BALKANTRIB'O5
5th INTERNATIONAL CONFERENCE ON TRIBOLOGY
JUNE.15-18. 2005
Kragujevac, Serbia and Montenegro

GALVANIC CATHODIC PROTECTION INFLUENCE ABOUT DIMINISHING WEAR IN CORRODING MEDIUM

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Abstract

In corroding medium wear presents a corrosive compound. In electrolytic medium corrosion mechanism is electro-chemical.

For metallic couple each material surface has its own electro-chemical potential. Between two materials, corrosion current is smaller if materials potential are closer.

Paper establish for five materials, electro-chemical potential at different temperatures in order to fix the best materials couple.

Because even when we choice the best materials couple, corrosion still remain at a great value it is presented a method to reduce corrosion wear using galvanic cathodic protection. Experiments were made in static and dynamic conditions. Galvanic anode alloy was obtained and manufactured in our laboratory.

The results shows that cathodic protection with active anode Al-Zn alloy, reduce wear at all materials couples in different values depending on materials and working conditions.

KEY WORDS: *corrosive wear, cathodic protection, active anode.*

1. INTRODUCTION

Systems for well fluids extraction are: natural flow, artificial lifting, deep-well pumping with rod-pump or hydraulic and electro-centrifugal, submerged. Deep-well pumping is used in final phase of oil-field exploitation, when oil recovery by artificial lifting continuous or intermittent efficiency became non-economical.

Nowadays 65% of Romanian crude-oil production is obtained by deep-well pumping with rod-pumps, pumping wells representing 86% of wells for petroleum exploitation, [6]. From total pumping wells number, at 32% the working medium is severe abrasive and corrosive, at 46% is abrasive and corrosive and at 22% is normal, [6]. Well fluids classification it is made depending on contents of corrosive substances and sand like this, [1]:

Normal fluid:
- less than 30% mineralized water;
- without H_2S, CO_2, O_2 in water;
- water-floated sand less than 0,3%.

Abrasive fluid:
- water-floated sand above 0,3%;
- water and non-corrosive gases.

Corrosive fluid:
- above 30% mineralized water;
- salinity above 20g/l water;
- presence of H_2S, CO_2, O_2;
- pH < 7;
- contamination with stimulation fluids (HCl < 10%).

Abrasive - corrosive fluid:
- water-floated sand above 0,3%;- salinity above 20g/l water;
- presence of H_2S, CO_2, O_2.

All over the world at oil field with deep-well pumping with rod-pumps, 40% failures due to piston bore-hole pumps, [5]. In figure 1 is presented the elements participation at wells failure.

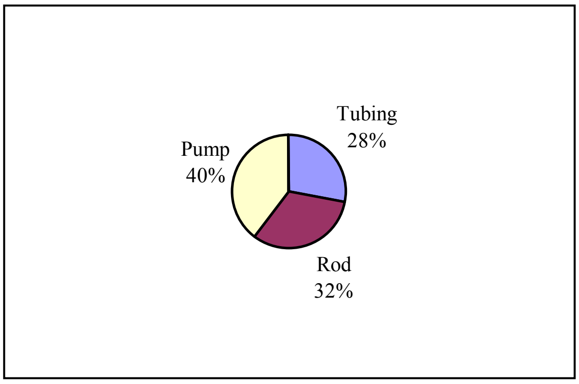

Fig.1: *Failure in deep-well pumping with rod-pumps*

Average percentage of impurities in recovery fluid rise continuous along the time and represent 60…90%, existing wells with 96…98% impurities. Thus, a main failure cause of rod-pumps is abrasive and corrosive wear of couple's piston-cylinder and valve cage- ball.

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.

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.

Corrosive wear participation in total wear is 25…50%, [1] 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;
- electro-chemical methods such as cathodic protection.

Less expensive are choosing proper couple of materials for piston and cylinder and also cathodic protection with active anode.

2. ACTIVE ANODE

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 timelife.

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

In figure 2 is presented the anode geometry.

Active anode material is an alloy Al-Zn6,5. Alloy casting, liner extrusion and machining were made in the laboratories of Oil Equipment Engineering Technology Department of Petroleum-Gas University.

The main anode characteristics are:

- theoretic drain………….2300Ah/kg;
- real drain……………….1100Ah/kg;
- efficiency…………………40-60%;
- anode consumption………..5,9kg/A.year.

Anode liner is fixed on a steel screw stay and has weight 87g/100mm.

The cathodic protection method with active anode for down-hole pumps and anode construction are paper author patent owner.

