

CHAPTER (2)

USED OIL DISPOSAL AND ENVIRONMENT

2-1 Waste Management

2-1-1 Introduction

Human activity inevitably produces wastes. These could be simply defined as items unwanted by their owner that cannot be readily sold or given away to someone else. Throughout history, the basic approach to waste has been to dispose it, and the methods have been dump, bury or burn, in combination with moving either the people or the disposal site if proximity of living and disposal became too unpleasant.

In our era the fundamental limitations to this approach to waste have become unavoidably obvious. The growth of populations and the finite capacity of land and water to act as repositories for dumped or buried waste mean that we can no longer simply move our rubbish or ourselves somewhere else. We have realized that the air too is finite and that discharging burnt, particulate or gaseous matter into it is not only discomforting but increasingly unhealthy. To make matters worse (or perhaps to bring them to a head) our "sophisticated" lifestyle has enabled us to discard much that earlier generations would have reused.

Possibly even more threatening than limited disposal capacity, our technological progress has altered the nature of the waste we produce to include chemicals and other products that are either poisonous or non-degradable or both. So we find that toxins we dump seep back into waterways and those we wash away return in the fish we eat. Other toxins have to be stored for the future, but the hoped-for means of disposal remain elusive while the stockpiles grow and the containers rust.

In the face of the obvious many changes are occurring. Waste is no longer

being defined simply as unwanted or useless materials, but rather as those that the immediate owner cannot economically use and which cannot be disposed of without taking into account the true costs of disposal. The implication is that many of these materials could become a resource for someone else.

2-1-2 Strategy for Waste Management

Waste management has been defined as "the control or management of wastes using technological solutions". This background information brief explores the concepts, methods, problems and promise of the emerging technology of waste management in our post throw-away era.

Further, two new approaches have been added to the traditional dump, bury and burn, and a hierarchy of treatments has been conceived (Figure 2.1). The first new approach, at the top of the hierarchy, is waste minimization, which includes methods of avoiding or at least minimizing the creation of waste in the first place. The second is recycling, which includes the household concepts that our grandparents knew such as composting, reuse and repair, but is expanded to include industrial processing of materials that is impossible within households. As well, the old approaches (dump, bury and burn) have been refined so that a range of technologies is available to lessen their impact when they still cannot be avoided.

The degree of change is such that new terminology is required. The age of waste disposal (as a primary concept) is over, that of waste management has arrived. It would be helpful to have a precise definition of these terms, but many varying definitions have been published. Even the term "waste" has a range of descriptions depending on the context in which it is used. Among the simple definitions available for "waste" are the following:

- "Expendable or useless remains" ^[49].
- "Unavoidable material for which there is no economic demand and for which disposal is required" ^[50].

- "Any matter (whether of value or not) discarded or left over in the course of industrial, commercial, domestic or other activities" ^[51].

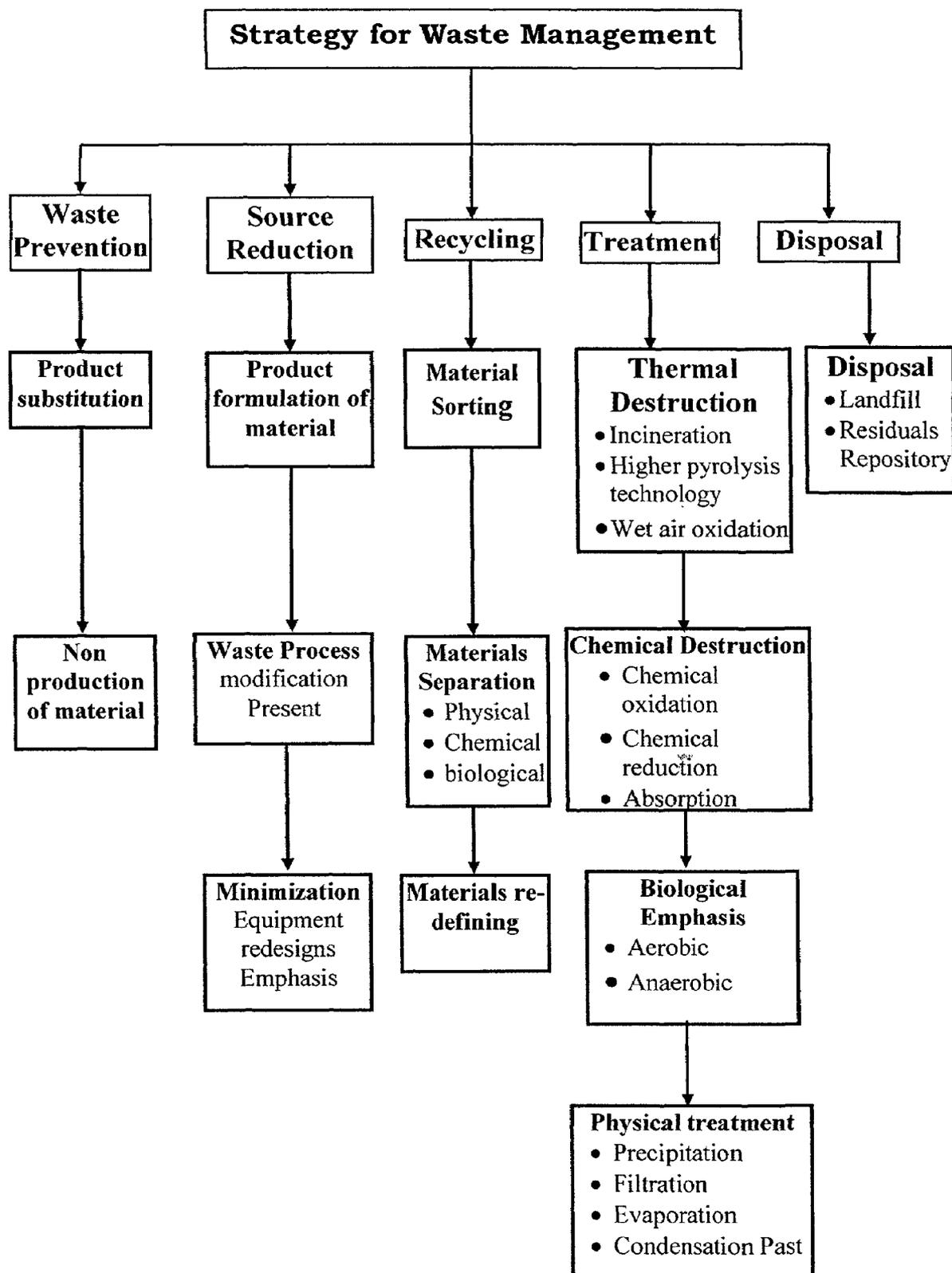


Figure 2.1 Waste Management

Definitions are also available for several of the more common categories of wastes. Solid waste is a term that is sometimes used for municipal wastes and sometimes for virtually all wastes, for example, "any garbage, refuse, sludge from a waste treatment plant, water supply treatment plant, or air-pollution control facility and other discarded material, including solid, liquid, semisolid or contained gaseous material resulting from industrial, commercial, mining and agricultural operations, and from community activities" ^[51].

2-1-2-1 Waste Minimization

The term "waste minimization" is used here to include the concepts of avoiding and/or reducing the amount of waste produced at source. These are the top two approaches of the waste management hierarchy. In 1989 waste reduction was described as "the environmental ethic of the next decade" ^[52].

These concepts do not imply an idealistic hope that all waste production will ultimately cease, rather the extremely practical concept that any reduction in the source production of waste lessens the amount that ultimately has to be managed in some way. All waste management investigations ("audits") should firstly consider whether any waste production can be avoided, reduced, or replaced by alternative materials that are easier to manage, before considering methods of managing waste that is produced.

2-1-2-2 Recycling

When the production of waste materials cannot be avoided, the best management option is to recycle them in some way. Recycling helps achieve the two objectives of the conservation of virgin resources and the minimization of landfill. We should not think about recycling solely in terms of the paper, plastic, glass and metal that we are most familiar with. This section explores some of the complex issues involved in the recycling debate, including a few of the more unusual recyclable materials.

Definitions: Two definitions of "recycling" are given. The first is a technical definition. Technically speaking it could be argued that for something to be recycled it should be put to the same end-use. Recycled glass is used for the manufacture of new bottles; aluminum cans are recycled into aluminum feedstock for the manufacture of more cans. PET therefore is not recycled, according to the definition, because it is not used for the production of PET bottles the second time around. Paper could be considered as recycled when it is used for paper production, but is it recycled when it ends up as cardboard^[53].

The second definition is the recovery of used products and the reprocessing of materials back into their original form or into new forms or products, and to the reuse of, products after cleaning or similar treatment.

