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Modeling of separation processes and chemical removal of paraffin

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Abstract— During the exploitation of a hydrocarbon deposit and during the transport through pipes, from the fluids that move from the layer, in the well and in the surface installations (processing and transport) a large amount of particles in solid form. They are deposited at different points of this route. Paraffin or petroleum wax is the best known solid phase that separates and has the formula C_nH_{2n+2} (starting from $C1_6H_{34}$ to $C_{64}H_{130}$).The article presents a numerical model regarding the formation of paraffin and especially a way to eliminate it by using a polymer added to crude oil.Also presented are the results of chemical experiments that had the role of observing the behavior of paraffin during heat desorption and especially the behavior of paraffin oil during polymer treatment.

Index Terms— paraffin, oil, wax, modeling, polymer.

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1 INTRODUCTION

During the exploitation of a hydrocarbon deposit and during the transport through pipes, from the fluids moving from the layer, in the well and in the surface installations (processing and transport) a large amount of pressure is separated, under certain conditions of pressure and temperature. particles in solid form. They are deposited at different points of this route.

Paraffin or petroleum wax is the best known solid phase that separates and has the formula C_nH_{2n+2} (starting from $C_{16}H_{34}$ to $C_{64}H_{130}$) [1].

Paraffin as waste (as found in the mining and transportation industry) differs from paraffin obtained in the refinery by the following characteristics [2]:

a. Paraffin from oil sites is a mixture of liquid components, solid products (paraffin, cherries) in the form of fine crystals, to which are added asphalt substances, resins, sand, marl, clay.

b. Paraffin obtained in the refinery consists of mixtures of hydrocarbons extracted from certain products of distillation of petroleum oils or of oils from bituminous minerals. It is a translucent substance, white or yellowish, with a rather pronounced crystalline structure.

Considering the paraffin content of crude oil, in order to determine their behavior during extraction, transport and processing, Romanian crude oil was divided into three categories, namely:

- paraffinic oils (containing more than 2% paraffin);
- semi-paraffinic crude oils (which have a paraffin content between 1-2%);
- non-paraffinic crude oil (having a paraffin content of less than 1%).

The separation and deposition of paraffin from crude oil is influenced by temperature and pressure.

By decreasing the temperature, a starting point of paraffin crystallization is reached, and by decreasing the pressure, some of the hydrocarbons come out of the solution, so that the dissolution capacity of the solid particles decreases.

The initial crystallization temperature is between 35 °C-38 °C.

This temperature is reached:

- during oil extraction between 600 and 1000 m, according to the geothermal gradient and depending on the quality of the oil,
- during the transport of crude oil on pipes it is reached after about 5 km of pumping (crude oil taking the soil temperature, which is not higher than 24 °C).

Paraffin separates from crude oil into small crystals. These, due to the movement of the fluid, come into contact with each other and agglomerate around a core (this can be a foreign body such as sand, marl or even fine metal particles due to corrosion).

These agglomerations of paraffin crystals are deposited on the interior walls of oil installations, the phenomenon being accentuated by their roughness.

Paraffin deposition is accentuated:

a. for intermittently producing wells due to repeated oil spills on the inner walls of the extraction pipes,

b. For pipes that pump only paraffinic crude oil and intermittently due to the shutdown of crude oil and its stationary for longer periods of time (in which the crude oil temperature reaches values equal to soil temperature).

The areas where the paraffin deposit takes place in the oil extraction and transport installations are, according to the mentioned conditions, the following:

- in the pores of the layer - in the area in the immediate vicinity of the wellbore;
- at the exit of the layer on the operating column at shallow wells
- inside the column of extraction pipes on the pumping rods at the wells that produce in deep pumping;
- inside the surface installation and mixing pipes.

Paraffin deposits produce:

a. the decrease of the production capacity of the probes, due to the clogging of the pores at the exit of the layer

b. reducing the flow section of the fluids through the transport pipes,

c. increasing the viscosity of crude oil by increasing paraffin deposits.

2 PARAFFIN PROPERTIES

2.1 Definition

Paraffin is a solid, white, translucent substance consisting of a mixture of saturated hydrocarbons obtained from the distillation of crude oil or coal and used in the manufacture of candles, the impregnation of paper and fabrics, as a raw material in the chemical industry [3].

