ANNUAL OPERATING PLAN

Advanced Biochemical Processes for Geothermal Brines

FY 1998

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Prepared by
Brookhaven National Laboratory
for the
U.S. Department of Energy
Office of Geothermal Technologies

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Advanced Biochemical Process for Geothermal Brines

FY 1998 Annual Operating Plan

Submitted by

Brookhaven National Laboratory
for
The U.S. Department of Energy

October, 1997

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Advanced Biochemical Processes for Geothermal Brines

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1. OVERVIEW

1.1 Objectives

The NES No Policies Change Case suggests that roughly 250,000-MW of new capacity will be needed between 1990 and 2010. Geothermal/hydrothermal resources are currently providing 3800-MW and can play a significant role in providing additional capacity. The No Policies Change Case projects hydrothermal capacity to grow to 10,000-MW by the year 2010 with continuation of the R&D program at the base level. 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.

As part of the overall Geothermal Energy Research which is aimed at the development of economical geothermal resources production systems, the aim of the Advanced Biochemical Processes for Geothermal Brines (ABPGB) effort is the development of economic and environmentally acceptable methods for disposal of geothermal wastes and conversion of by-products to useful forms. The interaction of the various aspects of ABPGB based technology is shown in Figure 1. This figure indicates that methods are being developed for dissolution, separation and immobilization of geothermal wastes suitable for disposal, usable in inert construction materials, suitable for reinjection into the reservoir formation, or used for recovery of valuable metals.

1.2 Background

The BNL/ESTD Geothermal Energy Project is part of the DOE Geothermal Energy Program conducted by the office of Geothermal Technologies, U.S. Department of Energy (DOE). The BNL/ESTD program addresses specifically the development and the needs of the "Advanced Biochemical Processes for Geothermal Brines" (ABPGB) project.

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. In other areas, such as the Geysers in Northern California, wastes

Annual DOE Program Review
 Headquarters Program Review
 Field Program Review (CET, Env.)
 Field Program Reviews (CALEN/C.E. Holt)
 Preparation of Peer Reviewed Papers
 Geothermal Resources Council Meeting

TBD, 03/98
 TBD, 1998
 Several TBD
 (video and field)
 05/98
 10/98

1. Gold, Platinum, Zinc, Manganese, etc.
2. High grade silica

Figure 1. Objectives of "Advanced Biochemical Processes for Geothermal Brines" Activity

containing only a few toxic metals are generated which, likewise, are subject to regulatory restraints.

It is known that certain microorganisms can interact specifically with metals via mechanisms such as surface adsorption, oxidization, reduction, solubilization and/or precipitation. These mechanisms have served as a basis for the development of a technology which allows the use of biochemical processes for solubilization of the geothermal wastes in which metals are transferred into the aqueous phase. The solubilized metals can be recovered and the remaining aqueous phase reinjected. The undissolved residue is then further processed to yield a high grade commercial silica.

Such biochemical technology 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 microorganisms 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, therefore, cross-contamination by undesirable species is ruled out by processing conditions, making this technology particularly environmentally acceptable. The stated objectives of the R&D program for the application of the new biochemical technology 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.
- The FY 1998 for APGB project is \$700K for operating expenses and \$130K for capital equipment for a total of \$830K. The applicable BNL Field Work Proposal for this work is Contractor No. AS-174-BPSD, B&R No. AM-10-01.

1.3 Strategy

(a) Selection of 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. Valuable metals, such as gold, platinum, silver and others can be recovered in commercially viable quantities.
- Gross residues from the biochemical processing can be further treated and converted to a high grade silica product.
- 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 CALEN/C.E. Holt for the development of field testing facilities is current.

- Cooperative research and development agreement is in place between CET Environmental Inc. and BNL. The aim of this effort is to jointly construct a field facility and test the BNL biochemical process in the Geysers area and elsewhere. The BNL/CET process is applicable in any of the industrial streams where the Stratford and/or a similar hydrogen sulfide abatement process is used.

1.4 Impacts

The new technology reduces significantly the cost and long term liability of surface disposal of sludges derived from geothermal brines. Concurrent processes for the concentration and recovery of valuable metals and salts and 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 depigmented silica product of a quality which has applications potential in other industries. The aqueous product from the primary process can be pooled with the bulk of the spent brine and 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 nonhazardous waste. The nonhazardous 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 represents 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 at the present scale of operations.

Further process cost savings are being 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 depigmented byproduct. The benefits that result are both environmentally and economically attractive. Not only that the detoxification process is less expensive, but the end products are useful. Current information also indicates that the emerging biochemical technology may find applications in other industries, particularly in the treatment of similar geochemical materials.

2.0 TASK DESCRIPTIONS

2.1 CALEN/C.E. Holt/BNL Program (Silica Production)

- A CALEN/C.E. Holt plant serves as a resource of geothermal brines and sludges. The company has made available a site for a pilot scale processing plant for the production of silica.
- A conceptional design for a 1300 kg/h sludge processing plant is shown in Figure 2. This process utilizes two biocatalysts, BC1 and BC2, in 85:15 ratios in the presence of different reagents (Reagent 1 and 2, Figure 2).
- The processes for the production of biocatalysts (BC1 and BC2) are summarized in block diagrams shown in Figures 3 and 4.
- In FY97, R&D efforts have shown that a single biocatalyst can be used in conjunction with proprietary chemical reagents (1 and 2; 1 or 2). A conceptual design for a silica production process is shown in Figure 5.

The significance of the use of a single biocatalyst and available "free" reagents will be discussed in Section 2.2.

2.2 Economics of Biochemical Waste Treatment Process

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. Initially, the primary process utilized 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 silica, and (5) use of existing facilities and "free products". Options 3, 4, and 5 generate revenues which offset the cost of initial investments. 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 may have economic and technical advantages.

Typical examples of economic analysis and appropriate calculation used by BNL R&D team are shown in Tables 1, 2, 3 and 4. In this example the costs have been calculated for a two biocatalyst (BC) process and a BC1:BC2 mix of 85%:15%. The corresponding analysis for the use

Fig. 2 The Production of Pure Fillers and/or Additives from 1300 kg/h of Geothermal Sludge
 (BC1 : BC2 = 85% : 15%, Sludge/Reagent = 1 kg:5L)

Figure 3 Process for the generation of 249 gal/h of Biocatalyst 1 (Full Scale)

**Figure 4 Process for the generation of 44 gal/h of Biocatalyst 2
(Full Scale)**

Figure 5. The production of silica from 1300 kg/hr of geothermal sludge using a single biocatalyst

**Table 1. Silica Production from Geothermal Brines (BC1 : BC2 = 85% : 15%):
(Equipment List and Type) (Full Scale : 1300 kg/h Sludge) (Sludge:Reagent = 1kg:5L):Biocatalyst Process**

