Industrial waste management in PVC production process by focusing on caustic flake waste (Case study: Ghadeer Petrochemical Company, Mahshahr, Iran)

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Abstract

Rapid growth of oil extraction has recently led to dramatic increase in petrochemical units' development in Iran. Polyvinyl Chloride (PVC) is one of the most widely produced synthetic in petrochemical complexes. As different industrial wastes are generated during PVC production process, characterization, classification and management of related wastes must be proposed regarding Waste Management Act of Iran. In this research, different industrial waste generated in Ghadeer Petrochemical Company (located in Mahshahr, Iran) was determined and then encoded by using EPA and Basel Convention classification. Amongst different wastes, caustic flake waste generated during Vinyl Chloride Monomer (VCM) production was considered as an indicator waste. Approximately 60 tons of caustic flake wastes are generated annually from activities associated with this plant. Different management methods were evaluated based on economic, technical and environmental aspects. These methods can be classified to four categories: Recovery through distillation and sublimation; incineration; chromatography; and landfilling. Results show that regarding readily available facilities (shortage of equipment and skill-labours) and current environment situation in district of Mahshahr (i.e. high groundwater level), recovery is the best methods for caustic flake waste management. Details of proposed method have been expatiated in this paper.

Keywords: Vinyl Chloride Monomer (VCM), Caustic flake, Waste management, Recovery.

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1. Introduction

Since the early twentieth century, petroleum and natural gas as a raw material for preparation of different compounds has become more important. The oil industry is expanding providing energy and raw materials for other industries and plays the most important role in industries as the driving force. Iran has fourth largest oil reserves and the second largest gas reserves in the world. It has earned much progress in the oil industry and according to country's 1404 scope of development; Iran needs 500 billion dollar investment in this industry (1). Petrochemical industry is a part of chemical industry and produces its productions by petroleum and natural gas. This industry produce materials for other industries and it is the world's third-largest industry, after the automobile and food industry. One of the most distinguishing features of petrochemical industry is its high value-added. As well as physical and chemical changes in the oil and gas hydrocarbon, the value increases up to 10 to 15 percent. In petrochemical industry, a main unit provides the raw material for other units. Industries which depends on oil industries provides more job opportunities and less costing one, as the products tends to consume more in the market. Polyvinyl Chloride (PVC) is one of the most extensive petrochemical products and one of the most consumed artificial polymers. It has two forms, soft and hard. PVCs most usages are in the construction sites. In PVC production process, di-ethylene (which is one the petrochemical products) converts to Ethylene Di Chloride (EDC) at the beginning and then to Vinyl Chloride Monomer (VCM). Finally PVC is made by using VCM. As other petrochemical industries processes during the manufacture of PVC, contaminants produce in various phases, solid, liquid and gas. So far much research has been conducted to control petrochemical industry contaminant like Emissions of volatile organic carbon (2-4). But solid wastes are one of the most important parts of petrochemical industry pollutants that containing domestic and hazardous wastes forms. Clearly, the proper management of these solid wastes is necessary to protect the environment and local people's health.

Also MAHSHAHR located in a Coastal region and there are many petrochemical facilities nearby this city so not paying attention to ecological rule can bring damage to the environment. This is in contrasts with the approach of sustainable development. Hence Management of solid wastes generated in the PVC production process is an important strategy. Greenpeace Research Institute has been studied the PVC production process and its environmental impacts widely. According to these researches the PVC industry which is the largest consumer of chlorine in the United States of America is the most important source in the production of dioxins and PCB (Polychlorinated Biphenyls). In this study, the most important solid waste produced have been identified that including coke, mineral sludge from wastewater treatment operations and (reboiler drilling).

In another research, the impact of pollution caustic treatment on the marine environment has been investigated. The caustic was used in the oil refining process and it included the impurities such as Phenol, NaSH, NaOH and suspended hydrocarbons. As a result, the polluted compounds becomes in gas form and caustic refined. The H2S gas is burned in flare or furnace burning trash and caustic refined with minimal contamination excreted in the sea. The main topic of this paper is to identify solid waste generated in the manufacture of PVC and then they were classified and coded. Then the index waste was introduced and its management strategy was provided. Solid waste produced in the Ghadeer petrochemical company has been chosen In this case study. Obviously, the result of this study will also be used for other PVC production petrochemical.

