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CONSTRUCTED WETLANDS THAT EMPHASIZE SULFATE REDUCTION: A STAGED DESIGN PROCESS AND OPERATION IN COLD CLIMATES

Thomas R. Wildeman[1,2], Laura A. Duggan[2], Judith L. Bolis[2], James Gusek[1]

1. Denver Knight Piesold, Suite 800, 1600 Stout Street, Denver, CO 80202 (303-825-6914)

2. Colorado School of Mines, Golden CO 80401 (303-273-3642)

ABSTRACT

At the Big Five wetland, which was built to treat drainage from a metal mine, encouraging results have been attributed to sulfate reduction. Cu and Zn are reduced to below detection limits of 0050 mg/L, Fe is reduced by at least 90 % to below 3 mg/L, and the pH is raised from below 3 to above 6. When it was realized that treatment was primarily through microbial processes within the substrate and that plants were not needed to insure success, the concept of taking a process through design stages has been a development that has accelerated the use of these reactor cells for acid drainage remediation. In staged design, laboratory experiments are initiated to determine what would be reasonable substrate materials for remediation of a particular water. When a reasonable substrate is found, bench scale experiments are initiated as the next stage in the design. In these studies, removal efficiency, permeability, and flow are analyzed to see if a candidate substrate will support sulfate reduction and be hydraulically reasonable. Using this design method, an acid drainage of pH 2.5 was raised to a pH of above 7. The total heavy metals concentration in this drainage was above 900 mg/L and Cu, Zn, Fe, and Mn were all reduced by 99 %.

Determining how well these anaerobic cells operate in the winter is done at the pilot plant site in Idaho Springs, CO. It's been found that over the last four winters, those cells that emphasize anaerobic removal within the substrate have operated continuously and effectively the year round. Winter operation is added by the fact that the water temperature of the acid drainage is always between 14 and 16 ° C, and the cell can be readily insulated from the cold. Activity of the sulfate reducing bacteria may decrease during the winter, however it appears that organic complexation of metals helps to maintain low concentrations of metals in the effluent.

INTRODUCTION

For contaminant removal, use of a constructed wetland allows one to maximize one or two processes over the many that occur in a natural wetland. Consequently, over the last decade, constructed wetlands have received considerable attention (Hammer, 1989). The Big Five Pilot Wetland in Idaho Springs, CO, was built to demonstrate the removal of heavy metals from a metals mine drainage (Wildeman and Laudon, 1989, Howard et al., 1989). The original design and construction was completed in the summer and fall of 1987 (Howard et al., 1989), and consisted of three cells 18.6 m^2 in size. From the beginning, Cell A, which contained a mushroom compost substrate performed better than Cells B and C which contained a substrate consisting of equal parts of peat, aged manure, and decomposed wood. Selected values for the mine

TABLE 1. CONCENTRATIONS (mg/l) OF METALS, PERCENT REDUCTION OF METALS, pH, AND FLOW RATES (GALLON/MINUTE) IN THE BIG FIVE MINE DRAINAGE AND WETLAND CELL OUTPUT WATERS.*

