J4 – 30-Day Post Treatment Results Technical Memorandum



An Environmental Construction Company

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Mr. Greg Wallace, R.G. Arrowhead Contracting, Inc. 10981 Eicher Drive Lenexa, Kansas 66219 Tel: (913) 814 9994 Fax: (913) 814 9997

RE: 30-Day Post Treatment Results and Discussion

Pre-Treatment In-Situ Chemical Oxidation (ISCO) Injection Project

Lawrence Aviation Industries Superfund Site

Port Jefferson, New York

Dear Mr. Wallace:

As a follow up to the August 13, 2010 letter from **Panther Technologies, Inc.** (**Panther**) to Arrowhead Contracting, Inc. (Arrowhead), we are providing this letter to summarize the results of the 30-Day Post Treatment sampling event and associated project details. We are providing the below information that details the conditions encountered at the site, injection related monitoring and observations and how those observations may tie to the results of the 30-Day Post Treatment sampling event. At this time and as shown on Table 1 attached, the results of the 30-Day Post Treatment sampling event do not meet the less than 50% greater than a 100-ug/l average for the five (5) source area monitoring wells (MW-ISCO-01,-02,-03,-04 and -05). Included herein is a discussion of the in-situ chemical oxidation (ISCO) program including a summary of the Bench and Pilot testing activities conducted, and the sequence and observations noted during Full-Scale injection activities that led to the completion of the ISCO program at the LAI site, as well as discussions as to why we believe the results being seen are present.

Full-Scale ISCO Program Summary

During injection activities within the source area adjacent to Buildings G and Building 10, **Panther** injected a total of 72,800-lbs of potassium permanganate as a 1.5% solution, or approximately 610,000 gallons of oxidant solution. Of the original treatment zone within the Contract Specifications, this represents more than 67% of the pore volume of the ISCO Treatment Area (120 x 168 x 20' thick) and double what both the Treatability Study and Pilot Study indicated was necessary to fully treat the area of interest with residual permanganate remaining following NOD and CVOC consumption. The source treatment was designed with a substantial injection array onsite that under relatively homogenous conditions should provide complete and extensive coverage and influence over the source area during injections. **Panther** has used this same method of ISCO program design at dozens of other sites with source areas greater than 5-acres that yielded very successful injection programs.

ISCO Injection Program Development

Over the duration of the project, **Panther** followed a stepwise approach to designing the ISCO injection program that built upon known fundamental design criteria, with each progressive step providing the necessary design criteria to scale-up to the next phase. The three phases included:

- o Bench Scale Treatability Study (TS);
- o Field Pilot Study; and
- o Full-Scale Injections.

A brief discussion of each step of the design process is included below.

Bench Scale Treatability Study

The TS setup was provided in more detail within the TS Workplan (February 2010) and the results were presented within the April 2010 Pilot Study Workplan which detailed the means and methods, and results of the TS. Selected excerpts of the TS setup and results include:

- Soil samples were collected and composited from five (5) soil borings including ISCO-SB-02, ISCO-SB-03, MW-ISCO-03, MW-ISCO-04 and MW-ISCO-05 for natural oxidant demand (NOD) testing in accordance with ASTM methods by a third party laboratory;
- An average NOD of 1.7 g/kg was reported for the composited soil samples;
- Reactors were setup using water from MW-ISCO-04, and composited soil samples from the source area and dosed at 50% and 105% of the Total Oxidant Demand (TOD);
- Reactors were allowed to react for five (5) days with intermediate samples collected for chlorinated volatile organic compound destruction kinetics;
- Within three (3) days, the reactors contained very low concentrations of CVOCs, including <1 ug/l TCE;
- Residual KMnO4 ranged from 49 192 mg/l after 3-days and 80 204 mg/l after 5-days reaction;
- Calculated TOD based upon residual KMnO4 ranging from 0.039 1.054 g/kg for the 3-day reactor vessels and -0.110 1.025 g/kg for the Day 5 reactor vessels;
- Based upon the complete destruction of CVOCs and residual permanganate in the Day 5
 reactor vessels, the Bench Scale TS indicated that the correct dosing of the vessels was
 achieved to satisfy the TOD at both the medium and high dosages and that the effective TOD
 was less than estimated during the initial ISCO design phase. Generally, a TOD of
 approximately 1 g/kg was sufficient to destroy all of the organics present with significant
 KMnO4 residual.