2. Material and Methods

Ghadeer petrochemical company located in the Mahshahr Special Economic Zone. The company has started its activity since 2010 and now is running at 100% capacity. This company produces 120000 ton/year PVC while total PVC production of Iranian company is 450000 ton/year PVC. Domestic consumer use 70% of the Ghadeer company products and 30% of its products exported to neighbor countries. This area has a warm and humid climae. The temperatures is between 50 ° C in summer and 0 ° C in winter and the relative humidity can be up to 100% during the summer. Average annual rainfall is 195 millimeter. In terms of topography it is almost a flat region and without steep slopes. This region has alluvial soil and contains gypsum and salty material. There are two important rivers in this area (Zohre and Jarahi). Average depth of groundwater level is 150 centimeter. A Sanitary landfill center with an area of 10 hectares has been established in this region which has been used for disposal industrial solid wastes of petrochemical companies.

2.1. PVC production process

Ghadeer petrochemical company has two production lines includes VCM production line and PVC production line. In VCM production line (Figure 1) EDC has been initially produced. There are two methods to produce EDC. The first method was called direct chlorination (section 100). In this method, chlorine, ethylene and iron chloride catalyst have been combined to produce EDC. The second method is called oxy-chlorination (section 200). In this method chlorine, Oxygen, ethylene, chlorine hydride and copper chloride catalyst have been combined to produce EDC. Sometimes the company uses imported EDC. However imported/ production EDC has entered into separation section (section 300) then water and other impurity include substances with a high boiling point and substances with a low boiling point has been separated from EDC. Then the produced water has been sent to pre-Treatment section and EDC has been sent to the final separation. In the next step (section 400), purified EDC with thermal cracking method using a furnace has become VCM and HCl. Efficiency of this process is %55. Output of this section is VCM, HCl and No cracking EDC. These material have been separatered in next section (section 500) and purified VCM has been sent to storage. EDC and HCl have been returned to production line too. Also wastewater of various section including alkaline, acidic and chemical waste have been sent to next section (section 600) to neutralization and recycling of EDC with it. Then wastewater of this section has been sent to section 800. In this section light and heavy material, OFF GAS and wastewater of sector 600 have been burned in a furnace. Material obtained from the combustion after cooling and steam generation have been become acid 18% in absorption tower (5).

In PVC production line (Figure 2), the VCM production in the former step through pipelines has been transferred to storage and charging VCM part (section A). As well as additives required for polymerization include buffer, emulsifier soluble, the catalyst soluble and reaction finalizing soluble have been produced in section B(section B). In polymerization step (section C) VCM has been scattered in liquid phase using a mixer and emulsifiers. Then catalyzer has been injected and VCM has been polymerized to PVC molecule and PVC suspension has been produced. The suspension also contains a large amount of unreacted VCM. After separation of VCM (section D), PVC suspension has been sent to centrifuge (section E). This suspension had 75% moisture and

dehydrated by mechanical method and centrifugal force. The result is a wet cake with 25% moisture. In next step (section F) moisture of the wet cake decreased to 1% and has been converted to powder. The resulting powder has been sent in testing silo (section G) and after sampling and confirmation, it has been sent to the storage (section H). Then it has been sent to packing section (section I). Final product has been stored in storage (section L) to be sent to the consumer. Also all wastewater of production line has been collected in special containers and after separation VCM the remaining water has been excreted.

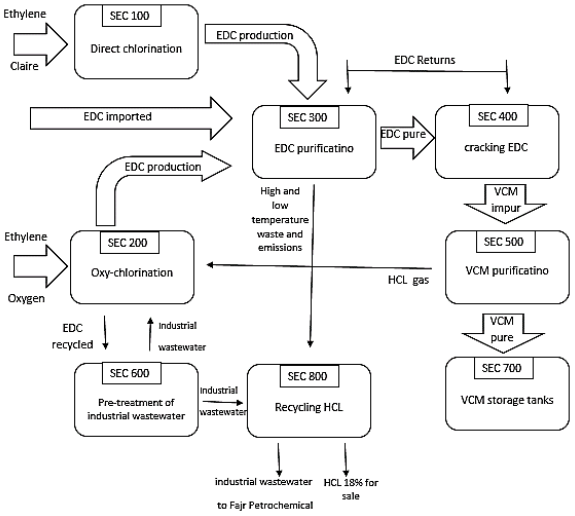

Figure1: VCM production process (6)

To identify solid waste of the company first we studied engineering reports of the company that explains the PVC production process. Also after the inspection of company, personnel have been asked to fill out questionnaires. According to the questionnaires solid wastes of company have been classified in 6 units include: VCM operation unit, PVC operation unit, UT operation unit, repairs unit, product store unit and restaurant unit. Also volume or weight of the solid waste per unit time has been identified.

