Lecture 40

Nanotechnologies in Ground Improvement and Site Remediation

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1.Introduction
General

- In 1959, Richard Feynman, a professor at Cal Tech, introduced the to the world, the concept of nanotechnology in his lecture, “Plenty of Room at the Bottom,” (Feynman 1959).
- Nanotechnology is an emerging field. It is an interdisciplinary science whose potential has been widely touted for well over a decade.
- Nanotechnology, which deals with understanding and control of matter at dimension of roughly 100 nm and below, has cross-sectoral applications and orientations.
- At the commercial level, the impact of nanotechnology, is evident in three major industry sectors, viz., materials and manufacturing (coatings and composites for products like automobiles and buildings), electronics (displays and batteries) and health care and life sciences (pharmaceutical applications).
- A nanometer (nm) is one thousand millionth of a meter. A single human hair is about 80,000 nm wide, a red blood cell is approximately 7,000 nm wide, a DNA molecule 2 to 2.5 nm, and a water molecule almost 0.3 nm.

2. The Science and Technology of Nanotechnology

2.1 *How Nanotechnology Works*

- Nanotechnology is a technology for making things by placing atoms precisely where they are supposed to go.
- By organizing individual atoms and molecules into particular configurations, these molecular machines are able to create works of astonishing complexity and size, such as the human brain, a coral reef, or a redwood tree.
- Nature shows that molecules can serve as machines because living things work by means of such machinery.
- Enzymes are molecular machines that make, break, and rearrange the bonds holding other molecules together.
- The key to the application of nanotechnology will be the development of processes that control placement of individual atoms to form products of great complexity at extremely small scale.

2.2 What Nanotechnology Can Do

- Full-fledged nanotechnology promises nothing less than complete control over the physical structure of matter.
- Known as “assemblers,” these tiny devices would be capable of manipulating individual molecules very rapidly and precisely.
- According to a programmed set of instructions, a nanotechnological approach would be able to produce substances that conventional biotechnology could not.
- After performing their tasks, the devices may be induced to self-destruct, or remain in a surveillance mode, or, in some cases, integrate themselves into the body’s cells. Such devices would have dramatic implications for the practice of medicine, and for society as a whole.

3.Application of Nanotechnology

- The automotive industry will certainly be influenced by the development and implementation of nanotechnology. Due to the small size of nano-materials, their physical / chemical properties (e.g. stability, hardness, conductivity, reactivity, optical sensitivity, melting point, etc.) can be manipulated to improve the overall properties of conventional materials.
- Coolants utilize nanoparticles and nano-powders to increase the efficiency of heat transfer and potentially reduce the size of the automotive cooling equipment.
- Metal nanoparticles are being considered for potential use in catalytic converters since the catalytic reactivity would be significantly enhanced due to the increased surface area of the metal.
- Some manufacturers are currently using nano-magnetic fluids in shock absorbers to increase vibration control efficiency.
- Wear-resistant, hard-surface nano-coatings are being investigated for applications in bearings, cylinders, valves, and other highly stressed components.
- High efficiency nano-layers of semiconducting materials provide electronic components and systems with a longer lifetime.

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- Sensors based on nano-layer structures find applications in engine control, airbag, anti-lock brake and electronic stability program systems.
- Nanoparticles may also assist in the optimization of conventional components like batteries, catalysts, solar cells or fuel cells.

3.1 In Civil Engineering

(a) Concrete

Addition of nanoscale materials into cement could improve its performance,

- Li (2004) found that nano-SiO_2 could significantly increase the compressive for concrete, containing large volume fly ash, at early age and improve pore size distribution by filling the pores between large fly ash and cement particles at nanoscale.
- It has also been reported that adding small amount of carbon nanotube (1%) by weight could increase both compressive and flexural strength (Mann S, 2006).
- When the microcapsules are broken by a crack, the healing agent is released into the crack and contact with the catalyst. The polymerization happens and bond the crack faces.
- The selfhealing polymer could be especially applicable to fix the microcracking in bridge piers and columns. But it requires costly epoxy injection.

