APPENDIX D

Ex Situ Biotreatment

1.0 Technology Background

Ex situ soil biotreatment involves excavation of soil, amending with water, electron donors, and/or optional nutrients, and placement in lined or unlined treatment cells. These conditions are created to stimulate anoxic biodegradation of perchlorate, chlorate, and other contaminants using indigenous microorganisms. Amendments are mixed with soil using various types of equipment such as composting machines and pug mills. Moisture content is monitored and water is added as needed to promote biological activity (Cox et al., 2000). Early evaluations of this technology simulated standard composting operations and involved mixing of soil with typical composting amendments such as wood chips, saw dust, manure, hay, and alfalfa (Cox et al., 1999; Smith et al., 2003; ITRC, 2008). Later developments involved addition of other electron donors such as calcium magnesium acetate (road deicer) along with composting materials (Smith et al., 2003). More recent developments eliminated the need for composting amendments which increase soil volume. Instead they depended on addition of electron donors, nutrients, and water alone (Geosyntec Consultants, 2006; Evans et al. 2008).

This technology is most applicable to relatively shallow and accessible contamination where soils can be excavated with reasonable effort. The limit of excavation is limited by the area available for side slope and the size of excavation equipment. There is a significant footprint requirement for containment cells and a significant amount of time (i.e., several months) may be required to reach remedial goals depending on the microbial community present, concentrations of contaminants, and temperature. Advantages include the ability to contain contaminated soils (i.e., no potential for off-site mobilization) and the low cost of implementation. In addition, the process is more easily controlled and monitored because it is an ex situ process. Several bench-, pilot- and full-scale studies have demonstrated the utility of the technology for treatment of perchlorate, and it has gained regulatory acceptance. Some example sites where full-scale implementation of ex situ bioremediation has been conducted are Aerojet in Sacramento, California; McGreggor Naval Industrial Reserve Plant in McGregor, Texas; Longhorn Army Ammunition Plant at Karnack, Texas; the former Bermite site in Santa Clarita, California; and the Olin/Standard Fusee site in Morgan Hill, California.

2.0 Technology Implementability

Appendix D to Vadose Zone Remediation Technology Screening Study Tronox LLC, Henderson, Nevada The primary application for ex situ bioremediation is treatment of contaminants in the shallow vadose zone soil; other technologies should be evaluated for deeper contamination. Relatively flat topography is required for excavation, staging, and treatment cells. The excavated soils are transported to a staging area where soils are screened, crushed (if necessary), amended, and mixed prior to placement in treatment cells. The placement of the staging area should be designed to limit transportation time. An area with relatively flat topography that can remain undisturbed for several months is required for the treatment cells. The amended soil can be placed into Ag Bags[™] or concrete containment cells underlain by asphaltic concrete and covered with tarp. Ag Bags[™] are typically 8 to 10-feet in diameter and may be up to several hundred feet long, depending on design requirements. Containment cells are constructed using stacking concrete construction blocks. Treated soils may be backfilled on-site.

Prior to full-scale implementation of the remedy, a laboratory bench-scale study is recommended to optimize the moisture content, nutrient requirements, degradation rates, and amendment type and loading for the treatment cells. Pilot testing can be conducted but is not necessary.

3.0 Technology Performance

At the McGregor Naval Industrial Reserve Plant in McGregor, Texas approximately 1,500 cubic yards of perchlorate contaminated soils were excavated, treated with amendment (citric acid, nitrogen, phosphorous, and soda ash as a buffer), and placed in a lined treatment cell . Perchlorate was reduced form an average of 500 mg/kg to concentrations below the detection limit of 0.1 mg/kg (ITRC, 2008).

Laboratory treatability tests and pilot-scale testing was conducted at the Longhorn Army Ammunition Plant in Karnack, Texas, Poultry manure, cow manure, horse manure, cotton waste, methanol, and ethanol were tested in the lab and ethanol, horse manure, and chicken manure were recommended for pilot testing. The pilot tests were conducted on six 18- by 18-foot cells using plastic liners. Perchlorate concentrations were reduced from 400 mg/kg to below detection limits in 10 months (ITRC, 2008).

The Olin/Standard Fusee site in Morgan Hill, California used ex situ bioremediation for treatment of 1,000 cubic yards of surficial soil (GeoSyntec, 2006). A pilot biocell test was conducted on approximately 100 cubic yards of soil and amendments including calcium magnesium acetate (CMA), active composting soil, saw dust (as a bulking agent), and hay (Smith et al., 2001). Perchlorate concentrations were reduced from 40

mg/kg in the amended soils to undetectable levels within 9 to 12 months. Soils were excavated and then treated with a total of 2,200 pounds of CMA and 1,000 pounds of citric acid; perchlorate concentrations were on average 7,000 μ g/kg in the mixed pile. The soils were deposited into a bioremediation treatment cell that had dimensions of 90 feet wide by 90 feet long and 4 feet high. Perchlorate concentrations were reduced to below the remediation goal of 50 μ g/kg (to 12 μ g/kg on average) within 9 months.

