

In the Matter of

PR Spring Tar Sands Project, Ground Water Discharge Permit-by-Rule

No. WQ PR-11-001

PREPARED SUPPLEMENTAL TESTIMONY

OF

WILLIAM JOHNSON

ON BEHALF OF

LIVING RIVERS

March 16, 2012

1 **I. Introduction**

2 **Q. Please state your name.**

3 My name is William P. Johnson

4

5 **Q. By whom are you employed and what is your position?**

6 I am a professor in the department of Geology & Geophysics and an adjunct professor in
7 the department of Civil & Environmental Engineering at the University of Utah.

8

9 **Q. For whom are you testifying in this proceeding?**

10 I am testifying on behalf of Living Rivers.

11

12 **Q: IN PREPARING THIS SUPPLEMENTAL TESTIMONY, WHAT DOCUMENTS HAVE YOU REVIEWED?**

13 In addition to the documents listed in my direct testimony (and the documents
14 referenced within them), I have reviewed the following:

15 Mr. Handl's February 27, 2012 Report

16 Perry's Chemical Engineer's Handbook, 1999

17 Perry's Chemical Engineer's Handbook, 1973

18

19 (Schwarzenbach R.P., Gschwend P.M., and Imboden D.M., 1993, Environmental Organic

20 Chemistry, Wiley Interscience, New York

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22 Johnson, W.P., and John, W.W., 1999, A Comparison of Humic Substances and Surfactants as

23 Remediation Agents: PCE Solubilization and Mobilization by Commercial Humic Acid, J. of Cont.

24 Hyd., 35, 343-362.

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Johnson, W.P., Cabral, K., Lion L.W., and Corapcioglu, Y.M., 1998, Reconciliation of Expressions for the Modified Retardation Factor and Incorporation of Non-linear Effects, J. Cont. Hydr.32, 247-266.

Johnson, W.P., and Amy, G.L., 1995, Facilitated Transport and Enhanced Desorption of Polycyclic Aromatic Hydrocarbons (PAH) by Natural Organic Matter (NOM) in Aquifer Sediments: Environmental Science and Technology, 29, 807-817.

Johnson, W.P., Amy, G.L., and Chapra, S.C., 1995, Model Simulation of Facilitated Transport and Enhanced Desorption of Polynuclear Aromatic Hydrocarbons (PAH) by Natural Organic Matter (NOM): ASCE, Journal of Environmental Engineering 121(6), 438-446.

Q. WHAT IS THE PURPOSE OF YOUR SUPPLEMENTAL TESTIMONY?

The goal of my testimony is to predict what will happen when water, such as rain water, contacts the residual tar/d-limonene mixture that will remain in the processed sands returned to the mine and deposited in the waste piles at the PR Spring site. The question to answer is whether bitumen compound would dissolve into that water. In my January 20, 2012 testimony, I determined that the bitumen compounds would indeed dissolve into water and therefore be available for transport. My conservative analysis showed that, in the presence of d-limonene, the concentration of bitumen in water would be 2000 times higher than the concentration would be if d-limonene were not present. The purpose of this testimony is to show the errors in Mr. Handl's analysis of the same issue and to show that my analysis better predicts what could happen when water contacts the processed sands.

1 **II. Rebuttal to Edward Handl**

2
3 **Q: Mr. Handl has filed a response to the testimony you filed in this case on January 20, 2012. Please**
4 **provide a brief summary of Mr. Handl's assertions and your reply to those contentions.**

5 Mr. Handl's February 27, 2012 response to my testimony contends that the only effect
6 of d-limonene on tar (bitumen) compounds in the residual mixture remaining in processed sands
7 is to dilute the bitumen compounds in that organic mixture (referred to as extract), and thereby
8 to simply dilute the compound concentrations in water (referred to as raffinate) that would
9 come into contact with (equilibrate with) the residual mixture. My testimony, in contrast,
10 demonstrates that the role of d-limonene is not merely passive dilution; but rather, that d-
11 limonene dissolved in water serves to "coax" bitumen compounds into the water; thereby
12 greatly increasing the concentration of bitumen compounds in the water that comes into
13 contact with the residual mixture.

14 Mr. Handl's assertion ignores the critical role of dissolved d-limonene in the water,
15 which is to concentrate bitumen in the water by many orders of magnitude relative to bitumen's
16 normal water solubility. In other words, the presence of d-limonene dissolved in water acts to
17 make bitumen more soluble than it would be were the d-limonene not there. The effect of d-
18 limonene on the solubility of bitumen cannot be demonstrated via Mr. Handl's ternary phase
19 equilibrium analysis because he assumes incorrectly that bitumen mixes with water "ideally,"
20 according to Raoult's Law. As I show below, bitumen does NOT mix with water ideally, and this
21 non-ideal interaction between bitumen and water refutes the raffinate boundary that Mr. Handl
22 assumed. Instead, this non-ideal interaction supports a raffinate boundary that in fact
23 demonstrates that bitumen compound concentrations will increase in the water as d-limonene
24 dissolves into the water. Hence, this effect (enhanced dissolution of bitumen compounds into

1 water via d-limonene dissolution into water) is supported both by the partition coefficient
2 approach I provided previously, as well as by a correct ternary phase equilibrium analysis.

3
4 **Q: Is your use of equilibrium partition coefficients standard practice in performing an analysis like the**
5 **one you present in your January 20, 2012 testimony?**

6 Yes. Mr. Handl, in his testimony, calls the use of equilibrium partition coefficients (as I
7 have done) "baffling", and implies that this treatment is unconventional. However, this
8 approach is highly conventional and appropriate, and is well demonstrated in the literature cited
9 below, as well as in the same section of the very text that Mr. Handl cited (Perry's Chemical
10 Engineer's Handbook, 1973); albeit my version of the text seems to be more modern relative to
11 Mr. Handl's version, and has a more extensive treatment of partition coefficients (Perry's
12 Chemical Engineer's Handbook, 1999).

13
14 ***The Problem with Mr. Handl's Use of Mole Fractions and Raoult's Law: Thermodynamics and Non-***
15 ***Ideal Mixtures***

16
17 **Q: Is Mr. Handl correct that the only influence of d-limonene is to reduce the mole fraction of**
18 **bitumen compounds in the extract?**

19 No, Mr. Handl is mistaken when he makes a significant issue out of the fact that I did not
20 account for specific mole fractions in the tar/d-limonene mixture (extract), which are of course
21 needed in order to calculate the specific concentration of a given compound that is achieved in
22 water (raffinate) that is in contact with the residual tar/d-limonene mixture (extract). However,
23 the issue is NOT the specific concentration of benzo(a)pyrene (B(a)P) or any other given bitumen

1 compound in water, because there is an entire class of compounds that are of concern.