Field Pilot Study

Following the Bench Scale TS, **Panther** utilized the data to scale-up and implement the Field Pilot Study. Details of the Field Pilot Study design were included in the April 2010 Pilot Study Workplan and the results were detailed within the June 2010 Pilot Study Results Technical Memorandum. Following mobilization and site setup, **Panther** mixed and injected a total of 33,580 gallons of a 1.5% KMnO4 solution, which corresponded to 4,000-lbs of 100% KMnO4 (50% of calculated TOD from the TS) into IW-ISCO-05 (Figure 1 attached). During and subsequent to injections into IW-ISCO-05, **Panther** observed the following trends:

- Downgradient monitoring well MW-ISCO-01, roughly 130-feet from the Pilot Study injection well realized a 90% reduction in TCE, from 240-ug/l to 23-ug/l. Additionally, MW-ISCO-01 also noted nominal increases in potassium and manganese (both components of KMnO4) and increases in measured oxidation-reduction potentials (ORPs). All of these factors indicated that MW-ISCO-01 was directly influenced by the injection testing.
- Downgradient monitoring location IW-ISCO-06, roughly 30-feet from the injection well, also noted significant influence during injections. Concentrations of TCE decreased from 270-ug/l to 28-ug/l, or a 90% decrease from Pre to Post-Pilot analysis. Additionally, IW-ISCO-06 was directly influenced by the injections indicated by the deep purple color within the well in addition to residual permanganate concentrations as measured on the colorimeter of up to 200 mg/l. IW-ISCO- 06 also noted significant increases in ORP.
- Sidegradient monitoring well MW-ISCO-04 noted lower decreases in TCE concentrations
 with Pre to Post Pilot results indicating a lower 23% reduction, but it did note some similar
 increases to other wells under the influence of the injections. Increases in potassium, ORP
 and residual permanganate concentrations were all noted. The lower reduction is likely due
 to groundwater velocities moving downgradient are higher than cross gradient and the Pilot
 Study tested was limited in duration.
- Monitoring of the source injection well (IW-ISCO-05) noted significant shifts in geochemical
 conditions, as expected. Increases in both potassium and manganese were noted along with
 increases in ORP and residual potassium permanganate. TCE concentrations decreased
 approximately 90% from 1,000-ug/l to 100-ug/l and with a longer duration of monitoring,
 would have like decreased further based on the residual potassium permanganate within the
 well.
- The final component of monitoring at the site included hydraulic measurements via downhole dataloggers in MW-ISCO-04, MW-ISCO-05 and IW-ISCO-06. During pilot testing, hydraulic influence was noted as far as 30-feet from the injection well (MW-ISCO-04, MW-ISCO-05 and IW-ISCO-06) even with the relatively high groundwater flow velocities and short test duration.

Based on the information obtained during the Pilot Test, the scale-up from Bench Scale TS to Pilot Study was successful at the lower dosage of 50% of the TOD and that the significant downgradient migration of permanganate observed was likely to continue during full-scale injections.

Full-Scale ISCO Injections

Following the successful Pilot Test in reducing CVOCs in both source and down gradient injection and monitoring wells, **Panther** finalized the Full-Scale ISCO injection program to initially include 50% of the TOD (same as the Pilot Test), corresponding to mixing and injection of 42,500-lbs of KMnO4, or approximately 354,000 gallons of a 1.5% solution. During this initial phase of Full-Scale injections, **Panther** noted significant influence within source area monitoring wells MW-ISCO-04 and MW-ISCO-05 and significant geochemical shifts with the presence of residual

permanganate in the monitoring wells during injections, verifying the Pilot Study radius of influence data.