Equipment Quantity I.D. No. (Tag No.) Name	Biocatalyst 1 Refer to Figs. 2&3			Biocatalyst 2 Refer to Figs. 2&4				
	Storage Tank 2	Storage Tank 2	Reactor 3	Storage Tank 2	Reactor 3	Storage Tank 3	Storage Tank 4	Reactor 3
	Nutrient Tank	Nutrient Tank	Fermentor 1	Nutrient Tank	Fermentor 2	Sludge Tank	Bacteria Tank	Bioreactor
Process Streams								
Stream number (IN)			1, 2		4		3, 5	6, 7, 8
Name			Nutrient feed		Nutrient feed		Biocatalyst feed	Mix feed
Stream number (OUT)	1	2	3	4	5	6	7	9
Name	Nutrient feed	Nutrient feed	Biocatalyst 1	Nutrient feed	Biocatalyst 2	Sludge feed	Biocatalyst feed	Mix reacted
Phase	Liquid	Liquid	Liquid	Liquid	Liquid	Solid	Liquid	Solid / liquid
Flow rate (total)								
Mass kg/h	188	753	941	166	166	1364	1107	2931
Volumetric m ³ /h	0.19	0.75	0.94	0.17	0.17	0.55	1.11	1.84
Residence Time, hr (per unit)	12	12	16	24	160	56	24	8
Residence Time, hr (total)	24	24	48	48	480	168	96	24
Equipment shape	Cylinder	Cylinder	Cylinder	Cylinder	Cylinder	Cylinder	Cylinder	Cylinder
Equipment size								
Length or height, L (m)	3	3	3	3	3	3	3	3
Width or Diameter, D (m)	1.2	2.3	3.0	1.6	4.0	4.3	4.0	3.0
Surface area, A, (m ²)								
Volume, V, (m ³)	3.2	12.9	21.5	5.7	37.9	44.1	37.9	21.0
Volume, V, (gal)	852	3409	5681	1504	10025	11661	10025	5545
Total volume, V, (gal)	1704	6817	17043	3008	30075	34983	40100	16636
Power consumption, P, (kW)	2.0	6.2	4.7	3.2	7.3		7.3	22.8
Total power consumed (kW)	4.1	12.4	14.0	6.4	22.0		29.3	68.5
Total power consumed (hp)	5.5	16.6	18.7	8.6	29.5		39.3	91.8
Temperature, (C)	In							
	Out							
Pressure, (barg)	In	1	1	1	1	1	1	1
	Out							
Orientation	Vertical	Vertical	Vertical	Vertical	Vertical	Vertical	Vertical	Vertical
Material of construction	Carbon Steel	Carbon Steel	Carbon Steel	Carbon Steel	Carbon Steel	Carbon Steel	Carbon Steel	Carbon Steel

**Table 2. Silica Production from Geothermal Brines (BC1 : BC2 = 85% : 15%):
(Equipment List and Type) (Full Scale : 1300 kg/h Sludge) (Sludge:Reagent = 1kg:5L):Sludge Process Refer to Fig. 2**

Equipment		Filter #1	Conveyor	Storage Tank	Storage Tank	Reactor	Filter #2	Conveyor
Quantity		1	1	1	1	1	1	1
I.D. No. (Tag No.)								
Name		Rotary Drum	Belt type	Sludge Tank	Reagent Tank	Bioreactor	Rotary Drum	Belt type
Process Streams								
Stream number	In	9	10		22	10, 15, 16	17	
Name		Mixed reacted	NS feed		Reagent feed	Mix feed	Mixed reacted	NS feed
Stream number	Out	10, 11	8	10	15	17	16, 18, 19	19
Name		NS, filtrate	NS feed	Sludge feed	Reagent feed	Mix reacted	NS, filtrate	NS feed
Phase		Solid / liquid	Solid	Solid	Liquid	Solid / liquid	Solid / liquid	Solid
Flow rate (total)								
Mass	kg/h	1725	461	1264	4214	7585	2107	1264
Volumetric	m ³ /h	0.69	0.18	0.51	4.21	6.83	2.11	0.51
Residence Time, hr (per unit)		0.25		3	3	1		
Residence Time, hr (total)				3	3	1		
Equipment shape				Cylinder	Cylinder	Cylinder		
Equipment size								
Length or height, L (m)				3	3	3		
Width or Diameter, D (m)		7.8		1.0	2.8	2.0	7.8	
Surface area, A, (m ²)		47.8					47.8	
Volume, V, (m ³)				2.17	18.1	9.75		
Volume, V, (gal)				573	4771	2577		
Total volume, V, (gal)				573	4771	2577		
Power consumption, P, (kW)					4.0	3.7		
Total power consumed (kW)					4.0	3.7		
Total power consumed (hp)					5.4	5.0		
Temperature, (C)	In							
	Out							
Pressure, (barg)	In			1	1	1		
	Out							
Orientation		Vertical	Horizontal	Vertical	Vertical	Vertical	Vertical	Horizontal
Material of construction		Carbon Steel	arbon Stee	Carbon Steel	Carbon Steel	Carbon Steel	Carbon Steel	Carbon Steel

Table 3. Silica Production from Geothermal Brines (BC1 : BC2 = 85% : 15%):

(Equipment List and Type) (Full Scale : 1300 kg/h Sludge) (Sludge:Reagent = 1kg:5L):Sludge Process Refer to Fig. 2

Equipment Type						
Equipment	Wash Tank	Filter #3	Pump	Air compressor	Air compressor	Air compressor
Quantity	1	1	3	1	1	1
I.D. No. (Tag No.)						
Name	Water Tank	Rotary Drum	Centrifugal			
Process Streams						
Stream number	19, 20	21				
Name	NS, Water	Mixed solution				
Stream number	21	22, 23, 24				
Name	NS, Water	Liquid, solid		Fermentor 1	Fermentor 2	Reactor
Phase	Solid / liquid	Solid / liquid	Liquid			
Flow rate (total)						
Mass	7585	4214				
Volumetric	6.83	4.21				
Residence Time, hr (per unit)	1	0.25				
Residence Time, hr (total)	1					
Equipment shape	Cylinder					
Equipment size						
Length or height, L (m)	3					
Width or Diameter, D (m)	2.0	3.4				
Surface area, A, (m ²)		9.2				
Volume, V, (m ³)	9.75			21.5	37.9	21.0
Volume, V, (gal)	2577			5681	10025	5545
Shaft power, Ws, (kW)			1.1	6.5	11.44	6.3
Power consumption, P, (kW)	12.4		1.1	6.5	11.4	6.3
Total power consumed (kW)	12.4		3.4	6.5	11.4	6.3
Total power consumed (hp)	16.6		4.5	8.7	15.3	8.5
Temperature, (C)						
Pressure, (barg)	In				1	1
	Out				4	4
Orientation	Vertical	Vertical	Vertical			
Material of construction	Carbon Steel	Carbon Steel	Stainless Steel			

**Table 4. Silca Production from Geothermal Brines (BC1 : BC2 = 85% : 15%)
(Cost Estimation - Ulrich)* (Sludge : 1300 kg/h) (Full scale/Continuous process)
(Sludge:Reagent = 1 kg:5 L) (CALEN)**

Fixed capital, Cfc	4044.2	Annual Capacity (ton/yr.)	10056
Working capital (10-20% of Cfc), Cwc	606.6		
Total investment, Ctc	4650.8		

Cost	k\$/yr.	k\$/ton
Manufacturing Expenses		
Direct		
Raw Materials (Nutrient & bacteria)	60	0.006
By-product credits		
Catalyst and solvents	3338	0.338
Operating labor	172	0.355
Supervisory and clerical labor (10-20% of operating labor)	26	0.358
Utilities		
Steam, barg, \$/kg		
Electricity, \$/kWh	318	0.389
Process water, \$/m ³	20	0.391
Demineralized water, \$/m ³		
Cooling water, \$/m ³		
Waste disposal, \$/kg		0.391
Maintenance and repairs (2-10% of fixed capital)	243	0.415
Operating supplies (10-20% of maintenance and repairs)	36	0.419
Laboratory charges (10-20% of operating labor)	26	0.422
Patents and royalties (0-6% of total expense)	127	0.434
Total, Adme	4366	4366 0.434
Indirect		
Overhead (payroll and plant),(50-70% of the sum of operating labor, supervision, and maintenance)	265	0.460
Local taxes (1-2% of fixed capital)	61	0.467
Insurance (0.4-1% of fixed capital)	28	0.469
Total, Aime	354	354
Total manufacturing expense (excluding depreciation), Ame		4720 0.469
Depreciation (approximately 10% of fixed capital), Abd		404 0.510
General Expenses		
Administrative cost (25% of overhead)	66	0.516
Distribution and selling costs (10% of total expense)	424	0.558
Research and development (5% of total expense)	212	0.579
Total, Age	702	702
Total expense, Ate		5826 0.579
Revenue from sales		11062
Net annual profit from sales, Anp		5236
Net profit from avoiding waste disposal		5455
Net profit from total process		10690
Income taxes (net annual profit times the tax rate), (35%) Ait		3742
Net annual profit after taxes (Anp - Ait), Annp		6949
After-tax rate of return, i = (Annp + Abd)/Ctc x 100 = %		158

*Best cost at time of calculation

of a single biocatalyst is given in Tables 5, 6, 7 and 8. This scenario also assumes that some of the chemical reagents are cost free.

