# USE OF ACOUSTIC EMISSION TECHNIQUE FOR IN-SERVICE EVALUATION OF THE MECHANICAL INTEGRITY OF EQUIPMENT GRP (GLASS REINFORCED PLASTIC)

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## Abstract

*Accidental breakage of tanks containing mineral acid is a dangerous problem in the chemical industry. Corrosion of glass fiber is thought to be responsible of this breakage. The consequences of glass fiber corrosion are cracks and failures leading to the collapse of the structure. We have shown that acoustic emission is a relevant technique for detecting the composite corrosion. Statistical analysis on acoustic emission has been performed.*

## 1. Introduction

### *1.1 Context*

Since the 1980, Glass Reinforced Plastic (GRP) has been used for manufacturing pipes and tanks in the chemical and petrochemical industry, including the storage of mineral acids. This composite material offers higher effective corrosion resistance. However, authors found accidental breakage of tanks (horizontal and vertical) containing mineral acids (hydrochloric and sulphuric) [1] [2]. These failures appear very quickly. For example, a collapse of tank in USA which contains 120000 litres of hydrochloric acid (17%) occurred after one and a half year [2]. Although tank in GRP have a thermoplastic barrier (thermoplastic envelope), sometimes acid migrates through it, due to the presence of defects. This incident can be very dangerous primarily for the industry workers, but also for the environment. These failures are attributed to environmental stress-corrosion cracking (ESCC) mechanism leading to the catastrophic failure before the ultimate stress dimensioning.

### *1.2 Corrosion mechanisms*

Corrosion or aging of the thermoset resin, like polyester and vinylester resins, is a phenomenon widely studied by J. Verdu [3]. These thermoset resins contain ester groups and styrene in their chains which can undergo hydrolysis or oxidation. These mechanisms have low kinetic [1] and cause chain split which is not expected to have strong direct consequences on mechanical properties especially for tanks operating conditions. Kumosa et al concluded that the deterioration of the resins (polyester, vinylester) by acid attack (nitric acid pH 1.2) was insignificant after 336h of immersion [4]. Hamadache observed a decrease of the tensile strength of a polyester resin after immersion in sulfuric acid (27%) during 960H (40 days) [5].

The corrosion of glass fibers in mineral acid solution is less known but very important. Indeed, this corrosion is thought to be responsible of GRP failure. The mechanism of the corrosion, called leaching, is thought to be an ion exchange reaction between the metal ions of the glass fibers ($Ca^{2+}$ and $Al^{3+}$) and the acid medium ($H^{+}$) (eq 1) [6][7][8][9][10].

$$\overline{M^{n+}} + nH^{+} \leftrightarrow \overline{nH^{+}} + M^{n+} \quad (1)$$

The bar shows the association with the glass fiber. This mechanism is thought to induce tensile stresses in the surface of the glass. These stresses could be large enough to cause cracking of the fiber glass. The presence of an external stress can accelerate the mechanism. However residual stress in the composite exists due to the shrinkage of the resin. This residual stress can be enough to cause cracks.
The consequences of corrosion fiber can be significant on the composite mechanical properties, especially with external mechanical stress.

### *1.3. Acoustic emission*

Acoustic emission is a non destructive testing (NDT) used in the chemical industry for many years. Standards exist such as CARP Code (Committee on Acoustic Emission from Reinforced Plastics). These standards are used to ensure the integrity of equipments. Various studies have shown that the corrosion of composites could be detected by this NDT method on composite specimens in tensile, flexural and fracture toughness test, with chemical attack [11][12][13]. Thanks to the progress of signal acquisition and treatment technology, it is now possible to save more information from recorded signals. Thus, it is possible to determine the specific acoustic signatures of observed phenomena.

## 2. Test cell and experimental methods

### *2.1 Material*

The resin used for the GRP material is an isophthalic polyester resin Synolit 1717. This resin contains ester groups which can undergo hydrolysis. The pure resin is tested in the acid medium.
The types of glass fiber used are E-glass. This type of glass fiber contains $Fe_2O_3$, $Al_2O_3$ and CaO. These elements react during the attack of the fibers by the acidic environment.
The composite material used has a fiber rate of 54% by weight. It consists of 10 layers of chopped strand mat (CSM) and 9 layers of woven glass.
The specimens used are cut from plates of 1m*1m. Specimen dimensions are as follows:

L = 300 mm, l = 50 mm, Th. = 11 mm.