Later the hazardous solid waste and normal solid waste have been separated. EPA Code, source code and risk code of any solid waste have been determined. The source code that shows how the waste have been produced, this code has been determined by the two marks: (I) for waste with industrial origin and (U) for waste with municipal origin. Also risk potential has been specified by 4 codes. (H) Code is for hazardous material. This solid waste has feature hazardous wastes and EPA has listed them as a hazardous waste. Non-hazardous material with code (1) which has combination with certain properties. And if concentrations of these compounds reach above the limits of concentration can be considered as hazardous waste. Non-hazardous material with code (2) which hasn't hazardous solid waste substances but they can cause environmental pollution. Non-hazardous material with code (3) which hasn't the potential to pollute the environment. Also hazardous solid waste has been classified according to Basel Convention.

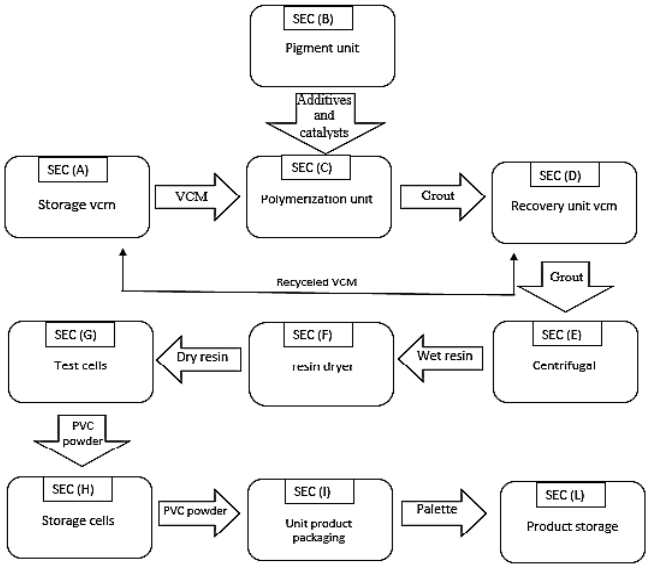

Figure 2: PVC production process (6)

3. Results and Discussion

According to questionnaires that company personnel has been answered, company's solid waste have classified in two groups: usual solid waste (Table 1) and hazardous solid waste (Table 2). Based on the data obtained from questionnaires answered by personnel of the company and coding, solid waste have been classified in two group: normal solid waste (Table 1) and hazardous solid waste (Table 2)

Table 1: Normal solid waste list

Risk code	Source code	EPA	Unit (weight / volume)	Amount	Unit	Waste name	No
2	I	407	Pieces/year	40	VCM operation	Bag tri-sodium phosphate	1
2	I	406	Pieces/year	4000	PVC operation	Empty barrels Catalyst	2
2	I	406	Pieces/year	20	PVC operation	Empty barrels Paxol	3
2	I	315	Pieces/year	86	PVC operation	Empty barrels Terminator	4
2	I	404,412	m3/4years	unlimited	UT operation	Peking cooling	5
2	I	407	Pieces/year	1440	UT operation	Empty bags of lime	6
2	I	406	Barrel/year	144	UT operation	Empty barrels of chemicals	7
2	I	406	Pieces/year	4	UT operation	1000-liter containers of materials chemical due to perforation	8
3	I	409	lit/4year	6300	UT operation	Cationic ion exchange resin	9
3	I	409	lit/4year	6400	UT operation	Anionic ion exchange resins	10
3	I	319	kg/month	100	Repairs	Bearing	11
3	I	308	kg/year	6	Repairs	Coated copper wire	12
3	I	309	unlimited	unlimited	Repairs	Aluminum or copper cable sheath	13
2	I	315	unlimited	unlimited	Repairs	Shells of oxygen and hydrogen	14
3	I	309	pieces/year	36	Repairs	Used equipment	15
3	I	319	kg/year	400	Repairs	Used Plate insulation	16

3	I	319	Ton/Year	10	Repairs	Scrap metal	17
3	I	307	kg/year	200	Repairs	Cutting metal chips	18
2	U	901	Kg/month	500	Restaurant	Bottles and plastic pallets	19
2	I	417	Pieces/year	3408	UT operation/ product store	Pallets	20
2	I	407	kg/year	2880	product store	Roll film packaging	21
2	I	418	Pieces/year	1344	product store	Packaging	22
2	I	407	Kg/month	500	product store	Jumbo Package	23

