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Performance, Material Degradation and Durability of a Biogas Chemical Scrubber Operated under Alkaline Conditions

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Abstract

Biogas upgrading to biomethane is commonly performed by alkaline chemical scrubbing. Four different types of materials were examined in the present work. Materials as steel (St-37), polyethylene, polypropylene and glass fiber reinforced polymer (GFRP) were immersed in alkaline environment for a period of 6 months. Extensive experimental analysis has been executed and properties such as tensile strength and Young's modulus have been determined and verified by numerical analysis using Abaqus software. During numerical analysis, a geometrically linear and nonlinear analysis has been employed to determine the tensile stress and strain distribution across the longitudinal axis. Numerical results verify the experimental findings.

Keywords: biogas upgrade, biomethane, CO_2 absorption, material degradation, thermoplastic, glass fibers, finite element method.

1 Introduction

Environmental protection and minimization of greenhouse gas emissions requires an increased share of renewable energy production and consumption [1,2]. Anaerobic digestion is a technology applied for the conversion of organic compounds (biomass) into methane rich biogas [3]. The European Union (EU) goal to increase biogas consumption from 18 Mtoe to 72 Mtoe by 2050, require major investments in anaerobic digestion technology [4]. According to the 2021 annual report of the European Biogas Association (EBA) there currently 19,000 anaerobic digestion facilities [5] and this number is expected to increase by a factor 3 to 4 until 2050.

Biomethane is a substitute to fossil natural gas that is produced after separation of biogas CO_2, and other impurities (e.g. H_2S, NH_3, siloxanes, moisture) [6]. It can be stored into the existing natural gas grid or be liquified for use as a vehicle fuel. The annual quantity of biomethane generated at EU level, is currently around 3 bcm and this number is expected to increase to 36 bcm by 2030, considering the Joint European action for more affordable, secure and sustainable energy [7]. The technologies applied for biogas upgrading to biomethane mostly include membrane separation, water scrubbing and chemical absorption [6]. Chemical (alkaline) absorption is simple to design and operate [6]. The most commonly used chemical for carbon dioxide absorption is sodium hydroxide (NaOH) [8]. In this case, gaseous CO_2 is dissolved in the liquid phase of the scrubber and converted to Na_2CO_3, thus retained in the liquid.

It is well known that chemical scrubber liquids are often corrosive. Scouring action as well as electrochemical corrosion are main causes of damages on component surfaces [9]. Metals, polymers and polymer composites are used in many applications [10-15]. Many existing studies in the broader literature examined mild steel (low carbon) in alkaline environments. Results showed that a passive form was formed which restricted the anodic dissolution rate to technically negligible levels.. On the other hand, polymers (thermoplastic, thermoset) or glass fibre reinforced composites, offer attractive potential and advanced properties such as lightweight constructions with high specific strength and stiffness, good resistance to corrosion and so on. However, there also exists a considerable body of literature where mechanical performance of polymer and polymeric composites analyzed in different environments (wet, high temperature and seawater) [16-21].

Aim of this study was to assess the performance of pilot-scale chemical (alkaline) scrubber for biogas CO_2 absorption and identify optimum operating conditions in terms of scrubber liquid pH. The optimum pH values were then selected to evaluate the aging effect of different scrubber construction materials (steel, polypropylene, polyethylene and GFRP). All scrubber material were tested with reproduced variable in an accelerated weather testing chamber. In this study the main aim is to understand the durability of four different materials exposed to an alkaline environment..

