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WASTE MANAGEMENT

HAZARDOUS WASTE MINIMIZATION: PART V

Waste Minimization in the Petroleum Industry

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The extractive nature of the petroleum industry sets it apart from other industries in many respects. The nature of this industry places it at somewhat of a disadvantage to other industries when attempts are made to foster waste minimization practices and programs. However, this is no excuse for the industry to not further vigorously pursue minimizing waste. This paper describes the petroleum industry and the products it makes along with their associated waste streams. The industry's commitment to waste minimization is described with examples of specific minimization projects provided. Although the opportunities for minimization are limited, the economic incentives for reducing waste disposal costs, not to mention long term liability from improper disposal practices, has put the petroleum industry on the road to waste minimization.

Since the passage of the Hazardous and Solid Waste Amendments of 1984, higher levels of management have become increasingly aware and more interested in their company's waste management practices. To a great extent, this interest has come about as a result of past disposal practices and involvement in tedious and expensive site cleanups and current skyrocketing costs to dispose of waste at properly operated disposal facilities.

This year will mark the beginning of compliance with newly issued hazardous waste Part B permits for most petroleum industry on-site treatment, storage and/or disposal facilities. Some on-site treatment, storage, and disposal facilities will not receive Part B permits. This will lead to expensive closure and post-closure care of these interim status units. In addition, such facilities will be forced to seek other means of treatment, storage and/or disposal which will likely involve costly use of offsite commercial facilities.

To reduce these escalating waste management costs, the petroleum industry is actively developing voluntary waste minimization programs to limit the quantity and toxicity of wastes to the extent economically practical. Because of the extractive nature of the industry, the fixed nature of the industry's raw materials and products, the maturity of the industry and competition in a world market where the industry has little control over the price of its raw material, the industry is aggressively seeking to further minimize its wastes through a combination of recycling and reuse rather than the more widely used approach of modifying processes so as to generate less waste. The petroleum industry also emphasizes environmentally sound methods of waste treatment.

Petroleum Industry Profile

The principal business areas of the petroleum industry are exploration and production (i.e., oil and gas extraction), refining, transportation and marketing. The majority of wastes produced by the petroleum industry are generated by the production and refining business areas.

The exploration and production area of the business explores for, develops and produces crude oil and gas resources from beneath the earth. In 1985, there were approximately 842,000 producing oil and gas wells in 38 states. These wells produced 8.4 million barrels of oil, 1.6 million barrels of natural gas liquids and 44 billion cubic feet of natural gas daily.[1] Crude oil production is traditionally expressed in barrels, wherein one barrel is equivalent to 42 U.S. gallons. The American Petroleum Institute (API) estimates domestic reserves at 28.4 billion barrels of oil, 7.9 billion barrels of natural gas liquids and 193.3 trillion cubic feet of natural gas. This area of the industry employed 451,618 people in 1985.[2]

The products (e.g., gasoline) manufacturing sector of the business is found in its refining operations. On January 1, 1987, there were 212 operable refineries in the United States with a total crude oil distillation capacity of 15.6 million barrels per calendar day. Of these 212 refineries, 188 were operating on January 1, 1987 with operating capacity listed at 14.9 million barrels per calendar day. These operable refineries are located in 36 states.[3] These refineries primarily produce gasoline, jet fuel, kerosene, distillate fuel oil, residual fuel oil, lubes, wax, petroleum coke and asphalt. In 1985, 138,191 people were employed in the manufacturing area of the industry.[2]

The transportation area of the business is responsible for moving petroleum fluids from the well site to the refinery and moving finished products from the refinery to wholesale and retail marketing outlets. Petroleum transport can involve pipelines, ocean-going tankers, inland waterway barges, transport trucks, and rail tank cars, or a combination thereof. In 1985, 183,266 people were employed in this sector of the industry.[2]

The marketing sector delivers the finished product to the customer. The customer most readily identifies the petroleum industry with its service stations along roadways that criss-cross the country. The full-service station of the past has given way to the self-serve station selling various staple items. In 1987, there were 93,864 service stations operating in the United States. In 1985, about 596,000 people were employed at about 99,987 retail gasoline service stations.[2]

The following discussion of the wastes identified for each industry segment and their attendant treatment and disposal options provides an overview. Gas processing operations are not specifically covered in this overview because these types of facilities rarely generate any significant amount of hazardous waste. Wastes generated are substantially similar to those discussed in the exploration and production section. This paper does not cover the waste disposal practices associated with spills of crude oil or petroleum products. Generally, if the material spilled can be recovered and recycled or reused, this will be preferred over disposal. If allowed, contaminated soil is treated utilizing in-situ biodegradation methods, otherwise the soil is excavated and properly disposed of.

Table I. Refining listed hazardous wastes projected disposal rates [(wet) tons/yr].[12]

K048-DAF float	308,000
K049-Slop oil emulsion solids	144,000
K050-Heat exchanger bundle cleaning solids	1,300
K051-API separator sludge	393,000
K052-Leaded gasoline tank bottoms	5,000
	851,300

Wastes from Exploration and Production Operations

On December 29, 1987, the U.S. EPA submitted its final "Report to Congress"[1] following the completion of its study of exploration and production wastes. Congress mandated this study in 1980 when it exempted these wastes—which include drilling muds, produced waters and other associated wastes—from the hazardous waste provisions of RCRA. In addition, EPA was instructed to make recommendations as to whether this exemption should remain in effect. These recommendations must be made to Congress by June 30, 1988, which, in turn, will decide whether to allow the exemption to continue or whether new laws need to be enacted to regulate these wastes.

