

DESIGN EQUATIONS FOR *IN SITU* THERMAL DESORPTION

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Computations that are required for design of ISTD processes utilize a large number of fundamental equations, both for operation of surface equipment and for design of the *in situ* process. The *in situ* processes are described by the fundamental fluid flow and heat flow equations. Although the actual computations are carried out in complex numerical simulators, the simplified analytical expressions will be used to illustrate the process mechanisms.

FLUID FLOW (Steady State)

Flow of fluids is described by a Darcy equation for each of the flowing phases. In most *in situ* processes, we need to account for flow of aqueous and oleic liquid phases and of a gas phase composed of air, water vapor, and lesser amounts of oleic vapors. The linear form of Darcy's equation, as given in Equation (1), generally describes flow in the thermal blanket process. The radial form, as given in Equation (2), describes flow in the thermal well process.

In the Darcy equations, the rock properties (absolute permeability and porosity) are differentiated from fluid properties (viscosity and density). The interference of dissimilar fluids in multiphase flow is described by a relative permeability correction that is a function of the saturations of each of the phases. All properties may vary with temperature, and in this way the flow of viscous oil, water, and vapors is properly described throughout the entire process.

HEAT FLOW

Conduction (Steady State)

Heat flow by conduction in porous media is described by the temperature–heat flow equations that are similar in form to the pressure–fluid flow equations. For steady-state, linear, conductive heat flow, Fourier's equation, given in Equation (3), is applicable. The Fourier equation for steady-state, radial, conductive heat flow, is given in Equation (4).

Conduction (Transient)

Because heat flow is so much slower than fluid flow, transient solutions are needed to describe the process. For linear flow, the rise in temperature as a function of time and distance from a plane heater blanket is given by Equation (5). This equation incorporates the bulk thermal properties of soil and the heat input rate per unit area of the heater. For pure conduction without convection, the temperature fall-off with distance is described by the complementary error function given in Equation (6) and Figure 1. The line source solution given in Equation (7) is a good approximation for radial conduction heat flow from a thermal well. The shape of the resulting temperature profile with radial distance from the line source is defined by the exponential integral function given in Equations (8) and (9) and Figure 2. When an array of heater wells is installed in a volume of soil, the temperature rise at any interwell location is the superposition sum of each of the heaters in the pattern, as shown in Equation (10) and Figure 3. Although the contribution to the temperature rise from distant wells is less than from closer ones, each well in the array contributes to the temperature rise. The effects of this superposition become most important after long heating times.

Radiation

Radiation heating is important only in the very high temperature region near the heaters. Typically, at heater temperatures less than 1000°F, radiation heat transfer becomes insufficient for practical heating rates from blankets or wells. The Stephan–Boltzmann equation shows radiation heat transfer to have a fourth-power dependence on the absolute temperatures. This is given in Equation (11).

VAPORIZATION

Dalton's Law

At moderate levels of heating, most *in situ* liquids will vaporize by boiling, evaporation into air, or steam distillation. For immiscible liquids, the fractions of individual components in the gaseous phase are described by Dalton's Law, which states that the total pressure of a gaseous mixture is the sum of the partial pressures of the components. See Equation (12). Because the liquids are immiscible, each component vaporizes independently of the others, as determined by its single-component vapor pressure, which is a function only of the temperature. The mole fraction of a component is directly related to the partial pressure as shown in Equations (13) and (14).

Raoult's Law

If the liquids are miscible, the partial pressure of a component is reduced by its mole fraction in the liquid phase. See Equation (15). For example, the slight solubility of benzene in water will reduce the partial pressure of benzene in the vapor phase, provided there is no excess liquid benzene present. This will retard vaporization of the last trace of benzene until all of the liquids are vaporized.