2 Materials and Methods

2.1. Chemical scrubber design and operation

The chemical scrubber used for the study had a total height of 4.0 m, diameter 0.4 m and a working volume of 250 L (Fig. 1). The chemical scrubber was packed with plastic pall-rings (1 inch diameter) and the biogas flow rate was maintained at 120 m^3/d during the study corresponding to an Empty Bed Contact Time (EBCT) of 3 min. The biogas CO_2 content at the scrubber influent was 25% (CH_4 = 75%) and the volumetric CO_2 loading rate 9350 g/ m^3 h. The alkaline liquid

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recycle flow rate was maintained constant at 0.75 m^3/h corresponding to a biogas to liquid ratio of (G/L) 6.7. The operational temperature ranged between 20-25 ºC during the study. The pH of the scrubber liquid was maintained at the desired level using 20% NaOH solution which was dosed using a peristaltic pump (Watson Marlow). pH monitoring was performed using a digital pH meter.

2.2. Specimen configuration

The testing configurations were based on ASTM standards E345-16 and ASTM D638-14 for metal and plastic materials, respectively. The specimen dimensions per type of material are shown in Fig. 2.

Fig. 1. Photographic representation of the alkaline chemical scrubber used for CO_2 removal from biogas.

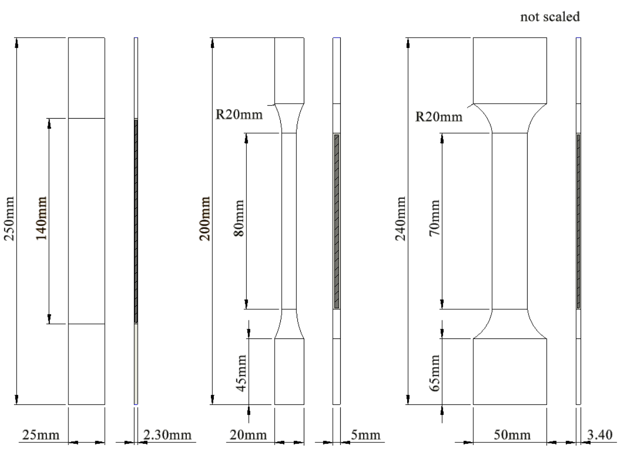


Fig. 2. Dimensions of specimens of (a) GFRP, (b) thermoplastic materials and (c) steel (St-37).

2.3. Materials and specimens' preparation

In this study, the influence of the alkaline environment was examined. Different types of materials were used: steel (St-37), polyethylene (PE), polypropylene (PP) and glass fibre reinforced polymer (GFRP) [22]. According to the ASTM standards, the free length (gauge length) of specimens was varied (see Fig. 2). A total of 112 specimens (7 specimens for each case) were manufactured and tested. Polyethylene (PE-100) and polypropylene (PP) sheets were provided by Stemplast company (Greece) while steel plates (St-37) were supplied by Chryssafidis company (Greece). The specimens were immersed in the alkaline environment for 2, 4 and 6 months, respectively. Glass fibre reinforced composite plates (Sigratex GE) were in a prepreg form. Twelve layers of 0º were cured on autoclave chamber for 1 hour at 1 bar and 120ºC.

2.4. Hydrothermal conditions

Hydration is the most common cause of steel degradation, while polymer diffusion is affected by conditioning temperature, environmental humidity and additives in polymers. Each factor directly affects the diffusion coefficient, which is function of temperature. As temperature increases, the diffusion coefficient increases too. During experimental procedure, a part of the specimens (seven) was used for control (unsoaked), while others were immersed in a metal bath containing alkaline scrubber medium with pH 12.5. The temperature was kept constant at 24ºC for the entire period of experiments (6 months) simulating the environment prevailing into a chemical scrubber unit (Fig. 3).

Fig. 3. Direct immersed of specimens in metal bath containing alkaline scrubber medium

2.5. Mechanical Testing

Further on, all specimens were tested on Universal testing machines Instron 8872 (for polymer material) and Instron 8802, with a load capacity of 25kN and 250kN, respectively. A displacement rate of 1mm /min was selected. The specimens were tested up to failure. The maximum load recorded by the machine was considered the strength of the specimen. Tensile load and elongation must be transformed to the tensile stress and strain in the gauge region, respectively, to obtain the tensile stress-strain curve. The results of the specimens of each material subjected to hydrothermal ageing will be compared with the corresponding reference material.

