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*SITE Technology Capsule*

# Texaco Gasification Process

## Introduction

In 1980, the U.S. Congress passed the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA), also known as Superfund. to protect human health and the environment from uncontrolled hazardous waste sites. CERCLA was amended by the Superfund Amendments and Reauthorization Act (SARA) in 1986-amendments that emphasize the achievement of long-term effectiveness and permanence of remedies at Superfund sites. SARA mandates implementing permanent solutions and using alternative treatment technologies or resource recovery technologies, to the maximum extent possible, to clean up hazardous waste sites.

State and federal agencies, as well as private parties, are now exploring a number of innovative technologies for treating hazardous wastes. The sites on the National Priorities List total over 1,200 and comprise a broad spectrum of physical, chemical, and environmental conditions requiring various types of remediation. The U.S. Environmental Protection Agency (EPA) has focused on policy, technical, and informational issues related to exploring and applying new remediation technologies for Superfund sites. EPA's Superfund Innovative Technology Evaluation (SITE) Program addresses these issues. The SITE Program was established to accelerate development, demonstration, and use of innovative technologies for site cleanups. EPA SITE Technology Capsules summarize the latest information available on selected innovative treatment and site remediation technologies. These Capsules are designed to help EPA remedial project managers, EPA on-scene coordinators, contractors, and other site cleanup managers understand the types of data and site characteristics needed to effectively evaluate a technology's applicability to their site.

In treating hazardous wastes, the Texaco Gasification Process (TGP) is an innovative extension of Texaco's conventional fuels gasification technology. According to Texaco, the TGP is capable of processing hazardous waste materials containing both organic compounds and heavy metal contaminants. The organics are converted into a synthesis gas (syngas)-a usable fuel or chemical intermediate-composed mainly of hydrogen and carbon monoxide. Most heavy metals mix with the residual mineral matter in the waste matrix and solidify into a glassy slag.

The TGP was evaluated under the EPA's SITE Program in January 1994 at Texaco's Montebello Research Laboratory (MRL) in South El Monte, CA, located in the greater Los Angeles area. The Demonstration used a soil feed mixture consisting of approximately 20 weight-percent waste soil from the Purity Oil Sales Superfund Site, Fresno, California and 80 weight-percent clean soil. The mixture was gasified as a slurry in water. The slurry also included coal as a support fuel and was spiked with lead and barium compounds (inorganic heavy metals) and chlorobenzene (volatile organic compound) as the Principal Organic Hazardous Constituent (POHC). Information on the TGP and results of the SITE Demonstration at the Texaco MRL are provided here.

## Abstract

The TGP is a commercial gasification process which converts organic materials into syngas, a mixture of hydrogen and carbon monoxide. The feed reacts with a limited amount of oxygen (partial oxidation) in a refractory-lined reactor at temperatures between 2,200° and 2,650°F* and at pressures above 250 pounds per square inch gauge (psig).

According to Texaco, these severe conditions destroy hydrocarbons and organics in the feed and avoid the formation of undesirable organic by-products associated with other fossil fuel conversion processes. At such high operating temperatures, the residual ash melts-forming an inert glass-like slag.

Texaco reports that the syngas can be processed into high-purity hydrogen, ammonia, methanol, and other chemicals, as well as clean fuel for electric power.

• A list of conversion factors is included at the end of the te:

SUPERFUND INNOVATIVE TECHNOLOGY EVALUATION

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The SITE Program evaluated the TGP's ability to treat hazardous waste materials containing both organic compounds and inorganic heavy metals. The primary technical objectives of the demonstration were to determine the TGP's ability to:

Produce a usable syngas product;
Achieve 99.99 percent Destruction and Removal Efficiencies (DREs) for organic compounds; and
Produce a non-hazardous primary solid residual-coarse slag-and secondary solid residuals-fine slag and clarifier bottoms.

Additionally, the demonstration test results and observations were evaluated to:

- Develop overall capital and operating cost data; and
- Assess the reliability and efficiency of the TGP operations.

The findings of the TGP SITE Demonstration are as follows:

- The TGP produced a syngas that can be used as feed for chemical synthesis facilities or as a clean fuel for the production of electrical power when combusted in a gas turbine. The average composition of the dry synthesis gas product consisted of 37% hydrogen, 39% carbon monoxide and 21% carbon dioxide. No organic contaminants, other than methane (55 ppm), exceeded 0.1 ppm. The average heating value of the gas, a readily **combustible fuel,** was 239 British thermal units (Btu) per dry standard cubic foot (dscf).
- The DRE for the designated POHC (chlorobenzene) was greater than the 99.99% goal.
- The average Toxicity Characteristic Leaching Procedure (TCLP) measurement for the coarse slag was lower than the regulatory levels for lead (5 milligrams per liter) (mg/L) and: barium (100 mg/L). The average California Waste Extraction Test (WET)-Soluble Threshold Limit Concentration (STLC) measurement for the coarse slag was lower than regulatory value for barium (100 mg/L) and higher than the regulatory value for lead (5 mg/L).
- Volatile heavy metals, such as lead, tend to partition and concentrate in the secondary TGP solid products-fine slag and clarifier solids. The average TCLP and WET-STLC measurements for these secondary TGP solid products were higher than the regulatory limits for lead, but lower than the regulatory limits for barium.
- Texaco estimates an overall treatment cost of $308 per ton of soil for a proposed transportable unit designed to process 100 tons per day (tpd) of soil with characteristics similar to that from the Purity Oil Sales Superfund Site, based on a value of $1.00/million Btu for the syngas product. Texaco estimates an overall treatment cost of $225 per ton of soil for a proposed stationary unit designed to process at a central site, 200 tpd of soil with characteristics similar to that from the Purity Oil Sales Superfund Site, based on **a** value of $2.00/ million Btu for the syngas product.
- In continuous operations, proposed commercial units are expected to operate at on-stream efficiencies of 70% to 80% to allow for scheduled maintenance and intermittent, unscheduled shutdowns.

The TGP technology evaluation applied the EPA's standard nine criteria from the Superfund feasibility study (FS) process. Summary conclusions appear in Table 1.

## Technology Description

Texaco maintains three pilot-scale gasification units, ancillary units, and miscellaneous equipment at the Montebello Research Laboratory (MRL), where the SITE demonstration was conducted. Each gasification unit can process a nominal throughput of 25 tpd of coal. The SITE Demonstration employed one of the three pilot-scale gasification units, the High Pressure Solids Gasification Unit II (HPSGU II), and support units as shown on the Figure 1 block flow diagram. The diagram identifies the key MRL process units that are part of the overall facility.