Steam Distillation/Air Evaporation

The weight fraction of an oleic contaminant that can be carried in a stream of air or of steam is given in Equations (16) and (17). This formulation assumes that a liquid contaminant residue is being evaporated in a stream either of air or of water vapor. Equation (17) shows that the weight fraction of contaminant in the vapor stream is dependent on the molecular weights and the pure component vapor pressures. (Subscript 1 refers to the contaminant and subscript 2 refers to either air or steam.) In the *in situ* thermal desorption processes, the total pressure of the vapor stream is slightly below one atmosphere. Therefore, for high boiling point contaminants, the partial pressure of the air or steam is very nearly equal to the total pressure. Because steam has a lower molecular weight than air, it is a more effective distilling medium than air. The large amount of water vapor present in the subsurface also makes steam distillation an important mechanism for recovery of contaminants at temperatures well below their boiling points.

CHEMICAL REACTION KINETICS

When high temperatures are generated *in situ* and sufficient air is present, most of the contaminants are destroyed in the subsurface. The long residence time of reactants at elevated temperatures in the ISTD process favors completion of chemical reactions. Assuming first-order reactions, we may represent the kinetic behavior as shown in Equations (18) and (19). These equations, when combined with Arrhenius' Equation (20), provide a combined expression for completion of a chemical reaction, as a function of time and temperature. See Equation (21). Our experience in field projects has shown that 90 to 99% of the chemical reactions take place in the subsurface soil. The remaining unreacted compounds are reacted in a high-temperature thermal oxidizer, achieving as much as 99.999999+% destruction efficiency for the combined process. The resulting products are carbon dioxide, water, and hydrochloric acid, all of which are readily vaporized at even moderate effluent temperatures.

A generalized stoichiometric equation for reaction of chlorinated hydrocarbons with air is given in Equation (22). This formulation assumes the air stream to be composed of 20% oxygen by volume. By monitoring the effluent stream for carbon dioxide, the amount of remediated hydrocarbon removed from the soil can be calculated. See Equation (23). Similarly, by monitoring the effluent stream for hydrochloric acid, the amount of remediated chlorinated hydrocarbon can be determined. See Equation (24).

Material balances of fluid components in the ISTD process are carried out at a particular site with the following conditions and assumptions:

1. The system volume is that bounded by the periphery of the treated volume of subsurface soil and the surface treatment equipment out to the effluent stack..
2. The simple balance consists of (the mass of a component initially present in the soil) + (the mass of component flowing into the treated volume from adjacent soil) = (the mass of component produced during the treatment) + (mass of component remaining in the treated soil at the end of the process).
3. Individual components include (a) the oleic contaminant, Equation (25), (b) water, Equation (26), and (c) air, Equation (27).
4. The initial mass of oleic contaminant in the soil is obtained by analysis of soil samples. Depending on the frequency of this sampling at the site, the total contaminant target can be readily obtained by construction of iso-concentration maps and comparing the initial amount in place with the produced amount as determined by Equation (23) or (24). In a well-designed project, essentially no contaminant is released to the atmosphere, no contaminant is allowed to resaturate the cleaned volume, and almost no residual contaminant will be left in the heated volume.
5. The initial amount of water in the target zone may also be determined from core sampling. Generally, there is much more water than oleic contaminant. In addition, the movement of groundwater exterior to the target region is prevalent at many sites and in some cases may even exceed the amount of water initially present in the target region. All of this water must be vaporized if it is not removed by dewatering wells. Typically, the amount of water in the product stream is 20 to 50% by volume. At the end of a successful project, all of the liquid water will have been vaporized. The mass of water vapor remaining in the target zone is negligible.
6. The mass of air initially in the soil is negligible, even in dry soils, because of the low density of air compared to the liquid components. Because of the high mobility of air, we normally expect to draw in a large volume from outside the heated region. Thus, the produced air almost entirely originates from outside the treatment area.

An energy balance for the process is more easily obtained than the mass balance of components. Since the soil temperatures are a good measure of the completeness of remediation, the energy balance, which takes into account electrical and thermal energies, provides an independent means of monitoring progress of the operations. This is accomplished by using the heat capacity of the soil and the thermal properties of the liquids and gas to estimate the average temperature attained from injection of a quantity of electrical energy. Equation (28) is a simple energy balance that does not take into account conductive heat losses from the surfaces of the heated region or water that originates from outside the treated volume.

