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CHAPTER 15

Ground Water Recovery and Treatment

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PERSPECTIVE OF GROUND WATER RECOVERY AND TREATMENT

Until the environmental revolution, the only ground water that was routinely treated to remove contamination was the impacted ground water that was extracted for beneficial use. With the recognition that contamination could cumulatively impact drinking water wellfields or entire areas and basins, there was an incentive to remediate ground water not yet extracted for use. Although it is now recognized that impacted ground water can be treated *in situ* or *ex situ*, at the time it was logical to extract impacted water, using wells similar to potable water wells, and treat and/or dispose of that water into surface waters. The underlying strategy was based on the concept that by removing the impacted water, you would gradually remove the underground contamination. Consequently, the first ground water remediation systems were generally extraction and *ex situ* treatment or simple discharge to surface water. This process is called pump-and-treat (Liu, 1997). As experience with these pump-and-treat systems accumulated, it became apparent that for many applications these systems were going to operate for a very long time, possibly decades or more, to approach the ground water standards for drinking water in the Safe Drinking Water Act regulations. In addition, it soon became clear that the rules of solubility still applied, and contaminant mass removed per mass of water diminished over time due, ironically, to the success of the prior removal. This was due in large part to the physics and chemistry of contamination by pure products of low solubility but high toxicity at low concentrations. Extractions became prolonged, not necessarily because the total mass of contaminant to be removed was very high, but because the dissolved mass of contaminants at any time was low. Then as the contaminant mass is lowered by treatment, the dissolved concentrations diminish correspondingly per constant time unit due to the lower equilibrium gradient. In addition, many free-phase or high concentration contaminants had penetrated lower permeability materials driven by gravity and/or high concentrations. Their extraction without a similar extraction driving force, *i.e.*, overcoming the hysteresis effect, meant that after the cleanup goals were apparently reached and the system was shut down, sequestered contaminant concentrations would gradually equilibrate with the recoverable ground water, again increasing the contaminant concentrations (USEPA, 1996).

The next trend was *in situ* ground water treatments that would facilitate destruction or immobilization of the contaminants in place in the ground. This was initially achieved by enhancing the naturally occurring bioremediation, by aerating or oxygenating and adding nutrients to the extracted water that was then reinjected.

Despite problems with all of these pump-and-treat techniques, in many circumstances the pump-and-treat *ex situ* systems are the practical mechanism for ground water treatment (USEPA, 2001a). For MTBE, with its high solubility and low adsorptivity, *ex situ* processes such as pump-and-treat processes appear to offer a rapid mechanism for preferentially removing MTBE from ground water compared to BTEX with its lower solubility and higher adsorptivity.

RELATIONSHIP TO POTABLE WATER

As discussed in the previous section, ground water pump-and-treat systems are closely related to ground water-based drinking water production and treatment systems. Much of the potable water in the U.S. comes from ground water, particularly in small towns and rural areas. In many locations, the shallow or first ground water is the preferred or sole drinking water source. This is often because shallower ground water is economical to reach and recover and because vertical recharge usually provides a local sustainable, renewing mechanism.

Compared to ground water remedial extraction wells, potable water wells are often larger diameter, frequently constructed of more robust and durable materials such as steel, and often deeper in the aquifer to facilitate the common practice of screening across a large vertical interval including more than one transmissive zone. In general concept and construction principles, potable water and remedial extraction wells are much the same. Treatment systems for potable water are where the two systems currently diverge. Typical treatment trains for ground water that is to be used as potable water include very few unit treatment processes. Potable ground water may not be treated at all or may undergo treatment for particulates (filtration, etc.) and possibly microbes (usually chlorination). In some locations there is treatment for natural organics (GAC) and/or nuisance characteristics such as odor, taste, and color (GAC, chlorination, ozonation). In general, the only treatment to reduce health risk is antimicrobial. Most treatments address aesthetic issues with the water. Natural organics are sometimes removed because they might be precursors of halomethanes from chlorination, not because they are toxic contaminants themselves. Under circumstances with significant anthropogenic impacts, treatment can be more extensive including nitrate removal, metals removal (coagulation, precipitation), and more contaminant specific variations of the above treatments.

GROUND WATER RECOVERY

General. Pump-and-treat has been one of the most widely used ground water remediation technologies in the past two decades. Ground water pump-and-treat is a group of technologies, including various ground water extraction methods as well as many aboveground or end of pipe treatment technologies. Figure 15-1 depicts a generalized ground water recovery and treatment system. Pump-and-treat systems remain a necessary component of many ground water remediation efforts, and are appropriate for both plume remediation and containment. Pump-and-treat has been most successful where it has been used to maintain a hydraulic control. In recent years, new *in situ* remediation technologies have emerged and have become more successful with ground water remediation/restoration projects.

Extraction. In general, the methods for extraction of ground water, the pump portion of the pump-and-treat technology, are not linked to or limited by the *ex situ* treatment technologies. Any method that gets the water out can supply the water to virtually any *ex situ* treatment system that can treat the contaminant(s). Because water is the only *in situ* transport medium for pump-and-treat, ground water extraction technologies are specific and optimized for the recovery of only one compound, water. Treatment technologies

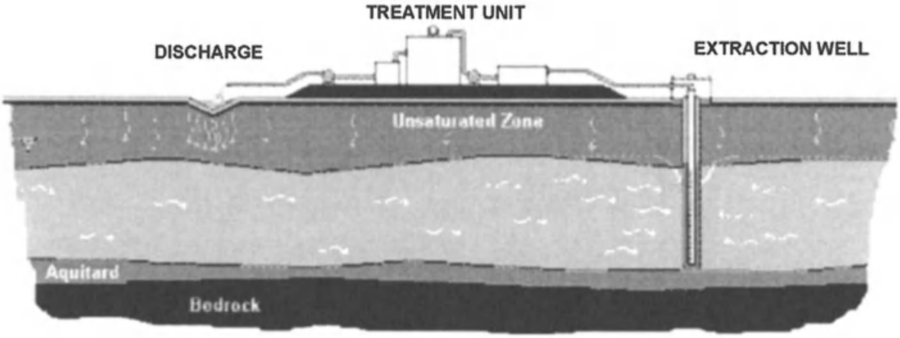

Figure 15-1. **Generalized Pump-and-Treat System**

are specific to the characteristics and concentrations of the contaminant or multiple contaminants of concern, and treatment design is often considered more challenging than design of extraction systems. While this may generally be true, one of the challenges of pump-and-treat is designing an efficient, effective extraction system at locations in intricate geological and hydrogeological locations such as karst or complexly faulted sites.

DESIGN

The real complexity of the pump-and-treat project is more the need to integrate the process from site characterization through design and operations to closure. To do this requires integration of the science (hydrogeology and geochemistry), regulatory analysis (cleanup goals, agreed endpoints), field services (construction and operations), and engineering design in one project team. Although ground water well systems are well understood, the design effort is different from the single drinking water well installation. The pump portion of pump-and-treat at most sites involves multiple wells and/or trenches for extraction and/or injection, often with differential control of extraction rates to optimize operations. Designing the extraction system to optimize contaminant mass or concentration recovery and/or containment can make for a very complex evaluation and design. Consequently, design of extraction still requires the full creative collaboration of the different skills: hydrogeologists, modelers, regulatory analysts, and civil, mechanical, and electrical design engineers.

Design Components. Most pump-and-treat systems involve extracting ground water via recovery wells constructed within the contaminant plume downgradient from the source. These are typically vertical wells, but in the last decade or so have included horizontal wells installed by horizontal boring or by trenching. In addition, simple trench drains with porous backfill media and pumps can be used for ground water recovery in areas where ground water is shallow enough to be economically reached by excavation. Even multi-phase and slurping extraction systems constitute ground water pump-and-treat operations. They just have more elaborate pump systems. Consequently, the components of a pump-and-treat system are:

- Extraction wells or trenches;
- Extraction pumps and controls;
- Collection piping and pumps;
- Collection tank(s);
- Treatment system with associated equipment;
- Post-treatment distribution piping and pumps, if needed;
- Injection/infiltration wells/trenches/fields, if needed; and/or
- Discharge point.

Well Array Design. The extraction wells/trenches, their locations, number, arrangement, and extraction rates, are designed and controlled so they act as a barrier to additional downgradient movement of the plume. Prior to installation of a pump-and-treat system, aquifer tests (slug tests, or preferably pumping tests) are conducted on enough wells or test trenches at the site to gather information on localized aquifer properties across the site. Through these tests, aquifer characteristics are determined and are used to model and/or design the extraction system configuration. Design factors include placement of recovery wells, number and size of wells, compatible well material (typically PVC or stainless steel), well screen placement, sustainable pumping rates, water transport systems, and well completion strategies.

Capture Zone Analysis. Appropriate well placement is designed using capture zone analysis, or fate and transport modeling, and data obtained from initial aquifer pumping tests. Numerous mathematical models are available to perform capture zone analysis and to evaluate recovery/injection system arrays. Capture zone analysis for MTBE is not different from plumes with other gasoline components since the contaminant type is not a factor in determining the well arrays capture zone(s).

Materials of Construction. Materials of construction for wells/trenches and the extraction pumps must be compatible with the contaminants of concerns. For MTBE at normal ground water concentrations, PVC well casings, high density polyethylene (HDPE) trench geotextiles, liners, and/or piping, and the usual gasket materials in ground water pumps are adequate. With MTBE, stainless steel is appropriate for ground water extraction pumps. Electrical and air driven submersible pumps are the two common types of pumps used in ground water recovery systems, and there is no particular reason to select one type over another with MTBE. More important is selection of pump properties as determined by the dimensions of the recovery well, required flow rate, depth to ground water, contaminants of concern, other groundwater chemistries, overall system configurations, and modes of managing and operating the system. For example, pneumatic pumps require careful adjustment initially, to avoid delivering water as well as air, and thus misleading the measuring system. Pneumatic pumps require a source of air that often requires a dedicated compressor station. Unless compressed air is available on site, electrical systems may be simpler at many sites, but may be less dependable than pneumatic pumps. Electrical pumps are inherently less safe and may require transformers to power multiple pumps located across large sites.

Typical Extraction Well Construction. Figure 15-2 depicts a typical recovery well design used in the industry today. The well can be completed below

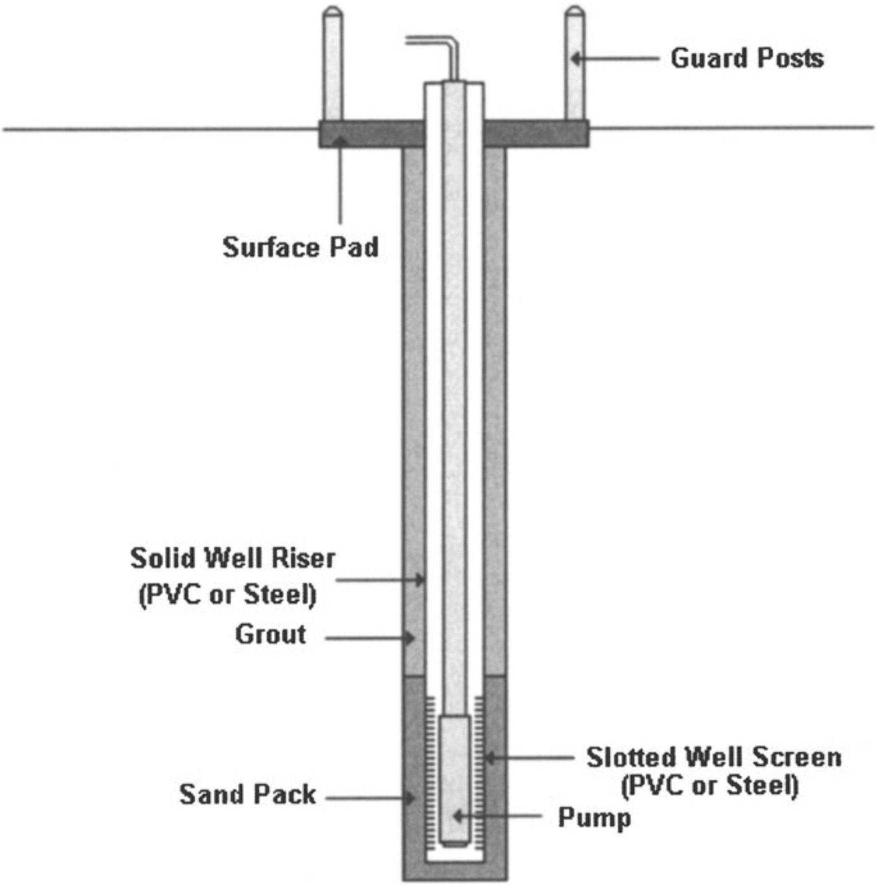

Figure 15-2. **Typical Recovery Well Design**

the ground surface in a vault, with a manhole cover, that houses the pump cables and controllers, valves, flow meter, and related components. The vault provides protection against weather, restricts access, deters vandalism at unmanned locations, and protects the well from vehicular traffic.

