Gas Thermal Remediation (GTR) Description

G.E.O. Inc.'s patented GTR™ system is used for In-Situ Thermal Remediation (ISTR) to significantly accelerate contaminant of concern (COC) mass removal by heating affected soils and/or groundwater.

In-Situ Treatment Background

During a soil vapor extraction (SVE) or pump and treat remediation project, COC mass removal rates are subject to rate-limiting properties resulting in asymptotic performance and often insufficient results. The process can be described in three phases of remediation: a mass removal phase, an asymptotic phase, and a rebound testing phase.
The initial phase of remediation is characterized by rapid COC removal due to high soil vapor and dissolved phase groundwater concentrations. Where the COC is present as a free phase, the concentrations will approach saturation as determined by the solubility limit or maximum gas phase concentration of the given COC(s).

During the second phase of remediation, the COC concentrations and mass recovery rates decrease rapidly in response to rate limiting desorption and diffusion of COCs from soil to vapor phase or dissolved phase.

The final phase is defined by diffusion-limited rates of COC removal with low effective removal of mass. It is difficult to estimate the total COC mass remaining in the target treatment zone (TTZ) during this phase due to subsurface soil and COC heterogeneities. This issue becomes problematic for deciding when to cease operations since early termination may result in significant rebound of the soil vapor and water COC concentrations thereby delaying site closure.

THE EFFECT OF THERMAL (ISTR)

The extent to which ISTR overcomes the rate-limiting step is a function of the specific COCs and the subsurface geology/hydrogeology of the TTZ and can be described by three influential rate-limiting physicochemical properties.

The solubility and vapor pressures of a COC significantly influence the COC concentrations in the extracted vapor stream and thus the mass removal rate. Increasing temperature will increase the vapor pressure and solubility thus increasing COC mobility by either dissolution of COCs to groundwater in the saturated zone followed by volatilization or volatilization of COCs to soil vapor in the vadose zone from the adsorbed phase.

The third property, diffusion, limits the mobility of the COC in low permeability areas with high silt and clay content. Increasing the temperature increases the rate of diffusion by lowering sorption coefficients.

ISTR significantly enhances mass removal by accelerating each of these rate-limiting steps. It should be noted that these processes occur simultaneously throughout the treatment period.

In-Situ Thermal Remediation Background

ISTR is a common and proven technology for the remediation of contaminated soil. The treatment process requires conventional SVE and sometimes pump and treat processes; SVE is
performed in parallel for the duration of the project and in some cases groundwater is being pumped from the saturated zone.

By definition, ISTR is the introduction of heat (or energy) into the subsurface to mobilize and recover volatile and semi-volatile organic compounds (VOCs and SVOCs) from soil and groundwater. The most commonly used methods of delivering the heat include thermal conductive heating (TCH), electrical resistant heating (ERH) and steam-enhanced extraction (SEE).

ISTR has been successfully applied to a wide range of COCs and hydrogeological conditions to reduce contamination to very low levels.

**ISTR REMEDIATION MECHANISMS**

Heating the subsurface to temperatures at or above the boiling point of water leads to significant changes in the thermodynamic conditions and can make non-aqueous phase liquids (NAPLs) (if present) more mobile for controlled removal.

In addition to increasing the recovery rate of COCs from the subsurface, in-situ thermal destruction may also occur. The most significant effects of heating are:

- In-situ thermal destruction of COCs via oxidation and pyrolysis.
- Vapor pressure always increases with temperature and the vapor pressure of NAPLs increases markedly with temperature. As the subsurface is heated from ambient temperature to temperatures in the range of 100°C, the vapor pressure of NAPL constituents will typically increase 10 to 30 fold.\(^1\)
- When soil contaminated with trichloroethylene (TCE) is increased from 20°C to 90°C, the Henry's constant increases an order of magnitude.\(^2\)
- Adsorption is, in general, an exothermic process. As such, adsorption coefficients are reduced during heating, leading to an increased rate of desorption of COCs from the soil.
- For most organic COCs, there is approximately a one percent decrease in viscosity per degree Celsius increase in temperature. Therefore, the higher the viscosity of a COC, the greater the decrease in viscosity with heating.
- Diffusion coefficients in both liquid and air are proportional to and increase with temperature.
- Steam stripping occurs when a NAPL is present along with water. Because both liquids are contributing to the vapor pressure of the mixture, it will boil at a lower temperature than either of the two liquids would separately.\(^3\)