### *Solids Grinding and Slurry Preparation Unit*

The slurry feed used in the demonstration was a blend of the Purity Oil soil slurry and a clean soil slurry. Coal and clean soil were precrushed in a hammer mill. For each slurry, the precrushed product (coal and clean soil; site-screened Purity **Oil** waste soil and coal) was combined with water, an ash fluxing agent, and **a** slurry viscosity reducing agent in a rod mill, where the mixture was ground and slurried. The mill product was screened to remove oversize material and transferred to the HPSGU II slurry storage tanks where the inorganic spikes (lead and barium) were added.

### *High Pressure Solids Gasification Unit II*

The slurry was gasified in MRL's HPSGU II. This unit includes equipment for slurry feeding, gasification, gas scrubbing, slag removal, clarifier solids removal, and process water handling. Figure 2 is primarily a schematic flow diagram of the process equipment and flows within the HPSGU II used in this demonstration. Secondarily, Figure 2 defines the interaction of the HPSGU II process streams with other MRL TGP process streams and units.

During the demonstration, the slurry was spiked with chlorobenzene as it was pumped into the gasifier. The gasifier is a two-compartment vessel, consisting of an upper refractory-lined reaction chamber and a lower quench chamber. Oxygen and slurry feeds were charged through an injector nozzle into the reaction chamber where they reacted under highly reducing conditions to produce raw syngas and molten slag. The oxygen-to-slurry ratio was controlled to maintain an operating temperature sufficient to convert the soil and coal ash into a molten slag. The average pressure was 500 psig.

From the reaction chamber, the raw syngas and molten slag flowed into the quench chamber, where water cooled and partially scrubbed the raw syngas. The raw syngas leaving the gasifier quench chamber was then further scrubbed of hydrogen chloride and particulates with additional water, cooled to near ambient temperature, and routed to MRL's Acid Gas Removal Unit. More than 99% of the chlorides in the syngas were transferred to the circulating water in these steps.

The water quench also converted the molten ash into glass-like slag particles, which then passed down through the quench chamber/lockhopper system. The lockhopper system discharged the slag solids to a shaker screen which separated the slag into a coarse fraction (coarse slag), and a fine fraction (fine slag). The fine slag was recovered using a vacuum belt filter. The filtrate from the vacuum belt filter was recycled to the lockhopper system.

Water from the quenching and scrubbing steps was combined and cooled. Solids in the combined stream were removed using a clarifier, which produced an underflow stream of concentrated solids and water, called clarifier bottoms, and an overflow stream of clarified water. Periodically, the clarifier bottoms were drawn off and filtered to produce clarifier solids

*Table 1. Evaluation Criteria for the Texaco Gasification Process Technology*

| | *Evaluation Criteria for Technology* |
|---|---|
| *Overall protection of human health and the enveronment* | • *Provides both short- and long-term protection by eliminating exposure to both organic and inorganic contaminants in* soil.<br>• *Prevents further groundwater contamination and offsite migration by destroying organic contaminants and demonstrating a potential to immobilize heavy metals into a non-leaching glassy, coarse slag.*<br>• *Requires measures to protect workers and community during excavation, handling, and treatment.* |
| *Compliance with ARARS** | • *Requires compliance with Resource Conservation and Recovery Act (RCRA) treatment, storage, and land disposal Federal regulations (of a hazardous waste).*<br>• *Excavation and construction and operation of onsite treatment unit may require compliance with location-specific ARARs.*<br>• *Emission controls are needed to ensure compliance with air quality standards, if volatile compounds and particulate emissions occur during excavation, handling, and treatment prior to slurrying.*<br>• *Wastewater discharge to treatment facilities or surface water bodies requires compliance with Clean Water Act regulations.*<br>• *CERCLA defines drinking water standards established under the Safe Drinking Water Act that apply to remediation of Superfund sites.*<br>• *Requires compliance with Toxic Substances* **Control Act** *treatment and disposal regulations for wastes containing polychlorinated biphenyls.*<br>• *CERCLA remedial actions and RCRA corrective actions are to be performed in accordance with Occupational Safety and Health Administration requirements.* |
| *Long-term effectiveness and permanence* | • *Effectively destroys organic contaminants and demonstrates a potential to immobilize inorganic heavy metals into a non-leaching glassy coarse slag.*<br>• *Site contaminants are destroyed or removed with residuals.*<br>• *The potential immobilization of heavy metals into non-leaching glassy, coarse slag requires further testing for anticipated long-term stability.*<br>• *Fine slag and clarifier solids may require further treatment. particularly when volatile heavy metals are present.*<br>• *Wastewaters require further treatment to effect long-term stability of contaminants and reuse of water.* |
| Reduction of toxicity, *mobility, or volume through treatment* | • *Effectively destroys toxic organic contaminants and demonstrates a potential to immobilize inorganic heavy metals into the primary solid product, a non-leaching glassy coarse slag.*<br>• *Reduction of soil to glassy slag reduces overall volume of material.* |
| *Short-term effectiveness* | • *Emissions and noise controls are required to eliminate potential short-term risks to workers and community from noise exposure and exposure to contaminants and particulate emissions released to air during excavation, handling, and treatment prior* to *slurrying.* |
| *Implementability* | • *Treatability testing required for wastes containing heavy metals.*<br>• *Large process area required.*<br>• *Large-scale transportable 100 tpd unit on multiple transportable skids requires large scale remediation with onsite commitment of more than 50,000 tons of soil and* 2 ***years*** *of operation.*<br>• *Initial transportable unit can be constructed and may be available in 24 months.*<br>• *Large size of unit and ex-situ thermal destruction basis for unit may provide delays in approvals and permits.* |
| ***Cost***** | • *Large-scale, complex, high-temperature, high-pressure, transportable thermal destruction unit at approximately $308 per ton of waste* soil. |
| *Community acceptance* | • *Large-scale, ex-situ, high-temperature, high-pressure, thermal destruction unit may require significant effort to develop community acceptance.* |
| State *acceptance* | • *If remediation* is *conducted as part of RCRA corrective actions, state regulatory agencies may require operating permits, such as: a permit to operate the treatment system, an air emissions permit, and a permit to store contaminated soil for greater than 90 days.* |

** Applicable or relevant and appropriate requirements.*
*** Actual cost of a remediation technology is highly site-specific and dependent on matrix characteristics. See Overall Unit Cost section of this Capsule. A complete cost and economic analysis can be found in the Innovative Technology Evaluation Report.*

