Testing pressure vessels operating in the HF acid environment by acoustic emission method

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Abstract. The article presents some results of using the acoustic emission method (AE) in testing of pressure vessels which use hydrofluoric (HF) acid as a catalyst to produce different oil products. The results of consecutive AE testing of vessels carried out with an interval of several years are discussed. The possibility of detecting some operational defects at different stages of their growth is considered. In particular, the possibility of early diagnosis of blistering and de-lamination of the vessel wall is shown. Elements of the AE testing data analysis are proposed, which make it possible separate signals from the evolution of two different types of metal damage (de-lamination and general corrosion) using the integral characteristics of the signals.

1. Introduction
The AE method in testing of real industrial facilities and laboratory studies of samples of several centimeters in size have significant differences. The main problem in using the results of laboratory studies in AE testing of industrial facilities is due to the fact that laboratory tests of materials are not strictly comparable with the actual conditions of their operation [1].

An adequate representation of the relationship between the facility properties and AE testing data using analytical models is practically impossible due to the large number of factors affecting the AE generation by a large-sized structure. Not for all, even known factors, it is possible to assess the degree of their influence on the test results. In addition, the process of AE generation may be influenced by factors that are unknown to specialists conducting testing [2, 3].

The information support of this application of the AE method is extremely limited. The number of articles on AE testing of industrial metal pressure vessels in the total mass of publications devoted to the AE method is insignificant. For example, out of 200 reports of the last three European conferences on AE (EWGAE-2014, 2016, 2018), 8 reports can be attributed to such works. For comparison, no less than an order of magnitude more theoretical works were presented. Perhaps this is a manifestation of certain limitations of the information policy of industrial enterprises on the use of this AE application and indirectly indicates the special importance attached to the results obtained.

An important difference is the significant difference in the degree of responsibility for the results obtained by specialists who control the state of dangerous industrial facilities in comparison with specialists who use AE in most other applications.

Accidents of the HF-acid vessels are potentially very dangerous and can cause significant material and ecological detriment [4, 5]. Serious measures are required to monitor their condition, including the use of NDT methods. One of such methods can be the method of acoustic emission (AE).

According to [5, 6] the damaging mechanisms of carbon steel in HF acid vessels are three types of defects associated with the action of atomic hydrogen on the metal structure: 1) hydrogen blistering
and de-lamination of the base metal of the wall; 2) stress-oriented hydrogen-induced cracking typically occurring in weld heat-affected zones; 3) hydrogen-assisted stress corrosion cracking in areas of increased hardness (usually in welds).

A significant influence on the evolution of defects formation processes is exerted by a layer of iron fluoride (FeF₂), which is formed upon the first contact of acid with a clean metal surface of a new vessel. It has a glassy structure formed by white tetragonal crystals; density 4.09 g/cm³; melts at 1100°C; slightly soluble in water. Fluoride is a product of the corrosive effects of HF acid on metal. However, in the future, it serves as a protective layer for the metal of the wall. The intensity of this type of corrosion at steady-state operating parameters mainly depend on the H₂O content in the working environment. Corrosion is negligible with content of H₂O below 1 ppm. Accordingly, the thickness of the fluoride layer does not increase and its structure does not change.

2. Results and Discussion

2.1. AE method using for early diagnosis of the vessel wall de-lamination

Fragments of the planar location graphs obtained during three serial AE tests of the vessel (vessel No. 1) used for the separation of hydrocarbons and HF acid are shown in figures 1 (a), (b), (c). The volume of the vessel is 23.5 m³, diameter – 2000 mm, wall thickness – 22 mm, steel – A-516 Gr.70.

According to the results of the first AE testing carried out 5 years after the start of operation of the vessel (figure 1 (a)), ultrasonic (US) testing was carried out. It found accumulations of inclusions of an acceptable size in the areas of AE activity. Therefore, for these sections, US testing was appointed during each subsequent planned stoppage of the vessel.

A feature of the de-lamination is the combination of a long incubation period for the evolution of a group of clustered discontinuities (sometimes tens of years) with accelerated growth at the stage of complete formation of discontinuities with a diameter of tens of centimeters (for a shorter time than the period between planned inspections) [7]. Moreover, higher AE activity during AE testing is observed, as a rule, at an early stage of de-laminations formation as a result of the growth and association of a large number of small neighboring discontinuities in the area of their concentration. It significantly decreases by the time the de-lamination reaches its maximum size, when rare sources of AE are recorded mainly at the boundaries of the de-lamination. Each de-lamination goes through the general stages of evolution, but can evolve according to an individual time schedule. Over time, the process of de-lamination’s formation can be activated in new areas of the vessel. Therefore, the total AE activity of the test object during the next tests may increase as a result of the involvement of these new sites of the de-lamination’s formation, where the destruction process began later.

