

March 18, 2002

Mr. John Burleson Stratford Army Engine Plant 550 Main Street Stratford, CT 06615

Re: Draft Technology Demonstration Plan In-Situ Chemical Reduction and Coprecipitation of Hexavalent Chromium in Groundwater Stratford Army Engine Plant

Dear Mr. Burleson:

The United States Environmental Protection Agency (EPA) has reviewed the draft document entitled "Technology Demonstration Plan, In-Situ Chemical Reduction and Coprecipitation of Hexavalent Chromium in Groundwater". This report was prepared by Geo-Cleanse International, Inc. for consideration at Stratford Army Engine Plant in Stratford, Connecticut. The report is dated February 5, 2002.

EPA has reviewed the *Technology Demonstration Plan* for the in-situ reduction and coprecipitation of hexavalent chromium (Cr(VI)) in groundwater at the former Stratford Army Engine Plant (SAEP), Stratford, CT. This document describes the planned technology demonstration and includes a thorough discussion of the chemical reactions involved. Overall, the authors have done a credible job of explaining the details of the in-situ reduction process, including both benefits and limitations. However, it seems that their approach is based largely on experience, while supporting data from other sites is not presented. EPA believes that SAEP is a good candidate site for this technology demonstration, but several recommendations are made that would provide confirmation of the hypothetical reactions involved in the process and possibly lead to modifications that would increase the success rate. Furthermore, confirmation of specific reaction products would increase confidence that the technology yields the desired long-term stability of the chromium left in place.

EPA's comments on the above-mentioned report are provided in Attachment I to this letter.

If you have any questions regarding these comments, please contact me at (617)918-1387.

Sincerely,

Higher & Cossidy

Meghan F. Cassidy Remedial Project Manager

Enclosure

cc: Ken Feathers/CT DEP Michelle Clemens/USCOE Peter Golonka/Gannett-Fleming

## ATTACHMENT I

The following are EPA's comments on the draft document entitled "Technology Demonstration Plan, In-Situ Chemical Reduction and Coprecipitation of Hexavalent Chromium in Groundwater" This report was prepared by Geo-Cleanse International, Inc. for consideration at Stratford Army Engine Plant in Stratford, Connecticut. The report is dated February 5, 2002

## **General Comments:**

1. Need for conceptual model. The Technology Demonstration Plan lacks a 'conceptual geochemical model,' i.e., a generalized picture of subsurface processes and mechanisms that act to control Cr mobility. Is the Cr(VI) present primarily in solution, or are there solid phases that might be controlling Cr(VI) solubility? Without a hypothesis to test, it may be difficult to interpret results. If the approach succeeds, why? If it fails, what is the cause and what needs to be changed in the procedure? For example, one possible explanation for the existence of the high Cr(VI) zone is that it represents a historic release from the plating facility that has remained more or less immobile, and in an unreduced state, in the groundwater since facility closure. If this is the case, then remediation by pump-and-treat, or the proposed in situ technology, may be appropriate. In an alternative scenario, the Cr(VI) release may have resulted in the precipitation of a solid phase (such as jarosite) in which hexavalent chromium substitutes for some of the sulfate sites in the crystal structure. This phase is relatively soluble, and the equilibrium solubility under site-specific conditions may be relatively high. In this case, slow movement of groundwater will continue to dissolve the solid phase, with the result that Cr(VI) will persist in solution as long as the solid-phase source is present. Injection of additional ferrous iron and sulfate may result in precipitation of additional jarosite (or other phases that could potentially incorporate significant quantities of hexavalent chromium), and thus perpetuate the groundwater problem by increasing the mass of solid-phase Cr(VI) source. In the Specific Comments listed below, EPA has proposed some specific recommendations for additional analyses to characterize Cr phases in both pre- and post-test soil samples.

2. *Need for geochemical modeling*. Nowhere is geochemical modeling used to support the planned demonstration. It is recommended that any of a number of available geochemical equilibrium programs (e.g. PHREEQC, MINEQL+, MINTEQA2, etc.) be used to predict what might happen (e.g., what reactions dominate? which phases might form?) during the test. The code could also be used to address the long-term stability of resulting phases under a range of plausible groundwater conditions. Finally, comparison of model results to field-derived data would validate or refute the conceptual geochemical model for the predominant processes.

