

PENTACHLOROPHENOL REMEDIATION AT A FORMER CALIFORNIA WOOD TREATING FACILITY

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ABSTRACT: The subject site is a former lumber mill and wood-treating facility that has undergone extended remedial efforts. Pentachlorophenol (PCP) levels ranging up to 2,200 mg/Kg remained within a smear zone located approximately five to seven feet beneath a concrete floor in the main mill building (the source area). Wet season (high groundwater) PCP groundwater concentrations in the source area averaged ~4,000 ug/L. Approximately 1,400 yd³ of PCP-contaminated soil was excavated from the vadose zone to the depth of the seasonal low water table, but approximately 600 yd³ of PCP-contaminated soil could not be removed without impairing the integrity of the building structure. The soil within the smear zone and the residual contamination in groundwater below the excavation were treated with a hydrogen peroxide-based chemical oxidation technology developed by Mr. Lundy. Approximately 8,000 gallons of peroxide solution were injected into the base of the excavation to address the contaminants remaining below the groundwater surface. Additionally, 4,000 gallons of peroxide solution were injected into the base of the column footings and the former excavation. Eighteen months post-treatment, groundwater concentrations in the source well have decreased from an average of 1,900 µg/L (one year pre-injection) to 0.59 µg/L.

INTRODUCTION

PCP (C₆HCl₅O) is a chlorinated hydrocarbon that was primarily used as a wood preservative at wood product facilities prior to the mid-1980s. Drips and spills from application systems (such as, dip tanks and spray booths) commonly resulted in the contamination of soil and groundwater at these facilities.

Site Description. The 6-acre site is located in Arcata, California, near a tidal estuary, in a lowland area approximately 4,000 feet from Arcata Bay (Humboldt Bay, North). Soil types are typical local bay muds of silt and fine sand with varying amounts of clay. Depth to groundwater ranges seasonally from approximately 2 feet Below Ground Surface (BGS) to 8 feet BGS. The historical groundwater gradient is to the southwest at 0.005 ft/ft.

The project site and adjacent land have been occupied and operated as wood manufacturing/production facilities by various tenants since 1902. In addition to milling operations, the mill treated lumber with an anti-stain and fungicide formulation of PCP and Stoddard Solvent (which was used as a carrier agent for PCP), and manufactured glue-laminated wood beams.

A leak in piping from an approximately 5,000 gallon, above ground, steel tank that stored solvent-based PCP was discovered by local residents and initiated regulatory action. Subsequently, PCP contamination was detected in soil and groundwater in the late 1980s. Contaminants of initial concern included PCP; 2,3,4,6 Tetrachlorophenol (TCP); phenols;

formaldehyde; petroleum hydrocarbons; and dioxins/furans. No phenols were detected; however, localized formaldehyde, petroleum hydrocarbons as Stoddard Solvent (TPHS), and dioxin/furans associated with the PCP formulations were documented. In 1990, 1,700 yd³ of contaminated soil were excavated from the north side exterior of the existing mill building (Figure 1). The excavation was backfilled with river-run gravel to increase the efficiency of the groundwater extraction and treatment system installed in 1993. Treated groundwater was discharged under permit to the City's sanitary sewer. This system operated until 1997. During that time, approximately 3 million gallons of groundwater was extracted and treated. Unfortunately, after seven years of remedial efforts, a significant contaminant source remained beneath the mill building.

Groundwater monitoring well MW-106, a target hot spot, was documented as having a PCP concentration of 24,000 ug/L (March 1990), and 2,500 ug/L (December 2000). An estimated 2,000 yd³ of soil with PCP levels ranging up to 2,200 mg/Kg remained within a smear zone, approximately five to seven feet beneath a concrete floor in the main mill building. The floor was underlain by fill material that extended to a depth of approximately five feet, where it interfaced with bay and estuary deposits, which primarily consisted of inter-bedded silt and silty sand.