Water Sample	Mn	% red.	Fe	% red.	Zn	% red.	Cu	% red.	pH	flow rate
INITIAL OPERATION			December 11, 1987							
Mine Drainage	34		32		10.6		1.02		2.8	
Cell A	27	21	18	45	7.8	27	0.44	57	4.6	1.0
Cell B	33	1	24	26	9.8	12	0.89	12	3.1	1.0
Cell C	34	0	22	32	9.6	9	0.91	10	3.3	1.0
			August 19, 1988							
Mine Drainage	26		37		8.1		0.91		2.9	
Cell A	25	4	20	56	<0.1	100	0.17	81	5.5	0.51
Cell B	26	0	15	59	6.1	24	0.55	40	3.2	0.24
Cell C	25	4	11	70	5.8	28	0.38	58	3.5	0.34
CELL A MODIFICATION		February 21, 1989								
Mine Drainage	27		32		9.3		0.56		3.0	
Cell A	22	19	12	63	4.5	52	<.05	100	5.1	0.28
Cell B	27	0	28	13	6.1	34	0.82	0	3.4	0.31
Cell C	25	7	31	3	7.2	23	0.26	53	3.5	0.32
			May 6. 1989							
Mine Drainage	30		42		10.4		0.76		3.0	
Cell A	33	-10	28	33	7.8	25	<.05	100	3.5	0.92
Cell B	27	10	10	76	6.2	40	0.36	53	3.0	0.83
Cell C	29	3	9	79	6.4	38	0.46	39	3.2	0.81
			August 1, 1989							
Mine Drainage	32		43		9.4		0.75		2.9	
Cell A	31	3	39	9	5.2	45	<.05	100	4.1	0.30
Cell B	26	19	24	44	6.6	30	0.46	39	3.1	0.48
Cell C	32	0	18	58	4.8	48	0.09	88	3.7	0.43
CELL B MODIFICATION		October 3, 1989								
Mine Drainage	35		46		9.9		0.66		3.2	
Cell B-Up	34	3	39	15	9.3	6	0.59	11	3.5	0.29
Cell B-Down	23	34	8	83	0.8	92	<.05	100	6.5	0.16
Cell E	24	31	<1	100	<0.1	100	<.05	100	6.3	0.062
			November 5, 1989							
Mine Drainage	32		38		8.7		0.61		2.9	
Cell B-Up	31	3	17	55	8.4	3	0.48	21	3.6	0.22
Cell B-Down	20	38	<1	100	6.0	31	<.05	100	5.9	0.24
Cell E	20	38	<1	100	<.1	100	<.05	100	6.5	0.11
			January 13, 1990							
Mine Drainage	31		33		9.0		0.59		2.9	
Cell B-Up	30	3	33	0	8.9	1	0.49	17	3.2	0.21
Cell B-Down	27	13	12	64	8.1	10	0.44	25	3.2	0.20
Cell E	28	10	10	70	<.1	100	<.05	100	6.0	0.10

*The area of Cells A, B, and C is 200 ft^2; the area of Cells B-Up, B-Down, and E is 100 ft^2.