2-2 Liquid Waste Management Plan Aspects

Since the environment's capacity to assimilate waste, is very limited therefore it would be of great benefits to follow a strategy to achieve zero pollution through designing a waste management plan. There are many kinds of wastes (solid liquid and gas). Since the concern in this research with liquid wastes, hence wastes to be addressed in the Liquid Waste Management Plan should include, but are not necessarily limited to:

- Municipal sewage.
- Urban storm water runoff.
- Combined sewer overflows.
- Septic tank pumpage.
- Pump station overflows.
- Sewage treatment plant sludge.
- Industrial or commercial wastes discharged to municipal sewers.
- Septic tanks and other sewage disposal systems not connected to the community sewer system; any other effluent specified by a manager.

The proactive strategy to achieve this goal includes:

Pollution Prevention:

This includes use of the 5Rs (Reduction, Reuse, Recycling, Recovery, and Residual management).

- **Best Available Control Technology (BACT)**

This is to facilitate pollution prevention, resource recovery and residuals management; and

- **The Principle of Polluter Pay**

Waste discharge permit fees will assist in achieving the goal of zero pollution. In exceptional cases, when retrofitting existing sources, waste discharge standards which are more lenient than BACT-based criteria may be prescribed.

Higher waste discharge fees will be payable under this situation, which will encourage compliance with BACT criteria over time.

2-2-1 Source Control and Pre-treatment

The possibilities of using source control to reduce the organic load, toxicity and volume of industrial commercial waste should be fully explored by laws to control quality of discharge to sewers may be required. Load reduction can mean significant cost savings in constructing and operating the treatment plant and in sewage sludge reuse or disposal.

2-2-2 Reduction, Reuse and Recycling - The 5Rs

The first 2Rs, Reduce and Reuse, are the most important, and should be given the highest priority. Recycling and utilizing waste materials can have long-term economic and social benefits. For instance, it may be preferable to treat the sewage in satellite plants for reuse as irrigation water on surrounding forests, farm land, or community facilities such as parks, golf courses and boulevards, even though this may incur additional costs.

Similar arguments can be made for recycling sewage effluent for its nutrient content, or recycling sludge for its humus and nutrient content.

The Liquid Waste Management Plan should address the potential for recycling and utilizing waste materials with particular attention paid to timing that is what might not be possible now may well be possible in the future. The final implementation costs of such programs will be lower if flexibility is considered when designing waste treatment works.

Reduction

All options to reduce the amount of waste, particularly toxic waste, entering a disposal system should be explored. Measures should be taken to ensure that the system is in good order and that infiltration or inflow to sewers is minimized. Public education campaigns can promote conservation, minimize consumption, prevent toxins from entering the system, curtail the use of garburators, etc. Source control programs can significantly reduce the toxicity of sewage.

Reuse, Recycling and Recovery

The greatest potential environmental, and to some extent economic, benefits can be achieved through the reuse, recycling and recovery of waste sewage and sludge. Options that can be explored include the use of treated effluent for irrigation, wetland development, industrial process or and cooling water. Treated sludge can be used for fertilizer and soil conditioner, and in the production of topsoil for disturbed lands.

Residual Management

Sewage residues include sewage, sludge, grit and scum. Provided the sludge is not unduly contaminated, it can be reused in a beneficial manner. Normal practice in the past has been to bury the grit and scum. Treatment processes which can recover these as useful materials should be explored.

2-2-3 Alternative Methods of Waste Treatment and Disposal

The Liquid Waste Management Plan should thoroughly review the alternatives for waste treatment and reuse or disposal.

Options to be investigated should include:

- opportunities for joint waste treatment with adjacent municipalities or regional districts;
- joint treatment with industry;
- waste reduction;
- possible land treatment;
- opportunities for reuse, recycling and recovery of waste resources;
- land and water disposal,
- on-site and other non-communal systems,
- options for staged development of the system.

Some disposal options may be rejected by some government agencies. Approval-in-principle for all options should be obtained from government agencies in the early stages of the planning process, prior to any public involvement. When the plan is presented to the public for review, it is prudent to present all alternatives in an easy-to-understand format clearly showing advantages and disadvantages of each option. Cost information should be broken down to individual households and industrial/commercial taxpayers.

Alternatives worthy of further investigation should be determined after evaluating public concerns, economic aspects, input from other agencies and environmental assessments.

Financial

All cost effective alternative waste treatment and disposal methods should be fully evaluated. Monetary costs should be calculated in terms of present dollar values or equivalent annual values over the planning period.

Monetary costs include capital construction costs and annual operating and

maintenance expenses, including routine replacement of equipment and parts. Such factors as use and recovery of energy and scarce resources, and the value of recycling water and nutrients should be included in the monetary cost analysis. Annual revenues generated by the system through energy recovery, crop production or other outputs shall be deducted from annual costs.

Communal systems can often minimize costs, while providing the necessary flexibility for alternative disposal methods, water reuse and future expansion. Non-monetary factors should be broadly defined to show their significance and impact. Non-monetary factors include social and environmental effects, implementation capability, operability, performance reliability and flexibility and some aspects of recycling/reuse opportunities.

2-3 Used Oil

2-3-1 Definition

Any oil that has been refined from crude oil or any synthetic oil that is used, and as a result of such use, is contaminated by physical or chemical impurities. In general, this includes:

- engine oil
- compressor oil
- transmission fluid
- hydraulic oil
- gear oil
- transformer oil
- cutting oil
- tempering or quenching oils
- brake fluid

2-3-2 Toxicity

Drained oils, if not reused, is considered as a great dissipation of national income. In addition, it is discarded in water network and in irrigation water

cannels changing its properties and causing severe pollution due to its harmful and hazardous materials.

It is difficult to get use of these oils in spite of their high economical value. Reclaiming used oil helps for energy conservation that the country need to conserve consumption rates which are considered to be the most important problem that our country faces in present time.

Used oil in developed countries are considered to be one of the natural resources used as furnace fuel after being specially treated when it can not be reclaimed for use as a oil by different chemical and physical methods. Some of the reasons of how reclaiming used oils are difficult for **four** reasons:

- 1) Lack of awareness of the majority of consumers to collect used oils.
- 2) Transportation and storage capacity is not proportional to the global consumed amount.
- 3) Shortage of reclaiming units suitable from the standpoint of production rates and of using a recent reclaiming methods where the present unit uses old-fashion techniques (Acid and clay treatment) in addition to its low reclaiming capacity and high out of order rates. Also the harmful high residual acidic rates (40 %) are difficult to be discarded.
- 4) Irrespective of law and legislations, which forbid the consumer from getting rid off used oil anywhere?

2-3-3 Recycling

The importance of a used oil recycling process is twofold. It salvages a valuable energy resource and significantly reduces environmental pollution caused by indiscriminate dumping.

One part of oil can contaminate a million parts of water. Oil that is poured down storm drains, emptied onto the ground, or carted off to garbage dumps event-usually seep into our streams, our lakes and our water supply.

If used oils are conserved through a recycling program, it can be re-refined

and put back to work as a lubricant or fuel. Also, it can be utilized as a feedstock in the manufacture of other petrochemical products.

The purpose of this research is to achieve the following main points.

- 1) Environmental protection against waste oils pollution.
- 2) Conservation of energy consumption by recycling and reclaiming used oils.
- 3) Economical value which will be gained from recycling and reclaiming used oils.

2-3-4 Environmental Protection against Waste Oils Pollution

All petroleum products, virgin and used can have adverse environmental effects and that used oil has a greater polluting effect for several reasons:

- Used oil shows higher levels of potential carcinogenic polynuclear aromatics (PNAs) than virgin oils.
- Used industrial oils have contained carcinogenic nitrosamines, and these can be present in used engine oils.
- Used oils contain such hazardous substances as lead, chromium, barium and cadmium.
- Halogenated compounds formed from breakdown of additives and fuel is present.
- Other hazardous or toxic substances not "natural" to used oil are added to the stream by unscrupulous or uninformed used oil collectors.

The toxicity of lubricants and some of the hazards associated with their use. In considering the toxicity of lubricants, it is convenient to look at the major components and review the potential hazards or concerns associated with each.

- Lubricant base oils.
- Additives for lubricants.

- Finished oils and greases.
- Fluid contamination or deterioration by toxic materials.

The past thirty years have been a period of increased public concern over environmental and health issues, especially with regard to the production and use of industrial chemicals. Desire for health, safety and an unpolluted environment has led to a wave of legislation during this period which resulted in the creation of new laws, such as the toxic substances control Act, the Resources Conservation and Recovery Act, and the subsequent implementation of many rules and regulations. Some of these have required extensive record keeping and have placed additional pressure on industry to discover potential hazards associated with the products that we make and the processes we use.

