Gravel Bed Reactors: Semi-Passive Water Treatment Of Metals and Inorganics

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Abstract

Diffuse impacts to surface waters are a critical issue facing mining industries, given rigorous environmental quality standards. Many conventional treatment technologies are expensive and difficult to comply with discharge criteria. Gravel Bed Reactors (GBR™) are a versatile semi-passive treatment technology capable of addressing a variety of water quality issues through altering the geochemistry of extracted mine water. GBRs™ offer simpler, cost-effective alternatives to water treatment facilities, packed or fluidized bed reactors and the possibility to re-use waste rock as packing media. GBRs™ allow installation of smaller systems in remote, challenging environments and the potential to treat mine water at source.

Keywords: Biological Treatment, pH Adjustment, Semi-Passive, GBR™

Introduction

Managing metal and inorganic mass loading in extracted mine water and reducing diffuse impacts to surface water present key challenges to mining globally. The geochemistry of mine water can vary widely including highly acidic or alkaline pH and elevated and variable concentrations of multiple constituents. Metal cations (e.g. cadmium, lead, zinc), transition metals (iron, manganese, copper, chromium, mercury), nonmetals (e.g. sulfur, nitrogen, selenium), metalloids (arsenic, antimony) and actinides (uranium) may be present in mine water. Where these constituents are present in the geological formation of the target resource, they can be mobilized through disturbance of the material and exposure to the atmosphere and/or aerated waters. Nitrogen compounds may also be present associated with degradation products of processing (e.g. gold cyanidation) or residual waste from nitrate- and ammonia-based explosives.

A wide range of commercially available solutions exist for treatment of mine water; however, operational requirements render most conventional technologies expensive and difficult to comply with regulatory constraints, including discharge criteria. Gravel Bed Reactors (GBR™) are a semi-passive water treatment technology capable of addressing the variety of water quality issues typically encountered in mine water. To date, the treatment of metals and inorganics using GBRs™ has focused on inducing microbial and chemical processes to alter mine water geochemistry to degrade and/or immobilize problematic constituents, that have proved to be effective in reducing mass loading in treated discharges to receiving environments/surface waters and the requirement for other treatment technologies to meet discharge criteria.

Methods

A GBR™ consists of an engineered bed of gravel/media within a lined container or cell through which mine impacted water containing constituents of concern is passed and treated through addition of biological and/or chemical amendments. Mine impacted surface water or groundwater (the influent) are typically diverted through the GBR™ under natural gradients or can be pumped to the GBR™ if necessary. Depending of the contaminants to be treated, amendments such as electron donors (typically carbon substrates), electron acceptors (typically oxygen, nitrate or sulfate) and/or pH buffers (e.g. carbon dioxide) are dosed into the influent within the upgradient portion of the GBR™ to promote the desired biological and/or geochemical reactions prior to discharge of the effluent.

GBRs™ are conceptually simple and very flexible reactors that can be engineered in varying ways to treat a wide variety of contaminants close to the source water, including in remote environments. GBRs™ can be either installed below ground surface within an excavation, onsurface within a natural depression, bunded or constructed cell, or a combination of both, i.e. some portion below ground level surrounded by a bund (Figure 1).

Key components of the GBR™ system typically include (Figure 2):

- A single or composite liner with a cover and insulating layer to hydraulically isolate the gravel bed from the surrounding environment, specifically exchanges with groundwater, precipitation infiltration and/or oxygen diffusion into the GBR™.
- Gravel bed media to support the growth and activity of microbes and biofilms and provide structural integrity of the treatment cell. Engineered material may be used or waste rock crushed to a consistent particle size, where design criteria for long-term geotechnical performance and leaching are met for its re-use in the treatment cell.
- Amendment delivery system(s) comprising storage and mixing tanks, dosing pumps and associated pipework in connection with a manifold header system within the upgradient portion of the GBR™ to deliver amendments uniformly into the saturated gravel bed media.
- Monitoring wells installed in the gravel bed media to permit measurement or sampling to assess water geochemistry and GBR™ performance.
- An upgradient equalization pond, with filtration if required, may be used to dampen fluctuations in influent volumes and water geochemistry entering the GBR™, with a downgradient effluent buffer pond or tank to adjust effluent geochemistry to meet regulatory criteria for discharge to the environment, in particular realignment of dissolved oxygen, pH, suspended solids and/or temperature to ambient conditions.
- In cold climates, heating equipment may be installed to prevent freezing of influent water and amendment delivery systems and/or to enhance sub-optimal reaction rates, with the potential to improve GBR™ operational efficiency and performance in challenging environments.