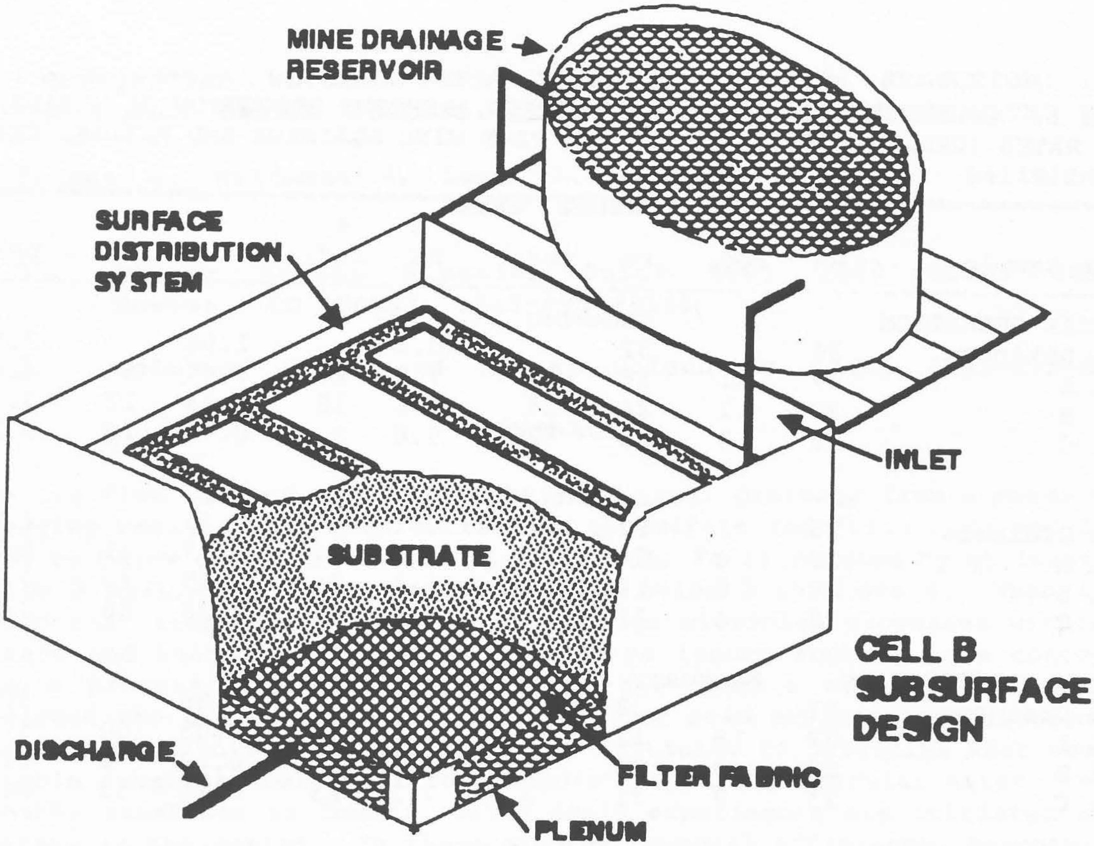

Figure 1. A cut-a-way view of the modification done to Cell B. Two identical subcells were constructed: the figure shows a downflow configuration.

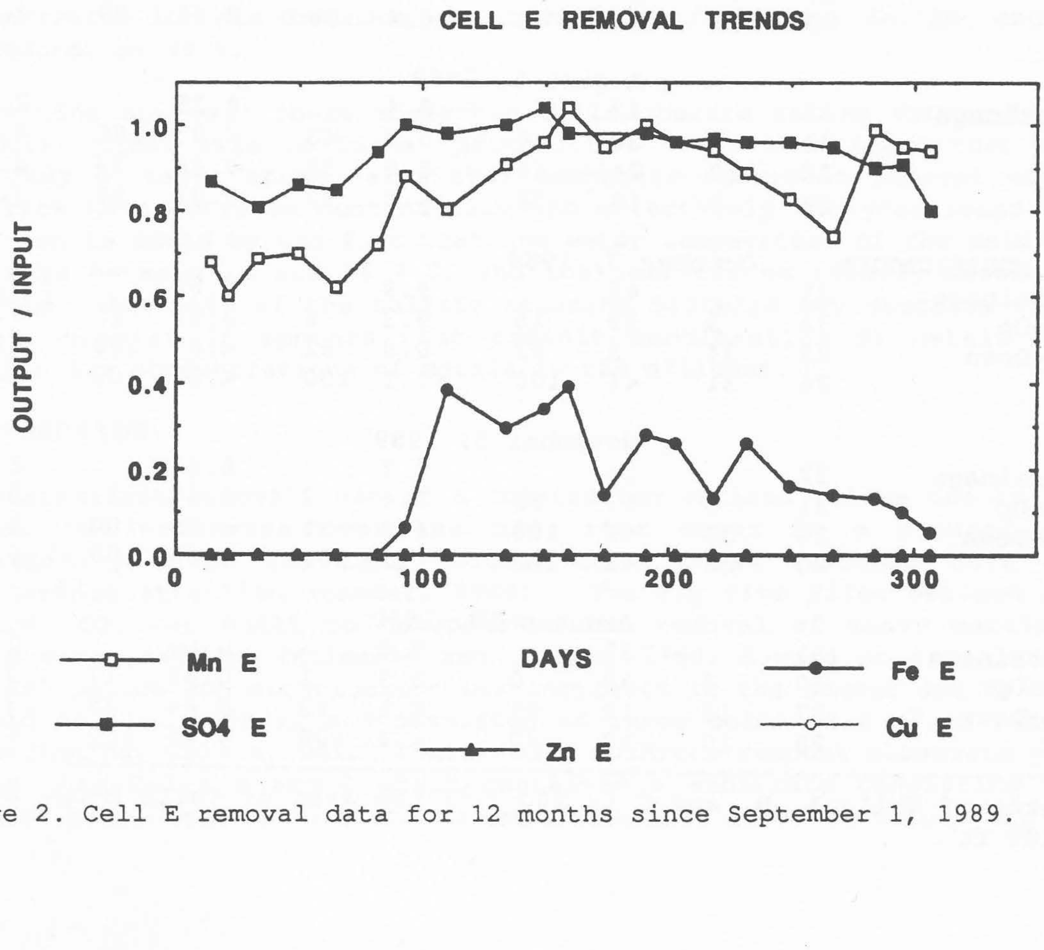

Figure 2. Cell E removal data for 12 months since September 1, 1989.

drainage input and the cell outputs are shown in Table 1. The results of various studies lead to the conclusion that sulfate reduction followed by sulfide precipitation is the primary heavy metal removal process (Machemer and Wildeman, 1991).

