Responding to Minnesota's Regulatory Sulfate Standard for Wild Rice Waters

Lucinda B. Johnson[1], Meijun Cai[1], Chan Lan Chun[1, 2], Adrian Hanson[2], George Hudak[1],
Igor Kolomitsyn[1], Shashi Rao[1], Beth Bernhardt[1], Tobin Deen[1, 2], Jerald Henneck[1]

[1]*University of Minnesota Natural Resources Research Institute, Duluth, MN 55811;*
[2]*University of Minnesota Department of Civil Engineering, Duluth MN 55812*

Abstract

A common challenge for industries and communities in Minnesota (USA) is a restrictive standard of 10 mg/L sulfate for waters associated with wild rice. This poses a substantial challenge for wastewater treatment facilities and businesses. Reverse osmosis and nanofiltration are expensive options and generate substantial waste. The work reported here is a suite of alternative materials and technologies for removing sulfate cost-effectively with reduced waste handling. This program encompasses development of new materials, barite precipitation, and biological reduction of sulfate to sulfide with iron dissolution by electrolysis. Minnesota's stringent regulatory standard will require application of multiple technologies.

Key words: sulfate, remediation, Minnesota (USA), water quality regulation, wild rice

Introduction

High levels of sulfate can alter sulfur cycling in natural systems, particularly freshwater. In northeast Minnesota, sulfate loading is largely associated with mining operations and increased interest has emerged for developing technologies to treat the high levels of sulfate in the circumneutral water (Bavin and Berndt 2008). A set of empirical observations of aquatic vegetation communities and water quality in Minnesota (USA) lakes in the 1940s found that few populations of wild rice (*Zizania palustris*) grew in areas with aqueous sulfate concentrations greater than 50 mg/L, and healthy populations were associated with water column concentrations of 10 mg/L or less (Moyle 1944). These observations led the state legislature to promulgate a Class 4A water quality standard, Minnesota Rule 7050.0224, which sets upper limits of water column SO_4 concentrations to 10 mg/L in waters with "wild rice present". Wild rice is a widely distributed annual emergent grass that provides habitat and food for waterfowl and wildlife. Wild rice (also known as manoomin), is economically and culturally important to the Ojibwe peoples, whose creation story is linked to this species (Schuldt et al. 2018). Declines in wild rice productivity and extent have implicated elevated sulfate levels, and the potential causal mechanism is associated with elevated concentrations of sulfide in the sediment pore waters (Myrbo et al. 2017; Pastor et al. 2017). Pore water sulfide is controlled by microbially mediated sulfate reduction, with sediment total organic carbon (TOC) and sediment iron concentrations serving as the dominant controlling variables (Pollman et al. 2017). The Minnesota Pollution Control Agency (MPCA) has proposed a revision to the sulfate rule, which would have taken into consideration site-specific TOC and Fe concentrations (MPCA 2019); however, an administrative law judge rejected this revision in 2018, therefore, as of March 2019, the restrictive 10 mg /L limit is still the current standard.

Chemical, biological and physical processes can reduce sulfate concentrations to below the US EPA drinking water standard of 250 mg/L. However, sulfate reduction below 200 mg/L primarily relies on membrane-based technologies such as reverse osmosis (RO) or nanofiltration (NF), which generate large volumes of liquid waste that is technically challenging and costly to manage (Aubé et al. 2018, mining waste); Bolton & Menk, Inc (2018, municipal wastewater).

The B&M report stated that the removal of sulfate from water in Minnesota using RO is especially difficult because the climate does not lend itself to evaporation of the RO reject, and the State has a prohibition against injection of the concentrate. This appears to make Zero Liquid Discharge (ZLD) the required option if RO is used. In a technology review for MN, Barr Engineering and BMI (2018) concluded that RO and NF were the most desirable technologies in the suite of technologies considered.

In comparison to the material- and energy-intensive RO and NF, biological sulfate reduction is a promising and more economical alternative for sulfate removal, and this process has been applied beneficially in both active (off-line sulfidogenic bioreactors) and passive treatment systems (constructed wetlands, permeable reactive barriers; Miao et al. 2012; Neale et al. 2018). However, the performance of these biological sulfate treatment systems is highly variable, which is particularly true in passive biological treatment. In a large part, this is due to technical challenges of supplying defined substrates (*e.g.* ethanol, lactate, hydrogen gas as electron donors) for promoting and sustaining biological sulfate reduction (Garcia-Saucedo et al. 2008; Eljamel et al. 2009).

