Calculations for DNAPL Flow in Fractures of the Lower HSU Unweathered Claystone

This Attachment to Appendix F of the Casmalia Final Remedial Investigation (RI) Report provides calculations used to assess dense nonaqueous phase liquid (DNAPL) flow in fractures of the unweathered claystone of the Lower Hydrostratigraphic Unit (Lower HSU) at the Casmalia Site. As further described in Appendix F and the main RI Report, free phase DNAPL is known to exist at the following locations:

- As a DNAPL pool overlying Lower HSU fractured claystone within the southern area of P/S Landfill. Free phase DNAPL occurs within the Gallery Well, RIPZ-27 immediately north of the Gallery Well, and RIPZ-13 approximately 150 feet north of the Gallery Well. The current measured DNAPL thicknesses are approximately 5 feet in RIPZ-27 and 14 feet RIPZ-13. DNAPL at the Gallery Well is kept pumped-down to a thickness of approximately 2 feet. The CSC measured a DNAPL thickness of 9 feet at the Gallery Well when initiating a DNAPL recovery on July 9, 1997. This DNAPL at the Gallery Well was likely present prior to the CSC's tenure at the site when liquid extraction from the Gallery Well was limited and the action level in the well was significantly higher. A liquid extraction test performed in RIPZ-13 was initiated on March 3, 2009 for a period of 10 days; during testing 42.3 gallons of DNAPL, 2.3 gallons of water and 0.1 gallons of LNAPL were captured. The DNAPL thickness declined from 13.60 feet to 2.5 feet at the end of the test period. The DNAPL thickness recovered steadily to a thickness of 8.47 feet when measured on March 9, 2010 and continued to steadily recover over a 1-year period to a thickness of 14 feet on June 18, 2010. The thickness of 14 feet was the DNAPL thickness prior to the start of the extraction test.

- Within fractures of the Lower HSU claystone in the Central Drainage Area between the P/S Landfill and the Perimeter Source Control Trench (PSCT). This free phase DNAPL occurs as measurable thicknesses within Lower HSU piezometers RGPZ-7C and RGPZ-7D, approximately 500 feet south of the clay barrier and 150 feet north of the PSCT. A review of fracture patterns observed within the optical televiewer survey (Table E-9) indicate that the majority of measurable fractures within the LHSU exhibit steep dip angles, while other fractures exhibit shallow and moderate dip angles. The nature of fracture continuity or connectivity with depth is unknown. Additional descriptions of fracture dips, continuity, and connectivity are provided in Sections 4, 5, and 6 o the main report.

DNAPL pooled within the southern area of P/S Landfill (or the Central Drainage Area if present) may have entered underlying fractures of the Lower HSU claystone, migrated through these fractures due to density-driven flow, and be the source of the free phase DNAPL that is measurable in RGPZ-7C and RGPZ-7D. The calculations presented in this attachment address the following:

- Thickness of DNAPL required to enter the underlying fractures within the Lower HSU unweathered claystone.

- Upward hydraulic gradient required to prevent continued downward DNAPL migration once DNAPL has entered underlying fractures within the Lower HSU.

- Upward hydraulic gradient historically and currently present in the Central Drainage Area where DNAPL is known to occur and whether this hydraulic gradient is sufficient to prevent continued downward migration of DNAPL within the Lower HSU claystone fractures.

The CSC used established mathematical equations governing DNAPL flow and data specific to the Casmalia site as input parameters to those equations to assess these issues. The site-specific data included measurements of DNAPL physical properties and unweathered claystone fracture widths. A summary of the equations and resulting conclusions regarding DNAPL movement at Casmalia is presented below.

I. Equation Development

To drive DNAPL from a free surface into a porous or fractured (subsurface) media, there are three driving forces that act concurrently on subsurface DNAPL. These include the force due to gravity (or density driving force), the capillary force (holding DNAPL in place), and the hydraulic force (influencing the DNAPL density driving force). The gravitational force will act to settle the denser material to the “bottom” of the containing media; the capillary force (or specifically the capillary action of water) will act to hold DNAPL in place and prevent DNAPL invasion due to water being the preferred wetting agent with the surrounding media (i.e., high surface tension); and the flow direction of the groundwater (i.e., the hydraulic gradient) will influence DNAPL flow being driven by gravity.