After laboratory tests anodes were used for down-hole pumps protection in many Romanian oil-fields [7].

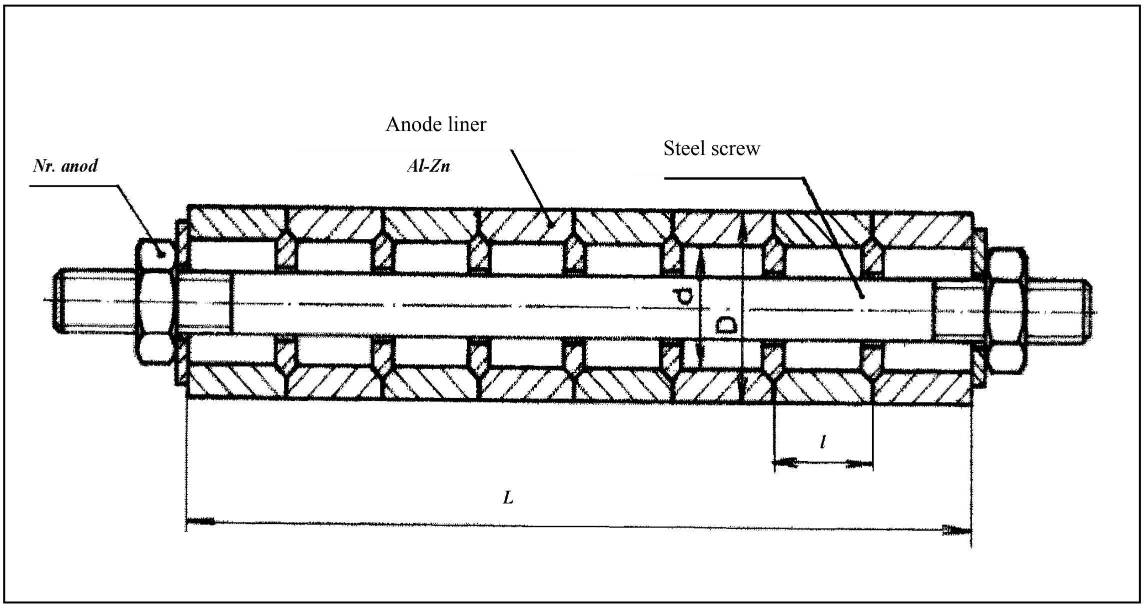

Fig. 2: *Active anode design*

3. EXPERIMENTS

3.1 Static corrosion wear tests

The direct contact or by an electrolytic medium between two materials with different electrochemical potential rise the intensity of the corroding wear.

Corrosion rate depends in proportion to electrochemical potential difference for piston-cylinder material couple.

From different material pistons and cylinders was prepared samples whose dimensions are presented in figure 3. At cutting and finishing it was not passed 150^{0}C, to not modify metallographic structure and the level of internal stress. In the middle of an inactive face, we braze a steel wire. The inactive faces and the wire were covered with synthetic resin.

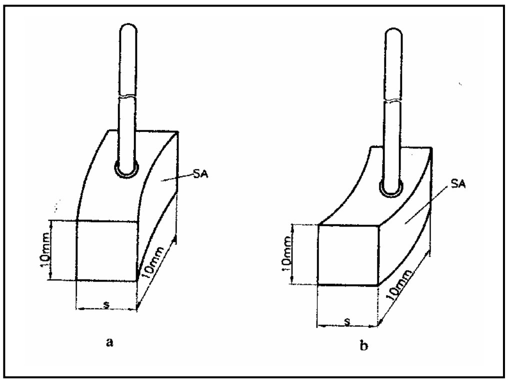

Fig. 3: *Sample dimensions*
a-cylinder; b-piston; SA-active surface

To evaluate kinetic corrosion parameters for metallic samples in petroliferous water it was used static-intensity method with calomel electrode as reference electrode and platinum electrode as control electrode. Was used a galvanic source and the intensity was given by a microammeter. Temperatures were 20^{0}C and 60^{0}C. Working medium was reached in CO_2 in a Kipp vase. Rising cathodic and anodic polarization curves, we could establish the corrosion current density i_{cor} (µA/cm^2). In table 1 it is presented the potentials and the corrosion currents for tested couples. These values result by drawing anodic and cathodic variation curve, as show in figure 4, [2].

