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Qualitative and Quantitative Characterization of Generated Waste in Nouri Petrochemical Complex, Assaluyeh, Iran

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Abstract**—**In recent years, different petrochemical complexes have been established to produce aromatic compounds. Among them, Nouri Petrochemical Complex (NPC) is the largest producer of aromatic raw materials in the world, and is located in south of Iran. Environmental concerns have been raised in this region due to generation of different types of solid waste generated in the process of aromatics production, and subsequently, industrial waste characterization has been thoroughly considered. The aim of this study is qualitative and quantitative characterization of industrial waste generated in the aromatics production process and determination of the best method for industrial waste management. For this purpose, all generated industrial waste during the production process was determined using a checklist. Four main industrial wastes were identified as follows: spent industrial soil, spent catalyst, spent molecular sieves and spent N-formyl morpholine (NFM) solvent. The amount of heavy metals and organic compounds in these wastes were further measured in order to identify the nature and toxicity of such a dangerous compound. Then industrial wastes were classified based on lab analysis results as well as using different international lists of hazardous waste identification such as EPA, UNEP and Basel Convention. Finally, the best method of waste disposal is selected based on environmental, economic and technical aspects.

Keywords**—**Spent industrial soil, spent molecular sieve, spent normal formyl morpholine solvent.

I. Introduction

THE petrochemical industry is one of the most important production centers which generate different kinds of hazardous waste, as most of the by-products and intermediates of this industry are toxic and dangerous. Already many studies have been done on the adverse effects of petrochemical wastes disposal. In the various petrochemical production processes, a wide variety of products are manufactured; as such, the petrochemical industry produces various wastes depending on the type of process and products produced. Various aspects of industrial waste management in different petrochemical complexes have been considered by previous studies emphasizing on hazardous waste characterization. For example, waste generation of the olefin production process has been identified and the potential of recycle, reuse and reduction methods were investigated [1]. Iran has 7.5% of the world's gas reserves, which is the second largest gas source [2]. These huge resources of gas as a raw material in the petrochemical industry lead to the development of the petrochemical industry in Iran. Most Iranian petrochemical complexes are located at the Pars Special Economic Energy Zone (PSEEZ). To date, limited research about the industrial waste generated in this region has been done [3]. Aromatic material is one of the most important products of the petrochemical industry. While the use of aromatic substances has increased, to the best of the author's knowledge, no research has been conducted about waste management in the petrochemical producing aromatics.

The aim of this paper is to identify the unique waste generated in the aromatics production process and determine the characteristics of each. The best method of waste management is then selected considering the lowest environmental risks and economic costs. For this purpose, industrial waste generated in NPC has been studied.

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II. Materials and Methods

The annual production capacity of NPC is 4.5 million tons, produced at the refining complex located in Bushehr Province, Iran. A special checklist was prepared to identify the waste products generated in the aromatics production process. In this checklist, the number of production units, amount and frequency of waste generation and the base compounds of the identified waste have been considered. This checklist was filled through site visit and interview meetings to responsible experts of NPC as well as literature review. Then the identified industrial waste generated at this complex has been sampled and waste density was measured by using ASTM B962 [4]. Also heavy metals including arsenic, barium, cadmium, cobalt, chromium, copper, mercury, manganese, nickel, lead, zinc are analyzed by using the instructions (ASTM D1976) and plasma mass spectroscopic method (ICP-MS) [5]. The Gas Chromatography (GC) is used in the detection of 26 organic compounds such as chloroiodomethane, decane and pyrene. Standards of the Basel Convention, EPA and UNEP have been used for waste classification and coding.

III. Result and Discussion

According to the findings, the most important NPC process wastes have been identified. Table I shows the checklist that has completed in this regard. As seen in Table I, each of the spent molecular sieve and spent NFM solvent have been generated in one of the production units, but both spent industrial soil and spent catalyst have been generated in several production units. Spent industrial soil comprises the most amount of waste generated in this petrochemical complex. Frequency of waste generation represents the period of time it is discharged and collected. This period is very different for various waste products.