A solution to achieving Minnesota's wild rice standard will likely be based on a portfolio of technologies, including physical, chemical, and biological processes. The Natural Resources Research Institute (NRRI) is working on such a portfolio, starting with testing of a bioreactor system (Hudak et al. 2017; not discussed further herein), and more recently focused on four different pathways (fig. 1). Below we briefly discuss 1) development of a new natural modified peat material that utilizes anion exchange properties for capturing sulfate at low pH; 2) preliminary testing of a barite precipitation process; and 3) development of a bioelectrochemical reactors.

New Material Development: Anion-Exchange

We have developed peat granular products designed to remove potentially toxic metals from mine and storm waters (Kolomitsyn 2017a, b, Kolomitsyn 2019). We are also developing a new peat-based material with introduced anion exchange properties that can be used as a weak anion exchanger for treatment of sulfate in acidic solutions. Peat does not naturally have any anion exchange capacity and by itself exhibits a nitrogen content of only 2.57%. Chemically, peats are largely organic material, which contain hemicellulose, cellulose, lignin, humic and fulvic acids. Lignin, humic and fulvic acids are naturally occurring phenol-containing polymers. Natural peat is susceptible to a hydrolysis reaction under pH 8.0 and higher. The hydrolysis releases humic acids into the solution and, therefore, colors the water. It also leads to destruction of the peat structure. In order to create a stable material, peat was granularized and treated with heat,

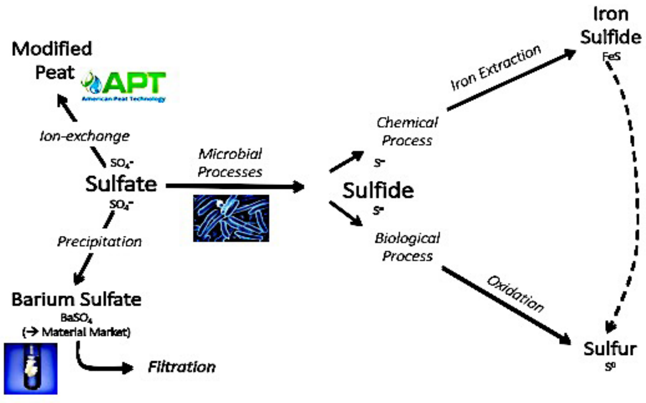

Figure 1 *Sulfate remediation program to meet Minnesota (USA) water quality standard for wild rice waters.*

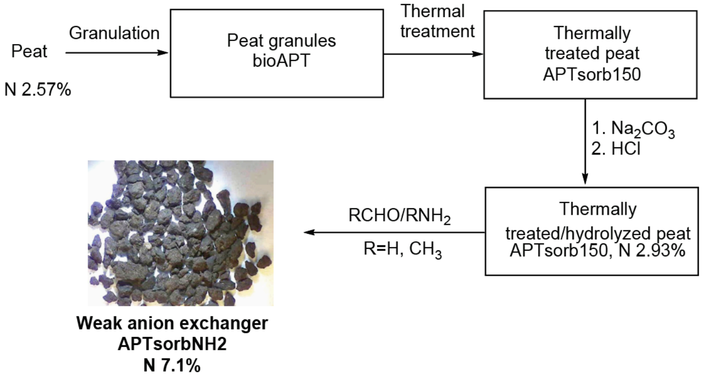

Figure 2 *General scheme to produce peat-based weak anion exchange (APTSorbNH2) by using modified Duff reaction conditions.*

