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ADVANCED BIOCHEMICAL PROCESSES FOR GEOTHERMAL BRINES

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KEY WORDS

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PROJECT BACKGROUND AND STATUS

Experimental data generated in an R&D program, established at Brookhaven National Laboratory (BNL), to identify methods for the utilization and low cost environmentally acceptable disposal of toxic geothermal residues, have shown that a biochemical process would meet the cost requirements and produce environmentally acceptable end-products. Insoluble chemical species of toxic metals including radionuclides found in geothermal residual brine sludges can be converted into soluble species which may be re-injected into existing wells or concentrated and re-processed. To accomplish this, several unique microorganisms have been identified which elaborate biochemical solubilization and concentration processes. The biochemical activities of these organisms served as models for the development of technically and economically feasible detoxification processes leading to advanced biochemical technology for geothermal waste treatment. The new technology reduces significantly the cost of surface disposal of sludges derived from geothermal brines. Concurrent processes for the concentration and recovery of valuable metals and salts are also being developed. Currently, the process removes better than 80% of total metal concentration in 8 to 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.

Geothermal waste is of the II-I type. In 1985, the cost for type II-I disposal was $200.00 per ton and $75.00 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. It is to be understood, that 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 $500.00 per ton. The corresponding non-regulated waste disposal cost was $100.00 per ton. If the sludge contains in addition to chromium and lead, say radium, then the cost of shipping and removal is $400.00 per cubic foot. Removal of the metals leaving radium alone produces waste costing $76.00 per cubic foot to dispose of or $10,800 and $2052 per ton, respectively. This represents a five-fold saving already achievable on a laboratory scale.

Further process cost savings have been 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 that result are both environmentally and economically attractive. Not only the detoxification is less expensive, but the end products are useful. The emerging biochemical technology could find applications in other industries, particularly in the treatment of similar geochemical materials.

PROJECT OBJECTIVES

Geothermal/hydrothermal resources are currently providing 2700-MW and can play a significant role in providing additional capacity. Moderate-to-high temperature hydrothermal resources are found in many areas of the United States, and are currently utilized for the generation of electric power as well as for direct heating.

Further, 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. Power plants which use lower salinity brines also generate wastes containing regulated contaminants. High disposal costs and the long-term liability associated with hazardous waste disposal provide the incentive for this study in which cost-efficient processing of geothermal wastes is being developed.

Technical Objectives

The objective of the Advanced Biochemical Processes for Geothermal Brines effort is the development of economically and environmentally acceptable methods for disposal of geothermal wastes and conversion of by-products to useful forms. These stated objectives are being accomplished by the development of biochemical processes which:

- 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, for example, 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

- Recent data generated at the laboratory pilot scale level show that a better than 25% reduction of disposal cost can be accomplished.
- The data also indicate that further cost reduction is feasible. This will greatly enhance the rate at which U.S. geothermal resources are developed.
- Conversion of geothermal sludges and brines into environmentally acceptable materials such as fillers, together with the metal salts recovery options, offsets the costs of initial investments associated with the installation of the biochemical processing plant(s).
- Integration of the biochemical processing recovery and recycling options into geothermal power producing plants, leads to a financial net gain with a concurrent satisfaction of regulatory requirements. This concept is illustrated by the examples given in Table 1, where high salinity geothermal sludges are converted to fillers.

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, such as the Geysers, 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 production of environmentally acceptable by-products from 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. This enhances and broadens the development and the utility of U.S. geothermal resources.

(c) Experimental Approach:

- The experimental strategy used at BNL for the development of a cost-efficient biochemical technology for the conversion of geothermal brines and residues into environmentally acceptable products is based on biochemical dissolution and concentration of toxic and valuable metals present 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 of a technology based on biochemical processes for the conversion of geothermal wastes from hazardous to non-hazardous wastes has been demonstrated. Laboratory-scale studies have shown that the new biochemical technology is versatile and is applicable to a variety of geothermal sludges containing few or many metals, including radionuclides such as radium, whose concentrations may exceed limiting threshold values as recommended by regulatory agencies. Metals such as chromium, copper, manganese, and others, can be removed with 80-90% efficiencies.