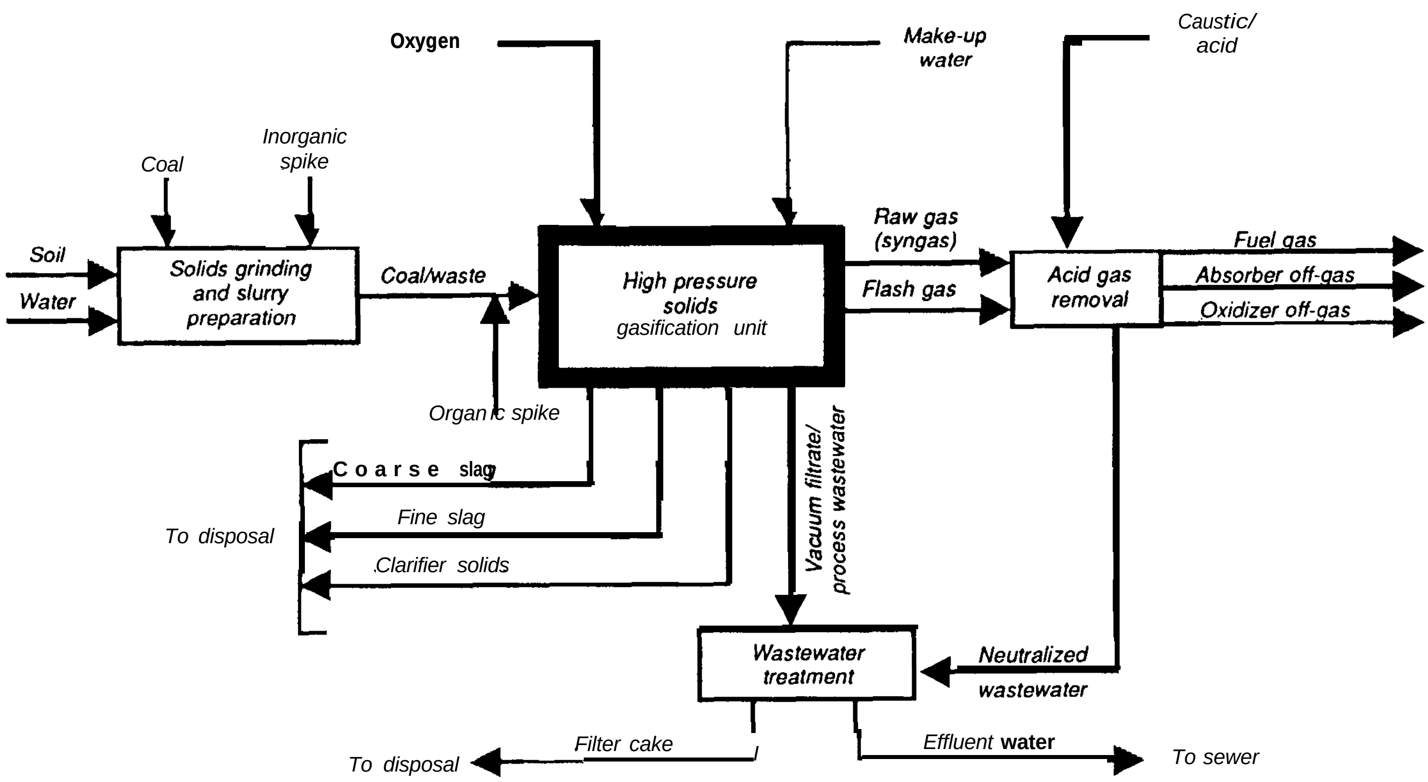


Figure 1. Block flow diagram of MRL TGP during SITE demonstration.

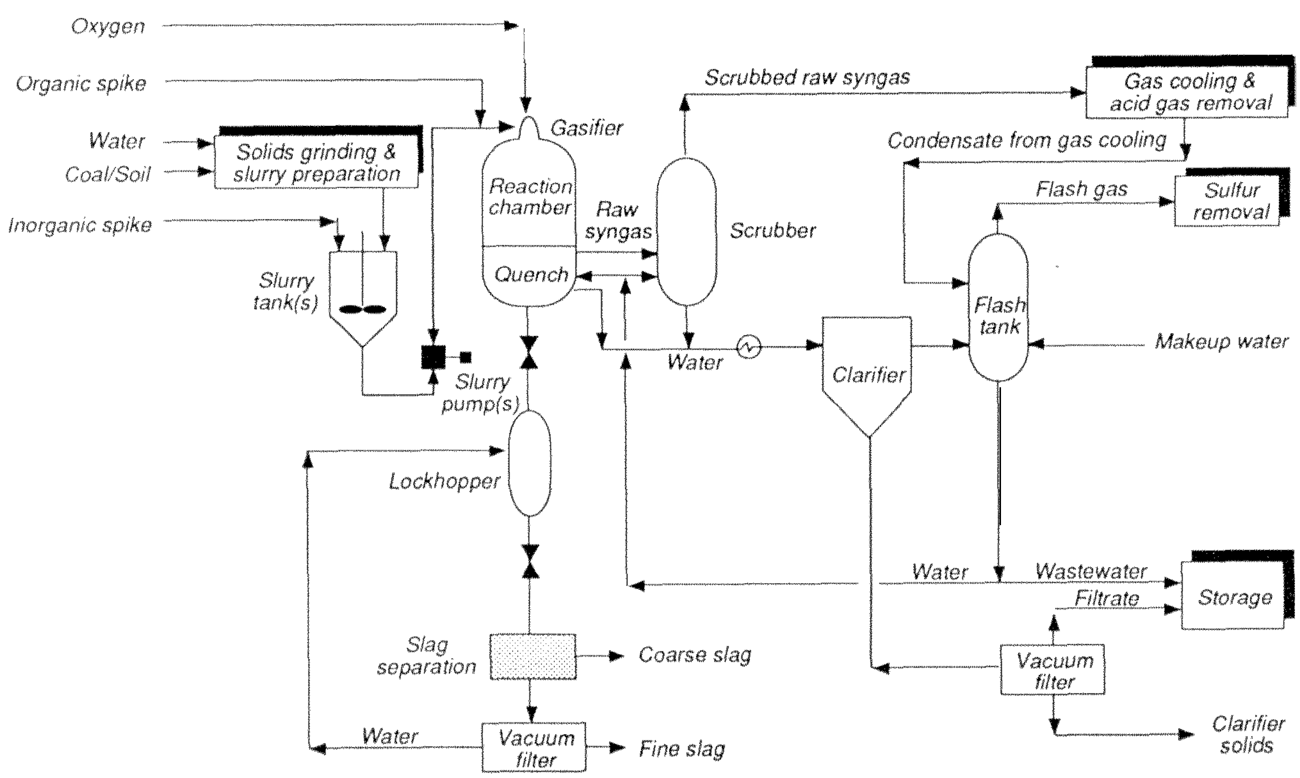


Figure 2. Schematic flow diagram of MRL's HPSGU II during SITE demonstration.

cake and vacuum filtrate. The clarifier overhead flowed to the flash tank where it combined with the condensate from the cooling of the raw syngas. In the flash tank, dissolved gases are removed from the water at low pressure (flash gas). Except for a small wastewater blowdow stream, the flash tank water was recycled to the gasifier quench chamber and raw gas scrubber.