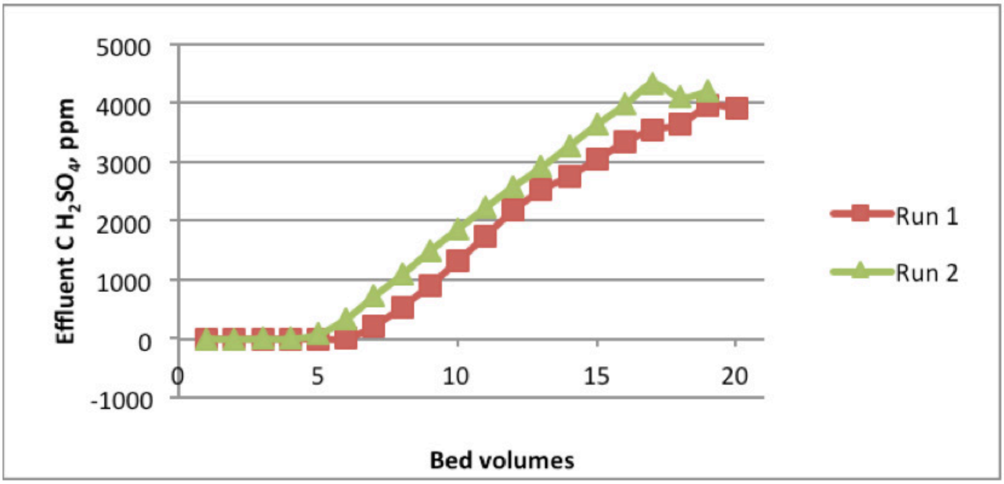

Figure 3 *Column data of sorption of H_2SO_4 on a peat based weak anion exchanger APTSorbNH2.*

leading to the development of APTsorb150 peat granules (fig. 2). These granules are stable without losing structural integrity at pH=10.2. When Na_2CO_3 pre-treated APTsorb150 granules were treated with a solution of HCl, and then subjected to the Duff reaction (Duff 1934, Grimblat 2016) with hexamethylenetetramine, the nitrogen concentration increased from 2.93% to 7.1% and the introduced anion exchange capacity rose from 0 mEq/100 g to 80 mEq/100g.

The total anion exchange capacity of APTsorbNH2 and the weak anion exchange nature of the introduced amine groups on the surface of peat granules were demonstrated through bench-scale column test using 4500 mg/L solution of H_2SO_4 in water (fig. 3). As can be seen from the Run 1 results depicted in fig. 3 the APTsorbNH2 granules for the column bed volumes 1-6 removed virtually all of the H_2SO_4 acid that was introduced into the column. The breakthrough was reached starting with bed volume 7, indicating that the anion exchange sites on the peat APTsorbNH2 granules began to saturate with the SO_4^{2-} anions. We detected that a portion of the acid introduced into the column remained in the aqueous solution and exited the column. At about bed volume 19, the concentration of the effluent plateaued at around 4000 mg/L, showing that all of the anion exchange sites on the peat granules had become saturated with the SO_4^{2-} anions.

Granules were regenerated by washing with a 0.1N solution of NaOH, followed by washing with deionized water until

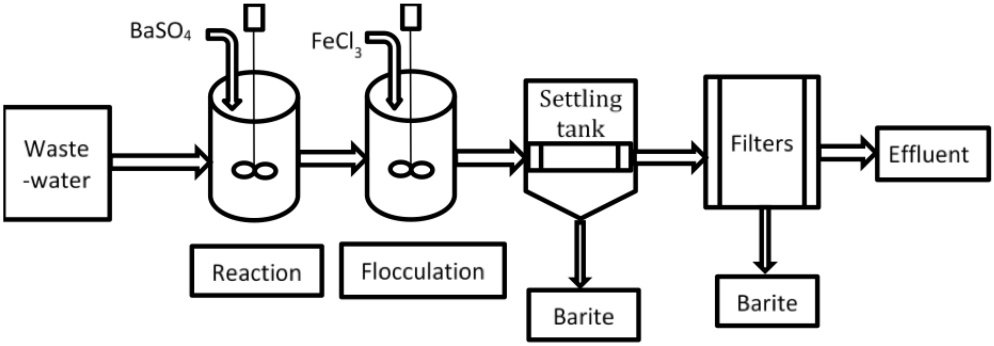

Figure 4 *Schematic of the barite precipitation process tested.*

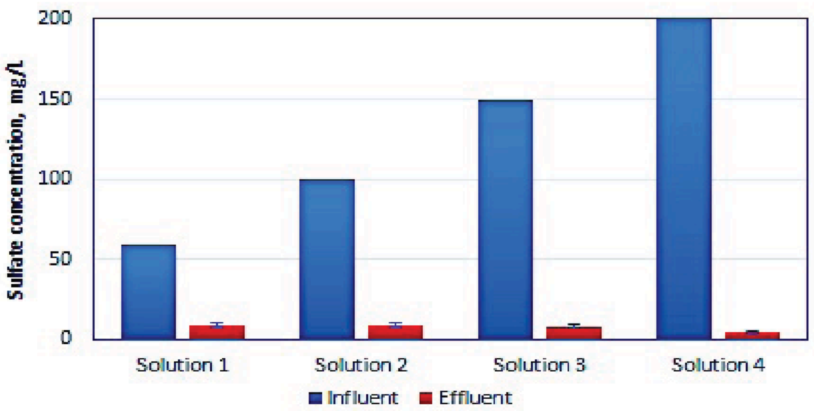

Figure 5 *The changes of sulfate concentration before and after chemical precipitation using four different wastewater sources.*

