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ADVANCED BIOCHEMICAL PROCESSES FOR GEOTHERMAL BRINES

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KEY WORDS

biochemical processing, decontamination, metal recovery, new products

PROJECT BACKGROUND AND STATUS

In 1987, an R&D program was begun at BNL to identify methods for the utilization and/or low cost environmentally acceptable disposal of toxic geothermal residues. Laboratory work has shown that a biochemical process would meet the cost requirements and produce environmentally-acceptable end-products. In this work, microorganisms have been identified which can interact with toxic metals (including trace radionuclides) in geothermal residual sludges and convert them into soluble species for subsequent reinjection or concentration. The biochemical activities of these organisms served as models for the development of economic detoxification processes for geothermal waste treatment. The new technology reduces significantly the cost of surface disposal of sludges derived from geothermal brines. Concurrent processes to concentrate and recover valuable metals and salts are also being developed. Currently, the process removes better than 80% of total metal concentration in less than 24 hours. The solid residue from this treatment can be subjected to a secondary treatment leading to a de-pigmented product with applications potential in other industries. The aqueous product from the primary process can be used for metal recovery. Economic and regulatory significance of the new technology is clearly defined by the following information.

In 1985, the graded cost for type II-I disposal was \$200 per ton and \$75 per ton for non-hazardous waste. The non-hazardous waste was defined as that not exceeding the total threshold limit concentration (TTLC) and soluble threshold limit concentration (STLC). For example, for chromium, STLC is 5 mg/L, which becomes 0.25 mg/L after the biochemical treatment, while the corresponding TTLC of 500 mg/L becomes 100 mg/L. Thus, an 80% removal of the metals represented a 60% saving. The cost of disposal and the long term liabilities are continuously increasing, while the available space for disposal is diminishing. For example, at BNL, recent disposal cost of a similar sludge was \$500 per ton. The corresponding non-regulated waste disposal cost was \$100 per ton. If the sludge contains in addition to chromium and lead, say radium, then it has to be shipped at a cost of \$400 per cubic foot (\$2052 per ton). On the other hand, removal of the metals leaving radium alone produces waste costing \$76 per cubic foot to dispose of (\$10,800 per ton). This represents a five-fold saving already achievable on a laboratory scale.

Further process cost savings may be achieved by (a) reactants recycling, (b) metal and salt recovery, (c) adjusting to specific needs as demanded by different chemistries of geothermal sludges and brines, (d) production of fillers from the de-pigmented byproduct. The benefits are both environmentally and economically attractive. Not only is the detoxification less expensive, but the end products are useful. The emerging biotechnology could find applications in other industries, particularly in the treatment of similar geochemical materials.

PROJECT OBJECTIVES

Geothermal energy is a major clean energy resource. However, disposal of toxic leachable solid waste in an environmentally and economically acceptable way may be a major impediment to large-scale geothermal development. Hypersaline brines lead to the generation of geothermal solid wastes in power plants. High disposal costs and the long-term liability associated with hazardous waste disposal provide the incentive for this study. Development of economically and environmentally acceptable methods for disposal of geothermal wastes and conversion of by-products to useful forms is being pursued.

Technical Objectives

- Solubilize, separate, and remove environmentally regulated constituents of geothermal sludges and brines.
- Produce a treated sludge which may be used as a feedstock for the production of revenue generating materials such as fillers and construction materials.
- Recover economically valuable trace metals and salts. The residues from such processing can be reinjected and/or converted to highly reduced volumes for disposal in the conventional manner.

Expected Outcomes

- A 25% or more reduction in disposal costs and less long-term liability associated with hazardous waste disposal.
- Conversion of geothermal sludges and brines into environmentally acceptable feedstocks, together with the metal salts recovery option.
- Integration of the biochemical processing recovery and recycling options into a geothermal power producing plant.

