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Appendix I

GEOHERMAL WASTE TREATMENT BIOTECHNOLOGY  
(Brookhaven National Laboratory)

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## SOME ASPECTS OF GEOTHERMAL WASTE TREATMENT BIOTECHNOLOGY

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ABSTRACT

Recent studies have indicated that biotechnological processes for detoxification of geothermal residual brine sludges are feasible. Preliminary studies have also shown that such processes are controlled by several factors which include the concentration of the residual sludge in the bioreactor, the type of bioreactor and the strain of acidophilic microorganisms used. A brief discussion of these factors follows.

## INTRODUCTION

Production of electricity by extraction of energy from underground geothermal reservoirs is a highly promising and growing industry. Large scale production of electricity from geothermal sources produces considerable wastes, which accumulate in the form of residual brine sludges containing different concentrations of toxic metals which makes it necessary to ship these residues to hazardous waste disposal sites at a considerable cost. Typically, a 50 MW liquid-dominated hydrothermal power plant in Southern California produces about 70,000 lb/day of solid residues containing in addition to silica and soluble salts, heavy metals, whose concentrations at times exceed the state regulation limits (Royce, 1985).

Work at the Brookhaven National Laboratory (BNL) has shown that acidophilic microorganisms can be used as the "active agents" in the detoxification of geothermal brine residues (Lin et al., 1987; Premuzic et al., 1988). A preliminary design for a process has been suggested (Premuzic et al., 1988). A technical and feasibility study of this process has been described elsewhere (Premuzic et al., 1988) and will only be mentioned here briefly. Thus a bioprocess for a plant producing 123,000 lb/day of a 65% wt. filter process cake was based on 5% sludge-to-liquid ratio and a 10 day residence time. Such a process represents about a one million dollar per year savings, or the equivalent of the 1986 regulated waste disposal cost. This estimate does not take into consideration the long-term liability associated with hazardous waste disposal, increases in the cost of shipping, dumping and the possibility of the dump-sites being closed. Earlier studies have also indicated that

the efficiency of the bioprocess depends on the concentration of the sludge, the type of bioreactor and the type of single and/or mixed cultures of bacterial strains used. Some results of recent studies will be discussed in this paper.

## RESULTS AND DISCUSSION

Three types of bioreactor systems are being considered as possible candidates to be included in the design of a biosystem for detoxification of geothermal residual sludges. These include a fluidized bed type, diagrammatically shown in Fig. 1., a column type batch bioreactor, Fig. 2, and a flat bed-type bioreactor, Fig. 3. In each case flow rates and air supply to the system have to be balanced in order to maintain a steady and active microbial culture supplied with nutrients as needed throughout the cycle. This is verified in all cases by routine sampling and monitoring for viable microbial growth and the metal concentration. The efficiency of metal solubilization by several strains of *Thiobacillus thiooxidans* and *Thiobacillus ferrooxidans* from the Brookhaven National Laboratory (BNL) collection have been studied. Different samples of residual brine sludge from proprietary sources, kindly supplied by the geothermal electrical power industry have been used in detoxification processes. The different sludges are site specific, with some containing more than ten toxic metals (Premuzic et al., 1988). In the work presented in this paper for sake of brevity, only a few representative metals have been used as process indicators.

In Table 1, the effect of eight strains of *Thiobacillus ferrooxidans* on a single residual brine sludge is shown. In this series of experiments a batch bioreactor with a 2-6% loading with stirring has been used. The most efficient metal solubilizing (removing) microorganisms for the metal are identified in Table 1 (square boxes). Results of similar experiments using strains of *Thiobacillus thiooxidans* and mixed cultures of *T. thiooxidans* (T.T.) and *T. ferrooxidans* (T.F.) are shown in Table 2. Tables 1 and 2 indicate that different strains solubilize metals, i.e., remove them from sludges in varying degrees (see square boxes) with a high efficiency for all the metals tested being exhibited by mixed cultures.

