REVIEW

Selected types of corrosion degradation of pipelines

Vybrané případy korozního poškození ocelových plynovodních potrubí

Hagarová M.[1], Cervová J.[1], Jaš F. [2]
[1] Technical University of Košice, Department of Materials Science
[2] Renojava, s.r.o.
E-mail: maria.hagarova@tuke.sk

The paper deals with corrosion degradation of gas pipeline. Pipelines play very important role as means transporting gas media over long distances from producers to end-users. Gas pipelines present a risk of potential corrosion degradation that can result in their failure. Corrosion on internal surfaces of steel pipes takes place in CO_2, H_2S, H_2O and chloride environment. Degradation of steel results in loss of mechanical properties, reduction in thickness and ultimate perforation and failure. Corrosion is the electrochemical process that involves the flow of electrical currents on a micro or macro scale. For corroding steel, the anodic and the cathodic reactions produces the electrochemical cell. Corrosion protection of internal pipeline surface is based mainly on chemical composition of gas and the use of inhibitors. Corrosion protection of the external steel surface of the product line involves coatings and cathodic protection.

Příspěvek se zabývá korozním poškozením plynovodního potrubí. Plynovody hrají velmi důležitou roli jako prostředek pro přepravu plynu na velké vzdálenosti od zdroje jejich výroby až ke spotřebiteli. Plynovodní systém představuje potenciální riziko možnosti korozní degradace, které může vést k jeho poškození. Koroze vnitřního povrchu ocelových potrubí probíhá v prostředí CO_2, H_2S, H_2O a chloridů. Degradace ocelí vede ke ztrátě mechanických vlastností, redukci tloušťky a nakonec k perforaci a porušení. Koroze je elektrochemický proces, který zahrnuje tok elektrických proudů na mikro nebo makro měřítku. Pro korodující ocel, anodické a katodické reakce vytváří elektrochemický článek. Protikorozní ochrana vnitřního povrchu plynovodů je založena především na chemickém složení plynu a použití inhibitorů. Protikorozní opatření vnějšího ocelového povrchu produktovodů zahrnuje použití povlaků a katodové ochrany.

INTRODUCTION

Gas pipelines are means of transporting gases over long distances from the source of their production to end-users. Specificities of gas pipeline systems include first of all their situation according to predetermined requirements on collection site and place of delivery, minor value regarding their alternative use, high investment and low operational costs and long return on investments [1]. Transit gas pipeline system constitutes potential risk related to operational pressure and corrosion degradation. Annual corrosion losses in gas industry in Slovakia constitute approximately 5 % of gross national product [2]. This implies high economic importance of maintenance costs of underground structures. The seriousness of gas pipelines corrosion issue involves both reduction of their service life and, particularly, pollution of the environment at emergencies [3].

Corrosion damage of gas pipelines

Sweet corrosion

Transported gases contain chemical components, such as CO_2, H_2S, S, H_2O, inorganic salts including chlorides $CaCl_2$, $MgCl_2$, NaCl, sand and bacteria, depending on composition of crude oil from which the gas is produced [4]. When the concentration of the above components exceeds the permitted limit, they cause corrosion of inner pipeline surfaces. Sweet corrosion of steel surface in CO_2 environment is referred to as pitting corrosion [5].

CO_2 found in natural gas dissolves in water which condenses on the surface of steel and the product of the following reaction is a highly corrosive carbonic acid:

$$CO_{2(aq)} + H_2O_{(aq)} \leftrightarrow H_2CO_3 \qquad (1)$$

This form of corrosion is accompanied by hydrogen depolarization with production of H_2 gas [5]. The quality of corrosion products developing on the surface of steel is affected not only by the partial pressure of CO_2 and temperature but also by a steady flow regimen that produces conditions for development of a protective layer of $FeCO_3$ according to formulas (2) and (3) [6,7]:

