BNL - 65740

BIOCHEMICAL PROCESSES FOR GEOTHERMAL BRINE TREATMENT

E.T. Premuzic, M.S. Lin, M. Bohenek, G. Joshi-Topé, W. Zhou, L. Shelenkova, and R. Wilke

Energy Science and Technology Division
Department of Applied Science
Brookhaven National Laboratory
Upton, NY 11973

To be Presented at the Geothermal Resources Council
San Diego, CA
September 20-23, 1998

This research was performed under the auspices of the U.S. Department of Energy under Contract No. DE-AC02-98CH10886

Biochemical Processes for Geothermal Brine Treatment

Eugene T. Premuzic, M.S. Lin, M Bohenek, G. Joshi-Topé,
W. Zhou, L. Shelenkova, and R. Wilke
Energy Science and Technology Division, Brookhaven National Laboratory

ABSTRACT

As part of the DOE Geothermal Energy Program, BNL's Advanced Biochemical Processes for Geothermal Brines (ABPGB) project is aimed at the development of cost-efficient and environmentally acceptable technologies for the disposal of geothermal wastes. Extensive chemical studies of high and low salinity brines and precipitates have indicated that in addition to trace quantities of regulated substances, e.g., toxic metals such as arsenic and mercury, there are significant concentrations of valuable metals, including gold, silver and platinum. Further chemical and physical studies of the silica product have also shown that the produced silica is a valuable material with commercial potential. A combined biochemical and chemical technology is being developed which (1) solubilizes, separates, and removes environmentally regulated constituents in geothermal precipitates and brines (2) generates an amorphous silica product which may be used as feedstock for the production of revenue generating materials, (3) recover economically valuable trace metals and salts. Geothermal power resources which utilize low salinity brines and use the Stretford process for hydrogen sulfide abatement generate a contaminated sulfur cake. Combined technology converts such sulfur to a commercial grade sulfur, suitable for agricultural use. The R&D activities at BNL are conducted jointly with industrial parties in an effort focused on field applications.

Background

Research and development strategy at BNL has focused on cost efficient processing of geothermal brines and sludges (Premuzic et al., 1996, 1997). This R&D effort led to the exploration of environmentally acceptable and cost efficient recycling and conversion technologies for the treatment of geothermal sludges and brines, summarized in Figure 1. This figure also introduces a new terminology, namely, "Geothermal Mineral Rich Precipitates (MRPs), rather than "Geothermal Sludges", and similarly, "Geothermal Mineral Rich Brines (MRBs). Using this strategy, a process (Figure 2) for high salinity brines has been developed. In this process, the brine is treated for metal recovery, while the silica rich precipitate, i.e., the MRP "cake" becomes the feedstock for the commercially viable products, e.g., silica. A significant modification of this process is being developed for the treatment of the by-product generated from low salinity geothermal resources. The by-product, a contaminated sulfur residue produced in the Stretford hydrogen sulfide abatement process, is treated first biochemically and then sublimed. The overall process is summarized in the block diagram shown in Figure 3. The end product is a commercial, agricultural grade sulfur. Currently, conceptual process designs are being explored in which by-products from either the MRP or the sulfur process will be fully recycled with zero, or, minimum yields of environmentally acceptable wastes.

Recent Activities

The process for the treatment of mineral rich precipitates (MRPs) leading to the production of amorphous silica is being developed jointly with CalEnergy Company, Inc., and is schematically summarized in Figure 4. The process yields amorphous silica in a quantity which is about one half of the original highly pigmented MRP feedstock. The dissolved "impurities" present in the liquid phase are reinjected. Biochemical treatment followed by chemical treatment applied at different concentrations and temperatures, leads to the production of a silica product with varying degrees of pigmentation. In the chemical composition of this product the major contribution to pigmentation is iron. Results of an inductively-coupled-plasma-mass spectrometric analysis (ICP-MS) of untreated and treated MRP with two different biocatalysts, BNL-3-25 and BNL-3-23 followed by chemical treatment R-1 are shown in Figure 5. The actual pigmentation is due to different chemical species of the responsible metals. For example, iron, the predominant metal present, under processing conditions appears in several forms, as shown in Table 1. The "effect" of the other metals, present in subtrace quantities, on the quality of the end product, is being investigated. For this purpose the use of BNL's Synchrotron Light Source (NSLS) in combination with other technologies is being explored (Bajt et al., 1994).

Under appropriate processing conditions the extent and the rates of depigmentation, expressed in terms of iron, are fast and efficient as shown in Figure 6a & b. There are several uses for the silica products. For example, the BNL silica product can be incorporated into acrylic wall paints. When compared to a commercial material, the produced silica rates very favorably, as shown in Table 2.

