M E M O R A N D U M

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FROM: Arthur C. Riese, Ph.D., C.HG., P.G.

RE: **Technical Memorandum and Response**
***ARWW&S Arsenic Source Investigation; Final Project Data Summary Report, dated 10-31-2013*; CDM Smith, April 9, 2014**

DATE: June 22, 2014

On behalf of Atlantic Richfield Company , Dr. Arthur C. (Sandy) Riese, President of EnSci , Inc., with consultation from Dr. Glenn Johnson of GeoChem Metrix, Inc. herein offers this Technical Memorandum and R esponse to the March 24, 2014 CDM Smith Report entitled *Agency Interpretive Report for MBMG's ARWW&S Arsenic Source Investigat ion; Final Project Data Summary Report, dated 10 -31-2013.*

CONTEXT

CDM issued an "interpretive report" that assessed the results from a coring study performed by the Montana Bureau of Mines and Geology (MBMG). The research cores were analyzed and describ ed by the MBMG to investigate potential arsenic sources within the ARWW &S. Undisputed in this following discussion is a recognition that weathered (oxidized) sulfide mineralization releases sulfate (SO4) and associated constituents such as arsenic (As) to the local groundwater. Arsenic is also sourced by active geothermal water, and by the weathering of sulfide mineralization that the fluids deposit. Finally, As is sourced by smelter emissions and mining wastes. The following statements respond to the CDM interpretations of As-sourcing in this geologically complex area.

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1) **CDM DATA INTERPRETATION IS FLAWED**

CDM states that *"Atlantic Richfield prepared a report that attempted to use selected MBMG data to develop a method of determining the source of the a rsenic; however, the correlations were weak and not supported by the data."* CDM Report at 1-1.

We disagree with this comment. In fact, it is the CDM methodology applied throughout their report that is weak and unsupported. The geostatistical classifica tions performed by Atlantic Richfield were all significantly discriminated at the 95% confidence limit, or higher. Many correlations between the primary geochemical constituents within an individu al classification demonstrated coefficients of determination (r^2) values of 0.8 or higher. These significant correlations were especially evident between the geothermal constituents, and with arsenic. CDM apparently chose to ignore the geothermal constituents and their chemistry in their entirety. **The CDM Report does not include a single statement addressing the presence of classical geothermal indicators within ARWW&S groundwater - even within the geothermal water itself.** Accordingly, CDM would have been unaware of any such correlations. On this basis alone, CD M's interpretation of the MBMG data is severely flawed and unreliable.

2) **CDM INCONSISTENTLY INTERPRETED THE DATA**

The CDM Report makes the following statement regarding the variation of groundwater arsenic concentrations with distance from the smelter stack:

"Groundwater arsenic concentrations varied across the site in a fairly predictable manner, at least for concentrations above about 20 μg/L. Figure 2 -1 shows that for groundwater arsenic concentrations above about 20 μg/L the concentrations generally decrease with distance from the stack. The relationship has a bit of scatter because only the distance from the stack is shown and not the direction . . . . Arsenic concentrations of about 20 μg/L and below tend to be fairly independent of distance from the stack. These results suggest that the lower arsenic concentrations have more than one source and cannot be attributed to the smelter emissions alone." CDM Report at 2-1 to 2-2.

CDM's statement that arsenic concentrations in groundwater below 20 ug/L are *"fairly independent of distance from the stack . . . and have more than one source and cannot be attributed to smelter emissions alone"* is correct. These samples ranged from 2 to 16 km from the stack, with no apparent trend with groundwater As concentrations.

CDM's statement that, *"Groundwater arsenic concentrations varied across the site in a fairly predictable manner, at least for concentrations above about 20 μg/L"* is incorrect and not borne out by the data. This statement implies that arsenic exceedances above 20 μg/L throughout the ARWW&S are related to former smelter emissions. An examination of Fig. 2 -1 reveals that arsenic groundwater concentrations in the 40 -70 μ g/L range are also non -predictable with stack distance (distances ranged from 1 - 12 km, with no correlation to arsenic). Had CDM examined the voluminous MBMG chemistry data for the samples that form the so -called *"predictable trend,"* they would have identified at least five very different groundwater populations having very different origins. Three of these include shallow groundwater populations associated with arsenic -bearing mining waste (two from Opportunity Ponds) that have no association with areal smelter deposition. In short, the same CDM conclusions about *"predicable trends"* hold true for samples with greater than 20 μg/l as they do for samples with less than 20 μg/L.