As one example, EPA's contractor has performed preliminary simulations using PHREEQC. Saturation indices (SI) were calculated for phases forming in the pH range from 5.0 to 7.0 when FeSO<sub>4</sub> is added to high-Cr(VI) groundwater. A plausible alkalinity was assumed. Calculated SI values were positive for FeCO<sub>3</sub> (indicating possible precipitation), as well as for the phase jarosite-H (stoichiometric formula (H<sub>3</sub>O)Fe<sub>3</sub>(SO<sub>4</sub>)(OH)<sub>6</sub>). These phases may be important in implementing the proposed remedial technology (e.g., precipitation of FeCO<sub>3</sub> may require additional reagent, and may contribute to fouling). If jarosite is present, the possibility that it contains some Cr(VI) (as  $CrO_4^{-2}$  substituting for  $SO_4^{-2}$ ) cannot be discounted. Later dissolution of this phase may remobilize Cr(VI)

3 Consideration of previous test results. The results of the previous pilot test conducted at this site (by Foster Wheeler and Harding Lawson Associates) are discussed, but the document would benefit from a more thorough discussion of the likely reasons for the limited success of the previous pilot test and the reasons that Geo-Cleanse believes its technology will address those shortcomings. What is similar and what is different about the proposed approach?

4 *Effects of elevated VOC concentrations.* The plan recognizes a lack of knowledge of the effects of high VOC concentrations on the proposed process. VOCs are included on the analyte list for pre-test sampling, and this is endorsed. However, it is noted that inorganics and VOCs have been addressed separately in previous programs, and there are few data from co-located samples in the pilot test area. Is the existing characterization in this area adequate to support design of the experiment? What contingencies have been considered in the event, for example, that VOCs in the proposed test area are much higher than anticipated?

5. Effects of elevated Cr(VI) concentrations. The plan acknowledges that the proposed in situ reduction process is optimal for application to groundwater with Cr(VI) concentrations of the order of 10 mg/L or less. Given the much higher concentrations detected in previous characterization of the chromium plume at SAEP, it is possible that the area designated for the technology demonstration may contain Cr(VI) at concentrations higher than anticipated. What contingencies have been considered if this is the case?

6. Relationship of the technology demonstration to ultimate SAEP site remediation. The document generally provides strong motivation and a well-conceived plan for a series of bench and pilot-scale experiments to test the proposed in situ reduction scheme. However, the relationship of the demonstration project to the ultimate cleanup goals for SAEP is not clear. In section 5.6.9, "scale-up" issues are addressed briefly; aquifer clogging, site characterization, site access, cost, and long-term stability of the precipitates are mentioned specifically. However, additional issues pertinent to application of the technology at SAEP are alluded to elsewhere in the text. In particular, it is stated several times (e.g., pp. 26-27, sec. 2.6, items 5 and 8) that the approach may be compromised by very high concentrations of chromium and/or by the presence of high concentrations of co-mingled organics. The SAEP site is certainly characterized by extremely high concentrations of both Cr(VI) and chlorinated solvents, both approaching  $10^3$ mg/L (e.g. WP-99-15 where Cr(VI) was detected at 950 mg/L). Geo-Cleanse indicates that their process works for relatively low Cr concentrations, of the order of 10 mg/L. How will the potential for full scale-up for application under the conditions prevalent at SAEP be evaluated? Will such an evaluation be part of the final report on the technology demonstration?

7. *Relationship of experimental time scales to long-term site concerns.* A key to determining the effectiveness of the technology is the long-term stability of the precipitate. How will the long-term stability be judged in a time frame that would allow this technology to be applied at the SAEP site, if in fact that is the intention?

8. *Applicable regulations*. Will leaving all chromium in the subsurface satisfy the Connecticut regulations for leachability? Will a waiver be required if soils in areas of higher chromium concentrations do not meet the regulatory standards?

## **Specific Comments:**

1. **p. 13, Section 1.3.3:** The text states that chromium background "...may include...'anthropogenic' background resulting from human activities either onsite or offsite." Chromium levels generated by onsite human activities should not be considered as "background."

