Energy & Technology Review

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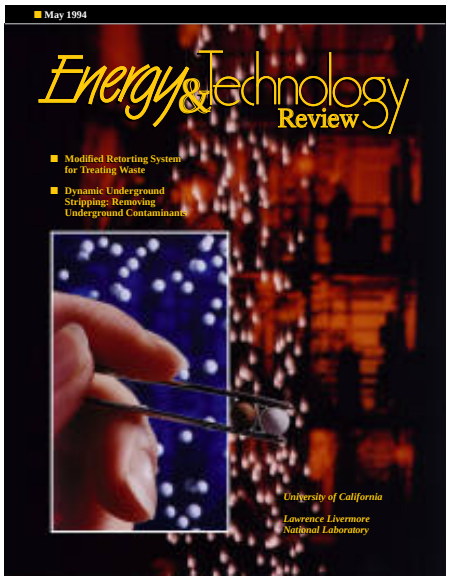
May 1994

Energy & Technology Review

- Modified Retorting System for Treating Waste
- Dynamic Underground Stripping: Removing Underground Contaminants

University of California

Lawrence Livermore National Laboratory



About the Cover

In the 1980s, LLNL developed the hot-recycled-solid (HRS) retorting process to produce liquid fuel from oil shale. Currently, we are demonstrating that the HRS process, if modified, can decompose or treat many harmful chemicals and compounds found throughout and beyond the DOE complex. The background image shows the pilot plant that was built to process oil shale. In October 1993, we collaborated with Sandia National Laboratories–California to adapt this pilot plant to demonstrate the feasibility of decomposing sodium nitrate. Using a circulating bed of hot ceramic spheres (shown in foreground), we vaporized and processed the liquid sludge. For more information about our modified HRS retorting system, see the article on p. 1.

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About the Journal

The Lawrence Livermore National Laboratory, operated by the University of California for the United States Department of Energy, was established in 1952 to do research on nuclear weapons and magnetic fusion energy. Since then, in response to new national needs, we have added other major programs, including technology transfer, laser science (fusion, isotope separation, materials processing), biology and biotechnology, environmental research and remediation, arms control and nonproliferation, advanced defense technology, and applied energy technology. These programs, in turn, require research in basic scientific disciplines, including chemistry and materials science, computing science and technology, engineering, and physics. The Laboratory also carries out a variety of projects for other federal agencies. *Energy and Technology Review* is published monthly to report on unclassified work in all our programs. Please address any correspondence concerning *Energy and Technology Review* (including name and address changes) to Mail Stop L-3, Lawrence Livermore National Laboratory, P.O. Box 808, Livermore, CA 94551, or telephone (510) 422-4859.

■ May 1994

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Energy & Technology Review

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We are developing an environmentally benign retorting system that can decompose hazardous wastes and many of the other harmful compounds found throughout the DOE complex.

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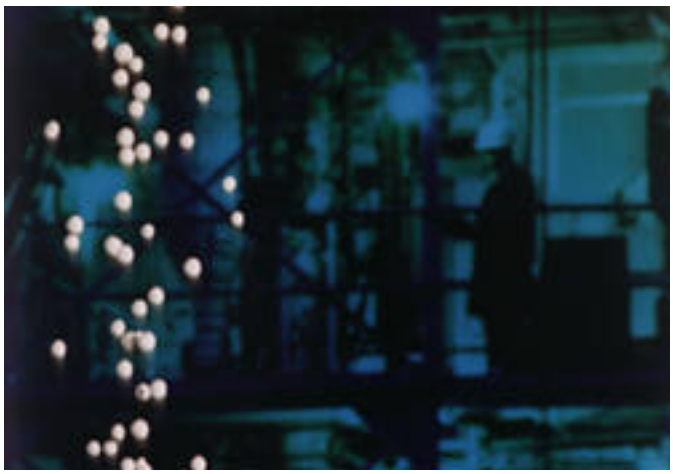
Modified Retorting for Waste Treatment



We are developing a technically sound, environmentally benign, and economically feasible retorting system, which uses a bed of hot ceramic spheres as the heat carrier, for decomposing hazardous wastes.

THE Laboratory has a number of programs to develop advanced technologies for environmental cleanup and waste treatment. In these efforts, existing LLNL technologies are being modified or adapted and new technologies are being developed to address pressing environmental issues. One such technology is retorting, in which the Laboratory has more than two decades of experience.

Retorting is the process by which substances are distilled or decomposed by heat, such as oil from oil shale, metal from ore, or gas from coal. Our retorting technology has focused on recovering oil from oil shale (see the box on p. 5 for a description of our oil-shale work). During the course of this work, we developed the LLNL hot-recycled-solid (HRS) retorting process, a rapid retorting system that uses hot recycled oil shale as the solid heat carrier (see the box on p. 9). We are now adapting the HRS process to address pressing problems in the field of waste treatment.

Evolution of the New Retorting System

During the course of our oil-shale work, we realized that the HRS process, if modified and extended, can be applied to several important problems in the field of waste treatment and environmental cleanup. For example, a preliminary laboratory study showed that the HRS process might be suitable for removing organic compounds and for decomposing sodium nitrate ($NaNO_3$). Organic compounds and sodium nitrate are major constituents of the mixed waste stored in underground tanks at the Hanford, Washington, facility. (Mixed waste is both radioactive and chemically hazardous.)

In 1993, we began to modify our on-site pilot plant that was built for processing oil shale. We have now adapted this pilot plant and are collaborating with researchers elsewhere to demonstrate the feasibility of pretreating Hanford tank wastes using a circulating bed of hot ceramic spheres. At the same time, we are pursuing several other applications of an HRS retort process for treating a variety of substances of environmental concern. We are demonstrating that the HRS process has potential applications for decomposing or treating many of the

harmful chemicals and compounds found throughout and beyond the DOE complex.

Advantages of Thermal Treatment

Maintaining a clean environment requires innovative techniques for treating and disposing of toxic substances. In recent years, LLNL researchers have developed several alternatives to long-term storage, landfill, or incineration. Some of our ideas come from basic research. Others, like the modified HRS process, are created by adapting an existing technology for a new application.

The modified HRS process applies heat to convert waste in a liquid state into nontoxic products. In thermal treatment, a high-temperature reducing atmosphere (that is, one with no oxygen present) is used to convert organic matter and other hazardous waste materials into a volatile vapor phase. Following thermal treatment, the volatiles are subjected to steam reforming, a process in which high-temperature (–1000°C) steam is applied to break down the volatiles into simpler, nontoxic species. After thermal treatment is applied to a large volume of waste sludge, all that remains is a small amount of ash. The volume reduction is considerable, ranging from 50 to 70 times less volume than the starting material.

Thermal treatment in the absence of oxygen has several other advantages beyond a large decrease in waste volume. For example, pyrolysis processes do not produce such highly undesirable products as dioxins and furans.

Figure 1. Photograph of the ceramic spheres (0.6 cm in diameter). In our pilot plant, these ceramic spheres are heated to and maintained at 555°C. Liquid waste is sprayed onto the spheres, and as they are circulated in a moving packed-bed reactor, they provide the energy required to thermally decompose the waste.

Thermal treatment involves one or more endothermic reactions. That is, the chemical reactions that take place absorb rather than generate heat. Such a process can be stopped immediately simply by shutting off the heat source. This safety feature is another reason that thermal decomposition is preferable to incineration for waste treatment. In addition, our HRS process operates at atmospheric pressure, providing enhanced worker safety. It also accommodates variable types of wastes—an important consideration for the different applications we have in mind.

Our HRS process uses a circulating bed of heated ceramic spheres, shown in Figure 1, as the heat carrier. We heat the ceramic spheres (using electric heat) until they reach a temperature that can vaporize and process the liquid sludge fed into the system. This technique—spreading out the liquid waste over the very large surface area afforded by the hot ceramic spheres—provides sufficient time for thermal treatment and avoids the problems of clumping and agglomeration that can occur when waste is treated alone.

In recent years, thermal treatment technology has advanced considerably as an economical alternative to incineration. Figure 2 diagrams a commercial, mobile detoxifier unit that can be used to treat gases, liquids, and solids. This unit handles waste in three ways:

- Industrial hazardous waste can be drum-fed or pumped from tanks.
- Medical waste, such as needles, gowns, and other contaminated solids, can be shredded and screw-fed counter to the flow of hot reactor gases.
- Liquid and slurried waste can be fed and processed in a circulating bed of ceramic spheres.

Compared to the disposal costs associated with incineration or landfill,

this commercial unit is a more economical alternative. Nevertheless, units on the market today cannot handle some types of hazardous waste or the mixed wastes plaguing the DOE complex.

Our goal is to develop the HRS system using hot ceramic spheres into a robust and highly reliable process for decomposing hazardous liquid waste, sludges, and contaminated soils. The HRS process can then be used to pretreat mixed waste (decomposing the chemically hazardous components, so the waste can be disposed of as radioactive-only waste).

HRS Process for Decomposing Sodium Nitrate

The 177 underground storage tanks at the Hanford facility contain various mixed wastes in the form of radioactive isotopes, organic chemicals, and sodium nitrate. The sodium nitrate in the tanks is a result of using the Purex process (which involves adding nitric acid) for extracting uranium from ore. When the waste materials were prepared for underground storage, sodium hydroxide was added to neutralize and buffer the acid solution and thereby reduce the likelihood that