Table 2: Hazardous waste list

Risk code	Source code	EPA	Unit (weight / volume)	Amount	Unit	Waste name	No
2	I	407	Pieces/year	40	VCM operation	Bag tri-sodium phosphate	1
2	I	406	Pieces/year	4000	PVC operation	Empty barrels Catalyst	2
2	I	406	Pieces/year	20	PVC operation	Empty barrels Paxol	3
2	I	315	Pieces/year	86	PVC operation	Empty barrels Terminator	4
2	I	404, 412	m3/4years	unlimited	UT operation	Peking cooling	5
2	I	407	Pieces/year	1440	UT operation	Empty bags of lime	6
2	I	406	Barrel/year	144	UT operation	Empty barrels of chemicals	7
2	I	406	Pieces/year	4	UT operation	1000-liter containers of materials chemical due to perforation	8
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3	I	409	lit/4year	6400	UT operation	Anionic ion exchange resins	10
3	I	319	kg/month	100	Repairs	Bearing	11
3	I	308	kg/year	6	Repairs	Coated copper wire	12
3	I	309	unlimited	unlimited	Repairs	Aluminum or copper cable sheath	13
2	I	315	unlimited	unlimited	Repairs	Shells of oxygen and hydrogen	14
3	I	309	pieces/year	36	Repairs	Used equipment	15
3	I	319	kg/year	400	Repairs	Used Plate insulation	16
3	I	319	Ton/Year	10	Repairs	Scrap metal	17
3	I	307	kg/year	200	Repairs	Cutting metal chips	18
2	U	901	Kg/month	500	Restaurant	Bottles and plastic pallets	19
2	I	417	Pieces/year	3408	UT operation/ product store	Pallets	20
2	I	407	kg/year	2880	product store	Roll film packaging	21
2	I	418	Pieces/year	1344	product store	Packaging	22
2	I	407	Kg/month	500	product store	Jumbo Package	23

3-1- identify index waste

Among the identified waste, caustic flakes with production of 60 ton per year was an index waste. This waste is considered as hazardous waste and its source code is (I) and Basel code is Y35. Its EPA code is 391 and hazardous code is H. This solid waste has been produced in VCM production line and in VCM purification section (section 500). Dryer towers of this section were filled by flake caustic and when VCM passes from bottom to top of the tower this flake caustic absorbs water and HCl and other impurity from VCM. Eventually Pure VCM went out of the top of the tower. Alternatively, caustic soluble produced in this process from the bottom of the towers. These flake caustics must be replaced every 3 months. Because over time Fe and NaCl have been absorbed by flake caustic and its effectiveness has been reduced. These flake caustic waste are stored now and there is no certain way to excretion them. In this study various methods of managing flake caustic as an industrial we have been investigated.

3.2. Waste management methods

In general, there are various methods of managing this flake caustic waste that is including three methods: landfill, incineration and recycling. The following each method have been described.

3.2.1. Sanitary landfill

In sanitary landfill, solid waste is buried in land so it does no harm to animals and the environment. The main problem with this method is the production of gas and leachate in place. As we know that Ghadeer petrochemical facilities located in a coastal area and groundwater level is just 150 centimeter and the possibility of discharge of leachate into groundwater and subsequent pollution of sea water is very high. If the latex wells arrive to groundwater or sea water it can be a hazard to humans and animals in the region. So if this method use in addition to the location and design principles of industrial landfill we should treat differently to leachate such as: aerobic or anaerobic treatment at different pH, advanced oxidation with hydrogen peroxide and iron, and coagulation, flocculation and etc [7-8].

3.2.2. Incineration

Waste incineration is the main method in waste management and it has higher priority than the landfill. Every year, more than 100 million tons of waste is incinerated around the world (9). In this method, waste should be dried at the beginning, then it will be ignition process starts and finally it will be burned as result their volume reduced up to 10%. Establishment and maintenance cost of equipment incinerator are very high and experts had been needed to use them. This method is mainly used for organic waste. But this flake caustic waste is included NaCl, Fe, NaOH and it is a inorganic waste thus to incinerate is not useful for this kind of solid waste. As a result ash which has been produced in the incinerator has a lot of salt so this salt well be dissolved in the underground water by interment it. And other way like recovery of elements of ash (10) or use of ash for product cement (11) should be experimented.