2. **p. 16, Section 2:** The second paragraph of this section indicates that the technology should be coupled with one that addresses a vadose-zone source (i.e., the proposed in-situ treatment of the groundwater plume does not eliminate vadose-zone contamination). If the latter is present, it is possible that it will continue to feed the groundwater plume. For this reason, further characterization of vadose-zone soils would appear to be essential to a complete demonstration. Furthermore, such sampling and analysis would be cost-effective if done in conjunction with the proposed program, as the equipment and personnel will already be mobilized, and the proposed borings will penetrate the vadose zone in any case. Split-spoon samples of vadose-zone soils should be collected from borings installed for the demonstration, and should be characterized to develop a better understanding of the potential continuing source in this domain. At a minimum, such samples could be archived for future analysis.

3. p. 17, Section 2.2: The text states that VOCs are often found in association with Cr(VI) and that these are "... efficient Cr<sup>+6</sup> reductants." GF notes that, while both VOCs and Cr are not reported from co-located samples in the Technology Demonstration Area, there are a few data that suggest that both Cr(VI) and VOCs may coexist – for example, in groundwater from WP-99-08, TCE is reported at 110,000  $\mu$ g/L (in the interval from approximately –16 to –20 ft MSL) and Cr(VI) is 300 to 500 mg/L (from –14 ft MSL to –33 ft MSL). Is there a threshold VOC concentration at which Cr(VI) reduction will take place? The occurrence of both Cr(VI) and high levels of TCE contradicts the statement that VOCs are efficient Cr(VI) reductants. This statement should be clarified.

4. **p. 17, Section 2.2:** It is true that, under specific circumstances,  $Cr^{+3}$  in groundwater may oxidize to  $Cr^{+6}$ ; to what 'natural oxidants' does this paragraph refer (e.g., manganese minerals)? Do these 'natural oxidants' exist at the SAEP site, and if so, in what concentrations? Is it anticipated that natural re-oxidation of Cr(III) in the Technology Demonstration Area will be problematic?

5. **p. 19, Section 2.3.3:** In this paragraph and elsewhere in this document, precipitates consisting of ferric iron and  $Cr^{+3}$  are referred to as "insoluble," ". not soluble" (Section 2.4 3, p. 22), or even ". very insoluble" While the solubilities of these phases are low relative to other, more highly crystalline Fe-Cr minerals, they <u>do</u> have finite solubilities in groundwater (e.g., as shown in Fig. 2-2) The site-specific redox and pH conditions that affect solubility of the anticipated Fe-Cr precipitate should be discussed with respect to potential for re-release of chromium to groundwater

6. p. 22, Section 2.4.3: It is stated that sulfate  $(SO_4^{-2})$  suppresses adsorption of Cr<sup>+6</sup> because  $SO_4^{-2}$  competes for surface sorption sites. What is the ambient sulfate concentration of site groundwater? Is marine sulfate present?

7. p. 22, Section 2.5, (1): The series of reactions that describe the reduction of  $Cr^{+6}$  by  $Fe^{+2}$  shown in Section 2.3.1, p. 18, suggests that a net effect will be a lowering of pH (Equation 5). Will groundwater during the pilot test be buffered to prevent pH from dropping below the optimal window of 5 to 6? How will this optimal pH be maintained during the pilot test? It seems that low pH could be problematic due to the potential for dissolution of any mixed Cr-Fe hydroxide phases forming during the test.

8. p. 22, Section 2.5, (2): The concentration of  $H_2O_2$  is anticipated to be ". .a maximum of approximately 3% depending on site conditions." What are the criteria for determining the peroxide concentration (e.g., TOC? COD?)? Are the site-specific data consistent with these criteria?

9. p. 23, Section 2.5: The first paragraph notes that the process utilizes specially designed injectors "...to generate a wide radius of influence for reagent dispersion." What is the risk of displacing the contaminated groundwater outward from the injection points and/or failing to obtain adequate mixing of reagents and contaminated groundwater?

10. p. 23, Section 2.5.1: Four advantages of the use of the Geo-Cleanse process are enumerated in this section. The fourth of these claims that the method is "...field-proven, reliable, and safe." Citations and/or summaries of the successful application of this methodology should be provided here. Under what conditions has it been proven successful? Were these successes achieved at sites that are comparable to SAEP? Are they at sites with similar groundwater, soil, and/or Cr and VOC concentrations? Additional details of previous experiences at other sites should be provided to support statement (4).