Trench Construction. Trenches can be thought of as wide long wells with a geotextile well screen and a porous internal sand/gravel pack. Biopolymer-stabilized trenching techniques are good for installations below the ground water table and particularly for deeper installations. The polymer can be digested (broken) after completion of excavation and installation of piping to restore the higher permeability of the trench base matrix. The MTBE-impacted ground water being transported from the well to the treatment system may be a hazardous waste if it contains other gasoline components. If the RCRA regulations apply to the site, this would require that underground piping be double-walled. Even if not required by regulation, double-walled piping is a good practice to minimize the possibility of a new leak and source. Figure 15-3 illustrates a typical trench extraction or re-infiltration system.

Optimization. Optimizing the recovery of impacted ground water is a dynamic process that uses the response of the ground water remediation system to improve the extraction and thus overall remediation efficiency. Optimization can be achieved by phased construction, by adaptive management of the well pumping rates, by periodic modeling of the initial and supplemented well arrays, and by pulsed pumping. These optimization practices work for MTBE just as with any contaminant.

Phased construction of extraction wells allows data from the response of the aquifer to pumping operations to be used in determining the location or in-filling of subsequent wells to address areas of poor recovery, high contaminant concentrations, or hydrogeological heterogeneities.

Adaptive pumping involves designing the wellfield with sufficient flexibility so that extraction and injection can be varied to reduce zones of stagnation. Extraction wells can be periodically shut off, others turned on, and pumping rates varied to ensure that contaminant plumes are remediated at the fastest rate possible.

Pulsed pumping has the potential to increase the ratio of contaminant

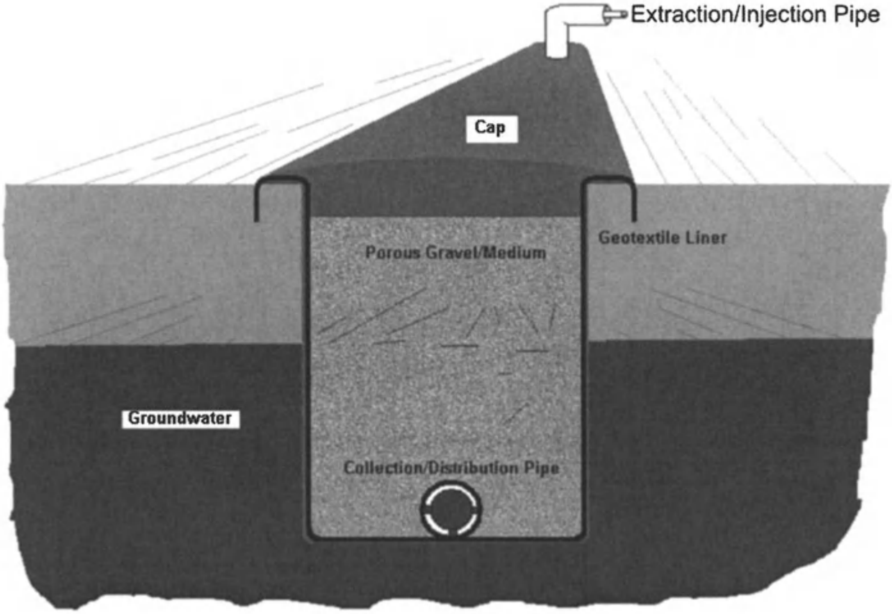

Figure 15-3. **Simple Trench Extraction/Reinfiltration System**

mass removed to ground water volumes removed where mass transfer limitations restrict dissolved contaminant concentrations during continuous pumping. During the resting phase of pulsed pumping, contaminant concentrations increase toward equilibrium due to diffusion, desorption, and dissolution from soils or free-phase materials into the ground water. Once pumping is resumed, ground water with higher concentrations of contaminants is removed. There is a practical limitation to the benefits available through pulsed pumping. As the water approaches equilibrium in dissolution, the rate of further dissolution declines, producing a diminishing return in contaminant mass for time.

The phenomena of tailing and rebound are commonly observed during pump-and-treat. Tailing is the progressive decline in dissolved contaminant concentration with continued operation of a pump-and-treat system. Tailing is primarily a product of the contaminant equilibria between water and soil and/or phase-separated contaminants. As the remediation reduces the concentration of contaminants adsorbed on the soils or in the free-phase, there is a proportionally lower concentration of contaminants in the ground water. Rebound is an increase in contaminant concentration after pumping is temporarily or permanently discontinued. Rebound is primarily caused by the continued, equilibrium-driven, dissolution of contaminants into ground water after the cessation of the steady-state pumping. Rebound can be exploited as an indicator of when remediation goals will be achieved by evaluating the curve generated by the sequential rebound peaks of a number of pulsed operations of the recovery system. Without an ongoing source, rebound diminishes with continued treatment and eventually becomes small enough to not recover beyond the cleanup goals.

REINJECTION/INFILTRATION

Recovered, impacted ground water, with any free-phase organics separated, and treated by one or more of the extensive array of treatment technologies, can then be discharged to a publicly owned treatment works, surface water, or injected/infiltrated back to the ground water, usually upgradient from the plume. Consequently, the injection/infiltration system is the alter ego of the extraction system, capable of using the same basic components, wells, trenches, pumps, and control systems to put water back into the ground water. This can promote an enhanced flow downgradient to the original extraction system, potentially speeding the remediation process.

SPECIALIZED EXTRACTION SYSTEMS

Modifications to ground water extraction systems have been developed and applied to tailing and rebound issues associated with NAPLs and strongly adsorbed contaminants. Typical modification to pump-and-treat is MPE including slurping, and surfactant-enhanced recovery (SER). The detailed discussion on MPE is provided in Chapter 9.

MPE is the simultaneous recovery of two or three phases; ground water, LNAPL, and/or soil vapor. MPE is applied with the well screen extending from below the water table to above the water table in the vadose zone. Ground water is pumped from the deeper screened interval (below the water table). This enhances LNAPL recovery and allows the designer to select the optimal ground water drawdown. An added benefit to three-phase recovery is that the lift of the recovered material is dependent on the mass being lifted, and the net lightening effect of the air mixed with the water and LNAPL product enhances the lift. MPE is applicable to MTBE particularly where both an LNAPL and dissolved plume exist in an area of the site. Since MTBE's solubility and high concentration in many gasolines are keys to its ability to form a plume, rapid removal of LNAPL concomitant with plume recovery is a plus.

SER uses injection of surfactant(s) and usually a cosolvent (such as ethanol or isopropanol) to mobilize contaminants adsorbed to the soils or present as a dense or light NAPL into the readily recoverable ground water flow. The cosolvent enhances contaminant solubilization. More importantly, it is a viscosity modifier for the usually viscous surfactant, allowing easier injection of the aqueous surfactant solution. SER enhances the recovery and shortens the time to recover contaminant mass by the formation of ground water-mobile micelles with contaminants sequestered within. This also increases the solubility of contaminants in water, and thus altering the surface activity properties of the water with soils and NAPL. This enhances the movement of water into sequestered areas, lessens the capillary interactions, and generally increases the ability to flow and recover dissolved contaminants. The surfactant and contaminants are subsequently extracted through pumping wells. Aboveground processes are used to treat the impacted ground water and recycle the surfactant if practical. SER is probably not useful for MTBE ground water recovery and treatment since MTBE adsorbs poorly and thus is readily mobilized in ground water.

MTBE SPECIFIC ISSUES

High solubility and low adsorption make pump-and-treat an effective approach for the remediation of MTBE impacted ground water. Tailing and rebound effects occur with MTBE, particularly when LNAPL is present, but are believed to be less significant for ground water dissolved plumes.

The most important consideration in designing an extraction system for MTBE or other contaminants is placement of wells/trenches and vertical screen or trench depth intervals. The extraction system is placed within the contaminant plume so it effectively captures the contaminants. Placement of the system wells and or trenches can incorporate two approaches. The design can incorporate a risk-based capture zone that allows areas of lower contaminant concentration, and lower risk, to escape the extraction system and naturally attenuate. With MTBE this needs to be considered carefully since its low taste and odor threshold make it liable to be a nuisance issue at concentrations that would probably not be of risk to humans or the environment. Alternatively, the extraction system can capture virtually all the ground water with detectable contaminants. This approach is used for sites where the contaminant is very high risk at low concentrations (acutely hazardous) or where escape of contaminants off-site would pose high liability, such as lawsuits. Although MTBE would not qualify as an acutely hazardous contaminant, its easy detectability by odor and taste in water could trigger lawsuits regardless of merit.

Well screens or trenches should be installed so they extend above the annual high water table to effectively capture LNAPL and accommodate seasonal ground water level fluctuations. They also must extend deep enough within the aquifer to capture the full, anticipated depth of the contaminant plume around or moving to the extraction point(s). MTBE, based on its specific gravity, does not produce a DNAPL itself and does not produce sinking plumes. Plumes of any dissolved contaminant sink only if there is significant downward movement of the ground water (along with all the constituents dissolved in it). A good example is drawdown by a heavily pumped well. However, MTBE, as with all dissolved contaminants, will tend to disperse and diffuse vertically and horizontally to produce a gradually deeper plume with time and distance. Extraction systems should be designed to capture the needed vertical and horizontal span of the plume.

Equally important is the design of the reinjection system if the treated water is to be reinjected back to the aquifer. Ideally, the reinjection wells/trenches are screened for the entire depth of the aquifer. Adequate reinjection capacity must be planned to accommodate this activity. The water management design must include plans for managing this excess water, such as discharge to a surface receiving water.

GROUND WATER TREATMENT

Although critical to the success of a remediation project, the extraction component is usually considered the simple part of pump-and-treat. This is because the extraction technologies are old and familiar, the variables are considered well-understood and definable, and the systems are considered to be forgiving, so that a few changes and additions can address operational issues. The challenges for extraction and reinjection are more likely to come in the hydrogeology and regulatory portions of the project.

The treat aspect of pump-and-treat has been the area of broadening technical possibilities in the last few decades. There are many new, potential, and refined treatment technologies applicable to extracted, impacted water. In this section, treatment technologies for MTBE in extracted ground water are discussed.

