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PHYSICAL MODEL OF PIPELINE STRESS CORROSION

Background
The proportion of main gas pipeline failures due to stress corrosion cracking (stress corrosion) has been steadily increasing during the past 20 years. However, the phenomenon is not observed in other pipelines, despite their almost identical characteristics. For a long time it was assumed that the corrosion can be effectively restrained by applying double protection: insulating coating + electrochemical protection. But electrochemical protection has proved ineffective against stress corrosion. Moreover stress corrosion accelerates with increase of the protection potential. Despite the large number of studies of this phenomenon a physical model that could explain the mechanism of stress corrosion of pipelines has not been found. This in turn did not allow offering effective protection methods. The paper presents such a physical model and its approval by a few examples.

Aims and Objectives
On the basis of analysis and generalization of the results of research in various fields of engineering to develop a physical model of stress corrosion of metals and to propose effective methods of main pipeline protection based on this model.

Methods
The research results presented in the paper were obtained by analysis of similar processes in different fields of engineering, as well as by direct physical experiments with metal samples exposed to stress corrosion.

Results
A physical model of stress corrosion of main pipelines that explains the mechanisms of the process and allows development of effective protection is offered and substantiated.

Key words: main gas pipeline, stress corrosion, stress corrosion cracking, hydrogen sulfide cracking, physical model, protons, internal pressure

Either philosophers or theoretical physicists are those from whom one can hear about the Unity of the world. Tech specialists usually do not think about it; they follow their industry regulations and guidelines without looking into similar documents
relating to other sectors. Meanwhile, sometimes it could be of great help in solving difficult, but important practical problems.

The authors of this paper in different years had to deal with problems in completely different fields, at first glance, not even close to similar to each other: in nuclear physics, welding procedures, and in the oil and gas industry. In implementing various contractual works they had also faced some problems of shipbuilding, electroplating, metallurgy, pipe production. One can ask what unites these spheres? What unites them so as to preoccupy esteemed readers? The answer is simple – the PROTONS.

For a long time, specialists of the oil and gas industry could not unravel the nature of phenomenon called stress corrosion. After 15 ... 25 years of operation, some gas pipelines begin to be covered by a network of parallel surface cracks, which then grow quickly and lead to the destruction of the pipeline. Metal exposed to stress corrosion can not go into rust but only cracks like a cracking log. In most cases, stress corrosion occurs with the general and localized corrosion as the background, as shown in Figure 1. In oil pipelines, water lines and other pipelines such phenomenon is not observed. Anyway, this is stated by many experts and researchers. A lot of research was done, and a number of patterns were identified, yet different authors came to different conclusions, sometimes contrary. And still occasionally heated debate flares up on the causes and mechanisms of this phenomenon.

Scientific disputes themselves are very interesting, but the problem of protection against stress corrosion is not yet solved. Therefore, the main focus is on the diagnostics, so that to detect timely the cracked areas of pipes and replace them before the destruction occurs. But this is just a fight against the consequences, not the phenomenon. With such approach, the volume of repair increases each year as stress corrosion covers more and more pipelines and sections. Repair requires shut-down of gas pipeline, and several lines are laid in one corridor in the most critical areas, so that one line could be shut down without reducing the volume of gas supplies to consumers.

Participation in the investigation of accidents of various pipelines almost all over the former Soviet Union, analysis of similar phenomena in other industries, physical experiments and study of the scientific literature [1 – 12] brought to the understanding of the nature of the phenomenon and to the construction of a physical model of stress corrosion. The model gives clear explanation of all patterns observed.

Main gas pipelines are laid underground, have
the insulating film coating, and, in addition are under the electrochemical protection (ECP). This

Figure 1 – The pattern of metal cracking under stress corrosion

means that the electric potential of $-1.0 \ldots -3.5$ V, with reference to the ground, is applied to the pipeline. Such negative potential creates the energy barrier for positive ions of iron ($\text{Fe}^{2+}, \text{Fe}^{3+}$) thus inhibiting dissolution of the metal in the ground water (via rust formation).

Double anti-corrosive protection is justified, as after 10...15 years the insulating film noticeably deteriorates, peels and lets the moisture in to the surface of the pipe. But even deteriorated insulation remains helpful as it maintains some contact resistance between the pipe and the ground. Without film the contact resistance is not sufficient to create protective potential along the length of the pipeline.

As the film deteriorates, the «protection shoulder» (the part of the pipeline where the necessary protective potential is maintained) becomes shorter, which requires the connection of additional stations. However, actions are often taken in the other way: the potential is increased (negatively) in attempt to compensate for its drop in distant areas. These two methods complement each other and improve the effectiveness of protection against general corrosion. But not against stress corrosion!

