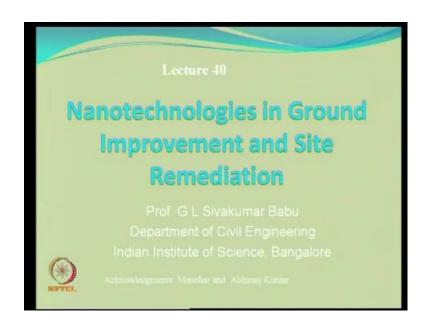
Ground Improvement Prof. G. L. Sivakumar Babu Department of Civil Engineering Indian Institute of Science, Bangalore

Lecture No. # 40

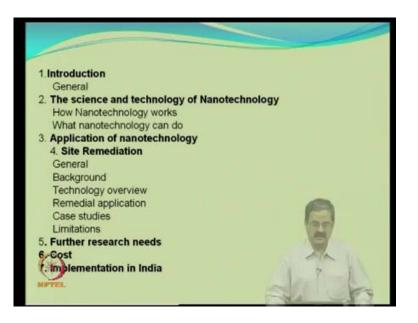
Nano-Technologies in Ground Improvement and Site Remediation

This is the fortieth lecture of the course, on ground improvement and geosynthetics and in fact, I am very happy that I would be talking about a new topic today, nanotechnologies in ground improvement and site remediation.

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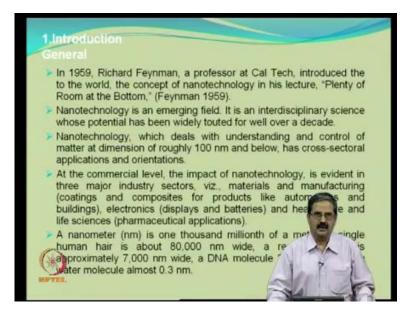
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We are all aware that, this the the nanotechnologies have made a significant difference sand people have been talking about ,the use of these technologies in the many areas of science and engineering, and definitely ground improvement is not an exception..

So, I would be trying to cover some introduction, the science and technology of the nanotechnology, the applications, particularly some geotechnical considerations and also how it can be very useful in ground improvement, and what is the research in its and what are the implications.

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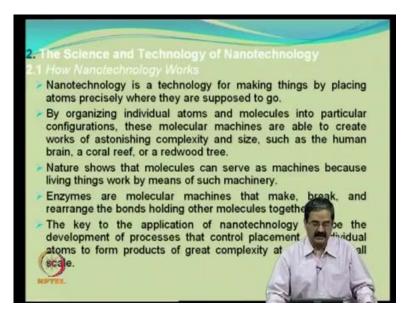
The, this technology of this technology of nanos ,are the finest, they will the finest materials, have the finite materials in that sense: has been initiated, when Richard Feynman a professor at Cal Tech introduced this ah, to this world the concept of nanotechnology, where he talked about the plenty of room at the bottom, and we are all aware that nanotechnology is an emerging field and it is an interdisciplinary field where it has lot of potential, for interdisciplinary and a cross-sectoral applications.

In some cases it deals with understanding control control of the matter at the finest dimensions roughly of the order of 100 nm, and below, and if you look at commercial aspects, major industries like materials, manufacturing and composites of products, for products, are taken big lead in this even electronics, particularly the nano electronics has been a well received area, health care and life sciences are also, me more applications.

And nanometer is nothing but, a one thousand millionth of a meter. So, if you want to understand what it means ,a as a human hair is about 80,000 nm wide, a red blood cell is about 7,000 nm wide ,and a DNA molecule is about 2 to 2.5 nm and the water molecule is about point 0.3 nm.

So, you can see that ,ah whatever dimension that we are thinking about particularly at the finest for the very very fine scales ,one can express in terms of the nano's, and the way that it works is that, is a technology for making things by placing atoms atoms precisely where they are suppose to go.

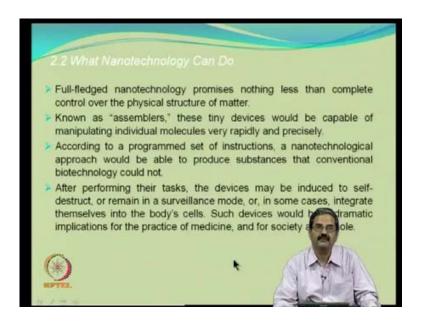
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By organizing individual atoms and molecules into a particular configurations, these molecular machines are able to create works of astonishing complexity in size, such as human brain, a coral reef, or a redwood tree.