In this example a feature of the first fully formed de-laminations was their location, as a rule, around the manhole under a wide patch ring. Therefore, their detection was unlikely by selective ultrasonic testing which is a traditional method of de-lamination detection. This is due to the fact that ultrasonic testing is carried out, as a rule, from the outside of the vessel wall, if there is no additional information for its use. Sites with de-lamination are closed outside by patch ring on this vessel. AE testing results provided additional information.

According to the results of the second AE testing (figure 1 (b)), the ultrasonic testing detected accumulations of discontinuities of acceptable sizes and the presence of a bottom signal in all areas of AE activity.

Figure 1 (c) shows the result of the third AE testing in the manhole’s area. By ultrasonic scan test that was conducted outside on the 300×300 mm site marked B1 in figure 1 (a), and by a visual internal inspection were found: blisters (photo in figure 1 (d)); an extended discontinuity measuring 70×20 mm at a depth of 16 mm in the absence of a bottom signal; numerous discontinuities at a depth of 6.1 to 19.2 mm.

Ultrasonic thickness measurement performed from the inside of the vessel determined the delamination in sites L1, L2, L3 and L4 (without blisters). Figure 1 (e) shows the result of one of the thickness measurements in these areas.

The early diagnosis of destructive processes in the vessel’s wall by AE method became the basis for additional control of the vessel. On the vessel already at the time of the third test for several years and until the replacement of the apparatus a system of continuous AE monitoring was used.
Figure 1. Location map’s fragments for 1st AE testing of vessel No.1 (a), for 2nd test after 9 year (b) and for 3rd test after 19 year (c). Marks L1, L2, L3 and L4 and the contours on location maps indicate the position of the de-laminations at the time of the 3rd AE test.

Figure 1 (d) is a photo of a blistering area; it is labeled B1 in figure 1 (a), (d), (c). Figure 1 (e) shows the measurement of the metal thickness in the area of one of the de-lamination.
2.2. Problem of identifying the type of damage

Figure 2 shows the results of planar location during AE testing of a horizontal vessel (vessel No. 2) with characteristics: V = 243 m³, diameter – 4200 mm, wall thickness – 23 mm, material – carbon steel A-516 Gr.70. In two previous tests of this vessel similar results were obtained in terms of the features of AE activity and the location of AE sources on its shell: numerous dense location clusters with a large number of high-amplitude events.

In general, similar results were obtained during testing of an other apparatus (No. 3) from the same technological chain (vertical vessel, V = 80 m³, diameter – 2600 mm, wall thickness – 20 mm, material – carbon steel A-516 Gr. 70). Previously, one vessel at this technological position has already been replaced due to the formation of de-lamination in several parts of the body. The AE method was one of the methods for diagnosing these bundles [8]. One of the bundles is shown in the photo in figure 3.

Some results of inspection of these vessels were presented in [8]. The most likely damage mechanism was called the process of formation of the bundle. However, in the future it became clear that the erroneous conclusion was made when determining the main damaging mechanism.

The main source of AE activity turned out to be the process of partial destruction of the layer FeF₂, which usually serves as a protective layer for steel against hydrogen-fluoride corrosion. However, the layer is destabilized and the protective function of the barrier layer decreases with an increase in the H₂O content in the process environment above 1 ppm [9]. As a result, new volumes of metal are corroded. Sometimes, to intensify the technological process, the content of H₂O in the process environment is increased. Correspondingly, corrosion intensifies, the vessel wall thickness decreases, and the fluoride layer due to new corrosion products increases in volume and acquires a layered structure (photo in figure 4 (a)).

![Figure 2. Location of AE sources on the reamer of vessel No. 2 (view from above, from above).](image-url)
Figure 3. One of the de-lamination sites of the wall of the previous vessel at the technological position of the vessel No. 3 [8].

After stopping the process unit for preventive maintenance the vessel is freed from oil products and acid. Then residues of HF acid are neutralized and non-solid neutralization products are mechanically removed from the vessel. A solid layer of FeF$_2$ is usually tried to preserve, given its protective function. But partial destruction or damage to the layer in some areas during cleaning still occurs.

AE testing is usually carried out before starting the equipment into operation after the necessary repair measures. By this time the fluoride layer is a randomly damaged inner quasi-shell, which in a complex pattern contacts the metal shell of the vessel (photo in figure 4 (b)). Cracking of this “shell” and de-lamination of its fragments from the vessel body generate AE signals under the action of tensile stresses during pneumatic tests. A fairly close contact of the fluoride layer with the inner surface of the vessel body allows these signals to propagate to AE sensors mounted on the outer surface of the vessel.