Since lubricants play an essential role in industrial processes and in our personal lives, it is reasonable to expect that this concern for safety would extend to our use of oils and greases. The toxicity of lubricants and some of the hazards associated with their use.

Some materials used as lubricants could present hazards have been known for more than 70 years ¹⁵⁴. This reference shows the dermatitis and skin cancer among workers in printing plants, cotton mule-spinners and other textile workers, and employees of metalworking plants who used the poorly refined process oils and lubricants of the period. Many of the earlier reports of toxicity related to "mineral oils suffer from lack of definition of the oils used, and some of this information creates a false impression today. For example, many articles deal with carcinogenicity of oils refer to them only as "mineral oils". However, it is known that many of the oils cited were petroleum or shale derived lubricants that had minimal processing. It is also known that poorly refined oils possess moderate carcinogenic activity. Currently, in the United States, "mineral oils" generally describe the highly refined white oils

used for medicinal or cosmetic purposes, which are not expected to be carcinogenic. The International Agency for Research on Cancer (IARC) has recently developed a monograph on lubricant base oils and derived products and has defined the various petroleum lubricants in some depth to overcome the previous nomenclature problems.

2-3-5 Toxicity Testing

Although, in some cases, we may be interested in possible toxic effects of a chemical on plants or other animal life, our interest is most often on the effect on humans. However, only in rare cases are it possible to carry out tests on human subjects and we must base our information about toxicity largely upon the results of studies conducted on laboratory on animal or on cell cultures. In some cases, epidemiological studies have proved useful in identifying chemicals and/or processes that are harmful to humans. However, epidemiological studies, while valuable, invariably involve uncertainty as to exposure levels, previous chemical experience, and a host of other compounding variables. Ultimately, the best characterization of a potential human health concern comes through the combination of both epidemiological and toxicity testing using animal models.

We often test a chemical on a small group of animals using relatively high exposure levels for a short period of time. Optimally, the conditions of exposure are such that they have some relevance to the anticipated human exposures. What we hope to determine is, "what will this chemical do to humans?" Human exposure may involve many people, exposed too much lower concentrations, but over a number of years or an entire working lifetime.

One of the biggest problems encountered in toxicology is determining how to extrapolate a risk calculated from a high exposure, small population animal study to a population of humans generally exposed at much lower levels.

Compounding the extrapolation process, we know that, unlike in animal studies where all possible variables (exposure, age, sex, diet, and genetic makeup) are standardized, human populations exist under particularly uncontrolled environments. People of different age, genetic makeup, and life styles are exposed under different and variable conditions to a chemical.

They are exposed to other chemicals: Cigarette smoke, alcohol, vitamins, varying types of diet. These other chemicals to which they are exposed may intensify the effect of a toxic chemical, or tend to counteract its effect. People may also be more or less sensitive than the test animals to a chemical. Toxicology is an extremely complex subject area and any prediction of human health risk based on animal data is subject to considerable uncertainty.

2-3-6 Toxic Hazards of Used Oils

Experimental work to study the toxicity of used oils has been relatively limited. There are, however, several areas where caution is indicated. These are summarized below.

1. Fluid contamination by toxic materials:

- a- Lead and combustion byproducts in motor oils.
- b- Metal swarf in cutting fluids.
- c- PCBs and solvent contamination.
- d- Bacterial and fungal growth.

2. Fluid deterioration to generate toxic chemicals:

- a- Oxidation/Nitration of motor oils and other lubricants.
- b- Lubricant cracking or coking at high temperatures.

A skin painting study sponsored by the American Petroleum Institute "API" on a composite sample of used motor oil has revealed an increased carcinogenic activity over the respective unused motor oil counterpart. The increased tumorigenic activity of the used oils is thought to be due to an accumulation of PAHs as a result of gasoline combustion and/or thermal

cracking of the oil. Similar work has been reported by the Institute of Petroleum (IP) in Great Britain.

Moderately increased levels of polycyclic aromatic hydrocarbons have been detected in used cutting oils.

The user of oils should exercise caution and avoid contact with oil that is highly degraded or "as been in service at extremely high temperatures.

Similar caution is necessary when the oil may become contaminated with toxic metals or bacteria.

2-4 Environmental Impact of Used Oils and Kiln Dust

2-4-1 Disposal of Used Oils

Figure 2.2 shows what happens to the lubricants sold every year in Western Europe. Only 49% are collectable and only 28% are actually collected ^[55]. The chart also includes process oils which are not lubricants. It is possible to identify the following objectives from these figures: the intensive gathering of collectable oils and an improvement in the environmental compatibility of the lubricants, of which more than 50% pollute the environment by way of total-loss applications, leaks, evaporation and other routes.

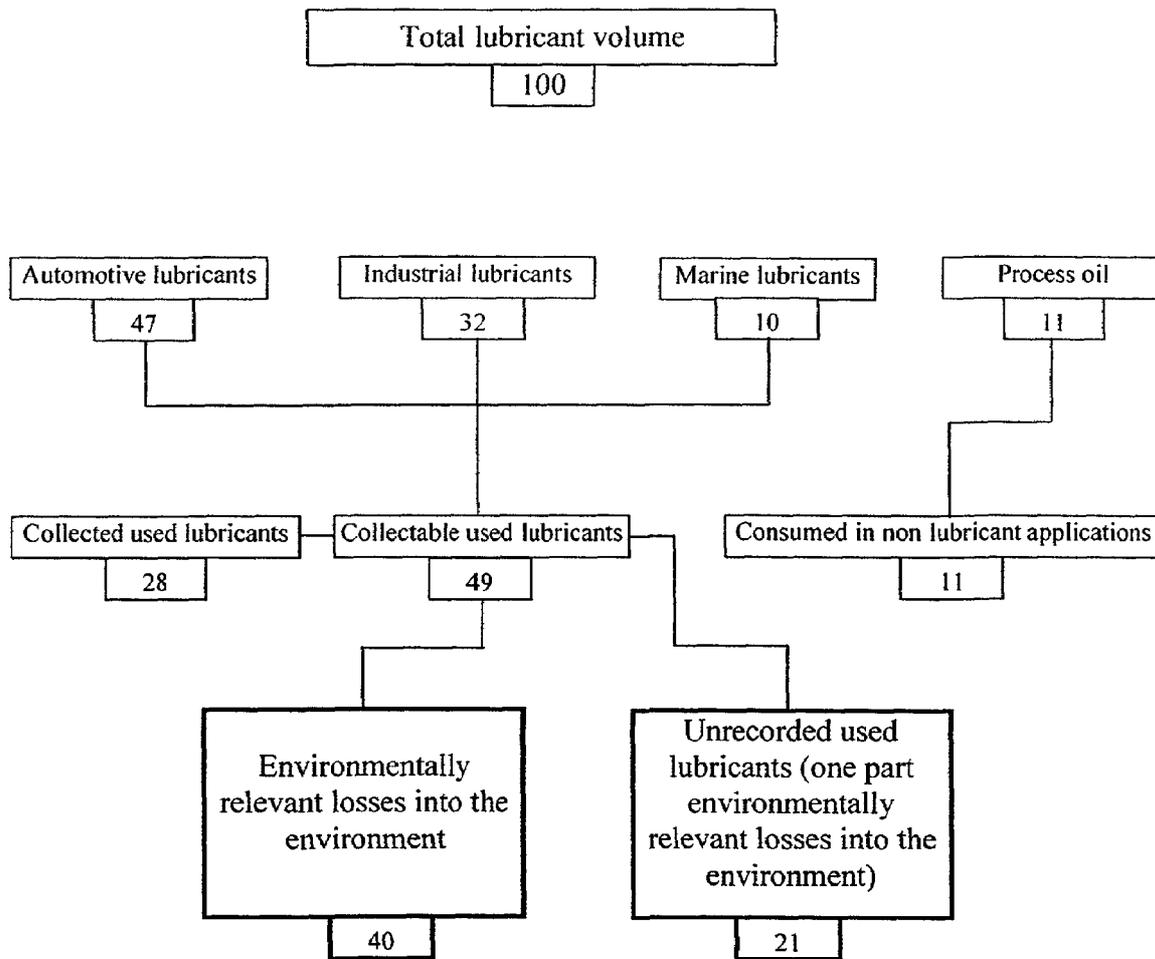


Figure 2.2 Lubricating oil supply, use and disposal in Western Europe (CONCAW 1996).

2-4-2 Possible Uses of Waste Oil

Used lubricants represent a problem for the environment. Their ecologically-compatible use is therefore an important environmental protection measure.