FY97 experiments have shown that the yield of high quality silica is about one half of the quantity of the original sludge feedstock. The dissolved "impurities" present in the liquid phase are reinjected. Earlier cost analyses, shown in Table 9, assumed a 100% conversion of geothermal sludge to silica. The revised cost analysis, based on FY97 data is given in Table 10. The importance of the new process which requires carefully controlled conditions will be apparent from the following brief discussion. Biochemical treatment converts physically and chemically the starting material (i.e., geosludge) as shown in Figures 6 and 7. This material when treated with an acidic reagent (reagent 1 or 2, refer to Figure 5) applied at different concentration and temperatures, leads to the production of a silica product with varying degrees of pigmentation as shown in Table 7.

In the chemical composition of this product the major contribution to pigmentation is iron. The inductively-coupled-plasma-mass spectrometric analysis (ICP-MS) of untreated and treated geosludge, with two different catalysts is shown in Figure 8.

The actual pigmentation is due to different chemical species of the responsible metals. For example, iron under the processing conditions may appear in several forms as shown in Figure 9.

Under appropriate experimental conditions (patent pending) the extent and the rates of depigmentation, expressed in terms of iron, are fast and efficient as shown in Figures 10 and 11. The temperature differences may be due to differences in the chemical properties at the experimental temperatures used. The end product, after neutralization is a high quality silica, as shown by preliminary analysis given in Tables 12 and 13. Table 12 summarizes the results of analyses carried out by DZ Laboratories which are accredited by the National Institute of Standards and Technology. Two BNL produced samples and a commercial silica (Imsil 1160 Silica, Unimin Specialty Minerals, Inc.) were each incorporated into a vinyl-acrylic latex wall paint, substituting the silicas for one another at equal weight. All preparations were then evaluated using ASTM Test Methods.

Although the differences from commercial samples are minor, current R&D is exploring modification in the procedure in order to improve further the scrub resistance and reflectance.

Table 12 summarizes chemical and physical properties as measured by International Testing Laboratories. Since these analyses have been carried out an improvement in the BNL treatment has led to further depigmentation of the trace amounts reported in Table 11.

Table 5 Silica Production from Geothermal Brines
(Equipment List) (Full Scale : 1300 kg/h Sludge): Single Biocatalyst Process, Refer to Fig. 5

Equipment Type								
Equipment Quantity	Storage Tank 2	Storage tank 1	Reactor 3	Reactor 3	Tank 3	Reactor 6	Tank 2	Filter 1
Name	Sludge	Nutrient tank	Growth tank	Bioreactor	Acid Storage	Acid reactor	Neutralizer	Filter
Phase	Solid		Liquid	Solid / liquid		Solid / liquid	Solid / liquid	Solid / liquid
Flow rate (total)								
Mass kg/h	1364	2045	2045	3409	17727	17727	2727	1364
Volumetric m ³ /h	0.55	2.05	2.05	2.59	17.73	17.73	2.73	1.36
Residence Time, hr (per unit)	168	80	120	2	2	2	2	0.25
Residence Time, hr (total)	336	80	360	6	6	12	4	
Equipment shape	Cylinder		Cylinder	Cylinder		Cylinder	Cylinder	
Equipment size								
Length or height, L (m)	3	3	3	3	3	3	3	
Width or Diameter, D (m)	7.5	10.0	12.2	1.8	4.6	4.6	1.8	3.4
Surface area, A, (m ²)								9.2
Volume, V, (m ³)	131.4	233.8	350.6	7.4	50.65	50.65	7.79	
Volume, V, (gal)	34718	61761	92642	1956	13382	13382	2059	
Total volume, V, (gal)	69437	61761	277926	5867	40145	80290		
Power consumption, P, (kW)		43.4	43.4	9.9	46.2	46.2	10.3	
Total power consumed (kW)		43.4	130.3	29.8	138.6	277.2	20.7	
Total power consumed (hp)		58.2	174.7	39.9	185.8	371.6	27.7	

Table 6 Silica Production from Geothermal Brines
(Equipment List) (Full Scale : 1300 kg/h Sludge): Single Biocatalyst Process, Refer to Fig. 5

Equipment Type				
Equipment	Heat Exchanger	Pump	Clarifier	Dryer
	14	18	5	1
Name	Teflon Tube	Centrifugal		rotary
Phase				
Flow rate (total)				
Mass			17727	17727
Volumetric			18	
Area(m^2)	10			
Diameter (m)			9.5	
				985
				1.7
Volume, V, (m^3)				6.6
Volume, V, (gal)				
Shaft power, Ws, (kW)		1.1		
Power consumption, P, (kW)		1.1	0.5	22.4
Total power consumed (kW)		20.1	2.3	22.4
Total power consumed (hp)		27.0	3.0	30.1
				total power
				660.2

**Table 7. Silica Production from Geothermal Brine
(Sludge : 1300 kg/h): Equipment Cost**

Equipment Identification	S.F.	Quantity	Capacity	Unit	Cost Index Value = 362					
					Cost, Cp	Cost, Cp	Material	Base Bare Module Factor, Fbm	BBM Cost Cbm	Total
					CE index = 315 \$1,000	CE index = 362 \$1,000				
Mixers										
Nutrient tank	1	1	43.4	kW	20.9	24.0	Stainless steel	2.5	60.1	60.1
Growth reactor	1	3	43.4	kW	19.3	22.2	glass-lined	3.5	77.7	233.0
Acid storage	1	3	46.2	kW	20.1	23.1	glass-lined	3.5	81.0	242.9
Biochemical Reactor	1	3	29.8	kW	17.8	20.5	glass-lined	3.5	71.7	215.0
Reactor (Sludge/Reagent)	1	6	46.2	kW	21.5	24.7	glass-lined	3.5	86.3	517.9
Wash Tank	1	2	20.7	kW	15.3	17.5	glass-lined	3.5	61.4	122.8
Total mixers										1391.7
Separator										
Dryer	1	1	6.6	m^3	16.4	18.9	brick-lined	4	75.6	75.6
Clarifier	1	5	9.5	m	60.8	69.8		3	209.5	1047.3
Filters	1	1	50.0	m^2	80.0	91.9	Polypropylene	3	275.8	275.8
Total separator										1398.7
Vessels										
Nutrient tank	1	1	350.6	m^3	78.9	90.7	Rubber-lined	2.4	217.6	217.6
Growth reactor	1	3	350.6	m^3	78.9	90.7	Rubber-lined	2.4	217.6	652.9
Acid storage	1	3	50.6	m^3	21.4	24.6	Rubber-lined	2.4	59.1	177.2
Biochemical Reactor	1	3	7.4	m^3	5.9	6.7	Rubber-lined	2.4	16.2	48.5
Storage Tank (Sludge)	1	1	131.4	m^3	40.7	46.8	Rubber-lined	2.4	112.3	112.3
Acidification Reactor	1	6	50.6	m^3	21.4	24.6	Rubber-lined	2.4	59.1	354.4
Wash Tank	1	2	7.8	m^3	6.1	7.0	Rubber-lined	2.4	16.7	33.5
Total Vessels										1596.3
Heat exchanger	1	14	10.0	m^2	3.0	3.4	Teflon tube	4	13.8	193.1
Pump (Centrifugal)	1	18	1.1	kW	3.1	3.5	Stainless Steel	4.5	15.8	283.9
Total bare module										4863.7
Contingency and fee								0.18	4863.7	875.5
Total module cost										5739.2
Auxiliary facilities								0.3	5739.2	1721.8
Grass-roots capital										7460.9

Table 8. Silica Production from Geothermal Brines
(Sludge : 1300 kg/h) (Full scale-Continuous process)