PCP Solubility. PCP is a weak organic acid (un-ionized form) and its aqueous solubility depends upon its pH. The solubility of PCP is 14 mg/L at 25°C. The basic ionized form of PCP is pentachlorophenate salt, which has a water solubility approximately 100 times greater than PCP (Watts, 1997). This is demonstrated by Hurst (Hurst et al., 1997), who shows that PCP solubility at pH 4.2 is 13.2 mg/L and at pH 7.65 is 1,465 mg/L.

PCP Degradation. Biodegradation, or the transformation of chemical compounds by living organisms, is one of the major processes that determine the fate of organic chemicals in soil and groundwater. In general, it has been found that most micro-organisms readily degrade PCP, with the PCP half-life ranging between 0.1 and 3 years (USEPA, 1991).

Although field and laboratory data indicate that microorganisms are capable of degrading PCP, it must be recognized that PCP is a fungicide and inhibits the activity of microorganisms above certain threshold concentrations. Although PCP was normally applied at a rate of 30,000 to 50,000 mg/L (Richardson, 1978), field studies conducted at contaminated wood product facilities indicate that PCP concentrations in water as low as 20 mg/L can inhibit microbial activity (Davis et al., 1994). Degradation of PCP is optimal between pH 6.5 and pH 8 and at a temperature between 10°C and 30°C (Brooks, 1998).