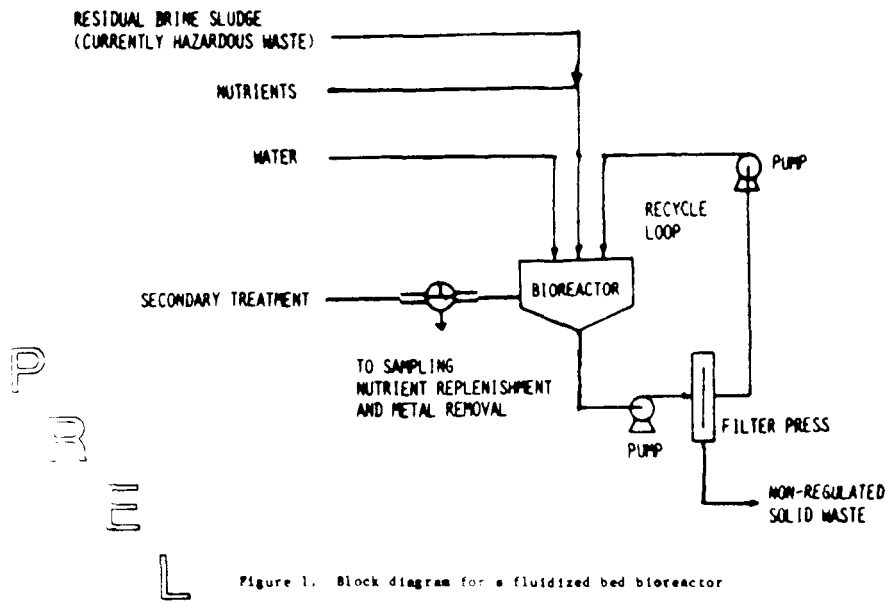


Figure 1. Block diagram for a fluidized bed bioreactor

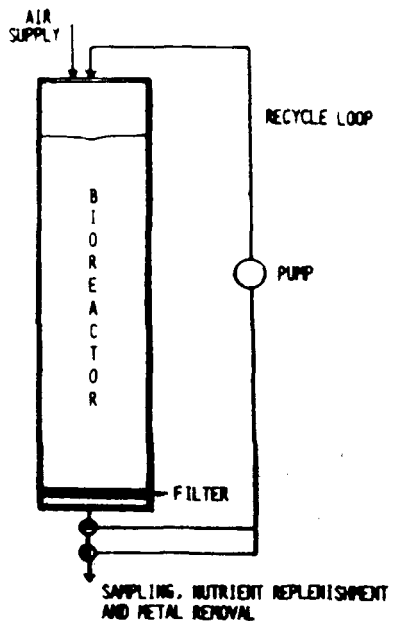


Figure 2. Block diagram for a column type batch bioreactor

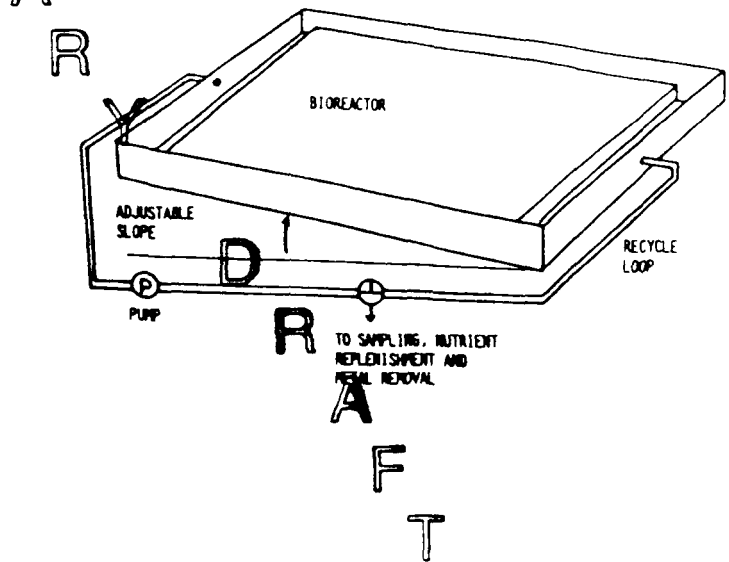


Figure 3. Block diagram for a flat bed type batch bioreactor

Table 1. % Removal of chromium, copper, manganese and zinc from residual brine sludge (BR-1) by the action of different strains of Thiobacillus ferrooxidans.