the effluent reached a neutral pH. A 4500 mg/L solution of H_2SO_4 in water was then introduced to the column (Run 2) and the loading cycle was repeated. The curves for the Run 1 and Run 2 are very similar, demonstrating that the performance by the APTsorbNH$_2$ granule media was repeatable after the media was regenerated using 0.1N NaOH solution. These data suggest that nitrogen introduced to peat granules under modified Duff reaction conditions exhibited amine like properties. The resulted new peat granular material, APTsorbNH2, behaves like a weak anion exchanger and the properties are retained even after media regeneration.

Chemical Precipitation, Barite Process

Since sulfate readily precipitate with barium ion, barite ($BaSO_4$) precipitation has been applied to treat high strength sulfate waste streams and has been extensively studied in the mining industry (Bosman, et al., 1990, Hlabela, et al., 2007, Swanepoel, et al., 2012). Barium salts such as barium sulfide, barium carbonate, barium hydroxide are known to remove sulfate from the solution from high levels (>1000 mg/L) to 100 mg/L. However, to date, no detailed studies have characterized the effect of the barite precipitation on sulfate removal from municipal wastewater. We have examined the potential of barite precipitation processes for achieving SO_4 concentrations below 10 mg/L in municipal wastewater containing SO_4 concentration below 200 mg/L.

A general schematic of the barite precipitation process is provided in Fig. 4. This process consists of the following unit operations: source water is chemically treated by the addition of barium salts in a rapid mixer with standard turbine paddles. Flocculatants such as ferrix and polymers are added to assist in forming larger and denser barite particles. We tested the effect of flocculant dose and mixing intensity to generate flocs of the suspended barite precipitates. The settling characteristics of the treated water were determined in settling column. The overlying water was filtered through a dual media filter to remove colloidal solids and floc fines. For each of the process approaches described above, performance data were collected and monitored for trends indicative of sulfate removal from the municipal wastewater. Data included conductivity, pH/temperature, turbidity, barium chemical doses, flocculant doses, mixing speed, sulfate concentration for the feed and the discharge flow streams. Other data collected, and monitored includes run times and sulfate recoveries.

Sulfate removal from municipal wastewater was initially studied using batch tests to establish baseline conditions for sulfate removal (molar concentrations, timing, mixing intensity). These tests were followed by continuous tests to quantify flocculation, precipitation and filtration conditions. We have demonstrated a barite precipitation protocol to remove sulfate from <200 mg/L to below the wild rice sulfate limit of 10 mg / L (fig. 5). Barium chloride was identified as a suitable reagent for the process. The removal of sulfate ions by precipitation strongly depends on the dosage amount of barium SO_4, mixing intensity, reaction time and other lab conditions, which are essential parameters for the design of a full-scale treatment system.

We are currently optimizing the process parameters to obtain information about the viability of the process, and identify design parameters needed for the field pilot-scale test at wastewater treatment plants. Moreover, sludge disposal methods including various pre-treatment options will be evaluated based on different regulatory requirements and the leachability of barite sludge.

Bioelectrochemical Reactors

We have developed a novel bioreactor to stimulate biological sulfate reduction and simultaneously facilitate the subsequent removal of the reduced sulfide by applying iron electrolysis under low electrical potential. Batch and flow-through bioelectrochemical reactors were developed to test the effect of low voltage on the efficacy of sulfate reduction and iron sulfide formation. Experimental bioelectrochemical reactors with stainless steel electrodes were composed of creek sediment affected by mining activities (Second Creek, MN) and were fed with a synthetic mine water medium with a sulfate concentration of 1000 mg/L. The reactors were operated at 0-2V producing cathodic

