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**A NEW SENSOR FOR HYDROGEN PERMEATION DETECTION AND  
MEASUREMENT AND CORROSION MONITORING**

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**Abstract:**

Many corrosive processes found in machines, equipments and pipings, used in the petroleum industry are directly influenced by hydrogen. The structural damages are caused, in many cases, by hydrogen inclusion into the metallic structures. These hydrogen is generated by acid means that contain free protons ( $H^+$ ), by chemical processes that lead to the protons formation, by formation of atomic hydrogen ( $H^0$ ), or even by absorbed gas hydrogen ( $H_2$ ). The structural damages caused by hydrogen may be: hydrogen induced cracking (HIC), blistering, sulfur stress cracking (SSC) and stress oriented hydrogen induced cracking (SOHIC). In practical terms the challenge is to detect, in a safe, fast and economically viable way, the formation of hydrogen close to a surface subjected to corrosion. This is necessary in order to use preventive control to avoid severe damages that can be caused. This work presents an experimental system designed for development and evaluation of a new sensor for permeated hydrogen determination and corrosion monitoring. This new experimental system enables performance comparison of bimetallic and traditional Devanathan-Stachurski sensors. The sensor is composed of two parts, each one built with a pair of dissimilar materials, being a sensor pair, for hydrogen flux measurement, and a reference pair, for temperature corrections. The results obtained showed good agreement with a traditional Devanathan-Stachurski sensor. The main advantages of this sensor are cheap construction, simple installation, external or internal set up (similar to pressure sensors), low maintenance cost, unlimited lifetime, precision and accuracy equivalent or better than obtained for methods currently used and online monitoring of hydrogen permeation and corrosion.

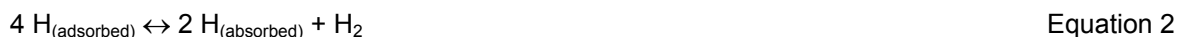
## INTRODUCTION

One of the greatest problems found in petroleum refineries is deterioration control of steel structures at units of the petroleum refining process. This deterioration is related to mechanisms involving the hydrogen penetration in steel and stress corrosion. The presence of cracks in steel vessels, which usually operates at high pressures, were identified as one of the largest problems in refineries. Approximately fifty percent of these cracks are due to hydrogen penetration in steel. Four types of hydrogen dependent corrosion mechanisms are normally found: Hydrogen Induced Cracking - HIC or StepWise Cracking - SWC, Hydrogen Blistering Induced Cracking - HBIC, Stress Oriented Hydrogen Induced Cracking - SOHIC and Sulfur Stress Cracking - SSC. The hydrogen is generated by acid media that contain free protons ( $H^+$ ), by chemical processes that lead to proton formation, by atomic hydrogen formation ( $H^0$ ), or even by hydrogen gas ( $H_2$ ) adsorbed in the metallic structure. These conditions are frequently found in liquid and gaseous currents flowing in a refinery, chemical or petrochemical plant.

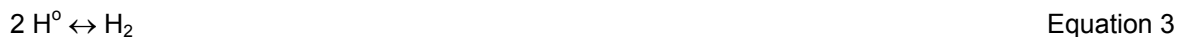
At industries that deal with hydrocarbons, a common source of hydrogen takes place when sulfide ions ( $S^-$ ) and water are present. When the steel in pipes is submitted to an atmosphere that contains humid  $H_2S$ , the following chemical reaction can happen:



The iron is removed from the steel surface and iron sulfide is formed, causing a mass loss that characterizes the corrosive process. The hydrogen is produced as atomic hydrogen ( $H^0$ ) or nascent hydrogen, which is absorbed by the metallic surface, configuring the reaction below:



The absorbed hydrogen diffuses through the steel, while the gaseous hydrogen is liberated in the liquid media. The atomic hydrogen,  $H^0$ , that diffused through the steel, when emerged from the outside external surface, it is recombined to form molecular hydrogen,  $H_2$ , as follows:



The detection of the hydrogen penetration using a hydrogen sensor is one of the more efficient ways used to control the deterioration process (corrosion) and increase the lifetime of the process vessels.

## STATE OF THE ART

The structural damages caused by hydrogen are varied and several processes were developed to control these damages such as a surface protective layer or to control the conditions of the media in contact with the corrosion material. The main problem here is how to measure in a safe, economically viable way and mainly, in the smallest possible time, the hydrogen formation close to a corrosion surface, in order to use control procedures to avoid damages. Great effort has been made to obtain a hydrogen sensor with short answer delay, easy installation, little maintenance, that provides precise and exact results, integrated to data processing systems and, of course, with low cost.