From the studies carried out by the Department of Bioengineering, Chemical and Physical Engineering [2], for the project "ARTERIAL BLOCKAGE in the PETROLEUM and NATURAL GAS INDUSTRIES Project", it is specified that paraffin (from the refinery) is a waste composed of paraffinic hydrocarbons (C_8 -C_{36}), and has a macrocrystalline structure.

Paraffin from the refinery is found in solid state entering liquid state at about 37 °C (99° F), being formed by alkanes that fall in the range $8 \leq N \leq 36$ of the chemical formula C_nH2_{n+2} [5].

Paraffin or petroleum wax, is the best known solid phase that separates and has the formula C_nH2_{n+2} (starting from $C_{16}H_{34}$ to $C_{64}H_{130}$) and is a mixture of liquid components, solid products (paraffin, cherry) in the form of crystals fine, to which are added asphalt substances, resins, sand, marl, clay. There are also wastes formed from naphthenic hydrocarbons (C_{30}-C_{60}) with a microcrystalline structure [4].

The paraffin I studied is petroleum wax and is different from the fuel known in the UK, Ireland and South Africa as paraffin oil or kerosene (refinery paraffin) in most of the US, Canada, Australia and New Zealand [6] .

The name paraffin is derived from the Latin parum ("barely") + affinis, which means "lack of affinity" or "lack of reactivity", indicating the non-reactive nature of paraffin [8].

Petroleum wax and paraffin are insoluble in water and soluble in benzene and have a density greater than 0.9 (Figure 1).

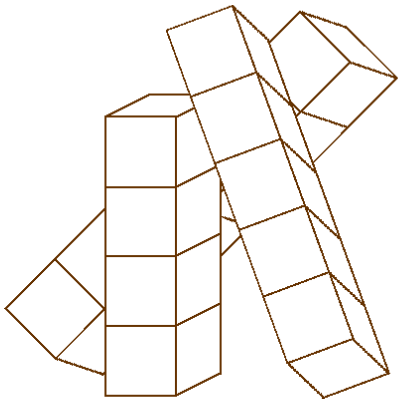

Fig.1.Paraffin microcristalyne

Pure paraffin is an excellent electrical insulator with an electrical resistivity of between 1013 and 1017 ohms / meter. [9] (being the best insulator except plastics and Teflon).

It is an excellent material for storing heat with a specific heat capacity of 2.14-2.9 J g-1K-1 (joule per gram Kelvin), and a melting heat of 200-220 g. J-1. [10] (Figure 2)

This property is exploited in drywall, paraffin is infused into drywall during manufacture, so that when it is installed, paraffin melts during the day, absorbs heat, and solidifies again at night, releasing heat [11].

Paraffin wax along with retractable radiators has been used to cool selenium vehicles [12].

The wax expands considerably when it melts and this allows its use in thermostats.

In pipes, paraffin is deposited on the interior walls due to the fact that in their lubrication area the speed is minimal (especially in the case of laminar flow).

As seen in Figure 3, the paraffin crystals are deposited on the inner walls due to their lower temperature than in the center of the flow axis (the temperature of the pipe wall is equal to that of the ground).

Fig.2. Paraffin treat

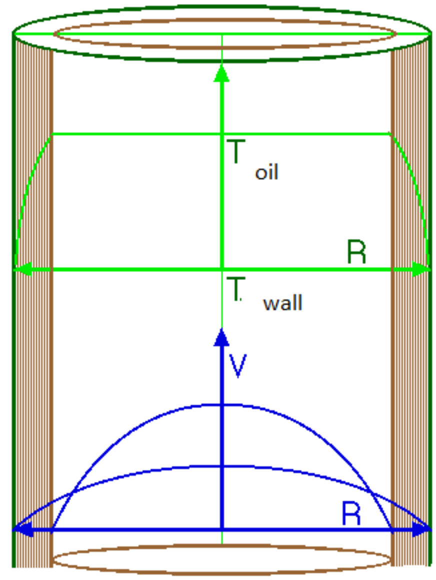

Fig.3.Oil Flow trough the pipe

2.2 Methods of disposal of paraffin-type waste from the activity of oil extraction and transport

Currently, the heat treatment of this type of waste is used to remove paraffin.