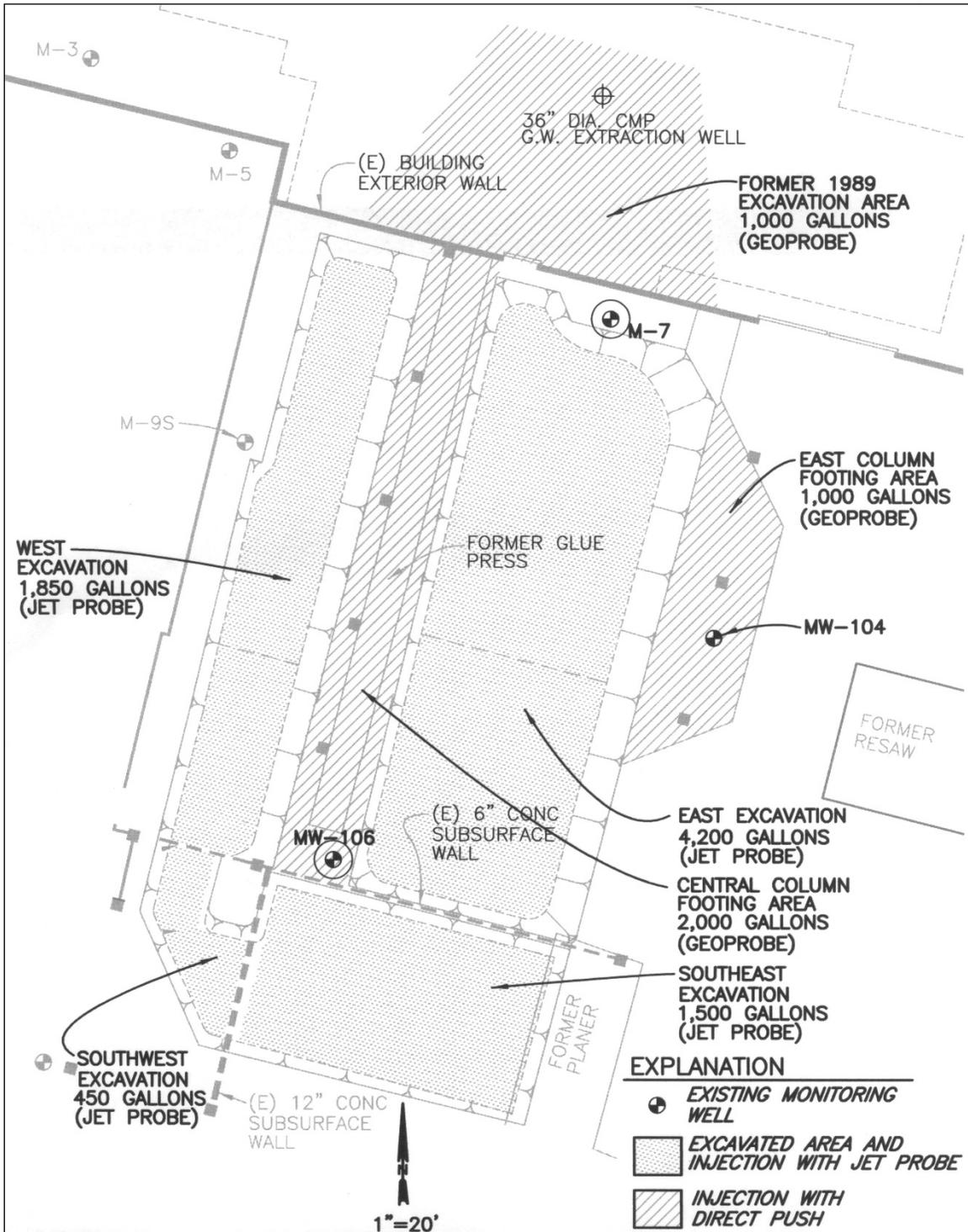


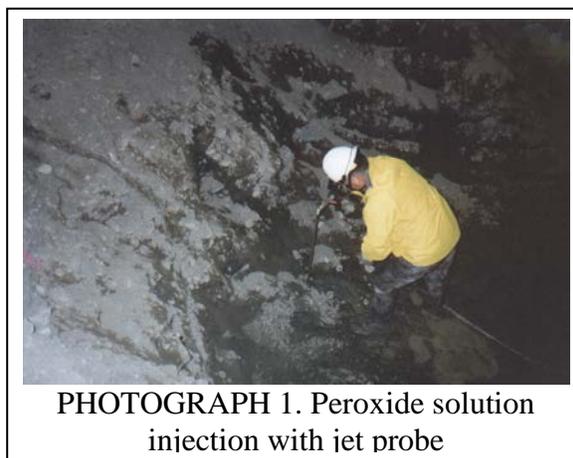
FIGURE 1. Remedial Site Plan, Beaver Lumber Company, Arcata, CA

Hydrogen Peroxide. The use of hydrogen peroxide for in situ chemical oxidation involves free radical generation and direct oxidation with hydrogen peroxide (ITRC, 2001). Fenton's Reagent uses a well-documented process that combines hydrogen peroxide with ferrous iron (Fe^{2+}), the reaction for which produces hydroxyl radicals. However, the naturally occurring iron present in site soils can be used as the catalyst for this reaction. Iron oxide minerals (such as, Goethite, Hematite, and Magnetite) are commonly found in soils as a byproduct of soil formation (Schwertmann et al., 1986). These oxides are usually found as iron coatings on the surfaces of sand or other soils. Goethite is the most common form of iron oxide and is found in many soils regardless of climatic region (Sposito, 1989). Thermodynamically, Goethite has the greatest stability under most soil conditions (Schwertmann and Taylor, 1977). Studies have shown that mineral-catalyzed Fenton-like reactions are not dependant upon maintaining soluble iron; therefore, hydroxyl radicals are generated at neutral pH regimes (Watts et al., 1999).

Peroxide Solution. The process involves injecting a blend of peroxides including low concentration hydrogen peroxide (H_2O_2) solution (~ 3% to 4% peroxide) and a blend of solid metallic peroxides including calcium peroxide (CaO_2) mixed with nutrients (such as phosphates) at a near-neutral basic pH (7.5 to 8.5). The low concentration peroxide solution is injected into the source area, causing several reactions to occur in the subsurface:

- 1) The calcium peroxide undergoes hydrolysis to form hydrogen peroxide as it slowly reacts with water.
- 2) Hydrogen peroxide at the near-neutral basic pH reacts with iron minerals present in the subsurface soils to generate a variety of radicals including perhydroxide and super hydroxide radicals. These radicals non-selectively attack the carbon-hydrogen bonds of organic molecules and are capable of degrading many petroleum products and pesticides, including PCP. Carbon/halogen bonds at the near-neutral basic pH are particularly susceptible to attack with an ensuing halogen/hydroxyl substitution reaction occurring. This reaction is aided by increased solubility of the PCP.
- 3) Oxygen is produced as a byproduct of hydrogen peroxide decomposition. In combination with the added nutrients from the peroxide solution formulation, the oxygen assists with biodegradation of residual contaminants and associated daughter products.

