A Solution of Inertisation of Petroleum Sludge Resulted from the Extraction of Petrol

RUS IOAN CRISTIAN, RADU SORIN MIHAI
Department of Mechanical Engineering,
University of Petroșani
Str.Universitatii, nr.20, Petrosani
ROMANIA
sorin_mihai_radu@yahoo.com

ABSTRACT: The contamination resulting from liquid petroleum products have a negative effect as much on elements above ground and on groundwater, due to infiltration, as it does on the atmosphere above ground through the evaporation of compounds from the pollutant. The paper realize a physical and chemical characteristics of the petroleum sludge and propose a solution in order to obtain inert waste, by mixing it with adsorbent materials. Inerted resulting product has real energetic characteristics and can be born mixed with coal in any power plant designed to burn coal with a volatile content of over 20%

Key words: **petroleum sludge, waste, decontamination, inert waste, oil**

1 Introduction

In the industrial activity there are numerous situations in which technical incidents are followed by the contamination of the surrounding environment with side products, oil and other liquid petroleum products.

The contamination resulting from this may have a negative effect as much on elements above ground and on groundwater, due to infiltration, as it does on the atmosphere above ground through the evaporation of compounds from the pollutant. Decontaminating of a polluted petrol site and the ecological reconstruction needed to bring the environment back to its original state is one of the most complex projects in the domain of Environment Protection, not only due to the economy and technology needed but also due to the impressive amount of organization involved. Determining which is the optimum method of decontamination, is also extremely difficult due to the large amount of variables and interactions that influence the system and make the end result impossible to precisely be predicted.

The elements found in the soils and their structure, together with the nature of the organic constituent and their humidity gives the ecosystem chemical and physical characteristics that are extremely diverse. However, the nature and quantity of the petrol product contributes to the creation of an ecosystem that is largely polluted.

Under the pressure of these largely diverse environments the process of choosing a decontamination technology is made largely on empirical principles that account first of all for the economy rather than the scientifically aspect of it.

Before a conclusion is reached about what technique is more adequate to a certain situation, there must be a diagnosis, inquiring the following:

- the composition and structure of the soil in the contaminated area
- the qualitative and quantitative characterization of the pollutant;
- the extent of the polluted area both at surface and in depth
- the grade of deterioration of the soil
- the negative effects of pollution upon the human activity in the area
- the danger of affecting the groundwater in the surrounding area

Currently the delimitation of the contaminated areas can be done with concern to a multitude of factors that depend on the type and location of the source of pollution, on the quantity and characteristics of the pollutant, the relief in the area, the composition and structure or the soil, subsoil and the groundwater.

Deciding on the spread of the contaminated zone, above ground as well as underground is done by combining the method of direct observation (done above ground, using means such as helicopters, planes or even pictures taken by satellites) with methods such as specific analysis for determining

the contents of the pollutant from ground samples, water samples (from above and below ground)

Considering the relatively high cost of effectuating the analysis of pollutant from soil and water samples, there must be a set optimal strategy regarding the number of times and precision necessary for the analysis, to delimitate the contaminated area.

For these situations it is recommended that the recoltation of soil samples or contaminated water to be done at the most concentrated zones in the polluted environment.

If the pollution is historical, when the position of the polluted area is not exactly known or in case of a distributed source, the delimitation of the contaminated zone is done on the base of information obtained through the analyzation of pollutant probes taken uniformly from the surface that is potentially polluted.

The information acquired through pollutant analysis has to be completed with information obtained from scenarios that shape the evolution of the pollutant in time and space.

The inventory of a contaminated area must contain elements that refer to:

- the site's inventory with detailed information regarding the location, technological flows with the related installations/equipment, adjacent sewerage system etc.
- the flows' inventory with exact information regarding the potential pollutants (identification, quantity, their variability in time etc.)
- the inventory of the pollution sources, effluents, the quantification, evaluation and validation of the causes of pollution
- the most accurate estimation of the contaminated area's extent, both at ground level and in depth

2 The physical and chemical characteristics of the petroleum sludge

Slurry comes out from the extraction of petroleum and it consists of deposition of particles, minerals (sand, clay) strongly impregnated with crude oil in separators, cisterns, collecting tanks related to the petroleum flow in the scaffold (colection and separation units crude oil treatment plant, sewage treatment plant). In terms of aspect, these slurries are semi-solid (pumpable sludge). The mechanical impurities found in petroleum are solid organic and inorganic matter (minerals) that form the sediment (slurry or sludge) which settles at the bottom of the tanks in which the petroleum is stored.

