VOL. 4, NO. 3, March 2014 ISSN 2225-7217
ARPN Journal of Science and Technology

http://www.ejournalofscience.org

Performance of Natural Zeolites in the Removal of Metal Ions from Crude Oil

Rose E. Ikyereve[1], Abubakar Mohammed[2], Chindo Nwankwo[3]

[1] School of Applied Sciences, University of Wolverhampton, Wolverhampton, United Kingdom
[2] Department of Mechanical Engineering, Federal University of Technology Minna, Nigeria
[3] Department of Environmental Engineering, University of Port Harcourt, Port Harcourt, Nigeria

ABSTRACT

The removal efficiencies of different natural zeolite materials for the selective removal of metal ions from crude oil were investigated. Three natural zeolite materials were used for the study; clinoptilolite, aluminum phillipsite and chabazite. The study was particularly focused on the metals that cause problems during processing of crude oil (nickel, vanadium and sulphur). The result shows that, clinoptilolite is efficient for the removal of nickel and sulfur at concentrations of 0.023ppm and 36.582ppm respectively. Aluminum phillipsite showed removal of vanadium and sulfur at concentrations of 0.2279ppm and 58.068ppm respectively, while chabazite was unable to remove any of the metal ions. The study thus showed the selectivity of the natural zeolites for the different metal ions, while one zeolite is good for the removal of a particular metal ion from the crude oil; the other is not, except for sulfur.

Keywords: *natural zeolite, clinoptilolite, philipsite, chabasite, nickel, vanadium, sulfur, crude oil*

1. INTRODUCTION

Despite the contribution from other fossil fuels such as coal and natural gas, the demand for petroleum continues to be higher as transportation fuel [1]. This has resulted in depletion of light oil reserves, scarcity and increase in oil price [2]. There is therefore a decrease in the light oil while the heavier oils increase with an increase in impurities such as metals, sulphur, asphaltenes, nitrogen etc. These impurities make the processing of the oils costly thus making the oil less desirable. New technologies to improve the quality and quantity of transportation fuel from natural sources other than the conventional crude have recently been explored [1]. Other fields like biofuels production, gas to liquid production or unconventional oil refining processes are currently been investigated [1, 3]. A number of technologies have been investigated to increase production of transportation fuel from heavy oil [4]. Of these technologies, hydrocracking is the most efficient yielding high selectivity to middle distillate and low selectivity to coke. Hydrocracking in most cases is said to be combined with other pre-treatment processes like solvent deasphalting and mild hydro treating [1]. The crude stock for hydro cracking most times contains high concentration of Ni and V metals (heavy oil) that conventional acid catalyst is easily poisoned/deactivated [5-7]. These among other metals have prompted the need for search of materials that can effectively remove them from crude oil during hydroprocessing. A solution to this problem would be to find a method of pretreating the heavy crude oil in order to reduce the concentration of the metal ions before it gets through to the downstream processing units. This would decrease cost, as catalysts would be less quickly poisoned and thus increasing lifetime and also throughput rate.

Zeolites, both natural and synthetic, with porous open framework, large surface area, catalytic and ionic exchange properties, known for industrial applications such as heterogeneous catalysis, separation, water softening, environmental remediation, etc. [8] could serve as good materials for the removal of these metal ions. Zeolites are inorganic aluminosilicates that are derived from silica (SiO_2) by the isomophous substitution of SiO_4^{4-} tetrahedra by AlO_4^{5-} tetrahedra. The composition of a zeolite is represented thus:

$$\text{Comp. of a Zeolite} = m/x^{x+}[(SiO_2)_n(AlO_2)_m]\cdot yH_2O \quad (1)$$