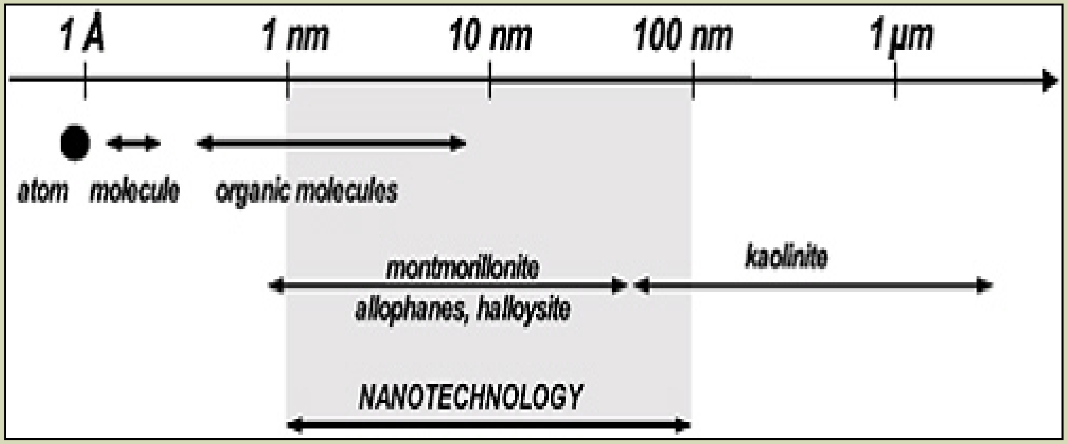
(b) Structural composites

- Sandvik NanoflexTM (NanoflexTM is new stainless steel with ultra-high strength, good formability, and a good surface finish developed by Sandvik Nanoflex Materials technology) is suitable for application which requires lightweight and rigid designs.
- Its good corrosion and wear resistance can keep life-cycle costs low. Attractive or wear resistant surfaces can be achieved by various treatments.

Applications in geotechnical engineering

- Although never considering themselves nanotechnologists, soil scientists and engineers, with their interest in the study of clay-size particles (< 0.002 mm), are among the earliest workers in the field of nanotechnology.
- Most material types and properties change with scale. For example, soil particles change in composition and shape from predominantly bulky quartz and feldspar to platy mica and clay over the range of particle sizes from sand and gravel down to silt and clay.
- A central challenge in geotechnical engineering is to understand the changes in properties and behavior in moving from large to small, whereas a central theme in nanotechnology is to take advantage of this transition and attain novel material performance through nanostructuring of new materials.

- Among the challenges to be met in introducing nanotechnology into geotechnical engineering is to be able to upscale the nano-level phenomena and process descriptions to the macroscale behavior, materials, and structures that are the usual end points of the engineer's efforts.
- The fundamental behavior of clays is a nanomechanics problem, suggesting that concepts and models developed in nanotechnology can provide new insights and enhanced understanding of the behavior of clay-size particles and, even more important, new means to manipulate or modify this behavior.



