BIOREACTOR ECONOMICS, SIZE AND TIME OF OPERATION (*BEST*) COMPUTER SIMULATOR FOR DESIGNING SULFATE-REDUCING BACTERIA FIELD BIOREACTORS

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ABSTRACT

BEST (bioreactor economics, size and time of operation) is an Excel™ spreadsheet-based model that is used in conjunction with the public domain geochemical modeling software, PHREEQCI. The *BEST* model is used in the design process of sulfate-reducing bacteria (SRB) field bioreactors to passively treat acid mine drainage (AMD) emanating from abandoned or active mine sites. While PHREEQCI calculates geochemical equilibria through the bioreactor, the spreadsheet portion of the model includes factors associated with cleanup criteria, designed flow rate, capital and operating cost, required time of operation, maintenance and media replacement schedule, and the size and configuration of the bioreactor. Depending on the design constraints, each factor can be considered an entry parameter or the result of calculations. The *BEST* simulator is public domain software available upon request via E-mail: zaluskim@mse-ta.com.

INTRODUCTION

Acid mine drainage emanates from abandoned and active mines, causing significant environmental problems by contaminating surface waters and groundwater with dissolved metals and raising their acidity. Because conventional treatment of AMD is often not feasible due to the remoteness of the site, lack of power, and limited site accessibility, a passive remedial technology needs to be used. One such technology uses SRB that have the ability to increase pH and alkalinity of the water and immobilize dissolved metals by precipitating them as metal sulfides, provided that a favorable biochemical environment is created.

When provided with an organic carbon source, SRB are capable of reducing the sulfate to soluble sulfide by using sulfate as a terminal electron acceptor. Acetate and bicarbonate ions are also produced. The soluble sulfide reacts with the metals in AMD to form insoluble metal sulfides (Equations 1 and 2). The bicarbonate ions increase pH and alkalinity of the water.

$$SO_4^{2-} + 2CH_2O \text{ -------> } H_2S + 2HCO_3^- \qquad (1)$$

$$H_2S + M^{2+} \text{ ---> } MS + 2H^+, \text{ where M = metal} \qquad (2)$$

Organic carbon, the organic electron donor, represented in Equation 1 by the formula $2CH_2O$, may be provided either by feeding a bioreactor with a chemical compound like lactate or methanol that delivers carbon directly or can be obtained from a selected organic matter that, if not used for this purpose, may be classified as waste. Because of the remoteness of many abandoned mine sites, the latter option is more appealing as it does not pose the risk of the misuse of methanol by irresponsible parties.

Research and successful demonstrations of this technology (Gusek et al., 2000; Canty, 1999; Zaluski et al., 2003) revealed the need for the development of a quantitative tool for the design and sizing of a bioreactor

The remoteness of AMD sites, their abundance, and economic aspects require that the design of a bioreactor be simple and inexpensive and that the bioreactor be capable of treating any AMD flow rate and the dissolved metals load. Therefore, it is preferred that bioreactors are prefabricated and designed to a size allowing for transportation using backcountry roads in mountainous regions. These conditions are met by bioreactors consisting of the number of modules or reactive cartridges (RC) that are assembled into one SRB treatment system at the mine site.

The *BEST* simulator (MSE, 2004; Zaluski et al., 2004) is tailored for designing such a treatment system based on the AMD chemistry and flow rate and the reactivity of the organic matter that is used as the organic carbon source – the electron donor for the sulfate reduction process.

CONSTRUCTION OF BIOREACTOR

Based on the results of the previous research, a new organic matter, a mix of English walnut shells and cow manure, was developed by the authors, and was selected as the reactive medium to be used in the bioreactor. Some advantages of using this mix are listed below.