Granular Activated Carbon (Liquid Phase). GAC is prepared from organic materials such as coal, lignite, wood, and coconut shell. The preparation involves controlled heating of the material to produce a porous high-carbon matrix that is activated by further treatment with heat and steam. Activation means that the carbon is altered by the treatment to maximize its potential to adsorb certain organic and inorganic compounds. The product of the preparation process can be ground and sieved to produce GAC or powdered activated carbon (PAC) of different sizes. The starting material and treatment processes produce GACs with varied properties, including porosity and pore size. There are experimental activated carbons impregnated with iron so that adsorbed materials can then be oxidized by peroxide to regenerate some of the adsorptive capacity. Despite relatively uniform production processes and starting materials, GAC purported to be of the same type can vary by manufacturer and by batch from a particular manufacturer. Usually these variations are not significant in changing the function of the GAC for actual field applications, but this should always be considered if new GAC batches do not behave as expected.

Adsorption of a substance is an interaction and accumulation of that substance at the surface of one phase, the solid phase, of a two-phase system interface, *i.e.*, liquid:solid phases or vapor:solid phases. The production of activated carbon results in a highly porous material with total surface areas reported up to 3,000 square meters per gram (m^2/g) (32,000 square feet per gram [ft^2/g]), but more typically 600 to 1,300 m^2/g (6,500 to 14,000 ft^2/g). The material is full of pores ranging from 10 to 1,000 angstroms that attract and adsorb organic molecules. Debate remains about the mechanisms of carbon adsorption, between a straightforward interaction with a surface and physical trapping of molecules in micropore spaces, or a combination of these mechanisms with others. It is critical to understand that some types and brands of GAC may perform better for adsorption of particular contaminants or contaminants from particular ground water sources. This is probably due to a variety of properties of the particular GAC and to water chemistry such as pH, natural occurring organics, mineralization, and similar characteristics. The current perception is that coconut shell GAC removes MTBE better than other GAC varieties (California MTBE Research Partnership, 1999).

TBA can be a degradative intermediate and co-contaminant of MTBE. Due to its higher solubility and lower Henry's Law constant than MTBE, TBA may be more difficult to remove by GAC than MTBE. Resin adsorption is demonstrated to better absorb TBA than GAC and thus may be a better option for sites with high concentrations of TBA.

GAC adsorption is not a destructive technology. Consequently, the GAC must be handled in a way that prevents release of the adsorbed materials to the environment again or must be regenerated for reuse in a way that removes but captures or destroys the released contaminants. Used GAC can be regenerated with heat and steam treatment, which releases and/or destroys the contaminants.

The efficiency of the GAC is defined as the mass of adsorbed material per mass of activated carbon. Generally, it declines with each subsequent regeneration and use, so that eventually it becomes cost-effective to dispose of the spent GAC. Spent GAC can be incinerated, burned as an alternative fuel, or, if free of contaminants, can be landfilled. In most applications for drinking water treatment, regenerated GAC cannot be used by regulation; only virgin GAC can be used. This is a precaution to be sure that the GAC does not itself become a source of contamination to the drinking water from residual contaminants from a previous use. If the water being treated for MTBE is to be used for drinking water, regeneration will probably not be a cost-cutting approach available to the operator.

Carbon adsorption is relatively nonspecific and has been shown to be effective for removing halogenated and nonhalogenated VOCs and SVOCs, and polychlorinated biphenyl (PCBs) compounds from liquid streams. From the perspective of MTBE treatment, this means that many other organic compounds, which may be co-contaminants, will also be consuming the GAC adsorptive capacity. Since BTEX and smaller alkanes and alkenes commonly accompany MTBE from gasoline and other fuels, sometimes this competition can be significant. In addition, free-phase hydrocarbons in the ground water can physically blind the GAC by accumulating as a layer on the surface of the GAC, limiting water and its contaminants access to the GAC porosity and thus limiting or preventing removal of dissolved components by the GAC.

Figure 15-4 is a simple diagram of a series of GAC beds in a simple treatment system such as might be used in a temporary ground water pump-and-treat remedial project. GAC beds can be operated either in parallel or in series. The usual design reason for using multiple bed approaches is to limit the frequency of the GAC changes or regenerations. For contaminants with lower affinities for GAC and with a breakthrough point at a fraction of GAC saturation, such as with MTBE, GAC reactors in series are appropriate. The series arrangement allows monitoring for breakthrough at the first carbon bed or canister while still protecting from total system effluent breakthrough with the second, third, or additional GAC beds or canisters.

The performance of a GAC system is affected by the properties of the GAC, chemistry of influent streams, and design parameters. The properties

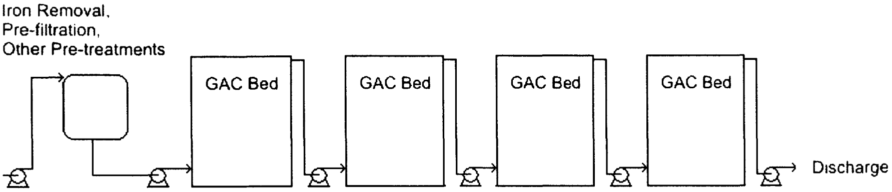

Figure 15-4. **Granular Activated Carbon Treatment Beds in Series**

of GAC include particle size, surface area, pore structures, surface chemistry, and also the type of carbon used. The adsorption capacity is dependent on the surface area accessible to organic molecules within the pore structures. The pH of the influent stream affects the affinity of weak organic acids or bases for activated carbon but probably is insignificant for MTBE.

Adsorption of anything, including MTBE, is a dynamic equilibrium phenomenon. In a static equilibrium (not flow through) with only one adsorbable constituent, the adsorption system comes to an equilibrium with some fraction of the constituent on the adsorbent and some fraction remaining in solution. At any given concentration, the equilibrium ratio, the fraction adsorbed and fraction not adsorbed, will be the same as long as the adsorption capacity of the adsorbent is not exceeded. Regardless of high or low total concentrations, the concentrations on the GAC and in the water will be proportional to the total available contaminant in the stream as long as the GAC adsorbent capacity is not exceeded. However, even in a static mode, individual molecules desorb randomly per unit time and others adsorb to maintain the equilibrium, basically an off and on phenomenon. In a mixed contaminant situation where the contaminants have different adsorption characteristics for GAC, this allows stronger adsorbers, such as benzene, to displace weaker adsorbers, such as MTBE. When an MTBE molecule desorbs, its place can be taken by a benzene molecule that is much less likely to desorb due to its equilibrium gradually and progressively shifting the equilibrium towards dissolution of the MTBE within the carbon bed. The equilibrium constant of a contaminant depends on its relative affinities for water and GAC but results in a constant proportional ratio in each phase, water or GAC. Thus, if the concentration in the influent drops significantly, MTBE, and other contaminants, now present on the GAC at considerably above the equilibrium ratio can desorb, increasing the water concentration until the equilibrium is reestablished. MTBE adsorbs to GAC and has a very early breakthrough relative to its saturation on GAC. The consequences of this are that MTBE is readily displaced by stronger adsorbing compounds and breaks through so early that GAC, if replaced at breakthrough, is prohibitively costly in most applications. Both problems can be resolved by designing longer or guarded systems. Since many of the compounds competing for MTBE adsorption locations are stronger adsorbers, placing multiple GAC beds ahead of the actual MTBE adsorption beds allows those beds to remove the displacing contaminants and allows MTBE to then adsorb on the later beds. The first beds must be monitored for breakthrough of the other contaminants and replaced when saturated to continue to guard the MTBE beds. Likewise, the guarded MTBE beds must be monitored for breakthrough of MTBE. By using a sufficient number of MTBE beds and enough guard beds, the first MTBE bed in each series can be operated after breakthrough until nearer saturation, maximizing use and minimizing cost per mass of MTBE removed per GAC mass.

Empty bed contact time (EBCT), bed depth, and hydraulic loading rate are design parameters for GAC adsorbers. EBCT is the time for the volume of water in a carbon bed to flow through the bed. Thus for a given flow, to increase the EBCT, the size of the bed and its associated water volume must be increased. Typically, an increase in EBCT will increase the bed life of the GAC for a given flow and contaminant concentration. However, as EBCT increases, at a constant hydraulic application rate, the capital cost increases for the larger tank and associated components of the system. Yet operating costs can decrease because of lower frequency GAC replacement and associated costs or downtime.

MTBE does not adsorb to activated carbon as well as hydrocarbons such as BTEX. Gasoline components including BTEX are usually present with MTBE and compete for adsorption locations. Natural organic matter in ground water will compete with MTBE for adsorption locations. Consequently, single component isotherms are not applicable for such mixtures. Bench jar or beaker tests can be conducted to estimate carbon usage, but dynamic column testing with natural site water is recommended for design of MTBE treatment systems. Poorer adsorption and co-contaminant competition causes a long mass transfer zone and early breakthrough of MTBE. Systems with three or more GAC adsorbers in series should be considered to enhance the total percent saturation of the first adsorber prior to its replacement. This decreases carbon usage rates and thus carbon replacement frequency, and prevents shutdowns due to potential breakthrough at discharge. Some regulatory agencies require shutdown when the next-to-last GAC bed in the series breaks through.

Coconut-based GAC is thought to have smaller pores that are more effective at adsorbing MTBE. Laboratory tests have demonstrated coconut shell GAC adsorbs more MTBE than coal-based GAC. However, variations in raw materials and manufacturing processes make it difficult to predict GAC performance without testing. Virgin carbon is preferred for the treatment of MTBE due to its higher adsorption capacity than regenerated carbon.

GAC is a well-developed and proven technology with a long history as a treatment for municipal, industrial, and hazardous waste streams. Modular

GAC column or bed reactors are readily available from a variety of vendors. The following factors may limit the applicability and effectiveness of the process:

- Spent carbon regeneration or disposal;
- Multiple contaminant competition;
- Fouling by suspended solids or solids formed by precipitation of reduced iron or manganese species;
- Free-phase hydrocarbon; and
- Poor adsorption for water-soluble compounds and small molecules.

For these reasons GAC is generally selected for lower concentrations of MTBE in water. A rule of thumb is 500 µg/l or less, and GAC may only be economical at half that loading.

INTERFERENCES

As with GAC applications for target contaminants other than MTBE, a variety of materials also present in the water to be treated may interfere with adsorption of MTBE.

Iron. Soluble reduced ferrous iron (Fe^{+2}) dissolved in the extracted water may oxidize to less soluble ferric iron (Fe^{+3}) forming iron hydroxide ($Fe(OH)_3$) during extraction and pumping by contact with oxygen introduced from the air. The $Fe(OH)_3$ can precipitate, both in piping and in or within the GAC bed. This can result in piping obstruction and/or progressive blinding of the flow channels for water and pore structure of the GAC, resulting in increased backpressure in the bed, poorer flow and distribution of flow, and inaccessible adsorption sites in the pore structure. Regeneration of the GAC may also be less effective because iron may remain trapped in the pore structures. During regeneration, such minerals, possibly acting as catalysts, in the GAC contribute to a degradation of the GAC carbon structure causing an accelerated and progressive loss of adsorptive capacity with each reuse, beyond the normal loss from regeneration. This type of deterioration can be determined by iodine or molasses tests, which essentially determine the small and large pore capacity of the carbon respectively.

If iron in the recovered water is expected to significantly interfere with the adsorption of MTBE, consideration should be given to using an alternate treatment technology or a pretreatment system to remove the iron. Iron concentrations of several mg/l in extracted water can usually be tolerated, but concentrations of tens of mg/l or higher will usually cause problems. Commonly used pretreatment systems can consist of aeration or chemical oxidation, followed by separation of the precipitated iron by filtering. In this application, removing MTBE by aeration or chemicals would not be the focus of the pretreatments since one aeration or stripper unit would generally not be adequate. One mechanical hydraulic stripper or aeration unit will probably be adequate for iron precipitation and could be designed to provide recirculation adequate to precipitate most of the iron. Pretreatment chemical oxidation with hydrogen peroxide or other oxidizers can be used to precipitate iron and has proven successful in this application for MTBE remediation. Following oxidation, the precipitate can be removed by a separator, clarifier, filtration, or other technologies. Coagulant technologies for iron should be carefully considered with respect to the impact of residual coagulant and its potential to also interfere with the GAC.