$$2HCO_3^- + Fe^{2+} \rightarrow Fe(HCO_3)_2 \quad (2)$$

$$Fe(HCO_3)_2 \rightarrow FeCO_3 + H_2O + CO_2 \quad (3)$$

Sour corrosion

Sour corrosion develops in H_2S environment which isn´t corrosive in itself; it becomes corrosive in a water-containing gas environment. Intensive corrosion can cause even perforation of the pipeline wall [8]. The resultant products of reaction of steel with $H_2S_{(ads)}$ are sulphides, such as FeS_2, $Fe_{3+x}S_4$, „mackinwite“ $Fe_{1+x}S$. Mackinwite layers can be converted to stabile cubic or hexagonal sulphides. Stability of the layers is affected by pH of the gas and then degree of solubility of H_2S and Fe [9].

In reality, the gas contains both CO_2 and H_2S. Fig.1 shows the influence of pH of the relevant environment on corrosion rate of carbon steel in the H_2S and CO_2 environment. The figure shows that the corrosion rate at pH=6 is lower than that at pH=11.5 because iron sulphide layers acquire better adhesive properties in the acidic environment [9]. According to [10] small quantities of H_2S (less than 500 ppm) contribute to development of a protective FeS layer. Another condition important for successfulness of anti-corrosion measures is elimination of H_2O from the gas by dehydration processes [10].

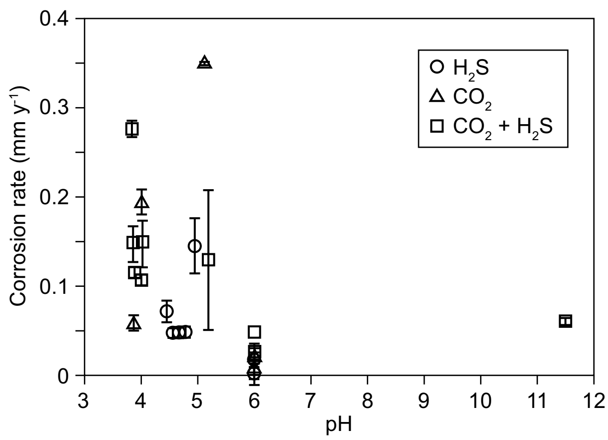

Fig. 1. Relationship between environmental pH and corrosion rate of carbon steel [9]
Obr. 1. Závislost mezi pH prostředí a korozní rychlostí uhlíkové oceli

Microbially influenced corrosion (MIC)

Microbially Influenced Corrosion is caused by a wide range of bacteria, various micro-organisms, fungi and algae. Bacteria produce waste products, such as CO_2, H_2S and organic acids, which increase toxicity not only of the flowing medium but also of the outer environment [11]. Corrosive aggressiveness of the environment produced by metabolism of bacteria and other micro-organisms is affected also by temperature, pH of soil electrolyte and concentration of salts [12]. Some authors [13,14] reported that Sulphate Reducing Bacteria (SRB) acting under anaerobic conditions is responsible for MIC corrosion. Bacteria of the following genera are mostly involved: *Desulphotomaculum species*, *Achromobacter species*, *Flavobacterium species* and other. Appearance of *Desulphotomaculum sp*. is documented in Fig. 2 [14].

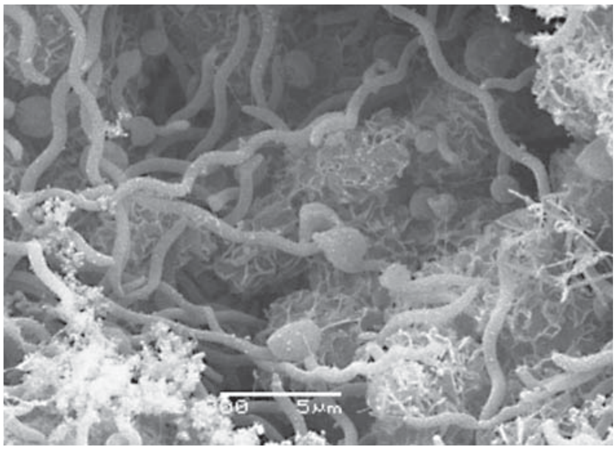

Fig. 2. Appearance of bacteria of *Desulphotomaculum species* [14]
Obr. 2. Vzhled bakterie Desulphotomaculum