- Cow manure is an easily biodegradable organic matter that ensures a quick startup of the bioreactor. It is widely available and inexpensive.
- Cow manure includes nitrogen needed by other microorganisms for the initial decomposition of manure. Moreover, the nitrogen is in the form of ammonium that is easier for microorganisms to use than nitrates.
- Walnut shells are more recalcitrant to biodegradation, thus supporting good long-term operation of a bioreactor.
- Walnut shells provide a solid matrix structure because individual shells actually rest on each other. This structure prevents time-driven compaction (settling), thus it works toward preservation of the initial permeability of the medium.

- Walnut shells contain a high percentage (56%) of total organic carbon (TOC). The TOC of manure is lower and varies, depending on the manure source, from 8% to 20%.

The mix of walnut shells and cow manure is referred to in this paper as W/M organic medium. A ratio value that often follows or precedes this term is the ratio of a bulk volume of walnut shells to the bulk volume of manure used for the given mix. The convention used in this paper is to express these ratios as decimal fractions of the bulk volume of walnut shells, e.g., 0.4, and the bulk volume of dry manure, e.g., 0.6, used for the mix before they were combined.

The RC uses a commercially available cylindrical or cuboidal plastic tank most often constructed of high-density polyethylene (HDPE) or polypropylene. Before the tank is brought to the AMD site, it is modified in a machine shop and equipped with necessary features to accommodate the W/M organic medium and serve as one SRB RC. The tank may be installed either above or below ground at the mine site, as required by the site conditions. An appropriate piping system conveys the AMD into the RC. Figure 1 illustrates a cylindrical RC that could be installed below or aboveground at the mine site.

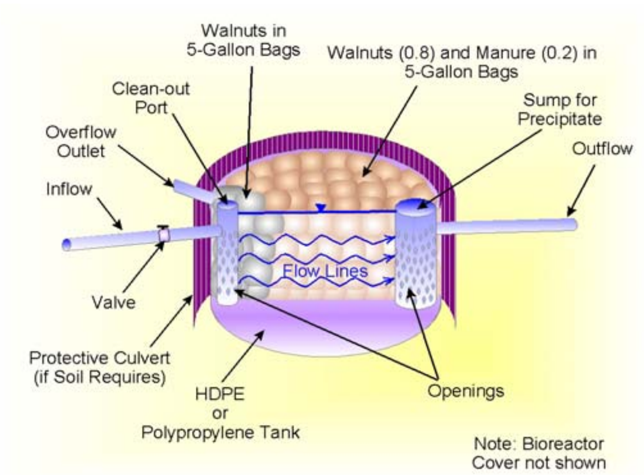

Figure 1 Illustration of a cylindrical RC.

The 5-gallon bags with W/M 0.8/0.2 organic medium shown in this figure may be prepared in advance and then transported to the mine site, or they may be made at the mine site. For the ease of the placement and removal, organic medium is packed in 5-gallon bags, which are made of plastic netting that is commonly used by grocery shops for prepacked fruits. A plastic tarp (not shown in the picture) placed on the top of the bags maintains anaerobic conditions. The cost of production and installation (excluding transportation to the site) of such an RC housed in a 2,500-gallon HDPE tank is approximately $8,000. The cost may vary depending on local supply and labor rates applicable at the given location.

A modular SRB treatment system consists of multiple RCs that are configured in parallel or in series depending on the AMD flow rate and its quality (metal load and pH), cleanup objectives, and space available at the given mine site. These RCs are filled with the W/M organic medium of the selected volumetric ratio of walnut shells and cow manure. The number of RCs and the system configuration is determined through modeling conducted using the *BEST* computer simulator developed for this purpose. The *BEST* simulator is public domain software available upon request via E-mail: zaluskim@mse-ta.com.

STRUCTURE OF THE *BEST* SIMULATOR

An SRB treatment system usually includes multiple RCs, configured in parallel. However, for a site with a low flow rate but high metals load, the RCs may be configured in series. Both the configuration and the number of RCs are determined using the *BEST* simulator. This simulator is a spreadsheet-based model that is used in conjunction with a public domain computer software package, PHREEQCI geochemical modeling program (Parkhurst and Appelo, 1999). While PHREEQCI calculates geochemical equilibrium for the advective-reactive transport of AMD through the bioreactor, the spreadsheet portion of the simulator handles issues of AMD flow rate, size of the bioreactor, its operational time, and its economics.