3 Results and Discussion

3.1. Effect of pH on chemical scrubber performance

The experimental results from the operation of the pilot-scale facility demonstrate that maximum CO_2 removal efficiency of 95% was achieved at pH = 12.5. Indeed, decreasing the scrubber pH resulted in lower CO_2 removal efficiency (see Fig. 4). During chemical scrubber operation the consumption of NaOH was calculated equal to 2.1±0.5 kg NaOH / kg CO_2 removed, corresponding to around 1 kg NaOH / m^3 biogas. Based on the above it was decided that the aging experiments were conducted using the alkaline scrubber liquid with a pH of 12.5.

3.2. Mechanical properties of scrubber construction material

In this section, the effect of an alkaline environment (pH value 12.5) on the mechanical properties of different materials was examined. Figures 5a-d show the experimental stress and strain curves of the specimens. As mentioned before, the specimens were subsequently loaded to failure in tension.

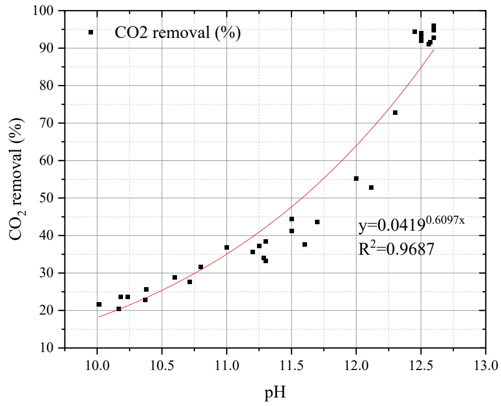
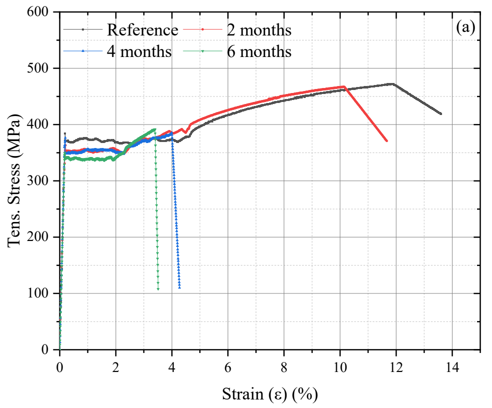
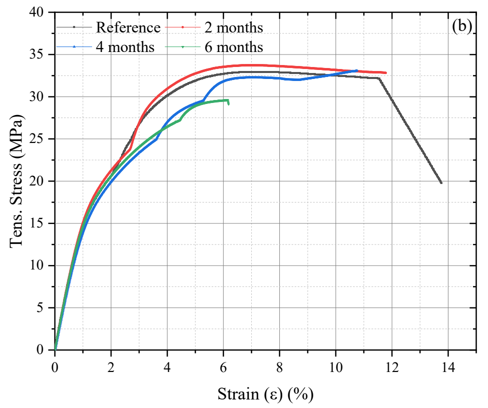
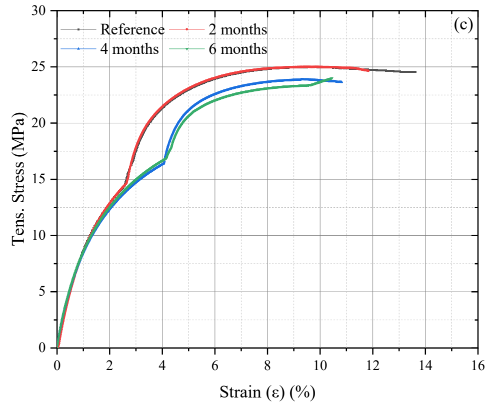


Fig. 4. Effect of pH on CO_2 removal efficiency using a chemical (alkaline) scrubber operated with biogas (CH_4 in = 75%, CO_2 in = 25%, EBCT = 3 min, T = 20-25 °C).