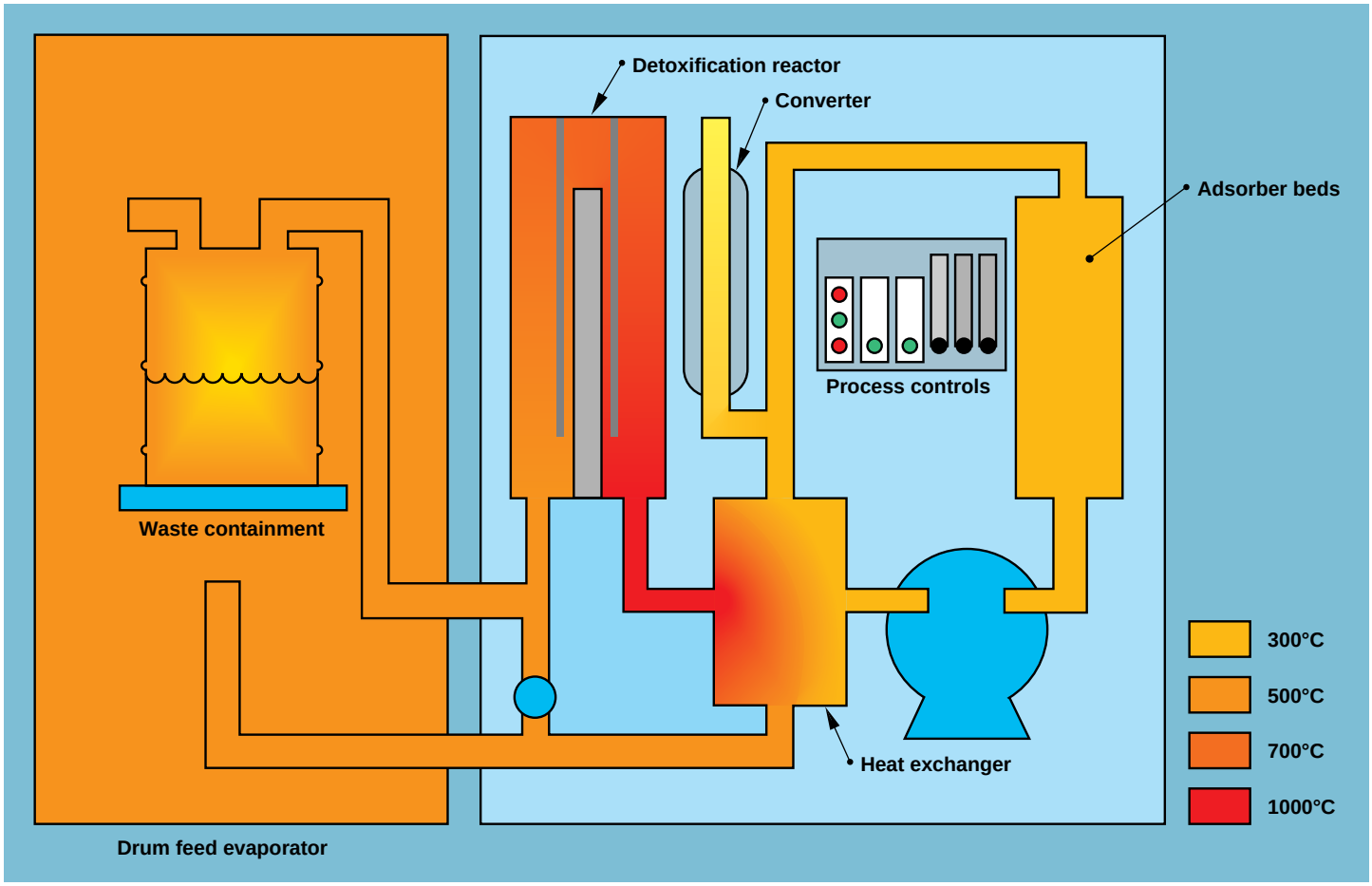


Figure 2. Diagram of the Synthetica Detoxifier, manufactured by Synthetica Technologies, Inc., of Richmond, California. This unit uses a multistep process to detoxify gases, liquids, or solids. Waste, such as liquid organics or shredded solids are vaporized in the evaporator (a drum feed is shown on the left in this example). Organic vapors are destroyed in the detoxification reactor shown on the right. The reactor uses electrical heat and has no fuel flame. The heat exchanger recirculates excess heat to the feeder. The converter oxidizes detoxified gases to CO_2 and H_2O. Activated carbon in the adsorber beds removes trace organics and metals. After thermal treatment of waste, a relatively small amount of dry, solid residue remains in disposable drums or can be steadily discharged, depending on the specific operation. Destruction levels are 99.99% or greater.

the storage tanks would leak over time. Nitric acid and sodium hydroxide, which are each highly corrosive, react to produce sodium nitrate. Despite the precautions taken to minimize risk, the tanks are now leaking, and there is concern that the contents will eventually contaminate the Columbia River (see Figure 3).

To solve this problem, the hazardous waste material—the organic wastes and sodium nitrate—must first be separated from the radioactive material. Once we rid the tanks of organics and sodium nitrate, the radioactive waste stream—in the form of a solid residue—can be processed in a vitrification plant to yield a glass waste product. Encapsulating radioactive compounds in either a ceramic or silica glass will prevent them from leaching into the environment for very long periods of time.

Preliminary Laboratory Study

The thermal decomposition of sodium nitrate is a complicated issue in itself. A wide variety of reactions and products are possible depending on temperature, the kinds and amounts of reducing gases that are added, and many other factors. The presence of steam, for example, is an essential component of our system because, without steam, unwanted solid products are formed (for example, peroxides and superoxides of sodium).

We performed a preliminary laboratory study to define some of the conditions needed to decompose sodium nitrate in a pilot plant using our modified HRS process. One of our main objectives during this study was to establish the optimum temperature at which more than 95% of the sodium nitrate is decomposed in less than 10 minutes. We also wanted to understand the kinds and relative amounts of product gases that would be generated.

We found that sodium nitrate could be almost completely decomposed under controlled laboratory conditions in less than 10 minutes at about 555°C. As a result, we chose 555°C as the operating temperature of our pilot plant.

The principal nitrogen-containing gas products from decomposition of sodium nitrate in the presence of steam and carbon dioxide (CO_2)

Figure 3. Aerial view of the Hanford, Washington, facility and its proximity to the Columbia River. This historic photo was taken on September 25, 1944. Mixed waste is now stored in 177 underground tanks at Hanford. Over time, the leaking contents could contaminate the Columbia River. Solving the problem involves several steps. With our modified HRS process, we can initiate remediation by separating the organic wastes and sodium nitrate in the tanks from the radioactive material they contain. The radioactive solids can then be encapsulated in a ceramic or silica glass to ensure environmental protection.

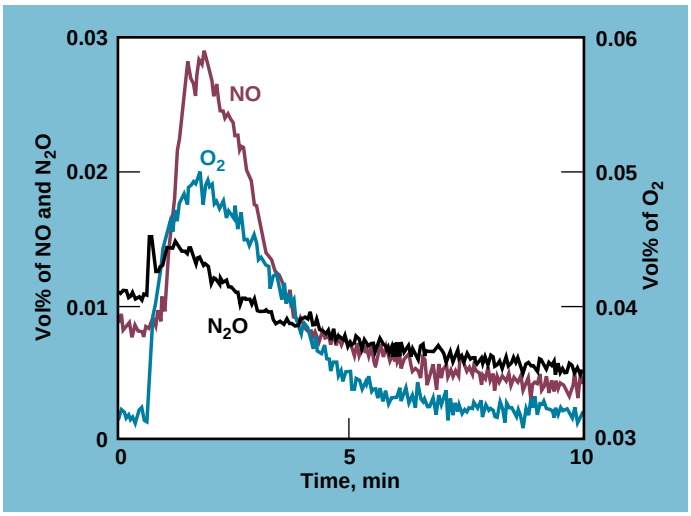


Figure 4. The evolution of several product gases from decomposing sodium nitrate over the course of 10 minutes. The figure shows the vol% of NO, N_2O, and O_2 of the total gas that is flowing through the fluidized bed. In this particular laboratory experiment—one of several in a series—we injected steam and argon, and the reaction was carried out at 555°C. This test showed that all the gases evolved similarly, and the sodium nitrate was decomposed in less than 10 minutes. This experiment established the temperature at which we would need to operate a pilot plant for decomposing sodium nitrate.

were determined by mass spectrometry to be:
- 70% NO.
- 15% N_2O.
- 5% NO_2.
- 5% N_2.
- 5% unreacted.

Figure 4 shows the evolution of several of these product gases from sodium nitrate over the course of 10 minutes. These mixtures of nitrogen-containing gases are of varying environmental concern and would have to be "scrubbed" prior to venting to the atmosphere. Scrubbing is a relatively straightforward process that can be done by chemical treatment or using a catalytic converter similar to those in automobiles.

The principal solid product of sodium nitrate thermal decomposition, in the presence of CO_2, is sodium carbonate (Na_2CO_3). This is an acceptable solid product. When processed in a vitrification plant, sodium carbonate would be converted to sodium silicates so that only CO_2 would be released into the atmosphere.

Demonstration at the LLNL Pilot Plant

In the fall of 1993, we applied what we had learned about sodium nitrate decomposition in the laboratory to larger-scale tests. In collaboration with researchers at Sandia National

LLNL's Work on Oil-Shale Processing

Interest in oil-shale retorting stems from the vast deposits of oil shale in the western states. The shale basins in Colorado, Utah, and Wyoming are the largest and richest oil shale deposits known, rivaling the petroleum reserves in the Persian Gulf. However, producing liquid fuel from western U.S. oil shale requires a technically sound and environmentally benign retorting system that can handle very large volumes of solids.

Several oil-shale processes developed by others in the 1970s were technically successful (i.e., they produced oil), but they proved to be too expensive for commercialization. Industry development of oil-shale retorting has been inhibited by the return to lower oil prices in the 1980s, uncertainty in the future price of crude oil, and the long lead time for commercializing new technology.

Our initial work on oil-shale processing, in the 1970s, focused on *in situ* technology. In the early 1980s, our efforts shifted to the broader field of advanced, aboveground oil-shale retorting. During the course of this work, we developed the LLNL hot-recycled-solid (HRS) retorting process. Retorts using hot solids as the heat carrier, as does our HRS process, have many advantages over earlier hot-gas retorts. For example, methods using hot solids are:
- Faster (minutes vs hours for heating).
- Yield more oil due to rapid heating (10–15% improvement).
- More energy efficient (use all the available carbon).

In addition, hot-solid retorts can:
- Process smaller particles, greatly reducing the heat-up time from hours to minutes.
- Process fines (particles smaller than about 0.5 mm in diameter that are thrown away by hot-gas retorts).
- Reduce environmental impact because of the self-scrubbing of sulfur.
- Be more easily scaled up to the large systems needed for a commercial plant.

In early 1991, we signed a three-year cooperative research and development agreement (CRADA) with Amoco Corporation, Chevron-Conoco Shale Oil Semiworks Joint Venture, and Unocal Corporation. Under this agreement, the first of its kind for LLNL, we continue to advance oil-shale technology and to explore ways to reduce the cost of producing liquid fuels from oil shale. This CRADA is now in its third year. During this time, we have developed a commercial concept that can:
- Produce oil from shale.
- Generate electric power.
- Produce high-value specialty chemicals (e.g., dyes, waxes, perfumes, and an asphalt additive that extends the life of roads, to name a few).

Our concept makes shale-oil processing economical at a modest scale of 10,000 barrels per day. We are currently seeking additional funding to continue with the work required to develop the technology fully for commercial application.

Laboratories–California, we adapted our on-site oil-shale pilot plant to demonstrate the feasibility of decomposing sodium nitrate in a small working-model system. Our demonstration tests were scaled to process approximately 1 to 2 kg per hour of liquid waste. (This rate is roughly one-hundredth the rate at which we would process actual waste in a commercial-scale plant.) Our tests lasted about four hours each day for four consecutive days.

Figure 5 shows the simplified HRS system we used to demonstrate sodium nitrate decomposition. Keep in mind that this modified system differs in several important ways from the system we developed earlier for oil-shale processing (compare Figure 5 with the illustration in the box, p. 9). To extract oil from shale, we needed air (oxygen) to burn the residual carbon and to lift the spent shale up around the loop to the top of the tower. In addition, oil-shale retorting is a solid process (with no added water). In contrast, our waste processing takes place in a reducing atmosphere (no oxygen) and involves liquids, not solids, because the waste in the Hanford drums is already in liquid form.