Thermal processes in paraffin treatment include incineration and pyrolysis [13].

By far the most important thermal process is currently the incineration of petroleum wax waste.

In the modern management of petroleum wax waste, incineration has the role of:

• inerting, minimizing air and water emissions;
• destruction because these materials are harmful organically,
• concentration of inorganic materials present in the wax;
• reduction of the mass of waste to be stored, especially of the volume;
• transfer of this residual waste in secondary raw materials in order to protect the other material resources.

This method was chosen because the currently existing installations ensure :

• safety of operation, co-incineration furnaces exist in the cement industry;
• does not require new investments;
• does not require new spaces;
• processed quantities are very small so no new investments need to be provided.

That is why this method of heat treatment is used, being the easiest method.

A waste incineration plant consists of the following areas of operation:

• waste collection;
• temporary storage, pre-treatment (if necessary);
• feeding in the incineration unit;

• disposal and treatment of residual ash;
• treatment and recovery of emissions

3 Methods for Reducing and Combating Paraffin Depozits

Methods for reducing and combating paraffin deposits are as follows :

- prevention methods by which precipitation and paraffin deposition are avoided or delayed;

a. Addition of polymer-type additives, in order to reduce the freezing temperature. It is known that in order to keep paraffin crystals in suspension, it is necessary to reduce the freezing temperature, a process that is very often used in the treatment of diesel and oils. In the particular case of paraffinic crude oil with a freezing point between 5 °C and 25° C, these additives are widely used to ensure transport through pipelines. A large number of low molecular weight copolymers have been created for this purpose, such as ethylene-vinyl acetate copolymer, copolymers of acrylic, methacrylic and maleic esters.

However, these copolymers ensure that the product is exceeded within limited limits (40° C and 60 °C) and do not ensure the removal of paraffin from the area of the pipe walls (where the temperature is close to that of the soil).

In the present study we used a copolymer of vinyl acetate as an example of freezing reduction.

b. methods of cleaning and removing paraffin deposited in the equipment through which paraffin oil circulates.

This procedure consists in inserting a plug of low, medium and high density polyurethane (Godevil-pig type).

In the literature this type of cleaning is less researched, being the prerogative of chemical engineers with applications in the oil industry and especially recently in medicine.

Most materials study how to deposit paraffin particles on the walls of pipes.

In the report Controlling Wax Deposition in the Presence of Hydrates, the effects that paraffin deposits have on oil tanker manifolds and unloading equipment, as well as how to reduce them.

This study describes methods to reduce paraffin deposits by:

a. Use of seawater mixed with crude oil,

b. The introduction of hydrated gases in the cold oil, the method used in Romania in the form of the introduction of gases in the solution for reducing the freezing temperature,

c. The introduction under pressure of hydrated gases for the elimination of paraffin deposits (biphasic transport), a method difficult to achieve due to the high pressures required,

d. Pipeline development,

e. Chemical cleaning of pipes,

f. Treatment of the interior of the pipes with substances that ensure the walls of the pipes without roughness (a polymeric film). This method is useful for large diameter and short length pipes, using phenols, epoxy and Teflon as paints.

In Romania until now, a series of researches have been carried out and a series of methods have been implemented in the field of cleaning pipes from paraffin deposits, the most frequently used being:

a. Cleaning by mechanical means,

b. Cleaning by chemical methods.

3.1. Reducing paraffin deposits by using water to create a crude water emulsion

The system consists of introducing salt water into the crude oil for the transport of crude oil (The temperature of crude oil T is higher than the temperature of the high water T).

This is to reduce the viscosity and freezing temperature by creating a water-like emulsion in crude oil (crude oil temperature T becomes equal to that of seawater).

So a natural depressant is created which will have the effect of agglomerating the particles in the emulsion (Figure 4).