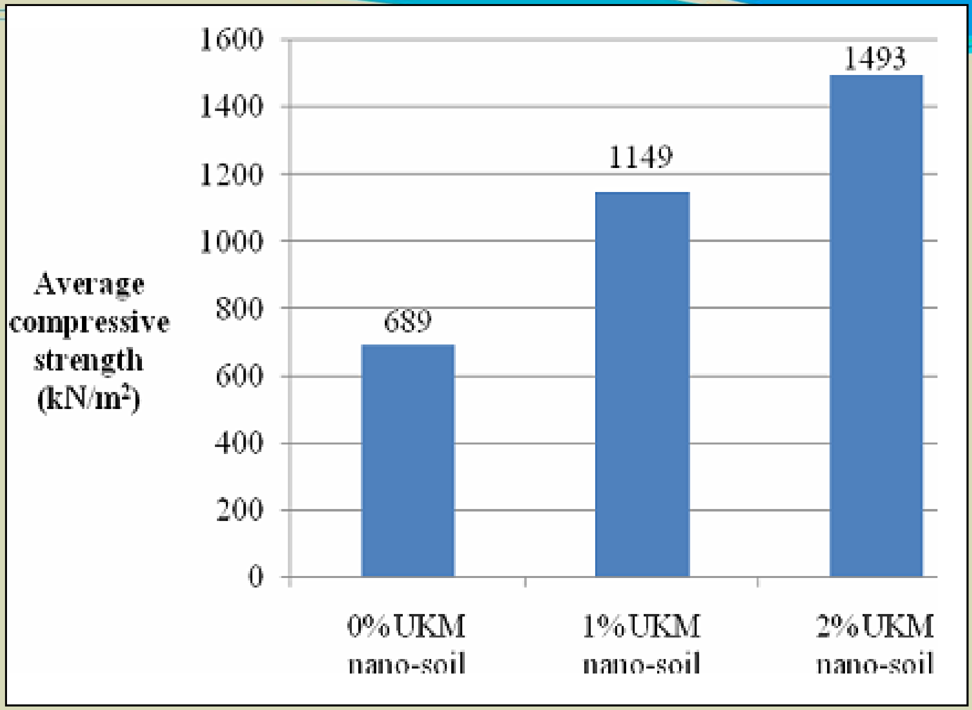
- Soil and rock are the world's most abundant and lowest-cost construction materials. In some states (e.g., dense, dry, and cohesive) they are strong and durable. In others (e.g., loose, wet, and soft) they are weak and unsuitable. Is it possible or even conceivable that new knowledge and the development of processes at the nanoscale may someday transform these materials in ways that can make them even more useful and economical?
- Developments in nanotechnology can aid in understanding the fundamental behavior of fine-grain soil at the particle level and lead to the development of engineered fine-grain soils. Readily available atomic force microscopes are now being used in mineral studies to explore local mineral variations in clays, such as surface charge and local hydrophobicity on mineral surfaces.
- Nanoparticles might also be engineered to act as functional nanosensors and devices that can be extensively mixed in the soil mass or used as smart tracers for in situ chemical analysis, characterization of groundwater flow, and determination of fracture connectivity, among other field applications.

- Two categories of soils have been investigated- 1. Normal Soil; 2. Nano-soil.
- Nano-soil: A product of milling of natural soil in which a greater portion of its particles are pulverized into nano sizes (1–100 nm)
- Additives are added to soft-clays and peat for soil stabilization because construction is impossible on these soils.
- Two criteria should be satisfied by any candidate material for soil improvement, viz. it should be inexpensive and non-toxic. Nano-soil satisfies both.
- Findings of laboratory experiments (carried out in accordance to BS 1377-1990) ('O' – Original soil; 'M' = Milled soil):

Test	Samples considered		Result when nano-soil is used
Atterberg Limits	100%O	98%O + 2%M	
Liquid Limit			Increases
Plastic Limit			Increases
Plasticity index			Decreases
Specific surface	See Fig. 1		Increases
Compressive strength	See Fig. 2		Increases

Table 1 Specific surface area of the soils

Kaolinite (m^2/g)		Montmorillonite (m^2/g)		UKM soil (m^2/g)	
Original	After milling	Original	After milling	Original	After milling
25.3	39.8	730.1	792.7	2.4	3.9



Study demonstrates that even a small addition of nano particles will show marked enhancement in soil behavior.
Reduction in Plasticity index has important implication in geotechnical engineering. This is because compaction of high plastic soils will generally results in high shrinkage upon drying.
Strength of soil-cement mixture almost doubled when 1% nano-soil was added.
Additionally, the soil with cement and nano-soil will have lower tendency for volume change and Plasticity Index in addition to increase in load bearing capacity.

4. Site Remediation

4.1 General

- For the next few decades, at the very least, many countries will be faced with serious issues regarding the cleanup of contaminated sites across the country.
- A number of contaminated areas await remedial action, and many still await identification.
- In the past ten years, emerging technologies such as phytoremediation, bioremediation, and permeable reactive barriers have become popular new tools. These novel treatments have begun to compete with more established technologies such as solidification/ stabilization, soil vapor extraction, and thermal desorption for soil, and pump and treat systems for groundwater (USEPA 2004).
- At the very forefront of these emerging technologies lies the development of nanotechnology for site remediation.

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- One emerging nanotechnology, nanosized zero valent iron and its derivatives, has reached the commercial market for field-scale remediation and studies.