Bacteria are capable of damaging the outer surface of pipes but also persist on their inner surfaces in the form of deposits. By their activities they support development of corrosion cracking and fissure corrosion [13,14]. The micro-organisms found in gas pipelines and soil can be classified differently. One can consider their tolerance for oxygen or their metabolism. The third way of classification is based on their shape [12]. By their growth, they contribute to the development of pitting corrosion and, eventually, they may cause complete clogging of the pipeline [5].

Corrosion of outer surface

Corrosion of outer surface of gas pipelines acquires an electrochemical character dependent on character of the soil, chemical composition of soil electrolyte, presence of stray currents and microbial activity of bacteria in the soil. Corrosion cells, that are the precondition of occurrence of corrosion processes, develop due to non-uniform aeration of soil with a place with higher concentration of oxygen acting as a cathode and a place with insufficient supply of oxygen performing as an anode. The character of soil affects its aeration, as shown in Fig. 3 [15].

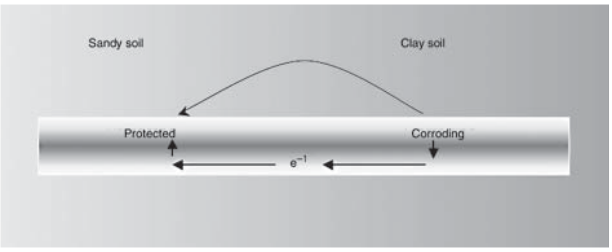

Fig. 3. Processes taking place on the outer surface of pipelines in sandy and clay soil [15]
Obr. 3. Proces probíhající na povrchu potrubí v písčité a jílovité půdě.

The up-to-date research of corrosion degradation of outer surface of gas pipelines focused on chemical composition of soil [16,17]. However, it was observed that the chemical composition has no dominant effect on kinetics of corrosion processes. In addition to aeration of soil, other important factors include specific electric resistance, elasticity index, content of moisture and clay in the soil, concentration of soluble salts, such as SO_4^{2-} and Cl^-, temperature, microbial population and the already mentioned pH of the environment [18,19]. Soil structure and its specific electric resistance, the so-called redox potential E_h, are a function of soil moisture, temperature and concentration of soluble salts. Low levels of soil resistance and small size of soil particles constitute a highly corrosive environment. Classification of corrosion environment in the soil in relation to soil specific resistance is shown in Table 1 [20,21].

Tab. 1. Classification of corrosivity of soil by value electrical resistivity [20,21] / *Klasifikace korozní agresivity půdy na základě hodnoty elektrického odporu*

Soil resistivity Rp [Ω m²]	Corrosivity of the soil
< 10	very aggressive
10 – 20	aggressive
20 – 50	medium aggressive
50 – 100	mildly aggressive
> 100	very mildly aggressive

Corrosion exposed to stray currents

Underground gas pipelines are frequently exposed to stray currents originating from various sources of unidirectional or alternating currents. The most common source of stray currents is electric traction (railway, urban) but one should consider also protective currents in the system of cathodic protection of pipes that can, for example at over-dimensioned protection, induce corrosion of other equipment [22]. The influence of stray currents originating from electrical line on corrosion of gas pipeline is illustrated in Fig. 4 [23].