Fixed capital, Cfc	7460.9	Tons/year	6077
Working capital (15% of Cfc), Cwc	1119.1	product	
Total investment, Ctc	8580.1		
<hr/>			
Cost		k\$/yr.	
<hr/>			
Manufacturing Expenses			
Direct			
Raw Materials (Nutrient & bacteria)			14
By-product credits			
Acid			2144
Base			19
Operating labor			175
Supervisory and clerical labor (15% of operating labor)			26
Utilities			
Steam			116
Electricity			560
Process water			20
Maintenance and repairs (4% of fixed capital)			448
Operating supplies (15% of maintenance and repairs)			67
Total, Adme			3589
<hr/>			
Indirect			
Overhead (payroll and plant), (60% of the sum of operating labor, supervision, and maintenance)			389
Local taxes (1.5% of fixed capital)			112
Insurance (0.7% of fixed capital)			52
Total, Aime			553
Total manufacturing expense (excluding depreciation), Ame			4143
Depreciation (approximately 10% of fixed capital), Abd			746
<hr/>			
General Expenses			
Administrative cost (25% of overhead)			97
Distribution and selling costs (10% of total expense)			499
Total, Age			596
Total expense, Ate			5485
Revenue from sales			6077
Net annual profit from sales, Anp			592
Net profit from avoiding waste disposal			5455
Net profit from total process			6047
Income taxes (net annual profit times the tax rate), (35%) Ait			2116
Net annual profit after taxes (Anp - Ait), Annp			3930
After-tax rate of return, $i = ([Annp + Abd]/Ctc) \times 100 =$			55

Table 9. Silica production from geothermal brines. Cost analysis of process changes

	Two biocatalysts no free reagent	One biocatalyst no free reagent	One biocatalyst and use free available chemical agents
Capital Investment thousands of dollars	4080	3606	3606
Total Expenses thousands of dollars per year	6751	6652	2980
Revenue from filler sales and savings from avoiding waste disposal thousands of dollars per year	16517	16517	16517
After tax net profit thousand of dollars per year	6347	6412	8799
After-tax rate of return on investment %	164	186	253

Table 9b. Silica production from geothermal brines. Corrected cost analysis

	Original Case Two biocatalysts no free reagent	Second Case One biocatalyst no free reagent	Third Case One biocatalyst and use free reagent
Capital Investment thousands of dollars	7752	7460	7460
Total Expenses thousands of dollars per year	6358	6271	5485
Revenue from filler sales and savings from avoiding waste disposal thousands of dollars per year	11531	11531	11531
After tax net thousand of dollars per year	3362	3419	3930
After-tax rate of return on investment %	46	49	55

Table 10. SUMMARY TABLEInterior Vinyl Acrylic Flat White Wall Paint

	<u>Imsil 1160</u>	<u>BNL Sample 1</u>	<u>BNL Sample 2</u>
Ease of Dispersion	5	5	5
Fineness of Grind	5	3	5
Viscosity Stability	5	5	5
pH Stability	5	5	5
Package Stability	5	5	5
Freeze-Thaw	5	5	5
Reflectance	5	3	5
Contrast Ratio	3	5	5
Pencil Hardness	5	5	5
Sheen - 85°	5	5	5
Burnishing	5	5	5
Scrubbability	7	5	3
Application Properties	5	5	5
TOTAL RATING	65	61	63

CONCLUSIONS

The following conclusions may be drawn from the results of this evaluation:

1. The differences in performance noted between the two Brookhaven National Laboratory products and the commercial silica product were few. The products were essentially equivalent for performance for all properties tested with the exception of the following.

Imsil 1160	-	Lower contrast ratio Superior Scrub Resistance
Pigment I	-	Poorer dispersion (grind) Lower reflectance
Pigment II	-	Poorer scrub resistance

Figure 6. Untreated Sludge

Figure 7. Biotreated Sludge

Fig. 8 Reagent 1 Treatment of Biotreated Sludge (L1)

Figure 9. Species of Iron Pigments

- $\text{FeO}(\text{OH})$ hydrous ferric oxide is brown
- Fe_3O_4 is a mixture of $\text{Fe}(\text{II})$ - $\text{Fe}(\text{III})$ oxide and is black
- $\alpha\text{-Fe}_2\text{O}_3$ is red brown
- $\text{Fe}(\text{III})$ chloride $\cdot 6\text{H}_2\text{O}$ is yellow
- $\text{Fe}(\text{II})$ chloride $\cdot 8\text{H}_2\text{O}$ is colorless
- $\text{Fe}(\text{II})$ chloride $\cdot 6\text{H}_2\text{O}$ and $\text{Fe}(\text{II})$ Chloride $\cdot 4\text{H}_2\text{O}$ are pale green
- Iron(II) and Iron(III) sulfides are black

Fig. 10 Silica Production: ICP-MS Analysis of Fe Concentration of Biotreated Sludge as function of R1 Treatment cycles

Figure 11. Reaction Rate vs. Temperature
Iron removal

Table 11. Results summary

Treatment	start weight	corrected for moisture	weight after treatment	% weight loss	comments
37%	10.05 g	8.54	6.67 g	22	yellow
18.5%	10.08 g	8.57	4.96 g	42	yellow
9.3%	10.10 g	8.59	4.24 g	51	brown yellow
4.7%	10.00 g	8.50	4.74 g	44	cream-yellow
2.35%	10.04 g	8.53	4.57 g	46	off white
1/2%	9.98 g	8.48	4.56 g	46	tan-white
0.6%	10.05 g	8.54	4.35 g	49	brown white

Table 12. Summary Table
Interior Vinyl Acrylic Flat White Wall Paint

	Imsil 1160	BNL Sample 1	BNL Sample 2
Ease of Dispersion	5	5	5
Fineness of Grind	5	3	5
Viscosity Stability	5	5	5
pH Stability	5	5	5
Package Stability	5	5	5
Freeze-Thaw	5	5	5
Reflectance	5	3	5
Contrast Ratio	3	5	5
Pencil Hardness	5	5	5
Sheen - 85°	5	5	5
Burnishing	5	5	5
Scrubbability	7	5	3
Application Properties	5	5	5
TOTAL RATING	65	61	63

Table 13. Report of Test

Parameter	Sample No. 1	Sample No. 2
1. Moisture and other Volatile matter (ASTM-D-208)	2.66%	5.35%
2. Loss on ignition (ASTM-D-719)	3.56%	3.45%
3. Matter soluble in HCl (ASTM-D-719)	2.95%	3.04%
4. Silica (ASTM-C-575)	58.11%	69.61 by digestion in HF and HNO ₃
5. Matter soluble in water (ASTM-D-1208)	0.392%	0.287%
6. Volume of settling in petroleum spirits (ASTM-D-719)	7.2 ml	11.0 ml
7. Acidity (ASTM-C-169)	13.7 mg NaOH/gram	13.54 mg NaOH/gram
8. Course particles (ASTM-D-185)	3.53%	0.65% >45µm
9. Color*	L = 86.9	L = 95.6
Hunter D25M	A = -3.1	A = -5.9
Colorimeter	B = +17.2	B = +16.2

* L = Whiteness : The higher the number the whiter from 0-100 scale

A = Red/Green : A minus number is on the green side 0-100
 higher the number the greener

B = Yellow/Blue : A positive number indicates yellow and 0-100
 the higher the number the more yellow

CONCLUSIONS

The following conclusions may be drawn from the results of this evaluation:

1. The differences in performance noted between the two Brookhaven National Laboratory products and the commercial silica product were few. The products were essentially equivalent for performance for all properties tested with the exception of the following:

Imsil 1160	-	Lower contrast ratio Superior Scrub Resistance
Pigment I	-	Poorer dispersion (grind) Lower reflectance
Piment II	-	Poorer scrub resistance

2.3 Metal Recovery

Cost-efficient options for metal recovery continue to be actively explored. Experimental data remain consistent and support the view that the aqueous phase produced by the ABPGB process should be pooled with the post heat exchanger brines, processed for metal recovery, and then re-injected.

Several different biosorbents are being tested. Selectivity of biosorbents is shown in Figure 12 and Table 14. Selectivity of the biosorbents used is further demonstrated by adsorption of platinum and gold at pH 1 and 100°C, as shown in Table 15. While the recovery of valuable trace metals from dilute solutions using biosorbents is very promising, further evaluation studies are needed. At the present time the quality of biosorbents varies from preparation to preparation. Further, the cost of production is still unattractive to make the process cost-efficient. However, based on the results generated thus far and discussions with biosorbent producers, both disadvantages may be resolved.