The process for treatment of the sulfur cake derived from the Stretford hydrogen sulfide abatement process is being developed jointly by BNL and CET International, Inc. A recent economic analysis of the MRP and the sulfur process is summarized in Table 3.

At BNL, metal recovery options continue to be actively explored. Experimental data remain consistent and support the view that the aqueous phase produced by ABPGB process should be pooled with the post heat exchanger brines, processed for metal recovery, and the remaining aqueous phase reinjected. Currently several different biosorbants are being tested. The overall selectivity of biosorbants is shown in Figure 7. Specific selectivity of the biosorbants used is further demonstrated by adsorption of platinum and gold at pH 1 and 100°C, as shown in Table 4. While the recovery of valuable trace metals from dilute solutions using biosorbants is very promising, further evaluation is needed. At the present time the quality of biosorbants varies from preparation to preparation. However, based on the results generated thus far and discussions with biosorbant producers, this disadvantage may be resolved.

Conclusions

1. A combination of biochemical and chemical processes has led to the design of a cost efficient technology for the treatment of geothermal metal rich precipitates (MRPs) and metal rich brines (MRBs).

2. The combined processes utilize full recycling options.

3. The emerging technology is environmentally attractive and yields commercially viable products.

4. Collaborations with industry enables a full development and field application of the emerging technology.

Acknowledgments

This work has been supported by the U.S. Department of Energy, Office of Conservation and Renewable Energy, Geothermal Technology Division, Washington, DC, under Contract No. AM-35-10 and by Brookhaven National Laboratory with the U.S. Department of Energy under Contract No. DE-AC02-98CH10886. We also with to acknowledge Ray LaSala, the U.S. DOE Program Manager for continued interest and encouragement.

References

Premuzic, E.T., M.S. Lin, and M. Bohenek, 1997. Advanced Biochemical Processes for Geothermal Brines: Current Developments, Geothermal Resources Council, Transactions, Vol. 21, 145-149.

Premuzic, E.T., M.S. Lin, and H. Lian, 1996. Geothermal Brines and Sludges: A New Resource, Proceedings of SWEMP 96, Cagliari, Italy, Fourth International Conference, Vol. 2, 1019-1025.

Bajt, S., S.R. Sutton, and J.S. Delaney, Premzic, E.T., 1994. X-ray Microprobe Analysis of Iron Oxidation States in Silicates and Oxides Using X-ray Adsorption Near Edge Structure (XANES), Geochimica & Comochemica Acta Vol. 58 (23), 5209-5214.

Table 1. Species of Iron Pigments

- FeO(OH) hydrous ferric oxide is brown
- Fe_3O_4 is a mixture of Fe(II)-Fe(III) oxide and is black
- α-Fe_2O_3 is red brown
- Fe(III) chloride·$6H_2O$ is yellow
- Fe(II) chloride·$8H_2O$ is colorless
- Fe(II) chloride·$6H_2O$ and Fe(II)Chloride·$4H_20$ are pale green
- Iron(II) and Iron(III) sulfides are black

Table 2. Comparison of the Geothermal MRP Silica Product Produced in the BNL Process with Commercially Available Amorphous Silica

The geothermal MRP product was comparable to the commercial product in the following areas

Ease of dispersion
Viscosity stability
pH stability
Package stability
freeze-thaw resistance
reflectance
contrast ratio
pencil hardness
sheen
burnishing
ease of application

The geothermal MRP product was inferior only in scrubbing resistance while it had a superior opacity (whiteness) of 97% as opposed to the commercial products 94%