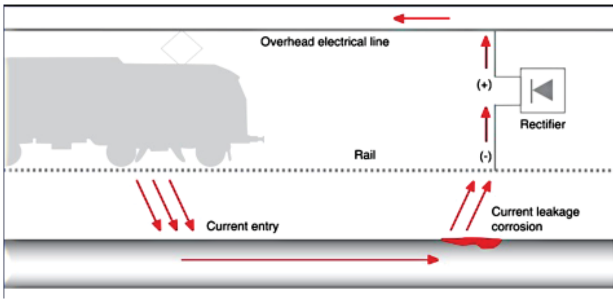

Fig. 4. Schematic representation of the impact of stray currents on the pipeline [23]
Obr. 4. Schematické znázornění vlivu bludných proudů na potrubí

Corrosion – mechanical damage stress corrosion cracking (SCC)

Corrosion – mechanical damage to gas pipelines include Stress Corrosion Cracking that occurs under the action of both corrosive environment and tensile component of stress. In acidic environment the SCC process is associated with diffusion of atomic hydrogen. In alkaline environment the damage involves anodic dissolution of pipe material [24]. A characteristic feature of both SCC forms is the development of cracks passing across pipe wall. In the environment with high pH the propagation of cracks is intercrystalline, as it is shown in Fig. 5, while in the environment with pH~7 the propagation of cracks is transcrystalline, as illustrated in Fig. 6 [15].

According to the source [25], corrosion cracking in H_2S (SCC) environment, which is a part of soil electrolyte, depends also on the level of potentials of cathodic protection. In alkaline environment, SCC occurs in relatively narrow range of potentials, approximately from -650 to -750 mV $Cu/CuSO_4$. On the contrary, in acidic to neutral environment with pH = 5.5 to 7, SCC occurs in the interval of potentials from -760 to -790 mV $Cu/CuSO_4$ [25].

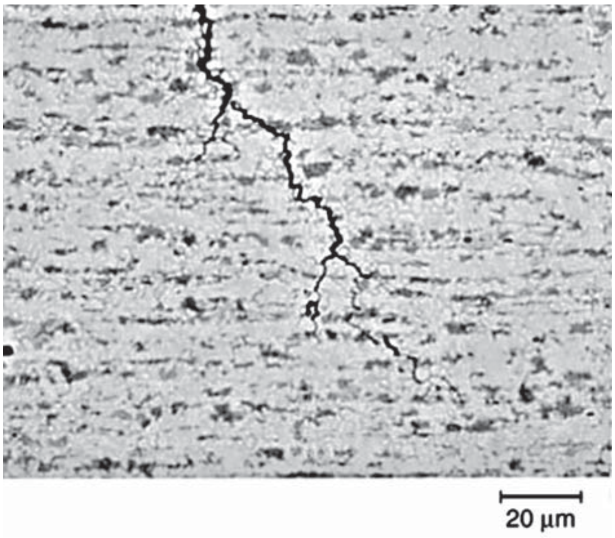

Fig. 5. Intercrystalline character of crack propagation in the high pH environment [15]
Obr. 5. Interkrystalický charakter šíření trhliny v prostředí vysokého pH

Anti-corrosion protection of outer and inner surfaces of gas pipelines

Inhibitors

Corrosion degradation of pipeline systems may acquire various forms and thus selection of the correct anti-corrosion measures is very important. Anti-corrosion protection of inner surfaces of gas pipelines includes the use of inhibitors, substances that limit rates of anodic and cathodic processes, for example by blocking active sites on pipe surfaces. Another possibility is based on production of a passive layer by chemical reaction between the inhibitor and the steel surface or on formation of an insoluble protective film by reaction of the inhibitor with aggressive components of the environment [26]. Corrosion of steel in aqueous media that contain dissolved carbon dioxide is an electrochemical process. As is known [7] CO_2 increases the amount of hydrogen formed on the cathode and forms the carbonate-oxide film on the surface of the steel. The most efficient ways of preventing sweet corrosion is using any available means to make the cathodic process efficiently inhibitive, while the second approach entails the formation of protective carbonate oxide films or deposits. The inhibitor for CO_2 corrosion should be chosen on the basis of the pH and temperature, as well as the initial condition of the metal surface (the type of film and/or deposits on the surface of the metal being protected). Most corrosion inhibitors used in oilfields are organic compounds, containing nitrogen or sulfur functionalities. The percentage inhibition efficiency (η %) of the inhibitors increases by increasing inhibitor molecule size [27].