APPROACH

(a) Selection Criteria

Brines from the Salton Sea geothermal area in California, may contain total dissolved solids up to 350,000 ppm. These hypersaline brines lead to the generation of regulated geothermal solid wastes in power plants. In other areas, major contaminants may be only a few metals, such as arsenic and mercury. Development of cost-efficient, flexible processes which meet regulatory requirements is the determining factor in the selection of geothermal waste processing technology.

(b) Rationale

The major thrust of this program is to develop low-cost processes for the concentration and removal of toxic materials and valuable metals from geothermal residues. In addition, methods and materials for the utilization of environmentally acceptable storage of these waste fractions are also investigated. The results from this effort reduce significantly the high disposal cost and the long-term liability associated with hazardous waste disposal.

(c) Experimental Approach

The experimental strategy used at BNL for the development of detoxification biotechnology for geothermal waste is based on the use of biochemical methods for dissolution of toxic elements found in geothermal residues. Thus, the produced solution containing toxic and valuable metals can be reinjected or pooled with bulk brines and be used for concentration and recovery of metals and salts. In the recovery mode, both chemical and biochemical methods are being developed.

Technical and economic feasibility has been demonstrated. Laboratory-scale studies have shown that biotechnology for detoxification of geothermal wastes is versatile and is applicable to a variety of geothermal sludges containing few or many metals, including radionuclides. Metals such as chromium, copper, manganese, and others, can be removed with 80-90% efficiencies. A laboratory-scale pilot plant has been constructed and is being used for the optimization of processes. The data generated in these studies serve as a basis for the design of full scale processing scenarios and projections for field applications. In terms of the latter, CRADAs and collaborative arrangements are in place.

RESEARCH RESULTS

The fourth comparative study of the agitated tank vs. fluidized bed type bioreactor was completed. For practical purposes, i.e., space restraints, the agitated tank is being used for routine studies. The two types of bioreactors are interchangeable in the BNL process.

Using a 40% loading and several hours residence time, a preliminary economic evaluation has also been completed. The results have been used to develop a computer program for the advanced biochemical processing of geothermal residual sludges. Differences in the cost of various processes stress further the importance of loading, residence time, the type of bioreactor,

biocatalysts production, process options and recycling. This study has also indicated the importance of process quality control and appropriate monitoring needs.

A first generation pilot-plant has been constructed and is being automated. A secondary process for the removal of radionuclides has been identified and is currently optimized. Sludge loadings of up to 40% are practical and at temperatures of $>50^{\circ}\text{C}$ fast rates of 10 hr or less have been achieved. Studies at elevated temperatures have confirmed that particular attention has to be paid to construction materials, compressors, pumps and other equipment needed for an efficient detoxification process.

The study of metal and salts recovery processes is very promising and indicated that an 80% to 90% metals recovery is possible from a small concentrate. The final aqueous phase meets drinking water standards. A complementary potassium and sodium chloride option is also very promising.

A process for the production of fillers has been designed. This process converts the bulk of the predominantly silica rich final residue into a new commercially viable feedstock.

FUTURE PLANS

Collaboration with industry will be expanded, e.g., cost-shared ventures. Complete process variables verification. Use best results from optimization studies for operating and field construction cost analyses. Continue "quality control" as per Salton Sea experience.

Additional and continuing attention is given to the environmental requirements and management of trace radionuclides. Conduct routine radioactivity measurements in the analysis of residual sludges with particular attention to radium.

Perform kinetic studies of biotransformation process at elevated temperatures particularly focused on short residence times and radionuclides removal. Optimize secondary processes particularly de-pigmentation technology.

Use laboratory plants to process and evaluate different types of sludges as supplied by industry, for example, MAGMA, P.G.&E. and others.

