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22 April 1994

Mr. Russell Hart
Remedial Project Manager (HSRW-6J)
U.S. Environmental Protection Agency
77 West Jackson Blvd.
Chicago, IL 60604

Re: Moss-American Site, Milwaukee, Wisconsin
Predesign Task 16 - Treatability Studies
of Bioslurry and Soil Washing Technologies

Dear Mr. Hart:

Roy F. Weston, Inc. (WESTON®) has prepared this transmittal on behalf of Kerr-McGee Chemical Corp. (KMCC), the settling defendant for the Moss-American site.

This transmittal provides an addendum to previously transmitted Technical Memoranda related to the Bioslurry and Soil Washing Treatability Studies for the Moss-American site. This addendum provides a single reference of technical responses addressing U.S. EPA's review comments on the treatability study findings. The technical responses to U.S. EPA's comment set No. 2 have been prepared consistent with the discussions and agreements made during our 18 February 1994 meeting with U.S. EPA, WDNR, and CH2M Hill, Inc. representatives. We propose that these sets of comments and technical responses be accepted by U.S. EPA as clarification and supplemental information to the Technical Memoranda previously prepared by IT Corporation and Bergmann USA, on behalf of WESTON and KMCC.

Please contact us with any further questions or comments on this transmittal.

Very truly yours,

ROY F. WESTON, INC.

Mark E. [signature]

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KERR-McGEE CHEMICAL CORPORATION

Addendum to Technical Memoranda

Predesign Task 16
Treatability Studies of Bioslurry and Soil Washing Technologies

U.S. EPA Review Comments and Technical Responses

Moss-American Site
Milwaukee, Wisconsin

April 1994

U.S. EPA Comment Set No. 2
Dated 10 February 1994

and

WESTON/KMCC Technical Responses
Dated 20 April 1994

RESPONSE TO COMMENTS ON THE TECHNICAL MEMORANDUM PREDESIGN TASK 16 - TREATABILITY STUDY OF BIOSLURRY AND SOIL WASHING TREATMENT TECHNOLOGY U.S. EPA COMMENT SET NO. 2 - DATED 10 FEBRUARY 1994

A. GENERAL COMMENTS ON TREATABILITY STUDIES

1. U.S. EPA Comment: *Coordination between the soil washing and bioslurry testing.* *EPA recognizes that the SOW states that soil washing and bioslurry will be performed in combination only if the separate tests are successful, but encourages Kerr-McGee to perform this further testing. This information would be most helpful in selecting a cost-effective treatment technology and determining the appropriate containment unit. For example, the analysis of soil washing in combination with bioslurry (page 2) suggests soil washing could be fairly effective as a separation step if the treatment standard is raised to more than 50 ppm.*

Response: WESTON and KMCC believe that before any further engineering evaluations or treatability work on bioslurry, soil washing, or any potential remedial technology for the site be performed, it is prudent to more thoroughly characterize the site soils and sediments. This was always the intent of WESTON's predesign schedule and sequence of work; however, site access restrictions have interrupted this planned sequence. Our goal is to achieve a more thorough site characterization during the 1994 field investigation season through implementing Predesign Tasks 3, 5, 6, 7, and 19. This will provide essential characterization of the potential "feed stream" for any remedial treatment system, and perhaps may substantiate that CPAH levels are below risk- or performance-based treatment standards, thereby precluding the need for treatment.

During our group meeting on 18 February, it was mutually agreed that postponement and perhaps elimination of any further treatability testing was acceptable until further site characterization was completed and further progress was made on selection of a revised site remedy.

Each of the tested technologies (bioslurry and soil washing) achieved some reduction in CPAH levels in their respective "product" fractions. Therefore, each could be expected to contribute to cleanup to the approximate order of magnitude CPAH levels demonstrated by this testing program. As discussed in the previous response to comments and concurred by U.S. EPA, the data obtained in these studies do not support the ability of these technologies to achieve the current treatment standard of 6.1 mg/kg CPAH. At the same time, the potential use of each of these technologies, particularly in conjunction, depends on more than the level of CPAH achievable in the final product.

Beyond technical feasibility, other site factors including the actual volume of soil requiring treatment would determine the practical feasibility and cost-effectiveness of these technologies. For relatively small volumes of soils, use of these relatively equipment-intensive technologies may be less favorable than simpler and more readily implemented technologies. Therefore, both soil volume and treatment standards, if differing from those currently established, should be considered in further evaluation of these and other technologies, alone or in conjunction.

2. U.S. EPA Comment: *Enhancements.* *Again, EPA recognizes that enhancements were not required. However, we are all aware of other researchers' conclusions that enhancements to the test might be required to achieve higher levels of removal. This limitation keeps us guessing as to how well the system might function if non-conventional operations were implemented. EPA would encourage Kerr-McGee to pursue the subject further.*

Response: The ongoing research on enhancements is acknowledged. For example, in the SITE Demonstration bioslurry study reported by Lewis et al. (as cited in the Technical Memorandum), two of the five parallel bioslurry test reactors were re-inoculated at week 10 of the study with organisms isolated from the site. Two additional reactors were both re-inoculated and amended with surfactant. The fifth reactor was not re-inoculated or amended. The authors reported that none of the enhancement protocols fostered any significant improvement in degradation over the unamended reactor. The authors further noted that the bioslurry system would normally be operated in a semi-continuous fashion or the batch operation would be truncated (following the initial PAH removal phase). This activity would be followed by solid-phase treatment to further reduce contaminant levels while minimizing cost. They also suggested the use of Fenton's reagent to partially degrade complex ring structures as a pretreatment step. It might also be noted that the work of Mueller et al. for soils from the American Creosote Site (also cited in the Technical Memorandum) was conducted using low soil concentration (±2 percent). These slurries were slurries prepared from site soils by washing with Triton X-100 to facilitate the availability of the contaminants in the aqueous phase. Under these conditions, the reported biodegradation of "Group 3" PAHs (which included the CPAH constituents) was 40%. The authors suggested that possible limitations on bioavailability and/or depletion of necessary cometabolites may have been responsible for the apparent cessation of biological activity and the resulting plateau in contaminant removal. Other possible causes noted by the authors included the accumulation of inhibitory metabolites (which may occur in batch systems) or the depletion of an "undefined rate-limiting element." Subsequent testing by SBP at this site under the U.S. EPA SITE program (as noted in SBP product literature) has included the development of specialized microbial cultures. A high degree of high molecular weight (HMW) PAH removal (98%) efficiencies have been reported for contaminated groundwater, instead of soil slurries (comparing influent to effluent data). According to the report, mass balance calculations indicated that 20% of the HMW PAHs were retained as residual in the reactor, resulting in a net removal of approximately 80%.

Testing of slurry phase treatment for the Southeastern Wood Preserving Site in Canton, Mississippi, conducted by Jergen and Woodhull[1], achieved CPAH removal to a residual level of 490 mg/kg, representing a removal efficiency of approximately 95% at 20% slurry density in bench scale tests following 30 days treatment. It might be noted that this testing was conducted using soil sieved through a 200-mesh screen. In subsequent full-scale testing, comparable performance (approaching 93% removal) was achieved for total PAHs. CPAH removal efficiency was approximately 71%, with residual soil PAH levels reduced to approximately 315 mg/kg from initial levels of 1,100 mg/kg. Slurry enhancements included a dispersant and defoaming agent in addition to nutrients. Performance was significantly diminished during winter (low temperature) operations. Data were not reported for the washwater from full scale operations. Bench scale data indicated <1 mg/L PAH in washwater.

Given the high level of ongoing research activity by these and other competent researchers, it is anticipated that improvements in bioslurry treatment technologies for CPAH will be developed in the future. Some of these "enhancements" under study may, with suitable development, result in lower final CPAH levels than achieved in this test. However, it is not expected that sufficiently fundamental or timely improvements would be made in the near term to achieve the degree of reduction required to meet the remediation goals for the Moss-American site. Further, as discussed at some length and agreed to during our meeting with U.S. EPA on 18 February, the scope of our bioslurry and soil washing treatability studies for the Moss-American site did include the evaluation of enhancements and nonconventional operations. This evaluation was particularly relevant once it was determined that we had reached treatment limitations under "conventional" modes of operation. For example:

- The use of a semi-continuous or semi-batch operating mode with the EIMCO reactor is considered a state-of-the-art enhancement.
- The use of surfactants and the comparative evaluation of surfactants versus water in soil washing tests was an enhancement.
- The evaluation of a froth-flotation step within our soil washing treatment operations is considered an enhancement in response to site-specific soil conditions.

Based on this evaluation of published literature on the subject of biological treatment of wood-treating constituents and our site-specific treatability study evaluations using

[1] Jergen, D.E., and P.M. Woodhull, "Slurry-Phase Biological Treatment of Polycyclic Aromatic Hydrocarbon in Wood Preserving Waste," OHM Remediation Services, Corp., Findlay, Ohio, 1994.

conventional and nonconventional modes of operation, we do not believe that we have left a substantive margin of doubt as to whether significantly higher levels of CPAH removal could be achieved with this site matrix.