In general, the *BEST* simulation process is based on the chemical composition of the AMD and its flow rate, TOC content in the organic matter, cost of material and production of a typical RC, the sulfate reduction rate (SRR) of the organic matter used in the treatment system, and the discount rate and operation and maintenance (O&M) cost for calculation of the net present value (NPV).

The *BEST* simulator was developed and formulated so it could be operated by a user with minimum modeling experience. The *BEST* simulator operation requires basic knowledge of the Excel™ program and some familiarity with the geochemical model PHREEQCI. Of course, a good chemical background is a bonus.

The *BEST* simulator is saved as a Microsoft Excel™ workbook, *BEST V1.xls*, and consists of 17 worksheets. Two of these worksheets (I and II) include charts showing the navigation between the 14 worksheets that are identified with letters A through L, (and numbers 1 and 2 for the worksheet series B and D) and their interaction with the PHREEQCI model and its input file.

Another worksheet (0) entitled "input and output" (I-O) allows for entering the majority of input data and having the most important results also printed on the same page. However, details of the design specification of the material, etc., are not listed in the I-O worksheet, and the user needs to refer to worksheets A through L to examine these details.

Most worksheets are linked together; however, the PHREEQCI model and its data input file are not automatically linked with the rest of the worksheets, thus required changes need to be input manually to PHREEQCI.

The time of operation calculated by *BEST* is based on the available organic carbon present in the W/M organic medium divided by the safety factor of 4. This safety factor is used because there is some uncertainty whether the organic carbon present in the medium is entirely available for the SRB.

MODELING PROCESS

The I-O worksheet (Figure 2) enables the user to enter data and read the most important results using a one-page printout. This worksheet consists of two main portions: Entry Data and Output Data. The Output Data consists of the Preliminary Design and the final Treatment System Design.

