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**BIO-LEACHING OF TOXIC METALS FROM GEOTHERMAL WASTE
A PRELIMINARY ENGINEERING ANALYSIS**

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February 1986

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SCHOOL OF CHEMICAL ENGINEERING PRACTICE
MASSACHUSETTS INSTITUTE OF TECHNOLOGY**

DEPARTMENT OF APPLIED SCIENCE

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**BIO-LEACHING OF TOXIC METALS FROM GEOTHERMAL WASTE
A PRELIMINARY ENGINEERING ANALYSIS**

MIT/BNL-86-1

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ABSTRACT

The feasibility of a biological facility to treat geothermal sludge from a base case 50-MW double-flash geothermal power plant in the Imperial Valley, California was evaluated. The effect of sludge and nutrient concentration, agitation air bubbling and sterility on the rate of metal solubilization by the bacteria Thiobacillus thiooxidans and ferrooxidans were examined. All experiments were performed in batch flasks and monitored daily for bacterial growth. T. thiooxidans leached 36% of the zinc in the sludge after 288 hr but leached little chromium. T. ferrooxidans removed 60% of the chromium in the sludge after 250 hr but did not leach zinc. Sludge to medium ratios of greater than 10% were toxic to the microorganisms studied. The experimental results were used to design a biological solid-waste treatment plant. The design basis used was 5 wt% sludge in the leaching vessel with a residence time of 10 days. The non-regulated waste resulting from the treatment plant could be used for land fill or construction materials. The total capital cost for the bio-leaching plant is \$3.3 million with an annual operating cost of \$690,000. The total cost of this plant is about 0.2¢/kWh of electricity produced, which is essentially the same cost as hauling the solid waste to a hazardous disposal site. This cost accounts for about 5% of the cost of producing electricity from geothermal power (4¢/kWh).

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1 SUMMARY

Electricity can be produced by expanding hot geothermal brines emanating from the interior of the earth in turbine generators. In the Imperial Valley of Southern California, there are nine known geothermal resource areas (KGRA). Brines from the Salton Sea KGRA in the Imperial Valley may contain total dissolved solids up to 350,000 ppm. These hypersaline brines lead to the generation of geothermal solid wastes in power plants. All of the solid waste produced must be analyzed for regulated metals using the California Department of Health Services (DOHS) analytical techniques, and if found hazardous the solid waste must be disposed of off-site in an approved waste management facility. Currently, the disposal of these wastes can cost over \$1 million per year for a 50-MW geothermal power plant operating in the Salton Sea KGRA. High disposal costs and the long-term liability associated with hazardous waste disposal motivate this study of a biological solid-waste treatment facility.

Microbial leaching or "bio-leaching" is the dissolution of metals catalyzed by microorganisms. Special importance is attached to the genus Thiobacillus in solid-waste treatment processes because of their ability to oxidize insoluble heavy-metal compounds into more soluble forms.

The objective of this project was to estimate the economic impact of a biological solid-waste treatment facility on a base-case 50-MW double-flash geothermal power plant operating in the Salton Sea KGRA. The bacteria Thiobacillus thiooxidans and ferrooxidans were used to study the effect of sludge concentration, initial nutrient concentration, non-sterile conditions, agitation and air bubbling on the rate of bio-leaching of chromium and zinc contained in solid geothermal waste. (The sludge waste used in these experiments was given to BNL by a geothermal source in the Imperial Valley.) All experiments were performed in batch flasks and monitored daily for bacterial growth. The leachate was analyzed for chromium and zinc using an atomic absorption spectrometry. Flow schemes were then proposed for a geothermal-waste treatment plant using this bacterium.

Experimental results indicate that T. thiooxidans leached out 36% of the zinc in the sludge after 288 hr but leached little chromium. T. ferrooxidans leached out 60% of the chromium in the sludge after 250 hr but did not leach zinc. The acidity of the medium must be low (less than 1.7) for zinc to be leached from the sludge. Air-bubbling has little effect on the rate of bio-leaching and sludge to medium ratios of greater than 10% are toxic to the microorganisms. Both strains of bacteria survived under non-sterile conditions, and for a limited period (5 days) in temperatures as high as 120°F. In all the successful leaching experiments, the maximum amount of metals were leached after 10 days. The ferrooxidans leached out chromium to below the California threshold limits for chromate. However, within the time frame of the experiments, the thiooxidans did not leach zinc to below the California threshold limits.

These experimental results were used to design a biological solid-waste treatment plant, using as a basis 80,000 lb/day of geothermal sludge generated from a 50-MW double-flash plant located in the Salton Sea KGRA of the Imperial Valley. In the proposed process, waste slurry (65 wt% solids) is sent to a thickener where nutrients, water, and inoculum are added so that the solids to

liquid ratio is 5%. Based on the experimental results, a residence time in the thickener of about ten days was chosen. The leachate from the thickener containing the dissolved metals is neutralized, filtered, and reinjected. The resulting waste from the filter press should be a small fraction of the original amount of waste generated by the double-flash plant. The nonregulated solids remaining in the thickener are pumped through a second filter press where they are concentrated to 65 wt%. These nonregulated solids can be used as landfill or for construction materials, such as concrete.

The capital costs involved in the proposed bio-leaching process include equipment costs, installation costs, working capital, and reinjection well costs. The thickener should be operated at the highest possible solids-to-liquid ratio to reduce the thickener size and to reduce the nutrient costs. In a sensitivity study, two solids-to-liquid ratios (5 and 10%) and two different liquid residence times (10 and 50 days) were examined. The total capital cost and annual operating cost of each design are tabulated in Table 1-1. The results show the economic advantage of having a biological waste treatment facility operating with a high sludge-to-liquid ratio and a high liquid residence time. The biological waste treatment plant is both technically and economically feasible. The total plant cost is small relative to the cost of generating geothermal energy. In addition, the long-term liability associated with disposal of hazardous solid waste is deemed significant; hence, the process is even more economically attractive. Future work should concentrate on finding bacteria that bio-leach under high solids-to-liquid ratios and at faster rates (lower sludge residence times). This would further enhance the economic feasibility of a biological solid-waste treatment plant.

Table 1-1 Capital and Operating Costs for Bio-Leaching Plants
with Different Solids-to-Liquid Ratios

Sludge in thickener (wt %)	5	5	10	10
Sludge residence time (days)	10	10	10	10
Liquid residence time (days)	10	50	10	50
Capital cost (millions of dollars)	3.3	3.2	3.0	2.9
Annual operating cost (millions of dollars)	0.69	0.47	0.55	0.44
Total Cost (¢/kWh)	0.23	0.18	0.20	0.17

The cost of a biological waste treatment plant (0.17-0.23¢/kWh) is about the same as the current cost of hauling the solid waste to a hazardous disposal site (\$1,022,000 per year or 0.23¢/kWh). Either cost accounts for about 5% of the cost of generating electricity from geothermal power (about 4¢/kWh in 1986).

2 INTRODUCTION

2.1 Background

2.1.1 Geothermal Energy

Geothermal energy refers to all of the thermal energy stored in the earth's crust. The major problem in utilizing this vast energy resource lies in its diffuse nature. For instance, in one year about 100 billion MWh of heat energy is conducted to the surface from the interior of the earth (DiPippo, 1980). This is roughly twenty times the electrical energy used by the entire world. The U.S. Geological Survey estimates a potential production of 21,000 MW of electricity in the United States for thirty years from the already identified geothermal systems. As of 1980, the installed geothermal electrical generating capacity in the entire world was 1750 MW and growing. Currently, geothermal energy accounts for almost 3% of the total electricity generated in California, Hawaii, Nevada, New Mexico, and Utah.

Geothermal energy is extracted from hot geothermal fluids (brines). The resources that produce these brines are termed hydrothermal systems. Hydrothermal systems are subsurface reservoirs of either steam (vapor-dominated) or hot water (liquid-dominated). Such systems are frequently located in areas near the boundaries of the earth's crustal plates. The water in these hydrothermal systems is usually the result of rain or melted snow percolating downward through sediments or fissures to a heat source such as hot dry rock or molten magma. Heated water sometimes rises towards the surface where it appears as geysers or hot springs (Figure 2-1). If the pressure in the reservoir is sufficiently high to prevent boiling, dry or superheated steam forms. Such vapor-dominated hydrothermal systems are the easiest to exploit for the generation of electricity, because the steam can be directly expanded in a low pressure turbine. However, very few of these systems are known to exist. Reservoirs in which the pressure exceeds the vapor pressure of brine (at reservoir temperature) do not form much vapor and result in liquid-dominated systems. Liquid-dominated hydrothermal systems are more difficult to utilize directly; they pose serious scaling and corrosion problems in production equipment and injection wells as a result of the amount of total dissolved solids (TDS) contained in the brine. The brine from a liquid-dominated system is usually flashed to produce a vapor phase which is then used to drive a turbine. The unflashed liquid may contain precipitated solids, rendering it inappropriate for reinjection into the earth due to potential injection-well clogging difficulties.

In summary, the elements necessary for a practical hydrothermal geothermal resource are: (1) a high-temperature chamber containing molten magma at a depth greater than 10 km; (2) fault boundaries to define the reservoir; (3) a permeable layer; (4) a thick layer of cap rock; and (5) a mechanism for reinjection of water to the reservoir after utilization (DiPippo, 1980).

The U.S. Geological Survey has designated areas in the United States identified as having potential for geothermal production of electrical energy as known geothermal resource areas (KGRA) (Royce, 1985). The Geysers KGRA, which is located about 90 mi north of San Francisco, is one of the few vapor-dominated systems known to exist. Nine liquid-dominated KGRA have been

A TYPICAL HYDROTHERMAL GEOTHERMAL SYSTEM

(DiPippo, 1980)

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FIG.

2-1

identified in the Imperial Valley of Southern California (Figure 2-2). This area has large amounts of TDS in its geothermal fluids. One of these, the Salton Sea (Niland) KGRA, contains hypersaline brines with between 250,000 to 300,000 ppm TDS (Ellis and Conover, 1981), which is over ten times higher than the TDS observed at any other KGRA. By comparison, sea water contains about 30,000 ppm TDS.

Future development of geothermal energy is dependent upon the technology to use resources that produce less desirable fluids, i.e., hypersaline brines. Early attempts to utilize the large resources in the Imperial Valley met with frustration and failure because of the corrosion and scale formation associated with geothermal brines. Renewed interest in the area developed in the 1970's when the world energy situation changed, and the development of alternative energy sources became a national priority (Whitescarver, 1984).

2.1.2 Description and Types of Geothermal Power Plants in the Imperial Valley

There are a variety of geothermal energy conversion systems, or power plants, in use and being developed in the Imperial Valley. The main geothermal power plants may be categorized as follows: (1) dry or superheated steam plants; (2) separated-steam/hot water "flash" plants; and (3) binary cycle plants with a secondary working fluid.

A dry or superheated steam geothermal power plant is used when the geothermal fluid is in a vapor phase. Vapor-dominated hydrothermal systems are the easiest to exploit for generating electricity. Steam from a production well is expanded directly in a turbine generator for the production of electricity. There are usually no problems associated with reinjection from a dry steam plant because the steam from a vapor-dominated system is usually free from any particulate matter. Dry steam power plants are scarce, since few vapor-dominated systems are known to exist. The geothermal power plants at The Geysers in northern California are currently operating with direct steam from a vapor-dominated hydrothermal system.