The main steps in the decomposition cycle for sodium nitrate can be best understood by referring to the principal pieces of equipment in Figure 5:

1. Heater. The moving-bed heater (upper left of Figure 5) heats the ceramic spheres using gas heated by an electric coil together with external wall heaters (not shown). The hot ceramic spheres then transfer their heat to the waste feed to reach a reaction temperature of 555°C.

2. Reactor. Just below the heater, sodium nitrate (the liquid waste to be decomposed) is injected onto the hot ceramic spheres, which then enter a moving packed-bed reactor. Thermal decomposition of sodium nitrate takes place in the reactor as the hot spheres, coated with sodium nitrate liquid, pass through the bed with an average residence time of 10 minutes. Steam and CO_2, injected from below, flow up and around the hot spheres to aid the decomposition and to produce sodium carbonate as the primary solid product.

3. Condensers. Gas and steam in the reactor pass through a cyclone separator and into condensers. The cyclone is a funnel-shaped device that uses centrifugal means to separate the gases and heavier solids. The condensers (at the right of the reactor in Figure 5) collect liquid condensate, which, for sodium nitrate destruction, is mostly water. Noncondensable gas is measured by Fourier transform infrared (FTIR) and mass spectrometry to determine its composition prior to venting.

4. Pneumatic Lift. Below the reactor, an LLNL-developed L-valve dispenses the hot spheres into a pneumatic lift pipe, which transports them to the top of the tower. The L-valve looks something like a miniature set of stairs. This valve uses puffs of compressed gas (such as CO_2 or an inert gas) to regulate the flow of spheres down the steps. The rate of discharge for the L-valve determines the recirculation rate of the spheres and the residence time of the spheres in the reactor. Hot recycled gas, air, or nitrogen is used as the driver gas for the pneumatic lift system. High velocities of the spheres in the lift pipe, as well as particle-particle interactions during pneumatic transport, remove the fine-grained crystalline sodium carbonate from the surface of the spheres, producing a fine dust.

5. Classifier. In the classifier (upper left of Figure 5), the spheres are separated from the lift gas and sent back to the heater. Discharge gas, carrying the small sodium carbonate crystals, passes through a cyclone separator and a dust filter. The solid waste products are collected, and the filtered, clean lift gas is recycled or vented.

During our demonstration tests, the HRS circulation system was operated 5 to 6 hours a day, without major problems. The off-gases were continuously analyzed to quantify the decomposition products of sodium nitrate. The distribution of nitrogen in the four product gases was:

- 70% NO.
- 0% N_2O.
- 30% NO_2.
- 0% N_2.

These results revealed that pilot-plant chemistry is significantly different from that of the controlled laboratory experiments. In particular, higher amounts of NO_2 are produced, and no N_2O was detected. The fact that we observed no detectable N_2O is highly desirable since its absence will aid in the conversion of nitrogen oxides into molecular nitrogen prior to release of gas into the atmosphere.

After examining the solids at the end of each day and following shutdown of the system, we found no signs of sticking, tacking, or agglomeration of the liquid waste. Our analysis showed that more that 95% of the sodium nitrate entering the system was decomposed. The primary solid product was sodium carbonate—the solid that we expected. These products would be converted into sodium silicates in a vitrification plant. From these tests, we concluded that the overall performance of the HRS process for sodium nitrate decomposition is highly promising.

Cold Test at the Sandia Facility

In addition to our pilot plant work, we are collaborating with researchers at Sandia to develop an integrated steam-reforming process for mixed

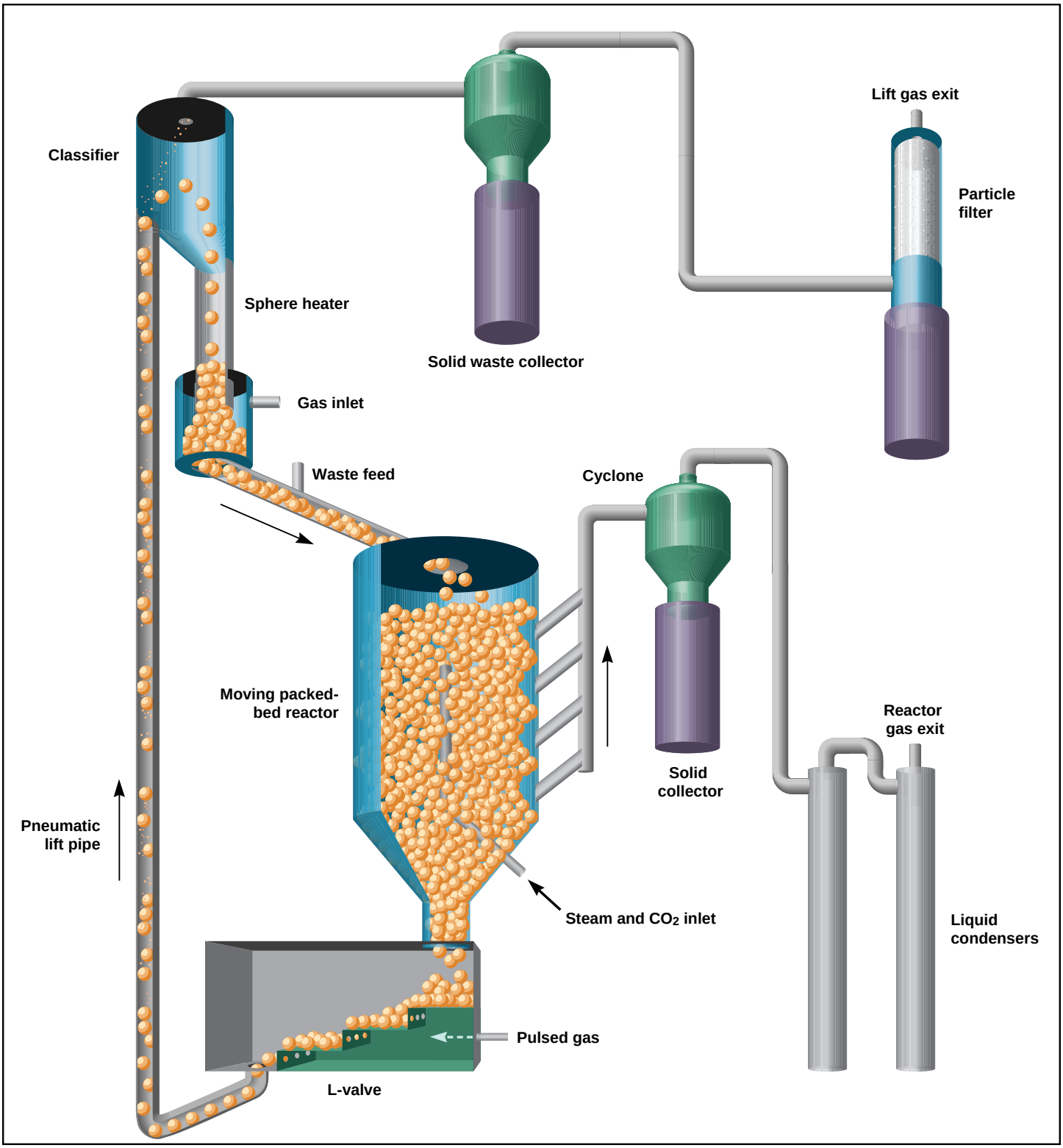


Figure 5. Schematic of the 4-story-tall HRS pilot plant at LLNL used, in October 1993, to demonstrate the decomposition of sodium nitrate. In this system, 50 kg of hot ceramic spheres, fed into the reactor from the heater, provide a large surface area for the thermal treatment and decomposition of sodium nitrate. The spheres are metered from the bottom of the reactor and are recirculated via a nonmechanical pneumatic lift back up into the heater. The off-gases and solids are separated in the classifier, cyclone, and filter (at top). The condensers (bottom right) collect liquid condensate. Noncondensable gas is measured and then vented.

waste. As shown in Figure 6, Sandia has built and is now operating a cold-flow system that can be used to study the functions of various pieces of HRS equipment at a larger scale. This is the next logical step toward a scaled-up waste-treatment HRS system that can be applied to the problem of sodium nitrate and other compounds.

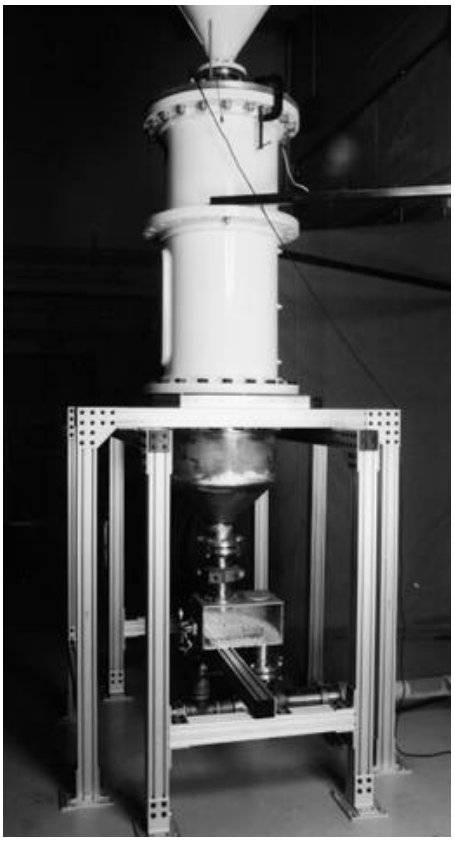


Figure 6. The cold-flow facility at Sandia National Laboratories–California. This unit is designed to simulate the processing of waste at a rate of 20 kg per hour, roughly ten times greater than that for our first demonstration tests at LLNL. Tests scheduled for later this year at the Sandia facility will further assess liquid–solid mixing requirements and evaluate the performance of a pneumatic conveyance system.

The Sandia facility is scaled to process material at a rate of approximately 20 kg per hour. This rate is about ten times larger than that for our first demonstration tests at LLNL and roughly ten times smaller than that required for a full-scale commercial unit.

We will use Sandia's cold-flow system to study various issues related to an increased mass-flow rate. A critical issue for any system that processes wastes containing radioactivity is ensuring its robustness and reliability. Once the unit itself becomes radioactive, maintenance becomes difficult, so it is desirable to eliminate mechanical complexity. Thus, the transport system, which includes the dispensing device (L-valve) and pneumatic lift, is a major issue in itself. The Sandia studies will include tests of the pneumatic transport system (with no moving parts) to circulate the ceramic spheres at a much larger scale than before.

The new tests will also look at another important issue: the liquid and solid mixing requirements in a ten-times larger system. We will study ways to inject the waste that avoid clogging of an injection nozzle as well as nonmechanical means to distribute the liquid over the ceramic spheres. These tests will improve our understanding of the overall process and enable us to identify the appropriate next steps toward the ultimate goal of a full-scale, stand-alone unit that can process waste at a rate of about 200 kg per hour.

