

# Valorization of Oily Sludge in Arzew Refinery



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**Abstract** The sludge treatment is a difficult phase in the fight against pollution. Indeed the scrubber with a difficult problem was solved for many reasons: scarcity of land available for application and filing need sets requirements of the environment and public hygiene. Moreover the economic importance of this problem is illustrated by the importance of the cost both in investment and operating it can represent. Oily sludge with a significant calorific value which represents 90% of methane (CH<sub>4</sub>) can be considered as an interesting fuel. The impact related to its combustion in poor conditions can be important. The main objective of this study is to thermally treat oily sludge from the oil industry at the level of the RA1/Z refinery and then make a characterization of sludge by: X-ray fluorescence (XRF) to determine the mineralogical composition mass in the form of oxides, e.g., percentages (% SiO<sub>2</sub>, % CaO, % Fe<sub>2</sub>O<sub>3</sub>, % K<sub>2</sub>O, etc.). X-ray diffraction (XRD) for sentencing phases, for example, silica, crystalline, or amorphous. Fourier-transform infrared spectroscopy in attenuated total reflection (FTIR-ATR) to determine functional groups, for example, O–H, C–H, C–Cl, Br–C, C–I, C–N, N–H, etc., and finally detection of heavy metals by atomic absorption spectroscopy (AAS). This study is to determine the sources of heavy metals in industrial wastewater which predictably sludge quality. Several origins can be identified such as industrial activities. In a second part, we're interested in studying the operating constraints due to the presence of the sludge contaminated as well as health and environmental risks. One is interested in identifying different Condit's other than spreading agricultural.

**Keywords** Agricultural, Environmental, Metal heavy, Mineralogical, Oily sludge, Wastewater

## 1 Introduction

Water was always synonymous with life and growth. This “blue gold” is first of all essential with the survival of the human being. Water is also essential to agriculture and breeding independent sources of food for any company. The

natural and drinkable fresh water is mainly contained in the icebergs and the glaciers. The remainder being in the lakes, rivers, and underground reserves. These sources of cumulated fresh water account for hardly only 2.5% of terrestrial water. For a long time, no one was hardly concerned with the manner of supplying itself out of water of quality. Nature has always been enough to provide this invaluable resource [1]. Following the industrial revolution and with the intensification of agriculture answers the needs of an increasing population. The fresh water worldwide consumption did not cease increasing since the beginning of the twentieth century. In the one century space, the world population has tripled, whereas the fresh water consumption was multiplied by six. The high standard of the population living conducts more water consumption for domestic and industrial uses, as a consequence more discharge of wastewater, which has an impact on the quantity and water quality. This phenomenon is worsened by the reduction in the capacity car purifier of the rivers (clearing out dredging's artificial drains of the rivers). Moreover, following the increasing urbanization with the erosion of the grounds and the deforestation, water infiltrates less and less deeply in the ground and more quickly joins the rivers and the seas. Also everywhere in the world, the fresh and drinkable water is an increasingly expensive and increasingly rare good. The first structured sewerage systems appeared about 1,850 primarily with the aim of cleansing of the cities. As for the precursory centers of purification of our modern stations, they developed in Europe at the beginning of the twentieth century [2]. If the man wanted to continue to enjoy this natural good, it was indeed necessary to reduce the polluting load of wastewater, as well domestic as industrial. In Algeria, there exists more than one hundred of wastewater treatment plant (WWTP) of which about 60 "known as urban" devoted to domestic wastewater. Others were installed in the production facilities. The need to purify wastewater will be increasing in Algeria and in other countries because of the demography and the increased consumption of the urban and industrial areas. Who says purification of water also says production of muds. However, the main objective of these stations is to reduce the environmental risk coming from wastewater discharge and to guarantee the rejection of treated water with defined quality by paying attention to the sludge generated by the purification processes. The current trend is different in the direction where muds as well as purified water are regarded as an element which contributes to the environmental impact of a purification plant. The activities listed in the industrial park of Arzew are at the origin of several pollution. Most important are industrial water of rejections coming from the processing centers of oil, the modules of treatment of gas and water services (industrial water for the desalting of the crude water of washing and water fire protection). Refinery is provided with a purification plant which will treat all; in particular, the effluents will split waste oil and muds [3]. Sludge treatment is a difficult phase for the fight against pollution. Indeed, the scrubber has a difficult problem to solve for multiple reasons: scarcity of land available for spreading and depositing, necessities and requirements of the environment, and public hygiene [4]. The purpose of this study is to characterize and investigate

the feasibility of converting oily sludge to clean fuel that meets energy and environmental requirements [5].

## 2 RA1/Z Complex Presentation

The Algerian economy is dominated by industries generated by gas of Hassi R' mel and the oil of Hassi Messaoud. In the northeast of Oran, the industrial center of Arzew, allows the liquefaction of gas and the refining of oil. In 1970 it was realized with the refinery of Arzew by Japan Gasoline Company(JGC) and inaugurated in 1973 and managed by NAFTEC after the reorganization of SONATRACH [3].

It was conceived to:

- Treat the crude oil of Hassi Messaoud
- Treat imported reduced crude (production of bitumen)
- Satisfy the needs for consumption out of fuels, lubricants, and bitumen of the national market
- Export the surplus products (naphtha, kerosene, fuel, and gas oil)

The refinery extends on a surface from 170 ha including/understanding production units of the fuel, lubricant, and bitumen. In 1978 following the needs important for lubricant, the construction of another unit integrated of production of 120,000 T per annum of basic oil was launched [3].

### 2.1 Production Capacity

The milked refinery:

1. 2.5 million tons per year of Saharan crude oil
2. 280,000 tons of reduced crude imported for the production of the bitumen [3]

### 2.2 Geographical Location

The refinery of Arzew is established in the industrial park to 2 km of Arzew; it is located on the plate of the locality of El Mohgoun at the crossroads of the trunk road N° 11 (Oran–Arzew) and the trunk road N° 13 (Arzew–Sidi Bel Abbas) and at approximately 40 km of Oran as shown in Fig. 1.

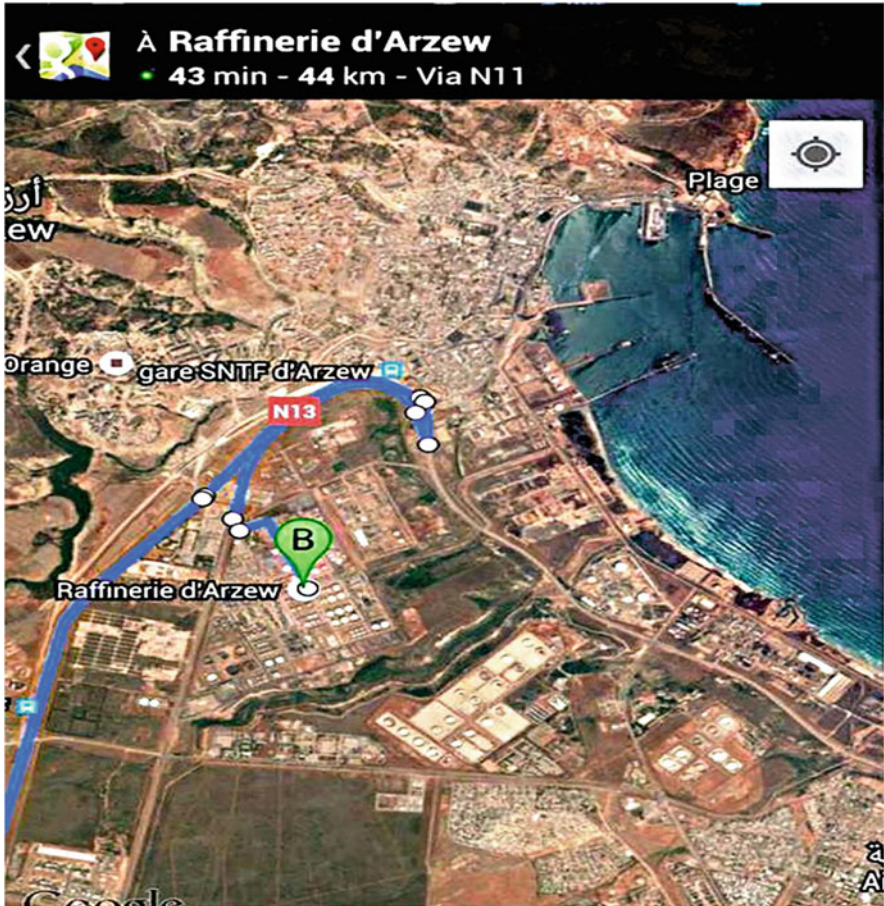


Fig. 1 Geographical location of the refinery of Arzew [3]

### 2.3 Description of the Production Areas of the Arzew Refinery

- Zone 1: Parking
- Zone 2: Standby station
- Zones 3 and 19: Utilities

Utilities are an important area within the Arzew Refinery producing steam, electricity, air service and instrument, and distilled water.

- Zone 4: Fuels

The Algerian crude from Hassi Messaoud is used as main load in zone 4. It consists of three (03) following units:

- Unit 11: atmospheric distillation (topping)

- Unit 12: platforming or catalytic reforming with three (03) reactors
- Unit 13: plant gas production (butane and propane)
  - Zone 07 and 05: Lubricants
- Unit 21/100 (vacuum distillation)
- Unit 22/200 (propane deasphalting)
- Unit 23/300 (furfural extraction)
- Unit 24/400 (MEP/toluene dewaxing)
- Unit 25/500 (hydrofinishing)
  - Zone 06/unit 3,000
- Unit 51/3,100: Finished oil mixing and conditioning unit
- Unit 52/3,200: paraffin treatment and conditioning unit
- Source treatment of acidic waters (acidic water depletion)
- Primary treatment in API separators
- Intermediate processing to complete the H&G removal
- Biological secondary treatment
- Clarification of the effluent

Other sources contribute to the pollution of the natural environment. It is the sanitary and domestic waters conveyed in underground networks separating toward sea [6].

