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Quantitative & Qualitative Study of Chemical Hazardous Waste in Refinery of Tehran to Propose Mitigation Plan

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In this study, waste product process, type, volume, source and their period of disposal as well as management methods have been identified. Moreover waste and chemical substance classification has been done according to RCRA(Resource Conservation and Recovery Act) law and Basel convention by considering certain codes for each substance.
In general, average produced waste in the study area is estimated about 1750 tones, which means 20.4g per each crude oil barrel. Annual average hazardous waste is estimated about 1338.7 tons/year, which is %76.5 of whole produced waste and average amount of non-hazardous waste is %23.5 of whole produced waste.
According to RCRA classification amongst all substances, only 9 of them has been categorized as hazardous waste listed in K list, 11 substances as hazardous waste from unknown source listed in F list, 25 substances classified as poisoned hazardous waste listed in U list and 4 substances classified as major hazardous has been listed in list P. Generally 49 substances of 133 substances have been identified and included in RCRA list. On the other hand according to Basel classification, 14 substances classified by Y codes, 6 substances by H code and 16 substances goes to both H and Y codes.
Results from examinations on soil samples show, that wastes produced by refinery includes heavy metal such as Cd, Co, Cu, Ni and Pb more than criterions limits.
Soil in Salvage area includes the highest average of Zn, and lowest of Cd.
Average density of TPH (Total Petroleum Hydrocarbons) in regional soil is about 230.58mg per each gram of soil; this clearly shows the polluted soil with oil-waste in Salvage area.

1. Introduction

Petroleum refinery in accordance with nature of its activities at different units including distillation, decreasing viscosity, purifying liquid gas, catalyst exchange, isomax and creating hydrogen produces large amount of chemical materials as waste materials which have dangerous environmental and health effects. Chemical waste materials are classified as dangerous industrial waste materials. According to problems as a result of chemical dangerous waste materials, compiling strategies for controlling and applying a national management system for keeping and transporting this group of material is very important. Applying programs for controlling waste materials has some expenses in

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which it is 10 times to 100 times lower than expenses for removing and cleaning these pollutions from environment after being entered to environment (Yaghmaiean and Khani,2003).By virtue of RCRA law, The U.S Environment Protection Agency has compiled by-law for management of harmful waste materials. By virtue of this law these materials shall have one of the following characteristics: flammable, erosive, activeness, explosive and poisonous. Some of the characteristics of chemical waste materials include: flammable, danger of explosion, creating dust at environment, dispersion by wind or air conditioner, firefighting care, bad effects on skin, mucus, eye and viscosity that in accordance with shape of waste material, the required regulations for management of them shall be observed (EPA, 2004). Considerable points for dangerous and chemical waste material management system include: specifying present status and quantity of waste material, compiling national strategy for dangerous and chemical waste material management, production management, collecting, maintenance, transporting and arrangement among persons in charge of production maintenance, transporting units and final discharge of chemical waste materials (Omrani,1995)(Yaghmaiean and Khani,2003).Therefore Tehran petroleum refinery due to adjacency with Tehran megacity and necessity of minimizing and industrial chemical waste material management of this city is selected for our research. This refinery is located at 15th km south of Tehran that by having 2 phases which were constructed in the year 1968 and 1973 with total daily production capacity of 225000 barrels. By conducting this study different waste material outputs, all resources, tanks, equipments, volume and their discharge period were specified, then RCRA classification, waste material and chemical material Basel was performed.

2. Goals of Research

The main goal of this research include recognizing chemical materials, studying the procedure of using them, recognizing consumption of chemical materials, recognizing centers, resources for circulating and producing chemical materials, classifying chemical waste materials that are produced in accordance with RCRA law and Basel, how to bury remains of additional materials and generally to offer image of present and future status of waste materials in Tehran refinery.

3. Materials and Methods

In the present research technical information of different sections of refinery is studied. Process of production, type and amount of consumed food under present condition is specified. Field visits and centers for producing chemical waste material were specified. Sampling and analysis of polluted soil in the area of keeping waste (Salvage) materials was performed. Then based on RCRA the chemical waste materials were classified and dangerous materials were specified. Finally based on health effects of dangerous waste materials the solutions for minimizing them were mentioned.

