

Treatment of Vapors from In Situ Thermal Remediation: Selecting the Best Option and Operating it Properly

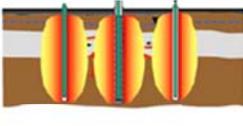
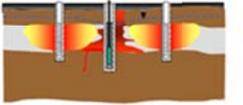
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ABSTRACT: In situ thermal remediation (ISTR) technologies are frequently used for treatment of highly contaminated source zones including sites with light and dense nonaqueous-phase liquids (LNAPL/DNAPL). Since thermal treatment often results in removal of tens or hundreds of thousands of pounds of chemicals from the subsurface in a period of several months, vapor treatment systems must be designed to handle dynamic process conditions including elevated temperatures, substantial moisture content, high contaminant mass loading and often acidic conditions. In addition, vapor treatment systems must be robust, providing reliable operational up-time because, unlike conventional “cold” vapor extraction systems, a hot ISTR site will continue to generate steam and contaminant-laden vapors even if the extraction system shuts down. An improperly or inadequately designed or operated vapor treatment system can cause schedule delays, cost over-runs and the potential release of uncontrolled fugitive emissions. Included is a discussion of lessons learned and means and methods to improve reliability of ISTR vapor treatment systems at both the design and field-operational stage. Knowledge and consideration of these critical design and operational parameters is important not only for thermal remediation contractors, but also for regulators, consultants and other remediation practitioners who may design, specify, evaluate or select contractors or vapor treatment systems for ISTR projects.

INTRODUCTION

The petroleum industry has used thermal methods for enhanced oil recovery for many years; however, consideration and development of ISTR methods only began in the late 1980s and early 1990s (Davis, 1997; Udell, 1996; Stewart & Udell, 1988). Over the last 10 to 15 years, ISTR has evolved from experimental tests and demonstrations to successful large-scale remediation projects delivered by a number of experienced practitioners. ISTR methods are robust, reliable, field-proven treatment technologies that have been used at approximately 200 sites (Kingston et al., 2010).

Figure 1 provides an overview of the three primary ISTR methods currently used for contaminant source zone remediation.

<p>Thermal Conduction Heating (TCH) or In Situ Thermal Desorption (ISTD)</p> <p><u>Applicability:</u> Heating governed by thermal conductivity ($f \sim 3$); wide range of target temperatures; low to moderate permeability settings if below the water table; otherwise any permeability (suitable for dewatered sites as well).</p>	
<p>Electrical Resistance Heating (ERH) – Joule or Ohmic Heating and convection heating, by means of the Electro-Thermal Dynamic Stripping Process (ET-DSP™)</p> <p><u>Applicability:</u> Heating governed by electrical conductivity ($f \sim 200$); boiling point of water; low to moderate permeability settings</p>	
<p>Steam Enhanced Extraction (SEE) – Steam Injection</p> <p><u>Applicability:</u> Heating governed by hydraulic conductivity ($f \sim 10^6$); boiling point of water; high permeability settings</p>	

Note: The factor f stands for the range of variation of the governing parameter in typical geological settings.

FIGURE 1. Overview of in situ thermal remediation methods.

Thermal treatment methods are often applied at highly contaminated source areas, including sites with high sorbed and dissolved phase concentrations and frequently with LNAPLs and/or DNAPLs present, including many sites with chlorinated contaminants. Heating such highly contaminated source areas results in rapid removal of contaminants over a period of months, rather than many years required for conventional “cold” remediation techniques.

Figure 2 depicts a typical contaminant mass removal over time for a thermal remediation project. As indicated on the figure, it is common on ISTR projects to experience contaminant removal rates of hundreds or even thousands of kg/day during peak periods.

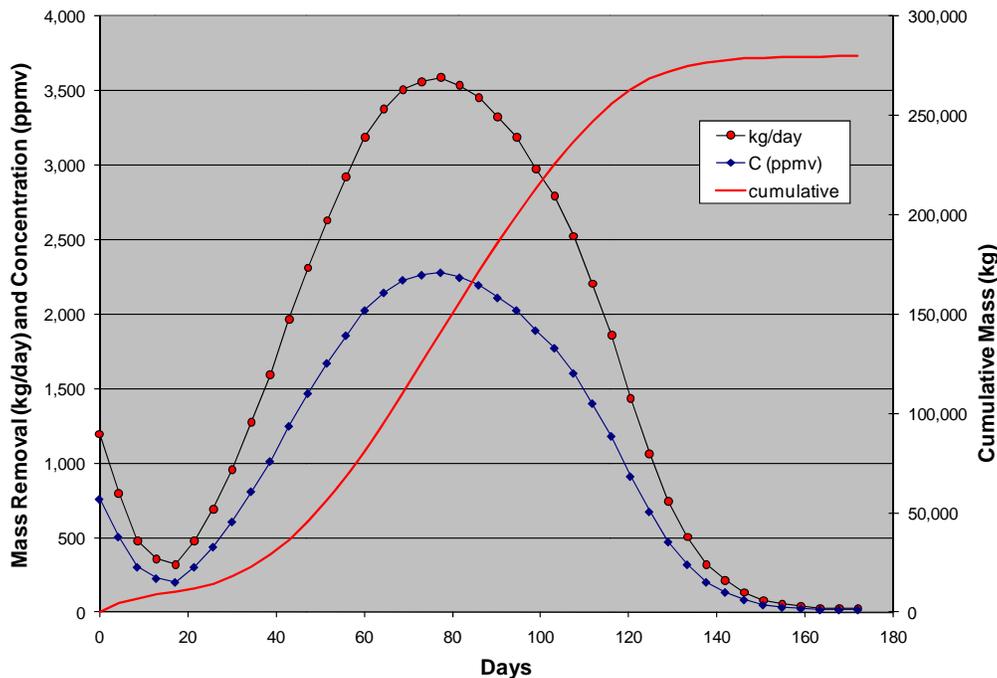


FIGURE 2. Typical thermal treatment site mass removal rate.

Figure 3 presents relative mass removal data versus average subsurface temperature for 5 chlorinated solvent remediation sites. Vapor pressure of NAPL constituents increases substantially with temperature leading to a significantly increased rate of contaminant volatilization. At the eutectic point, the sum of the partial pressures of the NAPL phase and water equal the local ambient pressure, allowing the NAPL phase to boil off at a temperature below either its boiling point or the boiling point of water (e.g., while the boiling point for pure PCE is 121°C, the eutectic [co-boiling] point for PCE in the presence of water is 87°C). The data in Figure 3 show that for these chlorinated solvent sites there is a rapid increase in the rate of mass removal beginning around 70°C, as portions of the subsurface reach the eutectic temperature and DNAPL begins boiling, resulting in high COC extraction rates in this temperature regime.

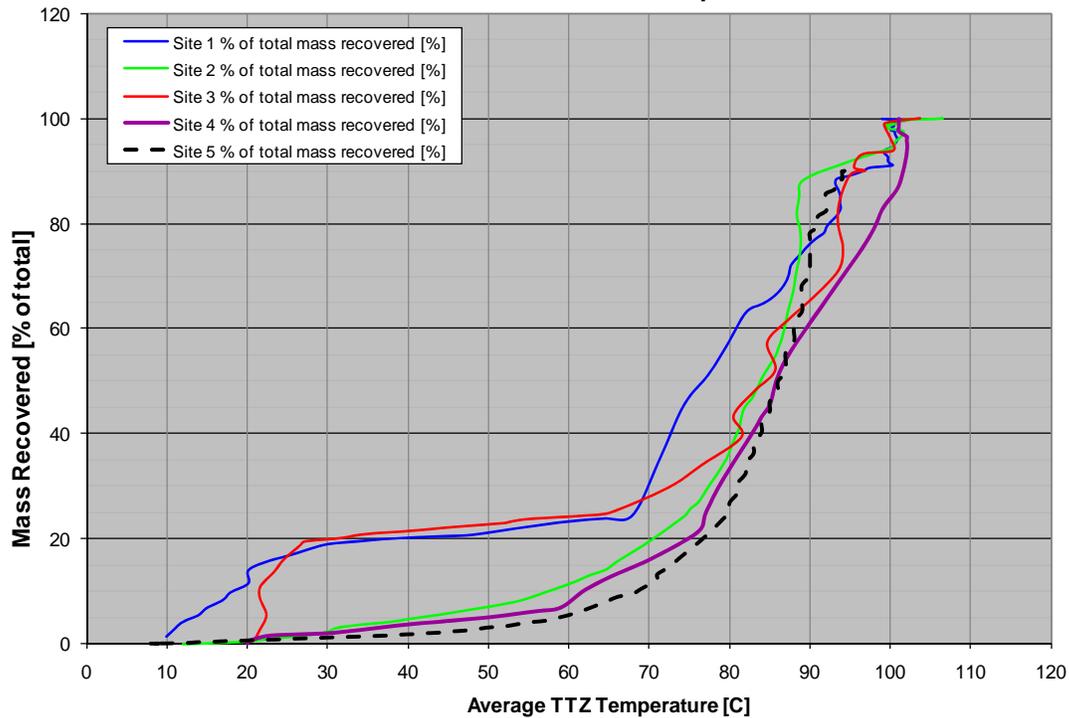


FIGURE 3. Mass removal vs. average in situ temperature for 5 chlorinated solvent Sites.

Vapor treatment systems for ISTR sites must be robust and reliable because, unlike conventional “cold” vapor extraction systems, a hot thermal remediation site will continue to generate steam and contaminant-laden vapors even if the extraction system shuts down. An improperly or inadequately designed or operated vapor treatment system can cause schedule delays, cost over-runs and the potential release of uncontrolled fugitive emissions. Incorporating installed spares and redundant components in our vapor and liquid treatment systems has enabled the authors to maintain vapor treatment system up-time in excess of 98% over more than 12 years operating at ISTR sites.

THERMAL TREATMENT OPERATING ENVIRONMENT

Heating the subsurface to temperatures of 100°C (212°F) or higher to boil groundwater and soil pore water generates significant amounts of steam by virtue of the fact that the expansion from liquid water to steam is approximately 1600:1 on a volume basis (i.e., 1 m³ of water equals 1600 m³ of steam).

