# ENVIRONMENTAL IMPACT ASSESSMENT: REFINING SECTOR

A project report submitted in partial fulfilment of the requirement of the

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In

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# CERTIFICATE

This is to certify that the project report on **Environmental Impact Assessment: Refining Sector** submitted to **University of Petroleum & Energy Studies** by **Shashank Kalucha**, in partial fulfilment of the requirement for the award of **Degree of Bachelor of Technology in Applied Petroleum Engineering (Academic Session 2006-2010)** is a bonafide work carried out by him under my supervision and guidance. This work has not been submitted anywhere else for any other degree or diploma.

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## ABSTRACT

"Environmental Assessments" or Environmental Reviews" have become a topic of increasing importance and relevance to the oil and gas industry. In this age of growing environmental awareness, the need for increased knowledge of the actual or potential impact of industry's operations on the environment is critical. The stakeholders requiring this information vary, from government agencies and local communities to company directors, management, and employees. One of the challenges facing industry is how to gather, assess, and then effectively act on environmental information as a strategic part of its business operation. The purpose of this dissertation is to clarify the concept of environmental assessments used in industries. It provides an overview of environmental concerns associated with petroleum industry and summarized common types of environmental assessments that are currently being performed in this industry. It also discusses some of the management criteria used to define the scope, approach, measurement standards, and reporting format.
Some key areas being covered are:

1. Environmental concerns of refining industry
2. Types of environmental assessments
3. Pollution control Techniques
4. Reuse of spent catalysts
5. Minimizing and treatment of sludge

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## 1. INTRODUCTION

It is being said that the most crucial issue of the 21st century will be negotiations of climate. Environmental issues have been talked about extensively in the recent past. All industries release pollutants during their operations and the refining & petrochemical industry is no different. The downstream sector has the potential to be amongst the most polluting industries but for the excellent practices involved.

The refining process releases numerous different chemicals into the atmosphere; consequently, there are substantial air pollution emissions and a notable odour normally accompanies the presence of a refinery. Aside from air pollution impacts there are also wastewater concerns, risks of industrial accidents such as fire and explosion, and noise health effects due to industrial noise.

Pollutants released from these installations have a detrimental effect on humans, animals, vegetation as well as property. The effects can be short term (exposure to toxic substances) or long term (global warming due to greenhouse emissions). Apart from pollutants being directly emitted or released another area of concern is safe disposal of waste and recycling of precious substances.

While refineries have usually adopted the best practices for minimization of emissions and reduction of wastage more still needs to be done. More investments in research for better technologies are required and it is essential that the environment be preserved.

## 2. TYPES OF ENVIRONMENTAL IMPACT ASSESSMENTS

Environmental assessment is defined as any review or study having the purpose of determining the environmental implications of an activity. The environmental assessments based on oil and gas industry practices can be broadly grouped into six major categories. These are:

### 2.1 Environmental Compliance Review

Compliance review is the most basic type of environmental assessment. Its purpose is to assess an entity's compliance to regulations, company policy, and/or operating practices. The assessment protocols for a compliance review may simply be a restatement of the local and national environmental laws, or facility permit, and compliance typically documented as a yes or no answer. The review scope should be defined in terms of locations/facilities reviewed, as well as the standards against which the facilities are to be judged. For example, a compliance review may be conducted at a single facility to determine and document its performance against the operating permit. The critical success factor of a compliance review program is its reporting and follow-up activities, as this type of review documents situations of noncompliance. Action plans and status reports focus on correcting the identified noncompliance issue and closing it out.

### 2.2 Environmental Site Assessment

Environmental site assessments (ESAs) are typically undertaken to evaluate and document the environmental conditions at a site. Also considered are potential environmental threats from surrounding properties. Such assessments are commonly commissioned by the legal and financial groups of the operating company for the purpose of trying to quantify potential environmental liabilities associated with the transfer of ownership. The scope of a site assessment is variable and can range from a paper due diligence review to a full groundwater and soil assessment and remediation plan. As the results from a site assessment are frequently used in business decisions, it is critical that the findings identify the current and future potential for financial risks, as well as, estimate the magnitude of the risk.

### 2.3 Environmental Management System Review

Environmental management system (EMS) reviews are designed to assess whether or not systems are in place to allow a facility or company to manage its environmental function. Unlike the compliance review, which focuses on compliance at an instant in time, an assessment of the management systems provides information on the ability to recognize, assess, and address environmental issues. This assessment assures that the company is able to maintain compliance to environmental standards, and its environmental aspects including performance, training personnel, and managing change are systematically monitored and documented. The scope of management system reviews is usually facility- or company-wide, as they usually extend into other disciplines such as occupational health and safety, quality, and operation. The critical success factor in this assessment is the ability of the reviewer to focus on the areas posing the greatest risk or opportunity for the operating company.

## 2.4 Environmental Design Review

Environmental design reviews or internal environmental impact assessments are internal reviews focused on confirming that the design of a new unit or facility meets company environmental objectives. These objectives can include not only current environmental regulatory requirements, but the company's own policies and standards. These reviews are frequently viewed as part of the ongoing activities of plant, their scope is usually fairly narrow. A more quantitative or methodical approach, similar to the hazardous risk assessments, would be required. Regardless of the depth of the review, an environmental design review is usually conducted as standard management of change procedure and the results integrated into the final design of the unit or facility.

## 2.5 Environmental Impact Assessment

Environmental impact assessments (EIAs) are becoming common requirements for financial institutions, government agencies, and other stakeholders in the facility. They can be extremely effective in ensuring the minimization of environmental impacts on the community, in the most cost-effective manner. The EIA also serves to ensure that the industry, government, and local community channels of communication are opened and remain established throughout the life of the project. The primary purpose of the EIA is to assess the potential impact of a new project in order to assure the stakeholders that the environment will not be unduly threatened by industrial development. EIAs are typically public documents which describe in detail a description and scope of the project, all relevant environmental regulatory requirements, a study and documentation of existing environmental conditions, a description of any potential environmental impacts of the project, plans and programs to manage and mitigate these environmental impacts, a monitoring plan to ensure compliance with these environmental management programs, and establishment of communications channels with government agencies and the community.

## 2.6 Decision and Risk Analysis

Decision and risk analysis (D&RA) process is a powerful tool used to compare the costs and benefits of a number of designs or strategies. Commonly used to assist in deciding the comparative financial benefits of varying business scenarios, the D&RA is becoming more frequently applied to the environmental costs and benefits of varying design approaches to a project. Experienced environmental professionals are required throughout the D&RA process to estimate the probable environmental implications of each scenario studied. Therefore, in this assessment, the environmental professional is just one component of the business team where the success factor is the right business decision.

## 2.7 Execution of Assessments

There is no single environmental assessment approach that can be applied to all companies and types of assessments. However, there is a best practice used in the oil and gas industry for executing a successful environmental assessment, which encompasses the following key steps: establishing the assessment objectives, defining its scope, planning for it, selecting the assessment team, conducting and documenting the assessment, and following up on its recommendations.

Planning the assessment involves estimating the time for the assessment, allocating resources, scheduling the assessment sessions, handling meetings, site visits, and other logistic matters, and collecting documentation, data, and records needed for the assessment. The assessment team leader is typically responsible for arranging these activities. Environmental assessments can be conducted on any site or facility and can be performed periodically or on an as needed basis. In conducting periodic assessments, typical activities include: proper people interviews, documents reviews, facility inspections, meetings, working sessions, and follow-up coordination.

In performing the remaining assessments, common practices include the use of one or a combination of the following techniques: project management, risk assessment, site assessment, engineering design concepts, cost-benefit analysis, statistical analysis, physical modelling, and utilizing results of relevant case studies and professional judgments. It is critical to follow up on the assessment recommendations to ensure its effective implementation. This is an important step in achieving the desired benefits expected from the assessment.