4.2 Background

- Over the years, the field of remediation has grown and evolved, continually developing and adopting new technologies in attempts to improve the remediation process.
- In the early 1990s, the reducing capabilities of metallic substances, such as zero-valent iron (ZVI), began to be examined for their ability to treat a wide range of contaminants in hazardous waste/water (Zhang 2003).
- The most common deployment of ZVI has been in the form of permeable reactive barriers (PRBs) designed to intercept plumes in the subsurface and subsequently remediate them (USEPA 1998b).
- The first full-scale commercial PRB was approved for use in the State of California by the San Francisco Regional Water Quality Control Board (RWQCB) in 1994.

4.3 Technology overview

- Nanoscale Zero Valent Iron (nZVI) and Reactive Nanoscale Iron Product (RNIP) comprise the most basic form of the nano iron technology (Zhang 2003, Okinaka 2004).
- Particles of nZVI may range from 10 to 100 nanometers in diameter or slightly larger. Figure 1 shows transmission electron microscope (TEM) images of nZVI.
- The most common route to nZVI synthesis employs sodium borohydride as the key reductant .
- By mixing sodium borohydride (NaBH4) with $FeCl_3 \cdot 6H_2O$, Fe^{3+} is reduced according to the reaction scheme below:

$$Fe(H_2O)6^{3+} + 3BH_4 + 3H_2O \rightarrow Fe^0 + 3B(OH)_3 + 10.5H_2$$

(Wang 1997)