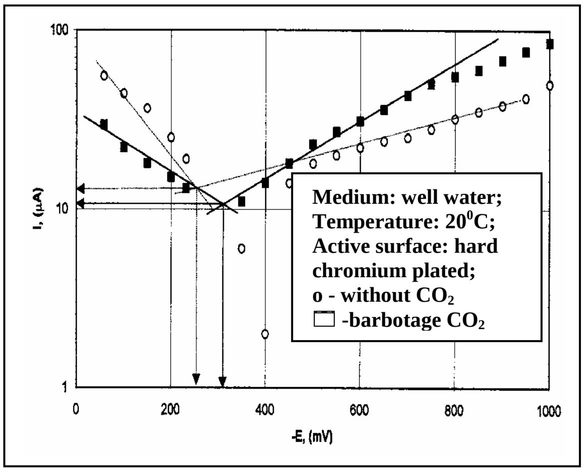

Fig. 4: *Tafel curve*

Table 1. Potential and current density

Surface material	Temperature ^{0}C	Medium, formation water	Corrosion potential, E_{cor}, mV	Current density, i_{cor}, µA/cm^2
Chromium plated	20	-	-580	12
		Barbotage CO_2	-380	14
	60	-	-603	15
		Barbotage CO_2	-480	18
Metal spray coating	20	-	-555	12
		Barbotage CO_2	-350	14
	60	-	-590	13
		Barbotage CO_2	-575	25
Nitrided	20	-	-430	33
		Barbotage CO_2	-390	47
	60	-	-500	45
		Barbotage CO_2	-360	80
Carbonitrided	20	-	-310	24
		Barbotage CO_2	-280	26
	60	-	-445	31
		Barbotage	-310	42

Analyzing parameters value from table 1. the conclusions are:

- corrosive medium temperature change corrosion potential. A greater temperature induces the rise of corrosion potential and corrosion current density for all materials;

- barbotage of CO_2 rise corrosion potential and corrosion current density for all materials;

- different samples have different corrosion potential and corrosion current density.

To determine corrosion rate in formation water from pistons and cylinder it were prepared samples whose dimensions are presented in figure 5. The inactive faces were covered with synthetic resin, stabile in formation water at maximum temperature.

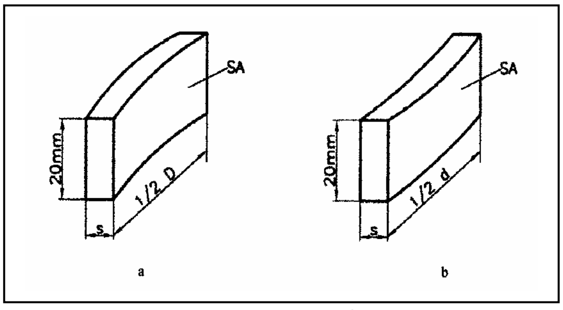

Fig.5*: Sample dimensions for corrosion rate a-cylinder; b-piston; SA-active surface*

In order to establish cathodic protection influence above corrosion rate, at samples was attached an active anode Al-Zn with a screw, shown in figure 6.

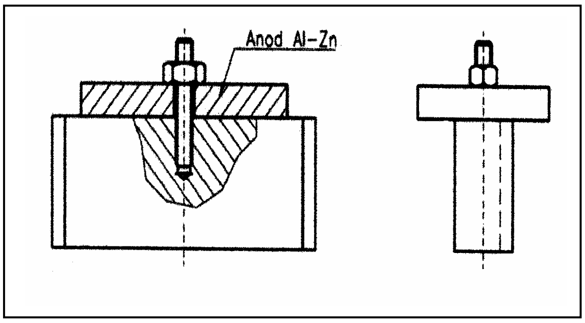

Fig.6: *Attaching active anode*

Samples were weighted with analytical balance with 0,1mg precision and were immersed in formation water putted in nonmetallic glasses. Heating was made in a thermostatic bath. CO_2 barbotage was made with CO_2 cylinder and pressure reducer.

Testing conditions to determine corrosion rate were:

- temperature 20, 30, 40 and 50^{0}C;
- atmospheric pressure with and without CO_2 barbotage;
- pressure of CO_2 - 2, 3, 4 and 5 MPa;
- with and without active anode.

Corrosion rate was calculated with relation:

$$v_{cor} = \frac{\Delta M}{A \cdot \tau} \quad \text{, g/m}^2\text{h}$$

were ΔM is mass loss, g;

A- sample active area, m^2;

τ - time, h.

In figure 7 is presented the corrosion rate at temperature 20^{0}C in formation water with CO_2 barbotage with and without active anode, [2].