P.I.'s discussions in Italy led to the analysis of Cesano samples. The ICP-MS analysis shown in Table 16, indicates that some valuable trace metals (e.g., Rb, Ti, V, Mn, Ag?, Au?) may be worth recovering, others, such as arsenic and selenium would have to be removed.

All of the processing options discussed in this sections 2.1-2.3 are summarized in Figure 13.

2.4 CET Environmental, Inc./BNL Process for Sulfur Recovery

The originally developed process for PG&E type residues involved two biocatalysts. Improvements in the original process led to further cost-efficient modifications. The new process uses a single biocatalyst and a sublimation step. This process is applicable to any sludge produced by the Stretford or a similar hydrogen abatement processes and is summarized in Figure 14. The

Figure 12 Selective biosorption of metals dissolved in the aqueous phase

Table 14 Metal concentration in the liquid phase, ppb.

Initial concentration				concentration after treatment with biosorbent				
Element	Std 1	Std 2	Ave. Std	P0102	P0102	Ave P010	P0201	Ave P020
Li 7	20.86	16.49	18.675	11.02	10.575	10.13	11.88	11.005
Be 9	21.79	18.12	19.955	4.991	4.922	4.991	4.853	4.922
B 11	567.4	753.6	660.5	641.7	673.75			
Mg 24	57.61	39.13	48.37	1360	1014.75			
Al 27	37.13	30.05	33.68	12.6	10.4385	12.6	8.273	10.4365
Sc 45	30.66	24.33	27.495	11.96	11.785	11.61	19.21	15.41
Ti 45	25.29	16.96	21.125	10.94	10.1895	11.99	14.05	13.02
V 51	27.99	22.41	25.2	13.73	14.375	18.14	18.34	18.24
Cr 52	29.3	22.33	25.815	12.63	12.675	18.62	18.87	18.745
Co 59	26.2	21.44	23.82	5.73	5.73	18.48	19	18.74
Ni 60	26.8	22.38	24.59	9.04	8.855	19.87	20.1	19.985
Cu 65	24.45	19.77	22.11	16.19	16.135			
Zn 66	19.58	16.7	18.14	10.85	10.865			
Ga 69	28.88	25.5	27.19	8.882	8.9595			
Ge 73	23.15	21.38	22.265	8.284	8.7755			

Table 15 Analysis of Brine Liquid for Platinum and Gold Using Different Biosorbents at pH1 and ~100°C

Sample	Standard Pt (ppm)	Standard Au (ppm)
Before Biosorption	5.04	0.335
Biosorbent P010	2.42	
Biosorbent P020		0.195
Biosorbent P030	4.79	0.063
Biosorbent P040	1.36	
Biosorbent P051	1.9	

Table 16. Cesano 1 Brine (in ppm)

Li	10.78	Sb	5.12
Be	4.4	Te	0.45
B	71.11	Cs	3.28
Mg	1.85	Ba	19.50
Al	18.6	La	0.32
Sc	1.49	Ce	0.64
Ti	102	Pr	0.05
V	185	Nd	0.18
Cr	14.8	Sm	0.02
Mn	0.46	Eu	0.01
Fe	4.5	Gd	0.02
Co	0.14	Tb	0.03
Ni	0.14	Dy	0.04
Cu	2.90	Ho	0.004
Zn	3.15	Er	0.01
Ga	0.31	Tm	0.003
Ge	0.84	Yb	0.01
As	46	Lu	0.003
Se	30.30	Hf	0.02
Rb	448	Ta	2.9
Sr	54.0	W	0.85
Y	0.03	Re	0.01
Zr	0.86	Ir	0.04
Nb	0.56	Pt	0.01
Mo	1.45	Au	0.14
Ru	0.04	Hg	0.85
Rh	0.01	Tl	15.5
Pd	0.2	Pb	0.21
Ag	0.12	Bi	0.06
Cd	0.06	Th	0.02
Sn	0.12	U	0.1

Fig. 13 Total Processing of Geothermal Sludges & Brines

Figure 14 Summary of the Sulfur Recovery Process

sublimation process (Figure 15) is an add on to the existing process based on the treatment of PG&E sludges. In the current experiments two sizes of sublimation apparatus have been used. One, a smaller, Barry #1 and the other larger, Barry #2. Averaged data generated in multiple experiments at different pressures, temperatures and time intervals are shown in Figures 16-20 and Tables 17-19. The results from these studies show that, in order to produce high quality agricultural sulfur, carefully controlled process condition must be maintained. This is because of the chemical and physical forms of sulfur and the arsenic and mercury sulfur compounds trapped in the original filter cake. Further optimization studies are current. At the present, it appears that the optimum processing conditions are low pressures, e.g., 5-10 mTorr and temperature of 160° and lower. It is interesting to note the composition of residue B (Table 18). Although the residue is a small fraction (<10%) of the original total, it contains substantial quantities of platinum (950 ppm) and gold (730 ppm). Since very few samples from the same locality and none from different localities have been analyzed, the statistical significance of the precious metal concentrations has yet to be verified. However, if such concentrations are consistent and occur in multiple sources, then recovery of gold and platinum may become an attractive option, and further offset operational costs. Preliminary cost-analyses of the sulfur recovery process are given in Tables 20-22.

2.5 Status

- Studies dealing with scaled-up theoretical projections of full silica producing processes are coming to a completion. The proposed processes would treat 3000 pounds (~1300 Kg) per hour of the geothermal sludge.
- Scaled-up projections are being analyzed by CALEN engineers. In FY97 Mary McCloud has been the coordinator and John Mortz the engineer responsible for interactions with BNL staff. Engineering staff at CALEN are currently generating an updated processing analysis. This analysis of the biochemical technology is based on experimental results being continuously generated at BNL lab. Silica production combined with metal recovery technology is now the major R&D thrust of this joint effort.
- CALEN is proceeding with the design and construction of progressively scaled-up (to 3000 lb/h) plants for the processing of geothermal brines and sludges. BNL's team will assist by constructing a small (~3 lb/h) laboratory plant. The system will include production of biocatalyst, multistep geosludge processing units and interfacing, leading to the commercial production of silica.
- The efforts to simplify ABPGB processes for high and low salinity brines have been intensified. Particular attention is being given to the use of a single biocatalyst, recycling and the maximum utilization of available materials (e.g., chemicals) and facilities.

Fig. 15A Block Diagram for a Sublimation Process

Figure 16 Sulfur Sublimation

Figure 17 Sulfur Sublimation

Figure 18 Sulfur Sublimation

Figure 19 Sulfur Sublimation

Figure 20 Sulfur Sublimation

Table 17 Sublimation Tests

PG&E Filter Cake at different temperatures and pressures,

Tests	Temp (Deg C)	Pressure (milli torr)	Feed (g)	Product S (g)	Residue (g)	Mass balance ***(%)
1*	180	20	3	2.1	0.33	87
2*	180	20	5	4.1	0.6	94
3**	160	60	54.55	46.27	7.84	99.3
4**	145	200	50	43.68	6.39	100.1
5**	150	75	51.07	44.23	5.88	98.12
6**	150	60	49.1	43	6.1	100
7**	164	45	49	42.8	5.91	99.2
8**	163	55	49.2	42.4	6.39	99.4

* 10 g vessel, ** 500g vessel, ***mass balance=(Product S+Residue)/Feed

Table 18 Analysis of Sulfur "tail" trace Residue B

Obtained at the end of sublimation 150 milli torr and 200 deg C

Elements	contents in ppm
Al	12660
Ti	2666
Fe	1216
Zn	1517
Ge	3483
As	717
Se	6850
Mo	1121
Cd	1900
Te	12550
Sm	1530
Pt	950
Au	730
Hg	2611