INDUSTRY INTEREST AND TECHNOLOGY TRANSFER

Organization(s)	Type and Extent of Interest
California Energy (CECI) C.E. Holt Company	One on one collaborative effort. Confidentiality Agreement signed. BNL assists the industry in their analytical chemistry needs and selected technical studies. The industry consults and exchanges materials and information. Field trials of a prototype biochemical process will be conducted by CECI at their site.
CET Environmental P.G.&E. Services	A CRADA between BNL and CET Environmental Services is in place. In this CRADA, CET will scale up a modified version of BNL's biochemical process specifically geared to the type of wastes generated by the Geysers types of operations. P.G.&E.'s management at the Geysers Geothermal Field have already identified the site for field testing of this process and their sludge waste stream.
EER, Inc., CA ENSOL, Inc., CA	CRADA

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APPENDIX 1

ECONOMICS OF BIOCHEMICAL WASTE TREATMENT PROCESSES

Previous and ongoing studies have shown that there are at least ten key process variables, ranging from the reactor size to the recycling of biocatalysts, which are essential in the determination of the cost-efficiency of the bioprocesses considered. In addition to these variables, several other parameters have to be evaluated and costed into the design of the overall biochemical process. Currently, the most efficient primary process utilizes two biocatalysts whose production and the rate of delivery influence the size and the number of bioreactors needed to be operational. In Figure 1, a process for the treatment of 5294 kg/h of geothermal sludge at a 40% loading and a residence time of 5 h in the biochemical reactor, requires an input of 946.5 kg/h of each of the biocatalysts. The rate of the Biocatalyst 1 production is fast and that of Biocatalyst 2 is slow. This fact influences the cost of productions. Further, a 50:50 or 85:15 mix of the two biocatalysts influences significantly the economics of the process. Three additional factors have to be also taken into consideration: (1) recycling of the biocatalysts, (2) recovery of valuable metals, (3) recovery of salts such as sodium chloride and potassium chloride, and (4) production of fillers. Options 3 and 4 generate revenues which offset the cost of initial investments as shown in Figure 2. Table 1 shows significant savings which can be achieved by different biocatalyst mixes and recycling. Further combination of the biocatalyst mixes and the potash recovery option, as shown in Table 2, makes possible to accomplish additional monetary gains by total processing of various byproducts generated in the operation of a power plant.

