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REVIEW ABOVE APPLYING ACTIVE ANODE PROTECTION AT SOME DYNAMIC PETROLEUM EQUIPMENT'S IN ORDER TO REDUCE WEAR

Razvan George RIPEANU[1,*], Vasile ISPAS[1], Dorina ISPAS[1]
[1]University Petroleum-Gas of Ploiesti, Ploiesti, Romania
*Corresponding author: rrapeanu@upg-ploiesti.ro

Abstract: *Paper presents a synthesis of studies made by authors, in order to reduce wear at some petroleum dynamic equipment's such as rod pumps and centrifugal pumps. Rod pumps and centrifugal pumps work in heavy conditions. Crude oil contains an important quantity of highly mineralized formation water, rich gases with a great percent of CO_2, grains of sand from petroliferous bed. Main failure cause of rod pumps is abrasive and corrosive wear and at centrifugal pumps erosion and corrosive wear. Are presented the tests developed, which show that cathodic protection with active anode reduces wear and is possible to be applied. Were established the influence above wear of temperature, pressure, CO_2 partial pressure, materials couples, sliding speed, impingement angles etc. Also it is presented the durability calculus of these equipment's and the patents obtained as a results of studies.*

Keywords: *durability, rod-pumps, centrifugal-pumps, active anode, corrosion, wear laws, roughness.*

1. INTRODUCTION

Friction and wear conduct at different pumps malfunctions. To raise durability were developed many technologies in order to reduce friction and wear. When working medium is corrosive applying cathodic protection is a solution to diminish wear [1-4]. In petroleum industry wear and corrosion represents major problems. These degradation forms lead at interrupting and production loses, at continuous reducing efficiency and rising expenses of maintenance and replacing equipment's. These affect not only economic budget but leads directly at environment pollution. Corrosion is considered as a natural degradation process of metallic materials under the action of chemical agents. Metallic materials are metastable in aggressive mediums and have the tendency to pass into a more stable form. The maximum intensity of this process took place in electrolytic mediums. Wear remove material and corrosion products from materials surfaces and degradation is accelerated and reliability is diminished. To prevent wear in electrolytic mediums are recommended materials recognized as resistant (noble) and which not generate galvanic corrosion in friction couples, using corrosion inhibitors, diminishing electrochemical potential of materials in the Pourbaix immunity domain etc. For a fixed materials couple cathodic protection could reduce degradation process with the condition to not produce hydrogen embrittlement because at cathode appear hydrogen.

Pumps good reliability, based on pumps construction and materials performances is a demand of all beneficiaries'. To respond at this demand, we have first to know and control the mechanisms developed at interfaces material-medium and then to develop and to apply new technics and technologies to rise wear resistance. To obtain good performances we have to use materials and technologies adequate to working conditions. Taking into account that in petroleum industry pumped fluids are highly corrosive and erosive, pumps parts are manufactured of materials with high hardness and good corrosion resistance. To fulfill only this tasks the pumps will became very expensive.

Durability of equipment's deserved by pumps works could be of 25 years or more (main pipes for ex.) and inspection costs, maintenance and repairing costs represent around 20 % of total costs on pumps life time. By non-conventional measures as cathodic protection is possible to reduce these costs for different pumps types [4,5].

To reduce costs and to evaluate durability first of all we have to analyze technical solutions based on theoretical and experimental studies in laboratory and then in real working conditions.

The paper presents a review of the tests and results obtained by the authors in order to raise durability of sucker rod pumps and centrifugal pumps by cathodic protection and by nitrating thermochemical treatment applied at austenitic stainless steels at centrifugal pumps.

2. SUCKER ROD PUMPS

An important percent from damages of production wells are caused by pumps failure and pump reliability depends on piston-cylinder and ball-valve couple durability [4]. For ceramics ball-valve couple, pump reliability depends only of piston-cylinder durability [4]. Crude oil contains an important quantity of highly mineralized water, rich gases with a great percent of CO_2, grains of sand from petroliferous bed.

Piston slipping along cylinder, theoretic is made in the presence of an, more or less, lubricate film. In fact, film thickness isn't constant. It's possible that piston to slip directly on cylinder and with abrasion wear to have adhesion wear. Materials for piston and cylinder are not proper for adhesion wear. Working fluid contains sand. Quantity and size of sand depends of existence and quality of sand filter. Sand grains smaller than radial clearance pass through piston and cylinder and remove chips from both surfaces, [1,4-6].

