

**Pass & Seymour (P&S) Boyd Ave Site  
ONONDAGA COUNTY, NEW YORK**

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**WORKPLAN FOR SUPPLEMENTAL  
IN-SITU CHEMICAL OXIDATION  
BROWNFIELD CLEANUP PROGRAM**

**NYSDEC Site Number C734102**

**Prepared For:**  
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## 1.0 INTRODUCTION

The purpose of this workplan is to describe the additional injection of permanganate into groundwater at the P and S Boyd Ave site (site) located in Solvay NY. This site was remediated under the New York State Brownfield Cleanup Program (BCP) as site number C734102 and issued a certificate of completion under the BCP in December 2010. The site, which is 18.07 acres, is located at 50 Boyd Avenue, Solvay, New York. The history of use of the site and the process of site investigation and remediation of the site is fully described in the Remedial Investigation and the Final Engineering Reports completed under the BCP. During the investigation of the site it was determined that two areas of groundwater impact remained as the result of past spillage of chlorinated organic solvents. Those two areas of impact are identified as AOC-1 and AOC-2 (figure 1). In order to address these occurrences of groundwater contamination it was determined that an In Situ Chemical Oxidation (ISCO) approach would be used to treat and destroy the chlorinated organics by injecting either potassium or sodium permanganate into the saturated zone within these AOC's. Permanganate is a relatively stable oxidant that may remain viable in the subsurface for months after injection. As part of the post COC monitoring and maintenance program, groundwater sampling in the vicinity of the AOC's was conducted and reported quarterly and summarized in a Periodic Review Report completed in March 2012.

ISCO has been proven to be an effective means of destroying chlorinated organics in groundwater and as a result has been recognized by the New York State Department of Conservation (DEC) as a presumptive remedy for addressing chlorinated volatile organics (CVOC's). As a presumptive remedy it is not necessary for a remedial party to prove that ISCO is a feasible option for destroying CVOC's in groundwater.

As described further in section 2.0 of this workplan an ISCO program was carried out in 2010. Based on groundwater monitoring results it has been determined that a supplemental injection of permanganate is warranted. This workplan describes the supplemental injection that is being proposed in conformance with the approved Remedial Design Document (May 2010) and as amended and described in the approved Final Engineering Report (September 2010), both of which were completed by S and W Redevelopment of North America, LLC (SWRNA). This workplan, when approved will supplement those approved documents.

## 2.0 ISCO SYSTEM DESIGN AND IMPLEMENTATION

Based on several phases of investigation it was determined that groundwater impacted with CVOC's existed in two discrete areas defined as AOC's 1 and 2. AOC 1 was comprised of two intervals i.e. a shallow zone of saturation in weathered shale and an underlying zone of fractured bedrock immediately underlying the weathered zone. AOC-2 reflected impact in a saturated fractured, weathered rock zone. The remedial design document targeted injection of permanganate to both the shallow and deeper zones in AOC-1 and the single zone in AOC-2. It was also determined based on installation and testing of two bedrock wells that impact to groundwater existed in monitoring wells BR10-46 and BR10-47 at levels warranting permanganate injection.

### 2.1 ELEMENTS OF ISCO DESIGN

The elements of ISCO design were described in the approved Remedial Design and adjusted somewhat during the course of injection based on the performance of the system. Those adjustments were described in the Final Engineering report and primarily relate to additional injection in wells BR10-46 and BR10-47 that was agreed to after the Remedial design was submitted. The amount of permanganate injected was increased based on the objective to oxidize CVOC's in the vicinity of BR 10-46 and BR10-47 but was not adjusted otherwise. However the number of injection points was adjusted as necessary to facilitate the process of injecting fluid in areas of lower hydraulic conductivity. The adjusted actual injection wells used were as follows:

AOC-1 OB	Wells OBIW-1, OW11-A
AOC-1BR	Wells BR07-30, IW1-3, IW1-4, BR09-40, BR09-43, OW30-C, OW30-D, plus injection into wells BR10-46 and BR10-47 which covered a zone that was treated as an extension of AOC1-BR
AOC-2	Wells M05-25, IW2-2, OB09-37, OW25-A, OW25-B, OW25-C

The amount of permanganate to be injected was calculated based on the amount of contaminant volume to be treated but adjusted for the permanganate natural oxidant demand (PNOD). As described in the remedial design the PNOD was calculated based on samples taken of the geologic material within which injection was to be completed. PNOD is a measure of the amount of material within the matrix of the saturated zone that will be oxidized by the permanganate due to the presence of organic carbon or inorganic reduced species such as iron. It is very common for the PNOD to use up most of the oxidizing power of the injected chemical. The amount of permanganate calculated to be injected was more than 95 percent determined by the PNOD as follows:

AOC-1 OB	117 pounds of potassium permanganate or 455 gallons of 3% solution
AOC-1 BR	16,055 pounds of potassium permanganate or 62,248 gallons of 3 % solution
AOC-2	16,201 pounds of potassium permanganate or 62,809 gallons of 3% solution; plus an additional amount for the area around BR10-46 and BR10-47 of 5,235 pounds of potassium permanganate or 20,300 gallons of 3% solution



## 2.2 SUMMARY OF ISCO INJECTION

As noted above the implementation of the ISCO process closely followed the elements of design with the exception of the use of some additional injection wells that allowed for the addition of the total amount of chemical to be introduced within the target treatment zones. The actual amount of permanganate injected was as follows: AOC-1 OB: 140 pounds, AOC-1 BR: 16,360 pounds, AOC-2: 16,170 pounds and BR10-46 and 47: 5,280 pounds. As described in the design document the potassium permanganate, which comes in solid form was mixed on site and then pumped through a manifold system into the distribution system. An option to the use of potassium permanganate was to use sodium permanganate, which is more expensive but comes already in solution and in a more concentrated form so that mixing is not necessary and less volume needs to be injected to meet the remedial objectives.

## 2.3 INJECTION OBSERVATIONS BY AOC

### AOC-1 OB

This interval has been often unsaturated and the result of injection confirmed what water levels in observation wells had already shown; that water in the overburden infiltrates downward to recharge the underlying fractured bedrock. During injection the distinctive purple coloration indicative of permanganate was observed in two bedrock monitoring wells. Overburden observation wells monitored after injection have often had too little water to allow for sampling. Groundwater samples obtained from overburden in AOC-1 are above groundwater standards for some CVOC's, but concentrations are much lower than in the underlying AOC-1 bedrock.

### AOC-1 Bedrock

Within seventeen days of the start of injection permanganate was observed in 12 observation wells. A number of those wells reflected brown or purple color remaining sixty days after injection indicating the viability of the chemical. Observations of permanganate dispersion indicate that injection resulted in migration of the chemical throughout the impacted zone.

### AOC-2

The results of injection indicated that permanganate coloration was observed throughout the portion of AOC-2 exceeding 1000 ppb of TCE. The purple or brown color persisted in most observation wells for 60—90 days after injection.

### BR 10-46 and BR 10-47

These two wells were used for injection and no wells could be monitored close by during or after injection due to the proximity of the northern property line. The targeted amount of permanganate was successfully injected in the two wells.

### 3.0 BASIS FOR SUPPLEMENTAL INJECTION

As discussed in the Periodic Review Report the injection of permanganate has produced reductions in some groundwater concentrations. As noted in both ITRC and USEPA guidance relative to ISCO the introduction of permanganate into an impacted aquifer oxidizes CVOC's dissolved in groundwater but also oxidizes aquifer matrix material that has sorbed chlorinated material. The result of matrix oxidation often causes a release of chlorinated organics causing a rebound in groundwater concentrations. Desorption of CVOC's is desirable because these contaminants are not readily oxidized until they are in solution. This type of rebound is much more pronounced in situations where residual non-aqueous phase liquid still exists, a situation that appears likely to exist in AOC-1 bedrock. Free DNAPL has never been observed in any wells or borings; however the concentrations of dissolved TCE particularly in AOC-1 bedrock are sufficiently high that residual material is believed to be present in proximity to wells OW1-2, OW1-3 and BR09-37. Supplemental ISCO injection should target these high concentrations in AOC-1 bedrock primarily and AOC-2 secondarily. It is not proposed that further injection be done in AOC-1 overburden for several reasons. This zone is largely unsaturated and evidence indicates that water in the overburden is recharging the underlying bedrock; however concentrations of contamination in overburden are much lower than in the underlying zone. Permanganate injected in the overburden is likely to end up in the underlying zone but most of its effectiveness is likely to be oxidized by the PNOD of the unsaturated zone.

#### 3.1 THE ROLE OF PNOD IN DETERMINING PERMANGANATE QUANTITY

The PNOD of the matrix and other dissolved substances (COD) in groundwater is well known. Prior to the implementation of the first ISCO injection, lab tests of PNOD were conducted by Carus Company. Based on those tests it was determined that for the targeted treatment zone of AOC-1 bedrock the total oxidant demand of the zone (PNOD plus contaminant mass) was 16,056.05 pounds of which only 107.15 pounds was the oxidant demand of the contaminant. For AOC-2 the total oxidant demand of the treatment zone was 16,200.05 pounds of which 30.79 pounds was the oxidant demand of the contaminant. Based on current USEPA guidance it appears that the PNOD is effectively higher with higher concentrations of permanganate and that PNOD exerts a decreasing effect over time. What appears not to be well documented is the degree to which multiple applications of permanganate reduce the PNOD of the aquifer. It would seem logical that this would be the case i.e. that permanganate injected in a first round of application would oxidize a portion of the organic matter and a reduced form of metals that are a component of the aquifer matrix such that the PNOD in subsequent injections would be lower. There does not seem to be a rule of thumb established relative to the percentage that PNOD might be reduced by multiple injections treating the same aquifer volume. However an EPA engineering issue paper on in-situ chemical oxidation by Huling and Pivetz notes that "soil with 1.6% TOC prior to oxidation had 0.6% TOC remaining after oxidation by potassium permanganate", or about 66%. It seems reasonable to assume that half of the PNOD would have been

Can PNOD  
be measured  
again?

