



CHARACTERIZATION OF THE SLUDGE DEPOSITS IN CRUDE OIL STORAGE TANKS

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Abstract

Sludge obtained from the crude oil storage tanks is semi solid waste. It is a complex emulsion of numerous petroleum hydrocarbons, water, and solid particles. Petroleum sludge is generated during crude oil transportation, storage, refining and production. It includes many poisonous species, xylene, polycyclic aromatic hydrocarbons, benzene, heavy metals, toluene, and ethyl benzene. The physiochemical characteristics of the sludge from oil and gas fields were investigated in this research. Basic sediments, water, and oil was determined by centrifuge, pH meter was used to evaluate the alkalinity. Total solid residue was calculated by evaporating the samples in drying oven after setting the temperature up to 105°C. Moisture contents were determined as a percentage of total solid residues (TSR). The fixed residue and volatile solids were analyzed by using electric muffle furnace after ignition on the temperature of 600°C. Moisture in the sludge was in the range of 32.23 to 34.92, Total solid residue was 67.7 to 65.08, Volatile solids 89.29 to 90.45 and fixed residue 10.71 to 9.55.

Keywords: sludge, characterization, crude oil, storage tanks

1. INTRODUCTION

Sludge that contain oil and water are generated through a variety of activities and processes on board ships, including sedimentation in tanks, tank dewatering processes, and leaks or cleaning cycles in backflush filters and separators for treating fuel oil and lube oil. The trend for combusting high density fuel oils of higher viscosity, as well as the use of residues as a fuel for medium-speed diesel engines, also increases the production of sludge from both fuel oil and lube oil. Organic materials affect many of the biological properties of the soil physical, chemical and. Some of the properties affected bioorganic materials include soil structure, soil compressibility and shear strength [1]. In addition, it also affects the ability to retain water, and contributions of food, and biological activity, and the price of water and air infiltration [1]. Identifies and record the mass porcelain bowl empty, clean and dry (MP). Put a part of or the whole oven-dried test sample from the experience of the moisture content in porcelain dish and the identification and registration of mass dish and soil sample (MPDS) [2]. Place the dish in the electrical muffle. Gradually increasing the temperature in the oven to 600°C. Carefully remove the porcelain dish using forceps (the dish is too hot), and allow to cool to room temperature to determine and record the mass of the dish containing thrashes (scorched soil) (MPA). Empty the bowl and clean it [1].

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The so-called solid content remaining after ignition (ash), where the remnants of the fixed and defined as the weight of organic material in the sludge [3]. This is the minimum weight of the solid, which will remain for the final disposal. And can be expressed either as a percentage of weight by weight of wet sludge ratio or TSR [4]. Sludge obtained from the crude oil storage tanks is semi solid waste. It is a complex emulsion of numerous petroleum hydrocarbons, water, and solid particles [1]. Most of crude oil have tendency to separate in to lighter and heavier hydrocarbons before refining. Low temperature may create problems, venting of volatile components generally contained by crude [3]. Sludge is settled on the bottom after the action of static condition of fluid and heavy ends that influence the solid particles and heavier hydrocarbon comes in the lowest part of the tanks or storages areas, that settled mass is generally known as sludge [4]. Petroleum sludge is generated during crude oil transportation, storage, refining and production. It includes many poisonous species, xylene, polycyclic aromatic hydrocarbons, benzene, heavy metals, toluene, and ethyl benzene [1]. Many countries recognized sludge as a hazardous waste because of its effects on the environment and health of the people working in the vicinity where the sludge is decomposed or treated. Worldwide production of sludge is increasing similarly in Pakistan [4]. As the years are passing then ratio of sludge formation is increasing. This might be due to the need of very refined oil production which leads to generate sludge [3].