Drilling wastes include fluids or "muds" used to drill a well, cuttings or rock fragments extracted from the borehole and, occasionally, various additives and chemicals used in the recipe for drilling muds to meet downhole conditions. The largest volume of drilling wastes are the spent fluids or muds. In its Report to Congress, EPA used the API method for estimating the national volume of drilling wastes. The API method estimates that 361 million barrels of drilling muds and cuttings were generated in 1985 from the drilling of 69,734 wells.[1]

In addition to drilling wastes, significant volumes of water are produced along with the oil and gas during the process of removing hydrocarbons from subsurface reservoirs. Over time, the ratio of produced water to oil and gas increases as the well matures. This produced water occurs naturally in the hydrocarbon reservoir and/or enters the reservoir from the injection of water into a nearby well which is known as waterflooding or secondary recovery. The recovery technique, geology of the formation and the maturity of the oilfield are the determining factors which control the quality of water expected to be produced. Produced water volumes calculated by EPA and API for 1985 were 11,671,641 and 20,873,243 barrels, respectively.[1]

Unlike drilling fluids and produced waters, Congress elaborated on the "other associated wastes" term. Specifically, "other associated wastes" refers to materials intrinsically derived from primary field operations associated with the exploration, development or production of crude oil or natural gas. These wastes include hydrocarbon-bearing soil in and around related facilities, drill cuttings, materials produced from a well, and accumulated material from production separators, fluid treating vessels, storage vessels and production impoundments.[4] According to the API, the exporation and production sector annually produces about 16 million barrels of other associated wastes.[5]

Currently, the above wastes are considered to be exempt from the hazardous waste provisions of RCRA. In the EPA Report to Congress, a partial list of nonexempt wastes was included. These wastes included waste lubricants, hydraulic fluids, motor oil, batteries, paint, solvents, off-specification and unused materials intended for disposal, incinerator ash, pigging wastes from transportation pipelines, sanitary wastes, trash, gray water, gas (SO_x and NO_x) and particulates from gas turbines or other machinery, drums whose contents are not intended for use, spent iron sponge, glycol and other separation media, filters, spent catalysts, wastes from truck and drum cleaning operations and spills from pipelines or other transport methods.[1] Indeed, these are the wastes which must be tested for hazardous waste characteristics when they become destined for disposal.

Waste Treatment and Disposal. Treatment and disposal of drilling wastes take place either on or off the drilling site. Onsite treatment and disposal methods include reserve pits, landspreading, annular disposal, solidification of reserve pit wastes, treatment and discharge of liquid wastes to surface water and closed treatment systems.[1] The most commonly used onsite disposal method involves depositing the used drilling muds and rock cuttings in earthen-walled reserve pits. Once drilling is completed, the pit(s) is closed according to state and local reg-

Table II. Refining non-listed wastes projected disposal rates [(wet) tons/yr].[12]

Primary O/S/W separator sludge[a]	69,000
Secondary O/S/W separator sludge[b]	6,600
Bio-sludge	699,000
Cooling tower sludge	14,400
HF alkylation sludge	31,000
FCC catalyst	131,000
Other spent catalyst	17,000
Stretford solution	38,000
Non-leaded tank bottoms	117,000
Treating clays	12,000
	1,135,000

[a] Sludges generated in separators other than API separators to include equalization tanks or lagoons, corregated plate interceptors (CPIs), parallel plate interceptors (PPIs), etc.
[b] Float (other than DAF float) generated from secondary treatment of refinery wastewater following separation in the primary oil/solids/water separator (before biological treatment).

Petroleum Refinery

Storage and Handling
- Tank bottoms, leaded gasoline
- Tank bottoms, unleaded gasoline
- Tank bottoms, crude oil
- Tank bottoms, distillates
- Tank bottoms, decant oil
- Tank bottoms, bunker
- Tank bottoms, slop oil (emulsion solids)
- Asphalt waste

Process units
- Desalter clean out sludges
- Caustic solution phenolic
- Caustic solution sulphidic
- HF acid (neutralized)
- H_2SO_4 acid (spent)
- Clay (spent)
- Activated carbon (spent)
- Amine filters
- Off specification sulfur
- Furfural (spent)
- Glycol (spent)
- Coke fines
- Stretford solution
- FCCU catalyst (spent)
- FCCU dust
- E.S.P. dust
- Poly unit catalyst (spent)
- H_2 plant catalyst (spent)
- Reformer catalyst (spent)
- Hydrocracker catalyst (spent)
- Hydrotreater catalyst (spent)
- Merox catalyst (spent)
- Copper chloride (spent)
- Claus plant catalyst (spent)
- HF acid soluble polymer

Utility plant
- Cooling tower sludge
- Lime sludge
- Anthracite filters
- Spent zeolite resins
- Sand from filters
- Ion exchange regenerant

Waste water Treatment plant
- Gravity separator sludge (API, CPI, PPI)
- I.A.F. and D.A.F. sludge
- Biotreater sludge
- Storm pond silt
- Sump sludge

Miscellaneous

Maintenance wastes
- Asbestos
- Refractory brick
- Oil contaminated soil
- Used drums
- PCB wastes
- Demolition scrap
- Heat exchange cleanings, solids and liquids

Laboratory wastes
- Spent chemicals (liquid)
- Spent chemicals (solid)
- Used drums

Administrative office bldg.
- General refuse e.g.:
- Waste paper
- Domestic waste
- Used office supplies

Figure 1. Sources of petroleum refinery wastes.

ulations and landowner agreements. Closures usually involve allowing the water in the pit to either evaporate or be decanted and properly disposed of. After this step is accomplished the pit is backfilled and the drill site is revegetated.

Off-site treatment and disposal methods include use of centralized disposal pits, injection and treatment facilities, commercial landfarms, and reconditioners of drilling muds.[1] These centralized-type operations are often established in conjunction with the development of an extensive oil and gas field.