3.2.3. Recycling

As noted above, the caustic waste containing iron and sodium chloride and by removal of this kind of impurities, it can be used again into the production process. This waste includes several types' molecules with different attributes such as differences in density, boiling point, magnetism and solubility and etc. Based on these differences these molecules can be isolated. The main chemical separation methods include: sublimation, chromatography, distillation, crystallization and extraction (12).

a) Sublimation: In this method impure material is heated to a temperature lower than the melting point and is sublimation. Produced Steam quickly accumulated on a cool surface and transformed to solid phase. This crystal is completely pure. This method is used for non-polar material with a relatively symmetrical structure. But our caustic waste is a polar material, this method would not be appropriate to purify it.
b) Chromatography: Chromatography is a method of separating mixtures that can be done by passing a mobile phase ups stationary phase. Depending on the mixture, different chromatographic methods are used. Due to the ionic nature of the caustic waste paper chromatography or thin layer chromatography ion exchange chromatography column is an effective method for separating its impurities (13). But we must keep in mind that this method is very costly Due to the high volume of the caustic waste produced.
c) Distillation: Distillation is a physical process to separate material with different boiling point. In this method a liquid mixture evaporates with heating then steam of every material which is compressed in a separate container and steam is compressed. Since distillation method is used for purification liquids with a relatively low boiling point we can not use this method for a solid sample that has a high boiling point.
d) Crystallization: In this way impure solid material dissolves in a hot solvent then this material re-precipitated by cooling the solution. The important point in this method is the selection suitable solvent. This solvent should dissolve slightly soluble at room temperature. But it should easily dissolve soluble in the high temperature. Also paying attention to polar or non-polar characteristics of material is so important. Because polar compounds dissolves in the polar solvents and non-polar compounds dissolves in non-polar solvents. Caustic waste is a polar compound so we can dissolves it in water, because water is a polar solution. In this condition due to Alkaline water Fe unable to be solution phase and it begins to sediment. But we con not use this method for separation of NaCl and NaOH because both of them are soluble in water. Therefore, in the following this method we should use another method to separate two salts such as use of resin and make pure NaOH.

Technical, economic and environmental aspects of proposed methods have been compared in Table 3. Then the best method for management of caustic solid has been chosen. There are several Criteria to technical aspect such as complicity technic, Capability of hazardous pollutants removal and necessity of land to each technic. As wall as there are different criteria to economic aspect such as current costs and investment costs and marketing for recovered product. There are environmental criteria in addition to economic and technical criteria, such as Potential of pollutants emission and replacement Energy recovery. In order to best alternative selection, different management methods were evaluated based on economic, technical and environmental aspects (Table 3). Many

approaches for evaluating mentioned criteria can be used to comprise different methods. Since various value judgment lead to different results, so these criteria were evaluated at three levels (law; medium; and high) due to uncertainty reduction.

Table 3: Comparison of the technical, economic and environmental management strategy

Crystallization	Chromatography	Incineration	Sanitary landfill	indexes	
medium	high	medium	medium	complicity technique	**Technical**
medium	high	low	low	Capability of hazardous pollutants removal	
high	medium	low	high	necessity of land to each technic	
medium	high	high	medium	Current costs and Investment costs	**economic**
high	high	low	low	Marketing for recovered product	
low	medium	high	high	Potential of pollutants emission	**environmental**
low	low	high	low	Replacement Energy recovery	

Regarding to Table 3 crystallization method has significant advantages for management of caustic waste in comparison with other methods from the technical and economical view. However necessity to land is the salient problem of this method, According to the location of the company this problem can be resolved.

4. Conclusions

Ghadeer petrochemical company is one of the largest PVC producers in Iran. VCM is a mater that is necessary to product PVC. Removal water and acid of VCM is one step of VCM production process, and it done by flake caustic. But after a few months due to impurities that have been added to the flak caustic it must be replaced with new caustic flakes. Disposal of these used flake caustic and choice a management method to this solid waste is one problem for this company. Among the different methods, recycling is the best way. Because it prevents to new pollutants in the environment. Through different recycling methods, crystallization and distillation methods are not applicable due to the nature of the waste. The extraction method is not applicable. Because we do not know the solvent that only solving caustic and don't solving other material. Also chromatography method Require large investments and flake caustic recovery costs is more than cost to buy flake caustic fresh. But Profitability is the most factors in economic project. Crystallization method is very effective for separating iron compound but sodium chloride will be remembered with caustic as an impurity. And if be used resin to separation NaCl, after a while we will forced to use the caustic for the restoration of the resin. In fact produced caustic well be used in this process again so so there is no justification for the use of resin for this purpose. However, since the sodium chloride would have significant impact in many chemical reactions we can use this combined (sodium hydroxide, sodium chloride) for chemical processes that required sodium

hydroxide like in Treatment. In Sanitary landfill method formation landfill requires a lot of capital. in addition to groundwater level is so high in this place and Leachate infiltration into the aquifers. If NaOH enter to underground water and then enter to coastal water, it will be undoubtedly effect on marine ecosystem. Also incinerate of this solid waste is not useful because it's an inorganic matter.

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