Used lubricants are created when all mechanical possibilities in a machine or at the user's premises no longer suffice to maintain the performance of the lubricant and especially when chemical additives have been used-up and aging by-products are present in the oil. The demand that new lubricants should be made of used products is based on the erroneous notion that re-refining can restore the original condition of a lubricant. In fact, lubricants lose value during use and re-refining, at best; can only restore the value of

base oil. In the case of conventional mineral oils, this value is only slightly higher than fuels or heating oils. This is also the reason why re-refining is hardly economical without legislative provisions or subsidies. From a global competition point of view, other disposal options include the direct incineration of untreated waste oils, the simple pre-treatment (cleaning) and alternative uses such as flux oils for bitumen or for the manufacture of secondary feeds in sec-feed plants for catalytic crackers and as blending stock for high-sulfur fuels.

2-4-3 Legislative Influences on Waste Oil Collection and Reconditioning

The EC Directive 87/101 contains a recommendation to all member countries concerning the regeneration of used oils insofar as economic, technical and organizational conditions allow. Emission thresholds for incineration plants (<3 MW) make the burning of untreated used oils difficult. However, in some European countries, incineration in smaller incineration plants is still possible. Legislation permits incineration in high-temperature furnaces and by the cement manufacturing industry. In some countries, fuels and heating oils reclaimed from used lubricants are not taxed and are thus subsidized.

The PCB problem which surfaced in Europe in 1983 significantly influenced European legislation on wastes. Polychlorinated biphenyls (PCB) which enter the re-refined oil chain as fire-resistant hydraulic oils or condenser oils, have changed German waste oil legislation. While the PCB problem has practically disappeared, the division of waste oils into two groups has had considerable consequences. Used oils which contain more than 0.2 % chlorine cannot be re-refined and are subject to expensive disposal procedures. This in turn has promoted the development of chlorine-free lubricants.

Re-refined used oils are subsidized in Italy. In Germany, the manufacturers

of lubricants (including distributors) have transferred their legal requirement to properly dispose of waste oils to collection organizations. In 1999, these received about US\$ 90 per tone from the lubricant consumers.

In the USA, state law on this subject differs. Since 1986, used oils have been classified as hazardous wastes in California and other states have since followed. In some states, the collector is paid up to 20 cents per gallon by the oil user, in other states the collector has to pay.

Viewed globally, some extremely differing situations exist. While some countries do not regulate the collection and disposal of used oil and used oil is generally not collected, other countries can point to high collection and disposal rates (in 1996, 99% of used oils were collected or properly incinerated in Germany, but only 60% in the USA).

2-4-4 Re-Refining

The re-refining of used oils to lube base oils started in 1935 ^[56]. The principal reasons why re-refining was unable to find acceptance were: high process costs and therefore high selling prices compared to relatively low virgin oil prices, in inadequate removal of carcinogenic polycyclic aromatics, the negative image of such oils in most markets and the increasing complexity of base oil blends in engine and other lubricants. In Western Europe, only 7% of base oil demand was satisfied by re-refined products in 1998.

Numerous re-refining technologies have been developed over the last 20 years. Many were patented but only few were suitable for large-scale application ^[57-62].

In general, the process stages are common to all the different method. General process stages for re-refining of used oils by:

- 1- Separation of larger solid impurities along with most of the water. This is normally achieved by sedimentation.
- 2- Separation of the volatile parts (fuel residues in engine oils, solvents and

low boiling-point lubricant components). This normally happens by atmospheric distillation. The separated light hydrocarbons can usually be used in-house for energy creation.

- 3- Separation of the additives and aging by-products. This can occur by acid refining, solvent (propane) extraction, vacuum distillation or partly also by hydrogenation.
- 4- Finishing process to separate any remaining additives, aging by-products and refining reaction products. This normally happens by hydrofinishing, with absorbents such as bleaching clay or mild, selective solvent extraction (e.g. Furfural).

2-4-5 Sulfuric Acid Refining (Meinken)

The sulfuric acid refining process was mostly developed by Meinken. Compared to older acid-based methods, various process stages reduce the amount of acidic sludge and used bleaching clay generated as well as increasing the lube oil yield.

Due to the acidic sludge problem, acid refining has largely been replaced by other methods. However, numerous such plants were still in operation in 1999. Figure 2.3 shows a Meinken flow plan.

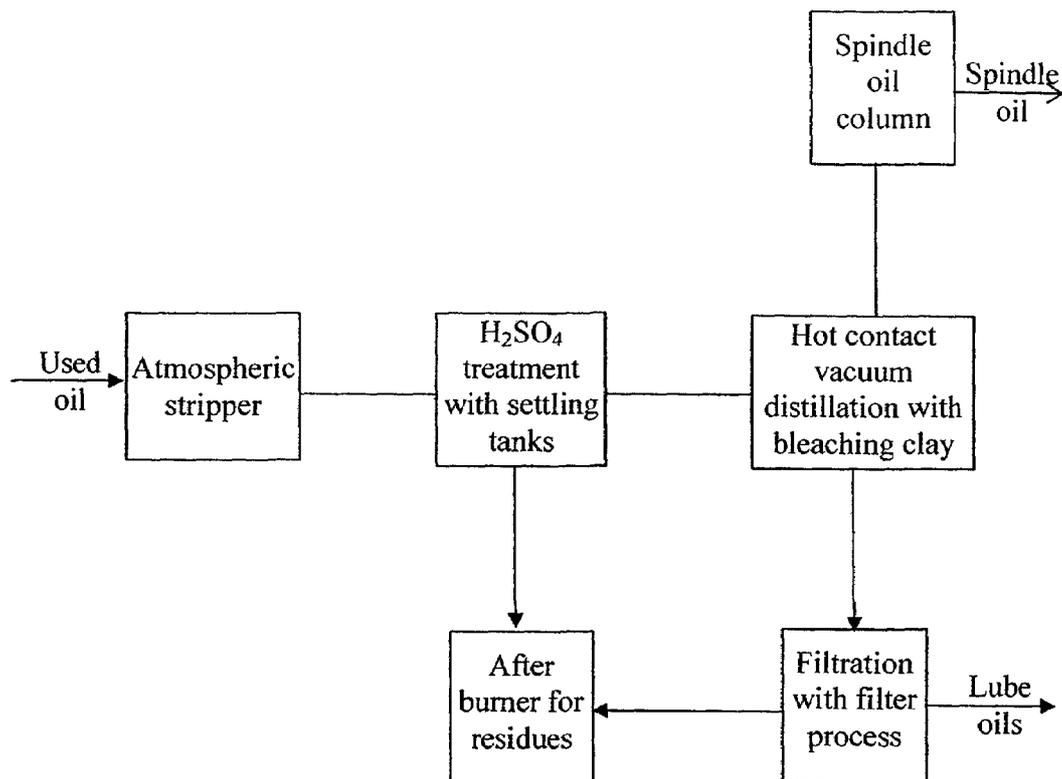


Figure 2.3 Sulfuric acid re-refining (flow chart of the Meinken process)

2-4-6 Propane Extraction Process (IFP, Snamprogetti)

Of the principal extractive refining processes, the IFP (Institut Français de Pétrole) technology is worth mentioning. This initially used propane extraction together with acid refining and later together with hydrofinishing. Propane extraction is also used by Snamprogetti (Italy) as the main refining step before and after vacuum distillation. Figure 2.4 shows the process with propane extraction.