The vast majority, nearly 90 percent, of produced waters are injected underground through approximately 168,000 injection wells.[5] This injection of produced water is permitted either by the U.S. EPA's underground injection control program or a comparable state program which is U.S. EPA-approved. Other methods of disposal include evaporation pits and permitted discharges into coastal and offshore waters. Another practice with produced water is reinjection into the same reservoir from which the water originated in order to enhance the recovery of hydrocarbons. In some areas of the country, low-salinity produced waters are used for irrigation and for drinking water for livestock under the beneficial use permitting program of the Clean Water Act.

Depending upon the type of other associated waste involved, similar methods are used in treating and disposing of these wastes. In general, these wastes are sold to reclaimers, landfarmed, landfilled or injected into underground wells. Currently, the API through an EPA request has undertaken a thorough review of what wastes should be considered "other associated wastes" along with establishing a better understanding of the waste management practices used by the industry concerning these wastes.

Treatment and disposal of nonexempt wastes depends on the hazardous waste characteristic of the waste and whether the material can be reused, recycled or reclaimed. The majority of these wastes are disposed of at permitted offsite commercial hazardous and/or industrial waste facilities.

Wastes From Petroleum Refineries

The refining sector generates the predominant share of hazardous wastes in the petroleum industry. The waste streams associated with refining and the major source categories from which they originate are depicted in Figure 1. Of these waste streams, EPA has identified five as listed hazardous wastes. These wastes include dissolved air flotation (DAF) float (K048), slop oil emulsion solids (K049), heat exchanger bundle cleaning solids (K050), API separator sludge (K051) and leaded gasoline tank bottoms (K052).[7]

On November 12, 1980, EPA proposed a change to the K048 listing from DAF float to secondary (emulsified) oil/solids/water separator sludge and a change to the K051 listing from API separator sludge to primary oil/solids/water separation sludge.[8] The U.S. EPA reopened the proposal on February 11, 1985 for further comments; however, the K048 and K051 listings remain unchanged.[9] Currently, EPA is revisiting its proposal. On April 13, 1988, a notice of data availability and request for comments was published by EPA after receiving additional data from API.[10]

The basis for listing these five wastes centers on two metal constituents, lead and hexavalent chromium.[11] The lead mostly comes from the use of tetraethyl lead as an octane booster in gasoline. Hexavalent chromium finds its way into these wastes in the blowdown from cooling towers that use hexavalant chromium compounds as a corrosion inhibitor.

The most current (1981) industry-wide estimates of listed hazardous waste disposal rates, adjusted for temporary storage, are given in Table I. In this same API survey, projected disposal-rate estimates of non-listed wastes were also made. These are given in Table II. Even though the wastes in Table II are not listed hazardous wastes, the survey testing summary of these wastes revealed all of them failed one or more of the hazardous waste characteristics (i.e., EP toxicity, ignitability, reactivity [sulfide] and corrosivity).

Waste Treatment and Disposal. Most refineries use decanting through gravity separation to treat their oily listed hazardous waste including DAF float, slop oil emulsion solids and API separator sludge. Slop oil emulsion solids are normally heat treated prior to decanting. Leaded tank bottoms are usually allowed to weather to oxidize the tetra-ethyl lead prior to disposal at an off-site commercial landfill. Heat exchanger bundle cleaning solids are commonly routed from a concrete cleaning pad in the process area to the refinery wastewater treatment system. When conducted in accordance with 40 CFR 261.3(a)(2)(iv)(c), this practice is exempt from hazardous waste regulations as long as the waste stream is a mixture of the refinery's wastewater, which is subject to regulation under either Section 402 or 307(b) of the Clean Water Act.

The most common "disposal" practice for most listed hazardous wastes in the API survey, previously mentioned, is land treatment or "landfarming" as it is commonly referred to in the industry. Even though by definition (40 CFR 261.10 and 268.2) land treatment is considered "land disposal," the technique uses biodegradation and immobilization to completely treat waste constituents. Many refineries pretreat their waste prior to landfarming to recover hydrocarbons for further processing. Listed wastes which are usually landfarmed include API separator sludge, DAF float and slop oil emulsion solids.

Other than minimal decanting, the non-listed wastes are not generally treated prior to disposal. For those refineries that do treat these wastes prior to disposal the methods include chemical, thermal and biological methods, weathering, thickening, centrifuging,

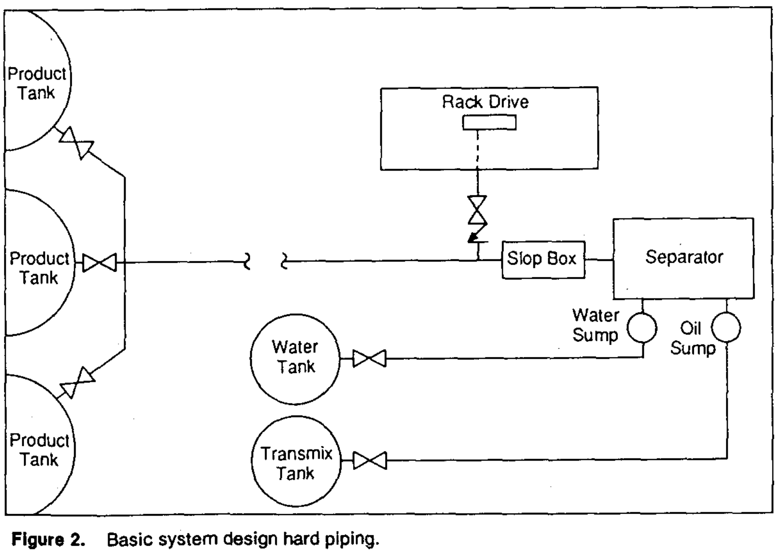

Figure 2. Basic system design hard piping.

and filtering. According to the API survey[12] most of the non-listed wastes are either landfarmed or landfilled at off-site commercial facilities. Other disposal methods used include deep well injection, metals reclamation, recycling into petroleum cokers and the use of nonhazardous sludges as road oil.