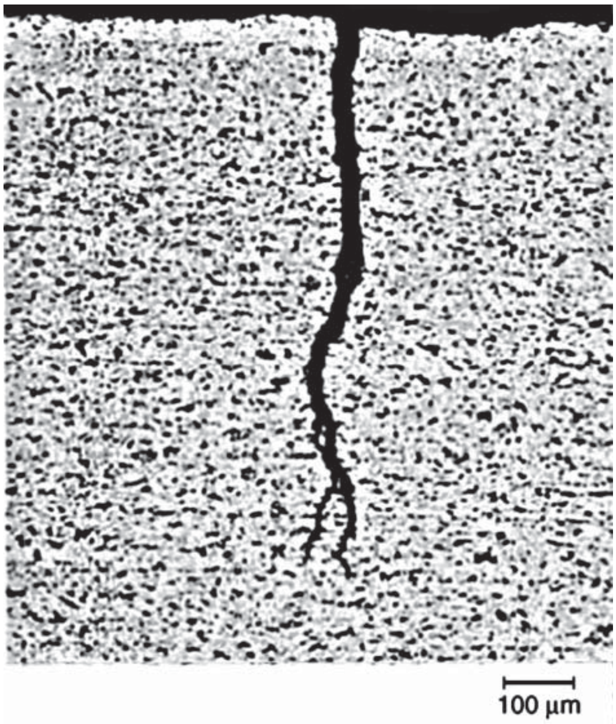

Fig. 6. Transcrystalline character of crack propagation in the environment with pH~7 [15]
Obr. 6. Transkrystalický charakter poškození v prostředí s pH ~7

Passive protection

Outer surfaces of gas pipelines are protected by building a barrier between soil electrolyte and the steel pipe that should be effective throughout service life of the pipeline. Such protective barriers consist of organic coats, metal and non-metal layers, e.g. glass fibres, epoxide and rubber. According to [5, 28, 29], three-layer polyolefins (3LPO) and Fusion Bonded Epoxy (FBE) belong among the coats most frequently applied to the surfaces of gas pipelines used for gas transit in Europe.

FBE coats are deposited to pipelines used in territories where sufficient plasticity of the coat is required at extremely low temperatures so as to prevent its cracking or detachment from the metal surface at changing temperatures. The multilayer polypropylene composite FBE coat is applied by thermally resistant technologies. Viscosity of individual layers of such coats, shown in Fig. 7, ensures sufficient resistance against shrinkage of the coat [5,28].

Modern methods of application of surface coatings include surface protection ZINGA. This involves application of one-component coat which reduces rate of corrosion attack owing to 92 % content of zinc dust of purity 99.995 %, presence of zinc salts, polyester resins and pigments. The service life of this one-component galvanic layer depends on adhesiveness of the coat and the environment in which the pipelines operate, see Fig. 8.

Service life of the layer under laboratory and field conditions has been verified according to the British standard BS 5493 [28,30].

Fig. 7. Thermotive five layer system buildup [5]
Obr. 7. Pětivrstvý systém povlaků