Other Waste Treatment Applications of the HRS Process

The DOE is in the process of dismantling a large fraction of the nation's nuclear stockpile. One waste component from the dismantlement effort is chemical high explosives. The current method for disposing of high explosives is by open burning and open detonation. Regulatory agencies may soon greatly restrict or eliminate open burning and open detonation as ways to dispose of propellants, explosives, and pyrotechnics (also called PEPs). The DOE uses primarily plastic bonded explosive, or PBX for short. Although much of this material—as much as 90%—may be sold to industry, a certain amount will have to be destroyed. (Many other materials, such as solvents and wipes that come into contact with the high explosives, become classified as hazardous waste and will also have to be destroyed.) Some high explosives can be pretreated with sodium hydroxide in a process called base (or alkaline) hydrolysis. This process destroys that material's explosive nature, but the resulting liquid and gaseous products are still hazardous and thus require additional treatment.

New regulations require the military to examine the life cycle of any new PEP developed. The Army is currently evaluating disposal methods for a new liquid gun propellant, LP XM46, which is used as a conventional propellant for field artillery. This material is a mixture of hydroxyl-ammonium nitrate and triethanol-ammonium nitrate in 20% water. Liquid gun propellant is not detonable, and once diluted in a ratio of one to three with water, it is neither explosive nor flammable. Nevertheless, the material is chemically hazardous, and a suitable method, other than incineration, is needed to dispose of the liquid material.

We are exploring the use of the HRS process with hot ceramic spheres to destroy liquid gun propellant and the

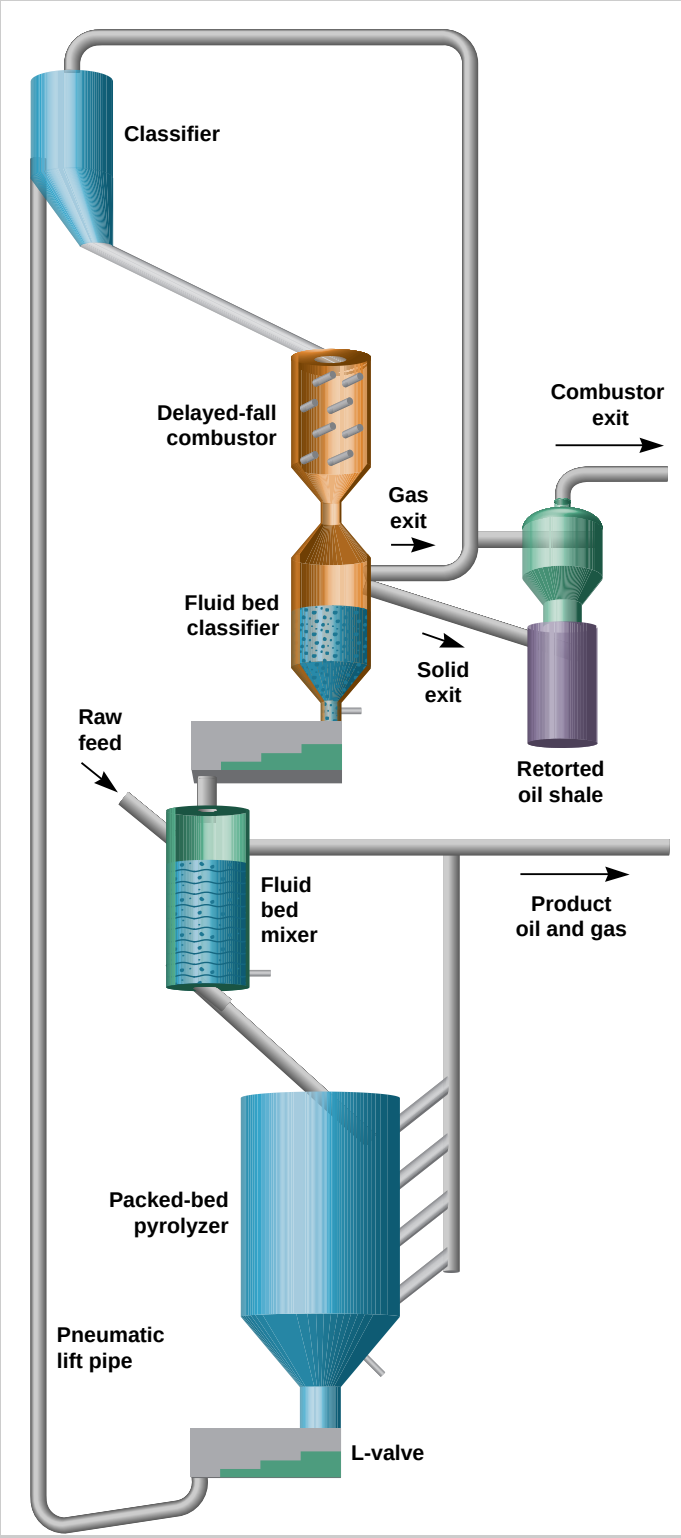
The Hot-Recycled-Solid Process

Our hot-recycled-solid (HRS) process offers major improvements in efficiency and reliability over other processes for extracting oil from shale. Processing improvements of the type embodied by the HRS system hold the promise of making shale oil competitive with the world price of crude oil early in the next century.

In experiments during the mid-1980s, we constructed and operated a 1-tonne/day retort at LLNL to study the chemistry of oil shale pyrolysis. (Pyrolysis is the use of heat to break apart complex molecules into simpler units.) This retort produced oils with better stability and lower viscosity than previously thought possible. In 1990, we scaled up to a 4-tonne/day facility, which allowed us to study, for the first time, pyrolysis and combustion chemistry using the actual particle size (up to 7 mm) of commercial scale and to produce enough oil (about 10 gallons per run) for detailed characterization studies.

The major components of the HRS oil shale retorting process are shown in the illustration. First, raw crushed shale and recycled hot, spent shale are combined in a mixer. The mixed shale is pyrolyzed for 3 minutes in a moving packed-bed pyrolyzer to generate oil. Whole oil is then condensed for subsequent analysis and characterization. Whereas reaction temperatures are reached in less than a minute by our process, previous systems required 30 minutes to several hours. Rapid heatup promotes high product recovery with a 10 to 15% improvement over previous retorting methods. From a ton of Colorado shale, three quarters to one barrel of oil can typically be recovered.

Shale leaving the packed bed is lifted pneumatically to and through a delayed-fall combustor during which residual carbon is burned to provide the process heat. Solid waste is discharged from a fluid-bed classifier, which also serves as a pressure block that separates the reducing (heating) and oxidizing (burning) atmospheres. In an actual production plant, the oil would be refined into high-octane gasoline, jet fuel, or other petroleum products.



products from base hydrolysis of high explosives as an alternative to open burning and incineration. We have completed one run of each of the two materials in our modified HRS pilot plant to determine the gas products, condensable liquids, and solid products of decomposition. The HRS process destroyed the base hydrolysate and produced a small amount of solid material composed of 75% sodium carbonate and a small amount of aluminum oxide. Gaseous emissions of NO_x and other EPA-regulated pollutants were small.

We operated the HRS pilot plant 7 hours at steady-state conditions and destroyed 36 kg of diluted liquid gun propellant. Our experiments showed that this material was better destroyed in an oxidizing system (such as molten salt oxidation, reported in the January–February 1994 issue of *Energy and Technology Review*, pp. 42–43). Pyrolysis caused 8% of the nitrogen in the propellant to form oxides of nitrogen. Diversion of the gases to the lift section of the HRS and the addition of oxygen greatly reduced the nitrogen oxide formation. This work has already given us a good head-to-head comparison with other decomposition methods. More tests with the base hydrolysis products are planned in the near future.

The Road Ahead

At present, the DOE complex has no operational treatment or permanent disposal capability for mixed wastes—those containing both radioactive and chemically toxic substances. To meet this critical need, the Laboratory is designing a pilot facility to demonstrate integrated, end-to-end treatment of mixed waste. An existing building at LLNL has been assigned for this Mixed Waste Management Facility. Our HRS retort process is a potential core technology for this facility.

Before the HRS process can be used to clean up actual mixed waste, it must first undergo rigorous testing in a research and development mode. The Mixed Waste Management Facility provides the mechanism for developing promising new technologies in a facility permitted to handle and process mixed waste.

We also plan to collaborate with other LLNL researchers in the area of waste management. We will study ways the HRS process can be applied to treat the on-site mixed wastes that have been generated by Laboratory research and development. At present, LLNL researchers are looking at the HRS process and at steam reforming as one technique to handle the on-site mixed waste.

Work funded by the Department of Energy's Richland Operations Office as part of Hanford's Underground Storage Tank Integrated Demonstration Program.

Key Words: hot-recycled-solid (HRS) process; high explosive; liquid gun propellant; oil shale retorting; sodium nitrate decomposition; thermal treatment; waste treatment.

For further information please contact Robert J. Cena (510) 422-7336.

Cleaning Up Underground Contaminants

Dynamic underground stripping combines steam and electrical heating of underground soils with vacuum extraction of vapors and fluids, guiding these processes by real-time monitoring methods.

AT hundreds of industrial and government sites across the United States, environmental consulting firms are designing permanent containment systems for underground contaminants such as hydrocarbon fuels, cleaning solvents, and industrial chemicals. In quantities of thousands of liters or more, these chemicals threaten to contaminate drinking water supplies for hundreds of years. Typical containment systems (e.g., deep walls of cement or clay, or hydraulic pumping to control groundwater movement) can keep the chemicals from further contaminating groundwater if they are properly maintained for many years, but they do not remove the contaminants. Clearly, removing the contaminants from the soil is a much preferable solution than containing them and attempting to prevent their spread.

In a fairly typical example of this problem, between 1952 and 1979, tens of thousands of liters of gasoline leaked from an underground tank at the former LLNL filling station. The amount of gasoline leaked is not well known. Estimates made using data from borehole core analysis placed the amount at about 30,000 liters; discrepancies in inventory logs from the 1970s gave the upper limit at 70,000 liters. In the 1970s, agricultural pumping in the vicinity ceased and the water table rose, trapping gasoline below it and "smearing" the gasoline through clay-rich soils of low permeability. (See the box on p. 14 for a description of the water table.) Figure 1 shows a diagram of this contaminated region.

Hydrocarbons trapped below the water table are especially difficult to clean up by traditional methods. The pump-and-treat method—now in use at some 300 Superfund cleanup sites—requires the pumping of huge amounts of groundwater up through an extraction well, followed by removal of whatever captured contaminant comes up with the water. Unfortunately, the pumped water carries very little contaminant—in the case of gasoline, no more than 10 liters of contaminant per million liters of water. We estimated that

removing the free-product gasoline from the LLNL spill site by the pump-and-treat method alone could take up to 200 years. (See the box on p. 15 for a description of free-product gasoline.)

