



ARCADIS U.S., Inc.
126 North Jefferson Street
Suite 400
Milwaukee
Wisconsin 53202
Tel 414 276 7742
Fax 414 276 7603

MEMO

To:
Nicholas Bertolas
Wisconsin Department of Natural Resources

Copies:
Alina Satkoski – Madison-Kipp
Michael Schmoller - WDNR

From:
Rebecca Robbenolt
Jennine Trask

Date:
July 8, 2015

ARCADIS Project No.:
WI001368.0026

Subject:
Sodium Permanganate Neutralization for Wisconsin Pollution Discharge Elimination System (WPDES) Discharge.

Sodium permanganate was used in 2012 and 2014 as part of an in-situ remedy at the Madison-Kipp site located at 201 Waubesa Street, Madison, Wisconsin. A permanent groundwater extraction and treatment system (GETS) was approved by the Wisconsin Department of Natural Resources as the long-term remedial strategy for the groundwater. The GETS system was permitted through Wisconsin Pollution Discharge Elimination System Permit Number WI-0046531-05-0. During initial startup and testing of the GETS, sodium permanganate was observed in the extracted groundwater at a concentration of approximately 0.75 to 3.8 milligrams per liter based on a visual scale in comparison to the color chart provided on page 5 of *Ground Water Sample Preservation at In-Situ Chemical Oxidation Sites – Recommended Guidelines* dated August 2012 (attached). In the July 6, 2015 email from the Wisconsin Department of Natural Resources, a limit of 16 micrograms per liter was added to the WPDES permit for the permanganate discharge. In order to achieve the discharge limit, the following neutralization process is proposed for the GETS.

Neutralization of the sodium permanganate (NaMnO_4^-) with hydrogen peroxide (H_2O_2) is proposed. Theoretical chemical reaction:

- $2\text{NaMnO}_4^- + 4\text{H}_2\text{O}_2 \rightarrow 2\text{NaOH} + \text{Mn}_2\text{O}_3 + 3\text{H}_2\text{O} + 4\text{O}_2$
- The molar ratio is 4 moles H_2O_2 : 2 moles of NaMnO_4^-
- Weight ratio: 0.48 parts H_2O_2 : 1 part NaMnO_4^- .

This approach has been confirmed with the sodium permanganate vendor, Carus Remediation Technologies, and this neutralization process is widely utilized in the industry. Based on the chemistry noted above, the proposed neutralization dosing is approximately 0.06 to 0.34 gallons per day of 32 to 35% industrial grade hydrogen peroxide solution (Safety Data Sheet attached). Hydrogen peroxide will be stored on site in limited quantities of approximately 15 gallons within a secondary containment structure. Hydrogen peroxide will be dosed by hand or using a small electric dosing pump to achieve neutralization of the sodium permanganate at Mix Tank T-101. Confirmation samples will be collected daily for the first week of system operation for visual inspection of the neutralization process per the attached color chart. Following successful demonstration of neutralization during this initial startup, one sample will be collected quarterly as presented in Table 3.1. All discharge monitoring requirements as outlined in Table 3.1 will be added to the site-specific discharge monitoring report for the Site. The information outlined below was referenced from permit WI-0046540-05-0. Please note that references to “potassium permanganate” in the permit language below should be revised to “sodium permanganate”.

Table 3.1 – Potable Water Treatment System Wastewater to Surface Water

| Monitoring Requirements and Effluent Limitations | | | | | |
|--|------------|-----------------|------------------|-------------|---------------------|
| Parameter | Limit Type | Limit and Units | Sample Frequency | Sample Type | Notes |
| Flow Rate | | gpd | Quarterly | Estimate | See 3.1.1 |
| Suspended Solids, Total | Daily Max | 40 mg/L | Quarterly | Composite | See 3.1.2 |
| pH | Daily Min | 6.0 mg/L | Quarterly | Grab | See 3.1.3 and 3.1.4 |
| pH | Daily Max | 9.0 mg/L | Quarterly | Grab | See 3.1.4 |
| Potassium Permanganate (KMnO ₄) | Daily Max | 16 µg/L | Quarterly | Grab | See 3.1.5 |
| Metals and Hardness | Daily Max | | Annual | Composite | See 3.1.6 |

3.1.1 Flow Estimate

Estimate means a reasonable approximation of the average daily flow based on a water balance, an uncalibrated weir, calculations from the velocity and cross section of the discharge, intake water meter readings, discharge water meter readings, or any other method approved by the Department.

3.1.2 Composite Sample

A composite sample means compositing individual flow proportional grab samples collected once per hour for eight hours or the duration of the discharge, whichever is less.

3.1.3 Grab Sample

A grab sample means a single sample taken at one moment of time or a combination of several smaller samples of equal volume taken in less than a 2 minute period.

3.1.4 pH Monitoring

The daily maximum pH limit for all wastewater discharges, except lime softening, is 9.0 standard units. The daily maximum pH limit for lime softening is 11.0 standard units.

3.1.5 Potassium Permanganate Monitoring

KMnO₄ monitoring is only required for discharges from filters where KMnO₄ is used. The permittee shall demonstrate compliance with the effluent limitation by visually inspecting the discharge sample against a white background under fluorescent lighting. The absence of any pink or purple color shall be considered to be in compliance with the daily maximum effluent limitation. The presence of pink or purple color in the discharge shall be considered an exceedance of the permit limit.

3.1.6 Metals and Hardness

Metals and hardness monitoring is only required for discharges from membrane filtration units. The parameters for metals monitoring are total recoverable copper, total recoverable lead, and total recoverable zinc. Metals monitoring will not be required under this permit issuance if two sets of metals data submitted under a previous permit issuance are below the Department's level of concern, and the water treatment has not changed significantly.