### **3 Industrial Sludge Generalities**

The environment is one of the pillars of sustainable development. For a long time, it was forsaken with the profit of economic and the social one. It is obvious today that the company and the economic activities will have to be built on a better balance of these three realities closely dependent. It is about a new and considerable challenge, which is carrying opportunities and innovations [7]. Industrial waste is a type of waste produced by the activity of industries. These industrial discharges are opposed to domestic waste coming from daily household activity, which originates mainly from the industry, construction, services, and agricultural activities. Within the framework of the responsibility widened for the producer who is responsible for the management of his waste until their elimination or their final valorization [8].

#### ***3.1 Principle and Objectives of the Regulation***

- To reduce
- To reuse
- To recycle [6]

### ***3.2 Effect of the Industrial Pollutant on Health***

Industrial pollution has very serious effects on the health of man. One distinguishes several types of pollution corresponding to several types of diseases [9].

### ***3.3 Air Pollution***

Industrial pollution is due to the presence of toxic particles in the air; it is caused by industrial smoke (refineries or exhaust fumes of the cars – CO<sub>2</sub>), manures or pesticides, methane, and ozone. This pollution increases the disease risks to man:

- Respiratory diseases: asthma, bronchiolitis, angina, respiratory insufficiency, and allergies
- Cardiovascular diseases: myocardial infarction, angina pectoris, and accident vascular cerebral
- Risk on the reproduction of the man
- Cancers
- Skin diseases [10]

### ***3.4 Pollution of Soil***

The pollution of soil is due to the artificial fertilizers or pesticides which are widespread on the arable lands to improve the output. Their use causes:

- Food poisonings
- Cancers
- Endocrine disturbances (glands) [11]

### ***3.5 Pollution of Water***

Pollution of water is related to that of the grounds because water infiltrates in the ground and will contaminate the groundwater. The risks on health are:

- The allergen's effects (causing allergies): rhinitides, conjunctivitis, asthmas
- Viruses and microbes, which make non-drinking water and cause many diseases [12]

### 3.6 *Muds Definitions*

- Muds: liquid-solid matter effluents strongly charged (with concentrations in solid of about 1–10% correspond 10–100 g/L)
- muds: inert chemically or ferment target (odors)

The treatment of muds is an additional problem with that of the water treatment. Various mud classes:

- Absorbent organic mud
- Absorbent oily mud
- Hydrophobic oily mud
- Absorbent mineral mud
- Hydrophobic mineral mud
- Fibrous mud

Mud indicates a residue organic or mineral, solid, liqui, or pasty.

A mud is characterized by its aspect, but specifically its origin supplemented by its chemical characterization, which will determine its die of treatment.

Broadly a mud is characterized by the following parameters:

- Concentration in polluting elements
- pH

Dry matter concentration (DM) is expressed, either in g/L for the slurries or in dryness (% in weight of DM):

- 6–10% of DM: liquid muds
- 10–20% of DM: pasty muds
- >20% of DM: solid muds [13, 14]

### 3.7 *Different Types of Muds*

One distinguishes here:

- Muds of industrial wastewater treatment plant WWTP by physicochemical treatment.
- Hydrocarbon muds and bottom of tanks resulting from the clearing out of unutilized fuel tanks.
- Muds of clearing out the hydrocarbon separators, sluices, grease removers located in particular in pretreatment before rejection at the natural environment and/or in the networks of rainwater.
- Muds of urban purification plant or agribusiness industry exits of the biological treatment of the effluents nonconformity to be épandues.



- Muds of clearing out and matters of drainings not spreadable are resulting from the maintenance of the urban and industrial networks of cleansing (clearing out of the networks) or installations of autonomous cleansing (septic tank).
- Muds of machining [13, 14].

### **3.8 Management of Muds**

The evacuation of muds is the last link of the purification of wastewater. In order to preserve the aquatic environments, the placement of lawful and perennial dies of evacuation of muds is essential. These dies indeed condition the good quality of the rejection of the purification plants (regular extraction of muds of the basins of purification) and guarantee a respectful destination of muds of the environment.

Muds come from the purification of domestic wastewater in the purification plants. The wastewater is brewed there in basins where one supports the development of the microorganisms which will degrade and absorb the organic matter. One then separates by decantation of muds of purified water which is rejected in the medium. Muds are primarily made up of water, rock salt, and organic matter. They contain nitrogen and phosphorus, which are fertilizing elements for the plants. Each one among us produces approximately 3 L of muds per day.

### **3.9 Industrials Muds**

The stages of industrial processing liquid waste generate by-products and waste which is recovered and forms industrial muds. These muds of nature specific to industries must undergo treatments or pretreatments so to reduce their quantity, to improve the public health and quality of muds, and to develop them if possible.

Muds can come from several sources:

- Industrial purification plant
- Hydrocarbons resulting from the basic clearing out of tank
- Machining
- Clearing out various and matters not spreadable whitebaits

One also distinguishes three types of muds according to the dry matter contained:

- slurries: 5–10%;
- pasty muds: 10–20%;
- solid muds: + of 20%.

The principal treatments of industrial muds are done with the upstream of the industrial process. Indeed, the control of the productions and the optimization of the processes often make it possible to reduce the volume of muds significantly to be treated.

The treatment of muds obtained is made to share several techniques. Their use depends on chemical and physical nature of muds thus obtained:

- Thickening
- Dehydration
- Anaerobic digestion
- Treatment of lubricating muds
- Oxidation by the wet process
- Drying
- Incineration
- Chemical conditioning and treatment of the odors
- Storage

The valorization of industrial muds is an important outlet. The muds obtained after treatment (mainly muds resulting from agribusiness industry) can indeed be used for agriculture thanks to their physicochemical properties.

### ***3.10 Technical of Reduction and Water Elimination of Muds Waste of Machining***

To reduce the volume of proceeded, different muds are implemented including/ understanding by order ascending of effectiveness and cost, thickening, dehydration, and drying.

### ***3.11 Wastewater Treatment Plant WWTP***

Each day the man consumes large quantities of water as well for his personal use as professional. This wastewater is collected in order to be purified. The collected wastewater has two origins: an origin domesticates (Urban Wastewater: UWW) and an industrial origin (Industrial Wastewater: IWW). In the case of zones little or fairly industrialized, this wastewater is mixed and treated together in a wastewater treatment plant (WWTP) which aims to reduce the polluting load that they convey in order to return in the aquatic environment water of good quality [15]. Muds come from the purification of wastewater. They result from the biological activity of the microorganisms living in these stations which transforms the matters transported by wastewater so that they can be extracted about it [16].

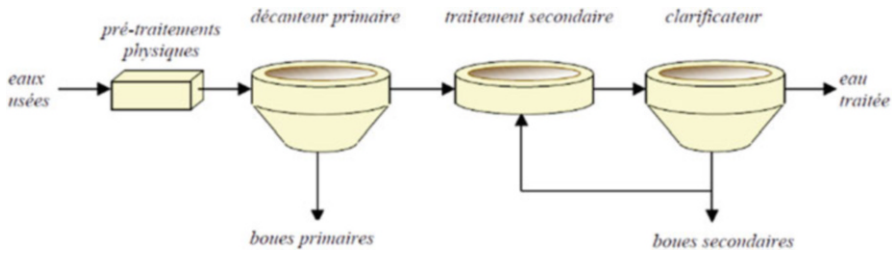


Fig. 2 Diagram of wastewater treatment plant WWTP Degrémont [17]

### 3.11.1 Fonctionnement of Wastewater Treatment Plant WWTP

Wastewater treatment plant WWTP consists in reducing the load out of organic matters and mineral. At the time of this stage, it occurs a transfer of pollution of the liquid phase (water) toward more concentrated phase (muds), and a gas phase ( $CO_2$ ,  $N_2$ , ...). The production of waste muds is thus completely dependent on the die of water treatment Degrémont [17] in Fig. 2.

### 3.11.2 Various Types of Muds of Wastewater Treatment Plant WWTP

Muds are mainly made up of solid particles not retained by the pretreatments upstream of the purification plant of not degraded organic matters, mineral suspended matter, and microorganisms (degradative bacteria essentially). They are presented in the form of a “thick soup.” which undergoes then treatments aiming in particular at reducing their water content Champiat [16].

Muds of purification plants are classified into four great groups Degrémont [17].

#### Primary Muds

They result from the primary education treatment and are produced by simple decantation at the head of the purification plant. These muds are fresh, i.e., not stabilized (strong content of organic matter), and strongly fermentable. From the nature of the new installations, they tend to disappear Degrémont [17].

#### Muds Secondary or Activated

These muds are stabilized biologically results from biological treatment by means of the properties épuratoires of the microorganisms consequently the mineral matter,

and the refractory organic matter are accumulated while the biodegradable organic matter is used as a substrate with the purifying microorganisms. These microorganisms mainly of the bacteria, use biodegradable pollution for their maintenance and their growth. The formed products are cells, carbon dioxide, and water [18, 19] as shown in Figs. 3 and 4 [18, 19].