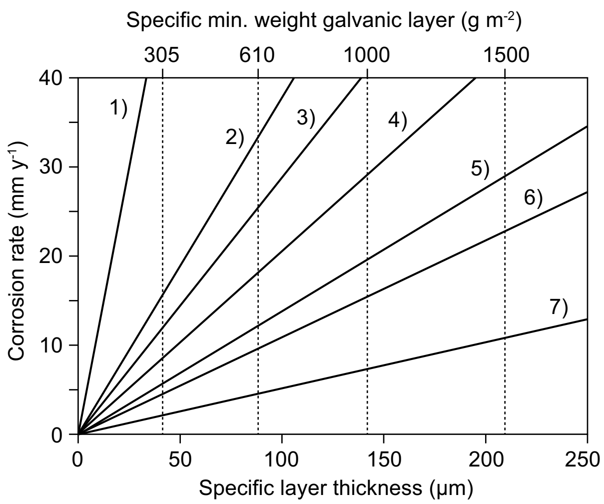

Fig. 8. Life galvanic system ZINGA depending on the thickness of the layer and environment [29] – 1) interior dry environment, 2) inland unpolluted exterior, 3) moist interior, 4) unpolluted marine exterior, 5) inland polluted exterior, 6) marine dirty exterior, 7) immersed in sea water
Obr. 8. Životnost galvanického systému ZINGA závislého na tloušťce vrstvy a prostředí [29] – 1) interiérové suché prostředí, 2) neznečištěný vnitrozemský exteriér, 3) vlhký interiér, 4) neznečištěný přímořský exteriér, 5) znečištěný vnitrozemský exteriér, 6) znečištěný přímořský exteriér, 7) ponořené v mořské vodě

Active cathodic protection

Protective coatings are frequently used in combination with active cathodic protection of pipelines [31]. In order to ensure effective cathodic protection (CP) of gas pipelines one must monitor not only processes taking place at the cathode, which is the object of protection, but also processes that occur at the anode. Monitoring of both cathodic and anodic processes is done because they affect each other [32]. Cathodic Protection is the electrochemical method of corrosion control in which the oxidation reaction in a galvanic cell is concentrated at the anode and suppresses corrosion of the cathode in the same cell. The CP system may be achieved in either of two ways: Sacrificial Anodes Cathodic Protection (SACP) and Impressed Current Cathodic Protection (ICCP) [33,34]. Schematic representation of these two types of cathodic protection is shown in Fig. 9 and Fig. 10. [35]

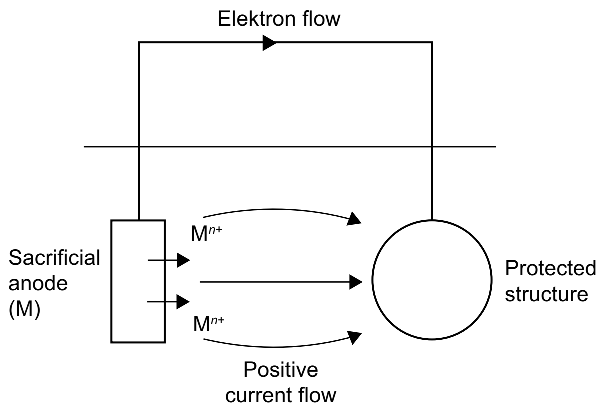

Fig. 9. Schematic diagram of Sacrificial Anodes Cathodic Protection – SACP [35]
Obr. 9. Schéma systému katodické ochrany obětovaných anod – SACP

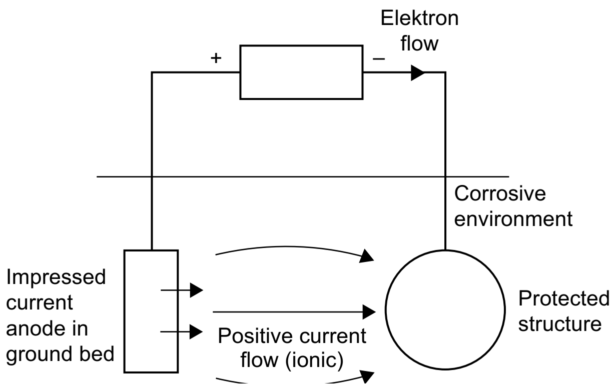

Fig. 10. Schematic diagram of Impressed Current Cathodic Protection – ICCP [35]
Obr. 10. Schéma systému katodické ochrany vnějším zdrojem proudu – ICCP

The galvanic cathode protection system is a sacrificial anode cathodic protection system because the anode corrodes sacrificially to protect the structure pipeline. Galvanic anodes are usually made of either zinc or magnesium, because of higher potential of these metals compared to steel structures. The ICCP system uses the same anode materials as the galvanic protection system. The principal difference between the two described methods is that ICCP uses an external power current source and SACP relies on the difference in potential between gas pipeline and the sacrificial anode [31-36].

