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Structured Packing Evaluation in Sour Gases Treatment from Kiln Emissions

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The burning of pieces manufactured with clays to be used in the construction industry, contributes to environmental imbalance because it contains combustible materials that produce emissions released in the atmosphere.

Up to now kilns have been used with combustion processes precarious and fuels highly polluting, which favor climate change emissions for CO_2, NO_x and acid rain by SO_x, endangering the health of those living near these facilities.

The treatment of combustion gases by means of a packed absorption column with a high efficiency liquid-gas contactor reduces pollutant emissions to the atmosphere, when combustion gases are in contact with aqueous amine solution of Mono Ethanol Amine (MEA).

The objective of this work is to study which one of three materials presents the lowest deterioration in the presence of combustion gases with MEA. The materials were tested according to American Society for Testing Materials ASTM G31-2004 corrosion testing, and the procedure NRF-194 PEMEX-2007.

The properties studied were tensile strength, hardness and elastic modulus, before and after structured packing materials were in contact with combustion gases in MEA aqueous solution. The results showed that in acid and basic medium, the metallic material was the most resistant to abrasion; it has the major tensile strength, and presented more resistance in the stress test.

1. Introduction

The study of gas-liquid contactors (structured packing), which are the elements directly contact with the acid gases with solution of Mono Ethanol Amine (MEA) (Chavez et al., 2005), lead the actions of delivering on environmental legislation regarding emissions into the atmosphere and increase the separation efficiency in the absorption columns (Back, 1972).

The burning of pieces manufactured (Orre et al., 2013) with clays to be used in the construction industry, contributes to environmental imbalance due to it is used combustible material that produce emissions released to the atmosphere, up to now kilns have been used with combustion processes precarious and fuels highly polluting, which favours climate change emissions for CO_2, NOx and acid rain by SOx, endangering the health of those living near these facilities (Chavez, 2008). The treatment of combustion gases by means of a packed absorption column with a high efficiency liquid-gas contactor reduces pollutant emissions to the atmosphere, when combustion gases are in contact with aqueous amine solution, using different structured packing material which can be metallic, polymeric or ceramic.

Some factors that decrease the lifespan of the materials and devices are radiation, thermal shock, pressure, velocity and turbulence of fluids, the presence of solid particles and action of air moisture (Kladkaew et al., 2009). Substantial corrosion problems (Veawab et al., 1997) in gas-liquid contactors such as wear, clogging and detachment of material, causing deterioration in the acid gases separation processes, due to loss of absorption efficiency (Wagner and Traud, 1938).

Corrosion problems are generated in the materials (Wellison et al., 2013), largely due to the presence of sour gases such as CO_2, SO_2, and other substances such as MEA, which in contact with water, become

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aggressive media that promote destructive oxidation of metallic alloys and the deterioration of non-metallic materials, into they are in contact (Mendoza et al., 2002). Table 1 presents the parameters of acceptance for materials tested in corrosive media PEMEX NRF-194-2007.

2. Methodology

In order to assess the interaction of the gas-liquid contactors in separating acid gases, there were considered two aspects: i) shelf life for corrosion problems and ii) physical-chemical properties of the materials contactors, to determine their abrasion resistance and mechanical strength.

2.1 Shelf life for corrosion by ASTM G5-1999 and ASTM G31-2004

For the study of materials contactors the Tafel extrapolation electrochemical technique was used, using two electrochemical corrosion cells, which were composed of a working electrode (sample), an electrode of graphite, a saturated electrode of Calomel, and one electrolyte aqueous solutions of an aqueous solution of MEA (monoethanolamine) at 30 % in weight, and electronic measurement was made. The sample was prepared so as to expose an area of 1 cm^2, as a reference electrode was used as saturated Calomel electrode and a counter electrode or auxiliary graphite electrode holder used a reference electrode (Wagner and Traud, 1938), partly immersed in electrolyte solution, to minimize ohmic resistance (Mendoza et al., 2002).

If the concentration of the reactants and products is uniform in the middle, the Butler-Volmer equation for the current density j is:

$$j = j_0 exp\left(\frac{\eta_a}{\beta_a}\right) - j_0 exp\left(\frac{\eta_a}{\beta_c}\right) \tag{1}$$

Were β_a y β_c, are the coefficients of anodic and cathodic Tafel, respectively. The equations are applied to the electrode reactions in which the speed is controlled by the charge transfer process at the electrode/electrolyte. This situation is often known as activation on corresponding potential as activation overpotential, η_A. The value of the coefficients Tafel, β_a y β_c, depend on the mechanism of the reactions taking place at the electrodes, which often include several stages. By means of Butler-Volmer equation, it is described the whole kinetics of charge transfer process, regardless of the mechanism, based on three easily measured variables: j_0, β_a y β_c (Mendoza et al., 2002).