3) **CDM MISCHARACTERIZES DIFFERENTIATION OF SOURCES**

The CDM Report makes the following statement with respect to the differentiation of sulfur dioxide from smelters and other industries:

"In general it is not possible to differentiate between sulfur dioxide fallout from smelters and other industries from leaching of abiotically-formed sulfides, which have $\delta^{34}S$ values ranging from about 0 to 14‰. $\delta^{34}S$ values in excess of 14‰ are associated with geothermal waters, while negative $\delta^{34}S$ values are associated with marine sulfates, such as gypsum, or biologically-formed sulfides." CDM Report at 2-11.

A review of the MBMG $\delta^{34}S$ values reported for local (Anaconda) sulfides and sulfide oxidation products, and a summary of the $\delta^{34}S$ values reported for Butte copper-sulfide ore (the material processed by the Anaconda smelter) provides the following list of $\delta^{34}S$ distributions that are specific to ARWW&S rocks and groundwater. (The RW Core is the Richard Walter MBMG research core, collected approximately two miles north of Anaconda):

- ✓ RW Core (0-90 m depth; oxidizing sulfide mineralization at 41 m depth): $\delta^{34}S$ values for jarosite minerals (-8.6 to -11.8 ‰)
- ✓ RW Core (+60m depths): $\delta^{34}S$ values for pyrite minerals (-1.0 to +6.8‰)
- ✓ RW Core (leachate of sulfidic rock at depth): $\delta^{34}S$ values of leachate -0.8‰ (71m depth) and -0.6‰ (90 m depth; corresponds to sulfide values at same depths of +3.1 and 0.0‰, respectively)
- ✓ Groundwater adjacent to RW Core (unreported by CDM) had $\delta^{34}S$ values of +14.6 and +17.1‰ (71-90 m depth range); attributed by MBMG to "fractionation during mineralization of jarosite" from over 100 ft above this level – ARC)
- ✓ Fairmont and Crackerville sulfides and outcropping ore samples (from the local Tuxedo mine): $\delta^{34}S$ values range between +5.3 – +6.4‰ (a +9.3‰ value had minimal sulfur for analysis – lab offered caution in applying the result)
- ✓ Crackerville matrix rock leachate (119 m; extensive hydrothermal alteration; non-sulfidic): $\delta^{34}S$ value of +14.3‰; leached 522 µg/L of As
- ✓ Butte ore (source material for Anaconda smelter and mine tailing wastes; unreported by CDM): $\delta^{34}S$ values range between -3.6 to +4.1‰ (Field, 1966; 21 samples)

The $\delta^{34}S$ values for local ARWW&S sulfide mineralization range between -1.0 (and lower) to +6.8 ‰; the Anaconda smelter emissions and mining waste should range between -3.6 to +4.1 (based upon Butte porphyry ore). CDM's dismissal of $\delta^{34}S$ for distinguishing waste/smelter fallout from natural, abiotic sulfide appears justified due to their overlapping ranges. These same criteria, however, place the upper bound of $\delta^{34}S$ from ARWW&S sulfide mineralization and emission wastes at approximately +7 (+6.8‰), based upon all the existing analyses known to Atlantic Richfield. Yet, CDM chose to represent *"smelter fallout and abiotic sulfide"* with a much larger range of 0.0 to +14 ‰ without any site specific justification.