SUMMARY SHEET: Input and output of the BEST simulator				
Explanations:	All fields but green are protected; to unprotect go to: Tools, Protection, Unprotect sheet			
	Input values are in italic and bold			
	BEST simulator is not automatically linked with the PHREEQCI input data file shown in Sheet F, therefore, all alteration to this sheet must be entered manually			
Entry data				
AMD source	***Strong synthetic AMD***	Atomic weight	Concentration	
	Al	26.98	***40.40***	mg/L
	Fe^{+3}	55.84	***0.00***	mg/L
	Enter other species if needed	*1.00*		mg/L
	Co	58.93		mg/L
	Pb	207.20		mg/L
	Ni	58.69		mg/L
	Enter other species if needed	***1.00***		mg/L
	Enter other species if needed	***1.00***		mg/L
	Enter other species if needed	***1.00***		mg/L
	Cd	112.41	***0.08***	mg/L
	Cu	63.55	***6.12***	mg/L
	Fe^{+2}	55.84	***39.48***	mg/L
	Zn	65.39	***17.78***	mg/L
RC dimensions	Height	Max (in center)	***7.5***	ft
		Wall	***6.8***	ft
		Active medium	***6.0***	ft
	Diameter		***8.0***	ft
Assumed sulfate reduction rate			***0.25***	mmol/(d*L)
AMD feed flow rate			***1.0***	gpm
Organic matter properties	Porosity		***0.50***	dimensionless
	TOC in fresh manure of the treatment system		***8***	%
	TOC in fresh walnut shells of the treatment system		***56***	%
	Volumetric moisture content of manure		***0.50***	g/cm^3
	Dry bulk density of manure		***0.21***	g/cm^3
	Dry bulk density of walnut shells		***540***	$Lb/yard^3$
	Volumetric ratio of manure in organic matter		***0.2***	dimensionless
Typical tank adaptation	Labor rate		***$60***	
	Date altered		***May,30,2003***	
Field installation	Labor rate for bagging organic medium		***$40***	
	Labor rate for field installation		***$70***	
	Time to make one bag with organic medium		***0.10***	hr
	Time to install one RC at the site		***16***	hr
Economical factors	Annual O&M (assumed)		***$1,000***	
	Discount rate		***3.2%***	
Output data				
Preliminary design				
For metal sulfides	Cost of a typical tank adaptation		3,813.5	
	Number of RCs		*5*	
	Years of operation for NPV calculation		*30*	
	Capital cost		$40,407	
	Net present value (NPV) of capital cost		$59,511	
For all metals precipitating	Cost of a typical tank adaptation		$3,814	
	Number of RCs		*17*	
	Years of operation for NPV calculation		*30*	
	Capital cost		$137,385	
	Net present value (NPV) of capital cost		$156,488	
Treatment system design				
Laboratory experiment	Influent sulfur concentration		***255.2***	mg/L
	Effluent sulfur concentration		***235.0***	mg/L
	Volume of the laboratory bioreactor		***9.1***	L
	Flow rate		***2.7***	mL/min
	Carbon oxidation required		1.263	mmol/L
PHREEQCI modeling	Carbon oxidation for PHREEQCI entry		0.126	mmol/L
	Run PHREEQCI and check metal removal			
Adequate metal removal	Number of RCs		1	
	Years of operation for NPV calculation		*12*	
	Capital cost		$8,081	
	Net present value (NPV) of capital cost		$17,918	
If an inadequate metal removal (repeat this step until an adequate removal is achieved)	Enter to PHREEQCI a larger value of carbon oxidation than before or adjust pH			
Adequate metal removal (last successful iteration)	Adjusted carbon oxidation for the adequate metal removal		***2.526***	mmol/L
	Number of RCs		3	
	Years of operation for NPV calculation		18	year
	Capital cost		$24,244	
	Net present value (NPV) of capital cost		$37,768	
Meets velocity and residence time criteria	Velocity value from the last design		3.0	ft/d
	Residence time from the last run		2.35	day
	Velocity criterion (maximum)		***2.5***	ft/d
	Residence time criterion (minimum)		***0.50***	day
If velocity and or residence time do not meet requirements (repeat this step until both do)	Enter a larger value for the number of RCs			
Meets velocity and residence time criteria (last successful iteration)	Increased number of RCs with velocity and residence time criteria met		***4***	
	Corrected velocity		2.3	ft/day
	Corrected residence time		3.13	day
	Years of operation for NPV calculation		30	year
	Capital cost		$32,326	
	Net present value (NPV) of capital cost		$51,429	

Extra items need to be input separately in Sheet C that will then calculate a new value for the cost of a typical tank adaptation

Measured from the bottom to the RC outlet

For a cuboidal tank enter value of $2(A/3.14)^{0.5}$ where: A is an area of the cuboidal tank base

This value must be manually entered to PHREEQCI data input file

If RCs are configured in series, divide and multiply the calculated residence time and velocity values respectively, by the number of RCs

This step is applicable only for the RCs configured parallel

Figure 2 Input-output worksheet for the *BEST* simulator.