A separated-steam/hot water geothermal power plant utilizes the well head mixture from a liquid-dominated hydrothermal system. The quality of the brine depends on the reservoir properties (e.g., temperature, pressure, and TDS). In most cases, the state of the brine in the reservoir is that of a compressed liquid. As the fluid rises up the production well, the pressure decreases causing steam to be produced. The mixture is then throttled into a flash vessel to a lower pressure where it is separated into vapor and liquid components. The vapor phase is expanded in a turbine and then condensed from reinjection. In a "single-flash" plant, the liquid is then reinjected without being utilized further. In a separated steam/double-flash plant (Figure 2-3a) another separator is included to flash the liquid exiting the first flash. The additional steam generated is then expanded in a low pressure turbine. The second stage of a "double-flash" plant captures a portion of the geothermal energy otherwise wasted by a "single-flash" system, thus increasing the utilization efficiency. Chevron Geothermal Company and Heber Geothermal Company have built the largest "double-flash" plant in the United States. The 52-MW plant was completed in 1984 and is currently operating in the Imperial Valley at about 80% capacity. A separated steam/multiple flash plant employs steam at three or more levels of pressure at the turbine entry points. "Multi-flash" plants are not economically attractive at the present time (DiPippo, 1980).

LOCATION OF KGRA IN IMPERIAL VALLEY

(Whitescarver, 1984)

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FIG.

2-2

TWO TYPES OF GEOTHERMAL POWER PLANTS

(a) Double-Flash Plant (DiPippo, 1980)

(b) Binary-Fluid Cycle (Tester, 1980)

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DATE 2-20-86	DRAWN BY SMR	FILE NO MIT/BNL-86-1	FIG. 2-3
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Binary cycle plants (Figure 2-3b) are closed loop Rankine cycles that involve a primary heat exchange step in which heat from the geothermal fluid is transferred to a secondary working fluid. The working fluid is typically a low molecular weight fluorocarbon or hydrocarbon such as butane or pentane. After the working fluid is vaporized by the geothermal fluid, it is expanded in a turbine generator. The advantages of a binary cycle over a steam cycle include (DiPippo, 1980): (1) better suitability for low-temperature hydrothermal resources, (2) turbine size is smaller for given output, (3) turbine is less expensive for given output, (4) no air leakage, (5) non-corrosive working fluid in turbine, (6) higher isentropic turbine efficiencies, (7) dry expansion, which eliminates erosion problems, and (8) lower condensing temperatures for better cycle efficiencies. Disadvantages of binary cycles include: (1) expensive suitable secondary working fluids, (2) major costs of heat exchangers, (3) large brine flowrates needed for a reasonably sized plant, which lead to disposal problems, and (4) flammability of secondary working fluid. The Magmamax dual binary cycle plant completed in 1979 in the Imperial Valley was the first geothermal plant of this type built in the U.S.

Table 2-1 summarizes geothermal power plant types currently in operation in the Imperial Valley. Some of these plants generate significant amounts of solid wastes due to the hypersalinity of the geothermal brines.

Table 2-1 Geothermal Power Plant Types in The Imperial Valley

Site	Utility or Plant Owner	Field Developer	Year of Start-Up	MW	Plant Type
East Mesa	Imperial Magma	Magma Power	1979	11	Binary
Brawly	Southern California Edison	Union Oil	1980	10	Single-flash
Niland	Southern California Edison	Union Oil	1982	10	Single-flash
Niland	San Diego Gas and Electric	Magma Electric	1982	50	Double-flash
Heber	Southern California Edison	Chevron	1982	45	Double-flash
Heber	San Diego Gas and Electric	Chevron	1984	50	Double-flash

2.1.3 Geothermal Waste

Waste from geothermal power plants is produced primarily during well drilling and plant operations. The well-drilling waste consists of drilling muds, brines, and residues, while operational waste consists of cooling tower and separator blowdown sludges (Royce, 1985). This study will concentrate on operational wastes generated in the Imperial Valley.

The geothermal fluids from the Salton Sea KGRA in the Imperial Valley contain unusually high amounts of TDS (up to 350,000 ppm). The operational waste generated consists of brine and associated solids. These solids precipitate out of the spent liquid from flash vessels, causing scale and corrosion

problems. In addition, the hypersaline brines pose serious problems for reinjection because solids can cause severe plugging of the reinjection well. For this reason, precipitated solids are removed in a clarifier and filtered before reinjection.

All the solid waste produced in the Imperial Valley must be analyzed for regulated substances using the California Department of Health Services (DOHS) standard analytical techniques (EPA, 1980). A solid waste is deemed hazardous if it contains a regulated substance (e.g., Zn, Cr, Pb, As, Cu) at a level exceeding the total threshold limit concentration (TTLC). A waste is also considered hazardous if the leachable level of any regulated substance is above the DOHS soluble threshold limit concentration (STLC). Table 2-2 gives the TTLC and STLC of regulated inorganic substances in California.

At present, all solid waste exceeding the TTLC or the STLC is disposed of by trucking to a type II-1 hazardous waste site. Any other solid waste below the DOHS concentration limits can be disposed of at a type II-2 hazardous waste site. Type II-2 sites handle less hazardous wastes and have lower disposal fees. The California Water Resource Board regulates the construction and operation of all waste disposal sites and requires that type II-1 sites have adequate ground water protection, including pit liners and leachate

Table 2-2 The California DOHS Soluble and Total Threshold Limit Concentration Values of Inorganic Toxic Substances in Hazardous Waste*

Inorganic Substances	STLC (mg/l)	TTLC (mg/kg)
Antimony and/or antimony compounds	15	500
Arsenic and/or arsenic compounds	5.0	500
Asbestos	-	10,000
Barium and/or barium compounds (excluding barite)	100	10,000
Beryllium and/or beryllium compounds	0.75	75
Cadmium and/or cadmium compounds	1.0	100
Chromium (VI) compounds	5	500
Chromium and/or chromium (III) compounds	560	2,500
Cobalt and/or cobalt compounds	80	8,000
Copper and/or copper compounds	25	2,500
Fluoride salts	180	18,000
Lead and/or lead compounds	5.0	1,000
Mercury and/or mercury compounds	0.2	20
Molybdenum and/or molybdenum compounds	350	3,500
Nickel and/or nickel compounds	20	2,000
Selenium and/or selenium compounds	1.0	100
Silver and/or silver compounds	5	500
Thallium and/or thallium compounds	7.0	700
Vanadium and/or vanadium compounds	24	2,400
Zinc and/or zinc compounds	250	5,000

Note: STLC and TTLC values are based on the concentrations of the elements, not the compounds. TTLC values are calculated on a wet-weight basis. The limits of asbestos and elemental metals apply only if the substances are in a friable, powdered, or finely divided state.

*Taken from Royce (1985).

collection systems. Some geothermal companies are developing processes for the use of solid waste as an ingredient in construction materials such as concrete. However, these processes are still in the research stage.

Due to high solid-waste disposal costs (and the long-term liability associated with hazardous waste disposal), the potential for further utilization of hypersaline geothermal brines from the Imperial Valley depends on the reduction or elimination of solid wastes generation. Actual waste treatment methods may prove to be less costly than the off-site hazardous waste disposal now being used.

2.1.4 Bio-Leaching

While investigating the causes of corrosion in pipes and other iron parts by mine water, Colmer and Hinkle isolated the bacterium Thiobacillus ferrooxidans (Bosecker and Kursten, 1978). The corrosion of the pipes was caused by the iron oxidizing activity of these microorganisms. Soon after Colmer and Hinkle's discovery, questions were raised relating to the utilization possibilities of these bacteria.

Currently, microbial leaching of low-grade ores using bacteria of the genus Thiobacillus is employed by industry for the recovery of copper and uranium. Microbial leaching or "bio-leaching" is the solubilization of metals catalyzed by microorganisms. Brookhaven National Laboratory (BNL) is investigating the feasibility of bio-leaching regulated metals from geothermal solid waste using Thiobacillus (T.) bacteria. Special importance is attached to the species T. thiooxidans and T. ferrooxidans in metal solubilization bio-leaching processes.

The major drawback of bacterial leaching is the slow rate of the biological process compared with some conventional chemical methods for extracting metals. However, in order to determine feasibility, economic comparisons between bio-leaching and conventional methods must be made for specific applications. In this respect, bio-leaching is viewed as plausible alternative for the removal of metals for dilute solid-waste streams. It seems probable that in the future, genetic manipulation may produce microorganisms with more desirable leaching characteristics, i.e., higher leaching rates and enhanced tolerance of toxic metals (Brierly, 1978; Summers, 1985).

2.2 Objectives and Methods of Approach

The objective of this project was to estimate the economic impact of a biological waste treatment facility on a base-case 50-MW geothermal power plant operating in the Salton Sea KGRA in the Imperial Valley of California.

In order to determine whether a biological waste-treatment plant using a geothermal fluid with 25-30% TDS would be technically feasible, batch kinetic studies have been performed with Thiobacillus thiooxidans and Thiobacillus ferrooxidans using a sample of geothermal sludge supplied to BNL by an Imperial Valley geothermal company. Experiments were performed to study the effects of sludge concentration, initial nutrient concentration, sterility, agitation, and air bubbling on the rate of zinc and chromium leaching. Zinc and chromium were chosen because preliminary sludge analysis indicated that these metals were found in high concentrations.

From these results, we have determined the leaching rate for zinc and chromium. An estimation of the residence time required to leach metals from the sludge samples supplied by an Imperial Valley geothermal source to below DOHS limit concentrations was then made. In addition, we have proposed a continuous process flow diagram for a biological waste-treatment plant.

An economic analysis illustrates the feasibility of the proposed bio-leaching process for treating geothermal solid waste and determines to which design variables the incremental treatment cost is most sensitive. The final cost of bio-leaching is compared to that of off-site hazardous waste disposal.

3 CHEMISTRY OF BIO-LEACHING

Bio-leaching is the dissolution of soluble materials catalyzed by micro-organisms. The two organisms used in this study are T. ferrooxidans and T. thiooxidans. As a result of their metabolism, Thiobacilli oxidize certain metallic sulfides into water-soluble sulfates by acting as catalysts in the production of sulfuric acid from elemental sulfur. These bacteria have been used to leach certain metals such as copper and uranium from low-grade ores (LeRoux, 1969).

These bacteria can tolerate very high concentrations of sulfuric acid and toxic metals. Most Thiobacilli are mesophilic, that is, they thrive at moderate temperatures; however, a few strains have been found at temperatures near the boiling point of water. Both T. ferrooxidans and T. thiooxidans are chemolithotrophic or "rock-eating"; they obtain their energy from the oxidation of inorganic compounds found in the surrounding rock. Both bacteria are autotrophic -- they obtain their carbon requirements from carbon dioxide in the air (Brierley, 1978). Their nitrogen requirement is supplied by inorganic salts, such as ammonium sulfate, that are provided in their growth media.

These two bacteria bio-leach metal into solution via different mechanisms. T. ferrooxidans affects metal solubilization by a series of redox reactions while T. thiooxidans produces sulfuric acid, which is responsible for metal leaching. If the metal sulfate resulting from bacterial action is soluble, then the metal ion is solubilized. However, if an insoluble metal sulfate is produced, such as lead sulfate, the problem of solubilizing the metal ion is unresolved.

