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RE: Comments on Potential Use of ISBS or Other Permanganate–based Remediation Approaches at the Gainesville Koppers Superfund site

EPA has proposed the use of ISBS, a permanganate-based treatment approach, for the Surficial Aquifer at the Koppers site. EPA has also indicated that ISBS or ISCO, using permanganate, may be used for the Lower Hawthorne formation. These comments demonstrate that ISBS is not a suitable remedy for any portion of the aquifer beneath the Koppers site. Key reasons for this include the complete lack of peer-reviewed scientific information demonstrating that ISBS provides any meaningful or effective long term chemical stabilization of creosote, particularly under the strongly reducing conditions at the Koppers site, the long-term instability of precipitated mixed-valence manganese oxides (MnO_x) resulting from permanganate oxidation, and the dissolved manganese plumes that result from application of permanganate in reducing aquifers, as described below.

ISBS is an experimental remediation method that is incompatible with the geochemical groundwater (Eh – pH conditions) at the Koppers site. No information has been presented in any peer-reviewed scientific or engineering journals that demonstrate that ISBS is capable of providing long term, permanent treatment for creosote, particularly within the highly-reducing geochemical conditions present in groundwater at the Koppers site.

To understand why ISBS is not suitable for the Koppers site, it is necessary to understand the impermanent nature of the MnO_x precipitates that form after permanganate reacts. Numerous studies have found that MnO_x particles that form through permanganate reactions can readily dissolve and form dissolved manganese plumes. This is especially true at sites with low Eh (redox potential) and with lower pH, such as within the Gainesville Koppers site groundwater. Therefore, manganese-based coatings cannot be expected to provide permanent "encapsulation" around DNAPL at the Gainesville Koppers site.

Although the solid MnO_x product of permanganate reactions is commonly considered to be a form of MnO_2, Loomer et al. (2010a) demonstrated that the valence of Mn in the MnO_x reaction products is between Mn+2 and Mn+4. This mixed oxidation state may be partly related to the presence of adsorbed Mn+2 (Loomer, et al, 2010b).

The implications of this research are significant with regard to the long term stability of MnO_x precipitates. While it is clear that extensive additional research into the precipitation and dissolution of these mixed valence Mn oxides remains to be done, available peer-reviewed scientific research is clear about several key issues. In anaerobic systems these precipitates may readily undergo dissimilatory reductive dissolution, where the solid phase Mn+4 or Mn+3 is reduced to the soluble Mn+2 ion. (Loomer et al., 2010b). What this

means for the ISBS process is that long term stability of manganese precipitates produced by the ISBS process cannot be expected or guaranteed. Because reliable long term stability of any stabilization applied to creosote at the Koppers site is critical to reduce long term threats to groundwater, permanganate strategies are not suitable for application at the site.

Many studies on permanganate have demonstrated the geochemical instability of MnO_x precipitates created by use of permanganate and these studies have been published in many journals, including peer-reviewed scientific journals. These studies include both laboratory and tests field tests. For example:

Hrapovic et al. (2005) conducted laboratory column tests on the use of permanganate oxidation for treating TCE. Following the application of permanganate, the formation of MnO_x minerals was visibly apparent in the columns. Reducing conditions were then established in the columns to stimulate in-situ anaerobic biodegradation of the remaining TCE. After reducing conditions were established, dissolved levels of manganese of up to 1600 mg/L were measured in the column effluent. Because Mn was not being added to the influent, the only source of Mn was the precipitated MnO_x solids.

Sahl, et al. (2007) conducted similar studies in a laboratory to evaluate the effects of permaganate on microbial populations. After applying permanganate to test columns containing sand and TCE, formation of manganese dioxide minerals was visibly apparent in the columns. Sand from the columns was also analyzed to confirm the presence of these manganese precipitates. Reducing conditions were established to evaluate post-ISCO impacts to microorganisms. Over the remaining course of the test, the MnO_x minerals began to dissolve and were determined to be almost completely dissolved by the end of the test.

Westersund et al. (2006) implemented full-scale permanganate treatment to treat chlorinated solvents at a contaminated site. Subsequently, due to evidence of reducing conditions and reductive dechlorination of remaining solvents, full-scale anaerobic reductive biological treatment was implemented to treat remaining contamination. After onset of reducing conditions, dissolved manganese levels reached as high as 173 mg/L, indicating that the manganese dioxides that had been precipitated by permanganate were dissolving.

A claim has been made by the site owner that ISBS achieves complete encapsulation of DNAPL by forming a crust of aluminum silicate hydroxides around the DNAPL. The vendor has claimed that it is only these aluminum silicate hydroxides that provide the necessary encapsulation of DNAPL and that there is no reliance on MnO_x solids for achieving complete, permanent, and stable encapsulation of DNAPL using ISBS. However, not a single peer-reviewed publication has confirmed that the ISBS process creates these aluminum silicate hydroxides. Observation of the presence of these minerals at the Koppers site after completion of an ISBS pilot test is not proof that they were created by the ISBS process. In fact, no soil cores were examined prior to the ISBS pilot test at the Koppers site to demonstrate that these aluminum silicate hydroxides were absent prior to implementing ISBS. Therefore, the conclusion that these aluminum silicate hydroxides were formed by ISBS is speculation.

