CHARACTERIZATION OF CATALYTIC CRACKING CATALYST AFTER ELETROKINETIC REMEDIATION BY X-RAY MICROTOMOGRAPHY

Renata Bachmann Guimarães Valt, revalt@bol.com.br
Nice Mika Sakamoto Kaminari, nice.kaminari@gmail.com
Alysson Nunes Diógenes, andiogenes@ufpr.br
Maria José Jerônimo de Santana Ponte, mponte@ufpr.br
Haroldo de Araújo Ponte, hponte@ufpr.br
Federal University of Parana, Laboratory of Environmental Technology (LTA), PO Box 19011, ZIP CODE 81531-990, Curitiba, PR, Brazil

Abstract. *One of the main uses of catalysts in the oil industry is in Fluidized Catalytic Cracking-FCC process, which generates large quantities of waste material after use and regeneration cycles. In this research the deactivated FCC catalyst was characterized before and after the electrokinetic remediation process, in order to assess modifications of its structure and possible adsorptive capacity. The electrokinetic remediation process consists of applying an electric field on the material to be treated through electrode plates. The contaminants are then transported by migration as charged species and removed out of system. It was performed analyses of X-ray Microtomography, Scanning Electron Microscopy and BET Surface Area measurement. The analyses showed no structural change due to the process applied and that electrokinetic remediation has recovered 40% of adsorption capacity of the material, by removing almost all heavy metals previously adhered in the catalyst surface.*

Keywords*: electrokinetic remediation, X-ray microtomography, catalyst*

1. INTRODUCTION

The remediation techniques provide for the recovery of contaminated areas by removing, reducing or eliminating the concentration of the contaminant. But in some areas due to soil structure, the conventional degradation of contaminants becomes inefficient or even unfeasible.

Several studies (Acar et al., 1995; Yang and Lin, 1998; Alshawabkeh et al., 1999; Pamukcu et al., 2004; Wang et al., 2007; Guaracho et al., 2009; Ma et al., 2010) related to electrokinetic technique have proven its viability and effectiveness in treating soil in situ, without having to remove it from the site, providing cost reduction when compared with other methods. However, it must indeed be realized in the area as it is acknowledged that some issues need to be taken into account such as soil characteristics, flow rate applied, depth of contaminant, metal concentration and removal time, among others, so someone can evaluate the technique adequately different types of situations and conditions (Pedrazzoli, 2004; Baptista, 2005; Guaracho et al. 2009).

The catalysts used in the process of thermal and catalytic cracking of petroleum accelerate chemical reactions by promoting the breakage and rearrangement of the molecules, so as to generate new product fractions. After a few cycles of use and regeneration, the metals present in the process, mainly nickel and vanadium accumulate on the catalyst surface and cause its deactivation by coke formation irreversible and must be replaced. Thus, large quantities of waste contaminated with metals are generated (about 120 tons per month) and classified as Class I (hazardous waste), justifying the research in new technologies that enable the reduction of hazardous waste produced, to avoid that they become a source of environmental and human contamination.

This research intends to apply the electrokinetic remediation technique in the treatment of petroleum cracking catalyst deactivated by removing heavy metals from its surface and measuring the efficiency of the process through analytical techniques such as X-ray microtomography.

1.1. Catalytic cracking catalyst

The fluidized catalytic cracking (FCC) is one of the major processes of refining industries (Biswas, 1990), converting oil fractions of low value, such as heavy gas in high-value products and market demand, such as automotive gasoline and liquefied petroleum gas.

The catalytic cracking uses heat, pressure, and an acid catalyst to affect the breaking up large hydrocarbon molecules into smaller molecules and lighter. The severe conditions of reaction and specially regeneration cause a rapid aging of the catalysts, being necessary to regularly introduce new catalytic reactor. Thus, according to Costa (2009), the cracking reactions are catalyzed by a mixture of catalyst particles with almost no use (low-polluting and high activity) and most commonly used catalyst particles (high oil content and low activity) which come from the regenerator. The catalyst is called catalyst disposed in balance, off, or exhausted thermodynamically stable, having exhausted its catalytic activity.