Unlike conventional “cold” SVE where it is often necessary to apply an elevated vacuum to establish a “radius of influence,” the subsurface steam generated at thermal treatment sites provides the primary motive force to deliver contaminant-laden steam and subsurface vapors to the extraction wells. For sites heated to, and held at, the boiling point of water, the extracted vapor stream is a hot saturated mixture with water (as steam) often comprising more than half of the total extracted mass flow rate.

Treating sites with chlorinated compounds also provides the potential for corrosion. Chlorine molecules liberated by the thermal treatment process have a high propensity to form hydrochloric acid (HCl) when in contact with water. Acidic HCl condensate is extremely aggressive, particularly against austenitic stainless steels (300 series), due to chloride stress corrosion cracking which can eat through standard wall stainless steel pipe/plate in a matter of days, even at low percent level HCl concentrations.

For ISTR sites where it is necessary to heat above the boiling point of water (e.g., for treatment of semivolatile organic compounds (SVOCs), coal tar, creosote, pesticides, PCBs and dioxins) it is frequently desirable to maintain a heated/insulated extraction manifold to prevent condensation of high boiling contaminants in the piping network. Thus, front end treatment plant equipment may receive incoming vapors at temperatures of 120°C to 200°C (250 °F to 400°F).

These conditions commonly encountered on ISTR sites necessitate careful evaluation of the mass and energy balance during the design process to select and size appropriate cooling, condensing, and treatment equipment. Vapor treatment systems for ISTR sites must be designed to handle hot, water-saturated vapors and must be sufficiently robust to manage contaminant loadings that can go from a few kg/day to hundreds or thousands of kg/day over a span of several weeks. Given the elevated temperatures, potential for chemical attack from recovered NAPLs and potentially corrosive conditions, materials of construction considerations are also critical for thermal treatment systems.

VAPOR TREATMENT APPROACHES FOR ISTR SITES

Vapor treatment options for ISTR sites may include sacrificial or steam regenerated granular activated carbon (GAC), adsorption onto synthetic media, cooling and condensation, thermal or catalytic oxidation or combinations of these systems. The following sections provide a brief overview of the various vapor treatment technologies and some lessons learned over years of implementing vapor treatment at ISTR sites.

Sacrificial GAC. GAC consists of a carbonaceous base material which may be formed from coal, peat, wood or nut shells (e.g., coconut shell). The carbon source material is first dried then heated at 400°C to 600°C in oxygen deficient atmosphere that cannot support combustion then activated, typically by exposing to steam or carbon dioxide at high temperatures (800°C to 1000°C), to develop the microporous structure needed to create the adsorption sites (Calgon Carbon Corp., 2007). The resulting GAC is a porous media with a very large surface area to volume ratio onto which many organic chemicals

readily adsorb. According to one manufacturer, “one pound of activated carbon provides a surface area equivalent to six football fields” (Calgon Carbon Corp., 1999).

Adsorption on GAC is a proven and effective technology for many chlorinated and non-chlorinated volatile organic compounds (VOCs) and SVOCs; however, adsorption isotherms must be reviewed for applicability to the selected contaminant. For example, highly volatile (high vapor pressure) compounds such as methylene chloride, vinyl chloride and MTBE do not adsorb well to activated carbon.

The primary design parameters for sizing vapor phase GAC vessels are the system flow rate, anticipated contaminant load, superficial velocity (typ. 5-50 cm/s), bed depth and pressure drop (US EPA, 1991; US EPA, 2006; USACE, 2001). Activated carbon systems typically consist of multiple media beds plumbed in lead/lag or series/parallel configurations. Adsorption on GAC can typically achieve contaminant removal rates of 98% to 99%, or higher if multiple beds are placed in series.

The hot, saturated vapors extracted from thermal treatment sites require conditioning for temperature and humidity to ensure efficient treatment by the GAC. For example, vapor influent conditions at the mid-heating phase at an ISTR site are typically 80°C to 90°C (180°F to 190°F) and saturated (100% relative humidity). For effective and efficient adsorption onto GAC, incoming vapors are typically conditioned to a temperature of 40°C to 50°C (100 °F to 120°F) and 50% relative humidity. This conditioning step utilizes a heat exchanger/condenser (e.g., shell & tube, fin/fan) and moisture separator, followed by a reheating step to boost the vapor temperature 5°C to 10°C [10°F to 20°F]) to raise the vapor above the dew point and optimize the relative humidity prior to the GAC media beds.

For high temperature thermal conduction heating (TCH) projects when soils will be heated above the boiling point of water and the incoming vapor stream is hot and dry, it may not be necessary or desirable to cool the vapors to 50°C (100°F) as the SVOC constituents may condense out of the vapor phase at these low temperatures. For some SVOC sites, the authors have operated vapor GAC polishing systems at temperatures up to 95°C (200°F) to prevent condensation of the COCs in the piping or treatment vessels (Bierschenk, et al., 2004).

Adsorption of most VOCs is an exothermic reaction; however, the heat of adsorption is especially high for ketones (e.g., MEK) and aldehydes (USACE, 2003). These constituents represent a special concern and must be examined closely to ensure that appropriate safety mechanisms are in place. Coconut shell based activated carbon can spontaneously ignite at temperatures in the range of 240°C to 300°C (460°F to 570°F), while coal based carbons typically have a higher autoignition temperature (Zerbonia, et al., 2001). Localized hot spots that develop within a GAC bed may cause contaminant vapors or carbon granules to spontaneously ignite. Once a GAC bed ignites, whether free burning of residual solvents or smoldering of GAC granules, it is very difficult to put out. This is a potentially dangerous situation that could lead to excess temperature and thermal stress on the vessel and, in extreme cases, structural failure or explosion of the vessel.

Lessons Learned – Sacrificial GAC. There are several concerns and lessons learned for utilization of vapor phase GAC on a thermal site.

- Effective conditioning is necessary to maintain efficient use of GAC. Preventing condensation of vapors inside GAC beds is important to minimize the potential for carbon pores to become saturated with water rather than contaminants. At the Memphis Depot site, ISTR was applied to residual CVOCs in the unsaturated zone. Over 5,600 kg (12,500 lb) of CVOCs were removed in the vapor phase and treated using sacrificial GAC, with GAC loadings in approaching 30% as a result of effective vapor conditioning (Heron, et al., 2009).
- Effective conditioning is especially important at sites with chlorinated contaminants. Acidic condensate can damage or destroy the GAC vessel and media support screens. Experience has shown that carbon steel vessels with appropriately rated coatings (e.g., epoxy, vinyl ester) and titanium media support screens have been effective at withstanding potentially corrosive conditions.
- For ISTR sites, especially high-temperature thermal treatment sites, it is most critical to include temperature monitoring and alarms upstream of, and inside, each GAC bed to protect against ignition of the GAC beds. Monitoring of carbon monoxide (CO) at the vessel effluent is another good early warning indicator of a potential bed fire. Rapidly rising CO levels can indicate smoldering combustion in the bed.
 - In the event of the bed fire, isolate the bed immediately to deprive it of oxygen and prevent extension of the fire.
 - Include provisions in the design of the vessel to allow introduction of water to quench burning media (e.g., internal sprinklers or quenching ports) along with appropriate venting provisions to relieve the large volume of steam that will result when quenching is initiated. Effective quenching of the bed fire will likely result in loss of the media (since it will be saturated with water) but should prevent a catastrophic failure of the vessel.
- GAC may be enhanced for treatment of compounds with poor adsorption characteristics. For example, the authors have used a potassium permanganate impregnated GAC for effective treatment of vapors containing vinyl chloride (LaChance, et al., 2006).
- Experience has shown sacrificial GAC to be most applicable for ISTR sites with lower contaminant mass, typically less than 4500 kg (10,000 pounds) of COC's. Steam regenerated carbon may be cost-effective for higher COC mass loads.

Steam Regenerated GAC. Steam regenerated GAC is used in place of sacrificial GAC for sites with moderate to high contaminant mass loadings, and may also be a cost-effective alternative for ISTR sites where steam injection is a component of the selected thermal remedy (for example: Heron et al., 2005). These systems use many of the same principles as sacrificial GAC, with the obvious added consideration of safely operating a boiler and steam delivery system. Steam regenerated GAC systems must be rated for the applied steam pressure and configured with appropriate venting and pressure relief devices. Steam regenerated vessels are typically insulated to minimize condensation in the vessel during the regeneration process.

Figure 4 presents a typical process flow diagram (PFD) for a steam regenerated GAC system. Steam regeneration is most often triggered automatically with actuated valves operated based on a timed cycle, but could be configured to regenerate based on effluent

VOC concentrations. The vessel undergoing regeneration is isolated and taken off-line while the other vessels in the system continue to operate. Steam at low to moderate pressure (typically 35-170 kPa [10-30 psig]) is flowed through the vessel, counter-current to the normal adsorbing flow direction for an appropriate time period (typically 2 to 4 hours—longer with higher boiling COCs or high mass load) to desorb the COCs off the GAC media. Once the steam cycle is complete (as determined by programmed cycle time or COC stripping concentration monitoring), warm heated air is swept through the vessel for several hours to remove residual moisture and dry the GAC, then cool ambient air is used to cool the media before the regenerated vessel is placed back in service.