High temperature hydrogen determination methods frequently use vacuum extraction. These methods measure the total amount of hydrogen in steel, including hydrogen at grain boundaries and microstructural inclusions. They are generally destructive and not very practical to be applied in industry. In contrast, electrochemical methods based on the oxidation of the hydrogen that emerges from the metallic

surface, just detects mobile hydrogen and hydrogen retained at reversible sites. Those hydrogen forms are believed to be more important, because they can diffuse to material defects and cause embrittlement.

The permeated hydrogen sensors in metallic structures can be classified in four main groups: pressure sensors, vacuum sensors, electrochemical sensors and combustible cells.

The main problems of internal pressure sensors (IPS) are the answer delay (it can take up to one month to reach measurable pressure levels) and the lack of sensibility. Due to these limitations, they can indicate the presence of a corrosive process when it is already irreparably advanced. When compared to the previous one external pressure sensors (EPS) have the advantage of being able to be externally set-up, without interference at the industrial process, but it still presents all other disadvantages. The answer delay is even larger, due to the largest wall thickness of process vessels subject to corrosion, when compared with wall thickness of the reactional tube of an IPS.

The disadvantages of vacuum sensors (VC) are the high cost of the peripheral electronic equipments and instrumentation needed for construction and operation and its fragility under severe operation conditions of an oil plant.

Electrochemical sensor uses a noble metal (Pd), resulting in high production costs. They have considerable answer delay, need external equipments for polarization of the electrodes and limited lifetime, once the electrochemical reactions imply on electrodes consumption. Besides the electrochemical processes can be very complicated and can be subject to interferences caused by the media, electrolyte contaminants or temperature. Several types were recently developed, such as the solid electrolyte sensor, but none of these efforts was able to eliminate the mentioned disadvantages.

The Devanathan and Stachurski Cell (DSC) is the widest electrochemical method used for hydrogen measurement. Its limitations include liquid media, costly and complicated instrumentation, reduced lifetime, besides this it has been used by several researchers as reference in development and test of other sensors.

## THE PROPOSED MODEL

The proposed model consists of a sensor that measures alterations in physical properties in a junction of dissimilar materials, the same principle largely used in thermocouples. Such alterations are function of the difference in electronic density of the atomic structure of each material, which is extremely influenced by the flow of atomic hydrogen ( $H^0$ ) through this junction. The proposed model should allow the potential measurement between a sensor pair and a reference pair.

The proposed was designed to overcome disadvantages of other sensors and processes. It is composed of two parts, being the main sensor (MS) welded to the metallic surface under hydrogen permeation, in such a way to form a metallurgical continuity with that surface, ensuring hydrogen diffusion through the metallic structure and the sensor. The second part, the reference pair (TCS), is bolt pressed to the metallic surface under hydrogen permeation, not allowing any hydrogen permeation through this pair. The sensor and the reference pairs are both connected to electric property meters, as for example potentiometers, being the difference of those electric properties a function of the hydrogen flow that crosses the surface.

## CONSTRUCTION OF THE SENSOR

The sensor (Figure 1.(A) to 1.(C)) consists of two parts in a "U" shape (2-A and 2-B), being one of the sides (2-A-1 and 2-B-1) and the base of the "U" (2-A-2 and 2-B-2) from the same material, and the remaining side of the "U" (2-A-3 and 2-B-3) from other material. These parts are welded in a corner of the "U" base – each one forming a bimetallic pair (2-A and 2-B). One pair (main sensor) (2-A) is welded in the external surface of the substrate under hydrogen permeation (1). The other pair (temperature compensation sensor – TCS) (2-B), is just fixed by the "U" base (2-B-2) onto the external surface (1). Both sensors (TCS and MS) are connected together and the farthest extremities are connected (3) (4) to a potential meter (5) that measures differences of electric potential.