Another paraffin recovery system is represented by the paraffin decanter-separation heat exchanger which then recovers the paraffin by introducing the heat exchanger into the sea,

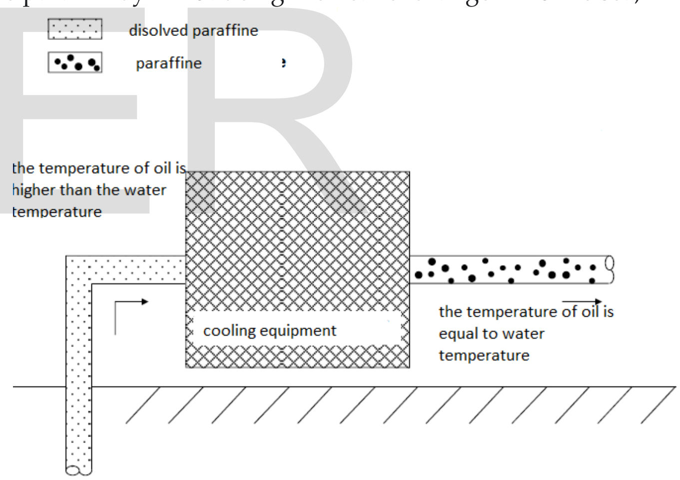

Fig.4. Reducing paraffine equipment (by cooling)

The hot oil is introduced into the exchanger, following the cooling of the oil and especially the low transport speed of the oil (in laminar regime) the paraffin is deposited on the walls of the exchanger. A paraffin sensor is mounted which, when the weight of the paraffin is higher than the one accepted in the pipe, is removed and the washing is washed with chemicals.

3.2. Reduction of paraffin deposits by gas dissolution

The system allows the use of a gas jet in the oil and thus ensures an agglomeration of paraffin particles by the fact that the fluid velocity decreases and therefore the paraffin particles are agglomerated (gas is used because the weight of the paraffin

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particle is higher than the oil-gas mixture, then the particle is deposited on the bottom of the pipe, and therefore it is then recovered by digging it) (Figure 5).

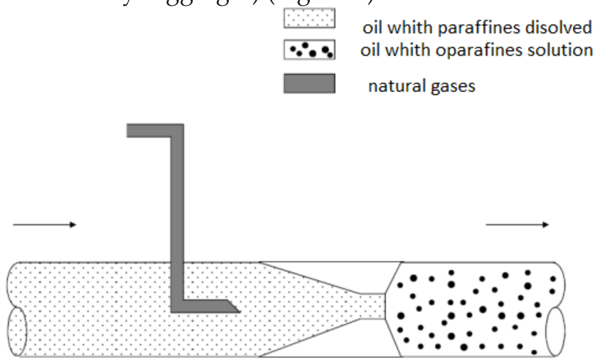

Fig. 5. Reducing paraffine equipment (by methane injection)

3.3. Reduction of paraffin deposits by ensuring a very fine inner layer of paint or other products (layer without roughness)

This method is intended to reduce the roughness of the pipe, where paraffin is stored (Figure 6).
This method is also useful in reducing internal corrosion (Figure 7).

Fig. 6. Reducing paraffine by epoxy layers

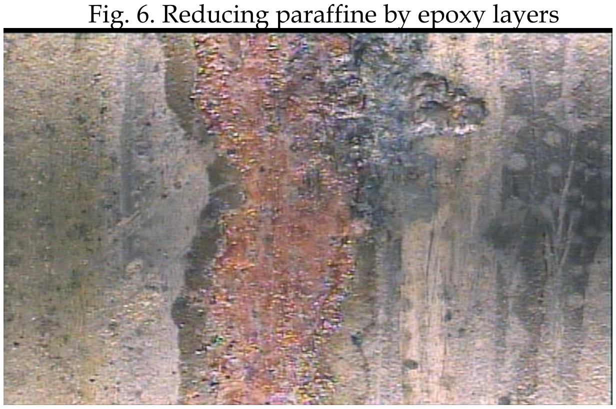

Fig. 7. Internal corrosion

3.4.Reduction of paraffin deposits by pigging pipelines

This method has the role of removing paraffin deposits by introducing a polyurethane cleaning device (Figure 8).
When the temperature of paraffin formation is equal to or lower than the temperature of crude oil, the deposition of perfin particles takes place, forming deposits (Figure 9).
These deposits solidify over time, consisting of paraffin and sand particles. Naphthenes were also found in these deposits, the structure being macrocrystalline.
Figure 8 shows that if TW is the oil temperature and TWAT is the paraffin precipitation temperature due to the decrease in temperature there is a reduction in pipe diameter .