Aggressive environments used are hydrochloric acid (37%). These environments are known to react with E-glass [6][7].

### *2.2 Test cell and experimental methods*

Cylindrical cells were designed to hold acid. There has been made in Teflon. The tightness between composite material and unit is ensured by Viton joint (Figure 1).

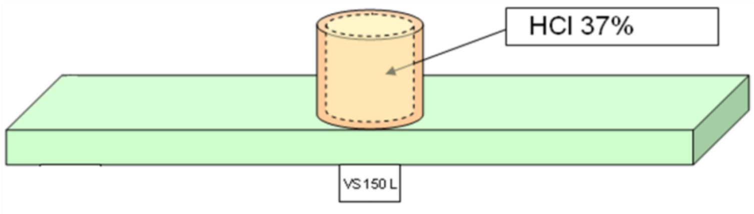



**Figure 1** Plan of the corrosion experiment monitored by acoustic emission

Acoustic emission due to corrosion is detected by a VS150L piezoelectric transducer (Vallen) positioned on the lower edge of the specimen, below the Teflon cell. The transducer has a resonant frequency of 150 kHz. He is connected to a pre-amplifier AEP3N with a fixed gain of 34dB and a pass band of 25 to 850 kHz. The acquisition system is an AMSY-6 with a threshold set to 34dB. The acoustic emission recorded is called a hit. Hit's parameters recorded are Amplitude (dB), Rise time (µs), Duration (µs), Count, Count to peak, Energy (eu) and max Frequency (kHz) (Figure 2). In order to have more information, 4 frequency parameters are used F1, F2, F3 and F4. The 11 parameters are standardized.

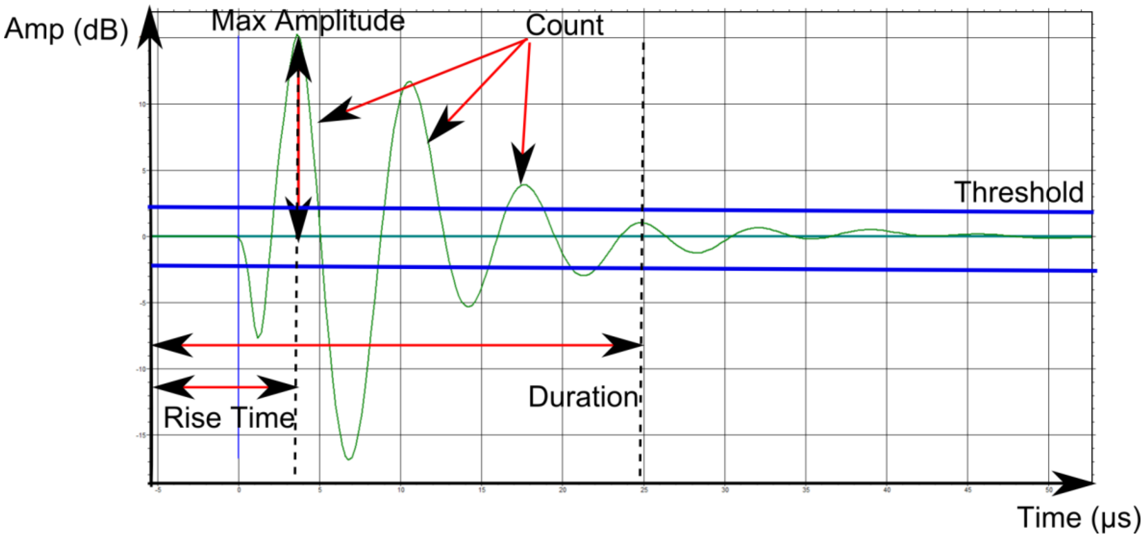



**Figure 2** Hit's parameters

Before clustering, a multivariate technique is used, called principal components analysis. This method reduces a large number of independent variables to a smaller set of variables. These principal components are a linear combination of the original variables. In order to do that, the Mathlab function "princomp" is used.