2.2 Physical-chemical properties of the materials contactors by ASTM E8-1998 and ASTM E384-1990

Mechanical properties: Hardness, tension and elastic modulus of three materials were evaluated as follows:

Hardness

The property of hardness of the materials was determined before and after contact with the MEA solution at 30 % by weight, in the presence of CO_2. Samples of the materials metallic, polymeric and ceramic were assembled on the resin of polymethyl methacrylate (PMMA) in a press Buehler to 150 °C and pressure of 28 MPa, in order to manipulate the samples during the polishing process with sandpaper 240 grit, 320, 400, 600, on up fine finish. Later they were given a polished mirror finish with Buehler microcloth cloth and aqueous alumina (Al_2O_3) of 0.1 microns. Knoop hardness (HK) was measured on a Shimadzu microhardness of the mark, using a diamond indenter diamond pyramid shape with angles of 172° and 130°, in accordance with ASTM E 384-90, at ambient temperature of 23 °C.

Tensile strength and modulus of elasticity measurements

Measuring the tensile strength and modulus of elasticity were performed with a Universal Testing machine Monsanto trademark and according to ASTM E 8-98. This assay was performed on specimens of 2 inches (0.05 m) long for each of the three materials, before being in contact with the aqueous solution of MEA at

Table 1: Accepted parameters for the materials tested in corrosive media NRF-194 PEMEX-2007

Materials tested in corrosive media	mpy	Mmpy
Exceptional	Less than 1	Less than 0.02
Excellent	1-5	0.02-1
Good	5-20	0.1-0.5
Acceptable	20-50	0.5-1.0
Poor	50-200	1.0-5.0
Unacceptable	Greater than 200	Greater than 5

30 wt% and after contact with the same solution with speed test of 5 mm/min, capacity from 0 to 10,000 MPa and ambient temperature of 25°C.

Morphology
The morphology of the materials was analyzed before and after being in contact with the aqueous solution of MEA with a Scanning Electron Microscopy (SEM) JEOLJSM5900LV brand, using secondary electrons to the metal material and backscattered electrons in the polymer and ceramic voltage 20kV (see Figures 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12).

3. Results

Table 2 shows the metallic material presented a rate of corrosion of 0.0642 mpy, 2.3 times more resistant than the polymeric material the polymer of 0.148 mpy, the second in resistant and the ceramic 0.56, 3.78 times less resistant than the polymeric material.

In Table 3, ceramic material decreased by 2.86 % as compared with the value before contact with the MEA. The hardness of the polymeric material decreased by 5 %, while in the metallic material rose 2.6 %. These results indicate that the metallic material resists most efforts to friction and pressure that are exhibited in the absorption column. Table 3 shows the analysis results of tensile strength. This parameter provides information on the tensile strength, rigidity and ductility of the materials. The metallic material showed the highest zone of plastic deformation, which means the more able to withstand higher pressures within the absorption column. The polymeric material was the most ductile causing not breaking easily. The ceramic one is the most fragile and prone to break easily due to the efforts within the absorption column.

Elemental composition of the structured packing before and after contact with the aqueous solution of MEA at 30 % by weight is shown at Table 4. It is observed that after contact with the MEA solution at 30 %, the metallic material introduced the presence of oxygen, corresponding to an oxidation process that results in a surface layer of chromium oxide and nickel, which serves to protect the material to reduce the corrosion process.

The morphology of the three materials before and after contact with the MEA solution at 30 % by weight and in the presence of acid gases are shown in Figures 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12. The ceramic material after contact with the MEA solution and acid gas has a morphology less rough surface, while the polymeric material does not change substantially and the metallic material introduced a greater surface roughness favoring the formation of liquid film to carry after the absorption process between the liquid and gas, helping to improve the mass transfer in the capture of carbon dioxide, is also dark areas of Cr_2O_3 and NiO, which provide protection against an acid medium.