TABLE I
SPECIFICATIONS OF THE PROCESSING WASTES IN NPC

Industrial waste	Production unit number	Amount (ton/year)	Frequency	Base compounds
Industrial soil	400, 600, 800	600	Annual	Silica and alumina
Catalyst	100, 300, 800	11	Weekly	Platinum on alumina
Molecular sieve	700	133	10 years	Silica and alumina
NFM solvent	500	3	Six months	Polymer

Density and physical features of the waste are presented in the Table II. Spent of NFM solvent and catalyst have the lowest and highest density respectively. Although spent NFM solvent is semi-solid at the beginning of production, after subjected to air, it becomes a stiff shape such as other three wastes (i.e. a solid form).

TABLE II
DENSITY AND PHYSICAL FEATURES OF THE PROCESSING WASTES IN NPC

wastes	density (gr/l)	physical features
Industrial soil	829	Black powder
Catalyst	1485	Cylindrical particles with cream grayish color
Molecular sieve	756	Cylindrical particles white
NFM solvent	502	Black sticky substance

The results of qualitative analysis to organic compounds are presented in Table III. In this table, 26 organic compounds were examined, while 15 combinations were not detectable in any of the waste. As it can be seen, there is no detectable organic compound in spent industrial soil. Only N-formylmorpholine waste is detectable in spent NFM solvent and the chloroiodomethane and methane, diiodo are detectable in the spent catalyst. However, a range of polycyclic aromatic compounds and alkanes compounds have been identified in spent molecular sieves.

TABLE III
QUALITATIVE ANALYSIS OF ORGANIC COMPOUNDS OF THE PROCESSING WASTES IN NPC

Compounds	Industrial soil	Catalyst	Molecular sieve	NFM solvent
Benzene, 1-methy1-4-(phenylmethyl)	N.D	N.D	N.D	N.D
Benzene, 1-methyl-2-[(3-methylphenyl)methyl]	N.D	N.D	N.D	N.D
Benzene, 1,1'-methylenebis[4-methyl]	N.D	N.D	N.D	N.D
Naphthalene, 1,2,3-trimethyl-4-propenyl	N.D	N.D	N.D	N.D
Methanone, bis-(3-methylphenyl)	N.D	N.D	N.D	N.D
Ethanol, 2,2'-bis-(methylimino)	N.D	N.D	N.D	N.D
Chloroiodomethane	N.D	D	D	N.D
N-Formylmorpholine	N.D	N.D	N.D	D
Methane, diiodo	N.D	D	D	N.D
Styrene	N.D	N.D	N.D	N.D
Ethylbenzene	N.D	N.D	N.D	N.D
Benzene	N.D	N.D	N.D	N.D
Naphthalene	N.D	N.D	D	N.D
Acenaphtylene	N.D	N.D	N.D	N.D
Acenaphthene	N.D	N.D	D	N.D
Fluoranthene	N.D	N.D	D	N.D
Pyrene	N.D	N.D	D	N.D
Toluene	N.D	N.D	N.D	N.D
Benzene, 1,1'-ethylidenebis	N.D	N.D	N.D	N.D
Phenanthrene	N.D	N.D	N.D	N.D
Trimethylbenzene	N.D	N.D	N.D	N.D
2-Phenylnaphthalene	N.D	N.D	N.D	N.D
Decane	N.D	N.D	D	N.D
Tetradecane	N.D	N.D	D	N.D
Hexadecane	N.D	N.D	D	N.D
Benzene, 1-methyl-3-(2-phenylethenyl)	N.D	N.D	D	N.D

N.D.: not detected; D: detected

The concentration of heavy metals is presented in Table IV. Comparing the amount of heavy metals with the standard values shows that spent industrial soil is contaminated by chromium, copper and lead. Spent NFM solvent is contaminated by metals, chromium, copper, lead and strontium. The spend catalysts and spent molecular sieves are also contaminated by copper and chromium, respectively.

After characterization of the waste, they can be classified and coding according to standards. Table V shows the classification and coding of the wastes according to standards of the Basel Convention, EPA and UNEP. According to this table, all the four wastes are classified as hazardous waste.