### Mixed Muds

The mixture of primary muds and secondaries leads to obtaining mixed muds. Their composition is dependent on the quantity of primary and secondary muds produced. Very fermentable, these muds undergo then the stabilizing treatment Degrémont [19].

### Physicochemical Muds

These muds result from a using treatment of the mineral flocculating agents (aluminum or iron salts). The physicochemical treatment is mainly used on industrial muds or for stage with under dimensioning of certain purification plants (for example, stations located in tourist areas) Degrémont [19].

### 3.11.3 Different Dies Treatment from Muds

Waste muds arise in a liquid form and with a highly fermentable organic matter load. These two characteristics are awkward and pose many engineering problems for their evacuation “whatever the destination among which them transport and their storage, which often lead to problems of handling and smell pollutions. This imposes the choice of a die of treatment as of the installation of the WWTP.

Generally, sludge treatment has two objectives:

#### Stabilization

To prevent or reduce the problems of fermentation and to avoid smell pollutions thus. Stabilization can be biological by aerobic or anaerobic way (methanization) or chemical (liming or other treatments)[22]. Biological stabilization has the advantage of limiting the later evolution of the composition of muds.

#### Dehydrations

The concentration of muds which aims to reduce their volume (more than water 97%) by thickening and/or dehydration to facilitate thereafter their transport and their storage. Conditioning is often used upstream to support separation liquid-solid using organic flocculating agents of synthesis or minerals and pressure-sealing.

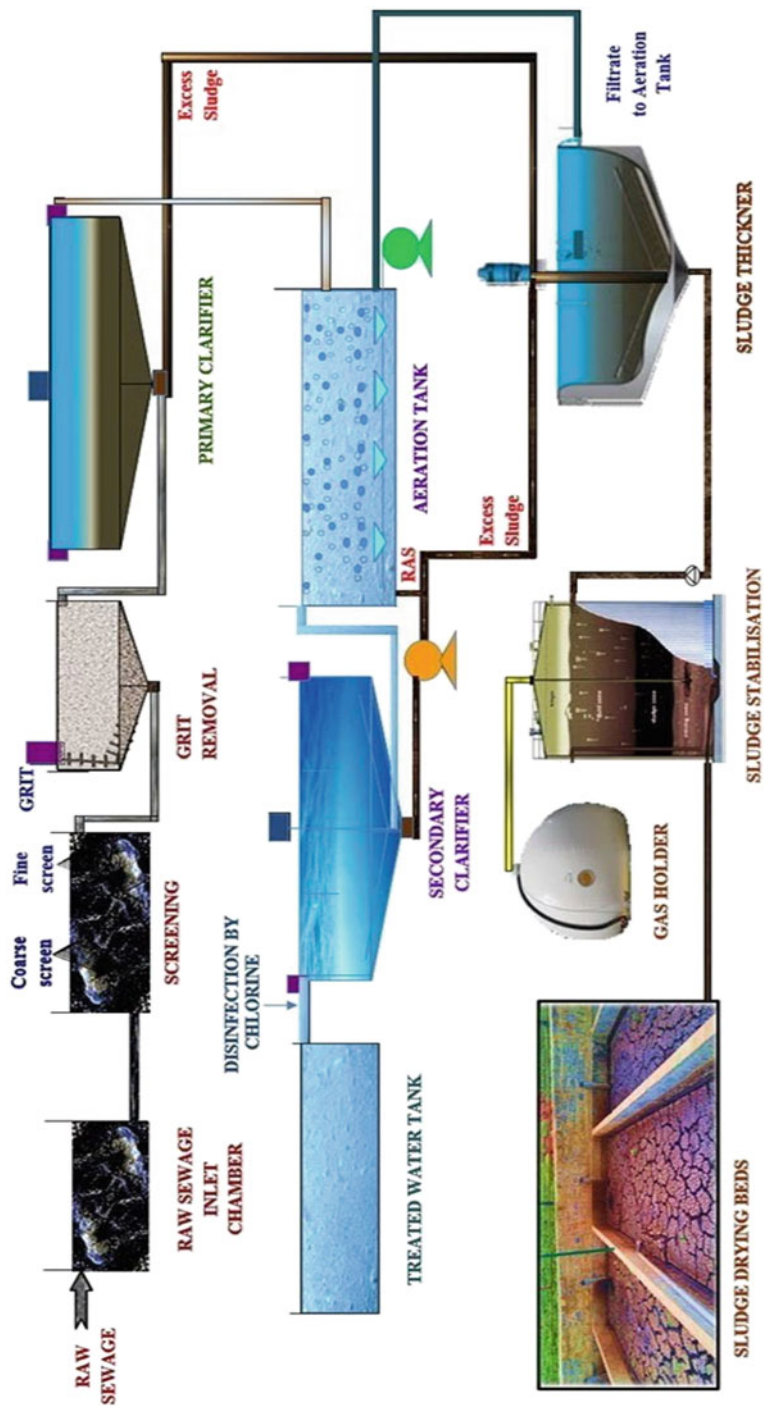
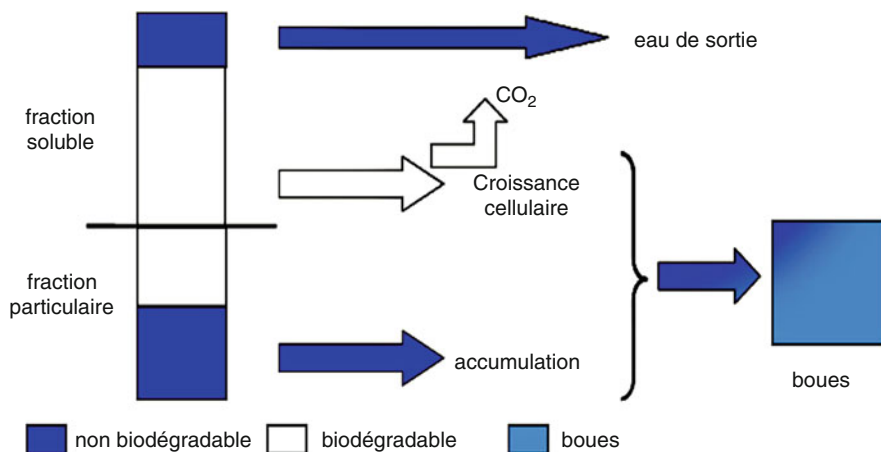


Fig. 3 Diagram of the wastewater treatment process and of production of muds [20]



**Fig. 4** Diagram of treatment biological of wastewater [21]

According to the power of the process of drying, it used thickening, dehydration, or thermal drying. One obtains muds with various percentages of dryness: slurries (4–10%), pasty muds (10–25%), and solid muds (25–50%) and granulated muds or powders some for a dryness higher than 85% [23].

### Spinneret of Elimination of Muds

If there exist many treatments to reduce volume upstream of the harmful effects and the harmfulness of muds, currently three dies are used to evacuate muds, according to whether one privileges a digestion mode based on elimination or recycling. It acts:

- Setting in controlled discharge
- Incineration
- Return on the ground by spreading [24]

#### *Put in Controlled Discharge*

The setting in pure mud discharge or mixture corresponds to a maximum concentration of all waste. Carbon leaves in the atmosphere in the form of methane. Remain the nitrogen and phosphorus (no recoverable). The stock room must be confined, and one is unaware of which can be to become to it in a long term nor duration of containment despite everything the precautions [25, 26]. Muds must be stabilized beforehand and dehydrated (maximum moisture of 70%). This solution has gradually lost its interest and is currently prohibited for financial reasons (closure procedure, etc.) and for environmental problems such as foul-smelling, breeding of mosquitoes, entrainment of fertilizing elements (nitrates, phosphates) and toxic products, which have an influence on the surface and groundwater [27–31].

### *Incineration*

It carries out the destruction of the organic matter of waste by combustion at high temperature (+ of 500°C) producing named smoke and residual mineral matter ashes. In the objective of an energy valorization of waste, produced heat is recovered in the form of vapor or of electricity for the operation of the furnace itself for the district heating or industrial [32]. The residues of the incineration (blast furnace slag) are usable for public works [33]. In France, 14–16% of urban muds are incinerated. In Europe, the percentage varies from 0% to 55% according to the countries. In Morocco, a treatment by incineration was not carried out yet. However, in spite of the interest of this process for an important reduction of volumes of waste, it has constraints mainly related to a very expensive investment. Muds alone are not car fuels. They require special furnaces and a mixture with other waste such as household waste. The elimination of ashes and the blast furnace slags require a controlled discharge of class 1 or one unit of inerting. This technique also remains harmful from ecological and environmental point of view since it contributes in addition to the organic matter wasting useful for the ground for the very toxic gas diffusion (NO, CO, SO, dioxane, etc.) which was covered by specific regulations [30, 31, 34].

### *Direct Spreading on the Soil*

In the current hour, the agricultural spreading of muds remains in Europe the principal die of elimination. This last is practiced that if those respect the principle “of agronomic interest” and are free from great contents of inorganic or organic pollutants.

This mode of recycling has adapted the most to rebalance the cycles biogeochemical (C, N, P) for environmental protection and of a very great economic interest. It aims to spare the natural resources and at avoiding any organic matter wasting due to the incineration or the hiding in discharges. Waste muds can thus replace or reduce the excessive use of expensive manure [34].