3.1 Thiobacillus ferrooxidans

T. ferrooxidans are gram-negative nonsporing rod-like organisms measuring 0.5-0.7 μm by 1.5 μm . They move about using a single polar flagella (Moss, 1969). Their energy requirements are obtained from the oxidation of inorganic sulfur, sulfide compounds, and iron compounds (Silver, 1978). T. ferrooxidans solubilize certain metal ions by the following series of oxidation-reduction reactions involving ferrous and ferric ions (Bosecker and Kursten, 1978):

where M is any metal of interest. Reactions (3-1), (3-2), and (3-4) are catalyzed by T. ferrooxidans; Reaction (3-3) proceeds without the bacterium. The ferric ions produced from the oxidation of ferrous ions in Reaction (3-2) are reduced in Reaction (3-3). The insoluble metal sulfides are oxidized in Reaction (3-3) to produce metal sulfates and elemental sulfur. The elemental sulfur is oxidized in Reaction (3-4) to form sulfuric acid. In the absence of iron, the acid produced can oxidize metal sulfides. Leaching is accomplished only when the sulfate produced is soluble.

3.2 Thiobacillus thiooxidans

T. thiooxidans were first isolated in 1922. These bacteria are gram negative, rod shaped, 1.0-2.0 μm long, and 0.5 μm across. Like T. ferrooxidans, they are mobile by means of a single, polar flagellum (Bosecker and Kursten, 1978). T. thiooxidans grow via the oxidation of elemental sulfur and thiosulfate, but are incapable of the oxidation of iron (Cripps, 1980). This bacteria catalyzes the formation of sulfuric acid (Reaction 3-4) that solubilizes the metal sulfides by the following reaction:

Again, leaching is accomplished only when the metal sulfate produced is soluble. Reactions (3-4) and (3-5) constitute the Thiobacillus catalyzed acid leaching cycle.

3.3 Mixed Cultures

Studies by Kelly and Jones (1978) have confirmed that mixed cultures of T. ferrooxidans and T. thiooxidans are more effective than either organism alone in leaching certain ores. This behavior is explained by the complementary nature of Reactions (3-2) to (3-4). The elemental sulfur generated in Reaction (3-3) is oxidized by both T. thiooxidans and T. ferrooxidans in Reaction (3-4) to produce sulfuric acid. If the rate of sulfuric acid formation with T. thiooxidans is faster than in the presence of T. ferrooxidans alone, an enhanced metal solubilization is expected for mixed cultures.

4 BATCH KINETIC EXPERIMENTS AND APPARATUS

A series of batch kinetic experiments were conducted to determine the bacteria-catalyzed leaching rates of zinc and chromium from a geothermal sludge slurry (60 wt% solids) obtained from a geothermal plant currently operating in the Salton Sea area of California. This sludge was supplied by an Imperial Valley geothermal source. Chromium and zinc were chosen because preliminary analysis of the sample sludge indicated that it contained high amounts of these metals relative to environmental regulations. All chromium was assumed to be present in the hexavalent chromate form, which is subject to the most stringent environmental regulations.

The bacteria used in this work are Thiobacillus thiooxidans and Thiobacillus ferrooxidans. All of the experiments were performed in 250-ml erlenmeyer flasks. The variables studied are: sludge concentration, initial nutrient concentration, non-sterile conditions, agitation, and air bubbling through the medium.

4.1 Experimental Procedure

Bacteria cultures of T. thiooxidans and T. ferrooxidans were acquired from the American Type Culture Collection (ATCC) and cultivated under sterile conditions by A. Gremme (BNL) for use in our experiments. The bacterial media was prepared as recommended by the ATCC; formulations are listed in Table 4-1. The waste sludge slurry (60 wt% solids) was oven-dried overnight and ground to a fine chalk-like powder with a mortar and pestle.

For sterile runs performed with T. thiooxidans, 1.0 g sulfur (precipitated) was placed in dry flasks, and 100 ml of the appropriate fermentation media was poured down the side of the flask without wetting the sulfur. Flasks were sterilized in flowing steam on three consecutive days for 30 min each day. The initial pH of the medium was approximately 4.2. Weighed amounts of sludge, autoclaved for sterility, were then added to the flasks. The mouth of each flask was plugged with sterile cotton.

For sterile runs performed with T. ferrooxidans, media was prepared in two solutions which were autoclaved separately and then mixed. One part consisted of FeSO_4 , H_2SO_4 , and 100 ml of distilled water and the other part

Table 4-1 Media Formulations for Thiobacillus

<u>T. ferrooxidans</u>		<u>T. thiooxidans</u>	
Component	Amount	Component	Amount
$(\text{NH}_4)_2\text{SO}_4$	0.4 g	$(\text{NH}_4)_2\text{SO}_4$	0.2 g
KH_2PO_4	0.2 g	KH_2PO_4	3.0 g
$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	0.08 g	$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	0.5 g
$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	10.0 g	CaCl_2	0.25 g
1 N H_2SO_4	1.0 ml	FeSO_4	0.005 g
Distilled Water	500 ml	Tap Water	1000 ml

contained the remaining nutrients listed in Table 4-1 and 400 ml of water. The pH was adjusted to 2.8 (as required) by the addition of 1 N H₂SO₄. Weighed amounts of sludge were placed in flasks and autoclaved for sterility. After the mouth of each flask was flame sterilized, 100 ml of medium was added. The mouth of each flask was then plugged with sterile cotton.

Media, sludge samples, and flasks were not steam sterilized or autoclaved for those experiments performed under non-sterile conditions with either T. thiooxidans or T. ferrooxidans.

The sludge and medium mixtures were inoculated with bacteria cultures in 5 or 10-ml aliquots when cell density had reached the exponential growth stage (approximately 1000 cells/mm³). A sterile pipette was used to transfer the inoculum from the bacteria culture to the experimental flasks; care was taken not to touch the sides of the flasks. Inoculation was performed within an hour after mixing the sludge and medium.

Following inoculation, flasks were placed on a horizontal shaker set at 600 RPM. While the liquid medium was well mixed, due to limited shaker speed the agitation was insufficient to cause a slurry to be formed.

Sampling was performed immediately after inoculation by removing the cotton from the flask and inserting a sterile pipette to remove a 5.1-ml liquid sample. The cotton was then replaced, and care was to insure the sterility of the flask and medium when appropriate. Approximately 0.1 ml of the sample was pipetted into a labelled 12.75-mm culture tube for bacterial counts. The remaining 5 ml was pipetted into a clean labelled centrifuge tube. Samples were centrifuged to remove suspended sludge and cells from the liquid media. The supernatant from each sample was filtered through a 0.22-micron filter into another labelled test tube in order to remove any remaining particulates. The sample was then ready to be analyzed for Cr and Zn by a Perkin-Elmer 560 Atomic Absorption spectrophotometer (AA). Hydracid papers were used to determine the pH of samples by pipetting a small amount of leachate onto the pH paper. Flasks were sampled every 24-48 hr thereafter for bacterial growth and Cr and Zn concentration measurements.

4.2 Experimental Conditions

The standard conditions used to grow the bacteria were: (1) 26°C, (2) shaker agitation, (3) sterility, (4) 100 ml of media as recommended by the ATCC, and (5) no air bubbling. Temperature was controlled by a room thermostat. The following experiments were performed to study the effects of sludge concentration, nutrient concentration, air-bubbling, agitation, and sterility on the bacterial growth rates and the rate of Zn and Cr solubilization. Only one variable was changed in each experiment.

Both bacteria were grown with 0, 2, 4, 10, 20, and 30 wt% sludge on a dry weight basis (Table 4-2). These experiments examined the limits of sludge concentration under which the bacteria can survive.

Table 4-2 Sludge Concentration Experiments

Bacteria	Sludge dry weight (g)	Comments
<u>T. thiooxidans</u>	0	Control
<u>T. thiooxidans</u>	2	
<u>T. thiooxidans</u>	4	
none	4	Control
<u>T. thiooxidans</u>	10	
<u>T. thiooxidans</u>	20	
none	20	Control
<u>T. thiooxidans</u>	30	
<u>T. ferrooxidans</u>	0	Control
<u>T. ferrooxidans</u>	2	
<u>T. ferrooxidans</u>	4	
none	4	Control
<u>T. ferrooxidans</u>	10	
<u>T. ferrooxidans</u>	20	
none	20	Control
<u>T. ferrooxidans</u>	30	

The effect of reduced nutrient concentration (Table 4-3) was studied with 2 and 4 wt% sludge. The main component in the T. ferrooxidans media is FeSO_4 (95 wt%). The effect of adding no FeSO_4 and 50% of the recommended amount was studied. Elemental sulfur accounts for 70 wt% of the T. thiooxidans media. The effect of no elemental sulfur in the media was studied. If leaching could be accomplished with reduced nutrient concentration, then the cost of a bio-leaching process would be decreased.

Table 4-3 Reduced Nutrient Concentration Experiments

Bacteria	Sludge dry weight (g)	Comments
<u>T. thiooxidans</u>	0	No sulfur added to media
<u>T. thiooxidans</u>	2	"
none	2	"
<u>T. ferrooxidans</u>	0	50% of FeSO_4 added
<u>T. ferrooxidans</u>	4	"
none	4	"
<u>T. ferrooxidans</u>	0	No FeSO_4 added to media
<u>T. ferrooxidans</u>	4	"
none	4	"
<u>T. ferrooxidans</u>	0	No H_2SO_4 added to media
<u>T. ferrooxidans</u>	2	"

Figure 4-1 shows the apparatus used to study the effect of air bubbling and Table 4-4 outlines the experimental conditions. No agitation was provided during the air bubbling experiments. The air flow rate to each flask was 0.5 l/min. This was done to determine whether increased carbon dioxide transfer in the media would increase bacterial growth. The effect of non-sterile conditions was studied with 2 and 4 wt% of sludge (Table 4-5).

The geothermal sludge was oven-dried from a 60 wt% paste. Since there are dissolved solids in the waste before drying, the ability of distilled water to dissolve any of these dried solids from 4 grams of sludge was studied. To determine whether soluble salts in the sludge were inhibiting bacterial growth, the effect of rinsing the 4 grams of sludge with distilled water before adding the bacteria was studied. The effect of no agitation was also studied with 4 grams of sludge. In order to determine if the bacteria can survive the maximum temperatures reached in the Imperial Valley, the bacteria were grown in a 120°F (50°C) oven with no sludge. In addition, an experiment was run to determine if both organisms could be grown together with and without sludge. The conditions for these experiments are given in Table 4-6.

Table 4-4 Air Bubbling Experiments

Bacteria	Sludge dry weight (g)	Comments
<u>T. thiooxidans</u>	0	No agitation
<u>T. thiooxidans</u>	4	"
none	4	"
<u>T. ferrooxidans</u>	0	No agitation
<u>T. ferrooxidans</u>	4	"
none	4	"
<u>T. ferrooxidans</u>	0	No agitation and 50% FeSO ₄ in media
<u>T. ferrooxidans</u>	4	"
none	4	"

Table 4-5 Non-Sterile Experiments

Bacteria	Sludge dry weight (g)	Comments
<u>T. thiooxidans</u>	0	Control
<u>T. thiooxidans</u>	2	
none	2	Control
<u>T. thiooxidans</u>	4	
<u>T. ferrooxidans</u>	0	Control
<u>T. ferrooxidans</u>	2	
none	2	Control
<u>T. ferrooxidans</u>	4	

AIR BUBBLING BIO-LEACHING APPARATUS

Table 4-6 Other Non-Sterile Experiments

Bacteria	Sludge dry weight (g)	Comments
<u>T. thiooxidans</u>	0	Grown at 50°C
<u>T. thiooxidans</u>	2	No agitation
<u>T. thiooxidans</u>	4	Sludge rinsed*
<u>T. ferrooxidans</u>	0	Grown at 50°C
<u>T. ferrooxidans</u>	2	No agitation
<u>T. ferrooxidans</u>	4	Sludge rinsed*
Mixed culture	0	Mixed culture
none	4	Distilled water

*Sludge rinsed with distilled water before addition of bacteria.