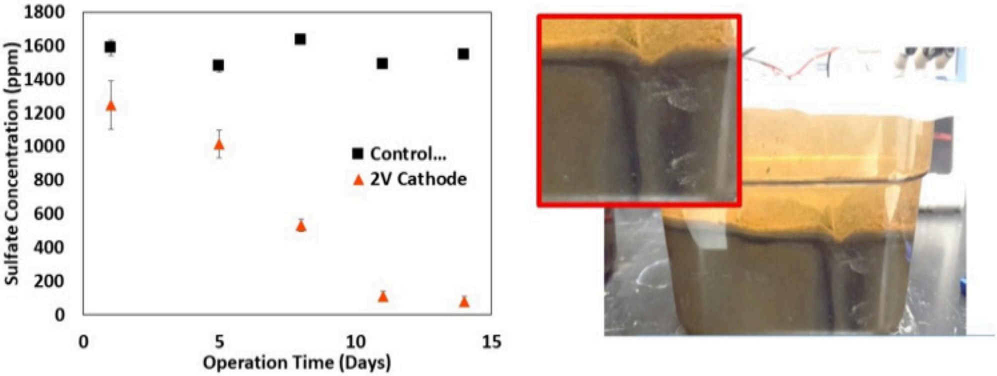

Figure 6 Change in pore water sulfate concentration at the cathode throughout the duration of sediment bioelectrochemical batch reactors operated at 2V and 0V (left) and black band precipitate formation in the reactor after 14 days of 2V applied to system (right). Black band precipitation is identified as iron sulfide through acid volatile sulfide analysis and SEM equipped with energy dispersive X-ray spectroscopy.

hydrogen and anodic iron dissolution.

The sulfur chemistry in the pore water of the reactors was assessed to determine indigenous microbial activity. The application of electrical potential resulted in active sulfate reduction in 14 days in comparison to control reactor (fig. 6). Iron sulfide formed in the reactors were examined with scanning electron microscopy and x-ray diffraction. Based on 16S rRNA amplicon sequencing analysis, the enhanced sulfate reduction appears to be associated with an increased population of sulfate reducing bacteria (*Desulfovibrio* and *SRB2*) in the response of a constant supply of hydrogen through electrolysis. In addition, the experimental results were used to validate a mathematical model of the system, which will then be used for process optimization. Sediment batch and packed-bed bioelectrochemical reactors demonstrated biological sulfate reduction enhancement, with subsequent iron sulfide capture. This work presents a proof of concept application of electrical potential to enhance the performance of biological sulfate treatment in a controlled manner.

Conclusions

We have successfully developed and patented a novel peat-based particle that can be used to remove sulfate from acidic mine water. The material can be regenerated to extend their life cycle beyond a single use. In addition, we have successfully demonstrated that barium chloride can be used to reduce sulfate concentrations from ≈100 mg/L to below 10 mg/L. Finally, we have successfully completed bench-scale tests of a bioelectrochemical process to remove sulfate from sediment pore water with the simultaneous production of iron sulfide. Further pilot testing is ongoing to extend the range of sulfate concentrations of the influent waters, to extend the applications from municipal wastewater treatment systems to industrial applications. We envision a set of cost-effective solutions will be available within the next few years to address Minnesota's unique wild rice standard.

Acknowledgements:

We wish to thank the State of Minnesota for funding the Minerals & Water Innovation Initiative. American Peat Technology is a partner in the development of new peat-based anion exchange materials. Matthew Santo provided valuable assistance with the chemical precipitation experiments.

References

Aubé, B, Lameres, M, Sang, SL (2018) A pilot comparison of sulphate removal technologies at Neves Corco. Pages 983-990, In: Wolkersdorfer, et al. (editors) 11th ICARD/IMWA/MWD Conference Proceedings. Pretoria, SA.

Bavin T, Berndt, M. (2008) Sources and fate of sulfate in NE Minnesota Watersheds: A mineral coordinating committee Progress Report MN-DNR.

Bolton & Menk, Inc. and Barr Engineering Company (2018) Analysing Alternatives for Sulfate Treatment in Municipal Wastewater. 84 pp. https://www.pca.state.mn.us/sites/default/files/wq-rule4-15pp.pdf. (Accessed March 3, 2019).

Bosman, DJ, Clayton, JA, Maree, JP, Adlem, CJ (1990). Removal of sulphate from mine water with barium sulphide. Intl J Mine Water, 9(1-4): 149-163.

Duff, JC, Bills, EJ (1934) Reactions between hexamethylenetetramine and phenolic compounds. II. Formation of phenolic aldehydes. Distinctive behavior of p-nitrophenol. J. Chem. Soc. 1305-8.