In summary, the design of an *in situ* thermal remediation project uses a wide range of technical concepts that are applied to complex geological models. The use of comprehensive numerical simulators that incorporate all of the formulations given above is essential for the successful design of a project.

EQUATIONS USED IN CALCULATION OF *IN SITU* THERMAL DESORPTION

FLUID FLOW (Steady State)

Linear

$$q_L = \frac{k k_r A \Delta p}{\mu \Delta l} \quad (1)$$

Radial

$$q_R = \frac{2\pi k k_r h \Delta p}{\mu \ln(r_e/r_w)} \quad (2)$$

HEAT FLOW (Steady State)

Linear

$$q_{hL} = \lambda A \frac{\Delta T}{\Delta L} \quad (3)$$

Radial

$$q_{hR} = \frac{2\pi \lambda h \Delta T}{\ln(r_e/r_w)} \quad (4)$$

HEAT FLOW – Conduction (Transient)

Linear

$$\Delta T(x,t) = \frac{2 F_o}{\lambda} \left\{ \left(\frac{\alpha t}{\pi} \right)^{1/2} e^{-\frac{x^2}{4\alpha t}} - \frac{x}{2} \operatorname{erfc} \left(\frac{x}{2\sqrt{\alpha t}} \right) \right\} \quad (5)$$

$$\operatorname{erfc}(X) = 1 - \frac{2}{\sqrt{\pi}} \int_0^X e^{-t^2} dt = 1 - \frac{2}{\sqrt{\pi}} e^{-X^2} \sum_{k=0}^{\infty} \left\{ \frac{2^k X^{2k+1}}{(2k+1)!!} \right\} \quad (6)$$

where $(2k+1)!! = 1 \cdot 3 \cdot 5 \cdots (2k+1)$

and $X = \frac{x}{2\sqrt{\alpha t}}$

Radial

$$\Delta T(r, t) = \frac{-F_1}{4\pi\lambda} Ei \left[-\frac{r^2}{4\alpha t} \right] \quad (7)$$

$$Ei(-X) = \ln(\gamma X) + \sum_{n=1}^{\infty} \left[\frac{(-X)^n}{n \cdot n!} \right] \quad (8)$$

$$\text{where } X = \frac{r^2}{4\alpha t}$$

$$\text{and } \ln \gamma = \int_0^1 \frac{1-e^{-t}}{t} dt - \int_1^{\infty} \frac{e^{-t}}{t} dt \quad (9)$$

$$\ln \gamma = 1 + \sum_2^{\infty} \left[\frac{1}{n} + \ln \left(\frac{n-1}{n} \right) \right] \quad (9a)$$

Well Patterns

$$\Delta T(x, y, t) = \frac{-F_1}{4\pi\lambda} \left[\sum_{n=1}^m \left\{ Ei \left(-\frac{(x-x_n)^2 + (y-y_n)^2}{4\alpha t} \right) \right\} \right] \quad (10)$$

HEAT FLOW – Radiation (Steady State)Linear

$$F_o = S(T_1^4 - T_2^4) \left(\frac{1}{\frac{1}{e_1} + \frac{1}{e_2} - 1} \right) f \quad (11)$$

VAPORIZATIONDalton's Law

$$p_t = p_1^\circ + p_2^\circ + \dots + p_n^\circ \quad (12)$$

$$f_1 + f_2 + \dots + f_n = 1 \quad (13)$$

$$f_1 = \frac{p_1^\circ}{p_1^\circ + p_2^\circ + \dots + p_n^\circ} \quad (14)$$

Raoult's Law

$$p_t = x_1 p_1^\circ + x_2 p_2^\circ + \dots + x_n p_n^\circ \quad (15)$$

Steam Distillation

$$f_{w_1} = \frac{w_1}{w_1 + w_2} \quad (16)$$

$$f_{w_1} = \frac{1}{1 + \left(\frac{M_2}{M_1} \cdot \frac{p_2^\circ}{p_1^\circ} \right)} \quad (17)$$