However, **Panther** also noted limited to no indicators present in down gradient wells MW-ISCO-01 and MW-ISCO-02, or side gradient well MW-ISCO-03, seemingly due to influence being caused by excessive and variable hydraulic conductivities and subsurface channeling. **Panther** elected to increase the mass of permanganate injected through mixing and injection of an additional 30,300-lbs of KMnO4 (additional 252,500 gallons of 1.5% solution) in an attempt to overcome these subsurface anomalies. The additional 30,300-lbs represented nearly twice the mass of KMnO4 deemed necessary during Treatability and Pilot Testing activities to complete remediation of the entire ISCO Treatment Area bringing the total volume of oxidant solution injected to 645,000 gallons of solution (Pilot Study and Full Scale). Some additional observations are included below:

- Based on the limited CVOC concentrations encountered at the site (up to 1,000 ug/l noted in IW-ISCO-05 during Pre-Pilot groundwater sampling), a very small quantity of KMnO4 (less than 1,000-pounds) is needed for complete destruction of CVOCs in groundwater, assuming no sorbed phase mass of TCE is present beneath Building 10, certainly significantly less than the difference between the KMnO4 necessary to satisfy the NOD and the amount of KMnO4 actually injected.
- Based on the Bench Scale TS result of approximately 1.0 g/kg effective NOD, only 33,485 lbs of KMnO4 was required to satisfy the NOD. Note that Carus Chemical confirmed similar but slightly higher results after soil mixing in their labs of 1.7 g/kg, which corresponded to approximately 56,930-lbs of KMnO4 was required to satisfy the NOD. After adding roughly 1,000-lbs to account for known COD, the total maximum mass of permanganate necessary was 57,930-lbs (based upon higher Carus NOD). We ultimately injected 76,000 pounds (4,000 lbs in Pilot and 72,000-lbs in Full-Scale) in the ISCO Treatment Area, or 33% more than what should have been required by the TS.
- Panther injected greater than 67% of the pore volume of the ISCO Treatment Area as 1.5% KMnO4 solution. This is dramatically higher than typical injection programs that recommend injecting <20% of the pore volume. An added concern for the LAI site based on the extremely heterogeneous nature of the site is if too much oxidant solution is injected without being able to track where it is going, then oxidant transport may migrate to either extraction wells or down gradient receptors unknowingly. Under relatively homogenous conditions and non-channel style flow regimes, we would not normally be concerned with this as downgradient NOD demands would utilize permanganate before it reached downgradient receptors. Under channel style flow regimes, this may not hold true.
- Some geochemical indicators were noted in MW-ISCO-01 during full-scale injections with no colorimetric change and short-term increases in oxidation-reduction potential (ORP), however, shortly after injections ended (within the 30-day monitoring timeframe), MW-ISCO-01 returned to its natural background conditions with lower ORP signifying significant recharge of non-oxidant laden water migrating through its screen.