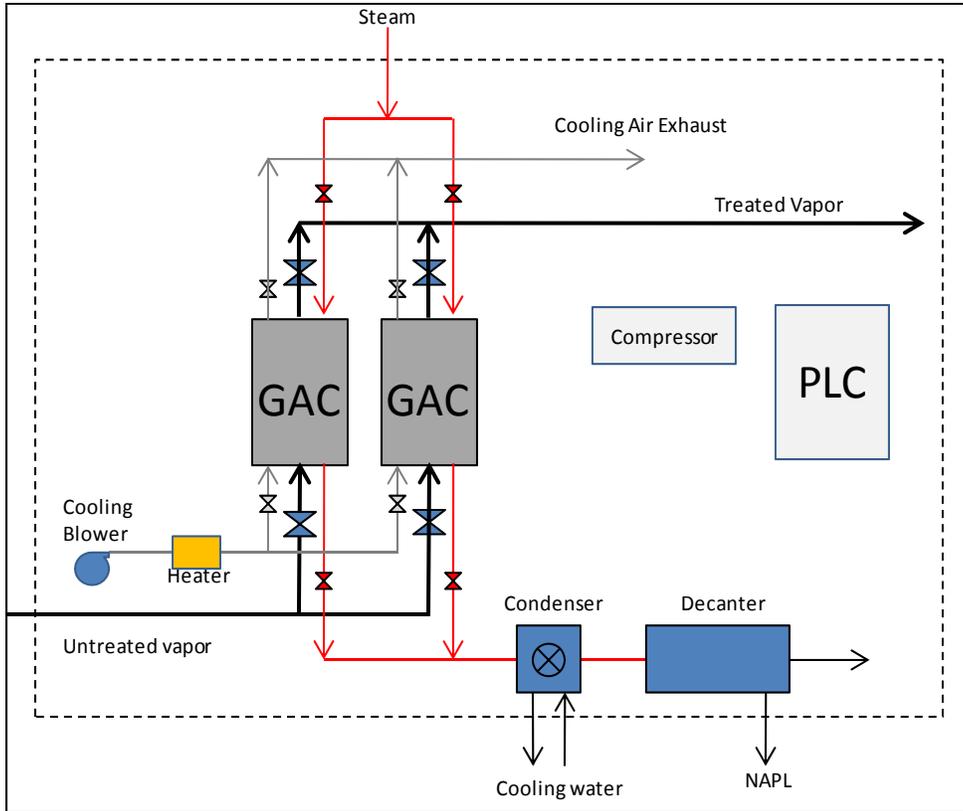


FIGURE 4. Typical steam regenerated GAC process flow diagram.

Effluent steam leaving the vessel is passed through a condenser and moisture separator to condense the water and COCs. The condensate then flows to a decanter to separate the recovered NAPL from the water. NAPL is drummed for disposal or returned to the plant if the recovered solvent is reusable. Effluent water is generally treated as required for compliance with discharge permits.

While on-site steam regeneration does not typically restore GAC to its full factory-new adsorption capacity, it can typically reach 50% to 70% of new capacity and withstand hundreds of regeneration cycles before the carbon needs replacement (USEPA, 2006).

Lessons Learned – Steam Regenerated GAC.

- In years past, there were a number of manufacturers of packaged steam-regenerated GAC systems. Through consolidation in the carbon industry and changes in business models, several carbon manufacturers have exited the business of providing engineered and packaged steam regenerated carbon systems. With that in mind, some attention must be paid to selection of a vendor with demonstrated design and implementation experience to ensure procurement of a high-quality steam regenerated GAC system.
- Due to the presence of residual moisture and residual COCs in steam regenerated GAC beds, and therefore lower adsorption capacity, it is good practice to include a downstream moisture separator and a large sacrificial GAC bed (typically 5 to 10 times larger than the primary steam regenerated beds), for effluent polishing.
- In some cases, NAPL recovered in a steam regenerated GAC system may be used as supplemental fuel to fire the steam generator, lowering overall project costs. Recovered NAPL may require additional filtration for water removal prior to use as a combustion fuel. However, if the NAPL is not reusable, potential long-term liability issues and costs for off-site disposal must be considered.
- Capital investment in a steam-regenerated carbon system is substantially more than a low pressure sacrificial GAC system. Pricing for a steam regeneration system capable of treating 600-1800 m³/hr (1000-3000 scfm) may range from \$300-\$700K, depending on materials of construction and automation options selected. However, for thermal sites with moderate to high contaminant mass (5,000-50,000 kg) [10,000-100,000 lbs], where permitting of a thermal oxidizer may be difficult or time consuming, steam regenerable GAC may be applicable.

Synthetic Adsorbent Media. Synthetic adsorbent media comprises a class of engineered adsorptive media with capability to remove specific organic compounds from liquid and vapor streams. Synthetic adsorption media is typically a hard, spherical, polymeric bead with good physical, chemical and thermal stability properties, designed to be used in a packed bed arrangement similar to GAC. However, in addition to their enhanced micro- and macro-pore structure, a primary advantage of many synthetic adsorbents is that they are engineered to be organophilic and hydrophobic—meaning that these synthetic adsorbent media are not as susceptible to water fouling as vapor phase GAC.

This moisture resistant quality allows these adsorbent media to be used in elevated humidity environments and helps provide synthetic media with an adsorption capacity often 5 to 10 times higher than comparable GAC media. Although synthetic media is able to provide generally higher adsorptive capacities than GAC, it does come at a higher cost. Pricing for synthetic media varies based on the specific media selected, but may range from 10 to 40 times the unit price of GAC (USACE, 2001; EPA, 2006). Given the significantly higher unit cost of synthetic media compared with GAC, it is most frequently deployed in a steam regenerated configuration (similar to that described above for GAC). As a result of its hydrophobic qualities and typically larger pore structure than GAC, synthetic media may return to 50% to 90% of its original adsorptive capacity after regeneration (US EPA, 2006).

Lessons Learned – Synthetic Absorbent Media.

- One consideration that arose on a recent thermal project employing synthetic media is the higher pressure drop that results from the small nominal diameter of the media beads. The smaller particles required the use of custom-designed fine mesh support screens. While this is not generally an issue with synthetic media used in liquid phase applications where liquid can be pushed through the media vessel under pressure in a down-flow configuration to ensure thorough distribution and contact, it does pose challenges for vapor phase applications where higher pressure pumping may not be possible. Increasing vapor delivery pressure too high may channeling and/or media carryover to the exhaust. Typical vapor phase media beds are configured in an up-flow treatment arrangement with down-flow (counter-current) regeneration. On advice of the manufacturer, the synthetic media bed for this application was designed for down-flow treatment and down-flow (co-current) regeneration.
- Synthetic media is generally not subject to inter-bed hot spots and is therefore less susceptible to bed fires than GAC. However, the polymeric construction of many synthetic adsorbents does impose process temperature limitations. As such, temperature control is necessary when using synthetic media on ISTR projects. At one site where synthetic media is used, incoming vapors from the thermal system had to be cooled to below 38°C (100°F) prior to entering the synthetic media beds. While this may be acceptable for some VOC constituents, synthetic media is not likely to be a good choice for vapor treatment on a high temperature thermal site treating SVOCs, as the cooling required to allow use of the media would likely result in condensation of the SVOCs prior to the media bed.

Cooling/Condensation Systems. Cooling and condensing are frequently used in industry to facilitate recovery and reuse of solvents (e.g., in the printing and coating industries), to capture and recover product during bulk transfer operations (e.g., tanker fill and discharge) and for capturing and recovering products from bulk storage tank vents. One advantage of such a system is its ability to safely treat vapors at very high concentrations, even at or above the lower explosive limit (LEL) concentration range. In addition, condensing systems can be especially cost effective where the recovered product can be reused by the facility or recycled at low or no cost. However, while cooling/condensing systems may still be effective at recovering chemical constituents at sites with a mix of subsurface contaminants (e.g., a drum disposal site), it is not likely that such a blend would be recyclable and therefore disposal costs, often as a hazardous waste, must be included in consideration of the technology.

Application of such cooling and condensing systems to the remediation industry has been practiced by several vendors. The authors have experience with the cryogenic-cooling and compression technology (C3 technology) developed and marketed by G.E.O. Inc. of Corona, CA. In the G.E.O., Inc. C3 process (Kessel, 2008), extracted vapors are first condensed to approximately 1000 kPa (150 psi, 10 bar) with a conventional piston or rotary screw air compressor, then passed through an air-cooled after-cooler to reduce the temperature of the vapor stream to near ambient temperature. Condensed water vapor is removed during the compression and after-cooling steps. The vapor stream is then cooled

to -40°C (-40°F) in staged, cryogenic refrigerated heat exchangers. At this low temperature, the majority of the solvent contaminant is condensed to liquid form and delivered to a receiver vessel and decanter for separation. The cold vapor is then passed through a regenerative adsorber vessel containing a proprietary synthetic adsorbent media to remove residual VOCs. A slip stream from the adsorber is recycled to the vapor influent, while the primary stream is exhausted to atmosphere, typically after passing through one or more sacrificial GAC beds for a final polish.

Electrical consumption for the cooling/condensing system is higher than the other vapor treatment alternatives considered here, estimated at approximately 0.5-0.6 kW/m³/hr [0.3-0.4 kW/SCFM of vapor] (G.E.O., Inc., 2012). While this may be a relatively large electric service in comparison with typical remediation systems, it is not overly large in relation to the electric service needs for electric powered ISTR systems.

Lessons Learned – Cooling/Condensation Systems.

- Extracted vapors from the ISTR wellfield must be cooled to a maximum of approximately 40°C (100°F) prior to entering the G.E.O., Inc. C3 system to prevent overheating of the air compressors. Thus, utilization of this system is limited to contaminants that do not condense at this pre-conditioning temperature.
- The chilled vapor recycle on the G.E.O., Inc. C3 system returns a slip stream from the adsorbent media to the process influent at nearly the full discharge pressure of the air compressor—roughly 1000 kPa (150 psi, 10 bar). Since most elements of the ISTR vapor treatment system are designed for moderate to low vacuum, it is necessary to ensure that all elements of the vapor extraction train are designed to withstand this elevated system operating pressure.
- On several thermal sites where the chilling/condensation system has been used, the condensed NAPL has been recovered as an oil/water emulsion. The reason for this is uncertain, as the system has been used successfully on unheated sites to recover “clean” NAPL. It may be related to the extraction method or the high proportion of water in the extracted vapor steam making it more difficult for the condensing system to separate water from the NAPL. In any case, the NAPL emulsion is typically not suitable for recycling and results in an increased volume of NAPL solution for disposal.
- The authors have evaluated, and will consider in the future, the potential use of a cooling/condensation system for reducing VOC load to a thermal oxidizer during the peak contaminant mass removal period at an ISTR site. This approach would only require the high energy demand of the cooling/condensation system for one or two months, and reduce the required VOC-loading capacity of the thermal oxidizer.

Thermal Oxidation Systems. Thermal oxidation systems comprise systems that raise the temperature of an organic compound above its autoignition temperature in the presence of sufficient oxygen, and maintain that elevated temperature for sufficient time to complete combustion to carbon dioxide (CO₂) and water (USEPA Fact Sheet, n.d.). Along with the specific compound or mix of compounds, primary design criteria for thermal oxidizers include residence time, combustion/reaction chamber temperature, turbulence

(i.e., mixing) and availability of sufficient oxygen. These parameters combine to determine the achievable destruction/removal efficiency (DRE) by thermal oxidation.