From the extraction process, the collection and treatment of sludge resulting in varying amounts depending upon the amount of oil extracted and processed, for slurries that are stored in pits located apart from separation units.

The stored waste material is composed of:

- liquid phase - residual water, rainwater, crude oil;
- semisolid phase – detritus material, heavy petroleum fractions, drilling fluid.

Using gravity separation a pellicle of oil forms at the surface of pits, which is captured and evacuated periodically through a pump with mobile sip on the right in the park.

In general, the obtained slurry has the following characteristics:

- variable water content, due to different origins of the sludges stored in pits;
- the content of volatile substances and petroleum products of sludge varies greatly from one sample to another;
- different calorific values from one sample to another;
- variable sulphur content;
- variable density 1,17 - 1,22 kg/dm^3;
- percentage of water 25 - 39%;
- volatile substances 15 - 31%;
- minerals 60 - 84%;
- sulphur 0,05%;
- calorific value 720 - 900 kcal/kg;

Sludge resulting from the cleaning of collecting, separation and storage of extracted oil tanks, as well as the sludge resulted from the cleaning of cellar wells is collected and stored in pits specially designed to further oil recovery.

These pits are located within the separator parks, warehouses and storage of crude oil treatment and sometimes near the extraction wells and / or central battle.

The sludges' characteristics determined in the laboratory are:

Table 1.

Sample	Win [%]	Aanh [%]	mcin [%]	Qinf [kcal/kg]
sample 1	34,45	51,99	31,47	2262
sample 2	11,87	43,93	49,41	3819
sample 3	6,99	53,18	43,55	3347
sample 4	25,69	73,47	19,72	1312
sample 5	20,10	60,66	31,43	2302
sample 6	24,59	69,27	23,18	1603
sample 7	45,14	25,33	40,96	3017

2.1 The characteristics of the petroleum sludge

The results of the physico-chemical analysis carried out on the raw material are presented in the table 2:

Table 2.

Sample	1	2	3	4	5	6	7
A anh	73,4680	43,9348	53,1827	60,6604	69,2659	51,9899	25,3271
MgO	0,0410	0,0811	0,0571	0,2188	0,0306	0,0000	0,0000
Al2O3	0,9861	1,0810	1,3806	1,7340	1,7103	0,6884	0,1544
SiO2	6,5104	4,5398	6,9098	7,4924	8,8604	3,5236	0,7823
P2O5	0,0586	0,0832	0,0727	0,0444	0,0456	0,0504	0,0000
SO3	2,8307	1,1277	0,8716	1,1991	1,4398	1,1363	0,7340
Cl	0,1561	0,0282	0,0386	0,0570	0,0563	0,0243	0,0222
K2O	1,2944	0,7613	1,4923	1,2767	1,5792	1,0136	0,0000
CaO	9,0034	11,5887	5,3302	7,6842	7,1774	9,8464	1,0425
TiO2	3,8440	2,0776	2,8396	2,0082	3,4084	3,0045	0,9264
V2O5	0,6606	0,3847	0,1200	0,4563	0,2610	2,7330	0,0000
Cr2O3	0,7710	1,2448	0,0000	0,7624	1,2669	0,0000	0,7809
MnO	0,9325	0,2492	0,3774	0,5696	0,5980	0,4171	0,1207
Fe2O3	25,7830	16,4362	27,6780	25,4778	34,6262	19,3288	8,2948
Co2O3	0,0000	0,0000	0,0000	0,0000	0,1565	0,0000	0,0000
NiO	0,1382	0,0550	0,1256	0,1746	0,1460	0,1759	0,1111
CuO	0,2281	0,0000	0,0000	0,0920	0,2049	0,1251	0,0537
ZnO	0,0000	0,0000	0,0000	0,1074	1,0878	0,0731	0,2529
Ga2O3	0,1610	0,0000	0,0666	0,0000	0,1343	0,0831	0,0000
GeO2	0,4782	0,2838	0,3774	0,3920	0,4435	0,4542	0,2790
As2O3	0,0000	0,2310	0,4986	0,5639	0,6052	0,0000	0,0933
SeO2	0,1397	0,0532	0,0589	0,0000	0,0000	0,1255	0,0000
Br	0,1067	0,0457	0,0498	0,0000	0,1157	0,0594	0,0446
Rb2O	0,2013	0,0000	0,0000	0,0000	0,0000	0,0327	0,2839
SrO	0,3729	0,1559	0,1630	0,1696	0,2460	0,2599	0,0902
ZrO2	0,0000	0,0000	0,1325	0,0000	0,0000	0,0000	0,3679
MoO3	0,0000	0,0000	0,0000	0,0495	0,0366	0,0000	0,0000
CdO	0,4540	0,0000	0,0000	0,3096	0,0000	0,0000	0,9739
BaO	9,4409	1,0787	2,1908	1,6694	0,5969	3,9407	1,0901
PbO	1,4288	0,0000	0,0000	0,0000	0,0000	0,0000	0,1056