Operation of the GBR™ consists of monitoring and sampling influent, effluent and GBR™ geochemical conditions (flow

***Figure 1** Example construction of a subsurface GBR™.*

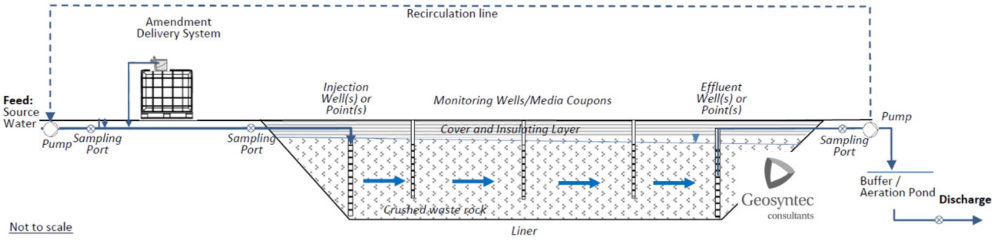

Figure 2 Schematic Cross-Section of a Typical GBR™.

and concentrations) and altering amendment dosing requirements to ensure the treatment remains in compliance with discharge criteria. Experience has shown that real-time measurement and data acquisition instrumentation linked to a programmable logic controller (PLC) with remote access may allow for more efficient GBR™ operation, permitting real-time control and adjustment of the system in response to often dynamic changes in influent conditions.

A wide variety of biological and geochemical processes can be implemented for mine water treatment in the GBR™ (e.g. Rittman & McCarty 2001, Simon *et al.* 2002, Skousen *et al.* 2017):

1. Reductive processes initiated in the presence of electron donors within GBRs™, e.g. natural organic matter, added carbon substrates:

- Biologically mediated degradation of anions (e.g. nitrate, nitrite, phosphate, chlorate, perchlorate and sulfate) to their elemental constituents under anaerobic conditions in the presence of natural or added electron donors, e.g. carbon substrates;
- Redox sensitive metals can be reduced under appropriate redox conditions from soluble forms to insoluble forms that precipitate, e.g. soluble species of hexavalent chromium ($Cr^{VI}_{(aq)}$) and selenite ($Se^{VI}_{(aq)}$) may be reduced to insoluble forms of trivalent chromium ($Cr^{III}_{(s)}$) and elemental selenium ($Se^{0}_{(s)}$);
- Transition metals (e.g. iron, manganese, copper, chromium, mercury) and divalent cations (e.g. cadmium, lead, zinc) can be precipitated as metals sulfides by inducing microbial sulfate reduction to sulfide, where sulfate is present or added in addition to electron donors.

2. Adjusting the pH of the influent water:

- Metalloids present as oxyanions (e.g. arsenate, AsO_4^{3-}) can be immobilized through shifting pH to the acidic range promoting adsorption onto charged mineral surfaces such as iron oxides or clays.
- Metals present as divalent cations (e.g. copper, zinc) can be immobilized by adsorption on mineral surfaces by shifting pH towards neutral or the alkaline range.
- Alkalinity and acid rock drainage-related issues such as acidity, can also generally be adjusted in GBRs™ through addition of various buffers and reactants.

3. Other treatment reactions:

- Phosphate induced stabilization of lead, uranium, plutonium, zinc and cadmium using Apatite II is capable of binding metals within insoluble new minerals.
- Organic constituents associated with mine operations (e.g. petroleum hydrocarbons, wastewater effluent) can be degraded with addition of electron acceptors such as oxygen nitrate or sulfate, to reduce biological oxygen demand (BOD) and chemical oxygen demand (COD) to achieve discharge criteria.

The potential to treat multiple contaminants using the same process is a key benefit of GBRs™, e.g.in anaerobic GBR™ fed with electron donors and sulfate, it could be possible to treat anions, certain redox sensitive metals and divalent metals.

The treatability of contaminants is typically determined through performance of bench-scale studies. Once the treatment reactions have been selected, the GBR™ design is governed by the mass loading of constituents of concern, the target concentrations in the effluent and the rate(s) of treatment. Estimation of the time required to reduce the influent concentrations of constituents to effluent targets at the anticipated flow rate and mass degradation/removal rate inform the hydraulic residence time required to achieve treatment goals (Vasquez *et al.* 2016).

