R3MEDIATE

21ST CENTURY IN-SITU SOLUTION FOR HYDROCARBON SPILLS

WHITE PAPER

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BACKGROUND & LITERATURE REVIEW

Hazardous wastes, toxic spills, contaminated water, contaminated soil, and pollutants are but a few of the environmental problems we face today all over the world. Since the late 1970's, great concern was expressed over the disposal of hazardous or toxic wastes. Common pollutants in soil and in water include asbestos, polychlorinated biphenyls ("PCB'), chlorinated hydrocarbons, petroleum products, pesticides, herbicides, and heavy metals. Most of these pollutants are man-made and have relatively long half-lives. Development and dissemination of such sophisticated and sensitive equipment as gas chromatographs, coupled with flame ionization and electron capture detectors, have allowed detection of pollutants with unheard of precision and accuracy (Rosenfeld & Feng, 2011).

Asbestos was used extensively prior to the 1980's to insulate structural steel and heating ducts, as a fibrous material in acoustical ceilings, in various applications on space heating and cooling units, in roofing papers, and in vinyl tiles adhesives (Dahlgren, 2016). Asbestos can be analyzed and identified rapidly and inexpensively by microscopic analysis. Removal of the asbestos from a contaminated site is possible, but the task is invariably expensive. Further, it is never the best solution if the job is not properly done.

PCB’s are widely used as insulation in electrical equipment, such as transformers and capacitors. If an electrical equipment contains PCB's, the equipment, its support platform, and the soil under and around the area most likely will contain these pollutants. The polymers are, to a certain extent, fire resistant. When they are burned, however, some toxic dioxin is formed as a by-product of the combustion, along with phosgene and hydrochloric acid. The toxic dioxin produced is the toxin reported in "Agent Orange.” PCB's biodegrade very slowly. Their very low vapor pressure precludes their loss to the atmosphere. Thus, cleanup of PCB's is particularly expensive since incineration is the normal method of decontamination of removed material (Zhao, et.al., 2015).

Chlorinated hydrocarbons have been widely used for at least five decades. These materials are used in paint thinners, paint strippers, degreasers, and 'dry cleaning' solvents. Chlorinated hydrocarbons generally include dichloromethane, chloroform, carbon tetrachloride, dichloroethanes, and others. Carbon tetrachloride is very toxic and when burned forms phosgene and hydrochloric acid. Chlorinated hydrocarbons have relatively high vapor pressure, and their density is greater than that of water. These solvents are very likely to enter soil and groundwater. These materials enter the soil rapidly and move downward as liquid. Decontamination soil containing this class of pollutants is usually done by excavation and gas extraction. (Ma, et.al., 2015) At one time, the decontamination was done by volatilization to atmosphere. Now, this old method is not considered acceptable in in most areas.

Petroleum hydrocarbon pollutants are common in virtually every area used by man.

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Petroleum products include crude oil, crude condensate, motor fuels, standard solvents, kerosene, and paint thinners. Benzene, a constituent of gasoline, is carcinogenic. A prevalent risk today is from leaking tanks. There is usually very little opportunity for degradation deep in the soil column or in an underground water column (Chapelle, Bradley, Lovley, O'Neill, & Landmeyer, 2002).
Pesticides and herbicides have been in general use since the early 1940's. They were used on farm crops, for right-of-way control, for forest management, and even for decorative management in houses and gardens. Pesticides are not only toxic but degrade slowly. Cleanup of these pollutants is exceedingly expensive (Fenster, et.al, 2006).

The most common heavy metal pollutants include lead, chromium, and mercury. Lead has been widely used in car batteries and paints. These heavy metals do not degrade because they are basic elements. Some, such as mercury, are, however, capable of biotransformation from inorganic to organic forms (Rajpert, Schaffer, & Lenz, 2018). One of the techniques to decontaminate such pollutants is adjustment of the pH. Oxidation and reduction actions are also used to decontaminate these pollutants.

Although not considered a pollutant, forest fires, oil-field fires and other fires are likewise hazardous. They are hazardous not only because of the damage they cause to the properties and materials, but also because of the gases generated by them (Schweizer, Cisneros, Traina, Ghezzehei, & Shaw, 2017).

HISTORICAL EX-SITU LIMITATIONS

For large scale decontamination of soil pollutants, one of the ways currently used is to excavate the soil, spread the soil out on a polyethylene film sheet, then allow the low boiling hydrocarbons to be released into the air. Afterward, the soil must be taken to a hazardous waste landfill or even transported to an incinerator where the remaining pollutants are burnt. In burning this soil, gases, some toxic, are released to the air. Even after this costly procedure, the remainder still may have to be deposited into a hazardous waste landfill.