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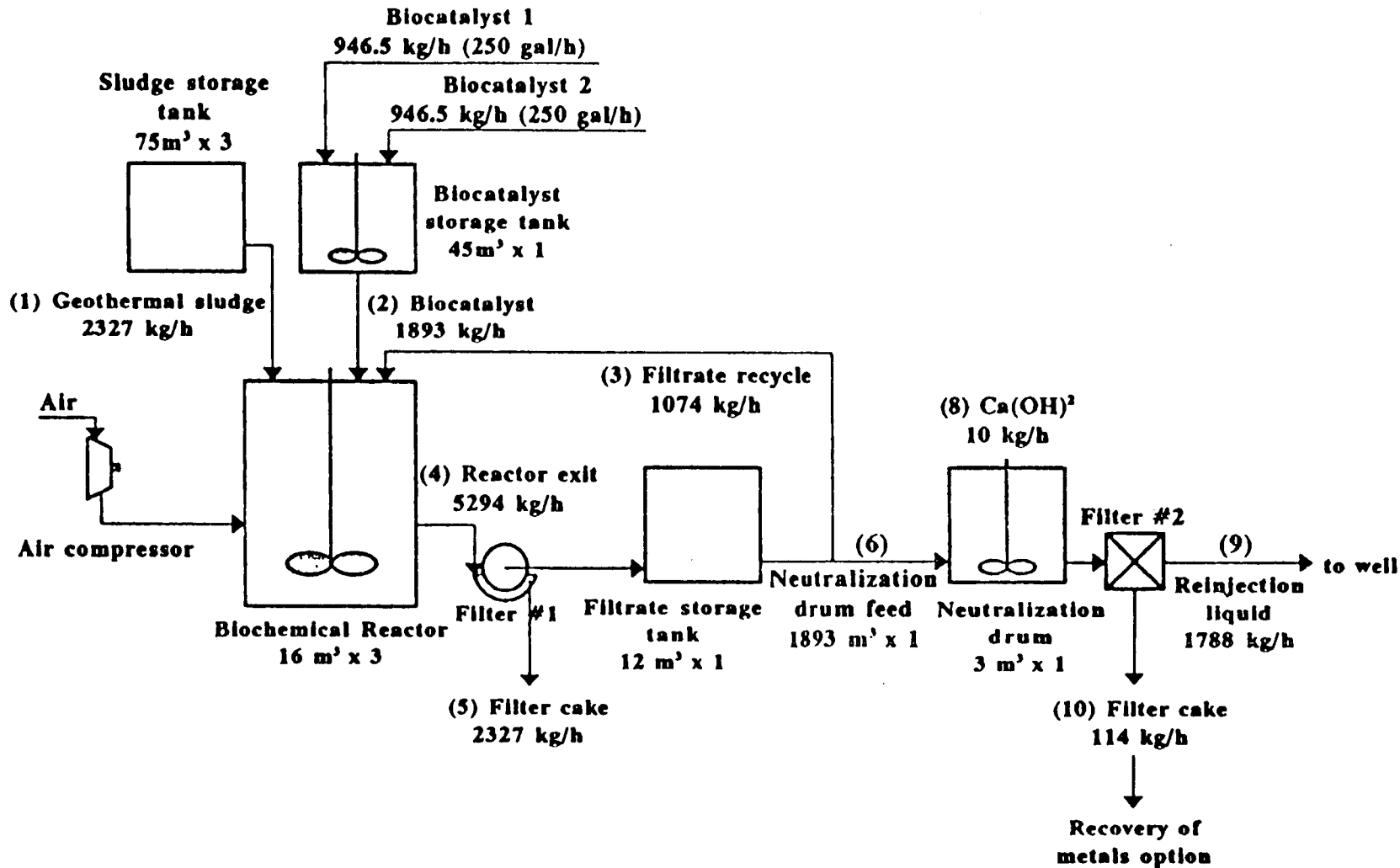


Figure 1. Total biochemical process for geothermal sludge (5130 ib/h). Treatment: Biocatalyst 1 (50%): Biocatalyst 2 (50%).