*3. **U.S. EPA Comment:** Mass balance. There appears to have been significant problems with the accuracy of the mass balance. Concerns about protocol (e.g., the need for more replicate analyses) were discounted. In retrospect, this appears to have compromised the quality of the data, and makes it necessary to address it in a qualitative fashion instead of quantitative. This does not reflect well on the technical expertise of the IT Corporation, WESTON's subcontractor.*

Response: The mass balance will be discussed in response to item C.4.

*4. **U.S. EPA Comment:** Clarifications. The following subjects require further discussion and clarification:*

a. Preferred mode of operation (semi-continuous versus semi-batch versus batch).

b. Practical reductions in PAH/CPAH that can be expected from bioslurry treatment.

c. Feed material characteristics and effects on treatability.

d. Page 17 includes the statement that "the inability of the bioslurry system to treat the fines makes additional development of soil washing to support bioslurry treatment unwarranted." Is this conclusion saying that the -28 mesh/+200 mesh fines are not amenable to either soil washing or bioslurry treatment?

Response:

a. Based on the data from this test, the preferred mode of operation would be batch. The use of continuous flow operation was based on several factors, including:

- The goal of maintaining an acclimated microbial population in the reactor.
- The goal of minimizing the potential effects of toxic shocks which could hypothetically result from changes in feed characteristics across the site or the accumulation of inhibitory metabolites.

(Note that the use of recycle was also intended to help maintain an acclimated population.) Even if batch operation were used, a form of recycle or reseeding would likely be used to provide a suitable, acclimated microbial population.

b. Based upon the results of bioslurry treatability testing, the practical reduction in PAH/CPAH that could be expected is similar to the reduction demonstrated by the data (i.e., final PAH/CPAH levels of approximately 320 mg/kg for PAHs and 180 mg/kg for CPAHs). The achievable treatment may be determined by contaminant desorption from soils, solubilization, and the residual bioavailability of the contaminant. If so, the final residual PAH/CPAH level following treatment may be relatively constant regardless of initial (influent) concentration, so that the use of constant "percent reduction" as a definition would be misleading. It must be noted that the final (week 6) CPAH levels in both the initial and final batch studies were quite similar (150 to 210 mg/kg), even though initial CPAH levels were different (averaging 460 mg/kg for the initial batch study and 210 mg/kg as a single value for the final batch study). The average CPAH level in the treated soil from the reactor study prior to the upset (1 February 1993 to 11 February 1993) was 175 mg/kg from an influent level of 267 mg/kg.

c. This test program did not experimentally evaluate the effect of feed material characteristics on achievable CPAH levels. Feed material characteristics for the bioslurry test were defined based upon the equipment manufacturer's recommendations regarding slurry properties. Based upon these recommendations, it is presumed that substantial deviations from the defined characteristics may reduce the effectiveness of reactor operation (in terms of mixing, homogeneity, and similar characteristics). Therefore, these deviations may also reduce the effectiveness of treatment.

Assuming that the sorption of the contaminant to soils will vary among different soil fractions, it is also possible that pretreatment size separation may affect product CPAH levels. For example, soil washing at a 200 mesh size separation would be expected to result in a feed to the reactor which is enriched in CPAH since the contaminants theoretically partition to the fine clay portion (see response to Comment B.2 for a discussion of actual data). The strong sorption of the contaminant to this fraction may also interfere with its bioavailability for treatment purposes.

d. The intent of the previous response to comments was to assert that under the current cleanup criterion, additional testing would not be productive since it is not likely that treatment of the fines from soil washing (<u>presumably</u> enriched in CPAH) would meet that criterion. Furthermore, if the coarse -28 mesh/+200 mesh material also does not meet the cleanup criterion, additional treatment or alternate redisposal would be required, rendering the soil size separation unuseful and uneconomical, other than for modifying size distribution for slurry feed purposes.

B. GENERAL COMMENTS ON RESPONSES

1. U.S. EPA Comment: *General Comment No. 2, regarding removal rates. The response states that "the PAH/CPAH removal in this study was a few percent below that reported in those literature sources." This requires clarification with regard to stages of the tests. This statement is valid for the bottle studies, but it is not valid for the latter stage of pilot-scale reactor operation, when contaminant biodegradation essentially ceased.*

Also, the report should address the impact of initial concentration on the treatment of efficiency. Our review of other projects involving bioremediation of creosote-contaminated soils suggests that lower percent reductions in PAH and CPAH concentrations can be expected for soils having lower initial concentrations. The significance of this in terms of attaining revised treatment goals needs to be addressed.

Response: It is agreed that the comment regarding percent removal of CPAH/PAH achieved applies only to the initial batch (bottle) study and possibly the early phase of continuous flow testing in the reactor. This, of course, means that the best performance achieved in this test is still a few percent below those of other studies.

The comment regarding lower CPAH removal for lower influent concentrations has several implications:

- That treatment is limited by desorption of the contaminant from the soils. Therefore, in the absence of the research-level solubility enhancements, treatment (noted previously) will essentially "bottom out" at some residual level, regardless of where the initial concentration. As noted previously, both initial and final batch studies exhibited similar final CPAH levels, although initial concentrations differed.

- That treatment is limited by the availability of other co-metabolites or enzyme inducers (such as the other simple PAHs). Once they are depleted, little further treatment of complex PAHs occurs. However, final data from the batch studies indicate slightly higher final total PAH levels in the final batch study than in the initial study (390 mg/kg versus an average of 320 mg/kg). This difference, however, is within the range of analytical variability.

- Either of the above possibilities also implies that a simple first order kinetic rate calculation, which is most often used, is not only simplistic but may be misleading.

Most immediately, the reviewer's comment reinforces the fact that it may not be valid to assume a constant percent removal regardless of initial PAH/CPAH concentration. Consequently, it should not be presumed that the existing treatment standard could be achieved under the tested conditions, even if lower feed soil PAH/CPAH concentrations are finally determined to apply.

2. U.S. EPA Comment: *General Comment No. 3, regarding integration of technologies.* *The comment states that the fines fraction would have a higher contaminant concentration than the original soil. We agree that this should be the case, but the data in the soil washing treatability study does not support this, as illustrated in the following data summary.*

Soil Washing Results for BRG-TS02 (Attrition with Water)		
Sample	*Total PAH (mg/kg)*	*CPAH (mg/kg)*
Initial	*197*	*66*
Treated Coarse Fraction	*<86.3*	*<23.3*
Treated Fines Fraction	*<151.3*	*<23.3*
Source: Table 3-3, 14, and 15; 9/29/93 Soil Washing Treatability Study Memorandum.		

However, if the wash water is combined with the fines fraction, there may still be an enrichment with respect to the contaminant concentrations in the feed to the slurry reactor. One would expect good removal of the aqueous phase contaminants, resulting from increased bioavailability compared to the soil phase.

Response: Refer to Figure 2-4 and Table 11 in the Soil Washing Treatability Study Technical Memorandum. The bulk feed sample for the optimized soil washing study was initially split into two portions. One portion, designated 2AS1PB, was used for sieve analysis/CPAH distribution as reported in Table 12, and exhibited a CPAH level of <34.3 mg/kg. The other portion, designated 2AS15PB, was subjected to the optimized soil washing and flotation test. Comparison of the fines product fractions from these tests (represented by samples 2AS16PB, 2AS20PB, and 2AS24PB [Table 14]) to the feed for these tests (2AS15PB) substantiates the statement regarding enrichment as technically accurate. A similar observation could be drawn for total PAH data. However, the slight degree of the apparent enrichment, combined with the variation in PAH/CPAH levels between the initial split samples, reduces the impact of this assertion. It is agreed that the extent of enrichment, if occurring, was slight.

RESPONSE TO COMMENTS ON THE TECHNICAL MEMORANDUM PREDESIGN TASK 16 - TREATABILITY STUDY OF BIOSLURRY AND SOIL WASHING TREATMENT TECHNOLOGY U.S. EPA COMMENT SET NO. 2 - DATED 10 FEBRUARY 1994 (Continued)

C. SPECIFIC COMMENTS ON BIOSLURRY TREATABILITY STUDY RESPONSES

1. U.S. EPA Comment No. 1, Soil Characterization. If soil washing and slurry bioremediation are to be evaluated accurately, subsequent nature and extent investigations should include assessment of the distribution and variability in soil/sediment conditions across the site and the impact of those varying conditions on the efficacy of the technologies.

In the second paragraph of the response, a general criterion for soil washing is discussed. It appears that WESTON and KMCC continue to view soil washing and slurry bioremediation as separate remedies, rather than two technologies that would be used in an integrated fashion.

Response: It is agreed that additional information regarding the distribution and variability in soil/sediment conditions is required in order to properly pursue these or other treatment technologies. Additional data should include not only contaminant levels and distribution, but also geotechnical information regarding soil characteristics and data which may relate to the partitioning and sorption of contaminants to soils (such as particle size distribution and measures of organic carbon).