Table 3. Economic Summary

Mineral Rich Precipitate (MRP): Silica Recovery Process

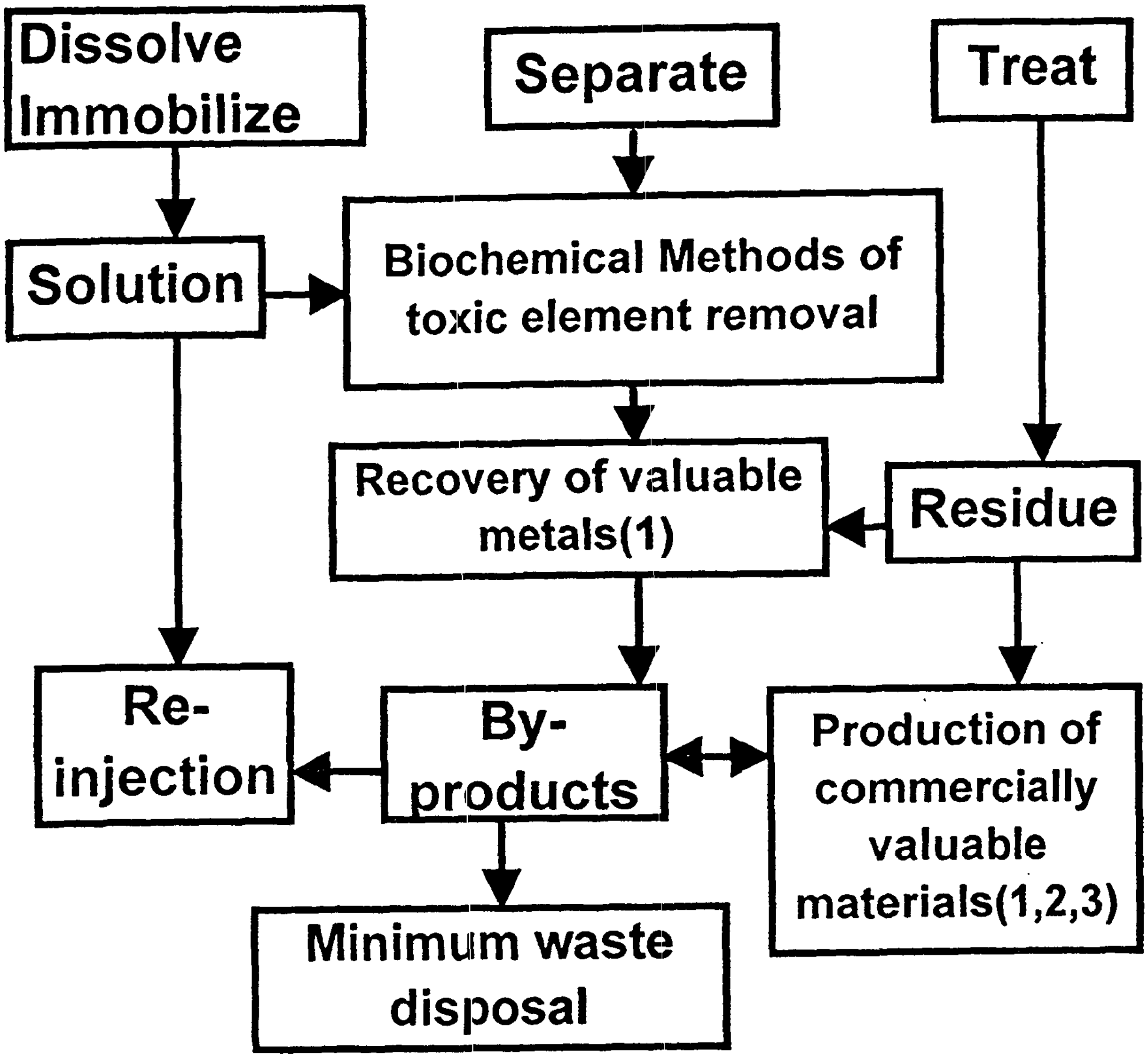
Capital cost $7 million dollars
Operating expenses $6 million/yr
Revenues:
$6 million/yr saving from disposal
$6 million/yr sale of silica
$6 million/yr pretax profit
55% yearly return on investment

Stretford H2S Abatement Technology: The Sulfur Cake Process

Capital cost $700 thousand
Operating expenses $331 thousand/yr
Revenues:
$164 thousand/yr saving from disposal
$190 thousand/yr sale of sulfur
$23 thousand/yr pretax profit
11% yearly return on investment

Table 4. Analysis of Brine Liquid for Platinum and Gold Using Different Biosorbents at pH 1 and 100°C

Sample	Standard Pt (ppm)	Standard Au(ppm)	% Uptake of Pt	%Uptake of Au
Before Biosorption	5.04	0.335		
Biosorbent P010	2.42		52	
Biosorbent P020		0.195		42
Biosorbent P030	4.79	0.063	5	81
Biosorbent P040	1.36		73	
Biosorbent P051	1.9		62	



1. gold, platinum, zinc, manganese etc.
2. high grade amorphous silica
3. agriculture grade sulfur