Instead of using the pump-and-treat method, a team of researchers from LLNL and from the University of California (UC) at Berkeley demonstrated a new and unique combination of technologies—collectively called dynamic underground stripping—to rapidly remove some 29,000 liters of free-product gasoline from beneath the LLNL site. As shown in Figure 2, our experiment targeted a portion of the LLNL spill area, which contained the majority of the free-product gasoline. Pools of free-product gasoline are known to lie outside the targeted area, as indicated by the circles in Figure 2, and a small fraction (much less than 1%) of the gasoline is known to have dissolved into the groundwater outside this region. The purpose of our demonstration was not to perform an entire cleanup of the spill area but to prove that dynamic underground stripping is successful in removing the free-product gasoline. This first demonstration of the new method on an actual spill site accomplished in less than a year what the conventional method would have taken decades to do. (In 1991, we tested the dynamic underground stripping technique on an uncontaminated underground site.[1])

Dynamic Underground Stripping: A General Description

In dynamic underground stripping, a targeted volume of earth is heated to vaporize the trapped contaminants. Two methods of heating—steam injection and electrical resistance—are used to heat all layers in the soil. Permeable layers (e.g., gravels) are amenable to heating by steam injection, and impermeable layers (e.g., clays)

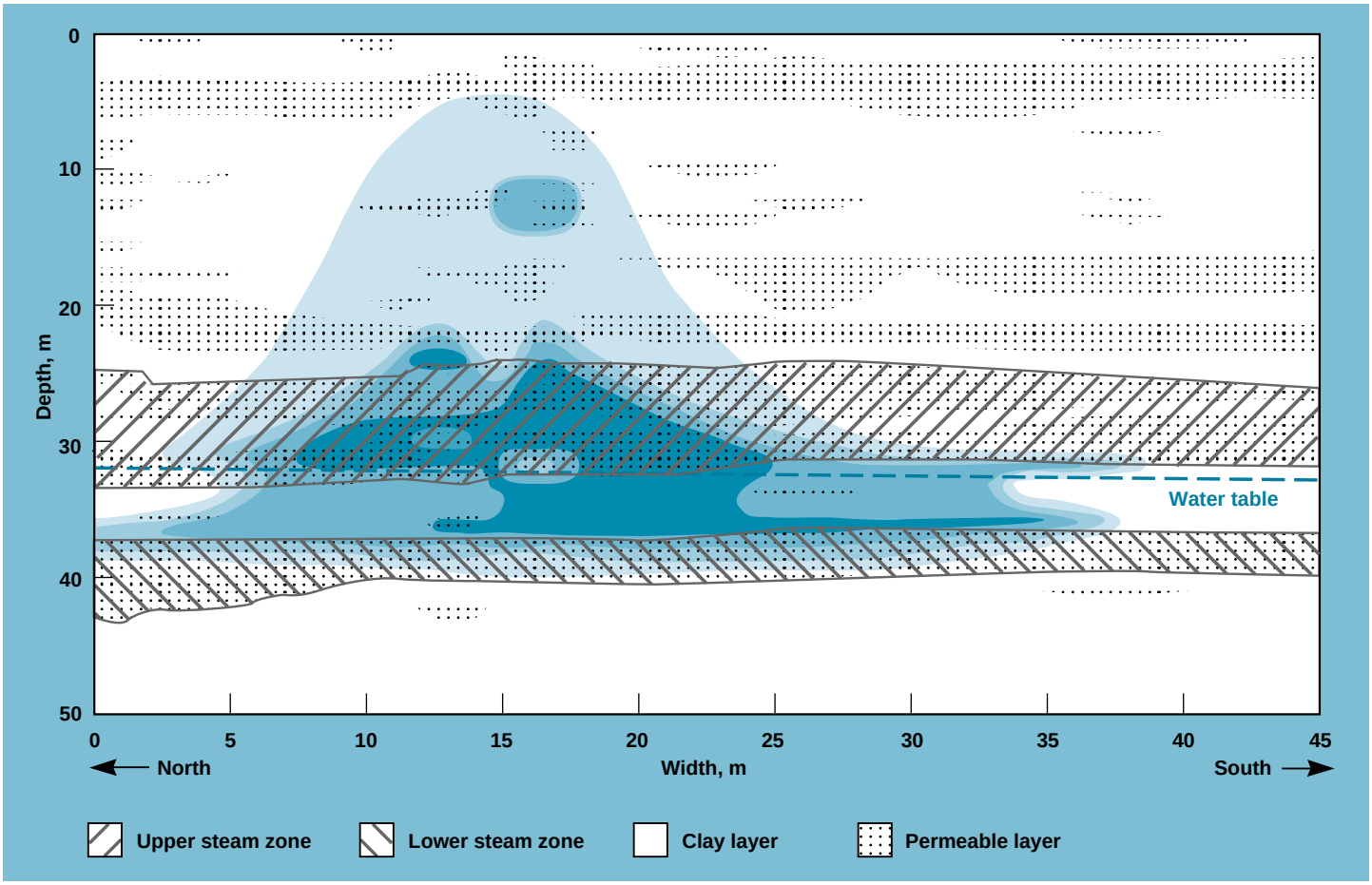


Figure 1. Cross section showing an approximation of the gasoline contamination at the treatment site before dynamic underground stripping began. The darker areas represent higher concentrations or free-product gasoline. The dashed line denotes the level of the water table.

can be heated by electric current. Because of these complementary heating techniques, dynamic underground stripping is the best technique available to treat heterogeneous soils. Once vaporized, the contaminants are removed by vacuum extraction. All these processes—from the heating of the soil to the removal of the contaminated vapor—are monitored and guided by underground imaging.

Researchers from UC Berkeley, led by Professor Kent Udell of the Mechanical Engineering Department, developed the powerful steam-injection technique by combining vacuum extraction with a steam-injection method that oil companies sometimes use in late stages of oil recovery. LLNL researchers developed the electrical resistance method of heating and an underground imaging technique—electrical resistance tomography.

Steam Injection and Vacuum Extraction

Injection wells drilled around an area of concentrated contamination are used to supply both steam and electric current. Extraction wells placed as close as possible to the center of the contamination are used to extract the contaminant. The steam is pumped in through the injection wells and advances in a wall, or front, toward the extraction wells. Concurrently, groundwater is pumped and vapor is extracted from the extraction wells. As the steam front advances, the permeable soils are heated to the boiling point of water (100°C), and volatile organic contaminants are vaporized from the hot soil. After the steam front reaches the extraction wells, steam injection is stopped; vacuum continues to be applied at the extraction wells. The lowered vapor pressure (resulting from the applied vacuum) forces the contaminants to boil, and the concentrated, contaminant-carrying vapor is then pumped to the surface and treated. When the steam zone collapses, groundwater reenters the treatment zone. The steam injection/vacuum extraction cycle is repeated, and additional contaminants are vaporized and removed.

Electrical Resistance Heating

Electric current is used to heat the impermeable soils. It operates on the same principle that makes a heating coil work—heat builds up in a conductor that resists current flow. For this technique, the clay itself supplies the resistance. In the steam injection wells, electrodes are sunk into the ground. Each electrode supplies several hundred amperes of current at up to 600 V, heating the impermeable clays. Water and contaminants trapped in these (relatively) conductive regions are vaporized and forced into the steam zone for vacuum extraction.

These combined heating processes achieve a hot, dry zone surrounded by cool, damp, untreated areas. Electrical heating and steam injection are repeated as long as underground imaging shows that cool (and therefore untreated) regions remain.

Underground Imaging and Monitoring

Several geophysical techniques are used to monitor the underground movement of steam and the progress of heating, including temperature measurements, electrical resistance tomography, and tiltmeters.

Temperature measurements made in monitoring wells throughout the treatment area reveal details of the complex heating phenomena in the alternating gravel and clay layers.

Figure 2. Top view of LLNL spill area, showing regions of known or suspected free-product gasoline contamination (circled in blue) and where we applied dynamic underground stripping (in pink). As noted by the circles outside the treatment area, additional free-product gasoline remains at the site.

These measurements are difficult to make in areas of high thermal gradients, such as in a steam flood. UC Berkeley researchers developed an optical temperature-logging system that can provide detailed daily borehole-temperature logs. In addition, thermocouples permanently installed in boreholes throughout the treatment area record temperatures around the clock.

Electrical resistance tomography provides near-real-time images of the underground processes and permits the identification of areas that are affected by the dynamic stripping process. Because electrical conductivity varies with temperature, measuring the resistance of the soil can reveal the progress of the steam front and the heated zones. Electrical measurements thus provide good measurements of steam movement and reveal changes in formation properties over a broad zone. Because the electrical properties of the soil are controlled by soil type, fluid saturation, and chemistry, electrical resistance tomography is also useful for characterizing a given site and for predicting steam pathways.

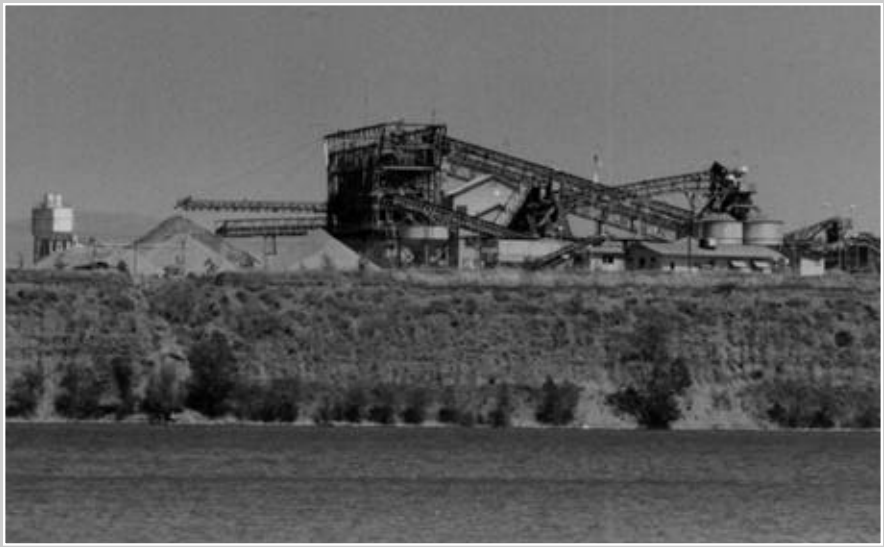
Tiltmeters are used to track the movement of the steam front. These devices are capable of detecting very small angular deformations in the ground surface that result from subsurface pressure changes, such as those that occur with the movement of the underground steam front. They are sensitive enough to detect pressure changes as small as a few hundred pascals (~0.05 psi) in the heated zone.

The Water Table

A child digging a hole at the beach will eventually reach a depth where the hole fills with water despite all efforts to bail it out. This is an early experience with the "water table"—the depth at which all the space between the medium (in this case, the sand grains) is water-filled. At any point on Earth, one can dig a hole deep enough to encounter such standing water.

The depth of the water table varies greatly from region to region. On the south side of the LLNL site (the location of the gasoline spill), the depth of the water table is about 30 meters; in more arid regions, the water table can be more than ten times as deep. During periods of rain and drought, the water table might rise and fall, respectively. Also, in areas where water is pumped for agricultural reasons, the level of the water table might change, as occurred at the LLNL site in the 1970s when agricultural pumping in the region ceased.