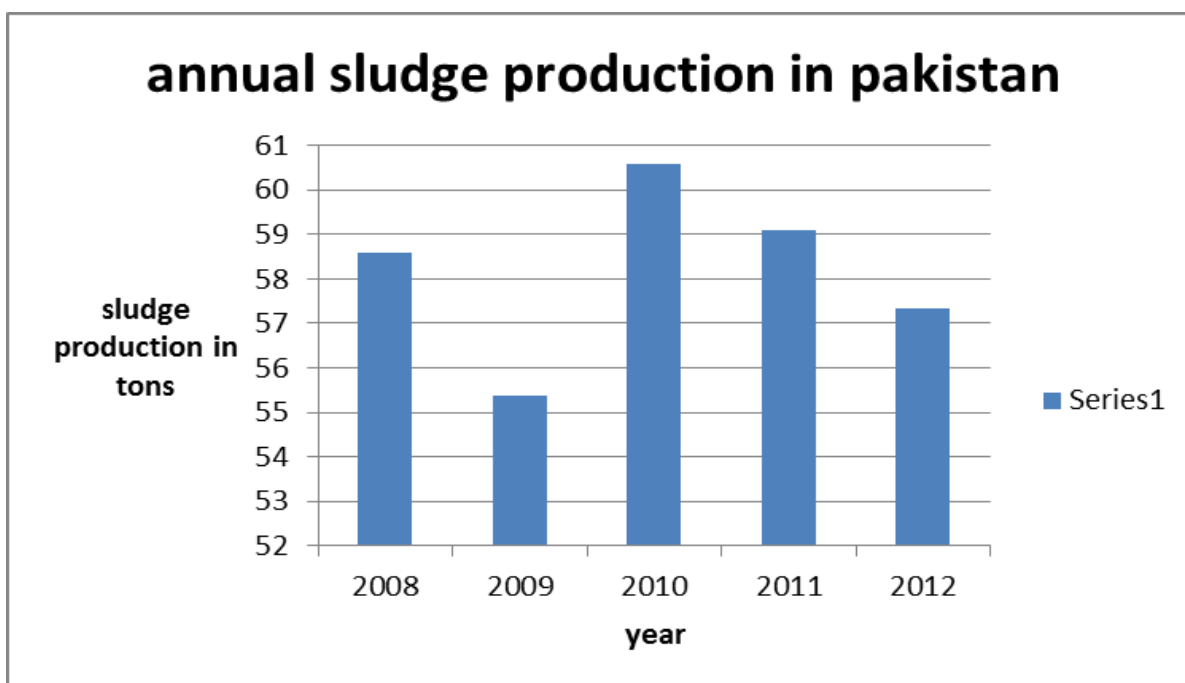


Figure. 1. Annual production of sludge in Pakistan

2. Material and Methods

2.1 Materials

The material that had been used in the research work is the sample of sludge from different oilfields. Hexane is used to dilute the sludge for experimental purpose.

2.2 Methods

2.2.1 Collection of Sample

Various sludge samples were collected from the XYZ field of OGDCL after collecting the samples, these were mixed thoroughly. Material was obtained in sample bags with the help of shovel of stainless steel. Sample buckets transferred in to the laboratory for performing experimental work on it.

2.2.2. The Characterization of Sludge

Sludge sample that was collected from the crude oil storage tank in stainless steel clean and dry bucket and analyzed in detail for the physio-chemical characterization. It is the mechanical method to separate materials from each other on density bases, what happens when any mixed liquid is centrifuged with high speed or at high RPMs then they goes away from each other and separation comes a head. The electronic centrifugal machine was used to separate the different components of the sludge like water, free oil and basic sediments. The machine was set on the 4000 revolutions per minute and run for One hour continuously in order to recover centrifuged material. The pH scale measures how acidic or basic substance. It ranges from (0 to14) pH of 7 is neutral. And a pH less than 7 is acidic, and a pH greater than 7 is basic that creates an conducive environment to the survival of organisms and retards the adsorption of oil after disposal. Thus, the purification sludge does not create odors or even a long-pH more than 12. Is a way to measure the total solid content, and this is determined by evaporating to constant weight is measured by the amount of sludge, weighing residue and expressed as a percentage of weight by weight. In this method first we will identify and record the mass porcelain bowl empty, clean and dry (MP). Then we put the sludge in the bowl then again weigh this sample filled porcelain bowl, the amount of sludge was dried and weighed to constant weight at 105 °C in the porcelain bowl. The residue was weighed and expressed as a percentage of original weight wet sludge. Equals $(100 - \text{TSR}) \%w / w$ and alternative parameters are usually quoted as a measure of the total composition of the sludge. Volatile solid content is measured by weight loss on ignition of dried sludge test TSR in 600 °C, is a measure of the organic content. And so it came to possible reduction in the mass of sludge. It quoted volatile solid content as percentage of TSR. This test is performed to determine volatile solid content of the sludge. Volatile solid contents the ratio, expressed as a percentage, of the mass of organic material in the sludge of a certain mass to the mass of dry sludge solids.

