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# Silicate minerals for $CO_2$ scavenging from biogas in Autogenerative High Pressure Digestion

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ABSTRACT

Autogenerative High Pressure Digestion (AHPD) is a novel concept that integrates gas upgrading with anaerobic digestion by selective dissolution of $CO_2$ at elevated biogas pressure. However, accumulation of $CO_2$ and fatty acids after anaerobic digestion of glucose resulted in pH 3–5, which is incompatible with the commonly applied high-rate methanogenic processes. Therefore, we studied the use of wollastonite, olivine and anorthosite, with measured composition of $CaSi_{1.05}O_{3.4}$, $Mg_2Fe_{0.2}Ni_{0.01}Si_{1.2}O_{5.3}$ and $Na_{0.7}Ca_1K_{0.1}Mg_{0.1}Fe_{0.15}Al_{3.1}Si_4O_{24}$, respectively, to scavenge $CO_2$ during batch AHPD of glucose. Depending on the glucose to mineral ratio the pH increased to 6.0–7.5. Experiments with wollastonite showed that $Ca^{2+}$-leaching was caused by volatile fatty acid (VFA) production during glucose digestion. At 1, 3 and 9 bar, the $CH_4$ content reached 74%, 86% and 88%, respectively, indicating $CO_2$ scavenging. Fixation of produced $CO_2$ by $CaCO_3$ precipitation in the sludge was confirmed by Fourier Transferred-InfraRed, Combined Field emission Scanning Electron Microscopy-Energy-dispersive X-ray spectroscopy and Thermogravimetric Analysis-Mass Spectroscopy.

## 1. Introduction

As reported by the International Energy Agency (Wellinger and Lindberg, 2001), corrosivity, condensation of water and reduced calorific value are main reasons why $H_2S$, $NH_3$, $CO_2$ and $H_2O$ should be removed in order to use biogas as a substitute for natural gas. The biogas composition depends on the average oxidation state of the carbonaceous substrate, as well as the degree of substrate pre-acidification and the presence of alternative electron acceptors, such as $SO_4^{2-}$ and $NO_3^-$ (Van Lier et al., 2008; Vavilin et al., 1995).

Due to fluctuations in wastewater composition, biogas composition can strongly vary over time and robust upgrading systems are required, adjusted to these quality fluctuations. Conventional methods such as pressure swing adsorption or gas-selective membranes can be used, but these are only cost-effective at biogas flows above 100 $m^3$/h (Zeeman et al., 2008).

In previous work (Lindeboom et al., 2011), we studied autogenerative high pressure digestion (AHPD) to produce high quality pressurized biogas in a single reactor system by integrating biogas scrubbing and storage into an anaerobic digester. By sealing the gas phase the produced biogas

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autogenerated biogas pressures up to 90 bar and can be used directly (1) to separate $CO_2$ and $CH_4$ based on Henry's constants of 0.031 mol $L^{-1}$ $bar^{-1}$ and 0.0016 mol $L^{-1}$ $bar^{-1}$, (2) dry the biogas based on the Clausius Clapeyron equation and (3) be used to exclude membrane pumps in AnMBR setups (Lindeboom et al., 2012). Furthermore, in practice $CH_4$ losses up to 20% have been reported for external upgrading, transport and storage of biogas altogether (Börjesson and Berglund, 2006). Therefore, on top of offering the above-mentioned advantages, AHPD could also reduce potential losses during transport, storage and upgrading of biogas, because production, upgrading and storage are performed in a single step bioreactor.

Although 90 bar biogas pressure can be produced, reactor costs and $CH_4$-dissolution would offset all potential benefits. However, experiments performed at moderate pressures (~5–10 bar), thereby reducing reactor costs and $CH_4$-dissolution to a minimum, showed that the potential benefits could be maintained (Lindeboom et al., 2012). However, under these economically more attractive conditions, control of the carbonate equilibrium and acid neutralizing capacity (ANC) is a prerequisite to maintain a proper pH for digestion (Lindeboom et al., 2012). Conventional industrially produced bulk-chemicals like sodium hydroxide (NaOH), carbonate ($Na_2CO_3$) or quicklime (CaO) could provide the required ANC. However, these are produced by the energy-intensive chloralkali, solvay and $CaCO_3$ thermal decomposition processes, respectively. Combined with the required transport, and safety requirements, this potentially offsets the environmental benefits of local biogas upgrading in remote areas. Lackner et al. (1995) and Schuiling and Krijgsman (2006) explored natural minerals for their potential for $CO_2$ sequestration in industrial processes. Moreover, for minerals such as wollastonite ($CaSiO_3$) and olivine ($Mg_{1.8}Fe_{0.2}SiO_4$) and large alkaline waste streams such as steel slags cost estimates for the total mineral carbonation process are 50–100€/ton avoided $CO_2$ (Huijgen et al., 2007; Mazzotti et al., 2005). Whereas based on the current market price, and assuming 100% reactivity one could expect 400–700€/ton $CO_2$ avoided for NaOH and $Na_2CO_3$ and 50–150€/ton avoided for CaO (Alibaba, 2013). Although quicklime, has a comparable current market price to silicate minerals, the thermal decomposition of $CaCO_3$ intrinsically emits 1 mol of $CO_2$ per mol of CaO on top of the heat demand of >850 °C (Whitfield and Mitchell, 2009).