You can really create something different or something same or new or whatever. So, 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 bonds holding other molecules together. So, the key to application of the nanotechnology will be the development of processes that control placement of the individual atoms to form products of great complexity at extremely small scale.

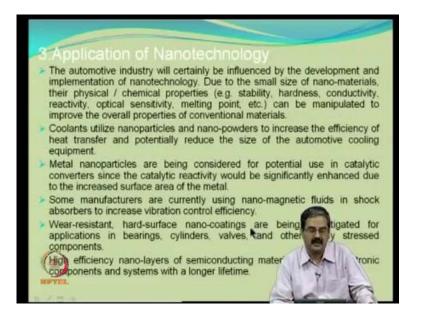
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What nanotechnology can do? You know a Full-Fledged nanotechnology promises nothing less than complete control over the physical structure of the matter this is something astonishing and amazing known as "assemblers" these tiny devices would be capable of manipulating individual molecules very rapidly and precisely.

According to a program set of instructions, a nanotechnological approach would be to produce, substances that conventional biotechnology could not .After performing the tasks, these devices may be induced to self destruct, or remain in 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 the society as a whole.

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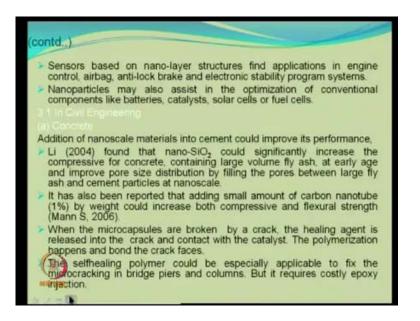


The Applications of Nanotechnology ,the automotive industry will be certainly be influenced by the development and implementation of nanotechnology. Due to a small size of the nano-materials, their physical / chemical properties like stability, hardness, conductivity, reactivity, optical sensitivity, melting point, etc can be manipulated to improve the overall properties of the conventional materials.

Coolants utilize nanoparticles and nano-powders to increase the efficiency of the heat transfer and potentially reduce the size of the automotive cooling equipment. Nanoparticles of metals 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 nano-magnetic fluids in shock absorbers to increase the vibration control efficiency. Water-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 long lifetime.

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Sensors are being used, and they based on nano-layer structures finding applications in engine control, airbags, 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.

So when it comes to civil engineering they are they have been useful in concrete there is some research that is being done addition of nano scale materials to cement could improve its performance, for example, Li found that nano SiO_2 could significantly increase the compressive strength of concrete containing large volume fly ash, at an early stage improve pore size distribution by filing the pores between the large fly ash and cement particles at nanoscale. It has been reported that adding a small amount of carbon nanotube by weight say for example, 1 percent could increase the both compressive and flexural strength. When the microcapsules are broken by crack, the healing agent is released into the crack and contact with the catalyst. This polymerization happens and they bond and they and they bond the crack faces.

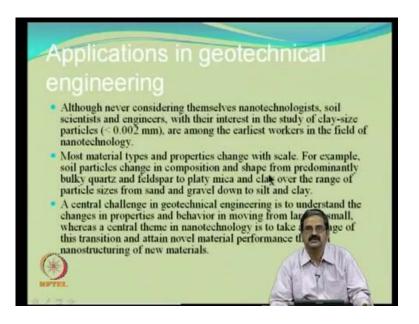
So, the self healing polymer could be especially applicable to fix the micro cracking in bridge piers and the columns but, it requires costly epoxy injection. So what I would like to say is that the nanoscience nanomaterials say for example, in nano SiO2 could definitely increase the strength of the concrete stiffness of the concrete, it can be used for you know crack healing as well ah where its required.

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And when you try to think of steel, there is a material called Sandvik Nanoflex TM, which is something a new stainless steel material with ultra-high strength, good formability, and a good surface finish finish developed by Sandvik Nanoflex Materials technology. It suitable for applications which requires lightweight and rigid designs. It has good corrosion and wear resistance and can keep life-cycle costs low. Alternatively Attractive or wear resistance surfaces can be achieved by various treatments.

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So, what do we do in geotechnical engineering, this is a very interesting to observe that in geotechnical engineering or even in soil scientists they have though they themselves do not call them as nano themselves as nanotechnologists, people who are trying to we have people who are trying to study the clay size particles (<0.002 mm), and and this has been there for more than thirty forty years and they are among the earliest workers in the field of nanotechnology.