## **4 Sludge Problematic**

The treatment of muds is a difficult phase for the fight against pollution. Indeed the purifier with a difficult problem has to solve for multiple reasons: rarefaction of the grounds available for spreading and the deposit need set requirements of the environment and the public health. In addition the economic importance of this problem is illustrated by the importance of the cost as well in investment as in exploitation as it can represent. Oily muds with an important calorific value, which represents 90% of methane (CH<sub>4</sub>) that can be regarded as an interesting fuel. The impact related to its combustion under bad conditions can also be important. The main aim of this study is to thermically treat oily muds of oil industry with the level

of refinery RA1/Z and then to make a characterization of these muds by X-ray fluorescence (XRF) to determine the mineralogical composition in mass percentages in the form of oxides, for example (% SiO<sub>2</sub>, % CaO, % Fe<sub>2</sub>O<sub>3</sub>, % K<sub>2</sub>O, ...). X-ray diffraction (XRD) for the determination phases, for example, crystalline or amorphous silica. Fourier-transform infrared spectroscopy in total mode of reflection attenuated (FTIR-ATR) to determine the functional groupings, for example, O-H, CH, C-Cl, C-Br, C-I, CN, N-H, etc. and finally detection of heavy metals by atomic absorption spectroscopy (AAS). This study is to determine the sources of emission of heavy metals in the industrial wastewater which downgrades the quality of muds. Several origins can be identified such as industrial activities. In a second part, one is interested in studying constraints of exploitation due to the presence of the muds contaminated as well as the health hazard and environmental. We are interested in identifying the various ways of valorization other than agricultural spreading.

## 5 Material and Experimental Methods

One studied oily mud resulting from the purification plant of the refinery of Arzew RA1/Z as shown in Fig. 5. Thus for an oily comparison between two muds in the furnace with two different temperatures with 200°C during 4 h and with 600°C during 1 h (as shown in Figs. 6 and 7).



**Fig. 5** Local of taking away of oily mud [3]





Fig. 6 Oily mud before putting it in the furnace



Fig. 7 To put mud in the furnace

### 5.1 Objective and Analyses

The knowledge of the chemical compounds of oily mud helps to characterize this waste. In this work, we have dried the mud in two different high temperatures by using blast furnace gas and the cement plants.

## 5.2 *Sampling and Analyses*

### 5.2.1 *Material and Taking Away*

- A shovel of collecting
- Bottle

### 5.2.2 *Mode of Taking Away*

- A manual taking away

## 5.3 *Point Intake*

Oily mud at summer taken on the level of the bed of final drying of the phase of the treatment of the mud of complex RA1/Z of Arzew as shown in Fig. 5.

## 5.4 *Muds Analysis Methods*

### 5.4.1 *Preparation of the Mud Powder for Various Analyses*

The level of the laboratory of GL2/Z carried out the drying of this oily mud.

One put oily mud in a furnace at 200°C during 4 h (as shown in Figs. 6 and 7) and another oily mud with 600°C during 1 h (as shown in Figs. 8 and 9).



**Fig. 8** Oily mud dries with 200°C



**Fig. 9** Oily mud dries with 600°C



**Fig. 10** Crusher mortar has agate

Once they are dried, using a mortar one crushed the mud to prepare it in various analyses for oily mud at 200°C and at 600°C (Figs. 8, 9, 10, 11, and 12). This operation makes it possible to homogenize the taken matter.

This powder will be used:

- Analyses by Fourier-transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD)
- The chemical composition by Energy Dispersive X-ray (EDX)
- For the chemical analysis by atomic absorption spectroscopy (AAS)
- Oily mud has 200°C
- Oily mud has 600°C



**Fig. 11** Crushed oily mud



**Fig. 12** Crusher with agate mortar and rammer oil

#### **5.4.2 Test Performed on the Mud**

##### Determination of the Rate of Waste Oils in Oily Mud

This method is used to determine the existing oil concentration in mud by extraction with a solvent (toluene). We take  $M = 5$  g muds in a beaker, then we add a toluene excess, and we carry out the agitation of the mixture. After the separation of the phases, we balance the quantity of mud collected after filtration as shown in Figs. 14 and 15.





**Fig. 13** Crushed mud at 600°C



**Fig. 14** Oily mud rate of 200°C

- Calculate of the oil concentration in mud with:

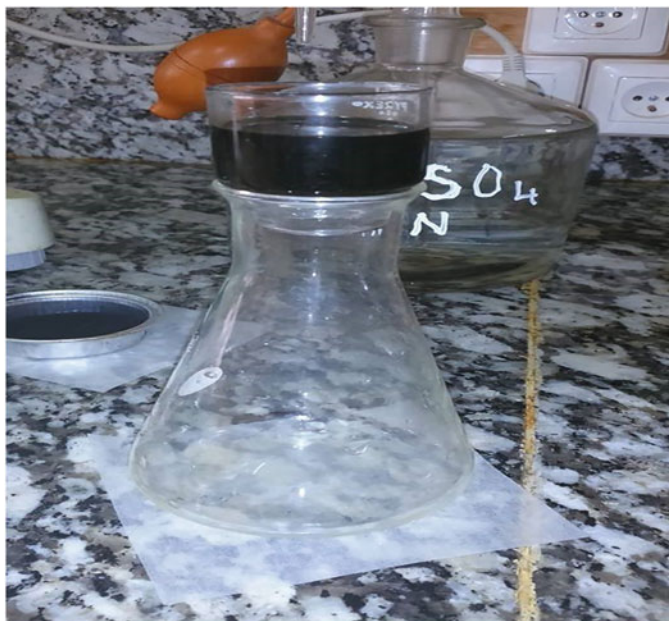
$$\text{Oil rate (\%)} = \frac{M - M_1}{M_2} \quad (1)$$

$M$ : mass of mud powders

$M_1$ : mass of mud after drying

$M_2$ : mass of oil to extract

$M_2 = M - M_1$



**Fig. 15** Oily mud oil rate of 600°C

### ***5.5 Determination of Heavy Metals in Oily Mud by Atomic Absorption Spectroscopy (AAS)***

(AAS) is a technique described for the first time by Walsh (1955). AAS studies absorptions of light by the free atom. It is one of the principal techniques bringing into play the atomic spectroscopy in the UV-visible field used in chemical analysis. It makes it possible to proportion about 60 chemical elements (metals and non-metals). The applications are numerous since one usually reaches concentrations lower than the mg/L (ppm). In its principle AAS spectroscopy consists in vaporizing the liquid sample and heating it using a flame or of a furnace. In flame mode the equipment can be used in the spectrometry of absorption and emission. The flame is directed toward a light emitted by a suitable lamp emitting the wavelengths characteristic of the required element. While crossing the flame, the light waves – of which the wavelengths correspond to the proportioned element – are absorbed by the excited ions present in the flame. Absorption is measured using a dispersive prism and of an electric eye; it is directly proportional to the concentration of the element. When the atoms of an element were excited, their return at the fundamental state is accompanied by the emission of light of a frequency  $F$  well defined and specific to this element. The same element dispersed in a flame has the property to absorb any of the same radiation frequency  $F$ . It results in an absorption from it from the incidental radiation related to the concentration of the element considered. In flame mode the



**Fig. 16** Preparation of water levels [Step 1]

limit of detection is about the ppm. The sensitivity of proportionings in flame mode is limited by secondary reactions (evaporation) and by time every court of passage in the flame. To increase the sensitivity of proportion, it is necessary to reduce or eliminate these two factors by atomization. This one is carried out in furnace graphite of a volume reduced under inert atmosphere. The limit of detection is then about Pb.

The developed applications in our laboratory allow us to determine the following elements: Na, K, Ca, Mg, Mn, Fe, Cd, Cr, Cu, Ni, Pb, Co, Zn, and As, by using the flame mode and the graphite furnace. These proportionings supported several studies on the operation of the grounds: the characterization of liquid samples (solution of the ground water of river and navy) and the behavior of metal elements traces in the grounds and the estuaries [35].

Before passing the two samples in the apparatus of atomic absorption spectroscopy (AAS), one prepared the water treatment which will be used for this analysis and which is prepared in the following way:

There is prenaït 1 gram sample that we add hydrochloric acid 21mL to him (HCl) 6N and 7 mL of nitric acid (HNO<sub>3</sub>) 3N, then we heat until complete drying. We take the operation again, but this time by using 10 mL HCl (5N) and demineralized water 50 mL (see Figs. 16 and 17).



**Fig. 17** Preparation of water levels [Step 2]

### 5.5.1 Preparation of Water

One has taken 1 g sample that we add hydrochloric acid 21 mL to him (HCl) 6N and 7 mL of nitric acid (HNO<sub>3</sub>) 3N, then we heat until complete drying. We take the operation again, but this time by using 10 mL HCl (5N) and demineralized water 50 mL (see Figs. 18 and 19).

Rough I let boil the whole then I filtered the filtrate once collected. We add 10 mL to him HCl, then we measure until 100 mL with demineralized water. I would obtain a yellowish mud solution then (see Figs. 20 and 21).

One diluted the solution 2 mL to the solution of 100 mL.