Thermal oxidizers are available in a wide variety of designs, each with specific advantages and disadvantages. Oxidizers may be electrically heated or natural gas/propane fired; although, typically only smaller devices are electrically powered. For ISTR sites, the authors have used a variety of devices including direct fired thermal oxidizers, flameless thermal oxidizers, as well as recuperative and regenerative thermal oxidizers. Achievable DRE's vary based on the type of oxidizer and design parameters selected, but DRE's of 98% to 99% are readily achievable and DRE's up to six-9's (99.9999%) can be achieved with high temperature and long residence times (e.g., 2 sec at 1200°C [2200°F]).

For sites with chlorinated or fluorinated compounds, a caustic scrubber is typically required. Hot oxidizer exhaust vapors must be rapidly cooled in a water and/or caustic solution spray quench vessel to minimize potential for formation of products of incomplete combustion (PICs, e.g., dioxins). The cooled vapors then flow in a counter-current manner through a high-surface-area packed bed scrubber tower where the vapors are contacted with a caustic solution (typically 20% to 50% NaOH). Acid gas neutralization efficiency of 95% to 99% is typically achievable. Due to the highly aggressive nature of hydrofluoric acid (HF), thermal oxidizer and scrubber systems treating fluorinated compounds cannot use standard glass-fiber (i.e., silica) based insulation materials, and therefore require HF-resistant (i.e., high alumina) cast refractory insulation.

Catalytic oxidizers, which are commonly used on remediation projects are notably absent from the list of oxidizer types used by the authors for ISTR sites. Catalytic oxidizers, which typically utilize a noble metal or noble metal on ceramic catalyst, allow combustion to occur at lower temperatures, typically in the range of 200°C to 500°C (400°F to 1000°F) and can typically achieve DREs in the range of 95% to 99%. The lower operating temperature requires less supplemental fuel to maintain the required reaction chamber temperature and is often well suited to remediation projects with longer duration or low contaminant concentrations. Catalytic oxidizers are sensitive to the heating value and concentration of incoming vapor streams and can typically only tolerate a modest (250°C) [450°F] temperature differential across the catalyst, which can pose a conflict for thermal treatment sites where contaminant mass removal rates may overwhelm the device. In addition, for sites treating chlorinated constituents, catalytic oxidizers must operate at approximately 480°C (900°F), which reduces the fuel savings benefit and also forces the oxidizer to operate very close to the temperature limit of the catalyst (typically ~670°C [1200°F]) (Herbert, 2012). For these reasons, the authors have not had occasion to utilize catalytic oxidizers for ISTR sites.

Regenerative thermal oxidizers (RTOs) consist of dual ceramic-packed beds, with a switching valve arrangement. Hot exhaust gasses exiting the primary treatment bed are used to preheat vapors entering through a ceramic-filled pre-heat bed. The valve positions and flow direction through the media beds reverse every 3 to 5 minutes to maintain stable temperatures and optimize heat recovery. RTOs can typically achieve DRE's of 95 to 99% and, by virtue of their switching bed design, RTOs are typically the most thermally efficient oxidizers, with heat-recovery efficiencies well above 90%. However, given their high thermal efficiency, RTO's may not be best suited for processing high-concentration vapor streams (as the energy content in the stream can overheat the beds).

Direct fired thermal oxidizers are perhaps the simplest variety of thermal oxidizer. Extracted VOC laden vapors are introduced into a hot combustion chamber and mixed with supplemental fuel and combustion air as required to maintain the desired combustion chamber temperature, typically 870°C to 1000°C (1600 to 1800°F), and up to 1100°C (2200°F) where required. A preheat heat exchanger which uses hot oxidizer exhaust gases to preheat the incoming fume stream may be added to increase the thermal efficiency of the device to a typical range of 50% to 65%.

Lessons Learned – Thermal Oxidizers.

- While thermal oxidizers may be the most capital intensive of the vapor treatment alternatives considered, they provide a robust and reliable system capable of handling the hot, moist, variable concentration vapor streams generated on ISTR sites.
- Incorporation of redundant sensors and components increases system reliability and minimizes down time. For example, incorporation of multiple flame sensors, multi-point thermocouples and back-up sensors for critical alarm functions improves system safety and reliability. Maintaining a kit of critical (or long-lead time) spare parts on site is also important to ensure maximum operational service.
- Increasing temperature and/or residence time to gain increased DRE impacts the physical size of the oxidizer and scrubber components and interconnecting piping. The increased size and weight must be considered in the system layout and the supporting pad structure.
- For ISTR sites, an induced draft design is generally preferred, such that the entire treatment train (including oxidizer and scrubber) is under negative pressure, thus any leaks are inward to minimize potential for fugitive emissions. In this configuration, it is generally advisable to install an additional moisture separator between the scrubber exhaust and the induced draft fan or vacuum blower.
- At several ISTR sites where RTO's were used for vapor treatment, a hot gas bypass valve was installed between the packed media beds allowing the hot exhaust vapor to bypass the heat recovery step and pass directly to the oxidizer outlet to prevent overheating of the RTO. In addition to this consideration, the external plenum and valve train on the RTO must be insulated to prevent condensation. This is especially important for chlorinated sites, as significant corrosion can occur at cold spots in the external valve train.
- Caustic scrubbers are available in a variety of designs. Scrubber systems with a venturi quench may not be well suited for the variable flow conditions experienced over the duration of ISTR projects. Whereas, so-called “washed wall” designs have proven to be robust in handling changes in flow rate and composition (i.e., varying moisture load) and have been resistant to corrosion of the quench vessel.
- Caustic soda (NaOH) is available in a variety of compositions and strengths, but is generally produced for industry use at 50% strength. The 50% NaOH solution freezes at 11°C (54°F), which can cause problems with outdoor storage at remediation sites. The 50% NaOH is often diluted to approximately 25% strength for use at remediation sites for safety reasons and to improve the freezing point to about -

16°C (3°F). The authors have also used a blend of NaOH and KOH to improve freezing point performance. It is also important to note the maximum specific gravity and density of the caustic blend (e.g., specific gravity of 50% NaOH is 1.52), and ensure that the selected storage tank is rated for the caustic solution density.

DISCUSSION

Each ISTR site deserves specific consideration with regard to contaminants, extracted vapor conditions (e.g., flow rate, temperature, humidity), available equipment space, regulatory environment and other site-specific factors. However, the authors' experience has taught them a number of things that can be summarized here.

- Vapor treatment systems for ISTR sites should be designed with built-in redundancy. ISTR vapor treatment systems should include installed duplex blowers, pumps and other critical components to maximize system uptime.
- An emergency back-up power supply (i.e., emergency generator) should be provided to allow continued operation of the vapor treatment system in the event of a loss of grid power (to prevent fugitive emissions).
- Careful consideration must be given to costs and potential long-term liability for disposal of residuals and waste products if selecting sacrificial GAC or one of the on-site regenerated alternatives that produce a NAPL condensate (e.g., steam regen GAC, synthetic adsorbent or cooling/condensing). Effective thermal treatment of source zones often removes more contaminant mass than conservative models may predict to be present in the subsurface, and disposal of large quantities of NAPL as a hazardous waste may be costly.
- Thermal oxidizers may be the most capital-intense and operationally complex treatment method and often (but not always) require a significant quantity of supplemental fuel. However, oxidizers provide destruction of site contaminants without generating a residual waste requiring disposal. For chlorinated treatment sites, the scrubber blowdown will include water with elevated salt content which may pose discharge concerns at some locations. Permitting for thermal oxidizers, particularly for sites with chlorinated contaminants, may also be time consuming. However, many public and regulatory agency concerns can be addressed with a thoughtful thermal oxidizer design.
- It is most important to have trained and skilled system operators to maintain and optimize operation of the selected vapor treatment alternative to achieve maximum up-time and ensure compliance with applicable discharge permits.

As a general rule of thumb, the authors have found that simple sacrificial GAC or cooling/condensation methods to be most applicable for pilot and full-scale ISTR sites with contaminant loadings around 4500kg (10,000 lb) or less. Steam regenerated carbon (or synthetic media, where applicable) may be well suited for sites with modest to high, but well-defined, contaminant loading (>4500 kg, [>10,000 lb]). Use of steam-regenerable media may be especially cost effective at ISTR sites where steam injection is a component of the remediation or where the recovered product can be re-used (e.g., either by the owner's plant or as fuel for the steam generator). In general,

where contaminant loadings are expected to be high (>20,000 kg, [>50,000 lb]), where contaminant mass is uncertain or where the waste is comprised of a mixture of many organic contaminants (as is often found at drum disposal and waste pit sites), thermal oxidizers provide the highest range of flexibility and minimal off-site waste disposal costs. The trade-off for this flexibility and capacity is that thermal oxidizers are capital intensive and often (but not always) consume a significant amount of supplemental fuel which must be included in the total cost evaluation.

