International Journal of Basic and Applied Sciences. Vol. 6 No. 3. 2017. Pp. 125-128

Full length Research ***Paper***

Measurement of Radioactivity and Heavy Metals in Refinery Effluents from petroleum Refining Companies in Egypt

Hassan, H.B; Salama, S*and Ahmed, A. Taha**

*Siting and Environmental Department & **Radiation control Department, Nuclear and Radiological Regulatory Authority, *Radiation Protection & Civil Defense Department, Nuclear Research Center, Atomic Energy Authority, P.O. 13759, Cairo, Egypt.*

Article history
Received: 04-7-2017
Revised: 15-07-2017
Accepted: 21-07-2017

Corresponding Author:
Hassan, H.B
Siting and Environmental Department, Egypt.

Abstract

The petroleum refining industry converts crude oil into petroleum products such as liquefied petroleum gas, naphtha, kerosene, diesel oil and residual which, generates different kinds of waste. Petroleum refinery effluents (PRE) are wastes originating from industries primarily engaged in refining crude oil. They are hazardous compounds containing waste which are a major source of environment pollution. The object of the present work is measurement some important physico-chemical parameters as pH, TDS, heavy metals such as Ni, V, pb, Cu, Cr, Co, Fe and Cd and activity concentration of radionuclides (U-238, Ra-226, Th-232 and K-40) in the (PRE) samples. The (PRE) samples collected during refining processes and final discharge from waste water treatment system of Refining Petroleum Company in Egypt. Heavy metal concentrations and activity concentrations of radionuclides of these samples are analyzed by using (ICP) optical emission spectroscopy and HPGe detector Gamma ray spectrometer. It was found that the concentrations of Ni, V, pb, Cu, Cr, Co, Fe and Cd in final discharge (PRE) sample after passing on wastewater treatment system in this Refining Petroleum Company were 0.006 0.0, 0.008, 0.012, 0.0014, 0.006, 0.005 and 0.006 ppm respectively and activity concentrations of radionuclides U-238, 226Ra, Th-232 and K-40 were 0.0, 1.2, 1.4 and 18Bq/l respectively. These obtained values for heavy metals concentration and activity concentrations of radionuclides U-238, Ra 226, Th-232 and K-40 in final discharge effluents approximately within the international recommended standard limit.

Keywords: *Crude oil, petroleum Refining, Norm, trace element, radioactivity*

Introduction

Petroleum oil is formed by thermal cracking of organic matter trapped in sedimentary rock. During thermal cracking the uranium or thorium remain with the residual organic matter (Bloch, S. et.al 1981). The metals present in the crude oils are mostly Ni (II) and VO (II) and other metal ions include copper, lead, iron, magnesium, sodium, molybdenum, zinc, cadmium, titanium, manganese, chromium, cobalt, antimony, uranium, aluminum, tin, barium, gallium, silver and arsenic (Treibs et.al 1936).

The petroleum refining industry converts crude oil into more than 2500 refined products, including liquefied petroleum gas, gasoline, kerosene, aviation fuel, diesel fuel and fuel oils. Petroleum refining is the physical, thermal and chemical separation of crude oil into its major distillation fractions which are then further processed through a series of separation and conversion steps into finished petroleum products. (Wake, 2005) presented a broader categorization, in which refineries were classified into four units. Therefore, each PRE is a function of the number of units and the configuration of the refinery, which results in a lack of uniformity of the composition of the discharged effluent. The final waste stream generated is the contribution of the units involved with crude oil processing, e.g., hydro-skimming, hydro-skimmer flare, hydro-cracking, hydro-cracker flare, sour water, condensate, flare and the desalter. Other units not directly involved with processing, e.g., sanitary, crude tank and laboratory water, also contribute significantly to the total volume of the effluent (Al Zarooni et.al, 2006). The wastewater comprises of storm water basin, stripped sour water and domestic wastewater. All these are channeled through the refinery wastewater treatment unit before it is discharged into the environment. A typical refinery wastewater treatment plants in a Typical Refining Petroleum company in Egypt consists of primary and secondary oil/water separation, followed by biological treatment.