In August, 1989, Cell B was remodeled to incorporate a number of design features that should improve contact with the substrate. The original cell was divided into two identical cells that can be operated in either the upflow or downflow configuration. It is comparable to a trickling-flow filter process. Values on removal of Mn, Fe, Cu, and Zn and increases in pH for Cell B-Upflow and Cell B-Downflow are given in Table 1. Just as for the original Cell A design, removal has been impressive from initiation of flow.

When Cell B was remodeled, Cell E was constructed using the original substrate from Cell B. It was designed to operate as a downflow, subsurface wetland. Construction was completely accomplished with materials found locally. From the initiation of flow on September 1, 1989, removal of Cu, Zn, and Fe has bee 100 %, and Mn removal averages 25 %. Removal results are given in Table 1, and are shown for a full 12 months in Figure 2. Again, laboratory experiments have confirmed that sulfate reduction with subsequent precipitation of metal sulfides is the predominant removal process in Cell E (Machemer and Wildeman, 1991)).

Once it was determined that sulfate reduction and subsequent precipitation of sulfides was the primary removal process, project objectives concentrated on how to employ knowledge of the biochemistry of sulfate reduction in the wetland design process. This is currently being done through the use of two ideas particularly suited to wetlands that employ anaerobic removal processes such as sulfate reduction: The limiting reagent concept, and staged design of wetlands.

THE LIMITING REAGENT CONCEPT

In the design of wetlands for wastewater treatment, there is a strong emphasis on determining the loading factor which gives an indication of how large a wetland should be to remove the contaminants of concern (Hedin and Nairn, 1990). This can be stated as the amount of square feet of wetland per gallon per minute of water to be treated or as the grams of contaminant removed per day per square meter of wetland (Hedin and Nairn, 1990). In our experiences, at the Big Five site typical measures of loading factor do not seem to explain the removal of metals even though heavy metals such as Cu and Zn are reduced by greater than 99 % (Wildeman, et al., 1990). We have discovered that a key factor in sulfate reduction is to insure that the optimum microenvironment for sulfate-reducers must be maintained. The most important environmental conditions are reducing conditions and a pH of around 7. Since the wetland cell is receiving mine drainage of pH below 3 and Eh of above 700 mV, the water can easily overwhelm the microenvironment established by the anaerobic bacteria. This leads to the limiting reagent concept for determining how much water can be treated, as an alternative to the use of typical loading factors.

Consider the following precipitation reaction:

$$Fe^{2+} \quad + \quad S^{=} \quad \text{------>} \quad FeS$$

At high flows of mine drainage through the substrate, sulfide will be the limiting reagent, the microbial environment will be under stress to produce more sulfide, the pH of the microenvironment will drop, and removal will be inconsistent. At low flows of mine drainage through the substrate, iron will be the limiting reagent, the excess sulfide will insure a reducing environment and a pH near 7, the microbial population will remain healthy, and removal of the metal contaminants will be consistent and complete. Using this idea, loading factors should be set to insure that the heavy metal contaminants are always the limiting reagents. The question then is how much sulfide can a colony of sulfate-reducing bacteria produce per cubic cm of substrate per day?

Recent studies suggest that a reasonable figure for sulfide generation is 300 nanomole sulfide / cubic cm / day (Reynolds, et al., 1991, McIntire and Edenborn, 1990). This number, the volume of the wetland cell, and the metals concentrations in the mine drainage are used to set the flow of mine drainage through the wetland cell. Using this concept in a subsurface wetland cell to determine the loading factor has resulted in year round complete removal of Cu and Zn, a nearly complete removal of Fe, and a rise in pH from 3 to 6 (Machemer, et al., 1990, Machemer and Wildeman, 1991).