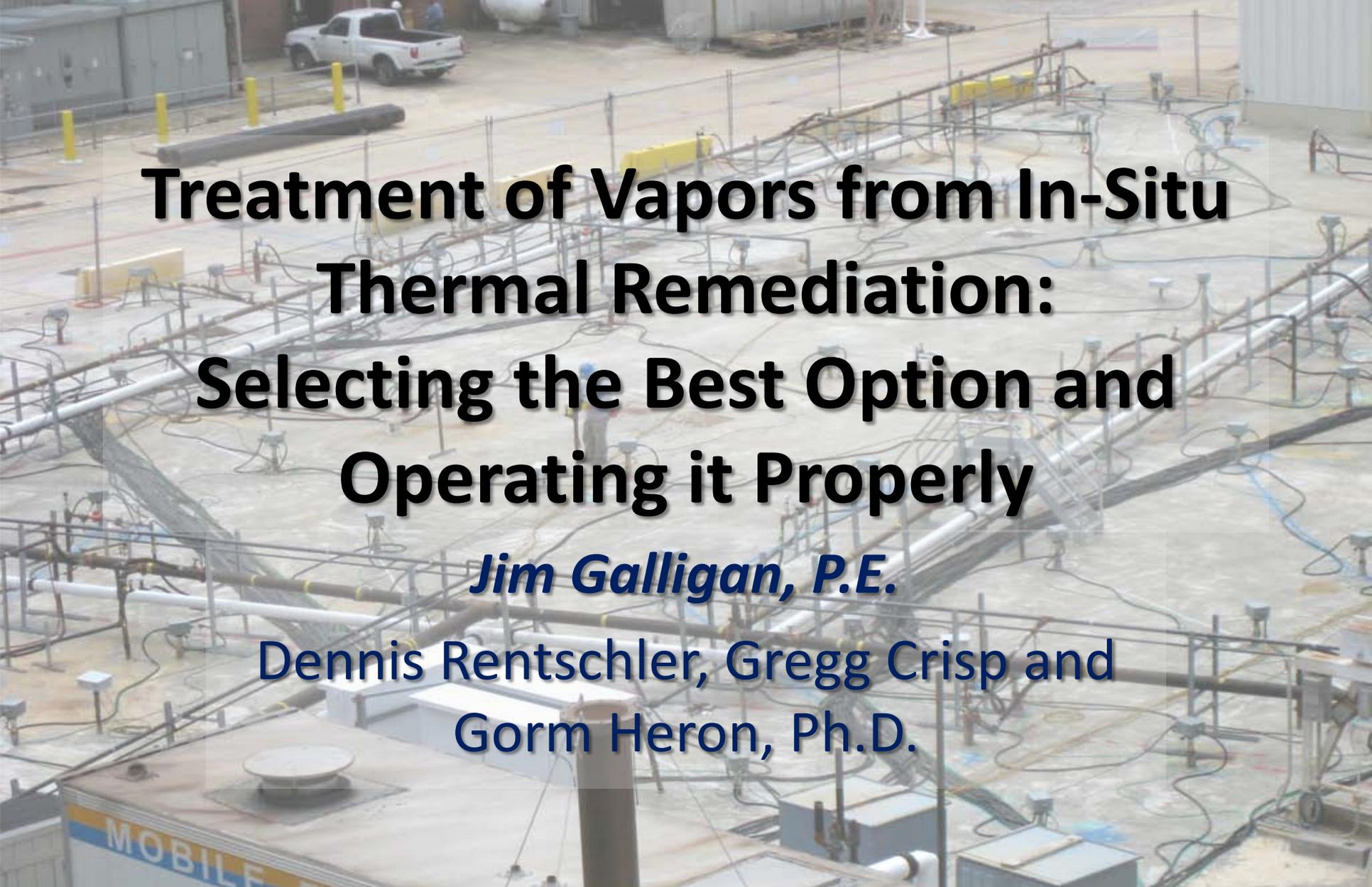
CONCLUSIONS

The authors have nearly 40 years of combined experience designing and operating vapor treatment systems for use at ISTR sites. Their experience has taught them that selecting and operating vapor treatment systems at these sites poses some particular challenges. ISTR projects are typically high-intensity, short duration projects when compared with conventional “cold” remediation technologies. Therefore, vapor treatment systems for ISTR sites must be designed to be robust and highly reliable, capable of handling significant changes in both vapor flow rate and contaminant concentration over the duration of a project and be able to withstand elevated temperature while resisting chemical attack from recovered COCs and potentially acidic condensate. Regardless of which vapor treatment system is selected, it is critical that the system be designed to handle the full range of expected operating conditions, with some contingency to accommodate unanticipated site conditions. The vapor treatment system must then be tended by skilled and experienced operators to maintain the system and optimize its performance.

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Treatment of Vapors from In-Situ Thermal Remediation: Selecting the Best Option and Operating it Properly

Jim Galligan, P.E.

Dennis Rentschler, Gregg Crisp and
Gorm Heron, Ph.D.



Think Thermal When...

- ✓ You have a Contaminant Source Zone or Hot Spot(s)
- ✓ Site is Heterogeneous and/or Low Permeability
- ✓ Stringent Cleanup Levels Must be Achieved, Quickly
(or you just need to remove a lot of mass)
- ✓ Costly Soil Disposal as Hazardous Waste

Thermal is Especially Well Suited if:

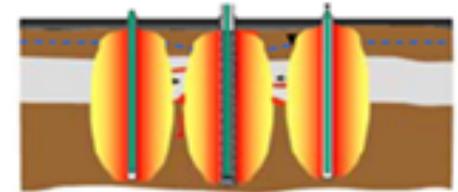
- ✓ The Treatment Zone is Deeper than 10 feet bgs
- ✓ There's a Mixture of Contaminants
- ✓ The Site is Complex, and/or
- ✓ Long-Term O&M is Too Costly



In-Situ Thermal Remediation Methods

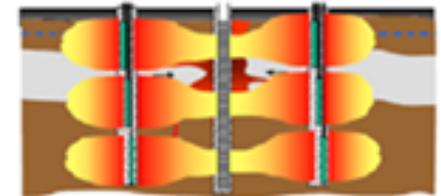
Thermal Conduction Heating (TCH) or In Situ Thermal Desorption (ISTD)

Applicability: Heating governed by thermal conductivity ($f \sim 3$); wide range of target temperatures; low to moderate permeability settings if below the water table; otherwise any permeability (suitable for dewatered sites as well).



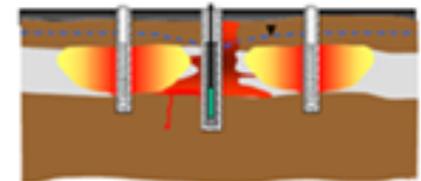
Electrical Resistance Heating (ERH) – Joule or Ohmic Heating and convection heating, by means of the Electro-Thermal Dynamic Stripping Process (ET-DSP™)

Applicability: Heating governed by electrical conductivity ($f \sim 200$); boiling point of water; low to moderate permeability settings



Steam Enhanced Extraction (SEE) – Steam Injection

Applicability: Heating governed by hydraulic conductivity ($f \sim 10^6$); boiling point of water; high permeability settings



Note: The factor f stands for the range of variation of the governing parameter in typical geological settings.



TERRATHERM

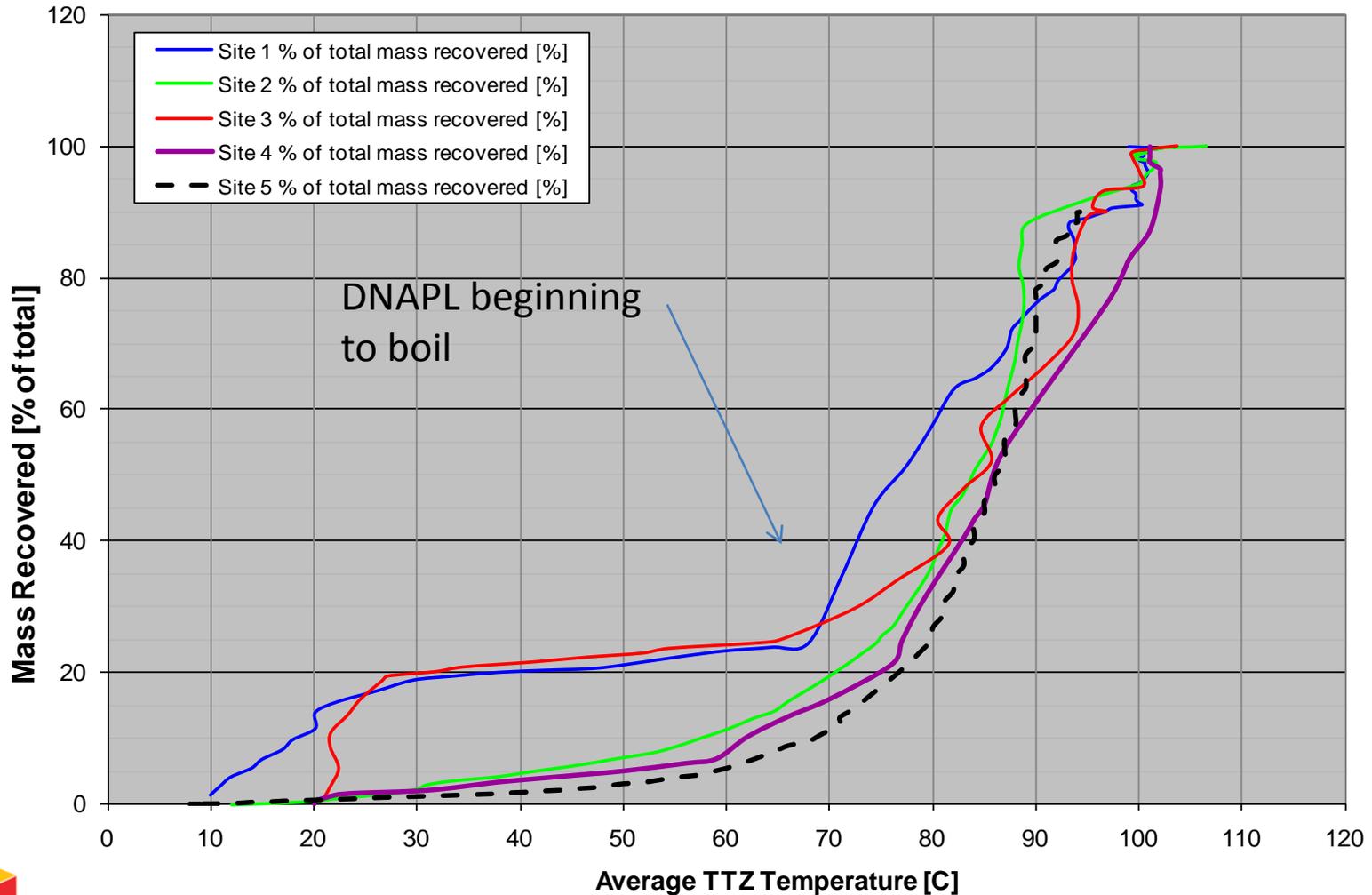
Think Thermal

How is Vapor Treatment at Thermal Sites Different than “Cold” Sites?