The required amendment concentrations and frequency of dosing depends on the influent conditions, the concentrations of the constituents of interest and co-contaminants that might compete to utilize the amendments. Under-dosing of the amendments can result in incomplete treatment, so it is important to account for uncertainties by applying safety factors to the amount of amendment theoretically required to complete the treatment. However, over-dosing not only incurs unnecessary costs, but can cause undesirable reactions to occur, e.g. with excessive addition of electron donors, it is possible to generate hydrogen sulfide gas and methane. Balancing amendment addition is thus a critical element to the success of a GBR™ design. Reduced scale GBR™ pilot tests provide cost-effective means to refine key design parameters and inform full scale implementation (Figure 3).

GBR™ Applications

GBRs™ have been used to treat industrial effluent and mine water since the late 2000s (Table 1). Pilot tests have been conducted in North America for treatment in GBRs™ of other contaminants including perchlorate.

Case Study 1 – Urban stream, California, USA

A subsurface GBR™ system was designed and implemented to treat selenium in an urban stream. Selenium had been mobilized from anoxic sediments that were exposed to atmosphere during urban development of the area. Laboratory treatability studies were conducted to evaluate potential methods to reduce selenium concentrations to <5 µg/L and reduce nitrogen loading by 50%. Initially mesocosm studies confirmed potential to reduce selenium in sediment mixed with organic material (electron donor). Subsequently, column studies were

Figure 3 *Example of a GBR™ pilot test system.*

Table 1 *Examples of Full-Scale GBR™ Applications.*

Location	Constituents Treated	Influent Conditions	Effluent Conditions	Flow rate	Media Bed Dimensions
				m³/d	m, L × W × D
Urban stream, California, USA	Selenium Nitrate	20-40 µg/L 5-15 mg/L	2.3-12 µg/L <8 mg/L	730-1,250	12 × 60 × 3
Mine site, West Virginia, USA	Selenium Nitrate	15-25 µg/L 6 mg/L	<5 µg/L <6 mg/L	270 (average)	28 × 8 × 1.5
Cement plant, USA	Arsenic Alkalinity	>300 µg/L pH ≈13.9	5-10 µg/L pH 7-8	Variable (passive)	14 × 26 × 3

performed to confirm selenium reduction in sand and gravel media, which had more predictable flow characteristics and provide GBR™ design and operational information, including electron donor selection and dosing, acceptable oxidation-reduction potential (ORP) ranges, potential for bio-fouling of the bed media, gas generation and selenium remobilization.

The GBR™ was designed as a lined excavated pit underneath the planned location of an athletic fields. The reactor bed was constructed inside a geomembrane lined containment system, overlain by 1 m soil cover. The bed media was 2 cm gravel and the electron donor sodium benzoate. The influent flow was fed by a header pipe and equalized in a distribution reservoir to discharge horizontally through the GBR™ to an outlet where the treated water was collected and then discharged.

The performance of the GBR™ under start-up, steady-state and upset testing conditions was assessed over a 14-month period (Figure 4). Following the performance evaluation, the GBR™ was operated for more than 6 years, achieving the target reductions in selenium and nitrate concentrations during steady state operations.

The GBR™ was considerably smaller than the constructed wetland alternative treatment under consideration (≈2,200 m^3 compared to ≈80,000 m^3) and enabled the overlying land to be redeveloped during treatment. The system installed relied upon regular sampling and analysis of the influent water to determine electron donor dosing, that resulted in periods of under- and over-dosing and suboptimal treatment. With real-time monitoring of the influent geochemistry, it is anticipated that this GBR™ would have consistently achieved non-detect concentrations of selenium and nitrate in the effluent.

Case Study 2 – Mine Site, West Virginia, USA

Surface water affected by selenium in newly exposed rock was treated within a GBR™ constructed beneath a parking lot to minimize disruption of mining operations. The excavation was lined with a geomembrane and gravel placed allowing the parking area to be reinstated above the GBR™. The GBR™ was designed to treat influent flows