Manganese. Like iron, dissolved manganese can precipitate and blind or plug flow paths and pores in the GAC. The same pretreatment technologies as used for iron generally will work for manganese. Both iron and manganese should be evaluated when one or the other is suspected to be in the water as often the same geochemical conditions and parent soils or rock can produce both soluble iron and manganese.

Total Organic Carbon. TOC or dissolved organic carbon includes the contaminants and naturally occurring organic materials. Naturally occurring organic materials can include tannins, a range of humic materials, particularly the more soluble humic and fulvic acid ranges of compounds, and in some areas naturally occurring concentrations of hydrocarbons from native shales, sands, limestones, and sandstones. These smaller humic and other materials are usually GAC adsorbable and thus consume adsorption capacity on the GAC. In addition, if their affinity for GAC is strong, they may significantly contribute to displacement of MTBE from the GAC. Co-contaminant gasoline range hydrocarbons may also contribute to the TOC and displace or replace MTBE on the GAC. Some fraction of the TOC may not be adsorbable on GAC and will emerge as breakthrough. Consequently, TOC as a measured parameter should generally be avoided as an indicator of breakthrough and particularly in areas with natural TOC or non-target contaminants in the ground water.

Pretreatment can help prevent MTBE from simply being displaced or non-contaminant TOC consuming the GAC capacity intended for MTBE. TOC can be removed by using a guard GAC bed that pretreats, leaving the subsequent beds for adsorption of MTBE.

Mineralization. In addition to iron and manganese, hard water compounds such as calcium carbonate and similar compounds may precipitate or scale in the equipment due to oxygenation and pH changes. Treatments for excessive mineralization include standard pretreatment with ion exchange systems and pH control to minimize precipitation.

Coagulants and Additives. Coagulants and additives, used to pre-treat water for removal of metals or turbidity, could interfere themselves with the GAC adsorption. These coagulants, just like turbidity, can adsorb to the GAC, blinding pores and blocking adsorption sites. Discussions with and between vendors of GAC systems and pretreatment systems should be expedited to select and match the appropriate systems to minimize the chances of interference caused by pretreatment for another interference.

Turbidity. Turbidity can include natural organic or inorganic turbidity components such as fine clay particles, particulate plant decay debris, silts, and even fine sands. However, it can also include free-phase organic material dispersed as droplets, micelles, or fine emulsions in the recovered water. Fine soil particles can physically bind the GAC pores, thus limiting the water flow channels, and generally disrupting good water distribution throughout the GAC bed. Free-phase organic material can smear over the surface of the bed face, coat GAC particles, and generally blind pores and cover adsorption sites. In addition, the organics may contain compounds that specifically adsorb, competing with MTBE.

Turbidity can be pretreated using sand, diatomaceous earth, or similar filter systems and/or coagulation systems.

Co-contaminants. Related to the free-phase organics discussed above are the dissolved organics, particularly those considered co-contaminants. It is appropriate to use the GAC system to remove co-contaminants along with MTBE, but the behavior and impact of the expected mix and individual components targeted for removal must be assessed. Generally, the design of the treatment system for mixed contaminants will be driven by the treatment fate of the contaminant most likely to breakthrough. This will usually be MTBE. Its breakthrough during interactions with the other contaminants will probably dictate the design (*e.g.*, the number of beds needed to maximize carbon usage while protecting from an unguarded breakthrough) and the need to use alternative technologies. It may make sense to design a GAC system knowing that the first bed will be used to remove BTEX, for example, and only subsequent beds will be expected to adsorb MTBE at significant concentrations, as discussed above. The first bed would then be monitored for BTEX breakthrough, and the bed changed when that happens. In essence such a system uses the first bed to guard the other beds from MTBE co-contaminants, freeing up the remaining beds for MTBE with minimal adsorption competition.

Biological Growth. Adsorbed contaminants, renewing oxygenated flows of water, and high surface area GAC combine to provide very good locations for biological growth. This is exploited in fluidized bed reactors (FBRs) with

GAC but can become a problem or a blessing in a simple GAC adsorption system. To some extent this can be a problem related to the lifetime of the first bed and the biodegradable nature of one or more of the contaminants. If the first bed is in place for weeks or months, this allows time for selection, adherence, and growth of a fixed biofilm on the GAC with the resulting blinding of pores and some water flow. Growth can occur across the interface of the GAC bed in extreme cases, suggesting that perhaps the wrong treatment system was selected. However, if the growth does not significantly impact the operation of the GAC, it can extend the life of the carbon by degrading adsorbed contaminants, allowing for additional adsorption at freed up locations. In addition to growth within the GAC, growth can occur within the recovery wells, piping, and tanks, becoming a source of sloughed biomass and inoculum to the GAC with similar effects as discussed for growth on the GAC. Simple filtration systems can remove biomass sloughed from upstream sources. These filters can be sand or mixed media but will need to be backwashed periodically. Such filters are often a standard component of GAC systems and can usually be supplied by the vendor of the GAC beds and equipment.

Costs. The costs of GAC treatment are generally well-understood for simple adsorption of the contaminants, even for MTBE with its recent emergence as a contaminant of concern. The California MTBE Research Partnership assembled cost numbers for GAC treatment.

Estimated costs for MTBE treatment with GAC vary from $0.41/3,800 liters (1,000 gallons) to $2.80/3,800 liters (1,000 gallons) treated. By comparison to the estimated costs of other technologies, GAC should be considered for sites at which influent MTBE concentrations are 200 μg/l or less. Other organic matter concentrations in ground water should be taken into account during the design. System design life will also affect the technology selection. GAC systems are more likely to be cost-effective for sites requiring short duration treatment compared to other systems, such as advanced oxidation, which require higher capital cost.

RESIN ADSORPTION

Resin adsorption is an adsorptive technology similar to GAC adsorption. Resin adsorption uses synthetic adsorptive resins to adsorb contaminants from ground water. Figure 15-5 illustrates the basics of such a system that typically uses at least two beds, so one is adsorbing while the other is being regenerated. The resins are typically spherical, microporous beads or prills, produced with a high surface area and a high adsorption capacity for organic molecules. The resins are polymer matrices with side functional groups that bind the contaminants, adsorbing them from the water. They adsorb selec-

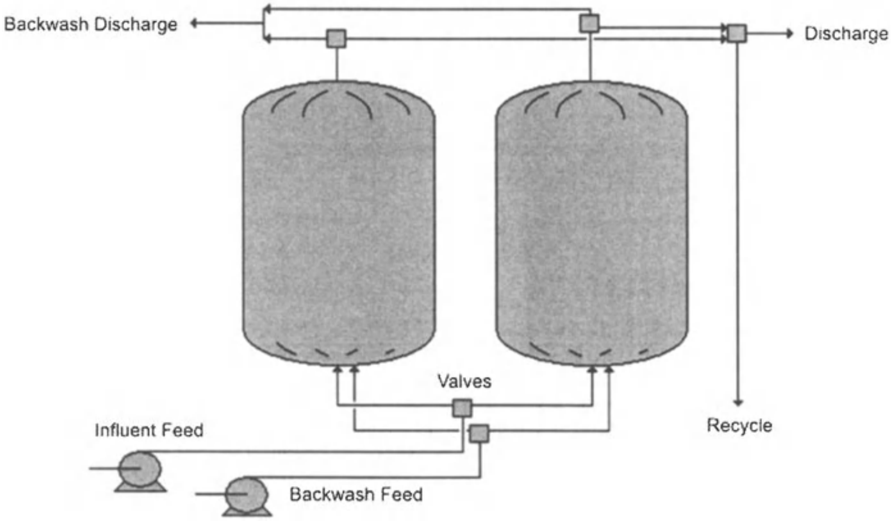

Figure 15-5. **Resin Adsorption System**

tively based on the chemistry, structure, and steric position of these side functional groups and the contaminant.

Resin adsorption is applicable for removing halogenated and nonhalogenated VOCs and SVOCs, PCBs, and explosive compounds from water. The synthetic resins typically provide 5 to 10 times higher mass loading of contaminants than does GAC at low contaminant concentrations. The affinity of the resins is higher for the contaminant molecule compared to GAC. Some resins have a higher capacity for MTBE compared to GAC. In addition, resin adsorbents are less likely than GAC to adsorb competing inorganic matter. Resins can be regenerated on-site through microwave irradiation or steam stripping. However, data are limited on the effectiveness and efficiency of MTBE treatment with synthetic resin adsorbents, suggesting that treatability studies need to be done if it is to be used for a specific application. Ground water impacted by MTBE is likely to contain TBA as well. For sites impacted by both MTBE and TBA, synthetic resin adsorption should be considered as a possible treat component of pump-and-treat.

There are some factors limiting the applicability and effectiveness of the process. Unit costs of resin are higher than GAC, typically requiring resin regeneration. Preliminary experience indicates that resins can be regenerated more times than GAC and with less loss of adsorption capacity than GAC. The economic tradeoff of resin's higher capacity, more regeneration cycles, and sustained adsorption capacity to the resin's higher cost has not been fully assessed. Suspended solids or solids formed by precipitation of reduced iron and manganese species in solution can physically foul a resin bed, requiring pretreatment to remove the fouling agents. Finally, there is the issue of treatment or disposal of the concentrated waste stream from the regenerated resin. Suggested options, but not demonstrated in the field, have included biological treatment of the waste stream from steam regeneration and thermal oxidation after microwave regeneration/volatilization.

AIR STRIPPING

Air Stripping is a process that exploits the phase equilibrium of contaminants between water and air. The transfer of contaminants from water to air is a surface area mass transport process. Impacted water is contacted by air, typically a larger volume of air, in a manner that greatly increases the two phases' interface surface area. This greatly increases the mass transport of the contaminants from water to air in response to the equilibrium gradient. The treatability of a contaminant by air stripping is indicated by its Henry's Law constant. The higher the Henry's Law constant, the easier the compound is to air strip. The dimensionless Henry's Law constants for MTBE and TBA are approximately 0.026 and 0.0009 respectively. Stripping is best for compounds with dimensionless Henry's Law constants of greater than 0.05. Nevertheless, MTBE can be air stripped and the CDHS has approved air stripping as their best available technology for MTBE. Recycling of water may be necessary to strip the MTBE down to the needed concentration for discharge. A typical volumetric ratio of air to water for effective MTBE stripping is greater than or equal to 200:1.

Air strippers of several types are commercially available. Types of air stripping methods include packed tower, tray stripper, diffused aeration, low profile aeration, and mechanical stripping.

STRIPPING TECHNOLOGIES

Packed Tower Stripper. A PTS usually consists of a cylindrical tower containing a perforated plate, near the bottom, to support the packing material. Packing materials can be various ceramic, stainless steel, or plastic shapes that promote turbulent flow of the water and air and maximize air:water interface surface area. Typical packed towers includes water distribution mechanisms at the top to distribute impacted water over the packing in the column. Water descends as air is blown up through the column, stripping off the volatile compounds. A sump at the bottom of the tower collects decontaminated water for recycling and/or discharge. PTSs can be permanent, or skid or trailer mounted. Most states require capture and treatment of the PTS off-gas prior to discharge to the atmosphere. Typical off-gas treatment technologies applicable to MTBE are GAC, thermal oxidation, catalytic oxidation, and biofilter treatment. Figure 15-6 illustrates a PTS.