The initial peroxide injection step is not intended to completely mineralize the parent compound (PCP). The chemical oxidation step is followed with enhanced biodegradation by the indigenous microbes. The biodegradation step is enhanced because PCP and its chlorinated hydrocarbon daughter products are converted into alcohols; thus, allowing a much wider variety of microbes to metabolize the PCP and its associated daughter products.



MATERIALS AND METHODS

The client wanted a remedial solution that would provide the quickest pathway to site closure. Our remedial strategy included excavation of contaminated soils to the furthest extent possible and subsequent injection of a peroxide solution to address residual PCP contamination.

Excavation activities began on August 22, 2002, and resulted in the removal of 1,400 yd³ of PCP-contaminated soil from the vadose zone to the depth of the seasonal low water table (7 feet BGS). Equipment consisted of a limited access excavator, loader, and 10- yd³ dump truck. Additionally, because site work was primarily inside the main mill building, large fans were used for ventilation during excavation and injection activities.

Approximately 600 yd³ of PCP-contaminated soil could not be removed without impairing the integrity of the support columns and perimeter foundation of the building structure. This soil (which was within the vadose zone) and the residual contamination in the soil and groundwater located beneath the excavated areas were treated with the peroxide solution.

Injection activities began on August 27, 2002, and concluded on September 13, 2002. The peroxide solution was prepared in 50-gallon batches and injected using either a jet probe or a Geoprobe®. The reagent included liquid hydrogen peroxide (~3% - 4%), calcium peroxide (powder form), a blend of nutrients including phosphate and urea, and municipal water. A centrifugal pump was used to keep the solution in suspension in the mixing tank. The peroxide solution was delivered using a high-pressure pump, and hoses to the jet probe or Geoprobe® injection points. The application rate was approximately 3 gpm at ~150 psi.



PHOTOGRAPH 2. Peroxide solution Injection with Geoprobe®

Approximately 8,000 gallons of peroxide solution were injected into the base of the excavation to address the contaminants remaining below the groundwater surface. A hand-held jet probe was used to place the peroxide solution at a depth of four feet into the saturated zone (7 to 11 feet BGS) with injection points spaced three feet apart. It should be noted that during the injection process, Stoddard Solvent NAPL (nonaqueous phase liquids) was displaced and accumulated on the groundwater surface, where it vigorously reacted with the peroxide solution to form a heavy foam.

Additionally, 4,000 gallons of peroxide solution were injected into the soil at the base of the column footings and into the former excavation area (circa 1990) located immediately north of the mill building. The injections in these areas were accomplished using a truck mounted Geoprobe® direct push unit. The injection depth was six to 10 feet BGS. Figure 1 shows the location of the excavations and associated jet probe injection areas, and the areas where the Geoprobe® was used around the column supports. Table 1 summarizes the injection specifications for each location.

TABLE 1. Injection specification

Parameter	Floor of Excavation (Deep)	Ground Surface (Shallow)
Injection Surface Area	7,000 ft ²	3,500 ft ²
Injection Depth	0-4 feet beyond floor of ex. (7-11 ft below original grade)	6-10 ft below grade
Injection Equipment	Hand Held Jet Probe	Geoprobe [®]
Point Spacing	2-3 feet	4-5 feet
Number of Injection points	~2,000	116
Vol. of Peroxide Solution/point	~ 4 gallons	~35 gallons
Vol. of Peroxide Solution Injected	8,000 gallons	4,000 gallons

Groundwater samples were collected and sent to a California-certified Laboratory for the following analysis:

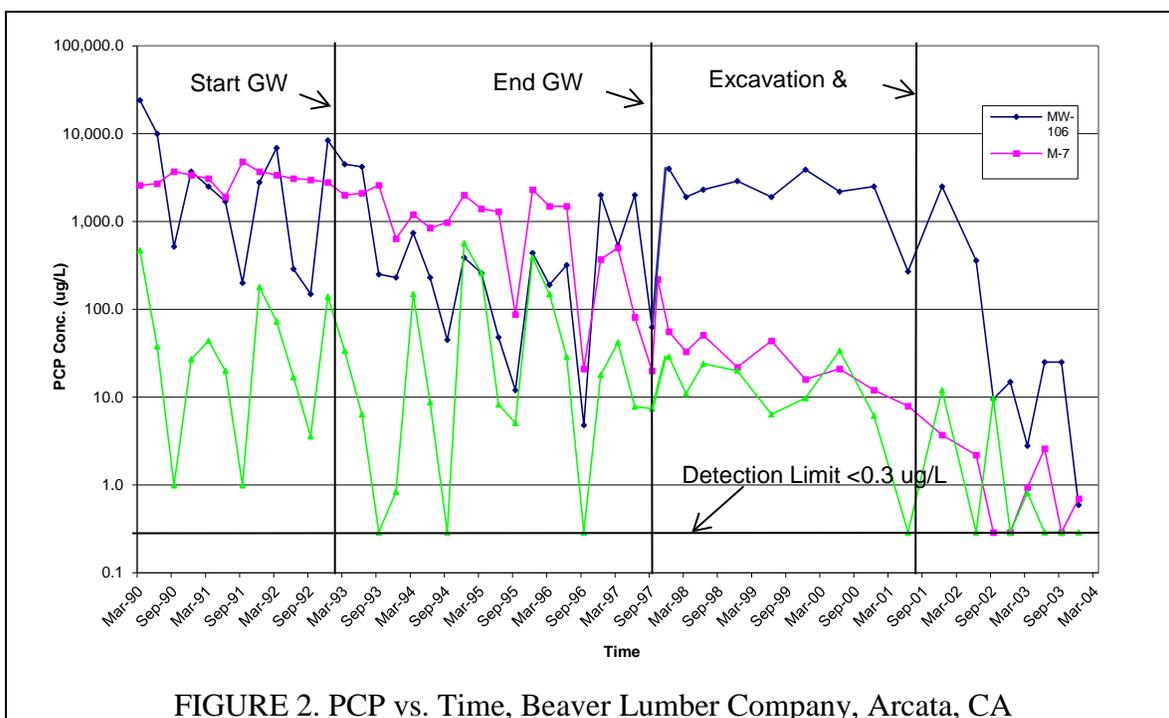
- PCP and TCP using the Canadian Pulp Report Method.
- TPHS using EPA Method No. 5030 GCFID.

RESULTS AND DISCUSSION

Soil. Interior perimeter portions (along the former glue press location) of the west and east excavations did not meet the target level of 1 mg/Kg because the areas could not be excavated due to the location of the roof truss column supports and footings. Most of these samples were collected prior to peroxide injection. Soil concentrations in the sidewall samples in the vicinity of the inaccessible column support areas ranged from 51 mg/Kg to 730 mg/Kg, with an average concentration of 200 mg/Kg. Generally, fill material above the existing gravel fill/native interface, and sidewalls located on the outer perimeter of the excavation were documented as being within the target PCP residual concentration range (<1 mg/Kg).

Groundwater. Prior to the remedial activities in 2002, the only groundwater monitoring well impacted by the 1989 soil excavation and groundwater extraction activities was M-7, which was located approximately 5 feet downgradient of the 1989 excavation limit. Previous remedial activities had limited effect on monitoring wells MW-104 and MW-106. Figure 2 illustrates the historical trends in these wells since the original excavation in 1989.

Eighteen months after the remedial activities were completed, the PCP concentrations in the source well MW-106 decreased from an average of 1,900 µg/L (year prior to injection) to 0.59 µg/L (December 2003). TPHS was not historically analyzed in groundwater monitoring wells prior to the peroxide injection. Post peroxide injection groundwater monitoring indicates that TPHS has only been detected in two of the injection perimeter monitoring wells (M-7 and MW-104) following the peroxide injection process. TPHS has not been detected in the source well MW-106 since the peroxide injection in September of 2002.



