Background

The 2013 Record of Decision Amendment includes enhanced bioremediation (EBR) "quote from RODA". The approved May 2014 RD/RA included an outline of how EBR would be implemented, which included 61 injection and extraction wells to distribute the terminal electron acceptor (TEA) during 1.5 to 3 years of recirculation, which would also provide containment of the contaminant plume. Modeling had been used to determine that the well spacing should be no greater than 75 feet and that the pumping rate should be 160 gallons per minute (gpm). The TEA to be used had not been determined, but comparisons were provided between the use of aerobic biodegradation by supplying oxygen as peroxide, or anaerobic biodegradation using sulfate.

Commented [DE1]: Carolyn, I bet you have a good quote from the RODA we can use here

July 2014 Field Test

Amec in July 2014 (before SEE implementation) conducted a field test of anaerobic biodegradation to support the anaerobic EBR modeling that was performed as part of the ST012 RD/RAWP due to the fact that significant assumptions were made in the analysis (Addendum #2, Appendix C, page 1-1; "Modeling results for both processes indicated that the remediation goals could be met; however, there were **significant assumptions made for the anaerobic approach.**" (emphasis added)). This field test was comprised of two push-pull tests performed at existing wells W-11 and W-30, both of which are completed in the lower saturated zone (LSZ), and both of which were known to be impacted by LNAPL. The purpose of the field test was to determine sulfate utilization rates. While microbial data collected during the field test showed increased populations of sulfate reducing bacteria, the data collected during the extraction phase could not be used to determine sulfate utilization rates. Pumping rates during the extraction phase from W-30 could not be sustained due to well fouling, and the limited amount of groundwater extracted from W-30 'did not provide a sufficient data set to estimate sulfate utilization' (lines 475-476). At W-11, sulfate concentrations increased during the pull portion of the test, which 'indicate that background groundwater sulfate concentrations were being pulled into the well and prevent the accurate estimation of sulfate utilization' (lines 477-478).

Instead, sulfate utilization was estimated from the shut-in portion of the test. Data presented from W-11 show that the TPH and benzene concentrations remained essentially constant during the shut in period (Table 2-1), while normalized sulfate concentrations were greater than the normalized tracer concentrations during most of the shut in phase of the test (Graph 3-4). Thus, very little sulfate utilization was demonstrated from the results at this well.

Data from W-30 show that the DRO and TPH concentrations increased substantially during the shut-in period of the test and benzene concentrations approximately doubled (Table 2-2), while the sulfate concentration decreased exponentially with time (Table 2-6). While the results at this well showed sulfate utilization during the shut in period (Graph 3-5), the results did not demonstrate that TPH or benzene were consumed by the sulfate that was utilized. After review of the field test report, EPA commented: "The results of the EBR Pilot Test are equivocal, difficult to interpret for practical use, and result in high uncertainty when used to model and plan full-scale EBR, and MNA." (CSS: *Review of Documents for Operable Unit 2, Site ST012, at the Former Williams Air Force Base, Mesa, AZ* May 17, 2016).

Addendum #2, which was first submitted to the Agencies for review in November 2015, proposes a very different approach for implementation of EBR than was contained in the May

Commented [DE2]: Carolyn – is this correct?

2014 work plan. First, based on the field test, sulfate is chosen as the TEA. Based on the fact that a very large amount of TEA will be required, which would be difficult to provide via oxygen injection, the use of sulfate appears reasonable. However, modeling performed at the conclusion of the Thermally Enhanced Extraction (TEE) pilot test indicated that while sulfate is depleted in the LSZ within the LNAPL plume, it is not depleted within the LNAPL plume in the upper water bearing zone (UWBZ) (BEM, 2010, Appendix M, see Figure M.5.1.2.4). Second, the amount of TEA required was reduced from 7600 tons of sulfate to 840 tons. A third change was to significantly reduce the number of injection and extraction wells from 61 to 18. A fourth change was that instead of 1.5 – 3 years of recirculation and plume containment at a pumping rate of 160 gpm, it was proposed to perform limite pumping during the injection of a very high concentration of sulfate (320,000 mg/L), and then to allow diffusion and dispersion to distribute sulfate throughout the LNAPL plume over approximately a five year period (see Addendum #2, Appendix E).