Preliminary Design

This stage of the bioreactor design focuses on the selection of the treatment scope as presented in Chart I (Figure 3). This process determines whether, for economic feasibility, the removal should be limited to only those metals that precipitate as sulfides, e.g., zinc (Zn), cadmium (Cd), and copper (Cu), or if the removal should include all metals, e.g. aluminum (Al) and ferric iron. Removal of metals such as Al and ferric iron would in general require a larger system to produce adequate bicarbonate to sufficiently raise the effluent pH. The screening process starts with data collection to characterize the AMD chemistry. These data, entered through the I-O worksheet, are used to calculate organic carbon oxidation (OCO) required to reduce an adequate amount of sulfate to precipitate metals that may form sulfides as shown by the net reaction (3) written for Cd.

$$Cd^{+2} + SO_4^{-2} + 2CH_2O = CdS + 2H_2CO_3 \qquad (3)$$

Also calculated at this stage of the design process is the OCO required to generate an excess of hydrogen sulfide that is needed to precipitate other metals as hydroxides as shown by the net reaction (4) written for Al.

$$2Al^{+3} + 3SO_4^{-2} + 6CH_2O + 6H_2O = 3H_2S + 6H_2CO_3 + 2Al(OH)_3 \qquad (4)$$

The results of these simplistic calculations, based only on concentrations of dissolved metals rather than their activities and pH, are used in calculations for the first estimation of the size and cost of the treatment system. This estimation also uses information on the AMD flow rate, the results of the chemical analysis for TOC in the organic mix used for the treatment system, and the dimensions and cost of production of a typical RC.

The first estimation of the treatment system size and cost is initially done for the alternative that precipitates only metal sulfides. This procedure follows the shapes drawn with the solid line in Figure 3. Next, the alternative of precipitating all metals is evaluated. This process follows the shapes drawn with the dashed line in Figure 3.

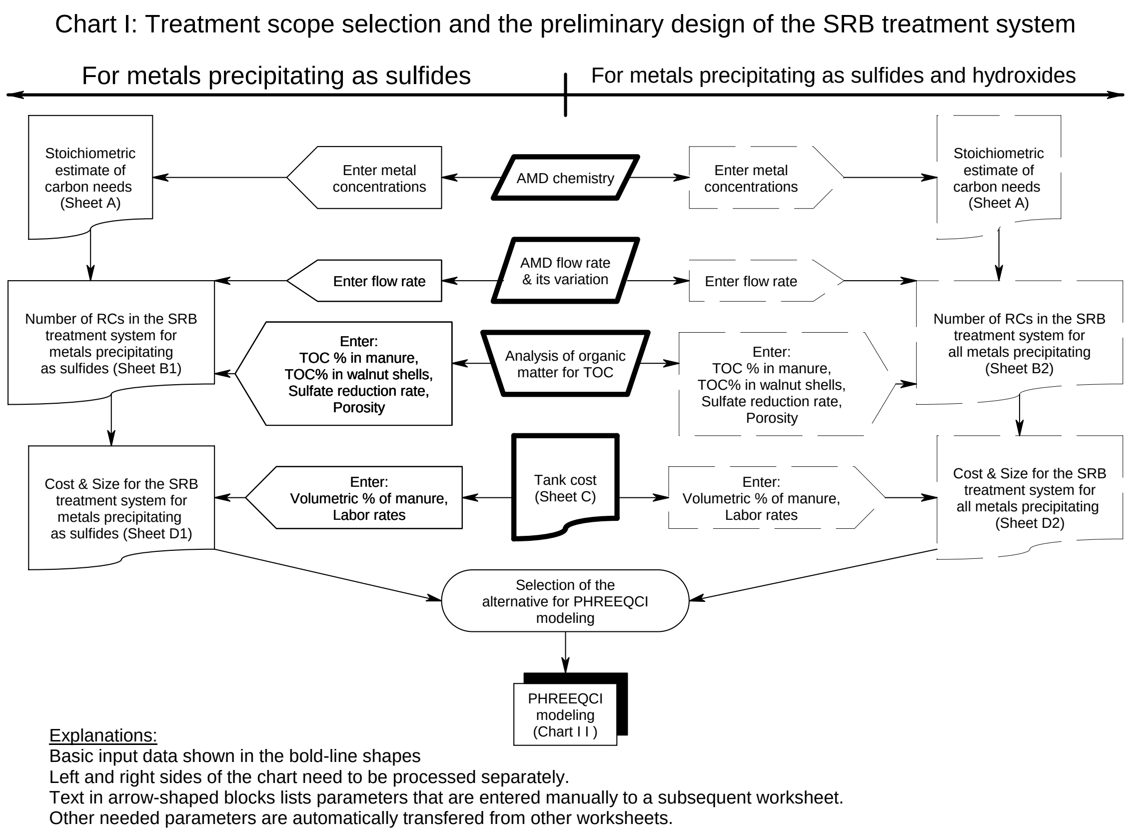

Figure 3 Chart I - Treatment scope selection and preliminary design.