STAGED DESIGN OF WETLANDS

Upon determining that precipitation of metals by sulfide generated from sulfate-reducing bacteria is the important process, it was realized that establishing and maintaining the proper environment in the substrate is the key to success for removal. This means that processes operating on the surface of the wetland are not that important. In particular, plants are not necessary in a wetland emphasizing subsurface processes. If this is the case, then a large pilot cell, such as was built at the Big Five site, is not necessary to determine if a wetland that emphasizes anaerobic processes for removal will work. Consequently, study of wetland processes and design of optimum systems can proceed from laboratory experiments to bench scale studies to design and construction of actual cells. We call this "staged design of wetland systems".

In current laboratory studies, culture bottle experiments are used for fundamental studies on how to establish simple tests to determine the production of sulfide by bacteria, and of what substrate will provide the best initial conditions for growth of sulfate-reducing bacteria. (Reynolds, et al., 1991) In these experiments, the production of sulfide at 18 °C has been 1200 nanomole/gm of dry substrate/day. Currently, the culture bottle experiments are being repeated using S-35 to establish that all the sulfide is produced by microbial processes.

Other laboratory studies have concentrated on the practical aspects of wetland design. One industrial concern was interested in whether cyanide concentrations typical of milling-waste effluents would kill sulfate-reducing bacteria. Culture bottle tests showed that sulfate reduction was retarded until the concentration of total cyanide was below 10 mg/L. Another industrial concern wanted to determine whether Cu concentrations above 100 mg/L would kill or retard sulfate-reducing bacteria. Culture bottle tests conducted over the course of one month showed that sulfate reduction was still vigorous at heavy metal concentrations above 100 mg/L.

Table 2. Constituent concentrations in mg/L in the Quartz Hill Tunnel mine drainage and in effluents from the bench scale tests.

Sample	Days Operated	Mn	Fe	Cu	Zn	SO_4	pH
		<------	Concentration in mg/L			--------->	
Mine Drainage	24	80.	630	48	133	4240	2.4
Cell A	24	0.94	1.6	0.06	0.27	450	7.4
Cell B	24	0.91	1.9	<0.05	0.17	770	7.5
Cell C	24	0.99	1.0	<0.05	0.16	412	7.4
Mine Drainage	43	80.	640	50	135	4300	2.5
Cell A	43	0.97	0.87	<0.05	0.18	1080	7.2
Cell B	43	0.64	0.96	<0.05	0.24	660	7.4
Cell C	43	1.6	0.46	<0.05	0.14	1180	7.2
Mine Drainage	71	70.	820	70.	101	NA	2.6
Cell B	71	0.48	0.40	<0.05	0.21	NA	8.0
Cell C	71	1.6	0.40	<0.05	0.25	NA	7.9

For bench scale studies, plastic garbage cans are used to conduct experiments to provide answers necessary to the design of a subsurface cell. (Bolis et al., 1991) Typical design parameters include determining the optimum loading factor, substrate, cell configuration, and the permeability of the substrate. In a bench scale study just recently completed, garbage cans filled with substrate were used to determine whether using the sulfide generation figure of 300 nanomole sulfide/cubic cm of substrate/day could be used to set the conditions for treating severely contaminated effluent that flows from the Quartz Hill Tunnel in Central City, CO. Contaminant concentrations for this drainage are shown in Table 2. Using the limiting reagent concept described above and the amount of substrate contained in the garbage can, flow could not exceed one milliliter/minute to insure that sulfide would always be in excess. Contaminant concentrations from the outputs of three different bench scale cells are shown in Table 2. For cell A the mine drainage was passed through the cell with no delay. For cell B the substrate was soaked with city water for one week before mine drainage started passing through the cell. For Cell C, the substrate was inoculated with an active culture of sulfate-reducing bacteria and soaked with city water for one week before mine drainage started passing through the cell. Preparations on cells B and C were done to insure that there would be a healthy population of sulfate-reducing bacteria before mine drainage flowed through the substrate. All cells were run in a downflow mode of the mine drainage through the substrate. In all three cells removal of Cu, Zn, Fe, as well as Mn is greater than 99 %. The increase in pH is from about 2.5 to above 7. These results were consistently maintained for over ten weeks of operation.