Petroleum refinery effluents (PRE) from the refinery are hazardous compounds containing waste. The discharge of these waste waters into the environment adversely affects the ecosystem (El-Naas et al., 2009b). Untreated or inefficient treated wastewater poses great threat to the environment because of its known hazardous constituents. Treatment is therefore necessary to correct these wastewater characteristics in such a way that the use or final disposal of the treated effluent can take place in accordance with the rules.

Wastewater can sometimes also be reused after passing through the wastewater treatment plant, sometimes requiring additional treatment to remove suspended solids and other contaminants the relevant legislative bodies without causing an adverse impact on the receiving bodies (Njau et.al, 2003). The aim of this paper to measure heavy metal concentrations and activity concentrations of naturally occurring radionuclides (226Ra, 228Ra and 40K) in final discharge (PRE) before and after passing on wastewater treatment system of Refining Petroleum Company in Egypt which help in assessment of their effects on human health and environment.

Material and Methods

Crude oil is used as a raw material by the refinery for production. Crude oil is transported to an oil refinery where complex hydrocarbon compounds are separated and converted through various refining operations (fractional distillation, cracking, solvent extractions, then other treatments including formulating and blending) to become useable fuel sources (Epstein PR. 2002). The Petroleum refinery effluents (PRE) from the refinery are composed of oil and grease along with many other toxic organic compounds. They are treated by the Wastewater Treatment Unit before it is being discharged into the environment (Venkatesh, 2010) as shown in Figure (1).

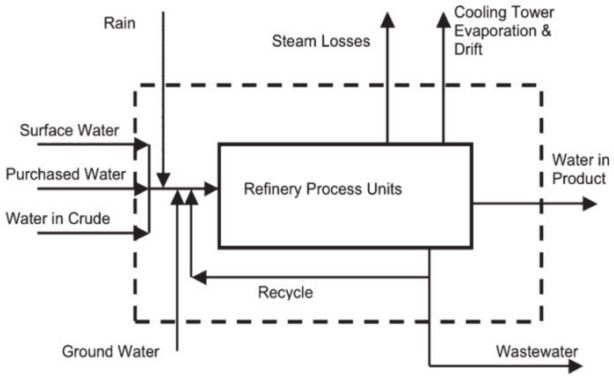

Fig 1: A schematic configuration of the typical water balance in a Petroleum Refinery

Collection and Preparation

Petroleum refinery effluents (PRE) samples were collected from Typical Refining Petroleum Company in Egypt on 2016 from different units as samples 1, 2 and 3 gathered from desalting unit which is used to remove salt, minerals, grit, and water from different types of crude oils. Sample 4 is collected from cracking unit. Cracking unit is used to break heavy oil molecules. Sample 5 is the final discharge water which has undergone both chemical and biological treatment to eliminate or reduce waste contents to acceptable levels. These samples were analyzed for physico-chemical parameters such as pH, conductivity and heavy metals concentration of Ni, V, pb, Cu, Cr, Co, Fe and Cd. For measurement activity concentrations of radionuclides ^{238}U, ^{226}Ra, ^{232}Th and ^{40}K and their decay products in these samples, they are, packed in a plastic container, sealed well and stored for 30 days before analysis. This allows the in-growth of uranium and thorium decay products. Then they were mounted into clean containers and measured.

Sample analysis

- *Physico-chemical parameters*

pH and EC of the studied PRE samples are measured using pH and EC electrodes (WTW) with accuracy $\pm$ 0.1^{o}C.