For the AMD whose chemical composition (Calliope mine site [Zaluski et al., 2003]) is presented in Figure 2, the cost of the treatment system would more than triple if the removal of aluminum is required. The capital cost is $40,407 and $137,358 for the "metal-sulfides" and "all-metals" alternatives, respectively. Additional negative effects of the treatment system for "all-metals" would be the production of carbonic acid that would decrease the pH of the treated AMD and the excess of hydrogen sulfide (reaction 4) that could affect air quality. Consequently, in the example of the *BEST* model (Figure 2), the selected alternative for the SRB treatment system is the option of precipitating metals as sulfides. In this case, metal hydroxides could be precipitated using a less expensive technology, e.g., a limestone cell (Desmier et al., 2003) that is not a part of the *BEST* design package.

TREATMENT SYSTEM DESIGN

The modeling process of the treatment system final design (Figure 4) starts with the selected alternative for the treatment scope, in this case to precipitate only metal sulfides. Therefore, the criterion for a successful operation is an adequate decrease of only those metals that precipitate as sulfides, i.e., Zn, Cd, and Cu, and to increase the pH to an acceptable level.

In addition to the dissolved metal concentration, pH, and oxidation-reduction potential (pE) of the AMD, the input data requires quantifying the OCO needed for sulfate reduction. This value can be acquired through the laboratory experiment for the SRR. Data from such an experiment, influent and effluent sulfur concentrations, are entered in an I-O worksheet and used to calculate the SRR [millimole per day per liter (mmol/(d*L)] and OCO [millimole per liter (mmol/L)] that will be used for PHREEQCI modeling.

For the example, as shown in the *BEST* model (Figure 2), the initial values calculated are 0.541 mmol/(d*L) and 1.263 mmol/L for the SRR and OCO, respectively. If no experiment was conducted, the value 0.25 mmol/(d*L) for SRR and the