The substrate used was a mix of 3/4 cow manure and 1/4 planting soil. The results from cells B and C show that the cow manure has an indigenous population of sulfate-reducing bacteria that are quite active. Inoculation with an active culture of bacteria is not necessary in this case. Also, since the results from cell A are comparable to those of cells B and C, the population of sulfate reducers can withstand immediate exposure to severe mine drainage and still produce sufficient quantities of sulfide. The key to good initial activity is to endure that the flow of mine drainage is low enough that its low pH does not disturb the micro-environment established by the bacteria.

Another feature of the results shown in Table 2 is that Mn is removed in all three cells. Typically, Mn is the most difficult contaminant in mine drainage to remove (Machemer and Wildeman, 1991, Machemer, et al., 1990, Hedin and Nairn, 1990, Wildeman, et al., 1990, McIntire and Edenborn, 1990). It is usually presumed that removal of Mn has to be achieved by raising the pH to above 7, and then introducing the effluent into an aerobic wetland cell so that Mn will be oxidized to MnO_2. Removal in an anaerobic cell must be as Mn(II). Analysis of possible species at a pH above 7, suggest that removal could be as MnS or $MnCO_3$. In this case, it is hypothesized that $MnCO_3$ is the precipitate because it is more insoluble than the sulfide. In either case, a key to Mn removal in an anaerobic cell appears to be the ability to raise the pH of the effluent above 7. If raising the pH to above 7 can be consistently achieved, then all the contaminants in mine drainage can be removed in one anaerobic cell.

OPERATIONS DURING THE WINTER

The last four winters have allowed observations on how well wetland cells operate during the winter. Not all of the cells have kept operating during the winter. Two key factors allow winter operation: The mine drainage water is about 12 to 15 °C the year round, and portions of the site are in winter sun throughout the day. Below, the winter success of each cell is described.

Cell A has operated continuously through all four winters. This is the case even when the flow was cut back from 4 L/min to 1 L/min. Three reasons can be given for the winter success of Cell A:

1. It is continuously in the sun.
2. More of the water flows through the substrate rather than across the surface.
3. The inlet is small and insulated so the energy within the water is not lost.

When the flow into Cell C was cut back to 1 L/min, it has frozen over the last two winters. This cell is more shaded during the winter. Also the dense growth of Typha in Cell C inhibits solar radiation from reaching the substrate-water interface. In addition, Cell C still has the original rock box inlet. This inlet allows much of the water energy to be lost.

Cell D was built in the summer of 1989 and in both winters it has frozen. This is primarily a surface flow cell and the depth of the substrate is only 0.5 meter. Also it is not well insulated.

Cell E has worked well over the last two winters. It is shallow, but is a subsurface flow cell. The important feature that keeps Cell E operating during the winter is that much of the water that enters the cell flows across the surface and over the spillway. This excess water insulates the substrate.

The modified B Cells have operated over the winter primarily because the surface of the cells was insulated with hay and plastic. In fact, the temperature of the outlet only dropped 4 to 5 °C during January and February. On Cell B-Upflow the new outlet installed in the spring of 1990 was not insulated. It froze in December, 1990 and the cell had to be turned off for the winter. Cell B-Downflow did have an insulated outlet, and it has continued operations throughout both winters.

Guidelines for Winter Operation

From these observations, a number of guidelines can be established for insuring the operation of wetland systems in cold winter climates.

- Use the thermal energy within the mine drainage water to best advantage. Insure that delivery systems are insulated. Keep inlet structures small and insulated.
- Place wetland cells so they receive winter sun. If this cannot be completely achieved, at least insure that outlets are in winter sun.
- Insulate the top of the cell with excess mine water as in Cell E or with hay and plastic as in the B Cells.
- Insulate the outlet and allow a method for the effluent to flow away from places where it could cause freezing problems. This is especially important if it is planned to sample water during the winter.
- If possible, design subsurface flow systems such as Cells B and E. The thermal energy within the substrate will aid operation, whereas in a surface flow system the waters are exposed to the elements.