Figure 1. MRP's and MRB's Treatment Options

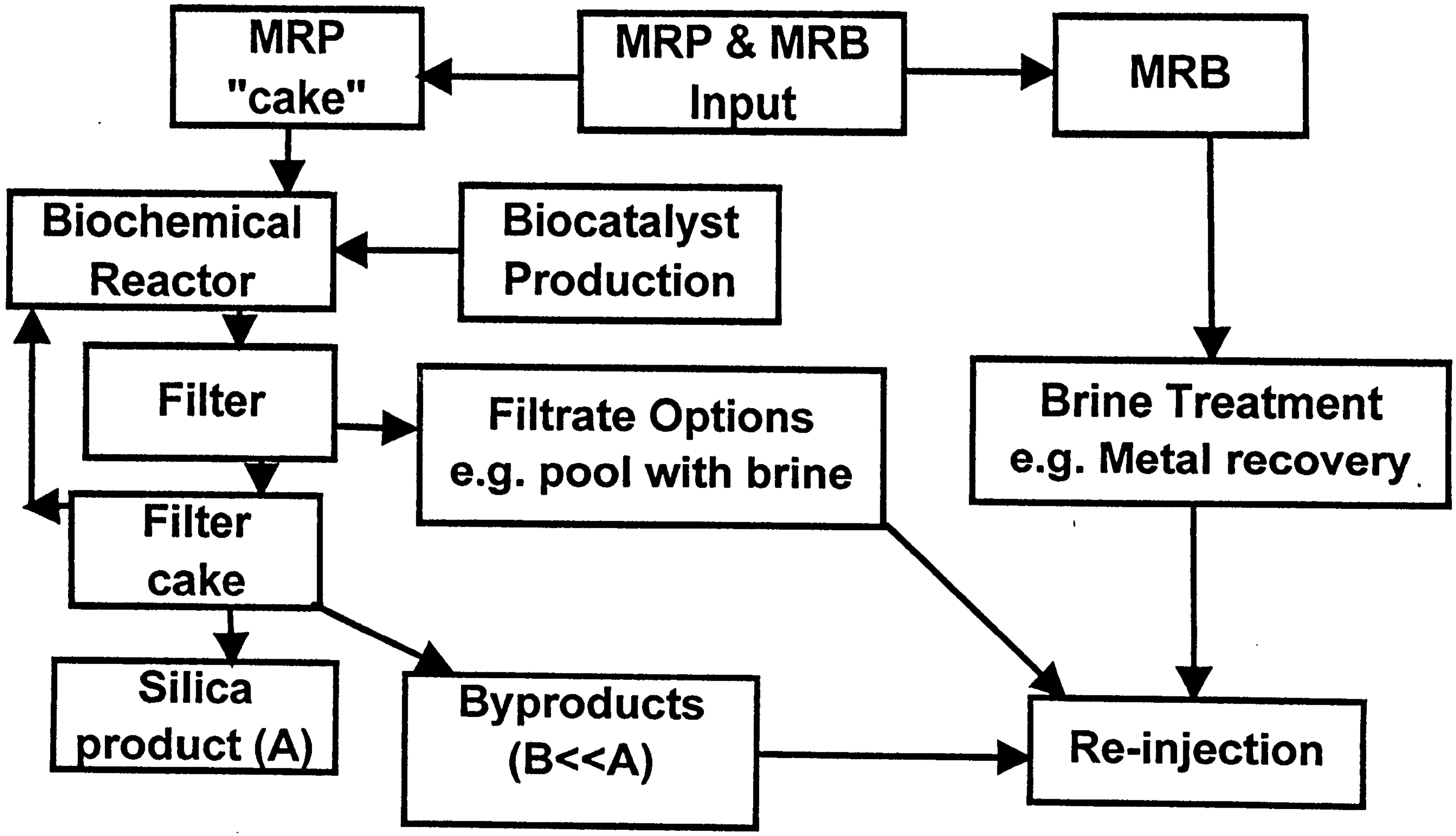


Figure 2. Total Processing of Geothermal Sludges and Brines