It was found that the increase in negative «protective» potential initiates other phenomena. Hydrogen H$^+$ cations in ground water begin «flow» speedily to the negatively charged surface of the...
pipe metal. On the metal surface they receive an
electron and are reduced to neutral state. After that,
the «coat» of the polar water molecules surrounding
the H\(^+\) cation is thrown off, and the cation transforms
into atom of hydrogen. Yet the electron cloud of the
metal is not inclined to let the valence electron of
hydrogen. Therefore, the nucleus of the hydrogen
atom (proton) also can not go far from the metal.
Mobility and penetrating ability of proton are
much higher than that of molecules and atoms. It is
an elementary particle and can penetrate into the
metal and migrate there searching for energetically
favorable state. There appear several such states.
One of them is the union of two stray protons in
the H\(_2\) hydrogen molecule, thanks to the electrons
available in excess inside the metal. The hydrogen
molecule immediately loses mobility and «is
cought» in dislocations or intercrystalline
micropores.
Another state is related to the carbon that is
always available in steels in the form of cementite,
and is ready to unite with four protons to form
methane molecules according to the formula
Fe\(_3\)C + 4H = 3Fe + CH\(_4\). The reaction in accordance
with this formula takes place in several stages
(CH\(_2\), CH\(_2\),
CH\(_3\)) and ends with the formation
of methane molecules. These molecules are also
accumulated in the intercrystalline micropores.
Thus, gases (hydrogen and methane) are
accumulated in the metal, and the internal pressure
is greatly increased. According to some estimates,
this pressure can reach tens and hundreds of
thousands of atmospheres. Simultaneously, the
decarburization of the metal occurs, which was
repeatedly observed during metallographic testing
of samples with stress corrosion cracking. At the
same time the crystal structure of the metal is
distorted, and additional dislocations are formed.
The density of dislocations increases, and the
dislocations lose their mobility. This is because the
dislocations are blocked by poorly mobile «extra»
formations. Locking dislocations leads to the loss
of metal ductility. The metal becomes brittle. High
internal pressure (due to gas accumulation) creates
mechanical stresses, which add up to the mechanical
stresses from the workloads and easily reach a
critical level. Internal bonds in the metal are broken,
and cracks appear. As protons penetrate farther
inside, the cracks in the metal are growing. The
moment comes when the strength of the metal is
exhausted, and the pipeline breaks.
Taking into account that pipelines are buried,
long and have an insulating coating, it is very
difficult to control the process of crack initiation
and development. However, in recent years they
have learned to detect cracks by special flaw detectors passing through the pipeline together with the pumped product.

Now, the reader should have clear understanding how this relates to nuclear physics. There protons are formed in nuclear reactions and bombard the reactor, supporting structures, vessels and pipes. The only difference is that these are high-energy speedy protons penetrating into the metal more easily. If metal articles are loaded, the mechanism of their embrittlement and cracking will be the same.

Welding experts know well that welding electrodes must be dry. Dry must also be the surface of the metal structure for welding. If the humidity is high, water molecules are decomposed into ions and individual atoms under the influence of the welding arc. Also, hydrogen atoms are formed, which in the arc and on the metal surface are decomposed into protons and electrons. Electrons are involved in welding currents, and protons penetrate into the metal. The weld is brittle. High residual stresses remain in the metal. Under workload such weld cracks and breaks.

In the shipbuilding industry, over a hundred years ago, it was first noticed that after attempts to use sacrificial anodes as a protection of steel hulls from corrosion in seawater, the hulls broke up after some time. Steel hull became brittle and weak. There the mechanism of the phenomenon is exactly as in trunk gas pipelines. Sacrificial anodes create on the hull negative potential relative to sea water. H⁺ cations from seawater are attracted to the hull and transform into protons; further scenario is as described above.

Electrochemical plating is used to cover a steel product with a thin layer of chromium, nickel, and other metals resistant to atmospheric corrosion. Therefore, nickel- and chrome-plated products shine and do not rust. Plating technique consists in that a product is immersed in the solution of chromium or nickel salts, and the negative charge is applied. Here, the cations of nickel and chromium move towards the product and are transformed into molecules of Ni and Cr. These molecules are big and do not have the ability of penetrating into the metal, so they are accumulated only on the product surface and form the desired coating.