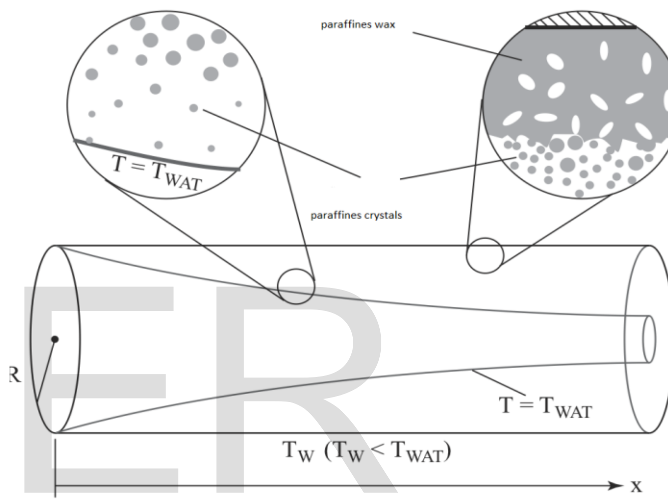

Fig. 8. Formation of paraffin deposits on the oil transport pipeline

4. Modeling of Chemical Separation Processes Removal of Paraffines

During the mechanical cleaning of the pipe, it is found that areas with uncleaned paraffin remain (areas of internal corrosion or roughness).
That is why the chemical cleaning of the pipes is also accepted by introducing mixtures of solvents.
The most commonly used solvents are the following:
a. Carbon disulphide is one of the best known solvents for removing petroleum wax deposits; however, it is extremely dangerous and its use is banned in most countries. It is explosive, with a flash point of -22 ° F (-30 ° C) and a self-ignition temperature of 212 ° F (100 ° C). It is also very poisonous.
b. Chlorinated solvents are excellent solvents, but they damage the catalysts used in the refining process and are considered a fire and health hazard. Therefore, their minimal detection in any crude oil leads to its rejection by refineries.
c. Benzene is an excellent solvent, however, it is highly flammable and is a carcinogenic (cancer-causing) compound.

d. Xylene and toluene are also excellent solvents, however, the saturation point is quickly reached, so large amounts are needed to clean the pipes.
When solvents come into contact with the deposits, they dissolve deposits (of heavy hydrocarbons) until the solvents reach their level of saturation.
If the solvents are not removed immediately after their saturation level is reached, then some of the dissolved paraffin will precipitate out of the solution (sap recrystallize).
Sometimes, recrystallization leads to a clogging problem that is worse than what was present before the treatment, due to the agglomeration of deposits in areas that did not previously have any deposits.