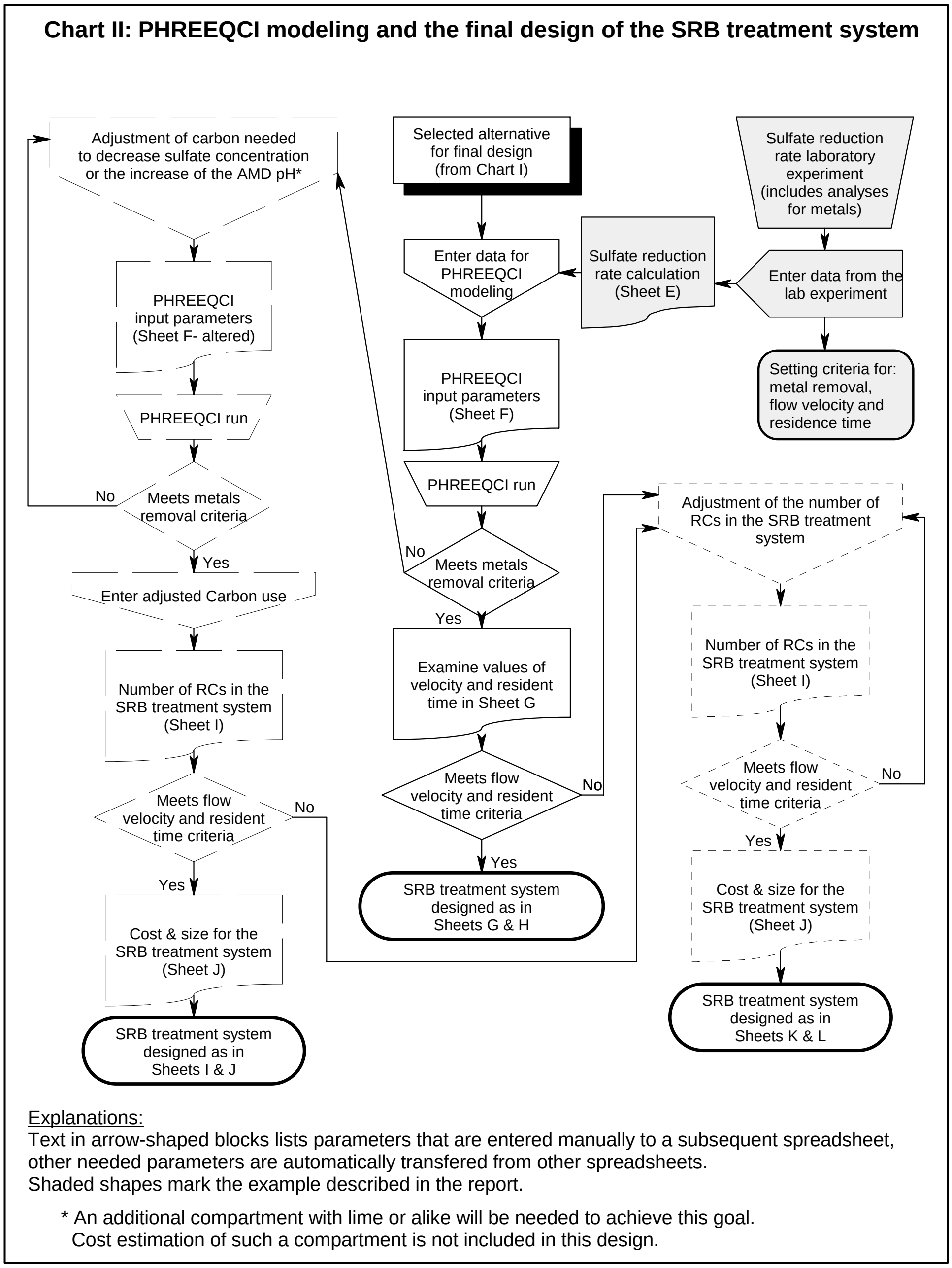

Figure 4 Chart II - Final design of the bioreactor.

corresponding value of 0.575 mmol/L for OCO could be used for PHREEQCI. These values fall within the lower range of the SRRs measured during the laboratory experiment (MSE, 2004) and, therefore, are considered conservative for the organic mix of walnut shell and cow manure (W/M) tested in the laboratory and used for the bioreactor described in this paper.

It is recommended that the laboratory experiment for the SRR also include analytical work for dissolved metals. This information can assist in establishing realistic criteria for metals removal by the treatment system being designed. Certainly, criteria like maximum contaminant level (MCL), suggested maximum contaminant level (SMCL), secondary maximum contaminant level, or any other industry project-specific requirements may be used.

This initial stage of the final design of the bioreactor, i.e., the SRR determination and setting criteria for adequate metal removal, is depicted in Figure 4 with shaded shapes.

In general, the design process may consist of the following five main activities:

- Laboratory determination of the OCO for the organic matter used in the bioreactor.
- Initial geochemical modeling using PHREEQCI, the AMD characteristics, and the laboratory defined OCO.
- Additional loop of PHREEQCI modeling with adjusted OCO values until the cleanup criteria are met, if not met for the original OCO value. An adjusted OCO value will then result in the increased number of RCs in the bioreactor.
- A checkup or adjustment of the size of the bioreactor until criteria for the flow velocity and AMD residence time are met.
- Calculation of the capital cost, NPV, and an estimated time of effective operation. The last is calculated based on the available carbon present in the W/M organic medium divided by the safety factor of four. The safety factor is used because of the uncertainty whether the organic carbon present in the medium is entirely available for the SRB.