Wastes From Transportation Facilities

The transportation sector of the petroleum industry generates the following waste streams which on occasion exhibit one or more hazardous waste characteristics. These wastes include tank bottom sludge and water from crude oil and product (i.e., leaded and unleaded gasolines, jet fuels and diesel) storage tanks, oil/water separator sludge and solvent degreasers. Data on nationwide volumes associated with these waste streams are not available.

Waste Treatment and Disposal. Tank bottom sludge is normally generated when a crude oil or product storage terminal undergoes a tank clean out and maintenance program. Separator sludge is normally removed by vacuum truck and handled in much the same manner as tank bottom sludge. The sludge is usually disposed of at a commercial or company-owned landfarm, drummed and sent to a commercial landfill depending upon the sludge's hazardous characteristic, and/or it is treated using a filter press or centrifuge. The filter press and centrifuge are usually mobile units which come on site and are used to dewater the sludge and in the process recover oil or product which is recycled. The filter cake or centrifuged solids are drummed and sent to a landfill while the water is treated at a commercial, public, or company-owned wastewater treatment plant or it is placed in on-site evaporation tanks.

To a great extent tank water draws are discharged to the secondary containment area around a tank's perimeter where it is allowed to evaporate and percolate into the ground. Under the Waste Minimization Projects, a description of a unique system for handling tank water draws used by Conoco Pipe Line Company is provided.

Solvent degreasers are a relatively low-volume waste stream generated as a result of parts and equipment cleaning. Many terminal operators have gone to a system where the solvent supplier retains ownership of the solvent. The solvent is in a container which is replaced by the supplier on a periodic basis. The solvent supplier exchanges solvent containers and returns to his facility to reclaim the spent solvent. This system has proven to be an effective means by which the terminal operator effectively manages his or her spent solvent.

Other methods for disposing spent solvent have included injecting it into a crude stream pipeline going to a company-owned refinery, mixing it with fuel for industrial boilers and furnaces and disposing of it at a commercial hazardous waste disposal facilities.

Used oil from routine oil changes is also generated at truck terminals. Used oil is normally placed in the truck's diesel tanks or arrangements are made with a recycler or re-refiner.

Wastes From Retail Marketing Facilities

Marketing facilities in the petroleum industry generate several waste streams which may occasionally exhibit one or more hazardous waste characteristics. These wastes include tank bottom sludge and water, separator sludge, contaminated and off-specification product, used oil and other lubricants, used batteries, used tires, spent antifreeze, solvent degreasers, used drums and used clay filtration elements. Accurate data on nationwide volumes of these wastes are not available.

Waste Treatment and Disposal. The only treatment that is normally found at a marketing facility is an oil/water separator which is used in conjunction with the facility's drainage system. Tank bottom sludge and water is usually encountered when tanks are cleaned, which is very rarely, and when tanks are replaced. Depending upon its hazardous characteristic, tank bottom sludge and separator sludge are drummed and sent to a commercial industrial or hazardous waste landfill. If the rinse water tests nonhazardous it is allowed to drain to the sanitary sewer following approval from the local municipality. If hazardous, the rinse water is disposed of at a commercial hazardous waste facility.

Used oil and other lubricants are handled by recyclers or re-refiners under contractual arrangements. Contaminated and off-specification product is often reworked back into the manufacturing process. Used batteries are normally sent to regenerators under contractual arrangements. Used tires are sent to a shredder, if available, for blending into asphalt or, for the most part, they are disposed of at the nearest municipal landfill. Spent solvents from parts cleaning are handled in much the same manner as discussed above. Spent antifreeze is often reclaimed for its glycol content. Also, it is usually acceptable to dispose of spent antifreeze in municipal sanitary sewers. If empty used drums can be reused they are sent to a drum reconditioner, otherwise they are crushed and sent to a municipal landfill. Used clay filters and other filters are allowed to drain to recover the product and then discarded at a municipal landfill.

Waste Minimization Commitment

The petroleum industry is strongly committed to voluntary rather than mandatory waste minimization programs. The 1984 RCRA amendments required the implementation of voluntary waste minimization programs. In many respects, the petroleum industry had already initiated practices and process modifications to avoid the generation of wastes, examples of which are described below.

Congress has begun to review legislative proposals dealing with waste reduction in conjunction with this year's RCRA reauthorization initiatives. EPA believes further statutory authority in this area is premature at this time. To support EPA's contention, the petroleum industry has undertaken the task of developing its waste minimization story.

Public interest groups that are advocating more regulation (e.g., mandatory waste minimization programs) presume certain regulatory incentives will spark industry to eliminate the majority of its wastes through source reduction (i.e., process modification, product reformulation, new product design, input substitution and improved management practices) and on-site recycling. The only problem with this presumption is that it fails to take into account the extractive nature of the petroleum industry. This extractive nature makes it inherently difficult to reduce the generation of wastes.

As a part of the petroleum industry's experiences, it is extremely important that Congress, EPA, and public interest groups become aware of the industry's progress in waste minimization. Coupled with this progress, these same groups need to understand the obstacles encountered by the petroleum industry in reducing the volumes of waste it generates.

These obstacles are given here as explanations rather than excuses as to why the petroleum industry's waste minimization/reduction programs will not realize significant reductions in waste volumes. It is for these reasons the industry's programs emphasize recycle and reuse practices in addition to source reduction and innovative treatment technologies.

Most source reduction methods are often unique to specific products or production processes. Even so, these methods can be grouped into four major categories as was done is S.1429, the Hazardous Waste Reduction Act (1987). These categories included:

- Substitution of raw materials;
- Reformulation or redesign of products;
- Equipment, technology, process, or procedure modifications; and
- Improvement in management, training, inventory control, materials handling, or other general operational phases of industrial facilities.