- Following the completion of injections and within the 30-day monitoring timeframe, MW-ISCO-02 changed to a deep purple with very high ORPs (>500 mV). Note that MW-ISCO-01 and MW-ISCO-02 are only approximately 30-feet apart and the lack of indicators in MW-ISCO-01 and significant geochemical shifts in MW-ISCO-02 likely indicate preferential pathway exists from the source area, bypassing MW-ISCO-01 that passes through MW-ISCO-02.
- Throughout the duration of injections including groundwater mounding monitoring presented in the September 13, 2010 letter, **Panther** noted no influence in MW-ISCO-03. In fact, during the second round of injections of the additional 252,300 gallons of oxidant solution (30,300-lbs of KMnO4), **Panther** attempted to influence MW-ISCO-03 by injecting in the wells only immediately adjacent to it (IW-ISCO-03, -07, -08, -09 and -10) while extracting groundwater (e.g. 10 15 gpm) from MW-ISCO-03 in an attempt to hydraulically force permanganate migration into the MW-ISCO-03. Even under hydraulic influenced conditions, **Panther** was unsuccessful in influencing MW-ISCO-03 and could not overcome the influence of subsurface hydraulic channeling that appears prevalent throughout this area.
- The potential for channel flow and highly variable hydraulic conductivities has been noted in other areas of the site during drilling operations as evidenced by problems with boulder layers and circulation losses in the groundwater extraction and treatment system well installation, and final constructed well specific capacities ranging from approximately 6-8 gpm/foot in IW-2 to 62-67 gpm/foot in IW-3 (less than approximately 50-feet apart) for identically constructed wells. It is these highly variable and heterogeneous conditions within very short distances that we are likely the cause of the inconsistent readings within the source area during ISCO injections.
- As shown on Table 1 (attached) significant rebound was noted in MW-ISCO-04 and MW-ISCO-05 during the 30-Day Sampling Event (increase of over an order of magnitude). Based on the historical downward trend in CVOC concentrations from the Pre-Pilot Sampling Event (April 2010) through the Interim Groundwater Grab Sampling Event in (July 2010), to the trend reversal following completion of injections and possible migration of KMnO4 out of the source area, it appears that a saturated zone source area, or an area of higher dissolved phase groundwater previously unknown, is causing increasing concentrations within the source area. Without significant additional investigation and significantly more wells, the area of higher concentrations cannot be located.
- It appears that focusing on injections in areas that would influence MW-ISCO-01 and MW-ISCO-02 were successful based upon the 70 ug/l TCE concentration in MW-ISCO-01 and the ND concentration with residual permanganate in MW-ISCO-02. The concern related to residual permanganate only in MW-ISCO-02 is that a distinct channel may in fact exist near MW-ISCO-02 connected to the source area that could be a preferential pathway away from the source area.

It is **Panther**'s opinion based upon the information provided herein along with the sheer volume of permanganate injected into the source area, that significant variation in subsurface hydrologic conditions (channeling to MW-ISCO-02) and a potential saturated source beneath Building 10

(rebound source near monitoring wells MW-ISCO-04 and -05) both represent a change condition that precluded **Panther**'s ability to meet the contractual requirement for reductions in the ISCO monitoring wells. The reason reductions may not be realized have to do with not only the hydraulic limitations and associated contact time associated with getting sufficient oxidant to overcome the channeling and high conductivities present, but also the potential source of significant rebound conditions in MW-ISCO-04 and MW-ISCO-05. The limitation is not associated with the ability of KMnO4 to treat the CVOCs, as that was proven in all phases of the project and through post treatment monitoring of the source area monitoring wells. Due to the concerns related to hydraulic limitations and potential channel driven flow, **Panther** does not believe that simply continuing to pump permanganate into the ground is a viable solution since much of the oxidant mass is being lost to unknown flow channels and not affecting the monitoring wells of interest. If continued attempts to treat those areas that have rebounded are attempted, as we run the risk of residual permanganate preferentially migrating into an area that could impact the extraction wells (direct connection through channel flow) that is not acceptable give the treatment system has not been designed for oxidant neutralization, or worse oxidant could migrate to other unknown discharge locations.