However, they began to notice that the chromeor nickel-plated products were more fragile and less strong than the same products without coating. Experts in physical metallurgy could not understand for a long time what was going on, but our dear readers have already guessed that again our friends – protons are at play. The solution contains water hence, there are H⁺ cations. They move to the product even faster than the cations of nickel and
chromium, and are transformed into protons which easily penetrate into the product and reduce its strength characteristics.

Some readers may think: A fine fairy tale! Where is the evidence? Has anyone seen these mysterious omnipresent protons?

Of course, no one saw protons. And can not see. However, it is quite possible to detect hydrogen and methane in the metal. For this purpose there is a method of spectral analysis. This method determines the composition of substances, not only the earth ones, but those of stars, of suns. Great Lomonosov already could measure the amount of substance. Any laboratory assistant can do it using modern methods and instruments. And this work was done, of course, by the authors of this paper.

One of the experiments consisted of the following steps [5].

1. Two groups of metal samples were cut from different places of the pipeline. One group was taken from the place where stress corrosion cracks had developed, the other – from the place without cracks.

2. Samples were cleaned by special procedure and weighed on the analytical (accurate) balance.

3. All samples were exposed to vacuum heat treatment. The temperature, vacuum pressure and retention time were selected such that hydrogen might get mobility in the metal, and the rest elements remain motionless. So, hydrogen gradually «evaporated» from the metal.

4. After that, all samples were again weighed and the change in weight was determined. The change in weight corresponded to the amount of hydrogen released from the metal.

Such experiments were repeated many times and on different pipelines. The samples were cut from different places at different distances from the fracture, from the inner and outer parts of the pipe wall. Also, mechanical tests of samples were carried out in order to check the changes in the strength of the metal. The results are a convincing proof of correctness of the physical model of stress corrosion, described above.

Firstly, in the zones of metal cracking the concentration of hydrogen was significantly higher than in the remote areas.

1 – pipeline wall; 2 – branch pipe; 3 – reinforcing collar; 4 – fillet weld «pipe – collar»; 5 – weld portion with the highest concentration of stresses

Secondly, the hydrogen concentration is always higher on the outer part of the pipe walls (in this
case, hydrogen comes from outside, from the ground water).
Thirdly, the higher is the concentration of hydrogen, the lower are ductility and strength of the samples.
This is the essence of the physical model of stress corrosion, proposed by the authors. Like every new theory, this model needs to be verified and approved. Let’s analyze, as an approval, some phenomena and events.
1. It was noted above that in other lines, except for the main gas pipelines, stress corrosion is not observed. It is time to explain this phenomenon. The explanation is simple and also has signs of unity.
All phenomena occur only under certain conditions. These conditions are limited to the critical values of the respective physical quantities. For example, the plastic deformation of metal takes place only at stresses exceeding the yield strength of the metal. Failure occurs when the ultimate strength is reached. Fatigue failure occurs at stresses above the fatigue limit. A crack propagates when the limit of crack resistance is reached. There are other «limits». It turns out that there is also an ultimate stress corrosion, which is about 0.7 of the yield strength. Trunk pipelines differ from all other pipelines by large diameters and high working pressures. Here, stresses in the pipe wall reach and exceed the stress corrosion range. On all other lines operating stresses do not reach the range of stress corrosion.
It was found that under mechanical stresses lower than the stress corrosion range slow protons had not penetrability sufficient for appreciable stress corrosion development during «lifetime» of pipeline.
2. The reader, who has studied the course of resistance of materials, may recall that the distribution of stresses (mechanical) is rarely uniform. Almost always, there are areas with concentration of stresses. Such zones, in particular, are welded joints. The coefficient of stress concentration in the welded joints is usually in the range of 1.2 ... 3.0. This means that in local zones stresses are as many times higher than the average stress. That is, by the stress level these zones will be in the same conditions as the main gas pipelines. Hence, stress corrosion may develop in these zones.
If the proposed physical model is correct, then this line of thought can not be argued. But why no notice of stress corrosion was taken on oil pipelines with a lot of welded joints and seams? The answer is really on the surface. Suppose there was a failure due to stress corrosion on the weld of an oil pipeline. In this case the crack will be on the welded joint,
and it will be visible to the naked eye. To what conclusion shall a supervisory body inspector arrive? Yes, he will blame the welder. Can the welder argue? No, he cannot, because the destruction of the seam is real. Will anyone drag his brains about stress corrosion? The reader is right – no one will. The welder will be deprived of bonus, his boss be reprimanded, penalty for damage be imposed on the pipeline company and the column «welding defects» in the statistics of failures will be supplemented. With this everybody go away with a sense of their duty done. Until another similar accident happens.

