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Research Paper

Biogenic acid attack on concretes in biogas plants

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Concretes in biogas plants (BGP) are subjected to chemical damage through acids which are formed by microbiological processes. Four-year-old grass silage clamp and different concretes samples were analysed. The tests allow statements on the plant-specific damage potential and the performance of the concretes used. Acetic and lactic acids were produced in the grass silage clamp through the microbiologically-induced ensilaging process. Damage decreased inversely with pH despite the presence of rainwater (dilution effect) due to the greater microbiological activity. At pH < 4.0, significant damage (depth of 12.8 mm after four years) was found in the silage clamp. The damage potential of organic acids is based on the buffering effect (subsequent dissociation) and the high solubility of the resulting salts. If atmospheric oxygen was used inside the fermenter for desulphurisation, various bacteria of the genus *Thiobacillus*, such as the bacterium *Halothiobacillus neapolitanus*, at first produced elementary X-ray amorphous sulphur (S) and later sulphuric acid, which dissolved the hydrate phases of the hardened cement paste. The dissolved calcium reacted with sulphate to gypsum. Concretes with a low equivalent water/cement ratio, a low calcium-content in the hardened cement paste and incorporated steel fibres performed the best resistance. The results can contribute to the prevention of damage in future and for the development of new, more resistant concretes.

1. Introduction

Biogas is a regenerative and easy-to-store energy source which is produced from local renewable raw materials. It can be used locally to provide electricity, heat and gas. Renewable raw materials from agriculture and/or residues (from agriculture or from industry, commerce or municipalities) are used as initial substrates to produce biogas (Table 1).

These initial substrates are usually stored in silage clamps, bunker silos for high solid content or in reservoirs for low solid content. Animal residues from agriculture (liquid manure, dung) are pH neutral and usable after a short storage time. Renewable resources have to be preserved after ensilaging based on the seasonal availability. Under anaerobic conditions bacteria produce silage saps with low pH because of the formation of organic acids, e.g. lactic acid. The acidic anaerobic conditions prevent the formation of yeasts and moulds as well as inhibiting the reheating of silage.

The production of biogas from renewable raw materials and/or residues takes place in fermenters. A fermenter consists of a liquid phase (initial substrate) and a gas phase

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Nomenclature table

BSC	Biogenic sulphuric acid corrosion
CEM I	Ordinary Portland Cement (OPC) according EN 197-1
CEM II/B-M (S–D)	Portland-composite cements with blastfurnace slag and silica fume according EN 197-1
CEM III	Blast-furnace cement according EN 197-1
C–S–H	CalciumeSilicateHydrate
DAfStb	Deutscher Ausschuss für Stahlbetonbau (German)
DBFZ	Deutsches Biomasseforschungszentrum gemeinnützige GmbH (German)
DMC	Dry matter content
DTA	Differential thermal analysis
EDX	Energy dispersive X-ray spectroscopy
GC	Gas chromatography
ILM	Incident light microscopy
MALDI-TOF	Matrix-assisted laser desorption/ionisation with mass spectrometry with time-of-flight analyser
pH	Is a measure of the acidity or basicity of an aqueous solution
SEM	Scanning electron microscopy
SF	Silica fume
SRB	Sulphate-reducing bacteria
TG	Thermogravimetry
w/c	Water cement ratio
(w/c)eq	Equivalent water cement ratio according EN 206-1
XA3	Exposure class for very high levels of chemical attack according EN 206-1
XRD	X-ray diffraction
λKā	Wavelength

(biogas). This is usually a single-stage fermenter in which the four microbiological process steps (hydrolysis → acidogenesis → acetogenesis → methanogenesis) take place with different types of microorganism simultaneously. In order to achieve maximum efficiency, the optimum conditions for methanogenic bacteria are aimed at liquid phase pH value of approx. 6.8 to 7.2 (Wellinger et al., 2013). Depending on the initial substrate, the biogas produced by microbiological processes consists of approximately 40–70% methane (CH_4), 25–45% carbon dioxide (CO_2), 5–10% water vapour (H_2O) as well as 0–5% minor constituents, namely ammonia (NH_3), nitrogen (N_2), oxygen (O_2) and hydrogen sulphide (H_2S) (König, 2013).

Various buildings are needed for the sustained production, storage and utilisation of the biogas. Long-term operation depends on the resource used and the mode of action and it has to be guaranteed.

Because of its short history (Bond & Templeton, 2011; German Biogas Association, 2015), complex anaerobic processing and the great variety of possible modes of action, currently little experience exists with respect to effect of the process on the concrete structures used (König, Rasch, Neumann, & Dehn, 2010; König, 2013). Knowledge of similar structures used in agriculture (De Belie, Debruyckere, Van Nieuwenburg & De Blaere., 1997; De Belie et al., 2000a; De Belie et al., 2000b), waste water plants (De Belie et al., 2004; Fernandes et al., 2012; Fjerdingstad, 1969) and sewage plants leads to the assumption of high levels of exposure to acidic materials. In this work, mechanisms were analysed for a silage clamp and two fermenters with different desulphurisation processes in order to ensure the sustainability of the concrete structures used and the energy sources. Using exposure tests in fermenters the resistance of different concrete mixes against the acid milieu was determined.

2. Materials and methods

2.1. *Materials*

2.1.1. *Silage clamp*

A silage clamp (length/height = 60/4 m), that has been in use for four years was investigated in terms of the damage mechanisms which took place. The tests were performed in-situ (i.e. on site) or ex-situ (i.e. in the laboratory) on material (twelve cores with a diameter of 100 mm and six powder samples from three different depths) and four extracted substrate samples (only grass silage). The storage time of grass silage was approximately ten months from October until August, year after year. The samples were taken in August 2010.

Table 1 – Initial substrates for biogas plants according (acc.) to Wellinger, Murphy, and Baxter (2013) and Omer (2014).

Renewable resources	Residues	
Agriculture		Industry, commerce, municipalities
Plant cultivation Corn, Grain, Sudan grass, Sweet sorghum	Animal residues Farmyard manure, Animal excrements Plant residues Grain strippings, Straw	Food industry Product wastes, Market wastes, Leftovers Municipal waste management Organic waste bin, Green cuttings, Landscape conservation Special sectors of industry e.g. pharmaceutical industry