- Laboratory-scale pilot plant has been constructed and is being used for the optimization of processes used in the emerging biochemical technology. The data generated in these studies serve as a basis for the design of full scale processing scenarios and projections for field applications.

- Joint R&D effort with CalEnergy/C.E. Holt for the development of field testing facilities is current.

- Cooperative research and development agreement (CRADA) is in place between CET, Environmental, Inc. and BNL. The aim of this effort is to construct jointly with PG&E a field facility and test the BNL biochemical process at an already chosen site in the Geysers area.

RESEARCH RESULTS

- A CalEnergy/C.E. Holt plant serves as a resource of geothermal brines and sludges and will be the site of a pilot scale processing plant for a concurrent removal of metals and production of fillers.

- Design for a full operating filler production plant is shown in Figure 1. BNL is contributing technical assistance to CalEnergy in the development of this plant.

- The total integrated process based on the new biochemical technology being developed under the present DOE funded programs is shown in Figure 2. This process, utilizes two biocatalysts and assumes both metal recovery and filler production options. Comparison of potential income values from metal and salt recovery options (Figure 2) with those of process modifications and integration with existing facilities (Table 1) shows the net profit potential of the new technology.

- Current R&D effort for the processing of high salinity feedstocks utilizes two biocatalysts BC1 and BC2 in 50:50 and 85:15 ratios in the presence of different reagents (Reagent 1 and 2, Figure 1).

- The originally developed process for PG&E residues involved two scenarios. The block diagram for the proposed processes is given in Figure 3. The difference between the two is that scenario 1 produces a crude sulfur cake and scenario 2 produces a high grade sulfur cake. Initial biochemical treatment is identical and the current overall process designed by CET, Environmental Inc. and based on BNL's R&D efforts is shown in Figure 4.

- Details of research, engineering designs, development, and cost-efficiency analyses are given in the reference section of this report.

- Educational programs have proved to be successful and are continuing as part of the ongoing R&D under the auspices of BNL and DOE, Office of Geothermal Technologies' educational programs.

FUTURE PLANS

- In collaboration with industrial partners, optimization and modification of currently designed and proposed processes will continue and will be intensified.

- The CET Environmental, Inc./BNL/PG&E process has to be limited to scenario 1 (Figure 3) because of environmental constraints placed on scenario 2 (solvent extraction).

- CalEnergy/C.E. Holt/BNL process will focus on utilization of existing resources, e.g. acid (Table 1), production of fillers and the recovery of metals.

- BNL will provide technical assistance in several areas, specifically:

    1. Laboratory plants will be used to further develop and integrate the biochemical processing of geothermal sludges.

2. Due to cost, space, and regulatory constraints, the laboratory model plant has to be substantially reduced in scale. However, engineering studies and design will ensure that appropriate scaling up can be projected and will satisfy the field requirements. This is being accomplished by a close interaction between BNL staff and the CALEN/CET/PG&E engineering staff.

3. Process modifications will allow the biochemical technology to specifically handle different types of geothermal wastes and convert them to commercially viable products.

4. The area of technology using controlled variables will be maintained and further automation/computerization of the pilot plant will be emphasized.

5. This effort will address the maintenance and optimization of variables includes design of scaled-up processes using corrosion resistant process units.

6. Strategies for the modification of the processes will particular focus on the possible elimination of process streams, use of single biocatalysts, recycling, and the utilization of existing facilities in the field.

7. If and when necessary (due to feedstock variations) optimize further variables for the removal of trace metals such as thorium, radium and uranium by a secondary process.

INDUSTRY INTEREST AND TECHNOLOGY TRANSFER

Organization	Type and Extent of Interest
California Energy/C.E. Holt CET Environmental Services, Inc. Pacific Gas and Electric	One on one collaborative effort. BNL assists the industry in their analytical needs and laboratory scale technical studies. The industry consults and exchanges materials and information. Field trials of a prototype biochemical process are currently being planned at their site.