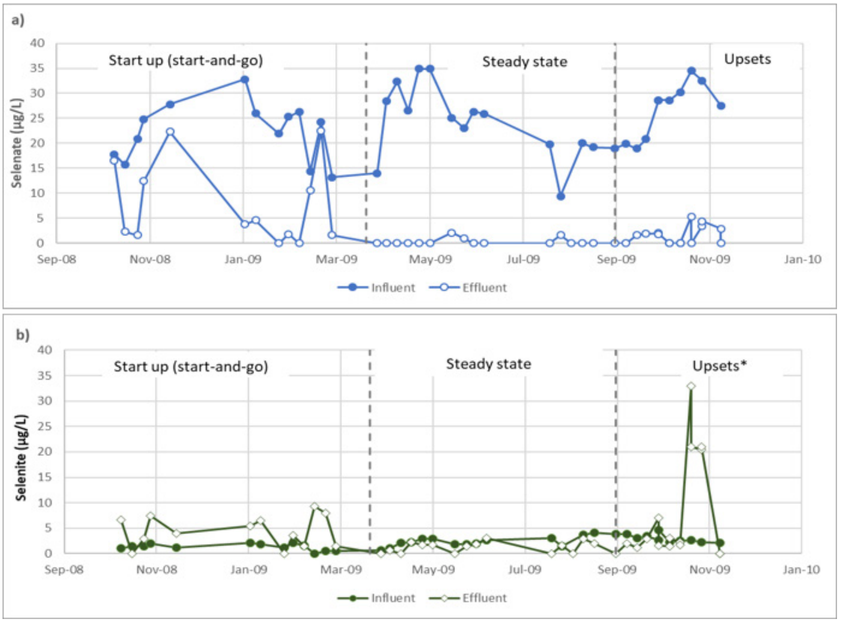

Figure 4 *Performance Evaluation for Selenium treatment in a GBR™. Upset testing involved shocking the system with hydrogen peroxide to oxidize immobilized selenium within the GBR™.*

up to 550 m^3/day, with a hydraulic residence time of 11 hours with the reactor bed. The selenium affected seep water from the newly exposed rock was collected and pumped to the GBR™, where citric acid and acetic acid (electron donors) were added to support bacteria in selenium and nitrate reduction. The GBR™ was operated for 8 months; after a 2-month stabilization period, selenium and nitrate concentrations in the effluent were consistently <5 μg/L and <6 mg/L for the remaining 6 months of operation.

Case Study 3 – Cement Plant, USA

A cement plant operated for more than 80 years in a remote area of the USA. The plant generated cement kiln dust, a fine-grained cement byproduct consisting of highly alkaline material, that was deposited in a nearby ravine. The cement kiln dust caused groundwater to become highly alkaline (pH 13.9) and leaching of metals from native soils, including arsenic, threatening water quality in a nearby pristine mountain stream.

Treatability studies indicated that the arsenic solubility and mobility was linked to the elevated pH and that by reducing pH, arsenic could be immobilized. A field pilot test was conducted to confirm the effectiveness of carbon dioxide (CO_2) diffusion at lowering pH and treating the arsenic in the groundwater.

The GBR™ comprised a 220 m wide funnel-and-gate design to capture the affected groundwater and direct it into the GBR™ under natural flow gradients. The GBR™ comprised soil-cement-bentonite retaining walls enabling the treatment bed to be constructed in place. The treatment bed comprised gravel with baffles to reduce dead flow zones within which silicone membranes were installed to diffuse CO_2 into the groundwater to neutralize the pH and promote immobilization of arsenic, chromium, lead and manganese to achieve compliance with water quality criteria. Given the remote location of this site, the GBR™ was required to be durable, require little maintenance and controllable remotely. The in-situ groundwater remedy produces no waste byproduct and the treated water is discharged directly to surface water without need for further treatment.

Conclusions

GBRs™ have been demonstrated to be capable of treating a wide range of constituents commonly present in mine water, by inducing microbiological and geochemical processes with biological and/or chemical amendments. GBRs™ are simpler, less-engineered solutions, requiring less tankage and equipment, compared water treatment facilities, packed bed bioreactors and fluidized bed reactors, while providing enhanced treatment control and requiring less space than passive treatment options (e.g. engineered wetlands, permeable reactive barriers [PRBs]). Comparatively small GBR™ systems can be installed and operated in remote locations, allowing for mine water treatment at or close to the source, and therefore offer a cost-effective, alternative option for mitigating diffuse impacts of mine water.

References

Rittman BE, McCarty PL (2001) Environmental Biotechnology: Principles and Applications. McGraw-Hill Education

Simon FG, Meggyes T, McDonald C (2002) Advanced Groundwater Remediation: Active and Passive Technologies. Thomas Telford Publishing

Skousen J, Zipper CE, Rose A, Ziemkiewicz PF, Nairn R, McDonald LM, Kleinmann RL (2017) Review of Passive Systems for Acid Mine Drainage Treatment. Mine Water and the Environment 36:133—153. https://doi.org/10.1007/s10230-016-0417-1

Vasquez Y, Escobar MC, Neculita CM, Arbeli Z, Roldan F (2016) Biochemical passive reactors for treatment of acid mine drainage: Effect of hydraulic retention time on changes in efficiency, composition of reactive mixture, and microbial activity. Chemosphere 153:244–253. https://doi.org/10.1016/j.chemosphere.2016.03.052