KINETICS – 1st-Order Reactions

$$-\frac{dc}{dt} = k_1 c \quad (18)$$

$$\frac{c}{c_o} = e^{-k_1 t} \quad (19)$$

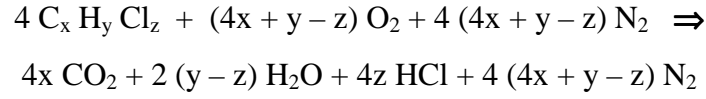
Arrhenius Equation

$$\ln\left(\frac{k}{k_o}\right) = -\frac{\Delta E}{RT} \quad (20)$$

Combined Equation

$$\frac{c}{c_o} = e^{-k_o t e^{-\frac{\Delta E}{RT}}} \quad (21)$$

STOICHIOMETRIC REACTION OF CHLORINATED HYDROCARBONS



$$w_{HCl} = w_{CHC} \cdot z \frac{M_{HCl}}{M_{CHC}} = w_{CHC} \cdot \frac{(36.5 \cdot z)}{(x \cdot 12 + y \cdot 1 + z \cdot 35.5)} \quad (22)$$

$$w_{CHC} = \left(\frac{M_{CO_2}}{V_{M@STP}} \right) \left(\frac{M_{CHC}}{x \cdot M_{CO_2}} \right) \int_0^t c_{CO_2} q_p dt \quad (23)$$

$$w_{CHC} = \left(\frac{M_{HCl}}{V_{M@STP}} \right) \left(\frac{M_{CHC}}{z \cdot M_{HCl}} \right) \int_0^t c_{HCl} q_p dt \quad (24)$$

MATERIAL BALANCE

Contaminant

$$m_c + \rho_c \int_0^t i_c dt = \rho_c \int_0^t q_c dt + r_c \quad (25)$$

Water

$$m_w + \rho_w \int_0^t i_w dt = \rho_w \int_0^t q_w dt + r_w \quad (26)$$

Air

$$\int_0^t i_a dt = \int_0^t q_a dt \quad (27)$$

ENERGY BALANCE

$$lwh \left\{ [\rho_R C_R (1 - \phi) + \rho_w C_w \phi S_w] (T_f - T_i) + \rho_w h_w \phi S_w \right\} + q_a t \rho_a C_a (T_f - T_i) = \frac{lwh}{A} F_1 t \quad (28)$$

NOMENCLATURE

Fluid Flow

$q_{L,R}$	=	flow rate [$\text{l}^3 \text{t}^{-1}$]
k	=	absolute permeability [l^2]
k_r	=	relative permeability [-]
A	=	area [l^2]
Δp	=	pressure drop [$\text{m l}^{-1} \text{t}^{-2}$]
Δl	=	flow path length [1]
μ	=	viscosity [$\text{m l}^{-1} \text{t}^{-1}$]
r_e	=	outer radius [1]
r_w	=	well radius [1]
h	=	length of well [1]

Conductive Heat Flow

ΔT	=	temperature change [T]
x	=	linear distance [1]
t	=	time [t]
F_o	=	heat injection rate / unit area [m t^{-3}]
λ	=	thermal conductivity [$\text{m l t}^{-3} \text{T}$]
α	=	thermal diffusivity [l^2/t]
F_1	=	heat injection rate / unit length [m l t^{-3}]
q_{hL}	=	linear heat flow rate [$\text{m l}^2/\text{t}^2$]
q_{hR}	=	radial heat flow rate [$\text{m l}^2/\text{t}^2$]
r	=	radial distance [1]
x,y	=	well distances N-S and E-W [1]
m	=	total well count [-]
X	=	argument of erfc and Ei functions [-]
k, n	=	integers [-]
$\ln \gamma$	=	Euler's constant = 0.577215665 [-]