The energy of AE signals from the destruction of corrosion products is usually much less than the energy released during the growth of cracks in the metal, and so is more difficult to detect in the field environment [10]. However, a large number of high-energy signals were recorded in the tests under consideration. Therefore, there were certain reasons to conclude that we are dealing with the process of formation of de-laminations, which are precisely crack-like defects. Besides:

- there was a history of damage to pressure vessels at these technological positions by stratification;
- the configuration of the AE activity sites had the form that is characteristic for the zones of de-laminations formation in the areas of concentration of atomic hydrogen collectors;
- according to the literature [5,6], blistering and de-lamination are among the three main types of damage in the environment of HF-acid;

Figure 4. The structure of the fluoride layer in a state of destabilization (a) and a photo of the inner surface of the vessel: areas of the destroyed layer are visible (b).
the most large-scale of the ultrasonic testing (13 sites with a total area of about 10 m²) according to the results of the third AE testing of vessel No. 2 showed thicknesses from 17.2 to 19.8 mm; while within the same area the difference between the maximum and minimum thickness ranged from 0.4 to 1.2 mm; these results left some chance for de-lamination, since the passport wall thickness was 23 mm; such a fast decrease to its measured values as a result of general corrosion was also not expected.

However, the described ultrasonic testing results already indicated that the main damaging mechanism for vessels No. 2 and No. 3 was general hydrogen fluoride corrosion [9] with a high probability. It was decided to replace the vessels. Samples cutting and study of metal from the walls of demount vessels confirmed the conclusion about general corrosion. Prior to the time required for the replacement of equipment, continuous monitoring systems including AE systems were installed on the vessels. Then these systems were reinstalled on new vessels due to the high potential danger of the equipment.

The results of the location of AE sources during testing of the new vessel after 2 years of its operation are presented in figure 5. This vessel replaced the dismantled vessel No. 2. AE activity is recorded, mainly due to frictional processes in the areas where the supports are located. The AE activity in this test is lower than it was when testing a new vessel (before contact with acid), since in two years there was a relaxation of the stresses usual for the new design. Therefore, the fluoride layer is in a stable state. This indicates compliance with the regulatory parameters of the operation of the vessel and the absence of damage of the layer during cleaning of the vessel at a stopping.

The following causes of error in the initial assessment of AE testing data may be indicated:
- incomplete knowledge of the features of defect formation in environments in which test objects were operated;

![Figure 5. Location of AE sources on the reamer of the shell of vessel No. 2 (view from the outside, section along the bottom line of the shell).](image)
- dogmatism in the interpretation of data (formal interpretation of information from literary sources or insufficient study of them);
- applying the method of analogies in areas where more stringent methods of analysis are required; for example, when analyzing the history of test’s objects or in assessing the position and configuration of location clusters;
- incorrect interpretation of some direct or indirect information collected; this applies, in particular, to the results of arbitration testing or such obvious facts as a very large area of AE activity, which is not typical for a real industrial vessel; also migration of sites of AE activity from test to test;
- some fortuities that affected the results of AE testing; for example, the localization of AE sources at the phase separation level (a frequent zone of defect formation) was due to the removal of the fluoride layer during vessel cleaning to the same height;
- as a rule, AE testing is carried out shortly before the end of a planned preventive stops of equipment, the timing of which is dictated by economic conditions. Therefore, the possibility of additional studies of the object to clarify the results of AE testing is significantly limited in time. Moreover, for these vessels special conditions are required for inspection. For example, an internal inspection requires the use of special protective suits, etc.

Regardless of the fact that the specific damage mechanism was first determined incorrectly, an unconditional positive result of AE testing of vessels No. 2 and No. 3 was the decision on additional measures to monitor their condition: the scope of ultrasonic testing during planned stops was expanded and continuous monitoring systems were installed. These systems combined registration of the main technological parameters and AE measurements.

2.3. Use of AE signal parameters to determine the type of damage
The combination of two types of damage in the material of one object of AE testing produces a serious problem in the analysis of data: the main array of AE activity generated by damage of one type can mask signals that generate damage of another type. A defect that is less dangerous in terms of the unpredictability of its evolution dynamics can “obscure” a more dangerous defect. This situation is quite typical for the considered group of equipment.

In the features spaces “Duration vs. Rise Time” (figure 6) and “Duration vs. Amplitude” (figure 7), formed by the integral parameters of AE signals, it is possible to separate the signals recorded during cracking of the fluoride layer from the signals accompanying the formation of bundles, which is satisfactory for the practice of AE testing of industrial pressure vessels. The parameter values are taken in double logarithmic axes.