2 Specifically, Raoult's Law for compounds dissolving into water for under ideal conditions is:

$$3 \quad C_{raf} = X_{ext} C_w^{sat}(L) \quad (1)$$

4 Applied to the present inquiry, C_{raf} is the concentration of the bitumen compound (e.g.
5 B(a)P or any other compound one might want to consider) in the raffinate (the water phase that
6 is in contact with the extract), X_{ext} is the mole fraction of the bitumen compound of interest in
7 the extract (tar/d-limonene mixture), and $C_w^{sat}(L)$ is the solubility in pure water of the pure liquid
8 form of the bitumen compound of interest. Hence, as Mr. Handl pointed out, the concentration
9 of any given compound in the organic phase would be relatively small (scaled to its X_{ext}).

10 However, there are expected to be many carcinogenic compounds in the organic
11 extract. As a result, to be accurate, one must sum the resulting concentrations for ALL
12 compounds of interest made using Raoult's Law above. In determining the absolute
13 concentration in the raffinate (in his February 27, 2012 response to my testimony), Mr. Handle
14 considered the mole fraction of a single compound only (B(a)P), and obtained a concentration of
15 5.7×10^{-4} $\mu\text{g/L}$ in the raffinate. The sum of the concentrations for all compounds of interest
16 would be considerably higher than the concentration that Mr. Handl calculated. Rather than
17 perform the calculation for a myriad of compounds, I simply represented that class of
18 compounds with B(a)P's water solubility, as my goal was not to obtain the precise concentration
19 of B(a)P in the water phase, but rather to demonstrate the critical effect of d-limonene on the
20 concentration of B(a)P in the water phase.

21 Furthermore, as I show below, Mr. Handl's incorrect assumption of ideal mixing leads to
22 further underestimation of the value of C_{raf} (the concentration of bitumen compound in the
23 raffinate, which I referred to as C_w^* in my previous testimony). This means that Mr. Handl
24 substantially underestimated the concentration of bitumen compounds in the raffinate because

1 he did not sum the concentrations for all the bitumen compounds of interest that will dissolve
2 into the water phase AND because he did not account for the fact that dissolved d-limonene in
3 the water phase (raffinate) would provide an ideal phase for the bitumen compounds, thereby
4 increasing the concentration of bitumen compounds in the raffinate. Had Mr. Handl summed
5 the concentrations of the many compounds in the tar, and had he accounted for solubilization
6 of bitumen compounds by d-limonene in the raffinate, his calculations would have shown a
7 significantly higher concentration of bitumen compounds in the raffinate.

8
9 **Q: For the purposes of further explaining the errors in Mr. Handl's analysis, will you adopt his**
10 **distinction between water and raffinate?**

11 Yes. Mr. Handl's February 27, 2012 response to that testimony refers to the
12 concentration of bitumen compound in the raffinate as " C_w ". However, Mr. Handl's distinction
13 between water and raffinate is useful, and so I have adopted " C_{raf} " to refer to the concentration
14 of bitumen compound in the water phase (raffinate) that is in contact with (equilibrated with)
15 the residual extract (tar/d-limonene mixture). Below I will use the term " C_w " to refer to water
16 that is in contact with tar (but without d-limonene in either phase).

17
18 **Q: In your January 20, 2012 testimony, how did you analyze the effect of d-limonene on the**
19 **concentration of bitumen in water?**

20 For the present purposes, the primary issue is the CHANGE in the concentration of
21 bitumen compounds in water before, versus after, the addition of d-limonene. My testimony
22 used partition coefficients (equilibrium coefficients for distribution of an example bitumen
23 compound between water and d-limonene) to demonstrate that the addition of d-limonene to

1 water increases the solubility of bitumen compounds in the water solution by multiple orders of
2 magnitude.

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4 **Q: Is Mr. Handl's approach capable of demonstrating the effect demonstrated in your testimony –**
5 **calculating the change in the concentration of bitumen in water caused by the addition of d-limonene**
6 **by using partition coefficients?**

7 Yes, but not under the incorrect assumptions that were made by Mr. Handl. Mr. Handl
8 inexplicably denies the validity of my partition coefficients approach despite its being well
9 established in the literature. Instead, Mr. Handl provides a ternary phase equilibrium analysis
10 that incorrectly assumes the bitumen compound partitioning follows Raoult's Law above for
11 ideal conditions. As a result, he incorrectly concludes that only effect of d-limonene is to dilute
12 the bitumen compounds in the organic residual (extract) and the water phase (raffinate). Mr.
13 Handl's conclusion is wrong because he fails to acknowledge deviation from Raoult's Law for
14 non-ideal interactions, such as those between bitumen compounds and water.

15
16 **Q: Can you show what information is needed to account for the interactions that are not included in**
17 **Raoult's Law?**

18 Yes. To explain further the impact of non-ideal conditions, I show that the above
19 expression of Raoult's Law, equation (1), is derived from a thermodynamic basis by considering
20 chemical potentials (μ_o and μ_w) of the bitumen compound of interest in the organic and water
21 phases, respectively (assuming that both the organic and water phases are liquids):

$$\mu_o = \mu^o + RT \ln \frac{\gamma_o X_o P^o(L)}{P^o(L)} \quad (2)$$

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$$\mu_w = \mu^0 + RT \ln \frac{\gamma_w X_w P^0(L)}{P^0(L)} \quad (3)$$

where μ^0 is the standard chemical potential for the bitumen compound of interest, R is the universal gas constant, T is temperature. The parameters γ_o and γ_w are the activity coefficient of the bitumen compound in the organic and water phases, respectively, and $P^0(L)$ is the vapor pressure of the pure liquid bitumen compound of interest.

At equilibrium, the chemical potentials of any bitumen compound of interest are equal in the organic and water phases ($\mu_o = \mu_w$). Therefore equilibrium is represented by equating the two expressions (2 & 3) above, which boils down to:

$$\gamma_w X_w = \gamma_o X_o \quad (4)$$

And re-arranging further yields

$$X_w = \gamma_o X_o \frac{1}{\gamma_w} \quad (5)$$

Q: What does this equation mean?

What the above expression says is that the concentration of B(a)P (or any other bitumen compound in the water phase) is proportional to its mole fraction in the organic mixture (X_o), its activity coefficient in the organic mixture (γ_o), and the inverse of its activity coefficient in the water phase (γ_w). Here, the organic mixture may be tar (in liquid form), or may be the tar/d-limonene liquid mixture, depending on the context one wishes to address. Both contexts are ruled by the above relationship. This expression is nearly equivalent to Equation 1 (Raoult's Law), but to make this obvious I need to explain further the activity coefficients.

1 **Q: What do activity coefficients tell us?**

2 Activity coefficients represent the compatibility of a compound for a given phase, i.e.
3 the organic mixture and water are the two phases with which the bitumen compound interacts.
4 A cardinal rule is that "like dissolves like." Therefore, polar substances such as water and
5 vinegar dissolve well into each other (are compatible), and non-polar substances such as
6 bitumen and d-limonene dissolve well into each other (are compatible). However, non-polar
7 substances do not dissolve well into polar substances; oil and water do not mix, nor do bitumen
8 compounds mix well into water. This is why the tar remains in the sand after millennia of
9 precipitation; the water does not dissolve the bitumen, and this is why d-limonene is such a
10 great agent for extracting bitumen compounds from the sand; i.e., bitumen and d-limonene are
11 compatible.