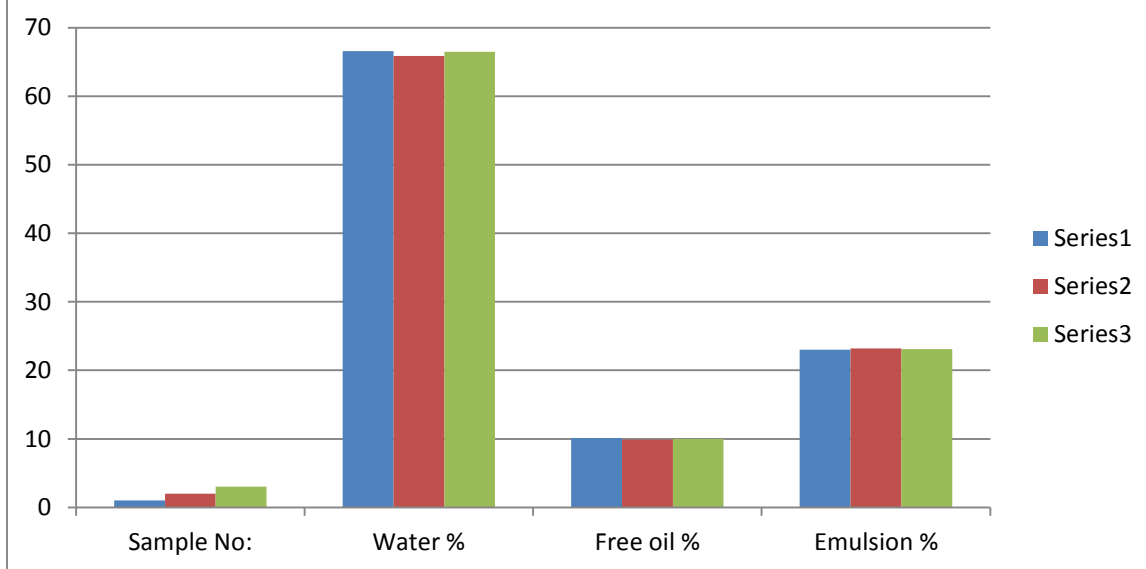
3. Results and Discussion

3.1. Analysis of basic sediments, water & oil

The centrifuge is equipment which is driven by electric motor and provides rotation to sample and separate the substance in to water, oil and sediments according to density, the solid at bottom and water between the oil and sediments. Centrifugal machine used to determine the water, oil and emulsion present in to sludge, centrifugal can also use to reduce the volume of the sludge for the treatment of sludge. 30ml of sludge was taken and mixed thoroughly at ambient temperature and put it in to centrifuge for 40 minutes at 3000 rpm.

Table 1: Water, oil and emulsion % of sludge sample

Sample No.	Qty., ml	RPM	Time, min.	Water %	Free Oil %	Emulsion %
1.	30	3000	40	66.6	10.1	23.0
2.	30	3000	40	65.9	09.9	23.2
3.	30	3000	40	66.5	10.0	23.1
4.	30	3000	40	65.5	10.2	24.3
5.	30	3000	40	64.9	10.9	24.2
6.	30	3000	40	66.2	09.9	23.9

**Figure. 2. Water, oil and emulsion % of sludge Samples**

In above Table 1 it is clear that the material can easily be distributed and separated from each other, here RPM are fixed having value 3000 RPM, it can be extended. Literature shows clear idea that if the centrifugal machine that produce high intensity of centrifugal action then the separation will be high, molecules of same weight will rush to each other and denser molecules apart to the bottom and lighter molecules float on the surface, In this test Oil came on the top and water took its place in the mid of test tubes while the residue and thick material containing dust & heavier particles settled in the bottom. The percentage of each separation was displayed in the Table 1 which concludes all the values.