For measuring heavy metals concentrations Ni, V, pb, Cu, Cr, Co, Fe and Cd of the PRE samples must be digested using the microwave digestion method. Milestone Digester (Ethose-D) which is used by specific program (Kingeston, H.M. et al, 1997) for digesting saline wastewater. The Leeman (ICP) optical emission Spectroscopy (USA) which has measuring concentration error from 1- 5% was used to measure concentration heavy metals in wastewater samples.

- *Gamma-Ray Spectrometer System and sample analysis*

The gamma ray spectra were analyzed by using a ORTEC coaxial High-Purity Germanium detector (HPGe) (Hamlat M. S., 2003). The energy and intensity of various gamma-ray lines have been measured to calculate the concentrations of U, Th, K and their decay products. The energy resolution of 2.1 keV Full-Width at Half Maximum (FWHM) for the 1332 keV gamma-ray line of ^{60}Co. Gamma vision software is used for data acquisition, analysis and to calculate the concentrations of U, Th, K and their decay products. The calibration of the detector was carried out by using certified standard point sources ^{60}Co (1173.2 and 1332.5 keV), ^{133}Ba (356.1 keV), ^{137}Cs (661.9 keV) and ^{22}Na (1368.6keV). The counting error for this instrument (HPGe) is ranged from 1- 5%.

The activity levels for radionuclides in the selected (PRE) samples are computed using the following equation (Carturan, S. 2010).

$$A = CR/\varepsilon(E)\, I\gamma\, W \quad (1)$$

Where; A = The activity level of a certain radionuclide; CR = The net count rate of the sample (Bq/ kg)(counts /seconds); ε (E) = The detector efficiency for the specific gamma ray energy; Iγ =The intensity of gamma-line in a radionuclide; W = The dried sample weight in kg.

Activities concentration due to the presence of ^{226}Ra, ^{232}Th, ^{238}U and ^{40}Kwas determined by measuring the 295.2 keV (18.7%) and 351.9 keV (35.8.1 %) gamma-rays from ^{214}Pb and the 609.3 keV (45 %) and 1120.3 keV (14.9%) gamma-rays from ^{214}Bi. ^{232}Th activity was determined from the gamma rays of 238.6 keV (45 %) from ^{212}Pb and 338.4 keV (12 %), 911.1 keV (29 %) and 968.6 keV (17.5 %) from ^{228}Ac and 583.1 keV (30 %) gamma-rays from ^{208}Tl. ^{40}K concentration was measured from its 1460 keV (10.67%) gamma-ray line.

Result and Discussion

Some important physico-chemical parameters as pH, conductivity, heavy metals such as nickel, vanadium, lead, copper, chromium, cobalt, iron and cadmium and activity of radionuclides (U-238, Th-232 and K-40) were measured in the collected (PRE) samples during refining processes and final discharge from waste water treatment system of Refining Petroleum Company in Egypt as shown in Table1.

Table 1: Concentrations of heavy metals and radioactivity of radionuclides in PRE samples

	Name of samples	No	Some physico-chemical properties		Concentrations of heavy metals (mg/L)								Activity concentration (Bq/l)			
			pH	TDS mg/l	Ni	V	Pb	Cu	R Cr	Co	Fe	Cd	^{238}U	^{226}Ra	^{232}Th	^{40}K
Before treatment	PRE1	1	6.8	25000	ND	0.03	ND	0.2	0.015	0.03	0.45	0.002	1.68	0.34	1.96	16.4
	PRE2	2	7.1	26000	ND	0.03	ND	0.12	0.008	0.02	0.50	0.005	9	6.5	6.4	160
	PRE3	3	7.2	24000	ND	0.08	ND	0.07	0.003	ND	0.75	0.003	0.0	21	0.0	152
	PRE4	4	7.2	27000	0.15	0.20	0.4	0.27	0.033	0.04	2.3	0.015	8	0.0	0.0	120
After treatment	PRE5	5	7.8	10000	0.006	ND	0.008	0.012	0.0014	0.006	0.005	0.006	0.0	1.2	1.4	18
			FEPA (1991)& JRC (2015*)										WHO 2008			
	Permissible limits		**6-9**	**2000**	1.0	1.0*	0.5	1.5	0.2*	0.5	5*	1	1	1	1	10