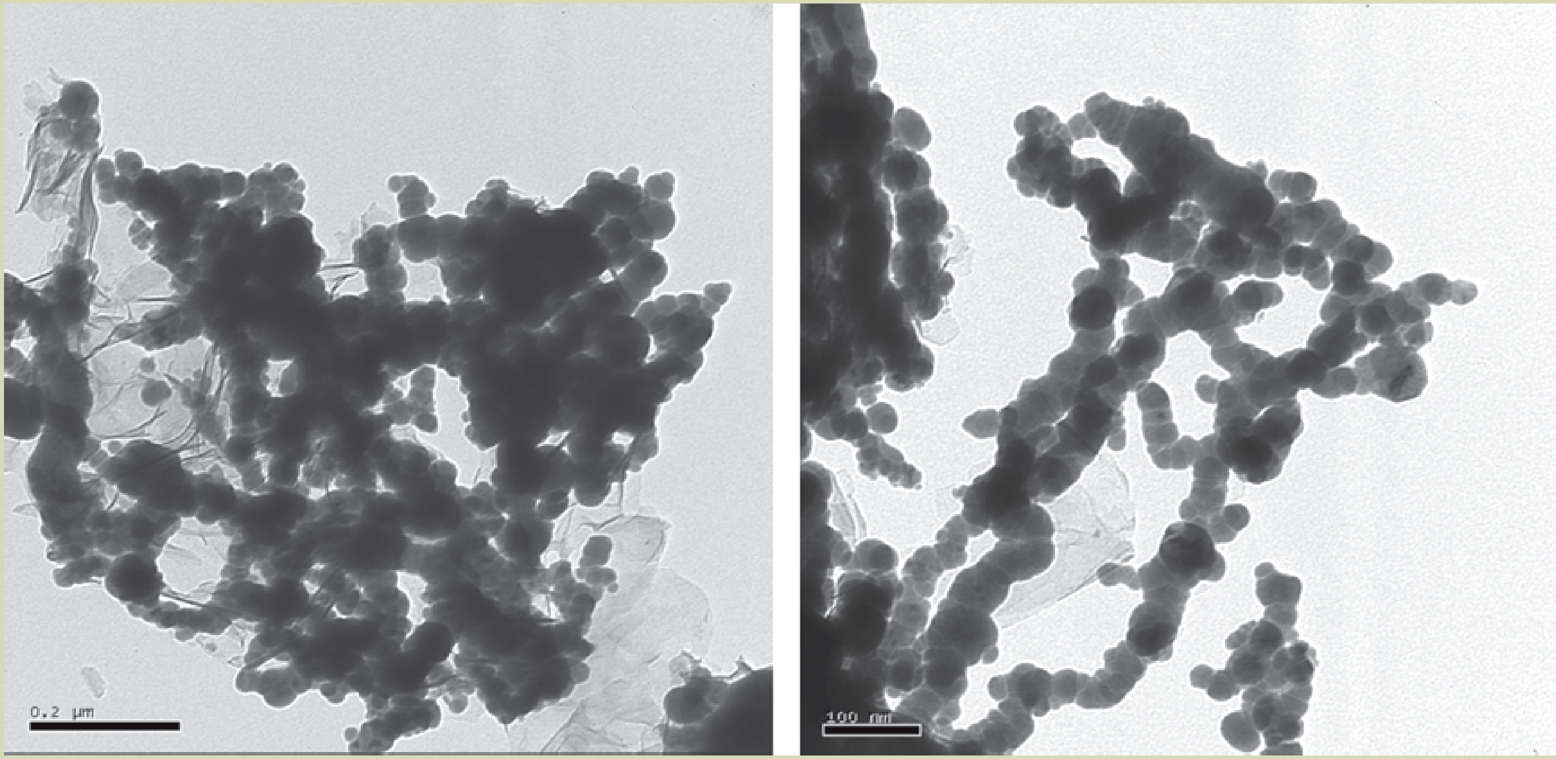

Figure 1: Transmission electron microscope (TEM) images of iron nanoparticles (Zhang, 2006b)

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- Following the reaction, the reduced particles of iron (Fe^0) created could be directly used for contaminant destruction.
- The stoichiometry of the reduction of trichloroethene (TCE) to ethane, a typical decontamination reaction, would proceed as follow:

$$C_2HCl_3 + 4Fe^0 + 5H^+ \rightarrow C_2H_6 + 4Fe^{2+} + 3Cl^-$$ (Elliott 2001)

- A recent study by Liu et al. compared the efficiency and degradation capabilities of nZVI synthesized using sodium borohydride reduction and the RNIP particles produced from ferrous sulfate.
- It was concluded, though, that the presence of boron and the shell thickness were the most likely explanations for observed differences in reactivity. The nZVI particles demonstrated rapid dechlorination of TCE and no deactivation; however rapid H2 evolution was observed.

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- Other methods of producing nanosized iron particles also have been developed.
- Ball milling represents another technique. In this process, micron-size iron powder is reduced to the nanoscale through an attrition or abrasion process using a ball mill (Liles 2004).
- A vacuum/gas condensation process also has been used to produce nanosized iron and other metals (Canano Technologies 2005).
- As with the addition of metal catalysts to nZVI particles, the formation of emulsified zero valent iron (EZVI) also represents an enhancement to the existing nZVI technology.

4.5 Remedial application

- The small particle size and high surface area to mass ratio make iron nanoparticles highly reactive and extremely versatile.
- The high surface area and surface reactivity compared with granular forms enable the nanoparticles to remediate more material at a higher rate and with a lower generation of hazardous byproducts .
- The ability of the nanoparticles to act as strong reducers also enables the remediation of an extremely wide range of contaminants.
- Table 1 lists many of the pollutants potentially remediated by nano iron.

Table 1. Contaminants remediated by nanoscale iron (Zhang 2003)

Carbon tetrachloride	Chrysoidine	*cis*-Dichloroethene
Chloroform	Tropaeolin	*trans*-Dichloroethene
Dichloromethane	Acid Orange	1,1-Dichloroethene
Chloromethane	Acid Red	Vinyl Chloride
Hexachlorobenzene	Mercury	PCBs
Pentachlorobenzene	Nickel	Dioxins
Tetrachlorobenzenes	Silver	Pentachlorophenol
Trichlorobenzenes	Cadmium	NDMA
Dichlorobenzenes	Bromoform	TNT
Chlorobenzene	Dibromochloromethane	Dichromate
DDT	Dichlorobromomethane	Arsenic
Lindane	Tetrachloroethene	Perchlorate
Orange II	Trichloroethene	Nitrate