3.1 Sampling and Analyzing Soil at Domain of Salvage Refinery and Specifying Igeo Index

Soil sampling was performed in 12 stations at the area of keeping waste material at Salvage refinery and by using atomic absorption machine the amounts of heavy metals including Cd, Co, Cu, Ni, Pb and Zn and by using spectrophotometer the amounts of TPH in sample of taken soils were measured. Then by using equation 1 the intensity of soil pollution at region under study was calculated.

$$Igeo = Log_2\left[\frac{Cn}{Bn \times 1.5}\right] \quad (1)$$

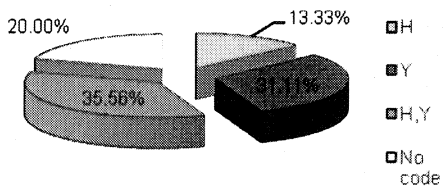
Igeo= Mueller geochemical index
Cn= Concentration of element in soil under study
Bn= Concentration of element in shale
1.5= Correction factor
Finally based on results the dendogram for cluster analysis of heavy elements are drawn.

4. Results

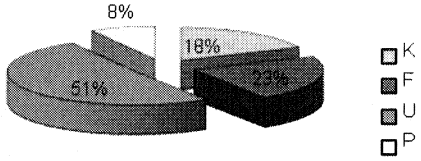
Total annual average amount of produced waste material from all of the units were approximated 1750 ton annually in which 20.4g was per barrel of petroleum. Also average amount of produced hazardous waste material was approximated as 1338.7 ton annually that include 76.5% and average produced non-hazardous waste material was approximated as 23.5% from total share of produced waste material.(F.Jafarigol,2009)

4.1 Recognizing Waste Materials in Units

As it was mentioned at section of materials and methods, in order to recognize different kind of produced materials, we have intended to study all tanks, equipments, all outputs, volume, discharge period and the procedure of present management for each of the waste materials. On this basis graph 1, indicate classification of waste materials with danger code based on RCRA in percentage mode and graph 2 indicate percentage of dangerous waste materials based on Basel classifications.(F.Jafarigol,2009)



Graph1 percentage of dangerous waste materials based on Basel classifications.



Graph 2 percentage of waste materials with danger code based on RCRA

Table 1 indicates level of measured heavy metals on 12 stations at Salvage area and table 2 indicate their comparison with present criterions. Also intensity of pollution is calculated based on relation 1 and is offered at table 3.

Table 1: Level of measured heavy metals and TPH on 12 stations at Salvage area

Station No.	Unit	Pb	Zn	Ni	Cu	Co	Cd	TPH
1	mg/kg	21	104	245	255	37	0.9	393.39
2	mg/kg	10	503	29	103	41	0.5	112.28
3	mg/kg	40	870	905	624	12	0.7	423.13
4	mg/kg	35	1500	148	680	13	0.85	343.39
5	mg/kg	30	210	330	250	19	0.9	254.40
6	mg/kg	65	3450	2200	1144	55	0.58	472.54
7	mg/kg	19	359	194	91	23	0.9	124.36
8	mg/kg	60	3345	1194	945	44	0.6	362.50
9	mg/kg	22	210	65	80	14	0.75	96.23
10	mg/kg	9	556	286	134	15	0.8	143.62
11	mg/kg	42	162	234	98	10	0.65	85.30
12	mg/kg	45	610	150	220	15	0.5	180.85
Min	mg/kg	9	104	29	80	10	0.5	85.30
Max	mg/kg	65	3450	2200	1144	55	0.9	423
Ave	mg/kg	33.16	989.91	498.33	381.16	24.5	0.7	249.33

Table 2: Comparison with present Criterions

Criterion	Unit	Zn	Pb	Ni	Cu	Co	Cd
Concentration of element in crust of Earth1	mg/kg	75	14	80	55	20	0.2
Agricultural soil 2	mg/kg	0.6-1	0.01	-	<125	-	0.01
Natural soil	mg/kg	90	35	50	34	-	0.35
Concentration of element in shales 3	mg/kg	130	80	29	45	19	0.2

Results of tests that were conducted at sample of soil indicate that in produced waste materials of refinery there were some heavy materials include Cd, Co, Ni, Pb and Zn. Based on table 1 the highest average of heavy metals available at soil of Salvage area was lead and the lowest heavy metals was cadmium. After comparing average density of heavy metals in natural soil polluted with petroleum waste materials it was clearly indicated that discharging waste materials in Salvage area was result in increasing amount of heavy metals in soil and amount of aforesaid metals in polluted soil was more than non-polluted surround soils. Discharging industrial waste materials to salvage area resulted in increasing amount of aforesaid metals. Results of these tests clearly certified percentage of pollution and poisonous soil of this area.