As discussed in response to these and previous comments, there are two sets of criteria under which soil washing or related approaches could be used at this site:

- As a direct treatment technology for contaminated soils. In this case, maximum recovery of clean material and minimal production of products requiring further treatment would be the goal. Under this scenario, washing to the 200 mesh criterion would likely be targeted.

- As pretreatment to provide the soil particle size reduction/distribution specified for downstream treatment process(es). Depending upon the requirements of the downstream process, this could be as simple as screening and may or may not involve a true "soil washing" step. For comparison, the soil preparation step used by Lewis et al. (previously noted) in EIMCO Biolift reactors included wet milling in a ball mill because the bioreactors at that time could not keep heavy sands in suspension (improvements in the reactor design were subsequently made by EIMCO). For the bioslurry process tested in this project, the recommended feed material was <28 mesh (see Appendix C of Technical Memorandum). It should also be recognized that the oversize material from whatever preprocessing is specified for this purpose must also meet the cleanup criterion. Otherwise, another (additional) treatment process would be required for the oversize material.

The results from the soil washing treatability test indicate that soil washing at a 200 mesh separation will not result in a "clean" fines fraction meeting the 6.1 mg/kg CPAH treatment standard. Additional "soil washing" testing to address the second of the above scenarios should be considered only in conjunction with the definition of feed requirements for the subsequent treatment process (if differing from bioslurry).

2. U.S. EPA Comment No. 2, Slurry Treatment Terminology. The response is adequate, assuming the report will be revised accordingly. In the true batch operations (the bottle studies and the initial charge of the reactor), significant contaminant biodegradation was evidently occurring. In the extended treatment of the 4/1 reactor contents, there was not clear evidence of any contaminant biodegradation. This is the reason we suggested using terminology that would reflect the differences in these treatment modes.

Response: It is agreed that, based upon the data presented in the Bioslurry Treatability Study Technical Memorandum, both the bottle study, which represented true batch operation, and the initial phase of the reactor study, which began with a batch charge of contaminated soil followed by daily feeding, exhibited contaminant removal. By contrast, the latter phase of the reactor study exhibited little or no apparent contaminant removal. As previously discussed, the reason for the onset and persistence of the poor performance in the reactor study is not known, particularly in light of continued positive evidence of biological activity. Furthermore, conditions in the reactor at the onset of the "extended operating phase", in terms of PAH levels and operating parameters, were similar to those in the batch study.

3. U.S. EPA Comment No. 3, Influent and Effluent Concentrations. Qualitatively discussing the observing trends in the reported $(C_i - C_e)C_i$ data would be an improvement over the current data presentation. However, there would be greater benefit in providing valid, quantitative rate data. Given the lack of steady-state condition, it appears most appropriate to generate quantitative rate data using the "organic loss" values in the mass balance (see discussion below).

Response: For the period 2/1/93 to 2/11/93 (prior to the beginning of the upset condition), the calculation of $(C_i - C_e)/Ci$ results in a calculated total PAH concentration reduction of 70%, using average influent and effluent PAH levels of 923 mg/kg and 275 mg/kg. At an average daily soil slurry feed flow rate of approximately two liters and an average total solids content in the feed and effluent of approximately 27%, the daily PAH removal rate would be approximated at 0.43 g/d. Since the relationship between active biomass and total solids is ambiguous in a slurry system, estimation of specific removal rate (gPAH/gbiomass/day) was not performed. As shown in response to Comment 4, a calculation of $(C_i - C_e)/Ci$ for the period following 2/15/93 is not appropriate.

4. <u>U.S. EPA Comment No. 4, Mass Balance</u>. The response did not directly address the most important issue raised in the comment. Increasing the negative "organic loss" values to zero in the "organic removal" column of the mass balance appears to have been inappropriate. For the period of 2/11 to 4/1, it appears that both the negative and positive values in the "organic loss" column are due to sampling/analytical variability and the use of too many significant digits in the mass balance, rather than contaminant biodegradation. Increasing the negative values to zero in the "organic removal" column, and then using the "organic removal" values in data interpretation appears to have resulted in an overestimation of the true degree of contaminant removal that was occurring. For the period 2/11 to 4/1, correct use of the mass balance data (use of the "organic loss" values) indicates there was no contaminant biodegradation attained in the reactor after 2/11.

If the above interpretation is correct, as we believe, it is misleading to characterize this as a "decline in performance." A termination of any further contaminant biodegradation in the reactor, compared to the significant contaminant removal that occurred in the true batch studies, suggests there were fundamental problems with the slurry biotreatment test approach.

Response: In order to respond to the reviewer's comment, a new mass balance approximation was constructed by WESTON for the period 2/15/93 through 3/29/93. This mass balance was constructed from PAH data in Tables 4-15 through 4-16 and from the flow, volume, and solids data in Appendix I. No attempt was made to alter the original mass balance spreadsheet calculations. Rather, a new balance was prepared based on data in the spreadsheets. This approximation estimated the total PAH mass into the reactor from the reactor feed streams, total PAH mass out of the reactor in the effluent, and the net accumulation of PAH in the reactor. The PAH mass in the recycle stream was also estimated. Sampling losses were neglected. Average influent PAH data were used for this balance. The rate of increase in reactor and recycle PAH concentrations was approximated as a linear event (regression coefficients, r = 0.96 and 0.98 for reactor and recycle PAH levels, respectively). The total reactor PAH mass accumulation was estimated from this rate of increase. This rate of increase was used to estimate the daily PAH concentrations in the effluent and recycle streams, and the individual estimated daily values were summed to estimate the total PAH accumulation for this period.

Based upon these approximations, the net PAH input to the reactor during this period was estimated at approximately 32 g from the feed. The net PAH mass removed in the effluent mass was estimated at 15.8 g. The net accumulation within the reactor was approximately 11.6 g. Neglecting CPAH losses in samples (approximated at less than 2 g), and considering the relative insensitivity of this mass balance procedure, this balance (27.4 g vs. 32 g feed) suggests minimal PAH biodegradation during this period.

This calculation is in agreement with the previously-acknowledged apparent failure in reactor CPAH performance, but does not establish the cause for that failure. Beyond the possibility of toxic or inhibitory effects in the reactor (which were investigated to the extent possible through additional chemical analyses during operation), the possibility of a form of reactor washout might be considered. Basically, for aqueous phase biological reactions, reactor washout occurs when the reactor net growth rate (established by influent and recycle rates for a given reactor volume) exceeds the maximum specific growth rate of the microbial population responsible for biodegradation (strictly true for aqueous phase reactions). Complete reactor washout would imply the complete loss of viable biomass from the bioreactor. The operational response to impending washout would be to attempt to reduce growth rate (increase mean cell residence time) by decreasing the feed rate (or increasing recycle).

While suitable kinetic data for microbial growth on mixed PAHs in soils may not be available to adequately predict washout, the residence time established for this study was selected as a conservative estimate. Based upon the available biological activity indicators, complete biomass washout did not appear to have occurred. Despite this, as well as the complete cessation of reactor feed and the demonstrated presence of biodegradable PAH constituents, no recovery of reactor PAH performance was observed.

5. U.S. EPA Comment No. 5, Contaminant Removal During Extended Treatment. If there was no credible evidence of further contaminant biodegradation in the reactor after 4/1, this should be explicitly stated.

Response: It is acknowledged that the reactor operating data for the period after 4/1/94 do not substantiate continued contaminant removal. This failure is a source of concern relative to full-scale implementation of this technology, even in light of the more successful performance in the original batch test.

6. U.S. EPA Comment No. 6, Oxygen Uptake Rate. We did not mean to suggest the oxygen uptake rate data should be used for quantitative predictive purposes. Rather, we intended to suggest that evaluation of the factors identified could potentially provide insight into the discrepancy between the mass balance data (which suggested no contaminant biodegradation after 2/11) and the oxygen uptake data (which correlated to a significant rate of potential contaminant biodegradation).

Response: It is agreed that the apparent oxygen uptake rates cannot be attributed to removal of PAH constituents during the period following 2/11/94. We feel that the level of oxygen uptake may not be fully attributable to PAH removal even during periods when PAH removal was occurring, nor would it be expected to, in the presence of other organics as indicated by the high TOC:PAH ratio. At the same time, the TOC data from the batch study and the reactor study may not fully account for the reported oxygen uptake rates. The other mechanisms postulated by the reviewer, while valid and undoubtedly contributing to the observed oxygen uptake, are not likely to be of sufficient magnitude to account for the observed oxygen uptake rates.

7. U.S. EPA Comment No. 7, Discussion of Reactor Performance. We believe it is somewhat misleading to characterize the slurry reactor effectiveness after 2/11 as a "decline in performance." One of the most significant findings of the test is the essentially complete shutdown of contaminant biodegradation in the pilot reactor with the semi-continuous mode of operation. This finding should be made evident in the report.