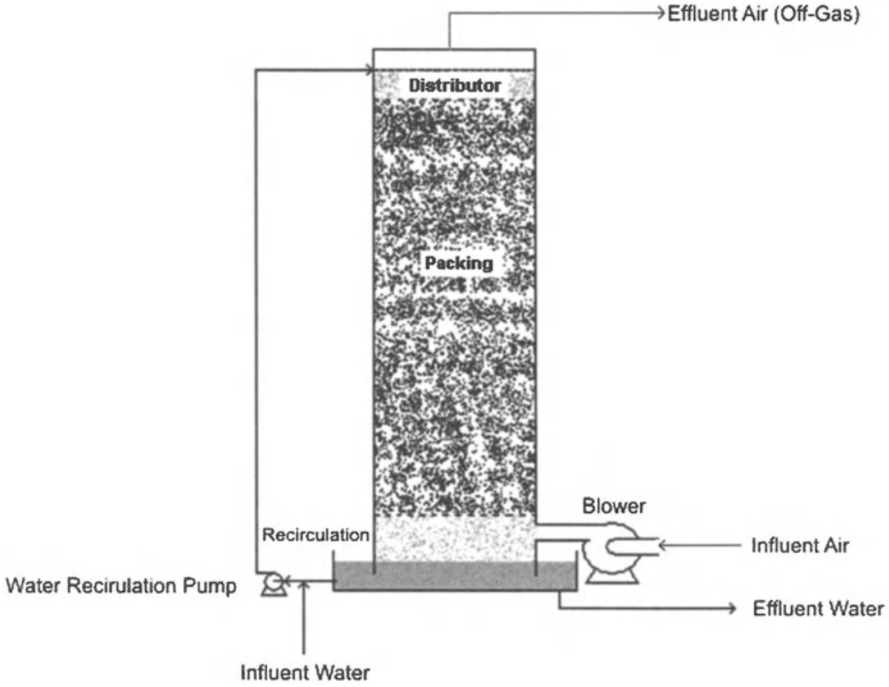

Figure 15-6. **Packed Tower Air Stripper**

Low-Profile Air Stripper. Low-profile air strippers (LPSs) operate on the same principles as PTSs. LPSs flow impacted water across stacks of trays that are perforated with small aeration holes. Water flows over a weir on each tray to the next lower tray until the water exits the bottom of the stripper. Air is bubbled through holes in the trays to facilitate stripping. The trays are packed in a very small chamber to maximize air-water contact while minimizing space. Because of the significant vertical and horizontal space savings, these units are increasingly being used for ground water treatment. LPSs may also be a good choice regarding concerns for visual impact at sites located in residential areas. These systems can also use heated trays to increase the stripping efficiency. Figure 15-7 illustrates an LPS.

Diffused Aeration Stripper. Diffused aeration strippers (DASs) are tanks or reservoirs with fine bubble or other air diffusers placed near the bottom. Air bubbles move up through the liquid, stripping contaminants, are captured by the tank roof, and then exit at the top of the vessel to off-gas treatment. Stripping efficiency is increased with deeper tanks or reservoirs (longer contact time) and finer bubbler or air diffuser systems (higher contact surface area). DASs are generally unimpacted by suspended solids. How-

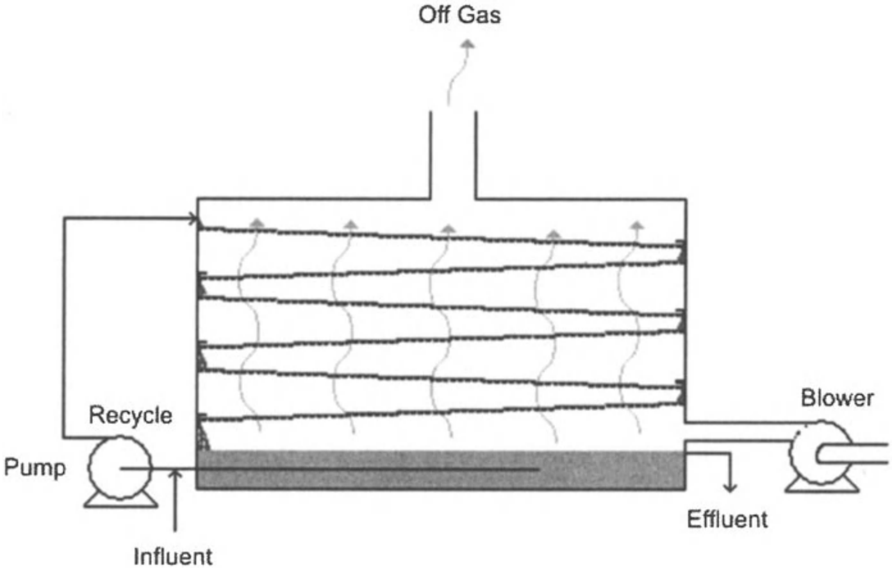

Figure 15-7. **Tray Stripper**

ever, for stripping MTBE, which needs a higher ratio of air to water, DASs are generally not effective unless the starting MTBE concentrations are very low, near the target discharge or cleanup concentration. As with any stripper system, poorer stripping performance can be overcome by larger, deeper tanks and extended air to water contact and residence time. Figure 15-8 illustrates a simple tank DAS.

Mechanical Stripper. Mechanical strippers are devices that exploit thin film or venturi effects to transfer contaminants from water to air. An example of a mechanical stripper is the Hazleton Maxi-strip® System. The venturi devices are mounted on the tops of tanks. The impacted water is jetted down the inside of a venturi by ring nozzles, producing highly turbulent jets of water that shear in the open venturi bore. The turbulence achieved in the venturi creates the large surface area needed to enhance mass transfer. The water jetting also induces airflow down the venturi, eliminating the need for blowers. The water can be recycled from the attached tanks to the venturies as many times as needed to achieve the treatment concentrations. Units can be assembled in series to meet the needed water capacity. The system has series of air intake hoods to allow outside air to be drawn directly to the strippers. In a stripper series, off-gas from the least contaminated module can be recycled counter to water flow as stripper gas. This minimizes the amount of total off-gas flow and increases the concentration of the contaminants in the eventually discharged off-gas, usually making for more efficient off-gas treat-

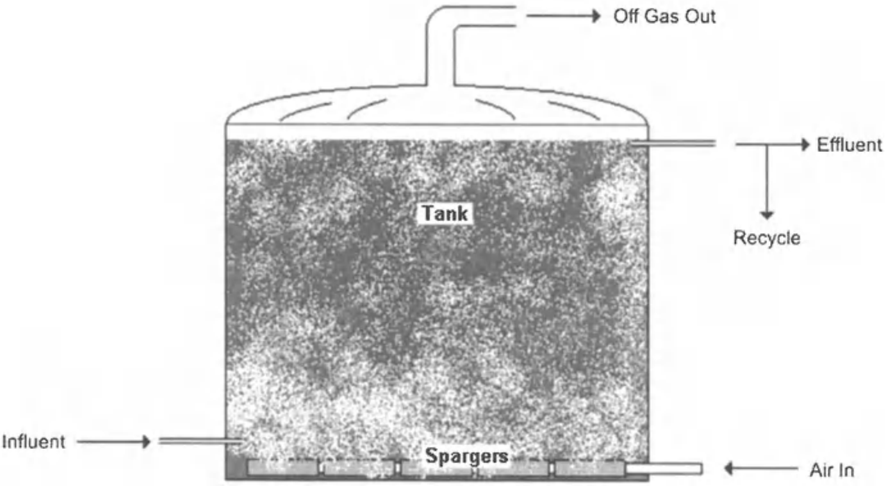

Figure 15-8. **Diffused Aeration Stripper**

ment. The off-gas can be treated as needed by GAC or other technologies. The mechanical stripper system is flexible for different influent concentrations or flows. Additional stripper modules can be added and modules can be turned off as required. Figure 15-9 illustrates the principles of a mechanical venturi air stripper system.

OFF-GAS TREATMENT

The air stream leaving the stripping system may require off-gas treatment if contaminant levels exceed regulatory emissions standards. Several treatment processes, such as GAC, catalytic and thermal oxidation, and biofilters can be cost-effective for treating the off-gas emissions.

Thermal and Catalytic Thermal Oxidation. Both thermal oxidation and catalytic thermal oxidation can be used to destroy organic compounds. In a thermal oxidizer, VOCs are oxidized in a flame at high temperature. In catalytic oxidation, VOCs in the emission stream are oxidized at lower temperatures with the aid of a catalyst. Catalysts typically employ platinum, palladium, or other metal oxides. The performance of a catalytic oxidizer is affected by several factors including: operating temperature, space, velocity, VOC type and concentration, catalyst properties, and presence of catalyst inhibitors or "poisons" in the emission stream. Typical poisons are metals and other inorganics that can deposit on the catalyst and reduce its reactivity with the hot organics. Figure 15-10 presents a simple illustration of a catalytic (thermal) off-gas treatment system. Thermal only systems are similar but without a catalyst to lower the temperature needed for destruction. Thermal

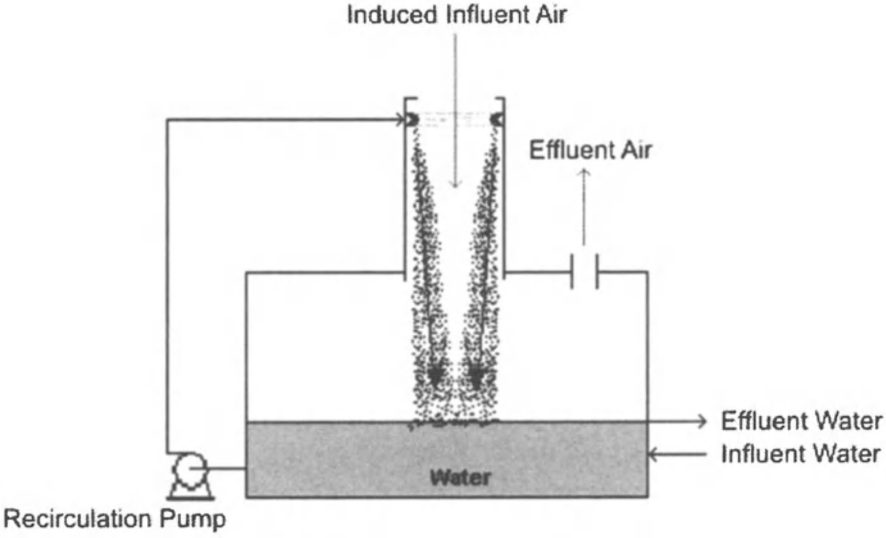

Figure 15-9. **Mechanical Venturi Air Stripper**

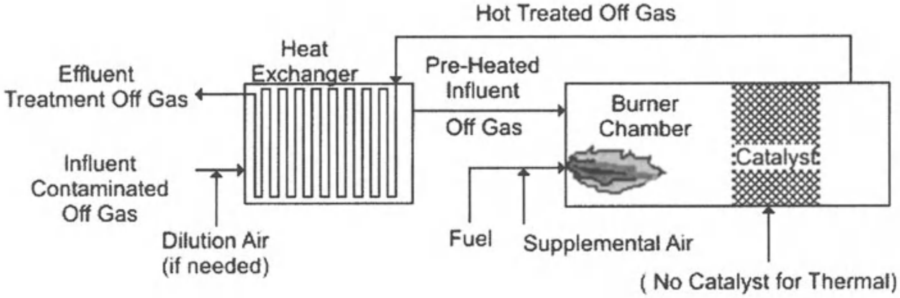

Figure 15-10. **Catalytic and Thermal Off-Gas Treatment System**

systems often use specially designed burners to assure destruction of the gas stream.