Biological treatment of wastes has also been tried. In this method, the pollutants are exposed to some microorganisms. The method will fail, however, if the annual rainfall is high and the erosion potential is not minimal. Difficulties also arise when the technique is applied in a careless manner. It is thus clear that there is an urgent need for an effective pollution remedial composition.

The five commonly used techniques utilized in the process of remediating hydrocarbon contamination (microbes, hydrogen peroxide, persulfate, permanganate, and ozone as O3) have limitations to their effective use in certain "in situ" applications. These include altering the soil pH, soil temperatures, microbe cannibalism, and additional aquatic life threats. R3MEDIATE works differently to avoid these typical threats.

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R3MEDIATE SCIENCE

Rather than creating additional process problems and environmental threats, R3MEDIATE uses a combined approach, utilizing a uniquely designed reactive silica-based formulation to initiate a high-energy redox reaction, allowing it to react to hydrocarbon and trap the hydrocarbon within the silica cell. This “micro-encapsulation” renders the hydrocarbon both insoluble and immobile. Consequently, R3MEDIATE has been demonstrated to be safe in aquatic/marine environments, as well as land-based applications. Measured total petroleum hydrocarbon (TPH) concentrations may be effectively reduced to at or under regulatory guidelines, when applied correctly.

EPA APPROVED METHODOLOGY

In formal remediation projects, the United States Environmental Protection Agency (USEPA) has accepted and issued guidelines for clean-up technologies using chemical oxidation (USEPA, 2004). The overall issue is to identify what is being treated, the site factors, Chemical oxidation design, permitting issues, and a written performance monitoring plan. Over twenty years ago the USEPA reported chemical oxidation is an “innovative” technology to combat and treat hazardous waste in water, sediment and soil (USEPA, 1998).

Chemical oxidation involves reduction oxidation or REDOX reactions. In REDOX hazardous substances are converted to non-hazardous, less toxic and inert. The USEPA reports stabilization agents include soluble silicates and allows for in-situ remediation techniques and processes (USEPA, 2006).

INDEPENDENT STUDY OF SILICA ENCAPSULATION

Recent studies have evaluated the effectiveness of hydrocarbon remediation by a silica encapsulation (SE) technique. Medjor, Akpoveta, and Medjor (2018) conclude SE method are better remediation technologies than other chemical methods such as the Fenton Oxidative since it does not emit greenhouse gases. Other important observations related to the performance of silica encapsulation technology are: 1). Encapsulation is by silica, an economic and environmentally safe material whose physical and chemical characteristics resemble soil, provides a metal and hydrocarbon impermeable coating of the soil-sorbent mixture therefore exposure to the environment poses no threat to the environment. 2). Remediation is accomplished within a short period of time and with minimal environmental disturbance. 3). SE is effective in the acidic environment. 4). SE can be used to remediate the environment contaminated by both hydrocarbons and metals; and, 5). The silica coating is stable over a broad pH range; contaminants cannot be released even when the environment is subjected to harsh acidic and basic conditions.

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PROPRIETARY PATENT ANALYTICAL FINDINGS

	PPM CONTROL	PPM TREATED	RESULT
ENDOSULFAN RESIDUALS	54,410	95	-99.825%
BENZENE RESIDUALS	38,477	3,556	-90.758%
ETHYLENE GLYCOL RESIDUALS	37	0.1	-99.729%
TRICHLOROETHANE RESIDUALS	173	12	-93.063%
BENZENE	0.008	0.0004	-95.000%
TOLULENE	0.03	0.004	-86.667%
ETHLYBENZENE	0.01	0.001	-90.000%
M,P-XYLENE	0.027	0.004	-85.185%
0-XYLENE	0.017	0.003	-82.353%

R3MEDIATE FOR HYDROCARBON CONTAMINATED SOIL

Confidential client field trials and customer testimonials indicate R3MEDIATE effectively brings total petroleum hydrocarbons to at or under regulatory applications, when applied correctly. Base R3MEDIATE will effectively treat hard surfaces such as piping, rock and gravel as well as soil contaminated with substances up to the C6 level of the hydrocarbon chain. For hydrocarbons beyond C-7 and beyond; a proprietary formula is added to base R3MEDIATE to allow the hydrocarbon to be effectively reduced and allow for effective and efficient micro-encapsulation.