In a pilot study at the Aerojet site, perchlorate-contaminated soils were mixed with carbon amendments and water, placed in a 7-foot wide by 5-foot high compost pile, and then covered with tarp. Perchlorate levels decreased from an initial concentration of 23 mg/kg to below the reporting limit of 0.1 mg/kg within 7 days (Cox et al., 2000).

Full-scale implementation of ex situ bioremediation was conducted at the former Bermite site north of Los Angeles, California and is described further under the case study below (CDM, 2009; Evans et al., 2008).

4.0 Case Study

Bench- and pilot-scale studies and full-scale implementation was conducted at the former Bermite site in Santa Clarita, California (CDM, 2009). Microcosm studies were conducted to evaluate different electron donors including high-fructose corn syrup, molasses, glycerin, acetic acid, and isopropanol. High-fructose corn syrup, glycerin, and isopropanol had the greatest reduction of perchlorate. High-fructose corn syrup was eliminated for full-scale use because it is perishable and isopropanol was eliminated due to permit requirements for flammable liquids and its classification by the California South Coast Air Quality Management District as a volatile organic compound. Glycerin was chosen for full scale implementation because of its stability, safety, low cost (\$0.585/lb for 99.5 percent solution in May 2006) and regulatory acceptance. However, the glycerin needed to be diluted to 90% by volume with water to decrease viscosity for application. Additional bench-scale microcosm studies were conducted where the amount and type of amendment (glycerin at 0, 500, and 1,000 mg/kg), nutrient additions (e.g., diammonium phosphate [DAP] at 0, 50, and 100 mg-N/kg), incubation time (0, 1, 2, and 4 weeks) and moisture content (10, 13, and 15 percent) were tested on soils with 5 mg/kg of perchlorate. Findings from the study indicated that perchlorate was reduced to below detection limits within four weeks when the moisture content was greater than 10 percent for all electron donors. While nutrients may provide favorable growing conditions for microorganisms, their addition should be tested to address site-specific requirements.

Appendix D to Vadose Zone Remediation Technology Screening Study Tronox LLC, Henderson, Nevada



Full-scale operation involved soil excavation followed by, screening, rock crushing (approximately 15 percent of soil required crushing), mixing screened soil and crushed rocks with water and amendments in the pug mill, placement in the treatment cells, incubation to promote biodegradation, drying, and backfilling. Water (15 to 17 percent moisture) glycerin (500 mg/kg), and DAP (50 mg-N/kg) were used as amendments to the soil using a custom automatic metering system to continuously measure the rate of soil and amendments conveyed to the pug mill. After soils were mixed in the pug mill, amended soils were placed into either an Ag BagTM or a concrete treatment cell covered with plastic. The Ag BagTM was approximately 10-feet in diameter and 200 feet long, storing approximately 375 cubic yards (500 tons) of soil. The concrete treatment cells were made of interlocking concrete blocks that were each 25 feet wide, 115 feet long, and 5 feet high and underlain by asphaltic concrete.

Perchlorate concentrations ranged from 471 to $10,000 \,\mu g/kg$ in the first set of treatment cells. In these cells, water and glycerin but not DAP were added as an amendment as noted above. Perchlorate removal ranged from 100 to 26 percent with an average concentration reduction of 78 percent following an incubation period of up to 65 days. Incomplete degradation was attributed to being limited by low total Kjeldahl nitrogen (TKN) in the soils at the Bermite site (Evans et al., 2008). DAP was subsequently added to the amendment at a rate of 50 mg-N/kg, which resulted in consistent and complete perchlorate removal within approximately two to four weeks of incubation. The rate of perchlorate destruction in full-scale operations was about 200 μ g/kg/day. The total amount of soil successfully treated was over 500,000 tons in Operable Unit 1 which led to OU1 closure. Continued operation is planned for remaining OU2 through OU6. A key finding from this study was that moisture content and nutrients were important for performance enhancement. However, at the Aerojet site in Azusa, California, DAP was shown to inhibit perchlorate destruction due to nitrification of DAP to nitrate (Amec Geomatrix, 2009). This finding highlights the variability of site-specific conditions in designing amendment type and application rate for bioremediation. A treatability study is recommended to optimize performance for full-scale operations.

5.0 Regulatory Acceptance

Ex situ bioremediation has been established in full-scale operations at multiple sites. The California Regional Water Quality Control Board and the California Department of Toxic



Substance Control have accepted this technology to meet remediation goals at multiple sites in California (e.g., Olin/Standard Fusee, former Bermite, and Aerojet sites).

6.0 Costs

The primary cost drivers for ex situ bioremediation are construction-related (excavation and backfill), infrastructure for mixing the amendment (a pug mill), and installation of the treatment cells (either Ag Bags or concrete treatment cells). These factors will be largely variable from site to site. Estimated costs for the former Bermite site activities were \$35 per ton (approximately \$26 per cubic yard; Evans et al., 2008). The distribution of costs were 44 percent associated with bioremediation, 20 percent oversight, 11 percent excavation, 10 percent backfill, 9 percent removing and drying, and 6 percent crushing. Later optimization reduced costs to about \$20 per ton.

7.0 References

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