With the exception of the last category, the extractive nature of the petroleum industry raises significant obstacles, some of which are impossible to overcome, to make significant reductions. These categories are characterized below in a petroleum industry context.

Raw Material Substitution

The petroleum industry has no control over the basic composition of crude oil which is determined by geological forces. The production sector of the business is faced with having to separate water produced with the crude oil which typically increases as the well matures. This waste generation is being further compounded because older domestic oilfields are not being replaced by younger fields as rapidly as in the past. Much of the oily wastes generated during refining occur as a result of the inherent lack of control over the basic nature of feedstock crude oil, the increased use of heavier crude streams with lower gravities, and the associated removal of naturally occurring contaminants in the crude oil. Other wastes, such as filter media and spent caustics, are generated as a result of removing sulfur and nitrogen contaminants present in crude oil. In addition, the quality of crude oil feedstocks is lower now than in past years, which translates into higher amounts of sulfur and nitrogen compounds and other impurities. These crudes require additional processing. Hence, greater amounts of wastes will be generated.

Product Reformulation or Redesign

The products of the petroleum industry are fixed by their very nature. Crude oil is the product of the production sector which is extracted from oil-bearing formations and separated from produced water. Fuels, lubricants, asphalts and petrochemicals make up the majority of refinery products. Although the amount of each product processed from a barrel of oil can be highly controlled, the fixed nature of these products cannot be controlled. Some fuels are so chemically simple, such as propane and butane, their composition cannot be changed. Further, these products must meet stringent product and regulatory specifications such as limits on sulfur, nitrogen, solids, and specific ranges of octane, boiling point, vapor pressure, and viscosity. With these restrictions and the general range of petroleum product composition, the refining sector is left with limited flexibility in product redesign or reformulation.

Process Modifications

The nature of the petroleum industry's products is such that they are small in number but high in volume. The products are produced on a very low value-added basis and have commercial lifetimes measured in decades. These factors results in very large and capital intensive process equipment dedicated to achieve maximum efficiency. This proccss equipment is designed with expected lifetimes of years or decades. These products and process time scales make it extremely difficult to introduce process modifications which could achieve source reduction. Indeed, industry experience has shown that modifying process units does not lead to reduction in volumes of wastes generated. There are insufficient economic incentives for the refining sector to launch massive capital intensive process modification or replacement of existing equipment projects to achieve marginal reductions in the amount of wastes generated. In addition, because the marginal profitability of petroleum products is relatively low and to a large extent controlled by international competition, companies may be unable to pass the cost of a major process change on to the consumer.

Management Practices

Improving management practices, inventory control, materials handling, training and employee awareness is one area the industry has no particular obstacles to overcome. However, the potential level of further waste reduction attributable to these practices is relatively small. Considerable effort has already been expended by the industry toward improving these practices to husband product losses.

In summary, while source reduction is an integral component of overall waste minimization and management strategies, the opportunities available to the petroleum industry are not as great as in most other industries. Therefore, the key elements of the petroleum industry's waste minimization and management strategy focus on recycling/reuse and treatment.

Waste Minimization Projects

At the national level the API, the National Petroleum Refiners Association (NPRA) and the Petroleum Environmental Research Forum (PERF) are aggressively promoting a variety of waste minimization projects. To a great extent these organizations through specific committees are tasked with raising the level of awareness concerning waste minimization within the petroleum industry with industry representatives and government officials at the federal, state and congressional level.

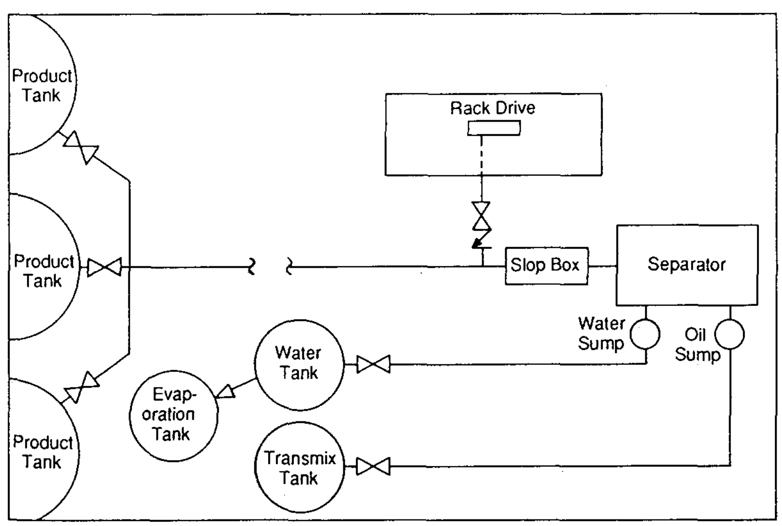

Figure 3. Basic system design hard piping with evaporation.

On February 25, 1987, the API and the NPRA conducted a workshop with the purpose of informing their memberships of the statutory and economic incentives for waste minimization and to provide information on opportunities and approaches for waste minimization.[13] On March 23 and 24, 1988, PERF convened the Refinery Waste Minimization Conference with the purpose of covering the overall role of waste minimization in refining, source reduction opportunities and various recycling approaches.

In addition, the API is documenting the scope and degree of success the petroleum industry is achieving in waste minimization. Under this effort a data base of petroleum industry generated wastes is being developed for the refining and marketing sectors. A compendium of waste minimization practices and equipment now used in the petroleum industry is also being prepared. Finally, API is establishing contacts with other organizations, such as the Chemical Manufacturers Association, National Governors Association, National Association of Manufacturers, Business Roundtable, etc., to further communicate the positions and practices of industries involved with this issue and increase overall awareness.