Fluids have also a strong corrosive action on metallic materials. Electro-chemical reactions generate brittle and hard compounds. In static conditions this compounds realize a passivated coating. In dynamic conditions, friction tangential force between piston and cylinder local remove oxide coating. Coating reconstruction needs time and sliding is continuous. Surface without coating oxide is exposed to corrosive action. Current density on not coated area is much bigger than coated area. In these conditions the corrosion rate on not coated area is bigger.

In conclusion in rod-pumps piston-cylinder couple there are three main wear tips, abrasive, corrosive and adhesive [1,4-6].

Corrosive wear participation in total wear is 25…50 %, [1,4-6] and if fluid contains H_2S even more.

Result that diminishing wear is possible by diminishing corrosive wear.

To reduce corrosive wear there are three possible methods to apply:

- proper materials with high corrosion resistance;
- reduce fluid aggressiveness with corrosion inhibitors;
- electrochemical methods such as cathodic protection.

To rise working life of rod pumps in abrasive and corrosive medium is recommended to use materials with high hardness and resistant at corrosion as hard-chromium plating steel for cylinder or piston, carbonitrided and nitrided cylinder and metallic carbide layers type METCO for pistons in order to resist at heavy duty condition [1,4-6]. Paper purpose is to present the methodology used to establish wear laws in order to predict piston-cylinder durability and also to present the cathodic protection method with active anode.

2.1 Piston-cylinder corrosion laws

For static corrosion tests were prepared samples manufactured from real pumps pistons and cylinders. Were used metal sprayed and hard chromium plated steel pistons and carbonitrided, nitrided and hard chromium plated steel cylinders which are most used materials for piston-cylinder couples in sucker rod pumps in Romania oil fields. Also were prepared specimens made of Al-Zn alloy as galvanic anode.

Each materials surface was studied in order to establish microgeometry parameters, microhardness and thickness of the coatings or nitrided or carbonitrided stratums.

Because were many factors involved, the experiments were leaded in order to establish each factor influence.

In the first phase were established electrochemical parameters at 20 °C and at 60 °C in formation water with and without CO_2 barbotage. The results are presented in papers [1,4-9]. Were observed that corrosive medium temperature modifies corrosion potential. Temperature rising induce corrosion potential and corrosion current density rising, barbotage of CO_2 rise corrosion potential and corrosion current density and different materials samples have different corrosion potential and corrosion current density and in couples will form galvanic cells.

In the second phase were tested in formation water at different temperatures (20, 30, 40 and 50 °C) , CO_2 pressures (0, barbotage, 2, 3, 4 and 5 MPa) couples of materials in different combinations with and without active anode presence.

Corrosion rate was calculated with relation:

$$v_{cor} = \frac{\Delta M}{A \cdot \tau} \text{ [g/m}^2\text{h]} \qquad (1)$$

were ΔM is mass loss [g]; A is sample active area [m^2]; τ is time [h].

In Figure 1 it is presented the corrosion rate at temperature 20 °C in formation water with CO_2 barbotage with and without active anode, [1,4].

Analyzing the influence of parameters above corrosion rate experimental results were formulated a Weibull type relation which shows the temperature influence, [4]:

$$v_{cor} = a_{p,c} - b_{p,c} \cdot e^{-c_{p,c} \cdot t^{d_{p,c}}} \text{ [g/m}^2\text{h]} \qquad (2)$$

were coefficients a_p, b_p, c_p, d_p are for piston material and a_c, b_c, c_c, d_c are for cylinder material.

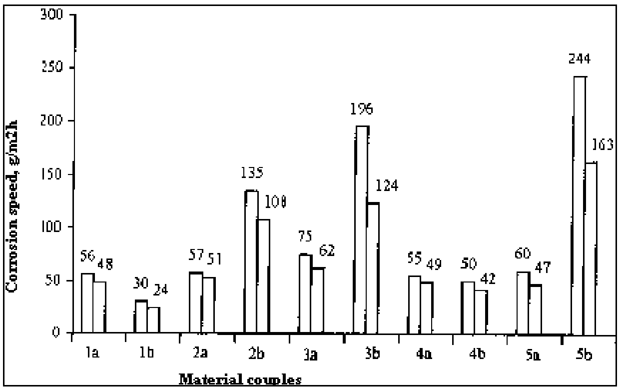

Figure 1. Corrosion rate at 20 °C and CO_2 barbotage; 1a-piston metal sprayed; 1b-skirt chromium; 2a-piston metal sprayed; 2b-skirt carbonitrided; 3a-piston metal sprayed; 3b-skirt nitrided; 4a-piston chromium-plated; 4b-skirt carbonitrided; 5a-piston chromium-plated; 5b-skirt nitrided

In Figure 2 it is shown the corrosion rate variation with temperature for carbide sprayed piston in couple with hard chromium cylinder [4].

