Low-concentration sulfate removal from wastewater with barite precipitation technology

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Extended Abstract

The State of Minnesota in the US contains abundant natural resources like iron ore and wild rice. The state produces about 40 million t of high-grade iron ore annually, contributing roughly 75% to the total U.S. iron ore production. Also known as one of the world's largest cultivated wild rice producers, Minnesota yields over 3 thousand t of wild rice annually. However, the growth of wild rice is highly sensitive to sulfate levels, which are highly influenced by iron mining activities. Research has shown a substantial decline in wild rice populations when sulfate concentrations exceed 10 mg/L.

To protect wild rice, which is an important part of the Ojibwe peoples' creation story, the State of Minnesota set a stringent sulfate standard of 10 mg/L for wild rice waters in 1973 (Minnesota Pollution Control Agency, 2023). Achieving this standard poses a substantial challenge for small industries and municipalities due to a lack of cost-effective technologies. Membrane-based technologies, such as nanofiltration or reverse osmosis, are capable of treating water to conform with the Minnesota wild rice water sulfate standard; however, these technologies often require high capital and operation costs. Recognizing the need to develop cost-effective sulfate treatment alternatives, our project team investigated the feasibility of chemical precipitation technologies to reduce sulfate to below 10 mg/L via a combination of laboratory and field pilot testing.

Chemical precipitation using lime, aluminum or barium chemicals is often used to treat mine drainage or wastewater with relatively high and medium concentrations of sulfate (Bowell, 2004; de Beer et al., 2010, Norris, 1972). Typically, sulfate was precipitated as gypsum ($CaSO_4$) in the lime treatment process, reducing concentrations to approximately 1,500 mg/L or higher. Further refinement to levels below 200 mg/L involved processes like ettringite or barium precipitation (Runtti et al., 2018). However, there is a gap in research regarding water treatment at low sulfate concentrations (< 200 mg/L), especially aiming to achieve levels below 10 mg/L. Additionally, most treatment processes have been designed for mining drainage (Bologo et al., 2012; Hlabela et al., 2007; Kefeni et al., 2015), which typically contained little or negligible organics. To explore the feasibility of the chemical precipitation process in treating sulfate at low concentrations and to quantify the operational parameters, a treatment system has been developed based on barite chemical precipitation reactions with barium chloride dehydrate followed by ferric chloride flocculation to remove sulfate from municipal wastewater (Fig. 1).

The lab scale batch and continuous tests examined various process parameters, including the selection of chemicals used, chemical dosage rates, the necessity of nucleation promotion, mixing rates, residence rates, and the influence of temperature. Using the parameters defined from the laboratory tests, a mobile pilot system was designed and manufactured. The system comprises one reaction tank and one flocculation tank, each divided into three cells. Additionally, it includes a clarification tank equipped with inclined plates, two parallel filtration columns, and a final effluent tank for storing treated water used in column backwash. The system is controlled by two control panels, which are accessible on-site and remotely.

The pilot system was installed in a trailer and deployed in three wastewater treatment plants over summers of 2021 and 2022 to treat both domestic wastewater and a mixture of industrial and domestic wastewater at a flow rate of 4–7.5 L/min. The selection of three wastewater treatment plants was based on distinct factors: the remarkably low sulfate concentration (around 60 mg/L) in one plant, the presence of chelating organics from a paper mill in the second plant, and the utilization of a mining pit lake as the primary drinking water source for the third plant (Table 1). Pilot testing was conducted continuously at each plant for 1.5–2.5 months with a single condition tested each week.

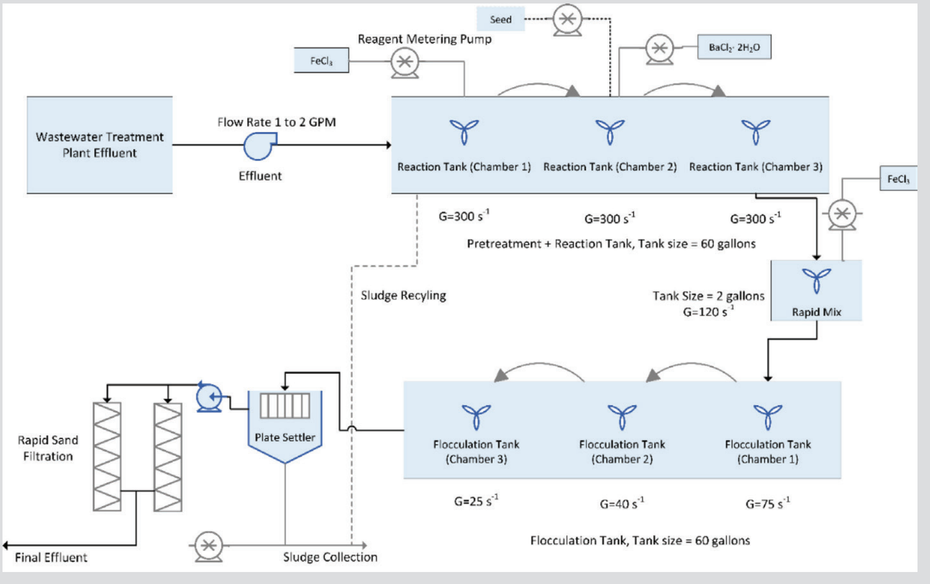

***Figure 1** The flow diagram of the pilot treatment system for sulfate reduction by barite precipitation technology*

The designed barite precipitation process successfully reduced sulfate levels from 60–350 mg/L to below 10 mg/L (Table 1), with some modifications necessary for different wastewater compositions and chemistries. For instance, an excess dosage of barium chemical and the introduction of nucleation seeds were required to treat water containing sulfate with concentrations below 100 mg/L. Additionally, the presence of organic chelates interferes with the reaction, necessitating the addition of ferric chloride to remove organic chelates prior to the precipitation reaction to effectively remove these chelates. The barite particles produced from the precipitation reaction tended to accumulate on the tank walls, forming a thick layer of scale that required frequent manual scrubbing for removal. However, the introduction of ferric chloride prior to the precipitation reaction can partially inhibit the scale built-up and also loosen the scale.

The findings from laboratory and pilot-scale testing will be key scientific and engineering foundations to develop a full-scale or industry-relevant treatment system based on barite precipitation technology in sulfate removal. Based on process and engineering design parameters derived from the pilot testing, the project team is moving toward the development of generic designs for integrating this treatment process into existing wastewater treatment facilities.

Keywords: Sulfate, wastewater, chemical precipitation, low concentrations, pilot testing

Table 1 Summary of the pilot testing performed in three wastewater treatment plants

Plant No.	Inflow water source	Inflow SO_4 concentrations, mg/L	Pilot testing conditions tested	SO_4 concentrations in effluent
1	Domestic wastewater	60	Seed dosage rates, Seed type, Overdose of barium chloride	Mostly below 10 mg/L
2	Mixture of domestic wastewater and paper mill discharge	80–120	Pretreatment $FeCl_3$ dosage rates to remove chelating organics, Seed dosage rates	Mostly below 10 mg/L
3	Domestic wastewater using pit lake water as drinking water source	170–360	Barium chloride dosage rates to achieve different concentration levels in effluent, dosage rates of $FeCl_3$ pretreatment to inhibit barite scale built-up	10, 50, 100, 150 mg/L

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