The wastewater blowdown and vacuum filtrate were routed to temporary storage for testing prior to treatment and disposal.

## Acid Gas Removal/Sulfur Removal

During the demonstration, MRL used a regenerable solvent process to separate hydrogen sulfide and carbonyl sulfide from the raw syngas. The raw syngas was contacted with the solvent, which removed the hydrogen sulfide, carbonyl sulfide, and some carbon dioxide (acid gases) producing a low-sulfur-content combustible fuel gas. The fuel gas was then flared. The acid gases stripped from the solvent and combined with the gasification system flash gas were fed to the Sulfur Removal Unit where the sulfides were absorbed using a caustic solution. The dissolved sulfides were oxidized with air and steam, producing a solution of sodium thiosulfate that was neutralized and routed to wastewater treatment.

As with the fuel gas stream, the Sulfur Removal Unit absorber and oxidizer off-gas streams were flared.

## Technology Applicability

The versatile TGP can process a variety of waste streams. Virtually any carbonaceous hazardous or non-hazardous waste stream can be processed in the TGP as long as adequate facilities are provided for pretreatment and storage.

Depending upon the physical and chemical composition of the waste stream, it can either be used as the primary feed to the gasifier or it can be co-gasified with a high-Btu fuel such as coal, petroleum coke, or oil. The combined feed must be slurried successfully, high enough in heating value to maintain gasifier temperatures, and composed of an ash matrix with a fusion temperature that falls within operational limits.

In general, the ratio of waste feed to fuel can be adjusted over a wide range. Although a waste stream can be used as the sole feed to the gasifier, blending the waste with another feed can ensure continuity and stability of operation.

The TGP can treat wastes that fall into three categories,

(1) Solid or liquid wastes that contain sufficient energy to sustain gasifier operation as the sole feed without adding another higher-heating-value fuel.
(2) Solid wastes with heating values too low to sustain gasifier operation that can be supplemented with a higher-heating-value fuel, such as coal.
(3) Liquid waste with insufficient heating values that can be combined with a higher-heating-value fuel. In this case the liquid waste can be used as the fluid phase of the primary feed slurry.

The TGP has operated commercially for nearly 45 years on feeds such as natural gas and coal, and non-hazardous wastes such as liquid petroleum fractions, and petroleum coke. Texaco's gasification process is currently licensed in the U.S. and abroad. The syngas is used for the production of electric power and numerous chemical products, **such as ammonia, methanol, and high-purity hydrogen.** As **an innovative** process gasifying less traditional and hazardous wastes, Texaco reports that the TGP has processed various waste matrices containing a broad range of hydrocarbon compounds including coal liquefaction residues, California hazardous waste material from an oil production field (petroleum production tank bottoms), municipal sewage sludge, waste oil, used automobile tires, waste plastics, and low-Btu soil. Texaco licensees in Europe have had long-term success in gasifying small quantities of hazardous waste as supplemental feedstock including PCBs, chlorinated hydrocarbons, styrene distillation bottoms, and waste motor oil.

Texaco expects to design TGP facilities with flexible and comprehensive storage and pretreatment systems capable of processing a wide range of waste matrices slurried with coal or oil, water, and additives. If the specific waste exhibits unusual physical or chemical characteristics that would affect the ability of the pretreatment module to slurry the feed, additional pretreatment equipment may supplement the existing design.

## Technology Limitations

The TGP can process all waste stream matrices based on the availability of adequate materials-handling, pretreatment, and slurrying equipment. The unit's complexity and costs, and the economic benefit of a tie-in to its syngas product, mandate that on-site remediations be limited to relatively large sites with a minimum of approximately 50,000 tons of waste feed and about two years of operation.

## Process Residuals

Solid TGP products such as coarse slag, fine slag, and clarifier solids are stored and characterized to allow proper disposal based on their hazardous or non-hazardous characteristics. In most cases, any excess water residuals will be treated by conventional wastewater treatment technologies.

## TGP Support Requirements

The TGP support requirements include site conditions (surface, subsurface, clearance, area, topography, climate, and geography), utilities, facilities, and equipment.

For a proposed 100-tpd transportable unit, surface requirements would include a level, graded area capable of supporting the equipment and the structures housing it. The complexity and mechanical structure of a high-temperature, high-pressure TGP unit mandate a level and stable location. The unit cannot be deployed in areas where fragile geologic formations could be disturbed by heavy loads or vibrational stress. Foundations must support the weight of the gasifier system, which is estimated at 50 tons, as well as other TGP support facilities and equipment. The transportable TGP unit would weigh approximately 300 tons and consist of multiple skid-mounted trailers requiring stable access roads that can accommodate oversized and heavy equipment.

The transportable 100-tpd TGP unit would require an area of approximately 40,000 square feet ($ft^2$) (275 ft x 150 ft), with height clearances of up to 70 ft. This area should accommodate all TGP process operations, although additional space could be needed for special feed preparation and waste residuals storage facilities.

The transportable TGP unit could be used in a broad range of different climates. Although prolonged periods of freezing temperatures might interfere with soil excavation and handling, coal handling, slurry preparation, and water-related operations, they would not affect a TGP design that incorporates adequate heating, insulating, and heat-tracing capabilities at critical locations.

The proposed transportable 100-tpd TGP unit would require the following utilities: 91 tpd of oxygen, 39 tpd of coal, 5 tpd of lime, 410 kilowatthours per hour (kWh/h) of electrical power, 40 gallons per minute (gpm) of make-up water, and less than 1 tpd of nitrogen.

Support facilities would include staging areas for contaminated soil and coal prior to pretreatment, materials-handling, and slurry preparation. Syngas product would be routed by pipeline directly off-site without any support facilities for storage or transport. Solid products would be stored in roll-off bins. Wastewater would be collected in appropriate tank storage. All support facilities must be designed to control run-off and fugitive emissions. Support equipment would include excavation/transport equipment such as backhoes, front-end loaders, dump trucks, roll-off bins, and storage tanks.

## Performance Data

To assess the TGP operation and its ability to process a RCRA-designated hazardous waste feed that does not comply with TCLP and WET-STLC regulatory limits, non-RCRA hazardous soil from the Purity Oil Sales Superfund Site in Fresno, CA was spiked with lead nitrate and barium nitrate during slurry preparation to create a surrogate RCRA-hazardous waste feed. For the extended SITE demonstration, additional slurry was required and prepared using a mixture of clean soil and oil spiked with barium nitrate since further supplies of Purity Oil soil could not be obtained. To ensure a sufficient concentration of the designated POHC for DRE determination, chlorobenzene was added to the Purity Oil/clean soil mixed test slurry at the slurry feed line to the gasifier. Table 2 shows the overall composition of the mixed, spiked test slurry processed during the TGP SITE Demonstration.

