Original Article

Waste Management & Research
0(0) 1–15

DOI: 10.1177/0734242X12448517
wmr.sagepub.com

A review of the technological solutions for the treatment of oily sludges from petroleum refineries

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Abstract

The activities of the oil industry have several impacts on the environment due to the large amounts of oily wastes that are generated. The oily sludges are a semi-solid material composed by a mixture of clay, silica and iron oxides contaminated with oil, produced water and the chemicals used in the production of oil. Nowadays both the treatment and management of these waste materials is essential to promote sustainable management of exploration and exploitation of natural resources. Biological, physical and chemical processes can be used to reduce environmental contamination by petroleum hydrocarbons to acceptable levels. The choice of treatment method depends on the physical and chemical properties of the waste as well as the availability of facilities to process these wastes. Literature provides some operations for treatment of oily sludges, such as landfilling, incineration, co-processing in clinkerization furnaces, microwave liquefaction, centrifugation, destructive distillation, thermal plasma, low-temperature conversion, incorporation in ceramic materials, development of impermeable materials, encapsulation and biodegradation in land farming, biopiles and bioreactors. The management of the technology to be applied for the treatment of oily wastes is essential to promote proper environmental management, and provide alternative methods to reduce, reuse and recycle the wastes.

Keywords

Oily sludge, petroleum, biodegradation, hazardous waste management, heavy metals, environmental impact, reuse, recycling

Introduction

The various activities involved in the petroleum industry, such as drilling, production, transport, processing and distribution, create considerable amounts of hazardous solid waste. The disposal of these waste materials into the environment can cause serious environmental problems (Mariano, 2005). For this reason, it is important to raise awareness of the environmental impacts caused by the activities involved in petroleum extraction, refining and waste treatment and the search for solutions that might minimize these effects.

A specific analysis of industrial activity at a petroleum refinery reveals that these activities clearly cause strong environmental impacts because the petroleum production process generates large amounts of waste, effluents, atmospheric emissions and risks inherent to the transport of petroleum products (Szklo and Uller, 2008). Oily sludges, the most abundant oily wastes generated in refineries, are a pasty, semisolid material made of sand (a mixture of clay, silica and oxides) contaminated by oil, the water produced and the chemicals used in petroleum processing (Heidarzadeh et al., 2010). The reduction, reutilization and recycling allow the development of sustainable policies for petroleum companies (Ladislao, 2008).

In the early days of petroleum refining, the management of oily sludges was improperly performed by dumping it into dykes, onto the ground or into ditches, trenches or casks for subsequent burial without any prior preparation of the area. The accumulation of oily sludges resulted in the contamination of local bodies of water, which caused silting of rivers, death of aquatic species, persistent heavy-metal contamination and damage to environmental preservation areas (Ayotamuno et al., 2007).

Therefore, the treatment and management of oily sludges are both essential to promote the sustainable management of the profitable extraction of natural resources, with a preference for the reduction, reutilization and recycling of these oily wastes. Biological, physical and chemical processes can be used serially and/or in parallel to decrease environmental contamination by petroleum hydrocarbons and other contaminants to levels permitted by environmental agencies (Mariano, 2005). The

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management of oily wastes involves the characterization of oily sludges (physical, physicochemical and chemical properties) and the technologies to treat it. The literature describes a wide range of possibilities for oily sludge treatment processes, including landfilling; incineration; co-processing in clinkerization furnaces; microwave liquefaction; centrifugation; destructive distillation; thermal plasma; low-temperature conversion; incorporation in ceramic materials; development of impermeabilization materials; encapsulation; biodegradation in landfarming; biopiles; and bioreactors.

The analysis and characterization of oily sludges, the amounts produced and the availability of equipment are important variables for defining the technology that will be applied to the treatment of oily sludges generated by a given petroleum refinery (Gusti, 2009). In the characterization of oily sludges, the quantification of the most relevant parameters must be prioritized to correlate them with the specificities of each treatment method. The classification of oily sludges consists of identifying each process that generates it, determining the physicochemical characteristics of the wastes and comparing the physicochemical characteristics to those of wastes and substances with known impacts on health and the environment as described by the NBR ISO 10004 technical standard (ABNT, 2004a), SW-846 guidelines (USEPA, 2007) and Directive 91/689/EEC (EU, 1991).

The search for technological innovations that permit the reutilization and recycling of oily sludges has resulted in better compliance with legal requirements for environmental protection. The development of such technologies is still a major goal of the agencies responsible for environmental surveillance, control and monitoring as well as the scientific community and the petroleum companies themselves, especially those that introduce the greatest amount of oily wastes into the environment. Some treatment solutions, including the reutilization and recycling of oily sludges, have yielded satisfactory results from technological advancements. The petroleum industry and the environmental control agencies have been focusing on reutilization and recycling techniques rather than on traditional methods such as industrial landfilling (Ruffino and Zanetti, 2008).

The aim of this study is to propose a methodology for the management of oily sludges generated during petroleum refining. The specific goals of this study are to analyse and characterize the formation of oily sludges at each step of the refining process; to discuss notions of environmental management, sustainability and ethics according to the '3 R' policy of reduction, reutilization and recycling; to map out technologies available for the treatment of oily sludges and to define the variables that must be taken into account in the selection of the most appropriate treatment. Thus, this study contemplates the mapping of available technologies by evaluating master's dissertations, doctoral theses, scientific articles, patents, ANP (National Agency for Petroleum, Natural Gas and Biofuels) and ABIQUIM (Brazilian Association of the Chemical Industry) annual reports, technical reports and professional field experience. Future analysis of the technical solutions will be performed to develop a methodology for treatment selection.

The petroleum industry: a focus on refining

According to ANP, petroleum refining consists of a set of physical and chemical processes aimed at transforming this raw matter into petroleum-based products. Petroleum processing begins by atmospheric distillation, which consists of fractionating the raw oil that will be processed by every refinery. This operation is performed in fractionation columns of different sizes that have several separation stages, one for each desired fraction (ANP, 2010). According to the separation stage of the petroleum components and the operational capacity of the refinery, different types of petroleum-based products are produced for the consumer market or for the petrochemical industry, such as liquefied petroleum gas (LPG), petrol, diesel, aviation kerosene and petroleum asphalt cement.

There are four stages in petroleum refining: separation, conversion, treatment and auxiliary processes (Jones and Pujadó, 2008; Maples, 2000). Refining plants are not identical; they differ depending on the type of raw petroleum that they process and the design of units as a function of the production of different products (Mishra, 1989). To help in the identification of oily sludges formation, an illustrative scheme describing the stages of refining, shown in Figure 1, was constructed for this study.

Oily sludges production must be reduced at its source or eliminated during processing. The methods for this reduction include process modifications, raw matter improvement by way of purification (lighter oils form less oily sludges), improvement of management practices, increase of equipment efficiency and recycling during the process (Bartilucci et al., 1989). The International Petroleum Industry Environmental Conservation Association (IPIECA) has identified the primary sources of the petroleum industry's oily wastes, as shown in Table 1.

The minimization of waste generation is an important waste management strategy based on the adoption of techniques that reduce the volume and/or toxicity of waste, i.e., the pollutant load. According to Azevedo (2003), the ISO 14000 standards integrate principles of sustainable economic development in a free-market system. The standards stimulate the self-organization and self-regulation of environmental conservation mechanisms, thus comprising a series of standards and reference documents aimed at reducing the global environmental load of a given process, stimulating the use of new materials, designing products to facilitate their recycling, improving the design of processes to optimize their environmental performance and perfecting the logistics of each stage of the product lifecycle (Guerin, 2008).