Table 1 shows pH of PRE samples are ranged from 6.8- 7.8 that level of the alkalinity of the effluent might be due to the salt in the raw material (crude oil) which could be suitable for the existence of most biological life or activities according to Tchobanogolous *et.al.,* 2003). The pH value of final discharge PRF 5 is slightly alkaline within the FEPA (1991) standard pH range of 6 to 9. Refineries generate TDS could be due to high concentrations of dissolved inorganic and organic molecules and ions present in the PRE samples (1, 2, 3, 4 and 5) reached to 10000 mg/l in final discharge PRF 5 sample (Agyeman*et al.,* 2013) and thus, unacceptable which contribute to more organic matter and salinity in water thereby having a major effect on the environment. However, a slightly high TDS value of 10000 mg/l was recorded as against the (FEPA) standard of 2000mg/l.

The concentrations of heavy metals (Ni, V, pb, Cu, Cr, Co, Fe and Cd) in collected PRF (1, 2 ,3 and 4) samples from raw petroleum during refining processes before passing wastewater treatment system are determined in PRE samples 1, 2, 3and 4. These samples containing heavy metals levels of 0.0–0.15 mg/l for nickel; 0.03–0.2mg/l for vanadium; 0.0– 0.4mg/l for lead; 0.07– 0.27 mg/l for copper; 0.003–0.033 mg/l for chromium; 0.0– 0.04 mg/l for cobalt; 0.45–2.3 mg/l iron and 0.002– 0.015 mg/l for cadmium. The concentration of heavy metals in PRE 5 after passage through waste water treatment system to reduce the effluent contamination level to allowable limits for discharge into environment are represented in PRE sample 5. The concentrations of heavy metal Ni, V, pb, Cu, Cr, Co, Fe and Cd in PRE sample (5) is 0.006, 0.0, 0.008, 0.012, 0.0014, 0.006, 0.005 and 0.006 respectively. These concentrations of heavy metal were less than the permissible limits of the FEPA (1991) and JRC (2015) as shown in figure (2). The activity concentrations values of radionuclides ^{228}U,^{226}Ra, ^{232}Th and ^{40}K in the PRE 1,2, 3, 4 samples were ranged between 0.0-9, 0.0- 21, 0.0-6.4, and 16.4 – 160 Bq/l, respectively as shown in Table (1), and in the final discharge PRE sample 5 were 0.0, 1.2, 1.4, and 18 Bq/l respectively as shown in figure (3). The activity concentrations of ^{228}U, ^{226}Ra, ^{232}Th and ^{40}K in the final discharge PRE sample 5 within the international standard limits WHO, 2008 expect values of ^{40}K at level slightly higher than those recommended standard limits.