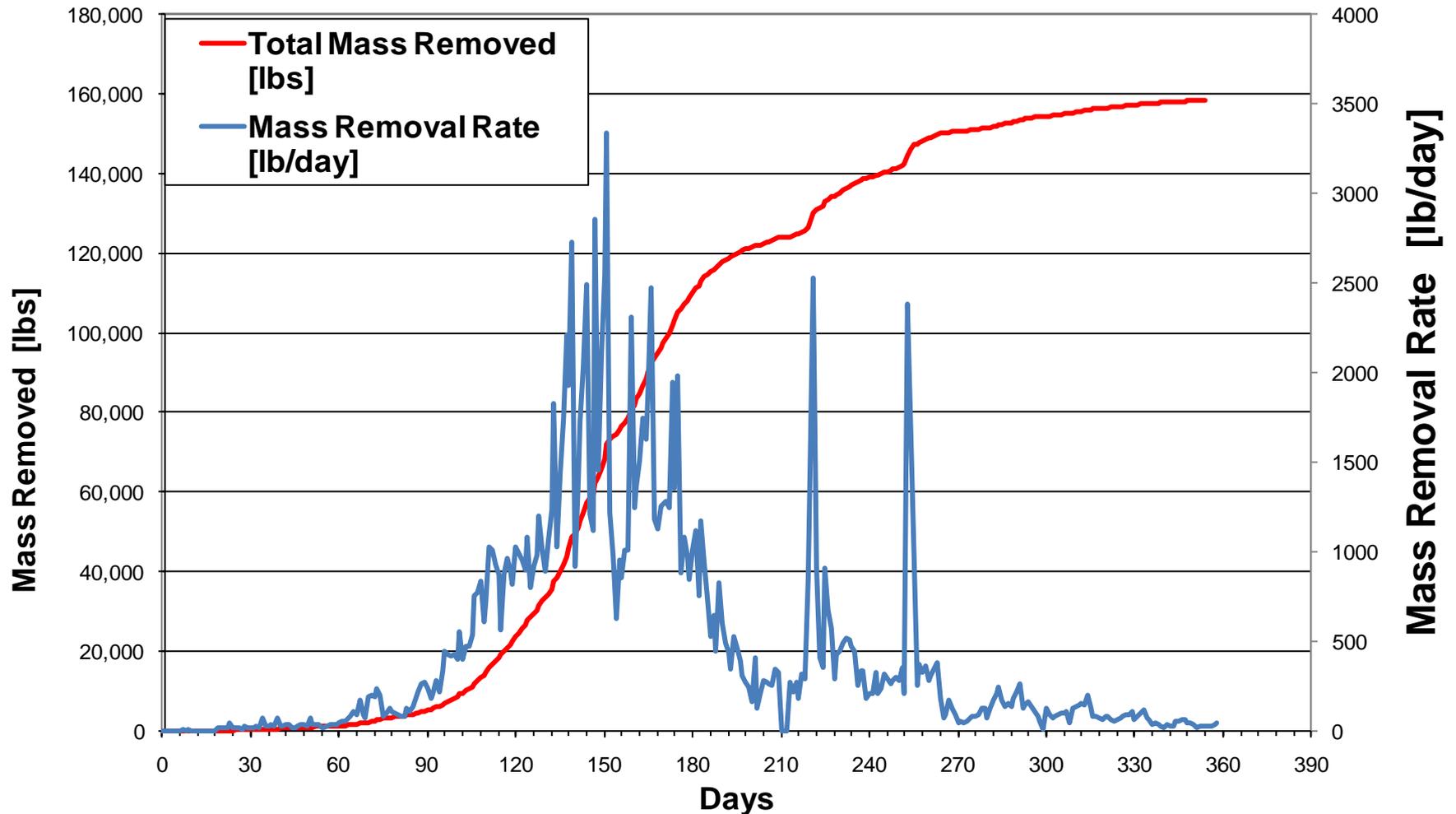
- Target: High Mass Source Zones
- Project: Short Duration, Dynamic Conditions
- Extracted Vapors:
 - **Hot:** 160 - >200F (250 - 400F for SVOC & PAH sites)
 - **Wet:** More steam (water) than air, on mass basis
 - **Corrosive:** HCl, HF
- Hot sites continue to generate steam & contaminant vapors even if extraction system shuts down
- High Contaminant Loading



Temperature vs. % Mass Removal for 5 CVOC Sites



Example COC Mass Removal at a Thermal Site



Vapor Treatment Options for Thermal Remediation Sites

- Adsorption on GAC
 - Sacrificial GAC
 - Steam Regenerated GAC
- Adsorption on Synthetic Media
- Condensing Systems
- Thermal Oxidation

Applicability, Selection & Lessons Learned



Sacrificial GAC



- Typical COC loading:
 - ~10-15% by mass
- Performance impacted by water content (i.e., humidity)
- Potentially combustible

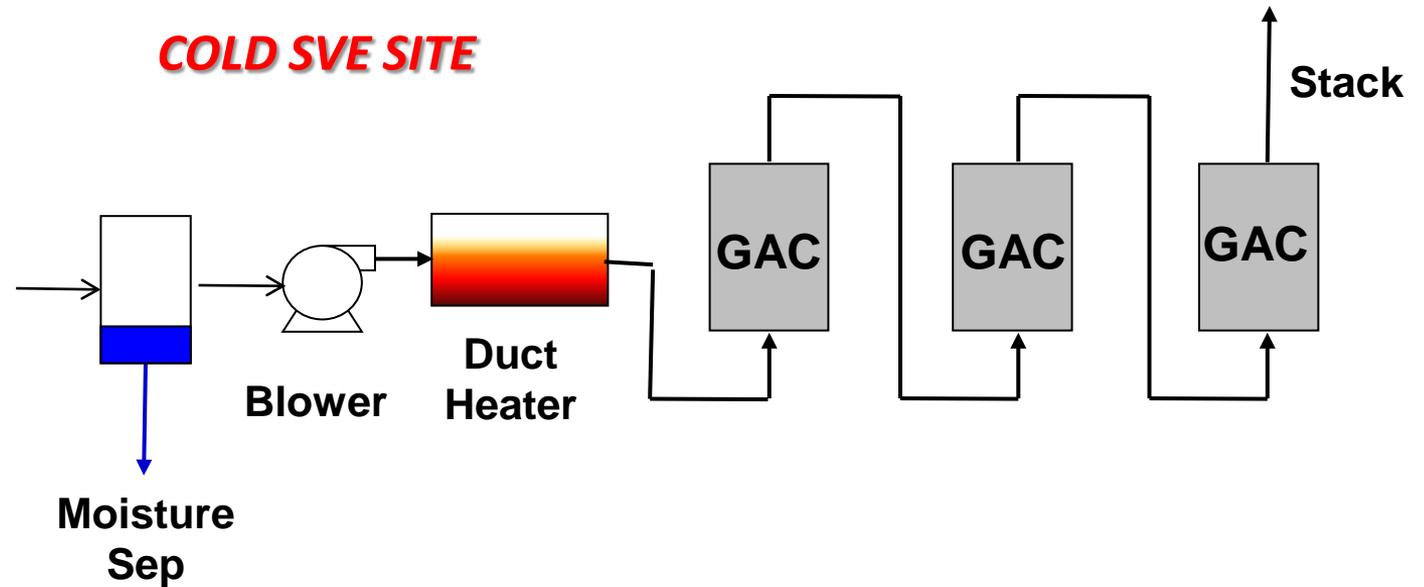
- Simple to install/operate
- Regulatory acceptance
- Spent GAC waste requires recycling or disposal



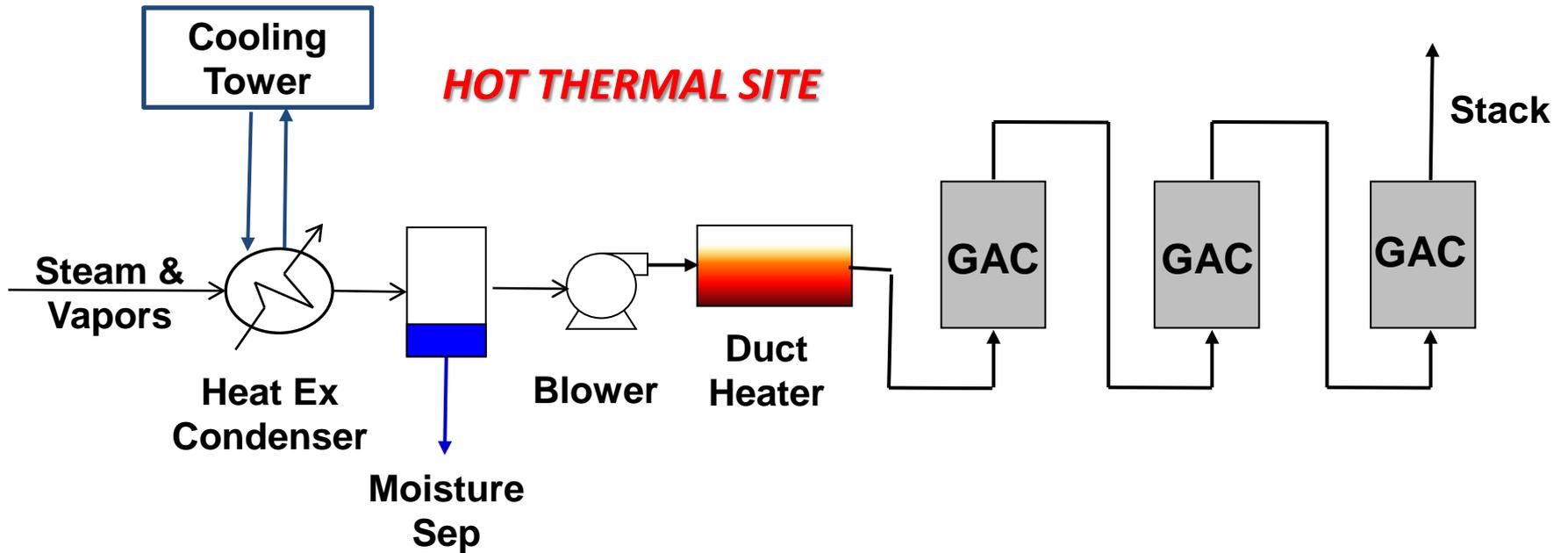
1 lb of GAC has surface area equal to 6 football fields (Calgon, 1999)



Sacrificial GAC PFD



Sacrificial GAC PFD



Critical Considerations for Sacrificial GAC for Thermal Applications

- **Proper conditioning of incoming vapor**
 - Target <120F, <50% RH
 - GAC loadings up to 30% by mass, achieved with effective conditioning
- **Monitor bed temperature**
 - Must have high temperature alarms
 - Include provisions to isolate & flood vessel in the event of bed fire
 - CO monitor may also be good early warning
- **For moderate to high COC mass load, consider steam regenerable carbon or synthetic media**