3.2. Determination of pH of sludge sample

pH is very important property of the liquid, which tells us about the nature of the given sample, like if pH is 7 than the given sample is neutral and if it is greater than 7 the sample possess basic nature if it is less than 7 the sample is acidic nature.

Table 2: pH values of oil sludge.

Sample No.	Quantity of sample	Solvent (hexane) ml	pH of sludge	Status
1.	30	40	7.1	Neutral
2.	30	45	7.4	Slight basic
3.	30	35	7.3	Slight basic
4.	30	30	7.3	Slight basic
5.	30	25	7.4	Slight basic
6.	30	20	7.4	Slight basic

Digital pH meter used for analyzing pH of the samples. As sludge is a thick and viscous semi solid in order to make it dilute hexane solution was used, which is organic solvent and having no effect on the pH value of given sample. For preparing sample of the sludge 40 ml of the hexane was mixed with 30 ml of the oil sludge to check the pH easily. The results obtained are given in the Table 2.

From the results of pH given in the Table 2 it is clear that the pH of sludge remains slight basic throughout the sample and also solvent dose was varied but the result remained same while Average pH of the sludge remained 7.3 which is considered as slight basic in nature, which create the problems for the land where we dispose it, the pathogen and the pH which is basic in nature may create the environment which is favorable for the growth of microorganism they may produce some toxic effects. In order to suppress the odor, pathogen and prevent of the growth of microorganisms, we can mixed it with lime to increase the pH value up to 12, to reduce odor problem.

3.3. Total solid residue (TSR)

The total solid residue present in the sludge was determined in the laboratory by drying samples in oven at the temperature of 105 °C for two days.

Calculated values are summarized in the Table 3. The average solid residue contained by the samples is 63 %. Electric furnace was set on the temperature of 105 °C and porcelain dishes were heated in it for twenty four hours continuously in order to get the required results.

3.4. Calculations for of TSR, pm, vs and FR

Initial weight of empty dish was calculated and mentioned in the table and then the dish was again weighted with material named W1 and W2 respectively. W3 was given to the material weight which is weight of dried material at 105°C while W4 is the weight of sample after ignition in muffle furnace at 600°C formula of Total Solid Residue will be equal to

$$\text{TSR \%} = (W3-W1) / (W2-W1) * 100$$

Moisture percentage was determined by subtracting the TSR % from

$$100 \text{ PM\%} = (100-\text{TSR}) \%$$

Volatile solid contents (VS) were calculated by final weight

$$VS = (W3 - W4) / (W3 - W1) * 100$$

Fixed Residue Contents were calculated by subtracting VS % from 1 all samples were checked by using furnaces, weighting scales and calculated the results from experimental data were tabulated in the Table 3.

Table 3: TSR, PM, VS and FR

Sample no.	W1	W2	W3	W4	TSR %	PM %	VS %	FR%
1.	59.19	122.43	101.05	63.67	67.7	32.23	89.29	10.71
2.	56.40	118.84	90.94	61.13	55.31	44.67	86.30	13.70
3.	47.18	123.99	97.13	51.95	65.09	34.90	90.63	9.37
4.	52.19	115.43	94.05	56.7	66.19	33.1	89.22	10.78
5.	54.90	116.84	88.94	59.13	55.31	44.69	86.30	13.70
6.	50.18	126.99	100.17	54.95	65.08	34.92	90.45	9.55