## 3. ENVIRONMENTAL CONCERNS OF REFINERY SECTOR

Oil and gas industry operation and activities has the potential to impact the environment, if its impacts are not adequately assessed and managed. The magnitude of the impact increases if the facility located near sensitive receptors, such as drinking water sources, residential areas, or protected environments. The presence of appropriate environmental protection measures at the facility level assists in reducing such impacts. Those impacts are typically produced during routine operation or as a result of maintenance or modification activities or accidental releases. The common environmental concerns/impacts associated with this industry can be grouped into the following areas:

1. Air emission of gases and particulates such as volatile organic compounds (VOC), hydrocarbons (HC), hydrogen sulphide ($H_2S$), sulphur oxides ($SO_x$), nitrogen oxides ($NO_x$), particulate matter (PM), carbon monoxides (CO), and carbon dioxides ($CO_2$). The impacts of these gases can vary from local effects (as in the case of CO and VOC) to global warming effects (as in the case of $CO_2$ and $N_2O$). In addition, since petroleum hydrocarbons possess flammable nature, their vapors have the risk of causing explosions and fires, if not properly managed.

2. Industrial wastewater discharges, which can result into release of constituents such as hydrocarbons, caustics, phenol, ammonia, and metals into the environment. This discharged wastewater can impact nearby surface and groundwater quality and surrounding marine environment, if not treated properly prior to disposal.

3. Waste generations, such as tank bottom sludge, oily wastes, and spent catalysts. Some of these wastes are hazardous, especially those containing hydrocarbons and heavy metals, and required special management and disposal.

4. Accidental releases, such as oil spills, sudden product releases, vapour releases or product leaks. Those releases can lead to air, water, or/and soil contamination, if not controlled promptly and effectively.

## 3.1 AIR POLLUTION

Air pollution refers to any process which adds to or subtracts from the usual constituents of air and may alter its physical or chemical properties sufficiently to be detected by occupants of the medium. It is usual to consider as pollutants only those substances added in sufficient concentration to produce a measurable effect on man, animal, vegetation and/or property. These pollutants can be classified in two general groups:-

a) Those emitted directly from identifiable sources

b) Those produced in the air by interaction among to or from primary pollutants or by reaction with atmosphere constituents.

### 3.1.1 Air Pollutants from Refining Operations

Major air pollutants that may be emitted from refining operations are sulphur compounds, hydrocarbons, nitrogen oxides, particulate matter and carbon mono oxide. Other emissions are aldehydes, ammonia and odours.

#### 3.1.1.1 Sulphur Compounds

Sulphur dioxide constitutes the maximum proportion of Sulphur compounds emitted from refineries. The main source of Sulphur dioxide are from combustion operations such as fired heaters, boilers and catalytic cracking regenerators and from sulphur dioxide extraction plants. Refinery flares, incinerators and Decoking operations are other minor sources. Other sulphur compounds emitted from refineries include hydrogen sulphide, sulphur trioxide and mercaptons.

#### 3.1.1.2 Hydrocarbons

The emissions of hydrocarbons result mainly from evaporation of light oils during Storage and handling of crude and petroleum products and from leaks. Sources of hydrocarbon emissions include loading, facilities, sampling, storage tanks, air blowing operations and compressor engines.

#### 3.1.1.3 Oxides of Nitrogen

Combustion of fuels in fired heaters and boilers and in internal combustion engines used to drive compressors and electric generators, are the main sources of nitrogen oxides emissions in the petroleum refineries.

The formation of Nitrogen oxides is mainly dependent on the flame temperature, residence time and excess air present in the flame.

#### 3.1.1.4 Particulates

The major sources of emissions of particulates in refineries are catalytic generators. Minor sources include asphalt oxidisers, sludge burners, emergency flares and incomplete combustion.

### 3.1.1.5 Carbon mono oxide

The only significant source of Carbon mono oxide is the catalytic cracking regenerator. . The minor sources include internal combustion engines used to drive compressors and electrical generators and incinerators.

### 3.1.2 Effects of Air Pollution

**The various effects of air pollution are:-**

Human health:

a) Reduction in visibility
b) Irritation of respiratory tract
c) Nose and throat irritation
d) Carcinogenic agents cause cancer
e) Respiratory diseases like silicoses asbestosis
f) Hydrogen sulphide, ammonia and mercaptons cause odour nuisance
g) Diseases like bronchitis and asthma are aggravated due to $SO_2$, $NO_2$

Effect on Plants:

a) Bleaching of leaves
b) Premature aging suppression of growth
c) Dropping of leaves
d) Collapse of tissue
e) Loss or reduction of chlorophyll

Effect on Material:

a) Corrosion, spoilage of surface, loss of metal
b) Discolouration and leaching
c) Deterioration and reduced tensile strength
d) Cracking of materials
e) Change in surface appearance

## 3.2 Water Pollution

Water pollution is defined as the addition of any substance to water or changing of water's physical and chemical characteristics in any way which interferes with its use for lawful purposes.

Water is used in petroleum refineries for variety of purposes. Water does not enter into the final product so 80-90% of the water supplied to a refinery comes out as waste water. Large volumes of waste water which are discharged contain a variety of objectionable and toxic organic and inorganic substances. If these waste waters are not treated to the desired degree, the pollutants reach the water course and bring out a number of changes in the quality of receiving water, which ultimately render the water for aquatic life and for domestic and industrial use.

### 3.2.1. Types of Water Pollution:-

1. Physical pollution
2. Chemical pollution
3. Physiological pollution
4. Biological pollution

#### 3.2.1.1 Physical Pollution

It occurs due to temperature, turbidity, suspended particulate matter, colour, foam & froth and radioactivity. The rise in temperature decreases the solubility of oxygen in water. This makes fishes migrate to other areas. Due to this, tolerance limits for temperature are prescribed for waste water discharge.

Turbidity in waste water decreases the penetration of solar radiation in water and clogs the gills of fish.

Colour reduces the photosynthetic activity and is considered as aesthetic pollutant.

#### 3.2.1.2 Chemical Pollution

It can occur due to inorganic or organic chemicals. Inorganic acids accelerate corrosion of metals and burn or irritate the skin of animals and humans. Organic chemicals are not toxic to aquatic life but can be dangerous because it can deplete the dissolved oxygen content. These chemicals also give rise to mal-odours and make the stream unfit for any type of use.

#### 3.2.1.3 Physiological Pollution

Distortion in taste and odour constitute physiological pollution. The presence of small amounts of sulphides which give rise to Hydrogen Sulphide at a low pH is the cause of undesirable odours in water.

#### 3.2.1.4 Biological Pollution

Biological pollution is a result of discharge of waste water containing pathogenic forms of bacteria, algae, viruses and protozoa. This type of pollution is often a secondary result due to contamination by sewage of industrial waste.

### 3.2.2 Effects of Water Pollution

The various effects of water pollution are:-

- Radioactive substances present in the water can lead to leukaemia and cancer.
- High levels of unsaturated cycloparaffins can result in irritation and anaesthesia.
- Damage to liver and kidneys.
- Diseases like cholera, typhoid, polio-myelitis and dysentery can occur.
- High toxicity can result in killing of aquatic life.
- Decrease in the amount of dissolved oxygen
- Alkalinity of soil increases
- Corrosion of metals

# 4. POLLUTION CONTROL TECHNIQUES

## 4.1 Air Pollution Control Techniques

### 4.1.1 Control of Emissions from Refinery Process Gases:-

Nearly all refinery processes generate gases which contain hydrogen sulphide or other low molecular weight sulphur compounds. These gases are normally used as a fuel in fired heaters and boilers. Sulphur dioxide emissions therefore result if the sulphur compounds are not removed. The most common procedure for removal of Hydrogen Sulphide and light mercaptons involves scrubbing the gases with an absorption solvent.

**Wet Scrubber**

Wet scrubber is a form of pollution control technology. The term describes a variety of devices that remove pollutants from a furnace flue gas or from other gas streams. In a wet scrubber, the polluted gas stream is brought into contact with the scrubbing liquid, by spraying it within the liquid, by forcing it through a pool of liquid or by some other contact method, so as to remove the pollutants.