Table 19 Mass Balance* for Mercury and Arsenic

Sulfur Sublimation Process in 500 g. vessel

Test	Hg in Feed (mg)*	As in Feed (mg)*	Conc. Of Hg in S (ppm)	Hg in S (mg)	Conc of Hg in Resid (ppm)	Hg in Resid (mg)	Mass balance of Hg (%)	Conc. Of As in S (ppm)	As in S (mg)	Conc of As in Resid (ppm)	As in Resid (mg)	Mass balance of As (%)
3	6.82	90.55	31.4	1.45	648	5.08	96%	56.1	2.60	11547	90.5	103%
4	6.25	83	48.5	2.12	599	3.83	95%	50.9	2.22	14321	91.5	113%
5	6.38	84.78	71.3	3.15	695	4.09	113%	64.7	2.86	16400	96.4	117%
6	6.14	81.51	38.4	1.65	678	4.14	94%	31.9	1.37	16485	100.6	125%
7	6.13	81.34	36.9	1.58	598	3.53	83%	22.0	0.94	12345	73.0	91%
8	6.15	81.67	38.4	1.63	727	4.65	102%	22.8	0.97	12112	77.4	96%

Feed: Untreated PG&E contains 125 ppm Hg and 1660 ppm As

Mass balance (as % recovery)=(Hg or As in S+Hg or As in Resid)/Hg or As in Feed

*Note the conc. given in mg is the amount present in actual (50g) feed of the starting material

**Table 20 Production of sulfur from geothermal sludges
(Equipment List and Type) Full Scale : 38 kg/h Sludge**

Equipment Quantity		Storage Tank 2	Storage tank 1	Reactor 2	Reactor 2	Filter 1	Pump 7	Sublimers 1
Name		Sludge	Nutrient tank	Growth tank	Bioreactor	Filter	Centrifugal	Turbo
Phase		Solid		Liquid	Solid / liquid	Solid / liquid		
Flow rate (total)								
Mass	kg/h	38	57	57	94	38		38
Volumetric	m ³ /h	0.02	0.06	0.06	0.07	0.04		
Residence Time, hr (per unit)		24	7	7	7	0.25		
Residence Time, hr (total)		48	7	14	14			
Equipment shape		Cylinder		Cylinder	Cylinder			
Equipment size								
Length or height, L (m)		3	3	3	3			0.2
Width or Diameter, D (m)		0.7	0.5	0.5	0.6	0.4		0.2
Surface area, A, (m ²)						0.1		0.1
Volume, V, (m ³)		1.0	0.6	0.6	0.7			0.1
Volume, V, (gal)		269	150	150	189			
Total volume, V, (gal)		538	150	299	379		1.1	
Power consumption, P, (kW)			0.3	0.3	1.5		1.1	1.0
Total power consumed (kW)			0.3	0.5	3.1		7.8	1.0
Total power consumed (hp)			0.3	0.7	4.1		10.5	1.4

Table 21 Production of sulfur from geothermal sludges
Full Scale : 38 kg/h Sludge

Equipment Identification	S.F.	Quantity	Capacity	Unit	Cost Index Value = 362		Material	Base Bare Module Factor, Fbm	BBM Cost Cbm \$1,000	Total \$1,000
					Cost, Cp CE index = 315 \$1,000	Cost, Cp CE index = 362 \$1,000				
Mixers										
Nutrient tank	1	1	0.3	KW	2.4	2.7	Stainless steel	2.5	6.8	6.8
Growth reactor	1	2	0.3	KW	0.6	0.7	Stainless steel	2.5	1.7	3.5
Biochemical Reactor	1	2	3.1	KW	6.8	7.8	Stainless steel	2.5	19.6	39.1
Total mixers										49.4
Separator										
Sublimar	1	1	0.1	m^3	150.0	172.4	carbon steel	1.5	258.6	258.6
Filters	1	1	0.1	m^2	10.0	11.5	Polypropylene	3	34.5	34.5
Total separator										293.0
Vessels										
Nutrient tank	1	1	0.6	m^3	1.0	1.2	carbon steel	1.9	2.3	2.3
Growth reactor	1	2	0.6	m^3	1.0	1.2	Rubber-lined	1.9	2.3	4.5
Biochemical Reactor	1	2	0.7	m^3	1.2	1.4	Rubber-lined	1.9	2.7	5.3
Storage Tank (Sludge)	1	1	1.0	m^3	1.5	1.8	Rubber-lined	1.9	3.4	3.4
Total Vessels										15.4
Pump (Centrifugal)	1	7	1.1	KW	3.1	3.5	Stainless Steel	4.5	15.8	110.4
Total bare module										468.3
Contingency and fee								0.18	468.3	84.3
Total module cost										552.6
Auxiliary facilities								0.3	552.6	165.8
Grass-roots capital										718.4

Table 22 Production of sulfur from geothermal sludges
(Sludge : 38 lb/h) Full scale/Continuous process

Fixed capital, Cfc	718.4	Tons/year	328
Working capital (15% of Cfc), Cwc	107.8	product	
Total investment, Ctc	826.2		
Cost		k\$/yr.	
Manufacturing Expenses			
Direct			
Raw Materials (Nutrient & bacteria)			2
By-product credits			
Operating labor			45
Supervisory and clerical labor (15% of operating labor)			7
Utilities			
Steam			24
Electricity			10
Process water			5
Maintenance and repairs (4% of fixed capital)			43
Operating supplies (15% of maintenance and repairs)			6
Total, Adme			143
Indirect			
Overhead (payroll and plant), (60% of the sum of operating labor, supervision, and maintenance)			57
Local taxes (1.5% of fixed capital)			11
Insurance (0.7% of fixed capital)			5
Total, Aime			73
Total manufacturing expense (excluding depreciation), Ame			215
Depreciation (approximately 10% of fixed capital), Abd			72
General Expenses			
Administrative cost (25% of overhead)			14
Distribution and selling costs (10% of total expense)			30
Total, Age			44
Total expense, Ate			331
Revenue from sales			190
Net annual profit from sales, Anp			-141
Net profit from avoiding waste disposal			164
Net profit from total process			23
Income taxes (net annual profit times the tax rate), (35%) Ait			8
Net annual profit after taxes (Anp - Ait), Annp			15
After-tax rate of return, $i = ([Annp + Abd]/Ctc) \times 100 =$			11

- The BNL pilot plant for silica production is now fully operative, producing 0.8-1.0 Kg per run of high quality amorphous silica. The process at present is semicontinuous. We are working on a design for a continuous process which should be analogous to the larger scale process being developed by CALEN.
- The efficiency of the treatment is currently inventoried by analysis of iron and iron species contents believed to be the major contributors to pigmentation. Recent results indicate that a three cycle process removes most of the metal species of concern.
- Senior technical and management from the CALEN/C.E. Holt team has been formulated during april (1997) and consists of the following people:

Dave P. Maystrick, CALEN, Project Manager, Omaha office;
 Andrew E. Scherer, CALEN, Project Development Manager, Omaha office;
 Mary E. McCloud, C.E. Holt Company, Senior Development Chemist, Pasadena office;
 John R. Mortz, C.E. Holt Company, Principal Process Consultant, Pasadena office;
 Bob Emmett, Emmett Process Consulting, Salt Lake City

- The group visited BNL on May 20th and 21st (1997). The BNL team and the CALEN group had a series of meetings in which the CALEN group learned a great deal about the ABPGB process. The group had also a chance to observe the whole process in the laboratory. Specific topics which have been covered included:
 1. Mass balance and recovery of silica efficiency
 2. Bioreactors: batch vs. continuous flow; loading; residence time; temperature; pressure; and conditions.
 3. Production of biocatalyst
 4. Barium sulfate inhibitor
 5. Shipment of additional geothermal sludge. There are some "new" requirements. Basically both groups use the same protocols.
 6. Silica specification and results produced in laboratory
 7. Outside commercial analysis of the "Produced Silica"
 8. Visit to the BNL silica facility and discussion of experimental work
 9. Laboratory review
 10. Discussion of business technology transfer terms
 11. Summary and discussion of future activities by CALEN and BNL
- At CALEN request we have sent a liquid sample of our biocatalyst to Calipatria. This has been done under our Confidentiality Agreement, however, against our advice. Biocatalyst handling and subsequent application and processing is a specialized and carefully controlled process which requires unique expertise. Testing and processing of the liquid sample without the appropriate expertise failed.