So, that way I must say that geotechnical engineering has started the area of nanotechnology quite long back whereas, others could do it in the recent times most material types and properties change it with scale. In geotechnical engineering, for example, soil particles change in composition shape from predominantly bulky quartz and feldspar to platy mica and clay over a range of particle sizes from sand and gravel down to silt and clay.

So the challenge in geotechnical engineering is to understand the changes changes in properties and behavior in moving from large to small, whereas, the central theme in nanotechnology is to take advantage of this transition and attain novel material performance through nanostructuring of new materials.

So, there is a an interesting difference here that, you are trying to manipulate the structure of the materials and by using this nano particles and so for this one needs to understand the various particle sizes that are available in nature in soils.

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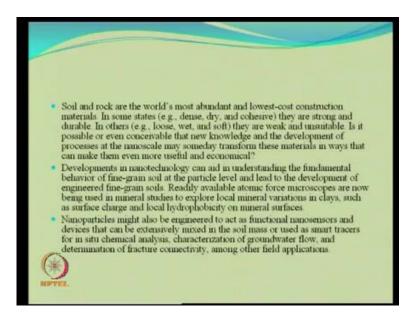
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The challenge as I just mentioned is to what you see observe in nanolevel needs to be upgraded to processes and physical phenomena that occur at macro scale behavior, and materials, and structures that are usually the end points in the engineer's efforts.

So, the fundamental behavior of clays is a nanomechanics problem, as I just mentioned suggesting that the concepts and modules developed in nanotechnology can provide new insights and enhanced understanding of the behavior of clay-size particles and, even more importantly, new means to manipulate or modify the behavior.

You can see that here, that 1mm and less than hundred nanometers if you take definitely you have materials like montmorillonite, allophones, hallow sites, organic molecules, and some of them are already there. So these these people have been using in geotechnical engineering practice particularly in the area of geo environmental engineering to modify the soil properties.

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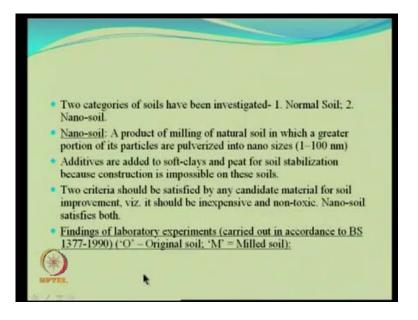


Soil and rock are the most abundant and lowest-cost construction materials and in some stages like dry, dense, and cohesive states they are strong and durable. In other cases loose, wet, and soft they are weak and unusable or unsuitable. Is it possible or even conceivable that the new knowledge and the development of process 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 be used in mineral studies to explore local mineral variations in clays, such as surface charges and local hydrophobicity on mineral surfaces.

And nanoparticles might also be engineered to act as functional nanosensors and devices, that can be extensively mixed in soil are used as smart tracers for the in-situ chemical analysis characterization of groundwater flow and determination of fracture connectivity among other field applications.

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There is a small example in literature in one of the case studies from in literature and they have just taken two types of soil. One is the normal soil, one is a nano-soil. Nano-soil is nothing but, a product of milling of the natural soil with a greater portion of its particles are pulverized into nano sizes 1-100 nm.

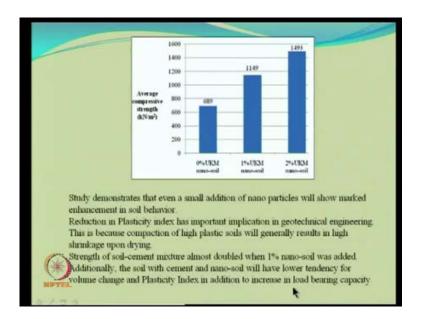
Additives are added to soft clays and peat for stabilization because construction is impossible with these soils. So the two criteria should be satisfied to any candidate material for soil improvement, one it should be non-toxic and also inexpensive and nanosoil satisfies both and the, in one of this papers its indicated that, the liquid limits, plastic limit and plasticity. If you add liquid limit increases definitely, it is about known well that you know they are much more final particle so the surface area increases so liquid limit increase plasticity also increases.