Suppose the authors of this physical model (or like-minded persons) find themselves on the site of such accident. And such opportunities really arose. Recently, there have been several accidents on the main oil pipelines, one of them in Bashkortostan. Dimensions of pipes on site were Ø1220×14.8 mm; service period of 38 years. The accident occurred on the vent assembly (Figure 2). As a result of break the crack appeared with the length of 1430 mm and the opening up to 350 mm. The center of the destruction was on the longitudinal section of a fillet welded seam, by which reinforcing collar of the vent was weld to the line (point 5). Technological welding defects such as cracks, incomplete penetration, pores, cuts, poor fusion were not detected.

Figure 3 – Hydrogen cracking of metal (300 x magnification)

When mounting vent the insulation was removed from the surface of the pipe and was not restored after the vent was assembled. However, corrosion defects dangerous for the pipeline are not observed; there are only traces of corrosion. This is due to the fact that the pipeline was under electrochemical protection. The mechanical properties of the pipe metal are in compliance with standard requirements and certificate and passport data. The fracture in the pipe wall at the place of the destruction is brittle, without any visible traces of plastic deformation. In the fracture microcracks are observed, representing hydrogen lamination of the pipe metal. Microsections demonstrate partial decarburization of pearlite grains, which is a sign of interaction with hydrogen (protons). We found numerous defects in the form of metal lamination, occurred due to hydrogen accumulated to very high pressures (Figure 3). This phenomenon is called hydrogen lamination of metal, hydrogen cracking, stress corrosion cracking, or stress corrosion. These names describe virtually the same phenomenon,
but emphasize different sides of its manifestation. The results show that the following factors played a key role in the destruction of oil pipeline:
– high stress concentration in the fillet weld «collar – pipe»;
– the absence of insulation along the fillet weld «collar – pipe»;
– the presence of a negative electric potential.
All this is nothing but conditions for the development of stress corrosion. Hence, it appears that local stress corrosion can be not only on main gas pipelines, but on oil pipelines and other lines, as well.

3. It is clear that the development of stress corrosion requires the sources of atomic hydrogen (or protons). What other sources exist? Some oil and gas fields are featured by high content of hydrogen sulfide H$_2$S. When pumping products with high content of hydrogen sulfide, steel pipes (also, other process equipment) become brittle as cast iron. The cause is that hydrogen sulfide–iron reaction produces hydrogen atoms (protons and electrons):
\[ 2Fe^{++} + 2HS^- \rightarrow FeS + 2H^+ + 2e; \]
\[ Fe^{++} + 2HS^- \rightarrow FeS_2 + 2H^+ + 2e. \]
These protons are formed on the inner surface of the pipe and then penetrate into the metal. And our reader already knows how they behave themselves there. The only difference from the cases considered above is that embrittlement and cracking occurs on the inner surface of the pipe, and, therefore, the network of cracks is very difficult for observation. Hydrogen sulfide corrosion (such is the name of phenomenon in this case) does not essentially differ from the external stress corrosion.

If the physical model is comprehended, then it is possible to offer methods of control of such dangerous phenomenon as stress corrosion. The methods should be based on the following requirements.
1) Do not allow the appearance of hydrogen atoms and protons on the metal surface; high-quality and durable insulation should be provided for this purpose;
2) If they are there already, slow down their penetration into the metal. To achieve this, reduce the stresses to the level lower than the range of stress corrosion;
3) If you can not reduce the load, you have to agree that after some time failure will occur. Hence, you must learn to determine the remaining service life of the pipeline in view of this phenomenon. For this, you must develop diagnostic methods and computation methods.
Some progress may be noted in the development of insulating materials. It was found that some
polymers of Asmol type have chemical bonding with iron and form an additional thin protective layer that is impervious to ions. With time, this protective layer does not lose its strength, if compared with classic insulating film, but becomes stronger due to its chemical nature. Metallurgists do not give up their attempts to develop such new steel qualities that would not lose their strength in hydrogen-containing environment. In other words, the new steels must have high limit of stress corrosion. So far, no notable success is achieved in this line, yet one proposal is interesting. It is proposed that the thin surface layer of the pipe wall be enriched with carbon (to bring it to the state of iron). This thin layer will act as a scavenger of hydrogen atoms (protons).

We hope that the offered physical model will help not only to understand some complex processes, but also to solve the problems successfully.

**Conclusion**

Offered and substantiated physical model of stress corrosion explains all observed mechanisms of stress corrosion in the gas mains and allows development of effective methods of protection.

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