Multistep process for waste minimization and material recovery

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Our country is facing a problem of growing proportions: more hazardous wastes and fewer locations to store or treat them. As the number of storage sites diminish, treating the waste or hauling it greater distances to the remaining sites will require large amounts of energy, which in the long-term is a limited and expensive resource.

Disposal management strategy should refocus to look ahead 30 years instead of 30 days. Today's short-term expenditures for disposal are not addressing the deferred costs of cleanup of contaminated land areas and aquifers. The Love Canal case may be all too typical of massive cleanup costs that could have been avoided by treatment at the time the waste was generated.

What is required is a coordinated program that will encourage and reward processes emphasizing volume reduction, product recovery for reuse, and minimum overall energy consumption. Inevitably, society will have to bite the bullet and expect to pay "up front" for waste treatment. The goal now should be to find or develop processes or combinations of processes that will separate out recyclable materials, detoxify waste material, be low in energy consumption, and be capable of handling huge volumes of material.

It is unreasonable to expect any single process to accomplish this task, so the need is for multi-step or cascaded processes. Many treatment processes now available are either too energy intensive and expensive (incineration and solvent extraction), or too slow to handle the volumes generated (land farming and filtration). In addition, land farming and incineration processes are both faced with emission problems. It is estimated, for example, that 20 percent of the hydrocarbons in a land farm might be emitted into the air.

Other new processes under development such as high-temperature fluid wall, plasma arc and super critical fluids (see *Pollution Engineering*, Dec. 1986, pg. 37) are cost and energy-intensive and tend to be specific for certain product streams. While this may be useful and cost justifiable in some cases, large-scale application to less specialized waste streams is not expected to be practical.