The factor of dilution (Fd) = 50

Thus the result to calculate the concentration of this solution:

Concentration of the solution in ppm (mg/L) = la value obtained \*factor of dilution (Fd)

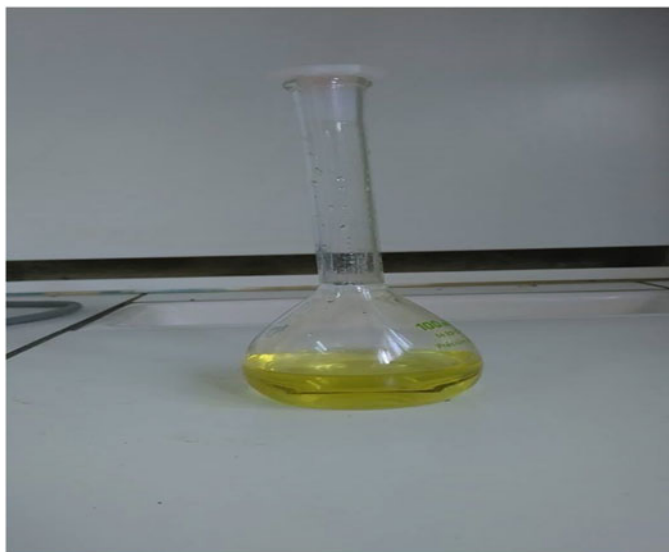
## 6 Results and Discussions

### 6.1 Determination of the Rate of Waste Oils in Oily Mud

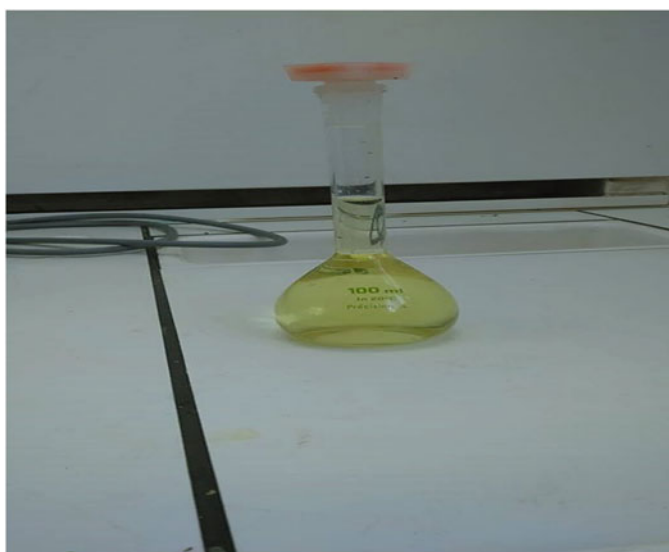
Calculation of the oil concentration in mud with: Eq. (1).

*The oily mud at 200°C (OMX200):*





**Fig. 18** Preparation of water levels [Step 3]



**Fig. 19** Preparation of water levels [Step 4]

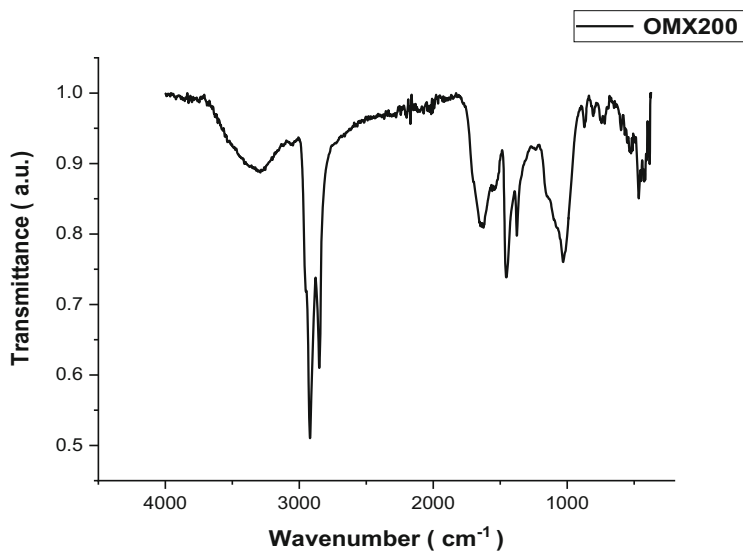
$$\text{Oil rate (\%)} = ((5 - 4.5) \div 5) \times 100 = 10\%$$

$$\text{Oil rate (\%)} = 10\%$$

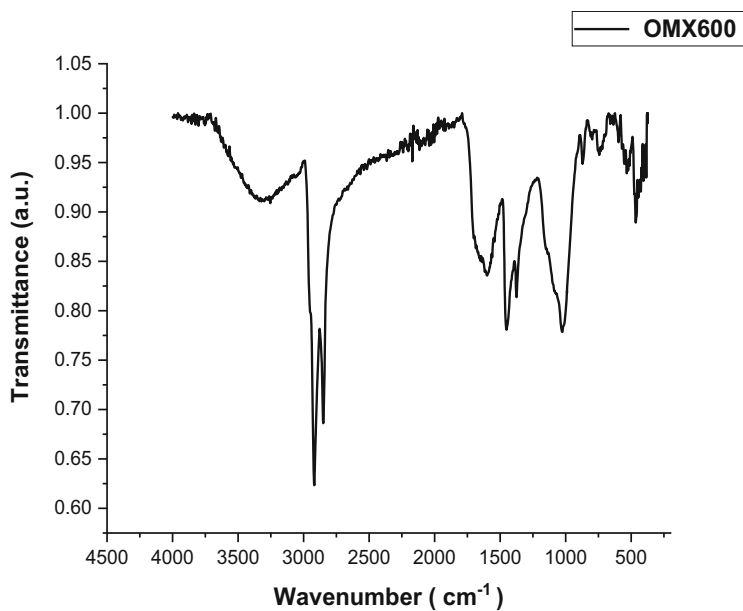
The oily mud at 600°C

$$\text{Oil rate (\%)} = ((5 - 4.8) \div 5) \times 100 = 4\%$$

$$\text{Oil rate (\%)} = 4\%$$



**Fig. 20** Spectrum of oily mud dries with 200°C (OMX200)



**Fig. 21** Spectrum of oily mud dries with 600°C (OMX600)

## 6.2 X-Ray Fluorescence (XRF)

Quantitative mineralogical analysis by X-ray fluorescence (XRF) of oily mud dries at temperature  $T = 200^{\circ}\text{C}$ . The mineralogical composition of dry oily mud at temperature  $200^{\circ}\text{C}$  (OMX200) studied refinery RA1/Z was determined by fluorescence of X-rays quantified in the form of oxides and is deferred in Table 1.

The mineralogical analysis of oily mud dries at  $T = \text{temperature } 200^{\circ}\text{C}$ ; watch the prevalence of silica ( $\text{SiO}_2$ ) with the value of 16.16% and the presence of oxides of small mass percentages which are iron oxide (III) ( $\text{Fe}_2\text{O}_3$ ) 4.46%, alumina ( $\text{Al}_2\text{O}_3$ ) 4.22%, calcium oxide ( $\text{CaO}$ ) 3.70% , potassium oxide ( $\text{K}_2\text{O}$ ) 0.70%, magnesium oxide ( $\text{MgO}$ ) 0.35%, sulfur trioxide ( $\text{SO}_3$ ) 0.19%, and finally sodium oxide ( $\text{Na}_2\text{O}$ ) 0.02%. The loss of ignition of dry oily mud at temperature  $T = 200^{\circ}\text{C}$  is of 63.09%.

## 6.3 Analysis by Fourier-Transform Infrared Spectroscopy (FTIR)

In oily mud dries with  $200^{\circ}\text{C}$  (OMX200) as shown in Fig. 20.

According to this result, one obtains a spectrum which contains various bands to be explained: The absorption band to  $3,290.59\text{ cm}^{-1}$  indicates the presence of a O-H of the carboxylic acid because of the various chemicals used [36]. The absorption band to ( $2,919.18\text{ cm}^{-1}$ ;  $2,850.87\text{ cm}^{-1}$ ) correspond to the vibration of elongations C-H; generally they are hydrocarbons of language chains carbonaceous of  $\text{C}_{11}$  to the  $\text{C}_{30}$  [36].

The absorption band to  $1,625.34\text{ cm}^{-1}$  corresponds to the vibration of carbons of double connections  $\text{C}=\text{C}$  [36]. The absorption band to  $1,560.07\text{ cm}^{-1}$  indicates the radicals of amines N-H [36]. The absorption band to  $1,455.03\text{ cm}^{-1}$  corresponds to the C-H vibration [36]. The absorption band to  $1,375.83\text{ cm}^{-1}$  corresponds to the vibration of radicals  $\text{CH}_2$  and  $\text{CH}_3$  [36]. The absorption band to  $1,030.60\text{ cm}^{-1}$  corresponds to the vibration of C-F [36]. Five absorption bands to ( $871.94\text{ cm}^{-1}$ ;  $806.23\text{ cm}^{-1}$ ;  $778.21\text{ cm}^{-1}$ ;  $743.14\text{ cm}^{-1}$ ;  $719.82\text{ cm}^{-1}$ ) correspond to the C-Cl

**Table 1** Chemical composition of oily mud dries for  $T = 200^{\circ}\text{C}$  (OMX200) by XRF

Composants	(%) mass
$\text{SiO}_2$	16.16
$\text{Fe}_2\text{O}_3$	4.46
$\text{Al}_2\text{O}_3$	4.22
$\text{CaO}$	3.7
$\text{K}_2\text{O}$	0.70
$\text{MgO}$	0.35
$\text{SO}_3$	0.19
$\text{Na}_2\text{O}$	0.02
LOI	63.09

vibrations [36]. Five absorption bands to ( $597.91\text{ cm}^{-1}$ ;  $570.11\text{ cm}^{-1}$ ;  $552.50\text{ cm}^{-1}$ ;  $523.19\text{ cm}^{-1}$ ;  $512.22\text{ cm}^{-1}$ ;  $512.22\text{ cm}^{-1}$ ) correspond to the C-Br vibrations [36].