Summary

While we understand that we have a limited set of empirical data from information collected during drilling and subsequent testing/ISCO injections, a full and complete hydrogeologic study of the area was not an intended component of the scope to understand or evaluate this type of significant heterogeneity. We relied on the information for groundwater flow, formation characteristics and the multi-tiered design process to guide the dynamic conditions of the ISCO program. We can certainly perform additional RI, if requested, as a component of understanding this complex flow regime to better detail the interaction and potential for channel flow, but as with all out-of-scope elements, there is a time and cost impact to running such a study and given this effort was for pre-treatment that is backed up by a pump and treat program, the cost of such a study does not seem appropriate. At a minimum, a significant number of additional injection wells would be required to even begin to determine how flow is moving about the site including wells beneath the buildings to determine oxidant transport and mass loading emanating from the building. While **Panther** is one of the most experience ISCO vendors in the country, we are not experts in the area of complex hydro-geological situations such as what the source area at LAI requires to more fully understand the data.

The specifications and specifically the log for the only well in this area, MPW-07; indicated a silty-sand matrix with a relatively low conductivity (up to 6.5 ft/day). This soil matrix and reasonable conductivity are the prime elements we utilized when designing an ISCO injection program for this area. We were not aware that there could potentially be channel flow, boulder zones or areas of significant conductivity changes (order of magnitude higher) over the screen lengths that may result in different, non-uniform distribution of oxidants. To be honest, even with our current knowledge of the site about the wide range of conductivities in this area, it may not be possible to accurately determine what is necessary to achieve complete oxidant coverage over the square footage desired. Screen intervals within existing injection wells appear to partially penetrate wide zones of varying conductivity so a complex hydrological assessment would be necessary along with modeling to even attempt to try to figure out what exactly is occurring. What we do know is that with nearly 650,000 gallons of solution injected, we still do not know where the permanganate is migrating too.

Based on all the various issues and site specific hydraulic information presented above that is completely outside of our control, **Panther** respectfully requests release from the 30-day average

concentration guarantee of not exceeding 50% of a 100-ug/l average in the five (5) source area ISCO monitoring wells since our ability to overcome the channel flow issues at the site and the rebound conditions noted in MW-ISCO-04 and MW-ISCO-05 indicate that a saturated source zone may be present and that excessively high hydraulic conductivities exist that were not anticipated. While we certainly do believe that ISCO can be a significant component of pre-treatment to reducing the final O&M timeframe of the recently installed pump and treat system, we believe that we are being impeded by natural conditions at the site that were not expected, nor are currently understood, with the assessment of such not currently a part of the scope of work for this effort.

If you have any questions or require additional information, please feel free to contact the undersigned at (609) 714-2420.

Sincerely,

PANTHER TECHNOLOGIES, INC.

Kevin D. Dyson, P.E. Project Manager

Attachments Table 1

Figure 1

Cc: Peter J. Palko, P.E., CHMM – **Panther**

Jack Twomey - Panther

Table 1. Historical VOC Concentrations is Source Area Monitoring Wells. Lawrence Aviation Superfund Site. Port Jefferson, New York.

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Well ID	Assumed Location	Pre Pilot Sampling - April 2010		Post Pilot Sampling - May 2010		Baseline Groundwater Sampling - June 2010		Interim Groundwater Grab Sampling July 2010*	Interim Groundwater Grab Sampling* (August 17, 2010)	30-Day Post Injection Groundwater Sampling Event - September 2010	
		VOC Results (ug/I)	ORP (mv)	VOC Results (ug/I)	ORP (mv)	VOC Results (ug/I)	ORP (mv)	VOC Results (ug/l)	VOC Results (ug/l)	VOC Results (ug/I)	ORP (mv)
ISCO-MW-01	Downgradient	240	91	23	162	110	186	349	173	70	201
ISCO-MW-02	Downgradient					490	161	1060	637	0	684
ISCO-MW-03	Side Gradient					460	231	407		550	123
ISCO-MW-04	Source	530	207	410	301	240	249	34.4		690	669
ISCO-MW-05	Side Gradient					82	203	63.7		200	388
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ISCO-IW-05	Injection Well	1,000	206	100	596						
ISCO-IW-06	Injection Well	270	214	28	726						

All Samples in ug/l

⁻⁻ denotes not sampled

^{* -} Interim sampling not completed per QAPP procedures