TABLE IV
CONCENTRATION OF HEAVY METALS OF THE PROCESSING WASTES IN NPC

Waste type	Industrial soil	Catalyst	Molecular sieve	NFM solvent	EPA standard for TCLP
As (ppm)	<1	<1	<1	5	5
Ba (ppm)	98	5	5	2	100
Cd (ppm)	<0/1	<0/1	<0/1	3	1
Co (ppm)	4	61	<1	<1	-
Cr (ppm)	6	4	11	15	5
Cu (ppm)	21	132	3	7	5
Hg (ppb)	<100	<100	<100	<100	200
Mn (ppm)	381	4	14	646	-
Ni (ppm)	429	-	2	7	-
Pb (ppm)	6	<1	<1	6	5
Zn (ppm)	-	245	12	60	300

Finally, the best method of waste management should be selected considering priorities in comprehensive waste management hierarchy. In the foregoing hierarchy, maximum rate of resource recovery (i.e. material and energy) is more preferable in comparison to land disposal. According to this fact, the recovery of spent industrial soil as the most appropriate waste management method is selected. In similar studies, the use of spent industrial soil as a building material, such as brick and ceramic, can improve some of its parameters and controls the environmental impacts of the disposal of these wastes [6]-[8]. In fact, using the clay to make bricks or ceramics can stabilize the heavy metals of the wastes.

Since spent catalyst contains very valuable metals, extraction of these metals has economic benefit, despite its high cost. By recycling the heavy metals, the emissions are controlled and the volume of waste remaining decreases. Hydrometallurgy, Pyrometallurgy, biological treatment and microwave radiation methods can be used to recycle the heavy metals [9]-[13].

Due to the zeolite structure, spent molecular sieves can be used instead of cement [14] or sand [15] to preparation of mortar. The use of spent molecular sieve along with cement and sand in mortar results in improvement of the mortar physical characteristics. Also, toxic emission to environment could be reduced due to stabilization of potential pollutants in spent molecular sieve.

Spent NFM solvent is another industrial waste which is generated during treatment process of this solvent and impregnated with various materials. However, recycling potential of this waste has not reported in previous researches, but due to hydrocarbon structure of the solvent, it can be used as a thermal energy source. Thus, using standard incinerators which are equipped to control system release of toxic pollutants into the atmosphere is recommended as the best method of disposal.

TABLE V
CLASSIFICATION AND CODING OF PROCESSING WASTES IN NPC

Waste type	Basel Convention			EPA			UNEP	
	Attach 1 (Y)	Attach 3 (H)	Attach 8 (A,B)	K	F	Nature T-C-R-I	T.M	T.I
Industrial soil		H6.1 H11 H12		K170		T	A	F
Catalyst		H11 H12 H6.1 H4.1		K172 K171		I-T	A	F
Molecular sieve	Y9	H6.1 H4.1	A2030	K170		T	A	F
NFM solvent	Y42	H4.1	A3140		F003 F004 F005	I-T	C	F

T.M.: type of material; T.I.: type of industrial

IV. CONCLUSION

Four different wastes including industrial soil, spent catalysts, spent molecular sieves and spent NFM solvent are generated in the process of aromatics production. All of four wastes are considered in the hazardous waste group. The best way to manage each of the wastes is proposed that include the use of spent industrial soil and spent molecular sieves in the making of some building materials, recovery of valuable metals from spent catalyst and thermal recovery through burning the NFM solvent in the standard incinerator.

Obviously, further researches should be done in the laboratory and on a pilot scale before implementation of the proposed waste management methods. In this regard, determination of optimum percentage for using spent industrial soil and spent molecular sieves as an additive in building materials, different lab analysis on engineering specifications of made materials (i.e. brick, concrete and etc.) and the monitoring of its environmental impacts are the most important researches can be considered in next stages.

In addition to the study of modern methods to increase the efficiency of extraction of heavy metals from spent catalyst, measuring emissions from the combustion of NFM solvent and determining the nature of the generated ash and also the optimal method for its disposal must be carried out. Also, further examination is recommended to asses other harmful aspects of hazardous wastes including toxicity, flammability and corrosiveness.

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