12 The activity coefficient for a perfectly compatible substance is 1, and the activity
13 coefficients for incompatible substances are greater than 1, ranging up to around 10^9 (one
14 billion) for large non-polar compounds like those in bitumen when they interact with water.
15 Hence, γ_o (activity coefficient of bitumen compounds in the organic mixture, that is, the non-
16 water phase) is approximately 1 (because they are perfectly compatible or nearly); whereas, the
17 value for γ_w (the activity coefficient of the bitumen compound in the pure water phase) is very,
18 very high (approaching 1 billion).

19

20 **Q: So how do the activity coefficients in water and the organic mixture relate to Raoult's Law and**
21 **ideal versus non-ideal conditions?**

22 What precisely is the value of γ_w in the raffinate is at the heart of the dispute between
23 Mr. Handl and me. Mr. Handl contends that this value is nearly one billion in the raffinate (as in
24 pure water) despite the presence of highly compatible d-limonene in the raffinate. In contrast,

1 my analysis shows that the value in the raffinate drops significantly below that in pure water
2 due to the presence of highly compatible d-limonene in the raffinate. The decreased activity
3 coefficient of bitumen compounds in the raffinate (relative to that in pure water) yields a much
4 higher concentration of bitumen compounds in the raffinate than one would predict for pure
5 water. Mr. Handl's assumption of ideal conditions predicted a concentration of bitumen
6 compounds in the raffinate that approximate the concentration of bitumen in pure water, and
7 ignored the effect of d-limonene dissolved in the water.

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9 **Q: But still, can you clarify how exactly this relates to Raoult's Law?**

10 This is done by considering pure water in contact with (equilibrated with) a pure liquid
11 bitumen compound, and in this case γ_w is referred to as γ_w^{sat} . From equation 5, recognizing that
12 that γ_o and X_o are each approximately equal to 1 for a drop of pure liquid bitumen compound,
13 the value of γ_w^{sat} can be obtained as the inverse of the solubility of the bitumen compound (in pure
14 liquid form) in water (expressed as a mole fraction):

$$15 \quad \gamma_w^{sat} = \frac{1}{X_w^{sat}(L)} \quad (6)$$

16 Substituting concentration for mole fraction, because solubilities are given as concentrations:

$$17 \quad \gamma_w^{sat} = \frac{1}{X_w^{sat}(L)} = \frac{1}{C_w^{sat}(L) V_w} \quad (7)$$

18 where V_w is the molar volume of water, and where this conversion between mole fraction and
19 concentration is appropriate for dilute concentrations such as for dissolution of bitumen
20 compounds in water.¹

¹ This approach is appropriate because this simple conversion between mole fraction and concentration is accurate only in dilute solutions like the raffinate.

1 Note that equation (6) substituted into (5) gives Raoult's Law in terms of mole fractions,
2 that is: $X_w = \gamma_o X_o X_w^{sat}$. Notice also that substitution of the relationship between mole fraction
3 and concentration given in Equation (7) yields Equation (1): $C_w = \gamma_o X_o C_w^{sat}$, with the
4 understanding that $\gamma_o \sim 1$.

5
6 **Q: O.K. But then where does the deviation from Raoult's Law come in?**

7 To show this I need to first establish the value of the activity coefficient of the bitumen
8 compound in pure water (γ_w^{sat}). Fortunately, this is obtained directly from Equation (7), using
9 B(a)P (again as a representative of many compounds of concern in the bitumen):

10
$$\gamma_w^{sat} = \frac{1 L_w}{1.95E - 7 mol_{B(a)P}} \frac{1 mol_w}{1.8E - 2 L_w} = 10^{8.45} \quad (8)$$

11
12 **Q: What does this calculation show us?**

13 Note that the result of this calculation is $10^{8.45}$, which equals 2.85E8 or 285,000,000.
14 This is a very large activity coefficient, representing highly non-ideal interaction between B(a)P
15 and water. Remember, however, the critical point here is that this value represents the activity
16 coefficient for B(a)P in pure water. It DOES NOT represent the activity coefficient for B(a)P (or
17 other bitumen compounds) in raffinate (water with d-limonene) as was assumed by Mr. Handl.
18 Before quantifying the value of γ_w in the raffinate, I will show conceptually how this analysis
19 relates to the ternary phase equilibrium analysis provided by Mr. Handl.

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21 **Q: O.K. but before you do, would you summarize your points so far in your testimony?**

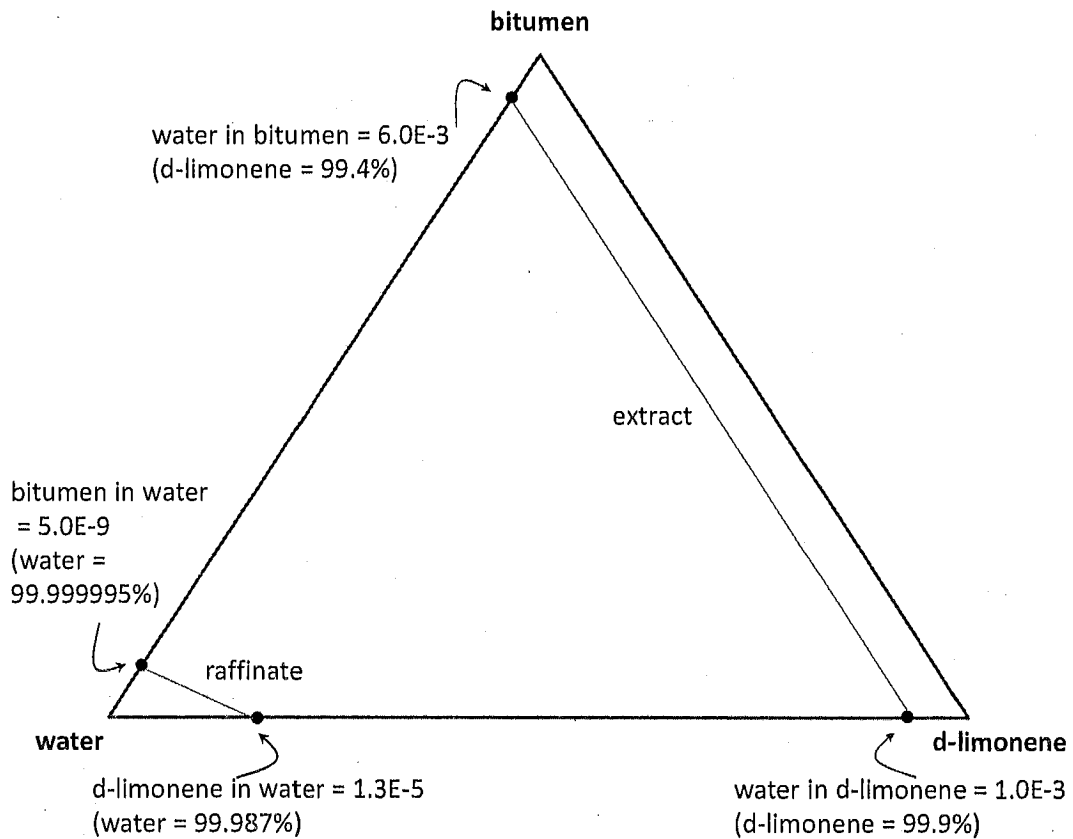
22 As indicated above, I demonstrated that Mr. Handl substantially underestimates the
23 concentration of bitumen in the raffinate because he does not sum or add up the

1 concentrations for all the bitumen compounds of interest that will dissolve into the water. I also
2 have further shown that bitumen and water are not an ideal mixture and indeed, are far from
3 ideal. This sets the basis for demonstrating that the non-ideality of interaction between
4 bitumen and water needs to be accounted for. Below I show how this would need to be done
5 using Mr. Handl's ternary phase equilibrium approach, as via thermodynamic relationships.