Granular Activated Carbon. Vapor phase GAC adsorbers can be used to treat off-gas streams. The activated carbon removes contaminants from the gas stream by adsorption, just as from water, until available active sites are occupied. Commercial grades of activated carbon are available for specific use in vapor-phase applications. As with GAC use in water systems, MTBE can be removed from off-gas by GAC. Many of the same principles apply for GAC adsorption from air streams as for water steams. Figure 15-4 illustrates a water based adsorption system. An air adsorption system would be similar except pretreatment would include a knockout pot or other demisting/dehumidifier system to remove moisture in the off-gas stream. This is particularly critical when off-gas is originating from a stripper system.

Biofilters. Biofilters are high surface area beds with wet biofilms that degrade the organic contaminants in air streams as they pass through the filters. The bed and biofilm must be moist so that organics will partition from the air stream to the thin water layer over the surface of the microbial biofilm where the microbes can rapidly access and degrade them. Uptake and degradation by the biofilm is a sink for the contaminant, effectively maintaining a steep mass transfer gradient from the air to the water to the biofilm. A blower and an air dispersion system are used to move the air through the biofilter and evenly distribute the flow. Water is misted or sprayed over the beds and/or the off-gas is humidified to increase transfer to the microbial biofilm. The biofilm is attached to the bed materials, which can be plastic, wood chips, or similar inexpensive and durable materials with high surface areas. Figure 15-11 illustrates an engineered tank system and a pile system for treatment of off-gas.

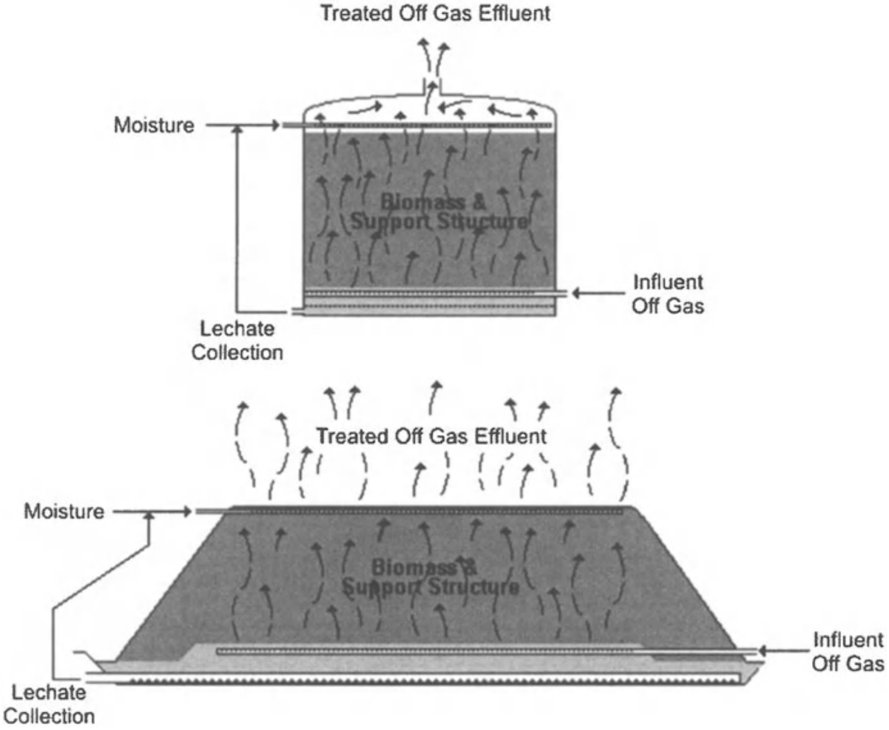

Figure 15-11. **Off-Gas Treatment with Biofilters**

Off-Gas Treatment Costs. The startup costs are comparable to conventional technologies such as GAC and thermal, but operations and maintenance costs are often substantially lower. There are no external fuel costs such as those associated with thermal oxidation technologies. Biofiltration becomes more economical than GAC or oxidation when airflow rates are high and pollutant concentrations are low. Biofilters can treat MTBE but may require larger filters for increased residence time to degrade MTBE and prevent accumulation in the water phase. At least one of the consortia and one of the microbes capable of degrading MTBE in a pure culture were isolated from a large biofilter application where the organisms were presumably degrading MTBE in the off-gas from a wastewater treatment plant. With appropriate conditions, trickling biofilters can be used directly to treat MTBE impacted water, eliminating the need to strip MTBE.

INTERFERENCES FOR STRIPPING

Interferences for effective stripping are water conditions or constituents that impact effective stripping of the target contaminant(s).

Iron. Ferrous iron dissolved in the extracted water may oxidize to produce iron hydroxide during extraction and pumping and will almost certainly be oxidized by contact with oxygen introduced from the air stripping processes. The iron hydroxide can precipitate before reaching the air stripper or within the stripper (resulting in progressive accumulations or fouling on the packing or trays), or as turbidity in the water. The result is decreased stripping efficiency as surface area is reduced and air and water flow and distribution are reduced. Since effective stripping of MTBE requires a very high air to water ratio, MTBE stripper systems are potentially more sensitive to losses of stripper effectiveness due to fouling compared with BTEX stripper systems.

Iron concentrations in extracted water of several mg/l can usually be tolerated, but concentrations of tens of mg/l or higher will usually cause problems. If iron in the recovered water is expected to generate significant solids and interfere with stripping of MTBE, consideration should be given to using an alternate treatment technology or a pretreatment system to remove the iron (see discussion in GAC treatment section). Pretreatment systems can consist of mechanical hydraulic stripping (*e.g.*, Hazleton-type systems), or chemical oxidation/precipitation, followed by separation of the precipitated iron. With a mechanical hydraulic stripper as a pretreatment system, the separation can be integral to the tank beneath the stripper module. In this application, one unit is usually adequate for iron precipitation and can be set up to provide adequate precipitation of most of the iron. Pretreatment chemical oxidation with hydrogen peroxide or other oxidizers can be used to precipitate iron. Following oxidation, the precipitate can be separated by corrugated plate interceptor or other physical separation technologies.

Manganese. Like iron, dissolved manganese precipitate can accumulate on packing and piping in strippers. The same pretreatment technologies used for iron generally will work for manganese. Both iron and manganese should be evaluated when one or the other is suspected. Often the same geochemical conditions and parent soils or rock could produce both soluble iron and manganese.

Mineralization. In addition to iron and manganese, hard water compounds, such as calcium carbonate, may precipitate or scale in the equipment due to oxygenation and pH changes. Treatments for excessive mineralization include pretreatment with ion exchange systems and pH control to minimize precipitation.

Temperature. Low temperature decreases the stripping efficiency and the removal of contaminants from the stream. Winter operations may require pre-heating the air and/or pre-heating the water prior to the treatment. Heating can also enhance the overall stripping efficiency year-round.

MTBE APPLICATIONS

Air stripping is a proven technology, successfully used to remove MTBE from drinking water. PTSs appear to be the most cost-effective for MTBE removal, in part because of their simplicity and robustness and in part because they are well understood. At low flows and removal efficiencies, prefabricated LPSs are competitive with PTSs, despite their slightly higher treatment costs. This is because of their availability as premanufactured package units, simple installation, ease of operation, and small space requirements.

Selection of a treatment system for off-gas containing MTBE is dependent on the off-gas MTBE concentration and flow rate. At low (less than 0.5 ppm) off-gas MTBE concentrations, vapor phase adsorption is the most cost effective off-gas control technology because of very low initial capital cost. For higher off-gas flow (greater than 300 cubic meters per minute [cmm] [10,000 cubic feet per minute {cfm}]) and higher MTBE concentrations (greater than 5 ppm), thermal oxidation becomes the most cost-effective treatment technology.

BIOREACTORS

Biological reactors have been widely used in the treatment of domestic and industrial wastewater. Organic pollutants in wastewater can be converted to biomass and mineral end-products, such as carbon dioxide and water, through microbial metabolism. Common types of wastewater bioreactors include activated-sludge, fluidized bed, and fixed-film reactors (rotating disk or trickling filter) systems.

Activated Sludge. An activated sludge process treats wastewater in an aeration basin, tank, or pond with an active mass of microorganisms (the activated sludge or mixed liquor volatile suspended solids [MLVSS]) capable of aerobically degrading organic matter into carbon dioxide, water, new cells, and other end products. Diffused or mechanical aeration maintains the aerobic environment in the basin and keeps reactor contents (mixed liquor) mixed. After a specific residence time (average time of water in the basin), the mixed liquor passes into a gravity clarifier of some type, where the activated sludge settles under relatively quiescent conditions and a clarified effluent is produced for discharge or tertiary treatment. The process recycles a portion of settled activated sludge back to the aeration basin to maintain the required activated sludge (MLVSS) concentration and discharges or wastes the remainder for disposal. Figure 15-12 illustrates a simple activated sludge system. These can usually be purchased as packaged or modular systems intended for small municipal utility districts but suitable for remediation sites.

MTBE can be treated with an activated sludge process. Most facilities that manufacture MTBE are successfully treating wastewater with significant MTBE and TBA concentrations using the activated sludge process. With MTBE, the residence time is usually extended to assure adequate time for treatment. In some activated sludge applications for TBA and MTBE, zoned aeration and zoned recycled activated sludge appears to enhance treatment efficiencies and end concentrations. A benefit of biological systems over other non-biological systems is that they typically improve their treatment capacity with time due to selection and adaptation. This is particularly true with activated sludge systems where a portion of the microbial biomass is returned to the treatment to maintain a designed MLVSS, allowing continuing adaptation and selection of the returned biomass. A second benefit of biological systems is that intermediates produced are usually rapidly degraded as well, since their generation also selects for an activated sludge population capable of degrading them.

The activated sludge process is a well-understood, conventional treatment process. The major design parameters for an activated sludge process include:

- Organic loading (food) (usually milligrams biological oxygen demand [BOD] per liter);

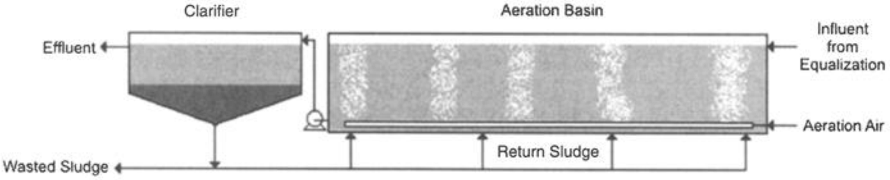

Figure 15-12. **Simple Aerated Activated Sludge Biotreatment System**

- Microbial biomass (MLVSS or mixed liquor suspended solids) concentration (mg/l);
- Food to (bio)mass ratio (mg BOD/mg MLVSS), also called sludge loading rate (SLR);
- Hydraulic (contact) retention time (HRT) or hydraulic loading rate;
- Mean cell retention time (MCRT) or sludge age (ratio of total MLVSS/ wasted MLVSS per day; and
- Rate of aeration (total pounds per hour) or as pounds per hour of oxygen transferred to water.

Simplistically, what these parameters mean, in sequence, are how much food is entering the system, how much biomass is there and is that enough active biomass (some of the biomass is dead at all times) to treat that food, is the food and biomass together in the reactor long enough to treat the food, is enough of the biomass active (not to old) to treat the food, and is there enough oxygen to support the biomass in oxidizing the food.