Figures 6 and 7 show the graphs of the characteristics of the first signals of localized AE events as a result of compilation of data recorded for two vessels: for vessel No.3 (its location map in Figure 2) the destruction of fluorides is mainly recorded and for the vessel No.1 (location diagram in figure 1 (c)) de-lamination processes are recorded. The observed intersections of the data indicate the presence of a different type of damage in each of the vessels along with the dominant mechanism.

The nature of AE events located in areas R3 (figure 6) and R6 (figure 7) is identical to events from areas R3 and R5. The release is due to the scale of the energy characteristics of these events, probably related to the process of combining discontinuities or the increment of long cracks.

Area R7 (figure 7) contains data on the most large-scale acts of destruction of the fluoride layer.

These graphs allow detecting the presence of two types of damage at the test object at the qualitative level. The graphs contain AE events that are not included in any of the clusters also, because it is possible to register events whose nature does not coincide with any of the main damage mechanisms.
Figure 6. Separation of signals associated with fluoride cracking (area R1) and with the growth of discontinuities (area R2) in the Duration vs. Rise Time. Comment about the area R3 in the text.

Figure 7. Separation of signals associated with fluoride cracking (area R4) and the growth of discontinuities (area R5) in the Duration vs. Amplitude. Comment about the areas R6 and R7 in the text.

The choice of features for data separation is associated with the idea of the nature of the destruction of structures that generate the corresponding signals. The growth of a crack in a metal is realized, as a rule, in the form of an abrupt of its length [11] by the size of the plastic zone at the crack tip, followed by braking at the zone boundary. Accordingly, the form of the AE signal in this case reflects the registration of a rapidly decaying stochastic process. In the process of cracking and destruction of even local sections of the fluoride layer, as a rule, a whole ensemble of cracks and micro-cracks is included. This is due to the significant heterogeneity and saturation of this structure with closely spaced fractures of various sizes. The cracks that begin to advance first are likely to reach the zones of the nearest cracks and instigate their growth. The process can take on an avalanche-like character without encountering areas of deceleration in a significant volume of the layer material. As a result, signals from several events are superimposed, and a long-term signal is recorded, with alternating sections of
Figure 8. Examples of waveforms of signals associated with a fluoride layer cracking (a) and processes of discontinuities growth (b) and (c).

attenuation and amplitude growth. Also, due to the presence of an ensemble of sources with different geometric characteristics, these signals are characterized by a wide frequency range. An example of such a signal is shown in figure 8 (a). In figure 6 and figure 7, the position of this particular signal in the area of the regions R1 and R4 is indicated by a circle.

Figures 8 (b), (c) show examples of two signals that are typical for the registration of stochastic events, namely the growth of cracks in the metal. They are registered in the areas of the delamination of the shell.

The position of the signal from figure 8 (b) is marked with small circles in the R2 and R5 areas in figure 6 and figure 7. The position of the high-amplitude signal from figure 8 (c) is marked in the R3 and R6 regions. In this case the form of the signal (the presence of two peaks on the graph) indicates a high probability of combining two cracks in the metal. However, unlike the processes of coalescence of cracks in the fluoride layer this process is not massive and the signal retains the form of a stochastic process.

The proposed method separates the data at a qualitative level. However, its use can be useful in practical AE testing of HF pressure vessels.
3. Conclusion

For early diagnostics of the evolution of such defects as blistering and de-lamination of the shell in industrial vessels operated in HF-acid environments the AE method can be successfully used.

Also the AE method can be used to detect the general corrosion evolution that causes thinning of the vessel wall by changing the state of the iron fluoride layer. It is possible to register the process of destabilizing this layer using the AE method. It is possible to control this process in the online mode if the presence of a continuous AE monitoring system. It makes possible to adjust the technological parameters in order to prevent their negative impact on the state of the equipment material.

Also, the AE method can be used to detect an increase in general corrosion, which causes a thinning of the vessel wall, since this process is accompanied by a change in the state of the iron fluoride layer. The registration of the process of destabilization of this layer is possible using the AE method. It is possible to monitor this process online if there is a system of continuous AE monitoring. This makes it possible to regulate the technological parameters in order to prevent their negative impact on the state of the equipment material.

The possibility of using some characteristics of AE signals as features for forming spaces in which the separation of signals recorded during cracking of the fluoride layer and signals accompanying the processes of formation of delamination occurs is considered. As such spaces it is proposed to use the dependencies “Duration vs. Rise Time” and “Duration vs. Amplitude” constructed in double logarithmic axes.

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