6
7 ***The Problem with Mr. Handl's Ternary Phase Equilibrium Analysis***

8
9 **Q: You stated that you would demonstrate how your determination of the that the activity**
10 **coefficient of bitumen (the value of γ_w) in water relates to Mr. Handl's ternary phase equilibrium**
11 **analysis. Please proceed.**

12 To argue in his response that addition of d-limonene only decreases the concentration
13 of bitumen in water, Mr. Handl's utilizes ternary phase equilibrium analysis, where the
14 solubilities of: 1) water in bitumen; 2) bitumen in water; 3) d-limonene in water; and 4) water in
15 d-limonene are plotted on a triangle with water, bitumen, and d-limonene on the vertices, as
16 shown schematically below.



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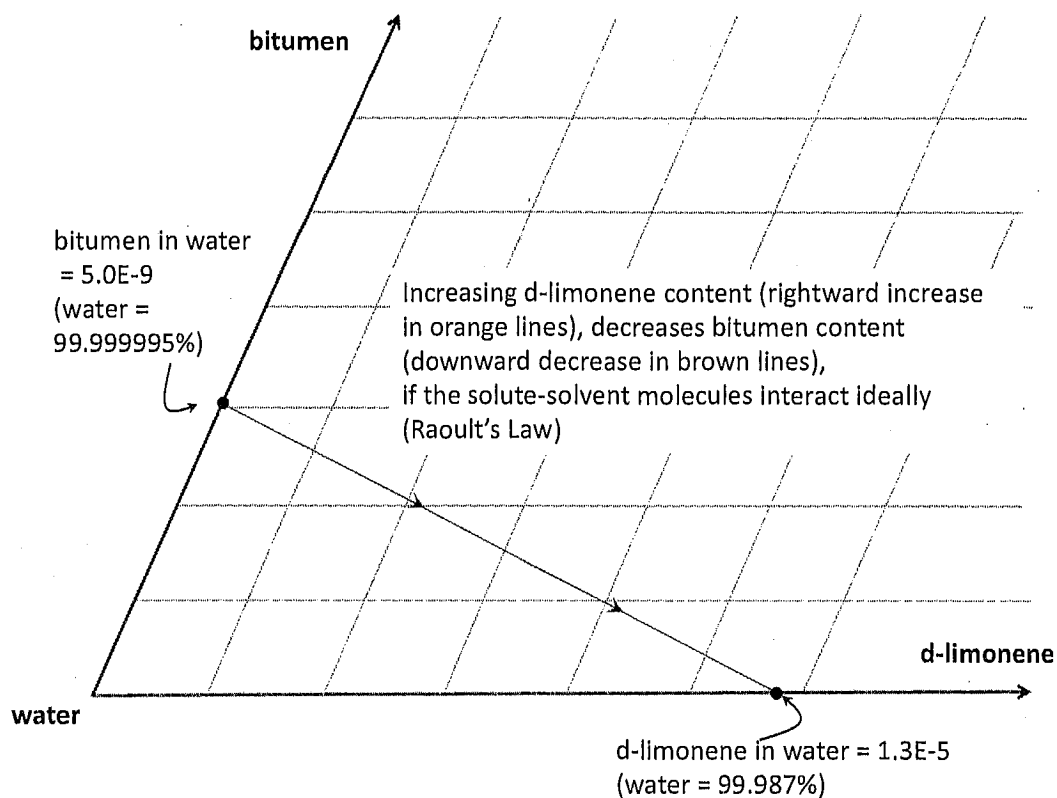
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Q: How does Mr. Handl depict the effect of d-limonene on the degree to which bitumen will dissolve into the raffinate?

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Mr. Handl's contended effect of d-limonene on dissolution of bitumen compounds into water is shown below:



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Mr. Handl assumes that the relationship between bitumen content and d-limonene content in the raffinate must follow the linear trajectory shown above, and states: "It can thus be seen that Dr. Johnson's assertion that limonene effects to "coax" compounds such as B(a)P into solution, is effectively refuted. In fact, as can be seen from this ternary system analysis, d-limonene will act to suppress the dissolution of other organics (present in bitumen) from the water phase". (Handl response February 27, 2012).

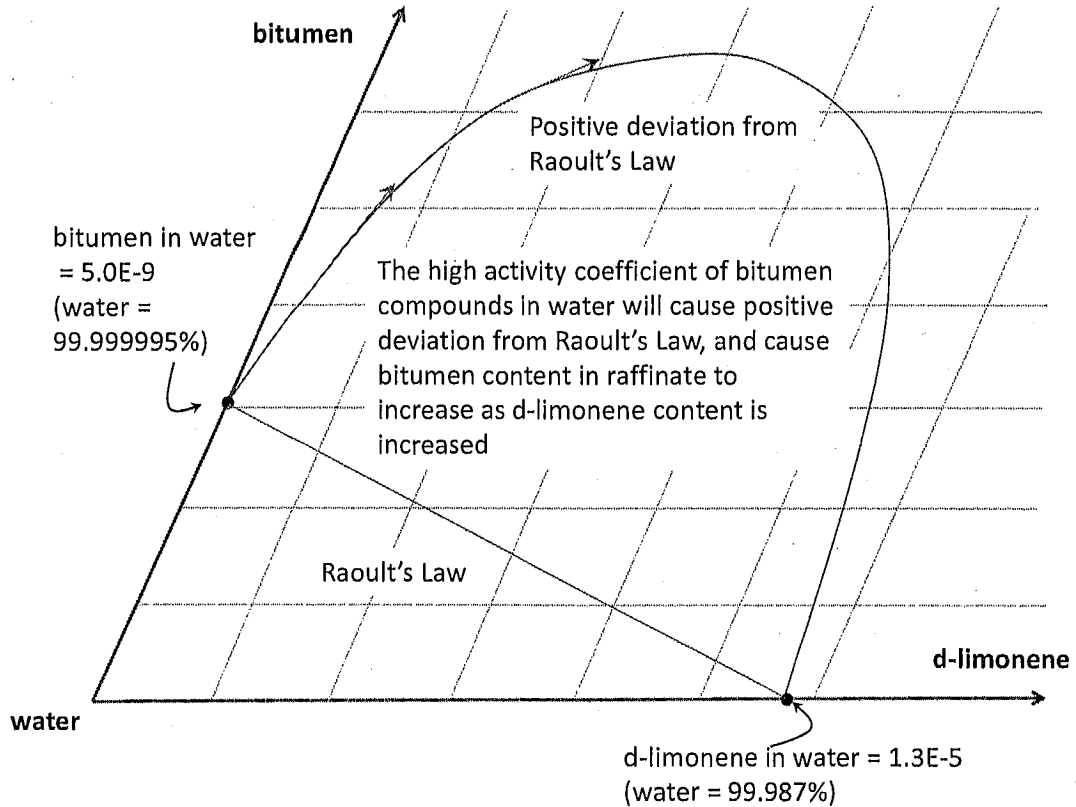
Q: Is Mr. Handl's assertion accurate?