The set's absorption bands to ( $494.58\text{ cm}^{-1}$ ;  $465.79\text{ cm}^{-1}$ ;  $447.47\text{ cm}^{-1}$ ;  $425.90\text{ cm}^{-1}$ ;  $418\text{ cm}^{-1}$ ;  $406.35\text{ cm}^{-1}$ ;  $384.48\text{ cm}^{-1}$ ) correspond to the vibrations of Cl [36].

In oily mud dries at  $600^\circ\text{C}$  that the absorption band to  $3,254.15\text{ cm}^{-1}$  indicates the presence of a O-H of absorption to carboxylic acid R-COOH. The formation of carboxylic with the cause of different chemicals used. Two absorption bands ( $2,918.15\text{ cm}^{-1}$ ;  $2,849.91\text{ cm}^{-1}$ ) generally corresponds to the vibrations of CH elongation; they are the hydrocarbons of the language chains carbonaceous of  $\text{C}_{11}\text{-C}_{30}$ .

The new absorption bands ( $2,566.95\text{ cm}^{-1}$ ;  $1,600.30\text{ cm}^{-1}$ ) corresponds to the vibrations of carbons doubles connections  $\text{C}=\text{C}$ . A new absorption band with ( $1,451.43\text{ cm}^{-1}$ ) corresponds to the vibration of C-H. The absorption band with ( $1,025.70\text{ cm}^{-1}$ ) corresponds to the CH vibration. The absorption band with ( $871.88\text{ cm}^{-1}$ ) corresponds to the C-Cl vibration. A new absorption band with ( $797.72\text{ cm}^{-1}$ ) corresponds to the C-Cl vibration. Absorption band with ( $743.55\text{ cm}^{-1}$ ) corresponds to the C-Cl vibration. Two absorption bands ( $597.11\text{ cm}^{-1}$ ;  $570.36\text{ cm}^{-1}$ ) correspond to the C-Br vibrations. A new absorption band with ( $533.64\text{ cm}^{-1}$ ) corresponds to the C-Br vibration. An absorption band with ( $512.80\text{ cm}^{-1}$ ) corresponds to the C-Br vibration. An absorption band with ( $465.34\text{ cm}^{-1}$ ) corresponds to vibration Cl. Two new absorption bands ( $445.49\text{ cm}^{-1}$ ;  $426.54\text{ cm}^{-1}$ ) correspond to the vibration of Cl. An absorption band with ( $418.33\text{ cm}^{-1}$ ) corresponds to the vibration of Cl. Two new bands correspond to the vibration of Cl as shown in Fig. 21.

The comparison between two oily muds dry with  $200^\circ\text{C}$  and the other has  $600^\circ\text{C}$  According to what this superposition sees, some of the difference between the two spectra of oily mud at  $200^\circ\text{C}$  (OMX200) and at  $600^\circ\text{C}$  (OMX600); which shows us that there are disappeared bands during heating, and we obtain new bands at  $600^\circ\text{C}$  which is explained by the effect of heat on the oily mud as shown in Fig. 22.

## 6.4 X-Ray Diffraction (XRD)

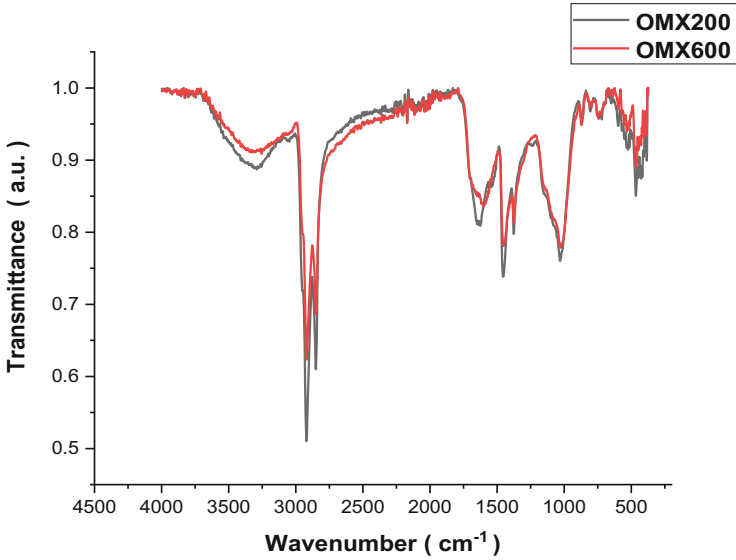
Figures 23 and 24 correspond the diffractograms of two oily muds present and their superposition as shown in Fig. 25.

Tables 1 and 2 represent the characteristics of the two diffractograms.

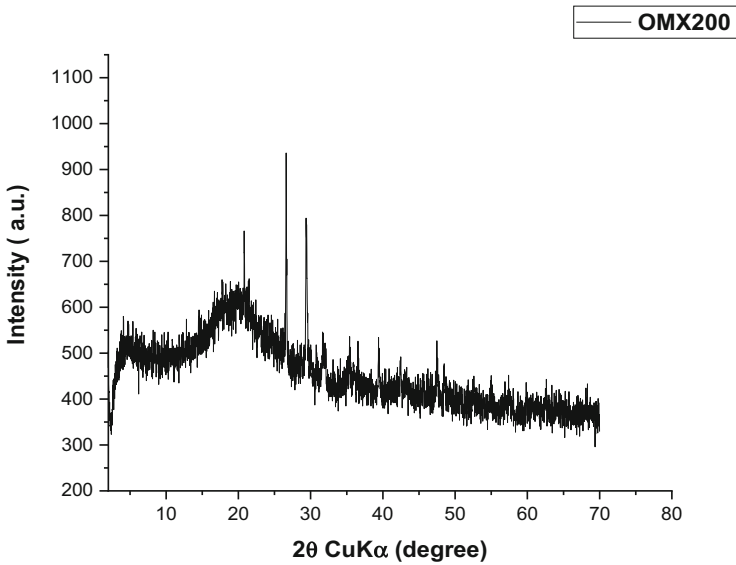
X-ray diffraction is a method of nondestructive analysis of solids in powder form based on Bragg's law (Eq. 2):

$$2d_{hkl} \sin \theta = n\lambda \quad (1). \quad (N = 1. \lambda = 1.54 \text{ \AA}). \quad (2)$$

$d_{hkl}$ : outdistance between 2 plans of index of  $d_{hkl}$  in  $\text{\AA}$ .



**Fig. 22** Spectrum of oily mud dries at 200°C (OMX200) and at 600°C (OMX600)



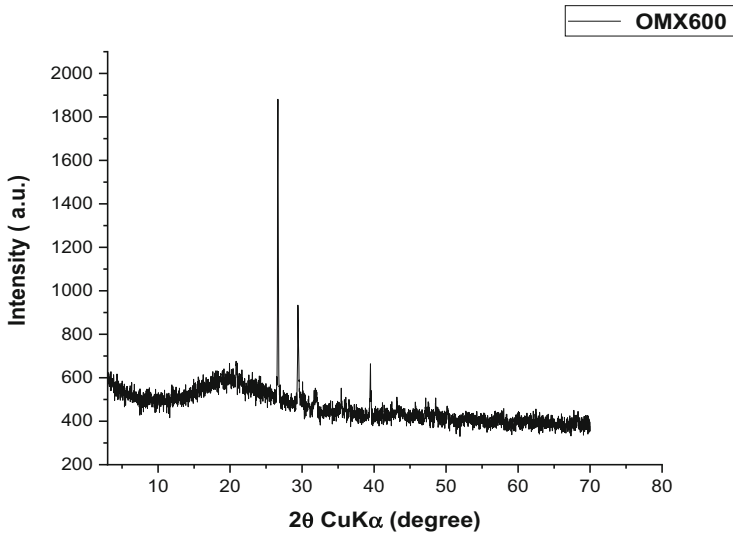
**Fig. 23** Diffractogram of oily mud dries with 200°C (OMX200)

$\theta$ : Bragg angle.

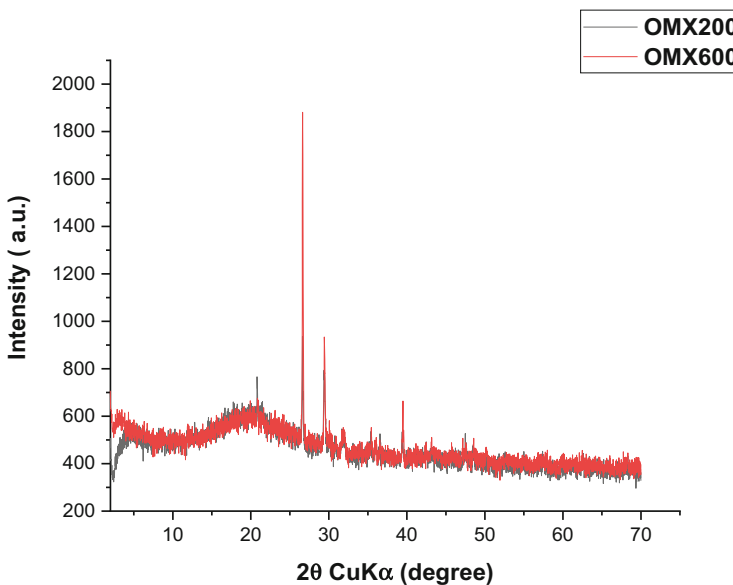
$\lambda$ : Wavelength of the radiation in Å.