11. p. 24, Section 2.5.2, and elsewhere in the document: The process requires the injection of a solution of hydrated ferrous sulfate (FeSO<sub>4</sub> 7H<sub>2</sub>O), thus providing a source of SO<sub>4</sub><sup>-2</sup> for desorption of Cr(VI) from mineral surfaces, and a source of Fe<sup>+2</sup> for the reduction of Cr<sup>+6</sup> to Cr<sup>+3</sup>. The target range of groundwater pH is 5 to 7. In this pH range, has the potential for precipitation of the ferrous iron as FeCO<sub>3</sub> been considered?

12. **p. 26, Section 2.6:** Among the limitations of the methodology listed here, the authors acknowledge (statement (5)) that the technology is not suitable for sites with "... extremely high groundwater chromium contamination..." What is the upper limit of Cr concentration where they feel that they have a reasonable chance of achieving successful reduction? Is this based on previous experience, and if so, at which site(s) and what were the conditions? What is the possible effect of the high VOCs on chromium reduction at the SAEP site?

13. **p. 26, Section 2.6:** (also refer to the comment pertaining to p. 19, Section 2.3.3) EPA agrees with the statement regarding the uncertainty inherent in making predictions of the long-term stability of Cr-Fe precipitates under field conditions. Long-term monitoring is necessary in order to demonstrate stability, as post-test changes in groundwater chemistry (i.e., as pH and redox conditions return to ambient levels) could indeed affect solubility of the newly-created phases. For example, the extremely slow groundwater velocities may favor low-ORP conditions in the absence of either injected or release-related oxidants such as  $H_2O_2$  or chromate. EPA notes, as did Geo-Cleanse, that ORP appears to be positively correlated with Cr(VI). Although none of the ORP values reported in Table 4-1 are negative, groundwater samples with low or nondetectable chromium also report ORPs less than 100 mV. The possibility that a Cr-Fe phase (e.g.,  $(Cr_xFe_{1-x})(OH)_3$ , precipitated during the pilot test) may dissolve as groundwater redox conditions reestablish to ambient, low levels after the conclusion of the pilot test should be addressed. As noted in the General Comments (above), EPA recommends use of any of the currently available software for geochemical modeling for several reasons:

- model results may identify Cr phases that are already present in soil in the target area;
- model results, based on site-specific data, may also indicate which phases are likely to form as a result of the pilot test;
- predictions of phases that may precipitate and subsequent confirmation by laboratory analysis lend confidence to predicted long-term stability (i.e., assuming that the equilibrium solubility under site-specific groundwater conditions is an upper limit);
- in the event that neither geochemical model predictions nor post-test analytical results support the hypothetical reaction series, model results may help to guide modifications to the proposed technology.

14. **p. 27, Section 2.6:** The authors note that "... sites impacted with VOC or SVOC contamination may require treatment (prior to the chromium treatment)..." If this turns out to be the case for the SAEP technology demonstration, how will VOCs be treated?

15. **p. 37, Section 3.0:** Geo-Cleanse acknowledges the potentially complicating fact that the  $Cr^{+6}$  and VOC concentrations at SAEP are higher than desirable for their methodology, but correctly states that the co-mingling of these contaminants is probably reasonably representative of metals-contaminated sites in general. At this point, is it possible to speculate on the extent to which they feel that their process will achieve Cr(VI) reduction under the conditions expected to be encountered at this site?

16. **p. 39. Section 4.2:** Concrete coring has revealed the presence of Cr(VI) within the floor slab at various locations throughout the former plating facility. Has any of this material been analyzed for identification of discrete Cr(VI) phases? As noted elsewhere in this review, the potential for remobilization of residual Cr(VI) presently sequestered in solid phases in the vadose zone should be considered

17. **p. 39, Section 4.2:** This section describes the pilot test performed in December 1999 and January 2000 by Foster Wheeler Environmental Corporation and Harding Lawson Associates. This test involved the use of potassium permanganate to oxidize the VOCs present, and a FeSO<sub>4</sub>- $H_2SO_4$  solution to reduce Cr<sup>+6</sup> and achieve the desired pH. From the summary of the results (p. 40), it seems clear that the test was only moderately successful. In particular, the authors note that iron precipitation was evident by the time the reagents reached a monitoring point (item (4), p. 40) and the solution was clear (but was it colorless, or was it yellow, indicating the persistence of Cr(V1)?).

It is also noted (item (6)) that  $Cr^{+6}$  concentrations dropped by at least two orders of magnitude but the target level of 0.11 mg/L (the Connecticut SWPC standard) was not achieved. To what is this failure to meet the target level attributed? On what basis does Geo-Cleanse propose greater success with their process? This issue should be discussed in greater detail, in order to resolve problems encountered during the Foster Wheeler / Harding Lawson pilot test that may be repeated by the Geo-Cleanse effort.