Steam Regenerated Media

Activated Carbon

- Inexpensive: <\$1/lb
- Sensitive to water/humidity
- Regenerate to 50-70% of new capacity
- Potential for bed fires
- Include sacrificial GAC polish on steam regen systems
 - 5-10X larger vessel

Synthetic Media

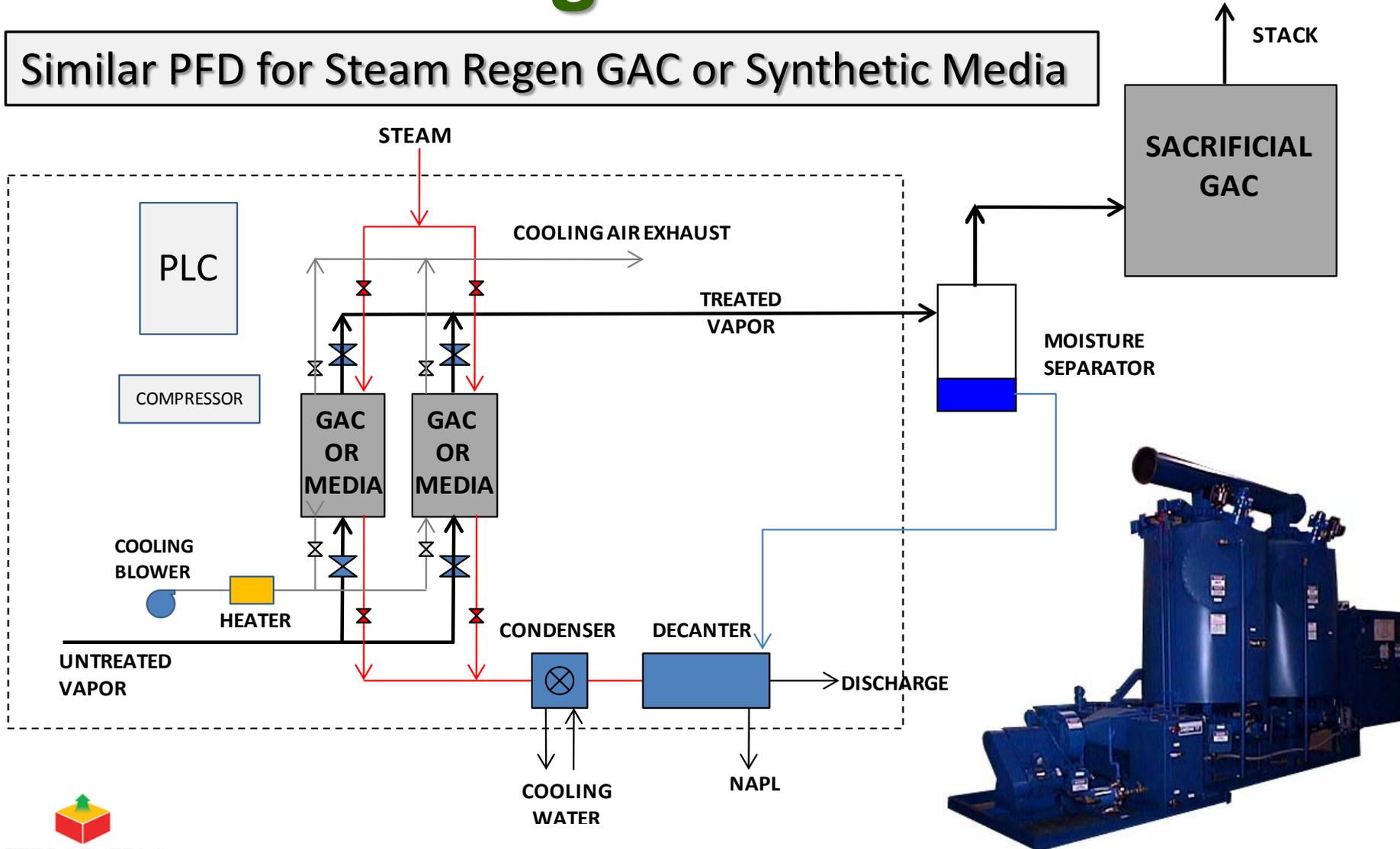
- Expensive: 5-40X GAC
- Hydrophobic, not as sensitive to humidity
- Hard, durable – more regen cycles than GAC
- Regenerate to 70-90% of new capacity
- Limited fire concern, but can melt at high temp.
- Small particles, higher dP, custom support screens

Requires capability to safely operate steam delivery system



Steam Regenerated Media

Similar PFD for Steam Regen GAC or Synthetic Media



Steam Regenerated Media



- *Much higher capital cost for integrated steam regen systems than sacrificial GAC system*
 - *1000-3000 scfm steam regen media (GAC or synthetic media) system: ~\$300K to >\$700K*

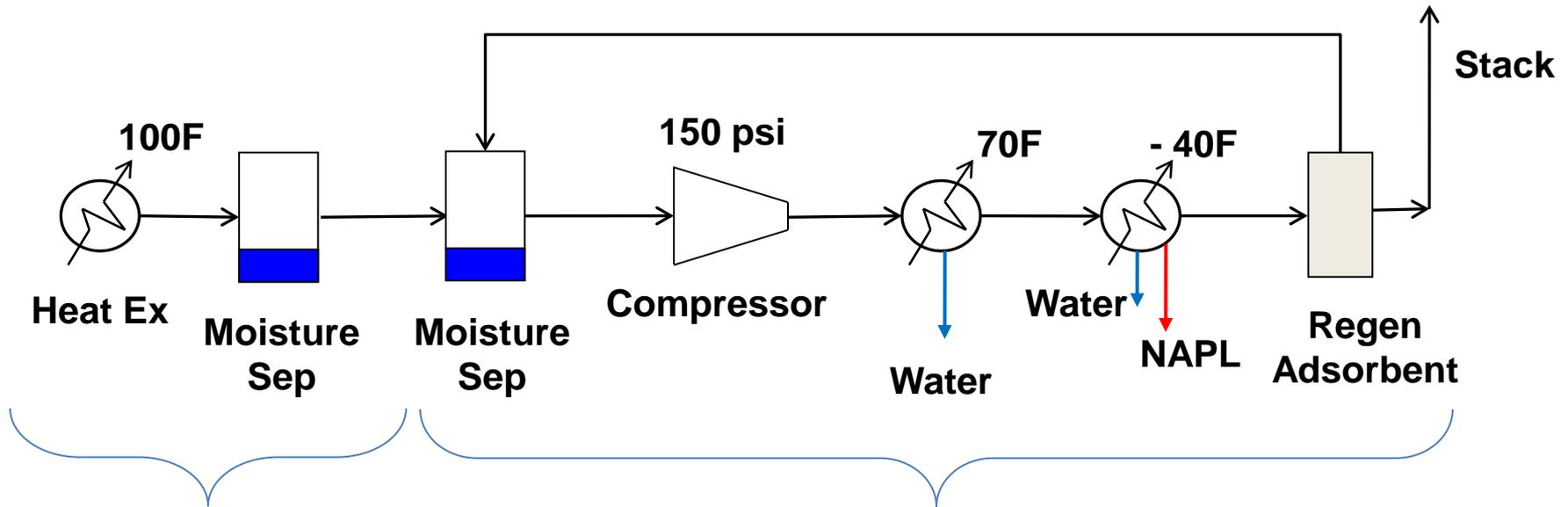
Steam regen media systems can be cost effective when:

- *Used at steam remediation sites,*
- *Where plant steam is available, or*
- *Where recovered product can be re-used (e.g., in plant or to fire steam generator)*



Manchester Corp, Harvard MA

Condensing System at Thermal Project



**Added Components
for Thermal
Application**

Basic G.E.O. Compression/Condensing System

- Handles high concentrations – up to LEL range
- Cool extracted vapor to ~100F prior to compressor
- Design extraction system to manage recycle loop discharge pressure (150 psi)

Condensing System at Thermal Project

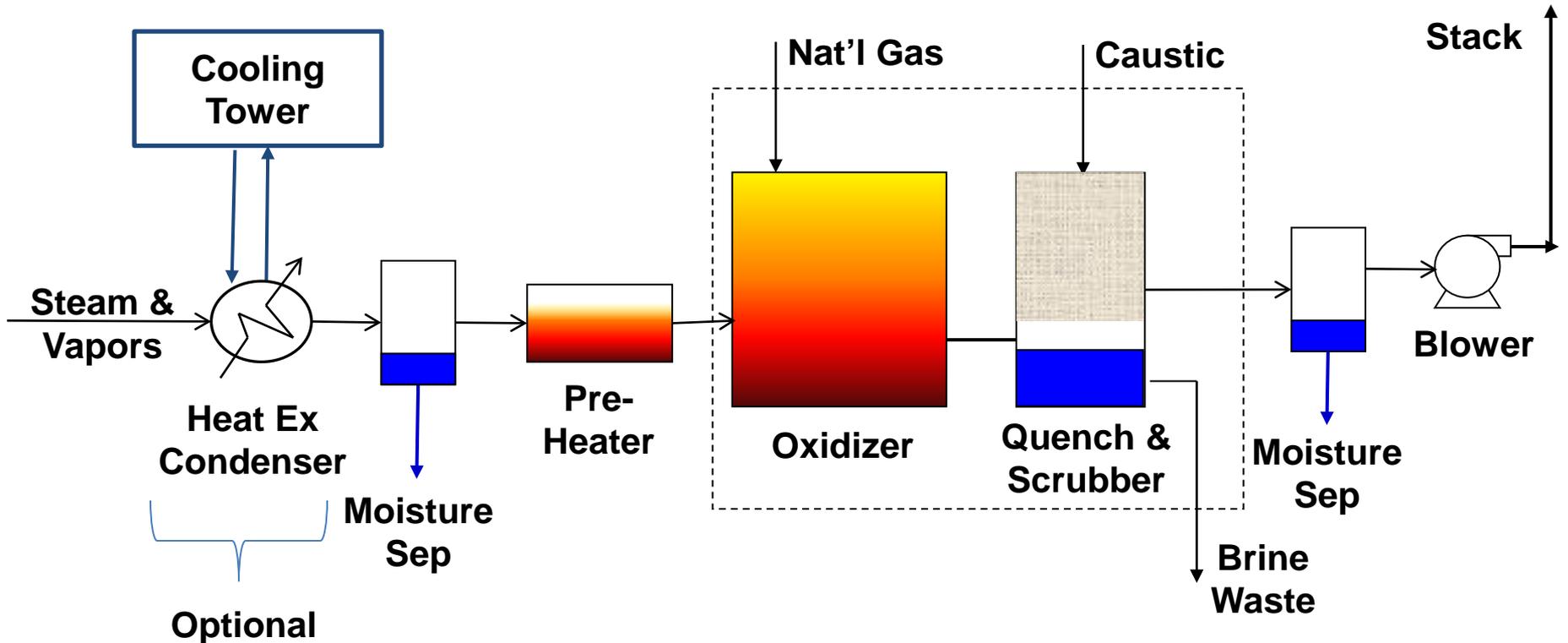


200 scfm G.E.O. System at thermal pilot site

- Higher electrical loads, but manageable on thermal site
 - Approx. 0.3 - 0.4 kW/SCFM
- NAPL waste requires recycling/disposal
- NAPL may form emulsion – extra disposal volume/cost