CDM provides no rationale for extending the range beyond +7 ‰. Their Figure 2-10 shows a large $\delta^{34}S$ range for the hydrothermally-altered Crackerville core based upon only two analyses (+7.5 and +14.3‰; from non-sulfidic matrix rock). Apparently, this +14.3‰ value was selected as their "upper limit," even though the CDM emphasizes that a value of 14 ‰ or greater clearly represents geothermal activity (CDM Report; page 2-11). **CDM's use of +14 ‰ exceeds the MBMG maximum $\delta^{34}S$ value reported for ARWW&S abiotic sulfide mineralization by a factor of two and exceeds the $\delta^{34}S$ range**

for Butte ore by a factor of three. CDM's upper limit is unjustified and falsely represents the actual data. It is difficult to understand the reasoning behind CDM's approach.

The CDM Report dismisses $\delta^{34}S$ for discriminating between ARWW&S waste /smelter-derived SO_4 and natural, abiotically-weathered SO_4 from local sulfide mineralization (CDM Report; pages 2-10 – 2-12). CDM's conclusion is based, in large part, upon a literature review of reported $\delta^{34}S$ values from six locations scattered across the globe (includ ing geothermal, waste sulfur emissions fall -out, natural sulfur occurrences, etc.). CDM's review also included a partial summary of $\delta^{34}S$ analyses from the MBMG core and leachate data. CDM improperly dismissed the usefulness of $\delta^{34}S$ over the range of 0 to +14‰ because of the overlap between locally and globally reported waste and natural sulfide values.

The CDM Report states that geothermal waters tend to have the greatest $\delta^{34}S$ values of all, with values exceeding +14‰ and in some cases much higher. The Dogger geothermal aquifer in the Paris Basin France (47 – 85° C) had $\delta^{34}S$ values ranging from +22.4 to +48.9‰ , while a geothermal water in New Zealand had a single measured value of 22.5‰. (p. 2-12; *see also* Figure 2-10).

As discussed above, the CDM Report dismisses $\delta^{34}S$ as a viable tool for discriminating between waste/smelter emissions and natural, abiotic sulfide, over an un-justified range of 0 to +14‰ (instead of 0 to +7‰, as the data suggests). Disturbingly, CDM chose to represent the lower limitof their $\delta^{34}S$ range for geothermal water at precisely the same value of +14‰. We find itboth curious and more than coincidental that CDM chose to represent these two limits with the same, poorly justified value. **CDM has attempted to eliminate $\delta^{34}S$ as a viable tool to identify mixtures of geothermal water with natural, background water.**

MBMG chose to expand the ARWW&S $\delta^{34}S$ "waste" signature over a range of +2 to +10‰ on the basis of: 1) a (weak) visual "break" in a $\delta^{34}S$ scatterplot population; and, 2) their interpretation that several samples with +10 to +14‰$\delta^{34}S$ (and one exceeding +14‰) were the product of biogenic isotopic fractionation, even though the samples included elevated concentrations of geothermal metals.

An accepted upper limit of +7.0 for $\delta^{34}S$ in the local Anaconda waste/smelter emissions and local sulfide mineralogy would demonstrate that arsenic is being sourced by geothermal water in certain locations. For example, a 50:50 mixture of geothermal ground water (assume $\delta^{34}S$ = +14 ‰) and natural or waste impacted groundwater ($\delta^{34}S$ = +4 ‰) will generate a $\delta^{34}S$ value of +9‰. A 40:60 mixture will generate values of about +8‰. Numerous ARWW&S groundwater samples in the MBMG study exceed +8.0‰, and many of these samples include elevated concentrations of geothermal metals and arsenic. Artificially elevating the upper limit of $\delta^{34}S$ to +14‰ limits its effectiveness in confirming mixtures of geothermal water and background water; however, it does not mask the presen ce of globally recognized geothermal indicators (below).

In sum, CDM misrepresents and mischaracterizes the $\delta^{34}S$ range for *"smelter fallout and abiotic sulfide."* The upper limit of the range in the CDM Report is not consistent with the data and CDM provides no supportable rationale for extending the range. As a result, CDM's conclusion that *"[i]n general it is not possible to differentiate between sulfur dioxide fallout from smelters and other industries from leaching of abiotically -formed sulfides"* is unfounded. To the contrary, the utility of $\delta^{34}S$ data in the range of +7 to +14‰ for demonstrating mixtures of geothermal groundwater and background water appears justified.