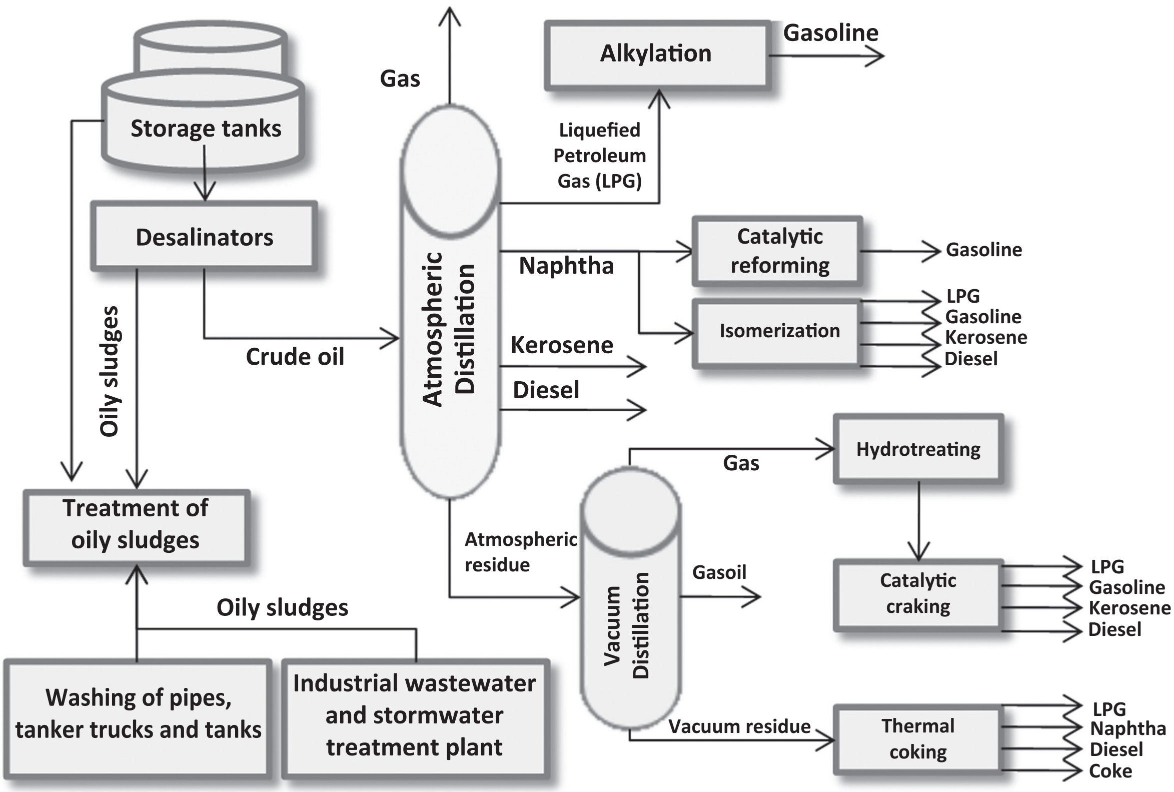

Figure 1. Illustrative scheme of the stages of petroleum refining and identification of the sites where oily sludges are formed.

Table 1. Types of oily sludge and the primary sources.

Type of oily sludge	Primary sources
Oily sludges with detergents or washing liquids, and it is carrying rust and reaction residues.	Oily sludge formed during the washing of the equipment used in refineries, such as distillation towers, cracking units and hydrotreaters as well as equipment used for catalytic reformation, isomerization, alkylation or delayed coking.
Oily sludges with non-mineral skimmed foam and grease.	In effluent treatment stations, oily sludge is formed in water–oil separators (WOS), floaters and/or flocculators.
Light oily sediments which contain mineral material.	In desalinators, an oily sludge containing high levels of sediments is formed during the desalinization process.
Heavy oily sediments which contain mineral material.	In tanks bottom used to store the raw petroleum and dark petroleum products (combustible oils, petroleum asphalt cement and lubricants).

Source: IPIECA (2004); Joseph (2009); Zhang et al. (2009).

Sites of oily sludges formation

According to the ANP Statistical Annual Report, the effective refining capacity worldwide in 2009 was 14 400 000 m^3 day^{-1} with a worldwide petroleum production of 12 600 000 m^3 day^{-1}. It is estimated, that at least 190 000 m^3 of sludge is generated daily, which corresponds to 1.5% of the total produced. The United States maintained first place in the rankings of world refining capacity (19.5% of the total), followed by China (9.5%), Russia (6.2%), Japan (5.1%) and India (3.9%). Together, these five countries represent 44.3% of the world refining capacity, with 3.6% growth from 2008. Brazil ranked tenth worldwide in refining capacity, with 333 900 m^3 day^{-1} or 2.3% of the world capacity (ANP, 2010).

To quantify the sludge generated in industrial plants, the petroleum density must be estimated. However, there are several types of petroleum, and their compositions are intrinsically related to their viscosity and density (Bhattacharyya and Shekdar, 2003). Aires (2002) assessed 12 samples of (heavy and light) petroleum from several randomly chosen Brazilian states to estimate the density of petroleum and found an average density of 0.8806 ton m^{-3}. From these data, Aires (2002) produced three estimates of the amount of sludge generated every day in Brazilian refineries based on the processed loads:

Table 2. Estimation of oily sludges generation in Brazilian refineries.

Refineries	Refining capacity[a] (m³ day⁻¹)	Processed load[a] (m³ day⁻¹)	Oily sludges[b] (m³ day⁻¹)		
			0.1%	0.5%	1.5%
Ipiranga (RS)	2 700	2 179	2.2	10.9	32.7
LUBNOR (CE)	1 300	961	1.0	4.8	14.4
RECAP (SP)	8 500	6 630	6.6	33.2	99.5
REDUC (RJ)	38 500	33 272	33.3	166.4	499.1
REFAP (RS)	30 000	26 607	26.6	133.0	399.1
REGAP (MG)	24 000	22 858	22.9	114.3	342.9
REMAN (AM)	7 300	6 512	6.5	32.6	97.7
REPAR (PR)	35 000	30 029	30.0	150.1	450.4
REPLAN (SP)	66 000	55 029	55.0	275.1	825.4
REVAP (SP)	40 000	38 899	38.9	194.5	583.5
RELAM (BA)	44 500	35 161	35.2	175.8	527.4
RPBC (SP)	27 000	26 388	26.4	131.9	395.8
Guamaré (RN)	4 328	1 484	1.5	7.4	22.3
Univen (SP)	1 100	1 094	1.1	5.5	16.4
Dax Oil (BA)	275	–	–	–	–
Total	332 703	287 106	287	1 436	4 307

[a]Source: Statistical Annual Report (ANP, 2010).
[b]Volume of oily sludges estimated from processing at each refinery.

0.1% (an optimistic view), 0.5% (more realistic) and 1.5% (pessimistic).

An estimate of oily sludges formation based on the 2009 refining capacity of Brazilian refineries is shown in Table 2.