CET is scaling up a modified version of BNL's biochemical process specifically geared to the type of wastes generated by the Geysers types of operations. PG&E's management at the Geysers Geothermal Field have already identified the site for field testing of this process.

Spin-offs from "Advanced Biochemical Processes for Geothermal Brines" have led to other CRADAs and collaborative ventures particularly in the processing of Fossil Fuels and hydrocarbon wastes. These include:

EER, Inc., CA	CRADA
ENSOL, Inc., CA*	CRADA

*The ENSOL process developed by BNL's group has been awarded the best 100 Popular Science Award for 1996.

REFERENCES

Premuzic, E.T., Lin, M.S., Jin, J.Z., and Hamilton, K. Geothermal waste treatment biotechnology. Proceedings of the World Geothermal Congress 1995, 4, 2769-2772, Eds. R.D. Wilken, U. F'rstner and A. Kn'chel, CEP Consultants Ltd., Edinburgh, UK 1995.

Premuzic, E.T., Lin, M.S., and Lian, H. Biochemical technology for the detoxification of geothermal brines and the recovery of trace metals. Heavy Metals in the Environment 2, 321-324 (1995). (BNL #61285).

Premuzic, E. T. Advanced biochemical processes for geothermal brines--Annual report FY 1994. Informal Report, Jan 1995. (BNL #61509).

Premuzic, E. T., Lin, M. S., and Lian, H. Biochemical processing of geothermal brines and sludges, Proc. Geothermal Program Review XIII, The Role of Cost-Shared R&D in the Development of Geothermal Resources, March 1995, U.S. DOE, p. 8-5 - 8-12. (BNL #61531).

Premuzic, E. T. Advanced biochemical processes for geothermal brines--Annual operating Plan FY 1995. Informal Report #61534, Feb. 1995. (BNL #61534)

Premuzic, E.T., Lin, M.S., Lian, H., and Miltenberger, R.P. Geothermal Brines and Sludges: A New Resource. Geothermal Resources Council Transactions 19, 77-80 (1995). (BNL #61972).

Premuzic, E.T., Lin, M.S., and L.H. Lian. Recent Advances in Biochemical Technology for the Processing of Geothermal Byproducts. Proceedings of the U.S. Department of Energy Geothermal Program Review XIV, April 8-10, 1996, Berkeley, California. (BNL #62987).

Premuzic, E.T., Lin, M.S., Lian, H., and Miltenberger, R.P. Geothermal Brines and Sludges: A New Resource. Proceedings of the Fourth International Symposium on Environmental Issues and Waste Management, October 7-11, 1996, Cagliari, IT, pp. 1019-1025, in SWEMP, Vol. 2, Ed. R. Ciccu, DIGITA, Cagliari, Italy 1996.

Patents

Premuzic, E.T. Biochemical Solubilization of Metals from Residual Geothermal Brines and Sludges. U.S. Patent No. 5,366,891 (1994).

Premuzic, E.T. and Lin, M.S. Conversion of Geothermal Brines and Sludges to Commercial Products. (1995).

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 primary process utilizes two biocatalysts whose production and the rate of delivery influence the size and the number of bioreactors needed to be operational. 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 e.g. gold, (3) recovery of salts such as sodium chloride and potassium chloride, (4) production of fillers, and (5) use of existing facilities and "free products". Options 3, 4, and 5 generate revenues which offset the cost of initial investments as shown in Table 1 and Figure 2. Current information which deals with biocatalyst production indicates that a separate industrial plant is needed for their production and that in the particular case of geothermal materials, the use of a single biocatalyst has economic and technical advantages.

Table 1. Fillers production from geothermal brines. Cost analysis of process changes.