Test	Samples con		Result when nano- soil is used	
Atterberg Limits	-			10106
Liquid Limit	- Annalese		Increase	8
Plastic Limit	100%+0	98%60 + 2	16H Increase	HS .
Plasticity index			Decrease	Decreases Increases
Specific surface	See Fig. 1		Increase	
Compressive strength	See Fig. 2		Increase	15
Kaninže (n ² ig) Original	sariace area of the soils Montor (te ² ig) After Original milling	Acnite UX (m ¹	M sol B) ginul After miller	

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But on other hand plasticity index which is a difference between liquid liquid limit minus plastic limit decreases and specific surface also you can see that its increases and compressive strength also increases that is an important point like you have a kaolinite clay which is the original specific surface 25.3 meter square per gram after milling it has increased to 39.8 and for example, original montmorillonite it is about seven thirty mili square square meters per gram. After milling the same increases to 792 and if you add the original soil you know the for example, you have taken a original soil it is about 2.4 after milling it has become increased to 3.9.

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Now, when you look at the impact of this nanoparticle addition to the soil, you can see that, the average compression strength is in range of 689 kilo Newton per meter square when there is no nano soil but, then if it is one percent it is increased to 141149 and then with two percent it is increased to 1493.

So what it shows is that, a small study, the small addition of the nanoparticles show a marked increase in strength response and reduction plasticity index is another important useful contribution and because we expect that plasticity less plasticity means less problem.

So strength of the soil cement mixture almost doubled when 1 percent nano-soil was added and additionally, soil with cement and nano soil will have lower tendency for volume change and plasticity index in addition to increase in load carrying capacity. So, this is an useful thing.

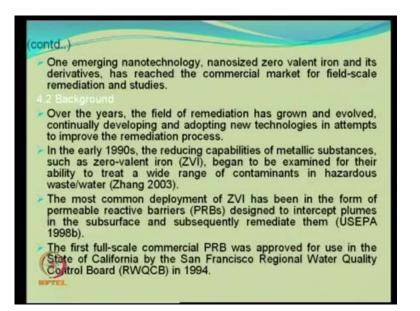
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But, as you just mentioned this area of nanoscience and technology has has been being a perceived in more in the area of site remediation because of the impact it has , because many countries have lot of contaminated sites which need to be cleaned up.

And in the past ten years, emerging technology such as phytoremediation, bioremediation, permeable reactive barriers have become popular new tools. These novel treatments have begun to compete with more established technology such as solidification / stabilization, soil vapor extraction, and all that. And off course, forefront of these methods emerging technologies is a development of nanotechnology for site remediation.

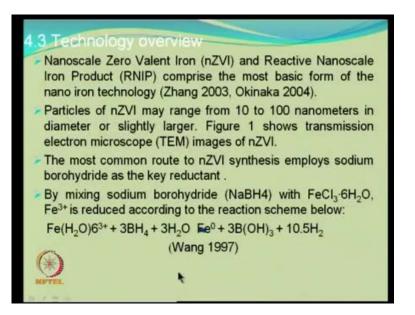
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One emerging nanotechnology, nanosized zero valent iron iron and its derivatives, has reached the commercial market for field-scale remediation and studies. I I will give a big big small background in this. Over the years, the field of remediation has grown and evolved, continuously developing and adopting new technologies in attempts to improve the remediation process.

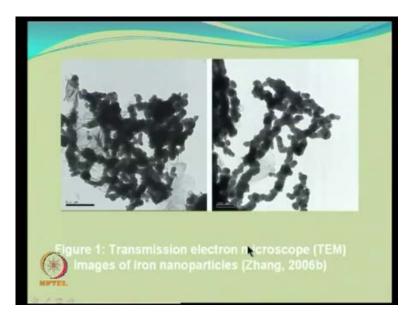
In the 1990's, the reducing capabilities of metallic substances, such as zero-valent iron (ZVI) began to be examined, for their ability to treat a wide range of contaminants in hazardous waste /water .The most common deployment of ZVI you know, zero-valent iron has been in the form of permeable reactive barriers (PRBs) designed to intercept plumes in the into the surface and subsequently remediate them. The first full-scale commercial PRB was approved for use in the state of California by the san Francisco Regional Water Quality Control Board.