4.3 Atomic Absorption Spectrophotometer

The atomic absorption spectrophotometer (AA) was calibrated in the linear working range for a specific metal before any readings were taken. Stock standard solutions of Cr and Zn were prepared as described in Table 4-7 and diluted to 5 and 1 ppm, respectively. These values represent the maximum concentrations of the linear working range of aqueous solutions and were used in calibration of the AA.

Table 4-7 Operating Parameters and Stock Standard Solution Preparation for the Atomic Absorption Spectrophotometer

Metal	Chromium	Zinc
Wavelength	358 Å	214 Å
Slit setting	0.7 nm	0.7 nm
Light source	Hollow cathode lamp	Hollow cathode lamp
Flame type	Air-acetylene flame reducing (rich, yellow)	Air-acetylene flame oxidizing (lean, blue)
Stock Standard	1000 µg Cr/ml	500 µg Zn/ml
Solution	Dissolve 3.735 g K ₂ CrO ₄ in one liter deionized water	Dissolve 0.500 g Zn metal in a minimum volume of HCl and dilute to one liter with 1% (v/v) HCl

Once the reference solution was prepared, the appropriate lamp was inserted into the spectrophotometer and the burner control unit turned on. The operating amperage, as noted on the lamp bulb, was adjusted with the lamp knob. The slit size and the wavelength were set according to the values listed in Table 4-7. The lamp's horizontal and vertical position were then adjusted until the maximum gain was attained. Once the hood, air flow, and acetylene flow were opened, the burner was ignited. The flame was then adjusted (see Table 4-7).

The capillary tube was inserted into distilled water to set the zero calibration. It was wiped dry before inserting into a 5-ml sample of the reference solution. The maximum value of the linear working range was then input to set the upper calibration limit. The capillary tube, wiped dry before insertion, was transferred to distilled water between each sample reading. Leachate samples of approximately 4-5 ml were prepared as described in Section 4.1. If a sample exceeded the maximum value of the linear working range, it was diluted with a measured amount of distilled water until an absorbance reading was obtained that fell within the linear working range.

4.4 Sludge Analysis

To determine the concentrations of zinc and chromium in the dried sludge, an AA analysis was performed on an acid digested sludge sample. The sample was prepared by placing 0.3 g of sludge in a beaker and mixing with 10 ml of 10% (w/v) tartaric acid and 6 ml of concentrated nitric acid for 15 hours. The beaker was placed in a steam bath for two to three hours until the sulfur turned white. At this time, the solution was filtered and the filtrate was diluted with distilled water to make a 100-ml solution.

5 EXPERIMENTAL RESULTS AND DISCUSSION

5.1 Thiobacillus Thiooxidans Batch Kinetic Studies

5.1.1 Bacterial Growth

In the batch kinetic experiments conducted under sterile conditions, T. thiooxidans exhibited exponential growth with 0, 2, and 4 wt% sludge (Figure 5-1). All three concentrations showed an initial lag phase. The flask without sludge began exponential growth after approximately 50 hr; and 2 and 4 wt% samples began exponential growth after 70 and 120 hr, respectively. The exponential growth phase in the control flask with no sludge lasted about 20 hr, and the average growth rate was measured to be 547 cells/mm³/hr. In contrast, exponential growth phases for the 2 and 4 wt% samples lasted approximately 80 and 100 hr, respectively. Average growth rates during these periods were observed to be 284 cells/mm³/hr for the 2 wt% sample and 294 cells/mm³/hr for the 4 wt% sample. No growth was apparent when 10 wt% or more sludge was used. These and all subsequent growth measurements have an estimated average error of 48% (Appendix 12.4.1).

Lower growth rates within flasks with higher sludge concentrations were thought to result from higher concentrations of salts in the medium caused by the solubilization of mostly chloride salts contained in the sludge. On this assumption, experiments were conducted in which the oven-dried sludge was rinsed with distilled water prior to the addition of medium or inoculum. It was expected that samples containing the rinsed sludge would exhibit higher growth rates. In fact, however, no difference in growth phases or rates was observed over a 230-hr period (Figure 5-2). In both cases, exponential growth began at about 65 hr and growth rates were 485 cells/mm³/hr and 327 cells/mm³/hr for the rinsed and non-rinsed samples, respectively.

One possible explanation for the lower growth rates is the presence of metals in the sludge that have been shown to be highly toxic to T. thiooxidans, even in concentrations as small as 1 ppb (Norris, 1978). Cadmium, mercury, and silver are toxic in small quantities and are present in typical geothermal waste.

In addition to sludge concentration, several other variables including temperature, sterility, agitation, and nutrient content affect bacterial growth.

Experiments conducted at 50°C (122°F) with no sludge present showed that T. thiooxidans were able to survive at this elevated temperature. However, the bacterium never reached exponential growth during the 230-hr experimentation period. Because temperatures in the Imperial Valley occasionally reach 120°F, bacterial growth may be halted in a bio-leaching process located in this region, but this poses no problem since these high temperatures are not sustained.

In experiments performed under sterile and non-sterile conditions, growth rates during the exponential phase were comparable: 325 cells/mm³/hr under non-sterile conditions and 284 cells/mm³/hr under sterile conditions (see Figure 5-3). This is a significant result because it would be impractical to design a sterile industrial process to treat the regulated sludge.

T. THIOOXIDANS
EFFECT OF SLUDGE CONCENTRATION ON BACTERIAL GROWTH
(STERILE CONDITIONS)

F. THIOOXIDANS
EFFECT OF RINSING SLUDGE ON BACTERIAL GROWTH
(4 wt% SLUDGE)

T. THIOOXIDANS

EFFECT OF STERILITY ON BACTERIAL GROWTH

We also studied the effect of mild agitation on bacterial growth. The agitation was insufficient to cause a slurry to be formed, but did cause the medium to be well mixed. As in the case of sterility, growth phases and rates were comparable in those experiments conducted with and without agitation (see Figure 5-4). During the exponential growth phase, which lasted from approximately 65 to 120 hours, growth rates for the agitated and non-agitated samples were 600 and 800 cells/mm³/hr, respectively. This indicates that maximum growth can be attained without agitation.

When no sulfur was added to the T. thiooxidans medium (in the hope of reducing raw material costs), the bacterium was unable to utilize the sulfur present in the sludge and died. This result indicates that sulfur must be included as a nutrient in a bio-leaching process involving T. thiooxidans.

Air-bubbling through the flasks without agitation had no effect on bacterial growth. This indicates that there are sufficient amounts of CO₂ and O₂ in the medium for maximum bacterial growth to be attained. Provided that equilibrium amounts of CO₂ and O₂ exist in the water used in the medium, aeration will not affect bacterial growth in a bio-leaching process.

5.1.2 Zinc Leaching

After 288 hr, 36% of the zinc originally in the waste sludge had been leached into the medium for experiments with both 2 and 4 wt% sludge (see Figure 5-5). Zinc measurements had an estimated average error of 9% (see Appendix 12.4.2). We detected a marked increase to 62% zinc leached for the 2 wt% sample at 211 hr, before decreasing to 36% at 288 hr. This sudden increase cannot be explained by experimental error, but we believe that it can be neglected, based on the zinc leaching behavior of all other experiments with T. thiooxidans. In the control flask containing no bacteria, only 1% of the zinc was removed after 288 hr. This indicates that the zinc is being leached through the acid leaching cycle catalyzed by the T. thiooxidans (see Section 3.1). This is illustrated again by Figure 5-6 which shows a notable increase in the percentage of zinc leached at about 65 hr, the same point at which the pH begins to decrease from 4.0 to 1.6.

Under both sterile and non-sterile conditions, 36% of the zinc had been leached from the sludge after 288 hr (see Figure 5-7). This was also true under agitated and non-agitated conditions after 113 hr. This observation is supported by the result (see Section 5.1.1) that bacterial growth is not affected by sterility or agitation and emphasizes the feasibility of designing a non-sterile biological waste treatment process utilizing T. thiooxidans.

As expected, depleting the medium of sulfur greatly reduces the percentage of zinc leached. Only 6% of the zinc had been leached from 2 wt% sludge after 113 hr when no sulfur was added to the medium. These results are supported by the lack of bacterial growth under the same conditions and stress the need for sulfur addition in any T. thiooxidans medium if bio-leaching of zinc is to occur.

The results on the effect of air bubbling in the leaching of zinc are not conclusive because no agitation was provided for these flasks. However, since air bubbling was seen to have no effect on bacterial growth, we would not expect agitation to affect Zn leaching.

T. THIOOXIDANS

EFFECT OF AGITATION ON BACTERIAL GROWTH

T. THIOOXIDANS

EFFECT OF SLUDGE CONCENTRATION ON ZINC LEACHING

(STERILE CONDITIONS)

T. THIOOXIDANS
EFFECT OF pH ON ZINC LEACHING
(4 wt% SLUDGE, STERILE CONDITIONS)

T. THIOOXIDANS

EFFECT OF STERILE CONDITIONS ON ZINC LEACHING

(2 wt% SLUDGE)

5.1.3 Chromium Leaching

Chromium was not leached by T. thiooxidans or the thiooxidans medium under any conditions studied. Thus, chromium bio-leaching, unlike zinc bio-leaching, does not utilize the acid leaching mechanism described in Section 3.1.

5.1.4 Process Applications

Based on the above results, T. thiooxidans will leach 36% of the total amount of zinc from the sludge in a 288-hr period under non-sterile conditions using sulfur in the medium. This reduced zinc concentration in the sludge from 10,000 ppm to 7,400 ppm, which is still above the California DOHS TTLC of 5,000 ppm Zn. However, more typical zinc concentrations in geothermal waste are below 10,000 ppm, so that T. thiooxidans may be useful in a biological waste treatment process for other sludges (Royce 1985).

5.2 Thiobacillus Ferrooxidans Batch Kinetic Studies

5.2.1 Bacterial Growth

In the batch kinetic experiments performed under sterile conditions T. ferrooxidans exhibited exponential growth immediately when no sludge was present and remained in this phase for approximately 140 hr (see Figure 5-8). Samples containing 2 and 4 wt% sludge, however, remained in a lag phase for 240 hr. It appears that these two samples began to grow exponentially at this time, but the experiment was terminated before further growth measurements could be taken. Growth in the control flask containing no sludge showed an average rate of 273 cells/mm³/hr during the exponential growth phase. The T. ferrooxidans did not survive when 10 wt% or greater sludge was used.

Lack of bacterial growth was thought to result from an excess concentration of salts in the medium. To investigate this possibility, we conducted experiments in which the sludge was rinsed with distilled water prior to addition of medium or inoculum. However, no difference in bacterial growth was observed and exponential growth was not reached over a 230-hr period (see Figure 5-9).

The existence of certain metals in the sludge, such as cadmium, silver and mercury, may account for the lack of bacterial growth. Kelly and Jones (1978) have shown that these metals are toxic to T. ferrooxidans even in extremely low concentrations.

The effects of sterility, temperature, agitation, and nutrient content on bacterial growth were also studied. Under both sterile and non-sterile conditions, T. ferrooxidans exhibited comparable growth over 232 hr (see Figure 5-10). At this point, neither sample had reached the exponential growth phase; no conclusions concerning the effect of sterility on the growth rates of T. ferrooxidans can be drawn.