	Original Case Two biocatalysts	Second Case One biocatalyst	Third Case One biocatalyst and use free available HCl
Capital Investment thousands of dollars	4,080	3,606	3,606
Total Expenses thousands of dollars/year	6,751	6,652	2,980
Revenue from filler sales and savings from avoiding waste disposal thousands of dollars/year	16,517	16,517	16,517
After tax Net Profit thousands of dollars/year	6,347	6,412	8,799
After tax rate of return on investment %	164	186	253

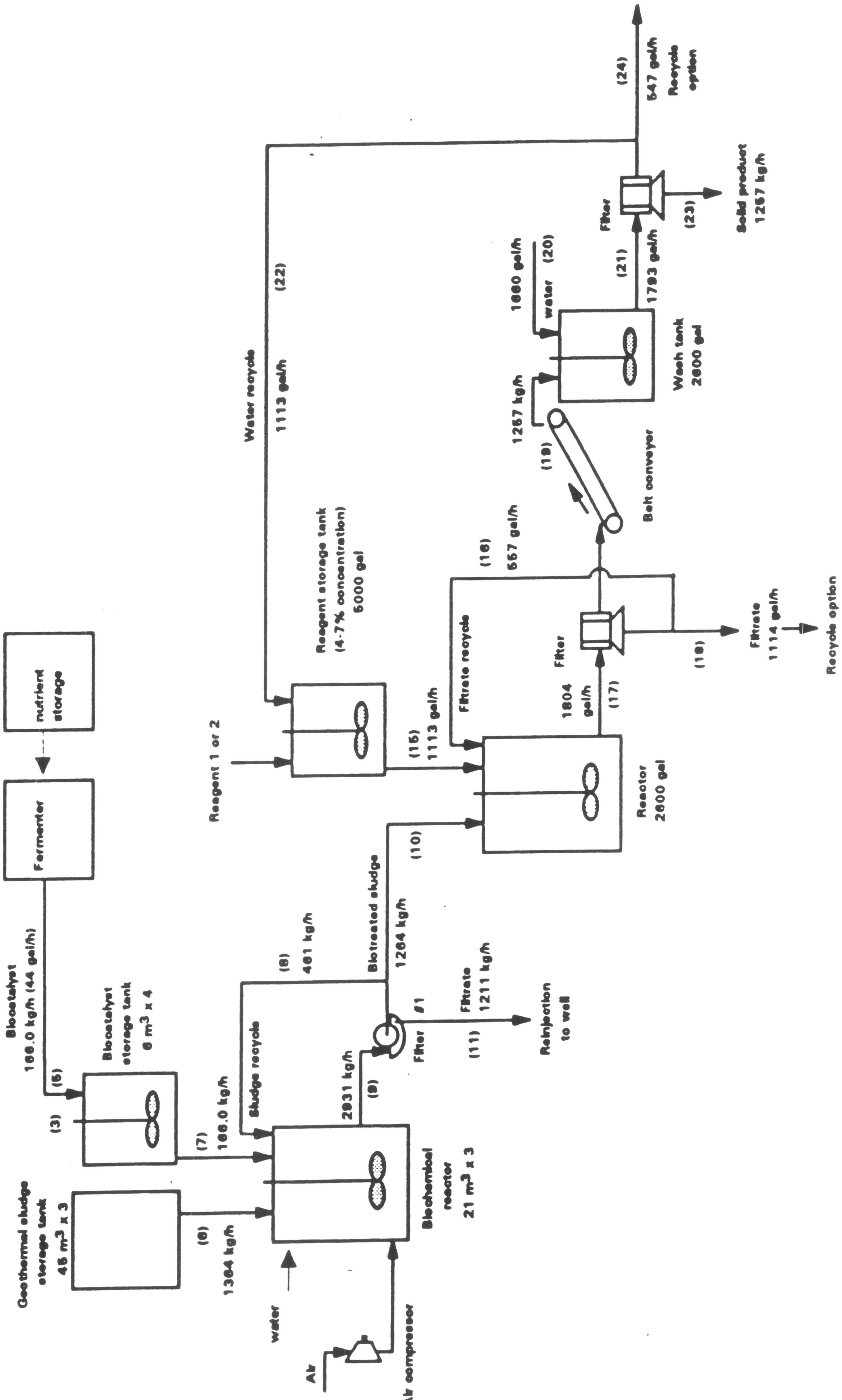

Figure 1. The production of pure fillers and/or additives from 3000 lb/h of geothermal sludge (BC1:BC2 = 85% : 15%, sludge:Reagent = g:5ml).