Radiant Heat Flow

S = Stephan–Boltzmann constant [$\text{m t}^{-3} \text{T}^{-4}$]

e = emissivities [–]

f = shape factor

T_1 = emitting temperature [T]

T_2 = absorbing temperature [T]

Vaporization

Dalton's Law

p = total pressure [$\text{m l}^{-1} \text{t}^{-2}$]

$p_{1,2,Kn}^{\circ}$ = vapor pressure of pure components [$\text{m l}^{-1} \text{t}^{-2}$]

$f_{1,2,Kn}$ = mole fraction of pure components in vapor [–]

Raoult's Law

$x_{1,2,Kn}$ = mole fraction of miscible pure components in liquid [–]

$p_{1,2,Kn}^{\circ}$ = partial pressure of component in vapor [$\text{m l}^{-1} \text{t}^{-2}$]

Steam Distillation/Air Evaporation

w_1 = weight of high boiling point oleic contaminant in vapor [m]

w_2 = weight of water or air in vapor [m]

f_{w_1} = weight fraction of oleic contaminant in vapor [–]

M_1 = molecular weight of oleic contaminant [m mole^{-1}]

M_2 = molecular weight of water or air [m mole^{-1}]

Kinetics

c	=	concentration [eq m ⁻¹]
c_o	=	base concentration [eq m ⁻¹]
k_1	=	kinetic constant [t ⁻¹]
k_o	=	reference kinetic constant [t ⁻¹]
ΔE	=	activation energy [m l ² t ⁻² mole ⁻¹]
R	=	gas constant [m l ² t ⁻² T ⁻¹ mole ⁻¹]
T	=	temperature [T]