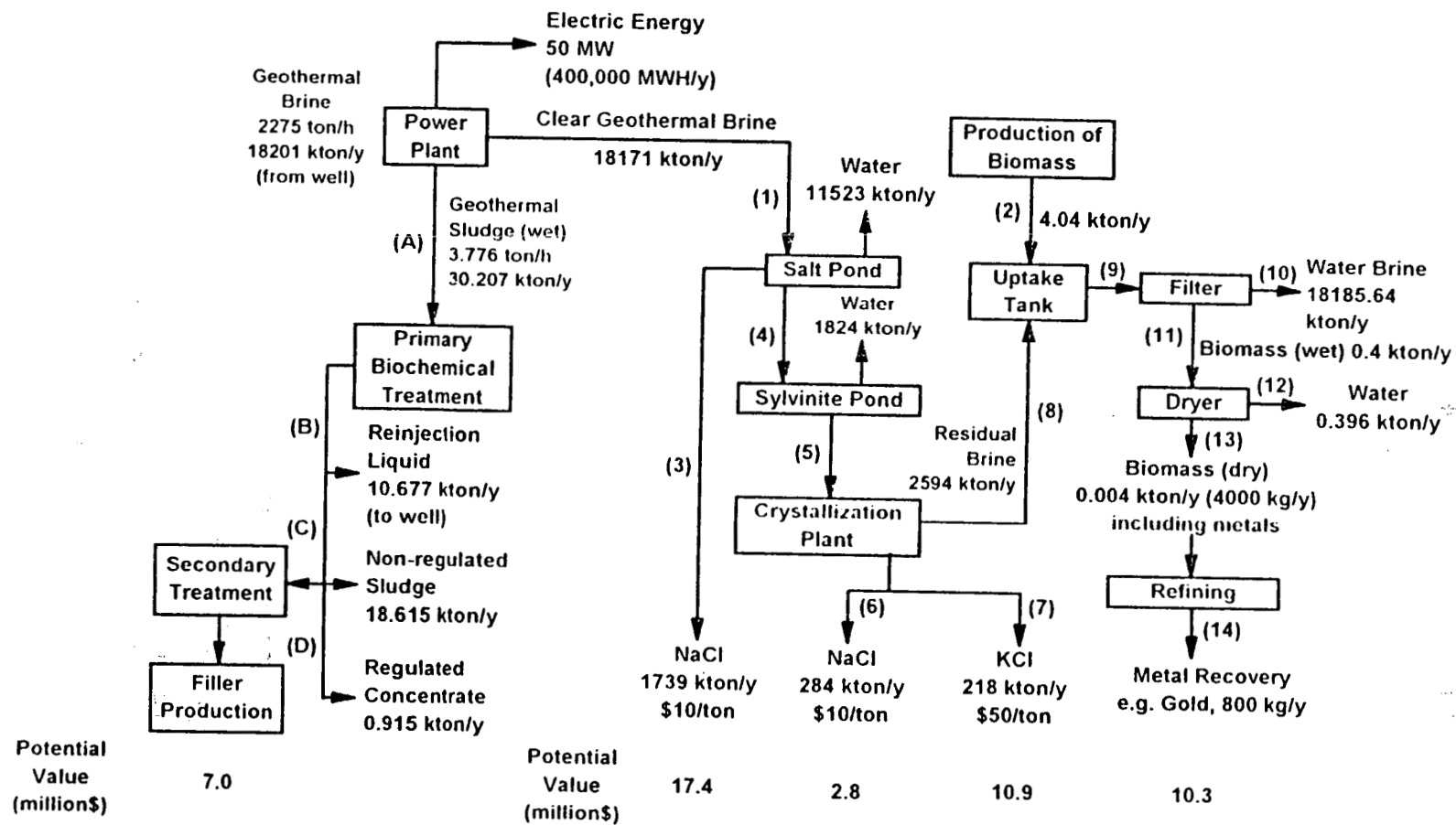


Figure 2. Biochemical processing for geothermal sludge and brine. Scenario C: Combined processes for sludge and brine.

Table 1. Cost Comparison for Different Biocatalyst Mixes and Corresponding Total Bioprocess Costs Per Metric Ton of Sludge

	*BC1:BC2	BC1:BC2	BC1:BC2
	50:50	85:15	85:15 (3 recycles)
	250 gal/h: 250 gal/h	425 gal/h: 75 gal/h	106.25 gal/h: 18.75 gal/h
BC1			
Capital Cost (CGR)	1,838,000	2,556,000	1,196,000
Annual Treatment	1,097,000	1,778,000	820,000
Fee	145	138	255
Unit Treatment Fee (\$/metric ton culture)			
BC2			
Capital Cost (CGR)	7,017,000	2,573,000	1,002,000
Annual Treatment	3,683,000	1,687,000	736,000
Fee	486	743	1,298
Unit Treatment Fee (\$/metric ton culture)			
BC1 + BC2			
Capital Cost (CGR)	8,855,000	5,129,000	2,199,000
Annual Treatment	4,449,000	3,466,000	1,556,000
Fee	316	229	411
Unit Treatment Fee (\$/metric ton culture)			
Total Bioprocess Costs Including Biocatalyst Production			
Capital Cost (CGR)	10,195,000	6,493,000	3,415,000
Annual Treatment	5,882,000	4,578,000	2,614,000
Fee	316	246	140
Unit Treatment Fee (\$/metric ton sludge)			

*BC = Biocatalyst

**Table 2. Total Biochemical Process Profit Estimates
Including Potash Plant Option for a 50-MW Power Plant**

BC1:BC2	Net Gain in \$ Millions/year
50:50	1.83
85:15	2.74
85:15 3 cycles	5.51