material), but were generally more variable for the red soil+SCM than for cg5.

3.3. Applications

There is great potential for biogas use at Australian piggeries, which could help to reduce greenhouse gas emissions by up to 64% across the pork supply chain (Wiedemann *et al.*,

560 2016). However, whilst several larger Australian pig producers (>1000 sows farrow to finish,
561 Gopalan *et al*, 2013) have readily embraced biogas technology, it has been uneconomical for
562 smaller producers (<500 sows, farrow to finish). The availability of simple, safe and cost-
563 effective H_2S treatment systems could greatly encourage on-farm biogas use at Australian
564 piggeries.
565
566 The results of trials at piggery A showed 90% H_2S removal from raw piggery biogas in a
567 single oxidation step, using infrastructure that is simple enough to fabricate, with minimal
568 detailed engineering design, and installed using local labour (Section 3.1). It may be possible
569 to further optimise system performance, but this would require longer term testing. For
570 example, an oxidation vessel with a higher aspect ratio than used in the present study, may
571 improve gas contact and thereby achieve lower H_2S concentrations in the treated outlet gas.
572 The prevention of an explosive methane-oxygen mixture is always critical; however, only
573 small amounts of air are required so that fuel-rich mixtures can be maintained (Wellinger and
574 Lindberg, 2005). The trials at piggery A showed that the suction of a downstream biogas
575 blower could draw in sufficient air for effective H_2S removal (Section 3.1, post-test). The
576 advantage of this approach (when operating correctly) is that air is only being added when the
577 biogas is flowing. When biogas is not flowing, air ingress is instead minimised by the slight
578 positive pressure (0.025-0.1 kPa, data not shown) under an anaerobic pond cover, instead
579 venting raw biogas to a safe location so that persons or livestock are not exposed to harmful
580 H_2S concentrations. The trial at piggery A also showed that valve settings around the air inlet
581 might require semi-regular adjustment to ensure that the venturi suction draws sufficient
582 amounts of air into the flowing biogas (Section 3.1). Oxidation systems would require
583 periodic maintenance to remove solids, such as elemental sulphur, minerals such as struvite
584 and biofilm from the packing. Commercial variants such as the BIOREM® process (2010)

585 and the THIOPAQ® process (Paques, 2015) have means to purge and recover sulphur. The
586 present work value-adds to commercial concepts, by showing that piggery CAP effluent
587 provides the necessary nutrients, moisture and inoculum for H_2S removal. The typically high
588 alkalinity in digested manure effluent also helps to buffer pH (Section 3.1).
589
590 Results of the chemisorption trials at piggery B showed that red soil removed H_2S, but had a
591 substantially lower sorption capacity than a commercial medium, cg5 (Section 3.2).
592 Accordingly, red soil is unlikely to be feasible for primary treatment to remove the bulk of
593 H_2S from raw piggery biogas, because of the excessive volume of red soil required to limit
594 media change-outs to manageable intervals, or alternatively, high change-out labour
595 requirements. Media quantities and/or ongoing labour could be reduced by a factor of 10 by
596 instead using red-soil+SCM to polish biogas after a separate primary treatment step has
597 removed the bulk of the H_2S (e.g. using oxidation). The lower sorption capacity of red
598 soil+SCM compared to cg5, resulted in less heat being released during regeneration.
599 Consequently, the red soil+SCM did not require wetting before being exposed to air when the
600 chemisorption column was opened at the end of the field trials. This demonstrates a safety
601 benefit of the less reactive red soil, compared with highly reactive commercial media.
602
603 As there are no heavy metals in cg5, some jurisdictions may allow land application of the
604 spent media (ACP Technologies, 2012). As on-farm crop production is commonly practiced
605 at Australian piggeries, carefully managed land application would be the preferred method
606 for utilising the spent cg5 or red soil media. This would involve minimal cost to the producer
607 in comparison to disposal in landfill.
608

While the concept of using a soil sourced on-farm, for treating biogas captured and used on-farm, has obvious benefits, ultimately, the feasibility of using red soil for biogas treatment will depend on a range of factors such as the sorption capacity, treatment volume limitations, labour costs, proximity to supplies of suitable soils and reuse/disposal costs.

4. Conclusion

This field trial study showed that oxidation in an external treatment vessel is effective at removing 90% of the H_2S in raw piggery biogas. The results showed that air was needed for H_2S oxidation (3-6% of the biogas volume) and could be drawn in by the suction of a downstream blower. The results also showed that effluent from an onsite CAP is a cost-effective moisture, nutrient and inoculum source for H_2S treatment by oxidation. At another piggery, chemisorption trials showed that a red soil chemisorbs H_2S, but at a 100 times lower capacity than a commercial chemisorption medium, cg5. It may be feasible to use oxidation as a primary treatment step to remove the bulk of the H_2S, prior to using red soil for final polishing of the biogas to a consistently high quality. In this way, red soil requires less frequent change-outs, and the combination of treatment steps could be practical and cost-effective. Pressure drop is higher across a bed of red soil mixture than across a bed of cg5, which affects the supply pressure required from a biogas blower. The cost feasibility of red soil depends on the cost of procuring the red soil. In the present study, the red soil was readily available from a local source.

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