- Currently BNL is discussing collaborative arrangements with CALEN. The plan is to formalize an agreement in which BNL will assist and advise in the conduct of a field experiments.
- Subject to the success of the first field experiments, BNL will continue working with CALEN and assist in the development of the new technology.
- The amorphous silica production plant requires a continuous supply of the biocatalyst. Logistics for a steady production of the biocatalyst will have to be worked out. In a continuous process in which geothermal sludge is converted to amorphous silica, the total processing time (biochemical/chemical) is fast (hours), while the production of biocatalyst is slow (2-3 weeks). Therefore, a separate plant and holding facilities for the production of biocatalyst are essential. The output from these plans must be timed in such a manner that it satisfies the hourly demand of the amorphous silica production facility. For example, the 2 lb/h plant being considered as the first test requires the following: A 40% loading of sludge to liquid needs 0.6 gallons (2.3 liters) of biocatalyst at a concentration of 1×10^7 /ml. This volume of biocatalyst would be required for each hour of continuous production. Thus, a 24 hours operation needs 54.2 liters of biocatalyst preparation at the same concentration.
- Italy/Sardinia trip.
- ENEL expressed interest in using the BNL/CET, Inc. process at 30 different sites, each being a 20 MW power plant.
- At Cessano, there also exists a metal recovery option. We have completed analyses of their samples.
- ENEL is also interested in our oil upgrading technology.
- ENEL would like to initiate/or lay groundwork for formal discussions which should lead to the development of an international project.
- Sardinia's aluminum processing plant produces large quantities (thousands of tons per many acres) of "red mud". At BNL, we have tested a combination of our geothermal bioprocess and a chemical process which would convert the "red mud" into an agriculturally useful product. The Sardinia plant is now being taken over by Alcan, which is a good setting for the transfer of American technology.
- CET International engineers together with the BNL group have designed first pilot plant. This plant design is ready for field testing.
- Production of agricultural grade of sulfur by CET-BNL technology is currently a major thrust of the R&D effort.

- Discussions between CET/PG&E and BNL were at the best slow. Although PG&E insisted over a period of many months (year) that they are interested in the new technology, recently because of their reorganization, they appear to be hesitant.
- CET International and UNOCAL have initiated a dialogue. CET-BNL technology can be applied at the Geysers and other plants (globally) which utilize Stratford or a similar process for the abatement of hydrogen sulfide.
- CET Environmental is initiating a dialogue with ENEL to explore further the possibilities of applications of the CET-BNL technology at ENEL sites in Italy. To accomplish this more efficiently, CET is considering to engage an engineer in Italy as their representative.
- Frequent exchange of information between the industrial and BNL teams occurs through telephone and video conferences as well as written information.
- BNL has won the National Award for Environmental Sustainability for its "Advanced Biochemical Process for Geothermal Brines" in 1997. BNL has been granted a "Certificate of Environmental Achievement" and the ABPGB program is recognized in the Renew America 1997 Environmental Success Index.
- Recovery of Metals program: Current
- Comparative economic studies for the use of multiple and single biocatalyst completed. A single biocatalyst and the use of a co-produced reagent has been recommended. The economic studies encompass silica production and the recovery of valuable metals.
- Refinement of the sulfur recovery technology currently addresses the variations in temperature and pressure range. The cost-efficiency and economic analysis strategies are being defined.
- Collaboration with educational institutions: Joint graduate student programs with Howard University and Polytechnic University active. Hayden Garriques of Howard University is completing his M.S. thesis in Chemical Engineering. He has made important contributions in the development of the sulfur recovery technology.

2.6 Summary

- Pilot plant operating at 10 l volume levels has been constructed and is used for operation studies.
- Development of a continuous process for the production of silica is a major thrust of the R&D effort of BNL/CALEN.

- 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.
- Secondary processes for the removal of radionuclides when and if necessary have been identified and are currently optimized.
- Corrosion resistant materials are being studied and their potential in bioprocessing is being evaluated.
- Analysis of metal and salts recovery processes indicate that an 80% to 90% recovery of valuable metals is possible from the original brines or small concentrates. A complementary potassium and sodium chloride option is also very promising. Final aqueous phase may be reinjected.
- Sulfur recovery (BNL/CET) applications pilot plant designed.
- Conceptual processes for the production of silica have been designed. Continuing expansion of confidentiality and business agreements and joint R&D efforts by BNL/CALEN, in progress.
- Details of research, engineering designs, development, and cost-efficiency analyses are given in the reference section of this report.

2.7 Spin-Offs/Meetings/Reviews/Reports/References

Spin-offs from "Advanced Biochemical Processes for Geothermal Brines" have led to other collaborative ventures.

EER, Inc., CA

CRADA - completed in FY1997

ENSOL, Inc., NY*

CRADA - completed. In FY1997 new company formed

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

References

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- Premuzic, E.T., Lin, M.S., Bohenek, M., Bajsarowicz, V., and McCloud, M. Advanced biochemical process for geothermal brines—current developments. Geothermal Resources Council Transactions, Volume 20. 1997.

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Premuzic, E.T., Lin, M.S., Bohenek, M., Bajsarowicz, V., and McCloud, M. Advanced biochemical process for geothermal brines--current developments. Geothermal resources council transactions, Volume 20. 1997, in press.

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, pending.

2.8 Key Issues and Strategy

Engineering disposal technology of by-products and waste is needed to meet the objectives for the production of safe and economically attractive power from geothermal operations. The data being generated in this program provide the basis for technology which will meet the requirements. To maximize limited resources, several strategies have been activated which include, (i) utilization of summer students; (ii) joint R&D on a subcontract basis, such as support of graduate students; (iii) arranging for visiting scientists to spend time on the project; and (iv) maximize collaboration and cost sharing with the geothermal industry.

2.9 Project Description

- Laboratory plants are used to further develop and integrate the biochemical processing of geothermal sludges.
- Laboratory processing is modified as needed so that engineering studies and design will ensure that appropriate scaling up can be projected and will satisfy the field requirements.

- Process modifications also allow the biochemical technology to handle different types of geothermal wastes and convert them to commercially viable products.
- The area of technology using controlled variables will be maintained and further automation/computerization of the pilot plant will be emphasized.
- This effort will address the maintenance and optimization of variables including design of scaled-up processes using corrosion resistant process units.
- Laboratory model for the CET, Inc./BNL process will follow analogous strategy as that for the silica production.
- Optimize further the variables for the removal of trace toxic metals such as thorium, radium and uranium by a secondary biochemical process.

2.10 Statement of Work

1. Optimize the semi-continuous sludge to silica process.
2. Further investigate and define the silica depigmentation process.
3. Initiate construction of biocatalyst production miniplant at a 1/10 scale of the FY1997 projection.
4. Construct a laboratory version of the BNL/CET, Inc. field plant. The plant will serve as an R&D model for the field operations.
5. The plant, constructed under (4) will be a batch plant. However it will also be used for engineering projections necessary for the design of continuous process(es) in which recycling, and biocatalyst recovery options have been factored in.
6. Use data obtained from model plants for optimization studies and economic analysis. The economic analysis will also project requirements for field applications.
7. Data generated by BNL/Industry (CET, Inc. & CALEN) joint efforts in field experimentation will guide projections and designs for full scale construction of plants in the field.
8. The metal recovery processes will concentrate on the selectivity of sorbants.
9. Cost-efficiency studies dealing with different sorbants will be initiated.
10. Expand CET Environmental Services, Inc. and BNL efforts in identification of broader applications of the sulfur treatment process.

11. Collaboration with CALEN will be expanded to field experimentation and joint R&D effort for the construction and operation of silica processing plants.
12. Continue tests of suitable materials for coating and/or construction of corrosion resistant reactor vessels and accessory equipment.
13. Expand the data base essential for pilot/field scale designs. Include field input.
14. Continue "Quality Control" effort as per Salton Sea experience.