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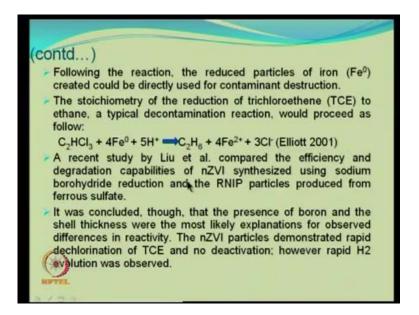
And the way that, the technology works is that Nanosize Zero-Valent Iron valent iron and the Reactive Nanoscale Iron Product comprise the most basic form of the nano iron technology. Particles of nZVI may range from 10 to 100 nanometers in diameters or slightly larger. And figure 1 shows the transmission of electron microscope images that I will show. The most common route to nZVI synthesis employs sodium borohydride as a key retardant reductant. So, by mixing sodium borohydride with ya this FeCl3 6H2O,and iron ferric the ferric ions are reduced according to the reaction that, we have here in this form.

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And, you can see in this, figure that the way that am the images are there and following this reaction, the reduced particles of iron created could be directly used for contamination contaminate destruction.

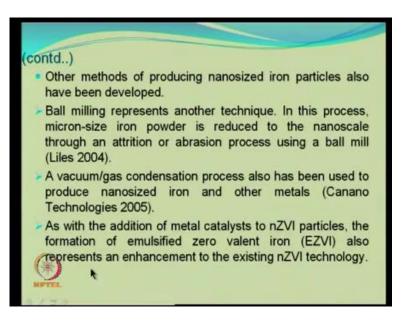
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So you have stoichiometry of the reduction of the TCE trichloroethane to ethane a typical decontamination reaction would proceed, this is a chemical reaction that we have and a recent study by Liu et al compared the efficiency and degradation capabilities of nZVI synthesized using sodium borohydride reduction and the RNIP particles produced from ferrous sulfate.

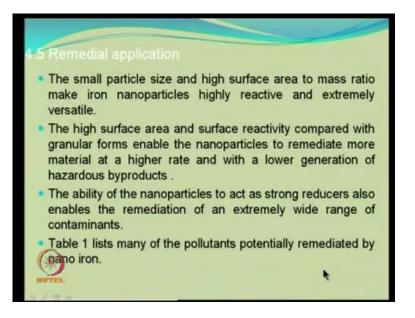
It was concluded though that the presence of boron and the shell thickness were the most likely explanations for observed differences in reactivity. The nZVI particles demonstrated rapid dechlorination of the TCE and no deactivation; however rapid H2 evolution was observed.

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So, 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 nanoscale through an attrition or abrasion process using a ball mill that is what I give an example just now how a milled material can increase the strength of the soil. A vacuum/gas condensation process has also been used to produce nanosized iron and other materials or metals. As with the addition of metal catalysts to nZVI particles, the formation of emulsified zero valent iron also represents an enhancement to the existing nZVI technology.

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So, the applications the remedial applications is that, the small size particle size and high specific area to mass ratio make iron nanoparticles highly reactive and extremely versatile. The high surface area and the surface activity compared with the granular forms enable the nanoparticles to remediate more material at higher rates and with a lower cons generation of hazardous hazardous products.

The ability of the nanoparticles to act as strong reduces also enables the remediation of extremely wide range of contaminants. So, the table one which I will show now has that one what are the contaminates that can be remediated by nanoscale iron. You have a number of contaminates here Carbon tetrachloride, Chloroform and DDT, orange II many things Mercury, Nickel, Silver, Cadmium all all of these contaminates PCB's, TNT's all that .You have a whole range of applications here.

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Table 1. Contam	inants remediated l	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	
Chlorobenzene	Dibromochloromethane	Dichor
DDT	Dehlorobromomethane	Ar
Lindane	Tetrachloroethene	
Orange II	Trichloroethene	

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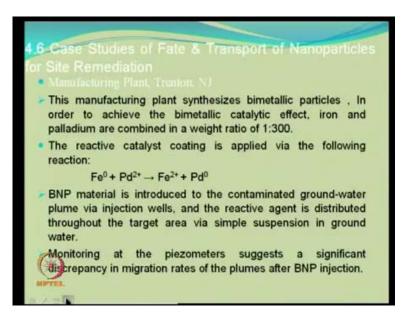


So, in conjunction with nano iron's diverse group of target contaminats, the field scale of may deployment of the particles can be achieved by varieties of ways. Nanoparticles were mixed with water to form a slurry that can be injected using pressure or gravity into a contaminated plume.

Once injected, the particles remain in suspension, forming a treatment zone. Particles of iron can also be used as ex in ex situ slurry reactors to treat soil, sediment, and solid waste. The injection of the nano iron into the ground represents the most common deployment of this technology thus far like this injection well you have and if there is a contamination plume it can have a barrier reactive barrier like this.