Response: Acknowledged, see response to Comment 5 above.

8. U.S. EPA Comment No. 8, Attainment of Treatability Study Objectives. Including the information presented in the response would improve Section 4.1.3. It appears that an important finding, that should be highlighted in this section, is the essentially complete shutdown of contaminant biodegradation in the reactor with the semi-continuous mode of operation.

Response: Acknowledged, see response to Comment 5 above.

9. U.S. EPA Comment No. 9, Last 6 Weeks of Continuous Flow Operations. This issue is covered in previous comments.

Response: Acknowledged.

10. U.S. EPA Comment No. 10, Alternative Selection. The response is adequate, assuming the report will also be corrected.

Response: Acknowledged.

11. U.S. EPA Comment No. 11, Recommendation on Enhanced Methods. If slurry biotreatment is to be considered further, recommendations are clearly in order. For example, one potential recommendation would be to avoid use of the semi-continuous mode of operation.

Response: As discussed in the response to previous comments, the data from this study indicate that bioslurry treatment may achieve reduction in CPAH levels to approximately 170 mg/kg. While the use of chemical and/or microbial enhancements may improve performance to some extent, it is not considered likely that in the near term such enhancements will result in attainment of the treatment standard of 6.1 mg/kg CPAH. Furthermore, the problems encountered in the latter phase of the bioreactor study, for which the cause could not be determined, must be considered. Based upon these conclusions and other data and observations, if bioslurry treatment is to be pursued further:

- Additional site characterization should be conducted. This characterization should include the contaminants of concern, other constituents (contaminants or otherwise) which may inhibit biological activity, and physical/chemical soil properties which may affect biological treatability.

- Based upon the results of additional site characterization and the results of this bioslurry treatability study, a revised design basis for bioslurry treatment should be established to include soil/sediment volume and characteristics, typical CPAH loading, and CPAH treatment goal.

- An updated evaluation should be made as to the status of bioslurry methods following the site characterization phase. This evaluation should include all proven reactor operating modes and the feasibility, performance, and practicality of any chemical/biological enhancements. This evaluation should also consider whether other biological treatment methods may be preferable to bioslurry treatment.

- Additional bioslurry testing should then be considered only in light of the above findings and, if appropriate, testing should be implemented within the above context regarding operating conditions and treatment standards.

Additional site characterization may also substantiate that CPAH levels in a large volume of site soils and sediments are at or below risk- or performance-based treatment standards. This finding may preclude the need for additional evaluation of bioslurry and soil washing technologies.

Additional recommendations drawn from this study which may influence future work include the following:

- At present, it seems that the preferred mode of reactor operation is batch, rather than continuous or semicontinuous. This recommendation is based upon the failure of the semicontinuous reactor during the latter operating phase. As discussed in response to these comments, the reasons for this failure are not known. It must also be recognized that the advantage of and need for microbial acclimation indicates that even in batch mode, some means of providing or returning acclimated biomass to the reactor must be considered. While this could be accomplished by operating a continuous flow feed reactor, it may prove simpler to retain within or recycle to the reactor a portion of biomass from previous treatment cycles.

- Improved methods of monitoring microbial "health" and activity are needed for future work. In this study, microbial population counts proved problematical due to spreading growth and the low sensitivity which resulted from measures taken to avoid spreading growth. The use of radiolabeled substrate appears to have given reasonably sensitive results. However, this method indicated continued capability against anthracene even during the reactor failure period and the subsequent extended operating period, when reactor anthracene levels were relatively high. As noted on Page 4-6 of the Bioslurry Treatability Study Technical Memorandum, naphthalene degraders as measured by gene probe analysis remained below the 10^4 cfu/g detection limit. Naphthalene levels were low in both the influent and effluent [reactor] throughout the study. Apparent oxygen uptake rates throughout the studies were high enough to indicate reasonably high overall biological activity (though this does not provide information on PAH capability). Areas of concern regarding these microbial activity indicators include their sensitivity and their correlation with each other and with observed performance in the reactor(s).

12. <u>U.S. EPA Comment No. 12, Screening</u>. There is still a lack of clarity on the material preparation steps. "Uniform size distribution" implies soil mixtures having the same percentage of soil particles in different size ranges. However, the description of the wet sieving procedure suggests that the objective was simply to screen out particles larger than 30 mesh. Please clarify.

Response: The intent of the wet sieving procedure during the bioslurry study was to remove the oversize material and meet the particle size recommendations of the bioslurry equipment manufacturer (summarized in Appendix C). It was not the intent of the procedure to achieve a "uniform" particle size distribution.

13. <u>U.S. EPA Comment No. 17, Oxygen Concentration and Uptake</u>. The report should include a discussion of these uncertainties.

Response: As acknowledged in previous comments and responses, apparent oxygen uptake rates throughout these studies were indicative of biological activity, even when apparent PAH/CPAH removal was low or negligible. This apparent discrepancy is of concern, since the level of oxygen consumption may not correlate directly with observed organics removal. It is acknowledged that a variety of metabolic processes other than PAH/CPAH degradation may result in oxygen consumption. These include bio-oxidation of other reduced compounds in soil and endogenous microbial activity (although the latter is likely to be relatively small).

Since influent TOC data were not taken during the reactor study, the significance of other organics removal in contributing to oxygen demand during the reactor study cannot be directly evaluated. Reactor TOC levels were somewhat lower than the initial TOC levels at 30% solids in the initial bottle study (see Table 4-1); however, these data should not be considered as directly comparable. Furthermore, TOC data through the initial batch study (Tables 4-1, 4-2, and 4-3) are equivocal with respect to the magnitude of the change in TOC during these studies. It should be recognized that the fraction of the total carbon contributed by PAH/CPAH is relatively small and therefore changes in PAH/CPAH may not be accurately reflected in TOC data.

14. U.S. EPA Comment No. 18, Anthracene Mineralization. It was not our intent to suggest that the anthracene mineralization should be used for projecting CPAH removal performance, but rather that results could be more readily compared (from test to test, project to project) if the results were presented as a rate versus a flat percentage.

Response: The available data from anthracene mineralization tests allow only a comparison of total mineralization (measured as $^{14}CO_2$ evolution) over 14 days incubation (the standard test period). While it is a significant oversimplification to use starting and ending data alone to calculate rates, the values in Table 1 represent such an approximation for purposes of this discussion.

Table 1

Sample	Average $^{14}CO_2$ Evolution (Percent)[1]	Approximate Net $^{14}CO_2$ Evolution Rate (Percent/Day)[2]
Week 3 Batch Study	13.73	0.98
Week 6 Batch Study	22.44	1.60
Final Reactor Slurry	21.20	1.52

[1] Average of multiple (5 to 6) test flasks or replicates.
[2] Total average CO_2 evolved divided by 14 days.

It is interesting, but not conclusive, to note that the data suggest that anthracene degradation capability persisted in the reactor through the end of the test, including the period when PAH levels (including anthracene) in the reactor were rising (during the apparent reactor failure).

D. SPECIFIC COMMENTS ON SOIL WASHING TREATABILITY STUDY RESPONSES

U.S. EPA Comment: *Use of bioslurry treatment has not been eliminated from consideration on this project. As stated above, it seems appropriate to further evaluate the likely performance of soil washing and bioslurry treatment, when the two are used in an integrated fashion. This further evaluation should include an assessment of the coarse fraction cleanup level that could be attained using soil washing at a 28 mesh separation point.*

Also, see discussion of specific Comment No. 1 on the bioslurry study, regarding soil characterization.

Response: The data presented in the Soil Washing Treatability Study Technical Memorandum shows that conventional soil washing at a 200 mesh separation size can reduce CPAH in the residual coarse fraction, although not to levels required to meet the current CPAH cleanup standard. Therefore, whether soil washing could be used as a primary component of a site remedy would depend upon findings of further site characterization/extent-of-contamination investigations and the final treatment standard. As discussed in response to previous comments, it is acknowledged that a soil pretreatment step (possibly but not necessarily "true" soil washing) may be required to meet feed requirements for downstream treatment processes, with the specific size distribution and processing step dependent upon the downstream unit. In such a case, the "reject" stream from the soil preparation stage must either meet the CPAH treatment standard or be reprocessed or managed by another treatment/disposal option. Available data on CPAH distribution among varying size fractions, drawn from the optimized soil washing test (see Figure 4-1), are presented in Table 12 of the Technical Memorandum. Total PAH/CPAH levels by size fraction drawn from these data are as follows.

Fraction	CPAH (mg/kg, Dry Basis)	PAH (mg/kg, Dry Basis)
Raw Head Sample	68	198
¼" x 10	103	237
10 x 50	57	134
50 x 100	75.5	179.5
100 x 200	88.7	208.7
200 x 325	84	202
325 x 0	2.05	11.55

[1] All < values used at full value for averaging.