18. p. 40, Section 4.2, item (6): The text notes that the HLA pilot test may have encountered limitations due to heterogeneous hydraulic properties, with slower domains relatively isolated from the flushing due to extraction and from the delivery of reagents. The same issues are likely to arise for the proposed injection scheme. What assurance is there that the injected reagents will be dispersed adequately through the target zone, rather than bypassing contaminant mass by localizing along more conductive pathways? Similarly, what assurance is there that the post-test monitoring will be adequate to capture any rebound due to slow "bleedout" from tighter subdomains?

19. p. 40, Section 4.2, item (7): The text indicates that a  $Fe^{+2}$ :Cr<sup>+3</sup> molar ratio of 30:1 was used during the Foster Wheeler - Harding Lawson pilot test. The apparent discrepancy between this ratio and the proposed ratio of 6:1 (Section 2.5.4, p. 25) should be resolved.

20. **p. 41, Section 4.3.2:** The need for additional characterization of soils from both the vadose zone and below the water table in the Technology Demonstration Area has already been noted (Comment 2, above). It is noted that there are some soil analyses in the June 2000 FW-HL report, in which both total Cr and Cr(VI) are reported. In most of these analyses, Cr(VI) is only a small fraction (a few percent) of the total, but for a few samples (e.g., PZ9910032XX), Cr(VI) is greater than 10% of the total. Also, the Technology Demonstration Plan document states that vadose zone soils from beneath the plating facility contain Cr(VI) as high as 640 mg/kg. These observations suggest that Cr(VI) is present in a stable, solid phase, and this phase should be identified for assessment of future solubility.

21. p. 41, Section 4.3.2: In this section, the development of reducing conditions is attributed to the presence of ". very high VOC concentrations. ." which, in turn, facilitate the reduction of  $Cr^{+6}$  to  $Cr^{+3}$  The implications of this statement are unclear. Do the authors mean to imply that the high VOC levels 'cause anaerobic, reducing conditions' through microbial degradation? The possibility that reduction of hexavalent chromium is caused by direct, abiotic interaction (i.e, oxidation) between chromate and the VOCs should be discussed.

22. p. 42, Section 4.3.2: The text notes that ORP is positively correlated with Cr(VI) concentration. Does this imply that the ORP is controlled to some extent by the presence of chromate or bichromate? Or, do the contaminants tend to localize in domains of higher hydraulic conductivity, which are also pathways for more recently infiltrated groundwater with a shorter residence time in the subsurface? This bears on important issues regarding the ambient redox conditions to which the site might be expected to return in the long term. These questions again highlight the need for a conceptual model framework within which to interpret site observations.

23. **p. 42, Section 4.3.2:** This section again poses the general question regarding the efficacy of the proposed reduction process in the presence of high levels of VOCs in the Technology Demonstration Area.

24. **p. 42, Section 4.3.2:** The third sentence in the sixth paragraph of this section appears to be missing words. "The two sampling locations that encompassed [???] within Chlorinated VOC Hot Spot..."

25. **p. 53, Section 5.1:** A specific demonstration objective is an evaluation of the ability of the treatment methodology to reduce  $Cr^{+6}$  and precipitate the resulting  $Cr^{+3}$  along with ferric iron as a stable hydroxide or oxyhydroxide phase (Item (3)). The goal, as stated here, is to reduce dissolved total and hexavalent chromium *to ambient background levels* or to other regulatory standards. The text indicates that ambient chromium levels have not been established for SAEP groundwater, but that additional background analyses will be conducted "...to evaluate total Cr and  $Cr^{+6}$  background." How will this background data set be established? Which wells will be sampled, and at what depth intervals? How will background locations be chosen? Finally, how is 'background' defined, particularly with respect to the statement (as noted in a previous comment referring to p. 13, sec. 1.3.3) about "anthropogenic' background resulting from human activities either onsite or offsite"?