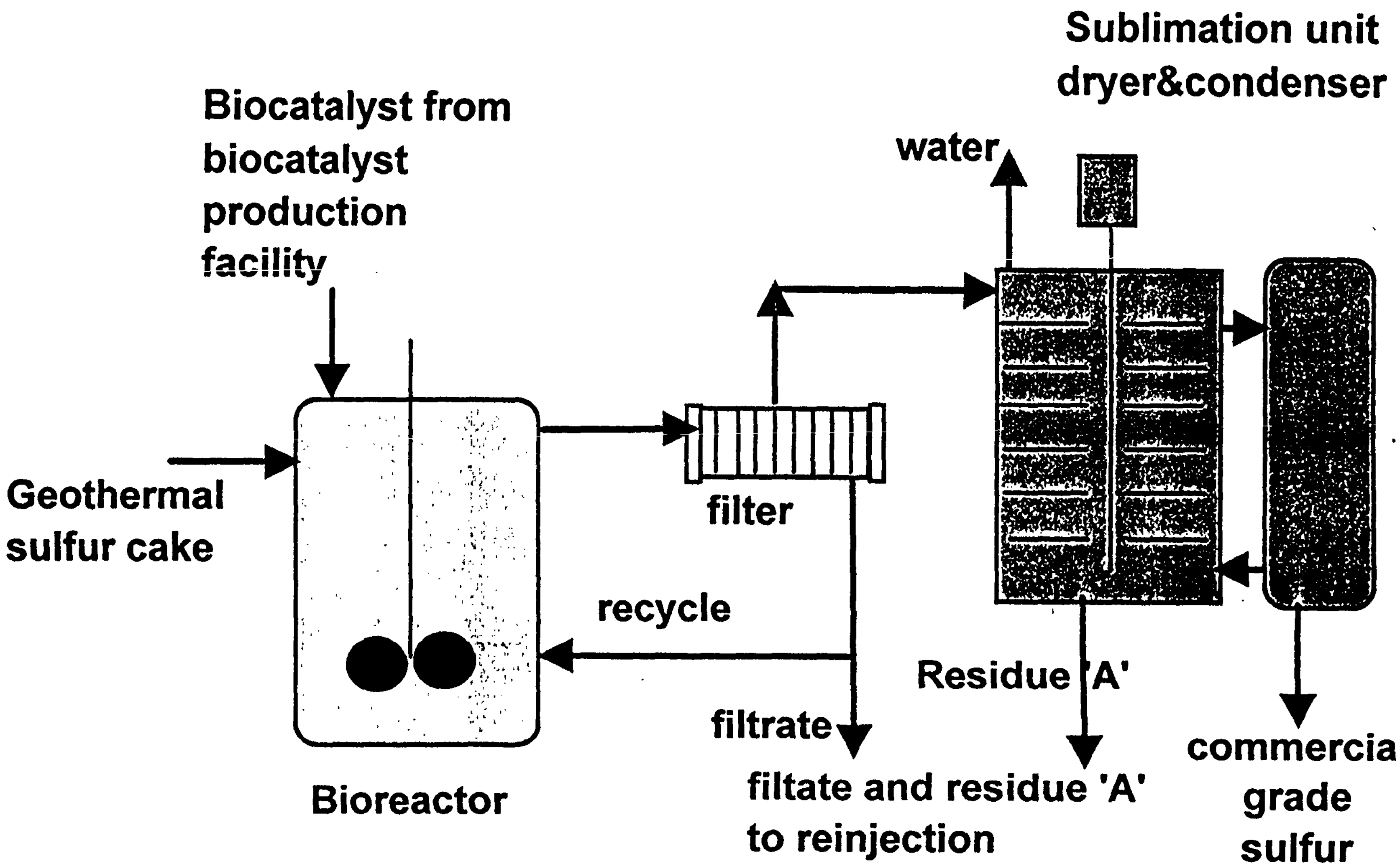


Figure 3. The Sulfur Cake Process

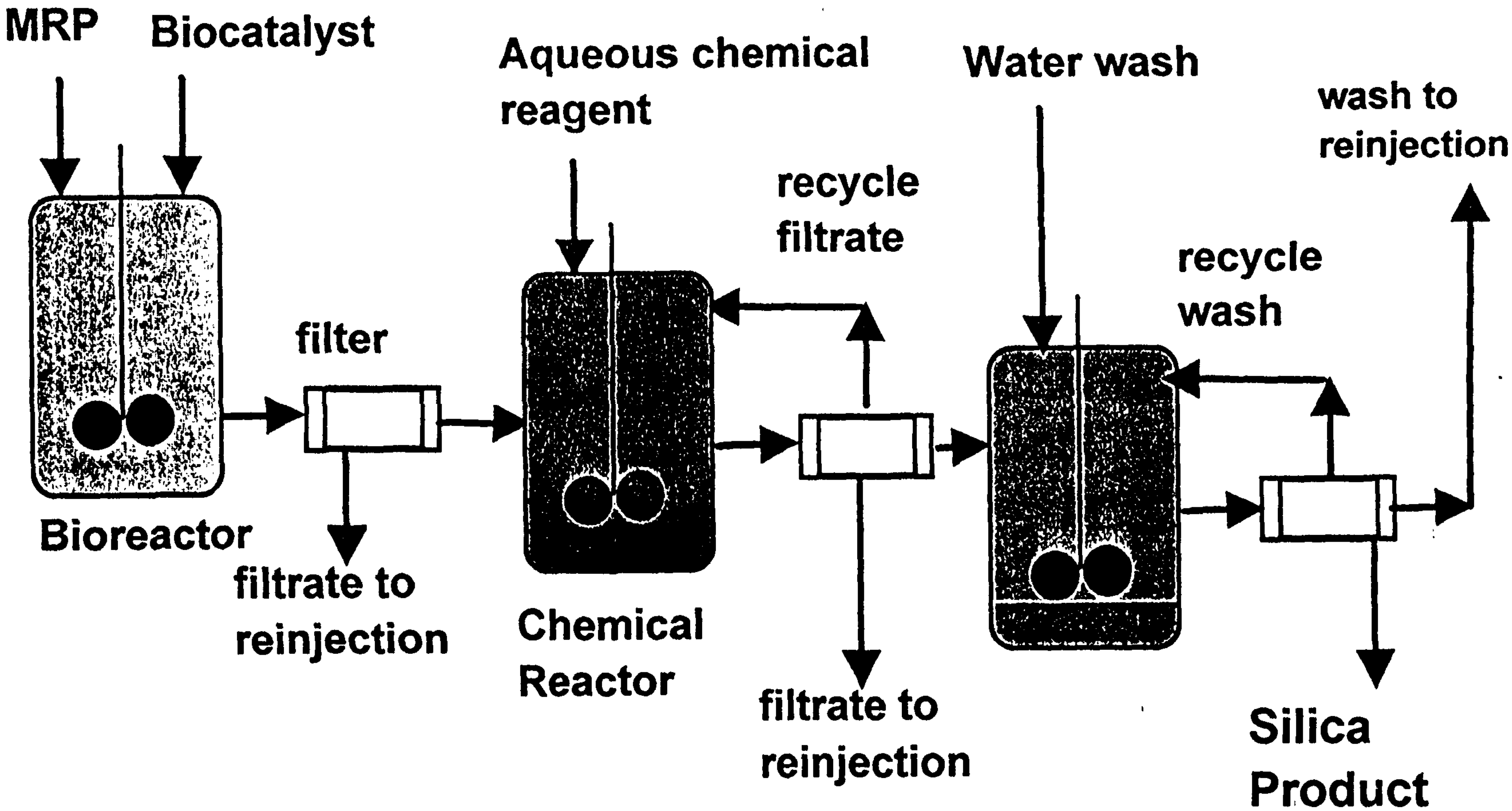


Figure 4. Treatment of