$$\sin \theta = \lambda / 2d.$$

$$\theta = \arcsin (\lambda / 2d).$$



**Fig. 24** Diffractogram of oily mud dries with 600°C (OMX600)



**Fig. 25** Diffractogram of two oily mud dries with 200°C (OMX200) and at 600°C (OMX600)

For dry oily mud that has 200°C (OMX200), according to this result, one obtained a diffractogram which contains different distances interarticular to explain: the peak with  $2\theta = 2^\circ$  with the interarticular distance  $d = 50.95$  corresponds for the smectite ((K, H<sub>3</sub>O) (Al, Mg, Fe)<sub>2</sub>O<sub>10</sub> [(OH)<sub>2</sub>, H<sub>2</sub>O]) [37]. The peak with  $2\theta = 2.5^\circ$

**Table 2** Elements analyses (Cu, Zn, Fe, Ni, Pb, Cd) in the oily mud at 200°C (OMX200) of RA1/Z by atomic absorption spectroscopy (AAS) in mg/L

Elements	Oily mud at 200°C (OMX200) [RA1/Z] (mg/L)
Cu	1.0575
Zn	0.8765
Fe	1.04
Ni	0.37
Pb	0.243
Cd	0.0075
Cr	0.05642

with the interarticular distance  $d = 33.18242$  corresponds for the smectite ((K, H<sub>3</sub>O) (Al, Mg, Fe)<sub>2</sub> O<sub>10</sub> [(OH)<sub>2</sub>, H<sub>2</sub>O]) [37]. The peak with  $2\theta^\circ = 3.3^\circ$  with the interarticular distance  $d = 26.41$  corresponds for the smectite ((K, H<sub>3</sub>O) (Al, Mg, Fe)<sub>2</sub> O<sub>10</sub> [(OH)<sub>2</sub>, H<sub>2</sub>O]) [37]. The peak with  $2\theta^\circ = 18^\circ$  with the interarticular distance  $d = 4.97$  corresponds for kaolinite Al<sub>2</sub>Si<sub>2</sub> O<sub>5</sub>(OH)<sub>4</sub> [38–41]. The peak with  $2\theta^\circ = 21.2^\circ$  with the interarticular distance  $d = 4.26$  corresponds for the illite (K<sub>2</sub>, H<sub>3</sub>O) (Al, Mg, Fe)<sub>2</sub>O<sub>10</sub> [(OH)<sub>2</sub>, (H<sub>2</sub>O)] (ASTM N° = 9–343). The peak with  $2\theta^\circ = 21.1^\circ$  with the interarticular distance  $d = 4.26$  corresponds for quartz (SiO<sub>2</sub>) (ASTM N°=5–490). The peak with  $2\theta^\circ = 21.1^\circ$  with the interarticular distance  $d = 4.26$  corresponds for the opal has (SiO<sub>2</sub>.n H<sub>2</sub>O) [40]. The peak with  $2\theta^\circ = 26.5^\circ$  with the interarticular distance  $d = 3.340$  corresponds for the rutile (TiO<sub>2</sub>) (ASTM N° = 8–98). The peak with  $2\theta^\circ = 26.5^\circ$  with the interarticular distance  $d = 3.340$  corresponds for the lepidocrocite ( $\gamma$ -FeOOH) (ASTM N° = 4–55). The peak with  $2\theta^\circ = 26.5^\circ$  with the interarticular distance  $d = 3.340$  corresponds for quartz (SiO<sub>2</sub>) (ASTM N° = 5–490). The peak with  $2\theta^\circ = 26.5^\circ$  with the interarticular distance  $d = 3.340$  corresponds for the akaganeite ( $\beta$ -FeOOH) [41]. The peak with  $2\theta^\circ = 29.4$  with the interarticular distance  $d = 3.03$  corresponds for diopside (Ca MgSi<sub>2</sub>O<sub>6</sub>). The peak with  $2\theta^\circ = 29.4$  with the interarticular distance  $d = 3.03$  corresponds for calcite (CaCO<sub>3</sub>) (ASTM N° = 5–490) [42].

The peak with  $2\theta^\circ = 29.4$  with the interarticular distance  $d = 3.03$  corresponds for opal-A (SiO<sub>2</sub>.nH<sub>2</sub>O) [40]. The peak with  $2\theta^\circ = 30.1^\circ$  with the interarticular distance  $d = 2.97$  corresponds for the opal-A [40]. the peak with  $2\theta^\circ = 30.1^\circ$  with the interarticular distance  $d = 2.97$  corresponds for calcite (CaCO<sub>3</sub>) (ASTM N° = 5–490) [42]. The peak with  $2\theta^\circ = 30.1^\circ$  with the interarticular distance  $d = 2.97$  corresponds for diopside (Ca MgSi<sub>2</sub>O<sub>6</sub>) (ASTM N° = 11–654). The peak with  $2\theta^\circ = 31.1^\circ$  with the interarticular distance  $d = 2.89$  corresponds for diopside (Ca MgSi<sub>2</sub>O<sub>6</sub>) (ASTM N° = 11–654). The peak with  $2\theta^\circ = 31.1^\circ$  with the interarticular distance  $d = 2.89$  corresponds for the Opal-A (SiO<sub>2</sub>.n H<sub>2</sub>O) [40]. The peak with  $2\theta^\circ = 31.1^\circ$  with the interarticular distance  $d = 2.89$  corresponds for calcite (CaCO<sub>3</sub>) (ASTM N° = 5–490) [43]. The peak with  $2\theta^\circ = 31.9^\circ$  with the interarticular distance  $d = 2.82$  corresponds for the Opal-A (SiO<sub>2</sub>.n H<sub>2</sub>O) [40]. The peak with  $2\theta^\circ = 31.9^\circ$  with the interarticular distance  $d = 2.82$  corresponds for calcite (CaCO<sub>3</sub>) (ASTM N° = 5–490) [43]. The peak with  $2\theta^\circ = 35.6^\circ$  the interarticular distance  $d = 2.53$  corresponds for kaolinite (Al<sub>2</sub> SiO<sub>5</sub> (OH)<sub>4</sub>) [54].

The peak with  $2\theta^\circ = 35.6^\circ$  with the interarticular distance  $d = 2.53$  corresponds for hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) [37].

The peak with  $2\theta^\circ = 36.8^\circ$  with the interarticular distance  $d = 2.45$  corresponds for the rutile (TiO<sub>2</sub>) (ASTM N° = 4–55). The peak with  $2\theta^\circ = 36.8^\circ$  with the interarticular distance  $d = 2.45$  corresponds for lepidocrocite ( $\gamma$ -FeOOH) (ASTM N° = 8–98). The peak with  $2\theta^\circ = 36.8^\circ$  with the interarticular distance  $d = 2.45$  corresponds for the goethite ( $\alpha$ -FeOOH).

The peak with  $2\theta^\circ = 39.5^\circ$  with the interarticular distance  $d = 2.28$  corresponds for the aragonite CaCO<sub>3</sub>) [46,60]. The peak with  $2\theta^\circ = 39.5^\circ$  with the interarticular distance  $d = 2.28$  corresponds for quartz (SiO<sub>2</sub>) (ASTM N° = 5–490). The peak with  $2\theta^\circ = 39.5^\circ$  with the interarticular distance  $d = 2.12$  corresponds for the opal-A (SiO<sub>2</sub> n H<sub>2</sub>O) [40].

The peak with  $2\theta^\circ = 47.1^\circ$  with the interarticular distance  $d = 1.91$  corresponds for quartz (SiO<sub>2</sub>) (ASTM N° = 5–490). The peak with  $2\theta^\circ = 47.1^\circ$  with the interarticular distance  $d = 1.91$  corresponds for illite (K<sub>2</sub>. H<sub>3</sub>O) (Al. Mg. Fe)<sub>2</sub>O<sub>10</sub> [(OH)<sub>2</sub>. (H<sub>2</sub>O)] (ASTM N° = 9–343). The peak with  $2\theta^\circ = 48.1^\circ$  with the interarticular distance  $d = 1.91$  corresponds for calcite (CaCO<sub>3</sub>) [33].

The peak with  $2\theta^\circ = 48.1^\circ$  with the interarticular distance  $d = 1.87$  corresponds for quartz (SiO<sub>2</sub>) (ASTM N° = 5–490). The peak with  $2\theta^\circ = 50.5^\circ$  the interarticular distance  $d = 1.87$  corresponds for kaolinite Al<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub> (ASTM N° = 9–343).

The peak with  $2\theta^\circ = 54.5^\circ$  with the interarticular distance  $d = 1.66$  corresponds for quartz (SiO<sub>2</sub>) (ASTM N° = 5–490). The peak with  $2\theta^\circ = 57.5^\circ$  with the interarticular distance  $d = 1.60$  corresponds for quartz (SiO<sub>2</sub>) (ASTM N° = 5–490). The peak with  $2\theta^\circ = 62.6^\circ$  with the interarticular distance  $d = 1.48$  corresponds for quartz (SiO<sub>2</sub>) (ASTM N° = 5–490).

*For dry oily mud that has 600°C (OMX600)*, according to this result, one obtained a diffractogram which contains different distances interarticular to explain:

The peak with  $2\theta^\circ = 1.8^\circ$  with the interarticular distance  $d = 49.07$  corresponds for the smectite ((K. H<sub>3</sub>O) (Al. Mg. Fe)<sub>2</sub> O<sub>10</sub> [(OH)<sub>2</sub>. H<sub>2</sub>O])) [37]. A new peak with  $2\theta^\circ = 11.8^\circ$  with the interarticular distance  $d = 7.43$  corresponds for quartz (SiO<sub>2</sub>). The peak with  $2\theta^\circ = 20.8^\circ$  with the interarticular distance  $d = 4.25$  corresponds for quartz (ASTM N° = 5–490) [41].