In the study of Creplive (2008) it was determined that the FCC catalyst deactivated evaluated at this research is composed of zeolites and it has three-dimensional structure of the faujasite type, as shown in Fig. (1):

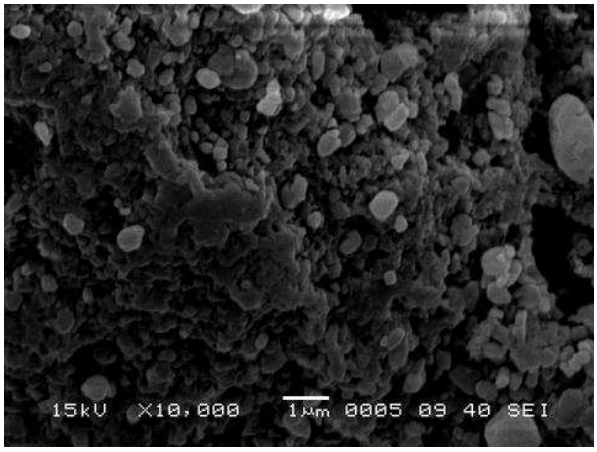

Figure 1. Deactivated catalyst obtained by scanning electron microscope

The structure of zeolites is commonly called aluminosilicates and consists of Si and Al atoms linked by oxygen bridges. After use, especially in petrochemical plants, such catalysts become potential pollutants (one of the worst contaminants from the oil refinery) due to three basic factors according to Afonso et al. (2003): the heavy metal content, the presence of highly carcinogenic compounds found in coke deposits that lodge on its surface and high acidity of these materials, far superior to the soil.

Considering the amount of catalyst used in the 350 FCC units worldwide, about 1400 tons per day according to Costa (2009), there is the importance of studying both the use of new material on treatment of the material already used.

1.2. Electrokinetic remediation

According to Acar (1995), electrokinetic remediation, which is also called electrokinetic processing, electromigration, electrokinetic decontamination or electro-correction may be used to separate (extract) metals and some types of organic waste saturated or unsaturated soil, sludge and sediment.

The technique consists of applying a direct current of low intensity or an electrical potential difference on the order of a few volts per centimeter, through the introduction of electrode plates, as Baptista (2005). The contaminants are then mobilized in the form of charged species or particles. Some variations of this technique involves the direct extraction of metal ions already in the form of metal and others involving the extraction of metal ions using a later process of ion exchange resins. According Pedrazzoli (2004), the electrokinetic remediation can also be used to slow or prevent the migration and / or diffusion of contaminants, directing them to specific points and diverting them from groundwater.

A representative scheme of the electrokinetic remediation technique is shown in Fig. (2):

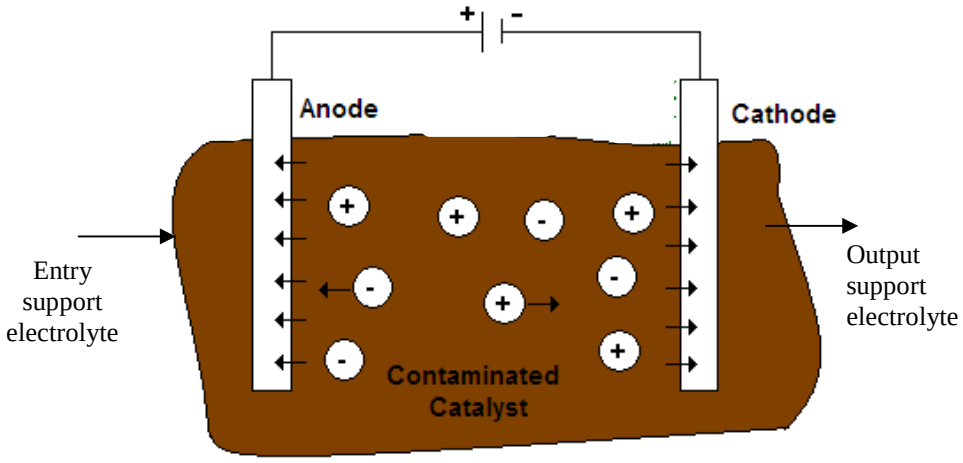

Figure2. Electrokinetics remediation technique

The main driving forces for the removal of contaminants from the pores of the material during the electrokinetic remediation process are, according Alshawabkeh (1999), the electroosmosis and electromigration, and the cations move toward the cathode and anions toward the anode through a combination these two forces.