Eljamel, O, Jinno, K, Hosokawa, T. (2009) Modeling of solute transport and biological sulfate reduction using low cost electron donor. Environ Geol 56:1605-1613.

Garcia-Saucedo, C, Fernández, FJ, Buitrón, G, Cuervo-Lopez, FM, Gomez, J. (2008) Effect of loading rate on TOC consumption efficiency in a sulfate reducing process: sulfide effect in batch culture. J Chem Toxicol Biotechnol 83:1648-1657.

Grimblat, N, Sarotti, AM, Kaufman, TS, Simonetti, SO. (2016) A theoretical study of the Duff reaction: insights into its selectivity. Organic & Biomolecular Chemistry 14(44): 10496-10501.

Hlabela, P, Maree, J, Bruinsma, D. (2007) Barium carbonate process for sulphate and metal removal from mine water. Mine Water Environment, 26(1): 14-22.

Hudak, G, Estepp, L, Schoff, P. (2017). The MnDRIVE Transdisciplinary Project Implementation of Smart Bioremediation Technology to Reduce Sulfate Concentrations in NE Minnesota Watersheds. Univ MN Duluth. Retrieved from: http://hdl.handle.net/11299/190404.

Kolomitsyn, IV, Jones, PW, Green, DA. (2017a) Particulate sorption medium prepared from partially decomposed organic matter. US Patent # 9,649,620, May 16, 2017.

Kolomitsyn, IV, Jones, PW, Green, DA (2017b) Particulate sorption medium prepared from partially decomposed organic matter. US Patent # 9,561,489, February 7, 2017.

Kolomitsyn, IV, Jones, PW, Green, DA (2019) Particulate sorption medium prepared from partially decomposed organic matter for selective sorption between competing metal ions in aqueous solutions. US Patent # 10,173,213, January 08, 2019.

Miao, Z, Brusseau, ML, Carroll, KC, Carréon-Diazconti, C, Johnson, J. (2012) Sulfate reduction in groundwater: characterization and applications for remediation. Env Geochem Health 34:539-550.

Minnesota Pollution Control Agency Governor's Task Force on Wild Rice. (2019). https://www.eqb.state.mn.us/sites/default/files/documents/FINAL%20Governor%27s%20Task%20Force%20on%20Wild%20Rice%20Report%20January%203%202019%20v2.pdf.

Moyle, JB. (1944). Wild rice in Minnesota. Journal of Wildlife Management 8(3):177-184.

Myrbo, A., Swain, EB, Engstrom, DR, Coleman, JW, Brenner, J, Shore, MD, Peters, EB, Blaha, G. (2017). Sulfide generated by sulfate reduction is a primary controller of the occurrence of wild rice (*Zizania palustris*) in shallow aquatic ecosystems. J Geophysical Res: Biogeosciences 122 (11): 2736-2753.

Neale, JW, Gericke, M, Muhlbauer, R. (2018) On-site pilot scale demonstration of a low-cost biological process for the treatment of high-sulphate mine waters. Pages 164 -170, In: Wolkersdorfer, et al. (editors) 11th ICARD/IMWA/MWD Conference Proceedings, Pretoria, SA.

Pastor, J., Dewey, B., Johnson, N. W., Swain, E. B., Monson, P., Peters, E. B., & Myrbo, A. (2017). Effects of sulfate and sulfide on the life cycle of *Zizania palustris* in hydroponic and mesocosm experiments. Ecol. Appl. 27: 321–336

Pollman CD, Swain, EB, Bael, D, Myrbo, A, Monson, P, Shore, MD. (2017). Evolution of sulfide in shallow aquatic ecosystem sediments. J. Geophy. Res: Biogeosci. 122. https:// doi.org/10.1002/2017JG003785

Schuldt, N. et al., 2018. "Expanding the Narrative of Tribal Health: The Effects of Wild Rice Water Quality Rule Changes on Tribal Health Fond du Lac Band of Lake Superior Chippewa Health Impact Assessment," Fond du Lac Band of Lake Superior Chippewa, http://www.fdlrez.com/RM/downloads/WQSHIA.pdf.

Swanepoel, H, de Beer, M, Liebenberg, L. (2012) Complete sulphate removal from neutralised acidic mine drainage with barium carbonate. Water Practice and Technology, 7(1).