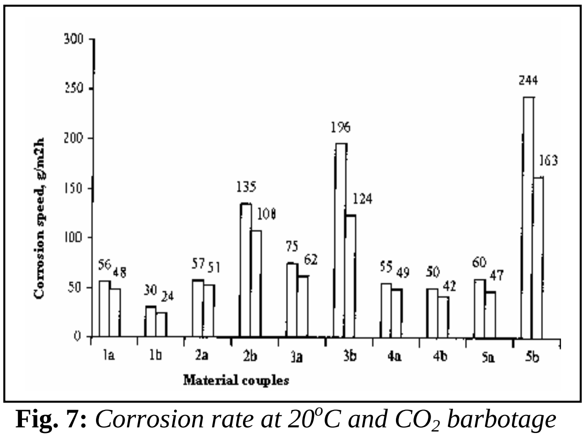

Fig. 7: *Corrosion rate at 20^{o}C and CO_2 barbotage 1a-piston metal sprayed; 1b-skirt chromium; 2a-piston metal sprayed; 2b-skirt carbonitrided; 3a- piston metal sprayed; 3b-skirt nitrided;*

4a-piston chromium-plated; 4b- skirt carbonitrided; 5a- piston chromium-plated; 5b- skirt nitrided.

In table 2 is presented the reduction percentage for corrosion rate when it was used cathodic protection with active anode, [3].

Table 2. Reduction percentage for corrosion rate

Materials couple		Conditions		Corrosion rate cut-off, %	
Piston	Cylinder	Temperature, ^{0}C	Pressure CO_2, bar	Piston	Cylinder
Metal sprayed	Chromium plated	20	-	15,0	24,0
			barbotage	14,3	20,0
			20	11,7	11,8
			40	5,7	8,6
		50	-	11,5	15,0
			barbotage	12,6	18,8
			20	17,2	15,0
			30	10,0	17,0
			40	8,9	13,8
			50	20,6	20,7
	Carbonitrided	20	-	13,5	12,7
			barbotage	7,0	20,0
			20	14,3	15,0
		50	-	21,0	15,7
			barbotage	21,3	18,7
			20	23,0	15,0
			30	18,2	25,1
			40	14,9	15,9
			50	27,7	23,9
	Nitrided	20	-	22,8	24,2
			barbotage	17,3	36,7
			20	18,7	17,8
			40	18,4	28,4
		50	-	28,3	15,1
			barbotage	34,6	38,3
			20	15,9	35,0
			30	17,6	26,8
			40	10,4	33,7
			50	18,3	22,0
Cromat	Carbonitrided	20	-	5,9	17,1
			barbotage	10,9	16,0
			20	27,0	18,8
			40	18,2	26,2
		50	-	12,3	30,0
			barbotage	17,8	25,2
			20	12,1	16,8
			30	20,0	21,0
			40	22,6	16,8
			50	14,7	28,3
	Nitrided	20	-	19,4	42,5
			barbotage	21,7	33,2
			20	41,7	43,7
			40	36,4	35,0
		50	-	21,1	23,5
			barbotage	21,6	28,8
			20	35,1	27,4
			30	26,2	27,6
			40	18,9	23,2
			50	22,5	19,6

3.2 Dynamic wear tests

Wear process was study on a testing machine designed and completed for that purpose.

Active anode Al-Zn was attached to the piston or to the cylinder, depending on the electrochemical potential of the two materials.

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

Testing conditions were:

- load, 50N;
- double stroke per. min., 54;
- temperature, 20^0C;
- barbotage of CO_2;
- with and without active anode.

In table 3 is shown the effect of cathodic protection with active anode in reducing wear.

Table 3. Cut-off wear by cathodic protection

Material couple		Cut-off wear, %	
Piston	Cylinder	Piston	Cylinder
Metal sprayed	Chromium	8,2	7,8
	Carbonitrided	11,5	8,3
	Nitrided	2,2	22,7
Chromium plated	Carbonitrided	2,3	19,3
	Nitrided	4,2	15,4

4. CONCLUSIONS

Cathodic protection with active anode reduces corrosion rate at all material couples. Cathodic protection effect depends on material couples and on testing conditions.

CO_2 barbotage at 20^0C rise corrosion rate. Rising temperature rise corrosion rate.

Rising CO_2 pressure, corrosion rate depends on pressure value.

At maximum testing temperature, corrosion rate presents high values.

Chromium plated piston is better to work with nitrided cylinder instead of cylinder carbonitrded 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.

5. REFERENCES

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