Mineral Rich Precipitates

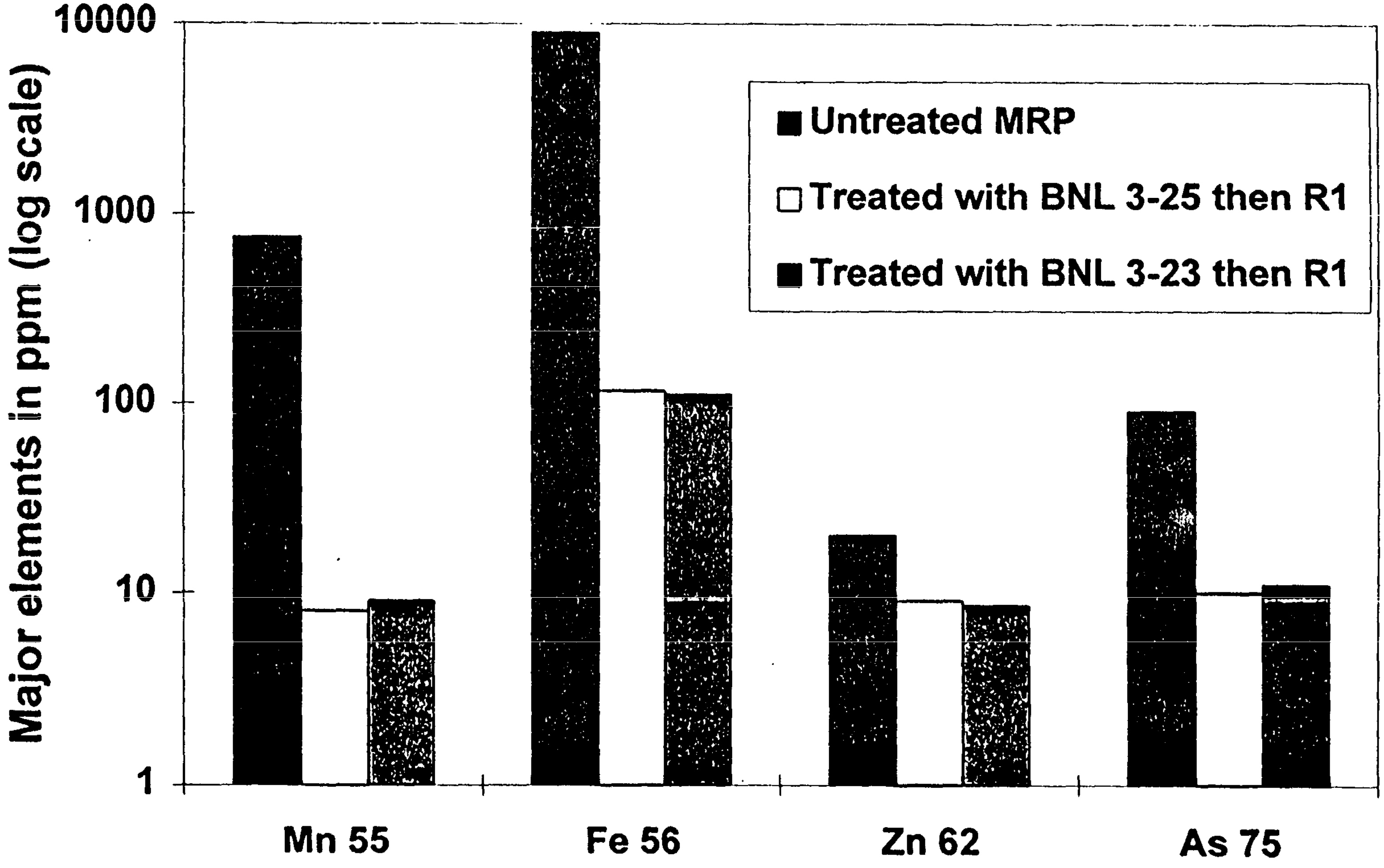


Figure 5. Reagent R1 Treatment of Biotreated MRP

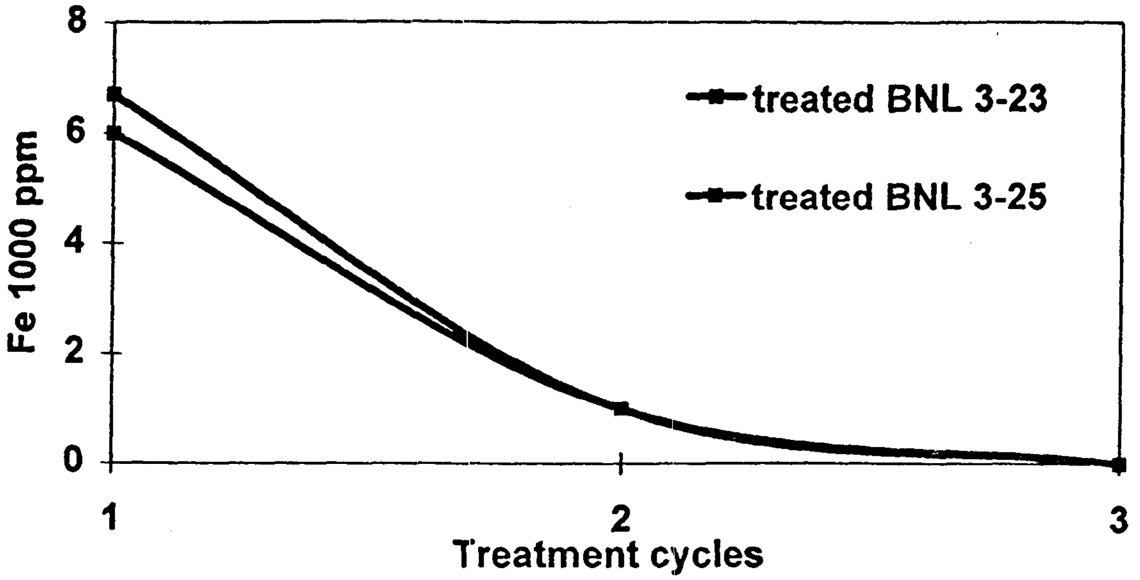


Figure 6a. Silica Production: ICP-MS Analysis of Iron Concentration of Biotreated MRP as Function of R1 Chemical Treatment Cycles