Clustering is made by using k-mean's method. This method separates n observations in k clusters. The criterion used is the minimum Euclidian distance between hits and the cluster's center. Toolbox "kmeans" is used in Matlab. The initial cluster centroid positions are selected from the n observations at random.

The exposure time varies from 350 to 1000h. Afterwards, they are washed with clean water and dried at room temperature.

After exposure, a visual observation is done. Samples are cut for observation by scanning electron microscope (SEM), FEI XL30. Energy-dispersive X-ray analysis (EDX Bruker Spirit) is also used in order to provide an X carthography under the SEM. Analysis of the chemical resin's degradation is performed by infrared spectrometry and durometer with a portable Barcol GYZJ 934-1 (following the recommendations LABOMAT).

## 3. Performed experiments

The different test performed are shown in table 1

| Test number | Environment | Exposure Time (h) | Polishing |
|---|---|---|---|
| 1 | HCl 37% | 350 | Yes |
| 2 | HCl 37% | 350 | No |
| 3 | HCl 37% | 1000 | No |
| 4 | HCl 37% | 1000 | Yes |

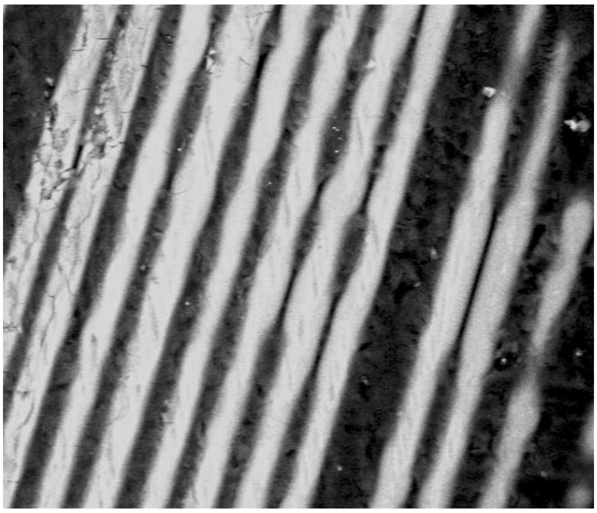
**Table 1** Experiment performed

The different exposure time is performed in order to observe the effect of the medium diffusion through the material. Polishing is made on two tests in order to remove the upper resin layer.
Test on pure resin (Synolit1717) is also done.

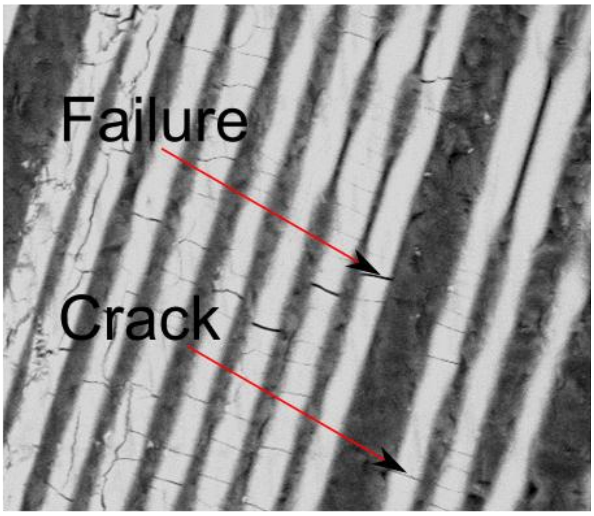
## 4. Results

*4.1 Observation and physicochemical analysis*

After exposure to Hydrochloric acid, test samples become yellow. The Hydrochloric acid solution becomes also yellow. When the sample is polished, a fiber's whitening is observed. Chandler et al show by ultraviolet and visible absorption spectrum that the yellow color is due to the formation of ferric chloride (FeCl3) [15].
Cracks and failure are seen by SEM (Figure 3).