Further, the geochemical mechanisms and chemical basis and processes for the alleged formation of aluminum silicate hydroxides have not been scientifically explained, demonstrated, or proven. The specific type of aluminum silicate hydroxides claimed to be formed by ISBS and the long term mineral properties of these aluminum silicate hydroxides are undemonstrated. There are no peer-reviewed published data

confirming that any aluminum silicate hydroxides that can be formed by an ISBS process have the stability to last for even a few decades, and certainly not for the hundreds of years necessary to effectively stabilize creosote at the Koppers site.

The claims made by the site owner about these alleged aluminum silicate hydroxides that form using ISBS are couched with speculative, wishful, and hopeful language - "the coatings are **not expected to be affected** by changes in redox potential of the aquifer"…..therefore **considered to be** stable"…. This highly qualified, wishful language is necessary because there are no peer-reviewed publications available to support any of these claims. In fact, there are no reliable scientific data confirming that these coatings, if they are formed at all by ISBS, are stable or not affected by redox potential, dissolution, ion exchange, and other geochemical processes that can lead to failure of this remedy.

What has been observed at nearly all permanganate injection sites has been the formation of manganese oxide minerals. The available research indicates that MnO_x minerals are geochemically unstable under reducing conditions. The Eh must remain elevated for these solids to remain geochemically stable over the long term (the hundreds of years that the creosote will remain in the aquifer). Given the highly reducing conditions at the Koppers site and large amount of organic material in the aquifer, including creosote and other organic chemicals at the site that act to suppress the redox potential, there is no way to expect or guarantee that the Eh and pH at the site will remain elevated and in the range at which MnO_x solids may remain stable over the next hundred to two hundred years during which the creosote will be present at the site.

The Surficial Aquifer at the Koppers site has been found to have Eh and pH characteristic of the range in which Mn^{+2} is the stable form of manganese and under which conditions dissolution of MnO_x will be favorable. Evidence of the reducing conditions in Koppers site groundwater include:

- Elevated dissolved iron is known to be present within the Surficial Aquifer and Upper Hawthorne. Iron reduction occurs only under anaerobic conditions and occurs at a lower redox potential than manganese reduction.

- the ORP of the groundwater has been reported in many groundwater monitoring reports prepared for the site to be in the reducing range, in some cases highly negative values were reported.

- Sulfide odors, indicative of sulfidogenic conditions, have been noted during purging of groundwater monitoring wells at the site by the field teams conducting the sampling. The presence of hydrogen sulfide is a strong and reliable indicator of reducing groundwater conditions. Sulfide reduction occurs at an even lower redox potential than iron reduction and well below the redox potential of manganese reduction.

Groundwater samples collected during the ISBS pilot test indicate that pH of the shallow aquifer in many wells ranges from 4.6 to 6. A groundwater pH in this range is favorable to enhanced dissolution of MnO_x solids.

All of these observations indicate that the Eh and pH of the aquifer at the site are such that dissolution of precipitated MnO_x will be geochemically favorable and that MnO_x precipitates will not be stable over the long term.

A key cause of MnO_x dissolution under anaerobic conditions is biologically-mediated manganese reduction, which occurs when manganese is used as an electron acceptor by bacteria. It is important to note that biodegradation of naphthalene, a primary COC at the Koppers site, has been found to occur under manganese-reducing conditions (Langenhoff, et al, 1996). Thus a key biological pathway that may lead to large amounts of dissolved manganese being generated at the Kopper site after application of any permanganate technology is biological-mediate manganese reduction. Naphthalene, toluene, phenol and other chemicals present in creosote may serve as electron donors in this reaction, as they are present in site groundwater and large reservoirs of naphthalene and other chemicals will remain onsite within the creosote DNAPL. Much of the naphthalene and other organics from the creosote will be in close contact with any MnO_x solids that precipitate on the DNAPL surface. The proximity of these electron donors will increase the likelihood of manganese reduction occurring and it will likely be impossible to prevent manganese-reduction reaction from occurring in this aquifer. Because of this, the MnO_x solids that form on the creosote surface may be the most likely to begin to dissolved due to dissimilatory manganese reduction.

In addition to naphthalene, other chemicals present in creosote and in Koppers groundwater, such as toluene and phenol, have been shown to be substrates that can be used by metal-reducing bacteria to promote dissimilatory manganese reduction (Stone, 1987; Langenhoff, 1997). Therefore, reduction of MnO_x precipitates is likely to occur at the Koppers site if permanganate is used in any manner as a treatment chemical in the ground.

Based on the foregoing discussion and facts from peer-reviewed literature, the following sequence of events has a high probability of occurrence after application of ISBS or ISCO with permanganate at the Koppers site.