The design of wet scrubbers of any air pollution control device depends on the industrial process conditions and the nature of air pollutants involved.

Inlet gas characteristics and dust properties (if particles are present) are of primary importance. Scrubbers can be designed to collect particulate matter and/or gaseous pollutants. Wet scrubbers remove dust particles by capturing them in liquid droplets.

Pollutants are either dissolved or are absorbed by the liquid.

Any droplets that are in the scrubber inlet gas must be separated from the outlet stream by means of another device referred to as a mist eliminator. Also, the scrubbing liquid, must be treated prior to any ultimate discharge or reused in the plant.

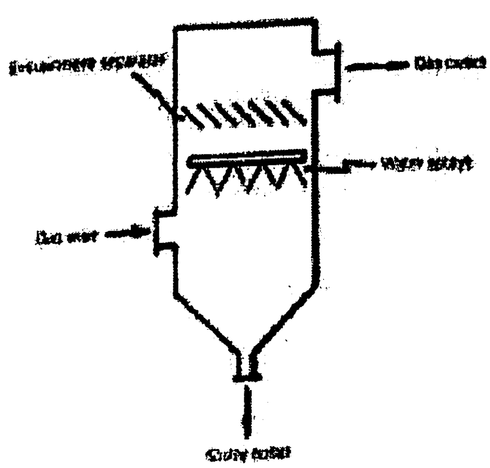


Fig 4 (1)

### 4.1.2 Control of Emission from Fuel Combustion:-

Combustion of fuel and residual fuel oils in particular can be significant source of sulphur dioxide emissions from refineries. The major options available in this case are changing of fuel type or improving fuel oil quality. Changing fuel type usually means switching to a cleaner type of fuel such as from residual oil to distillate, distillate to naptha, naptha to gas. Cleaner fuel can also be obtained by switching from higher sulphur to a natural low sulphur fuel.

The quality of fuel can be improved by treatment of the fuel to remove potentially polluting substances, prior to combustion. Hydrogen processing is a prime example of such an option. Technology for hydrodesulphurization of both distillate and heavy residual fractions of crude is also available.

### 4.1.3 Control of Carbon Monoxide Emissions

The only significant source of carbon monoxide emissions in petroleum refineries is the catalytic cracking regenerators. Carbon monoxide emissions from catalytic cracking units can be eliminated by incinerating the flue gases in waste heat CO boilers at temperatures of 1100 K to 1400 K. The heat of combustion of the Carbon Monoxide and other combustibles, and the sensible heat of the regenerator gases is restored by generating steam or heating the oil charged unit. Carbon monoxide is completely charged to Carbon dioxide.

### 4.1.4 Control of Emissions in Storage

Hydrocarbons are the products of a refinery and hence there is an obvious economic incentive to prevent their loss to the atmosphere. More air pollution control measures are therefore necessarily employed as adopted practice.

Emissions from storage vessels are generally caused by evaporation of liquids or liquefied gases. The control of emissions from oil & gas storage facilities result in reduction or eliminations of fire and recovery of valuable products. This reduction is normally achieved by the use of floating roof or pressure storage for light hydrocarbons.

### 4.1.5 Control of Emissions by Dispersion

The dispersion of excess pollutants by use of taller stacks is another means of abatement of pollution levels. This technique has been successfully used in controlling ground level concentrations. It is the simplest and most economic. Tall stacks, however, maybe a hazard to air or inadequate in certain topographical conditions. Further, since tall stacks do not eliminate but only disperse the pollutants. They may also transfer the problem from one locality to another.

### 4.1.6 Sulphur Recovery

Sulphur recovery from some refinery steams is a part of refining from consideration of product quality rather than abatement. Two important areas in this respect are nitro-fining and amine extraction. Both these yield a sour gas rich in Hydrogen Sulphide.

## 4.2 CONTROL OF WATER POLLUTION

The uses of water in a refinery can be categorized as drinking, cooling boiler feed, direct processing, sanitary and fire protection. The effluent water generated can be classified as under:

- Water free from oil
- Sanitary Sewage
- Process Effluents

The water free from oil includes storm water from oil free catchment areas, water treatment plant effluent, boiler blow down etc. The sanitary sewage includes wastewater coming from administrative buildings, canteens, toilets etc. The process effluents are basically oily waters originating from different sources, such as drainage from product storage tanks and loading facilities, storm water from oily areas, water from pump houses, blow down from cooling systems, desalter water, overhead condensate water from process units, spent caustic etc.

For effective treatment of effluent water, the streams are segregated through separate drainage systems and treated accordingly. The effluent treatment is usually divided into three categories:

- Primary
- Secondary
- Tertiary

### 4.2.1 Primary Treatment Methods:

This treatment consists of oil removal in two stages by physical methods. Various physical methods are available and these can be classified as baffling, floatation, skimming, stripping and extraction.

The first stage of oil removal is done in small pond or basin where major portion of the oil is removed by baffling, floatation and skimming methods. The second stage of oil removal is mainly by the API separators or other gravity seperators, where the remaining oil is removed through baffling, floatation and skimming methods.

### 4.2.2 Secondary Treatment Method:

It is the process in which microorganism play a very important role for the treatment of effluent. Microorganism like bacteria, fungi decompose the organic waste and convert into simpler form. The main function of secondary treatment is to convert the reaming organic matter of sewage into stable form by oxidation and nitrification.

**Aerobic Treatment :**

The treatment which is carried out by microorganism in the presence of oxygen.

**Anaerobic Treatment :**

The treatment which is carried out by aerobes in the absence of oxygen. The need of oxygen is supplied by oxidation of oxygenated compound for e.g $SO_2$

### 4.2.3 Tertiary Treatment Method:

This treatment has been limited to activated Carbon filtration process and ozonation which are effective in removal of the taste and odour and organics from biologically treated waste waters. The treated water which satisfy the relevant tolerance limits are finally disposed by controlled dilution into the stream.

### 4.2.4 Control through Reduction of Hydrocarbon Losses:

Various measures for reduction of hydrocarbon losses are listed below:-

a) Careful drainage from storage tanks while draining water/sludge.
b) Regular gland leak survey of process pumps and follow up for rectification of leaks to reduce oil loss from seals and glands.
c) Improved maintenance practices for pump gland packing.
d) Installation of mechanical seals in light hydrocarbon pumps to reduce gland leakage losses.
e) Accurate filling of tank wagons and tank lorries- surprise checks and control.
f) Use of fixed/floating roof for tanks as service requirement and keeping tank seals in good condition.
g) Provision of double valves on sampling points.

# 5. MINIMIZATION, TREATMENT & DISPOSAL OF SLUDGE

Petroleum sludge is a complex mixture of hydrocarbons, water, metals, and suspended fine solids. Petroleum industries are burdened with the problem of handling large quantities of sludge. The severity of the problem depends on the nature of the crude oil, the processing capacity, the downstream capacities, and the design of the effluent treatment plant. Sludge usually accumulates in refineries because of pump failures, desalter failure, oil draining from tanks and operation units, periodic cleaning of storage tanks, and pipeline ruptures.

This sludge has been categorized by regulatory agencies as hazardous waste. These petroleum sludge wastes typically are water-in-oil emulsions that are stabilized by fine solids. In view of this situation, it is necessary to develop and commercialize new combination schemes for processing oil sludge in refineries, with the following required features:

- Constant and continuous removal of sludge
- Consolidation and dewatering of sludge
- Utilization of coagulant from consolidated oil sludge
- Thermal dewatering of thickened oil sludge

Several process technology options for treating petroleum sludge have emerged during the past several years in response to the enhancement of environmental regulation governing these wastes. Some of these technologies are centrifugation, thermal desorption, solvent extraction, and hydrothermal processing.

Sludge must be characterized for pathogenicity, toxicity and various rheological properties. The suitability of sludge for incineration or other thermal treatment requires the determination of combustibility of sludge which includes gross calorific value and Carbon, hydrogen, sulphur, nitrogen, oxygen, halogen, moisture and ash content.