CONCLUSIONS

Research indicated that the most common causes of damage and failure in gas transmission pipelines in Slovakia and abroad are corrosion and external mechanical damage. Corrosion of buried steel pipelines is an important issue with regard to the number and seriousness of caused damages. Without effective means of fighting corrosion uncontrolled gas escapes may occur resulting in social-economical and environmental consequences. The basic precondition for sufficient reliability and safe service of gas pipeline systems is correct selection possibilities of protective inner and outer surface. Application of inhibitors is based on the knowledge medium composition, pH and temperature, as well as the initial condition of the steel surface. Cathodic-protection system may be monitored effectively by the measurement of structure-to-electrolyte potentials. Adjustments are made to the cathodic-protection current output to ensure that protective potentials are maintained at a sufficiently negative level as defined by the project specification. The level of protection in soils, used in protection of pipelines in Slovakia, is accepted at steel potentials of minus 850 mV with respect to (Cu/CuSO4).

REFERENCES

1. Gas and Oil Pipelines in Europe, *Current Issues in Education* **2013**, [Online], Available: www.europarl.europa.eu. [Accessed Dec, 2013].
2. Burda T. Development of a model for evaluation of risk in Slovak gas transport systems, *Slovgas* **2007**, 6, 12-13 (In Slovak).
3. Pipeline Performance in Alberta, Alberta Energy Regulator Report 2013-B, *Current Issues in Education* **2013**, [Online], Available: http://www.aer.ca/documents/reports/R2013-B.pdf. [Accessed Aug, 2013].
4. Tawancy H.M. et al. Analysis of corroded elbow section of carbon steel piping system of an oil–gas separator vessel, *Case Studies in Engineering Failure Analysis* **2013**, 1, 6–14.
5. Popoola L.T. et al. Corrosion problems during oil and gas production and its mitigation, *International Journal of Industrial Chemistry (IJIC)* **2013**, 4:35, 1-15.
6. Farelas F. et al. Corrosion Behavior of Deep Water Oil Production Tubing Material under Supercritical CO_2. Environment: Part II. Effect of Crude Oil and Flow, *Corrosion 2013 NACE International* **2013**, 2381, 1-14.
7. Moiseeva L.S., Rashevskaya N.S. Providing Protection against Carbonic-Acid Corrosion for Equipment in the Oil-and-Gas and Chemical Industries, *Chemical and Petroleum Engineering* **2001**, 37, 1, 54-59.
8. Kvarekval J. Kjeller Localised Corrosion Project (KLOC), *Current Issues in Education* **2011**, [Online] Available: http://www.ife.no/en/ife/departments/materials_and_corrosion_tech/projects/kloc [Accessed, 2012].
9. Sridhar N. et al. Effects of Water and Gas Compositions on the Internal Corrosion of Gas Pipelines – Modeling and Experimental Studies, *Corrosion Science* **2001**, 57, 3, 221-235.
10. Recommended Practice for Mitigation of Internal Corrosion in Sour Gas Pipeline Systems, *Current Issues in Education* **2009**, [Online], Available: http://www.capp.ca/getdoc.aspx?DocId=155644&DT=PDF [Accessed Dec, 2013].
11. Cathodic Corrosion Protection of earthburried Pipelines, *Current Issues in V&C Kathodischer Korrosionsschutz Ges.m.b.H* [Online], Available: http://www.vc-austria.com/fileadmin/media/downloads/broschueren/englisch/vc_pipeline_protection.pdf [Accessed Oct, 2013].
12. Repčík R. Microbiologically induced corrosion on buried steel structures, *Slovgas* **2010,** 5, 28-31.
13. Antony P.J. et al. Corrosion of 2205 duplex stainless steel in chloride medium containing sulfate-reducing bacteria, *Electrochimica Acta* **2007,** 52, 3985–3994.
14. Cetin D., Aksu M.L. Corrosion behavior of low – alloy steel in the presence of Desulfotomaculum sp., *Corrosion Science* **2009**, 51, 1584- 1588.
15. Beavers J.A, Neil G. T. External Corrosion of Oil and Natural Gas pipelines, *Current Issues in Education* **2006**, 13C, [Online], Available: www.asminternational.org [Accessed 2006].
16. Ferreira C.A.M. et al. Vaitsman D.S., Pérez, D.V. Evaluation of the Corrosivity of the Soil Through Its Chemical Composition, *Science of the Total Environment* **2007,** 388, 250-255.
17. Liu T.M. et al. Effect of Soil Compositions on the Electrochemical Corrosion Behavior of Carbon Steel in Simulated Soil Solution, *Materials Science and Engineering Technology* **2010,** 41, 4, 228–233.
18. Cole, I. S., Marney, D. The science of pipe corrosion: A review of the literature on the corrosion of ferrous metals in soils, *Corrosion Science* **2012**, 56, 0, 5-16.
19. Kleiner Y. et al. Impact of soil properties on pipe corrosion: Re-examination of traditional conventions. *WDSA proceedings of the 12th Annual International Conference on Water Distribution Systems Analysis: Tucson, AZ* **2010**, 968.
20. Ahmed, A. Review: Electrical study of pipe - soil - earth system, *Life Sciences Journal* **2011**, 8, 2, 695-723.
21. Shreir L.L. et al. Metal environment reactions. Jarman, R.A., Burstein, G.T Publishers **2000**, Oxford.
22. Bertolini L. et al. Corrosion behaviour of steel in concrete in the presence of stray current, *Corrosion Science* **2007**, 49, 1056-1068.
23. Beavers J., Harle B. Mechanisms of high-pH and near-neutral-pH SCC of underground pipelines, *Journal of Offshore Mechanics and Arctic Engineering Transactions of the ASME* **2001**, 123, 3, 147-151.
24. Baker M. *Pipeline Corrosion*, 2008. [E-book], Available: https://primis.phmsa.dot.gov/gasimp/docs/FinalReport_PipelineCorrosion.pdf.