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FIELD CASES

WYOMING CALICHE PAD SITE (JULY 2019)

Client called with hydrocarbon release around wellhead and sporadic spot releases on pad. R3 Technicians arrived on location and observed black, oily, dirt around wellhead (Fig. 1) and spot releases or older oily releases around open area of the pad site (Fig. 3). The pad site was well-packed, caliche, and in good condition and well-maintained, excluding the oil releases mentioned.

R3 Technicians conducted tailgate safety meeting and proceeded to train third-party applicators and the client on R3MEDIATE processes and chemistry. Applicators began R3MEDIATE application and process. Figure 2 displays results seventy-two (72) hours post treatment while Figure 4 shows results a mere six (6) hours post treatment.

MIDSTREAM GAS PROCESSING PLANT (WEST TEXAS REGION, JULY 2019)

Client operates a gas processing plant in West Texas. The problem involved a hydrocarbon release causing significant hydrocarbon staining to the piping, soil, and gravel at the site (Fig. 5). R3 Technicians arrived and began a full-service R3MEDIATE Treatment after the required client safety orientation. After twenty-four (24) hours the surfaces display significant improvement with vast redox and subsequent micro-encapsulation of hydrocarbons occurring (Fig. 6).

FIELD SERVICE MIDSTREAM CLIENT (OKLAHOMA, JUNE 2019)

Client is a midstream client requiring field service secondary to a hydrocarbon release on soil and vegetation in Oklahoma (Fig. 7). R3 Technicians arrived on location and conducted required client safety orientation.

R3 Technicians began the R3MEDIATE application and process. Figure 8 details results only five (5) hours into the process. Significant redox reaction and encapsulation is present as evidence of the soil restoring to light brown from its original black, oily, sheen. Client placed additional order of the R3MEDIATE the same day as treatment for self-service within their processing plant. Corporate wide the client continues to order both full-service and self-service R3MEDIATE.

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CONCLUSION AND RECOMMENDATIONS

Chemical oxidation, which involves oxygen reduction or “redox reactions” are an approved in-situ remediation technology by the United States Environmental Protection Agency (USEPA, 1998, 2004 & 2006). R3MEDIATE uses a combined approach, utilizing a uniquely designed reactive silica-based formulation to initiate a high- energy redox reaction, allowing it to react to hydrocarbons and trap the hydrocarbon within the silica cell. This “micro-encapsulation” renders the hydrocarbon both insoluble and immobile. R3MEDIATE is safe, non-toxic, and safe in aquatic environments.

R3MEDIATE mitigates several limitations present in commonly used in-situ hydrocarbon remediation. When compared to ex-situ alternatives R3MEDIATE defers a significant amount of capital and also enhances safety conditions by eliminating personnel required, heavy equipment, and significant lease traffic.

For companies and service providers seeking innovative solutions; R3MEDIATE is recommended for good environmental stewardship via housekeeping scheduling, revolving preventative maintenance schedules and turnaround job tasks. With regard to formal remediation jobs; R3MEDIATE may be utilized as part of a formal work plan including site closure.

For technical and/or regulatory assistance; it is recommended utilizing R3 Industrial Cleaning Services, LLC third-party provider. R3’s third-party provider is a professional, contract research organization comprised of a highly diversified interdisciplinary team of solely P.E. (professional engineer), M.S. (masters) and Ph.D. (doctoral) degreed scientists. Their scope of expertise in a support role extends broadly for R3 Clients in both domestic and international markets.

R3MEDIATE SOIL-BASED APPLICATION PROCESS

The preferred method of application of R3MEDIATE is spraying. It can be applied with a power spraying system or even with garden type sprayers to effectively treat organic hydrocarbon contamination. Spray the product on the contaminated soils in atomized form. A fine mist spray nozzle is recommended to get a better distribution of chemical in contact with the oil. This also increases the presence of oxygen in the chemical processes which enhances its effectiveness.
Alternatively, oxygen can be brought into the process by the addition of aeration or by adding hydrogen peroxide to the formulation. For best results, agitation of the soil after spraying with product will:

Help promote direct contact with all of the contaminated soil, and increase the exposure to oxygen. In non-porous and/or heavily contaminated soils, it will be necessary to rake or till the soil to the level of the depth of contamination.

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Rain water will continue the activation of the R3MEDIATE by helping disperse the product throughout the soil and by the introduction of additional oxygen. Clay soil, being much denser and less porous than sandy type soils, will require more R3MEDIATE and more agitation than sandy soils to ensure complete contact of all of the contamination with R3MEDIATE.