The REPLAN refinery processed the largest amount of petroleum in Brazil: 55 029 m³ day⁻¹, or 19.3% of the total processed volume. The next-largest-volume producers were REVAP (13.3%), RELAM (12.4%), REDUC (11.2%), REPAR (10.6%), REFAP (9.4%), RPBC (9.3%) and REGAP (8%); the remaining refineries represented 6.6% combined. Even based on these optimistic estimates, assuming that oily sludges generation is 0.1% of the processed load, the daily production of 287 m³ of oily sludges is substantial. These data reinforce the need to establish an efficient methodology to treat oily sludges that take into account the particularities of each refining unit. Solid wastes generated at petroleum refineries arise from several refining processes, including petroleum handling at the producing units and the treatment of the effluents that they generate. It should be emphasized that refineries produce both hazardous and non-hazardous wastes; however, both types must be properly managed.

Oily sludges are produced by different water–oil separation processes (arising from the effluent treatment stations); by accidental spills; during cleansing of the different types of equipment used for petroleum separation, conversion and treatment and in storage tanks for raw petroleum and dark derivatives, such as lubricant oils, combustible oils and petroleum asphalt cement (Kriipsalu et al., 2008).

Physicochemical characteristics of oily sludges

Water is commonly found in oil sludges at concentrations between 30 and 90%. Oil sludges also contain 4 to 7% sediments by concentrations that are mostly composed of halite, calcite, kaolinite and quartz (Monteiro et al., 2007). The remaining sludge is naturally composed of petroleum hydrocarbons at concentrations between 5 and 60%. The oily phase of petroleum sludge contains 40 to 60% saturated hydrocarbons, 25 to 40% aromatic hydrocarbons, 10 to 15% resins and 10 to 15% asphaltenes (Shie et al., 2004; Speight 2006). According to Shie et al. (2004), benzene, toluene, ethyl/benzene and xylene (BTEX) are commonly found among the aromatic compounds, as are phenols and polycyclic aromatic hydrocarbons (PAH), which are partially responsible for the flammability of petroleum sludge and its consequent classification as a hazardous waste (Xia et al., 2006).

Technical standards are helpful for identifying oily sludges components throughout the entire cycle, from sampling (NBR ISO 10007;ABNT (2004b)) to lixiviated extract solubilization (NBR ISO 10005; ABNT (2004c)) and solubilized extract (NBR ISO 10006; ABNT (2004d)). The analytical results allow oily sludges to be classified according to the NBR ISO 10004 standard (ABNT, 2004a), which defines oily sludges as class I (hazardous) because of the presence of toxic components such as PAH and BTEX. According to the NBR ISO 10004 standard, waste is classified into the categories described in Table 3. Waste hazard is defined as a function of physical, chemical or pathogenic properties of the waste that may pose a risk to public health and the environment. This is the case of oily sludges.

According to the NBR ISO 10004 standard, petroleum sludge is listed as a hazardous waste with identification code K170 and is described as clarified sludge from the oil tank waste and/or solids from the separators/filters of the petroleum-refining operations line. This classification is the result of the presence of benzo[a]pyrene, dibenz[a,h]anthracene, benzo[a]anthracene,

Table 3. Classification of wastes by their hazardousness.

Wastes	Characteristics
Class I	Hazardous, inflammable, reactive, corrosive, toxic or pathogenic.
Class II A	Non-inert: may have properties of biodegradability, water solubility and combustibility.
Class II B	Inert: do not pose risk of inflammation, corrosiveness or combustibility and do not affect potability standards when water-soluble.

Source: ABNT (2004a).

benzo[a]fluoranthene, benzo[k]fluoranthene, 3-methylbenzyl-cyclopentaneanthracene and 7,12-dimethylbenz[a]anthracene, among other toxic compounds.

In the characterization of oily sludges must be quantified parameters, such as: pH; dry solid matter; total phosphorus; total nitrogen; total carbon; sulphur; metals (As, Pb, Cd, Co, Cu, Cr, Ni, Zn, V, Hg); polycyclic aromatic hydrocarbons (PAH); total petroleum hydrocarbons (TPH); benzene, toluene, ethyl-benzene, xylenes (BTEX) (ABNT (2004a); SW-846 guidelines USEPA (2007)). These are the most relevant parameters to correlate with the specificities of each treatment technology. For example, oily sludges that contain a high concentration of sulfur, Cr, Pb, Hg, PAH and BTEX must not be treated by thermal process such as incineration, co-processing in clinkerization furnaces, microwave liquefaction, destructive distillation and low-temperature conversion.

Management of oily sludges within the context of sustainable development

Human health and environmental quality are constantly degraded by the increasing amount of hazardous waste generated by several industrial processes. Rational waste management is one of the most important issues to consider for maintaining environmental quality, with the goal of achieving sustainable and environmentally sound development worldwide. Effective control of the production, storage, treatment, recycling and reutilization, transport, recovery and disposal of hazardous waste is important for human health and environmental protection (Guerin, 2008). One of the highest priorities in hazardous waste handling is the minimization of waste generation as part of a wider approach of modifying industrial processes and consumption patterns through pollution prevention strategies and clean technologies (Gusti, 2009).

Brazil has specific legislation and standards for dealing with waste. The Brazilian Constitution (Brazil, 1988) legislates on environmental protection in its Article 225th. There are other laws associated with this matter, such as Law 6,938 (Brazil, 1981), which establishes the National Policy for the Environment; Law 6,803 (Brazil, 1980) on basic guidelines for industrial zoning in critical pollution areas; Law 12,305 (Brazil, 2010a), which establishes the National Policy for Solid Waste; Decree 7404/2010 (Brazil, 2010b), which establishes the National Policy for Solid Waste Inter Ministry Committee and the Steering Committee for the Implementation of Reverse Logistics Systems; and the National Council on the Environment (CONAMA) Resolutions. This subject is extensively addressed in Chapters 19, 20, 21 and 22 of Agenda 21.

The handling and final disposal of industrial waste follow the ‘polluter must pay’ principle established by the National Policy for Solid Waste Law 12,305 (Brazil 2010a). This principle means that ‘the one generating [waste] is responsible for its handling and final disposal’. The Brazilian states intervene in this matter through environmental control agencies that require hazardous waste producers to use proper handling, storage, transport and final disposal systems. Crelier and Dweck (2009) claim that a broad consensus currently exists on the importance of measures focused on the reutilization of water and recycling of solid waste; therefore, this ideal is expected to be embodied in real actions that demonstrate the efficiency of the decisions made in this regard and strengthen the management mechanisms that support them.

Environmental management of solid waste is based on waste minimization and energy recovery whenever possible. In waste minimization, the prevention of hazardous waste production is emphasized, together with the use of disposal alternatives excluding the soil as a destination. Minimization consists of diminishing the amount of waste and/or its contamination potential by reduction at the source, reutilization and recycling, thereby minimizing toxicity and/or hazardousness. To achieve effective waste minimization, Pinheiro and Holanda (2009) suggest that hazardous waste generators must first establish whether or not the production of waste can be avoided (reduction at the source); then, the possibility of finding a new application for the product (reutilization) should be evaluated; and finally, the possibility of generating profit from the raw material that composes the waste (recycling) should be evaluated. The combination of these three principles forms the 3 R concept: reduce, reuse, recycle.