No. Mr. Handl reaches this flawed conclusion based on the erroneous assumption that the boundary of the raffinate phase is precisely the line connecting the solubilities of bitumen in water and d-limonene in water. This assumption is further based on the false conclusion that the water-rich solution must be ideal, and therefore follow Raoult's Law (that is he assumed γ_w

1 = γ_w^{sat}). However, the fact is that the raffinate boundary does not, should not, and cannot
2 follow Handl's assumed line.
3

4 **Q: What is the nature of the real boundary that characterizes the raffinate phase?**

5 The boundary is non-linear. This is because a nonlinear boundary arises from the
6 extremely high non-ideal interactions between bitumen compounds and water, and the ideal
7 interactions between bitumen compounds and dissolved d-limonene. The boundary of the
8 raffinate phase is not the line identified by Mr. Handl (reflecting Raoult's Law), but rather a non-
9 linear boundary as shown below (positive deviation from Raoult's Law), which demonstrates
10 that bitumen compound solubility will increase with increasing d-limonene concentration in the
11 raffinate.



12

1 **Q: Is Mr. Handl's assumption of this linear boundary in keeping with what is known about the effects**
2 **of dissolved solvents like d-limonene on extent to which a hydrophobic solute like bitumen will**
3 **dissolve into a water solution?**

4 No. Mr. Handl's assumption and corresponding conclusion conflict with the large body
5 of existing literature regarding co-solvent and co-solute effects (from dissolved solvents like d-
6 limonene) that increase hydrophobic solute (here, the bitumen) dissolution to aqueous (or
7 water) solutions (Schwarzenbach R.P., Gschwend P.M., and Imboden D.M., 1993, Environmental
8 Organic Chemistry, Wiley Interscience, New York).

9
10 **Q: Can you make this more intuitive to a non-expert?**

11 Yes. Note that the diagram above (which uses Mr. Handl's own numbers) shows that
12 the d-limonene (solubility of $1.3E-5$ as mass fraction) is more than four orders of magnitude
13 more soluble in water than bitumen compounds ($5.0E-9$ as mass fraction). This means that
14 there will be a large amount of d-limonene in the water relative to the bitumen. **Because we**
15 **know that d-limonene is an excellent solvent for bitumen, it even makes intuitive sense that**
16 **the dissolved d-limonene in water will create an excellent environment for bringing the**
17 **bitumen into the water, thereby increasing the solubility of bitumen by many orders of**
18 **magnitude.** This is why the non-linear boundary of the raffinate (shown above) must apply.
19 Conceptually it is obvious that the bitumen concentration in the raffinate must increase as d-
20 limonene is added to the system. Below I will use the thermodynamic constructs to rigorously
21 show that this must be the case.

1 **Q: Are there other limitations in Mr. Handl's ternary phase equilibrium analysis?**

2 Yes. Furthermore, the ternary phase equilibrium analysis used by Mr. Handle
3 corresponds to two immiscible or partially miscible LIQUIDS (miscible meaning that they dissolve
4 into one another), and so fails to recognize that tar compounds under ambient (pre-processed)
5 conditions in the vast majority of rock at the site exist in a mixture that is dominated by
6 compounds with melting temperatures above the ambient temperature; i.e. they behave more
7 akin to solids than liquids under ambient conditions.² Hence, for the tar compounds
8 encapsulated in the majority of the rock matrix at the site, mixing with d-limonene (a compound
9 with melting temperature below ambient conditions), causes a profound change in their
10 behavior, as demonstrated below. Mr. Handl's ternary phase equilibrium analysis does not
11 account for this change.

12
13 **Q: Please summarize the further points you have made.**

14 I have pointed out the errors in Mr. Handl's ternary phase equilibrium analysis. I
15 showed that he was mistaken to assume a linear boundary depicts the interactions between
16 bitumen compounds and water. In reality, the boundary is a non-linear boundary. This non-
17 linear boundary indicates that bitumen compound solubility will increase with increasing d-
18 limonene concentration in the raffinate.

19 I also note that Mr. Handl's analysis does not account for the fact that the bitumen
20 being processed acts like a solid before the d-limonene is added; whereas it behaves as a liquid
21 after it is mixed with d-limonene

22

² The exception is at tar seeps where sufficient content of "lighter" liquid petroleum compounds remains to allow the tar to flow.

1 **Q: Can you substantiate this further (beyond a conceptual approach)?**

2 Yes, I can do so using a thermodynamic approach, as follows:

3 ***Thermodynamics and Non-Ideality – Quantitative***

4

5 ***Equilibration of Tar (without d-limonene) and Water (without d-limonene)***

6

7 **Q: You stated that Mr. Handl's analysis does not account for the fact that the bitumen (before it is**
8 **processed) acts like a solid; whereas, addition of d-limonene results in a tar/d-limonene mixture that**
9 **is in a liquid state. Please substantiate this and explain its significance.**

10 The effect of solid to liquid phase transition is easily incorporated into the
11 thermodynamic basis for partitioning, as shown below, where the chemical potential of the
12 representative bitumen compound in the organic phase (semi-solid bitumen) before d-limonene
13 is added is given by μ_o , and the chemical potential of the bitumen compound in pure water is
14 given by μ_w .

15
$$\mu_o = \mu^0 + RT \ln \frac{\gamma_o X_o P^0(S)}{P^0(L)} \quad (9)$$

16
$$\mu_w = \mu^0 + RT \ln \frac{\gamma_w X_w P^0(L)}{P^0(L)} \quad (10)$$

17 In this case, for dissolution of bitumen compound from tar into water (e.g. rainwater)
18 (both lacking d-limonene), the relationship (after equilibration) is:

19
$$\gamma_o X_o P^0(S) = \gamma_w X_w P^0(L) \quad (11)$$

20 Re-arranging gives the mole fraction ratio of bitumen in the tar versus the water (both
21 phases without d-limonene):

$$\frac{X_o}{X_w} = \frac{\gamma_w}{\gamma_o} \frac{P^0(L)}{P^0(S)} \quad (12)$$

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3 **Q: What does Equation 12 tell us?**

4 This equation shows that the mole fraction ratio is the distribution coefficient for the
 5 representative bitumen compound between water and the organic phase (tar), or more simply,
 6 the partition coefficient for the bitumen compound between water and tar. This better
 7 represents the fact that the bitumen is a tar and therefore in a semi-solid state when exposed to
 8 pure water.

