

Evaluation of Quicklime Application as a Method of Treating Contaminated Soils

A Proposal Prepared for:
The Florida Department of Transportation

Project Manager: Curtis Barnes

FDOT Advisors: Terry Zinn and Luis Reis

Submitted by:
The Department of Environmental Engineering Sciences
University of Florida

1.0 Overview

Research is proposed to evaluate the use of quicklime to treat contaminated soil excavated during remedial activities. Field data gathered as part of remedial activities at a Department of Transportation (DOT) site in Alachua County found that the addition and mixing of quicklime to excavated soils resulted in the removal of several organic pollutants to levels below that required for cleanup. The dominant mechanism of pollutant removal (e.g. destruction, volatilization, entrapment in the soil matrix) was not identified. A limited amount of previous research indicates that quicklime addition does have remediation potential for some types of pollutants in terms of cost and performance effectiveness in comparison to many traditional soil treatment systems.

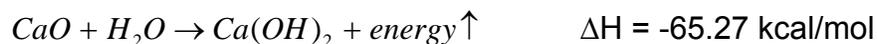
A two-phase research approach is proposed. In phase I, the extent of pollutant removal and the dominant mechanism(s) occurring during the quicklime treatment process will be examined. Soil samples collected from existing contaminated sites and clean soils spiked with various pollutants will be utilized. The effects of various design variables, including commercial quicklime type, loading amount and method, moisture content, soil type, and contaminant properties on pollutant removal by volatilization, chemical reaction, and entrapment in the soil matrix will be assessed. For some samples, concentrations of contaminants in the soil and vapor phase will be measured as a function of time. The resulting rates of transformation will be directly related to the design variables tested to determine an optimum treatment scheme. Phase II of this proposed work will be conducted at a pilot level in the field to further evaluate cost and feasibility of the quicklime treatment. Two sites will be chosen for the pilot study, and their selection will be based on performance of the soils during the laboratory feasibility studies, availability of the site for the phase II work, etc. Emphasis will also be placed on the ultimate disposition of the treated

soil, particularly in terms of any requirements for post-treatment (e.g., pH adjustment) and on the effects of the quicklime treatments on microbial populations.

2.0 Background

2.1. Quicklime: Production and Current Applications

Quicklime (CaO) is a high-pH mineral¹ produced by heating calcium carbonate (CaCO₃; limestone). Quicklime is frequently used in water treatment operations and in agriculture when pH control is needed. Quicklime reacts with water in an exothermic reaction to yield calcium hydroxide (Ca(OH)₂, sometimes referred to as hydrated quicklime), as shown below (Anthony et al., 2002):



Over time, Ca(OH)₂ may be “carbonated” by naturally occurring CO₂ to form limestone.

Quicklime is sometimes used to “treat” soils with high clay contents. The addition of quicklime can greatly improve soils of moderate-to-high plasticity. Modification occurs because the normally present cation adsorbed on the surface of the clay mineral is exchanged for the calcium cations supplied by the hydrated quicklime. Desired results of treatment of soils with quicklime include plasticity reduction, drying, swell reduction, and improved stability (NLA, 2002). At a number of sites, the process of adding quicklime to soils as part of remedial activities (to change physical properties of the soil) also resulted in the reduction in concentrations of pollutants. The addition of quicklime was shown to be successful in stabilizing liquid organics and heavy metals by the U.S. Army Corps of Engineers (Marion et al., 1997).

2.2 Observations at the Fairbanks Site

During a recent excavation of contaminated soils at the FDOT Fairbanks Site in Alachua County, FL, soils were remediated to below action levels by mixing with quicklime (WRS, 2002). The soils contained such contaminants as 1,1-dichloroethene, 1,1-dichloroethane, 1,1,1-trichloroethane, benzene, trichloroethene, toluene, tetrachloroethene, ethylbenzene, and *o*-, *m*-, *p*-xylenes. As soils were being excavated, they were power-screened by a trommel and placed in a lined pond awaiting vacuum extraction as a treatment step. When the excavation neared depth, the soil clay content increased, thus decreasing its ability to be effectively screened. Quicklime was added to improve the soil properties (physically) for screening and vacuum extraction, and an immediate temperature increase, caused by the exothermic reaction between the quicklime and moisture content of the soil, was noted. Soils were tested for contaminants

¹ pH = 10.5 – 12.4 depending on purity

of concern after mixing, and all were below action level concentrations. Soils that had been previously slated for vacuum extraction were mixed with approximately 5% quicklime until all the soil at the site was below action levels for the contaminants. Air monitoring for health and safety reasons indicated that workers were not exposed to contaminants through volatilization.