The 3 R policy sanctioned by Agenda 21 aims to reduce the negative environmental impact of human activities. The application of the 3 R policy generally involves saving non-renewable resources and reducing pollutant emissions into the soil, water and atmosphere. The strategy of reducing or eliminating waste at its source consists of developing actions that promote waste reduction, preserve natural resources, reduce or eliminate toxic substances (present in raw materials or auxiliary products), reduce the amount of waste generated by processes and products and, thus, reduce the amount of pollutants released into the air, soil and water. Reutilization includes any technique that allows waste reutilization without treatments that alter the physicochemical characteristics of the waste. Recycling is any technique that allows the generation of profit from a waste after it is subjected to a treatment that modifies its physicochemical characteristics.

Recycling might be performed separately from or within the refining process. Recycling within the process allows a profit to be generated from waste and then utilized in the same process that produced the waste. Recycling separately from the process allows a profit to be generated from waste and for it to be used in a process other than the one that generated the waste.

Technologies for treating oily sludges

The treatment of oily wastes is needed to prevent soil contamination to maintain the functionality of the soil and to protect the quality of superficial and subterranean water, which are public assets and strategic reserves for public supply and environmentally sustainable development. Our analysis of the technological solutions applied to the treatment of oily sludges begins by mapping out the available technologies from master's dissertations, doctoral theses, scientific articles, patents, technical reports and professional field experience. Many physical, physicochemical and biological processes are available to treat oily sludges, such as landfilling; incineration; co-processing in clinkerization furnaces; microwave liquefaction; centrifugation; destructive distillations; low-temperature conversion; thermal plasma; incorporation in ceramic materials; development of impermeabilization materials; encapsulation; biodegradation in landfarming; biopiles and bioreactors.

These processes are described in detail in the following sections.

Landfilling

Landfill sites are impermeabilized areas prepared for the deposition of waste in cells. These horizontal areas are planned and constructed specifically for the disposal of compatible industrial solid waste according to NBR ISO 10,157 (ABNT, 1987). This system consists of a particular way of disposing of waste in the soil that, based on engineering criteria and specific operational standards, aims to guarantee safe confinement in terms of environmental pollution and public health protection. It is also the least expensive among the employed techniques (Businelli et al., 2009). Oily sludge is not likely to be disposed of in soil, at least not in clean soil, and not in landfilling. However, it may be landfilled in confirmed cells, alone or mixed with other wastes.

Moses et al. (2003) proposed a landfill disposal system for 600 tons of oily sludge that results from tank cleansing. The system consisted of a low-permeability (10^{-7} to 10^{-8} cm s^{-1}) 40-cm clay layer followed by a high-density polyethylene layer. To decrease the potential migration of leachate into subterranean aquifers, a plant (*Acacia auriculiformis, Bamboo, Polyalthia* sp. and *Casuarina*) belt was installed to absorb and metabolize petroleum hydrocarbons. However, this technique has limitations for some types of industrial waste that require pre-treatment before landfilling can be performed. Consequently, landfilling is only performed when no other reuse or recycling technique is available.

In Brazil, legislation discourages the disposal of petroleum sludge in landfill sites. According to Kriipsalu et al. (2008), many European countries have banned the disposal of oily sludges in industrial landfill sites. Law 12,305 (Brazil, 2010a), Article 9 establishes that the following order of priorities must be observed in the management and administration of solid waste: non-formation, reduction, reutilization, recycling, solid waste treatment and environmentally adequate final disposal of wastes. Thus, the disposal of oily sludges in industrial landfilling sites must be avoided as much as possible because reduction, reutilization and recycling must be prioritized.

An important feature of solid waste contained in landfill sites is the decomposition of the organic matter, which results in the production of gas and leachate, which is a dark-coloured, foul-smelling fluid of varying chemical composition that includes heavy metals and organic matter. Leachate is a cause for concern because it might infiltrate the soil and contaminate subterranean and superficial water. A further disadvantage of industrial landfilling is the need for physical space (Butt et al., 2008).

Incineration

Incineration is a treatment method that utilizes thermal decomposition via oxidation under high temperatures to decrease the volume of waste, make it less- or non-toxic or even eliminate it, in some cases. The NBR ISO 11,175 standard (ABNT, 1990) establishes criteria for the incineration of hazardous waste. CONAMA resolution no 316/2002 legislates the procedures and criteria to be applied to the functioning of thermal waste treatment systems (CONAMA, 2010). Wastes for incineration can be solid, liquid or pasty. Their characteristics and behaviour during combustion determine how they must be mixed, stored and introduced to the burning area. Some liquids are easily destroyed, whereas others must be inserted through a hot gas stream or sprayed directly over the flame. In this case, new toxic substances might be formed by way of molecular cracking. Thus, control systems are required, the most important of which control the temperature to be attained and the time of exposure.

When sulfur-, fluorine-, chromium-, bromine- and iodine-containing wastes are incinerated, they form gaseous emissions containing these same pollutants. To eliminate these pollutants, the gases must be washed (Gomez et al., 2009). The resulting compounds are gases (CO_2, SO_x, NO_x, PAH, BTEX, dioxins and furans) and ash (mostly metals). When the combustion is incomplete, carbon monoxide (CO) and particulates composed of finely divided carbon released into the atmosphere as soot might appear. In general, two major types of incineration are used: conventional and other types that incorporate energy-recovery procedures. In the latter type of incineration, a steam generator is placed in the path of the combustion gases to generate a profit from a considerable fraction of the gases thermal energy via their cooling. This procedure suffers two major disadvantages. First, it involves a high expenditure of energy during the burning stage. Second, even when there are engineering criteria and specific operational standards, they are not sufficiently safe to prevent air pollution from the persistent threat of PAH, the formation of even more hazardous compounds such as dioxins and furans and the inadequate landfill disposal of more toxic wastes such as heavy metals, which are still found in fly ash or bottom ashes (Gusti, 2009). Incinerators to treatment of oily sludges must be equipped with flue gas cleaning systems with high-tech.

Chen et al. (2008) studied operational variables for new incineration technologies that employ pure oxygen injection and recycling of the gas derived from waste combustion. Their results indicated that increasing the oxygen concentration to 40% and the recycled gas concentration to 35% in the input stream reduces the emission of benzene, toluene, trichlorobenzene, 2,4-dinitrophenol, phenol, dichlorophenol and other aromatic and chlorinated organic compounds.

Co-processing in clinkerization furnaces

The industrial process for the fabrication of cement comprises the calcination and fusion of a material composed of about 94% calcareous materials, 4% clays and 2% iron and aluminium oxides in a rotating furnace operated at a temperature of 1450 °C for solids and where the flame temperature oscillates at approximately 2000°°C. This furnace produces clinker (Rocha et al., 2011). Wastes are processed in rotating furnaces because the specific conditions of the process, such as high temperatures, an alkaline environment, an oxidizing atmosphere, an optimal mixture of gases and products and a long residence time, are usually sufficient to destroy hazardous wastes. However, the use of these alternative fuels in the cement industry has limitations, such as the volume of the secondary fuel that feeds the furnace and other limitations related to environmental safety. Waste fuels are selected specifically not to influence or compromises the quality of a cement product. Therefore, utilization of oily sludges is strictly monitored. During waste combustion, the most volatile materials follow emission paths that are damaging to the properties of cement and occupational and environmental health. Many of these wastes are classified as hazardous and contain heavy metals and organochlorine compounds with vinyl or aromatic chains, such as dioxins and furans.