9

10 ***Equilibration of Extract (tar with d-limonene) and Raffinate (water with d-limonene)***

11

12 **Q: So how does addition of d-limonene to this system change this analysis?**

13 In contrast to the above analysis that equilibrated chemical potentials for water
 14 interacting with tar, the analysis for equilibrating chemical potentials of organic extract (tar with
 15 d-limonene) (μ_{ext}) interacting with raffinate (water with d-limonene) (μ_{raf}), yields the following
 16 expressions, where the activity coefficients and mole fractions are defined for the bitumen
 17 compound of interested in the extract (γ_{ext}, X_{ext}) and raffinate (γ_{raf}, X_{raf}) phases:

$$\mu_{ext} = \mu^0 + RT \ln \frac{\gamma_{ext} X_{ext} P^0(L)}{P^0(L)} \quad (13)$$

$$\mu_{raf} = \mu^0 + RT \ln \frac{\gamma_{raf} X_{raf} P^0(L)}{P^0(L)} \quad (14)$$

20 Yielding:

$$\gamma_{ext} X_{ext} = \gamma_{raf} X_{raf} \quad (15)$$

21

1 Re-arranging gives the mole fraction ratios of bitumen compound in the extract and
 2 raffinate (both phases with d-limonene):

$$3 \quad \frac{X_{ext}}{X_{raf}} = \frac{\gamma_{raf}}{\gamma_{ext}} \quad (16)$$

4
 5 **Comparing Bitumen Compound Concentrations in the Water Phase in the Presence versus Absence of**
 6 **d-limonene**

7
 8 **Q: How is this analysis relevant to the present inquiry?**

9 For the case of water in contact with tar (d-limonene absent), we know that $\gamma_o \sim 1$
 10 because the bitumen compounds are compatible with the tar. Substituting the above
 11 information into equation (12) (absence of d-limonene) yields:

$$12 \quad \frac{X_o}{X_w} = \frac{\gamma_w}{1} \frac{P^0(L)}{P^0(S)} \quad (17)$$

13 Likewise, for the case of raffinate in contact with the residual extract (tar/d-limonene
 14 mixture), we know that $\gamma_{ext} \sim 1$ because bitumen compounds are compatible with the tar/d-
 15 limonene mixture. As Mr. Handl pointed out, $X_{ext} < X_o$ (the mole fraction of a given bitumen
 16 compound in the extract is less than that in the tar), and X_{ext} decreases with increasing d-
 17 limonene in the extract. Hence, $X_{ext} = X_o * (1 - X_{ext}^{d-limonene})$. Substituting into (16) (presence of d-
 18 limonene) yields:

$$19 \quad \frac{X_o (1 - X_{ext}^{d-limonene})}{X_{raf}} = \frac{\gamma_{raf}}{1} \quad (18)$$

20 Combining (17) and (18) yields:

$$21 \quad X_o = \frac{X_w \gamma_w^{sat} P^0(L)}{P^0(S)} = \frac{\gamma_{raf} X_{raf}}{(1 - X_{ext}^{d-limonene})} \quad (19)$$

1 Re-arranging yields the mole fraction of a bitumen compound in raffinate (water plus d-
2 limonene) relative to pure water (e.g., rainwater), which is the ratio (X_{raf}/X_w) that quantifies the
3 increase in bitumen compound dissolution into water in the presence versus absence of d-
4 limonene:

$$\frac{X_{raf}}{X_w} = (1 - X_{ext}^{d\text{-limonene}}) \left(\frac{\gamma_w^{sat}}{\gamma_{raf}} \right) \left(\frac{P^0(L)}{P^0(S)} \right) \quad (20)$$

6
7 **Q: What does Equation 20 show?**

8 Equation 20 shows that the ratio of bitumen concentration in the water phase in the
9 presence versus absence of d-limonene scales oppositely to the mole fraction of d-limonene in
10 the extract (as Mr. Handl pointed out in his response to my testimony February 27, 2012).
11 However, Mr. Handl failed to acknowledge that the ratio also directly scales to the ratio of the
12 activity coefficients of the bitumen compound in water relative to raffinate phase (second term
13 on right hand side), which is greater than unity (thereby increasing the ratio of bitumen
14 concentration in the water phase in the presence versus absence of d-limonene). Furthermore,
15 Mr. Handl neglected to confirm that the ratio also directly scales to the ratio of liquid versus
16 solid vapor pressures for the pure bitumen compound (third term on right hand side), which is
17 also greater than unity (thereby further increasing the ratio of bitumen concentration in the
18 water phase in the presence versus absence of d-limonene).

19
20 **Q: But your testimony pointed to equation 1 as representing Mr. Handl's approach. Can you relate**
21 **the above equation to Equation 1?**

22 Yes. To further clarify these omissions by Mr. Handl, re-arrangement of (20) yields:

$$X_{raf} = (1 - X_{ext}^{d\text{-limonene}}) X_w \left(\frac{\gamma_w^{sat}}{\gamma_{raf}} \right) \left(\frac{P^0(L)}{P^0(S)} \right) \quad (21)$$

By combining (5) and (6), which describes the equilibrium between liquid bitumen and water, we obtain

$$X_w = \gamma_o X_o X_w^{sat}(L) \quad (22)$$

Substituting (22) into (21) yields:

$$X_{raf} = \gamma_o (1 - X_{ext}^{d\text{-limonene}}) X_o X_w^{sat}(L) \left(\frac{\gamma_w^{sat}}{\gamma_{raf}} \right) \left(\frac{P^0(L)}{P^0(S)} \right) \quad (23)$$

Recognizing that $(1 - X_{ext}^{d\text{-limonene}}) X_o = X_{ext}$ (from text prior to equation 18) yields:

$$X_{raf} = \gamma_o X_{ext} X_w^{sat}(L) \left(\frac{\gamma_w^{sat}}{\gamma_{raf}} \right) \left(\frac{P^0(L)}{P^0(S)} \right) \quad (24)$$

And recognizing that $\gamma_o \sim 1$, $C_w^{sat}(L) V_w = X_w^{sat}(L)$, $C_{raf} V_{raf} = X_{raf}$, and that $V_w \sim V_{raf}$, where V_w and V_{raf} are the molar volumes of the water and raffinate phases, we obtain:

$$C_{raf} = X_{ext} C_w^{sat}(L) \left(\frac{\gamma_w^{sat}}{\gamma_{raf}} \right) \left(\frac{P^0(L)}{P^0(S)} \right) \quad (25)$$

Q: How precisely does Equation (25) relate to Equation (1)?