26. **p. 53, sec. 5.1, item (4):** The document states that TCLP and SPLP procedures will be used to evaluate the long-term stability of the chromium-bearing precipitates that form. While these leaching tests will serve to characterize the potential for remobilization under the conditions of the test (oxidizing, lower pH than ambient SAEP groundwater), they may not test under conditions appropriate to future groundwater geochemistry at the site. For applicability at any particular site, and for assurance that the solid phases formed are likely to remain stable, it may be essential to identify the specific phases present, and to evaluate their solubility under a range of potential future geochemical conditions. For example, if the oxidizing conditions prevailing at

present are due to the presence of the chromate, and the natural condition is more reducing (e g, due to the low groundwater velocity, long residence time for groundwater, presence of organic carbon within the aquifer, etc.), the potential for remobilization of chromium due to dissolution of the Cr-Fe phase and release of Cr (as well as any other coprecipitated metals) should be evaluated for the latter conditions.

27 **p. 54, Section 5.1:** In theory, the successful implementation of the proposed pilot test <u>should</u> yield a decrease in Cr(VI) in both soil and groundwater at the site. However, as noted elsewhere in this review, the possibility that Cr(VI) is already present in solid phases in the aquifer soils as a consequence of leakage from the former plating facility, or that such phases may precipitate as a result of the injection of ferrous sulfate during the pilot test, should be examined critically (e.g., through geochemical modeling and pre- and post-test characterization of aquifer solids).

28. **p. 54, Section 5.2:** Item (2) states that hexavalent chromium concentrations in the pilot test area, between Buildings B-2 and B-12, range from nondetectable to a maximum of 56 mg/L. How was this value obtained? It is apparent from the cross-sections presented as Figures 4-6 and 4-7 that this maximum value may be representative of the groundwater concentration at, say, MW-99-11, to the northeast of the proposed Technology Demonstration Area. However, data from Table 4-1 report Cr(VI) concentrations as high as 450 mg/L in groundwater from MW-99-20 (on the south side of the Technology Demonstration Area). Inasmuch as there are no analyses from directly beneath this area, the possibility that groundwater Cr(VI) may be much higher than 56 mg/L should be addressed. While it is agreed that the SAEP site may be a good place to test this remedial technology, the potentially high levels of Cr(VI) may render the methodology less than optimal for the site overall

29. **p. 54, Section 5.2, items (2) and (3):** It is stated that the pilot test area is chosen to meet the criteria that Cr(VI) and VOC concentrations are not too high. While this may prove to be the case when further characterization is done in conjunction with the test, these restrictions may bear on the ultimate applicability to the site as a whole. Other domains of concern have been shown previously to have much higher Cr(VI) and VOC levels (both approaching  $10^3 \text{ mg/L}$ ) in the groundwater. If results from the demonstration are encouraging, what will be done to test the applicability of the approach under more extreme conditions (i.e., higher Cr(VI) and VOC concentrations)?

30. **p. 56, Section 5.3.5:** Although alkalinity is listed among the "Process Monitoring Parameters" in Table 5-4, it is not mentioned as an analyte in this section or in Table 5-1 ("Analytes and Analytical Methods"). It is recommended that alkalinity be added to the groundwater analyte list, because it is necessary for any calculations predicting the formation/dissolution of carbonate phases, e.g., FeCO<sub>3</sub>. In addition, chloride (Cl<sup>-</sup>) should be added as an analyte in order to track potential effects of tidal mixing with seawater.

31 **p. 58, Section 5.4:** As noted elsewhere in this review, it is not clear that the VOC concentrations in the vicinity of the proposed pilot test have been measured at points co-located with chromium analyses. Since samples collected for the bench-scale tests will not be preserved according to EPA guidelines for organic samples, how will the effects of treatment on VOC concentration and vice versa be evaluated?

32. p. 59, Section 5.4.1: The plan states that soil samples will be analyzed just prior to the experiments so that the appropriate baseline conditions are established. While this is well motivated for the purpose of the bench experiments, these analyses may not provide accurate characterization of the in-situ conditions, which might prove to be an important consideration for the proposed field-scale tests. Splits of the soil samples should be collected, transported, and analyzed under standard soil-analysis protocols in order to characterize further the current subsurface conditions, and to support the design of the proposed field testing.

33. **p. 59, Section 5.4.2:** If groundwater samples are not preserved by acidification, is sorption of inorganics to the sample container walls likely to bias results?

34. **p. 60, Section 5.4.4:** Type 3 (of the four general types of groundwater to be used in the bench scale testing) purports to contain "...relatively high  $Cr^{+6}$  concentrations (greater than 50 mg/L)." How much greater than this value does Geo-Cleanse anticipate this concentration to be?