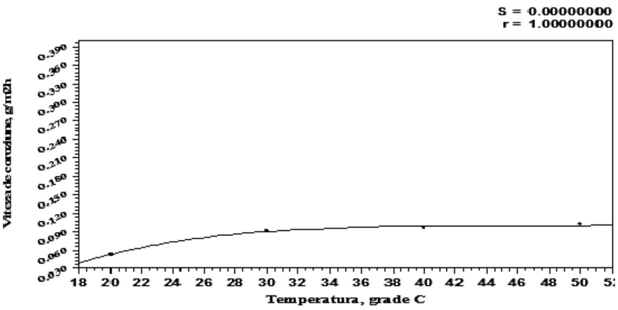

Figure 2. Corrosion rate vs. temperature for carbide sprayed piston in couple with hard chromium cylinder

The CO_2 pressure influence above corrosion rate is expressed with polynomial relation, [4]:

$$v_{cor} = a_{p,c} + b_{p,c} \cdot p + c_{p,c} \cdot p^2 + d_{p,c} \cdot p^3 + e_{p,c} \cdot p^4 \text{ [g/m}^2\text{h]} \qquad (3)$$

were $a_{p,c}$, $b_{p,c}$, $c_{p,c}$, $d_{p,c}$, $e_{p,c}$ are coefficients depending of tested materials couples and working medium.

In Figure 3 [4] it is exemplified the corrosion rate variation with CO_2 pressure for carbide sprayed piston in couple with hard chromium cylinder.

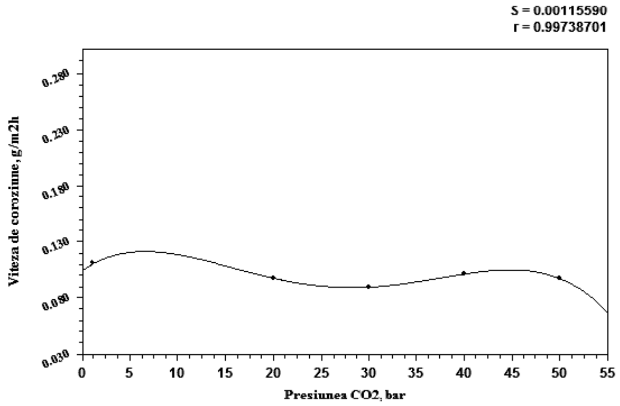

Figure 3. Corrosion rate vs. CO_2 pressure for carbide sprayed piston in couple with hard chromium cylinder

The temperature and CO_2 pressure influence above corrosion rate relation obtained is [4]:

$$v_{cor}=a+b/x1+c\cdot x2+d/x1^2+e\cdot x2^2+f\cdot x2/x1 \ [g/m^2h] \quad (4)$$

were $a_{p,c}$, $b_{p,c}$, $c_{p,c}$, $d_{p,c}$, $e_{p,c}$, $f_{p,c}$ are coefficients depending of tested materials couples and working medium; *x1* is temperature [°C]; *x2* is pressure CO_2 [bar].

The corrosion rate curve depending on temperature and corrosion rate it is shown in Figure 4 [4] for carbide sprayed piston in couple with hard chromium cylinder.

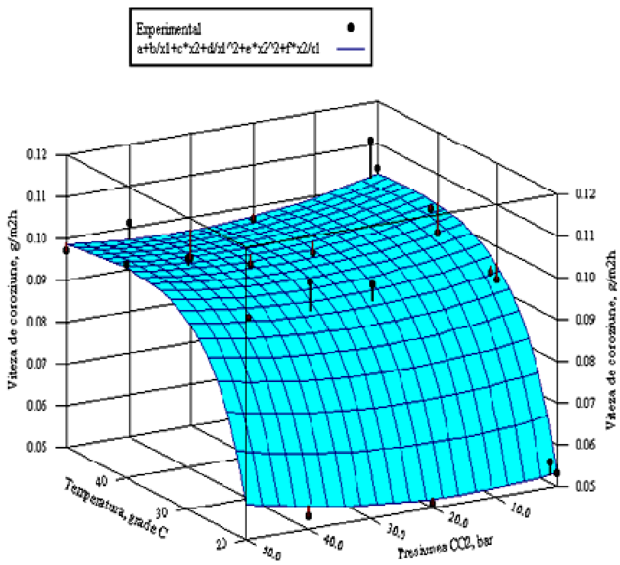

Figure 4. Corrosion rate vs. temperature and CO_2 pressure for carbide sprayed piston in couple with hard chromium cylinder

In Figure 5 [4] it is shown the corrosion rate variation with temperature and CO_2 pressure for carbide sprayed piston in couple with hard chromium cylinder in active anode Al-Zn presence.