DNAPL migration will occur if the sum of the driving force (gravity and possibly downward hydraulic force) exceeds the restricting force (capillary force and possibly upward hydraulic force). The hydraulic force due to hydraulic gradient can promote or resist DNAPL migration, depending on its principle direction. A downward hydraulic force will increase the potential for downward density-driven DNAPL migration while an upward hydraulic force will decrease the potential for this DNAPL migration.

1. **DNAPL Thickness Required to Penetrate Underlying Fractures or Porous Media**. Potential DNAPL penetration (entry) from larger pore openings into smaller pore or fracture openings in water-saturated porous media requires displacement of the water-saturated porous matrix or fractures. DNAPL is able to displace water only when the DNAPL pool height generates sufficient pressure to overcome the minimum capillary pressure (i.e., entry pressure or displacement pressure, P_d), which can be expressed as:

$$P_d = (\rho_n - \rho_w) g Z_t \qquad (1)$$

where g is the gravitational constant, Z_t is the required DNAPL pool height to initiate entry into saturated pores (also called the threshold thickness), and ρ_n and ρ_w are the density of NAPL and water, respectively.

We have considered and propose two separate equations to calculate the threshold thickness of DNAPL. The equation based on rough-walled fracture aperture openings used in CSC RI/FS Work Plan (CSC, 2004) and the Technical Memorandum, Interim Collection/Treatment/Disposal of Contaminated Liquids Component of Work (ICF Kaiser, 1998) is expressed as (Kueper and McWhorter, 1991)

$$Z_t = \frac{4\sigma_{nw}\cos(\alpha)}{bg(\rho_n - \rho_w)} \qquad (2)$$

where *b* is the fracture aperture and *α* is the contact angle between water and NAPL, and σ_{nw} is the interfacial tension between water and NAPL.

Alternatively, the threshold thickness may be derived based on hydraulic conductivity of the media and the pore radius, and is expressed as (McWhorter and Kueper, 1996)

$$Z_t = 9.6\frac{\rho_w}{(\rho_n - \rho_w)}\frac{\sigma_{wa}}{\sigma_{nw}}(\frac{K}{\phi})^{-0.403} \qquad (3)$$

where *K* is the hydraulic conductivity (cm/s), σ_{wa} is the interfacial tension between water and air (65 dynes/cm), and *Φ* is the fracture porosity.

2. **Upward Hydraulic Gradient Required to Prevent Downward DNAPL Migration.** When neglecting the capillary pressure gradient, downward DNAPL movement will be driven by the density difference between DNAPL and water (gravity force and buoyancy force). The upward hydraulic gradient, i_g, necessary to counteract the gravity gradient is given by (Chen and Mercer, 1993):

$$i_g = (\rho_n - \rho_w)/\rho_w \qquad (4)$$

Where ρ_n and ρ_w are the density of NAPL and water, respectively. This equation was suggested by USEPA in their comments to request the CSC to quantify the upward groundwater gradient (necessary) to halt migration of DNAPL "by balancing the downward DNAPL density-driven force with the upward groundwater gradient force". This equation is used below with site data to evaluate the upward hydraulic gradient required to prevent continued downward DNAPL migration in fractures in the Central Drainage Area.

3. **DNAPL Migration Influences by Density and Capillary Pressure Gradients.** The CSC used established mathematical equations to develop an additional equation to also consider the resisting force of capillary action on DNAPL flow, in addition to the gravity and buoyancy forces considered above in Equation 4. The development of this additional equation is described below, although it is not used in actual calculations because the derived equation is essentially equivalent to Equation 4 given the physical subsurface features at the Casmalia site.

When the resisting force of capillary action is included, the movement of DNAPL is determined by the interaction of all the forces exerting on it. Considering both the density and capillary pressure gradients, the upward hydraulic gradient required to prevent DNAPL continued downward migration through a "capillary barrier" (i.e., low permeability barrier or aquitard) is given by (Chen and Mercer, 1993):

$$\frac{\Delta h}{L} = \frac{\rho_n - \rho_w}{\rho_w} + \frac{P_c - P_d}{\rho_w g L} \qquad (5)$$

where P_c is the capillary pressure at the base of a DNAPL pool overlying the capillary barrier, P_d is the entry pressure of the capillary barrier, and Δh is the hydraulic difference over L, the vertical length (i.e., thickness) of the capillary barrier.