At the individual company level a variety of efforts are underway. These efforts include:

- Establishing corporate policy and goals for waste minimization,
- Conducting waste minimization audits,
- Developing company-wide waste data bases on quantities of wastes generated,
- Identifying various waste minimization techniques presently being used,
- Identifying opportunities for implementing techniques or practices,
- Conductng employee awareness sessions at the operator level,
- Establishing employee incentive compensation programs (bonuses) for waste minimization suggestions which are implemented, and
- Funding research projects which may lead to effective recycling endeavors.

Following is an overview of waste minimization projects in the petroleum industry which have proven to be successful. Some states' rules and/or states' interpretation of U.S. EPA regulations may preclude the use of some of the following waste minimization projects.

Exploration and Production Projects

The industry's offshore operations are primarily faced with disposing of paint and spent solvent wastes and used nickel/cadmium batteries. Under contractual arrangements the spent solvent is sent to a solvent reclaiming company. Rather than having to land dispose batteries, many operators are switching to lead acid batteries which are sent to battery regenerators when they no longer can be used. Onshore painting projects are not on the order of magnitude of painting offshore platforms; therefore, onshore operators normally use contractors who contractually agree to be responsible for their paint wastes.

Used lubricants, hydraulic fluids and motor oils generated offshore are collected and sent to a company's shorebase where they are stored prior to transporting to a recycler. Onshore facilities usually put these used oils in their field crude oil tanks where the used oil ultimately makes its way to a refinery for processing via the crude stream.

Other practices which have been implemented and proven to be successful include using smaller reserve pits and produced water pits, recycling drilling muds in closed systems, segregating muds for disposal as nonhazardous waste prior to entering a hydrocarbon zone, and solifying wastes in reserve pits.[13]

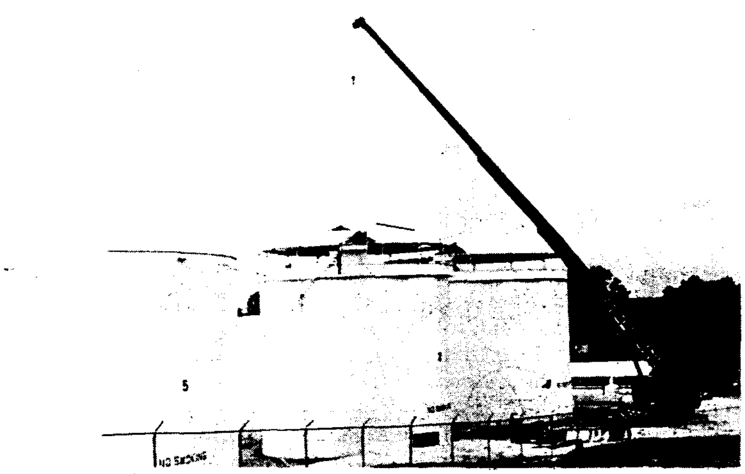

Figure 4. Geodesic dome for external floating roof storage tank.

Refining Projects

In general, the opportunities for waste reduction in the refining area currently reside in changing operator habits and practices rather than in process modifications as discussed earlier. Indeed, the most promising area refiners are working on is waste segregation. Most refinery hazardous waste comes from oily sludges found in combined process/storm sewers. Steps are being taken at many refineries to prevent the mixing of relatively clean rainwater runoff with oily wastes. Where it is feasible, separate stormwater and process wastewater sewers are being installed.

Refineries that have a coker can enjoy the petroleum coke exemption under 40 CFR 261.6(a)(3)(ix). This exemption allows for refinery hazardous wastes that contain oil to be used as feedstock to a coker as long as the wastes are generated at the same facility at which the coker is located and the resulting coke does not exhibit a hazardous characteristic. The oily wastes that a coker can normally receive includes DAF float (K048), slop oil emulsion solids (K049), API separator sludge (K051), tank bottom sludge and bio-sludge. The process modification is relatively inexpensive and is currently used in the industry by Mobil. The process has been shown to be extremely effective for recycling the above listed and non-listed hazardous wastes.

In the area of product substitution, major efforts are under way to reduce and eventually eliminate the use of lead in gasoline as an octane enhancer. To accomplish this federally mandated lead phase-down, refineries are installing technology process modifications such as reformers and alkylation units, along with using other octane enhancers, such as methyl-tertiary-butyl-ether (MTBE). Although more acid wastes are expected to be produced from the alkylation unit; offsetting this increase is the elimination of wastes due to tetra-ethyl lead production, leaded gasoline storage tank sludge

(K052) and the emission of lead into the environment by way of combustion.[14]

Phosphate-based corrosion inhibitors are being substituted for chromate-based ones used in cooling water systems at refineries. This substitution eliminates the source of the hazardous characteristic (i.e., EP toxicity for chromium) often found in refinery wastewater treatment sludges. On March 29, 1988, EPA began the rulemaking process to prohibit the use of hexavalent chromium-based water treatment chemicals in comfort cooling towers.[15] In the preamble of this proposed rule, EPA states that it is continuing its evaluation of the need for listing chromium (hexavalent or total) as a hazardous air pollutant and for subsequent national emission standards for hazardous air pollutants for industrial cooling towers. Regulatory initiatives like this will likely lead to eliminating the use of hexavalent chromium-based chemicals in industrial process cooling towers.

Sulfidic and phenolic caustics from the refining industry are being used as effective substitutes for other commercially available chemicals. Companies use these caustics as feedstocks for the production of new chemical products. No regeneration, reclamation or materials extraction takes place in the production process nor are any of the materials land disposed or burned. When a refinery has to dispose of these caustics they usually fail one or more of the hazardous characteristics resulting in having to handle the material as hazardous wastes. Depending upon the strength of the caustics, refineries have found this to be an effective use of a material that otherwise would be a hazardous waste if disposed of.