2. METODOLOGY

The material under study consists of a Fluid Catalytic Cracking catalyst with its catalytic activity exhausted. The catalyst was obtained by President Getulio Vargas Refinery - PETROBRAS / REPAR, being composed primarily of oxides of alumina and silica, being saturated with heavy metals - mainly nickel and vanadium - and other elements such as coke.

The electrochemical reactor used for the electrokinetic remediation following the model developed by Yeung (1997) and adapted by Baptista (2005) and Creplive (2008), see Fig. (3):

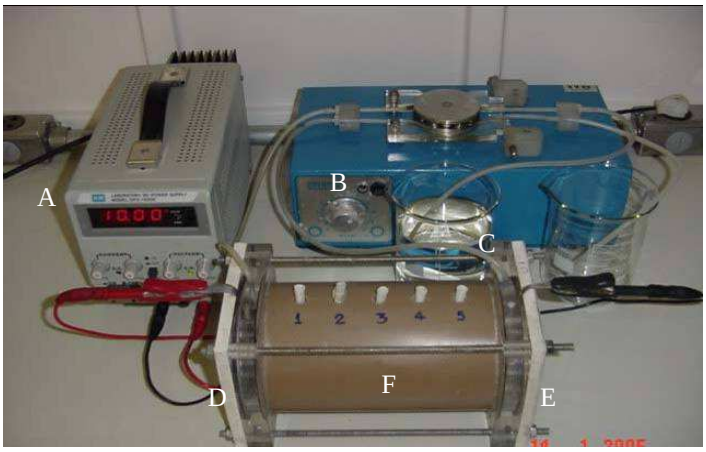

Figure 3. Electrokinetic reactor

The letter A represents the source potential, B represents the peristaltic pump, C represents the electrolyte, D represents the anode chamber, E represents the cathode chamber and F represents the body of the electrokinetic reactor.

The studies of Baptista (2005) and Creplive (2008) indicate that the best removal of heavy metals is achieved by using sulfuric acid 1M as electrolyte, with flow 100 mL/h and potential application from 10 to 11 V for 48 hours.

After this treatment, the material was washed with distilled water inside the reactor, without applied potential.

The catalyst deactivated and remedied was submitted to analysis of X-ray microtomography and scanning electron microscopy for evaluation of the process employee.

The microtomography equipment used was a SkyScan model 1072, with the following acquisition parameters: 80KV Power, 124μA current, copper filter (1 mm) with an average of 2 images per acquisition, 1475 ms integration time per frame, 360º overall rotation angle with 0.5º step size of rotation angle. It was reconstructed 847 images of sample slices with 5.78 μm spatial resolution. This setting was used for the two acquisitions in order to compare the results across gray levels in the reconstructed image.

3. RESULTS

The analysis of scanning electron microscopy indicated that the remediation process of the deactivated catalyst did not affect his morphological aspect, according to Fig. 4, i.e., remained its external morphology.

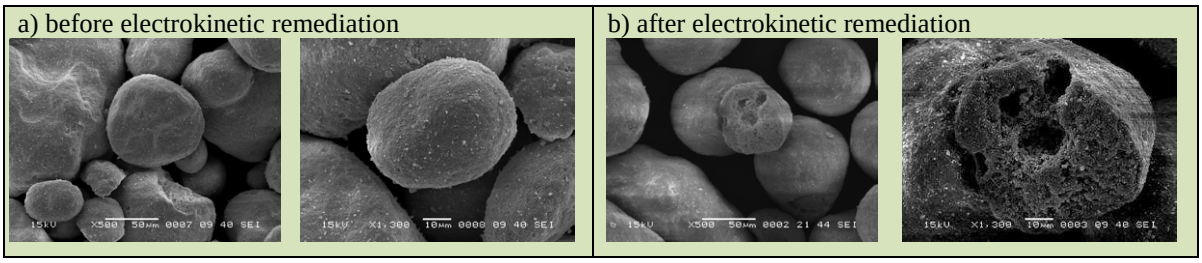

Figure 4. Scanning electron microscopy of the catalyst

With respect the surface area available for adsorption, the BET tests demonstrated effective recovery of pores after remediation. The new catalyst showed 300 m². g^{-1} surface area, the catalyst deactivated 148 m². g^{-1} and the catalyst remedied 208 m². g^{-1}, i.e., there was a recovery of 40% of surface area comparing the material deactivated.