2.11 Technical Support

Staff

E.T. Premuzic, Scientist, Chemist/Biochemist, Principal Investigator
M.S. Lin, Chemist
J.H. Yablon, Microbiologist
W. Zhou, Technician, Spectroscopy
L. Shelenkova, Microbiologist
M. Bohenek, Chemical Engineer

Educational Programs

In the overall effort dealing with R&D biochemical technology for detoxification of geothermal brines and promotion of scientific research in general, we have established continuing projects suitable for undergraduate and graduate students, high school students, and high school teachers.

All of the participants in our R&D effort are supported through the educational programs at BNL which have a broad spectrum, ranging from opportunities for university students to high school science teachers and educational funds of the DOE Geothermal Technology Division.

Visiting Scientist/Collaborator:

1. Dr. John Tharakan, Howard University
2. Dr. Allan Meyerson, Brooklyn Polytechnic University
3. Dr. Robert Benenati, Brooklyn Polytechnic University
4. Dr. David Schwartzman, Howard University
5. Adolph Peter Irsa, Instrumentation

College Students:

1. Bin Dong
2. Marc Silver
3. Christine Stokes*
4. Christine Liu*
5. Angie Parlatore

High School Students:

1. Victoria Chin
2. Denise Gluck
3. Fang Lu
4. Daniel Durand**

Hayden Garriques*, a graduate student under the HBCU program, is completing a M.Sc. degree in Chemical Engineering from Howard University.

*Minority teachers or students

**Daniel Durand has made it to the final list of the Westinghouse Science Contest

2.12 Program Management

BNL conducts R&D and provides technical assistance in several areas, specifically:

1. In collaboration with industrial partners, optimization and modification of currently designed and proposed processes will continue and will be intensified.
2. The CET Environmental, Inc./BNL process uses a single biocatalyst and a modified step for production of agricultural grade sulfur.
3. CALEN/C.E. Holt/BNL process will focus on utilization of existing resources, production of silica and the recovery of metals.
4. Laboratory plants will be used to further develop and integrate the biochemical processing of geothermal sludges.
5. Due to cost, space, and regulatory constraints, the laboratory model plant has been reduced in scale. However, engineering studies, and design 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 and CET engineering staff.
6. Biocatalyst production strategies will be defined further.

7. Process modifications will allow the biochemical technology to specifically handle different types of geothermal wastes and convert them to commercially viable products.
8. The area of technology using controlled variables will be maintained and further automation/computerization of the pilot plant will be emphasized.
9. This effort addresses the maintenance and optimization of variables including design of scaled-up processes using corrosion resistant process units. This portion of the program is carried out in collaboration with Marita L. Allan of BNL, P.I. in the geothermal materials program.
10. Strategies for the modification of the processes focus particularly on the possible elimination of process streams, use of single biocatalysts, recycling, and the utilization of existing facilities in the field.
11. 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.
12. Prepare Field Work Proposals (FWPs)
13. Conduct operational planning jointly with industry.
14. Prepare technical reports
15. Prepare peer reviewed papers
16. Prepare monthly reports
17. Develop safe operating procedures
18. NEPA review and compliance
19. Technology transfer

INDUSTRY INTEREST AND TECHNOLOGY TRANSFER

<u>Organization</u>	<u>Type and Extent of Interest</u>
California Energy/C.E. Holt Company	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 Environmental Services, Inc.
Richmond, CA
and
Pacific Gas and Electric Geysers
Power Plant, Healdsburg, CA

CET has scaled up a modified version of BNL's biochemical process specifically geared to the type of wastes generated by the Geysers types of operations. Although the BNL/CET process is ready for field application, its implementation at PG&E sites is not progressing due to the companies reorganization. CET/BNL are exploring other avenues and commercial application sites.

3.0 MANAGEMENT SUMMARY

3.1 Management Structure

- The Geothermal Technology Division at the Department of Energy (DOE) Headquarters formulates the overall geothermal program policy, provides program guidance and financial resources, and coordinates activities with other government agencies. Through the annual budget cycle, DOE Headquarters (HQ) establishes budgets and priorities, and assigns program responsibilities to Operations Offices and National Laboratories.
- The Idaho Operations Office (IDO) serves as the focus for coordination of the Geothermal Brine Chemistry Activity which includes Advanced Biochemical Processes for Geothermal Brines with other Operations Offices (Chicago, IL; Richland, WA), National Laboratories (Brookhaven, NY; Pacific Northwest, WA), Universities (Univ. of California at San Diego), and Contractors. With their assistance, IDO develops planning options and cost estimates; reviews and recommends program activities; and procures, administers and manages projects, consistent with Headquarters' program guidance.
- The technical and administrative management of the long term/high risk R&D phases of the task are under the direction of BNL with task policy established by the Geothermal Technology Division (GTD) Task Manager. To provide overall guidance to the task and to assure relevance, industrial and technical society advisory panels have been established.
- Fiscal control is exercised in the form of monthly comparisons, over the task term, of actual costs incurred against corresponding line items of the budget. Technical results are monitored through a periodic review, by the Contractor Task Manager, of accomplishments by measuring actual performance as compared to expected progress. All work is conducted in conformance with generally accepted standards for R&D and other investigative or analytic procedures, as observed by universities and large independent research facilities including BNL.

- Brookhaven National Laboratory will develop recommendations for future research as requested by the Operations Office; conduct in-house geothermal waste detoxification research projects; subcontract tasks as agreed with HQ; conduct cooperative research, field tests and information exchange with the research community and geothermal industry; and participate in DOE technical reviews.

3.2 Budget

Funding and Manpower Requirements

Funding obtained from DOE's Geothermal Division is being used to design and construct laboratory scale plants capable of operation at 50-60°C at pH 1-2 to be used as models for the development of full scale processes for the treatment of geothermal residues.

Experimental protocols have been developed to study the kinetics of multi-element removal. These studies also included removal of metals such as uranium, thorium, and radium. In addition to measurements by ICP-MS which measures masses and, therefore, different isotopes, radioactivity measurements are also scheduled. This is particularly important in the case of radium which is present in low concentrations (3×10^{-4} - 9×10^{-4} μ Ci/g) and, therefore, counting methods for its determination are preferable. All of these analytical procedures as well as building of new bioreactors are person-hour intensive.

Modifications and process optimization requires capital equipment investment. In FY 1997, to be continued in FY 1998, collaboration with industry will be intensified. A joint program between CET International and BNL makes possible to field test the BNL process. Further, BNL has a Confidentiality Agreement with CALEN which allows for extended collaboration in several areas. This is a one-to-one fully shared effort.

	<u>FY96</u>	<u>FY97</u>	<u>FY98</u>
Operating	755	675	700
Capital	75	125*	130
Educational	100	60K	TBD
Total	912	800K	830
FTE(s)	5.4	5.4	5.4

*Additional \$200K end of the year allocation for capital equipment.

FTE's may vary depending on the staff utilized, such as the staff from concurrent programs in Fossil Energy, Visiting Scientists, and students supported by the Educational Programs.

The funding needs for manpower, materials, and supplies are estimates. Funding for capital equipment, construction of bioreactors, compliance with environmental and safety requirements, as

well as analytical investigation and servicing will have to be costed in. The additional FY97 allocation of 200K for capital equipment has been used for upgrading of ICP-MS and purchase of instruments which have significantly expanded and improved programmatically important analytical capabilities. More accurate projections for pilot scale construction will be possible after additional economic studies of a number of prototype biosystems operating under optimum conditions have been completed. Current data base indicates that the field testing and subsequent conversion to a continuous process will require a full engineering complement. A continuous process would have to be fully automated with full back-up facilities. This means multiple, parallel processing streams involving a series of bioreactors in sludge processing, biocatalyst recycling, and metal/salts recovery modes. Therefore, costs may have to be modified according to the results generated. In these modifications, the industrial contributions will have to be costed in.

3.3 Milestones and Deliverables

- Preparation of peer-reviewed papers dealing with bioprocess conditions and designs to be submitted to Geothermics and Geothermal Science and Technology 5/98
- Annual Operating Plan 10/98
- Complete analysis based on the first generation of a complete operating laboratory model scaled-up processes including metal recovery, biocatalyst recycling, and filler production 11/98
- Fiscal Year Update 12/98