[1]. Taylor,1964
[2]. Alloway,1995
[3] .Faust & Aly.1981

Table 3: Intensity of pollution based on Mueller index

	Zn	Pb	Ni	Cu	Co	Cd	Unit
Average of concentration	989.91	33.16	498.33	381.16	24.5	0.7	mg/kg
(Igeo)	2.34	-1.8	3.52	2.5	-0.19	1.22	-
Intensity of soil pollution based on Mueller index	low pollution	No pollution	Moderate pollution	low pollution	No pollution	Very low pollution	-

Finally dendrogram for cluster analysis of heavy metal and TPH in figure 1 is shown. Cluster analysis is composed of 2 branches including A,B. In branch A there are elements including Pb, Ni, Zn, Cu and Co with similarity coefficient and meaningfulness to TPH and branch Ni is regarded as index for petroleum pollution, on the other hand presence of TPH is regarded as petroleum hydrocarbon index. Therefore Pb, Zn, Cu and Co are originated from petroleum pollution. Weak relationship of Cd with branch A indicates that density of this element is not under control of petroleum pollution.

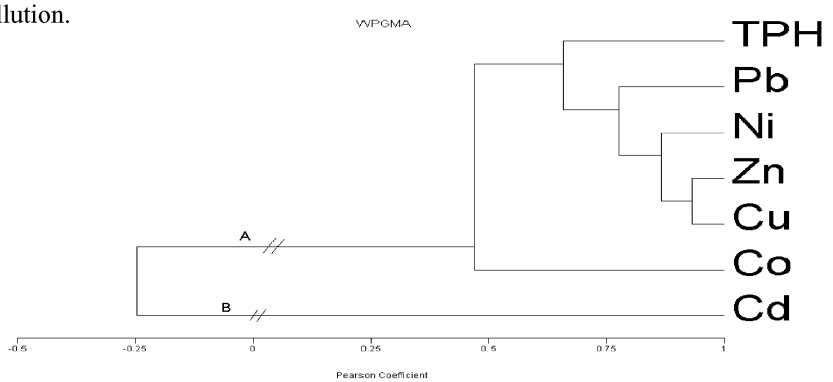


Figure 1: Dendrogram for cluster analysis of heavy metal and TPH

5. Discussion & Conclusion

Based on RCRA classification from total recognized materials in Tehran refinery, 18% were among dangerous waste materials with specified resource or K list, 22% were among dangerous waste materials with unknown resource or F list, 52% were among poisonous dangerous waste materials or U list and 8% were among acute waste materials or P list and generally 49 materials from total 133 recognized materials were among RCRA list. Also based on Basel classification, 14 waste materials were recognized in which code Y included 6 waste material, code H included 16 waste materials that included both code H and Y and among total recognized waste materials, 9 waste materials were lack aforesaid codes. Results of tests on samples of soil indicated that in produced waste materials in refinery there were some amount of heavy metals including Cd, Co, Cu, Ni, Pb and Zn. The highest amount of heavy metals in soil of Salvage area was related to zinc and the lowest amount of heavy metal was related to cadmium. After comparing average density of heavy metals in natural soil and soils polluted with petroleum waste material it was clearly indicated that discharging waste

materials in Salvage area resulted in increasing amount of heavy metals in soil and amount of aforesaid metals in polluted soils was very higher than non-polluted soils. Discharging industrial waste materials related to Salvage area resulted in increasing level of heavy metals. The highest level of TPH was related to station 6 and the lowest amount was related to station 11 and generally average density of TPH in soil of area was 230.58mg in per gram of soil in which it clearly indicated pollution of soil at Salvage area to petroleum waste materials. Based on danger codes and waste materials it was indicated that 39% of waste materials were flammable, 33% were poisonous materials, 14% were erosive materials, 10% were acute dangerous materials and 4% were oxidant waste materials. Based on aforesaid results correct management of waste materials in refinery shall be based on strategy in which the following elements shall be observed for management of waste materials (EPA, 2004):

1- Production of waste materials within Process Design shall be minimized

2- Production of waste materials by Change to Equipments and Procedures shall be decreased

3- Up to possible amount the waste materials shall be recycled

4- Output of process and operation shall be recover

5- Finally waste materials after applying aforesaid methods, shall be purified and buried

According to aforesaid main elements, management of solid waste materials at Tehran refinery for minimizing chemical waste materials shall cover the following items:

- Decreasing Production of Waste Material in Resource
- Recycle
- Reuse
- Purification

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