Overall the process provides a number of remedial benefits. Most importantly, the technique facilitates source zone remediation, which is a very important a clear benefit in the case of site cleanup.

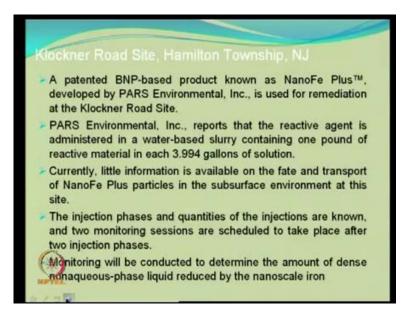
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A few case studies here in the Case Studies of the Fate and Transport of a Nanoparticles for Site Remediation it is in manufacturing plant trenton new jersey. This manufacturing plant synthesizes bimetallic particles, in order to achieve the bimetallic catalytic effect iron and palladium are combined in the ratio of weight ratio of 1:300.

The reactive catalyst counting is applied via the following reaction: you have the reaction here. 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 ground water. Monitoring at the piezometer suggests the significant discrepancy in migration rates of the plumes after the BNP injection.

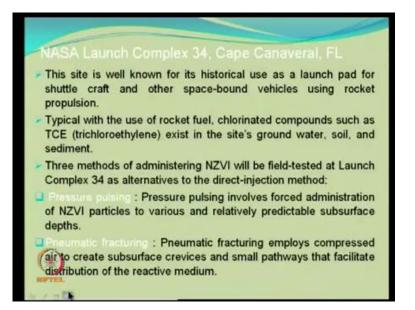
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A patented BNP-based product known as NanoFe $plus^{TM}$, developed by one company pars internationally international is used for remediation at the Klockner Road Site. PARS Environmental, Inc., Reports that the reactive agent is administered in a water-based slurry containing one pound of reactive material in each about four gallons of solution.

Currently, little information is available on the fate and transport of the NanoFe Plus particles in the subsurface at the site. The injection phases and quantities quantities of injections are known, and two monitoring sessions are scheduled to take place after the two injection phrases phrases. So, monitoring will be conducted to determine the amount of dense nano aqueous-phase liquid reduced by the nanoscale iron.

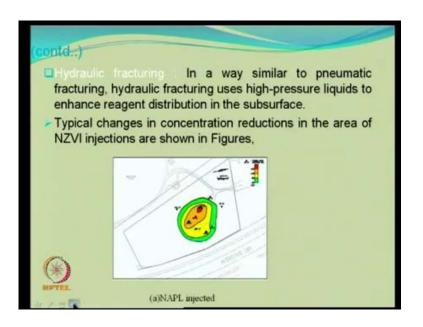
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So ,efforts are being done on this but, now I tell as one should understand that yes it has been attempted in the field and there is a case study available to understand may be one should just take the update from the company itself, and what is going to happen what is happening at the site. The other one was the NASA Launch Complex in the florida cape canaveral the site is well known for its historical use. Typical with the use of rocket fuel the chlorinated compounds such as TCE this is a contaminate exist in the site's ground water soil and sediment.

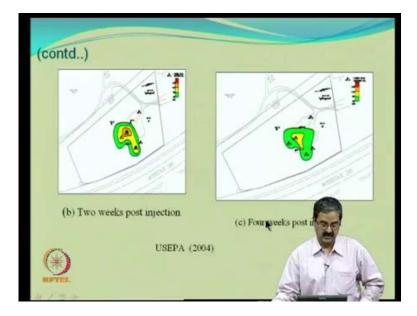
So, three methods of administering NZVI. I will will be field-tested at the large complex as alternatives to the direction direct injection method. One is the pressure pulsing the pressure pulsing involves forced administration of NZVI particles to various and relatively predictable subsurface depths. 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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So, another one is the hydraulic fracturing: In a way similar to pneumatic pneumatic fracturing, hydraulic fracturing uses high-pressure liquids to enhance reagent distribution in the subsurface subsurface.

Typical changes, in concentration reductions in the area of NZVI are shown in the figures, like you can see that there is some concentrations here NAPL is in the injected.