The following substitutions were made as the terms P_c and P_d are not readily measurable from field measurements:

$$P_d = (\rho_n - \rho_w) g Z_t \qquad (6a)$$

where Z_t is the required DNAPL pool height to initiate entry into saturated pore or fracture, and

$$P_c = (\rho_n - \rho_w) g Z_n \qquad (6b)$$

where Z_n = thickness of DNAPL body

To derive Eq. (7), with the appropriate substitutions, the two pressure terms P_c and P_d are replaced by an equivalent head term, Z_t and Z_n, respectively. Substituting Eq. (1), Eq. (4), and Eq. (6) into Eq. (5), we derive the equation to calculate the required upward hydraulic gradient (i_h) in terms of liquid densities and thickness, as:

$$i_h = \frac{\rho_n - \rho_w}{\rho_w}\left(1 + \frac{Z_n - Z_t}{L}\right) \qquad (7)$$

It is noted that the application of Eq. (7) requires that the threshold thickness of DNAPL, Z_t, can be estimated from either Eq. (2) or Eq. (3).

In essence we have transformed the Eq. (5) in to a buoyancy term, $(\frac{\rho_n - \rho_w}{\rho_w})$, and geometric term, $(1 + \frac{Z_n - Z_t}{L})$, that represents the thickness of the DNAPL pool with respect to the fracture length to derive Eq. (7).

The derivation is valid, under the assumption that the surface tension forces P_c and P_d can be represented by equivalent hydrostatic forces, i.e., Eqns (6) and (7). Similar substitutions have been made by others and published in articles (e.g., The Behavior of Dense Non-Aqueous Liquids (DNAPLs) in Fractured Media, by Kueper and McWhorter NGWA Water Issues Publication, 1989)).

However, we should note that the methods used in the Draft-Final RI Report and RI/FS Work Plan may not be completely appropriate to the Site. Firstly, the empirical equation

$$Z_t = 9.6 \frac{\rho_w}{(\rho_n - \rho_w)} \frac{\sigma_{wa}}{\sigma_{nw}} \left(\frac{K}{\phi}\right)^{-0.403}$$

does not take into account the impact of NAPL under the influence of a hydraulic gradient. To address this, the CSC attempted to incorporate the effects of hydraulic gradient into the evaluation, i.e., by modification of eqn (5).

However, the conceptual model for eqn (7) (and by default eqn (5)) may not readily translate to the Casmalia Site. The conceptual model for eqn (7) is based on a submerged DNAPL pool resting on a low permeability fractured surface, with the fractured aquitard having a defined thickness (L). (Note that the term L is represented as both a variable and an unknown, which is not ideal).

At the Casmalia Site an “aquitard” per se does not exist (that is, there is not a high-low-high permeability series of geologic units). Instead, hydraulic properties over much of the area of interest are governed by the transition from weather claystone to unweathered claystone, i.e., from a moderate porosity and permeable soil profile to a largely low porosity impermeable rock. Thus, for eqn (7) to be completely applicable the fracture length L becomes the thickness of the unweathered claystone (900+ feet), and as such, the geometric term in eqn (2) tends to zero, and the required upward gradient to arrest DNAPL down movement is that required to counteract the buoyancy term (i.e., Eq. 4).

II. <u>Equation Application</u>

1) DNAPL Thickness Required to Penetrate Fractures or Porous Media

<u>Previous DNAPL Pool Height Calculations from RI/FS Work Plan</u>

Previous CSC estimates for the required DNAPL pool heights to infiltrate the Upper or Lower HSU where initially presented in the RI/FS Work Plan (CSC, 2004); these estimates were based on a set of measured physical properties of the DNAPL and interpreted aquifer physical properties, as follows:

- Using the fracture equation [i.e., Eq.(2)], a DNAPL density of 1.1 g/cm^3, an interfacial tension between water and DNAPL of 4.95 dynes/cm, and fracture apertures from historical core borings (CB-4 and CB-5i to CB-8i), the required DNAPL pool height to initiate DNAPL entry to the Lower HSU ranges from 0.09 to 0.23 feet.