3.1.7 Floating Solids and Foam

There shall be no discharge of floating solids or visible foam in other than trace amounts.

3.1.8 Solids Removal

Solids shall be removed from settling equipment to maintain treatment capacity and efficiency of the system.

plan, or in general EPA documents such as the Resource Conservation and Recovery Act (RCRA) guidance document (U.S. EPA, 1992) or EPA SW-846 (U.S. EPA, 1982). Additional direction on ground water sampling techniques can be found in Yeskis and Zavala (2002).

2.1. Permanganate (MnO₄⁻)

Data and information presented below are reported in terms of the permanganate anion (MnO₄⁻; 118.9 grams per mole (g/mol)). Permanganate is purchased either as sodium permanganate (NaMnO₄; 141.9 g/mol) or potassium permanganate (KMnO₄; 158.0 g/mol) and as a result conversion to the permanganate anion concentration is needed to determine sample preservation needs as per the *Issue Paper*. Specifically, the ratios 118.9/141.9 (g-mole/g-mole) and 118.9/158.0 (g-mole/g-mole) are used to convert NaMnO₄ and KMnO₄, respectively to MnO₄⁻.

2.1.1. Analysis by Visual Observation

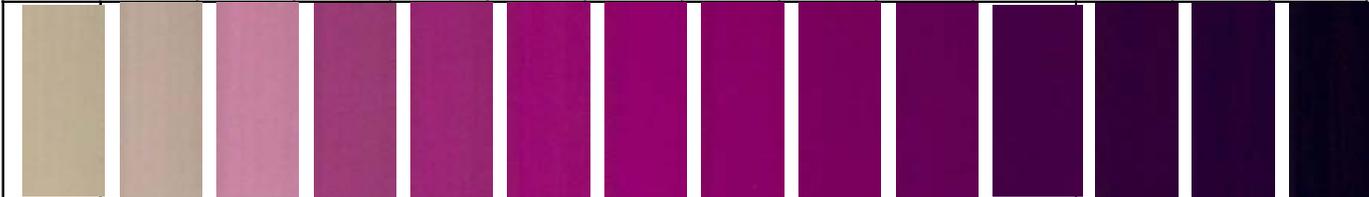
The characteristic pink or purple color of MnO₄⁻ in a 40 mL VOA vial can be used as a general guideline to

estimate the concentration by using the MnO₄⁻ colorimetric scale (Table 1). This method should be used with caution because ground water turbidity and colloidal manganese dioxide solids (MnO₂(s)) can affect sample color and result in deviations from the tabulated color scale. Field filtration can help minimize these interferences, but may not fully remove all color if sub-micron colloidal and/or dissolved constituents are present.

2.1.2. Spectrophotometric Analysis

The permanganate concentration can be determined using commercially available field test kits (SenSafe™, 2011; CHEMetrics, 2011). Additionally, an accurate measurement of the permanganate concentrations can be determined using a field spectrophotometer (maximum absorbance wavelength (λ) = 525 nanometers (nm) (A₅₂₅)) and a calibration curve involving a linear correlation between MnO₄⁻ concentration and A₅₂₅ (Figure 2, Table 1). Filtered samples (0.2-0.45 micron) may be required to eliminate background colloidal or suspended solid materials that can absorb light at 525 nm and interfere with permanganate measurement. Volatilization of

Table 1. Permanganate concentration, spectrophotometric absorbance at 525 nm, and required amount of ascorbic acid required to neutralize the oxidant in a 40 mL vial. The color scale represents actual photos of MnO₄⁻ vials and is included for conceptual guidance. Actual colors vary based on background lighting, and color printers. Additionally, photographs of low concentrations (i.e., clear solutions) do not accurately capture transparency.

| | | | | | | | | | | | | | |
|--|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
|  | | | | | | | | | | | | | |
| [MnO₄⁻] (mg/L) (millimolar in parentheses) | | | | | | | | | | | | | |
| 0 | 0.75 | 3.8 | 7.5 | 11.3 | 18.8 | 30.1 | 37.6 | 56.4 | 75.3 | 113 | 151 | 188 | 376 |
| (0) | (0.01) | (0.03) | (0.06) | (0.09) | (0.16) | (0.25) | (0.32) | (0.47) | (0.63) | (0.95) | (1.27) | (1.58) | (3.16) |
| Absorbance⁽¹⁾, wavelength (λ) = 525 nm | | | | | | | | | | | | | |
| 0 | 0.011 | 0.059 | 0.134 | 0.197 | 0.329 | 0.516 | 0.627 | NL | NL | NL | NL | NL | NL |
| Ascorbic Acid Stock Solution (M)⁽²⁾ | | | | | | | | | | | | | |
| - | 0.015 | 0.015 | 0.15 | 0.15 | 0.15 | 0.15 | 0.15 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 |
| Volume of Ascorbic Acid solution (μL) | | | | | | | | | | | | | |
| 0 | 30 | 150 | 30 | 46 | 76 | 121 | 152 | 23 | 30 | 46 | 61 | 76 | 152 |
| Mass of Ascorbic Acid (mg) | | | | | | | | | | | | | |
| 0 | 0.08 | 0.4 | 0.79 | 1.21 | 2.1 | 3.32 | 4.17 | 6.1 | 7.9 | 12.2 | 16.1 | 20.1 | 40.2 |
| (1) [MnO ₄ ⁻] (mg/L) = 58.8 × A ₅₂₅ ; A ₅₂₅ is the absorbance at 525 nm; non-linear above 38 mg/L MnO ₄ ⁻ . | | | | | | | | | | | | | |
| (2) To minimize sample dilution, the ascorbic acid stock solution used was 0.015, 0.15, and 1.5 M. | | | | | | | | | | | | | |