In waste combustion, heavy metals are redistributed. The most volatile metals (such as Hg and Tl) are emitted together with gases through the main furnace chimney, whereas the semi-volatile (Cd, Pb, Sb and Se) and non-volatile (As, Cr, Cu and Ni) metals are usually incorporated into the clinker. The levels and characteristics of atmospheric pollutant emissions depend on the technological and operational characteristics of the industrial process, especially the characteristics of the clinker rotating furnaces, the chemical and mineralogical composition of the inputs and the chemical composition of the fuels. In this regard, the burning of hazardous waste involves a significant emissions load with a correspondingly high environmental and social cost.

To measure the impact on human health of the inhalation of these pollutant-rich materials, Winder and Carmody (2002) studied the causes of contact dermatitis in civil construction workers arising from the alkaline nature of cement combined with chronic exposure to the irritating action of chromium(III) and chromium(IV) compounds commonly found in cement. This study also indicated a strong correlation between chronic exposure to dioxins and furans and increased incidences of cancer, reproductive disorders, immune deficiency and endocrine system disorders. In terms of environmental health, these authors observed a negative impact on the quality of the air breathed by the population close to the plant.

Dioxins and furans accumulate in fatty tissues, especially in animal-derived food products. It is not fully known whether dioxins and furans are already present in wastes or instead formed from precursors (such as biphenyl polychloride and chlorinated benzenes) or compounds not directly considered hazardous, such as chlorinated hydrocarbons, inorganic chlorine ions or plastics. Although the temperatures in cement furnaces are sufficient to destroy dioxins and furans, these compounds can form anew during the process of gas cooling (Sweetman et al., 2004).

The problem posed by the emission of mercury in combustible gases has been investigated and was a focus of intense surveillance by the European Union. Usually, mercury is generated by the treatment of metals, waste incineration and fossil-fuel burning, among other sources. The mercury in mud studied by Zabaniotou and Theofilou (2008) was derived from processing at a sewage treatment plant, where the emissions of heavy metals were only 16% (w/w) and 6% of the maximum acceptable levels of dioxins and furans, respectively. Thus, these authors concluded that the co-processing of sewage mud as an alternative fuel for cement furnaces is satisfactory. This practice helps to save energy during fuel combustion in addition to providing the environmental benefit of proper disposal of a waste that might cause environmental damage if it were discarded in an irregular manner.

Microwave liquefaction

Microwave liquefaction is a technique developed in the United States that consists of a process for separating the water contained in oily sludges by means of an emulsifier combined with a microwave bundle. Such treated sludge can be reused for energy purposes, and the separated water can be sent to an industrial sewage treatment station (ISTS) (Robinson et al., 2008; Sandroni and Smith, 2002; Wolf, 1986).

Mutyala et al. (2010) noted that microwave technology has broad applications in the petroleum industry, such as the in situ recovery of oil in schist; the separation of water–oil emulsions; the removal of naphthenic acids; hydrodesulphurization; hydrodenitrogenation and the cracking of heavy oils. These authors reviewed the scientific and technological literature on microwave radiation processes and described some results indicating that microwave radiation technology exhibits a higher efficiency in separating systems containing water, oil and solids than those involving gravitational sedimentation and traditional heating processes.

According to Ladislao (2008), the microwave technique can be applied to accelerate the release of organometallic compounds that affect the carbon–metal bond. Moreover, to avoid the loss or transformation of species, some extraction parameters have been optimized, such as exposure time and microwave power.

Fortuny et al. (2007) studied the effect of some variables (pH, salinity and aqueous fraction) on the performance of demulsification by microwave irradiation in an industrial reactor. The best results were observed with a neutral pH, zero salinity, 45% aqueous fraction and a temperature of 130 °C that resulted from an increase of the applied microwave power.

Centrifugation

The centrifugation technique allows the separation of gaseous, aqueous and pasty phases by physical means. This technique is a reasonably clean process with relatively low cost. The use of centrifugation is advantageous because it does not require a large space; however, some precautions must be taken when installing the equipment because it can generate noise and vibrations (Ripley and Needham, 1998). According to Alshammari et al. (2008), this technique is less efficient for the separation of oil and water than the technique of microwave irradiation with an emulsifier. Zubaidy and Abouelnasr (2010) reported a process for the recovery of oily sludge from the bottom of a tank using steam, organic solvents and tensioactive chemicals to reduce the viscosity of the sludge and thus allow removal of the oil solids. This process employs centrifugation for separation and is able to produce a solid with only 1500 ppm of total petroleum hydrocarbons (TPH). The recovered oil is approximately 16% of the total volume and approximately 50% of the emulsion oily fraction, and it is incorporated into the process of production because it has compatible quality. Centrifugation generates 7% heavy oily sludge. The oil resulting from this process can be used for burning in boilers and other energy-producing processes.

Destructive distillation

Destructive distillation, pyrolysis or thermal oxidation is the chemical decomposition of an organic compound induced by heat at temperatures between 300 and 1600 °C. In the treatment of petroleum sludge, factors such as the size of waste particles, the humidity (up to 5%), the abrasion capacity of the processing unit, the presence of heavy metals and the corrosion of the ducts and reactor might limit the application and the efficiency of this process (Bridle and Mantele, 1999; Punnaruttanakun et al., 2003; Shie et al., 2000).

Wallace (1978) described the process of pyrolysis under high temperatures or destructive distillation for a variety of high-molecular-weight organic materials. Processes are conducted under non-oxidizing conditions. Organic compounds are exposed to microwave and ultrasound radiation to promote the cracking of high-molecular-weight molecules. Volatilized components are collected in an appropriate compartment, and the main resulting molecules are H_2, CO, CO_2, N_2, O_2, CH_4, C_2H_6 and C_3H_8.

In 2003, Petrobras developed a three-stage technique in which petroleum sludge is subjected to high temperatures, which allows the separation of water, oil and solid compounds. In addition to oily sludges, this technique has also been applied to the treatment of oil-contaminated soils. This method consists of initially heating the sludge to evaporate most of the water (90–150 °C), followed by a second stage of thermal distortion (250–350 °C), which is performed at temperatures higher than those used in the first stage to crack the hydrocarbon chains. Finally, prosthesis is performed, in which the heavy material resulting from the previous treatments is cracked at very high temperatures (500–800 °C). The solid waste that results from these three stages forms an inorganic material (Pickler et al., 2004).

Shie et al. (2004) studied the treatment of oily sludge under different oxygen concentrations (4.83–20.95% O_2) at temperatures between 107 and 850 °C and with heating constants from 5.2 to 21.8 K min^{-1}. This process resulted in less-viscous oil that exhibited increased quality as the oxygen concentration was increased. The optimal temperatures for the thermal treatment process reactions varied between 315 and 425 °C (laboratory unit) and 190 and 360 °C (pilot plant) under a nitrogen atmosphere, which promoted waste minimization as evidenced by a greater than 40% reduction of the initial oily waste mass. The main resulting compounds were N_2, CO_2, H_2O, CO and low-molecular-weight paraffinic and oleifinic hydrocarbons. Crelier and Dweck (2009) assessed the influence of water content on the process of oily sludge pyrolysis using thermogravimetry. Differential thermal analysis (DTA) revealed that the water content of oily sludges can significantly affect the thermal balance in the industrial pyrolysis process.