So, assuming reactions rates are compatible with anaerobic digestion rates, a wide range of alternatives can be selected for adding ANC in AHPD, but also in conventional anaerobic digestion, nitrogen removal, desulfurization and bioelectrochemical systems (Salek et al., 2013). The rate and degree to which silicate minerals react are dependent on the mineral stability (Essington, 2004). This is a function of, amongst others, the cation to silicate ratio and the mineral structure (mainly characterized by the Si:O ratio). Based on the position in the Goldich series, overall wollastonite carbonation is an exothermic process with $\Delta Hr$ of −87 kJ/mol (Huijgen and Comans, 2006; Lackner, 2002), not requiring external heat input. Silicate minerals (like wollastonite, $CaSiO_3$) that are exposed to acid react according to the following reaction equation:

$$CaSiO_3(s) + 2H^+(aq) \rightarrow Ca^{2+}(aq) + SiO_2(s) + H_2O \qquad (1)$$

The required $H^+$ in this reaction could be provided by undissociated fatty acids, produced for example during typical anaerobic glucose digestion (Thauer et al., 1977).

$$C_6H_{12}O_6(s) + 2H_2O \rightarrow 2CH_3COO^- + 2H^+ + 4H_2 + 2CO_2 \qquad (2)$$

Due to the $H^+$ consuming reaction, accumulating fatty acids may dissociate, meanwhile maintaining an optimal pH (6–8) for methanogens in AHPD reactors. Besides, an increasing pH also shifts the carbonate equilibrium towards $HCO_3^-$ and $CO_3^{2-}$, possibly resulting in the precipitation of secondary carbonates (Eq. (3)).

$$Ca^{2+}(aq) + CO_3^{2-}(aq) \rightarrow CaCO_3(s) \qquad (3)$$

So, Eq. (3) provides on top of $HCO_3^-$ formation, a mechanism to store produced $CO_2$ as solids. In AHPD, this is particularly relevant, at lower ratios between ANC and produced $CO_2$, when the calorific value of the produced biogas is becoming diluted (Lindeboom et al., 2012).

From a perspective of $CO_2$-valorization and AHPD reactor calcium carbonate can precipitate in 6 different forms, having different characteristics. Amorphous calcium carbonate (ACC), hexahydrate calcium carbonate (HCC), monohydrate calcium carbonate (MCC) and the polymorphs vaterite, aragonite and calcite have respective $pK_{sp}$ values at 25 °C of 6.28, 6.59, 7.15, 7.91 ± 0.02, 8.34 ± 0.02 and 8.48 ± 0.02 (Nehrke, 2007). It is therefore essential to realize, that bacteria and archaea, induce precipitation by altering intra- and extracellular conditions and can thus influence the type of calcium carbonate formation.

The influence of anaerobic digestion conditions on $CaCO_3$ precipitation at atmospheric pressure is already widely studied (De Graaff et al., 2011; Ismail et al., 2008; Van Langerak et al., 1999, 2000). Deviations from $pK_{sp}$ of calcite and aragonite in water have been reported as a consequence of the complex biological liquid composition (Dupraz et al., 2009; Van Langerak et al., 1999). The sole presence of $PO_4^{3-}$ is reported to alter the $pK_{sp}$ from 8.4 to 6.5 due to inhibition of calcite formation from amorphous calcium carbonate (Van Langerak et al., 1999).

The aim of this work is to demonstrate the feasibility of using various silicate minerals, wollastonite (W), olivine (O) and anorthosite (A) for buffering the reactor pH in autogenerative high pressure digestion. Additionally, dissolution of wollastonite under AHPD conditions was studied, focusing on the secondary precipitation of $CaCO_3$, the role of fatty acid intermediates and the $CO_2$ content of the biogas.

## 2. Material and methods

### 2.1. *Reactors*

For AHPD experiments three pressure vessels with a total volume of 0.6 L were used (Parr 910908, Moline, USA). The volume of the liquid phase was manually controlled at 0.5 L. The reactors were equipped with a heating cylinder (Julabo MP, Seelbach, Germany), an online pressure sensor (Ashcroft A-series 1000 PSI, Stratford, USA), a high pressure pH probe