Not all holes make good wells, however. At the site of the LLNL gasoline spill, for instance, a 35-meter-deep hole could end in a fine-grained, clay-rich soil in which the water would not flow—but only seep. It could also end in a gravely soil; a hole in this medium would fill rapidly and would not be emptied even by pumping the water out at a rate of 100 liters/minute.



At Shadow Cliffs Regional Park—an old gravel quarry near LLNL—the local water table forms the surface of the lake.

Demonstration of Dynamic Underground Stripping at a Contaminated Site

In this first application of dynamic underground stripping at a contaminated site, our goals were to:

- Determine how well the process removes gasoline.
- Determine how well the monitoring methods can be used to control heat input and map heated zones.
- Determine whether there are any deleterious effects with this process (such as dispersal of contaminant).
- Determine how the several components of this technique can be varied in relation to one another to maximize extraction efficiency.
- Demonstrate the engineering and operational practices required for safe and effective operation of this cleanup technique.

Site Characterization

The soils at the gasoline spill site are alluvial, ranging from very fine silt and clay layers to coarse gravels, with permeabilities ranging over several orders of magnitude. There are two principal permeable zones: one above and one below the water table.

Our aim was to remove all the free product gasoline at the treatment area (see Figure 2). Approximately half of this gasoline was above the water table (at a depth of 30 m) and half was trapped below. The treatment zone was in the shape of a distorted cylinder about 40 m in diameter and extending from a depth of 20 to 45 m.

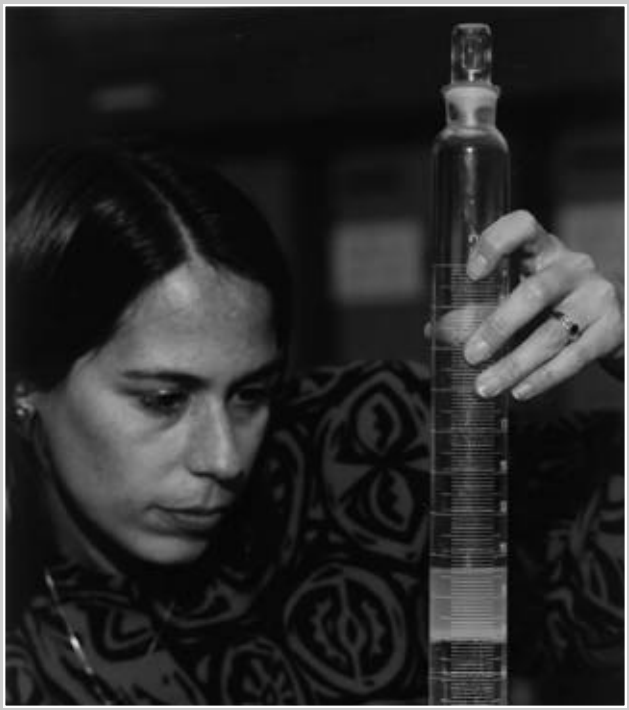
We drilled six injection wells around the spill perimeter to deliver both steam and electric current. Three extraction wells were drilled close to the center of the spill site.

Electrical Preheating

In November 1992, we began the electric preheating of the site. Electricity preferentially flows in areas of high conductivity; the hotter the soil, the higher the conductivity. Initially, the clays are much more conductive than the gravels. Our preheating ensured that the conductivity in the clay-rich zones would remain higher than in the gravel zones even after they were elevated to steam temperatures. Had we not taken this step and simply started with steam heating, the gravel would have been more conductive than the clay, electricity would have flowed into the gravel, and the clay would not have been heated. In November and December 1992, the electrical heating system operated at a maximum power of 800 kW, heating the clay layers in some areas to temperatures exceeding 70°C.

First Steam Pass

We began injecting steam into the lower of two permeable layers in early February 1993. For 37 days, a gas-fired boiler of ~8 MW put out 11,000 kg/h (190 liters/min) of steam. The spreading steam rapidly heated the permeable layers to the boiling point of water, and, within just 12 days, the steam front reached the extraction wells. A small fraction (about 15%) of the free-product gasoline was pushed ahead of the steam front and recovered as liquid; most of the gasoline was removed as vapor after the steam zone was fully established. Prior to the experiment, we did not know that the fraction of vapor would be so high. The amount of water and gasoline vapor removed during this phase (~6400 liters) was limited by the capacity of the vapor treatment system (~95 liters/day); subsequently, the vapor treatment system was redesigned to increase its capacity. Figure 3 shows the daily and cumulative volumes of gasoline removed during this and the other two extraction phases of the project.



Free-Product Gasoline

When large amounts of gasoline contact water, most of the gasoline remains as a separate liquid (see photo to the left). Often called “free product” because it is independent of the water, this gasoline can exist in soils as droplets, coatings on soil particles, or pools of underground gasoline. Because gasoline does not dissolve readily in water, it is very difficult to remove free product by pumping water. It can be pumped out as a separate liquid when there are large underground pools of gasoline, but some gasoline remains trapped in small spaces between soil particles. Held there by the strong forces of surface tension, this trapped gasoline can only be removed by dissolving it in thousands of times its volume of water or by boiling it away, as is done with dynamic underground stripping.

Robin Newmark, a key researcher on the dynamic underground stripping project, holds a sample of free-product gasoline and water recovered from the LLNL treatment area. The yellow gasoline floats on the heavier water, with a salad-oil-like emulsion—a mixture of droplets of both—between. The water below is tainted by dissolved gasoline (about 1 part gasoline per 1000 parts water).

Second Steam Pass

After a three-month shutdown, during which we upgraded the effluent treatment facility and improved the in-process sampling and analyses, we began the second steam pass, which ran from May into July 1993. During this pass, we intended to establish better control of the effluent stream by applying the knowledge gained during the first steam pass. We also wanted to explore ways of increasing the cost effectiveness of the dynamic stripping process.

Extraction rates were high at the beginning of the second pass because the residual heat in the soil had vaporized the gasoline during the shutdown period. To maximize the extraction rate during this second pass, we increased the amount of time the treatment zone was kept under vacuum. We also used a pulsed mode of operation, alternating steam injection and vacuum-only phases on a five- to six-day cycle. We found that the extraction rate varied considerably depending on the amount of steam injected and the total vacuum applied; more gasoline was extracted when steam was not being injected and thus the vacuum effect was greater. During this pass, the average extraction rate was more than 380 liters/day of gasoline (compared to 3 liters/day for pump-and-treat).

The effluent from the extraction wells was first directed to heat exchangers. Most of the gasoline was removed as vapor, and some of the gasoline vapor was condensed along with a large amount of water in the heat exchanger. A gasoline–water separator allowed us to measure the volume of the condensed gasoline. The stream of gasoline vapor out of the heat exchanger was used to help power two internal combustion engines that created the vacuum for extraction. Figure 4 shows the vapor extraction and treatment system.

At the end of this second steam-injection phase, we drilled six boreholes across the treated site from which we made temperature measurements and took core samples for analysis. We found that most of the soil within the treatment volume was heated to the boiling point of water. Only a thick clay layer at 30 to 34 m was not, having reached only 80°C in places. This "cold spot" was where the largest concentration of free-product gasoline remained, an estimated 3000 liters. Recovered soil samples revealed that free-product gasoline had been removed from the edges of the spill and from the zone above the water table. They also revealed that gasoline concentrations had not increased in the soil outside the treatment volume, a very important finding because we wanted to demonstrate that our method did not spread the contaminant. Figure 5 shows a geologist's interpretation of the data from the six boreholes in the treatment area.

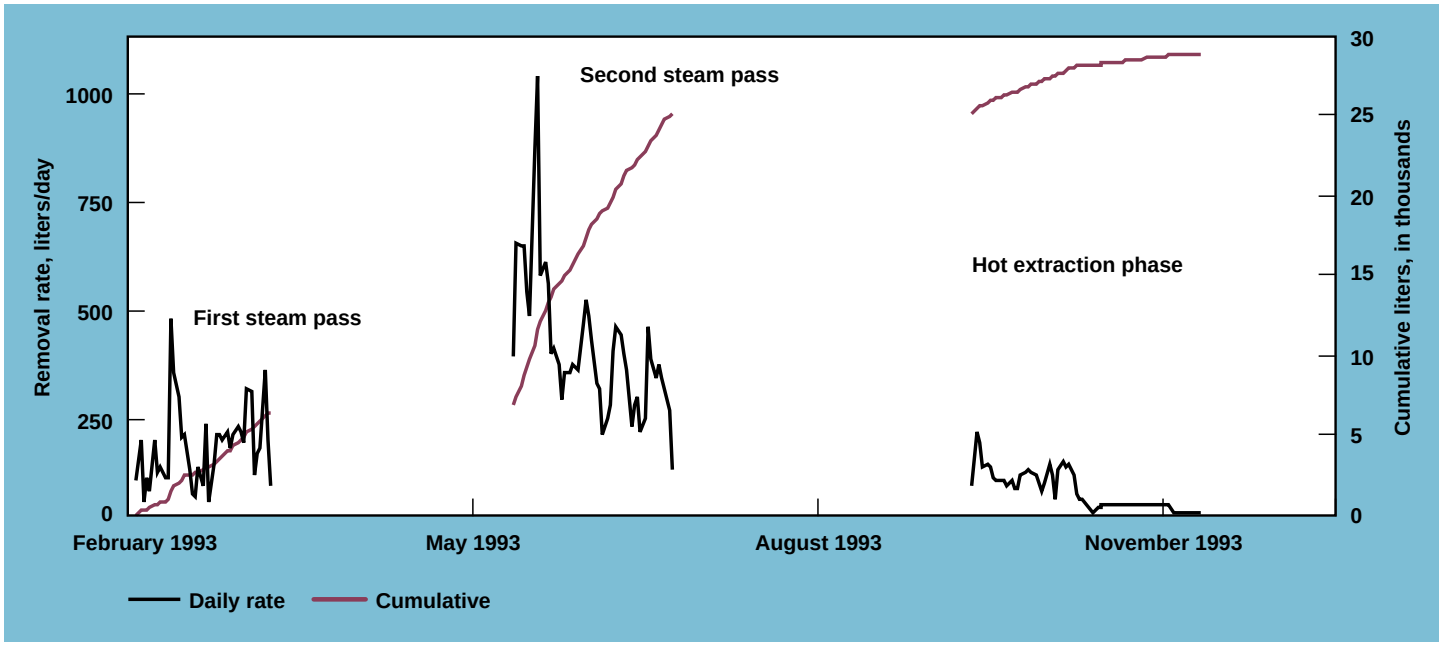


Figure 3. Daily extraction rates and cumulative volumes of extracted free-product gasoline show the three extraction phases. Extraction rates were highest during the second phase, when extraction systems were optimized and we used a pulsed mode of operation, alternating steam injection and vacuum-only phases.