For MTBE, because of its apparent slower degradation rate, the design and operational issues that may greatly impact an activated sludge system are HRT or hydraulic loading rate, MTBE and other food concentration(s), effluent treatment goal, and use of a sludge recycling system for maximum adaptation. These issues will determine whether a temporary system or a large, complex, and more permanent system is needed. The latter can greatly increase costs, particularly if the treated water is not reused or recycled for later use. One could expect that, in a mixed contaminant food stream, MTBE will be the target compound that determines the HRT or hydraulic loading rate (*i.e.*, the critical target compound) since it will probably be the slowest to degrade of the target organics. However, this should be confirmed with treatability studies when treating a complex mixed organic wastewater stream containing MTBE. Activated sludge systems are not applicable to the low concentrations of MTBE often seen at field sites unless additional degradable organic carbon is available in the wastewater or can be added to supplement the feed. To maintain an activated sludge system, typically a minimal mass of food (*e.g.*, 100 mg/l of BOD) is needed to sustain a viable biomass. As the BOD concentration goes down, the biomass concentration declines and becomes unhealthy. The use of fluidized bed GAC systems can typically spare this effect so that lower concentrations can sustain the system, but again this is more typically in the 10 to 100 mg/l range, still requiring additional contaminants in the mix or supplementation of the food.

Fixed-Film Reactors. Fixed-film reactors are those that biologically treat wastewater using a thin biological film fixed (self adhered) to a solid surface. Microbes prefer to adhere to solid surfaces and readily do so if the surface has fine structure that allows attachment. The more surface area the more biomass that can attach. Consequently, a supporting solid surface with the maximum surface area in contact with water is the optimum for these systems. Such systems occur naturally in ground water and streams where microbes adhere to soil particles and rocks in the flow of the water. The two most common engineered fixed-film reactors are packed trickling filter systems (trickling filters) and rotating disk systems.

Trickling filters range from older, low concrete tanks with crushed, sized rock packing to modern tank systems with tortuous, complex, high surface area plastic packing over which contaminated water flows. A rotary or stationary mechanism distributes wastewater across the top of the filter, from which it percolates, generally as a thin film, through the interstices of the film-covered medium. Trickling filters can be designed with vertical plug flow, but this makes aeration difficult and control of water feed more complex. Most trickling filters operate with thin film flows over most of the packing. As the wastewater moves through the filter, the organic matter diffuses into the film where it is available to the microbes and is degraded by those microbes. The oxygen can be supplied in the wastewater or by air forced up through the filter, but most typically is supplied by induced natural eduction of air into the interstices of the packing as water drains down over the packing, leaving voids between the packing. An underdrain system collects treated effluent for recycling for additional treatment and/or discharge. Biomass sloughs from the surfaces over time and must be separated from the discharge. Sloughing can generally be controlled by hydraulic loading to the filter but is desirable at some rate, since it removes aged and dead biomass just as wasting does in activated sludge systems. Figure 15-13 illustrates a

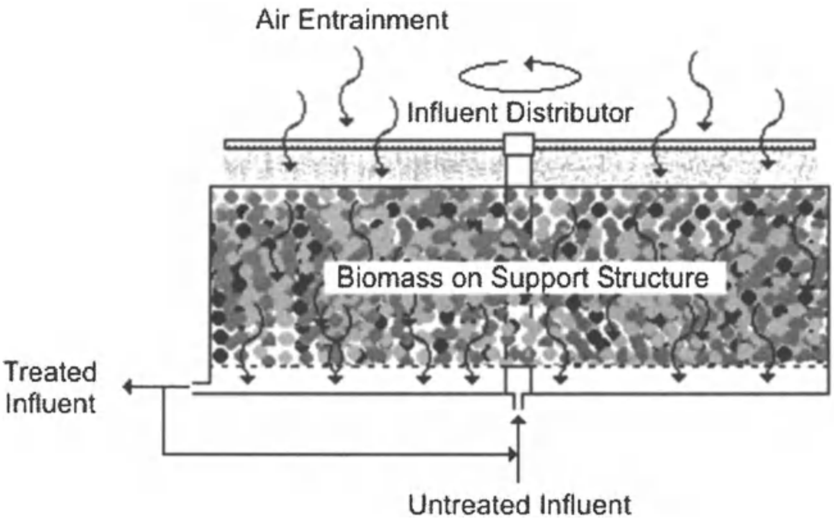

Figure 15-13. **Biological Trickling Filter**

simple biological trickling filter with a rotating overhead distribution of untreated influent water.

Rotating disk systems usually consist of closely spaced disks or perforated plates that rotate through a tank or trough carrying the impacted water. Microbial biofilm grows adhered to the disks or plates as they are repeatedly immersed in water. Aeration occurs as the disks are above water and entrain air into the water. Some systems are supplemented with aeration in the water flow and some are enclosed overhead in sheaths in which air or oxygen can be added. As with other fixed-film systems, the film biomass sloughs as it grows and must be managed prior to discharge of the treated water. Figure 15-14 illustrates the principle of rotating disk operation.

Fixed-film systems should be capable of treating MTBE, but the long residence times expected for MTBE and TBA treatment opposed to the typically low contact times in fixed-film systems indicate that such systems will require high recycle ratios and larger reactors than needed for rapidly degraded contaminants. However, these systems may be applicable to wastewaters with low concentrations of MTBE. Rotating disk systems are probably not good candidates for MTBE or TBA treatment particularly at MTBE concentrations in the mg/l range because of the slow degradation rate and low cleanup goals. The problem associated with any fixed-film system is the mass transfer limitation of oxygen into the inner layer of the attached biofilms. This can be critical for MTBE where high oxygen concentrations appear to enhance the degradation rate.

Fluidized Bed Bioreactor. FBRs use the water to be treated to suspend (fluidize) a bed of fine-grained material such as sand or GAC, using an upward water velocity. Chapter 29 describes a case study that employs an FBR. As

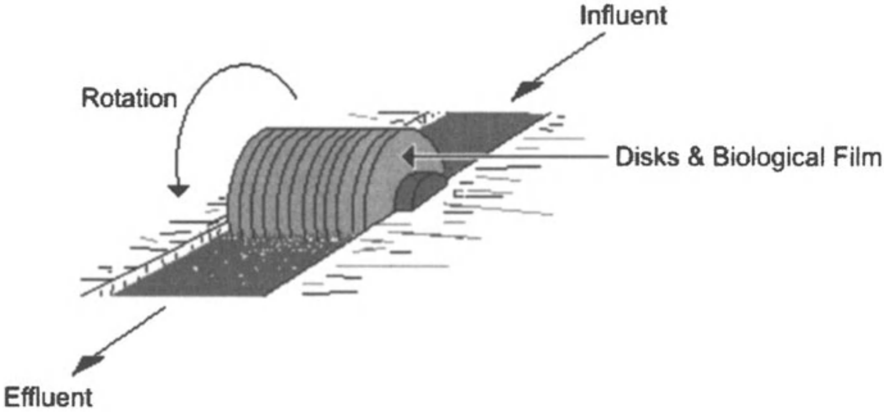

Figure 15-14. **Rotating Biological Disk Contactor**

with other fixed-film processes, the particles develop a microbial film. Fluidization significantly increases the specific surface area available for biomass and thus degradation of contaminants. Use of GAC as the fluidizing bed medium also adds to the specific surface area available for microbial colonization. FBRs avoid the bed plugging problems associated with a fixed bed bioreactor and trade it for a narrow range of operational flows due to the need to fluidize but not wash out the bed. Water being treated is usually recycled repeatedly to the fluidizing flow for extended treatment. GAC-FBRs have the added aspect of adsorbing the contaminants to potentially extend the contaminants' residence time in the reactor and possibly enhance the contaminants availability to the biofilm. The fluidization tends to abrade the biofilm, sloughing excess biomass that passes out of the reactor and which typically must be managed and disposed of. This sloughing is necessary to allow new growth and remove aged biomass. Figure 15-15 illustrates the operation of an FBR.

FBRs typically require a higher degree of operator maintenance and process control than other readily available treatment processes. Additionally, this process is sensitive to high variations in influent flow and contaminant concentrations and thus a substantial equalization capacity may be required.

FBRs using GAC potentially combine two technologies demonstrated to treat MTBE, biodegradation and GAC adsorption. FBRs have been used to treat an MTBE impacted ground water stream in Sparks, Nevada. GAC-FBRs have also been shown to be capable of degrading MTBE to below detection limit from high concentrations in bench studies.

MEMBRANE SEPARATION (REVERSE OSMOSIS)

A membrane, as discussed here, is a filter material with very small pores. It acts as a selective barrier that permits the diffusive separation of solutes in a fluid by mechanical size-sieving and/or charge effect mechanisms. Mem-

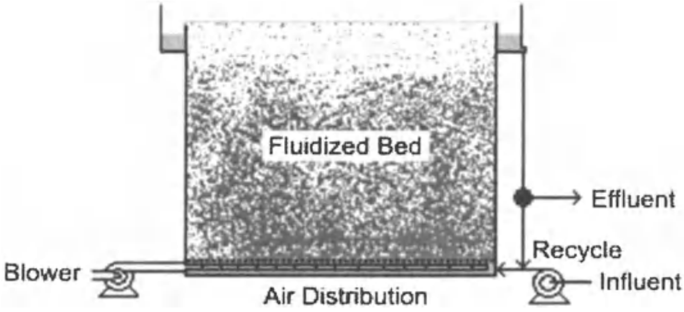

Figure 15-15. **Fluidized Bed Bioreactor**

branes can be selected to separate components over a wide range of particle sizes, molecular weights, and charges. Membranes are available in several different configurations — tubular, hollow-fiber, plate-and-frame, and spiral-wound.

RO is actually an ultrafiltration. Osmosis is the movement of some component (a solvent such as water) of a solution through a membrane from the more dilute solution to the more concentrated solution with a net long-term effect of equalizing the concentrations on both sides of the membrane. RO moves water or other solvent against the normal direction of flow by applying high pressures on the concentrated side of the membrane to overcome the high osmotic pressures across the membrane. At the same time it excludes the passage of most or all of the solute molecules by pore size and/or by charge effects. The solution passed through the membrane is called permeate or filtrate. The material retained is often called rejectate or retentate. Figure 15-16 illustrates the membrane mechanism for possible separation of MTBE from a water stream.

RO membranes can reject organic molecules greater than or equal to 150 molecular weight (MW) and a percentage of those between 25 and 150 MW. RO is a possible technology for the removal of MTBE (nominal MW equals 88) from ground water, but its practicality has not yet been demonstrated. RO membranes are subject to fouling by particulates, colloids, chemical scaling, and biological growth. Treatment may be required to remove the fouling agents. The concentrates of an RO process generally require post-treatment before disposal. In the case of MTBE, the higher concentration rejectate would require management by some other treatment.

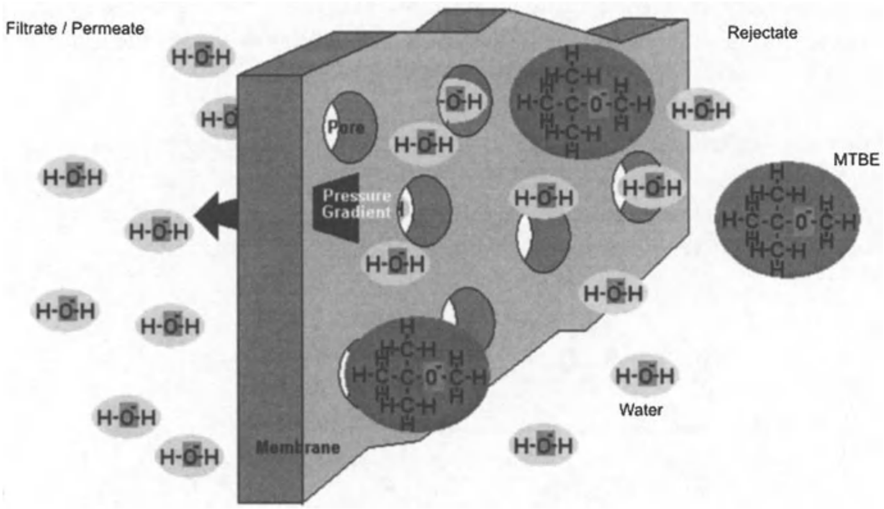

Figure 15-16. **Membrane Filter Separation**

ADVANCED OXIDATION PROCESSES

AOPs use oxidants (chemical or chemical/physical) to treat organic and oxidizable inorganic components in water. Although other oxidants can oxidize some organics, virtually all AOPs rely on hydroxyl radicals (OH•) to react with pollutants. The AOPs are capable of completely oxidizing organic materials to carbon dioxide and water, if treated long enough with enough oxidant. The common oxidants used as hydroxyl radical sources are hydrogen peroxide and ozone. Hydroxyl radical generation is stimulated by UV light, ferrous iron, cavitation, and sonication as well. A wide variety of AOPs are available to generate hydroxyl radicals for the oxidation of contaminants including: UV/hydrogen peroxide, UV/ozone, Fenton's reagent (peroxide and ferrous iron), and combined ozone and peroxide. The hydroxyl radicals react with organic contaminants, which by definition are more reduced than carbon dioxide, to oxidize them to carbon dioxide, thereby destroying them. If these organics contain elements such as chlorine, these become inorganic end products such as halide salts.