The term in square brackets represents the framework structure of the zeolite. The isomorphous substitution of Si by Al generates an excess negative charge on the oxygen framework. This negative charge is compensated by the cations (M of valence *x*) present during synthesis and held in the interstices of the structure on crystallization [9]. Water is also present in the structure of the zeolite though not part of the zeolite framework. The properties of the zeolites such as the ion exchange, adsorption, catalytic etc. are largely dependent on the nature of the charge balancing cations and the exchange capacity is governed by the Si/Al ratio [10-12]. Zeolites have already been successfully applied in the removal of heavy metals such as Cr^{3+}, Fe^{3+}, Co^{2+}, and Zn^{2+} among others from aqueous solutions [13-16] and for the catalytic cracking of heavy crude oils and bitumen [17-19]. However, to the best of our knowledge, no work has been done on the selective contributions of these three natural zeolites at removing catalysts poisons from crude oil. This paper presents the performance of natural zeolites in the removal of metal ions from crude oil.

2. MATERIALS AND METHOD

2.1 Materials

Clinoptilolite (K, Na, Ca) $_{2-3}$ [$Al_6Si_{30}O_{72}$].24H_2O), high-alumina phillipsite ($Na_{6.3}$ $K_{4\cdot2}$ [$Al_{10\cdot5}Si_{21.5}O_{64}$]. 23 H_2O) and chabasite (Ca, Na_2, K_2, Mg) $Al_2Si_4O_{12}\cdot 6H_2O$) and the crude oil samples were obtained from the UK. Ethylenediaminetetraacetic acid (EDTA) was purchased from sigma Aldrich, UK.

2.2 Experimental Method

The metal ions extraction/removal was done as shown by the setup in Fig.1. 1g of clinoptilolite powder was suspended in 50mL of the crude oil in a separating flask containing 25mL of EDTA. This mixture was properly mixed using the flask shaker for an hour at room temperature (18°C) to properly homogenize the mixture. The mixture was then left to stand for a day so as to attain equilibrium and enable the separation of the distinct layers. The aqueous layer was then carefully separated from the organic (oil) layer. This procedure was repeated for each of the three zeolites used and the aqueous layer used for metal analysis. A similar experiment was carried out but without introducing any zeolite. This was labeled as a 'control' since it was used to compare the effectiveness of the heavy metal immobilisation of the different zeolite materials used.

2.3 Characterization

The aqueous samples containing the metal ions were analyzed using the inductively coupled plasma atomic emission spectroscopy (ICP-AES), a spectrociros ICP-AES spectrometer.

Fig 1: Experimental setup

3. RESULTS AND DISCUSSION

The result from the ICP analysis in Figure2 clearly shows the effect of the different zeolites on the removal of metal ions from crude oil. This is evident from the appearance of metal ions such as nickel and vanadium that were initially absent from the 'control'. This can be explained based on the fact that, heavy crude oil is made up of three groups of compounds; oil, resins and asphaltenes. The resins and asphaltenes are the large molecules containing metal impurities. The metal ions, particularly vanadium and nickel in crude oil are described in two forms, porphyrinic and non-porphyrinic forms. These metal ions are believed to be associated with asphaltenes, most likely in the porphyrinic form. To get these metal ions removed from crude oil requires breaking down the higher molecular weight fractions such as the asphaltenes that forms aggregates with Porphyrins by non-covalent interactions. Zeolites due to their catalytic property are able to breakdown these large molecular fractions. The conversion of the higher molecular weight to lower molecular weight oil fractions exposes a significant amount of the metal ions for removal from crude oil. Thus, the metal ions which were not available for extraction in the control became available in the presence of zeolite catalysts.

It is observed from the Figures 2 to 4 that the efficiencies of metals removal by the different zeolites differed significantly, while one zeolite is good at the removal of a particular metal ion from the crude oil, the other is not. This could be due to the nature of acid sites for the different zeolites. From the study, clinoptilolite was found to be efficient in the removal of nickel at a concentration of 0.023ppm and sulfur at concentration of 36.582ppm. Aluminum phillipsite was found to effectively remove vanadium and sulfur at a concentration of 0.237ppm and 58.068ppm respectively. The concentrations of sulfur from the experiment were found to increase from concentration of 31.557ppm to 58.068ppm. Aluminum phillipsite sample was shown to remove the highest amount of sulfur compared to the other zeolite materials used. Chabazite from this study was only able to remove sulfur and not any of the other problem causing metals from the crude oil.