Stoichiometry

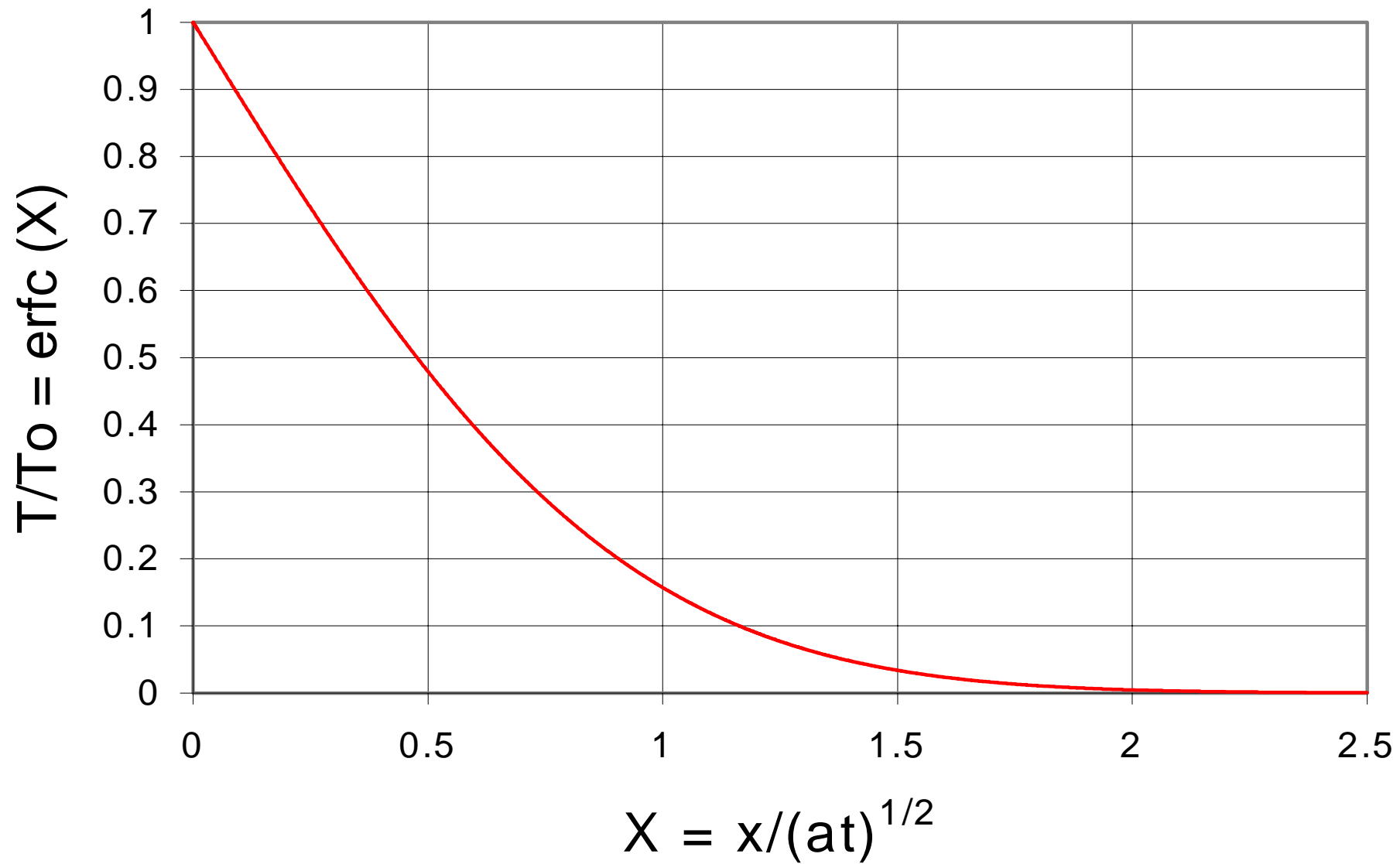
w_{CHC}	=	weight of chlorinated hydrocarbon produced [m]
w_{HCl}	=	weight of HCl produced [m]
M_{CO_2}	=	molecular weight of CO ₂ [m mole ⁻¹]
M_{CHC}	=	molecular weight of chlorinated hydrocarbon [m mole ⁻¹]
M_{HCl}	=	molecular weight of hydrogen chloride [m mole ⁻¹]
$V_{M@STP}$	=	molar volume of a gas [l ³ mole ⁻¹]
x	=	number of C atoms / molecule
z	=	number of Cl atoms / molecule
c_{CO_2}	=	fractional concentration of CO ₂ in product streams [-]
c_{HCl}	=	fractional concentration of HCl in product streams [-]
q_p	=	total flow rate of gas in product stream [l ³ t ⁻¹]