- Using the hydraulic equation [i.e., Eq.(3)] along with the hydraulic conductivity of 1.2 x 10^{-6} ~ 2.5 x 10^{-4} cm/s and the same DNAPL density and interfacial tension as in the fracture equation , the required DNAPL pool height for DNAPL to initiate DNAPL entry into the lower HSU ranges from 1.1 to 9.1 feet.

<u>Revised DNAPL Pool Height Calculations using RI Data</u>

The DNAPL pool height calculations from the RI/FS Work Plan are revised below using new DNAPL density data collected during 2004 RI activities. The calculations are revised using both the fracture equation Eq. (2) and the porous media equation Eq. (3) in the two text tables below. The calculations in these tables are performed using the following DNAPL densities:

- 1998 DNAPL density of 1.1 g/cm^3, for the Gallery Well (same density as above)
- 2004 DNAPL density of 1.085 g/cm^3 for the Gallery Well
- 2004 DNAPL density of 1.0184 g/cm^3 for RGPZ-7C

The other parameters used in Eq. (2) and Eq. (3) are the same as those presented in the RI/FS Work Plan (CSC, 2004) since no new information on these physical properties was obtained.

Revised DNAPL Pool Height required based on Fracture Aperture (Eq.2)

Required DNAPL Pool Height based on "Fracture Aperture"				
Data Source (cm/s)	Fracture Aperture (cm)	Required DNAPL Pool Height (ft)		
		Gallery (1998)	Gallery (2004)	RGPZ-7C (2004)
70th Percentile (CB-4)	0.001	2.27	2.66	12.31
Maximum (CB-4)	0.003	0.76	0.89	4.10
70th Percentile (CB-5i to CB-8i)	0.01	0.23	0.27	1.23
Maximum (CB-5i to CB-8i)	0.025	0.09	0.11	0.49

Revised DNAPL Pool Height required based on Hydraulic Conductivity (Eq.3)

Required DNAPL Pool Height based on "hydraulic conductivity"				
Hydraulic Conductivity (cm/s)	Porosity (Φ)	Required DNAPL Pool Height (ft)		
		Gallery (1998)	Gallery (2004)	RGPZ-7C (2004)
Upper HSU Max.: 6.0×10^{-3}	0.05	0.56	0.66	3.06
Upper HSU Mean: 4.5×10^{-5}	0.05	4.05	4.75	21.99
Lower HSU Max.: 2.5×10^{-4}	0.01	1.06	1.25	5.76
Lower HSU Mean: 1.2×10^{-6}	0.01	9.11	10.71	49.53
Clay Barrier Minimum: 1.0×10^{-6}	0.25	35.9	42.17	>150
Upper HSU Matrix: 3.4×10^{-8}	0.48	>150	>200	>900
Lower HSU Matrix: 3.4×10^{-8}	0.44	>150	>200	>900

For the Gallery Well, the difference in the results of the calculations presented in the RI/FS Work Plan performed using the 1988 DNAPL density of 1.1 g/cm^3 and the revised calculations performed using the 2004 DNAPL density of 1.085 g/cm^3 is small. Both sets of calculations indicate that the height of DNAPL in the P/S Landfill is potentially sufficient to initiate DNAPL entry into underlying fractures of the Lower HSU under the range of fracture widths and equivalent porous media permeabilities assessed. As described above, the current measured DNAPL thicknesses are approximately 5 feet in RIPZ-27 and 14 feet RIPZ-13.

As discussed in the RI/FS Work Plan, the difference in the required pool heights between the two equations (Eq. 2 and Eq.3) may be due to the over-estimation of in-situ fracture aperture openings. The 70th percentile is conservatively used because the fraction of aperture widths less than or equal to 0.01 cm is 70 percent. Additionally, apertures are considered high-end estimates and wider than in-situ equivalents due to relieving of compressive stress, and disturbance during drilling and during the measurement process. However, even though the two sets of equations use different inputs and assumptions, they both indicate the height of DNAPL in the P/S Landfill is potentially sufficient to initiate DNAPL entry into underlying fractures of the Lower HSU.