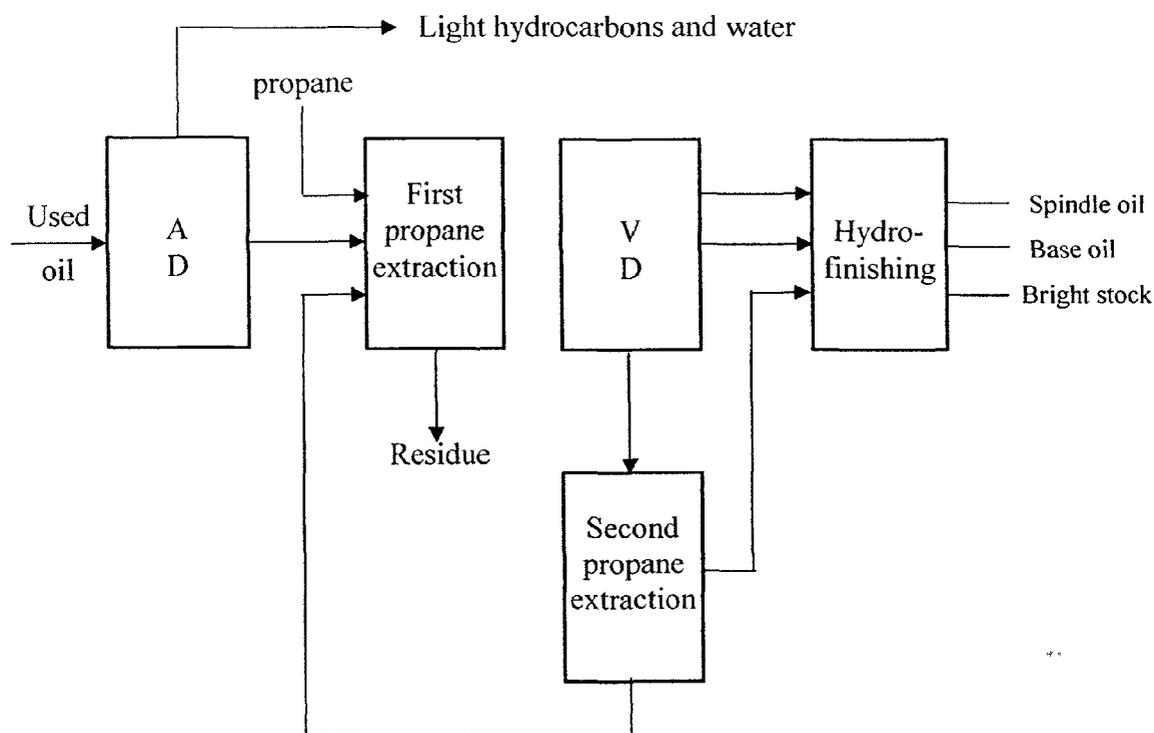


Figure 2.4 Re-refining by propane extraction (IFP, Snamprogetti)

2-4-7 Mohawk Technology (CEP-Mohawk)

The Mohawk Process (subsequently CEP Mohawk) using high pressure hydrogenation was introduced in the USA at the end of the eighties. The process begins with thin-film vacuum distillation (after flashing the light hydrocarbons and water). This is followed by hydrogenation of the distillate at 1000 psi over a standard catalyst. Special steps realized catalyst life of 5 to 12 months, which was essential for the economy of the process.

Marked reductions in the amount of water which must be treated as effluent as well as the cheaper materials for construction (absence of corrosion) are further advantages. The Mohawk process which is based on the KTI process has been licensed for Evergreen Oil (USA and Canada).

2-4-8 KTI Process

The KTI (Kinetics Technology International) process combines vacuum

distillation and hydro-finishing to remove most of the contamination and additives. The key to the process is the thin-film vacuum distillation to minimize thermal stress through mild temperatures not exceeding 250°C.

The hydro-finisher removes sulfur, nitrogen and oxygen. The yield of finished base oils is high (82% on a dry waste oil basis). Figure 2.5 shows the flow chart of this process.

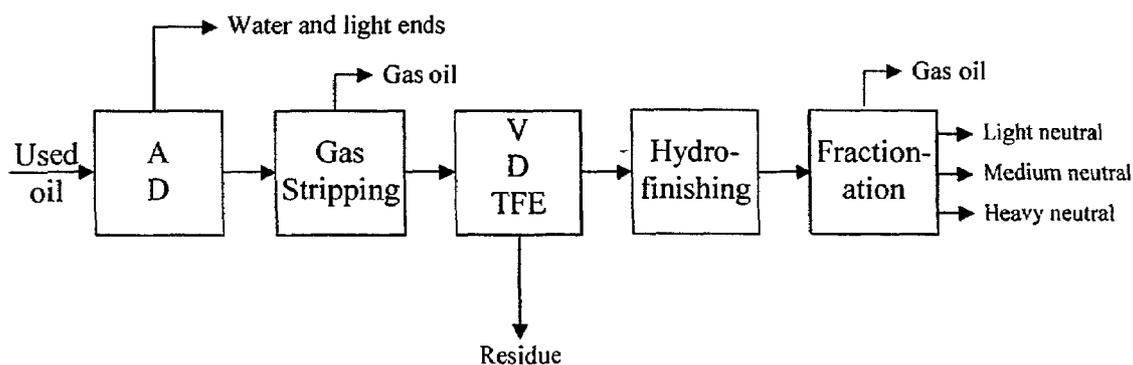


Figure 2.5 flow chart of the KT1 process: thin film evaporator (TFE) with hydro-treatment.

2-4-9 PROP Process

PROP technology was developed by Phillips Petroleum Company. The key elements of the process are the chemical demetalization (mixing an aqueous solution of diammonium phosphate with heated base oils) and a hydrogenation process. A bed of clay is used to adsorb the remaining traces of contaminants to avoid poisoning of the Ni/Mo catalyst. Figure 2.6 shows the PROP Process.

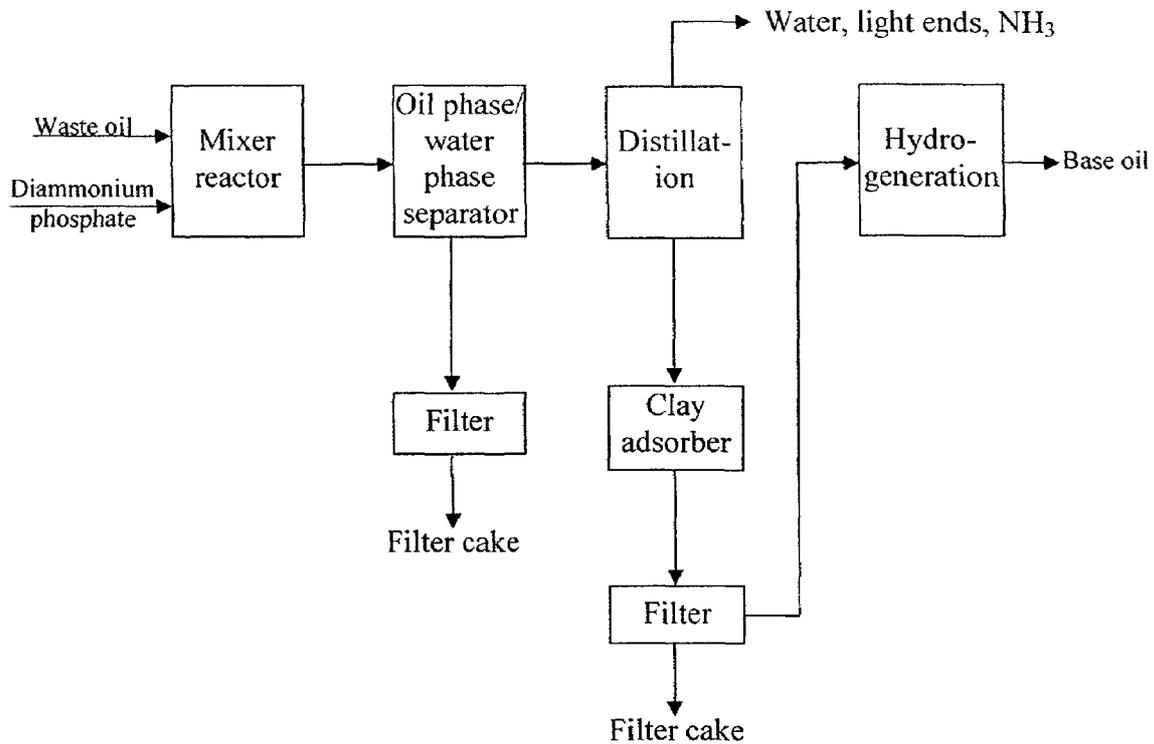


Figure 2.6 Flow chart of the PROP Process.

2-4-10 Safety Clean Process

This process uses atmospheric flash for removing water and solvents, a vacuum fuel stripper, vacuum distillation with two thin-film evaporators, hydrotreater with fixed bed Ni/Mo catalysts, figure 2.7. When using high severity the hydrotreater is in the position to reduce polynuclear aromatics; it also removes higher boiling chlorinated paraffins.