As indicated in Figure 4, these activities can be processed along two routes:

1. The direct path (shapes drawn with the solid lines) that does not require any adjustments for corrections for OCO values, residence time, and flow velocity.
2. A path that requires an iterative PHREEQCI MODELING (shapes drawn with the dashed lines), but does not need an adjustment for the flow velocity and the residence time.

Both routes can be supplemented by the adjustment for the AMD residence time and the flow velocity (shapes drawn with the short dashed lines).

The design of the bioreactor as presented in Figure 2 required following route number 2 supplemented with the adjustment for the flow velocity. Such a bioreactor would consist of four RCs whose capital cost would be $32,326, and the NPV for a 30-year operational period would be $51,429. This bioreactor, flowing at the rate of 1 gallon per minute (gpm), would be capable of lowering concentration of the most recalcitrant metal, Zn, from 18 milligrams per liter (mg/L) to 5 mg/L, which is a secondary maximum contaminant level.

CONCLUSIONS

The *BEST* simulator is a flexible tool for sizing SRB bioreactor systems, predicting water quality along the length of the bioreactors, and performing simple economic analyses to support engineering trade studies. Depending on the AMD feed composition, comparison of the required bioreactor size for removing only metals that form sulfides versus the required size to precipitate all metals is a significant element of the design process. Laboratory testing is very valuable for determining anticipated SRR and OCO values for available substrates for input into the simulator. The *BEST* simulator was developed and formulated so that it could be operated by a user with minimum modeling experience. The *BEST* simulator operation requires basic knowledge of the Excel™ program and some familiarity with the geochemical model PHREEQCI.

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REFERENCES

Canty, M. 1999. "Overview of the Sulfate-Reducing Bacteria Demonstration Project under the Mine Waste Technology Program." Mining Engineering, June 1999. pp. 61-80.

Desmier, R., B.C.T. Macdonald, T.D. Waite, and M.D. Melville. 2003. "Passive Treatment of Acid Sulfate Soil Drainage Using a Closed Tank Reactor. In Proceedings from the Sixth International Conference on Acid Rock Drainage. The Australian Institute of Mining and Metallurgy, Cairns, Australia.

Gusek, J., C. Mann, T. Wildeman, and D. Murphy. 2000. "Operational Results of a 1,200 gpm Passive Bioreactor for Metal Mine Drainage, West Fork, Missouri." In Proceedings from the Fifth International Conference on Acid Rock Drainage, pp. 1133-1137. Society for Mining, Metallurgy, and Exploration, Inc. Denver, CO.

MSE Technology Applications. 2004. Final Report-Improvements in Engineered Bioremediation of Acid Mine Drainage. The Mine Waste Technology Program report for U.S. EPA, Cincinnati, OH.

Parkhurst, D.,L. and C.A.J. Appelo. 1999. User’s Guide to PHREEQC (Version 2) – A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations. U.S. Geological Survey, Water-Resources Investigations Report 99-4259.

Zaluski, M.H., J.M. Trudnowski, M.A. Harrington-Baker, and D.R. Bless. 2003. "Post-Mortem Findings on the Performance of Engineered SRB Field-Bioreactors for Acid Mine Drainage Control." In Proceedings from the Sixth International Conference on Acid Rock Drainage. The Australian Institute of Mining and Metallurgy, Cairns, Australia.

Zaluski, M.H., B.T. Park, and D.R. Bless. 2004 "Designing Sulfate-Reducing Bacteria Field Bioreactors Using the *BEST* Model." In Proceedings from Remediation of Chlorinated and Recalcitrant Compounds. The Fourth International Conference, Monterey, CA.