25. Ossai Ch.I. Advances in Asset Management Techniques: An Overview of Corrosion Mechanisms and Mitigation Strategies for Oil and Gas Pipelines, *International Scholarly Research Network ISRN Corrosion* **2012**, 2012, 1-10.
26. Graeme W. Corrosion protection of metals in marine environment. J. Metal Corrosion Protection, *Chemistry* **2010**, ISSN: 2191-1363.
27. Hany M.A. Adb El-Lateef. Corrosion Properties of Steel Pipelines against CO_2 Corrosion, *Chemistry Journal* **2012**, 2, 52-63.
28. Westood J. Macro factors driving the global oil and gas industry and the subsea pipelines sector **2011**, Toronto.
29. Jaš F. Zinganization – renovation and depositing of new zinc coatings to steel products, *Transfer inovácií* **2013,** 27, 47-50 **(in Slovak).**
30. Heidersbach R.H. Cathodic Protection, *ASM Metals Handbook: Corrosion* **1987**, 13, 1059-1093.
31. BBA – Technical Approvals for construction. Corrosion protective coating for steel. Agrément Certificate 03/4047.
32. Liptáková T. et al. The granularity effect of the carbon packs on behavior of cathodic protection, *Corrosion of underground structures 2011: proceedings of the 17th international conference: Košice, Slovakia*, **2011**, 65-71.
33. Guyer J.P. et al. An introduction to cathodic protection, *Current Issues in Education,* **2009**, [Online], Available: http://ws012.cedengineering.com/upload/An%20Introduction%20to%20Cathodic%20Protection.pdf. [Accessed, 2009].
34. Lazzari L., Pedeferri P. Cathodic protection, *McGraw Hill Publishers* **2006**, New York.
35. Ashworth V. Principles of Cathodic Protection, *Elsevier B.V.* **2010**, 2, 2747–2754.
36. Choi J.B. et al. Development of Limit Load Solutions for Corroded Gas Pipelines, *International Journal of Pressure Vessels and Piping* **2003**, 80, 121–128.