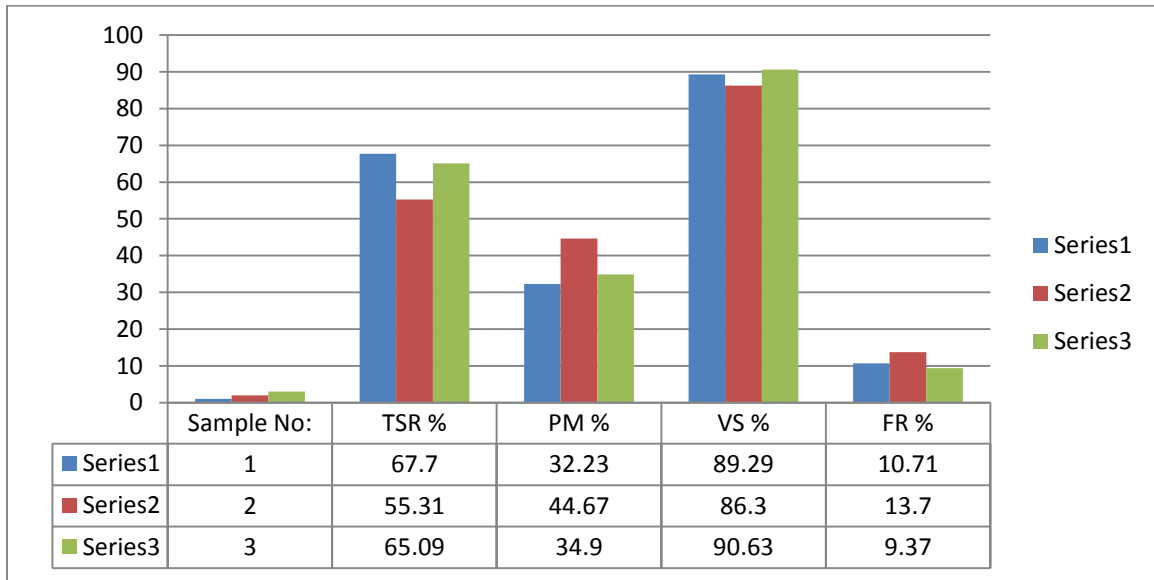


Figure. 3. TSR, PM, VS AND FR

Average values as given in Table 3 are Total solid residue 62.7%, Total Moisture contents are 37.26%, Total Volatile substances are 88.74% and Fixed Residues 11.26% these are results calculated in the laboratory and considered as average values.

3.5. Some useful applications of oil sludge

Oil sludge is made of water, solids and little percentage of oils it may contains heavy metals and heavy hydrocarbons. Due to solid particles and unwanted material it can't be

used directly hence it is not applicable without processing. After separation of water from it, sludge can be used in emulsion with other oils and it is also used for burning purpose after forming briquettes by mixing its ratio with biomass, coal or saw dust. Sludge has adhesive property hence it will help in binding as well as in combustion because of hydrocarbons.

3.6. Treatment of Oil sludge

It is recommended by researchers that the sludge can be treated by using biotechnology like bioremediation in which bacteria like consortium is used by suitable media like wheat bran, inorganic nutrients or fertilizer. Bacteria decomposes and degrades the oil while increasing the colony of bacteria. Excluding this sludge can be separated by mechanical means using decanters, centrifugal machines but this is costly process owing to use of heavy machinery. Sludge can be treated by induced floatation air to recover oil from it, this type of treatment is valid for the sludge whose viscosity is moderate or low, high viscous sludge can't be treated by this method [14]. Sludge can be treated with vacuum separation method. Filtration is done under vacuum or an applied inert gas pressure, filter cake is built on the filter media that is dried at lower temperature that cake is utilized as burning add to coal or other solid fuel.[15]

3.7. Environmental impact of oil sludge.

Oil sludge is considered as hazardous waste because of presence of oil it deteriorate the fertility of soil, increase soil pollution and if it is burnt in open atmosphere then CO² emissions will and SO² fumes will damage the equilibrium of atmosphere. In case of disposing it into the earth or in to the canal then there is chance of killing aquatic life. Again it will directly affect the ecosystem [16]

4. Conclusions

The optimum results showed that in sludge, the oil was 10%, water was 66% and remaining 33% was sediment with emulsified oil. The maximum pH value in the sludge was found as 7.4 which is alkaline in nature. With high alkalinity, the sludge cannot be disposed in to open pits. It may causes hazards and may increase the chances of fire and emission of volatile matter. It may cause environment pollution as well as damage the physical properties of the soil at the point of disposal. Proper treatment of sludge must be carried out before disposing the sludge. Furthermore, the sludge may be utilized to recover the value added product.

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