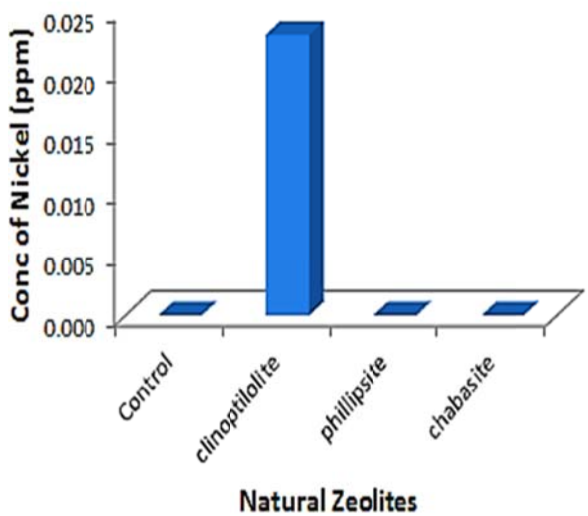

Fig 2: .Nickel concentrations in different zeolites

ARPN Journal of Science and Technology

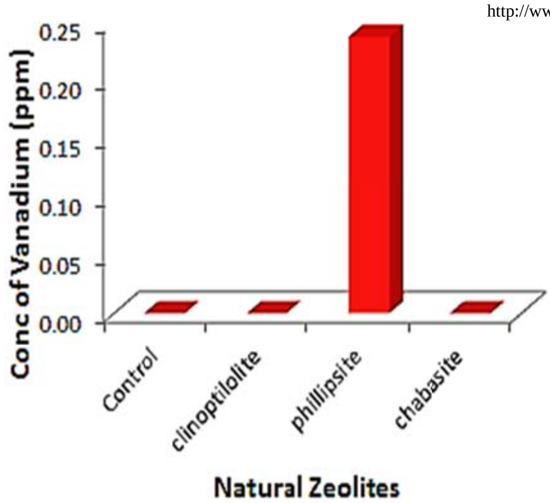

Fig 3: Vanadium concentrations in different zeolites

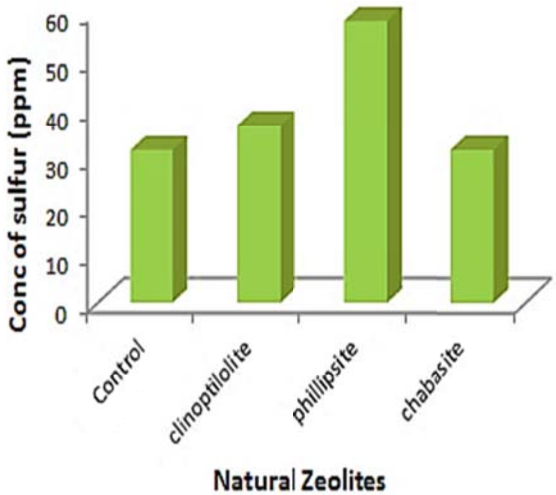

Fig 4: Sulfur concentrations in different zeolites

4. CONCLUSION

Natural zeolites such as clinoptilolite, aluminum phillipsite and chabasite have been shown to play a positive role in the removal of poisonous metal ions from crude oil. The different zeolites were observed to be selective at removing the metals. It is therefore possible that these zeolites have the potential to be used as catalysts in the processing of crude oil, maybe not as the conversional cracking catalysts but catalysts for the pretreatment of heavy crude oil. This will hopefully reduce the overall cost to crude oil processing.

ACKNOWLEDGEMENTS

The Authors would like to express profound gratitude to Prof. Craig D. Williams for his guidance and support during the course of this research. The technical staff of Environmental Science at the University of Wolverhampton is also being appreciated for the ICP analysis. The financial support received from Benue State University Makurdi, Nigeria is also appreciated.