Equation 25 is identical to Equation 1 (Raoult's Law) used by Mr. Handl except for two very important terms: a) $\gamma_w^{sat}/\gamma_{raf}$; and b) $P^0(L)/P^0(S)$. The first of the two terms reflects the influence of non-idealities on dissolution of a bitumen compound in water that contains d-limonene, and the second of the two terms reflects the influence of d-limonene in the residual extract (tar/d-limonene mixture) on the behavior of a bitumen compound (acting as a liquid versus a solid).

1 To account for the latter ratio, my testimony uses the normal water solubilities of solid
2 and liquid B(a)P as a basis for demonstrating the change in B(a)P solubility due to the addition of
3 d-limonene (the ratio of the solid and liquid vapor pressures is equal to the ratio of the solid and
4 liquid solubilities).

5
6 **Q: How does the difference between Equations (1) and (25) explain the differences in your testimony
7 and Mr. Handl's response?**

8 Mr. Handl failed to account for the above two terms in his analysis, and as shown below,
9 both terms greatly increase the amount of a given bitumen compound that will dissolve in
10 water. This means that Mr. Handl's analysis greatly underestimates the concentration of
11 bitumen compounds that will dissolve into water (raffinate) in contact with the residual extract
12 (tar/d-limonene mixture).

13
14 **Q: Can you estimate values that demonstrate the magnitude of these differences?**

15 Yes. We can determine the value for the liquid/solid vapor pressure ratio from the
16 following formula (Schwarzenbach et al., 1993):

$$\frac{P_{(L)}^o}{P_{(S)}^o} = e^{\left(\frac{\Delta S_{melt}(T_m)}{R}\right)\left(\frac{T_m}{T}-1\right)} \quad (26)$$

18 Where $\Delta S_{melt}(T_m)$ is the ratio of the entropy of melting (at the melting temperature, T_m), and T is
19 the temperature of interest. The ratio of $\Delta S_{melt}(T_m)/R$ is approximately 6.8 for bitumen
20 compounds (Schwarzenbach et al.), and $(T_m/T)-1$ ranges with the T_m of the compound of
21 interest, which is around 230 °C (~500 K) for bitumen compounds, yielding a $(T_m/T)-1$ value of
22 around 0.78 (assuming a temperature of interest of 10 °C).

23 Hence:

$$\frac{P_{(L)}^o}{P_{(S)}^o} = e^{\left(\frac{\Delta S_{melt}(T_m)}{R}\right)\left(\frac{T_m-1}{T}\right)} \approx e^{(0.78)(6.8)} \sim 200 \quad (27)$$

Q: Can you estimate values that show the effect of the activity coefficient ratio term?

Yes. But, the activity coefficient ratio $\gamma_{wf}^{sat}/\gamma_{raf}$ is not readily estimable for bitumen compounds in the absence/presence of d-limonene, because of limited data. However, this ratio is estimable from data for other compounds that interact with bitumen similarly to the way d-limonene does. Octanol is a reasonable representative for d-limonene in this regard, and data for interaction of octanol with bitumen compounds such as B(a)P is readily available. However, because octanol exhibits more polarity than d-limonene octanol will be more soluble than d-limonene in water, and will have a lower affinity for bitumen than d-limonene. Nevertheless, as demonstrated below, the octanol system will show that the activity coefficient ratio $\gamma_{wf}^{sat}/\gamma_{raf}$ is significantly greater than unity, which means, as Schwarzenbach et al. (1993) acknowledge, that the presence of co-solutes like octanol or d-limonene in water increase the concentration of bitumen compounds in water, in direct contradiction to Mr. Handl's testimony.

In order to obtain the above ratio of activity coefficients for the octanol system, consider a system with dissolved bitumen (e.g. B(a)P) in water that is equilibrated with pure liquid octanol (e.g., octanol being used to extract dissolved B(a)P from the water). Following equilibration (as derived above for d-limonene/tar/water system), the activity of B(a)P in the raffinate (water plus dissolved octanol) (γ_{raf}) relative to that in the octanol droplet (γ_{ext}) is equal to the mole fractions of B(a)P in the octanol (extract) versus raffinate phases.

$$\frac{\gamma_{raf}}{\gamma_{ext}} = \frac{X_{ext}}{X_{raf}} \quad (28)$$

Conversion of the mole fractions to concentrations yields:

1
$$\frac{\gamma_{raf}}{\gamma_{ext}} = \frac{X_{ext}}{X_{raf}} = \frac{C_{ext} V_{ext}}{C_{raf} V_{raf}} \quad (29)$$

2 where C_{ext} and C_{raf} are the concentrations of B(a)P in the extract and raffinate phases, and V_{ext}
 3 and V_{raf} are the molar volumes of the extract and raffinate phases. Recognizing that C_{ext}/C_{raf} is
 4 the well-known octanol-water partition coefficient (K_{ow}), substitution yields:

5
$$\frac{\gamma_{raf}}{\gamma_{ext}} = K_{ow} \frac{V_{ext}}{V_{raf}} \quad (30)$$

6 The values of V_{ext} and V_{raf} are well approximated by the molar volumes of octanol and water,
 7 0.16 and 0.018 (L/mol) respectively, because of the low solubility of water and octanol in each
 8 other (similar to the d-limonene/water system). The value of K_{ow} is approximately $10^{6.5}$ or
 9 1,250,000 (Schwarzenbach et al.), and the value of γ_{ext} is approximately 1. Substituting the
 10 above values into equation 30 yields:

11
$$\gamma_{raf} = (1250000)(0.16 / 0.018) = 11,200,000 = 10^{7.45} \quad (31)$$

12 Comparing the value of γ_{raf} ($10^{7.45} = 11,200,000$) to γ_w^{sat} ($10^{8.45} = 285,000,000$), derived
 13 above via Equation 8, shows that a small amount of octanol dissolved in water reduces the
 14 activity coefficient of B(a)P in the raffinate by one order of magnitude relative to pure water.
 15 Recall that whether the value of γ_w in the raffinate (γ_{raf}) is different than that in pure water (γ_w^{sat})
 16 is one major aspect of the dispute between Mr. Handl and me. Clearly these values (11,200,000
 17 and 285,000,000) are very different.

18 To understand the effect of the $\gamma_w^{sat}/\gamma_{raf}$ and $P^0(L)/P^0(S)$ terms on the concentration of
 19 bitumen compound in the raffinate, we can assume that $\gamma_w^{sat}/\gamma_{raf}$ in the octanol system reflects
 20 reasonably that ratio in the d-limonene system, and we can substitute (27) and (31) into
 21 Equation 25 to obtain:

1
$$\frac{X_{raf}}{X_w} = (1 - X_{ext}^{d\text{-limonene}})(10)(200) = 2000(1 - X_{ext}^{d\text{-limonene}}) \quad (32)$$

2

3 **Q: What does Equation 32 show?**

4

5

6

7

8 **Q: How does this calculation relate to your earlier testimony?**

9

10

11

12

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15

Equation 32 demonstrates that the concentration of bitumen compounds in water can be expected to be greatly enhanced (by three orders of magnitude) in the presence (X_{raf}) versus absence (X_w) of d-limonene.