Continued Hot Extraction Phase

After completing the initial experimental phase in July, we resumed extracting groundwater and vapor in October 1993 as part of the ongoing LLNL site cleanup. The initial spike in extraction rates at this time was smaller than after the first pass. In November 1993, we applied electric heating to the area. The overall temperature of the treated zone rose only slightly because the extraction systems were removing much of the deposited electrical energy. For this heating phase, we added four new, long electrodes; we are in the

Figure 4. View of the vapor-extraction treatment system. The internal combustion engines inside the trailer create the underground vacuum; the engines run directly off gasoline vapors pulled from the extraction wells.

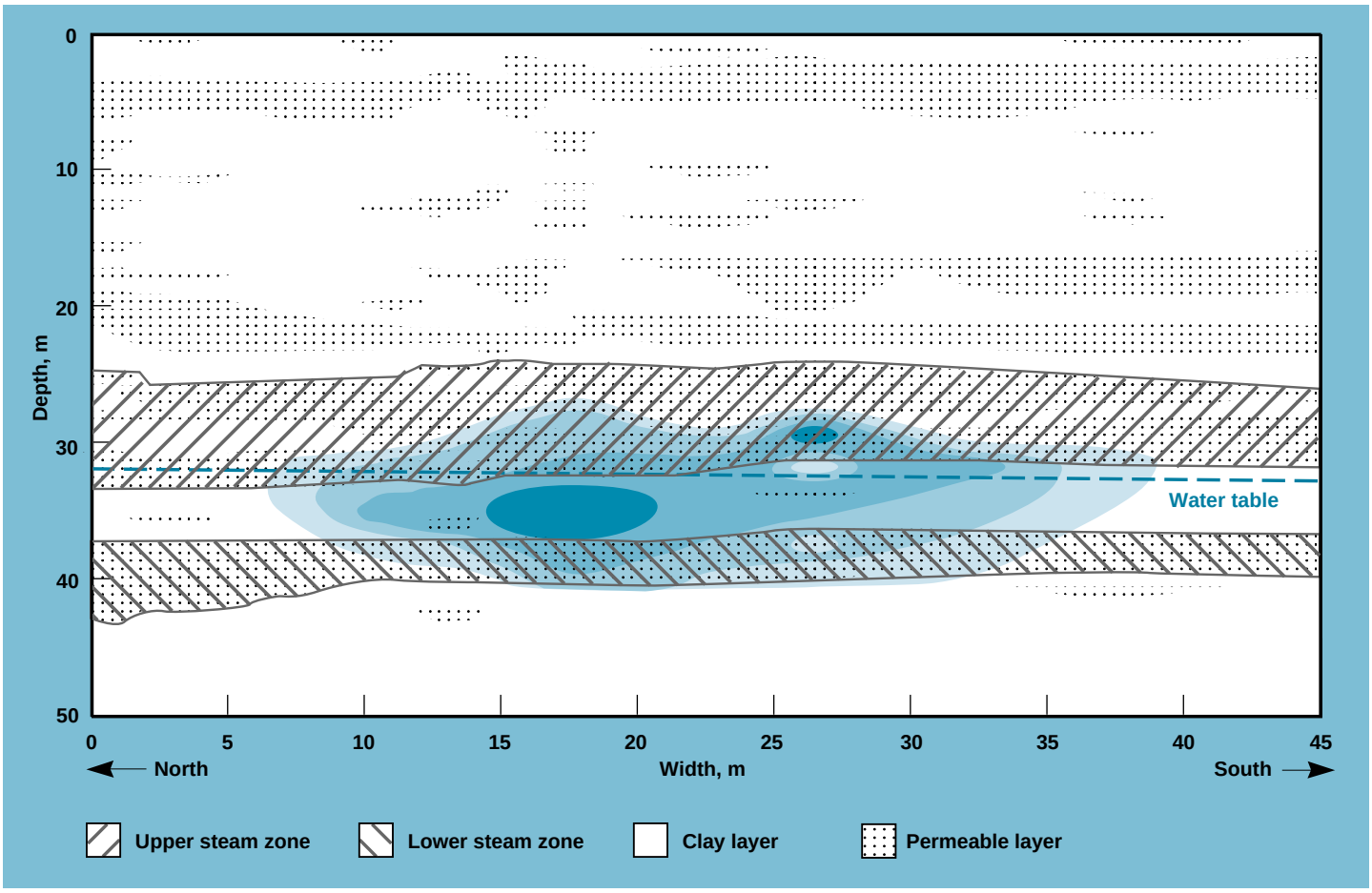


Figure 5. Approximate cross section of the treatment site after the two steam passes (compare with Figure 1). The area of gasoline contamination has contracted greatly.

process of modeling the effect these electrodes had on the process. We turned off all heating and extraction systems in mid-December 1993.

When we resumed groundwater pumping and vapor extraction in January 1994, gasoline concentrations in the recovered groundwater had decreased and the gasoline vapor concentrations increased only slightly, suggesting that no significant amount of free-product gasoline remained to be volatilized (unlike after the previous shutdown periods). Benzene concentrations in the extraction wells were less than 200 ppb, down from their peak of 7000 ppb before the first steam pass. (Benzene is the component in gasoline that is most closely regulated and thus is the chemical that we monitor to determine whether or not the cleaned-up site is within regulatory limits.) Similarly dramatic decreases in benzene concentrations were measured in the monitoring wells, from several thousand parts per billion before stripping to less than 300 ppb in January 1994. Although the site is not legally cleaned up—the regulatory limit for benzene is about 1 ppb—we have reduced the concentrations of free-product gasoline such that over a period of years microorganisms may degrade the remaining gasoline at the treatment area.

This last extraction phase removed about 3800 liters of gasoline, for a total of at least 29,000 liters. We believe that no significant free-product gasoline remains in the treatment zone (although this can only be confirmed by future drilling). We estimate that this cleanup procedure decreased the amount of gasoline in the treatment area by roughly 100 times. Sampling and analysis of cores from new boreholes must still be done to assess the cleanup/contamination status of this area.

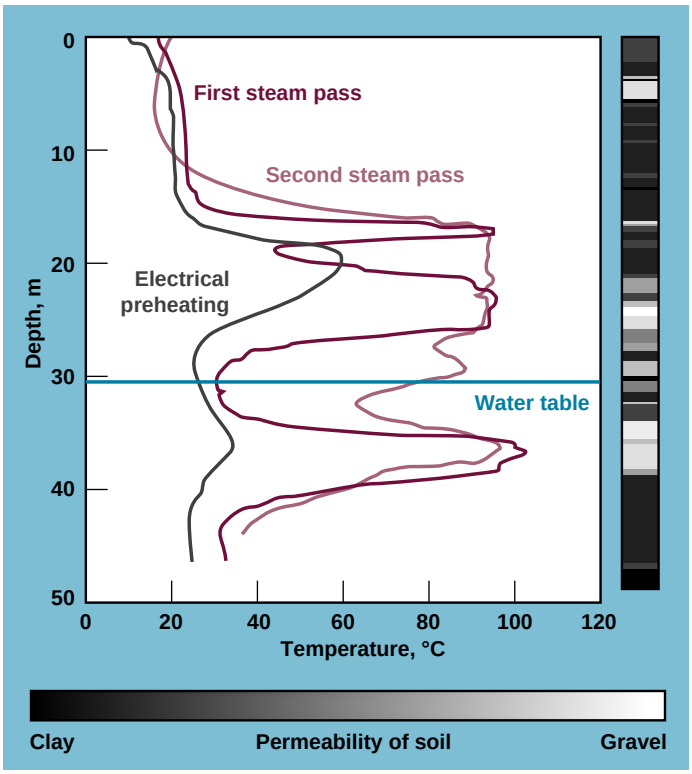


Figure 6.
Temperature logs from a monitoring well inside the ring of injection wells. These logs show electrical heating of the clay-rich layers during the preheat, steam passing through the most permeable layers during the first steam pass, and conductive heating, and later penetration, by steam into less permeable layers during the second steam pass.

Monitoring and Controlling the Cleanup Process

Day-to-day monitoring of the dynamic stripping process assured that we were injecting enough steam to drive contaminant to the center of the treatment zone without driving too much steam (and, perhaps, contaminant) outside the zone. For example, we had agreed not to drive steam under the Sandia–California site, adjacent to LLNL. Such a need for rigorous containment would likely occur in other applications.

Because of variations in local geology within the treatment zone, each of the 12 injection ports (two each in six wells) injected a different amount of steam at a given pressure, ranging from 300 kg/h to the entire output of the boiler. Although such a range in steam injection rates is expected in such a geologically heterogeneous site, it requires that the location and size of the underground steam zones be measured *in situ*.

The 11 monitoring/imaging wells housed fixed thermocouples and infrared sensor systems from which were generated continuous temperature logs. Figure 6 shows the temperature logs at one monitoring well for the electrical preheating phase and the two steam passes. These temperature logs provided the most detailed local measurements of the vertical distribution of the steam; for example, they revealed temperature gradients during the first steam pass of up to 80°C over just a meter or so in depth.

Between the wells, electrical resistance tomography, supported by temperature logs, mapped the progress of the steam and heating fronts rapidly

and accurately at resolutions of 1 to 2 m. Electrical resistance tomography provided images of the heated zones by comparing the electrical resistance distribution before and during heating. These images revealed several areas where steam was moving vertically in the treatment zone, which had not been detected by the borehole temperature logs or inferred from geological interpretations.

The speed of electrical resistance tomography made it the principal method for monitoring the dynamic stripping process. Data were obtained and analyzed in less than a day and were used to set the steam-injection rates for the next day. Figure 7 shows images that reveal the movement of the steam front. The placement of the electrical resistance tomography/temperature wells allowed good monitoring of the interior of the treatment zone (extending about 9 m outside the ring of steam injection wells) and lower-resolution monitoring of the surrounding area.

Surface-implanted tiltmeters—arranged in a larger array—monitored the full extent of the steam zone outside the treated area (Figure 8). These devices provided maps of the areal extent of the steam zone emanating from each well, particularly for the zone below the water table. They were extremely effective in mapping the lateral spread of the steam and the development of any preferential steam pathways.

Results of the Demonstration

By late 1993, dynamic underground stripping had removed about 29,000 liters of gasoline from the treatment site. We treated a volume of earth of about 80,000 m^3 between 20 and 45 m in depth. The maximum gasoline extraction rate was 950 liters/day. At the surface, about one-third of the fuel was condensed for recycling.

We believe that we removed virtually all the free-product gasoline from the treated area. After dynamic stripping has removed the bulk of the contamination, other methods of soil and groundwater cleanup (including pump-and-treat and bioremediation) can be used to remove the remainder.

This demonstration clearly showed that dynamic underground stripping quickly removes the concentrated, free-product contaminants, preventing them from continuously leaching into the soil. In larger-scale operations, such as removal of million-liter spills from refineries, the ability to recover usable fuel or solvents will be quite valuable.