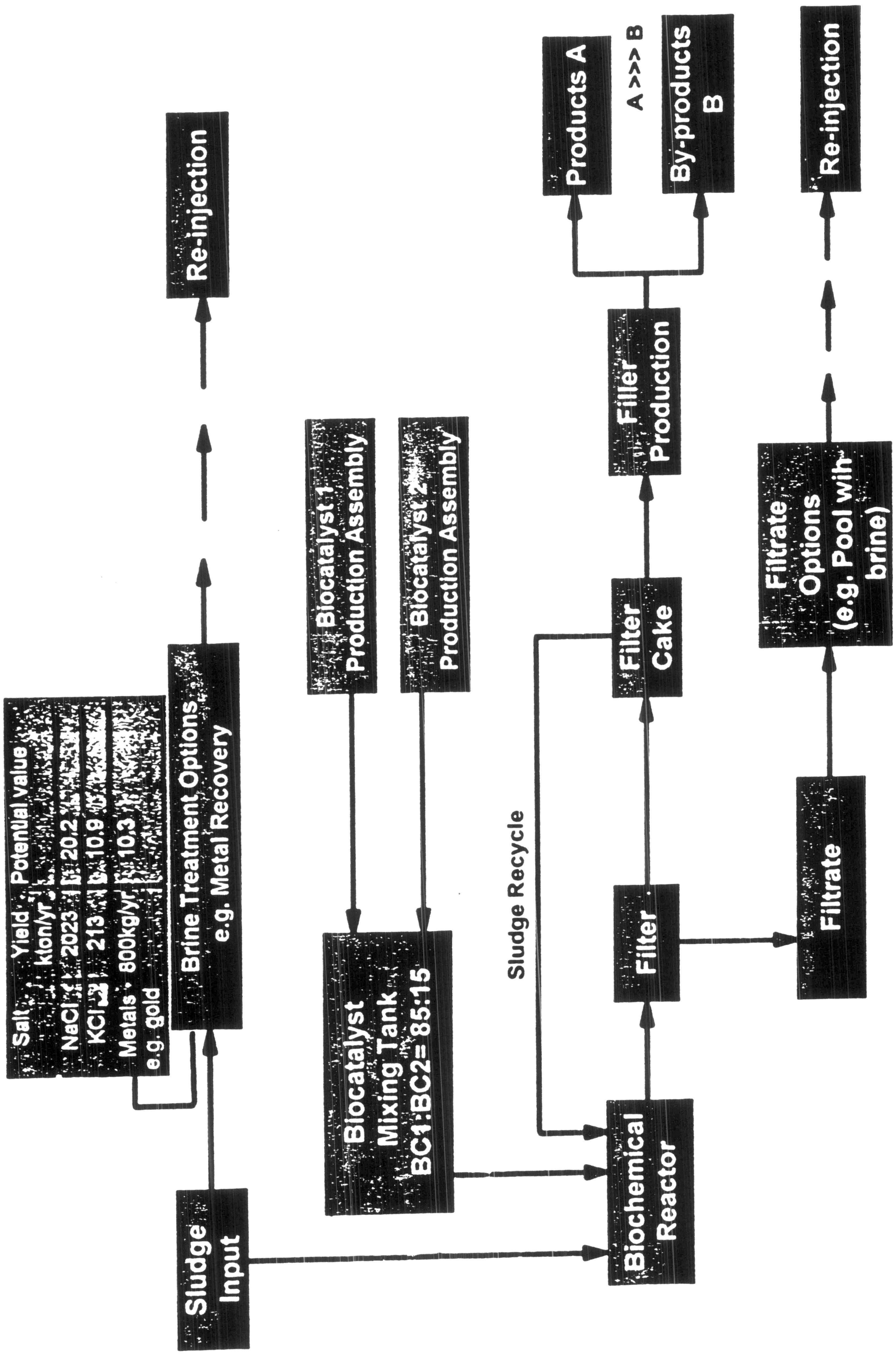

Figure 2. Total processing of geothermal sludges & brines.