A high volume refinery waste that shows promise as an effective substitute for other commercially available chemicals is spent catalyst, in particular, cat poly catalyst used in a refinery's catalytic polymerization unit. In its dry state this spent catalyst is not a hazardous waste; however, when it becomes wet the material will fail the corrosive hazardous characteristic. One of Conoco's refineries is currently using its cat poly catalyst as a pozzolan material in the manufacture of concrete. The concrete made at this refinery has exceeded Conoco's standards for strength; however, it is not used for structural support. It is used for on-site roadbase, utility/storage pads and non-loadbearing walls. FCC equilibrium catalyst also exhibits possibilities as an effective alumina source and admixture in the cement manufacturing industry.

Another use of cat poly catalyst is being researched by a university under a project funded by Conoco. This project involves the use of cat poly catalyst as a source of phosphorous fertilizer for agronomic crops. The catalyst is being compared to the use of a commercially available triple superphosphate fertilizer (0-46-0). Initial results reveal there is no significant difference in straw and grain yields between the two phosphorous sources. Nutrient uptake data reveal only small differences between the two sources; however, they were of no agronomic or environmental consequence.

The API has experimentally evaluated a number of technologies for the treatment of listed petroleum refinery oily wastes. The technologies studied were mechanical treatment (filtration), solvent extraction, thermal treatment (drying), and pyrolysis. In several cases the application of two treatment technologies in series was studied (e.g., filtration followed by drying and drying followed by fixation). Four of the technologies tested were effective in producing a residual of substantially reduced hazard level as measured by concentrations of hazardous constituents in the product solids. In addition, chemical fixation further reduces the level of hazardous materials leached from the solids in the toxicity characteristic leaching procedure (TCLP).[16]

Transportation Projects

In the summer of 1980, Continental Pipe Line Company (CPL), now known as Conoco Pipe Line Company, the operator of Conoco's petroleum product storage terminals and pipelines, undertook an extensive investigation of the wastewater generated at their product terminals. The study involved analyzing tank bottom water from 45 tanks around the country. The analyses included traditional wastewater parameters (e.g., BOD_5, COD, pH, etc.) and the four hazardous waste characteristics tests.

The wastewater found at the bottom of product storage tanks enters the tanks from two major sources (i.e., water entrained in pipeline deliveries to the tanks and rainfall entering the tanks around tank roof seals). Results of the analytical phase of the study revealed that the raw tank bottom water sometimes exhibited the ignitability characteristic and the EP toxicity characteristic for lead, arsenic and barium.

Historically, this wastewater was drained from the tanks and discharged into the tank dike area. After careful inspection for free oil, the wastewater was generally discharged from the dike, often in combination with stormwater. This practice was, and still remains, common throughout a large segment of the petroleum industry.

With the passage of RCRA in 1980, CPL discontinued this practice of disposing tank bottom water to the ground. This decision was based on the above-mentioned analytical results. Having made this decision, CPL undertook the design of a tank bottom wastewater handling system along with a procedure for evaluating treatment and ultimate disposal options.

Figure 2 describes the tank bottom wastewater handling system chosen by CPL. Most of these systems have been installed underground. This system has been installed at 35 of 50 terminals at a cost of around $40,000 per terminal. The majority of the systems were installed between 1982 and 1984.

The primary objective of CPL's wastewater handling system is the collection of tank bottom water, its separation and analysis, and its subsequent preparation for disposal. The system consists of five major components: the collection system, the slop box, the separator, the sumps and the collection tank (Figure 2).

As illustrated, the collection system consists of a network of "hard-piped" pipelines which connects the storage tanks to the separator by way of a slop box. In general, the pipelines, separator and slop box are installed with cathodic protection. The wastewater flow is controlled by manual valves which are operated by terminal personnel. Some terminals utilize a portable trailer in lieu of "hard-piping" to transport the waste to the separator.

The collection system also connects run-off waste material from the truck rack loading area. The waste material from this area generally consists of small product spills, water used to wash down the rack and some stormwater.

The function of the slop box is twofold. First, it provides a mechanism by which flow into the separator is equalized. Second, it provides a mechanism by which large solid material that might be entrained in the water will fall out prior to entering the separator.

The oil/water separator is a high efficiency vertical tube coalescing separator. It is designed to remove all free floating hydrocarbon and to lower oil and grease levels to a level which would be acceptable at most publicly owned treatment works (POTW). The separator has two discharge streams—the wastewater effluent, and the separated petroleum product. These streams are subsequently collected in the water and product sumps.

The water and product sumps are constructed of steel and are generally in the range of 5–10 barrels capacity each. In general, the sumps are installed with cathodic protection. Their purpose is to collect and temporarily store the separated water and petroleum product. A small pump, installed on each sump, is used to pump the petroleum product back to a petroleum storage tank and the water to the wastewater collection tank. The wastewater collection tank is a steel tank that is normally in the 250–500 barrel capacity range. The tank, like the piping and sumps upstream of it, is installed with cathodic protection to eliminate corrosion.

Once the wastewater reaches the collection tank, it is tested for hazardous waste characteristics. The ignitability characteristic is removed by the above mentioned high efficiency coalescing oil/water separator. Analytical results of this wastewater reveal that less than five percent of the samples exceed the EP toxicity limits for lead and/or arsenic. When this occurs the wastewater is disposed of at a hazardous waste disposal facility. Otherwise, the wastewater is disposed of in a manner consistent with applicable wastewater disposal regulations (e.g., evaporation systems, local POTW, hauled to a Conoco refinery's wastewater treatment plant, etc.)