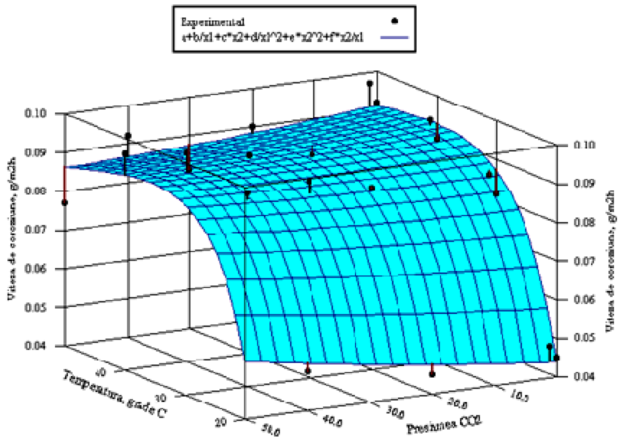

Figure 5. Corrosion rate vs. temperature and CO_2 pressure for carbide sprayed piston in couple with hard chromium cylinder in active anode Al-Zn presence

Corrosion tests proved that active anode Al-Zn presence reduce corrosion rate, and diminishing efficiency depends of materials couples and working parameters [1,2,4-9].

2.2 Piston-cylinder wear laws

Wear abrasion process was research on a testing machine designed and completed for that purpose. In Figure 6 [4] it is presented the cinematic diagram of the device.

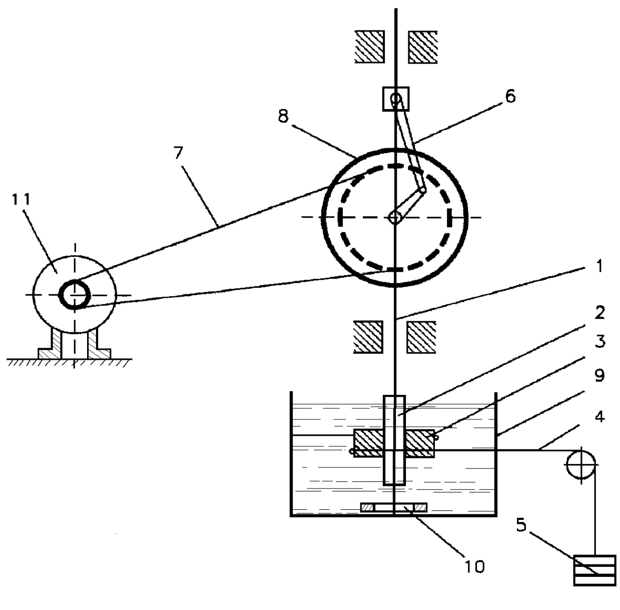

Figure 6. Cinematic diagram of the device

On vertical rod 1 is fixed the sample type piston 2. Sample type cylinder 3 slotted is tighten on piston with a flexible cable 4, tensioned with weight set 5. Alternative movement of the piston is provided by crank and connecting-rod assembly 6, moved by electric motor 11. Piston-cylinder system is completely immersed in formation water from tank 9. To maintain in suspension sand, we have a punched plate 10.

For wear tests it was used formation water with 3 % sand from rod pumps with grain size smaller than 63 μm.

Testing conditions were [4]:

- cable load, 50 N;
- double stroke per. min., 54;
- temperature, 20 °C;
- barbotage of CO_2.

Analyzing the experimental results at dynamic tests was formulated a wear relation, [4]:

$$u_{p,c} = a_{p,c} \cdot x + b_{p,c} \quad (6)$$

were, $u_{p,c}$ is piston respective cylinder wear, mg; *x*- time, min.; $a_{p,c}$, $b_{p,c}$ are coefficients depending of piston (*p)* and cylinder (*c)* materials couple and of testing conditions.

In Figure 7 [4] it is presented the wear curve for hard chromium plated cylinder in couple with metal sprayed piston, [4]. For this materials couple the relation (6) have R^2= 0.9390072263.

The obtained experimental results prove that the presence of active anode reduce wear depending on materials couples and working conditions, [1,2,4-9].