As with any type of chemicals or processes used to remediate oil spills, follow-up testing such as for TPH levels will be required to positively determine the final results. However, as a quick indicator that the product is working, you can see a visible change in the contaminated area within a relatively short period of time (usually 24 to 72 hours) by a significant change of color of the treated area. For typical medium to heavy grade dark colored oil spills, the color will change from a dark black color to a light to medium brown color silicate, or sand like residue. Odors from the hydrocarbons will no longer be noticeable. Depending upon the level of contamination, it may be necessary to apply a second treatment.

Soil type, moisture content, temperature, as well as types and ages of the hydrocarbon contamination, will help determine the concentration and application rates, as well as time frame that the product works.

For heavy clay soils that are saturated with hydrocarbons and where the soil is dry; spray directly onto contaminated soil. Application rate will vary between 1.5 US gallons to 5 US gallons of R3MEDIATE per cubic yard of contaminated material, depending on the temperature, moisture level of the soil, type, and amount of contamination.

For sandy soils that are saturated with hydrocarbons and where the sand is dry; R3MEDIATE application rates will vary from 1 US Gallon to 3 US Gallons.

Mechanical agitation will be required to the depth of contamination in order to expose all the contamination to R3MEDIATE and to introduce oxygen to the process. This will assure the greatest effectiveness of the product.

R3MEDIATE HARD SURFACE APPLICATION PROCESS

For metal skids, piping, concrete, rock, and gravel the preferred application method is spraying. This enhances the action of oxygen in the chemical processes. Alternatively, oxygen can be brought into the process by the addition of aeration or by adding hydrogen peroxide to the formulation.

For oil dispersed on concrete or asphalt, i.e. parking lots or drive through service businesses, R3MEDIATE should be sprayed over the stained areas. For an initial application on outdoor hard surfaces that are laden with oil or other hydrocarbons, apply R3MEDIATE directly to the contaminated area.

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If outdoors, do not apply if there is a chance of rain within 2 hours of application.

R3MEDIATE needs time for the redox reaction to work. Allow the treated surface to sit until you see a white, flaky residue (Can be as little as 30 minutes on hot surfaces or very windy conditions). The surface will turn white indicating that the product is working. Agitation of R3MEDIATE and the hydrocarbons will assure complete contact when treating loose gravel or rocks. Once the surface turns predominantly white, the surface can be rinsed, or power washed as the hydrocarbons have been converted into a non-toxic compound.

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FIGURES

FIG. 1 – HYDROCARBON RELEASE AROUND WELLHEAD ON A CALICHE PAD SITE IN WYOMING (R3ICS, LLC. 2019 JULY).

FIG. 2 – SEVENTY-TWO (72) HOURS POST TREATMENT WITH R3MEDIATE. NO DIG & HAUL. NO NEW SOIL. WELLHEAD ON A CALICHE PAD SITE IN WYOMING (R3ICS, LLC. 2019 JULY)

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FIG. 3 – HYDROCARBON RELEASE ON OPEN AREA OF CALICHE PAD SITE IN WYOMING (R3ICS, LLC. 2019 JULY)

FIG. 4 – SIX (6) HOURS POST TREATMENT WITH R3MEDIATE. NO DIG & HAUL. NO NEW SOIL. HYDROCARBON RELEASE ON OPEN AREA OF CALICHE PAD SITE IN WYOMING (R3ICS, LLC. 2019 JULY)

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FIG. 5 – WEST TEXAS GAS PROCESSING PLANT. HYDROCARBON RELEASE WITH SOIL, PIPE & GRAVEL STAINING. (R3ICS, LLC 2019 JULY)

FIG. 6 – TWENTY-FOUR (24) HOURS POST TREATMENT WITH R3MEDIATE. WEST TEXAS GAS PROCESSING PLANT. HYDROCARBON RELEASE WITH SOIL, PIPE & GRAVEL STAINING. (R3ICS, LLC 2019 JULY)

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FIG. 7 – FIELD SERVICE MIDSTREAM CLIENT OKLAHOMA. PRE-TREATMENT HYDROCARBON RELEASE ON SOIL AND VEGATATION. (R3ICS, LLC. 2019 JUNE)

FIG. 8- FIVE (5) HOURS POST-TREATMENT FIELD SERVICE MIDSTREAM CLIENT OKLAHOMA. HYDROCARBON RELEASE ON SOIL AND VEGATATION. (R3ICS, LLC. 2019 JUNE)

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