From Fig. 5a-c, a linear increase of the stress with the strain was observed, followed by a nonlinear behavior. Young's modulus also predicted by using stress-strain curves. According to Fig. 6a, in steel test specimens the main failure varies as a function of immersion period mode which takes place in the middle of the specimens, which confirms the model of the execution of the experiment and therefore the experiment is considered valid. Although for polymer and polymer composite specimens the necking occurs near the top or the bottom, and not near the center of the specimen, and this is observed across all the ageing intervals (Fig. 6b-d).







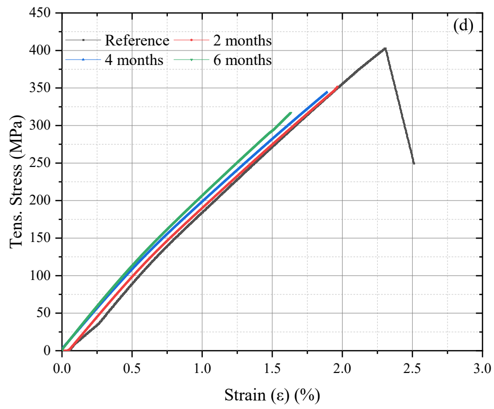


Fig. 5. Tensile stress versus strain for (a) steel, (b) polypropylene, (c) polyethylene and (d) glass fiber reinforcement polymer.

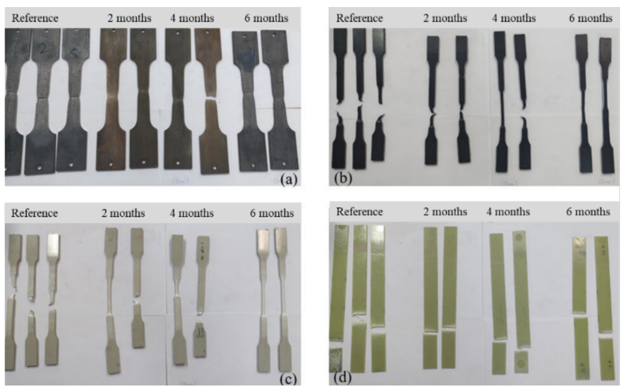


Fig. 6. Tensile test failure modes for (a) steel, (b) polyethylene, (c) polypropylene and (d) glass fiber reinforced polymer.

However, for polymeric composite specimens, response was observed, until failure. During experimental tests, delamination of the glass fibers was also observed while cross-section was completely severed. The tensile strength, as well as moduli of the materials, are presented in Tables 1 and 2. Table 1 shows that the tensile strength of materials was slightly increased during the first 2 months after soaking in the alkaline solution, and it reduced gradually afterwards. The tensile strength of steel and GFRP specimens will eventually decline to a very low level around 490 MPa and 300 MPa after 4 months of soaking in the alkaline solution at a constant temperature. It should be mentioned that metal failure is due to single propagation of the crack, compared with the additional failure of the GFRP effects and voids in the matrix, form microcracks. Microcracks may occurs by moisture, where induces swelling of the matrix. In this case, the fibre-matrix adhesion is weakened [23-25].

Generally, direct immersion of the polymer and polymer composites in aggressive environments (alkaline solutions) resulted in the degradation of the mechanical properties over a relatively limited time [26-33]. Furthermore, from Table 1, no further degradation in the tensile strength of the thermoplastic materials (PE,PP) was evidenced after 5 months of soaking in the alkaline solution. This is one reason why thermoplastic polymer matrices are suitable for biogas applications [39]. Generally, thermoplastic materials swelling capacity depends on the specimen preparation [35-39].

Table 2 shows the normalized Young's modulus as a function of the treatment time in alkaline solution at a stable temperature. From the experimental results, it is clear that tensile strength reduction is not proportional to the decrease of modulus of elasticity, which was less pronounced. Furthermore, Table 2 reveals only small variations in the elastic modulus after ageing (with a maximum loss of 9.42%, polyethylene).