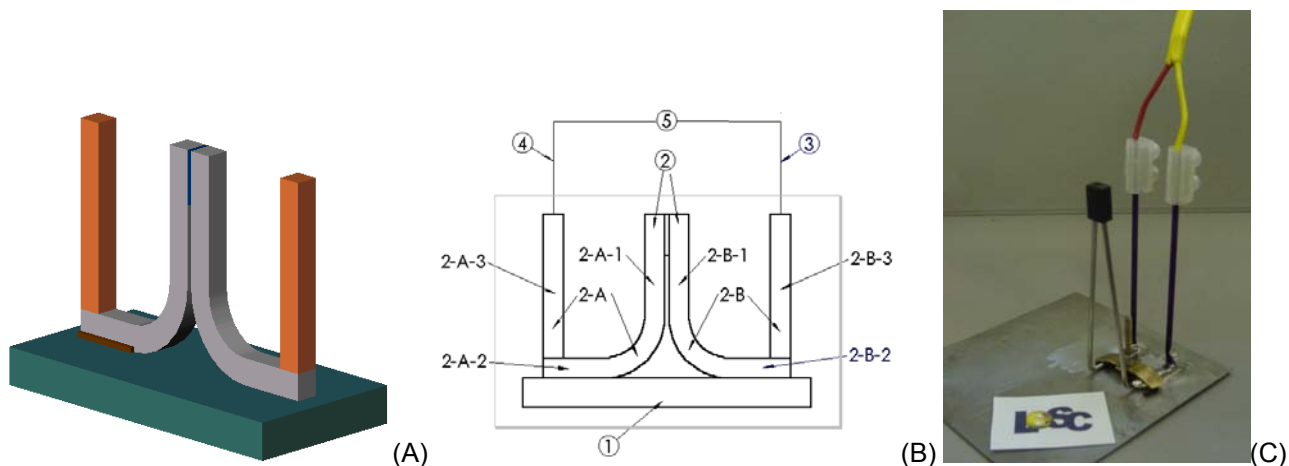


Figure 1 – 3D model. (A) Constructive concept of the sensor, showing the sensor pair (left - welded to surface) and the reference pair (right), (B) Electric diagram of the sensor, (C) Prototype of the sensor applied on a steel membrane

## RESULTS AND DISCUSSION

Figure 2.A presents a typical permeation curve under galvanostatic charging,  $i_{H_2} = 2 \text{ mA.cm}^{-2}$ , obtained in a Devanathan-Stachurski Cell (DSC).

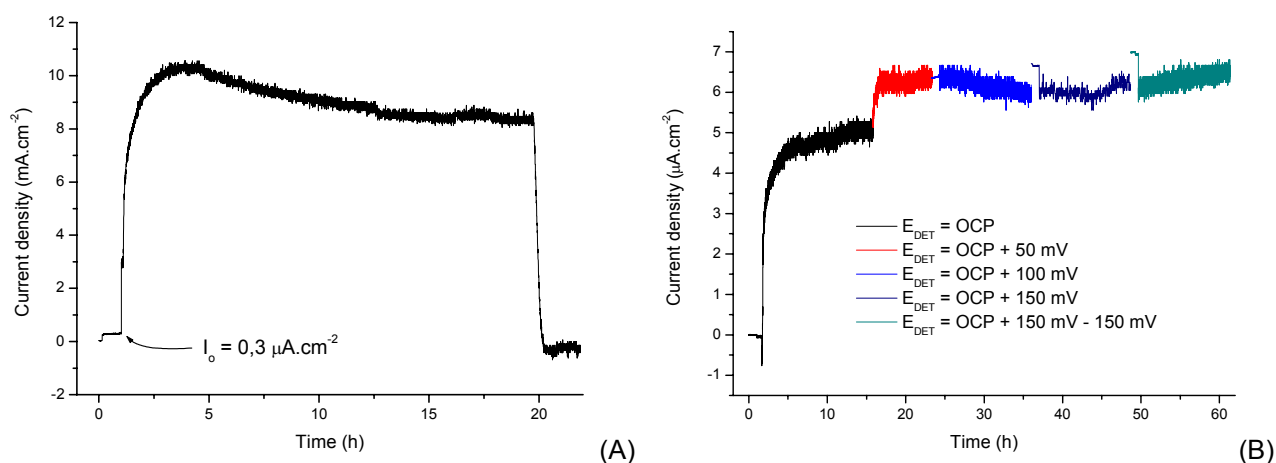


Figure 2 – (A) Typical curve for hydrogen permeation in a DSC. Exit surface covered with a 1-2  $\mu\text{m}$  Pd layer,  $\text{N}_2$  bubbling, 25  $^{\circ}\text{C}$ ,  $i_{H_2} = 2 \text{ mA.cm}^{-2}$  (B) Effect of the detection potential (vs. Lazaran) on the permeation current, exit surface with a 1-2  $\mu\text{m}$  Pd layer,  $\text{N}_2$  bubbling, 25  $^{\circ}\text{C}$ ,  $i_{H_2} = 2 \text{ mA.cm}^{-2}$

The used detection potential ( $E_{DET}$ ) was the open circuit potential (OCP) after 240 min and the background current was about  $0,3 \text{ mA.cm}^{-2}$ . Figure 2.B presents the effect of  $E_{DET}$  on the permeation current measured. The range studied was between OCP and OCP + 150 mV (vs. Lazaran). The charging conditions in the Figure 2.B were kept unchanged for all measurements and the membrane was not allowed to degass between experiments (continuous charging). The results indicate small influence of potential on the measured current, for the case of a membrane recovered with a thin Pd layer. These studies are necessary, considering that a DSC was used as the reference sensor in the development of the bimetallic sensors (BS).

The experimental set-up (computer controlled through LabView™) used in the development and comparison with DSC is presented in Figure 3.A. A Devanathan-Stachurski Modified Cell (DSMC) and two prototypes of the new sensor are shown in Figure 3.B. These sensors are under the same cathodic charging during the experiments, enabling performance comparison for the performance of the sensors.