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2 Heron, G., Christensen, T H, Enfield, C G 1996. Temperature effects on the distribution of organics in soils and groundwater and implications for thermally enhanced in-situ remediation. Environmental Science and Technology
• At boiling point temperatures (100°C above the water table and steam temperature below the water table), steam stripping depletes the NAPL of its more volatile and mobile constituents.⁴
• Rates of hydrolysis exponentially increase with temperature, acting as a decomposition mechanism for the identified COCs. Extended hydrolysis and bioactivity account for the well documented "polishing effect" of residual COCs in the months following ISTR.

For low boiling point COCs, the increase in vapor pressure and rate of vaporization are generally the most significant mechanisms by which mass recovery is enhanced by ISTR; for high boiling point COCs, the greatest enhancement is likely to be the reduction in viscosity in non-aqueous phase liquids (NAPL). However, all of these changes with increased temperature aid in the recovery of COCs from the subsurface.

Thermal Conductive Heating (TCH)

The proposed ISTR treatment design utilizes TCH. TCH is carried out by placing closed loop TCH wells in a grid-like pattern throughout the TTZ. The soil and groundwater are treated as follows:

- Thermal energy provided by steel TCH wells heat the soil, water, and COCs by means of thermal conduction and to a limited extent, radiation and convection. As the TCH wells reach temperatures between 100°C and 500°C, temperature gradients are created throughout the TTZ.

- Since the thermal conductivity of soil varies over a very narrow range - only by a factor of 3 - TCH is effective and predictable regardless of the permeability of the soil or its degree of heterogeneity.

- The superposition of heat from the TCH wells results in a relatively uniform temperature gradient from each TCH well (Figure 1). This heat flux propagates throughout the TTZ, until the desired target treatment temperature (TTT) is measured by thermocouples placed at the centroids (center points between thermal conductive heating wells) of the TCH well field. TTTs range from 50°C to 350°C depending on the COCs present and the goals of the project.

- As soil temperatures increase, COCs and a portion of water contained in the soil matrix are vaporized. Locations close to TCH wells may achieve superheated temperatures (above the boiling point of water)

- Groundwater that surrounds TCH well intervals into the saturated zone will be vaporized into steam.

- As water is vaporized from the TTZ, steam distillation will assist in the removal of COCs.

- SVE extracts soil vapor and steam from the subsurface through vertical and/or horizontal wells and creates a negative pressure on the TTZ during the heating process. The extracted off-gas is routed to the above-ground dedicated vapor and liquid treatment systems prior to discharge.

VAPOR TREATMENT OF OFF-GASSES
Contaminated soil vapor is removed from the extraction wells and transferred to the above-ground vapor and liquid treatment systems. A positive displacement blower is used to overcome the subsurface pressure produced by heating. Depending on the well configuration and subsurface geology/hydrogeology, free phase chemical laden water may be produced from the extraction wells.
G.E.O. Inc. typically uses one of three different vapor treatment methods to treat the extracted soil vapor. These include C3 Technology, vapor phase granular activated carbon (vGAC), and Gas Thermal Remediation+Fuel (GTR+F™).

The specific COCs being treated, the COC concentrations, air permitting, and site-specific constraints determine vapor treatment method selection. In some instances (specifically for larger, more complex sites), a combination of several treatment options may be the most cost effective method.