Thermal plasma

Thermal plasma technology has evolved during the 1980s to a well-established interdisciplinary science with a wide range of important applications in materials processing. Plasma is considered to be the fourth state of matter, consisting of a mixture of electrons, ions and neutral particles, although overall it is electrically neutral. This technology involves the creation of a sustained electrical arc by the passage of electric current through a gas in a process referred to as electrical breakdown. Because of the electrical resistivity across the system, significant heat is generated, which strips away electrons from the gas molecules resulting in the plasma (Huang and Tang, 2007). Thermal plasma offer a combination of advantages: the results are high processing rates, high fluxes of radical species, the potential for smaller installations, and high quench rates (Byun et al., 2011).

Nishikawa et al. (2004) conducted a study of using thermal plasma with steam for the treatment of carbonaceous wastes. The experiment was carried out in a hybrid plasma system, a gas control system, a steam generator, an exhaust system and a reaction chamber. Argon was used as the plasma gas and carrier gas and oxygen and steam were used as oxidants. Charcoal with sodium chloride was used as a test piece instead of carbonaceous wastes.

Three different conditions were tested. The first was treatment by argon thermal plasma alone, the second with argon thermal plasma and oxygen and the third by argon thermal plasma and steam. The results showed that the charcoal experienced a large weight loss when treated by thermal plasma with oxygen and by thermal plasma with steam. It was concluded that the gasification of carbon by thermal plasma with steam is very effective for the disposal of carbonaceous wastes.

Low-temperature conversion

Bayer and Kutubuddin (1982) began the development of the process of low-temperature conversion (LTC) in the 1980s. LTC is a thermal process performed at low temperatures under an inert nitrogen atmosphere; the temperatures are oscillated between 380 and 450 °C, without the addition of catalysts. LTC was developed to generate a profit from the industrial sludge obtained in urban and industrial effluent treatment stations (ETS). The treatment stations generate four products with potential for commercial reutilization: oil, coal, gas and water (Aires, 2002).

The chemical composition of oil and the quality of coal are functions of the origin of the waste employed as raw matter. Oil obtained by LTC might have several industrial applications according to its chemical composition. In general, oil from LTC is composed of hydrocarbons and fatty acids when the sludge comes from urban or industrial treatment stations with the same characteristics and can be used in the fabrication of soap, grease and other products. The calorific power value determines whether or not raw oil and coal can be used as fuels. One of the major advantages of this process is associated with the storage and transport of both oil and coal. Additionally, gases and treated water might be recirculated within an energy co-generation system, thus diminishing the final cost of the operation (Zhiqi et al., 2007). Pereira and Soriano (2002) indicated that in Brazil, this technology is being evaluated for application to urban, industrial and agricultural wastes. Their results indicate yields of 10–40% oil, 40–79% coal, 6–16% water and 3–10% gas.

Incorporation in ceramic materials

The ceramic industry has identified and tested some techniques that incorporate wastes as raw matter into clay mass to obtain refractory materials, such as in the fabrication of ceramic blocks. The use of oily sludges in the fabrication of ceramic materials also favours a reduction of the energy costs because products such as hollow bricks, solid bricks, slabs, tiles, ceramic pipes, gaskets and structural blocks and rustic floors often gather large amounts of energy. This method therefore reduces the distances for raw matter transport while resulting in products with higher technical quality (Silva et al., 2006).

The ceramic materials are produced by burning out the expanding clay in a rotary kiln at 1100–1200 °C. The emitted gases are blocked in pores due to a high viscosity of the liquid phase. The liquid phase blocked in the pores causes the expansion of granules. These ceramic materials are known as trademarks Leca, Fibo and Arlita (Latosińska and Żygadło 2009).

Mansurov et al. (2001) emphasized that the solution for the problem posed by the use of oily sludge and oil-contaminated soils is complex because of the instability of these wastes and their future composition and properties, which change constantly under the influence of the atmosphere when they are stored in open wells. At the same time, waste ‘ages’ because of the evaporation of its lighter components, the oxidation and resinification of the raw oil, the formation of micellar-colloidal conglomerates and the additional precipitation of mostly inorganic contaminants. Monteiro et al. (2007) observed that solubilization assays for incorporated red ceramic pieces comply with the technical specifications. However, their investigation of the microstructure of ceramic clay with inertized oily waste showed that the addition of this waste caused alterations in the chemical composition and the microstructure of the ceramic material. These authors also showed that the best proportion of oily sludge for incorporation in the fabrication of ceramic blocks is approximately 10 to 20% in weight because properties such as mechanical resistance and water absorption are maximized. In addition, ceramic blocks prepared from oily sludge at this concentration exhibited good chemical stability, as demonstrated by the results of lixiviation and solubilization analyses.

In general, the use of oily waste in the fabrication of red ceramics improves quality. The latest published articles show that oily waste without inertization treatment results in a 10% increase in the mechanical resistance when it is incorporated into ceramic material. This increase is the result of a better packaging of clay particles in the processed mass before burning arising from the lubricating action of oil films. For additions of waste greater than 10%, the oily contents of the sludge, in addition to a film, also form a hydrocarbon pocket that, after burning, results in pores (empty spaces) that are unfavourable for mechanical resistance (Monteiro and Vieira, 2005).

Development of impermeabilization materials

Oily sludges and oil-contaminated soils can be used to fabricate impermeabilization materials used in road construction. The United States uses most of its oily wastes in the maintenance of light-traffic roads in extraction and production areas; the waste is often mixed with added materials from the same sites. The case of California should be highlighted for its employment of compacted oily sludges materials in pavements for approximately a century (Mansurov et al., 2001).

The use of oily sludges for road improvement might be viable when it is applied to one of the paving layers or merely agglomerated with clay for compaction on the roadbed to increase resistance and to reduce the formation of particulate material. However, further care is required when using oily sludges for road maintenance because full knowledge of its physical and chemical characteristics and its environmental classification is required to guarantee that its use in roads will not result in any negative effect on the environment. Attention must also be paid to the geomorphology of roads and the surrounding environment, including the flora and fauna, and to data on local hydrogeology (Lynn et al., 2002; Partanen and Ellis, 2006).

According to Binet et al. (2002), molecular reactivity is strongly influenced by temperature: asphaltenes are the most reactive, followed by resins, aromatics and saturated compounds. Another important issue is the emissions caused by heating when oily sludge is used to prepare hot asphalt mixtures. Such emissions contain a large amount of organic compounds that could potentially damage the health of processing workers. Among these compounds, we highlight PAH compounds, which are considered to be mutagenic and carcinogenic (Wahlström et al., 2000).

Oily sludges used for road construction must be tested for properties such as flash point, permeability, density, proportion of organic matter, metals, pH, electric conductivity, lixiviation capacity and proportion of oils and greases. Al-Futaisi et al. (2007) evaluated the treatment of oily sludge containing 500 000 mg kg^{-1} TPH as well as high Pb, Zn and Hg and low Ni, Cu and Cr concentrations compared with the values reported in the literature. These authors suggested three possibilities for treating this oily sludge: physical mechanisms to extract oils that can be used as fuels, solidification/stabilization and the production of road construction materials. The results were satisfactory, which indicates that the use of this oily sludge in road construction is the best technique among those discussed.

Encapsulation – solidification and stabilization

Encapsulation is a term used to define a waste treatment technology that uses processes of solidification and stabilization of contaminants (Ball et al., 2011). In stabilization, the hazardous components of waste are transformed through chemical reactions and maintained in their less-soluble or less-toxic forms. Solidification produces a monolithic solid mass of treated waste, which improves the structural integrity in terms of physical and handling traits (Gusti, 2009).