## 5.1 Sludge Conditioning

Sludge conditioning may be used to increase solid concentrations, improve recovery, or reduce thickening time. This can be achieved by chemical addition or thermal treatment.

### 5.1.1 Chemical Conditioning

It involves the use of either inorganic or organic chemicals. The most commonly used inorganic chemicals for conditioning sludge include lime, ferrous and ferric sulphate, ferric chloride and aluminium. These chemical coagulants are employed to promote agglomeration of floc particles.

### 5.1.2 Thermal Conditioning:

The primary function of thermal sludge conditioning is to improve dewaterability. The advantage of this process includes reduced solid quantity, very low specific filtration resistance, sterilization and enhanced activated sludge digestion

## 5.2 Thickening of Sludge:

Thickening is defined as removal of water from sludge to achieve in moisture content of slurries. The resulting material is still fluid. Thickening is used to reduce the volume of sludge or for greater efficiency in subsequent processes. Sludges are thickened primarily to decrease the primary capital cost of subsequent sludge processing steps by substantially reducing the volume. The principal thickening methods are:

- Gravity thickening
- Centrifugal thickening
- Floatation thickening
- Gravity belt thickening

### 5.2.1 Gravity Thickening:

The thickening of sludge by gravity is carried out in tanks. The basic process is zone settling. This process is divided into four zones. These are clarification zone, transition zone, hindered settling zone and compression zone.

The clarification zone contains relatively clear supernatant. In the hindered settling zone, the suspension moves downward at a constant rate. The transition zone is characterized by a decrease in the solid settling rate. The compression zone involves consolidation of sludge as liquid is forced up around the solids.

### 5.2.2 Floatation Thickening:

The thickening by floatation is achieved by introducing fine air bubbles into the system. The air bubbles either adhere to or are adsorbed by the sludge solids, which are then lifted to the surface where they are removed. Dissolved air floatation is used extensively for sludge thickening.

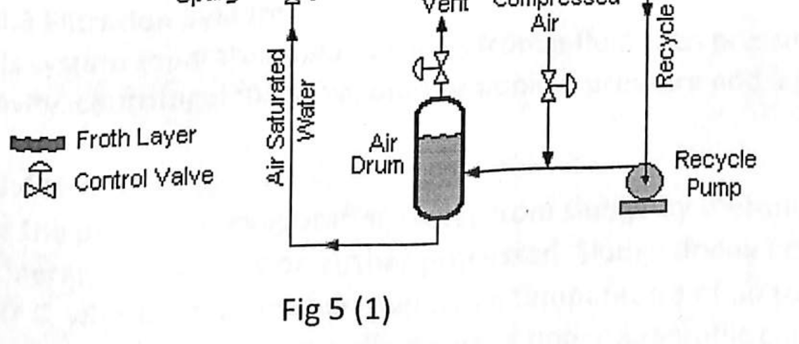


Fig 5 (1)

The process involves pressurizing a side stream of 30% thickening effluent by introducing air in air-water saturation tank. The supersaturated flow is then released to atmospheric pressure, either with or in close proximity to the sludge inflow. The process is generally used for thickening biological sludge although it can be applied to most sludge.

**5.2.3 Centrifugal thickening:**
This employs the solid bowl and imperforate basket decanter centrifuges. Typically, thickening centrifuges are restricted to activated sludge. The solid bowl decanter comprises a long, cylindrical bowl tapered at one end and rotated at high speed. An internal scroll moves at a differential speed to the bowl. Optimum performance is achieved with a consistent feed and so, upstream storage and mixing is desirable.

**5.2.4 Gravity Belt Thickening:**
This method requires low power. The woven polyester cloth belt provides a drainage medium for removal of water freed from the sludge by polymer addition. Sludge can be thickened to 5% dry solids, or better depending on sludge type.

**5.3 Dewatering of Sludge:**
The thickened sludge is dewatered for efficient handling. This achieved by centrifugation and filtration. The process of dewatering overlaps to some extent with sludge thickening. The selection of dewatering equipment depends on the requirement for subsequent treatment or disposal or both.

**5.3.1 Non-Mechanical Systems:**
The two common non-mechanical systems used for dewatering sludge are sludge drying beds and drying lagoons.
Sludge drying beds comprise an open air drying system in which an under-drainage system is covered with coarse gravel and topped by a layer of sand. Sludge is diverted to each bed via a channel or pipeline and the bed is filled to a depth of 200m to 300m.
Drying lagoons are similar to drying beds but without under drainage. They are filled to between 0.75m to 1.25 m depth. Untreated sludge, limed sludge, or sludge with poor quality supernatant is unsuited because of odour potentials. The system is most suited to digested sludge.

**5.3.2 Centrifugation:**
He two major types of centrifuges used for sludge dewatering are the sludge bowl decanter and the improved basket which are similar to the units for thickening sludge.

**5.3.3 Filtration System:**
This system separates solid particles from a fluid with pressure gradient produced by gravity, centrifugal force, vacuum or applied pressure and a porous filter medium.

**5.3.4 Heat Drying:**
It is the process of evaporating water from sludge by thermal means so that it can either by incinerated efficiently or further processed. Sludge drying occurs at a temperature of about 370° C, whereas incineration requires a temperature of up to 760° C.
Concentration sludge is usually digested under anaerobic conditions. Organic compounds produce methane and carbon dioxide. Bound water is released from the sludge (as shown in figure).

Single Stage, Standard Rate Anaerobic Digester

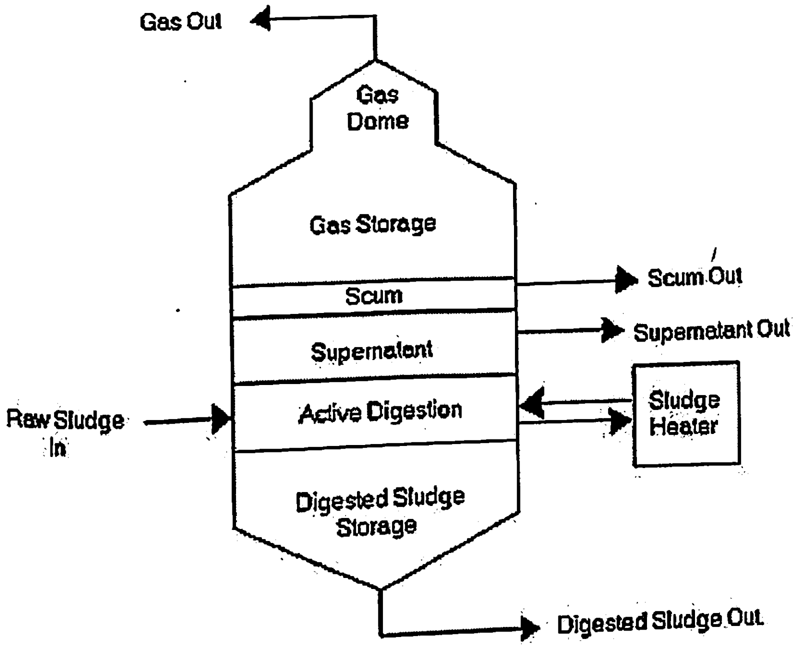


Fig 5 (2)

## 5.4 Oil & Hazardous Waste Separation from Sludge:

Oil content in the effluent is mainly responsible for sludge production. Complete free oil and maximum emulsified oil can be recovered by de-emulsification, gravity separation, air floatation, flocculation, coagulation so that sludge would be containing minimum oil content. If the sludge still has high oil content (>3 percent), this oil has to be recovered.

Various techniques being used are:-

- Three phase high speed separator
- Microwave radiation
- Solvent extraction process
- Low temperature thermal treatment process

None of these technologies are entirely successful. Some have operational problems and (or) produce low quality solids; others that produce high-quality solids are very expensive. There is a demand for a universally applicable technology for the treatment of petroleum sludge. The technology should be capable of recovering petroleum in a form that can be redirected to a refinery for further processing to produce higher quality petroleum products.