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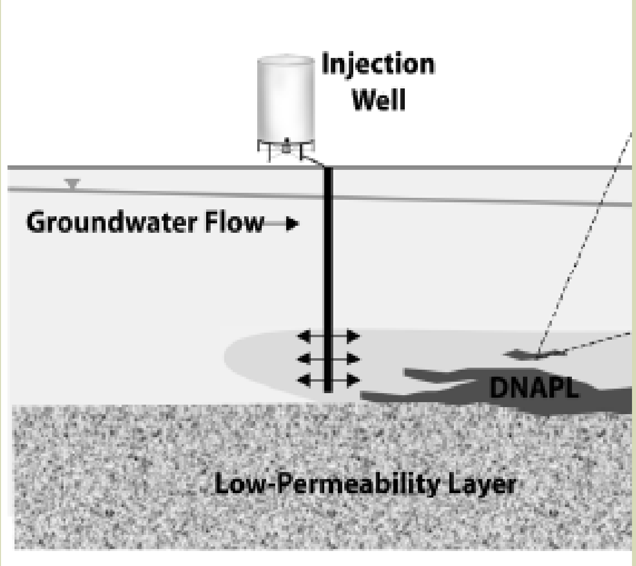
- In conjunction with nano iron's diverse group of target contaminants, the field scale deployment of the particles can be achieved in a variety of ways.
- Nanoparticles can be mixed with water to form a slurry that can be injected using pressure or gravity into a contaminated plume .
- Once injected, the particles remain in suspension, forming a treatment zone. Particles of iron also can be used in ex situ slurry reactors to treat soil, sediment, and solid waste.
- The injection of nano iron into the ground represents the most common deployment of this technology thus far.
- Overall the process provides a number of remedial benefits.
- Most importantly, this technique facilitates source zone remediation, a clear benefit for site cleanup.



Site remediation through inject process

4.6 Case Studies of Fate & Transport of Nanoparticles for Site Remediation

- Manufacturing Plant, Trenton, NJ

- This manufacturing plant synthesizes bimetallic particles , In order to achieve the bimetallic catalytic effect, iron and palladium are combined in a weight ratio of 1:300.
- The reactive catalyst coating is applied via the following reaction:

$$Fe^{0} + Pd^{2+} \rightarrow Fe^{2+} + Pd^{0}$$

- BNP material is introduced to the contaminated ground-water plume via injection wells, and the reactive agent is distributed throughout the target area via simple suspension in ground water.
- Monitoring at the piezometers suggests a significant discrepancy in migration rates of the plumes after BNP injection.

Klockner Road Site, Hamilton Township, NJ

- A patented BNP-based product known as NanoFe Plus™, developed by PARS Environmental, Inc., is used for remediation at the Klockner Road Site.
- PARS Environmental, Inc., reports that the reactive agent is administered in a water-based slurry containing one pound of reactive material in each 3.994 gallons of solution.
- Currently, little information is available on the fate and transport of NanoFe Plus particles in the subsurface environment at this site.
- The injection phases and quantities of the injections are known, and two monitoring sessions are scheduled to take place after two injection phases.
- Monitoring will be conducted to determine the amount of dense nonaqueous-phase liquid reduced by the nanoscale iron

NASA Launch Complex 34, Cape Canaveral, FL

- This site is well known for its historical use as a launch pad for shuttle craft and other space-bound vehicles using rocket propulsion.
- Typical with the use of rocket fuel, chlorinated compounds such as TCE (trichloroethylene) exist in the site's ground water, soil, and sediment.
- Three methods of administering NZVI will be field-tested at Launch Complex 34 as alternatives to the direct-injection method:

- Pressure pulsing : Pressure pulsing involves forced administration of NZVI particles to various and relatively predictable subsurface depths.
- Pneumatic fracturing : Pneumatic fracturing employs compressed air to create subsurface crevices and small pathways that facilitate distribution of the reactive medium.

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- Hydraulic fracturing : In a way similar to pneumatic fracturing, hydraulic fracturing uses high-pressure liquids to enhance reagent distribution in the subsurface.
- Typical changes in concentration reductions in the area of NZVI injections are shown in Figures,