The peak with  $2\theta^\circ = 20.8^\circ$  with the interarticular distance  $d = 4.25$  corresponds for the opal-A (SiO<sub>2</sub> nH<sub>2</sub>O) [40]. The peak with  $2\theta^\circ = 26.8^\circ$  with the interarticular distance  $d = 3.34$  corresponds for quartz (SiO<sub>2</sub>) (ASTM N° = 5–490). The peak with  $2\theta^\circ = 26.5^\circ$  with the interarticular distance  $d = 3.34$  corresponds for rutile (TiO<sub>2</sub>) (ASTM N° = 8–98). The peak with  $2\theta^\circ = 26.5^\circ$  with the interarticular distance  $d = 3.34$  corresponds for the akaganeite ( $\beta$ -FeOOH) [41].

The peak with  $2\theta^\circ = 29.5^\circ$  with the interarticular distance  $d = 3.03$  corresponds for diopside (Ca MgSi<sub>2</sub>O<sub>6</sub>) (ASTM N° = 11–654). The peak with  $2\theta^\circ = 29.5^\circ$  with the interarticular distance  $d = 3.03$  corresponds for the opal has (SiO<sub>2</sub>nH<sub>2</sub>O) [40]. The peak with  $2\theta^\circ = 35.4^\circ$  with the interarticular distance  $d = 2.52$  corresponds for hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) [43]. The new peak with  $2\theta^\circ = 35.9^\circ$  with the interarticular distance  $d = 2.48$  corresponds for rutile (TiO<sub>2</sub>) (ASTM N° = 8–98).



The new peak with  $2\theta^\circ = 35.9^\circ$  with the interarticular distance  $d = 2.48$  corresponds for lepidocrocite ( $\gamma$ -FeOOH) [66]. The new peak with  $2\theta^\circ = 35.9^\circ$  with the interarticular distance  $d = 2.48$  corresponds for goethite ( $\alpha$ -FeOOH) [58]. The peak with  $2\theta^\circ = 36.8^\circ$  with the interarticular distance  $d = 2.45$  corresponds for the rutile ( $\text{TiO}_2$ ) (ASTM N $^\circ = 8$ –98). The peak with  $2\theta^\circ = 36.8^\circ$  with the interarticular distance  $d = 2.45$  corresponds for lepidocrocite ( $\gamma$ -FeOOH) [66]. The peak with  $2\theta^\circ = 36.8^\circ$  with the interarticular distance  $d = 2.45$  corresponds for goethite ( $\alpha$ -FeOOH) [58]. The peak with  $2\theta^\circ = 39.4^\circ$  with the interarticular distance  $d = 2.27$  corresponds for quartz ( $\text{SiO}_2$ ) (ASTM N $^\circ = 5$ –490). The peak with  $2\theta^\circ = 39.4^\circ$  with the interarticular distance  $d = 2.27$  corresponds for aragonite ( $\text{CaCO}_3$ ) [58, 60]. A new peak with  $2\theta^\circ = 41.2^\circ$  with the interarticular distance  $d = 2.19$  corresponds for Opal-A ( $\text{SiO}_2 \cdot n\text{H}_2\text{O}$ ) [40]. A new peak with  $2\theta^\circ = 43.3^\circ$  with the interarticular distance  $d = 2.19$  corresponds for the opal-A [40]. The peak with  $2\theta^\circ = 47.1^\circ$  with the interarticular distance  $d = 1.92$  corresponds for quartz ( $\text{SiO}_2$ ) (ASTM N $^\circ = 5$ –490). The peak with  $2\theta^\circ = 47.6^\circ$  with the interarticular distance  $d = 1.91$  corresponds for quartz ( $\text{SiO}_2$ ) (ASTM N $^\circ = 5$ –490).

The peak with  $2\theta^\circ = 47.6^\circ$  with the interarticular distance  $d = 1.91$  corresponds for illite ( $\text{K}_2 \cdot \text{H}_3\text{O}$ ) ( $\text{Al} \cdot \text{Mg} \cdot \text{Fe}$ ) $\text{O}_{10}$  [(OH) $_2$  · (H $_2$ O)] (ASTM N $^\circ = 5$ –490). The peak with  $2\theta^\circ = 47.6^\circ$  with the interarticular distance  $d = 1.91$  corresponds for calcite ( $\text{CaCO}_3$ ) [33]. The peak with  $2\theta^\circ = 48.6^\circ$  with the interarticular distance  $d = 1.87$  corresponds for quartz ( $\text{SiO}_2$ ) (ASTM N $^\circ = 5$ –490). The peak with  $2\theta^\circ = 48.6^\circ$  with the interarticular distance  $d = 1.87$  corresponds for kaolinite ( $\text{Al}_2\text{Si}_2\text{O}_5$  (OH) $_4$ ) (ASTM N $^\circ = 9$ –343). The new peak with  $2\theta^\circ = 50.1^\circ$  with the interarticular distance  $d = 1.81$  corresponds for quartz ( $\text{SiO}_2$ ) (ASTM N $^\circ = 5$ –490).

#### 6.4.1 The Superposition Enters Both Diffractogram

According to this superposition, being able to see the diffractogram of mud that has 200°C (OMX200) and amorphous on the other hand the diffractogram at 600°C (OMX600) and crystalline, however, perhaps explains by the effect of heat on mud what one has understood of it that there has organic phases disappeared during heating of mud as shown in Fig. 25.

### 6.5 Determination of the Metal Elements in Oily Mud

(Cu, Zn, Fe, Ni, Pb, and Cd) atomic absorption spectrometry analyses in the oily mud of RA1/Z.

The masses of heavy metals in oily mud are summarized in the table of the results.

## 6.6 Quantification Table of the Metal Elements in the Oily Mud of 200°C (OMX200)

These values are represented in (mg/L), but standard Afnor gives us values in matter mg/kg dries; this is why we must convert them into mg/kg DM in the following way:

To prepare water treat, we have dissolve 1 g of mud in 100 final ml of solution in 1 L of solution of ms, and we calculate the quantity of these elements in dry mud 1 kg with the following formula as shown in (see Tables 3, 4, and 5), respectively:

$$\text{Valor in mg/kg of DM} = X \times 100/1,000 \quad (3)$$

**Table 3** Quantification of the metal elements in the oily mud of 200°C (OMX200) in mg/kg

Elements	Oily mud at 200°C (OMX200) [RA1/Z] in (mg/kg)	Norm in agriculture in (mg/kg)
Cu	105.75	1,000
Zn	87.65	3,000
Fe	104	/
Ni	37	200
Pb	243	243
Cd	0.75	0.75
Cr	5.642	1,000

**Table 4** Elements analyses (Cu, Zn, Fe, Ni, Pb, Cd) in the oily mud of RA1/Z at 600°C (OMX600) by atomic absorption spectroscopy (AAS) in mg/L

Elements	Oily mud at 600°C [RA1/Z] in (mg/L)
Cu	1.3691
Zn	1.09
Fe	2.3
Ni	0.40
Pb	0.347
Cd	0.065
Cr	00.0431

**Table 5** Quantification of the metal elements in the oily mud of 600°C (OMX600) in mg/kg

Elements	Oily mud at 600°C [RA1/Z] in (mg/kg)	Norm in agriculture in (mg/kg)
Cu	136.91	1,000
Zn	109	3,000
Fe	230	/
Ni	40	200
Pb	34.7	800
Cd	6.5	20
Cr	4.31	1,000

## 7 Conclusions

At the time of the realization of our memory of end of study, we became aware of the importance of the purification plant which with for objective to purify oily water so that they are not directly rejected in the natural environment, because they can generate serious environmental problems and handles public. On the other hand, this stations generate another waste (mud) rich in oily age of nature toxic and carcinogenic and can be neither stored nor put in discharge. The exact composition of muds varies according to the origin of oily water of the period of the year and the type of purification plant. Muds are very rich in organic matter (between 50% and 70% of matter dries) which supports the proliferation of micro the organizations which multiply and break up the organic matter. In the absence of sufficient ventilation, the decomposition releases from the organic compounds malodorous has jumps as well as gases with greenhouse effect (carbonic gas, methane, etc.). This situation illustrates clearly that an action plan became necessary fine to rehabilitate a system allowing an adequate exploitation for muds by respecting the standards of environmental protection. The contribution to the valorization of oily muds of the refinery of Arzew-like fuel of substitution in the furnaces of the cement factories or the blast furnaces of the foundries as a principle to develop the energy capacity of the organic matter of dried mud because its calorific value is very high of that of methane. The use of alternative fuels makes it possible to diversify the energy resources and to reduce these costs. On the one hand, in the furnaces, the organic components will be exposed by heat treatment with different temperature with 200°C, and 600°C will be burned completely, while the mineral components will undergo a chemical conversion which will integrate into the clinker without deteriorating the excellent quality of this one. The use of ashes of muds like an addition to the clinker in the manufacture of cement in goal to minimize the increasing quantity of waste of coordination with existing industries with the national territory by using the least expensive processes devoted of the very satisfactory results with the various studied percentages.

## 8 Recommendations

As an example the substitution of 13% of the raw material by ashes enables us to eliminate a quantity from 65,000 tonnes/year knowing that annual production of cement in a cement factory (e.g., cement factory of Saida) is estimated at 500,000 tonnes/year cements with ashes as addition obtained at 900°C and will be used preferably in the nonexposed works, for example, highways. Finally we can completely say that our study of valorization of muds eliminates this waste in an exemplary industrial process on the ecological and economic level. It is the most suitable way, ecologically and economically, in order to respond to the problem of removing heavy metals and sewage sludge ashes.

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