**5.5 CASE STUDY 1:**

A study was carried out to investigate a combination of various systems of electrokinetic cells, to which oily sludge, conditioning liquids, and different electrical potentials were applied. The developed electrokinetic phase separation is a new cost-effective technology, which in turn will permit the revitalization of petroleum sludge. This method can significantly reduce the amount of wasted sludge and can recover new fuels free of metals and water. Life cycle analysis of the recovered fuel shows that a new petroleum waste management protocol might reduce emissions of major greenhouse gases such as $CO_2$, $CH_4$, and $N_2O$.

**Methodology:**

Oily sludge was taken from the bottom of a crude oil storage tank in a refinery to fill up a series of electrokinetic cells with dimensions of 25 cm × 14.5 cm × 10.5 cm (*L* × *W* × *H*). Two stainless steel plate electrodes were installed at a distance of 19.5 cm in each cell. To find the optimal condition, different voltages, 0.5 and 1.5 V/cm, were applied to each electrokinetic cell (Table 1). Some cells contained amphoteric surfactant (C12-C14-alkyl-dimethyl-betain) as a conditioning liquid. In these cells, sludge and surfactant were mixed for 4 h to obtain a uniform texture. Two cells without connection to the power supply served as control cells. The choice of both the surfactant concentration and the voltages was based on previous extensive research on electrokinetic phenomena. Cells were connected to the electricity for 32 days. After disconnection, the cells remained untouched for further observation of electrokinetic processes for another 43 days.

The cells were equipped with probe electrodes to study continuous changes in sludge physical properties during the electrokinetic phase separation. Therefore, six silver probe electrodes were installed in each cell in two vertical lines (6.5 cm from both cathode and anode), where the distance between neighbour probe electrodes in each vertical line was 1.5 cm. The voltage distribution between the electrodes was monitored by direct measurements of the potential between electrodes and each probe electrode. Electrical potential at each probe and current supplied to each cell were measured daily using a digital multimeter. The changes within the cells were monitored continuously through pH and resistance measurements. After measuring the mass of each sample, 8 ml of hexane was added, and the vial was shaken manually for 1 min and then left for 24 h. The liquid part was then poured into another 20 ml vial.

Oily sludge is a mixture of different kinds of hydrocarbons (light and heavy fractions), water, soil, and suspended materials. The following fractions of sludge were assessed:

(1) Water content — The American Society for Testing and Materials (ASTM) standard method D95 was used for measuring the water content of the oily sludge. The oily sludge was heated with benzene (solvent), which distilled with the water in the sample. Condensed solvent and water were continuously separated in a trap, and the water settled as the bottom layer. The condensed liquid containing water and hydrocarbons was transferred to a graduated cylinder. A water layer with higher density was generated at the bottom of the cylinder. The volume of the water was used for calculating the water content of the sample (by assuming that the density of water is 1 g/cm3).

(2) Volatile hydrocarbon content — To determine the amount of light hydrocarbon inside the oily sludge, a sample of known mass was put in an oven (with ventilation) at 105 °C for 24 h. The reduction in mass indicated the moisture and light hydrocarbon content in the sludge. As water content was measured previously, the light hydrocarbon content (in wt %) was calculated as follows:

light hydrocarbon = [(reduced mass in g)/(mass of tested sample in g)] × 100% – (water content in wt.%)

The sludge contained a high amount of light hydrocarbons because it was taken from the bottom of the crude oil storage tank and was not in contact with air, so no evaporation took place.

(3) Solids content — Dried samples (105 °C) were placed in a furnace at 550 °C for 30 min. The residue showed the solids content of the sludge as weight percent: solids = [(residue remaining after burning in g)/(mass of tested sample in g)] × 100%

(4) Non-volatile hydrocarbon content — After measuring the water content, light hydrocarbon content, and solids content, the non-volatile hydrocarbon content can be calculated in weight percent as follows:
Non-volatile hydrocarbon = 100% – (light hydrocarbon in wt.% + solids in wt.% + water content in wt.%)

**RESULTS: Characteristics of oily sludge treated with the new technology**

The aforementioned analytical methods were used to assess the effectiveness of the separation of recyclable components under different conditions applied to electrokinetic cells. Comparing analyses of electrokinetically transformed samples with that of the initial oily sludge (Table 2), it can be concluded that the application of electrokinetic phenomena reduced the amount of water by almost 63% and light hydrocarbon content by almost 43% in the solid phase. Using electrokinetics in combination with amphoteric surfactant reduced the water content by 60% and light hydrocarbon content by 50% in the solid phase. It was observed that the variation of electrical potentials did not have a significant effect on the effectiveness of the system.

Gradual release of volatile hydrocarbons, which are trapped in the colloidal particles, causes a significant increase in the amount of greenhouse gases (GHGs) worldwide. Light hydrocarbons are important contributors to the GHG effect; for example, methane has a heat-trapping effect 21 times higher than that of carbon dioxide. Therefore, the capture of these gases could have a huge impact on global warming. It has been demonstrated that the amount of light hydrocarbons in the solid phase was significantly reduced after the electrokinetic application. Thus, the new technology permits the simultaneous collection and treatment (or reuse as fuel in other units) of these volatile fractions.

Table 2. Characteristics of the initial sludge and separated phases (wt.%).

| Sample | Water content | Volatile hydrocarbon content | Solid content | Nonvolatile hydrocarbon content |
|---|---|---|---|---|
| Initial sludge | 18.1 | 55.9 | 2.6 | 23.5 |
| Separated phases in cells without surfactant | 6.8 | 31.8 | 19.3 | 42.2 |
| Separated phases in cells with amphoteric surfactant | 7.5 | 29.1 | 17.5 | 45.9 |

This study investigated the effect of different electrical potential gradients and the surfactant on the effectiveness of phase separation. The solid phase remaining after the experiment was more compact and stable. It has been concluded that the application of the amphoteric surfactant does not improve the total efficiency of the system.

Analyzing the pH variations and resistance distribution led to a better understanding of the thermodynamics of the process. By considering the results of the experiment, it can be concluded that the lower electrical potential can produce a higher demulsification rate.

***Benefits from Application of New technology:-***

1. ***Value-added products:*** Waste reduction reduces the costs of treatment and disposal and the resources needed to permit and track the waste. If the refinery's oily sludge disposal could be reduced, the facility could save a substantial amount of money each year. With the proposed technology, the water content and light hydrocarbon content of the sludge can be reduced by almost 63% and 50%, respectively, and this will greatly reduce the volume of waste. The amount of the nonvolatile part of the remaining solid is almost 48% higher than that of the initial sludge. This higher amount of nonvolatile hydrocarbons and lower amount of water increases the heating value of the remaining solid and makes it more useful as a fuel.
A large part of these nonvolatile hydrocarbons is related to asphaltene, so the remaining solid also could be sent to an asphaltene unit for additional preparation. The separated volatile hydrocarbon phase could be captured and used as fuel in different parts of the refinery. One suggested method could be to blend these recovered lighter hydrocarbons with other appropriate streams of petroleum refineries to produce high-quality fuel. Since no additional hydrocarbon phase has been observed in the extracted water, it can be sent to a wastewater treatment plant.

2. ***GHG mitigation:*** The developed technology mainly concerns an oily sludge that is usually stored in open ponds. The application of the electrokinetic phase separation transforms the oily sludge to value-added products. The liquid phase could be redirected to the refinery and used as a fuel. In addition, the solid phase could also be used as a fuel or combined with other material for further applications (e.g., road materials). In all of these cases, the reuse of sludge results in preserving natural resources and would substantially decrease the emission of GHG. In the next paragraph, a potential case is presented to estimate the degree of GHG mitigation after the application of the new technology to petroleum oily sludge. This estimation is based on simple life cycle analysis (LCA) of a fuel product. If a refinery is assumed to produce 30 000 tons of oily sludge each year. The recovery of only 30% of these sludge components per refinery will lead to the generation of 10 000 tons of fuel products per year per refinery.