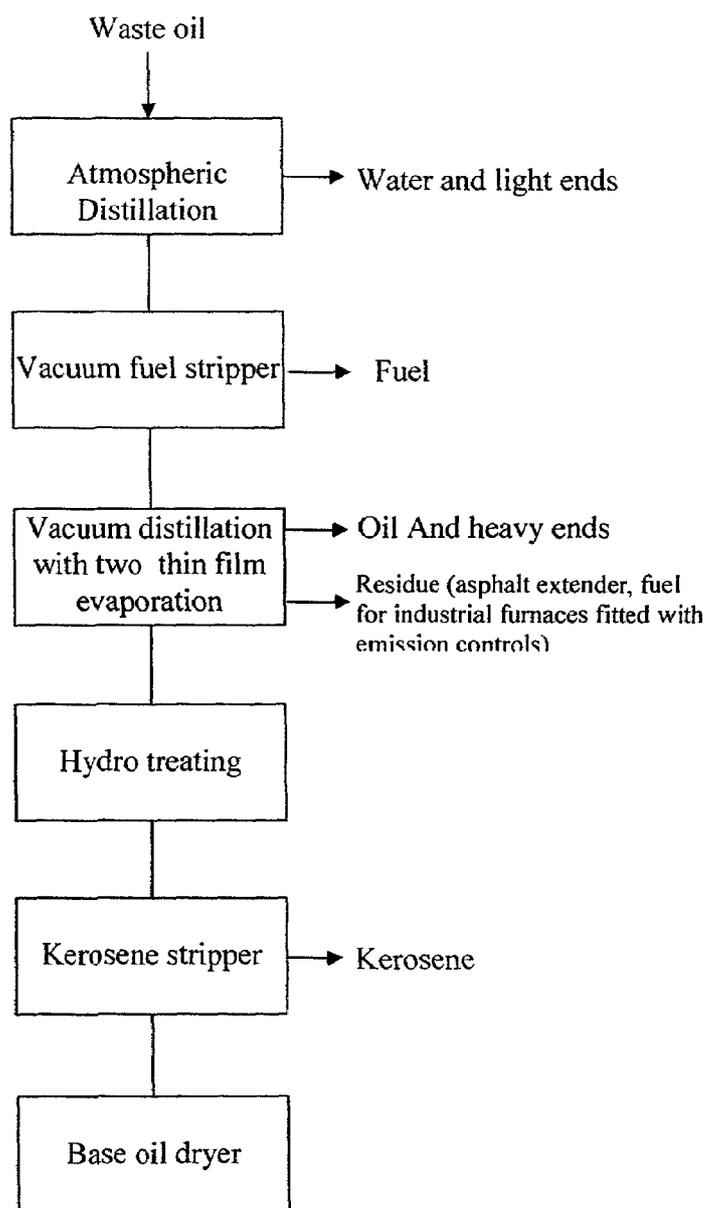


Figure 2.7 The safety Clean process.

2-4-11 DEA Technology

The best results with regard to the technical and environmental quality of the re-refined oil and the elimination of PAR are provided by a combination of thin film distillation followed by selective solvent extraction. In this process, the distillate from vacuum thin-film distillation towers equipment at the re-refinery (Doll Bergen/ Germany) are finally treated in a lube refinery

solvent extraction plant followed by hydrofinishing (DEA, Hamburg, Germany). After this extraction process, the PAR content is lower than that of virgin solvent neutrals. Figure 2.8 shows the corresponding flow-chart.

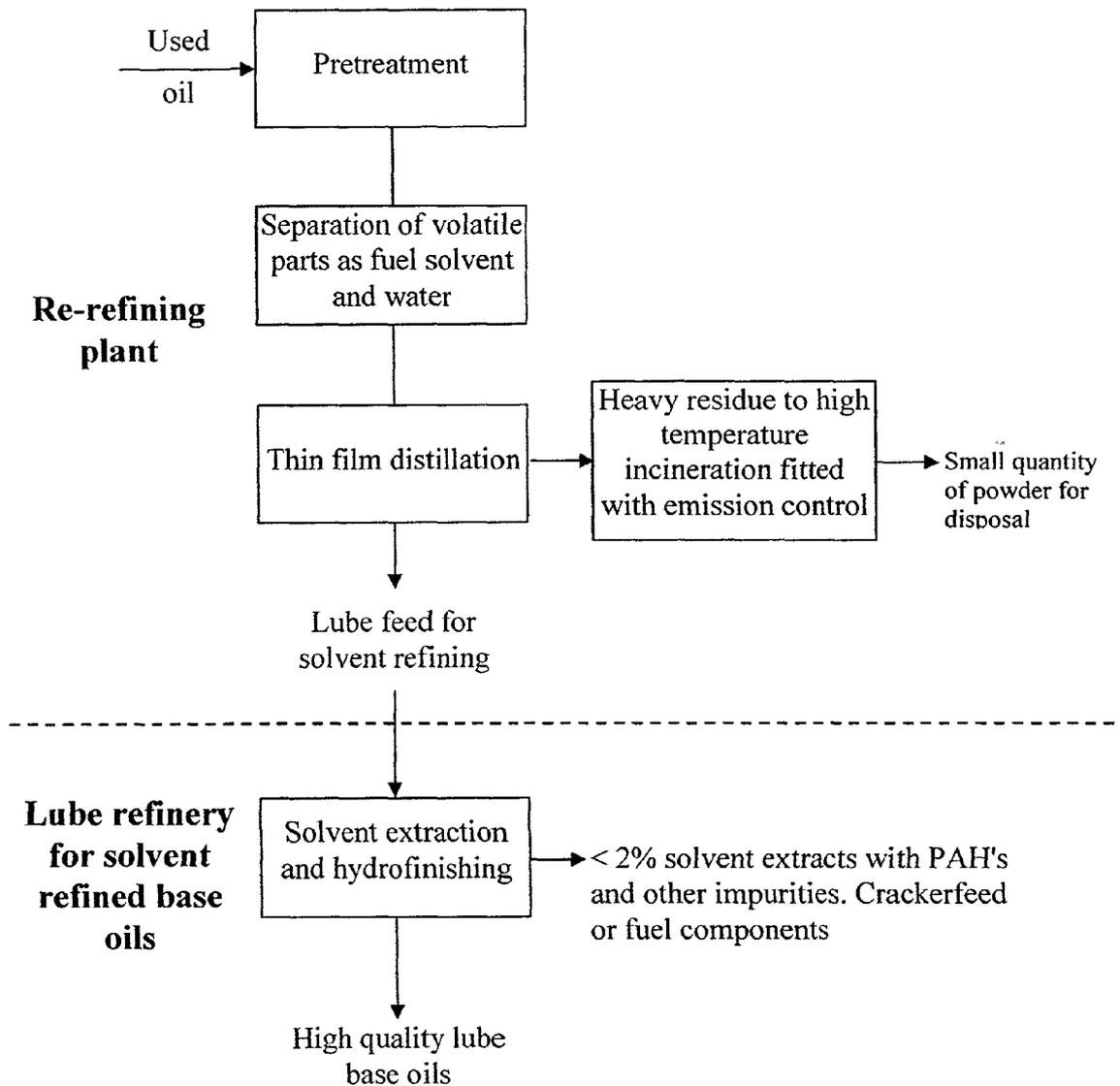


Figure 2.8 Introduction of selective solvent extraction in the re-refining process (DEA/mineralöl-Raffinerie Dollpergen, Germany).

2-5 Cement Kiln Dust

Up to few years ago, production of cement in Egypt was mainly conducted by the wet process. The shift to the dry process increased three times the amount of accumulated dust. The utilization of cement dust, from the various sectors of industry, is a present day concern involving the problem of energy and pollution. The enormous quantities of cement dust released into the atmosphere by cement manufacturing industries contribute substantially to the reduction of air quality. The cement dust, along with other air borne pollutants, may be responsible for many respiratory health problems suffered by residents of the metropolitan area. Other than obvious health hazards associated with poor air quality, there are also other aspects of air pollution that must be taken into consideration such as the difficulty in maintaining residences free from accumulation of dust, possible deterioration of structures and materials associated with air borne corrosive agents, and general diminishing of the quality of life by those persons continually exposed to intensive levels of air pollution.

To deal with the by-pass dust a precise knowledge of its chemical composition and properties are often required. However, it is not possible to list accurate chemical composition and physical data of the dust produced during clinker burning. The main reason, among others, for property variations of dust is its formation under conditions unique to its respective burning process, which may vary hourly for the same kiln, and from one kiln to another. In addition, the quantity of dust produced is dependant on the type and concentration of chemical components in the raw material which, again, may vary from one plant to another due to different quarrying locations, where Suez Plant disposes about 80-100 tons daily and Quattamia about 220-daily.

Dust:

The generation of dust from cement manufacturing plants is recognizable as the main problem and has received considerable attention, both from the

various regulatory authorities and from the industry itself. Dust emissions may be classified into one of the two categories depending on their sources:

Process dust emissions are those arising from the exhausting of gases directly integrated in the cement manufacturing process (spot point emission).

- Fugitive dust emissions are generally those resulting from entertainment and re-entertainment dust by wind or vehicle. This classification of dust categories is important, since the impact of the associated emission is likely to vary significantly, depending on the dust sources.
- Fugitive and dusty air emissions may be expected to settle mainly within the confines of the plant and its immediate vicinity whilst low density buoyant process emissions generated in cement kilns, once dispersed from tall stack, could contribute to long range and trans-boundary air pollution.
- It should be further noted that most of the dust are products of the various manufacturing stages which can be returned to the process, they are generally not wastes or by-products requiring Disposal. It is therefore economically desirable to design and operate with high dust capture efficiencies.

Cement producers world wide are deeply concerned about the amount of dust generated by the dry and wet processes in cement clinker production, because the amount of dust generated by the dry and wet processes in cement clinker production, because the amount of dust generated constitutes up-to 13% of the total amount of clinker produced.