As expected, post-excavation and hydrogen peroxide injection data indicates a significant decrease in the PCP/TCP concentrations in source well MW-106. No significant rebound in PCP concentrations has been observed during the eighteen months since the initial injection. Note, the chart scale is logarithmic.

CONCLUSIONS

To date, remediation (peroxide injection coupled with over-excavation of a portion of the source area) is on track for achieving the client's site closure goal.

The excavation portion of this remedial action project successfully achieved the target residual PCP concentration within accessible areas above the seasonal low groundwater surface. Peroxide solution injection and subsequent bioremediation of the residual contamination have degraded the post-excavation residual PCP/TCP/TPHS soil and groundwater contamination. The peroxide injection process has been documented as significantly reducing the target contaminant concentrations in the groundwater.

Prior to peroxide injection, soil confirmation sampling showed elevated PCP concentrations remaining in inaccessible areas (under column footings). The goal of peroxide injection was to reduce PCP concentrations in these inaccessible areas. Post-injection groundwater monitoring results to date indicate that these efforts were successful. Monitoring wells MW-106 and MW-104 were located outside of the excavation areas (within inaccessible areas under column footings), yet showed significant reduction in PCP concentrations following the peroxide injection.

If the monitored levels of groundwater PCP/TCP concentrations continue to demonstrate a steady decrease through the fall of 2004 (two years after the initial peroxide injection), SHN will request site closure from the lead regulatory agency.

REFERENCES

Brooks, Kenneth M. 1998. Literature Review, Computer Model and Assessment of the Potential Environmental Risks Associated With Pentachlorophenol Treated Wood Products Used in Aquatic Environments. Report prepared for Western Wood Preservers Institute. Port Townsend: Aquatic Environmental Sciences.

Davis, A., J. Campbell, M. Ruby, M. Bennet, and S. Tubin. 1994. "Attenuation and Biodegradation of Chlorophenols in Ground Water at a Former Wood Treating Facility," *Groundwater*. Vol. 32, No. 2, pp 248-257.

Hurst, Jestin C., R.C. Sims, J.L. Sims, D.L. Sorensen, J.E. McLean, and S. Huling. 1997. "Soil Gas Oxygen Tension and Pentachlorophenol Biodegradation," *Journal of Environmental Engineering*. Vol. 123, no. 4. pp 364.

Richardson, B. 1978. *Wood Preservation*. Lancaster: The Construction Press Ltd.

USEPA. 1991. *On-Site Treatment of Creosote and Pentachlorophenol Sludges and Contaminated Soil*. EPA/600/2-91/019.

Watts, Richard J. 1997. *Hazardous Wastes: Sources, Pathways, Receptors*. New York: John Wiley & Sons, Inc.

Watts, Richard J., M. K. Foget, S. Kong, and A. L. Teel. 1999. "Hydrogen Peroxide Decomposition in Model Subsurface Systems," *Journal of Hazardous Materials*. New York: Elsevier Science B.V.

Interstate Technology and Regulatory Cooperation Work Group, In Situ Chemical Oxidation Work Team. (June 2001). Technical/Regulatory Guidelines: Technical and Regulatory Guidance for In Situ Chemical Oxidation of Contaminated Soil and Groundwater. Washington, D.C.: ITRC.

Sposito, G. (1989). Chemistry of Soils. New York: Oxford University Press. pp. 22-40.

Schwertmann, U., et al. (1986). "Mutual Interactions Between Organics and Iron Oxides," Interactions of Soil Minerals with Natural Organics and Microbes. (Soil Science of America Special Publication No. 17). Madison: Soil Science Society of America. pp. 223-250.

Schwertmann, U. and R. Taylor. (1977). "Iron Oxides," Minerals in Soil Environments. Madison: Soil Science Society of America. pp. 145-180.

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