Experiments conducted with T. ferrooxidans at a temperature of 50°C (122°F) without sludge present, showed that the bacteria could survive for at least 120 hr but die after 120-230 hr at this temperature. Although similar temperatures are reached in the Imperial Valley, they are generally not sustained for long periods and should not kill the bacterium in a bio-leaching process located there.

T. FERROOXIDANS

EFFECT OF SLUDGE CONCENTRATION ON BACTERIAL GROWTH
(STERILE CONDITIONS)

T. FERROOXIDANS

EFFECT OF RINSING SLUDGE ON BACTERIAL GROWTH

(4 wt% SLUDGE, NONSTERILE CONDITIONS)

T. FERROOXIDANS

EFFECT OF STERILE CONDITIONS ON BACTERIAL GROWTH
(2 wt% SLUDGE)

T. ferrooxidans showed similar bacterial concentrations in experiments with and without mild agitation. However, in neither case was exponential growth apparent, and no conclusion can be drawn about the effect of agitation.

Experiments were conducted using the recommended amount of FeSO_4 (95 wt%), one-half the recommended amount (48 wt%), and no FeSO_4 in the T. ferrooxidans medium with 4 wt% sludge. Exponential growth was observed only in those experiments using one half the recommended amount of FeSO_4 , which may be an indication that ferric ion inhibition occurs. There is evidence that ferric iron inhibits the rate of ferrous iron oxidation. This could be a major factor limiting growth in cultures of T. ferrooxidans (Kelly and Jones, 1978). Kelly and Jones have shown that the lag before growth increases and the rate of development decreases as initial FeSO_4 concentration increases.

Air bubbling through the medium without agitation had no effect on bacterial growth. This indicates that sufficient amounts of CO_2 and O_2 exist in the medium for maximum bacterial growth. Provided that there are equilibrium amounts of CO_2 and O_2 in the water used in a scaled-up process, no aeration should be necessary to reach maximum bacterial growth.

5.2.2 Chromium Leaching

In samples containing both 2 and 4 wt% sludge with bacterium, 60% of the Cr was leached from the sludge after 250 hr as compared to only 12% of the Cr being leached from a 4 wt% sample without T. ferrooxidans in the same time period (see Figure 5-11). In this case, the bacterium catalyzes the Reactions (3-1), (3-2), and (3-4), which lead to the solubilization of Cr. Chromium concentrations were determined within 12% with 95% confidence.

Sterility did not affect the rate of Cr leaching. Under both sterile and non-sterile conditions, 23% of the Cr was leached after 150 hr. These results are supported by the bacterial growth observed under the same conditions (see Figure 5-10), and indicate that a bio-leaching process can be designed for non-sterile conditions.

Chromium leaching was not affected in the unagitated flasks. However, since the agitation mixed the liquid well but did not produce a slurry, we cannot infer that the leaching rates are not transport limited.

The effect of reducing the FeSO_4 concentration to 50% and 0% of the recommended amount on Cr leaching was also studied. After 220 hr, with or without bacteria present, 33% of the total Cr is leached from 4 wt% sludge using all of the recommended amount of FeSO_4 , 17% of the Cr is leached using 48 wt% FeSO_4 , and less than 3% of the Cr is leached using medium with no FeSO_4 . Thus, the FeSO_4 concentration in the medium cannot be reduced without also reducing the rate of Cr leaching. This follows from the mechanism involved in the leaching of Cr described in Section 3.1. FeSO_4 must be present for the bacteria-catalyzed Reaction (3-2) to occur, and hence, the metal-oxidizing Reaction (3-3) must also occur. Experiments were also conducted without adding sulfuric acid to the medium, which increased the pH of the medium to 3.4. However, this increase in pH did not affect the total amount of Cr leached.

T. FERROOXIDANS

EFFECT OF BACTERIUM ON Cr LEACHING

(STERILE CONDITIONS)

Results from air bubbling experiments are inconclusive because agitation was not provided. However, as with T. thiooxidans, the bacterial growth of T. ferrooxidans was not affected by air bubbling, so we would not expect to see an effect on Cr leaching.

5.2.3 Zinc Leaching

Under all conditions studied, including controls containing no bacteria, approximately 30% of the total amount of zinc in the sludge was leached after 24 hr. This indicates that the acidity (pH = 2.8) of the T. ferrooxidans medium, rather than bacteria-catalyzed leaching cycle, is responsible for leaching zinc. Experiments were also conducted without adding sulfuric acid to the medium, which increased the pH of the medium to 3.4. However, this increase in pH did not affect the amount of Zn leached.

5.2.4 Process Applications

In the above experiment, T. ferrooxidans did reduce the Cr concentration in the sludge from 830 ppm to 332 ppm over 250-hr period under non-sterile conditions. This falls below the required California DOHS TTLC of 500 ppm Cr (all chromium was assumed to be present as chromate) and suggests that T. ferrooxidans can be used to biologically remove Cr from geothermal waste. Under similar conditions, T. ferrooxidans will reduce the Zn concentration in the sludge from 10,000 ppm to approximately 7,000 ppm. However, this level still exceeds the TTLC for zinc of 5,000 ppm.

5.3 Combined Culture of T. thiooxidans and T. ferrooxidans

This experiment showed that T. thiooxidans and T. ferrooxidans can exist and grow together in a medium prepared with 50% of each strain's recommended media. Initial results show higher rates of leaching and approximately three times the total chromium leached than with T. ferrooxidans alone. Further work is required to establish the improved leaching rates of mixed cultures.

5.4 Design of Semi-Batch Laboratory Apparatus

The batch kinetic experiments required a low sludge to liquor ratio in order for the bacteria to stay alive. The main purpose of a continuous laboratory experiment is to investigate the possibility of increasing the sludge to liquor ratio without killing the bacteria. If feasible, the volume of the leaching vessel in an actual solid waste treatment plant could be reduced by using this system.

The proposed experimental apparatus is a percolating system, where the leaching liquor containing bacteria and media can trickle through a bed of sludge. If the high concentration of insoluble ions is toxic to the bacteria, then limited contact time of the sludge with the bacteria in this trickling system should enable the bacteria to recuperate when in contact with the medium. However, if the high concentration of soluble ions, such as potassium or chloride, leads to cell lysis, then initially washing the sludge with water would enable the bacteria to proliferate at high sludge to liquid concentrations. In the proposed system, fresh sludge and media may be introduced at any time. Some problems that might be encountered with this apparatus are that the bacteria may still die or the liquid may not trickle through the sludge. Agitating the sludge may be the solution to the second problem, but the first problem remains unresolved.

The proposed percolating apparatus (Figure 5-12) consists of a glass cylindrical tank or beaker with a volume of 2000 ml (10 cm in diameter and approximately 25 cm in height). In this tank, a removable plastic basket is used to hold the sludge. The basket is equipped with a handle which will make cleaning of the apparatus easier. The basket (approximately 9 cm in diameter and 8 cm in height) should be made of a material that will withstand a pH below 1.5. The bottom of the basket contains large holes for the liquid to flow through. A highly porous, thin sintered glass plate (1 cm thick) lines the bottom of the basket. A membrane filter (25 μ m pore size) separates this plate from the sludge; this filter allows the bacteria to flow but not the sludge. The whole assembly (plastic basket, sintered plate, membrane filter, sludge) is supported by a ring stand.

A pump is used to circulate the liquid from the bottom of the tank to the sprayer on top of the tank at flow rates between 10 to 500 ml/min. A reciprocating pump is used to prevent the rupturing of bacterial cell walls that may be caused by rotary pumps. The liquid passing through the sludge falls to the bottom of the tank. Samples are to be taken from the sampling port. A magnetic stirrer is included to maintain a uniform concentration in the liquid. The tank should contain 1000 ml of liquid during the experiment; however, during the course of the experiment, the volume of the system will decrease. This decrease in volume is caused by evaporation of water and sampling. To maintain a constant system volume during experimental runs, fresh media should be added into the tank regularly, especially after taking samples. Tygon tubing is used as piping.

PROPOSED SEMI-BATCH BIO-LEACHING APPARATUS

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FIG.

5-12

6 TYPICAL GEOTHERMAL POWER PLANT

6.1 Double-Flash Process

The design basis for our biological waste-treatment plant is a hypothetical 50-MW "double-flash" plant operating in the Salton Sea KGRA in the Imperial Valley (Figure 2-2). We chose the Salton Sea KGRA because it is here that the geothermal fluids contain the highest concentration of TDS (up to 350,000 ppm). Hence, we expect more solid waste to be generated from the Salton Sea KGRA than in any other KGRA in the Imperial Valley. Table 6-1 shows the geothermal fluid characteristics from three wells in the Salton Sea KGRA. Our design is based on the fluid from a Salton Sea well where the brine temperature is 500°F and the TDS is about 300,000 ppm.

Table 6-1 Characteristics of Geothermal Fluids from Three Wells in the Salton Sea KGRA (Royce, 1985)

FLUID CHARACTERISTIC	WELL SINCLAIR 1 (Flash Fluid)	WELL MAGMAMAX 1 (Flash Fluid)	WELL IID 1 (Flash Fluid)
<u>FLUID PROPERTIES</u>			
Temperature (°F)	536	509	600
Depth of well (ft)	690	2,900	5,200
Conductance (mhos/cm)	0.247	0.226	-
Specific Gravity (77°F)	1.114	-	-
pH	5.3	6.1	5.2
<u>CHEMICAL COMPOSITION (ppm)</u>			
<u>Key Species:</u>			
Chloride (Cl ⁻)	93,650	120,374	155,000
Sulfate (SO ₄ ²⁻)	58	10	56
Bicarbonate (HCO ₃ ⁻)	60	4,472*	150
Carbonate (CO ₃ ²⁻)	0	0	0
Hydrogen sulfide (H ₂ S)	-	-	16
Ammonia (NH ₃)	340	558	409
<u>Other Species:</u>			
Silica (SiO ₂)	350	426	400
Calcium (Ca)	14,550	23,090	28,000
Sodium (Na)	36,340	46,282	50,400
Potassium (K)	7,820	7,789	17,500
Magnesium (Mg)	780	108	54
Boron (B)	210	-	390
Iron (Fe)	166	168	2,290
Manganese (Mn)	410	-	4,100
Barium (Ba)	540	55	235
Stronium (Sr)	360	100	400
Total Dissolved Solids	183,700	203,406	257,800

* Total carbon dioxide.

Source: Ellis and Conover, 1981.

Eskesen (1977) gives the specific output for a "double-flash" plant operating with 500°F geothermal fluid as 53.61 BTU/lb of brine produced. Using Eskesen's specific output for a 50-MW plant, we estimated the total flowrate of geothermal fluid to be 3.18 million lb/hr (Appendix 12.3). In order to determine the rest of the stream properties of the plant, the following assumptions were made:

- (1) Geothermal brine characterized by saturated liquid water at 500°F
- (2) No boiling point elevation due to the presence of TDS
- (3) No effect of condensable gases
- (4) Isenthalpic throttling into each flash vessel
- (5) Turbine discharge temperature of 120°F
- (6) Constant liquid specific heat.

In order to determine stream properties, the temperature of each flash vessel had to be determined. Using the method of Milora and Tester (1976) we estimated the temperature of the high pressure flash to be 352°F and the temperature of the low pressure flash to be 226°F (Appendix 12.2).

