Maco Technology srl / Centexbel
Integrated sensors for the detection of ammonia and hydrogensulfide in biogas plants.

Context
Despite the development of a new generation of coated fabrics, the tensioned membrane structures for biogas plants are still quite problematic in terms of durability of the membrane, mechanical stability of the connections and overall structural behaviour of the structures.

The main failures are due to two main reasons: the early degradation of the coated fabrics, which lead to the progressive increase in the losses of gas and the subsequent reduction of the tensile strength of the membrane, and the rupture of the welded seams due to the decrease in the mechanical performance of the PVC coating due to the high temperature and chemical corrosion (Fig. 1 & 2).

Objectives
Maco Technology srl and Centexbel, within the activity of the EU funded research project MULTITEXCO, developed a new generation of sensors for the detection of ammonia and hydrogensulfide.

The main objective is to detect the misuse of a coated fabric through the irreversible colour change of the sensor and to simplify the legal controversies in case the manufacturer uses a coated fabric designed for other applications or when the client uses the biogas plant with a different substrate which releases concentration of gasses different from what considered for the initial design.

Existing Biogas plants as case study
Maco Technology is currently investing in the development of innovative structures for the biogas sector. Recent projects include Tensairity® roofs based on inflatable beams for square sewage basins with a span up to 50m or inflatable floating roofs for circular tanks with a diameter up to 65m.

The experience gained in the last years during the recladding of several existing biogas plants highlighted the inadequacy of numerous coated fabrics for heavy duty applications in presence of corrosive gases such as H_2S and ammonia. The problem has been investigated through detailed analyses of samples collected from biogas fermenters (where high corrosive gasses are likely to accumulate) selected as a case study due to the premature degradation of the coating.

Chemical analysis of deteriorated samples after biogas formation was performed using XRF, FT-IR and dynamic headspace. Samples showed various levels of deterioration, even on the same fabric. Despite the material used was specifically designed for biogas applications, the exposure to a different gas or to a higher concentration of corrosive chemicals, combined with inaccuracies during the manufacturing, lead to the early degradation of the PCV coating. The effect, which is anticipated by a change in the colour of the fabric, is more evident on the fabric panel with the edge of the fabric exposed to the internal atmosphere. The corrosive chemicals penetrated the fabric form the edge along the fibres and destroyed the protective coating from the inside.

The XRF analysis and the FT-IR analysis carried out highlighted that the failure of several membrane structures used in corrosive environments like biogas plants are related to the inadequacy of several coated fabrics for heavy duty applications in presence of corrosive gases such as H_2S and ammonia.

Development of sensors
For this reason, within the MULTITEXCO project, Maco Technology and Centexbel invested in the development of two sensors for the detection of ammonia and hydrogensulfide. The irreversible colour change allows to detect the exposure of the fabric to corrosive gases or to concentrations beyond the scenarios and the limits considered during the design.

For Maco Technology and for material producers the installation of these sensors offers an important technical and commercial advantage compared with other competitors. The irreversible colour change will prove the misuses of the fabric with no uncertainty and the consequent reduction of the costs related to expensive and time consuming legal controversies.