Agency Concerns about EBR

Although it was the Agencies' understanding at the time the RODA was signed that the majority of the LNAPL would be recovered by SEE and minimal residual LNAPL and dissolved phase at the periphery of the SEE treatment area would be addressed with EBR. Thus, the Agencies believed that EBR would be implemented in the area surrounding the SEE treatment zone where moderate temperature increases might be expected to further enhance microbial growth and hydrocarbon degradation. SEE was expected to reduce the benzene concentrations within the treatment area to 100 – 500 ug/L, and then transition directly to monitored natural attenuation (MNA). However, the actual SEE treatment zone include only approximately half of the LNAPL at ST12 (Final RD/RA Work Plan, May 2014). Also, according to estimates provided by Amec (February 2017 BCT meeting), Amec now states that approximately 200,000 gallons of LNAPL remain in the SEE treatment area. Thus, there is considerably more mass remaining in the subsurface than what the Agencies had understood would be treated by EBR, and approximately half of that mass is in the still-extremely hot SEE treatment area, which is likely too hot to support native sulfate reducing microbes. Amec recognizes this fact, as the first step in there implementation plan calls for stabilizing the temperature to no more than a 1°F increase per day before initiating EBR.

The Air Force has stated that they are committed to "achieving remedial action objectives within our ROD Amendment's estimated timeframe" (March 15, 2017 letter signed by Phil Mook). However, the Agencies have very significant concerns that the approach proposed in Addendum #2 will not only fail to meet the remedial goals within the remedial timeframe, but will actually make the contamination situation at ST12 worse by reducing degradation rates and allowing the contaminant plume to spread. These concerns are based on:

1) Site conditions in terms of the remaining LNAPL mass are different from those contemplated in the RODA for EBR/MNA.
2) EBR/MNA has not been tested and proven effective at a site of this size, complexity, and source mass – particularly in terms of the timeframe contemplated.
3) The extremely high sulfate injection rate proposed in Addendum #2 would be a 'shock loading' of sulfate which could have a detrimental effect on the microbial populations that they are trying to stimulate due to the geochemical changes this sulfate addition will

cause. The November 2016 response to comments (RTC) acknowledges that the high injection concentrations of sulfate will likely limit microbial growth at the injection wells. The "Decision Tree" for EBR provided on March 16, 2017 seems to indicate that sulfate concentrations must be below 30,000 mg/L to not cause inhibition. The conservative tracer transport model results presented in Appendix E of Addendum #2 indicate that significant portions of the site will remain at concentrations of this level for as long as 1990 days (approximately 5.5 years) after sulfate injection. Suthersan et al. (2011) states, **"sulfate application strategies that employ repeat injections at highly elevated concentrations may not be as effective as sulfate delivery strategies that achieve relatively steady sulfate concentrations over time in the range of 100 to 2000 mg/L. This can increase the efficiency of the process while limiting the geochemical footprint of the reactions."**

4) Research has shown that even when sulfate reducing microbes that can oxidize petroleum hydrocarbons are present, benzene reduction may not occur (ESTCP, 1999). It has not been demonstrated that sulfate-reducing bacteria that can degrade benzene are present at this site. Although it appears that benzene degradation is occurring, essentially all TEA (except CO_2) are depleted at this site (BEM, 2010), and thus, benzene degradation may be occurring via a different microbial population.
5) It is not clear that the UWBZ is deficient in sulfate (BEM, 2010), in which case sulfate addition will not stimulate hydrocarbon oxidation.
6) It is not clear that the proposed mass of sulfate to be injected – as large as it is – is sufficient to degrade the LNAPL mass that remains. Addendum #2, Lines 822-827: "Initial target TEA dosage is based on treating approximately 30% of the LNAPL mass in the CZ, UWBZ, and LSZ, on treating approximately 30% of the LNAPL mass in the CZ, UWBZ, and LSZ, accounting for the likelihood that BTEX+N will be preferentially consumed during bioremediation over longer chain hydrocarbons. **Although BTEX+N are the primary COCs, other compounds will degrade and consume sulfate in the process."** (emphasis added). According to the referenced ESTCP document, "***Ground water contaminated from gasoline contains not only BTEX compounds, but many other gasoline components as well. At the Seal Beach site, much of the injected nitrate and sulfate was utilized by bacteria to degrade non-BTEX hydrocarbons. This makes it difficult to predict the amount of electron acceptor(s) that will be needed for complete BTEX removal.***" In field experiments at a gasoline spill site, Reinhard et al. (ES&T, 31(1):28-36, 1997) found that only 13 to 40% of the sulfate consumed was used to degrade BTEX.
7) Numerical modeling using MODFLOW-SURFACT was used to support the contention that 1.5 years of sulfate addition/recirculation could reduce benzene concentrations to levels that could then degrade over the next 15 years to via MNA to reach the cleanup goal of MCLs. However, as was discussed during the March 16, 2017 BCT conference call, the model likely overestimates the degradation rate due to the assumptions of equilibrium between the LNAPL and dissolved phases (i.e., no mass transfer limitations), and the use of an estimate of naturally occurring organic matter (foc) of 0.0003, which leads to too low of an estimate of contaminant sorption and retardation. Also, there was extensive discussion during this call that the modeling, as performed, is not predictive. The modeling results can only legitimately be used as a tool to compare time frames under differing scenarios. ***Thus, the modeling that was performed cannot***