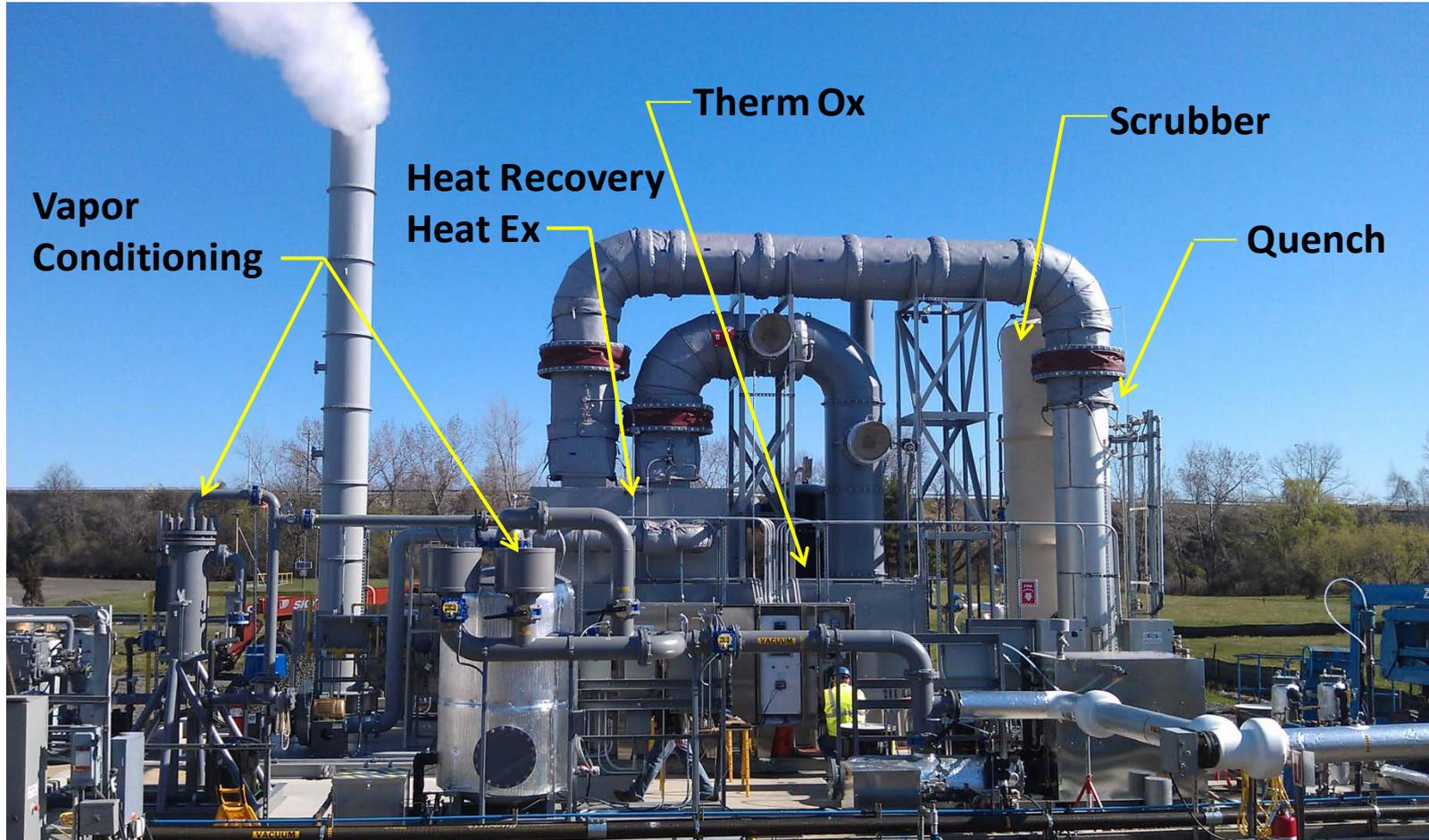
- Well suited to smaller flow rates (100 - 1000 scfm) or pilot scale sites
- Can be cost effective if recovered product is reusable/recyclable

Therm Ox at Thermal Project



- Time, Temperature, Turbulence & Sufficient Oxygen determine DRE
- Caustic scrubber required for CVOC, CFC sites

Thermal Oxidizer System Components

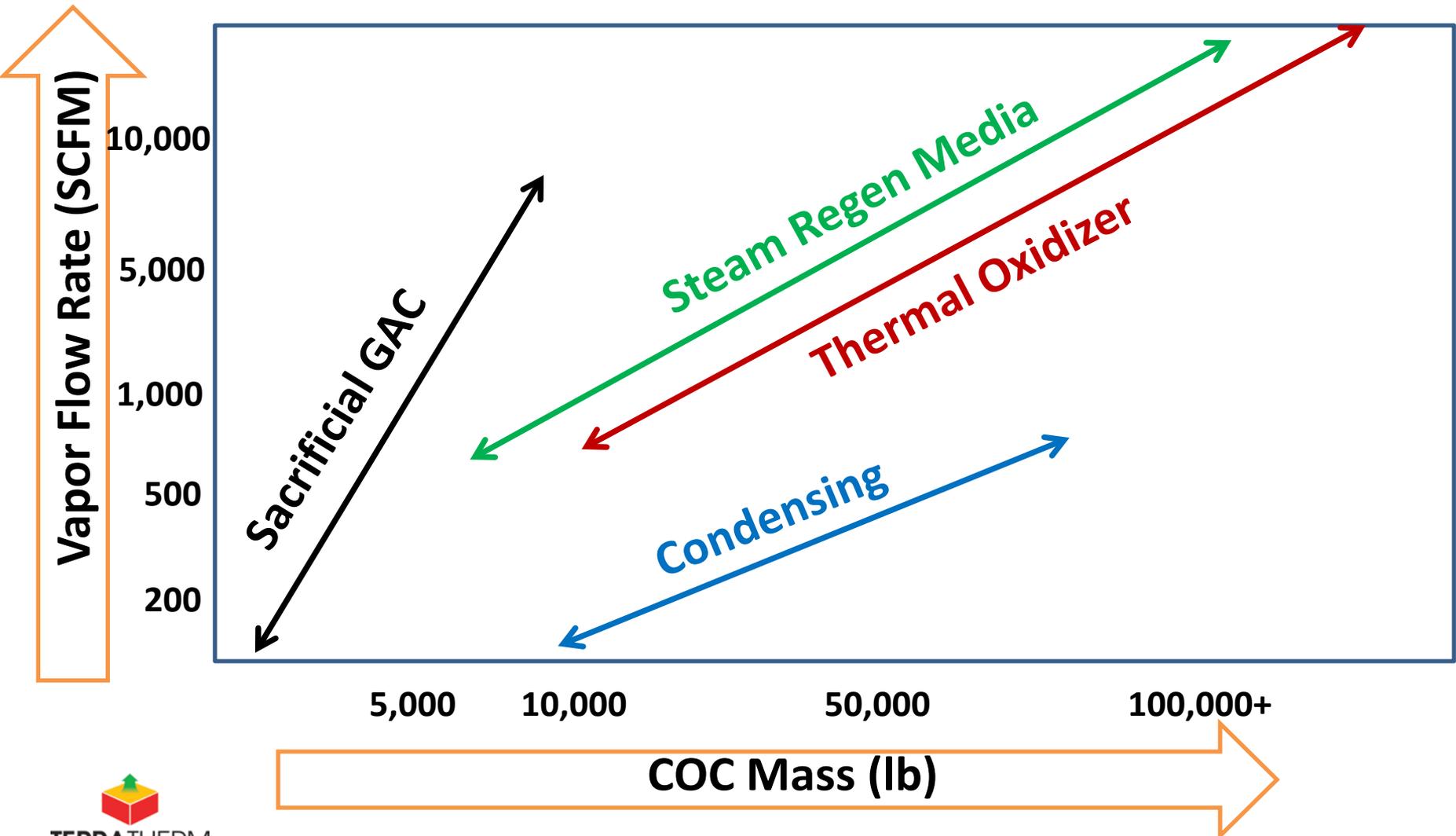


Thermal Oxidizers for In-Situ Thermal Sites

- Wide variety of designs for specific needs
 - Trade off between thermal efficiency and COC capacity
- High DRE's possible
 - Up to (6)-9's DRE
- Most capital & operationally intensive system
- No residual waste disposal
- Well suited for high or uncertain COC mass sites
- Design-in reliability & redundancy features
- Experienced operators to handle dynamic conditions at in-situ thermal sites



Which System to Choose?



Summary

- **In-Situ Thermal Sites are Dynamic**
 - Hot, wet vapor stream
 - High concentrations, rapid changes
 - Potentially corrosive conditions
- **Vapor Treatment System Must be Robust**
 - Installed spare blowers, pumps & components
 - Redundant sensors
 - Emergency back-up power supply
- **Condition Influent Vapors - Reduce Moisture Load**
 - Condense steam
 - Treat reduced non-condensable flow rate
- **Trained & Experienced Operators**



Questions