2.3 Active anode for sucker rod pumps cathodic protection

Protection efficiency depends on active anode geometry. With bigger anode surface area the current efficiency is bigger, but anode consumption is much important. For the same anode weight surface area has to be as possible as smaller to assure a great time life.

Minimum area for a maximum weight is spherical. For technological reasons it was adopted a cylindrical form.

In Figure 8 [2,4] it is presented the anode geometry. Active anode material is an alloy Al-Zn6.5. The cathodic protection method with active anode for sucker rod pumps and anode construction is patent RO118671-B.

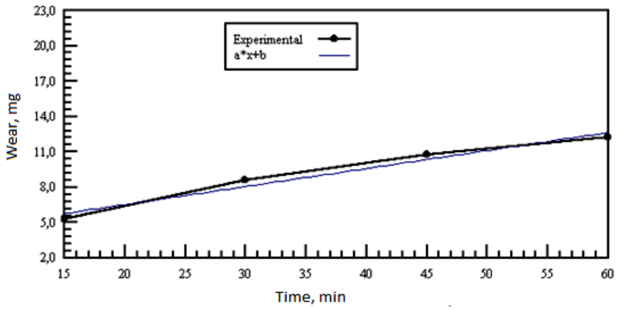

Figure 7. Wear for hard chromium plated cylinder in couple with metal sprayed piston

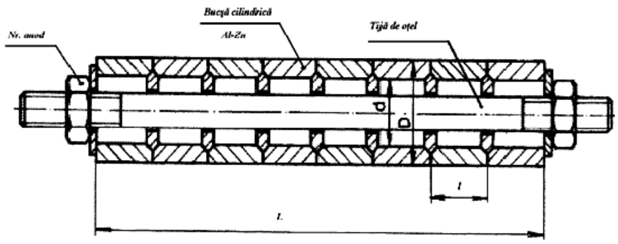

Figure 8. Active anode design

2.4 Evaluation of piston-cylinder durability

In order to evaluate piston-cylinder life time we put the condition to obtain a minimum surface pumping efficiency, η = 0,65 [4]. Based on laboratory tests results and taking into account of transformations to obtain similarity with a real pump working parameters was created a computer program for real pumps durability calculus. In Figure 9 is presented the program window simulation [4-6,9].

Program give us the possibility to evaluate pumps durability depending of pumps type (nominal diameter, length, materials couples), active anode presence, CO_2 partial pressure, deep of the pump in well, temperature, double stroke per. min. at pumping unit, etc.

3. CENTRIFUGAL PUMPS

In petroleum industry are used pumps with rotor and body made of carbon steel type OT450, gray cast type EN GJL HB 215, EN GJL HB 155, AISI 304 AISI 316, etc. Paper presents the erosion-corrosion wear results at tests made in the presence of formation water with 3% sand at different impingement angles, with and without active anode made on materials from rotor and body centrifugal pumps. Because sand particles and corrosive character of crude oil the wear mechanism is an erosive-corrosive one. The important quantities of formation water from crude oil make the aggressively of crude oil to depend of formation water aggressively.

To reduce corrosive wear of centrifugal pumps was proposed a cathodic protection with active anode.

Also at austenitic stainless steels hardened by nitride thermochemical treatments are presented the wear tests results.

3.1. Corrosion rates

Samples were made of carbon steel type OT450 from a real pump rotor, of gray cast type EN GJL HB 215 and EN GJL HB 155 from a real pump bodies. To evaluate materials corrosion behavior in formation water were made electrochemical tests using a potentiostat EG&G 350 Princeton and an ASTM cell with ECS reference electrode. In table 1, [3] are showed the values of electrochemical parameters. At samples made of mentioned materials were also established corrosion rate at different temperatures by immersion method. The values obtained were similar with the results obtained by electrochemical tests at 20 °C.

3.2. Erosion wear tests

To establish the erosion influence were made tests at 15°, 30° and 45° impingement angles at 1450 r.p.m. (7.6 m/s) with and without active anode attached at samples. Was establish wear for tested material samples and also was measured roughness on impact samples face. The working medium was formation water with 3 % sand wit size smaller than 0.125 mm.

In Figure 10 [3] it is shown the wear results obtained for samples of material GJL215 at 15° impingement angles and in Figure 11 [3] it is presented roughness modification curve for material GJL HB 215 at 15° impingement angles.