Portland cement kiln (by-pass) dust was found to be composed of finely ground cement raw materials (CaCO_3 and SiO_2) having lay out of alkali sulfate (K_2SO_4 and Na_2SO_4) in this form, it cannot be directly recycled to cement kilns because concrete is weakened by a reaction and the collected aggregates^[63]. This finely divided dust is emitted from cement kiln to prevent the buildup of excessive salts in the cement kilns. The alkali salts in the dust are driven from the clay raw materials, which include potassium and sodium feldspars^[64].

2-5-1 Recycling of Cement Dust

The utilization of by-products, from the various sectors of industry, is a present-day concern involving the problem of energy and sometimes even ecology. Cement plants generate solid waste air and water pollutants during the course of their operation. The cement kiln exhaust gas contains substantial quantities of particulate matter and constitutes the largest source of air pollution in the plant. The solid waste problems generally arise from the disposal of kiln dust (a mixture of finely divided raw feed, partly calcined raw meal cement clinker and condensed volatile salts) ^[65].

The cement industry usually uses mechanical collectors, electrostatic precipitators, filter baghouse collectors, or combinations thereof to control the particulate ^[66]. The types of collectors used depend on the emissions and the temperatures of effluents of the unit operation. In fact, approximately 12% of the kiln feed exists from the kiln with the gas (up stream of any air pollution control equipment). Throughout the industry, roughly 73% of the kiln dust is recycled to the cement-making process ^[67].

The clinker cooler is the second largest air pollution source in cement plants. Dust collected from this source is returned to the process (usually clinker storage) rather than wasted. The types of air pollution control equipment used to handle clinker off-gas include the following:

- 1- Granular bed filters.
- 2- Baghouse collectors.
- 3- Electrostatic precipitators.

Up to 15 years ago, general production of cement in Egypt is conducted mainly by the wet process. Nevertheless, the on-going shift, in our cement industry, to the dry method is expected to increase the accumulated dust. This is due to the fact that the dry process of cement production results in dust three times more than the wet process. Generally, a high proportion of cement

dust is recycled in the cement kiln and that; the part which is not recycled has excessive concentrations of alkali oxides, chlorides and sulphates that may prevent the final product to conform with the standard specifications.

2-5-2 Alkali Cycle

Oxides of potassium (K_2O) and sodium (Na_2O), commonly referred to as alkalis, are impurities that not only have deleterious effect on cement quality but can cause considerable operating problems particularly in preheated kiln. Of the two alkalis, potassium is by far the predominant impurity that needs close attention from the plant chemist. During the burning process, alkalis vaporize in the lower part of the burning zone, travel with the kiln gas to the near of the kiln, and condense again at a gas temperature of around $900\text{ }^\circ\text{C}$.

These alkalis react in the colder part of kiln with sulfur dioxide, carbon dioxide, and chlorides that are contained in the kiln gases. Thus, an internal alkali cycle is created that can lead to troublesome buildup and ring formation in the kiln. The inner cycle of alkalis depends on the kiln type as well as on the content of sulphates and chlorides in raw materials and in *Me* fuel. In dry and wet process kilns this condensation takes place in the lower stages of the pre-heater tower or grate pre-heater. There must not be too much of them in the clinker, they should not be recycled and allowed to accumulate in the kiln and yet they are found in great quantities in the raw materials. To combat these problems, various means are employed to keep these alkalis under control.

In long wet process rotary kilns, 70% of alkalis introduced to the kiln generally remains in the clinker, while 30% leaves the kiln with exit gases^[75]. In wet-and dry plants, part of all of the kiln dust collected in the bag-house or electrostatic precipitator must be wasted. Some plants are filtrated in that they have to waste only the last section of these dust collectors, i.e. the very fine dust particles that are richest in alkalis. Preheated and precalciner kilns are

equipped with alkali by-pass systems at the preheat tower to control all alkali cycle.

2-5-3 Sulphur Cycle

Sulfur (SO_3) is introduced into the kiln by the raw materials and the fuel. This impurity will also vaporize to form sulfur dioxide (SO_2) at a temperature of $\sim 1000^\circ\text{C}$ and condenses in the form of sulphates within the kiln system. They readily combine with calcium and potassium form CaSO_4 and K_2SO_4 both of which are the prime cluprits forming and buildup problems in the upper half of the kiln system.

Chloride originated primarily from the raw material and from the coal. For proper kiln operation, plant chemists usually try to hold the total chloride content in the raw mix below 0.02%. Chlorides also vaporize and react with alkalis to form alkali chloride. Alkali chlorides tend to remain in the internal kiln cycle for long time and can lead to heavy coating as well as ring formation in the upper part of the rotary kiln and the lower stages of the pre-heater. Chlorides, even in such small quantities as 0.02% in the kiln feed can become so troublesome on some pre-heater kilns that they are forced to operate with a by-pass of up to 15% at the pre-heater tower.

2-5-4 Cement Dust and its Circulation

Cement manufacture in Egypt discard annually approximately 2.5 million tons of cement dust collected from exhaust gases of cement kilns, no-dulizers and cooling towers. The collected dust contains excessive concentrations of alkalis that make it unsuitable for return to the cement making process. Utilization of this cement dust would eliminate costly pollution control measures that are required to prevent degradation of air, land and water in the vicinity of dust disposal sites. Typically, about 10-20% by weight of the raw materials leave the kiln as dust which must be scrubbed to prevent air

pollution. In case, removal of alkali content in this dust is affected, reuse of some of this dust in the cement manufacture becomes liable to take place. Kiln dust originates when finely ground raw materials become airborne in the stream of combustion gases traveling up the kiln. Carbon dioxide liberated by the decomposition of calcium carbonate adds to the agitation of the materials and thus to the amount of airborne dust. In the presence of excess alkali, an alkali aggregate reaction takes place causing the concrete to expand and loss in strength, hardness and is less durable.

In the literature, alkali removal from either the raw materials or from the airborne kiln dust has been published. The wet process involves leaching of the dust with suitable fluids mainly water followed by treatment with chemical and partial separation. The second method is hydrometallurgical in principle whereby alkali is vaporized with the temperature range 1300 - 1700°C. This method is called a fluidized bed reactor.

Some plants have installed leaching system to reprocess collected kiln dust for alkali removal, so that the dust can be recycled to the cement manufacturing process. Leaching involves mixing kiln dust with water, then clarifying the mixture. Clarifier underflow is recycled to the cement kiln while the overflow (which contains most of the sodium and potassium salts) goes to some form of waste water treatment process. The use of leaching processes has been declined over the last ten years due to the need for treating process waste water. Less than a dozen plants in the industry presently have leaching operations. Other leaching methods have been researched, but none have been commercialized.

Kiln dust has been or can be used in a number of different ways, including those listed below. The Portland cement association is conducting experimental work in the use of waste kiln dust for a number of these applications.

- Landfill and soil stabilizer,

- Sub-base roads,
- Dump in strip mines to neutralize acid mine drainage,
- Fillers for bituminous paving materials asphaltic roofing materials,
- Neutralize acidic waste of bogs, lakes, and streams,
- Neutralize certain industrial wastes such as spent pickle liquor, leather tanning waste and cotton seed delinting waste,
- Absorption of SO₂ from stack gas in wet scrubber slurries, and -replacement of soda in green glass.

Agricultural uses of cement kiln dust are being researched world-wide, and a number of research studies have been conducted by the U.S. Department of Agriculture. For example, researchers have found that some types of dust have 80 percent of soil neutralizing capacity of lime and about the same liming qualities as pulverized limestone. Dust also provides an inexpensive source of certain fertilizer nutrients, particularly potassium.

Cement dust has also been used in cattle feeding experiments by the Department of Agriculture. The experiments have shown that steers fed cement dust as part of a complete mixed diet had a higher average daily weight gain and an improved feed/gain ratio compared to steers fed a normal control diet. These experiments are continuing. Dust used in these experiments has been taken from a single source. It is not now known whether any heavy metals present in the dust used for agricultural purposes will have adverse environmental health effects.

The X-Ray diffraction analysis of the dust indicates that the dust consists of limestone as a main component, together with minor amounts of quartz CaSO₄, KCl, NaCl, K₂SO₄, 2(C₂S)CaSO₄ and 2 (C₂S)CaCO₃ ^[68]. The mineralogical constituents of kiln dust were identified as; calcium carbonate, quartz, feldspar, mica, glass beads and carbon, incompletely reacted raw mix such as free lime, B-C₂S, C₂F, C₄AF, mullets, and dehydrated clay, and CaSO₄ and Na₂SO₄ formed as a result of the reaction between fuel gas and

kiln feed.