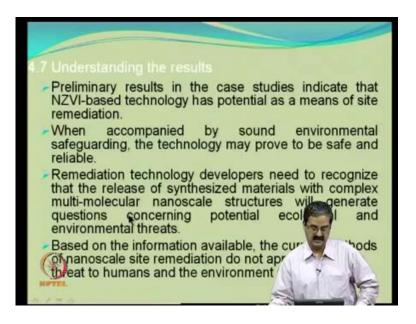


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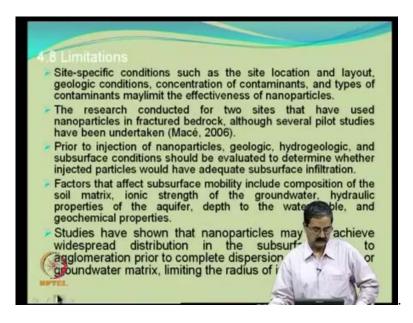
After two weeks after injection you can see that you know green line indicates its little better like you can see in the previous site Site, it is much lesser. So, I mean we can only

understand that there is some should be zone, green zone has increased with the result what it means is that it is from an USEPA study that this technique has been effective.

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(b) Two week	s post injection	(c) Four weeks post	
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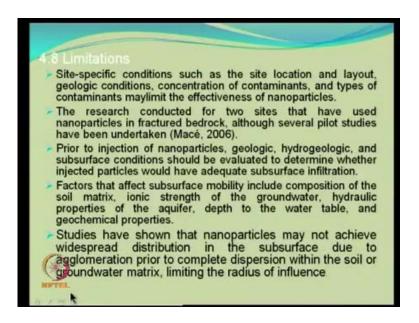
4.7 Understanding the results
 Preliminary results in the case studies indicate that NZVI-based technology has potential as a means of site remediation.
When accompanied by sound environmental safeguarding, the technology may prove to be safe and reliable.
Remediation technology developers need to recognize 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 currenthods of nanoscale site remediation do not apresent to humans and the environment

So, what it means is that, these case studies indicate that NZVI-based technology has potential as a means of remediation. When accompanied by sound environmental safeguarding the technology may prove to be safe and reliable.

And this remediation technology developers need to recognize that the release of the synthesized materials with complex multi-molecular nanoscale structures will be will generate questions concerning potential ecological and environmental threats.

Of course small is very very small is fine but, if it is going to cause bigger damages also one should be careful. Based on the information available, the current methods of nanoscale site do not appeared to pose a threat to humans and the environment there is some assurance available here.

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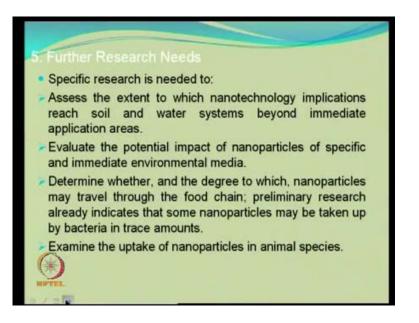


One of the limitation some of the limitations you should be able to understand that site specific conditions such as site location layout and geological conditions, concentration of contaminates, and types of contaminates may limit the effectiveness of nanoparticles. The research conducted for the two sides that have that have used nanoparticles in fractured bedrock although several pilot studies have been undertaken. Prior to injection of the nanoparticles geological hydrogeological and the 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 ionic strength of the groundwater hydraulic properties of the aquifer depth to the water table and geochemical properties.

Studies have shown that the nanoparticles may not achieve widespread distribution the subsurface due to the agglomeration prior to complete dispersion within the soil or groundwater matrix limiting the radius of influence.

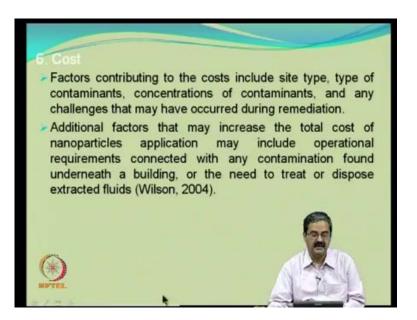
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What are the research needs, so of course, this area I know that is a beginning in this area but, then we need to understand what can be done. So to assess the extent to which nanotechnology implications reach soil and water systems beyond immediate application areas one needs to really have a a far sight ahead in this area.

Evaluate the potential impact of the 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 that is one thing one should see. Examine the uptake of nanoparticles in the animal species.

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When it comes to cost yes factors contributing to a costs including site type type of contaminates, concentrations of contaminates, and challenges that may have occurred remediation. Additional factors that may increase the total cost on the nanoparticles application may include operational requirements connected with any contamination found underneath a building or they need to treat or dispose extracted fluids.