Three runs were conducted over a 2-day period, treating approximately 40 tons of slurry. The total amount of slurry treated during the entire demonstration (scoping runs, initial shakedown, system startup, a pretest run, the three replicate runs, and post-demonstration processing of the slurry inventory) was approximately 100 tons. Critical process parameters included slurry feed rate; raw syngas, flash gas, and fuel gas flow rates; make-up and effluent water flow rates (except neutralized wastewater); weight of coarse slag, fine slag, and clarifier solids; and the organic spike flow rate. Critical chemical/analytical parameters included VOCs, polychlorinated dibenzodioxins (PCDDs), polychlorinated dibenzofurans (PCDFs). and metals in all feed and discharge streams (except neutralized wastewater); TCLP and WET-STLC analyses on waste feed, slurry feed, coarse slag, fine slag, and clarifier solids; and compositions of process gas streams.

*Table 2. Composition of Demonstration Slurry Feed*

| | Slurry, pounds (lb) | | |
|---|---|---|---|
| | *Purity Oil soil* | *Clean soil* | *Total mixed** |
| *Pittsburgh #8 coal* | 10,511 | 56,280 | 66,791 |
| *Hovoline SAE 30 oil* | — | 2,050 | 2,050 |
| *L.A. County soil* | — | 11,000 | 11,000 |
| *Fresno County soil* | — | 11,080 | 11,080 |
| *Purity Oil soil* | 5,264 | — | 5,264 |
| *Water* | 10,529 | 54,000 | 64,529 |
| *Gypsum* | — | 2,500 | 2,500 |
| *Surfactant* | 21 | 130 | 151 |
| *Barium nitrate* | 330 | 1,000 | 1,330 |
| *Lead nitrate* | 145 | — | 145 |
| *TOTAL* | 26,800 | 138,040 | 164,840 |

*. The total slurry feed does not include the chlorobenzene organic spike (L-5) that was added (at approximately 3,150 milligrams per kilogram (mg/kg) based on slurry flow) to the total mixed slurry flow to the gasifier at 6.20, 6.30, and 6.75 pounds per hour (lb/h) for Runs 1, 2, and 3, respectively.*

Note.-A list *of conversion factors is included at the end of the text.*

## *DRE*

The DRE was the measure of organic destruction during the demonstration test. This parameter is determined by analyzing the concentration of the POHC in the feed slurry and the effluent gas stream(s). For a given POHC, DRE is defined as follows:

$$DRE = \frac{W_{IN} - W_{OUT}}{W_{IN}} \times 100\%$$

Where:

$W_{IN}$ = Mass feed rate of the POHC of interest in the waste stream feed

$W_{OUT}$ = Mass emission rate of the same POHC present in the effluent gas streams prior to release to the flare.

For these TGP SITE tests, DREs were calculated in two ways. For the gasification process, the effluent gas streams included the raw syngas and flash gas; for the overall TGP operation, the effluent gas streams included the fuel gas, the absorber off-gas, and oxidizer off-gas. The POHC identified for the demonstration was chlorobenzene. This compound was selected as a representative stable compound for the purpose of evaluating the TGP's ability to destroy organic compounds. As shown in Table 3, all calculated DREs were greater than 99.99 percent for chlorobenzene.

## *Slag and Solid Residuals Leachability*

### Test Slurry Leaching Characteristics

The test slurry was spiked with lead nitrate and barium nitrate to create a surrogate RCRA-hazardous waste feed and to evaluate the TGP's ability to produce a non-hazardous solid residual in which heavy metals are bound in an inert slag resulting in TCLP and WET-STLC measurements that are lower than their respective regulatory limits. Table 4 shows that the test slurry feed measurements were higher than the TCLP

Table 3. Destruction and Removal Efficiencies (DREs) for Principal Organic Hazardous Constituent (POHC) - Chlorobenzene

| Run | DRE for gasification process | | | | |
|---|---|---|---|---|---|
| | $W_{IN}$* (lb/h) | Raw syngass (lb/h) | Flash gas (lb/h) | Total $W_{out}$** (lb/h) | DRE*** (%) |
| 1 | 6.20 | 0.00016 | 0.000013 | 0.000173 | 99.9972 |
| 2 | 6.30 | 0.00019 | 0.000010 | 0.000200 | 99.9966 |
| 3 | 6.75 | 0.00023 | 0.000014 | 0.000244 | 99.9964 |
| Average | 6.42 | 0.00019 | 0.000012 | 0.000210 | 99.9967 |

| Run | DRE for overall Texaco MRL operation | | | | | |
|---|---|---|---|---|---|---|
| | $W_{IN}$* (lb/h) | Fuel gas (lb/h) | Abs. offgas (lb/h) | Oxid. offgass (lb/h) | Total $W_{out}$** (lb/h) | DRE** (%) |
| 1 | 6.20 | 0.0000033 | 0.00010 | <0.000019 | <0.000 122 | >99.9980 |
| 2 | 6.30 | 0.0000620 | 0.00038 | 0.000018 | 0.000460 | 99.9926 |
| 3 | 6.75 | 0.0000 130 | 0.00023 | 0.000011 | 0.000254 | 99.9962 |
| Average | 6.42 | 0.0000250 | 0.00024 | <0.000016 | <0. 00028 1 | >99.9956 |

* $W_{IN}$ = Mass feed rate of chlorobenzene (POHC) in the waste stream feed.

** $W_{OUT}$ = Mass emission rate of chlorobenzene (POHC) in gas effluent streams.

*** $DRE = \frac{W_{IN} - W_{OUT}}{W_{IN}} \times 100$

Note -A list of conversion factors is included at the end of the text.

Table 4. TCLP and WET-STLC Results - Lead and Barium

| | TCLP Pb mg/L | | WET-STLC Pb mg/L | |
|---|---|---|---|---|
| | Range | Average | Range | Average |
| Regulatory value | 5.0 | | 5.0 | |
| Purity Oil soil* | 223 | | — | |
| Clean soil (S- 1)** | <0.03 | | <0.5 | |
| Slurry (SL- 1)*** | 8.1-8.4 | 8.3 | 54-6 1 | 56 |
| Coarse slag (S-3) | 3.3-5.8 | 4.5 | 6.7-11.1 | 9.8 |
| Fine slag (S-4) | 11-18.3 | 14.9 | 22.8-52.9 | 43.0 |
| Clarifier solids (S-5) | 691-1,330 | 953 | 903- 1,490 | 1,167 |

| | TCLP Ba mg/L | | WET-STLC Ba mg/L | |
|---|---|---|---|---|
| | Range | Average | Range | Average |
| Regulatory value | 100 | | 100 | |
| Purity Oil soil* | 329 | | — | |
| Clean soil (S- 1)** | 0.3 | | <5.0 | |
| Slurry (SL- 1)*** | 0.1-0.2 | 0.1 | <5.0-6.5 | <5.5 |
| Coarse slag (S-3) | 0.5-0.8 | 0.6 | <5.0 | <5. 0 |
| Fine slag (S-4) | 1.2-2.0 | 1.75 | 5.6- 10.4 | 9.3 |
| Clarifier solids (S-5) | 1.2-3.8 | 2.7 | 14-51.4 | 38.4 |

* Lead TCLP of Purity Oil soil (waste feed to produce Purity oil slurry with 15,000 mg/kg (as elemental lead) lead nitrate spike and barium TCLP of Purity Oil soil with 30,000 mg/kg (as elemental barium) barium nitrate spike-measured in pretest spike study.