These results suggest that all fractions except the <325 mesh filter cake exhibit CPAH levels well above the current treatment standard of 6.1 mg/kg. While no specific separation at 28 mesh was conducted in conjunction with the bioslurry test feed criterion, the results from this sieve analysis suggest that the reject from a 28 mesh soil pretreatment step may require further treatment or alternative management.

The reason for the residual CPAH levels in these fractions is not entirely known. As discussed in the Technical Memorandum, the soil sample used for these tests exhibited, in addition to a significant humic detritus fraction (also noted in the bioslurry study), a coal and a coal ash which would contribute to these PAH levels. Froth flotation had limited success in removing the coal and coal ash.

As is the case for bioslurry treatment, additional site characterization data will be important in further evaluation of the potential feasibility of soil washing at the site. In addition, since the presence of coal and coal ash in the treatability test samples may be one cause for the inability to achieve lower residual CPAH levels, it should be determined whether the presence of coal and coal ash is characteristic of site soils generally or is isolated in distribution.

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20 January 1994

Ms. Betty G. Lavis (HSRW-6J)
Project Manager
U.S. Environmental Protection Agency
Region V
77 W. Jackson Boulevard
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Re: Moss-American Site, Milwaukee, Wisconsin
Predesign Task 16 - Treatability Studies of
Bioslurry and Soil Washing Technologies

Dear Ms. Lavis:

Roy F. Weston, Inc. (WESTON®) has prepared this transmittal on behalf of Kerr-McGee Chemical Corp. (KMCC). It is presented in response to U.S. EPA and WDNR review comments provided in your letter dated 9 November 1993 and received on 22 November 1993.

The enclosure provides comment-specific responses to the technical issues raised by the reviewers. Following U.S. EPA review and concurrence with these responses, we will incorporate this information as an addendum to the previously transmitted Technical Memoranda.

As you suggested, it may be prudent to schedule a meeting to discuss these responses and the related technical comments. Please contact Gary Deigan at (708) 918-4114 when you are ready to arrange this meeting.

Very truly yours,

ROY F. WESTON, INC.

Gary Deigan

Gary J. Deigan
Principal Project Manager

Kurt S. Stimpson/SLR

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Enclosure

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U.S. EPA Comment Set No. 1
Dated 9 November 1993

and

WESTON/KMCC Technical Responses
Dated 20 January 1994

RESPONSE TO COMMENTS ON THE TECHNICAL MEMORANDUM PHASE I TREATABILITY STUDY OF BIOSLURRY TREATMENT TECHNOLOGY

I. GENERAL COMMENTS

1. **Comment:** There were a number of questions raised in the treatability study reports that were left unanswered. In most cases the reports did not attempt to resolve the questions.

   Response: WESTON and KMCC propose that the response to comments presented herein will address the questions raised by the reviewers.

2. **Comment:** The removal rates attained in the bioslurry test were less than reported by others in the literature (and in Chapter 1 of the WESTON report). This decreased efficiency should be discussed more thoroughly.

   Response: The reference to Chapter 1 of the WESTON report is unclear, but is presumed to refer to literature summarized in Section 1.3.3 of the Technical Memorandum. In that section, a range of removal efficiencies for various PAH constituents was summarized. It should be noted that this literature review was not intended to be exhaustive. The highest removal of total PAH reported in that summary is 93.4% (±3.2%) and the corresponding CPAH removal was 89.1% (Lewis, 1992). Additional literature in that section reports CPAH removal of 81.6% after two weeks and up to 89.1% after 10 weeks. All of the literature cited in that section support the concept that the majority of removal occurs in the first few weeks of operation, with minor removal thereafter.

   Other literature (not cited in the Technical Memorandum) generally supports the concept that biological treatment is most effective against the simpler PAH constituents of creosote. For example, Mueller, et al., (1, 2) reported that for creosote-contaminated soils, biodegradation of each PAH compound (except naphthalene) did not proceed after 14 days of incubation. The authors further report that lower molecular weight PAHs were more susceptible to biological attack than high molecular weight PAHs using indigenous organisms. The authors also surmise that the biodegradation of high molecular weight PAHs may occur during biodegradation of low molecular weight PAHs, which implies that once the low molecular weight PAHs are depleted, little additional treatment of high molecular weight PAHs may occur.[1]

---

[1] Reference

Mueller, J.G., S.C. Lantz, B.O. Blattmann, and P.J. Chapman, "Bench-Scale Evaluation of Alternative Biological Treatment Processes for the Remediation of Pentachlorophenol- and Creosote-Contaminated Materials: Slurry-Phase Bioremediation," Environmental Science and Technology, 25, 6, (1991).

Comparison of these results within Table 4-9 in the IT Corp. Technical Memorandum indicates that PAH/CPAH removal in this study was a few percent below that reported in those literature sources. The observed trend of removal (the bulk of removal occurring in the first few weeks with minimal removal thereafter) was entirely consistent with literature reports. It should be noted that the best removals reported in the cited literature (Lewis, 1992) were achieved under conditions beyond the scope of the Statement of Work (SOW) (including the use of bioaugmentation and surfactants) and that even if the use of such additional steps resulted in comparable removal efficiencies for the Moss-American site soils, the CPAH treatment standard would not be achieved. For example, a CPAH removal efficiency of 89.1%, starting with the initial CPAH concentration used in this study of approximately 460 mg/kg, would result in a treated soil CPAH level on the order of 50 mg/kg.

3. **Comment:** There is little discussion on how the results from each treatability test affects the other (i.e., the soil washing and bioslurry treatment) and yet these two technologies were intended to be used together.

   Response: As stated in the Statement of Work and the treatability Test Plan, the intent of Phase I testing was to test these technologies separately, then, if appropriate, combine the two in a subsequent phase(s). Based upon Phase I treatability studies, neither technology as tested will achieve the CPAH cleanup criterion. If soil washing (rather than soil screening as was employed in the bioslurry treatability study) were used prior to full-scale bioslurry treatment, the anticipated results based upon available information would generally be as follows.

   - Based upon the Phase I soil washing treatability study, soil washing at a 200 mesh size separation would result in the recovery of approximately 70% of the total soil input volume as "clean" product exhibiting a residual CPAH level on the order of 20 - 25 mg/kg (above the cleanup criterion).

   - The remaining 30% of the soil, representing the fines fraction, and having a higher PAH/CPAH level than the *original* soil would proceed to bioslurry treatment. Based upon Tables 14 and 15 in the soil washing Technical Memorandum, coarse (clean) soil CPAH levels ranged from 17 to 34 mg/kg, while fine CPAH levels ranged from 23 to 110 mg/kg. Assuming comparable total PAH/CPAH removal efficiency for these fines as was achieved for the bulk soil during bioslurry treatment, the treated fines product would likely be several times higher in CPAH concentration than the cleanup criterion.

- See Response to Comment on Soil Washing Treatability Study, page 15.

II. SPECIFIC COMMENTS

Comment: Soil Characterization. Soil properties and the physical nature of the contamination in the soil are critical in bioremediation. Discussion of these topics was limited in the report. From the information presented in Appendix A and the Soil Washing report, it appears that the soil used in the treatability studies included bark and coal. These materials, particularly coal, would impact test results if present. The description of the soils used in the study should be expanded, and should address the degree to which the soils are considered representative of other soils and sediments to be treated at the site.

Response: The importance of soil and contaminant characteristics is acknowledged. (It might be noted that since the two treatability studies were conducted simultaneously rather than sequentially, there was limited opportunity to incorporate all of the observations from one into the other.) However, the need to consider soil characteristics was recognized. As discussed in Section 3.2.2 and Appendix C, the preferred particle size distribution, based upon reactor operating characteristics, was defined through testing by the reactor manufacturer (Eimco Process Equipment Company), and their recommendations were incorporated into the test program. The soil pretreatment step removed large debris. As noted in Section 3.2.1, this screening resulted in only 42 lb. of pretreated soil for bioslurry testing from 150 lb. of soil.

The presence of coal particles within the soil matrix is expected to be a considerable factor in the final CPAH levels achieved. WESTON does recognize that the "unavailability" of residual CPAHs of low solubility may be one reason for the lower limitation on residual CPAH levels in the treated soil. During the collection of soil samples from Phase I treatability testing, coal and coal ash was found in the top two feet of soils across several areas of the site. The potential solution for this in terms of bioslurry operation would be removal (separation) of coal fines prior to bioslurry treatment, since essentially no treatment of the coal particles would be expected to occur in the bioslurry reactor. However, based upon data from the optimized soil washing test, the use of froth flotation to separate coal would not dramatically improve the situation with respect to the bioslurry reactor influent CPAH levels. Soils for treatability testing were composited from several areas of the site in an effort to produce test materials which were representative of site conditions. WESTON and KMCC believe that the soils composites utilized for the treatability studies are reasonably representative of site soil conditions at the site. Variation of soil characteristics across the site is recognized as an important factor. For example, based upon the limited particle size distribution data provided in the FS report, some of the soils on site may not be ideal candidates for soil washing based upon particle size distribution. (The general screening criterion for the successful use of soil washing is that the soil contain less than approximately 20% fines [<200 mesh]). Variations in PAH/CPAH levels across the site are also of importance. For this reason, two different soil samples were homogenized from numerous site test pits for treatability testing in order to provide a range of probable feed conditions.