Before exposure




After exposure

**Figure 3** Scanning electron micrographs showing failure, cracks of glass fiber

Energy-dispersive X-ray analysis (EDX) performed on fibers in contact with HCl (37%) show variations comparing to typical fiber. Indeed, the peak height obtained for calcium and aluminum clearly decreases compared to normal fiber. For example, the mass percentage of Calcium decreases from 40% for a typical fiber to 10% when he is in contact with HCl 37% for 350h.

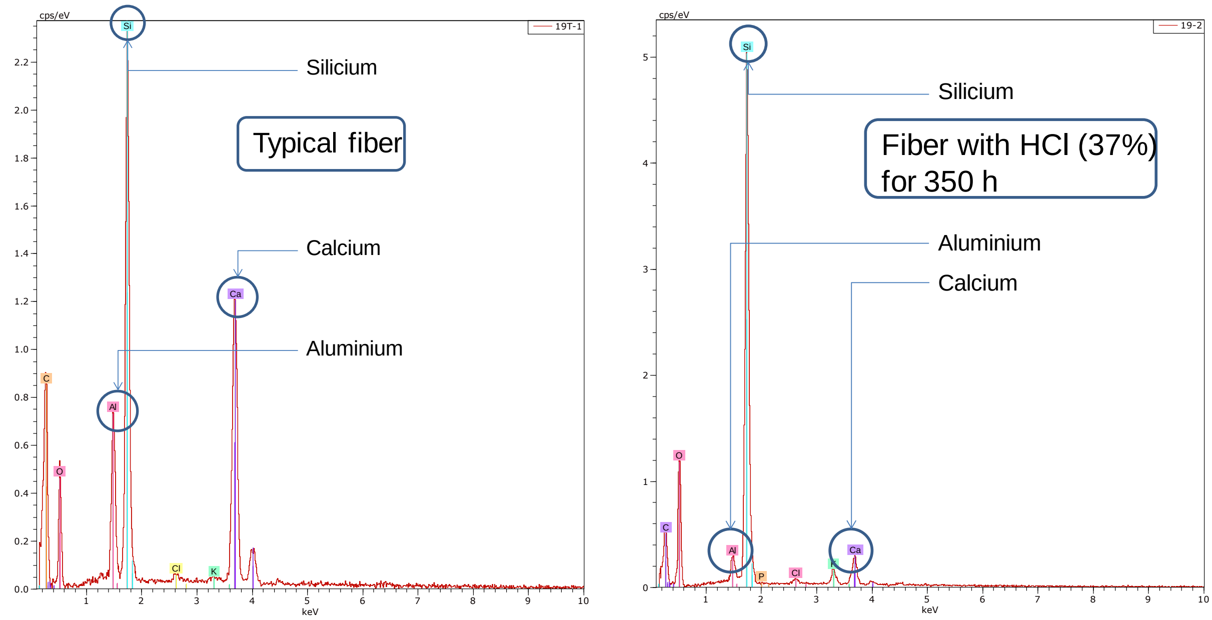



**Figure 4** EDX of typical fiber and a fiber with HCl (37%) for 350 h

Test with durometer Barcol and infrared spectrometry don't show any change of the resin. These methods don't provide evidence of resin degradation.
Observations by SEM don't show also any difference between pure resin and pure resin in contact with HCl 37% for 350h.

*4.2 Acoustic emission analysis*

We have shown in a previous work that the variation of cumulative events with time is proportional to the microstructure [16]. For example the percentage of fibers on the first 250µm of depth is more important in the Test 1 (20%) than the Test 2. So there are more events of the beginning of the test for the specimen 1. We notice that no acoustic emission is recorded on pure resin test.

Before clustering, principal component analysis is made in order to reduce the number of variables. For example in the 1st specimen, the five first principal components are chosen. Indeed, with the five first principal components we have 90% of the total variance which is sufficient for a statistical analysis.
Clustering is made by using k-mean's method. The number of clusters k is chosen by using the Davies-Bouldin index (D&B index) [17]. It takes into account both the distance between clusters and the within clusters scatter. The D&B index is calculated for different number of clusters. The "optimal" number of clusters is the one which minimizes this index. For the different corrosion tests, the index is minimal for 3 clusters (Figure 5).