** Clean soil is soil matrix used to produce clean soil slurry.

*** The SITE Demonstration slurry (SL- 1) is a mixture of lead nitrate and barium nitrate-spiked slurries produced using Purity Oil soil and clean soil. SL- 1 is composed of 26,800 lb of Purity Oil slurry mixed with 138,040 lb of clean soil slurry (See Table 2.).

Note._ A list of conversion factors is included at the end of the text

Pb: Lead

Ba: Barium

and WET-STLC regulatory limits for lead but lower than the regulatory limits for barium.

## Normalized TCLP and WET-STLC Values for Lead in Test Slurry

The test soil composed of approximately 20 weight-percent Purity Oil soil (lead TCLP of Purity Oil soil: 223 mg/L) and 80 weight-percent clean soil (lead TCLP of clean soil: <0.03 mg/L), could be expected to have a normalized, or corrected, TCLP value for lead of approximately 40 mg/L. The test slurry, composed of approximately 20 weight-percent total soil (normalized TCLP value for lead: 40 mg/L) diluted by the remaining slurry solution of 80 weight-percent coal, gypsum, and water (no lead TCLP value) could be expected to have a calculated TCLP value for lead of around 8 mg/L, which closely approximates the average TCLP measurement of 8.3 mg/L lead for the test slurry. Similarly, an expected normalized WET-STLC value of 280 mg/L lead, based on spiked soil blending, would be consistent with the average WET-STLC measurement of 56 mg/L lead for the test slurry, due to the dilution of the coal, gypsum, and water.

## Fate of Barium in Test Slurry

The fate of the barium contaminant indicates that significant changes occurred in the barium chemistry during slurry formulation. A pretest study TCLP value of 329 mg/L was measured in a leachate produced from the spiked Purity Oil soil. This contrasts with the much lower 0.1 mg/L measured in the TCLP leachate from the test slurry matrix, which included coal, gypsum, and water. The introduction of sulfur-containing gypsum and coal could have provided an environment in the slurry that changed the original soluble barium nitrate spike material to insoluble barium sulfate. The relative solubilities of barium nitrate and barium sulfate differ by ten-thousand fold. Since barium sulfate is relatively insoluble, it remains with the solids and does not transfer to the leachate during the TCLP test. The one thousand times reduction in the test slurry TCLP result for barium from the pretest level in the Purity Oil soil would be consistent with a partial speciation change to barium sulfate.

## SITE Demonstration Results

The SITE Demonstration showed that the mobility of the lead in the main residual solid product-the coarse slag-was lower than the mobility of the lead in the contaminated/spiked soil. The mobility of the barium essentially remained unchanged. The average TCLP and WET-STLC measurements for coarse slag, which comprised 62.5 weight-percent of the total solid residuals, were lower than the TCLP regulatory levels for lead and barium and the WET-STLC regulatory value for barium. The average TCLP and WET-STLC measurements for fine slag, which constituted 35.9 weight-percent of the total solid residuals, and clarifier solids, which amounted to 1.6 weight-percent, were higher than the TCLP and WET-STLC regulatory limits for lead but lower than the tests' regulatory limit for barium. The leach test results indicated mixed success in meeting the test objectives. Analysis of the effects of dilution by the non-contributing slurry components-coal, water, gypsum-on the TCLP and WET-STLC test results showed that the TGP can potentially produce-as its major solid residual-a coarse slag product with TCLP and WET-STLC measurements below regulatory limits. The TGP effectively treated a soil matrix exhibiting **a** normalized TCLP value of 40 mg/L for lead and produced a coarse slag with an average TCLP value of 4.5 mg/L lead and a fine slag with an average TCLP value of 14.9 mg/L lead.

The average WET-STLC measurements for all solid residual streams were higher than the WET-STLC regulatory values for lead. However, the TGP demonstrated significant improvement in reducing lead mobility as measured by WET-STLC results. The process treated **a** soil matrix exhibiting a normalized WET-STLC value of 280 mg/L for lead and produced a coarse slag with an average WET-STLC value of 9.8 mg/L lead and a fine slag with an average WET-STLC of 43 mg/L lead.

## Synthesis **Gas** Product Composition

The synthesis gas (syngas) product from the TGP is composed primarily of hydrogen, carbon monoxide, and carbon dioxide. For a commercial unit, the raw syngas would receive further treatment in an acid gas treatment system to remove hydrogen sulfide. This would produce a combustible fuel gas that could be burned directly in a gas-turbine/electrical-generation facility or be synthesized into other chemicals.

The raw gas from the gasifier was sampled and analyzed to evaluate the TGP's ability to gasify a slurry containing a RCRA-hazardous waste material and produce a synthesis gas product. This gas stream was then treated **in** the MRL Acid Gas Removal System; the resulting fuel gas product was flared. Table 5 shows the compositions of the raw syngas and the fuel gas product.

## Products of Incomplete Reaction (PIRs)

The TGP is a gasification process which converts organic materials into syngas by reacting the feed with a limited amount of oxygen (partial oxidation). In addition to the syngas mixture of hydrogen and carbon monoxide, other organic compounds appear as products of the incomplete partial oxidation reaction. The term "PIR" describes the organic compounds detected in the gas product streams as a result of the incomplete reaction process.

All gas streams, including the raw gas, flash gas from the gasification section, fuel gas, absorber off-gas, and oxidizer off-gas, contained trace amounts of volatile and semivolatile PIRs. Carbon disulfide, benzene, toluene, naphthalene, naphthalene derivatives, and acenaphthene concentrations were measured in the gas streams at parts per billion (ppb) levels. The POHC-chlorobenzene-was also detected. Small amounts of methylene chloride and phthalates were also detected but likely were sampling and analytical contaminants. Measured concentrations of PCDDs and PCDFs in the gas streams were comparable to the blanks, indicating that these species, if present, were at concentrations less than or equal to the method detection limits (parts per quadrillion). Other compounds such as xylenes, chloromethane, bromomethane, dibenzofuran, fluorene, and phenanthrene (expected from the thermal treatment of coal and chlorobenzene) were detected at lower concentrations in the flash gas and off-gases.