This technology is a treatment alternative for wastes that contain ionic contaminants such as heavy metals. Its application to oily organic contaminants present in petroleum-industry wastes has been the subject of recent research. In general, clays, soils and aquifer materials with little organic matter exhibit low adsorption capacities for the organic contaminants present in subterranean water (Poon et al. 2001). However, a small chemical modification that causes the dislocation of natural exchangeable ions in these soils results in a significant increase of the organic content and a substantial increase of the adsorptive properties of non-ionic organic solutes. The increase in the organic phase results from the exchange of cations present in the mineral structure with organic cations that act as a powerful adsorption medium with an absorption capacity 10 to 30 times higher than that of the soil natural organic matter (Leonard and Stegemann 2010). This process is effective for the removal of benzene, dichlorobenzene, percholorethylene and many other organic substances. Thus, this soil modification can also be used to treat solid waste before disposal in landfill sites to improve the containment capacity of soils that are poor in organic matter, to protect aquifers and also to increase the containment capacity of impermeabilization layers in landfill sites (Moses et al., 2003).

Thus, encapsulation technology may be defined as a treatment process to improve the physical and handling treatments of waste, reduce the surface area through which pollutants can migrate or leach, limit the solubility of the waste or even detoxify its hazardous components. According to Silva et al. (2006), inertization consists of the addition of 20% by weight of bentonite, which acts as an encapsulating agent for hazardous compounds in oily sludges. This material requires eight days to perform inertization by encapsulation, after which its colour becomes clearer and its pasty consistency becomes sandy. After this stage, the material is referred to as encapsulated sludge, which is classified as Class II A (non-inert), although it still requires space and care for proper disposal.

Landfarming

Landfarming is a bioremediation technique whereupon oily sludges are scattered and mixed into the reactive soil layer in a controlled manner for the microbiota in the ground to act as a degrading agent. This process is applied to large areas because biodegradation occurs in the upper soil layer, where aerobiosis is guaranteed. Soil hydrocarbons may undergo volatilization and biodegradation (Hejazi et al., 2003; Maila and Cloete, 2004).

The use of soil for treatment began in Europe at the end of the nineteenth century with the technique of irrigating cultivated areas with sanitary waste waters. At the beginning of the 1950s, this treatment process attracted the interest of petroleum-refining companies in the United States, which were the first to develop and apply treatment in the soil for their waste. They named this specific treatment process landfarming (Genouw et al., 1994; Picado et al., 2001; Sayles et al., 1999). However, the landfarming approaches to bioremediation of refinery and other petroleum sludges are not acceptable environmentally and are banned in most North American jurisdictions (Ward et al. 2003).

The NBR ISO 13.894 (ABNT, 1997) standard establishes that unit planning, construction, operation and maintenance must seek to attain maximal levels of degradation, transformation and/or immobilization of contaminants in the soil reactive layer. Landfarming construction prevents or minimizes the transference of contaminants to neighbouring areas via the existence of a lateral barrier and an impermeabilization layer made of high-density polyethylene or compacted clay. Operational techniques involve the addition of nutrients, humidification, aeration and pH correction of the soil. The added macronutrients are nitrogen, phosphorous and potassium compounds in the form of commercial fertilizers and/or urea (Harmsen et al., 2007; Maila and Cloete, 2004). Correction of the soil pH can be performed by the addition of calcium and magnesium oxides. Soil aeration is performed by means of a plough coupled to a tractor (Marin et al., 2005).

Silva (2009) evaluated the treatment of oily wastes in a 1000 m^2 area in a landfarming site at a Brazilian refinery. Biostimulation operational methods were employed through humidification, fertilization and aeration. In parallel, an area was isolated as a control cell. Results obtained after 225 days of treatment were encouraging with respect to time and the initial concentrations of contaminants. The TPH content decreased by 89.6% in the treated soil, with a degradation rate of 25.8 mg kg^{-1} day^{-1}, whereas the control soil exhibited 22.4% degradation (6.5 mg kg^{-1} day^{-1}). The population of aerobic bacteria, filamentous fungi and anaerobic bacteria exhibited average concentration values of 1.4×10^7 colony forming unit (CFU) g^{-1}, 2.6×10^5 CFU g^{-1} and 2.2×10^6 cells g^{-1}, respectively.

Hamdi et al. (2007) have evaluated the specific biodegradation of anthracene (ANT), pyrene (PYR) and benzo[a]pyrene (B[a]P) by employing biostimulation and bioaugmentation techniques to remove these compounds. Bioaugmentation is the introduction of a group of natural microbial strains or a genetically engineered variant to treat contaminated soil or water. These authors observed complete degradation of ANT and PYR in just 30 days; however, B[a]P decreased from 1000 to 420 mg kg^{-1} in 90 days. The rate of biodegradation was consistent with the number of benzene rings, which is greater in ANT and PYR with three and four rings, respectively; however, the rate was slower for B[a]P. The slow degradation of B[a]P might be related to the strong interaction of the five benzene rings with the solid matrix, which results in low mass transference to micro-organisms. Among the PAH studied, benzo[a]pyrene is the most worrisome because it accumulates along the food chain and exhibits physicochemical properties similar to those of many organochlorine pesticides such as DDT, dieldrin and atrazine (Haritash and Kaushik, 2009).

Biopiles

Biopile technology involves the construction of contaminated soil mixed with oily sludges in cells or piles to stimulate internal aerobic microbial activity by highly efficient aeration. Biostimulation operational methods are employed to improve the microbial activity through addition of humidity or nutrients such as nitrogen and phosphorus. Bacteria degrade hydrocarbons adsorbed in the soil particles, thereby reducing their concentration. Typically, biopiles are constructed on an impermeable base to reduce the probability of leachate migrating to the subsurface environment. A mesh of pierced ducts installed at the base of the pile and connected to a compressor guarantees optimal aeration of the system (Kriipsalu and Nammari, 2010). In some cases, a collection system is built for the leachate, mainly when a humidifier is used. Piles are usually covered with plastic to avoid the release of atmospheric contaminants and to protect piles from the weather (Seabra et al., 2006).

Ururahy et al. (1998) noted that the most common varieties of biotechnology applications for waste treatment (landfarming and biopiles) require long processing times, pose significant risks of aquifer contamination from leaching, are highly sensitive to climactic variations and require large areas of land and constant monitoring. The biopile technique has the following additional disadvantages: it might not be effective for high concentrations of contaminants (> 50 000 ppm TPH); heavy-metal concentrations greater than 2 500 ppm inhibit microbial growth; compounds that are too volatile tend to evaporate instead of being biodegraded and the gases resulting from aeration might require treatment before being released to the atmosphere. Oily sludges are usually poor in organic matter and exhibit low bacterial activity. Thus, the biodegradation rate of a pollutant might be negatively affected.

Kriipsalu et al. (2008) evaluated the biodegradation of oily sludge from flocculation–flotation units through biopiles generated from different structuring materials, including sand, matured oily waste, food wastes and cut wood wastes. The use of food wastes as the structuring material yielded better degradation of TPH and PAH.

Bioreactors

Different types of bioreactors have been developed, mainly for the treatment of liquid effluents, but these systems are also currently being used for solid waste. Slurry bioreactors are one of the most important types this technology for treatment of oily sludges. They might be useful for the degradation of highly resistant compounds (Riser-Robert, 1998; Rizzo et al., 2010).