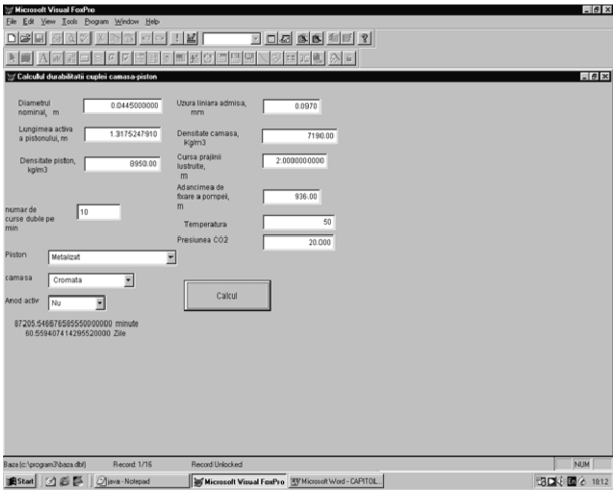

Figure 9. Program simulation for sucker rod pumps durability calculus

Table 1. The values of electrochemical parameters

Parameter	GJL HB 215	GJL HB 155	OT 450	Zn Anode
Corrosion current, i_{cor} [μA]	3.352	2.218	6.020	4.887
Corrosion potential, E_{cor} [V]	-0.160	-0.131	-0.190	-0.537
Corrosion rate, v_{cor} [mm/year]	0.045	0.030	0.080	0.074

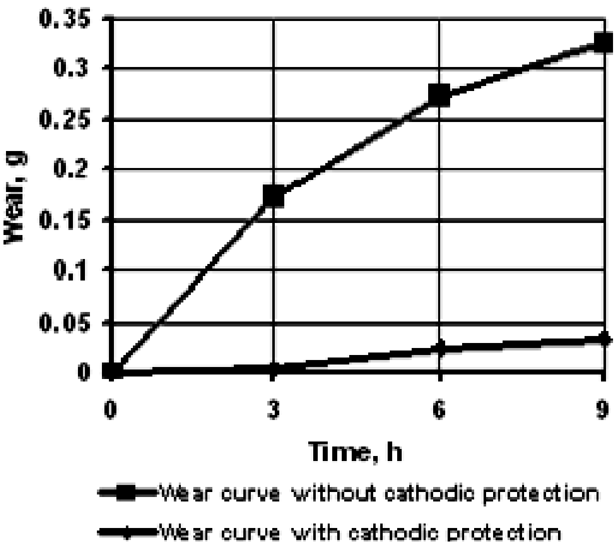

Figure 10. Wear curve for material GJL HB 215 at 15 ° impingement angles

From Figure 10 we could observe that cathodic protection reduce wear. Similar behavior was observed at all tested materials.

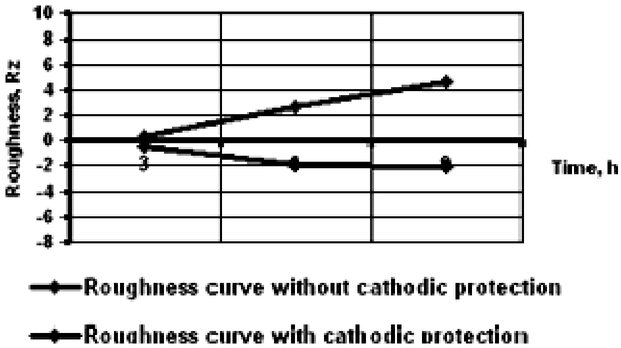

Figure 11. Roughness modification curve for surface of material GJL HB 215 at 15°

Cathodic protections with active anodes reduce erosion wear at all tested materials and impingements angles. Also cathodic protection improves surfaces roughness. For roughness the critical impingements angles for sample materials GJL HB 155 and OT 450 is 15° and for material GJL HB 215 without cathodic protection 15° and 30° and 15° with cathodic protection. These critical angles must be avoided.

The benefic results of cathodic protection with active Zn anode presented, was also confirmed at tests made on centrifugal pump stand (Fig. 12) and in industrial conditions [3].

Figure 12. Centrifugal pumps testing stand

The obtained results regarding cathodic protection efficiency give authors the possibility to formulate and to obtain the patent RO122867–B.

3.3. Nitrating treatments influence above tribologic behavior of austenitic stainless steels

Austenitic stainless steels have a good behavior in the presence of powerfully oxidant or corrosive environments, but with the disadvantage of a weak attitude in friction conditions due to the combined effects of the temperature produced by friction and of the superficial plastic distortions, especially in the presence of work environments presenting poor lubricant qualities.