The calculations performed for the claystone matrix using a hydraulic conductivity of 3.4 x 10^{-8} cm/sec indicate that DNAPL invasion into the claystone matrix is unlikely. Because DNAPL invasion into the claystone matrix is unlikely, the claystone matrix in the Lower HSU does not appear to be significant secondary storage mechanism.

2) Upward Hydraulic Gradient Required to Prevent Downward DNAPL Migration.

Calculations of the required upward hydraulic gradient required to prevent downward DNAPL movement is estimated using Eq. (4) for the following piezometer clusters:

- Located between the P/S Landfill and PSCT-1
  - RGPZ-6B, RGPZ-6C, and RGPZ-6D
  - RGPZ-7C and RGPZ-7D

- Located immediately downgradient of PSCT-1
  - RG-1B, RG-1C, and RGPZ-8D

Figures F4-1, F4-2, and F4-3 are hydrographs for each of these clusters, respectively. These hydrographs show the groundwater elevations for each piezometer, annual precipitation, and notations with reasons that select water level data are not in equilibrium. In general, groundwater elevations increase during wetter winters and decreases during drier winters.

The required upward gradient based on Eq. (4) is straight forward and equals to the ratio of the DNAPL and water density difference to the water density. Based on the DNAPL densities of 1.0851 and 1.0184 g/cc measured in samples collected from the Gallery Well and RGPZ-7C, the upward hydraulic gradient of 0.018 to 0.085 ft/ft in vertical direction is required to counteract DNAPL sinking due to gravity gradient only.

For a comparison of the observed upward hydraulic gradients and the calculated hydraulic gradients needed for DNAPL entry into the Upper or Lower HSUs; groundwater elevations nested wells are used.

Table F4-1 presents the detailed results for the required upward hydraulic gradient necessary to arrest the downward DNAPL migration and whether the upward gradient is sufficient to prevent downward DNAPL migration at each of the three well clusters. The calculations are performed using the densities from both the Gallery Well DNAPL and RGPZ-7C samples to encompass the range of densities that may exist in the area ranging from the southern part of the P/S Landfill to the PSCT. The calculations indicate the following:

- There is a downward gradient in the Central Drainage Area from the Upper HSU to the Lower HSU as indicated by the water levels in well pair RGPZ-6B/RGPZ-6C (Figure F4-1). These downward gradients will promote downward migration of DNAPL (Table F4-1).

- Historically there has been an upward gradient in the Central Drainage Area within the Lower HSU as indicated by the water levels in well pairs RGPZ-6C/RGPZ-6D and RGPZ-7C/D (Figures F4-1 and F4-2). This upward gradient still occurs at well pair RGPZ-6C/RGPZ-6D but became neutral at well pair RGPZ-7C/RGPZ-7D during 2006.

    - Since equilibrium data became available in late 2000, the upward gradient at well pair RGPZ-6C/RGPZ-6D has always been sufficient to prevent downward DNAPL migration assuming a DNAPL density of 1.0184 gm/cm^3 but not sufficient assuming a DNAPL density of 1.0851 gm/cm^3 (Table F4-1). The scenario with a DNAPL density of 1.0184 gm/cm^3 is more likely at this well pair.

    - Since equilibrium data became available in early 2001, the upward gradient at well pair RGPZ-7C/RGPZ-7D (Figure F4-2) has been sufficient through 2006 to prevent downward DNAPL migration assuming a DNAPL density of 1.0184 gm/cm^3 but insufficient after 2006 (Table F4-1). The upward gradient has not been sufficient to prevent downward DNAPL migration assuming a DNAPL density of 1.0851 gm/cm^3 (Table F4-1). The scenario with a DNAPL density of 1.0184 gm/cm^3 is more likely at this well pair.

- There is an upward gradient near PSCT-1 from the Lower HSU to the Upper HSU as indicated by well pair RG-1B/RG-1C (Figure F4-3). Deeper piezometer RGPZ-8D cannot be used to assess the vertical gradient within the Lower HSU because the RGPZ-8D water levels are not in equilibrium.