The present method has numerous advantages over known methods: (*i*) increasing the total recovery of hydrocarbon residue from oily sludge; (*ii*) recycling of hydrocarbon residue from a waste-stream product to a usable refinery product by reducing water content, in turn eliminating the potential liability for environmental contamination due to disposal of the waste-stream product; and (*iii*) decreasing the overall cost and time involved for recovery and disposal of hydrocarbon residue.
The results of this research permit the introduction of a new technology with the potential to (*i*) change the management of petroleum wastes and permit rapid dewatering, revitalization, and reuse of separated components and (*ii*) solve the waste disposal problems created by land bans.

## 5.6 DISPOSAL OF SLUDGE

Once the oil and hazardous organic and inorganic materials are removed from the concentrated sludge, it needs to be disposed off.

### 5.6.1 Direct Disposal

In direct disposal, the sludge produced is directly disposed off on agricultural systems, including forests and land reclamation projects. Sludge contains majority of essential nutrients for plant growth and so is a better supplement to fertilizers. However, the presence of high concentration of heavy metals in some sludge limit the amount of sludge that can be applied to any section of land.

### 5.6.2 Pyrolysis

Pyrolysis is the chemical decomposition of a condensed substance by heating. It occurs spontaneously at high temperatures (above 300$^{oc}$). It can be performed in a variety of reactors, including fluidized beds. It is a recovery process also because the mixture of gases produced can be used directly as fuel or as the raw material for the synthesis of other fuels.

### 5.6.3 Incineration

Incineration is a waste treatment technology that involves the combustion of organic materials. Incineration and other high temperature waste treatment systems are described as 'thermal treatment.' Incineration of waste materials converts waste into incinerator bottom ash, flue gases, particulates and heat which can in turn be used to generate electric power. The flue gases are cleaned of pollutants before they are dispersed in the atmosphere.
Incinerators reduce the volume of the original waste by 95% depending upon composition and degree of recovery of materials such as metals from the ash for recycling. This means that while incineration does not completely replace land filling, it reduces the necessary volume for disposal significantly.

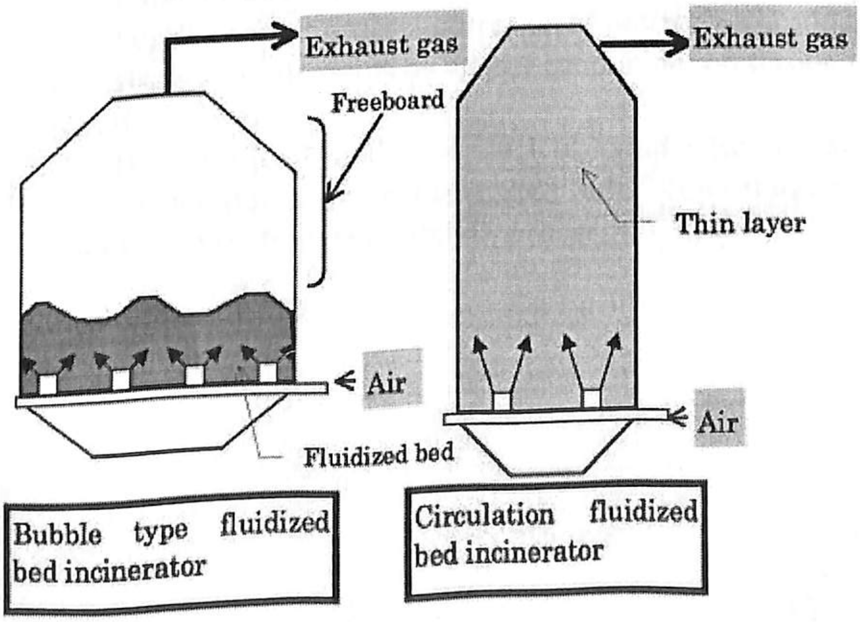


Fig 5

## 6. RECYCLING OF CATALYSTS

Precious metal catalysts are crucial for many technical syntheses. The main application fields in oil refining are catalytic reforming, isomerisation and hydrocracking. Such precious metal-bearing catalysts are also used in bulk and speciality chemicals productions such as vinyl acetate monomer (VAM), purified terephtalic acid (PTA) and many hydrogenation processes. The noble metals involved are mainly platinum (Pt) and palladium (Pd), but also the other platinum group metals (PGM) ruthenium (Ru), iridium (Ir) and rhodium (Rh), as well as gold (Au) and silver (Ag), either alone or in combination. Often, other metals (for example, Sn, Pb, Ni, Co, Ge) are used as promoters. All these metals are coated on various carriers such as alumina, silica, zeolites and carbon.

Due to the high value of precious metals, the recycling of the spent catalyst at the end of its useful life is crucial for the overall economic performance of a catalytic process. Refining companies specialising in precious metals recycling have developed suitable technologies for the efficient reclaiming of these valuable metals. However, selecting the right recovery process and recycling company for a specific spent catalyst is not easy Focus is usually on economical considerations – the total cost to be paid and the amount of metals finally returned from the recycling chain. I this context, the reliability and accuracy of the weighing and sampling preparation is crucial, since the analytical metals content obtained o the retained sample is the basis for al further calculations. Along with the economical questions, the environmental issues must not be neglected:

- What environmental, health and safety (EHS) risks arise in a certain recycling chain?
- What liabilities are the spent generator exposed to?
- How secure can the spent generator be about the technical, commercial and environmental performance of the selected refiner?

Besides their valuable content of precious metals (Pt, Pd, Au, and so on), spent catalysts also contain a complex mix of different substances, such as:

- Catalytic base metals and promoters: Sn, Pb, Ni, Co, and so forth
- Fe, Ni, Cr from process corrosion of reactor walls and tubes
- Hazardous elements by way of contamination through the feed/crude oil (As, Hg and more).
- Halogens (Cl, F, and so on) such as found in isomerisation catalysts
- Carbon (for example, high coked "heel" CCR catalysts) and hydrocarbon contamination from the catalytic process

In one way or another, the recycling chain (Figure 6.1) has to cope with these complex mixtures. Just reclaiming the valuable metals is not sufficient; the whole recovery chain has to be evaluated for its environmental soundness.