It can be seen in Fig. 5 two images obtained by X-ray microtomography. Figure 5a represents the deactivated catalyst. The arrows indicate the presence of metal in this sample. Having higher density than the catalyst, the metal has more shades of gray near the white than the rest of the sample. Figure 5b represents an image of the catalyst remedied. Note the absence of tones close to white indicating low amounts of metal.

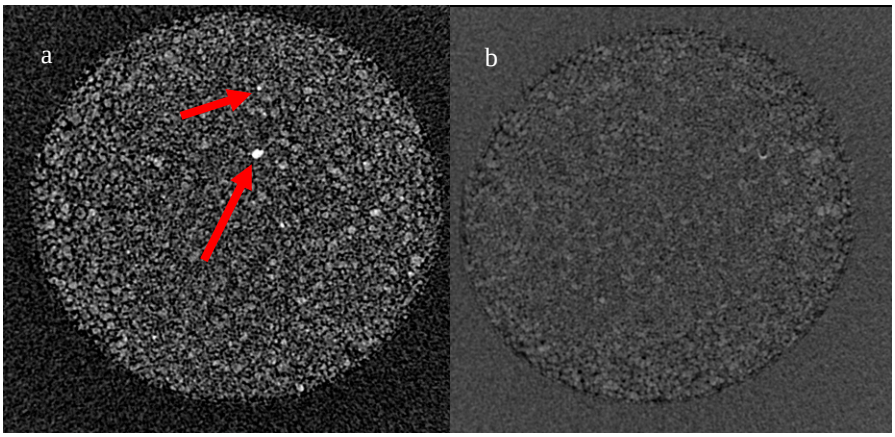

Figure 5. X-ray microtomographic section: a) deactivated catalyst b) remedied catalyst

The analysis results of X-ray microtomography carried in the deactivated and remedied catalyst are shown qualitatively in Fig. 6, after the reconstruction of images in three dimensions and subsequent targeting threshold gray levels. Each edge of the reconstructed cubes shows 0.3 mm in length.

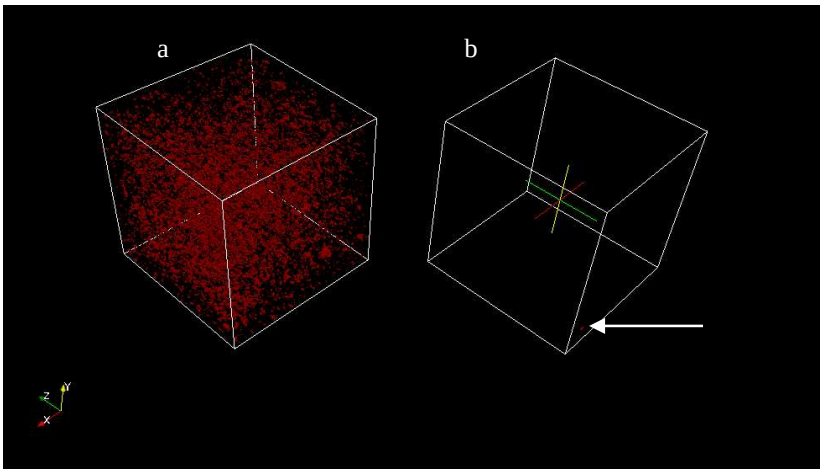

Figure 6. X-ray microtomography: a) deactivated catalyst b) remedied catalyst

Comparing the two images in Figure 6, it appears that electrokinetic remediation has promoted the removal of material of higher density, metals, indicated by the color red. In Figure 6b, the arrow indicates the amount of remaining metal.

4. CONCLUSIONS

The electrokinetic remediation technique, though relatively new, was efficient in decontaminating the catalyst, without damaging its structure. The removal of contaminants was indicated by the results of X-ray microtomography and BET, the latter showing an increase in surface area occurred probably by the release of blocked pores by metal particles.

The results showed that the use of images microtomographics for characterization of complex structures is a non-destructive method advantageous and effective for determining the presence of metals in the materials. Thus, the results of the research indicated that the technique was satisfactory regarding to best use of the deactivated

catalyst remainder of oil cracking process. So, the catalyst that although disabled for catalysis, remains a noble material which can be reused in a different purpose.

5. ACKNOWLEDGEMENTS

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