What are  
metals #'s?

arbitrary



Disagree -  
why do  
injection  
based on an  
arbitrary #?

oxidized by the permanganate and that there is no reason to plan for the necessity of treating for that PNOD repeatedly. Using less chemical but injecting it in the highest concentration areas of AOC's 1 and 2 will have the added benefit of injecting a lower fluid volume which should increase the contact time between the permanganate and the highest concentrations of CVOC's.

#### 4.0 SUPPLEMENTAL INJECTION APPROACH

As previously discussed the ISCO injection array as described in the remedial design was modified during the injection process with the concurrence of NYSDEC. That modified array simply increased the number of injection points within the highest concentration zones of each AOC. The modified array will be used for the second injection using a reduced amount of permanganate to reflect a lower effective PNOD.

#### 4.1 INJECTION ARRAY

Pilot testing and full scale injection results were used to adjust the array of injection wells in all AOC's. It is proposed that the array as described in the FER will be maintained as follows:

##### AOC-1 Bedrock

The following wells will be used for injection in accordance with the array used for injection number one; BR07-30, BR09-40, BR09-43, IW1-3, IW1-4, OW30C and OW30D. The spatial distribution of oxidant was verified during the first injection but for confirmation the nine observation wells will be checked at least daily for indications of permanganate color (OW30A, OW30B, OW1-1, OW1-2, OW1-3, OW1-4, BR09-36, BR09-37, and BR09-39).

##### BR10-46/47

These two wells will be used for injection and checked for color during post injection quarterly monitoring. There are no observation wells for this zone.

##### AOC-2

As described in the FER a total of six injection wells were used in 2010. The same wells will be used in the second injection: MW05-25, OW25-A, OW25-B, OW25-C, IW2-2 and OB09-37. During injection all wells located in the vicinity not being used for injection will be checked for color at least daily.

#### 4.2 INJECTED CHEMICAL QUANTITY

As discussed earlier the amount of chemical used in the initial injection was primarily driven by the need to adjust for the natural oxidant demand which is not believed to be a reversible process unless the eH of groundwater becomes negative. Groundwater monitoring of dissolved oxygen and eH since 2010 indicates that groundwater conditions are oxidizing. The amount of permanganate to be injected is targeted at 50% of the initial injection and is as follow:

AOC-1 Bedrock- 8180 pounds of potassium permanganate or the equivalent weight of sodium permanganate

BR10-46/47- 2620 pounds of potassium permanganate of the equivalent weight of sodium permanganate

AOC-2- 8085 pounds of potassium permanganate or the equivalent weight of sodium permanganate

*Include DO  
& eH data in  
this up.*

#### 4.3 DELIVERY SYSTEM

The delivery system to be used for handling and injecting permanganate will be the same or functionally equivalent to the system used during the first injection. It may be advantageous to use sodium instead of potassium to avoid the mixing process.

required for potassium permanganate and to reduce the amount of fluid injected because sodium permanganate has a much higher solubility in water than potassium. The manifold system for delivering fluid from storage to each well will include flow valves to equalize flow between injection points, to the extent possible and flow gauges for each line. Connections between manifold pipes and wells will be water tight to avoid overflows. Flow into each injection point will be measured daily. To the extent necessary, flow will be controlled to attempt to equally distribute the chemical across the injection zone.



## 5.0 CONFORMANCE WITH APPROVED REMEDIAL DESIGN DOCUMENT

This workplan describes a second round of injection of permanganate in conformance with the approach for ISCO described in the remedial design and final engineering reports both approved in 2010. All health and safety procedures described in the remedial design will be adhered to during the implementation of this workplan. All injections will be conducted with personnel present during injection and daily review of the injection process by the consultant.

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## 6.0 POST INJECTION MONITORING

Every attempt will be made to schedule the quarterly groundwater monitoring process such that the injection does not interfere with collection of groundwater samples as required in the Site Management Plan (SMP). However, as described in the SMP, any well that still shows purple coloration in groundwater will not be sampled until the purple has disappeared.

*Use an  
alternate  
well if one  
is nearby.*

## REFERENCES

Technical and Regulatory Guidance for In-Situ Chemical Oxidation of Contaminated Soil and Groundwater, 2<sup>nd</sup> edition, Interstate Technical and Regulatory Council, January 2005

In-Situ Chemical Oxidation, Huling S. G. and Pivetz, B.E. USEPA Engineering Issue Paper, August 2006

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Users Guide: Design Tool for Planning Permanganate Injection System, Borden, R.C., Simpkin, T. and Lieberman, M.T., Environmental Security Technology Certification Program, NCSU, August 2012