Table 2: Corrosion rate of materials contactors at MEA solution at 30 % in weight, mmpy (mm per year) and mpy (miles per year)

Contactor material	Corrosion rate in aqueous solution of MEA at 30 % weight	
	mm/y	Mpy
Metallic	1.63068 x 10^{-3}	6.42 x 10^{-2}
Polymeric	3.7592 x 10^{-3}	1.48 x 10^{-1}
Ceramic	1.4224 x 10^{-2}	5.6 x $^{10-1}$

Table 3: Results of change in the mechanical properties of structured packing before and after contact with the aqueous solution of MEA at 30% weight

Mechanical properties	Metallic	Polymeric	Ceramic
Knoop hardness (HK) before contact with MEA	190 HK	20 HK	700 HK
Knoop hardness (HK) after contact with MEA	195 HK	19 HK	680 HK
Change of hardness (%) after contact with MEA	+ 2.63 %	-5.0%	-2.86%
Tensile strength (MPa) before contact with MEA	841 MPa	35 MPa	90 MPa
Tensile strength (MPa) after contact with MEA	797 MPa	33 MPa	65 MPa
Change of tensile strength (%) after contact with MEA	- 0.36 %	- 5.71%	- 27.8 %

Table 4: Elemental composition of the structured packing before and after contact with the aqueous solution of MEA at 30 % by weight

Elemental composition	Metallic (%)		Polymeric (%)		Ceramic (%)	
	Before	After	Before	After	Before	After
Aluminum					16.62	11.83
Manganese	0.72	1.00				
Sulfur	0.015	0.31				
Carbon	0.07	0.19	87.34	96.15		4.5
Phosphorus	0.01	0				
Silicon	0.01	0.05			22.92	24.53
Chromium	18	14.3				
Nickel	13	8.0				
Potassium					1.69	2.26
Iron	66.775	71.01				0.65
Molybdenum	1.4	0.68				
Oxygen		4.46			58.76	55.1
Sodium						0.59
Magnesium						0.45

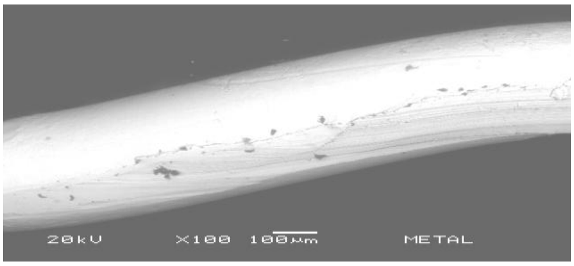

Figure :. SEM of the surface of the metallic material at 100X, before contact with MEA

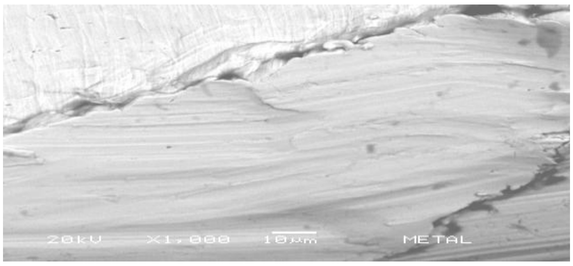

Figure 2: SEM of the surface of the metallic material at 1000X, before contact with MEA, with rough spots

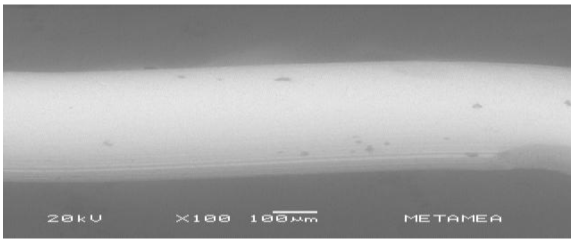

Figure 3: SEM of the surface of the metallic material at 100X, after contact with MEA

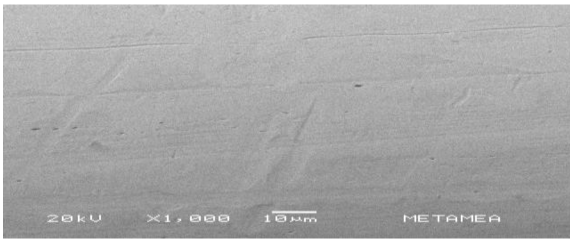

Figure 4: SEM of the surface of the metallic material at 1000X, after contact with MEA

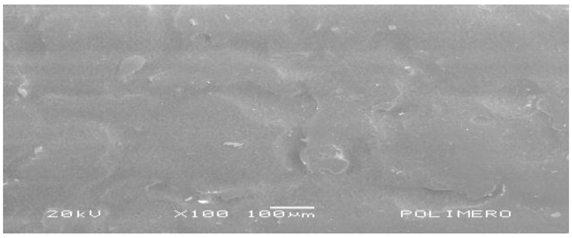

Figure 5: SEM of the surface of the polymeric material at 100X, before contact with MEA