For full-scale implementation, it is desirable to maintain reasonably consistent feed concentrations to the bioslurry reactor, and the importance of considering variable feed conditions across the site is a predesign phase consideration. While this issue is of concern, neither the representativeness of the test soils matrix, nor the overall impact of this issue on the feasibility of bioslurry treatment can be fully addressed until further predesign extent of contamination tasks are completed.

Comment: Slurry Treatment Terminology. Some of the terminology used in the report to describe slurry reactor operations is misleading.

- While operation of the reactor from 1/25 to 4/1 approximated continuous flow, the term "semi-continuous" is more appropriate to describe this mode of reactor operation.

- Reactor operation from 4/2 to 5/4 is described as a return to batch operation. True batch operation would include a fresh charge of the reactor. Reactor operation during this period would more appropriately be characterized as "extended treatment of the 4/1 reactor contents."

Response: The recommended changes in terminology are acceptable. It might be noted that, even at full-scale, semi-continuous rather than truly continuous operation would likely be employed. This is due to the practical difficulties in materials handling, particularly in continuous pumping of slurries at low flow rates.

While it is true that the "extended treatment period" did not begin with a fresh charge of soil, reactor conditions with respect to such factors as solids levels, overall PAH/CPAH levels, and substrate levels were similar to those which would have resulted from a fresh soil charge to the reactor.

Comment: Evaluation of Semi-Continuous Reactor Performance. The following comments on the discussion of reactor performance question the current evaluation of semi-continuous reactor performance.

Comment: ***Influent and Effluent Concentrations.*** The report's evaluation of reactor performance makes extensive use of percent removal based on the influent and effluent concentration data: $(C_i - C_e)/C_i$. In a continuous or semi-continuous mode of reactor operation, the reactor must be at steady state conditions in order for this percent removal calculation to be an appropriate quantification of contaminant biodegradation in the reactor. Steady state conditions (e.g., constant mass of reactor solids, stable reactor contaminant concentration, etc.) were never reached. Given the absence of steady state conditions, using this percent removal calculation to characterize bioreactor performance appears to be misleading.

Response: Comment accepted. It was acknowledged that steady state reactor operating conditions (solids/PAH/CPAH levels) were not achieved, for still unknown reasons and in spite of the maintenance of all controllable variables within acceptable ranges. Therefore, the reporting of average removal rates (e.g., Table 4-18) will be modified to qualitatively discuss the observed trends.

Comment: *Mass Balance.* The report indicates that a significant rate of contaminant mass removal (0.5 g PAH per day) was being achieved in the reactor during the later stages of semi-continuous reactor operation. A simple mass balance on the reactor was performed for the period 2/11 (when reactor PAH concentrations had reached a minimum) through 4/1 (when semi-continuous operation of the reactor was terminated). This mass balance indicates that there was very little or no contaminant mass removal during this period, and that the difference in the PAH concentration in influent and effluent streams was due almost completely to a build-up of PAH in the reactor solids.

While our mass balance was much simpler than the mass balance presented in Appendix I, but should be no less valid. Regarding the mass balance presented in Appendix I:

- The mass balance approach and the terms used in the spreadsheet should be explained and clarified. For example, the difference between "organic loss" and "organic removal" should be explained. It looks like the values are the same, with the exception that all the negative values in the "organic loss" column were increased to zero in the "organic removal" column. The rationale for deleting the negative values from the computation of the average rate of organic removal should be presented. This is the likely explanation for the discrepancy in the rate of contaminant removal presented in the report, and the rate calculated in the attached mass balance.

- The accuracy and precision of the mass balance data should be evaluated and described. Solids concentrations were reported at values having three significant digits. The accuracy and precision of solids sampling/analysis does not support use of three significant digits. It appears that solids data to three significant digits may have been used in the mass balance. If so, this would introduce much error into the mass balance. For example, the mass balance shows an increase in the reactor solids of 1.27 kg from 1/25 to 1/26. Based on our understanding of reactor operation, such an increase was not possible.

Response: The mass balance referred to in this comment was not provided in U.S. EPA's transmittal and therefore not reviewed by WESTON. It is acknowledged that some of the increase in PAH/CPAH concentrations in the reactor during the period 2/11 through 4/11 is likely the result of the net mass input from the feed, after the mass removed from the effluent is subtracted. The reviewer's comment that "the difference in the PAH concentration in influent and effluent (emphasis added) streams was due almost completely to a buildup of PAH in the reactor solids" is unclear, since the reactor PAH levels are themselves taken as the effluent level (for a completely mixed reactor, the reactor concentration is equal to the effluent concentration). WESTON acknowledges that the increase in reactor PAH levels results from their continued input without effective contaminant degradation.

As noted above, the agreement between this balance and that apparently prepared by the reviewer cannot be evaluated without receiving the reviewer's mass balance. The comment regarding accuracy/precision and in particular significant digits is acknowledged. While the mass balance computer spreadsheet calculated values without regard to criteria for significant figures, their accuracy can and should be considered in interpreting the results. For example, the cited anomaly of an apparent increase of 1.27 kg in reactor solids from 1/25 to 1/26 represents a change of approximately 6.7% from the previous day's value. This is likely to be within the range of normal variability given the accuracy of the respective analytical methods. While the mass balance computer spreadsheet can be re-run with the appropriate degrees of roundoff, we do not feel that the critical conclusions of the study have been erroneously drawn due to misapplication of significant figures.

Comment: ***Contaminant Removal During Extended Treatment of 4/1 Reactor Contents.*** The report presents performance data for the extended treatment of the 4/1 reactor contents. However, there is no discussion of how this data was generated. Examination of the contaminant concentration data for this period (see Figure 4-3) indicates that the sampling/analytical variability during this period was greater than any true change in the contaminant concentration in the reactor contents. The computational method for and the statistical validity of the performance data that is presented should also be presented.

Response: As indicated in response to previous comments, the discussion of removal during this phase will be limited to qualitative observations, as the calculation of average removal during this phase is inappropriate. It should be noted that the "lowest" reactor level for CPAH during this period represented an apparent reduction of 42% relative to the concentration on 4/1/93. The average removal presented in Table 4-18 is based upon the average difference between reactor levels during this period and that on 4/1/93 (which would strictly apply only if all of these data represent the "completion" of the batch removal process. Since this assumption cannot be verified, the discussion of results during this phase will be limited to the qualitative observation that the change in reactor operating mode did not result in restoring PAH/CPAH removal efficiency (which was the goal of this modification to the test program).

Comment: ***Oxygen Uptake Rate.*** The report states that the oxygen uptake rate throughout the study averaged at least approximately 4.5 mg/l-hr (page 4-7). Using the stoichiometry of contaminant biodegradation, this oxygen uptake rate may be used to compute a theoretical contaminant biodegradation rate. The theoretical rate is much higher (by nearly two orders of magnitude) than the rate of PAH removal determined in the attached mass balance. Potential causes of this discrepancy are the following:

- The method did not generate representative oxygen uptake rate data. However, the trend of decreasing pH in the reactor (page 4-2) is an indication of an ongoing oxidation process.

- The potential presence of significant concentrations of other, nonpriority pollutant organics in the reactor feed (e.g., the aliphatic in the carrier oil used in wood treatment operations). In retrospect, the absence of testing for the potential presence of nonpriority pollutants (e.g., TPH) in the feed was a fundamental flaw in the treatability test design.

- The potential presence of inorganic species that exerted a continuing oxygen demand (consider the sulfide data in Table 4-21).

- Biomass in endogenous decay.

These potential causes of the wide discrepancy between oxygen uptake and contaminant removal should be identified and evaluated.

Response: It is agreed that if the stoichiometry of degradation is known (particularly for a mixture of organics) and if assumptions are made regarding oxidation of other reduced compounds and regarding factors such as endogenous oxygen utilization, a theoretical contaminant biodegradation rate can be computed from oxygen removal data. The use of such calculations to quantitatively confirm measured PAH removal data was not intended. The rate calculations apparently made by the reviewer were not provided with the comments and therefore no specific response regarding those calculations can be made.

Relative to the reviewer's postulated causes for the apparent discrepancy, the following comments are offered:

- The method of oxygen measurements in the slurry head space (as well as in bioreactor slurries) is provided in Appendix G, with literature citations, potential interferences, and QC requirements. This method is as specified in the approved Test Plan.