The geothermal power plant extracts energy from a hot geothermal brine by expanding it through turbine generators. The brine (Stream 1) in Figure 6-1 is throttled into the first flash vessel at constant enthalpy where 19% of it is flashed to produce 600,000 lb/hr of steam (Stream 2), which is expanded in the high pressure turbine. A material balance fixes the liquid flowrate (Stream 3) from the first flash as 2.6 million lb/hr. This liquid is throttled isenthalpically into the second flash where 11% is flashed into vapor (Stream 4) producing 350,000 lb/hr of steam which is expanded in the low pressure turbine. The steam exiting the turbines at 120°F and 1.7 psia is sent to a condenser (Stream 6). Once the stream has been condensed and cooled in the cooling tower, it is recycled to the direct contact condenser to be used as makeup water. The latent heat released by the condensing steam vaporizes this makeup water in the cooling tower.

Energy balances on the turbines resulted in an isentropic (ideal) power production of 70.2 MW (Appendix 12.2). The real work of our base-case double-flash plant is 50 MW. This results in a turbine efficiency of 71%.

The flow rate of the spent liquid from the second flash (Stream 5) is 2.23 million lb/hr. This spent liquid contains all of the initial TDS from the original geothermal brine from the production well (Stream 1). A material balance fixes the solids in Stream 5 as 470,000 ppm or 47 wt%. It is typical for less than 1% of the TDS to precipitate (Brugman, 1986). Stream 5 is sent to a brine-solids separation process before it is reinjected. Table 6-2 summarizes the stream properties of the double-flash plant.

BASE CASE 50-MW DOUBLE-FLASH PLANT

Table 6-2 Base-Case 50-MW Double-Flash Plant Stream Summary*

Stream Number	Description	Flowrate (lb/hr)	Temp. (°F)	Press (psia)	Enthalpy (Btu/lb)	Entropy (Btu/lb°F)
1	Brine from production well (300,000 ppm TDS)	3,180,000	500	681	488	0.689
2	High pressure steam	600,000	352	138	1193	1.576
3	Liquid from Flash 1	2,600,000	352	138	324	0.506
4	Low pressure steam	350,000	226	19	1156	1.735
5	Liquid from Flash 2 470,000 ppm TDS (1% precipitated solids)	2,200,000	226	19	194	0.333
6	Steam exit from turbines	950,000	120	1.7	940	1.63

*See Appendix 12.2 for calculations.

6.2 Brine-Solids Separation Process

The spent liquid from the second flash vessel (Stream 5) is further processed by concentrating the solids in a clarifier, thickener, and filter press (Figure 6-2). Throughout the solid separation process, temperatures are maintained at 230°F in order to avoid additional precipitation of solids. Thus, all of the equipment in Figure 6-2 is well insulated. We expect that any metals contained in the solid waste are saturated in the clarifier solution due to the concentration of the original brine. Stream 5 is concentrated to be about 5 wt% precipitated solids in the clarifier. The overflow from the clarifier (Stream 7) is essentially a solid-free solution. However, it is further purified in a dual-media filter (coal and sand) before it is reinjected (Stream 8). The filter removes any particles with a diameter greater than 3 μ m. A back-flush tank containing filtered brine is present in order to periodically rinse the dual filter of any particulate deposits. The back-flush (Stream 9) is recycled back to the clarifier.

The underflow from the clarifier (Stream 10) enters a thickener vessel where it is further concentrated to about 15 wt% precipitated solids. The overflow from the thickener (Stream 12) is recycled back to the clarifier. The "washed thickener underflow" (Stream 13) is pumped through a filter press where it is concentrated to about 65 wt% precipitated solids. The liquid from the filter press (Stream 11) is recycled back to the thickener.

If the resulting filter-press cake (Stream 14) is found to exceed the California DOHS TTLC or STLC, it is hauled by truck to a type II-1 hazardous waste-disposal site. If the waste is below the DOHS limits, it can be disposed of in a type II-2 disposal site. The 65 wt% filter press cake is the geothermal waste that we wish to treat in a biological waste treatment facility. Table 6-3 summarizes the brine-solids separation stream properties of our base-case double-flash plant.

BRINE-SOLIDS SEPARATION SYSTEM

Table 6-3 Brine-Solids Separation Process Stream Summary

Stream Number	Description	Flowrate (lb/hr)	Temp. (°F)	wt% Precipitated Solids
5	Brine from Flash No. 2 (470,000 ppm)	2.2×10^6	230	0.15
7	Clarifier overflow	$\sim 2.2 \times 10^6$	230	0.001
8	Solid-free brine to reinjection	$\sim 2.2 \times 10^6$	230	(particles <3 μm)
9	Back flush	Intermittent	230	Variable
10	Clarifier underflow	11,000	230	5.0
11	Filter press recycle	6,200	230	Variable
12	Thickener overflow	Intermittent	230	Variable
13	Thickener underflow	11,000	230	15.0
14	Filter press cake	4,800	230	65.0

7 BIOLOGICAL SOLID-WASTE TREATMENT PROCESS

7.1 Basis of Design

Based on current operations, a 10-MW double-flash plant operating in the Salton Sea KGRA produces 14,000 lb/day (dry basis) of solid waste (Whitescarver, 1986). This scales to 70,000 lb/day for a 50-MW plant. John Bruggan of the Ben Holt Company estimates about 115,200 lb/day of 65 wt% solids filter cake (Stream 14) from a 50-MW double-flash plant in the Imperial Valley. This turns out to be 74,800 lb/day of dry geothermal waste.

The proposed biological waste-treatment process is a continuous process to be run at the ambient conditions (80°F) in the Imperial Valley. It is based on 80,000 lb/day of dry geothermal waste contained in a 65 wt% filter-press cake, which corresponds to 123,000 lb/day of a 65 wt% filter-press cake. Based on experimental results presented in Section 5, bio-leaching will occur at a 5% sludge-to-liquid ratio and residence times of both the sludge and leachate will be 10 days. Nutrients will be added by using the formulations recommended from the ATCC (Table 4-2). Irrigation water from the Colorado River will provide the water necessary for the process. Processing 80,000 lb/day of solid waste will require about 470 lb/day of nutrients and 66,600 lb/day of irrigation water in order to provide a 10-day residence time for the water.

7.2 Proposed Process Flow Scheme

The process flow sheet for the proposed biological waste-treatment facility is given in Figure 7-1. The filter press cake (Stream 14) is placed on a conveyor belt at an average rate of 5,130 lb/hr (65 wt% solid). This is an average rate because the filter press cake is removed as a batch operation. The filter cake is at a temperature of 230°F before it is removed and placed on the conveyor belt. While on the conveyor belt, it should partially cool before being added to the thickener. The conveyor belt leads to a thickener where the nutrients (Stream 15) and water (Stream 16) at 80°F are continuously added. Bio-leaching takes place in the thickener where the solid and liquid residence time is 10 days, and the sludge-to-liquid ratio is 5%. Since the reproduction rate of the bacteria is faster than the rate they are being removed (along with the liquid) the concentration of bacteria in the thickener should reach a steady state.

The thickener underflow (Stream 23) containing 15% precipitated solids is sent to a filter press where it is concentrated to 65 wt% solid cake. The resulting filter press cake (Stream 24) leaves the process at a flowrate of 5,130 lb/hr. The liquid (Stream 18) is recycled back to the thickener. The solids contained in the filter press cake now contain regulated metals at a concentration below the DOHS limits due to the bio-leaching in the thickener. Hence, the filter press cake is now a nonhazardous solid waste.

In order to protect the reinjection well from corrosion, the leachate from the thickener (Stream 17) is sent to a neutralization drum where the pH is raised to at least 4. It is then pumped through a filter (Stream 20) in order to collect any precipitated solids. These solids must be treated as regulated waste; however, their volume will be much smaller than the total volume of solid waste produced. The filtered leachate (Stream 21) is then

BIOLOGICAL WASTE-TREATMENT PLANT

Table 7-1 Biological Waste-Treatment Plant Stream Summary

Basis: 5% Solids

10-day residence time for liquids and solids

Stream Number	Description	Flow Rate (lb/hr)	Amt. of Solid (wt%)
14	Filter Press Cake From Brine-Solid Separation	5130	65
15	Nutrients	470	100
16	Irrigation Water	66,600	0
17	Thickener Overflow	67,100	0
18	Filter Press Recycle	17,100	0
19	Soda Ash	~400	100
20	Exit from Neutralization Drum	67,500	0
21	Reinjection Liquid	67,400	0
22	Regulated Solids from Filter 2	Very Small (<100)	65
23	Thickener Underflow	22,200	15
24	Filter Press Cake (Non-Regulated Solids)	~5100	65

pumped down a reinjection well drilled for leachate disposal. Due to solubility limitations, this reinjection well is not the same well used in the brine-solids separation process of the double-flash plant (Figure 6-2). Table 7-1 summarizes the stream properties of our biological waste treatment facility. Table 7-2 contains a list of the process equipment specifications.

7.3 Alternative Design

7.3.1 Leachate Recycle Alternative

One process alternative is to take the leachate after neutralization (Stream 20) and recycle it back to the clarifier (Figure 7-2). This stream represents only 2.8% of the total clarifier flowrate (5 wt% basis). This would eliminate the costs of both the additional filter press and reinjection well. However, there is a potential problem with this alternative. The concentrations of metal ions in the leachate (with sulfate counter ions) may exceed the concentration of metal ions (with sulfide counter ions) in the clarifier. If this happens, metals will precipitate in the clarifier and will eventually end up back in the filter cake.

RECYCLE ALTERNATIVE

Brine from 2nd Flash

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Table 7-2 Process Equipment Specification

Basis: 5% Solids

10-day residence time for liquids and solids

Equipment	Specification
Thickener Volume (gal)	1,936,000
Filter Press	Same as existing
Conveyor Belt	1 m x 20 m
Neutralization Drum Volume (gal)	16,400
Pump Load (GPM)	
Pump 1	134
Pump 2	45
Pump 3	134
Pump 4	34
Pump 5	133
Injection Well Depth (ft)	2,000

In particular, chromium could be a problem. We have estimated that the total concentration of Cr ions in the clarifier is 0.8 ppm. However, we have measured concentrations of up to 18 ppm in the leachate from our experimental results. If this stream contacted the clarifier, chromium salts would precipitate out of solution. This occurs because the solubility product of Cr is exceeded by increasing the concentration of Cr. This problem could be avoided if the metals in the leachate can be precipitated in the neutralizing drum and removed by a filter press.

7.3.2 Metal Recovery

Another process alternative is to send the leachate from the thickener (Stream 17) to a metal recovery plant (Figure 7-3). The stream leaving the metal recovery plant would then be recycled to the clarifier without precipitation occurring. However, the potential metal recovery from the leachate (Stream 17) has not been evaluated. Also, the utility operating the geothermal power plant may not own the mineral rights for the geothermal fluid they are utilizing and, hence, may not be able to pursue this alternative without added cost.

METAL RECOVERY ALTERNATIVE

Brine from 2ndst Flash

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FIG.

7-3

8 ECONOMICS OF A BIOLOGICAL SOLID-WASTE TREATMENT PROCESS

8.1 Costing Existing Waste Disposal

Currently, there are three costs associated with the disposal of geothermal solid waste: (1) hazardous-waste site acceptance fees (2) trucking, and (3) tax on hazardous waste generation.

Geothermal waste can be disposed of in two forms: solid or slurry. The acceptance fees are \$55/yd³ for regulated solid waste and \$0.105/gallon for a regulated slurry (I.T. Corporation, 1986). Trucking costs are about \$55/hr. These costs are current and could be increased in the near future. Using our basis of 80,000 lb/day of a 65% solids filter cake solid slurry produced from a 50-MW plant, the disposal cost is about \$1,022,000/yr, which amounts to 0.23¢/kWh. This estimated cost does not give credit for the elimination of liability associated with hazardous solid waste, which is likely to be significant.