Strain	Cr	Cu	% Metal removed	
			Mn	Zn
BNL-2-45	30	55	77	90
BNL-2-49	26	58	77	90
BNL-2-44	35	53	58	68
BNL-2-45	26	84	35	88
BNL-2-46	25	88	40	85
BNL-2-47	48	31	57	89
BNL-2-48	22	45	33	85
BNL-2-49	32	91	41	85

Table 2. % Removal of chromium, copper, manganese and zinc from residual sludges BR-1, BR-3, and BR-5 by Thiobacillus thiooxidans (T.T.) and mixed cultures of T. thiooxidans and T. ferrooxidans (T.F.).

Strain T.T.	Brine	% Metal removed			Zn
		Cr	Cu	Mn	
BNL-3-23	BR-1	2	50	30	77
BNL-3-23	BR-3	6	65	34	77
T.T. + T.F.					
BNL-2-49	BR-1	65	90	80	85
+	BR-5	20	90	78	60
BNL-3-24					
BNL-3-25	BR-5	85	82	85	72
+					
BNL-2-46					

Various concentration of residual brine sludge in the bioreactor also influence the extent of metal solubilization as shown in Tables 3 and 4.

CONCLUSIONS

Based on the current results the following conclusion may be drawn:

Table 3. The influence of different concentration of residual brine sludge (BR-2) on the extent of metal solubilization.

Strain T.T. + T.F.	% BR-2 (w/v)	% Metal removed			
		Cr	Cu	Mn	Zn
	1	56	40	62	69
BNL-3-26	2	51	42	61	65
+	4	53	48	67	72
BNL-2-45	6	58	52	74	67
	8	64	50	75	*
	10	56	46	66	*

\*not determined.

Table 4. The influence of different concentration of residual brine sludge (BR-5) on the extent of metal solubilization.

Strain T.T. + T.F.	% BR-5 (w/v)	% Metal removed			
		Cr	Cu	Mn	Zn
	1	91	40	88	73
BNL-3-25	2	83	46	90	75
+	4	80	57	86	79
BNL-2-46	8	75	51	76	72
	12	79	55	71	47

1. Choice of microorganisms may well be pre-determined by the composition of a particular residual sludge. Thus a sludge which, for example, is predominately rich in chromium may require a concentration of microorganisms most efficient for chromium and not necessarily efficient for other toxic metals, which may be present in trace amounts at concentrations well below the threshold limits;

2. The treatment cycle may also be shortened from say six to three days if only few metals are to be considered;

3. In terms of bioreactor design, efficient cycling, supply of nutrients and air will dictate a particular basic design concept, i.e., batch or continuous.

Preliminary results discussed above indicate that mixed cultures of different strains of microorganisms, the relative concentration of the residual brine sludges in a bioreactor and the number of toxic metals present in concentrations exceeding the threshold limits play critical roles

in scaled up processes and require further research and development studies. The results of these studies will generate information essential to the design of efficient biotechnology for detoxification of residual brine sludges.

**ACKNOWLEDGMENTS**

This work has been sponsored by the U.S. Department of Energy, under Contract No. AM-35-10 and by Brookhaven National Laboratory and the U.S. Department of Energy under Contract No. DE-AC02-76CH00016. We wish to acknowledge L. Kukacka of BNL for valuable discussion and advice. We also wish to acknowledge M. Moseley, a BNL semester student for technical assistance.

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BROOKHAVEN NATIONAL LABORATORY (BNL) INVOLVEMENT IN THE  
SALTON SEA SCIENTIFIC DRILLING PROJECT

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OBJECTIVE:

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Obtain a large geothermal waste sample from the BSSDP site to conduct scaled-up research studies, in which BNL uses biochemical techniques to remove toxic elements that exceed environmental regulations.

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BACKGROUND:

Disposal of toxic leachable solid waste in an environmentally and economically acceptable way may be a major impediment to large-scale geothermal development.

For example, 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 provide the incentive for this study.

It is known that microorganisms can interact with metals specifically by several mechanisms such as surface adsorption, oxidation, reduction, and solubilization and/or precipitation. These mechanisms serve as a basis for the development of biotechnology which allows use of biochemical processes for removal and concentration of toxic metals present in the waste or makes possible solubilization of the waste.

