Giving soils the shock treatment

The need to treat contaminated soils where they lie has inspired a novel approach to site clean-ups. **Chris Thompson** and **Dr Gary Low** describe the process.

Today's industries, before they are allowed to operate, must provide details of the potential impact of their activities on the environment. In the past, however, such regulations did not apply. The existence of many contaminated sites which cannot be re-used because of the concentrations of inorganic and organic wastes held in their soil is a legacy of these past uncontrolled industrial practices.

In New South Wales alone it is estimated that there are more than 900 metal finishing and metal foundry sites contaminated with metals such as cadmium, zinc, lead, nickel and chromium, and more than 1600 cattle-dip sites contaminated with inorganic and organic arsenic and pesticides. In addition, many brick yards and paint factory sites are contaminated with lead, and many railway storage yards, metal scrap yards and old gas work sites harbour polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) and heavy metals.

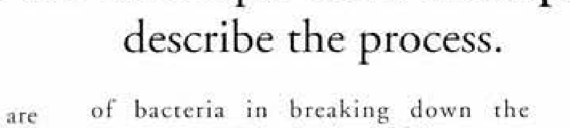
Thirty to 40% of sites listed by the NSW Environmental Protection Authority contain several contaminants, both organic and inorganic, in a hazardous mix. Some sites are no larger than a suburban backyard, while others cover two to three hectares. Many are in areas where land is too scarce to be left vacant.

A solution that might have sufficed a few years ago would have been to dig up the contaminated soil and dump it elsewhere. But that is no longer allowed. Contaminated soil is a hazard wherever it lies.

Today the emphasis is on '*in-situ*' cleaning'. Several on-site soil cleaning technologies are available, some of which are available commercially. Others, such as bioremediation, are still being researched.

Bioremediation involves adding nutrients to the soil to encourage the activity of bacteria in breaking down the contaminants. The drawback of this process is that it takes a long time and, to date, the results have been variable.

Other methods include soil venting, in which air or a selected gas is blown through the soil to remove volatile organics; passing radio-frequencies through the soil to increase the mobility of contaminants; and the extreme measure of vitrification. This involves heating the soil to high temperatures and treating it with additives so that it solidifies, preventing the contaminants from escaping. So far, however, none of these treatments has proved ideal. Better cleaning methods are therefore being investigated.



Strict regulations govern the environmental impacts of today's industries. A legacy of uncontrolled industrial practices in the past is the existence of many sites contaminated with hazardous wastes. Researchers at CSIRO's Division of Coal and Energy Technology are working with industry to develop efficient ways of dealing with the problems on site.

Seeking better ways to clean

An ideal process would remove all or most of a site's contaminants, obviating the need to tackle each one individually. It would also be inexpensive, and have no deleterious effects on the environment.

Three years ago, CSIRO's Division of Coal and Energy Technology, in conjunction with Caltex Australia, set out to develop a remediation process to remove hydrocarbons from soils at old garage sites or in fuel depots. Their approach involved using supercritical fluid to extract a full range of hydrocarbons including aromatics, phenolics and benzene, ethylbenzene, toluene and xylene (the volatile organic compounds) in a relatively short time.

A supercritical fluid is one that behaves in part like a gas and in part like a liquid. Substances enter a supercritical phase when subjected to high pressures at the same time as being heated. The density and solvent power of supercritical fluid are like those of a liquid, but its transport properties and compressibility are like those of a gas. Thus it can be an excellent solvent and as such is used widely in extraction processes.

The same team is experimenting with another process that pulls together two established technologies in a novel way. It is known as surfactant-enhanced electrokinetic soil washing.

Let's start with the electrokinetic part. This involves a direct current being applied across electrodes placed in the soil. In response, the various chemical species in the soil, either ionic or non-ionic, move from the pores and surface of the soil towards the electrodes. Ionic particles and charged particles will migrate to the oppositely charged electrodes (processes known as electromigration and electrophoresis). The bulk of the soil-water is induced, under an applied electric field, to flow through the soil to the cathode (negatively-charged electrode). This process is called electro-osmosis.