8.2 Proposed Process

The basis used for the economic analysis is the same as that used for the proposed process design (see Section 7.2). We assumed a 5 wt% solids in the thickener, as well as a 10-day solid and liquid residence time. These assumptions were all based on experimental results. The results of this analysis are presented in Table 8-1.

The potential savings of our process (Figure 7-1) is \$1,022,000/yr, which is the current regulated waste disposal cost. The total capital cost of our biological waste treatment plant is \$3,309,000. This cost includes equipment, installation costs (100% of purchased equipment), land, a reinjection well, working capital, and a 20% contingency. The thickener cost is based on stainless steel construction. The cost of the reinjection well is based on estimates by Tester (Edwards, 1982). The well depth is about 2,000 ft. The fluid being reinjected is less than 3% of the original fluid that was reinjected and therefore needs a much smaller reinjection well diameter. The working capital of the plant is 20% of the total capital cost.

The annual operating expenses (\$687,000/yr) include nutrient costs for Thiobacillus bacteria (estimated from current prices to be approximately \$130/ton nutrients), disposal of non-regulated waste, insurance, irrigation water and labor. The cost of irrigation water is negligible (the annual cost is below \$100).

The total capital cost of the treatment plant was amortized over the 30-year plant life at an interest rate of 10%. The annual cost of the process (amortized capital and annual operating) corresponds to approximately 0.2¢/kWh, which is 0.23¢/kWh or about 5% of the current cost of producing electricity from geothermal energy. (The 1986 estimated cost of electricity from geothermal energy is 4¢/kWh based on data obtained from a 1985 Meridian Corp. report prepared for the U.S. Department of Energy.) Therefore, the cost of a biological waste-treatment plant is small relative to the total cost of

Table 8-1 Cost of Biological Waste Treatment Plant

(1)	POTENTIAL ANNUAL SAVINGS (PAS)		\$1,022,000
(2)	CAPITAL COSTS		
2.1	Direct Costs (DC)		\$2,206,000
	Purchased Equipment (PE)		917,000
	Thickener (stainless steel)	\$260,000	
	Pumps (5)	49,000	
	Filter Press (2)	500,600	
	Neutralization Drum	18,000	
	Conveyor Belt	90,000	
	Installed Equipment	100% PE	917,000
	Land	8% PE	73,000
	Reinjection Well		300,000
2.2	Indirect Costs (IC) (Contingency)	20% DC	\$ 441,000
2.3	Fixed Capital (FC)	IC + DC	\$2,648,000
2.4	Working Capital (WC)	20% TCC	\$ 662,000
2.5	TOTAL CAPITAL COST (TCC)	FC + WC	\$3,309,000
2.6	Ammortized Capital Cost (ACC) ¹		\$351,000
(3)	ANNUAL OPERATING COSTS		
3.1	Nutrients		\$ 265,000
3.2	Irrigation Water	553,000 gal	<\$100
3.3	Disposal of Non-Regulated Waste		365,000
3.4	Insurance		26,000
3.5	Labor		30,000
3.6	TOTAL ANNUAL OPERATING COSTS (TAOC)		\$ 687,000
(4)	ANNUAL SAVINGS (LOSS)	PAS - ACC - TAOC	(16,000)

¹ Based on 30-year plant life and interest rate of 10%.

geothermal power generation. The yearly gain from operating the treatment plant instead of disposing of solid waste as hazardous material is small (a maximum of 0.06¢/kWh based on the data presented in Table 8-2). However, any long-term liability associated with hazardous waste disposal was not considered in this analysis. Thus, if this liability is deemed significant, a biological solid-waste treatment plant should be built.

In conclusion, the economic impact of a biological waste treatment facility on a 50-MW geothermal power plant operating in the Imperial Valley of California is negligible. This means that a decision to add such a facility

in an existing power plant or include one in a new power plant will be based on the desire to treat the plant's solid waste as opposed to trucking it to a hazardous waste site.

8.3 Sensitivity Analysis

The variables studied were percent sludge in thickener (5 and 10%), and liquid residence time in the reactor (10 and 50 days). The effects these variables on capital costs, operating costs, and total cost are presented in Table 8-2. A more detailed analysis is presented in Appendix 12.5. By increasing the sludge in the thickener to 10 wt%, the thickener volume and the capital cost is decreased. This reduces the total cost to about 0.20¢/kWh. The liquid residence time can be increased to 50 days by decreasing the make-up water flowrate five-fold and by not changing the thickener volume. This significantly decreases pump sizes and nutrient costs and reduces the total cost to about 0.1¢/kWh.

Table 8-2 Total Cost Sensitivity to Sludge Concentration in Thickener and Liquid Residence Time

Sludge in Thickener (wt%)	5	5	10	10
Liquid Residence Time (days)	10	50	10	50
Capital Costs (millions of \$)	3.3	3.2	3.0	2.9
Annual Operating Costs (millions of \$)	0.69	0.47	0.55	0.44
Total Cost (¢/kWh)	0.23	0.18	0.20	0.17

* Based on a 10-day sludge residence time

8.4 Alternative Designs

The leachate recycle alternative (Figure 7-2) eliminates approximately \$550,000 in capital costs (filter press and reinjection well) as well as the associated installation and other costs. The metal recovery alternative (Figure 7-3) also saves these capital costs, assuming the metal recovery plant can pay for itself. This slightly reduces the total cost of our basis process to about 0.22¢/kWh. However, further research must be done before any more can be stated about the economics of the metal recovery alternative.

Another economic alternative is to sell the non-regulated solid waste for construction materials. In the economic analysis for this alternative, we assume the cost for non-regulated disposal. This greatly reduces the total cost of our basis process to 0.15¢/kWh.

9 CONCLUSIONS

9.1 Experimental Conclusions

1. The bio-leaching of toxic metals from geothermal solid waste by bacteria of the genus Thiobacillus can be performed under non-sterile conditions.
2. Thiobacillus ferrooxidans can leach out chromium via a redox reaction involving iron (II) and (III) ions.
3. Thiobacillus thiooxidans can be used to leach out zinc from geothermal waste by producing sulfuric acid.
4. Combined cultures of ferrooxidans and thiooxidans leach out three times more chromium than ferrooxidans alone in a shorter time.
5. Both Thiobacillus bacteria used in this study cannot survive with high sludge to liquid ratios. They survived in 4 wt% of the geothermal sludge but died at concentrations of 10 wt% or greater.
6. T. thiooxidans and T. ferrooxidans can thrive at 120°F for up to 5 days. T. thiooxidans survive for longer periods, but die after 10 days.
7. Air bubbling did not increase bacterial growth. Therefore, we can conclude that sufficient CO₂ and O₂ exist in the liquid media to support maximum bacterial growth.
8. The mild agitation used was not enough to form a slurry in the erlenmeyer flasks. Leaching rates of zinc or chromium were not affected by this mild agitation. Further studies with stronger agitation should be performed.
9. The concentration of FeSO₄ in the ferrooxidans media cannot be reduced from that prescribed by the ATCC without affecting the rate of chromium leaching.
10. T. thiooxidans cannot grow in sludge without the presence of elemental sulfur.
11. Bacterial growth was not affected by rinsing the sludge with distilled water before inoculation. Any soluble salts in the dried sludge do not affect bacterial growth.

9.2 Process Design and Economic Conclusions

1. It is technically and economically feasible to build and operate a biological geothermal waste-treatment plant. The total cost of such a facility is about 0.2¢/kWh of electricity produced.
2. Further reduction in capital and operating cost should result from the use of a mixed culture of T. ferrooxidans and T. thiooxidans.

10 RECOMMENDATIONS

Further investigation of the feasibility of bio-leaching toxic metals from geothermal waste is required. This study consisted of preliminary experiments and designs in order to obtain a rough estimate of the technical and economic feasibility of a bio-leaching process. The strains of T. thiooxidans and T. ferrooxidans used in this work were able to leach out zinc and chromium, respectively. Specific recommendations geared to optimize the biological waste treatment facility are given below.

1. Further experiments with mixed cultures should be carried out due to the complementary nature of these two bacteria. T. ferrooxidans produce elemental sulfur, which is rapidly oxidized by the T. thiooxidans to produce sulfuric acid. The ferrooxidans then use the sulfuric acid to reduce Fe^{3+} ions.
2. Experiments with a bench-scale semi-batch reactor should be performed to further test the feasibility of using a continuous biological waste treatment facility.
3. Experimentation should be done with other strains of Thiobacillus. Some of these strains may have a increased tolerance to high sludge concentrations.
4. Attempt to genetically alter the T. thiooxidans and T. ferrooxidans that were used in this study by subjecting successive generations to higher sludge concentrations.
5. Perform experiments with strong agitation to produce a fine sludge slurry in order to determine if increased leaching rates can be achieved.
6. Conduct a series of laboratory kinetic experiments at elevated temperatures (up to 230°F) with Sulfolobus in order to test the feasibility of using thermophilic bacteria. The elevated temperatures may result in higher leaching rates.
7. Examine the leachate recycle and metal recovery design alternatives in more detail to determine the feasibility of significantly reducing capital and operating costs of a biological-waste treatment facility.
8. Use sludge that has not been dried in order to simulate real conditions. These results would determine whether sludge drying and grinding has an effect on the rate of bio-leaching.
9. An investigation into the use of microorganisms that adsorb metals out of solution is recommended in order to determine the feasibility of metal recovery by bio-accumulating the leachate metals. Certain microorganisms such as Cyanidium caldarium (green algae), Pseudomonas aeruginosa, and yeast are known bioaccumulators.
10. Only the bio-leaching of chromium and zinc was measured. In future experiments the leachate should be analyzed for all the metals regulated by the California Department of Health Services.

11 ACKNOWLEDGMENTS

We would like to thank our consultants, Eugene Premuzic and Lawrence Kukacka for their technical advice throughout the project. Special thanks go to Olin Whitescarver, Tom Henrichs, Ben Holt, Jeff Tester, and John Brugman for lending their expertise on geothermal energy production. We are grateful to Annette Gremme and Mow Lin for their assistance in our project and our appreciation goes to George Skaperdas, Barbara Royce, and Dan Slatkin for their time and cooperation.

12 APPENDIX

12.1 Location of Original Data

Original data can be found in databook MIT/BNL-86-1 (1986), Volumes 1, 2, and 3, on file with the MIT Practice School, Building 120, Brookhaven National Laboratory, Upton, NY 11973. Sample calculations and the literature file are also on file with the MIT Practice School.

12.2 Determination of Interstage Flash Temperatures

Interstage flash temperatures for a two-stage geothermal power plant were determined by utilizing the methods of Milora and Tester (1976). Our calculations were based on the following assumptions:

- (1) no condensable gases in geothermal fluid;
- (2) geothermal fluid characterized by saturated liquid water at temperature T and specific enthalpy $h_1(T)$;
- (3) specific heat of saturated liquid is constant;
- (4) entropy (S) not affected by pressure.

When a saturated liquid, with flowrate F is throttled to a lower pressure, the fluid is flashed into vapor and liquid reactions (Figure 12-1). These vapor and liquid flows (V_1 and L_1) at the flash temperature (T_1) are given by:

$$V_1 = F [h(T) - h(T_1)]/\lambda(T_1) \quad (12-1)$$

$$L_1 = F - V_1 \quad (12-2)$$

where $\lambda(T_1)$ = latent heat of vaporization at flash temperature. In a double-flash system, L_1 is then throttled into a second flash vessel where the temperature is T_2 . The vapor and liquid flowrates out of the second flash are given by:

$$V_2 = L_1 [h(T_1) - h(T_2)]/\lambda(T_2) \quad (12-3)$$

$$L_2 = L_1 - V_2 \quad (12-4)$$

Power from the first turbine is obtained by expanding V_1 to the sink temperature T_0 where heat is rejected. The amount of power generated (P_1) is equal to the product of the vapor mass flow rate (V_1) and the specific enthalpy drop of the vapor during the turbine expansion:

$$P_1 = V_1 [H(T_1) - H(T_0) - T_0(S(T_1) - S(T_0))] \quad (12-5)$$

where η is the average turbine efficiency accounting for moisture generated during turbine expansion (approximately 80%).