Micro-organisms can generally be used in bioreactors in two different states: free or immobilized. However, only the former state has been used in the treatment of solid waste. In this case, the micro-organisms are kept in suspension and are able to grow freely within the liquid medium or adherent to the soil in suspension. The bioreactors can be agitated mechanically or by continuous air injection (Lima et al., 2011; Upreti et al., 2009). The most common type of treatment of contaminated oil involves systems operating in a semisolid phase with 40–90% water (v/v). Ururahy et al. (1998) prefer the bioreactor treatment technique. In their view, bioprocesses are better than incineration because the latter has high-energy demands, and co-processing requires reprocessing of sludge during refining at the refinery itself or at other industrial units (cement and brick factories).

Nevertheless, bioreactor treatment has some disadvantages, such as higher costs than in situ treatments, because the transport of contaminated material involves additional expenses, the construction of equipment for a particular decontamination, additional manpower and additional energy (Alshammari et al., 2008).

According to Ward and Singh (2003), a bioreactor system with a 4.55×10^6 L capacity was used to treat oily waste at the Gulf Coast refinery, which is one of the largest in the world. The nominal solid volume was 10%, and an aeration and agitation system was used to increase biodegradation. This bioprocess was inoculated with hydrocarbonoclastic micro-organisms, particularly those of the genera *Acinetobacter, Alcaligenes, Ochrabactrum, Pseudomonas/Flavimonas, Rhodococcus* and

Stenotrophnomonas. A 50% reduction of oils and greases was achieved after 80–90 days.

Soriano et al. (2007) claimed that, compared with the classic bioremediation techniques of landfarming and biopiles, the use of bioreactors has advantages to improve the biostimulation and bioaugmentation: the control of atmospheric emissions and process water production; the control and maintenance of operational conditions (pH, temperature, humidity content); the guarantee of adequate mixing (continual or discontinued agitation); more effective monitoring of pollutant degradation; the possibility to place additives directly into the reactor (water, micro-organisms, biosurfactants, nutrients, pH correctors, co-substrates); a facilitated aeration system and a lack of direct contact between reactor contents (pollutants) and the environment during the treatment process, which results in environmental and safety gains.

Analysis of technological solutions applied to the treatment of oily sludges

The aim of any oil removal operation is basically to reuse, recycle or dispose of oily waste in the most efficient and environmentally proper manner. The choice of treatments depends on the amount and type of oily sludges, the presence of contaminated sediment, the site of oil waste formation, the legal and environmental considerations and the operational costs involved. The amount of oily sludges formed is an important variable for decision-making because each technology has a specific processing capacity. A large refinery may employ bioreactor technology, centrifugation, co-processing in clinkerization furnaces or destructive distillation. Ward et al. (2003) highlighted the LST (liquid/solid treatment) process developed by Petrozyme Technologies, Ontario, Canada. This technology was applied to treat 75% of oily waste produced by Venezuelan refineries over 6 years. The facilities included eight bioreactors with a total capacity of 1×10^6 L. The bioreactors were contained in a sparged air-lift aeration system with no mechanical mixing; and the optimal operating temperature was 28–32 °C. The fermentation nutrient formulation was optimized to maximize hydrocarbon accession by the micro-organisms, microbial growth rates and the rate and extent of hydrocarbon degradation. The initial TPH concentration was 10% (w/v); 12 days after bioprocessing, the TPH degradation was greater than 99%.

A small refinery can use biopile technology, landfarming, encapsulation, incineration or low-temperature conversion. The type of oil processed in the refinery must be taken into account because heavy petroleum (low API grade) gives rise to larger amounts of oily sludges. In the characterization of the parameters of oily sludges, such as: pH; dry solid matter; total phosphorus; total nitrogen; total carbon; sulfur; metals (As, Pb, Cd, Co, Cu, Cr, Ni, Zn, V, Hg); polycyclic aromatic hydrocarbons (PAH); total petroleum hydrocarbons (TPH); benzene, toluene, ethylbenzene, xylenes (BTEX) must be quantified (ABNT, 2004a; SW-846 guidelines; USEPA (2007)). Water content in oily

Table 4. Types of oily sludge and recommended treatment methods.

Type of oily sludge	Treatment method of oily sludges												
	Incineration	Co-processing	Microwave liquefaction	Centrifugation	Low-temperature conversion	Destructive distillation	Thermal plasma	Incorporation in ceramic materials	impermeabilization materials	Encapsulation	Landfarming	Biopile	Bioreactors
Oily sludges with detergents or washing liquids, and it is carrying rust and reaction residues.			×	×	×	×	×						×
Oily sludges with non-mineral skimmed foam and grease.				×							×	×	×
Light oily sediments which contain mineral material.			×	×	×	×	×	×	×	×			
Heavy oily sediments which contain mineral material.	×	×				×	×	×		×			

×, recommended treatment method

sludges is an important variable in treatment-technology decision-making. For example, centrifugation, bioreactors, landfarming and biopiles might be indicated for oily sludge with a high water content. However, sludge with high water content is not desirable for thermal processes such as incineration, co-processing, destructive distillation, thermal plasma or low-temperature conversion. If the concentrations of heavy metals such as Pb, Hg, Cr and Zn are high the biological processes become strongly affected (Zukauskaite et al., 2008). High concentrations of PAH and BTEX can also inhibit micro-organisms. The pH of the waste helps to determine which type of treatment is better suited. The optimal pH for biological treatments varies between 5.5 and 8.5 to permit the development of biological communities (Hamdi et al., 2006; Kriipsalu et al., 2007; Ollivier and Magot, 2005); if the pH is too high, co-processing treatment is not viable because it damages furnaces and compromises their durability. The concentration of TPH is also a decisive parameter because whenever their level is too high, microbiological inhibition might follow. However, in the case of physicochemical processes, the higher concentrations of TPH make technologies that recover oil by way of microwave liquefaction, centrifugation, destructive distillation or low-temperature conversion more preferable.

From the perspective of oily wastes characterization, there are four types of oily sludges: oily sludges with detergents or washing liquids, and carrying rust and reaction residues; oily sludges with non-mineral skimmed foam and grease; light oily sediments which contain mineral material; and heavy oily sediments which contain mineral material. In Table 4, the best indicated treatments for each type of oily sludge, taking into account possible reuse, costs and available techniques, among other features are suggested. Costs were evaluated according to the Remediation Technologies Screening Matrix and Reference Guide, Version 4.0 (FRTR, 2011).

Oily sludges lead to difficult decisions that require a survey of the available resources, the choice of the best practices, the choice of cleansing techniques and the safety of the involved personnel. More than one treatment type might be indicated for each type of oily sludge. Decision-making criteria still must include other variables, such as operational cost, legislation and environmental requirements (possible environmental impact remaining after the use of a given oily sludges treatment technology).

Conclusions

Available studies represent an important contribution, especially regarding the treatment, reuse and recycling of petroleum sludge. Improvement of the techniques is part of a body of actions involving policies that integrate the management of quality, health, safety and environmental systems. Furthermore, these policies seek more investment and attention to research to develop new clean technologies.

Oily sludges can be treated by different approaches, which make it necessary to survey the available resources and to select the most suitable treatment technologies as a function of the physicochemical characteristic of oily sludges. Characterization might result in four types of oily wastes that may require different treatment technologies. This alignment between oily sludge characteristics and available treatment technologies guarantees the most effective management of these oily wastes.

Funding

This research received no specific grant from any funding agency in the public, commercial, or not-for-profit sectors.

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