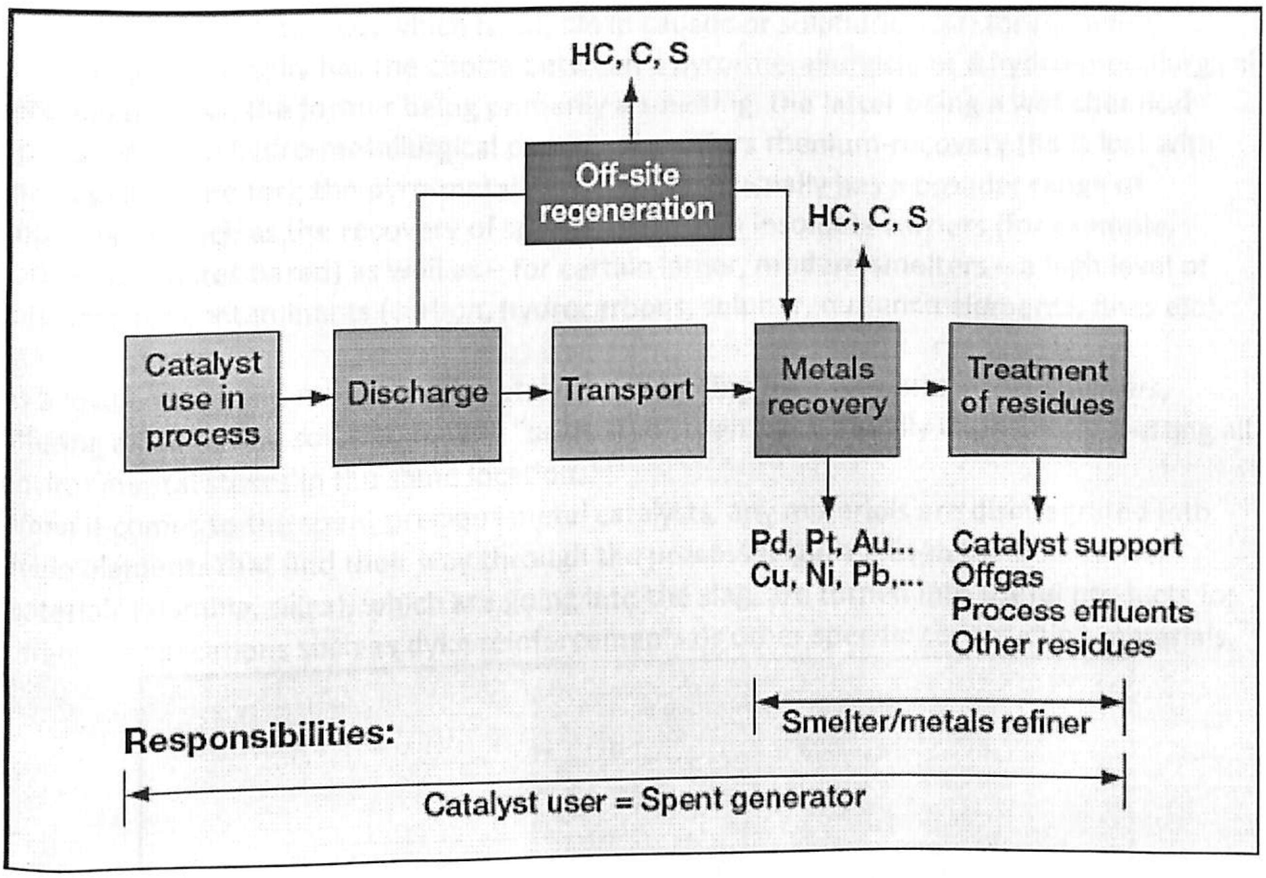


Fig 6 (1)

The generator of a spent catalyst has to ensure that all the operators involved in the recycling chain are acting in an EHS-compliant way when treating the spent catalyst. This responsibility is related to individual regulations in specific countries, to the Basel liability protocol as well as to the principles of responsible care, to which the chemical and oil-refining industry have committed themselves.

Whether the spent catalyst is sent for "off-site regeneration" or not (prior to shipping to a precious metals refinery) may render the whole recycling loop more difficult to monitor. It might be more appropriate to consider a one stop treatment at a precious metals refiner, taking care of the whole spent package in an environmentally sound way.

6.1 **Metals refining:**

When it comes to sending out precious metal-bearing spent catalysts on a "soluble" carrier (typically a γ-Al2O3- carrier, which is soluble in caustic or sulphuric acid) for recovery, the generator basically has the choice between a pyro-metallurgical or a hydro-metallurgical recovery process, the former being primarily a smelting, the latter being a wet chemical process. While a hydro-metallurgical process also offers rhenium-recovery (Re is lost with the slags in a smelter), the pyro-metallurgical process usually has a broader range of applications, such as the recovery of spent catalysts on insoluble carriers (for example, carbon or zeolites based) as well as – for certain larger, modern smelters – a high level of tolerance for contaminants (carbon, hydrocarbons, sulphur, nuisance elements, fines etc).

As a result, more and more soluble catalysts are finding their way into larger smelters, offering an all-in-one solution for the "untreated" spent and, equally importantly, putting all environmental stakes in the same location.
When it comes to the spent precious metal catalysts, any materials are disintegrated into single elements that find their way through the process (Figure ). Even the bulk carrier materials (alumina, silica), which are going into the slag, are turned into useful products for different applications such as dyke reinforcements or other specific construction materials.

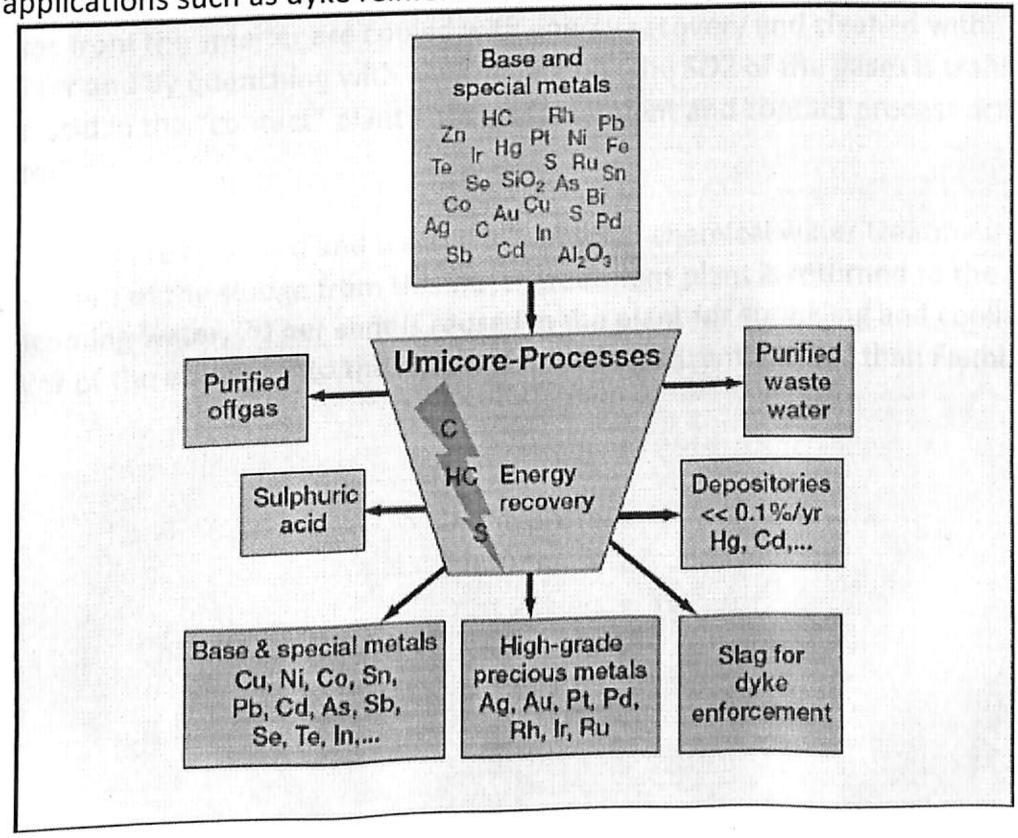


Fig 6 (2)

Process gas treatment generates sulphuric acid as a by-product, the caloric value of combustibles like carbon or sulphur is used as fuel, off-gases are cleaned, process waters are sent to a water-treatment plant, making the whole plant not only a 100 per cent materials-recovery unit but also a nearly zero-waste facility when it comes to the overall environment.

## 6.2 Environmental Liabilities

Finding the right balance between economical and ecological performance is crucial when dealing with all kinds of raw materials coming from various origins. To ensure a long-term commitment towards suppliers and people, EHS should have high priority in the recycling of spent catalyst.

**Case Study:** Umicore Hoboken Plant, Belgium

At the Hoboken plant, an environmental management system has been implemented in accordance with ISO 14001 and in close connection with the quality system (certified against ISO 9001). The plant has also been successfully audited by several large, international oil-refining companies. The environmental performance of the plant is continuously monitored by Umicore and by the authorities. This is reported to the Flemish authorities in detail and to the public in an annual environmental report. A whole range of measures is in place to prevent dust emission: dust-free emptying of the shipped drums or big bags, dust-free sampling procedures, storage of the spent catalysts in containers inside a warehouse, emptying of the containers under aspiration, transport in covered belt systems and more. Besides their environmental importance, these installations prevent any loss of precious metals with the dust fraction, which further improves sampling accuracy and metal yields. Process gases from the smelter are cooled with energy recovery and cleaned with an electrofilter and by quenching with water injection. The SO2 of the gases is transformed to sulphuric acid in the "contact" plant – the gas treatment and contact process act as a "perfect filter".

All process waters are collected and treated in a physico-chemical water treatment plant. About 75 per cent of the sludge from this water-treatment plant is returned to the smelter. From the incoming water, 70 per cent is reused in the plant for sprinkling and cooling. The metal content of the effluent into the river Schelde is significantly lower than Flemish standards.