In order to obtain inert waste (harmless) the following ingredients may be mixed:

1. slurry oil in proportion of 30 - 60%;
2. residues of petroleum coke, charcoal or sawdust in proportion of 35 - 65%;
3. quicklime in proportion of 5 - 10%

Mixing is being done on a concrete platform, covered as it follows:

1. 10 cm layer of residues of petroleum coke, charcoal or sawdust
2. 30 cm layer of slurry oil
3. apply quicklime by spraying
4. 10 cm layer of residues of petroleum coke, charcoal or sawdust

The pressing of the material is done by repeatedly passing over the mix with an auto compactor.

When the material reaches a compaction degree greater than 80% a compost turning machine will be used to make it loose. The thus obtained loose material should be allowed 3 days in order to complete the reactions of neutralization and adsorption of the volatile compounds by the coke.

The benefits of the proposed technology are:

- converting the oil sludge (hazardous waste) to recoverable composite material that has the characteristics of harmless waste;
- the final disposal of waste treated by conversion to solid fuel.

The ash resulting from the burning of the solid combustible material has the characteristics of an inert waste.

In order to determinate the recipe for inert waste there were performed three series of tests using coke

adsorbent material, in proportion of 35%, 25% and 15% respectively.

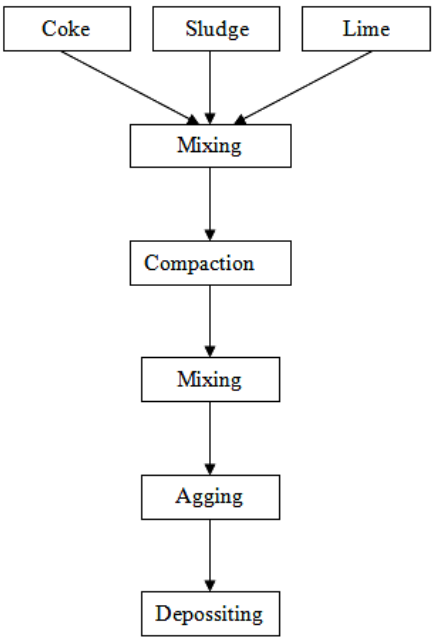

Figure 1. Scheme of proposed flow

The results of the inertization test performed using an adsorbant material in proportion of 35% are presented in the table 3:

Table 3. technical analysis

	Win	Aanh	Vanh	Qinf
sample 1	2,79	43,86	20,80	4275
sample 2	2,66	30,47	36,18	5364
sample 3	2,75	33,82	27,23	5087
sample 4	26,96	61,63	26,47	1998
sample 5	2,46	37,22	28,73	4829
sample 6	2,86	21,88	38,77	6044

The results of the inertization test performed using an adsorbant material in proportion of 25% are presented in the following table 4:

Table 4.

	Win	Aanh	Vanh	Qinf
sample 1	0,59	44,19	29,06	4357
sample 2	0,25	52,51	17,24	3685
sample 3	1,83	33,60	37,82	5158
sample 4	1,42	37,49	30,80	4865
sample 5	1,24	48,74	23,80	3952
sample 6	0,64	48,65	22,13	3986

The results of the inertization test performed using an adsorbant material in proportion of 15% are presented in the following table:

Table 5.

	Win	Aanh	Vanh	Qinf
sample 1	0,59	44,19	29,06	4357
sample 2	0,25	52,51	17,24	3685
sample 3	1,83	33,60	37,82	5158
sample 4	1,42	37,49	30,80	4865

From the previously presented data it is observed that by mixing it with an adsorbent material one may obtain products with obvious energetic characteristics.

3 Conclusions

1. The petroleum industry generates significant quantities of waste, amongst which petroleum sludges have the most powerful negative impact on soil or surface water.
2. Petroleum waste is included in the hazardous waste category, at the same time it is considered to be a persistent pollutant.
3. By mixing it with adsorbent materials, such as coke breeze, this waste can be stabilized and brought to the charcateristics of hazardous waste, except the parameter: „Total Organic Carbon".
4. Inerted resulting product has real energetic characteristics and can be cremated mixed with coal in any power plant designed to burn coal with a volatile content of over 20%.

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