- It is possible that other oxidizable substrates, including other organics as well as reduced inorganic species such as sulfide, may have exerted an oxygen demand which would be measured in this procedure. The assumed stoichiometry of each such reaction as well as the relative concentrations of each such specie would have to be considered in transferring measured O_2 uptake rates to presumed PAH/CPAH biodegradation rates. It should be recognized that O_2 uptake rates in this study were used in a manner analogous to microbial counts, as indicators of microbial activity, rather than for quantitative predictive purposes regarding PAH/CPAH removal. In addition, the presence of these other substrates in the soil would not necessarily be of any detriment unless it could be shown that their presence suppressed activity against the target constituents (i.e., by serving as a preferential substrate). If the latter did occur, this could pose a continuing problem with this technology which would have to be addressed before full-scale implementation. As to whether the lack of data on other contaminants is a fatal flaw, it is acknowledged that the sampling and analysis schedule was specified in the approved Test Plan.

- See response to second bullet.
- It is considered unlikely that endogenous metabolism (while undoubtedly occurring) would be responsible for the magnitude of the apparent effect.

Comment: ***Discussion of Reactor Performance.*** The attached mass balance suggests that very little or no PAH removal occurred after 2/11, as reactor began to approximate semi-continuous operation more than the initial batch loading and operation of the reactor. This significant and unexpected result merits discussion. Potential causes should be identified and discussed.

Response: It is acknowledged that the decline in reactor performance was unexpected. The measured increase in reactor PAH/CPAH levels was indicative of reduced biodegradative activity, particularly since the specific PAHs which increased in concentration included those compounds which had previously been removed in the process. As indicated in Table 4-15 and Figure 4-3, the majority of the increase was in noncarcinogenic PAHs. This unexpected trend was recognized as the data developed, and responsive efforts were made during the study to determine potential causes. These efforts, which were communicated to the Agency during the testing program, focused upon the following:

- Verification that reactor operating conditions and microbial activity parameters remained within normal ranges or similar to previous values.
- Analysis for potential toxicants which may have entered the reactor and inhibited biological activity. These included analyses of VOCs and halogenated organics (based upon very low levels of VOCs which were detected in a few instances during routine reactor headspace analyses) and analyses of selected heavy metals and sulfides. These data are presented in the Technical Memorandum. It should be recognized that the ability to track this problem analytically once it developed part way

through the study was limited by the availability of sample materials, particularly from earlier test phases. For example, only limited samples were available from early batch or continuous flow tests against which to compare analytical data for potential toxicants during the problematic period. However, within this limitation, the selected analytes (VOCs/metals/sulfides) were not found at levels grossly differing from those apparently present during more "successful" test phases. This data suggests that toxicity from the selected analytes was not the cause of diminished performance.

- Evaluation of whether the decrease in performance was related to the reactor operating mode. In order to address this question, the reactor was switched to the "batch" (i.e., un-fed) mode of operation, since previous batch testing at similar PAH/CPAH levels had demonstrated removal generally consistent with results reported in the literature for similar testing approaches, and no experimental or operational problems were encountered in those tests. At the time of the switch, routine reactor operating conditions were normal, and substrate (PAH/CPAH) levels, as discussed previously, were reading as high as in the feed soil. However, PAH/CPAH removal during this period continued to be negligible.

- As a further check, a second small-scale batch study (bottle study) was conducted using feed soils from the second drum of feed material. This bottle study was intended to either confirm the results of the initial batch study with regard to PAH/CPAH removal or provide evidence that the diminished performance in the reactor was a function of the characteristics of the second drum of feed material. While PAH/CPAH removal was achieved in this second batch study, the extent of removal was less than that achieved in the initial study with the first drum of feed soils.

Comment: Attainment of Treatability Study Objectives. Contrary to its title, Section 4.1.3 does not present much discussion of attainment of test objectives beyond the failure to meet the CPAH criteria.

- Regarding enhanced operation of the bioslurry reactor, it is clear that the attempt at semi-continuous treatment was no enhancement of a batch treatment approach, based on the mass balance showing no further contaminant removal after 2/11.

- Regarding determination of "optimal" set points, one could apparently conclude that reactor performance would be enhanced with batch treatment or a draw and fill mode of operation that more closely approximates batch treatment (semi-batch operation).

- There is no discussion of the objective of identifying requirements for additional physical/chemical pretreatment.

Response: As summarized in Section 3 of the Test Plan, and in Sections 2 and 4.1.3 of the Technical Memorandum, the following were the stated objectives:

Batch Bottle Study:

- Providing support data for enhanced operation of the bioslurry reactor.
- Determination of the impact of solids loading on operation.
- Calculation of preliminary substrate utilization rates.

Bioslurry Reactor Study:

- Estimation of hydraulic retention time (HRT) and BSRT set points for operation.

- Determination of the efficacy of meeting the specified treatment standard.

- Identification of requirements for additional physical/chemical pretreatment.

- Generation of performance data upon which pilot-scale design could be established.

The objectives of the batch bottle study were generally achieved. The study demonstrated PAH/CPAH removal. No significant performance differences were seen between slurry densities of 30% and 40%; solids loading for the reactor study were based upon this observation as well as recommendations from EIMCO regarding suitable slurry density for these soils. Preliminary substrate utilization rates were estimated. Test data indicated that the cleanup criterion would not be achieved even with an extended batch treatment.

While the findings observed in the bioslurry reactor study are of concern, useful information regarding the stated objectives was obtained. Continuous flow operation at long HRT/BSRT values would not provide adequate performance. Even during periods prior to the onset of the anomalous performance and in the batch testing, the data indicated that the specified treatment standard would not be met even at long retention or treatment times. Minimal soil pretreatment requirements in terms of screening, particle size, and slurry density for successful reactor operation were defined. Useful operating experience for such factors as reactor mixing, and settleability of the treated slurry was obtained. Information was also obtained on both airborne contaminant concentrations and aqueous (soluble) contaminant levels which would relate to full-scale treatment requirements for reactor off-gas and water separated from the slurry, respectively. While this information and data would be used in the development of pilot-scale design, their importance is diminished by the inability of this technology to meet the specified cleanup standard.

Other Comments. Other miscellaneous comments on the report are presented below.

Comment: Page viii. It is noted that "The last 6 weeks of continuous flow operation demonstrated increasing PAH and CPAH concentrations in the effluent stream." The reasons why this occurred were not fully explained. This raises some questions as to the validity of the data if left unanswered.

Response: See response to previous comments. The period of diminished performance is of concern. However, the early operating data, in conjunction with the initial batch operation indicate that the performance practically achievable by the tested process will not approach the cleanup standard.

Comment: Page 1-2. It is stated that alternative selection was driven by compliance with the mandated treatment criteria. This is not true, since incineration was one of the alternatives evaluated, but not selected, and could have met the cleanup criterion with more certainty than biological treatment.

Response: Comment acknowledged.

Comment: Pages 2-1 and 2-2. The recommendations suggest the possibility of testing enhanced methods, but falls short of making any real recommendation.

Response: It is questionable whether enhancements would provide the fundamental improvement in performance which would be required to achieve the specified treatment standard. While these recommendations suggest potential enhancements to the existing process, they are not considered to be within the realm of "conventional" bioslurry operation (as currently understood) to which this SOW treatability study was limited.

Comment: Page 3-2. Was the purpose of screening to achieve uniform particle size distribution, as stated in the report, or to remove the +30 mesh soil fraction? Please clarify.

Response: The intent of the screening operation was to remove oversize debris (bark, etc.) which could not enter the reactor. Wet sieving was used to achieve the desired particle size distribution for slurry operation.

Comment: Page 3-3. It is stated on several occasions that the mercuric chloride was ineffective as a biological inhibitor. But no explanation was provided.

Response: As stated and as evidenced by both biological indicators (microbial counts and O_2 uptake data) and PAH/CPAH removal, repeated additions of mercuric chloride, up to a final calculated concentration of 1,500 mg/l, were not successful in completely inhibiting biological activity. The difficulty in chemically sterilizing soils for treatability testing is recognized in U.S. EPA's Guide for Conducting Treatability Studies Under CERCLA: Aerobic Biodegradation Remedy Screening (EPA/540/2-91/013B).

Comment: Page 3-6. It is stated that "due to problems with solid separation, the equation was modified." Some elaboration is requested. Also, equation 3 appears to have been made dimensionless. Is this correct?

Response: Due to problems with effective solids separation which precluded the use of a conventional clarifier and recycle flow line, it was necessary to remove effluent in a "batch" manner, with a portion to be concentrated by centrifugation for return to the reactor. Under this mode, "wasting" of solids from the reactor was likewise accomplished on "batch" basis. As a result, the denominator of equation 2, which, in descriptive terms, represents the daily (or otherwise periodic) mass removal from the reactor, was changed from one employing waste flow *rates* to one using the daily waste *volume*. However, the discussion in the text fails to clarify that the denominator term Ve represents the <u>daily</u> sample volume (i.e., Ve = Volume of daily effluent sample, [l/d]). With this correction, equation 3 has the correct units (time).

RESPONSE TO COMMENTS ON THE TECHNICAL MEMORANDUM PHASE I TREATABILITY STUDY OF BIOSLURRY TREATMENT TECHNOLOGY (CONT.)