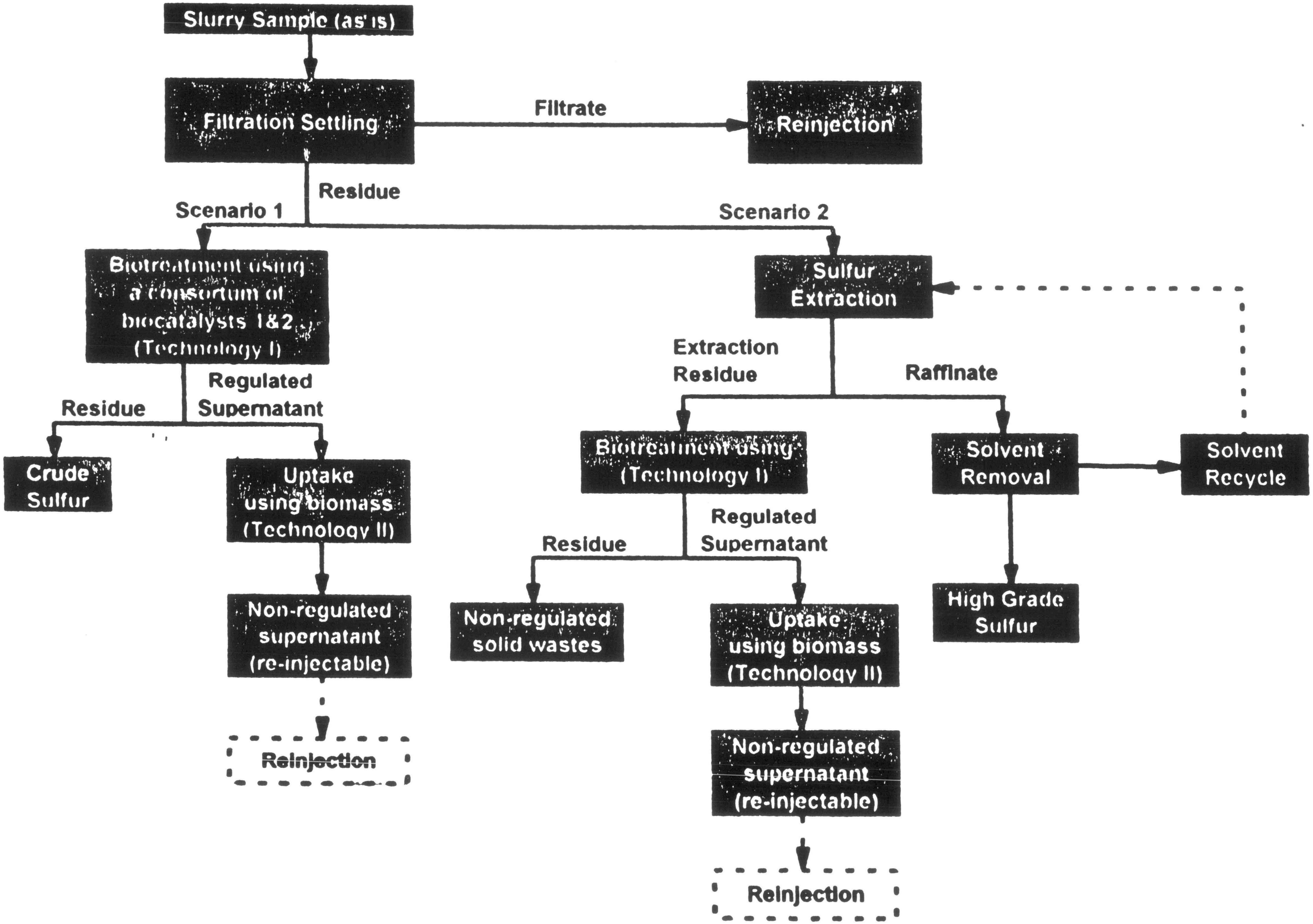

Figure 3. Proposed scheme for the treatment of geothermal waste slurry (CET/PG&E/BNL).