be interpreted as support for Amec's contention that the cleanup goals can be achieved in an estimated 20 years.

8) Approximately one year after termination of steam injection, large portions of the SEE treatment area remain at temperatures that are likely not conducive to the natively-occurring microbial populations, although some of the less-impacted areas may be experiencing increases in microbial growth. Amec's mass estimates indicate that 200,000 gallons of LNAPL remain in this area.

Path Forward

In order to go forward with EBR, the Agencies propose that a phased implementation approach be employed. The ultimate objective of using a phased implementation is to gather the information we need to ensure that EBR is being implemented in an optimal manner. From this information, we can establish milestones and criteria against which we can compare the full scale implementation to ensure that the remediation is proceeding in a manner and at a rate that will allow the remedial goals to be achieved in the estimated desired time frame. The "Decision Tree" states that the first step in implementing EBR would be "To establish location is ready for EBR injections". During this pumping/LNAPL removal and temperature stabilization step, Amec should provide well-documented case studies of specific sites where EBR, as Amec plans to do it, has actually remediated 100s of thousands of gallons of LNAPL/BTEX so as to reach 500-600 ug/L BTEX in groundwater, with no LNAPL remaining (or, at least, no LNAPL with COCs in the LNAPL). At the same time, laboratory experiments should be performed:

Commented [DE3]: I would really like to use a much stronger word here, like they are required to do a phased implementation, but that is for the managers to decide. As a technical person, my advice is to not let EBR go forward as they propose in Addendum #2.

a) In light of the inconclusive results from the field test on benzene degradation accompanying sulfate utilization, the first objective of the site specific testing should be demonstrating that the sulfate-reducing microbial consortia at this site is capable of degrading benzene, and if so, what conditions are necessary to maximize the degradation rate. If these laboratory experiments show that benzene degraders are not naturally present, it may be necessary to incorporate bioaugmentation into the EBR work plan.
b) Laboratory experiments could determine if the existing microbial system is deficient in sulfate, and if so, the amount of sulfate needed to maximize degradation rates, and the amount of sulfate required for degradation of BTEX.

These laboratory experiments must be performed utilizing soil samples from all four of the hydrologic zones: cobble zone (CZ), UWBZ, low permeability zone (LPZ), and LSZ.

Based on what is learned from the laboratory experiments, the first phase of the field implementation can be designed that will allow determination of benzene degradation in each of the hydrologic zones. Again, all four hydrologic zones should be targeted, as well as areas of heavy LNAPL saturation, and areas only affected by dissolved contaminants. Benzene degradation rates can be estimated using a flow-through field setup rather than a push-pull test as was used in the field pilot test. Estimates of benzene degradation derived from the field test can be used in an appropriate predictive model to estimate treatment times, although it must be kept in mind that, "***Anaerobic bioremediation is still not thoroughly understood, especially under field conditions, making clean-up times difficult to predict***" (ESTCP, 1999). The presence of significant LNAPL at this site and low permeability zones that are known to contain LNAPL will

limit the biodegradation rate (ESTCP, 1999, page 6). More details on the laboratory and first phase of the field implementation are provided below.