    - Since equilibrium data became available in November 2000, the upward gradient at well pair RG-1B/RG-1C has always been sufficient to prevent downward DNAPL migration from the Upper HSU to the Lower HSU assuming a DNAPL density of both 1.0184 gm/cm^3 and 1.0851 gm/cm^3 (Table F4-1).

    - Equilibrium water level data are not available to assess whether the gradients are sufficient to prevent downward DNAPL migration within the Lower HSU.

Water level data are not available prior to 2001 to assess the conditions before placement of the P/S Landfill cap in 1999 and since groundwater extraction began at the PSCT in the early 1990s.

III. <u>Summary</u>

1. DNAPL Thickness Required to Penetrate Fractures or Porous Media

Calculations performed to assess the DNAPL thickness required to penetrate underlying fractures within the Lower HSU indicate that the historical and current heights of DNAPL in the P/S Landfill are potentially sufficient to initiate DNAPL entry into underlying fractures of the Lower HSU under the range of fracture widths and equivalent porous media permeabilities assessed. A sufficient thickness of DNAPL to initiate DNAPL entry into the Lower HSU has likely been present since before 1997.

2. Upward Hydraulic Gradient Required to Prevent Downward DNAPL Migration

Calculations performed to assess the upward hydraulic gradient required to prevent downward DNAPL migration indicate the following:

- There is a downward gradient at the Central Drainage Area from the Upper HSU to the Lower HSU that will promote downward migration of DNAPL. However, there is an upward gradient to the south near PSCT-1 from the Lower HSU to the Upper HSU that has always been sufficient to prevent downward DNAPL migration from the Upper HSU to the Lower HSU assuming a DNAPL density of both 1.0184 gm/cm^3 and 1.0851 gm/cm^3.
- Historically there has been an upward gradient in the Central Drainage Area within the Lower HSU. This upward gradient still occurs at well pair RGPZ-6C/RGPZ-6D but became neutral at well pair RGPZ-7C/RGPZ-7D during 2006. Since equilibrium data became available in late 2000, the upward gradient at well pair RGPZ-6C/RGPZ-6D has always been sufficient to prevent downward DNAPL migration assuming a DNAPL density of 1.0184 gm/cm^3 but not sufficient assuming a DNAPL density of 1.0851 gm/cm^3. The upward gradient at well pair RGPZ-7C/RGPZ-7D has been sufficient through 2006 to prevent downward DNAPL migration assuming a DNAPL density of 1.0184 gm/cm^3 but insufficient after 2006. The upward gradient at well pair RGPZ-7C/RGPZ-7D has not been sufficient to prevent downward DNAPL migration assuming a DNAPL density of 1.0851 gm/cm^3. A DNAPL density of 1.0184 gm/cm^3 is more likely at these well pairs than 1.0851 gm/cm^3.
- Equilibrium water level data are not available in deeper piezometer RGPZ-8D to assess whether the gradients are sufficient to prevent downward DNAPL migration within the Lower HSU at PSCT-1.
- Water level data are not available prior to 2001 to assess the conditions before placement of P/S Landfill cap in 1999 and since groundwater extraction began at the PSCT in the early 1990s.
- Groundwater elevation data are not available to assess the vertical gradient conditions at the southern end of the P/S Landfill, at the Gallery Well, or between the Gallery Well and the RGPZ-6 piezometer cluster.

In summary, since landfill capping occurred from 1999 through 2002, groundwater gradients have been sufficient in the south part of the Central Drainage Area and in the vicinity of PSCT-1 to prevent downward DNAPL movement. These upward gradients have likely been present since liquids extraction from the PSCT began in the early 1990s. However, data necessary to perform this assessment are not available to the north (i.e., under the P/S Landfill) to assess whether there are upward gradients that are sufficient to prevent the downward migration of DNAPL into the Lower HSU. However, under present site conditions (i.e., capping of P/S landfill, Gallery Well extraction of NAPL liquids, placement of the PSCTs) DNAPL is likely contained to onsite boundaries.

IV. References

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