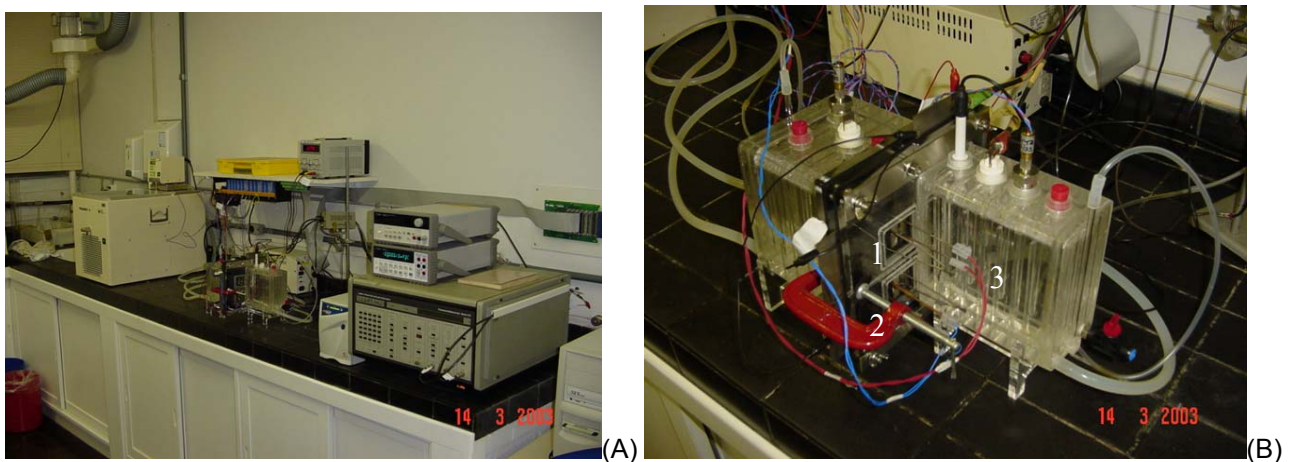


Figure 3 – (A) Experimental bench for development/test of the new sensors. (B) Devanathan-Stachurski Modified Cell (DSMC) with a traditional DSC (3) and two bimetallic sensors - Ni/Cromel – (1) and Constantan/Cromel (2) – subjected to cathodic charging

Figure 4.A shows results of a DSC and a bimetallic sensor, both subjected to the same cathodic charging, where a good agreement in the results (steel membrane 0,6 mm thick in both cases) can be seen.

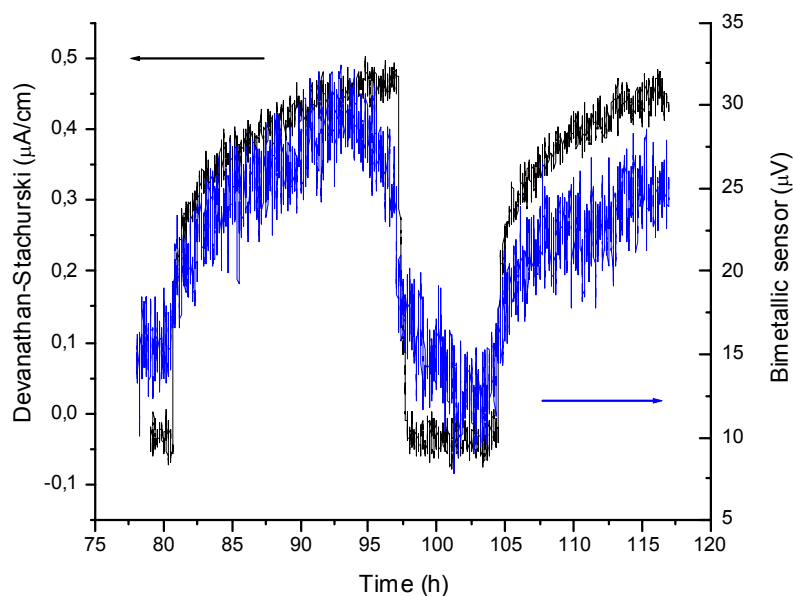


Figure 4 – (A) Comparison between a bimetallic sensor (Ni/Cromel) and a traditional Devanathan-Stachurski sensor. Cathodic charging at  $3 \text{ mA.cm}^{-2}$

## CONCLUSIONS

The new sensor presented promising results as can be seen in Figure 4.(A). The main advantages of this sensor are cheap construction, simple installation, external or internal set up (similar to pressure sensors), low maintenance cost, unlimited lifetime, precision and accuracy equivalent or better than obtained for methods currently used and online monitoring of hydrogen permeation and corrosion.

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