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I know that nanoparticles are available in many places and you know we need to really handle them in a way that you know lot of science behind that and its reactions with soil

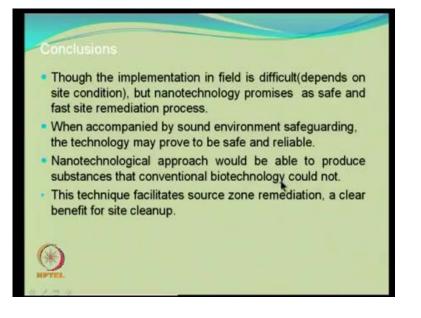
need to be understood to before we go for some more brought conclusions in this area and we have a lot of contaminated soils we should be able to work and see if nanoparticles can be effective and establish some sort of understanding there.

What is happening in India one should understand that, nanotechnology in India is a government led initiative in Indian institute of science there is a big interdisciplinary center in the area of nanoscience and engineering which is a quite a big center and which is support from the government.

And industry participation is very recently originated and industries also moving moving towards that enabling energy storage production and conversion with renewable energy frameworks is also there. Enhancement of agricultural productivity through pesticides is can it nanoparticles can it lead to agricultural productivity increase. Nanotechnology is slowly implemented in being implemented in medical field, textile industry.

Sectors such as health energy and environment have received greater attention by various technology departments in fact department of science and technology is looking it very seriously, department of biotechnology and SERC. They are all looking at nanotechnology with lot of curiosity and they they are looking at the implications they hope that definitely if you nanoscience can bring in a lot of change whether it is in the agriculture production or in trying to remediate contaminated sites it is going to be wonderful because or even health and energy and other issues.

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So, though the so I must say that when you have this technology, people should understand that the field implementation is not simple because the I mean in terms of the nano fabrication and other branches in mechanical engineering and electronics engineering it is difficult but, in the area of geotechnical engineering implementation in the field is not easy.

Because it depends on the site conditions but, nanotechnology promises as a safe and fast remediation technique or a process. When accompanied by sound environmental safeguarding the nanotechnology may prove to be safe and reliable I am sure about it and nanotechnological approaches would be able to produce substances that conventional biotechnology could not could not.

So definitely this technique facilitates source zone remediation a clear benefit for the site cleanup and I am sure that the references that I have indicated here particularly from wilson and zhang and also the some of this references are quite useful and actually in this preparation I must thank my students Mister.Manohar and Vinay for help in the preparation of this material and also say that the it it has been a quite a successful one ah.

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Referen Wilson G. 2004. Demonstration of in situ dehalogenation of DNAPL through injection of emulsified zero-valent iron at launch complex 34 in Cape Canaveral Air Force Station, FL. Presented at the Battelle Conference on Nanotechnology Applications for Remediation: Cost- Effective and Rapid Technologies Removal of Contaminants From Soil, Groundwater and Aqueous Environments. September 10, 2004. Zhang W-X. Nanoscale iron particles for environmental remediation: an overview. J Nanopart Res. 2003; 5:323-332. Zhang W-X, Elliot DW. Applications of iron nanoparticles for groundwater remediation. Remediation. 2006; 16(2). Zhang W-X, Durant N, Elliott D. A. In situ remediation nanoscale zero-valent iron: fundamentals and field ar tions. resented at the Battelle Conference on Remed Chorinated and Recalcitrant Compounds, Mor May 22-25, 2006.

With this I would like to conclude this lecture fortieth lecture in this series in this course and I would like to thank NPTEL, who have been a force behind this particular initiative with government of India level and their constant encouragement towards this course has helped me a lot in reaching this deadline and the staff of the NPTEL here in interest of science have been a great help help in trying to organize this lectures the institute has been of considerable help and student of my classes who took this ground improvement course and they have been quite helpful in the whole you know in participating in the discussions and preparations of material various stamps. And there are number of people from industry particularly in the area of ground improvement you need to interact with industry and many of them they supplied with their material and to be shown.

Because ground improvement techniques need lot of case studies and you have lot of support from many companies say for example, Keller and there also use some material from internet as well I some materials here and there have been used and I must thank all of them dare who have been very helpful in both indirect way and indirectly indirectly in the development of this course. So, I thank you again and I will be very happy to provide or improve this course further with inputs from everybody.

Thanks again one and all, bye.