It was reported that clinker was prepared directly in separate furnace. The clinker obtained had a lower hydraulic activity and higher water demand than conventional clinker due to its much higher alkali content. The problem was eliminated by Tettmar *et al* ¹⁶⁹ who first cabined the kiln dust in a fluidized bed reactor at 1225 °C in order to volatilize about 70% of the alkalis. The cabined dust was then added to the ground cement in the amount of 5% to 10%.

The effect of alkali content on cement quality was studied carefully which showed that the increased alkali content decreases the cement durability.

The loss in cements strength resulting from recycling large amounts of waste dust to the kiln was offset by the addition of flouring-containing mineralizes. An alternative method of burning waste dust has been described. In which the dust from several kilns were recycled to one kiln, which operated for 16 hours with recycled dust and 8 hours with standard kiln feed slurry. This procedure avoided the accumulation of alkali salts and improved the strength. Sell and Fischbach ¹⁷⁰, have suggested recycling waste kiln dust in the form of briquettes. The briquetting process simplifies handling of kiln dust, and enables it to be processed with the feed and burned with a little dust being regenerated. The process does not appear to be limited to freshly produced dust, but also to old stored in waste piles. Burning the peptized dust in grate process kiln, when already requires the use pellets, was also considered promising

2-5-5 Statement of the Problem

The raw materials and fuels entering into the cement burning process contain secondary constituents, such as alkalis, Sulphur and chlorine. These constituents are partially vaporized in the high temperature zones and then condense in the colder zones of the burning system. Successive evaporation

and condensation of secondary constituents between kiln and pre-heater calciner from is known as circulation phenomena. In fact, there are two cycles occurring in a clinker burning system, namely, internal cycle and external cycle. The internal cycle is formed by vaporization of secondary constituents in the rotary kiln and condensation in the colder zones of the process. On the other hand, the external cycle is caused through the return of dust transferred with the pre-heater exit gas to the raw mix via the raw mill, the cooling tower, and filter. The behavior of circulation elements depends on its degree of vaporization, its extent of adsorption by the hot meal and condensation in pre-heater mill and filter and also by its degree of combination in the clinker.

Intensive internal cycle of secondary constituents may cause serious operation problems due to coating formation. Clinker quality deteriorates in addition to emission problems. In cases of relatively high intakes of secondary constituents, it may be then necessary to break the cycles to avoid coating formation problems and to reduce the residual amounts of those constituents that end up in clinker. For this purpose, an effective technique which consists of installing a by-pass system is necessary ^[71-94]. On the other hand, the fuel energy consumption of the Thin Plant increases with increase of kiln gas by-pass. So, a kiln gas by-pass is considered, from the thermal point of view, as a heat loss from the process. It is represented by the loss of escaped sensible heat of by-pass gases and dust as well as the consumed heat of reactions of the dust ^[94].

2-5-6 Possible Uses of Cement By-Pass Dust

The cement industry produces a large amount of waste dust. This dust arises from two sources: ^[94] Cement dust from the rotary kiln, known kiln dust, that settles from the electrostatic precipitators used to purify the flue gases evolving from the kiln; and By pass dust, which constitutes a " purge " from the kiln in order to minimize the amount of alkalis (mainly in the form

of chlorides) in the effluent flue gases from the kiln, figure 2.9. One main factor that decides whether it is possible to recycle any dust the kiln, is the alkali chloride content of this dust. The first type can usually be recycled to the kiln since its alkali content is usually low. By-pass dust, on the other hand, cannot be recycled to the kiln, its alkali content usually exceeding 10 %. The rate of by pass dust production usually ranges from 3-8 % of the total as kiln production rate. Kiln of capacity 4000 ton/day clinker? will produce about 200 ton/day by pass dust. This large amount has to be disposed of, since it represents an environmental hazard, primarily because of its extremely low particle size ($\sim 10^{\phi}$ microns). The current state of affairs involves dumping the dust in open pits in desert regions.

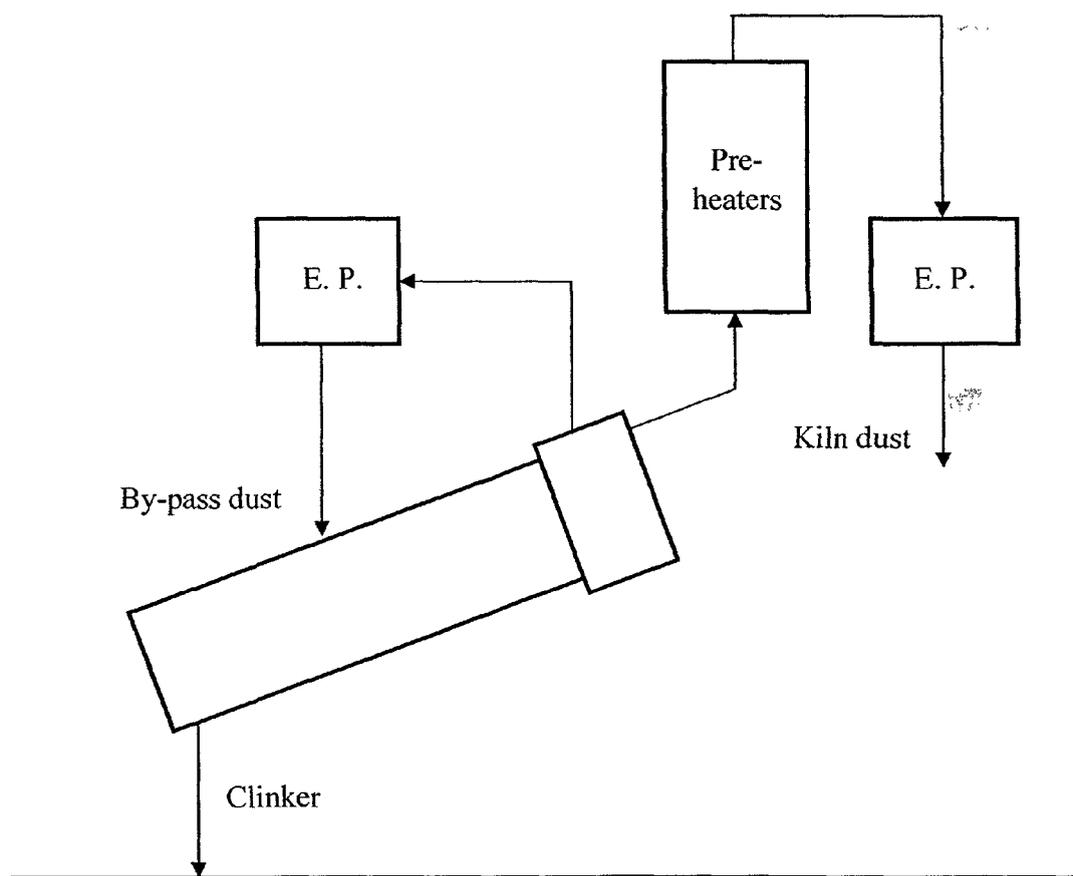


Figure 2.9 Cement By-Pass Dust

In the past three decades, and since the sweeping success of the dry pro-

cess, several alternatives have been proposed to make use of the waste dust. Davis and Hooks ^[88] have submitted a comprehensive review about the matter. Potential uses of kiln and by pass dust include soil stabilization, sub-base road fillers for bituminous and asphaltic materials, replacement of soda in low quality glass, etc.... On the other hand, a lot of work has been done to make use of the large amount of alkalis present in by pass dust in the ceramic industry, as a fluxing agent. Sabra *et al* ^[89] have used by pass dust in the manufacture of clay bricks and recently an optimum amount of dust to be used in clay bricks manufacture has been proposed by Elwan *et al* ^[90] ^[104]. The main drawback, in my opinion, seems to be the high fluorescence occasioned by the presence of alkalis that I have personally observed as the percentage of dust exceeds 5 %. Recently, adding by pass dust was tried at percentages reaching 15 % as a substitute for cement in cement bricks without impairing their properties. Also, up to 10 % dust was added as substitute feldspar in the manufacture of vitrified clay sewer pipes. The prototype pipe produced abided by the standards ^[105]. All these uses, and others, have one main drawback: Although they utilize the waste dust, they can hardly be expected to make use of any appreciable quantity of dust produced by even one single kiln. That is why the most promising applications seem to be those related to its use in the cement industry itself. In this respect, the work of Didamony *et al* ^[91] that uses by pass dust as a mineralizer in the cement industry, accelerating the Tinkering process, makes use of a large proportion of the dust produced. Also, recent research work at the chemical engineering department, Cairo University, has proved that a reasonable amount of by pass dust can be ground with clinker, and still keeping the resulting cement within the standards. I finally believe that joint work between the interested parties can have a positive impact on possible solutions for the dust problem.