Table 1. Summary of tensile test results.

Months	Tensile Strength [MPa]							
	St-37		PE-100		PP		GFRP	
	Avg. values	Std. Dev.	Avg. values	Std. Dev.	Avg. values	Std. Dev.	Avg. values	Std. Dev.
0	493.5	1.5	25.6	0.07	33.0	0.30	406.1	22.82
2	498.7	1.4	25.9	0.35	33.7	0.04	348.4	22.14
4	480.1	1.9	23.8	0.14	32.3	0.07	344.5	21.72
6	495.7	5.1	23.8	0.28	32.1	0.17	304.8	23.00

Table 2. Summary of Youngs' modulus results.

Months	Young 's Modulus [MPa]							
	St-37		PE-100		PP		GFRP	
	Avg. values	Std. Dev.	Avg. values	Std. Dev.	Avg. values	Std. Dev.	Avg. values	Std. Dev.
0	209.55	4.4	1.38	0.189	1.76	0.014	22.82	0.13
2	201.01	1.67	1.32	0.085	1.80	0.003	22.14	0.35
4	214.28	5.6	1.11	0.032	1.67	0.116	21.72	0.08
6	202.3	1.2	1.25	0.138	1.75	0.033	21.0	0.11

3.3. Finite element modelling

Implicit numerical simulations of the tensile test were carried out by using Abaqus. The dimensions of the specimens were presented in a previous section (Fig. 2). Two models were used in order to predict the progressive failure of the materials. The first model was an elastic-perfectly plastic model which predicts the failure of polymers and metals. On the other hand, a linear elastic model was selected to describe the failure of GFRP. The damage initiation standard options as well as damage evolution for ductile metals were also selected. By using such options, the damage caused by nucleation, growth, and aggregation of voids can be predicted. Two different elements were also used. More than 20000 linear eight-node elements (C3D8R) and four-node elements (S4R) were used for metal (and thermoplastic materials) and polymer composite, respectively. The models were analyzed according to the boundary conditions shown in Fig. 7.

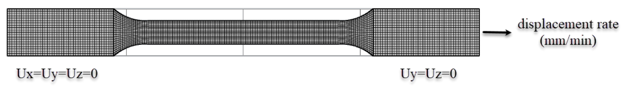


Fig. 7. Typical finite element mesh and loading and boundary conditions of the specimens.

The load is applied incrementally so that the stress-strain distribution monitors the increasing load, thus enabling the plasticity equations to be solved correctly. This process is needed in non-linear finite element analysis to avoid the possibility of convergence to an incorrect solution. Table 3 shows the finite element results of the tensile specimens compared with the additional experimental results. Numerical results verify the experimental findings.

Table 3. Comparison of Finite Element (F) and Experimental results (X).

Months	Tensile Strength [MPa]							
	St-37		PE-100		PP		GFRP	
	X	F	X	F	X	F	X	F
0	493.5	491.35	25.6	26.36	33.0	34.93	406.1	415.15
2	498.7	483.33	25.9	26.12	33.7	35.07	348.4	362.12
4	480.1	396.73	23.8	24.49	32.3	33.75	344.5	353.16
6	495.7	401.66	23.8	24.36	32.1	30.06	304.8	323.71

4. Conclusions

The aim of this study was to examine the durability of four different materials exposed to an alkaline environment (pH = 12.5). The experimental results reveal, that increasing the immersed time from 0 to 2 months, the tensile strength slightly increases. However, mechanical properties decreased as the immersion time increased. For GFRP specimens, swelling leads to decrease of adhesion bonding of fibre-matrix, where multiple microcracks can be formed in the matrix. On the other hand, steel failure can be described as a term of propagation of a single crack. Generally, results shows that thermoplastic materials (PP, PE) could be alternative solutions for biogas applications. It must be noted that all the experiments were made using raw materials and no coating was applied.

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