Electrokinetics is an excellent method of moving metals and water in the soil and gathering them at a common electrode where they can be collected and removed. As such it has already been applied to soil cleaning and dewatering. The limitation of

CSIRO and Caltex Australia are experimenting with a new 'soil-washing' process based on a technique called electrokinetics. Electrokinetics involves applying a direct current to electrodes placed in the soil, causing the chemicals to move towards the electrodes, where they can be collected and removed. This photograph shows earlier work in which electrokinetics was used to dewater coal slurry. In future trials electrodes will be used along with a surfactant to enhance the degradation of organic contaminants.

the process, however, is that it does not collect the organic contaminants which often are bound to the soil particles.

This is where the 'surfactant-enhanced' part comes in. A surfactant (short for surface active agent) is a substance that alters the surface tension of liquids or solids. Soap and detergents are good examples. When we wash with soap, the soap lowers the surface tension of the water so that it is better able to wet the skin and lift off the dirt.

When a surfactant is added to soil, it reduces the interfacial tension between the contaminant and the soil matrix, allowing the organic compounds to be 'washed' off the soil particles. These are then carried towards the cathode. Because the direction and rate of flow is controlled, there is maximum contact between the surfactant and the soil particles and hence maximum mobilisation of the organics. Thus, injecting a surfactant into the soil enhances the effectiveness of the electrokinetic process.

Seeking the ultimate surfactant

To date the research team has tested 11 surfactants in a 'model' soil containing known amounts and types of contaminants. They have been looking for surfactants that are available commercially; are not readily adsorbed onto the soil; interact well with organics; and are both biodegradable and reclaimable. Various analytical procedures have been designed to assess the effectiveness of the surfactant. These measure the type and amount of contaminant removed and the time required for the process to be completed.

The test results have revealed marked differences between surfactants. The best are able to remove 80-90% of such compounds as dichlorobenzenes, xylenes, toluene, n-decane, heavier hydrocarbons, napthalene and chloronapthalene (the main 'nasties'). Of the 11 surfactants tested, three show promise. These are needed only in low concentrations, are electrokinetically mobile, and are only slightly adsorbed onto the soil surfaces.

The experiments have been limited to a bench-scale electrokinetic unit capable of handling up to 20 kilograms of soil. In practice, getting results from this quantity of soil is a long process, each experiment taking more than a week. Therefore most of the tests have been done on half-kilogram samples.

In the coming year the aim is to identify why certain surfactants perform better, and to run pilot-scale tests with real, rather than laboratory-model, samples.

What will all this look like in real life? The configuration of the electrodes can vary. There may be one central cathode encircled by anodes (positive electrodes); the cathodes and anodes may be inserted in parallel lines; or the electrodes may be stacked horizontally through the soil. Where a larger area has to be decontaminated (say the size of a football pitch (it may be divided into more manageable units. It depends on the number of electrodes, and/or the time available.

The main advantages of the surfactant-enhanced electrokinetic process is that it captures the majority of the contaminants, whether organic or inorganic. It is able to be used with wet soils, it does not affect the integrity of the soil (the soil remains 'alive'); and there is a high degree of control of the movement of the contaminant through the soil. Costs are relatively low because the process requires little energy, and incurs neither excavation nor transport costs. Most importantly, the remediation process does not generate more pollution.

The complete solution, however, is some way off. Dr Gary Low, who has been involved in developing the project, says a better understanding of surfactants' behaviour is needed. Issues such as why some surfactants perform better than others; how to reclaim the surfactant once it has served its purpose; how the process is affected by soil characteristics; and how modifications of electrode design can achieve optimum performance, are yet to be resolved.

Eventually, mathematical models will be needed to enable site managers to plan the detailed operation of the process on specific sites.