Such biotechnology is particularly useful when large quantities of wastes are present which contain low, but nevertheless environmentally significant, concentrations of toxic metals, disposal of which is regulated. Another advantage of the biochemical processes considered in this program is due to the type of microorganism used. These microorganisms are acidophilic and thermophilic capable of living under very harsh conditions such as extreme acidic pH, high salt concentrations, and elevated temperatures. Such conditions are unsuitable to most other microorganisms which require mild conditions for their growth. This means that the new biotechnology developed at BNL does not require sterile conditions.

## STRATEGY:

- o The BNL experimental strategy is based on the use of biochemical methods (i.e. selected microorganisms) for dissolution of toxic elements found in geothermal residues. Thus, the produced solution, which contains toxic metals can be reinjected or the metals can be concentrated and recovered. The efficiency of the metal solubilization (i.e., removal from the waste) is determined by experimental conditions which enable removal of toxic metal (to at least below the regulatory level) in the shortest possible time. To optimize the process, compatible microorganisms must be identified, plus other variables, such as biomass to residual sludge ratio, different residence times, mixed cultures, ambient and elevated temperatures, must be considered.

## EXPERIMENTAL APPROACH:

- o Using sludge samples obtained from the GSEDP site, BNL will conduct scaled-up biochemical activities, some of which are covered below:
  - Kinetic studies will be conducted using mixed cultures of different strains of acidophilic and thermophilic microorganisms. The studies will be performed in the five to ten gallon range. Earlier BNL studies have been performed at the 250 to 500 milliliter range. During the kinetic studies, sampling will be carried out over extended periods of time. Timing will vary from hours to days, with 10 days being the common residence time. Aqueous and solid phase sample analyses will be carried out, using various analytical tools, such as atomic adsorption to determine the relative solubilization (i.e., removal) of toxic metals from solid brine, as seen in the culture media after microbiological treatment.
  - The solids will be examined after treatment to determine the efficiency data. In this process, the solid material is subjected to chemical treatment, such as acid solubilization or borax fission and then analyzed by atomic adsorption. Sampling is carried out at  $t = 0$  and  $t = 10$  days to evaluate the maximum concentration of solids vs. the viability of cycled biomass and nutrients. Since the residual sludges from geothermal plants are site specific, samples containing metal concentrations exceeding the environmentally allowable threshold limits are analyzed.
  - Three types of bioreactors will be considered during the upscaled experiments: column, flat bed, and fluidized bed reactors for the purpose of evaluating the process design efficiencies of each. Initially, the flat bed and fluidized bed reactors will be evaluated.

## RESEARCH RESULTS:

- o Preliminary research results using the GSEDP sludges will be presented later this year.

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Table 2. % Removal of chromium, copper, manganese and zinc from residual sludges BR-1, BR-3, and BR-5 by Thiobacillus thiooxidans (T.T.) and mixed cultures of T. thiooxidans and T. ferrooxidans (T.F.).

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T.T. + T.F.					
BNL-2-49	BR-1	65	90	80	85
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+					
BNL-2-46					

Various concentration of residual brine sludge in the bioreactor also influence the extent of metal solubilization as shown in Tables 3 and 4.

#### CONCLUSIONS

Based on the current results the following conclusion may be drawn:

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		8	64	50	75	*
		10	56	46	66	*

\*not determined.

Table 4. The influence of different concentration of residual brine sludge (BR-5) on the extent of metal solubilization.

Strain	T.T. + T.F.	% BR-5 (w/v)	% Metal removed			
			Cr	Cu	Mn	Zn
		1	91	40	88	73
BNL-3-25		2	83	46	90	75
+		4	80	57	86	79
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		12	79	55	71	47

1. Choice of microorganisms may well be predetermined by the composition of a particular residual sludge. Thus a sludge which, for example, is predominately rich in chromium may require a concentration of microorganisms most efficient for chromium and not necessarily efficient for other toxic metals, which may be present in trace amounts at concentrations well below the threshold limits;

2. The treatment cycle may also be shortened from say six to three days if only few metals are to be considered;

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