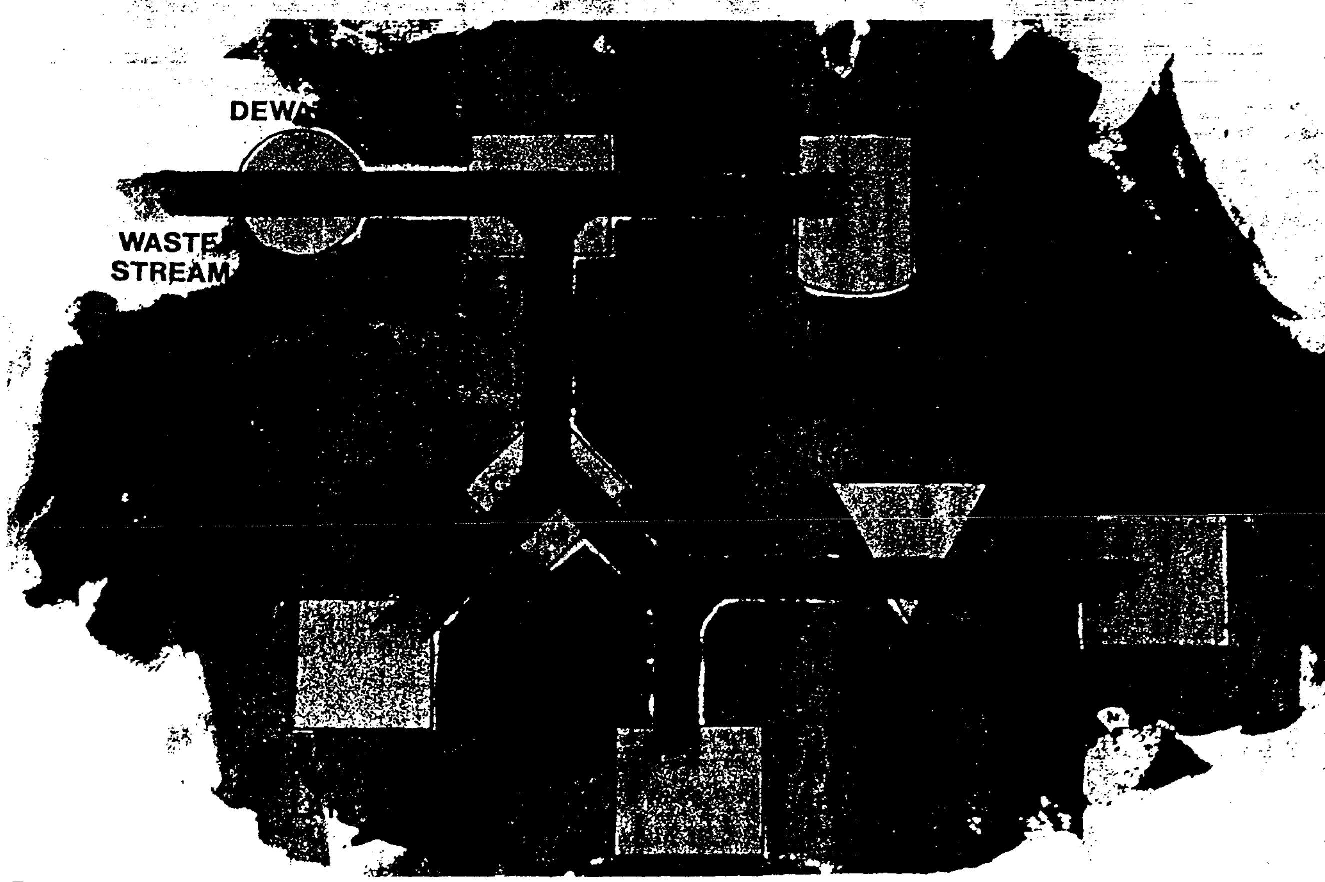

Figure 1. Multistep process for waste minimization.

Multi-step treatments

A multi-step waste treatment process, instead of the current single-step approach, offers an overall improved system of treating waste streams and results in much smaller waste volumes for disposal. While the present cost of this approach may be higher than current lowest cost disposal methods, the *total cost* of proper long-term treatment/detoxification of the same material at a Superfund site is surely well in excess of the cost of properly treating the material at the source as it is generated.

For instance, consider the treatment of heavy-end refinery wastes which contain wide range molecular weight hydrocarbons, water, and solids consisting of dirt, clays, rust and heavy metals. If we take 1000 tons of that waste, the current low-cost landfill is a poor investment toward the deferred and much higher cost of cleaning up that site later. The energy costs of incinerating the wet solids will be prohibitive in the long run, and doesn't take into account the loss of the valuable recyclable material. The scheme in Figure 1 shows a proposed multi-step treatment of oil refining wastes.

De-watering by centrifuging or filtering can reduce the volume considerably—to about 400 tons. The remaining hydrocarbon-saturated solids can then go through a separation process to return the hydrocarbons, (200-300 tons) back to the refinery as burner fuel or for reprocessing. This recycle component will help defray the costs, particularly as oil prices increase. The remaining solids (100-200 tons), if low enough in hydrocarbons, can be used as building material or taken to clean landfill.

If the material is such that the separation is incomplete, and the solids still contain significant amounts of hydrocarbons, these costs will be driven up as final treatment is considered—either incineration, land farm or as a last resort, disposal in a toxic waste dump. In any case, the overall volume has been reduced tenfold and the actual hydrocarbons reduced even more. If incineration does follow, this would mean less wasted hydrocarbon resources and fewer combustion products released to the atmosphere.

For land farms, the reduction of organic matter would ease the burden in the soil and allow a much smaller acreage to service a given refinery. Spreading materials of 30 percent hydrocarbons would eventually overwhelm a land farm that can only function at levels of up to about 20 percent average hydrocarbon loading. Spreading solids with 1 percent hydrocarbon could keep the farm functioning indefinitely. In the case of toxic waste disposal, the volume may be low enough to allow encapsulation.

New technology

The most difficult step in the multi-step disposal system is the separation of hydrocarbons from solids. New technology is needed. If possible, the process should be able to handle a wide range of materials. There are many different chemicals saturating a variety of solids such as catalysts and filter clays.

New processes must be conscious of the energy required as long-term supplies will be short and prices will be high. The emergence of a new industry such as waste treatment with high energy needs could shift a precariously balanced energy industry back into tight supply.

One new patented process for the separation of solids from water insoluble hydrocarbons results in recovery of 85 to better than 99 percent of the hydrocarbons (depending on the nature of the feed stream), and in some cases renders the solid portion of the stream reusable. The process is based on low-temperature aqueous chemical solutions that effect release (displacement) of hydrocarbons from solids followed by a three-phase separation. The hydrocarbon material can be skimmed off the top for recycle or for burner fuel depending on the purity and value of the recovered material. The releasing reagent is recycled in the process.

The concentrated solids in the lower phase are filtered out of the releasing reagent. Depending on the effectiveness of the release process and the type of material being separated, the solids can be dried and reused, or used as clean fill or for composite building material such as concrete. If the solids are still contaminated, economics will dictate whether a second release treatment is justified or whether land farm or incineration would be best. For both the latter cases, volume reduction is the important feature.

The releasing solution process has been shown to be appropriate for the industrial wastes shown in Table 1. The fluid catalytic cracker (FCC) fines and additive filter cakes have been treated successfully on a pilot plant scale. The others, as well as an oil-soil material from a hazardous dump site, have been treated successfully in the laboratory.

Catalytic cracker fines

Of the 15 million barrels/day of petroleum processed in U.S. refineries, five million barrels of residual stocks are cracked in FCC units. In the process a bed of fine inorganic catalyst is fluidized by a flow of heavy crude oil fractions which pass through the bed at temperatures approaching 1000 F.

