



Brief Technical Summary of Oil Remediation Treatment

The treatment is a stabilization and conversion but not a solidification. The product is a loose-flowing granular material which can be returned to the site from which it came, removed to landfill, or even used as a soil-building component in agricultural land. It will consistently decrease toxic materials removed by standard leaching tests by about three orders of magnitude (99.9% remediation). The treatment has proven effective on all the noxious materials listed by EPA.

The mechanism of trapping and holding (stabilization) is primarily ion-exchange for heavy metal cations. Zeolites, the major ingredient, are natural, inorganic ion-exchangers which attract and hold metallic cations, particularly divalent and trivalent cations. Clinoptilolite, a major component of the remediation treatment has potassium ion (K^+) and sodium ion (Na^+) as its major, charge balancing cations. These exchange rapidly and preferentially with Ca^{2+} , Mg^{2+} and Fe^{3+} in groundwater or Pb^{2+} , Ni^{2+} or Cd^{2+} in contaminated soils. These are held very tightly by a chelation effect (attachment to two or three cations' sites in the zeolite crystal structure) and are almost inert to reverse exchange. Removal is further inhibited by a glaze of sodium aluminosilicate which forms on the surface of the zeolite particle. This is formed at a slower rate by reaction of the sodium hydroxide and aluminum hydroxide components of the remediation mixture with the surface of the zeolite crystal. The gel material first formed is reduced to a glass by the heat of hydration of sodium hydroxide.

Trapping metal cations by ion-exchange within the zeolite crystal is distinct from their precipitation by soluble silicates or on the surface of calcium silicates (cement). Exchange is very rapid and distributes the metals through the zeolite crystal. There they are deposited at crystallographic sites in the zeolite structure replacing Na^+ . Very few chemical reagents will displace divalent or trivalent cations from these positions. Metal silicates on the other hand are non-stoichiometric compounds in which the metal is coordinated to silano groups ($SiOH$) in an amorphous silica matrix. (1)

A second mechanism is operative for molecular species such as benzene, toluene, and xylenes. These are adsorbed into the internal pores of the zeolite for small molecules and the pores of silica gel for large complex molecules. Clinoptilolite has pores $0.3 \times 0.7 \text{ nm}$ (2) which can readily accommodate simple aromatic molecules such as xylene. Its void volume in this pore size range is about $0.3 \text{ cm}^3/\text{g}$. (3) (surface area ca $300 \text{ m}^2/\text{g}$). Silica gel is well known for adsorbing and holding aromatic molecules, such as naphthalene and more complex polynuclear aromatics.

Polar aromatics such as chlorobenzene, nitrobenzene or pyridine are preferentially adsorbed on silica gel. The external surface of these particles, both zeolite and silica gel, is highly siliceous and is again aluminate is required to seal the internal surface against release of these trapped molecules. External surface is only about 1% of the total active surface of the particle. Calcination will remove occluded organics only if residual pores permit entry of oxygen molecules and egress of CO₂. More commonly, the trapped molecule is reduced to coke.

A third mechanism, caustic fusion, is operative for complex organic molecules reducing them to simpler, less toxic entities. It is particularly effective for highly polar molecules, such as chloroform or nitrobenzene. The net reaction forms a sodium salt (NaCl, NaNO₃, etc.) and CO₂ plus simple hydrocarbons. This reaction requires concentrated NaOH plus modest heat. It is not calcination in that air or oxygen is not required. It removes functional group from organic molecules which are often the focus of their toxicity. Limited water is a necessary condition for this reaction.

The treatment ratio, 100% of the mix per unit of soil to be treated, is in most cases a substantial overtreatment. For a large site, the treatment can be optimized at a lower level; but optimization is expensive due to laboratory and analytical charges. For many smaller sites, overtreatment is the more economical strategy. It provides assurance of the effect on this material. The stabilizing action does not depend on physical exclusion of water. Over long periods, modest leaching of sodium ion is to be expected. Where the treated product is important to agriculture, substitution of KOH for NaOH is suggested.

(1) J. R. Conner, Soil Remediation and Sludge Treatment, pp. 243-54 (ca. 1992)

(2) W.M. Meier & D.H. Olson, Atlas of Zeolite Structure Types, pp 106-7, Butterworth-Heinemann (1992)

(3) D.W. Breck and R.W. Grose, Molecular Sieves. (Advances in Chemistry, Series 121), pp 319-29, American Chemical Society (1973)



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