(a)NAPL injected

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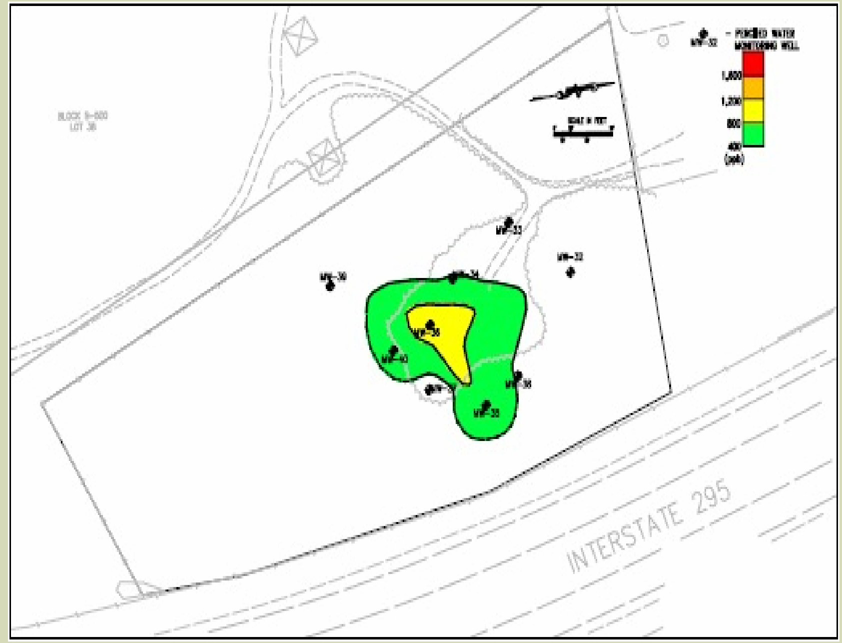
(b) Two weeks post injection



(c) Four weeks post injection

USEPA (2004)

4.7 Understanding the results

- Preliminary results in the case studies indicate that NZVI-based technology has potential as a means of site remediation.
- When accompanied by sound environmental safeguarding, the technology may prove to be safe and reliable.
- Remediation technology developers need to recognize that the release of synthesized materials with complex multi-molecular nanoscale structures will generate questions concerning potential ecological and environmental threats.
- Based on the information available, the current methods of nanoscale site remediation do not appear to pose a threat to humans and the environment (Beshoy Latif).

4.8 Limitations

- Site-specific conditions such as the site location and layout, geologic conditions, concentration of contaminants, and types of contaminants maylimit the effectiveness of nanoparticles.
- The research conducted for two sites that have used nanoparticles in fractured bedrock, although several pilot studies have been undertaken (Macé, 2006).
- Prior to injection of nanoparticles, geologic, hydrogeologic, and subsurface conditions should be evaluated to determine whether injected particles would have adequate subsurface infiltration.
- Factors that affect subsurface mobility include composition of the soil matrix, ionic strength of the groundwater, hydraulic properties of the aquifer, depth to the water table, and geochemical properties.
- Studies have shown that nanoparticles may not achieve widespread distribution in the subsurface due to agglomeration prior to complete dispersion within the soil or groundwater matrix, limiting the radius of influence.

5. Further Research Needs

- Specific research is needed to:
- Assess the extent to which nanotechnology implications reach soil and water systems beyond immediate application areas.
- Evaluate the potential impact of nanoparticles of specific and immediate environmental media.
- Determine whether, and the degree to which, nanoparticles may travel through the food chain; preliminary research already indicates that some nanoparticles may be taken up by bacteria in trace amounts.
- Examine the uptake of nanoparticles in animal species.

6. Cost

- Factors contributing to the costs include site type, type of contaminants, concentrations of contaminants, and any challenges that may have occurred during remediation.
- Additional factors that may increase the total cost of nanoparticles application may include operational requirements connected with any contamination found underneath a building, or the need to treat or dispose extracted fluids (Wilson, 2004).

7. Implementation in India

- Nanotechnology in India is a government led initiative. Industry participation has very recently originated.
- Enabling energy storage, production and conversion within renewable energy frameworks (solar heater).
- Enhancement of agricultural productivity through pesticides.
- Nanotechnology is slowly implementing in medical field, textile industry.
- Sectors such as health, energy and environment have received greater attention by various technology departments in the government (DST, DBT and SERC).

Conclusions

- Though the implementation in field is difficult(depends on site condition), but nanotechnology promises as safe and fast site remediation process.
- When accompanied by sound environment safeguarding, the technology may prove to be safe and reliable.
- Nanotechnological approach would be able to produce substances that conventional biotechnology could not.
- This technique facilitates source zone remediation, a clear benefit for site cleanup.

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