2.3 Results from Other Work

The addition of quicklime to soils was shown by the U.S. Army Corps of Engineers to stabilize liquid organics and heavy metals in contaminated soils (Marion et al., 1997). Although the quicklime did not change the chemical properties of the soils contaminated by solid organics (asphalt tar and pesticides), it did still improve the physical properties of the soils for potential reuse. Quicklime treatment of contaminated soils caused a major decrease in "TCLP-extractable" hydrocarbons, in which both volatilization and encapsulation may have played a role in the reduction of these compounds. Since results were not consistent among wastes, it was concluded that the specific nature of the wastes will play a role in the efficacy of quicklime to remediate wastes in the future.

2.4 Summary of Potential Benefits and Unknowns

The addition of quicklime to soils contaminated with organic pollutants has been shown to reduce the concentrations of many of these pollutants; however, field demonstrations have not successfully identified the dominant mechanism responsible for the reduction. Possible mechanisms that control contaminant reduction include (Sedlak et al., 1991):

- Volatilization of the chemical as a result of the increased temperature occurring during quicklime addition
- Enhanced abiotic destruction of the chemicals resulting from an increase in temperature
- Entrapment of the contaminants in the soil-Ca(OH)₂ matrix

Other unknowns are the resulting byproducts of conversion, their mobility and toxicity, the disposition of the treated soil for disposal, and the impacts of the treatment on the microbial populations present in the soil.

Quicklime addition may also prove beneficial for materials containing large-molecular organic compounds, such as asphalt, tar and similar petroleum-based materials. While limited previous work did not document significant destruction of these chemicals, the properties of the soils were favorably changed, and the concentrations of total petroleum hydrocarbons that leached were reduced (Marion et al., 1997).

Quicklime addition may be beneficial with respect to the mobility of heavy metals. Many heavy metals are amphoteric and highly soluble at very low and/or high pHs. The addition of quicklime may be used to adjust pH to a level where the metals are least likely to leach. Other minerals (e.g. Apatite II) have been shown to stabilize (through crystallization) metals such as uranium and lead for long periods of geologic time (Conca, 2000). Similar mechanisms may occur with quicklime as well. However, the long-term stability of this method and the effects of pH change by quicklime on the leachability of some metals are currently not well understood and, therefore, require further investigation.

3.0 Methods

The proposed research combines laboratory- and field-scale studies with the overall goals of 1) assessing the feasibility of quicklime addition as a cost-effective, efficient treatment scheme, 2) determining the dominant mechanism of contaminant removal by quicklime treatment, 3) optimizing the conditions for quicklime treatment of soils contaminated with pollutants representative of those present at DOT sites, and 4) assessing the disposition of treated soils in terms of the impacts of treatment on microbial populations and their readiness for disposal. Two phases are proposed to achieve these goals. Phase I will focus on laboratory testing, whereas phase II will be conducted in the field. Specifics of proposed activities in each phase are provided below. A project period of three years is proposed (18 months for each phase).

3.1 Phase I

3.1.1 Literature Review/Background Research

Past literature pertinent to the project will be reviewed and the researchers will keep current of any literature published or similar advances in research during the research period. People who have contributed or are contributing to this line of research (including Florida DOT (FDOT) personnel, U.S. Environmental Protection Agency (U.S. EPA) personnel, and Florida Department of Environmental Protection (FDEP) personnel) may also be directly contacted for further background research.

3.1.2. Laboratory Studies

Laboratory experiments will also be conducted in two components. The *first* component will employ batch studies to determine the degree of treatment efficiency of quicklime applied to different soil/pollutant combinations. The *second* component will utilize real-time experiments to assess the mechanism responsible for pollutant reduction (volatilization, abiotic destruction).

3.1.2.a Batch Studies. Batch experiments will be conducted on two types of soils samples: 1) clean soil spiked with known amounts of pollutant compounds and 2) soil samples collected from contaminated sites in Florida. The “clean” soils will be spiked trichloroethylene (TCE) and 2,2',4, 4'-tetrachlorobiphenyl

(TCBP). These test contaminants are chosen for their relatively large differences in properties (including vapor pressure, aqueous solubility, and octanol-water partition coefficient). Soil samples will be treated with various types of commercially available quicklime formulations to examine appropriate mixing rates, stability and fate of chemicals after mixing, and effects of different quicklime and soil types on contaminant removal. Soils and quicklime formulations will be tested for chemical and physical characteristics before treatment, and different mixing rates and methods will be examined for efficiency of removal of the test compounds (added at an average concentration present at contaminate sites) and possible metals (and other contaminants) present in the soil samples. A total contaminant concentration will be measured before and after treatment, and a leachable contaminant concentration will be evaluated after treatment, using an appropriate EPA-designed batch test, such as the Synthetic Precipitation Leaching Procedure (SPLP). Both solid and liquid samples will be analyzed for contaminants of concern, including various volatile organic compounds, polyaromatic hydrocarbons and total petroleum hydrocarbons.