The vapor from the second flash is expanded in the second turbine to produce additional power P_2 :

$$P_2 = V_2 [H(T_2) - H(T_0) - T_0(S(T_2) - S(T_0))] \quad (12-6)$$

TWO-STAGE FLASH SYSTEM

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FIG.

12-1

Optimum thermodynamic performance occurs at those values of T_1 and T_2 for which the partial derivatives of the expression for the combined power vanish. By setting the partial derivatives equal to zero and making a series of mathematical manipulations and simplifications, the interstage optimum flash temperatures can be determined (Milora and Tester, 1976). The optimum values of T_1 and T_2 are given by:

$$T_1^{\text{opt}} = (T_0 T_2)^{1/3} \quad (12-7)$$

$$T_2^{\text{opt}} = (T_0 T_1^{\text{opt}})^{1/2} \quad (12-8)$$

Thus, for any value of T and T_0 , the optimum flash temperatures can be determined.

For our base case double-flash plant (Figure 6-1), the optimum flash temperatures are determined using Eqs. 12-7 and 12-8. Hence, with $T = 500^\circ\text{F}$ (960°R) and $T_0 = 120^\circ\text{F}$ (580°R), the optimum flash temperatures are:

$$\text{Flash 1 Temp} = T_1 = [(580)(960)^2]^{1/3} = 352^\circ\text{F}$$

$$\text{Flash 2 Temp} = T_2 = [(580)(812)]^{1/2} = 226^\circ\text{F}$$

12.3 Material and Energy Balances for Base-Case "Double-Flash" Plant

Stream properties for our base-case "double-flash" plant were determined by performing material and energy balances. In this section we summarize the methods and assumptions used in determining the flowrates and temperatures given in Table 6-2.

12.3.1 Determination of Steam Flashing from Flash No. 1 and No. 2

The geothermal fluid at 500°F is throttled into the first flash vessel where the temperature was determined to be 352°F (Appendix 12.2). Assuming an isenthalpic expansion through the throttling valve, the enthalpy of the fluid in Flash No. 1 is the same as that of the brine (488 Btu/lb). Thus, the fraction of vapor (x) that is flashed can be calculated from an enthalpy balance between the geothermal fluid at 500°F and the saturated liquid and vapor enthalpies (H_1 and h_1 respectively) at 352°F .

$$h = x H_1 + (1-x)h_1 \quad (12-9)$$

Thus, with $h = 488$, $H_1 = 1192.7$, and $h_1 = 323.9$ Btu/lb (saturated values at 352°F), the fraction of vapor flashed is equal to 19% of the brine flowrate (3.18 million lb/hr) which is 600,000 lb/hr of steam.

Subtracting the steam flowrate to the first turbine from the brine flowrate gives 2.6 million lb/hr of spent liquid with an enthalpy of 323.9 Btu/lb entering Flash No. 2. This liquid is isenthalpically expanded to 226°F (Appendix 12.2) where more steam is flashed to the second turbine. From Table 6-2, the enthalpies of the saturated vapor and liquid (H_2 and h_2) at 226°F are 1155.6 and 194.3 Btu/lb respectively. An enthalpy balance determines the

fraction of steam (y) flashed in the second flash:

$$h_1 = y H_2 + (1-y)h_2 \quad (12-10)$$

Thus, the fraction of vapor flashed is 0.135 of the spent liquid from Flash No. 1 or 350,000 lb/hr. This establishes the liquid flowrate from Flash No. 2 as 2.2 million lb/hr (at 226 F).

12.3.2 Isentropic Ideal Work of Turbines 1 and 2

From Table 6-2, the entropy of the saturated steam from the first flash (S_1) is 1.576 Btu/lb^{°F}. The turbine exhaust is at 120 F (design basis). Expanding the steam to 120^{°F} by an adiabatic reversible process fixes the entropy at the turbine exhaust at 1.576 Btu/lb^{°F}. Thus, the quality of the steam (z) at the turbine exhaust can be determined by an entropy balance where the saturated vapor (S) and liquid (s) have an entropy of 1.9339 and 0.1646 respectively at 120^{°F} (steam tables).

$$S_1 = z s + (1-z) S \quad (12-11)$$

$$1.576 = z (.1646) + (1-z) 1.9339$$

Hence, the quality of the steam (z) from turbine 1 is 0.202. Using this quality at 120^{°F}, the enthalpy at the turbine exit can be calculated from:

$$H_1(T_0) = z h_s + (1-z) H_s \quad (12-12)$$

$$H_1(T_0) = .20(87.97) + (1-.20)1113.6$$

$$H_1(T_0) = 906.4 \text{ Btu/lb}$$

With the exhaust enthalpy determined to be 906.4 Btu/lb, the isentropic enthalpy drop across the turbine can be determined using the inlet enthalpy of the steam (H_1) at 352^{°F} as 1192.7 Btu/lb:

$$\Delta H_{\text{ideal}_1} = (1192.7 - 906.4) = 286.3 \text{ Btu/lb}$$

The steam flow rate was determined to be 600,000 lb/hr (Section 12.3.1). Thus, the ideal work of turbine no. 1 is calculated from:

$$\dot{W}_{\text{ideal}_1} = (600,000) (286.3) = 1.72 \times 10^8 \text{ Btu/hr}$$

A similar calculation using the steam from Flash No. 2 with enthalpy and entropy of 1155.6 Btu/lb and 1.735 Btu/lb^{°F} respectively produces a steam quality of 0.112 at 120^{°F}. The enthalpy at the exhaust of turbine 2 ($H_2(T_0)$) was determined to be 998.8 Btu/lb. The isentropic enthalpy drop across turbine no. 2 is then:

$$\Delta H_{\text{ideal}_2} = (1155.6 - 998.8) = 156.8 \text{ Btu/lb}$$

Using the steam flowrate of 350,000 lb/hr from Flash No. 2, the ideal work produced by the second turbine is determined:

$$\dot{W}_{ideal_2} = (350,000) (156,8) = 5.4 \times 10^7 \text{ Btu/hr}$$

Thus, the total ideal work (Turbine 1 and Turbine 2) is found to be:

$$\dot{W}_{tot} = \dot{W}_{ideal_1} \dot{W}_{ideal_2} = 2.27 \times 10^8 \text{ Btu/hr}$$

Converting this work into megawatts gives 66.4 MW of ideal power. Our base-case double-flash plant produces real work of 50 MW. Thus the cycle efficiency is 75%.

12.4 Error Analysis on Bacterial Growth Counts and Atomic Absorption Measurements

12.4.1 Bacterial Growth Counts

For each sample of leachate taken, nine separate counts were made on a hemocytometric slide. These counts were then averaged and the standard deviation calculated. To determine the 95% confidence level, a representative set of points was chosen (see Calculation File). Twice the standard deviation as a percentage of the mean was averaged for 15 points to give a 48% error.

12.4.2 Atomic Absorption Measurements

Atomic absorption measurements of Cr and Zn concentrations were calibrated using standard solutions. A 5 ppm Cr solution was used to set the maximum value of the linear working range. At the end of sample measurements, the stock standard solution was again measured. The average and standard deviation of these measurements were calculated. From these, the percent error at the 95% confidence limit was calculated. The maximum error of each measurement was calculated using a differential error approach. The error for Cr leaching ranged from 44% error at the lower end of the linear working range to 12% error at the higher end. For Zn, the maximum value of the linear working range is 1 ppm and the error for Zn leaching was 9%.

12.5 Detailed Economic Sensitivity Analysis for Biological Waste Treatment Plant

The table in this section details the economic analysis used to calculate simple payback. Table 12-1 shows the effects of varying the percent solids in the thickener as well as varying the liquid residence time in the thickness. This table includes the cost of disposing of the non-regulated waste. The last column of Table 12-1 shows the effect of neglecting the cost associated with disposing of the non-regulated waste.

Table 12-1 Cost of Biological Waste Treatment Plant

Conditions:		5%	5%	10%	10%	5%
Solids in Thickener						
Solid Residence Time		10 days	10 days	10 days	10 days	10 days
Liquid Residence Time		10 days	50 days	10 days	50 days	10 days
1	POTENTIAL ANNUAL SAVINGS/YEAR (PAS)	\$1,022,000	\$1,022,000	\$1,022,000	\$1,022,000	\$1,022,000
2	CAPITAL COSTS					
2.1	Direct Costs (DC)	2,207,000	2,149,000	1,991,000	1,951,000	2,207,000
	Purchased Equipment (PE)	917,000	889,000	813,000	794,000	917,000
	Thickener	260,000	260,000	182,000	182,000	260,000
	Pumps (5)	49,000	32,000	30,000	17,000	49,000
	Filter Press (2)	500,000	500,000	500,000	500,000	500,000
	Neutralization Drum	18,000	7,000	11,000	5,000	18,000
	Conveyor Belt	90,000	90,000	90,000	90,000	90,000
	Installed Equipment 100% PE	917,000	889,000	813,000	794,000	917,000
	Land 8% PE	73,000	71,000	65,000	63,000	73,000
	Reinjection Well	300,000	300,000	300,000	300,000	300,000
2.2	Indirect Costs (IC) 20% DC (Contingency)	441,000	430,000	398,000	390,000	441,000
2.3	Fixed Capital (FC) IC + DC	2,648,000	2,579,000	2,390,000	2,341,000	2,648,000
2.4	Working Capital (WC) 20% TC	662,000	645,000	597,000	585,000	662,000
2.5	TOTAL CAPITAL COST (TCC)	3,309,000	3,224,000	2,987,000	2,926,000	3,309,000
2.6	Amortized Capital cost (ACC) ^b	351,000	342,000	317,000	310,000	351,000
3	ANNUAL OPERATING COSTS					
3.1	Nutrients	265,000	53,000	113,000	26,000	265,000
3.2	Irrigation Water	<100 ^c	<100 ^d	<100 ^e	<100 ^e	<100 ^c
3.3	Non-Regulated Waste Disposal	365,000	365,000	365,000	365,000	0
3.4	Insurance	26,000	26,000	24,000	23,000	26,000
3.5	Labor	30,000	30,000	30,000	30,000	30,000
3.6	TOTAL ANNUAL OPERATING COSTS (TAOC)	687,000	474,000	552,000	444,000	321,000
4	ANNUAL SAVINGS (LOSS) PAS - ACC - TAOC (\$6,000)		\$206,000	\$153,000	\$286,000	\$350,000 ^a

^a Includes sale of non-regulated wastes^b Based on 30-year plant life and interest rate of 10%^c 66,600 lb/yr^d 13,300 lb/yr^e 33,300 lb/yr

13 TABLE OF ACRONYMS

AA	Atomic Absorption Spectrophotometry
ATCC	American Type Culture Collection
DOHS	Department of Health Services
EPA	Environmental Protection Agency
KGRA	Known Geothermal Resource Area
STLC	Soluble Threshold Limit Concentration
TDS	Total Dissolved Solids
TTLC	Total Threshold Limit Concentration

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