To improve tribological qualities, can be recalled the application of thermal and thermo-chemical treatments, in the desire to obtain a tough, ductile and homogenous layer, which:

- reduces the action of conjugated asperities of the surface;
- increases shear resistance;
- increases resistance at superficial fatigue;
- increases corrosion resistance.

Two austenitic stainless steels, stainless steel AISI 304 (SR EN 10088-1-X5Cr Ni 18-10) and stainless steel AISI 316 (SR EN 10088-1-X5Cr Ni Mo 17-12-2), have been elected having a spread use in the construction of equipment's from petrochemical and refinery industry. Test samples obtained from these steels have been submitted to a gases nitrating treatment in two stages, at a temperature of 505 °C, namely 545 °C for 14 hours, and in parallel to an ionic nitrating treatment at a temperature of 480 °C for 8 hours. Tribological parameters were establish on universal tribometers like tribocorrosion wear machine, ball on disk C.S.M. microtribometer, erosion wear testing machine.

Tests conditions on CSM microtribometer [10] were: disk samples made of 304 and 316 steels untreated, gas nitrided and plasma nitrided, Ø 6 mm ball of 100Cr6, normal load N = 4 N, sliding speed v = 0.366 m/s, dry friction length L = 100 m, temperature 20 °C, relative humidity RH = 33 %.

In Figure 13 it is shown the friction coefficients for AISI 316 material samples, [10,11].

In the presence of formation water the mentioned materials were tested on wear testing machine, at parameters: samples made of 304 and 316 steels untreated, gas nitrided and plasma nitride, normal load, N = 25 N, sliding speed, v = 0.42 m/s, cylinder diameter, D = 40 mm, speed of rotation, n = 200 r.p.m., formation water as working medium, temperature T = 20 °C. In Figure 14 [10,11] is presented the volumetric wear results obtained for AISI 316 cylinder material sample.

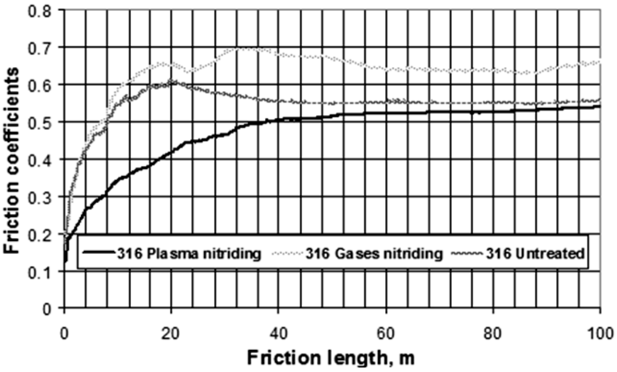

Figure 13. Friction coefficients vs. friction length

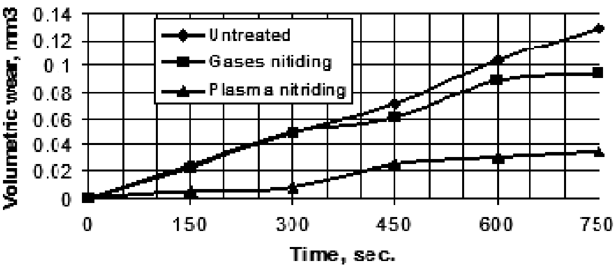

Figure 14. Wear curves for AISI 316 samples

At erosion wear tests the selected erosion wear test medium consisted of formation water from the water supply tank of an injection station, the latter having a high quantity of suspended sand particles and a high potential for corrosion. The main characteristics of the formation water used were: pH = 6.6, and the chemical composition with Na^+ 79.58 g/l, Ca^{z+} 4.41 g/l, Mg^{z+} 0.90 g/l, HCO_3^- 0.92 g/l and Cl^- 133 g/l with a sand content of 10 g/l collected from water supply tank [12]. The sand particles collected for erosion testing are silicon (SiO_2) based, chemically inert, possessing high hardness (7 Mohs scale or 1500 Vickers scale). The specimens were mounted at an angle of 15° and then 30° angles corresponding to the input-output angles of the blades of the centrifugal pumps.

In Figure 15 [12], it is shown the wear curves obtained for AISI 316 at impingement angle of 15° and in Figure 16 [12], at impingement angles of 30°.

Note that there is an important distinction between the erosion behaviors of the three states, and also depending of impingement angle. Increased surface hardness by nitrating treatments provides a significant reduction of wear by erosion. By increasing the impingement angle from 150 to 300, erosion wear increases both in untreated condition and also when gas or plasma nitrating thermochemical treatment was applied.