## Particulate Emissions

During the SITE demonstration, particulate emissions were measured for the raw syngas and fuel gas streams. These averaged 6.1 milligrams per cubic meter ($mg/m^3$) in the raw syngas, and 1.3 $mg/m^3$ in the fuel gas. By comparison, the

*Table 5. Synthesis Gas Composition*

*Raw syngas composition and heating value*

| Run | $H_2$ (vol. %) | CO (vol. %) | $CO_2$ (vol. %) | $CH_4$ (ppmv) | $N_2$ (vol. %) | Ar (vol. %) | COS (ppm v) | $H_2S$ (ppmv) | THC (ppmv) | Heating Value (Btu/dscf) |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 34.6 | 33.0 | 25.9 | 87 | 6.5 | 0.3 | 120 | 1,180 | 49 | 219 |
| 2 | 26.9 | 31.3 | 26.9 | 51 | 5.1 | 0.0 | 170 | 3,050 | 17 | 210 |
| 3 | 35.4 | 39.6 | 26.2 | 42 | 5.7 | 0.05 | 130 | 1,980 | 14 | 228 |
| Average | 32.3 | 34.6 | 26.3 | 60 | 5.8 | 0.1 | 140 | 2,070 | 27 | 219 |

*Fuel gas composition and heating value*

| Run | $H_2$ (vol. %) | CO (vol. %) | $CO_2$ (vol. %) | $CH_4$ (ppmv) | $N_2$ (vol. %) | Ar (vol. %) | COS (ppmv) | $H_2S$ (ppmv) | THC (ppmv) | Heating value (Btu/dscf) |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 376 | 39.1 | 21.0 | 71 | 4.9 | 0.2 | 33 | 490 | 32 | 239 |
| 2 | 363 | 35.0 | 20.9 | 49 | 5.6 | 0.05 | 44 | 580 | 16 | 239 |
| 3 | 34.7 | 41.3 | 21.2 | 44 | | 0.1 | 50 | 68 | 15 | 239 |
| Average | 36.9 | 38.5 | 21.0 | 55 | 5 4 | 0.1 | 42 | 360 | 21 | 239 |

*Note.- A list of conversion factors is included at the end of the text.*

$H_2$: Hydrogen
CO: Carbon monoxide
$CO_2$: Carbon dioxide
$CH_4$: Methane
$N_2$: Nitrogen
Ar: Argon
COS: Carbonyl sulfide
$H_2S$: Hydrogen sulfide
THC: Total hydrocarbons (excluding methane)

particulate emission standards for boilers and industrial furnaces processing hazardous waste (40 CFR Part 266 Subpart H), and industrial, commercial. and institutional steam generators processing coal and other fuels (40 CFR Part 60 Subpart Db) are higher than the average measured values for these gas streams. Since the fuel gas product would not be vented or flared in a commercial unit, but would be burned directly in a gas-turbine/electrical-generation facility or synthesized into other chemicals, it is expected that the treated vent gas from any of these downstream facilities will be treated to meet applicable particulate emissions standards. This must be assessed on a case-by-case basis.

## Acid Gas Removal

Hydrogen chloride gaseous emission rates measured from 0.0046 to 0.0117 lb/h. The chlorine concentration in the feed slurry, based on a chlorobenzene spike addition equivalent to 3,150 mg/kg in the slurry and the chloride concentration in the slurry, ranged from 4.3 to 4.7 lb/h. Using these figures, the TGP's hydrogen chloride removal efficiency exceeded 99 percent.

Sulfur-containing gas emission rates measured from 2.2 to 2.7 lb/h. The sulfur concentration in the slurry, based on the ultimate analysis for sulfur, ranged from 0.97 to 1.20 weight-percent. Using these figures, the TGP's sulfur removal efficiency averaged 90 percent.

According to Texaco, the MRL systems for acid gas removal are designed to process a wide variation (flow and composition) of gas streams based on the developmental-nature of the research activities conducted there. It is expected that systems designed to meet the specific requirements of proposed commercial TGP units will provide higher removal efficiencies.

## Metals Partitioning

The fate of the spike metals in the slurry (lead and barium) appeared to depend on their relative volatilities under TGP operating conditions. Lead- a volatile metal-concentrated in the clarifier solids, which were scrubbed from the raw syngas. Lead probably evaporated in the hot regions of the gasifier and condensed on the fine particles in the cooler areas of the process. The more refractory barium did not concentrate in any particular solid residue. It partitioned throughout the solid residual streams roughly in proportion to the mass of each residual stream.

As presented in Table 6, average lead concentrations were 880 mg/kg, 329 mg/kg, 491 mg/kg, and 55,000 mg/kg in the Demonstration slurry, coarse slag, fine slag, and clarifier solids, respectively. Although the clarifier solids comprised only 1.6 weight-percent of the solid residuals, they contained 71.1 weight-percent of the measured lead in all the solid residuals. The remaining 28.9 weight-percent of the lead partitioned to the coarse and fine slags.

Average barium concentrations were 2,700 mg/kg, 11,500 mg/kg, 15,300 mg/kg, and 21,000 mg/kg in the demonstration slurry, coarse slag, fine slag and clarified solids, respectively. The barium partitioned to the solid residual streams in approximate proportion to the mass flow of each stream. The coarse slag, which comprised 62.5 weight-percent of the solid residuals, contained 55 weight-percent of the measured barium in the

*Table 6. Mass Flow Rates and Total Concentrations of Lead and Barium in Slurry Feed and Solid Residuals**

| | Slurry (SL-1) | Coarse slag (S-3) | Fine slag (S-4) | Clarifier solids (S-5) |
|---|---|---|---|---|
| Now rate (/b/h) | | | | |
| Range | 2,212-2,291 | 250-307 | 151-167 | 3.1-10.5 |
| Average | 2,216 | 273 | 157 | 6.8 |
| % of Residuals | ____ | 62.5 | 35.9 | 1.6 |
| Pb concentration (mg/kg) | | | | |
| Range | 867-899 | 198-542 | 217-651 | 43,400-72,000 |
| Average | 880 | 329 | 491 | 55,000 |
| Pb mass rate | | | | |
| Average (lb/h) | 2.00 | 0.09 | 0.08 | 0.42 |
| % of Slurry Pb | — | 4.5 | 4.0 | 21.0 |
| % of Residuals Pb | — | 15.3 | 13.6 | 71.1 |
| Ba concentration (mg/kg) | | | | |
| Range | 1,750-3.580 | 8,090 - 16,300 | 11,800-18,300 | 15,100-26,300 |
| Average | 2,700 | 11,500 | 15,300 | 21,000 |
| Ba mass rate | | | | |
| Average (lb/h) | 6.1 | 3.1 | 2.4 | 0.14 |
| % of Slurry Ba | — | 50.8 | 39.3 | 2.3 |
| % of Residuals Ba | — | 55.0 | 42.5 | 2.5 |

* Mass flow rates and metal concentrations for slurry are on as-received basis; for **solid** residuals are on dry basis.
Note - A list of conversion factors is included at the end of the text.
Pb: lead
Ba: Barium

solid residuals. The remaining 45 weight-percent of the barium partitioned to the fine slag and clarifier solids in approximate proportion to their mass flow.