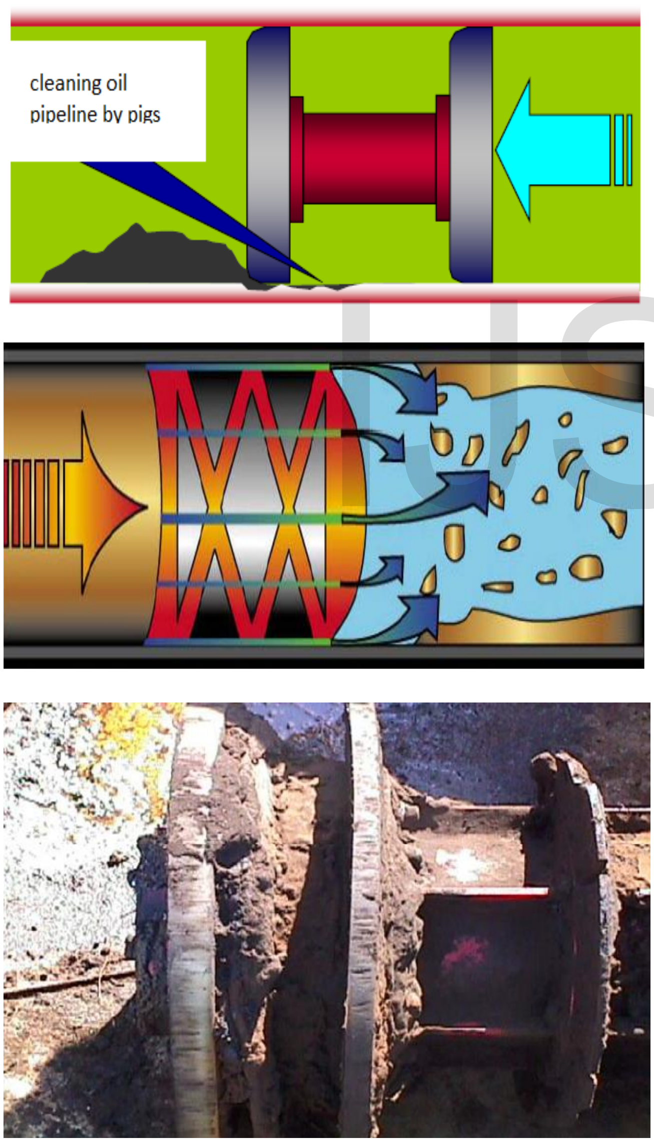

Fig.9. Cleaning paraffines by pig

5. Heat tratament of paraffines

To reducing paraffines quantity, We porposed two techniques:

- Thermal desorbtion,
- Combustion.

Thermal desorbtion is same to distillation of oil, but I modify installation (distillation to 100 °C) (Figure 10).
Combustion is process to fire paraffines (combustion to 100°C).
For burning we used 17.72 grams of parafines.
This parafines were taken and burned
After finsih, 16.69 grams of oil and parafiness is not recovery
Wax recovery = 1.03 grams.
Percent of oil recovery by paraffines (burning) 5,81 %

By thermal desorption we used 29.51 grams of paraffines and 24.31 grams recovery.
Wax disposal by distillation 5.2 grams.
Percent of oil recovery by paraffines (thermal recovery) 82,37 %


Fig.10. Thermal desorbtion of paraffines

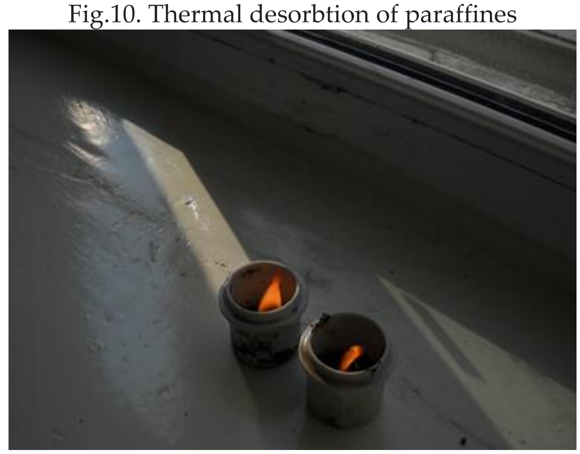
Fig.11. Combustion of paraffines

6. Conclusion

Considering that on a pipeline transporting paraffin oil for a distance of 50 km, about 50 kg of paraffin appears weekly during the cleaning operation, it is absolutely necessary to find methods to eliminate only in this case a quantity of at least 2600 kg per year. .

That is why this material has succeeded:

a. To determine the appearance of paraffin in the activity of transport and storage of crude oil,

b. To make a mathematical model regarding the behavior of paraffin in pipes,

c. To analyze in the laboratory the best method of disposal of this type of waste,

d. to observe which heat treatment methods are better.

Therefore, the operators in the oil industry tried to find methods to eliminate this waste, the most useful method being incineration in rotary kilns.

But this method used so far, in addition to destroying this waste, also brings problems in the elimination in the atmosphere of compounds such as SOx, NOx, CO_2, CO, produced during combustion in the furnace.

That is why this study aims to find other methods of disposal of this type of waste, describing the method of thermal desorption.

Another method of eliminating this type of waste is to reduce it to a minimum by treating paraffinic crude oil with polymers.

Following this process, the paraffin is transported to the refinery, being processed in the distillation column and resulting in the refining paraffin very useful in the composition of waxes, in the manufacture of food packaging, in articles for medical equipment and in cosmetics.

We described the current state of research in the field of paraffin removal as well as how it appears.

The article presents a numerical model regarding the formation of paraffin and especially a way to eliminate it by using a polymer added to crude oil.

Also presented are the results of chemical experiments that had the role of observing the behavior of paraffin during heat desorption and especially the behavior of paraffin oil during polymer treatment.

In conclusion the best method of disposal of this type of waste and future research in this field is thermal desorbtions.

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