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4) **CDM IGNORED GEOTHERMAL TRACER CONSTITUENTS DATA**

The CDM Report makes no menti on of geothermal tracer constituents. Many other groundwater constituents besides $\delta^{34}S$ are associated with geothermal activity. These include long-standing and widely established suites of hydrothermal metals, rare earth elements (REE), and anions, includ ing W, Cs, Rb, Li, B, F, Pd, Tl , Hg, As, etc. (See Barnes, 1979). **CDM neglected to consider the available MBMG geothermal tracer constituents data in its analysis .** CDM did not evaluate a single geothermal indicator from the MBMG core analyses, the core l eachate analyses, the soil leachate analyses, the hot geothermal vent water from the known geyser mounds, or the ARWW&S groundwater itself. The leachate results show strong correlations between the classic geothermal indicators (W, Rb, Cs) and arsenic in the Powell Vista (MS) core and the Fairmont (FR) and Crackerville (SH) cores. These data were apparently ignored. This is a fundamental flaw of the CDM Report.

5) **CDM'S SIGNIFICANT FLAWS IN ASSESSING ARSENIC TRENDS AT DEPTH**

CDM concludes, based on sediment leachate samples, that *"the MBMG samples are likely diluted by the deeper soils to some extent because the smelter impacts decrease rapidly with depth in the unplowed soils"* (CDM Report at page 2-4). The Report also concludes that *"the arsenic leached from the sediments could be adsorbed arsenic which was originally present within smelter -impacted soil, but was carried to depth by infiltration water and partially attenuated by the sediments."* (CDM Report Section 2.4). These two conclusions contradict one another.

CDM's omission in considering the geothermal indicator metals for discriminating among groundwater source types (noted above) resulted in CDM relying on very limited means to assess the origin of deep (>50 ft depth) and elevated (>10 ug/L) arsenic concentrations in groundwater and subsurface leachate tests. Without sufficient explanation of CDM's supporting rationale, CDM inappropriately chose to use the leachate arsenic concentrations measured on the upper six inches of surface soil to assess arsenic trends at depth.

The MBMG soil sample analyses included no basic soil-mineralogical analysis, no measurements of soil surface area, no determination of ion exchange capacity, no soil pH measurements, and no selective sequential extraction analyses. The analysis included only a simple measure of leachable arsenic. CDM related this limited data to arsenic leachate concentrations measured on complex mixtures of rock matrix and fracture filling cements at 200 -300 ft. depths. Application of a conventional vadose zone transport model w ould demonstrate that simple variations in sorptive phase concentrations (such as Fe-oxides provide for As) by only a few percent can diminish the concentration of a downward migrating constituent by orders of mag nitude over a depth of 50 ft. Once the constituent reaches the water table, a much more complex 2, 3 -D fluid transport model would be required to estimate the remnants of downward flux. The extrapolations proposed by CDM are not precise, and have no bear ing on the actual downward flux of arsenic. **Accordingly, CDM's conclusions on the origin of arsenic in ARWWS groundwater, based upon soil leachate analyses, are only speculation and not supported by data.**

6) CDM PROVIDES **NO JUSTIFICATION FOR EXPANDING THE BOUNDARY**

The CDM Report states that *"[s]oil data are sparse for the immediate Flint Creek Area, but range from 60 to 240 mg/kg and soil in the Fairmont and Crackerville areas both showed leaching potential for arsenic . . . Expansion of the southeast ern domestic well sampling boundary appears to be warranted to incorporate this area."* (p. 3-5)

There is overwhelming evidence of extensive hydrothermal alteration (including natural arsenic mineralization) reported by MBMG in their Crackerville (SH) and Fairmont (FR) research cores. **For these reasons, there is no technical or other justification for expanding the southeastern boundary of the domestic well program, especially into and beyond the known Fairmont and Crackerville geothermally-impacted areas.**