Volatile organic compounds (VOCs) will be analyzed using US EPA SW846 method 5035/8260B. A 5.0 g sample will be obtained in a vial with a septum-sealed screw cap in either the field or in the laboratory. The sample vial will be spiked with an internal standard and surrogate mixture, heated to 40 °C in a hot water bath, and purged with an inert gas (helium) combined with agitation of the sample to trap volatile organic compounds onto an absorbent trap. When purging is complete, the trap will be heated and backflushed with helium to desorb the trapped sample components into a gas chromatograph for analyte separation and analysis by mass spectrometry.

Polyaromatic Hydrocarbons (PAHs) and Total Petroleum Hydrocarbons (TPHs) will be extracted from samples using US EPA SW846 method 3550B. A 30.0 g sample will be weighed into a 250-mL flask and mixed with anhydrous sodium sulfate to form a free-flowing powder. The sample will then be extracted three times with 100-mLs of a 1:1 (v:v) Acetone/Hexane mixture using an Ultrasonic extraction unit. The sample extract will then be concentrated to a volume of 1.0 mL using a Zymark Turbovap II sample concentration unit. Analysis will be performed using US EPA Method 8270C using a Finnigan Trace 2000 GC/MS.

3.1.2.b Focused Real-Time Studies The batch studies described above will provide a “before-and-after” view of the quicklime treatment process, specifically in terms of the effectiveness of this method using various soils taken from field sites, commercially available quicklime formulations, and different moisture contents. Ideal optimum mixing rates, quicklime content, and moisture content will be determined in this first phase, as observed by maximum contaminant removal from the soils. Real-time studies will then be performed in the second phase of laboratory experiments at the optimum conditions determined in the batch studies to assess the relative degree of the three different removal mechanisms: volatilization, abiotic chemical transformation under anaerobic or aerobic conditions, and entrapment within the soil-Ca(OH)₂ matrix. The ultimate

goal of this portion of the laboratory work will be to assess the dominant mechanism(s) of removal for each soil-quicklime type combination and to determine the impacts of this method on pH levels and microbial populations in the soil.

The system designed for this work will consist of a quartz flow-through reactor with ports for a thermocouple and dissolved oxygen (DO) probe to allow "real-time" measurement of temperature and pH in the soil-lime mixture throughout the experiments. Both probes will be connected to appropriate meters, which will then be connected to an A/D converter board (DAS08-PGL, Computer Boards, Inc., Mansfield, MA) attached to a computer that is equipped with Labtech Notebook software (Wilmington, MA) for visual display of real-time measurements. Continuous mixing will be performed at the rate observed as optimum in the batch studies. Inlet and outlet ports of the reactor will allow flow of an inert nitrogen gas stream that will be fed to a gas chromatograph for automated sampling and analysis of TCE or TCBP and any possible daughter products, including lesser-chlorinated ethenes or BPs resulting from reductive dechlorination processes (anaerobic) or oxidized products resulting from aerobic processes.

Real-time measurements of the contaminant and possible products, temperature, and DO will provide a strong indication of the dominance of volatilization or chemical reaction mechanism. If the former proves the dominant mechanism, it is anticipated that TCE or TCBP will be the primary product observed throughout the quicklime reaction time; however, if chemical reactions do occur, the relevant daughter products will be observed in the head space over time. Temperature values measured with time will provide valuable information on the temperature gradients that form with each soil type and quicklime type that will, in turn, provide an indication of optimum temperature (and time) for maximum removal of contaminant. DO measurements will provide existing conditions in the soil and will allow better prediction of the relevant daughter products from either anaerobic or aerobic chemical transformation processes.

Upon completion of each experiment, the soil will be sacrificed for measurement of leachable contaminant concentrations (measured as described previously). These results, along with the headspace concentrations, will provide a basis for determining the amount of pollutant entrapped, chemically transformed, and volatilized by using mass balance methods. pH levels of the various soils tested will also be measured and compared to initial values. Finally, the diversity of microbial populations present before and after testing will be assessed using genetic analysis. DNA from soils will be isolated using a commercially available soil DNA isolation kit (Mobio, Solana Beach, CA, USA). Polymerase chain reaction (PCR) will then be performed on the extracted DNA to screen for 16S rRNA sequences, which will be compared to those in known populations.

Results of the laboratory experiments will provide not only optimum mixing, quicklime loading, and moisture content levels but also an indication of the

dominant removal mechanism, as previously discussed. Knowing whether volatilization is the dominant mechanism will enable effective design of the pilot-scale process that will possibly include a gas-collection system.