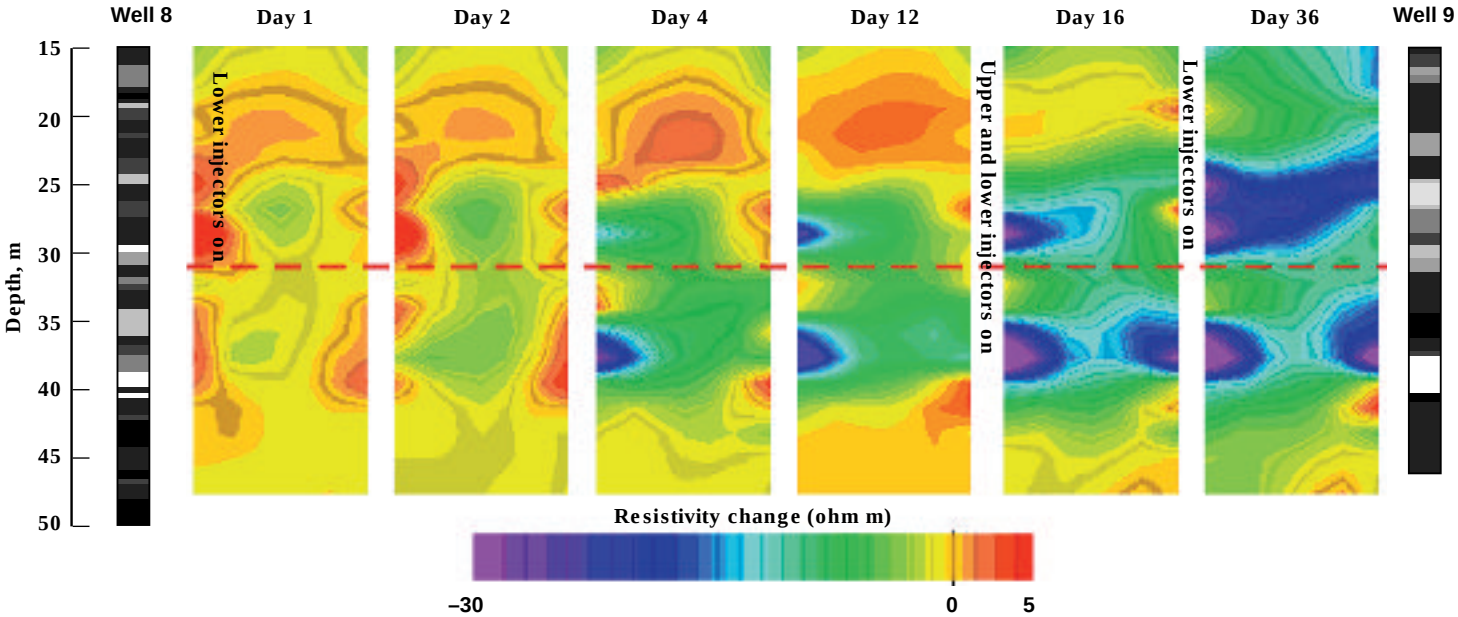


Figure 7. Electrical resistance tomography images show the passage of steam between two monitoring wells, starting from the first day of steam injection. The images compare initial baseline data with data taken during steaming. The steam zone appears as a zone of lower electrical resistivity (green, blue, and violet) passing across the image plane. This image plane is located about 6 m from the nearest injection well and is nearly perpendicular to a line linking it and the extraction wells. Small decreases in electrical resistivity are observed within hours of the start of steam injection. By the end of the first steam pass (Day 36), both the upper and lower steam zones were at or near steam temperature.

Effect of Dynamic Underground Stripping on Microorganisms

In areas where petroleum hydrocarbons exist naturally in soils, microorganisms have evolved to use these chemicals as food. Studies performed before we began stripping operations showed that on the edge of the spill, where gasoline was sufficiently dilute that it was not toxic to such organisms, bacteria were degrading the gasoline to some degree.

We expected that this flourishing ecosystem would be temporarily extinguished by the heating process. However, when we sampled the six post-test boreholes across the treatment site (drilled after the second steam pass, as mentioned above), we found a new and flourishing microbial ecosystem. We identified some species of bacteria and yeast that had been present before and others that had not. All were growing and were degrading gasoline at temperatures above 70°C. This unexpected assistance from nature is aiding in the continued cleanup of this treatment area.

Conclusions

This first application of dynamic underground stripping to a spill confirmed its value as a cleanup technology. We demonstrated that:

- Steam injection and electric heating effectively heat permeable zones and clay zones, respectively.
- Establishing a complete steam zone in very permeable materials requires large amounts of steam.
- Most of the gasoline is removed through vapor recovery (rather than being extracted as liquid).
- The extraction rate varies greatly according to the amount of steam injection, the total vacuum applied, and the cycle times.
- Alternating steam injection and vacuum-only phases maximizes the extraction rate.
- The treatment systems (e.g., the heat exchanger and the gasoline–water separator) must be able to handle large peak extraction rates and rapid changes in rate.

Dynamic stripping is relatively inexpensive. From experience at other cleanup sites, we estimate that using the pump-and-treat method with vacuum extraction at this site would have taken up to 200 years to achieve the same level of cleanup. Rough cost estimates for pump-and-treat range from $20 million to $60 million.

A "low-tech, brute-force" alternative would have been to scoop out the contaminated material—leaving a hole 100 m across and 50 m deep—and haul the diggings to a broad expanse of disused flat earth. There the soil would be spread out and periodically plowed to expose fresh material so that aerobic bacteria could degrade the contaminants. Once cleaned, the soil would be hauled back to the site to fill up the hole. This treatment site, however, contained a number of underground

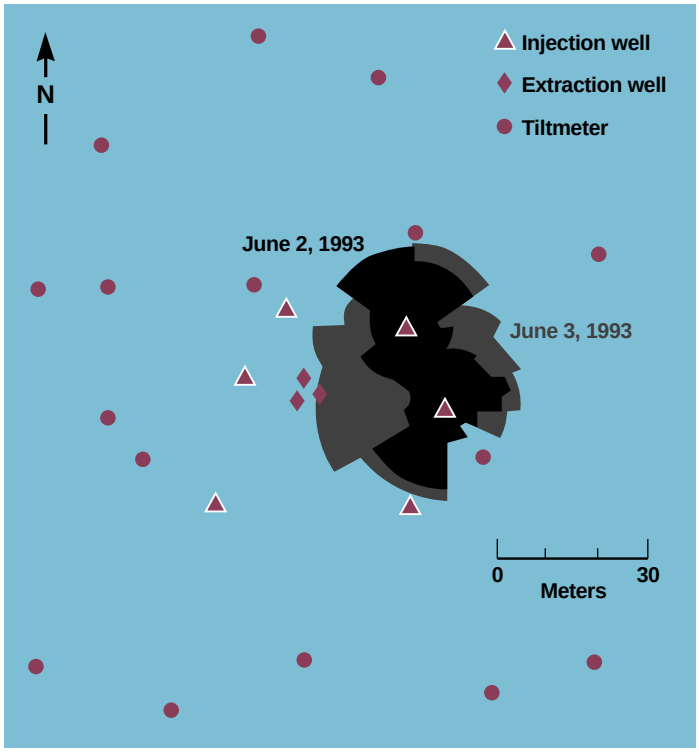


Figure 8. Tiltmeter maps show the growth of the steam fronts emanating from two injection wells on consecutive days. At this time, steam was being injected into only two wells. Steam broke through to the extraction wells the third day.

power, water, and sewer lines, which would have greatly complicated the excavation. This process would have taken a year and cost about $30 million.

In contrast, our dynamic stripping demonstration took 9 months of active time and cost $11 million for treatment and the supporting research. We are confident that if we applied what we learned from this first practical effort, we could perform the same cleanup in 6 months for about $6 million. In the future, improved commercial treatment systems optimized for high-effluent-volume, short-duration applications will probably yield further savings.

Future Work

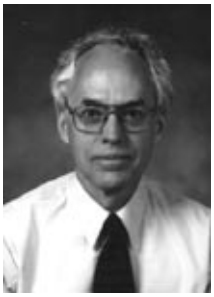
We are exploring the use of dynamic underground stripping to remove chlorinated solvents, which are used in common industrial processes (e.g., TCE or trichloroethylene, used in the manufacture of computer microchips) and are the most common contaminants at Superfund sites. These solvents have been difficult to remove using pump-and-treat methods because, unlike gasoline which is lighter than water, they are denser than water and tend to sink deeper and deeper into the earth. However, because they vaporize at 87°C (below the boiling point of water), they may well be amenable to extraction using dynamic underground stripping. We may also demonstrate dynamic underground stripping to remove solvents at a military base slated for closure.

Work funded by the Department of Energy's Assistant Secretary for Environmental Restoration and Waste Management.

Key Words: dynamic underground stripping; electrical resistance heating; electrical resistance tomography; environmental cleanup; steam injection; underground gasoline contamination—cleanup.

Reference

1. R. D. Aines and R. L. Newmark, "Rapid Removal of Underground Hydrocarbon Spills," *Energy and Technology Review* (UCRL-52000-92-7), July 1992, pp. 1–7.



For further information contact Roger Aines (510) 423-7184, Robin Newmark (510) 423-3644, John Ziagos (510) 422-5479, Alan Copeland (510) 422-8188, or Kent Udell (UC Berkeley) (510) 642-2928 (not pictured).

Abstracts

Modified Retorting for Waste Treatment

In the early 1980s, we began developing an oil-shale retorting process that uses hot solids as the heat carrier. This technology, called the hot-recycled-solid (HRS) retorting process, is now being modified and extended for application to important problems in the field of waste treatment and environmental cleanup. Current studies at the LLNL HRS pilot plant and at a related facility at Sandia National Laboratories–California are showing that the modified HRS process is suitable for removing organic compounds and for decomposing sodium nitrate ($NaNO_3$), both of which are constituents of the mixed waste stored in underground tanks at the Hanford, Washington, facility. Our small-scale pilot system uses 50 kg of hot ceramic spheres fed into a reactor to provide a large surface area for the thermal treatment and decomposition of sodium nitrate. This approach has many advantages over other technologies: it incorporates excellent safety features, is environmentally benign, and avoids sticking and agglomeration of liquid waste, which can be a problem with other approaches. Through collaborative studies, we are exploring several additional potential applications of our HRS retorting process, including the destruction of high explosives and liquid gun propellant as well as the decomposition or treatment of many of the other harmful chemicals and compounds found throughout and beyond the DOE complex.

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Cleaning Up Underground Contaminants

Beneath hundreds of industrial and government sites across the United States, pools of such contaminants as hydrocarbon fuels, cleaning solvents, and industrial chemicals threaten drinking water supplies. In a fairly typical example of this problem, between 1952 and 1979, tens of thousands of liters of gasoline leaked from an underground tank at a former LLNL filling station. Researchers from LLNL and from the University of California at Berkeley used a unique technology—dynamic underground stripping—to rapidly remove some 29,000 liters of gasoline in less than a year. This technology applies heat—by steam and electricity—to vaporize trapped contaminants in the soil. Once vaporized, the contaminants are removed by vacuum extraction. These processes are monitored and guided by underground imaging. Dynamic underground stripping is relatively inexpensive and promises to be the cleanup technology of choice at numerous sites in the future.

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