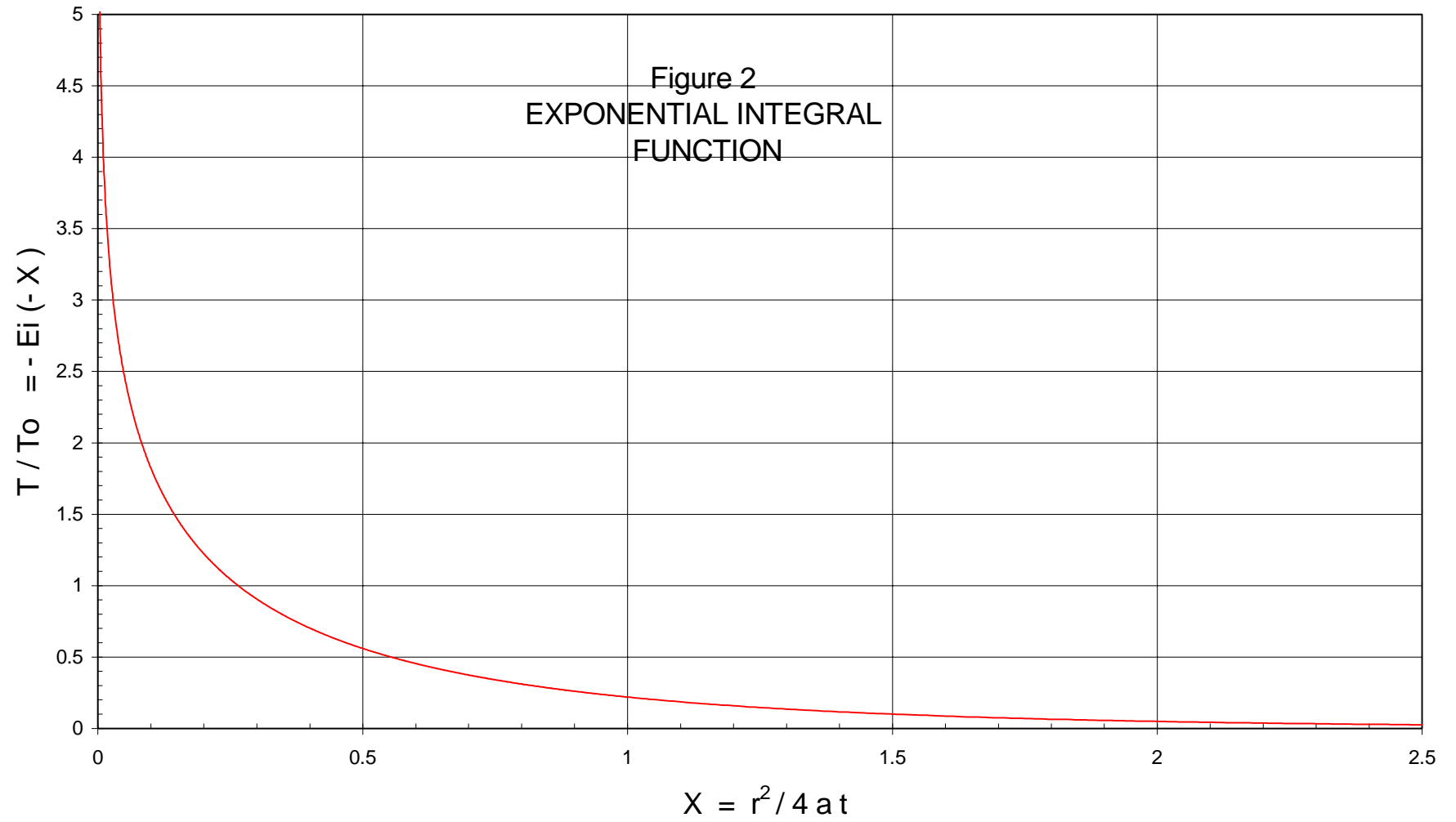
Material Balance

m_c	=	mass of contaminant [m]
ρ_c	=	density of contaminant [m l ⁻³]
i_c	=	inflow rate [l ³ t ⁻¹]
q_c	=	production rate [l ³ t ⁻¹]
r_c	=	residual contaminant [m]

Energy Balance

l	=	length of site [1]
w	=	width of site [1]
h	=	height of site [1]
ρ_w	=	density of water [m l^{-3}]
ρ_R	=	density of mineral grains [m l^{-3}]
C_R	=	heat capacity of mineral [$\text{l}^2 \text{t}^{-2} \text{T}^{-1}$]
ϕ	=	porosity [-]
ρ_w	=	density of water [m l^{-3}]
C_w	=	heat capacity of water [$\text{l}^2 \text{t}^{-2} \text{T}^{-1}$]
S_w	=	water saturation [-]
q_a	=	flow rate of air [$\text{l}^3 \text{t}^{-1}$]
ρ_a	=	density of air [m l^{-3}]
C_a	=	heat capacity of air [$\text{l}^2 \text{t}^{-2} \text{T}^{-1}$]
T_f	=	final temperature [T]
T_i	=	initial temperature [T]
h_w	=	heat of vaporization of water [$\text{l}^2 \text{t}^{-2}$]
F_1	=	well heat injection rate / unit length [m l t^{-3}]
t	=	time of heating [t]
A	=	area / injection well [l^2]