This is similar to the ratio I provided in my testimony, but differs because the present approach uses representative values for tar compounds; whereas my testimony used specific values for B(a)P as an example. The above expression further shows that the mole fraction of d-limonene in the extract would need to exceed 0.9995 to cancel the effects of solid/liquid transition ($P^o(L)/P^o(S)$) and solubilization of bitumen compounds by dissolved d-limonene in the raffinate ($\gamma_w^{sat}/\gamma_{raf}$).

16

Q: Would you expect a mole fraction of 0.9995 for d-limonene in the extract?

17

18

19

20

21

22

No. A mole fraction of 0.9995 for d-limonene in the extract is grossly inconsistent with USOS's claim that d-limonene readily vaporizes from the residual extract. Even if one assumes a mole fraction of d-limonene in the extract of 0.5, then one would still expect that the concentration of bitumen compounds in the raffinate to be 1000 times greater than their concentration in d-limonene-free water.

1 **Q: What is your conclusion based on the analysis above?**

2 Of course the specific values used in these calculations can be disputed, but what
3 cannot be disputed is that the dissolution of bitumen compounds in the raffinate is promoted by
4 the solid/liquid transition ($P^0(L)/P^0(S)$) and by solubilization into dissolved d-limonene ($\gamma^{sat}_{wl}/\gamma_{raf}$).

5
6 **Q: Are there any measurements that corroborate your calculations?**

7 The above calculated effect of d-limonene on the concentration of bitumen compounds
8 in the raffinate is corroborated by the values for percent bitumen content of return water
9 (900,000 $\mu\text{g/L}$) measured by USOS, and reported in documents provided to Living Rivers.
10 Johnson January 20, 2012 Testimony at 14.

11
12 **Q: How do the values measured by USOS equate with Mr. Handl's analysis?**

13 Such a high dissolved concentration of bitumen compounds is impossible to explain
14 using Mr. Handl's analysis. Mr Handl's analysis states that the maximum concentration of
15 combined bitumen compounds in the raffinate should be approximately 1.5 $\mu\text{g/L}$ in the absence
16 of d-limonene, and should decrease below that value as d-limonene is added to the system. In
17 contrast, the USOS data shows a bitumen concentration in the raffinate that is nearly a factor of
18 400,000 (more than five orders of magnitude) higher than the representative concentration 1.5
19 $\mu\text{g/L}$ chosen by Mr. Handl. Clearly Mr. Handl's analysis is greatly at odds with the data provided
20 by USOS.

1 **Q: Therefore, in addition to all of the other reasons stated above, is your analysis more in keeping**
2 **with the USOS findings?**

3 Yes. The data is explained by my analysis above. While my calculation estimated a
4 factor of 2000 increase in bitumen compound concentration (far lower than the observed
5 400,000 increase), my calculation assumed that d-limonene interacted with bitumen similarly to
6 octanol, which likely underestimates solubilization of bitumen compounds by d-limonene.
7 Furthermore, to accurately estimate the full extent of solubilization, my calculations would need
8 to include the mole fractions and vapor pressures of all bitumen compounds. The data provided
9 by USOS supports my claim that d-limonene will greatly increase the concentration of bitumen
10 compounds in water that comes into contact with the residual tar/d-limonene mixture.

11
12 **Q: Is there some test that would actually determine the degree to which the bitumen compounds**
13 **would dissolve into water in the presence of d-limonene?**

14 Yes. Such tests exist. For this reason, it would be prudent for the State of Utah to
15 require leach tests to be performed to quantify the potential for tar compounds to leach into
16 WATER from the residual tar/d-limonene mixture in the processed sand. These measurements
17 are not particularly difficult to perform, and would provide critical understanding of the
18 behavior of the tar compounds should the residual extract come into contact with water. A
19 leach test was previously performed using hexane; however, as recognized by DWQ, this test
20 provides no insight regarding what concentration of bitumen compounds would be expected in
21 water.

1 **Q: Please summarize your testimony.**

2 The goal of my testimony is to demonstrate what will happen when water, such as rain
3 water, contacts the residual tar/d-limonene mixture that will remain in the processed sands
4 returned to the mine and deposited in the waste piles at the PR Spring site. The critical question
5 to answer is whether addition of d-limonene will greatly increase the amount of bitumen
6 compounds that will dissolve into water when water comes into contact with the waste piles.
7 My January 20, 2012 testimony used specific values for benzo(a)pyrene (B(a)P) as an example
8 bitumen compound to demonstrate that the presence of d-limonene will greatly increase the
9 concentrations of these compounds that will dissolve into water in contact with the tar/d-
10 limonene mixture. My analysis showed that, in the presence of d-limonene, the concentration
11 of bitumen in water would be 1500 times higher than the concentration would be if d-limonene
12 were not present.

13 In his February 29, 2012 testimony, Mr. Handl disputes my findings. However, Mr.
14 Handl's analysis makes several errors in attempting to estimate the actual concentration of
15 bitumen in water contacting the residual tar/d-limonene mixture in the processed sands.

16 First, Mr. Handl did not sum the resulting concentrations for ALL compounds of interest
17 made using Raoult's Law. The sum of the concentrations for all compounds of interest would be
18 considerably higher than the concentration Mr. Handl calculates in his testimony.

19 Second, Mr. Handl treats the bitumen and water mixture as though it were ideal, which I
20 showed was improper. This mistaken assumption means that Mr. Handl's simplistic use of
21 Raoult's Law and his ternary phase equilibrium analysis lead to inaccurate results. As a result,
22 Mr. Handl greatly underestimates the effect that d-limonene has on expected concentrations of
23 bitumen compounds in water.

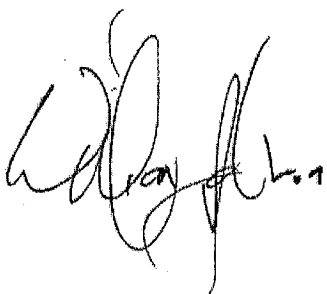
1 Third, Mr. Handl fails to account for the differences in the behavior of tar without d-
2 limonene (a semi solid) and the tar/d-limonene mixture (a liquid). This oversight further causes
3 Mr. Handl's calculation to severely underestimate the increase in the concentration of bitumen
4 compounds that will dissolve into water in the presence versus the absence of d-limonene.
5 I showed these flaws using both Mr. Handl's ternary equilibrium approach as well as an
6 approach using thermodynamic relationships.

7 I also showed that Mr. Handl's approach led to results that were not consistent with
8 USOC's own data and that my analysis more accurately reflect these company-provided results.

9 Finally, I stated that there are tests readily available that would determine the potential
10 for tar compounds to leach into water from the residual tar/d-limonene mixture in the
11 processed sand. I concluded that DWQ should order that such tests be run, reported and
12 analyzed before the agency permits the PR Spring mining operations.

13
14 **Q: Does this conclude your testimony for now?**

15 Yes.

16


17
18
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