Comment: Page 3-6. Explain the shift in pH.

Response: A moderate decrease in pH during biological treatment is a normal event.

Comment: Page 4-2. Explain why the "nitrogen concentration was considered excessive."

Response: There was concern over potential inhibitory effects of very high ammonia concentrations if the theoretical stoichiometric requirements were added all at once to the test system. Since the ammonia "demand" for metabolic purposes would be expressed over time during the study, the decision was made to add ammonia nitrogen in several smaller doses over time, thus providing the necessary mass of nitrogen while avoiding concentration-based toxicity.

Comment: Page 4-3. How could the oxygen concentration and the uptake rate both increase? Please clarify.

Response: The apparent uncertainties in the oxygen measurements can account for this trend. Also, see response to U.S. EPA's comment on oxygen uptake rates (pages 7 and 8 of this transmittal).

Comment: Pages 4-6 and 4-7. The results of the anthracene mineralization testing would provide more insight if presented as a rate, rather than as a straight percentage.

Response: While rate calculations could be provided, their direct utility in interpreting the results is not clear. It should be recognized that anthracene, as one of the more amenable PAH constituents, may be removed more rapidly and extensively than the target CPAHs. Removal rates based on anthracene mineralization would not be suitable for projecting CPAH removal performance.

RESPONSE TO COMMENTS ON THE TECHNICAL MEMORANDUM SOIL WASHING TREATABILITY STUDY

Comment: The conclusions of the soil washing treatability report tend to focus on how well the treatment system performed in terms of reducing PAHs and CPAHs to the treatment standard of 6.1 ppm. The ability of the soil washing process to separate the "clean" from the contaminated soil was summarized in Section 3.1.3, where it is stated that the soil washing process could not produce a coarse fraction having CPAH concentrations less than the cleanup goal. Because this does not appear to have been a main focus of the report, some elaboration on this should be provided to confirm that the process tested, or a modified version, could not produce a clean fraction at any given mesh size breakpoint, especially the 28 mesh used in the bioslurry test.

A thorough description of the soils used in the study, and a discussion of the degree to which the soils are considered representative of other soils and sediments to be treated at the site, was absent. It appeared that sample BRG-TSO2 was only marginally contaminated, and may not be very representative of site soils and sediments.

INTEGRATION OF SOIL WASHING AND BIOSLURRY TREATMENT

Soil washing was described in the Soil Washing report as an "adjunct" to bioslurry treatment. However, in the soil washing treatability study, soil washing was evaluated as an alternative, rather than an adjunct, to slurry biotreatment. In retrospect, it appears that study of the two techniques in an integrated fashion may well have improved the performance of each individual technology, as well as providing greater value in terms of assessing an overall remedy for the site. This observation is based on the following considerations:

- The study indicated the "cutoff" for feed to the bioslurry is 28 mesh. Approximately two-thirds of the soil is coarser than 28 mesh (+28 mesh, corresponding to a medium sand), and would require another treatment approach.

- Soil washing is commonly viewed as an adjunct to slurry bioremediation that is used for treating the soil that is too coarse to treat in a slurry reactor. Rather than focusing on the considerable soil fraction that is +28 mesh, the soil washing treatability study examined treatment of the +200 mesh soil fraction. (The 200 mesh corresponds to the cutoff between silt and fine sand.)

- The soil washing study included an evaluation of PAH concentration as a function of grain size. This evaluation indicated that the PAH concentrations are much higher in the 100 to 325 mesh range than in the coarser soils (see Table 5 of the soil washing report).

RESPONSE TO COMMENTS ON THE TECHNICAL MEMORANDUM SOIL WASHING TREATABILITY STUDY (CONT.)

Comment (cont.):

- The 100 to 325 mesh soils are suitable for treatment in a slurry bioreactor. Eliminating the -28 mesh fraction from the soils to treated with soil washing would significantly lower the initial contaminant concentrations in the soil, as this would exclude the 100 to 325 mesh soils. Coarser soils are also generally more effectively treated with soil washing than finer soils. These considerations suggest that using soil washing to treat only the +28 mesh soils would result in a higher probability of meeting or more closely approaching the target cleanup level in the coarse fraction.

- Soil washing at a cutoff of 28 mesh would produce a fines stream for bioslurry treatment that would be enriched in PAH. In bioremediation of creosote-contaminated soil, higher percent removal is generally achieved in more highly contaminated soils. Thus, using soil washing to generate a -28 mesh bioreactor feed stream could increase initial PAH concentration and percent removal achieved in slurry biotreatment. However, no benefit with respect to lower bioreactor effluent concentrations would be anticipated.

It appears that the soil washing report contains information that addresses many of the issues described above. Discussion specific to these issues, however, would be valuable for future discussions.

Response: As stated in the predesign Statement of Work (SOW), the initial treatability studies were to include separate tests of soil washing and bioslurry treatment, and, "if both processes are successful, soil washing with bioslurry in combination..." The SOW also stated that "Testing of the processes in combination will occur (if both processes are successful in achieving the cleanup criteria), to determine the effects of interaction between the two studies." The Phase I soil washing treatability test therefore examined "conventional" soil washing, with conventional size separation criteria (approximately 200 mesh). As noted in response to comments on the bioslurry study, a common screening criterion for soils washing as a candidate treatment process is a fines fraction (<200 mesh) in the feed soil of less than 20%. The size separation used in this study was as specified in the approved Test Plan. It should also be recognized that, since the soil washing and bioslurry treatability study were conducted concurrently, there was little opportunity to incorporate the bioslurry size distribution criteria recommended in the latter test into the soils washing study.

The data presented in the Technical Memorandum illustrate that soil washing did not meet the cleanup criterion. It should also be noted that, based upon the particle size distribution data presented in the report, the tested soils exhibit a fines fraction somewhat higher than would be considered optimal for soils washing. Limited particle size data presented with the RI/FS also suggest that some of the site soils may not meet the conventional screening criterion with respect to particle size distribution. By these criteria (cleanup level and recoverable "clean" soil volume), soil washing is not considered feasible at this site.

Response (cont.):

It is, however, acknowledged that soil preparation will be necessary for any bioslurry reactor application. At a minimum, this would include removal of large debris and, possibly, particle size reduction to provide the proper slurry density/size distribution. For purposes of the Phase I bioslurry study, these preparation steps were accomplished at the treatability test facility by screening/wet sieving.

The Moss-American FS (Alternative 3A and others using bioslurry treatment) stated that prior to bioslurry treatment, "the soil would be screened to remove oversize debris" (as was accomplished in the bioslurry study), "and then washed in an attrition scrubber to try to reduce the volume of soil requiring slurry treatment." The stated goal of the attrition scrubbing step to reduce the volume requiring bioslurry treatment (which is different from pretreatment to provide an optimal bioslurry density) would be useful only if the volume removed from bioslurry treatment meets the cleanup standard. Current information indicates that it will not meet the CPAH cleanup standard when washed at a 200 mesh separation size.

Based upon discussions with Bergmann USA, it would be technically feasible to provide a soil washing system to provide a 28 mesh separation point for feed to a bioslurry reactor. However, the volumetric recovery of "clean" product would be even lower than at the 200 mesh separation size. Based upon the data on PAH distribution as a function of size fraction as presented in the Technical Memorandum, it is not certain whether the +28 mesh fraction would meet the cleanup criterion (although these data do not provide a size break at exactly 28 mesh and do not reflect the potential effectiveness of surfactant on the coarse fraction). Furthermore, as noted in the reviewer's comments, the fines fraction going to the bioslurry reactor would be enriched in PAHs and "no benefit with respect to lower bioreactor effluent concentrations would be anticipated." Consequently, while additional testing could demonstrate whether soil separation at 28 mesh for purposes of bioreactor feed would provide an acceptably "clean" coarse fraction, the inability of the bioslurry system to treat the fines makes additional development of soil washing to support bioslurry treatment unwarranted. It should also be recognized that if another treatment technology were selected to replace bioslurry treatment, feed preparation requirements would be dictated by that technology (and neither the 200 mesh nor the 28 mesh criterion may apply). In such a case, the role of soil washing in the feed preparation scheme would require a technology- or remedy-specific reevaluation.

Regarding the general comment and concern over the degree to which the tested soils are representative of other soils and sediments to be treated at the site, this concern is acknowledged, both for the bioslurry and soil washing technologies. Both variations in contaminant concentrations and soil characteristics are of importance (and, as previously noted, RI/FS data on particle size distribution indicate that at least some site soils may not meet the optimal criteria for soil washing). It was for precisely this reason that a minimum of two different soil samples were collected from the site for use in testing. It was intended to examine an "average case" and a "worst case" with respect to CPAH levels, with the presumption that upon successful results under these scenarios, performance at intermediate levels could be confirmed as necessary in subsequent phases. Please also reference the response to comments on the bioslurry treatability study soils regarding representativeness of site soil samples.