Pilot case
For this reason, Maco Technolgoy decided to involve one of his main clients in the biogas sector and validate the sensors on field through a pilot case. The brand new biogas plant is based in the Milan area and is designed to transform agricultural waste into fertilizers
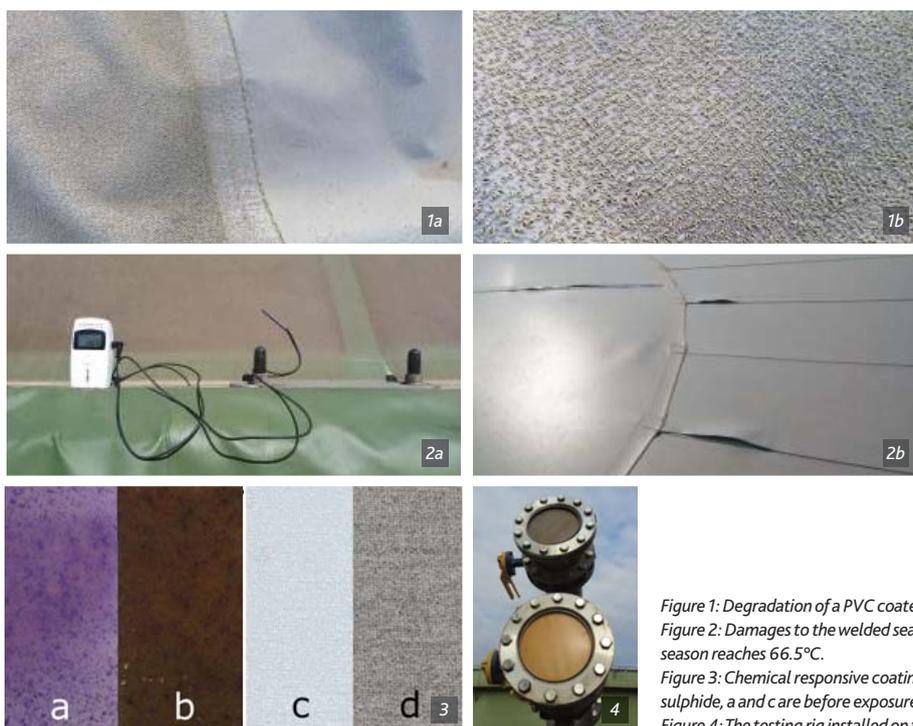
Figure 1: Degradation of a PVC coated polyester fabric due to the exposure to biogas.
Figure 2: Damages to the welded seams due to the high temperature that during a sunny day in the warm season reaches 66.5°C.
Figure 3: Chemical responsive coatings with irreversible colour change: left ammonia, right hydrogen sulphide, a and c are before exposure, b and d after exposure. Scale bar is 1cm.
Figure 4: The testing rig installed on the fermenter in correspondence of the membrane roof.

with the additional production of biogas used to generate the heat and electricity absorbed by the plant. Despite the "state-of-the-art" facilities, the client experienced a rapid degradation of the membrane roof which changed from green to brown in few weeks. A testing rig designed by Maco Technolgoy srl will offer the final validation of the first prototype of the sensors.

The sensors have been developed through a combined set of tests carried out at lab scale and in the pilot project. The XRF spectrum of the samples before and after the exposition to biogas highlighted that the damaged fabrics has a clear sulphur content that hint to the corrosive activity of sulphur containing products in the biogas fermenter. Therefore, the goal was to find two sensors able to detect ammonia and hydrogensulfide, the two main sources of corrosive chemicals. The task was not easy because the sensors had to be practical to install, irreversible and reliable during the expected life span of the structure (from 5 to 10 years).

The team selected a sensor based on an irreversible colour changing pigment to be integrated in the final structure by means of coated patches easy to apply in the key areas of the structures (Fig. 3).

The validation of the new sensors started with a set of preliminary tests at lab scale. To mimic the real conditions, a new test setup was constructed based on the fogging test. In this test, a known concentration of H_2S gas is formed at elevated temperatures (40°C) to which the fabric is exposed. The other side of the fabric is cooled down (18-20°C) to force condensation to occur (Fig. 4).

After the successful tests at lab scale, the sample has been installed in the pilot project be means of a testing rig designed by Maco Technology and able to put the sample directly in contact with the internal atmosphere of one of the fermenters (Fig. 4). The samples have been installed in August 2016 and the intermediate assessment carried out in November 2016 confirmed the expected long term performance of the sensors and the feasibility of the new product which will be sold by Maco Technology in 2017.

Credits

This new product has been developed by Maco Technology srl and Centexbel with the support of D'Apollonia spa and TexClubTec within the MULTITEXCO research project founded by the European Union through the FP7-SME funding scheme.

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Figure 1: Inflatable shelter for solar impulse plane @Solar Impulse.
Figure 2: Inflatable cushions, Le nuage @Nicolas Pauli.
Figure 3: Tea house, museum für angewandte Kunst Frankfurt @ Uwe Dettmar, Frankfurt
Figure 4: Inflatable structure in the CSTB wind tunnel, Nantes, pHD Alexis Bloch, GeM.
Figure 5: Finite Element Analysis of an inflatable beam, GeM.