REFERENCES

[1] Shimada, H., Sato, K., Honna, K., Enomoto, T. and Ohshio, N. (2009). Design and development of Ti-modified zeolite-based catalyst for hydrocracking heavy petroleum. Catalysis Today, **141**(1-2): 43-51.

[2] Dalai, A. K. and Chung, K. H. (2001). Heavy Oil Upgrading, Renewable Energy and Catalysis Symposium, 49th Canadian Chemical Engineering Conference. Fuel, **80**(8): 1041-1042.

[3] Agarwa, A.K. (2007). Biofuels (alcohols and biodiesel) applications as fuels for internal combustion engines. Progress in energy and combustion Science 33(3): 233-27.

[4] Rana, M. S., Sámano, V., Ancheyta, J. and Diaz, J. A. I. (2007). A review of recent advances on process technologies for upgrading of heavy oils and residua. Fuel, **86**(9): 1216-1231.

[5] Paweewan, B., Barrie, P. J. and Gladden, L. F. (1999). Coking and deactivation during n-hexane cracking in ultrastable zeolite Y. Applied Catalysis A: General, **185**(2): 259-268.

[6] Gawel, I., Bociaska, D., and Biskupski, P. (2005). Effects of asphaltens on hydroprocessing of heavy oils and residua. Applied catalysis 295: 89-94.

[7] Furimsky, E., Massoth, F.E. (1999).Catal. Today **52:** 381.

[8] Auerbach, S.M. Carrado, K.A. Dutta, P.K. (2003). Handbook of Zeolite Science and Technology, Marcel Dekker, New York.

[9] Dyer, A. (1988). An introduction to zeolite molecular sieves, Bath, Bath Press Ltd.

[10] Barrer, R.M. (1989). Zeolites and Clay Minerals as Sorbents and Molecular Sieves, Academic Press, FRS London.

[11] R. Szostak. (1989). Molecular sieves, Principles of Synthesis and Identification, Van Nostrand Reinold, New York.

[12] D. W. Breck. (1974). Zeolite Molecular Sieves, Structure Chemistry and Use, Wiley, New York, NY.

[13] M.A.S.D. Barros, E.A. Silva, P.A. Arroyo, C.R.G. Tavares, R.M. Schneider, M. Suszek, E.F. Sousa-Aguiar. (2004). Removal of Cr(III) in the fixed bed column and batch reactors using as adsorbent zeolite NaX, Chem. Eng. Sci. 59: 5959–5966.

ARPN Journal of Science and Technology

http://www.ejournalofscience.org

[14] M.A.S.D. Barros, P.A. Arroyo, E. Sousa-Aguiar, C.R.G. Tavares. (2004). Thermodynamics of the exchange processes between K+, Ca2+ and Cr3+ in zeolite A, Adsorption 10: 227–235.

[15] J.S. Kim, M.A. Keane. (2002). The removal of iron and cobalt from aqueous solutions by ion exchange with Na-Y zeolite: batch, semi-batch and continuous operation, J. Chem. Technol. Biotechnol. 77: 633–640.

[16] I.C. Ostroski, C.E. Borba, E.A. Silva, P.A. Arroyo, R. Guirardello, M.A.S.D. Barros. (2011). Mass transfer mechanism of ion exchange in fixed bed columns, J. Chem. Eng. Data 56:375–382.

[17] G.O Chivadze, TsINaskidashvili, E.K. Kvantaliani. (1990). Catalytic cracking of heavy petroleum fractions over modified natural zeolites. Izvestiya Akademii Nauk Gruzinskoi SSR Seriya Khimicheskaya, 16:186–189. Russian

[18] W. Wang. (2010). Catalytic cracking of Athabasca oilsands using clinoptilolite. MSc dissertation, Edmonton (AB): University of Alberta.

[19] A.S.M Junaid, M. Rahman, H. Yin, W.C. McCaffrey, S.M Kuznicki. (2011). Natural zeolites for oilsands bitumen cracking: Structure and acidity. Micropor, Mesopor Material, 144:148–57.