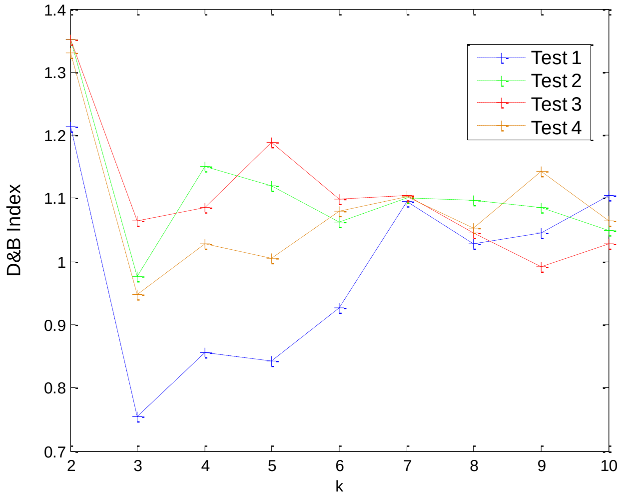
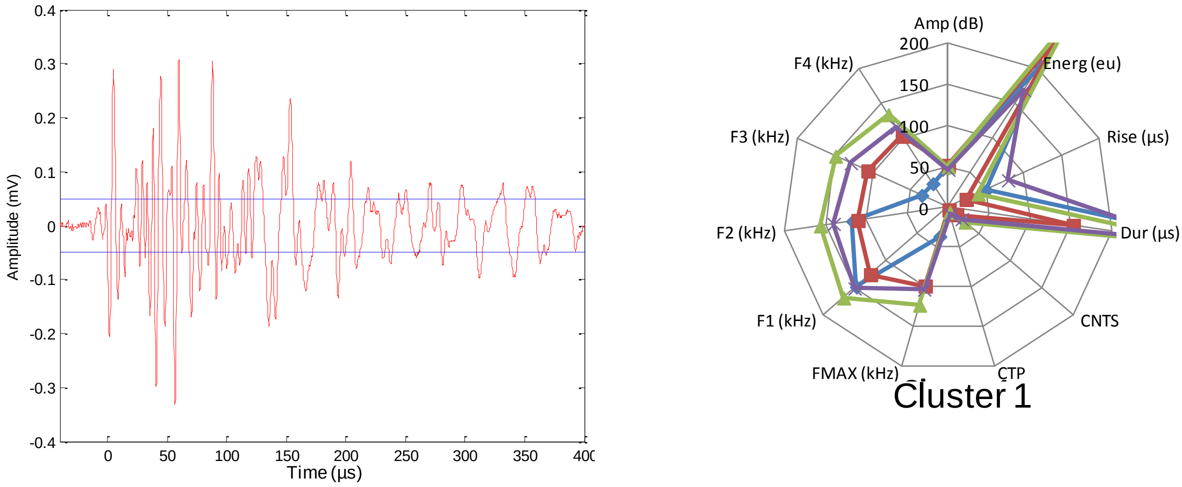



**Figure 5** Results of D&B index for the different tests

Several clustering (100) are performed in order to have stable results. K-mean's method is made on the hits in the principal component vector space. The Figure 6 shows the result of the classification (waveforms and cluster centers). The cluster centers are presented in a radar chart.