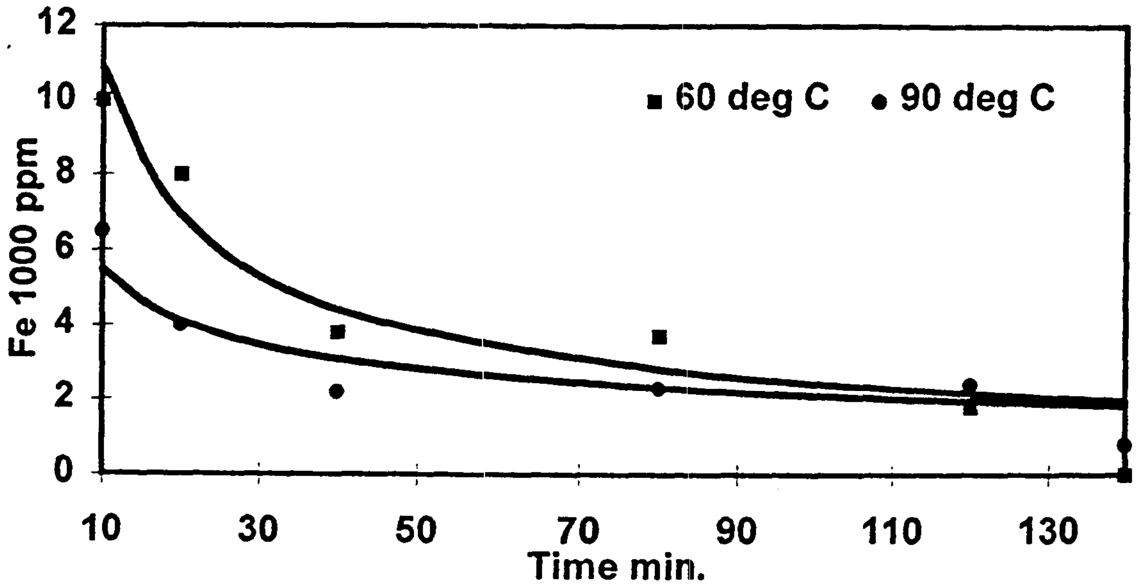


Figure 6b. Reaction Rate vs. Temperature Iron Removal

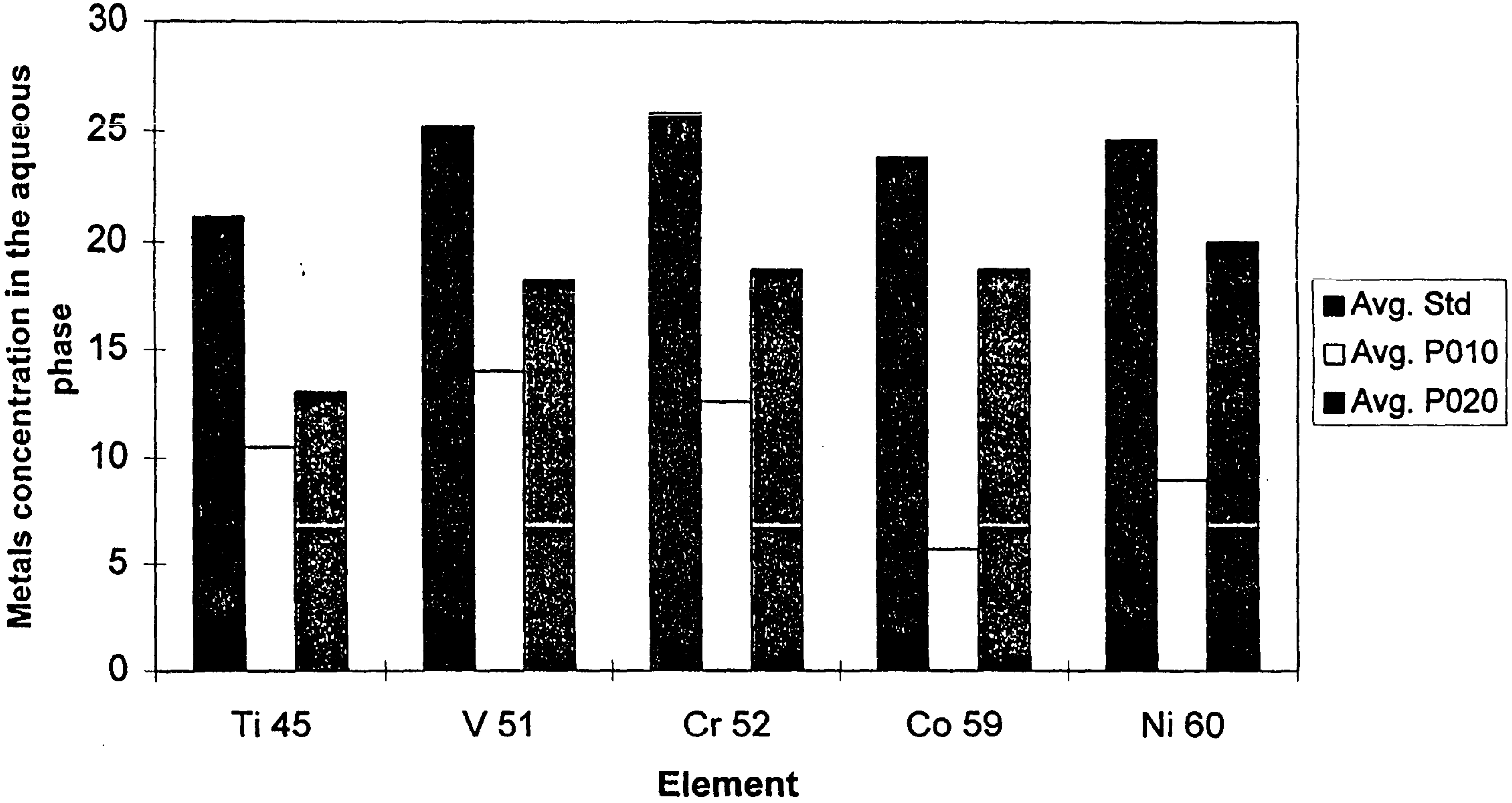


Figure 7. Selective Biosorption of Metals Dissolved in the Aqueous Phase