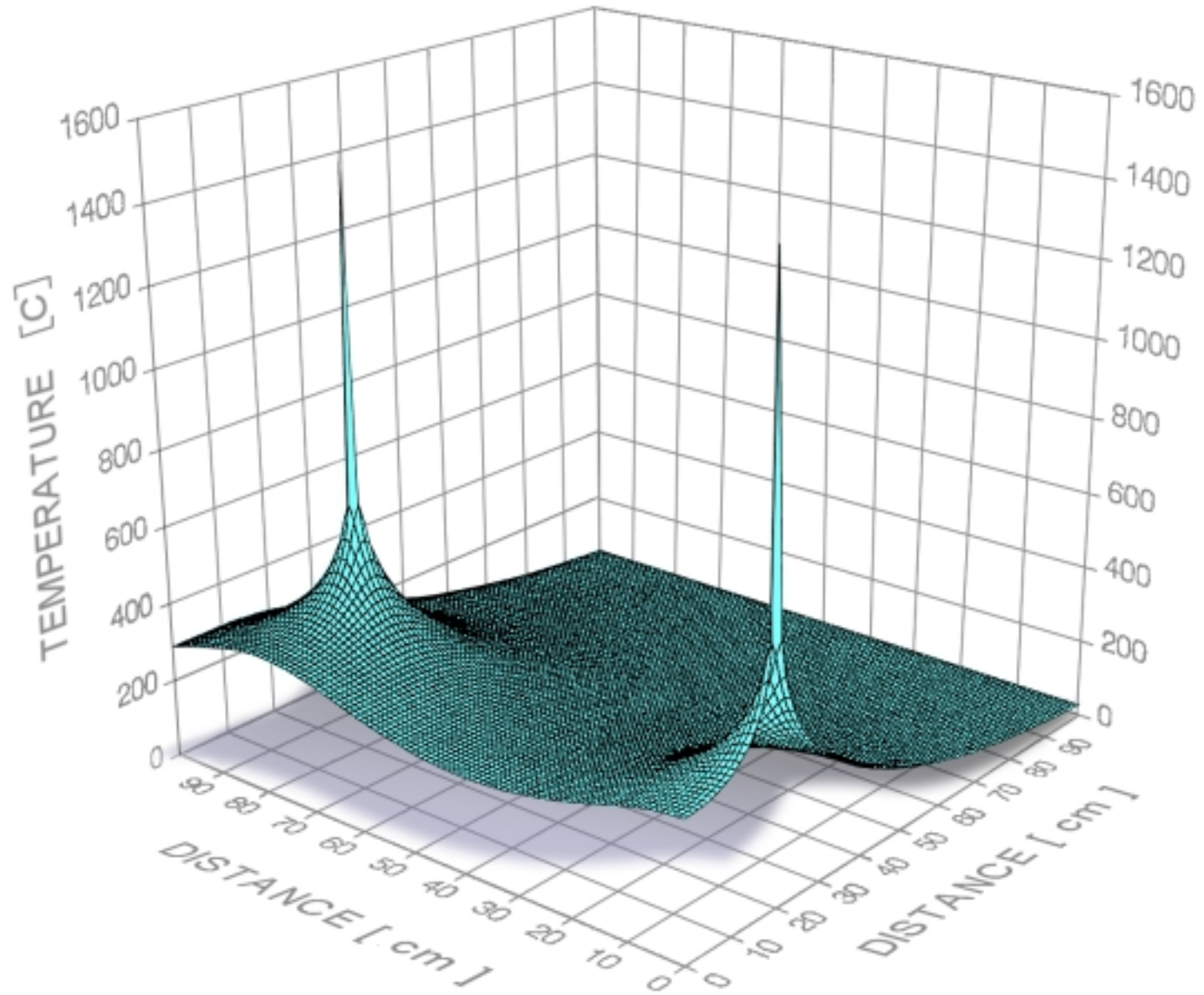


Figure 3 - SUPERPOSITION of EXPONENTIAL INTERGAL FUNCTIONS