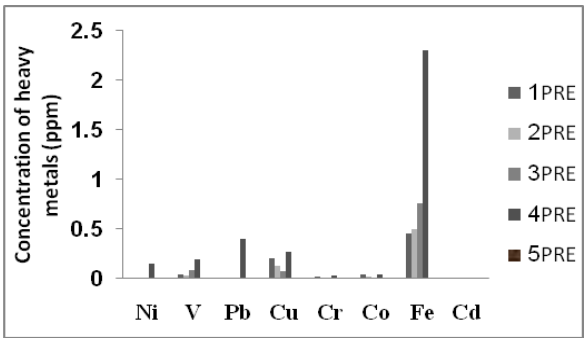

Fig 2: Concentrations of heavy metals (ppm) in PRE samples

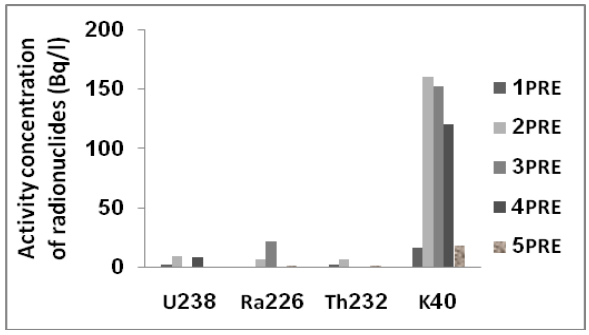

Fig 3. Activity concentrations of radionuclides (Bq/l) in PRE samples

Conclusion

This study has shown that final discharge effluents from Refining Petroleum Company in Egypt approximately contain low concentrations of pollutant. The long-term impact of the refining effluent on the surrounding environment is not known, though accumulation of these pollutants can be fatal to both aquatic and human life. Continued discharge of improperly treated effluent may further compound the environmental problems of the communities living around this company.

References

Agyemang E. O., Awuah E., Darkwah, L., Arthur, R., and Osei, G., 2013: Water quality assessment of a wastewater treatment plant in a Ghanaian Beverage Industry. International Journal of Water Resources and Environmental Engineering. Vol 5 (5) pp. 272 – 279

Al Zarooni, M. and Elshorbagy, W., 2006: Characterization and assessment of Al Ruwais refinery wastewater. J. Hazard. Mater. 136: 398.

Bloch, S. and Key, R.M, 1981: Radioactive springs in the watershed of a proposed reservoir in Sequoyah County, Oklahoma: Origin and environmental effect Am" Assoc. Petr. Geol. Bull, 65, 154.

Carturan, S., 2010: LNL Annual Report 81

EC Joint Research Center (JRC) 2015: Best Available Techniques Reference (BREF) Document for the Refining of Mineral Oil and Gas. Available at European Union (EU). "Directive2008/50/EC of the European Parliament and of the Council of 21 May 2008 on Ambient Air Quality and Cleaner Airfor Europe." Brussels/Strasbourg: European Union.

El-Naas, M.H., Al-Zuhair, S., Al-Lobaney, A. and Makhlouf, S. 2009b: Assessment of electro coagulation for the treatment of petroleum refinery wastewater. J. Environ. Manage. 91: 80.

Epstein, PR and Selber, J., 2002: Oil- A life cycle analysis of its health and environmental impacts. Report of centre for Health and the global Environment, Harvard Medical School Boston, and Massachusetts 73

Federal Environmental Protection Agency (FEPA) 1991: National Guidelines and Standards for Waste Management in Oil and Gas Industry in Nigeria. FEPA Nigeria. Official Gazette, Nigeria.

Hamlat, M. S, Kadi, H. and Fellag, H., 2003: Precipitate containing NORM in the oil industry: modelling and laboratory experiments" Applied Radiation and Isotopes 59: 93.

Kingeston, H. M..; Walter, P.J.; Chalk, S. J;, Lorentzen, E. M. and Link, D. D., 1997: Environmental microwave sample preparation fundamentals, methods, and applications. In microwave enhanced chemistry: Fundamentals.

Njau, K. N. and Mlay H., 2003: Wastewater Treatment and other research initiatives. Pp 213 – 215 (2014).

Tchobanologous, G., Burton, F. L. and Stensel H. D. 2003: Wastewater Engineering-Treatment and Reuse. McGraw Hill, Boston, USA.

Treibs, A., 1936: Chlorophyll and minerals in organic Hminderivate, AngewChemie, 49: 682.

Venkatesh, M., 2010: Petroleum refining water/waste water use and management IPIECA (International Petroleum Industry Environmental and Conservation Association) guide

Wake, H., 2005: Oil refineries: a review of their ecological impacts on the aquatic environment. Estuar. Coast Shelf Sci. 62: 131.

World Health Organization (WHO), 2008: Guidelines for drinking water policy 3rd ed., Incorporating the 1st and 2nd agenda, Vol.1 recommendation. WHO Geneva, Switzerland.