Where evaporation is used the additional equipment which has been installed is an open tank (Figure 3). As a result of the combined action of the sun and wind, in an arid climate, evaporation occurs resulting in a disposal method requiring minimal operating expense. Emissions to the air are insignificant from these open tanks. CPL has installed this system at several of its Rocky Mountain District terminals.

As these wastewater handling operations matured, CPL began to focus on reducing the amount of wastewater being generated at the terminal. A major source of terminal wastewater is tank bottom water that is generated when rainwater leaks around the seals on external floating roof storage tanks. To alleviate this source of wastewater, geodesic domes were considered. A geodesic dome is a type of vaulted fixed roof with a framework of straight-sided polygons (Figure 4). Geodesic domes can prevent virtually 100 percent of the rainfall from entering a tank. CPL has installed 15 geodesic domes throughout its terminal systems to date. A significant reduction in the volume of water generated from these tanks has been experienced. Savings generated by geodesic dome installations typically produce an internal rate of return in the 25–30 percent range. Geodesic domes also reduce evaporative emissions to the air.

CPL has also experimented with modification of truck loading racks at terminals to seek reduction in another contributing source of terminal wastewater: truck rack run-off. Many CPL terminals have installed one or a combination of the following modifications: (1) curbing around the truck rack, (2) larger canopies around the truck rack, or (3) extensions on the sides and back of existing canopies. These modifications prevent excess rainfall from being routed over oily areas and into the collection system. Experience has shown a 50 percent reduction in total wastewater from implementation of these modifications at some terminals.

CPL has also shown innovative and aggressive waste reduction alternatives for disposal of tank bottom sludge. Emphasis has been placed on more environmentally desirable alternatives to disposal, such as recycling. A contractual agreement was entered into with a tank bottom recycling service company to utilize their filter press operation for recycling CPL tank bottom waste. The press operation filters out usable product, and produces a nonhazardous solid cake suitable for disposal in a municipal landfill.

Spent solvent from degreasers used for cleaning parts and equipment is handled under contractual arrangements with the solvent supplier. On a periodic basis the supplier replaces the used solvent with a container of fresh solvent. The spent solvent is then reclaimed at the suppliers facility.

Marketing Projects

Waste segregation is an important strategy for waste minimization at retail outlets. By having an effective segregation program, the value of the materials generated can be preserved via recycling or reclaiming. These types of projects are being implemented at most full-service retail outlets.

Over the past several years, Conoco has undertaken an aggressive program to replace underground gasoline and diesel storage tanks at its retail outlets to limit the chances of product leaks reaching groundwater. As of the end of 1987, 864 underground tanks had been replaced. Plans are to replace an additional 81 tanks in 1988, as part of this ongoing effort.

Conclusions

Even though the petroleum industry faces a difficult task in minimizing and reducing waste, the projects described above reveal the industry's long-term commitment to waste minimization through recycling and reusing materials. To remain a competitive force in the world marketplace, the American petroleum industry has gone to great lengths to sustain this commitment.

Other incentives driving this recycle/reuse movement are anchored in meeting self-imposed waste minimization goals, land disposal bans (i.e., "first third"), the cost of commercial disposal, the difficulty in obtaining Part B permits, the lack of storage capacity and the inherent headaches associated with having to deal with hazardous waste.

The attitude of the petroleum industry's process engineers has shifted from the end-of-pipe approach to waste disposal, typical of the 70s and early 80s, to the minimization of waste through recycle/reuse options and, where possible, process modifications. For waste minimization to succeed in any industry, it must begin with a strongly committed management and be implemented fully at the operator level. Indeed, waste minimization in the petroleum industry is well on its way to being a grass roots movement that will succeed.

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Performance Audit Results for Volatile POHC Measurements

during RCRA Trial Burn Tests

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Audit materials containing principal organic hazardous constituents (POHCs) have been developed by EPA for use by federal, state, and local agencies or their contractors to assess the accuracy of measurement methods used during RCRA trial burn tests. Audit materials are currently available for 27 gaseous organics in five, six, seven, and nine-component mixtures at parts-per-billion levels (7 to 10,000 ppb) in compressed gas cylinders in a balance gas of nitrogen. The criteria used for the selection of 27 gaseous organic compounds is described.

Stability studies indicate that all of the organics tested (with the exception of ethylene oxide and propylene oxide below 10 ppb levels) are stable enough to be used as reliable audit materials.

Subsequent to completion of the stability studies, 89 performance audits have been conducted with the audit materials to assess the accuracy of the Volatile Organic Sampling Train (VOST) and bag measurement methods during or prior to RCRA trial burn tests. A summary of the audits conducted for each POHC and the measurement system audited is shown in this paper. The audit results obtained with audit gases during RCRA trial burn tests are generally within ±50 percent of the audit concentrations.

The determination of POHC at trace levels (<50 ppb levels) during hazardous waste trial burn tests requires sophisticated sampling and analysis systems. Agency personnel responsible for trial burn tests need to be concerned about the accuracy of POHC measurements. Accuracy of such measurements may be assessed by conducting a performance audit. A performance audit is a quantitative assessment of the accuracy of a measurement system. For volatile POHC, a performance audit consists of providing an "unknown" or "blind" cylinder gas to the organization being audited. The organization draws a sample from the cylinder gas through (VOST) or into (bag measurement) the POHC Sampling System and analyzes the collected sample. When a performance audit is conducted during or prior to a hazardous waste trial burn test, it provides an assessment of the measurement accuracy and indicates the presence of any bias for the combined sampling and analysis system.

The EPA's Environmental Monitoring Systems Laboratory operates a program to develop organic gas audit materials and provide these audit gases to federal, state and local agencies or their contractors for use in performance audits during hazardous waste trial burn tests. The Research Triangle Institute (RTI), under contract to the EPA, is the principal organization for development of audit gases and coordinating subsequent audits using these gases. Currently five, six, seven, and nine component gas mixtures have been de-

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