Controlled Jet Injection FRx

TECHNICAL BRIEF

Injecting Potassium Permanganate

Introduction

Slurry Injections are two-dimensional structures created in subsurface soils and rock by application of hydraulic pressure. In essence, these are new volumes created by displacing existing soil and rock, and the new space can be filled with materials that can affect in situ treatment of contaminated groundwater, soil and/or rock. For example, in situ chemical oxidation (ISCO) remediation processes can be implemented by creating the requisite hydraulic pressure with a slurry of potassium permanganate granules.

Features and Benefits

Potassium permanganate, when applied by slurry injection, offers at least four significant advantages relative to it cousin, sodium permanganate.

Potassium Permanganate Concentration

$$1\ gal\ liquid = 8.33\ lb$$

$$\frac{10\ lb\ solids}{2.74 * 8.33\ lb/gal} = 0.438\ gal$$

$$slurry\ vol = 1.438\ gal$$

$$10\ lb * \frac{AW_{Mn} + 4\ AW_O}{AW_K + AW_{Mn} + 4\ AW_O}$$

$$= 10 * \frac{54.94 + 4 * 16}{39.1 + 54.94 + 4 * 16}$$

$$= 7.53\ lb\ MnO_4^-$$

$$\frac{7.53\ lb}{1.438\ gal} = 5.23\ lb/gal$$

- A greater concentration of permanganate ion (MnO_4^-) can be delivered by slurry injection with potassium permanganate granules. Typical injection slurry comprises 10 lbs of potassium permanganate solids for every gallon of carrier fluid, which usually is a viscosified water system. Given the crystalline density of potassium permanganate of 2.74 g/cc and the atomic weights of manganese, oxygen, and potassium, an easy calculation shows that injection slurry contains 5.23 lbs/gal of MnO_4^-. A similar calculation for sodium permanganate solution, which is delivered as 40% aqueous solution, shows that only 3.41 lbs of MnO_4^- can be delivered with that material. The ratio of 1.5 (5.23/3.41) should be considered a lower limit, because slurry can be more heavily loaded with potassium permanganate granules – the upper limit is about 22 lbs of potassium permanganate per gallon of carrier fluid, which corresponds to insufficient fluid to separate the solid grains. At 22 lbs per gallon, the ratio of anion delivery is about 2.5.

- While the concentration is greater during delivery, the concentration realized in the remedial treatment process is substantially less because of the limited solubility of potassium permanganate. In situ, the permanganate concentration in the groundwater (where all remediation reactions take place) will not exceed 5%, depending upon groundwater temperature. While reaction rates do increase with increased anion concentration, optimal deployment – in terms of contaminant destroyed per mass of permanganate applied – is realized at lower concentrations.

- In contrast to aqueous solution that can be flushed down-gradient, solid potassium permanganate cannot be displaced by groundwater flux. Rather, the bulk of the potassium permanganate remains fixed and slowly dissolves, serving as a long-term, passive source of remedial agent.
- Potassium permanganate is safer to handle than sodium permanganate concentrate. Excess sodium permanganate needs to be managed carefully – slowly neutralized and brought under control – otherwise, violent exothermic reactions – indeed explosions – take place. Potassium permanganate, because of its limited solubility, much less readily establishes these dangerous conditions.

In addition, there can be cost differences between sodium permanganate and potassium permanganate. In general, potassium permanganate is less expensive because many manufacturers make sodium permanganate from the potassium form. Also, the shipping cost of sodium permanganate will be higher per unit of MnO_4^- because of the mass of accompanying water.

Methods

Creation of permanganate–filled injection slurries can be done with techniques first developed by research sponsored by the US EPA in the late 1980's and early 1990's. The critical steps include installing a suitable injection well to the targeted formation and creating a fluid system that reliably transports the granular potassium permanganate.

The former can be accomplished by any competent drilling method and well construction that 1) can preserve and, if possible, enhance the in situ state of stress and 2) establishes a competent seal that isolates the target interval from the surface. Direct push rods have proven to be a robust and viable approach, but other drilling methods may also be used.

The slurry used to create potassium permanganate injections differs somewhat from the slurry used in other injection work. Whereas guar often is used to viscosify water used to create slurries of iron, sand or other remediation materials, permanganate too readily oxidizes guar. While some modified guar compounds have shown some temporary resistance to permanganate oxidation, these still constitute an organic load that ultimately will consume oxidation capacity of the permanganate – thus imposing an additional cost upon the process. Instead, practical permanganate slurry can be created with water slightly viscosified with bentonite – usually less than 3% by weight. This dosing lends needed viscosity without delivering appreciable colloidal materials into the subsurface. Without viscosifier, permanganate granules cannot be transported reliably and tend to accumulate and plug equipment, hoses, and well components in the most inopportune places as well as fail to distribute optimally in situ.

Injection Size and Effectiveness

The volume – and thus mass - of any given material that can be delivered through injection slurries will be governed by soil conditions, depth, and practical limits of equipment, personnel and time allotted for the work. Based on FRx experience, slurry injections at a depth of at least 20 feet bgs can be created with as much as 4,000 pounds of potassium permanganate. Greater quantities may be achievable in more ideal soil conditions. Lesser quantities may be practicable at shallower depths due to the natural tendency for horizontal injections to dip upward even in the most ideal settings. More importantly, previously disturbed soils or highly variable soil structures may limit the viable volume of injections due to slurry returning to the ground surface or propagating away from the target interval.

The radius of influence (ROI) of an injection could be construed as the distance over which remedial conditions can develop due to the presence of an injection. In this sense, the ROI will grow slowly with time at a rate depending upon the amount of natural organic matter in the soil, until the emplaced permanganate is exhausted. In contrast, each injection can be expected to have a definable radius of extent (ROE). Different criteria can be used. One definition could be the extent of the tip of the created injection plane. Realizing that the tip has zero aperture, the tip is a location that cannot contain even a single grain of solid permanganate and, thus, does not constitute a good measure of the ROE. A better definition is the radius at which the injection aperture is sufficiently open to accommodate granular solids. At a minimum, the ROE corresponds to an aperture equivalent to the grain diameter of the permanganate. When using fine-grained permanganate, a somewhat larger aperture needs to be selected to establish a ROE that encompasses a significant quantity of permanganate. An aperture of two millimeters will accommodate sufficient mass to: (a) affect remedial conditions an appreciable vertical interval from the injection and (b) be observable in a core sample.

The distance between the center of the injection and the two mm ROE, which depends upon the volume of material in the injection, as well as local geotechnical parameters, typically extends between 15 and 45 feet. The potassium permanganate within the injection will treat surrounding soil, rock, and groundwater until it is exhausted. Depending upon the oxidant demand of the formation (both natural and contaminant), a single injection filled with a few thousand pounds of potassium permanganate may treat a column of media forty feet across and fifteen feet high.