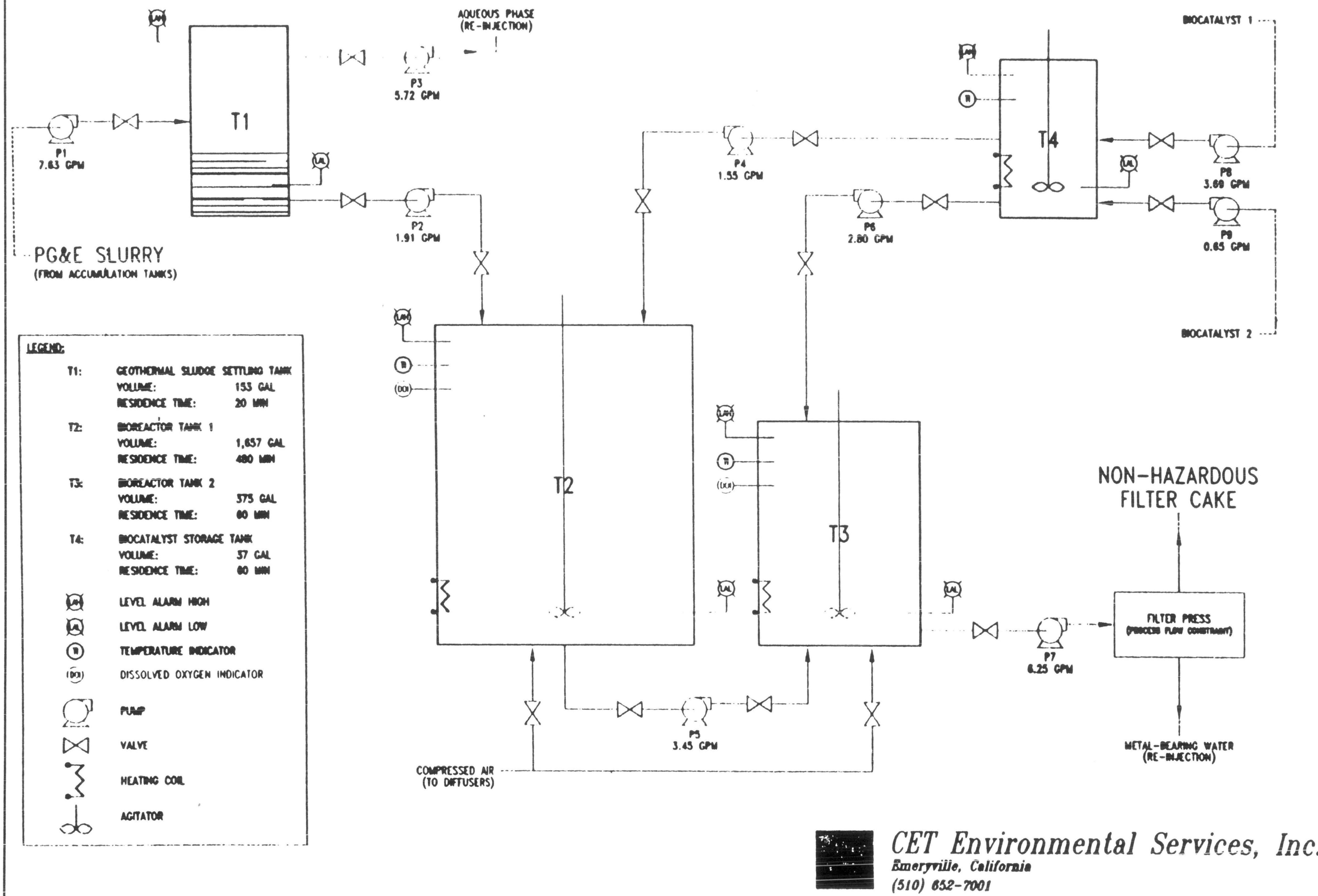

Figure 4. Basic process flow diagram. Bioremediation of geothermal sludges.