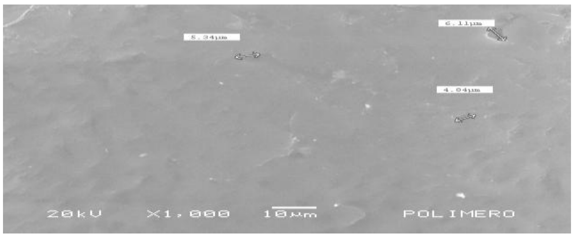

Figure 6: SEM of the surface of the polymeric material at 1000X, before contact with MEA

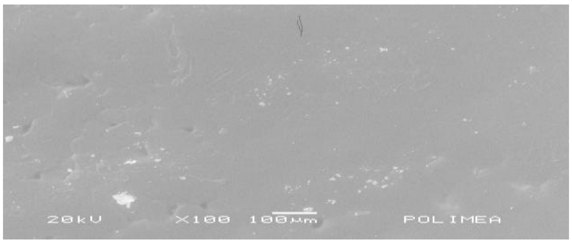

Figure 7: SEM of the surface of the polymeric material at 100X, after contact with MEA

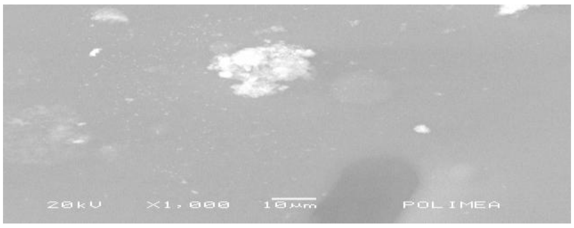

Figure 8: SEM of the surface of the polymeric material at 1000X, after contact with MEA

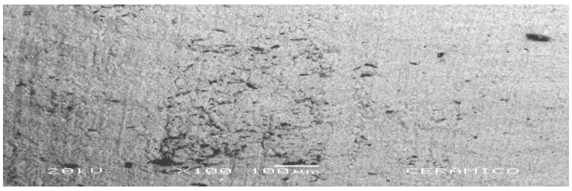

Figure 9: SEM of the surface of the ceramic material at 100X, before contact with MEA

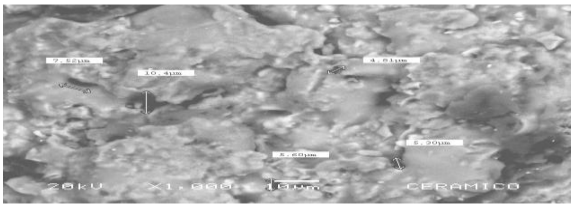

Figure10: SEM of the surface of the ceramic material at 1000X, before contact with MEA

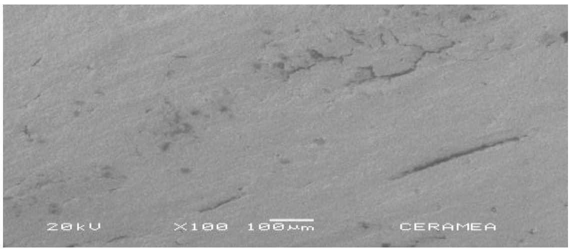

Figure 11: SEM of the surface of the ceramic material at 100X, after contact with MEA

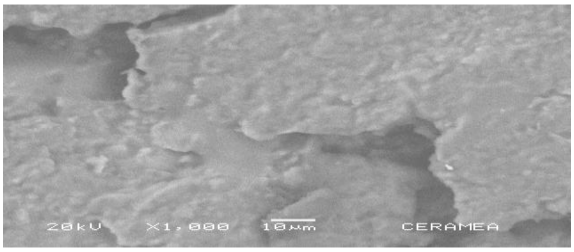

Figure 12: SEM of the surface of the ceramic material at 1000X, after contact with MEA

4. Conclusions

The ceramic was the most susceptible to be attacked when the concentration of MEA rose above the reference value and because of its fragility and porosity was found to be less suitable for use in the treatment of acid gas with MEA, in absorption processes.

The polymeric material showed higher resistance to attack in presence of MEA aqueous solution, which makes it suitable for treatment of acid gases.

The metallic material was identified as the best suited for the treatment of CO_2, due to their mechanical properties which can withstand higher loads before failing and able to withstand higher pressures within the absorption column. After contact with the aqueous solution of MEA, layers of Cr_2O_3 and NiO were formed on its surface due to react with a passive anode, and became resistant to corrosion.

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