TYPES OF AOPS

Fenton's Reagent. Figure 15-17 shows the cyclical chemistry of Fenton's reagent generation of hydroxyl radicals. This process is among the oldest and simplest to implement. This is because hydrogen peroxide is widely available in bulk at various strengths and can be mixed easily *in situ* or in a reactor system at the process site with ferrous salts to generate the active hydroxyl radicals. As shown in Figure 15-17, an advantage of this system is the cyclical regeneration of the ferrous iron by a reaction of the ferric iron with another hydrogen peroxide molecule, regenerating the ferrous iron to continue to produce more hydroxyl radicals. Disadvantages of the Fenton's reagent process are its sensitivity to pH and the issue of iron *in situ* in the aquifer if reinjected or discharged in the surface effluent stream.

Peroxide — Ozone. Mixing ozone and hydrogen peroxide can also generate hydroxyl radicals. However, ozone must typically be generated on site with an electrical ozone generator, and ozone is an air emission health problem in operations and a water discharge problem, resulting in the need for

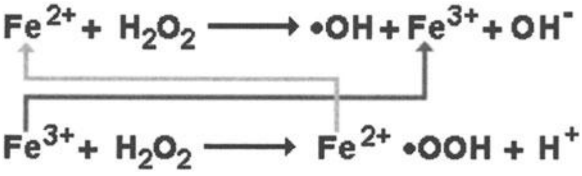

Figure 15-17. **Generalized Fenton's Reagent Chemistry**

treatment to remove ozone from the process effluent. This type of AOP has been successfully applied in the removal of MTBE from drinking water and extracted ground water (Liang *et al.*, 1999; Hydroxyl Systems and URS Corporation, 1999). The peroxone process is one that has been developed based on the use of ozone in conjunction with hydrogen peroxide to provide effective, economical treatment of MTBE. The peroxone process technology involves two essential steps, ozone dissolution and hydrogen peroxide addition in the water stream.

Cavitation/Sonication. AOPs can also be enhanced by cavitation and sonication. Both systems operate on a similar physical-chemical basis. By applying mechanical cavitation or high-energy ultrasonic vibrations to a water phase, microbubbles form, grow to a critical size (on the order of a few angstroms), and then implode. When these bubbles collapse, temperatures of approximately 3,000 to 5,000 Kelvin are generated, and products similar to those found in combustion systems are formed. Water vapor in the bubble is dissociated into hydroxyl radicals (OH•) and hydrogen atoms (H^+). The destruction of organic contaminants occurs within the bubble via thermolysis and in the bubble interface and bulk solution through reaction with hydroxyl radicals. These systems are more effective if combined with other AOPs to enhance the generation of hydroxyl radicals.

UV Driven Systems. Another mechanism for generating hydroxyl radicals is excitation of oxidants such as hydrogen peroxide with UV radiation. These systems mix the oxidant into the water to be treated and pass the water through reactors around powerful UV lamps whose radiation produces hydroxyl radicals that oxidize the contaminants. These systems have been used for years for chlorinated contaminants such as pentachlorophenol and chlorinated solvents. These systems also work on MTBE because the key is generation of the hydroxyl radical.

UV driven systems suffer from all the other hydroxyl radical issues, such as oxidation of non-target compounds and quenching reactions. In addition, turbidity and color can act as barriers to the transmission of light in the impacted water inhibiting the efficiency of oxidation. Finally, UV systems are capital intensive and expensive to operate, requiring substantial maintenance. For small footprint systems, treating low flows and low concentrations (μg/l) they can be an appropriate selection for MTBE or chlorinated contaminants. For high flows and concentrations, other technologies seem to have cost advantages.

Electron Beams. High-energy electron beams (E-beams) have also been utilized at pilot scale as an AOP. The radiolysis (radiation driven splitting) of water by an E-beam forms oxidizing hydroxyl radicals (OH•), reducing hydrated electrons (e_{aq^-}), and hydrogen atoms (H^+), also hydrogen radicals (H•), hydrogen gas, and H_2O_2. The high-energy E-beam irradiation has been demonstrated to simultaneously destroy an array of organic compounds due to the oxidation power of hydroxyl radicals and the reducing capacity of the various hydrogen forms generated. This technology is still in the research phase; reaction chemistry must be sufficiently understood prior to its availability for full-scale applications. This technology is very unlikely to ever be used specifically for MTBE or at a remedial field pump-and-treat site. First the electrical energy requirements are enormous, the system requires extensive radiation shielding (particularly massive in the target area), the technology control is a specialized technical area, and the size and cost of the systems are prohibitive for most applications. Their best applications are in mixed contaminants in sole source or high value drinking water where the extracted water can be expected to remain contaminated for decades.

LIMITATIONS OF AOPS

Chemical oxidations and the particular type to be used for a particular treatment can be limited or inhibited in their cost-effectiveness by various site and process characteristics including:

- *Contaminants* — Some contaminants, such as carboxylic acids and dicarboxylic acids, may be slower to oxidize, requiring longer residence (oxidant contact) times while others will oxidize very rapidly;
- *Intermediates* — Residence (contact) times or polishing treatments must take into account the time needed to oxidize potentially harmful intermediates. For example MTBE chemical oxidation may produce TBF, acetone, or TBA, all of which could be harmful in not sequentially destroyed as well;
- *TOC* — AOPs are indiscriminate oxidizers, leading to oxidation of non-target contaminants or natural organics (humic substances and natural hydrocarbons) along with the constituent of concern. As indicated by the bullet above, other compounds (*e.g.*, phenolics) oxidize rapidly and preferentially, rapidly consuming the oxidant;
- *Turbidity/Color* — Turbidity and color are indicators of other materials, possibly organic, in the stream that will consume the oxidants. In addition, for UV driven processes, turbidity and color can interfere with or quench the effective UV reaching the oxidant and contaminants, thereby reducing the efficiency of the oxidant system;
- *Free Radical Scavengers* — Free radicals are scavenged by specific chemicals such as the dissolved inorganics discussed below. However, excess chemical oxidant can also be a free radical scavenger, and the design dosing of the process should take this into account and change as needed as the treatment continues; and

- *Dissolved Inorganics* — Carbonates, bromine, and iron can quench oxidant reactions and alter the kinetics of oxidation of target compounds.

ADVANTAGES OF AOPS

The AOPs offer several advantages over biological or physical processes, including; destruction of contaminants, absence of secondary wastes, killing of bacteria and microorganisms, and process operability. However, AOPs are not cost-effective for high contaminant concentrations because of the large amount of oxidizing agent required. Free radical scavengers such as carbonate can inhibit contaminant destruction efficiency. The consumption of oxidants by natural organic matters in the water will also increase treatment costs and create the potential for forming undesirable byproducts. Suspended solids or solids formed by precipitation can interfere with UV transmission. There is also a concern of producing intermediates by incomplete oxidation of MTBE.

OTHER AOPS

Permanganate. Other AOPs are available, such as permanganate systems. However, preliminary testing of permanganate indicates that it is ineffective at MTBE treatment. This is not surprising, because permanganate oxidation is most effective when used to oxidize organics with double bonds (vinyl or alkene bonds).

COSTING PUMP-AND-TREAT SYSTEMS

The costs of ground water recovery are generally well-understood for the various recovery approaches (USEPA, 2001b). Variability in recovery costs is generally due to contaminant properties, localized geology, and water chemistry. These factors mostly impact the number of wells, depth of wells, simplicity/complexity of the pumping system, operation and maintenance of the recovery system, remediation time (time to capture a given volume of water and contaminant), and pre- or post-treatment for iron, suspended solids, and similar characteristics. Costs can be considerably higher for locations where the geology, ground water chemistry, or treated ground water disposal limitations require more elaborate recovery systems, pre- or post-treatment(s), or discharge fees, pipelines, extensive testing, and similar regulatory requirements.

Table 15-1 provides typical ranges of capital and operation and maintenance costs for the ground water recovery and treatment systems. The costs provided on Table 15-1 apply to approximately 70% of the pump-and-treat systems with varying treatment technologies discussed in this section and assume simple or no pretreatment or specialized post-treatment. However, the

Table 15-1. **Costs for Typical Pump-and-Treat System**

Recovery System	Capital Costs[1]	*Recovery Wells:* • \$2,000 to \$3,000/well (fixed costs) PLUS • \$100 to \$150/foot/well (variable costs)	Fixed costs include: System design, mob/demob, setup for drilling, well completion and development. Variable costs include: Labor for field oversight, well drilling and sampling, well casing and screen, pump, controllers, well piping, and disposal of waste generated during field activities.
		Transfer Piping: • \$15 /linear foot (aboveground piping) OR • \$60 /linear foot (below-ground piping)	Aboveground piping: 4-inch High Density Polyethylene pipe placed on ground or support. Belowground piping: Saw cut 6-inch concrete slab, trench, install double-wall (2½ inch, 4 inch) PVC piping, and backfill.
	Operation and Maintenance Costs[2] (per month)	• \$130/well/month (smaller system) to • \$100/well/month (larger system)	Operation and Maintenance costs include: Labor and equipment for inspection, routine mechanical maintenance, rehabilitating wells (50% each year), sampling and analysis for MTBE (semi-annual sampling), and utilities.
Treatment System	Low Costs[3]	\$0.37 /1,000 gallons	Simple system (600 gallons per minute [gpm]): High flow, no pretreatment, low influent concentrations, relaxed treatment goals.
	High Costs[4]	\$2.00 /1,000 gallons	Complex System (600 gpm): Low flow, pre/post-treatment required, high influent concentrations, and low cleanup goals.

Notes: [1] RS Means(r) Remediation Cost Data Assemblies Cost Book — 8th Edition: Recovery system cost is based on one (1) well drilled with hollow stem auger up to a depth of 100 feet bgs and installed with a 6-inch diameter recovery well with manhole cover as well completion.

[2] RS Means(r) Remediation Cost Data Assemblies Cost Book — 8th Edition: Operation and Maintenance costs are provided for a smaller system for retail stations (5 recovery wells, each pumping at 10 gpm, with total of 50 gpm) and larger system for industrial facilities (25 recovery wells, each also pumping at 10 gpm, with total of 500 gpm).

[3] From Table 6.1 California MTBE Research Partnership (2001). Assumptions: 30-year operation and maintenance life, 600-gpm flow rate, very clean effluent, no pre-treatment (See Appendix A of the report for details).

[4] From Table 6.1 California MTBE Research Partnership (2001), with 60% added for pretreatment and interference. Assumptions: 30-year operation and maintenance life. Smaller complex system (about 6 gpm) could easily be an order of magnitude more expensive/1,000 gallons.

cost drastically goes up with low flow, high concentration, and high interference to the treatment system.

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