1. Application of a permanganate solution into the subsurface will lead to oxidation of some natural organic material, some reduced metals that may be present in the injection zone, and some, but not all, dissolved site-related organic contaminants. The Eh of the aquifer will temporarily increase in areas where permanganate can be delivered and will not increase in areas that are bypassed due to inefficient injection methods. MnO_x particulates will form close to the permanganate reaction sites. MnO_x may form a partial crust around some, but not all, DNAPL. Lithologic heterogeneities, the presence of DNAPL, and plugging of the aquifer due to MnO_x formation will prevent injected permanganate fluids from contacting all, possibly most, DNAPL in the aquifer. Aluminum silicate hydroxides may or may not form around some of the DNAPL. Some DNAPL will remain untreated. This untreated DNAPL will continue to leach naphthalene and other organic contaminants such as benzene and toluene into groundwater and the DNAPL may also continue downward vertical migration towards the Floridan aquifer.

2. Over time, reducing conditions and bacterial populations will become re-established as the permanganate reactions become exhausted. The permanganate reaction produces acidity so the pH will likely decline, as will the Eh, which will be favorable to dissolution of MnO_x.

3. Over time, manganese-reducing bacteria in close proximity to creosote and MnO_x solids will begin to reduce the MnOx. The creosote will provide a large reservoir of naphthalene, phenol, toluene, and other chemicals known to induce manganese reduction. MnO_x precipitates that are located throughout the entire ISBS treated area and in areas with dissolved organics in groundwater also will likely begin dissimilatory manganese reduction.

4. Over time, dissolved manganese concentrations in groundwater will increase, indicating failure of the ISBS remedy. As this happens, further migration of DNAPL (downward) and dissolved phase contamination may proceed, including migration of contaminants towards the City of Gainesville's Murphree potable water well field.

It may take several or many years for steps 2, 3, and 4 to occur but the scientific data overwhelmingly suggest that this scenario will likely eventually occur at the Koppers site.

For the reasons described above, it is clear that the ISBS process is a fatally flawed and unsuitable long term remedy at the Gainesville Koppers site. The only statements supporting the long term viability of ISBS are unsubstantiated claims from the site owner. No peer-reviewed scientific literature has substantiated these claims.

A long-term, permanent remedy at the site that is based on a well-documented robust technology, such as soil stabilization, is required.

The residents of Gainesville will not allow EPA to make technology selection decisions that ignore fatal flaws that are clearly indicated by scientific peer-reviewed literature, while instead relying on unsubstantiated vendor claims. We are demanding that EPA begin addressing the unproven effectiveness and technical limitations of the ISBS process in a scientific manner, rather than relying on unsubstantiated vendor claims. EPA has technical experts on ISCO processes, such as Dr. Scott Huling, in EPA's Ada, Oklahoma research laboratory, that have the technical and scientific capabilities to provide unbiased opinions about this technology. We are copying Dr. Huling on these comments to solicit his independent opinion about the technical validity of ISBS and the concerns identified herein. We will not accept as valid any responses to these comments that are generated solely by the site owner.

To provide EPA with some guidance regarding the appropriate degree of scientific validation that ISBS requires before it can be considered a long term stable and reliable remediation technology for creosote, at a minimum the following items must be scientifically demonstrated and confirmed by independent scientists:

1. The formation of crystalline aluminum silicate hydroxides that encapsulate DNAPL by application of permanganate must be clearly proven and demonstrated under scientifically-valid research conditions. The chemical conditions that are required to form these aluminum silicate hydroxides

must be clearly explained and understood. Specific factors that limit or prevent formation of aluminum silicate hydroxides under in-situ conditions must be completely understood so that it is possible to determine whether appropriate conditions for formation of these minerals can be achieved in the field. This information needs to be published in peer-reviewed scientific journals before application of this technology is considered as a permanent and reliable remedy.

2. The degree to which aluminum silicate hydroxides can encapsulate DNAPL and limitations regarding the amount of DNAPL that can be encapsulated must be precisely determined, both in the laboratory and in the field. This is essential to allow for determining appropriate chemical doses for field application. Without a detailed understand of the precise stoichiometric doses and chemicals required, at best only incomplete, if any, formation of aluminum silicate hydroxides can be expected. This information needs to be published in peer-reviewed scientific journals before application of this technology as a permanent remedy.

3. The long term permanence of any aluminum silicate hydroxides coatings must be demonstrated by long-term, controlled scientific tests. Factors and conditions that can lead to failure of these coatings must be demonstrated and methods that can be applied to ensure that these coatings do not fail in the future must be demonstrated. Without reliable knowledge that any coatings that form are stable within the wide range of geochemical conditions that may occur in the future, the suitability of this remedial technology for any site is undemonstrated and unproven. This information needs to be published in peer-reviewed scientific journals before application of this technology as a permanent remedy.

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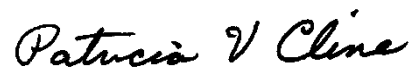
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Sincerely,

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