## Process Wastewater

The Demonstration produced three process wastewater streams: process wastewater (flash tank blowdown and quench/scrubber and lockhopper water inventory on shutdown); gasification vacuum filtrate (produced from the vacuum filtration of the clarifier bottoms); and neutralized wastewater from the sulfur removal unit. Samples from each of these streams were collected and analyzed for VOCs, SVOCs, PCDD/PCDF, metals, pH, and organic and inorganic halogens. Samples of the inlet water stream were also analyzed to determine if it was introducing any contaminants of concern.

Lead concentrations in the process wastewater and vacuum filtrate ranged from 12.4 to 38.9 mg/L and from 3.98 to 18.4 mg/L, respectively. Although the majority of the lead was found in the clarifier solids, small amounts of lead or lead compounds remained suspended in the clarifier overhead and traveled to the process wastewater as the flash tank blowdown. Similarly, small amounts of lead remained suspended in the vacuum filtrate and did not settle in the clarifier solids.

Trace concentrations of VOC and SVOC PlRs such as benzene, acetone, carbon disulfide, methylene chloride, naphthalene and naphthalene derivatives, and fluorene were found in the wastewater streams. No concentrations of PCDDs or PCDFs were found at or above the method detection limit of 10 nanograms per liter

Inorganic chloride concentrations in the wastewater streams ranged from 380 mg/L to 6,800 mg/L. These values were, in general, an order of magnitude higher than the concentrations found in the inlet water; they indicated the presence of additional chlorides in the feed. Ammonia was also detected in the process wastewater and vacuum filtrate streams; the pH values of these streams were fairly neutral. The inorganic chloride concentrations indicated the presence of chloride, but the neutral pH values indicate that the chloride species is not acidic. These results show that the HCl produced in the gasification process was removed in the quench and scrubber, neutralized by the ammonia, and discharged in the process wastewater/vacuum filtrate effluents.

Concentrations of organic chloride in the inlet water ranging from 680 mg/kg (Run 3) to 2,500 mg/kg (Pretest) were carried through the system to the wastewater streams. Similar concentrations appeared in the process wastewater, vacuum filtrate, and neutralized wastewater streams.

For proposed commercial units, the wastewater streams would be treated on-site for recycling or for disposal as non-hazardous water.

## Overall Unit Cost

Information available to date on capital and operating costs is preliminary. According to Texaco, an overall treatment cost of $308/ton of soil is estimated for a transportable unit designed to process 100 tpd of soil with characteristics similar to that from the Purity Oil Sales Superfund Site, based on the production of a marketable syngas product valued at $1.00/

million Btu. Texaco estimates an overall treatment cost of $225/ton of soil for a stationary unit designed to process 200 tpd of soil at a central site, with characteristics similar to that from the Purity Oil Sales Superfund site, based on a value of $2.00/million Btu for the syngas product.

These costs include amortized capital costs and all operating costs. They exclude waste soil handling, waste site-specific roads and facilities, and permitting and regulatory costs, which can be extremely variable and are the obligation of the site owner or responsible party at the waste site. Actual costs will vary depending on the site and the soil matrix being treated.

## Overall Unit Reliability

The SITE demonstration experienced three operational incidents which were identified and resolved prior to startup or during operation; they did not require the shutdown and disruption of the demonstration operations. A major earthquake also occurred one day prior to the scheduled demonstration test. Based on the minimal disruptions caused by these incidents and the continuous post-demonstration processing of the remaining slurry inventory, the reliability and efficiency of the proposed commercial TGP units will be consistently high, and they are expected to operate at on-stream efficiencies of 70% to 80%. The downtime allows for scheduled maintenance and intermittent unscheduled shutdowns such as those caused by materials-handling equipment problems due to variations in, and the abrasive nature of, soil and coal matrices.

## Technology Status

A demonstration was conducted in 1988 at MRL for the California Department of Health Services where petroleum tank bottoms from a California oil production field were: co-gasified with low-sulfur, western coal. This California-designated hazardous waste was fed to the gasifier at a rate of 600 lb/h mixed with 2,400 lb/h of coal. The dry syngas was composed of 39% carbon monoxide, 38% hydrogen, and 21% carbon dioxide. Texaco reported that the solids were non-hazardous, based on California Assessment Manual limits for total and leachable metals in effect at the time of the demonstration and the solids and wastewater were free of trace organics and EPA priority pollutants.

Texaco has announced plans to build a $75-million TGP power facility at its El Dorado, KS refinery, which will convert about 170 tpd of non-commercial petroleum coke and refinery wastes into syngas. The syngas, combined with natural gas, will power a gas turbine to produce approximately 40 MW of electrical power-enough to meet the full needs of the refinery. The exhaust heat from the turbine will produce 180,000 lb/h of steam-approximately 40% of the refinery's requirements. Construction will begin during the first quarter of 1995, with startup projected for the second quarter of 1996.

## Disclaimer

The initial conclusions presented herein are preliminary. The data will be reviewed by the appropriate EPA Quality Assurance/Quality Control Officer and addressed at length in the Innovative Technology Evaluation Report.

## Sources of Further Information

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## Conversion Factors

| | English (US) | x | Factor | = | Metric |
|---|---|---|---|---|---|
| Length: | 1 foot (ft) | x | 0.305 | = | meter (m) |
| Area: | 1 square foot ($ft^2$) | x | 0.0929 | = | square meter ($m^2$) |
| Volume: | 1 gallon (gal) | x | 3.78 | = | liter (L) |
| | 1 cubic foot ($ft^3$) | x | 0.0283 | = | cubic meter ($m^3$) |
| Mass: | 1 grain (gr) | x | 64.8 | = | milligram (mg) |
| | 1 pound (lb) | x | 0.454 | = | kilogram (kg) |
| | 1 ton (t) | x | 907 | = | kilogram (kg) |
| Pressure | 1 pound per square inch (psi) | x | 0.0703 | = | kilogram per square centimeter ($kg/cm^2$) |
| | 1 pound per square inch (psi | x | 6.895 | = | kilopascal (kPa) |
| Energy. | 1 British Thermal Unit (Btu) | x | 1.05 | = | kilojoule (kJ) |
| | 1 kilowatt hour (kWh) | x | 3.60 | = | megajoule (MJ) |
| Temperature: | (°Fahrenheit (°F) - 32) | x | 0.556 | = | °Celsius (°C) |

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