The extracted vapor stream is first cooled by a chiller after which any free phase liquid is separated by a vapor/liquid separator (VLS) positioned prior to the blower to prevent damage to equipment. The VLS is equipped with an automatic float actuated pump that directs the captured water to a water treatment system or an above ground recovery tank. Pump failure triggers an alarm to shut down the system. Following the blower is an air-to-air heat exchanger designed to cool the process air before being sent to the vapor treatment system.

**(1) C3 Technology**

C3 Technology was developed by G.E.O. Inc. and is a process which uses compression, cooling, and condensation to condense most of the COCs from the vapor stream in a recoverable liquid phase form. Residual COCs are captured by a proprietary adsorption technology that efficiently recovers VOCs from off-gas vapor streams, generally exceeding a 99.9% recovery rate.

The chemical is recovered as a NAPL that is temporarily containerized for recycling or off-site disposal. Dependent upon the COC and state or local agency, the final effluent stream may require polishing with vGAC.

C3 Technology is most advantageous at sites where the COC concentrations are high and/or the COC(s) have a low affinity for vGAC adsorption. C3 Technology has no upper concentration limit and can treat most VOCs present at contaminated sites with no dilution requirement. A characteristic trend of ISTR is for the soil vapor concentrations to increase steeply with heating, reach a peak, decrease steeply, and then level off to an asymptotic level that approaches zero. As a result, the average effluent COC concentrations will fluctuate significantly over the life of a project.

C3 Technology's ability to treat any COC concentration makes it an ideal vapor treatment option with ISTR since frequent vGAC change out can increase operating costs and reduce the efficiency of subsurface heating potential downtime.

**(2) Vapor Phase Granular Activated Carbon**

The most straightforward vapor treatment method is vGAC. In this configuration, extracted soil vapor is routed through vessels containing vGAC. Most air permitting regulations require at least two vessels in series (ie. Lead and lag configuration) and frequent sampling/monitoring of mid and effluent soil vapor concentrations. When COCs are detected in the effluent of lead vessel,
the spent vGAC must be regenerated or disposed of and replaced with fresh vGAC (either virgin or regenerated) and vessel configuration repositioned.

(3) Gas Thermal Remediation + Fuel

Gas Thermal Remediation plus Fuel (GTR+F™) can be utilized at sites where the contaminants have a significant energy content (i.e. petroleum sites) and pose no health or environmental risk after thermal oxidation (i.e. generally precluding chlorinated solvent sites).

In this configuration the extracted soil vapor is routed back into the burners where thermal oxidation of the contaminants occur. GTR+F™ reduces and often eliminates the need for additional vapor treatment since the destruction efficiency of most VOCs exceeds 99%. The combustion emissions are monitored to control the fuel supply since energy is being obtained by the system burner in the form of British Thermal Unit (BTU) obtained from the contaminant destruction. Typically, GTR+F™, is utilized at low concentration petroleum impacted sites (both in-situ and ex-situ) where there is limited moisture content in the soil being treated and the saturated zone is not being treated.

Treatment of Recovered Liquids

Liquid waste production is generated at all ISTR projects. The vapor treatment options will produce liquid waste with the exception of GTR+F™ in limited cases. All liquids extracted during the ISTR process must be treated prior to discharge. The two types of fluid wastes produced during treatment are:

1. An aqueous waste that, based on profile analyses, normally contains low concentrations of dissolved VOCs in water
2. A NAPL that may be eligible for recycling/reuse

The proportion of these two liquids is dependent on the specific COC profile at the site and the vapor treatment method being used. The aqueous waste can either be treated on-site with liquid phase granular activated carbon (LGAC) and discharged to a proximate point or collected and sent to a waste disposal facility. The NAPL can either be recycled/reused or also sent to a waste disposal facility. The greatest opportunity for NAPL recycling is at sites where the COCs are petroleum hydrocarbons (i.e. refineries).