35. **p. 60, Section 5.4.4:** Type 4 groundwater will have ". . VOCs and other characteristics of groundwater at SAEP." What concentration of VOCs is anticipated, and what VOC concentration will be used in the bench scale testing?

36. **p. 61, Section 5.4.4:** If the precipitate formed during the groundwater bench-scale tests is to be collected and weighed, it is recommended that the phase(s) formed be characterized and/or identified by powder x-ray diffraction (XRD), electron microprobe, scanning electron microscopy with energy-dispersive spectrometry (SEM/EDS), electron diffraction via transmission electron microscopy (TEM), or other suitable analytical method. Characterization of the product(s) formed during the test is critical to interpretation of test results and extrapolation to long-term behavior of the precipitated phase(s).

37. p. 62, Section 5.4.5: Inasmuch as a primary objective of the soil slurry batch tests is to determine resistance of the precipitated chromium minerals to mobilization, it is recommended (as noted elsewhere in this review) that characterization of Cr-bearing minerals present in pre-test soil samples as well as any phases forming as a consequence of the test, should be accomplished by XRD, TEM, SEM, electron microprobe, or other suitable method.

38. **p. 64, Section 5.4.6:** The planned experimental protocol appears to assume that equilibrium chemistry will prevail, and, implicitly, that the *rate* of water flow through the columns is not a significant variable. A few runs at different flow rates should be considered in order to verify that the experimental results are not influenced significantly by reaction kinetics (i.e., that residence time in the column is not a significant variable).

39 **p. 65, Section 5.5.1:** The text states that six injector wells will be installed, and refers the reader to Figure 5-1 for locations. Figure 5-1 shows seven symbols for injector wells, although only six are labeled Please check the figure for consistency.

40 **p. 66, Section 5.5.2:** Item (2) on this page suggests that the average groundwater  $Cr^{+6}$  (based on results from MW-99-10 and MW-99-11) is 9.9 mg/L. Results from MW-99-20 introduce the possibility that the average groundwater concentration could be much higher. What is the rationale for using the lower number?

41. **p. 66, Section 5.5.2:** To what GCI field experience do the authors refer in making the statement that "...approximately 10% of the groundwater volume is ...sufficient... to distribute the reagents..."? Is this estimate based wholly on field experience? Has any hydrologic modeling been invoked? What is the relationship between the volume injected and the number and distribution of injection points?

In addition, the average ferrous iron requirement cited here, 11000 mg/L, appears to translate to nearly 4000 kg of FeSO<sub>4</sub> 7H<sub>2</sub>O (at a solution concentration of 197 mM Fe<sup>+2</sup>, 72580 liters of solution, and molecular weight of FeSO<sub>4</sub> 7H<sub>2</sub>O equal to 278 g/mol) The discrepancy between this mass and the estimated 802 kg of FeSO<sub>4</sub> 7H<sub>2</sub>O in the preceding statement on this page (which is based on the minimum Fe<sup>+2</sup>:Cr<sup>+3</sup> ratio of 3:1, as shown in Table 5-3) needs to be clarified

42. **p. 68, Section 5.5.4:** One soil boring is planned to collect samples for post-test analysis. This introduces the possibility that the hole location may not be "representative" of the test area. Results from the HLA pilot test suggested that subsurface heterogeneity may have played a role in the distribution of reagents. In this event, it is possible, for example, that the single post-test boring may sample a domain that was bypassed to some extent during the injection and subsequent reaction stages of the test. At least one additional post-test boring should be considered in order to verify that results are not sensitive to the exact location of the sampling.

43. p. 71, Section 5.6.9: Issues related to scale-up from the bench test to the field extend beyond the concern for aquifer clogging due to excess iron precipitation. These issues include, but are not limited to, the high  $Cr^{+6}$  concentrations, presence of preexisting Cr(VI) solid phases in the aquifer, effects of high VOC levels, and lack of predictive capabilities for long-term success due to inadequate knowledge of the relevant phase equilibria, hydraulic considerations, etc. Will there be an evaluation of the applicability of this technology to this particular site at full scale? Is this a goal, or is this demonstration more or less independent of ultimate site cleanup goals?

44. **Table 9-2.** Will an OVM with a 10.6 eV bulb will detect TCA, which has an eV requirement of more than 11?