## 6.3 Economic Impact:

Determining the true bottom profitability of a spent catalyst-recycling job is not easy. It requires both experience and a complex calculation that has to consider not only costs but also the time of the precious metals return, as well as the total metal yield of the selected recycling chain. Figure 4 shows the main factors and interdependencies. It becomes obvious that not only the final refining step but also other parts of the selected recycling chain, such as off-site regeneration, have to be considered.

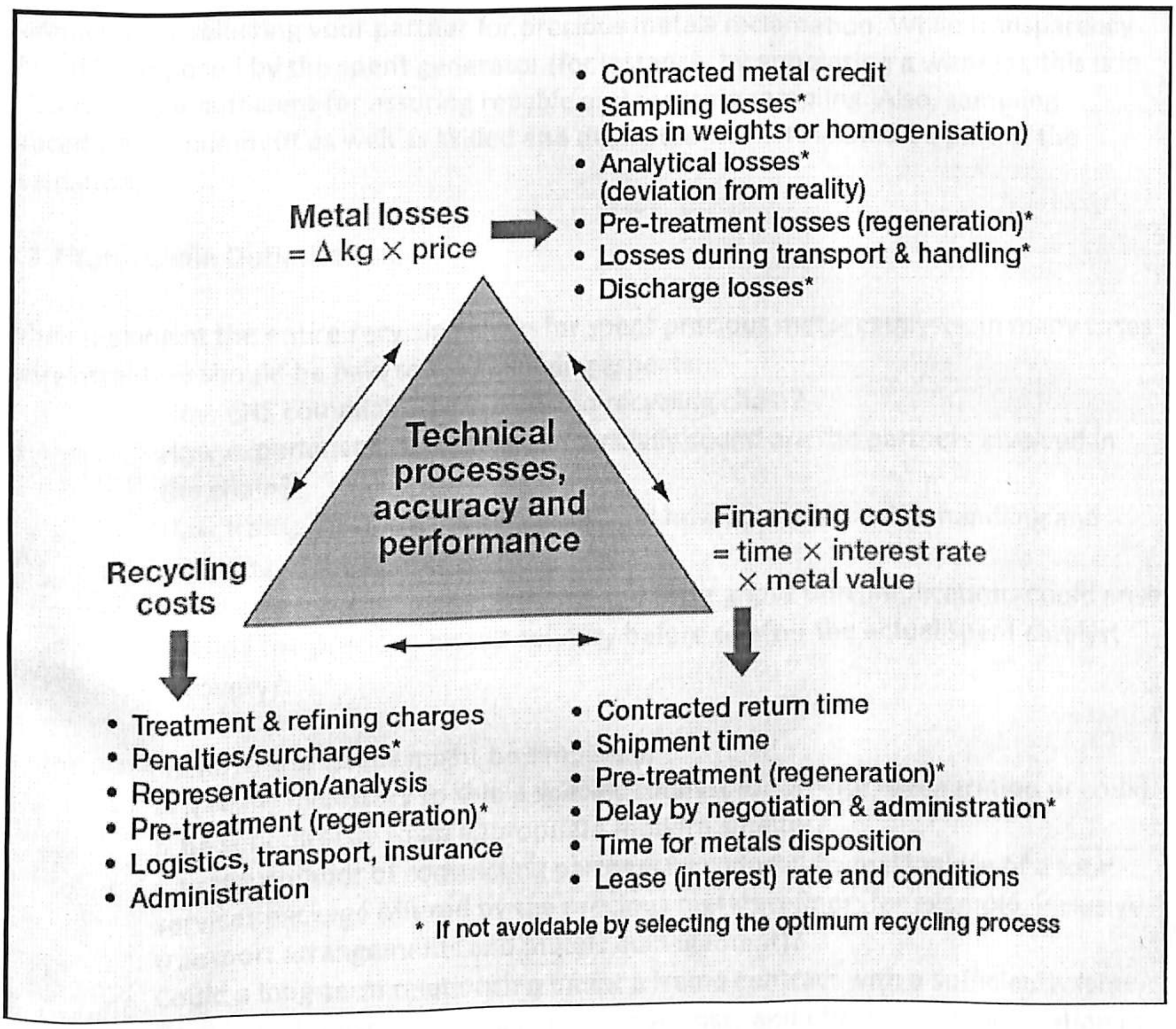


Fig 6 (3)

Compared to the intrinsic value of a spent precious metals catalyst, especially for Pt-spent, the reclamation costs in most cases are only a small part. Taking risks or uncertainties in the performance of the recycling chain could easily offset the recycling cost. In addition, the recycling cost could carry a hidden cost in case of inaccurate sampling. Hence, a bottom-line cost calculation is to be balanced against the general expertise, professionalism and financial soundness of the catalyst recycler as well as against the transparency and EHS compliance of the entire recycling chain.

#### 6.3.1 Weighing & Sampling:

One of the most important economical impacts is how to determine the true precious metal content of a spent catalyst. Any 2 per cent deviation during the catalyst handling, weighing and/or sampling logically corresponds with a 2 per cent deviation in the precious metal credit! For a typical reforming or isomerisation catalyst with a Pt content of about 0.3 per cent, at current Pt prices of around US$800/troz, a 2 per cent deviation would result in a discrepancy of US$1500/Mton of spent or – for a 50 ton lot – US$75 000 in total. Hence, an accurate, transparent and reliable sampling becomes the first and most inevitable parameter for selecting your partner for precious metals reclamation. While transparency should be imposed by the spent generator (for instance, by appointing a witness), this is in most cases not sufficient for assuring reliable and accurate sampling. Also, sampling procedures, equipment as well as skilled and dedicated workers should be part of the evaluation.

#### 6.3.2 Total Chain Optimization:

When looking at the entire recycling chain for spent precious metal catalysts, in many cases more attention should be paid to the following aspects:

- How EHS compliant is the selected recycling chain?
- How experienced, reliable and financially sound are the partners involved in the chain?
- How transparent are the processes and how accurate are the handling and sampling of the spent?
- What costs, potential metal losses and throughput time implications could arise outside the precious metals refinery before or after the actual spent catalyst recovery?

On the other hand, other issues might be simplified:

- Is it really necessary to ship a specific catalyst for off-site regeneration or could it be sent directly to an appropriate modern smelter?
- Can the number of contracting partners be reduced by making use of a total services package offered by the precious metals refiner (for example, inclusive transport arrangements and metals management)?
- Could a long-term relationship under a frame contract with a sufficiently large, flexible and reliable refining partner save costs and efforts in administration by the spent generator?
- Could an "early" technical discussion in a partnership between a generator and refiner determine any beneficial shortcuts in the handling and pre-treatment of the spent?

**The best approach for a true optimisation of the recycling chain is open and comprehensive communication between the partners involved in the chain.**

# 7. CONCLUSION

Refineries across the world try to adopt the best practices towards environmental preservation. However, given the various types of emissions and wastes and the sheer scales it has not been sufficient. There are various factors which restrict the sector. These are mostly dependent on technological limitations & economic viability.

The treatment and disposal of sludge has become a huge problem from refineries given the ever expanding output. With land being a limited resource this problem will only increase in prominence. The case studies above demonstrate that with innovative methods it is possible to tackle the problem in better ways. Research is required to continuously upgrade methods to solve this problem.

Catalysts used in refinery processes are usually expensive. Thus, not only from an environmental point of view but also from an economic point of view it is essential that catalysts be recycled and regenerated. Catalyst regeneration is a complex and expensive procedure and it is important to make improvements in the method.

Air and water pollution caused by refineries are fairly well known and considerable effort goes into curbing this. The fuels being produced in the refineries also have to meet stringent levels which can minimize emission of pollutants but also adds to the cost of the fuels.

With shrinking margins it is all the more a bigger challenge for the sector to meet all these demands and produce high quality fuels. The report looks at these challenges and the way refineries tackle them.

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