Gas Thermal Remediation (GTR™)

G.E.O. Inc. and their Certified Licensees are the sole providers of G.E.O. Inc.’s patented GTR™ system used to carry out ISTR projects. GTR™ is a method of TCH in which individual burners (Figure 3) are used to raise the temperature of the subsurface.
The individual burners are fueled by either natural gas or propane to provide heat to the TCH wells. The heat is transferred to the individual TCH wells (Figure 3) as hot combustion air is circulated within the enclosed steel tubing of each TCH well. The hot combustion air is completely isolated from the soil and heating of the subsurface occurs primarily through conduction. Throughout the heating process the individual burners and proximate temperature/pressure recording points are monitored via a wireless data system. A real time ftp website is used for accessing data remotely. Subzones within the TTZ can be individually controlled, so that temperature gradients and energy consumption may be optimized.

A typical GTR™ system uses the following equipment:

- GTR™-type burners and their respective TCH wells placed in borings
- Vapor extraction wells co-located within TCH well boring
- Separate vapor extraction trenches or vertical wells (as necessary)
- Natural gas connection or mobile propane tank(s)
- Mobile control center and programmable logic controller (PLC) data collection system
- Wireless monitoring, control, and communications system
- Thermocouples and their respective borings
• Vacuum induction blower to supply burner air
• Vapor extraction system to extract soil vapor and apply vacuum to the well-field
• Vapor treatment system to treat soil vapor
• Water/NAPL separator plus water treatment and discharge (Liquid GAC)

**BENEFITS OF GAS THERMAL REMEDIATION**
The benefits of using GTR™ for ISTR are summarized below:

• Scalable to fit any size ISTR project, even small sites in urban areas, under buildings.
• Natural gas or propane supply the energy for subsurface heating.
• Nominal electric power is required (i.e. blowers, burner controls, etc.) and when not available (remote sites), a mobile generator can be used for a completely off the grid ISTR system. Note that large and costly power upgrades are not required.
• The use of individually controlled burners allow for burners to be removed from operation as localized areas of the TTZ reach their treatment goals, which translates to energy and cost savings.
• Complete mobilization in as little as 2 weeks.
• No noise, smell and traffic nuisance for the neighborhood.

**Wellfield Layout and Estimated Treatment Time**
The well-field design (specifically the TCH well spacing) and treatment time are a function of subsurface geology/hydrogeology, the amount of water in the saturated zone (from both the vadose and saturated zone), the hydraulic conductivity (if treating into the saturated zone), and the COCs.

Modeling could be done via a software program to estimate the treatment time regarding all the characteristics of the subsurface and contaminants.
Based on the TTZ dimensions and the subsurface geology/hydrogeology, one GTR™ burner may be capable of heating more than one TCH well. The time to reach TTT is defined as the amount of time it will take for the centroid locations to reach the TTT. Thus, most soil in the TTZ will be at or above the TTT for longer than the Treatment Time at TTT, as indicated below.

The treatment time can be decreased by decreasing the TCH well spacing, however, this will increase total costs in most cases due to the additional equipment and increased labor costs for mobilization, demobilization, and operations.

Temperatures at the centroid locations will be continuously monitored with thermocouples to ensure complete heating of the TTZ. Several multi-function temperature and pressure monitoring points will also be installed in the TTZ to measure temperature at vertically discreet locations, and to monitor the subsurface vacuum to maintain pneumatic control.

Figure 4. Modeled average temperatures of a pilot study at 10, 60, and 90 days.
Figure 5. Illustration of how a Gas Thermal Remediation burner is used to heat the subsurface during ISTR.
Figure 6. Drawing of a TCH well placed in the vadose zone.
Figure 7. Drawing of a Vapor Extraction Well placed in the vadose zone.
Figure 8. Drawing of a Thermocouple and Pressure Transducer placed in the vadose zone.
Figure 8. a). Gas distribution system being assembled to feed burners. b). Dual redundant pressure regulators placed in series.