3.1.3 Regulatory Feasibility

Quicklime has been recognized by regulators as a physical treatment option for soils, but it may not be as well recognized for its chemical transformations. As a part of this research, the appropriate governing agency (i.e., FDEP) will be contacted to determine the steps that would need to be taken in order to implement quicklime treatment of soils at a remediation site. This information will be documented so that the quicklime technology, when developed, may be applied at other sites throughout the state.

3.2 Phase II

3.2.1 Site-Specific Pilot-Scale Study

As previously discussed, a portion of soil samples tested in phase I of this work will be derived from contaminated sites. Two of these sites will be chosen for a pilot-scale field work, based on amenability of the soil to this treatment, the availability of the site, and ease of obtaining proper regulatory approval for this treatment. A portion of the soils at each site will be excavated and remediated with the quicklime using the method(s) developed and information obtained in phase I of this research. The site soil characteristics will be evaluated before and after treatment for total and leachable contaminant levels.

3.2.2. Site-Specific Feasibility

The feasibility of the quicklime treatment option will be further evaluated based upon the results of the pilot-scale study. The assessment of the treatment option will include: economic, logistical, and regulatory feasibility.

4 Personnel and Facilities

Dr. Timothy Townsend and Dr. Angela Lindner will serve as the investigators on the project. Dr. Townsend is an associate professor in the Department of Environmental Engineering Sciences at the University of Florida. His area of specialty is solid and hazardous waste management. Dr. Lindner is an assistant professor in the same department. Her research interests are bioremediation and pollution prevention. Ms. Jenna Jambeck, a Graduate Research Fellow in the Department will serve as a project coordinator and regulatory specialist. Ms. Jambeck's research areas include solid and hazardous waste management, policy and regulation.

Laboratory activities will be performed in the Department's Shared Analytical Laboratory Facility. The Department of Environmental Engineering Sciences Analytical Support Laboratory is housed in a total of 2258 sq. ft. in the New

Engineering Building on the campus of The University of Florida. Analytical instrumentation consists of a Finnigan Trace 2000 GC/MS equipped with a CTC A200S Autosampler for the analysis of extractable organic compounds, a Tekmar 3100 purge-and-trap concentrator attached to a Finnigan GCQ GC/MS for the analysis of volatile organic compounds, a Finnigan INCOS XL GC/MS equipped with an Entech 7000 microscale purge-and-trap concentrator for the analysis of volatile organic compounds in air samples, a HP 5890 GC/TCD for the analysis of methane and carbon dioxide in landfill gas samples, a HP5890 GC/ECD/NPD for the analysis of pesticides and herbicides, a Finnigan SSQ7000 HPLC/APCI/ESI for the analysis of polar and thermally labile compounds, a Hitachi 7000 HPLC/UV/Fluorescence for the analysis of carbamate pesticides, a Thermo Elemental Trace ICP/OES for the analysis of metals, a Dohrmann DC-190 TOC for the analysis of total organic carbon, a Braun & Luebbe AutoAnalyzer 3 for the analysis of nutrients, a CEM MarsX Microwave Sample Preparation Unit, and a Zymark TurboVapII Concentrator.

5 References

- Anthony, E.I., L. Ha, L. Cyr, B. Smith, and S. Burwell. 2002. The Enhancement of Hydration of Fluidized Bed Combustion Ash by Sonication. *Environ. Sci. Technol.*, **36**(20), 4447-4453.
- Conca, J.L., Lu, N., Parker, G., Moore, B., Adams A., Wright, J., Heller, P., 2000. PIMS - Remediation of Metal Contaminated Waters and Soils, Reprinted from the Proceedings of the Second International Conference on Remediation of Chlorinated and Recalcitrant Compounds, May 2000 with an Addendum from ICAM 2000, <http://www.pimsnw.com/apatite2/>.
- Marion, G.M., Payne, J.R., Brar, G. S., 1997. Site Remediation via Dispersion by Chemical Reaction (DCR), U.S. Army Corps of Engineers, Cold Regions Research & Engineering Laboratory, Special Report 97-18.
- NLA (National Lime Association), 2002. Construction and Building Materials, from the "Lime Facts" bulletin, <http://www.cimprogetti.it/Construction.PDF>.
- Sedlak, D.S.L., K.E. Dean, D.E. Armstrong, and A.W. Andren. 1991. Interaction of Quicklime with Polychlorobiphenyl-Contaminated Solids. *Environ. Sci. Technol.*, **25**(11), 1936-1940.
- WRS Infrastructure & Environment, Inc. 2002. Source Area Remediation Report for FDOT Fairbanks Disposal Pit, September 27, 2002.