CONCLUSIONS

Using constructed wetlands for wastewater treatment is still a developing technology. However, the results from the Big Five Pilot Wetland that was funded by the Emerging Technology Program (ETP) of the U. S. EPA shows promising removal of heavy metals and increase of pH for acid mine drainage. Conclusions from the project include:

1. Toxic metals such as Cu and Zn can be removed and the pH of mine drainage can be increased on a long term basis.
2. The major removal process is sulfate reduction and subsequent precipitation of the metals as sulfides. Exchange of metals onto organic matter can be important during the initial period of operation.
3. A downflow, trickling filter style of configuration achieves the best contact of the water with the substrate.
4. Removal efficiency depends strongly on loading factors. For bacterial-sulfate reduction, a volume-instead of a surface-loading capacity works better. Using the limiting reagent concept also gives good removal results.
5. Permeability of the substrate is a critical design variable for successful operation. Using laboratory and bench-scale tests, a good indication of the soil permeability in a constructed wetland can be determined.
6. Solutions to problems such as plugging of plumbing by ferric hydroxides and freezing of discharge lines during winter have to be designed and constructed into the passive nature of wetlands to achieve long term operation.
7. Since the removal process is primarily bacterial, a staged deisgn process works well. Laboratory experiments gives good indications of

the removal capacities of substrate materials; bench-scale tests give flow versus removal values; and pilot scale experiments can be sized so that systems are the size of a typical wetland module. completion of the project consists of constucting more modules.

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REFERENCES

Bolis, J. L., Wildeman, T. R., and R. R. Cohen, 1991, "The Use of Bench Scale Permeameters for Preliminary Analysis of Metal Removal from Acid Mine Drainage by Wetlands," Proceedings of the 1991 National Meeting of the American Society of Surface Mining and Reclamation, ASSMR, Princeton, WV, pp. 123 - 136.

Reynolds, J. S., Machemer, S. D., Wildeman, T. R., Updegraff, D. M., and R. R. Cohen, 1991, "Determination of the Rate of Sulfide Production in a Constructed Wetland Receiving Acid Mine Drainage" Proceedings of the 1991 National Meeting of the American Society of Surface Mining and Reclamation, ASSMR, Princeton, WV, pp. 175 - 182.

Machemer, S. D., and Wildeman, T. R., 1991, Organic Complexation Compared with Sulfide Precipitation as Metal Removal Processes from Acid Mine Drainage in a Constructed Wetland," Jour. of Contaminant Hydrology, in press.

Hedin, R. S., and Nairn, R. W., 1990, "Sizing and Performance of Constructed Wetlands: Case Studies," Proceedings of the 1990 Mining and Reclamation Conference", West Virginia Univ Publications, Morgantown, WV, pp. 385-392.

Machemer, S. D., Lemke, P. R., Wildeman, T. R., Cohen, R. R., Klusman, R. W., Emerick, J. C., and Bates, E. R., 1990, "Passive Treatment of Metals Mine Drainage through Use of a Constructed Wetland," In EPA Document No. EPA/600/9-90-037, pp. 104-114.

Wildeman, T. R., Machemer, S. D., Klusman, R. W., Cohen, R. R., and Lemke, P., 1990, Metal Removal Efficiencies from Acid Mine Drainage in the Big Five Constructed Wetland," Proceedings of the 1990 Mining and Reclamation Conference, West Virginia Univ Publications, Morgantown, WV, pp. 417-424.

McIntire, P. E., and Edenborn, H. M., 1990, The Use of Bacterial Sulfate Reduction in the Treatment of Drainage from Coal Mines," Proceedings of the 1990 Mining and Reclamation Conference", West Virginia Univ Publications, Morgantown, WV, pp. 409-415.

Hammer, D. A., 1989, "Constructed Wetlands for Wastewater Treatment," Lewis Publishers, Chelsea, MI, 831 pp.

Howard, E. A., Emerick, J. C., and Wildeman, T. R., 1989, The Design, Construction, and Initial Operation of a Research Site for Passive Mine Drainage Treatment in Idaho Springs, Colorado," In "Constructed Wetlands for Wastewater Treatment", Lewis Publishers, Chelsea, MI, pp. 761- 765.

Wildeman, T. R., and Laudon, L. S., 1989, "The Use of Wetlands for Treatment of Environmental Problems in Mining: Non-Coal Mining Applications," In "Constructed Wetlands for Wastewater Treatment", Lewis Publishers, Chelsea, MI, pp. 221-230.