Laboratory Work
These tests would provide a baseline with which to compare data on microbial populations during implementation, as well as assessing benzene degradation and the effects of adding sulfate.
Eleanor (& Dan) – can you fill this in?

First Phase Field Implementation I've imported what Dan provided previously – needs re-writing
ask for a field study that involves actually remediating an LNAPL mass – pick a well with substantial LNAPL, put a transect of injection wells upgradient of the LNAPL well, and a transect of monitoring wells immediately downgradient of the well, and inject sulfate, etc., as planned for the full-scale EBR – or as found to be optimal based on lab tests? If AF can timely remediate that well so that no LNAPL is found in the well, and the COC concentrations in that well and the downgradient monitoring transect are below standards, then that would be strong evidence that a full-scale approach could work.

The chosen LNAPL well should have significant LNAPL – more than a sheen – at least two inches of LNAPL fairly consistently, so that actual *remediation of LNAPL* can be assessed.

> Note that my sense of where AF is going is that eventually they will claim that they don't actually have to get rid of LNAPL, but merely get GW concentrations of BTEX down to MCLs, "eventually". Encapsulation of LNAPL by microbial films (to degrade the BTEX moving from LNAPL to GW), by iron sulfide precipitates (to reduce flux of BTEX from LNAPL to GW), fouling and precipitates in and around LNAPL bodies (so that GW doesn't really flow close to the LNAPL) are things that could cause GW concentrations of BTEX to fall, while much BTEX remains in the remaining LNAPL. Hence my continued insistence on the idea that the details of performance monitoring make a huge difference in what "success" is.

Chosen well should be at elevated temperature, to correspond with the general site conditions.

Reagent injections (sulfate, etc.) should reflect those concentrations, rates, volumes, etc. that are proposed for full-scale EBR or as found to be optimal based on lab tests?.

Assuming the field study continues for at least a year, the changes around the injection wells in terms of microbiology, sulfate concentrations, sulfide production, hydrogen sulfide generation, precipitation of iron sulfides, possible aquifer plugging, changes in pH, etc., can be monitored and evaluated for viability of a full-scale remedy, and any likely dangers, showstoppers, etc.

Fouling should be assessed for all wells (injection, LNAPL, monitoring), to determine the likely needs for well reworking, refurbishing, eventual replacement, etc. This is particularly important for the follow-on contractor (after AMEC's contract expires) to have an idea of long-term costs,

Commented [WU4]: Note that AF intends to get the COCs down to 500-600 ug/L so that MNA can complete the remediation to MCLs in the required timeframe.

Of course that means that the MNA part is also significantly uncertain (i.e., a whole different bag of uncertainty), even if EBR performs just like AF models it.

Commented [DE5]: The decision tree states that <5 ft/week accumulation in wels is non-inhibiting to starting EBR – I think that has to be the standard

Commented [WU6]: AF has consistently denied EBR is planned for LNAPL source remediation, and consistently affirmed that indeed EBR will remediate LNAPL source materials. But if AF is not going back to SEE (or other actual source remediation technology – "actual" meaning in a few years, not some indefinite long-term "eventually"), then EBR has to remediate the LNAPL, and do it right away with minimum hiccups. So the field study should explicitly confirm that a significant mass of LNAPL has indeed been remediated (or not).

and how to bid. Also, corrosion of carbon steel wells should be assessed, as it is well known in the oil industry that sulfate reduction and the production of H2S accelerates corrosion.

The downgradient monitoring transect can not only monitor COC changes, but also assess the geochemical footprint of downgradient locations, which would be pertinent to evaluating possible enlargement of a sulfate/etc. plume at full scale.

> Also, the distribution and concentrations of sulfate achieved downgradient of the injection transect is of great interest. The AF model indicates they can get a reasonable (to them) sulfate distribution, but reality in subsurface environments is often different from the models. The field study should be designed to provide suitable data to design injection well spacing, injection rates, injection concentrations, pressures, etc., so as to achieve useful sulfate concentrations across the site.

If AF can timely remediate that well so that the COC GW concentrations in those representative wells and the downgradient monitoring wells are (and remain over time) below EBR goals, then that would be strong evidence that a full-scale approach could work.