As the gaseous hydrocarbons pass through the catalyst, fine catalyst particles (fines) are entrained in the gas and carried out of the catalyst bed into the effluent stream. The effluent gases pass through cyclone separators which knock down and recycle the larger particles. Particle sizes under 20 microns escape, however, and pass over with the cracked fractions into a distillation unit where the products are distilled. The bottoms from this distillation column is called a "slurry oil" and the fine catalyst particles accumulate in this fraction.

Most refineries send this material to large tanks where it is allowed to settle. Every three to five years the tank is removed from service and the oil is withdrawn from the top, leaving a residue of 3000 to 8000 tons of slurry oil/FCC fines mixtures.

The catalyst fines contain toxic metals such as nickel and vanadium, but they exist in solid solutions in the catalyst and cannot be eluted with water or acids. Thus, when free of hydrocarbon, the solids can be disposed of in landfill or used in concrete production at little or no cost to the refinery. The slurry oil is a heavy, black oil normally used as residual fuel for utility plants or bunker fuel for use on ships.

Table 1. Refinery Industry Waste Disposal Market

Material	Tons/yr
Refinery Fluid Catalyst Cracker Fines/ Slurry Oil	130,000
Attapulgus Clay/Jet Fuel Mixtures	12,000
API Separator Sludge	393,000
Bottoms from Tank Cleaning	122,000
Lubricating Oil Additive Filter Cake	50,000
Total	707,000

Oil recovered in the process, as shown in Figure 2, can be recycled back into the plant. The recovered fines, damp with water, can be disposed of much more readily than the original mixture. They are still hazardous, but the oil content has been reduced by at least 90 percent and the material does not have to be solidified. This result produces significant savings to the refiner because of the reduced disposal tonnage, in addition to the recovered value of the oil.

Lubricating oil manufacturing

Another application for the process is in the production of lubricating oil additives. A final filtering removes solid particles from the reaction mixture to produce a clear liquid. Filter material is diatomaceous earth, commonly called filter aid. The process produces a waste filter cake which contains about equal parts of lubricating oil additives and waste filter aid.

Some manufacturers wash the cake with a lubricating oil diluent to remove some of the additive. This procedure is relatively ineffective and rarely reduces the concentration of additive on the cake below 35 to 40 percent. Present disposal methods for the cake are burial or incineration.

Some additives are manufactured in a light solvent, and some companies have begun using centrifuges to remove the insolubles prior to filtration. The Claypro process recovers essentially all of the oil and additive from these waste centrifuge streams at a substantial savings to the additive manufacturer.

Hazardous waste site cleanup

This potential market for recovery and reuse dwarfs all others in size. The EPA has identified 850 sites requiring cleanup, and the eventual cost may reach over $8 billion over the next five years. Each site will have different soil types and likely will have different organic contamination. This material variability will pose the toughest technical separation challenges of all those described. But preliminary studies using the aqueous releasing solution technique have been encouraging.

Alternatives and incentives

As regulations curtail the easy, low-cost methods of waste disposal, it is up to industry to develop efficient alternatives to land fill. A stimulus to this effort should be government encouragement through tax incentives for companies reducing waste at the source. Also, direct sponsorship or tax-related support of research on new methods for treating hazardous waste streams is essential to attract private sector investment into companies working on new and innovative processes.

Concern about the cost of such programs should be offset by the reality of the expense of retroactive clean up programs such as Superfund. With economic incentives from government, and by concentrating on waste management and resource recovery processes, we can go a long way toward solving our disposal problems. **PE**

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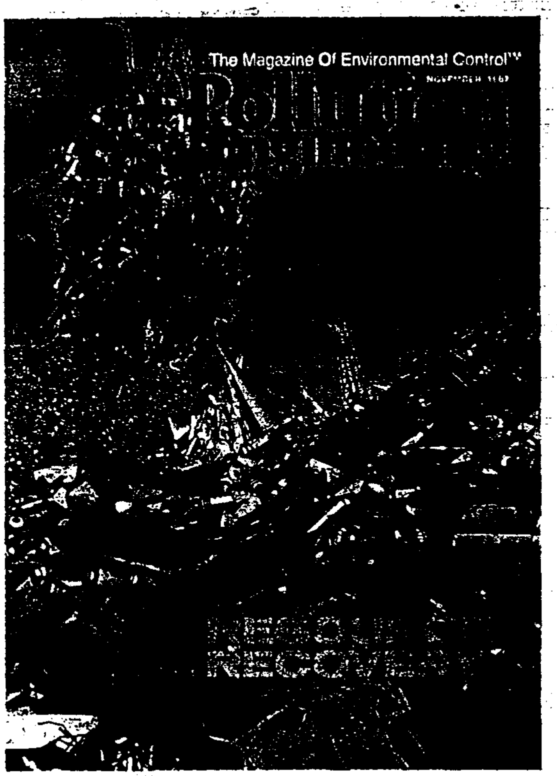

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CONTENTS

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