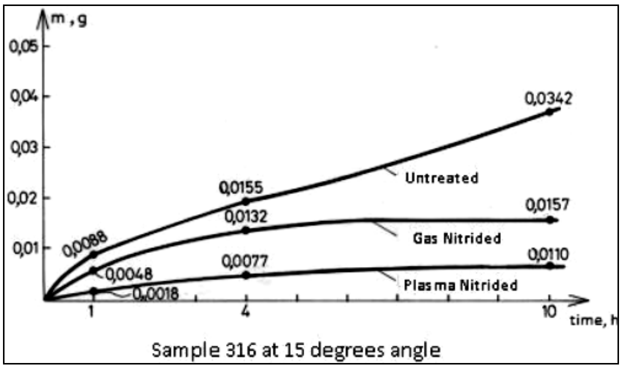

Figure 15. Erosion wear curves at impingement angle of 15°

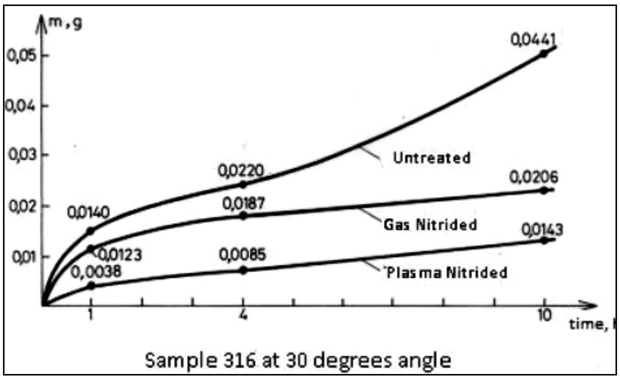

Figure 16. Erosion wear curves at impingement angle of 30°

4. CONCLUSIONS

In electrolytic aggressive liquid mediums, such as crude oil, industrial or urban residual waters, the corrosive part of wear could be reduced, with low costs, by applying cathodic protection with active anodes.

Zinc material has a anodic behavior in couple with tested materials for sucker rod and centrifugal pumps in formation water.

Chromium plated piston is better to work with nitrided cylinder instead of cylinder carbonitrided because electro-chemical potential are closer for nitrided cylinder. The same conclusion is for piston metal sprayed.

Cathodic protection with active anode reduces wear at all material couples.

Based on many experimental tests in laboratory and in more than 100 different wells from Romanian oil fields, the program created could evaluate with a error smaller than 12% the rod pumps lifetime, taking into account the piston cylinder materials couples, temperature, CO_2 pressure, deep of pump, double stroke per. min. at pumping unit, surface stroke and rod pump type. We can see also that corrosion rate is bigger with a smaller pipe flow section. Also a bigger roughness determines a bigger corrosion rate. The program created assures a fast instrument to evaluate corrosion rate.

Experimental tests establish that wear rise with temperature. With CO_2 pressure the influence above wear is different depending on the CO_2 pressure value and the materials couples. Because at CO_2 pressure tests was used only CO_2 gas the CO_2 pressure value is the same with partial pressure of CO_2. The maximum corrosion rate was obtained for 8…10 bar CO_2 pressure when the conductivity of tested formation water was maximum.

Cathodic protections with active anodes reduce erosion wear at all tested materials and impingements angles. Also cathodic protection improves surfaces roughness. For roughness the critical impingements angles for sample materials GJL HB 155 and OT 450 is 15° and for material GJL HB 215 without cathodic protection 15° and 30° and 15° with cathodic protection. These critical angles must be avoided.

The obtained results presented permit the authors to formulate a patent to protect sucker rod pumps and also a patent to protect centrifugal pumps with active anodes.

Increased surface hardness by nitrating treatments provides a significant reduction of wear by erosion.

By increasing the impingement angle from 15° to 30°, erosion wear increases both in untreated condition and also when gas or plasma nitrating thermochemical treatment was applied.

The wear in the same friction conditions decreased substantially in the case of plasma ionic nitriding. Also the wear and friction coefficients were smaller for AISI 316 than for AISI 304 material samples. This behavior is due to the thickness of formed expanded austenite *S* phase with good behavior at friction. This explains also the better tribological behavior of plasma nitrating then gases nitrating of austenitic stainless steels. Gases nitrating was performed at temperatures higher than plasma nitrating. This due to higher temperature at the surface appear also the phase γ' Fe_4N and reduce the thickness of S phase.

The 480 °C plasma nitrating temperature was optimum for AISI 316 but for AISI 304 was too high, the recommended value is 440 °C.

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