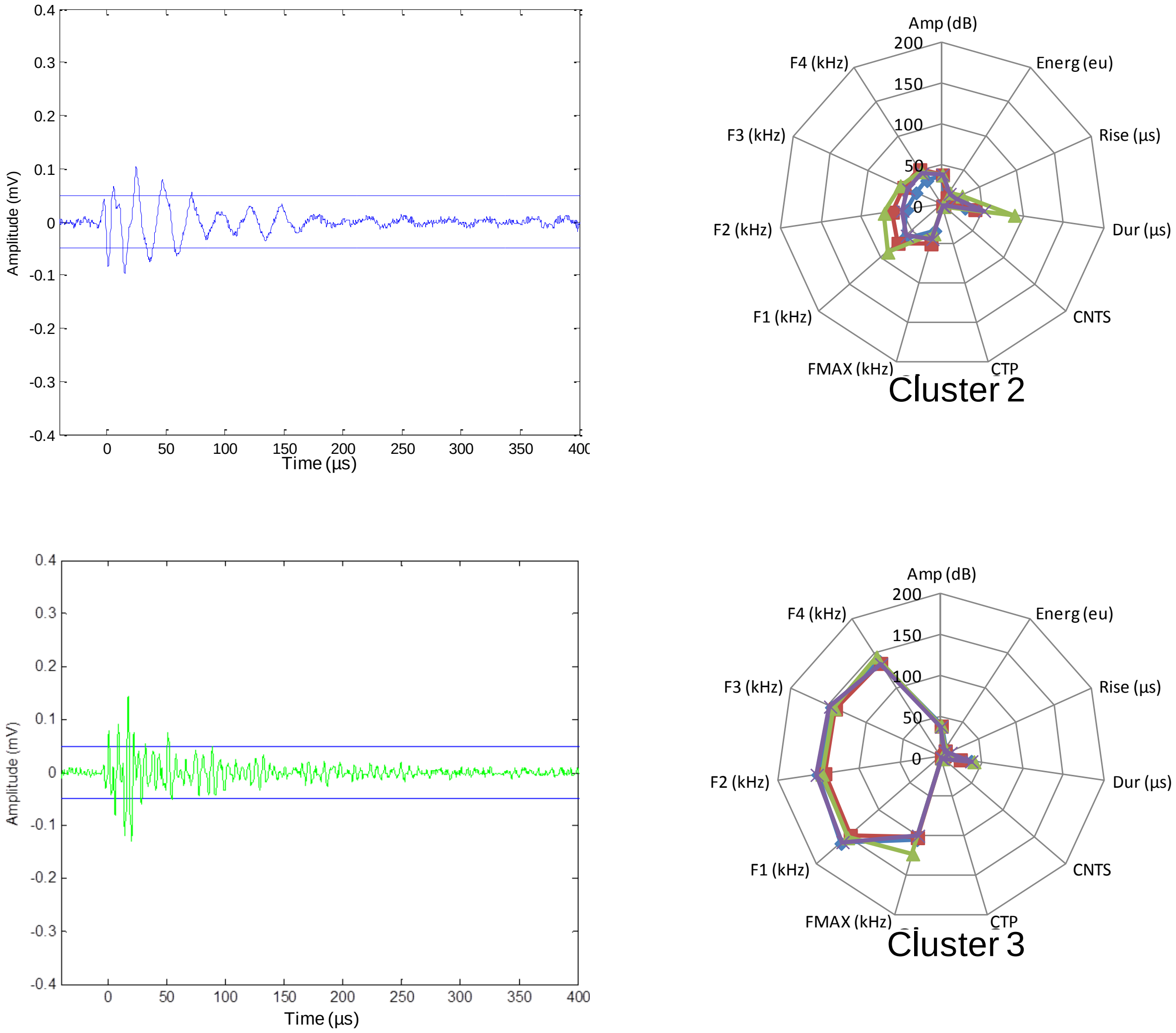



**Figure 6** Waveform and cluster center for each cluster

Cluster 1 (red) is characterized by signals with a high amplitude (≈ 40dB), energy (<200 eu) and duration (<150 µs). This kind of signals is very complex. The two other clusters have the same characteristics except the frequency parameters. Signals of the cluster 2 (blue) have a low frequency (50 kHz) compared to the signals of the cluster 3 (green) (150 kHz). The different colors on the radar chart represent the different tests. We may notice the remarkable reproducibility of these results.

## 5. Conclusion

Composite corrosion or aging in acidic medium is a phenomenon that can have serious consequences especially in the chemical industry. Corrosion mechanism of fiberglass has been confirmed by SEM and physical analysis. The use of acoustic emission in order to detect cracks and failures of fiberglass is relevant. 3 clusters have been found thanks to statistical analysis of acoustic emission signals.

Our ongoing work is to make the link between acoustic emission signatures with the observed defects. We will also study the effect of the distance between sensors and the corrosion area in order to locate the damage. Finally we will perform stress corrosion tests so as to study the synergy of stress and corrosion.

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