

# Passive Solar Photocatalytic Treatment in Mining Process-affected Water

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## Abstract

H2nanO Inc. has developed SolarPass, a floating reactive barrier comprised of buoyant photocatalyst beads that provides a passive, light-activated treatment process for target contaminants, while simultaneously blocking volatile emissions. Recently, H2nanO validated the efficacy of SolarPass for in-situ treatment of mining tailings water through an outdoor pilot-scale system in Alberta, Canada. Under natural sunlight illumination, target contaminants were degraded, including volatile sulfurous compounds and organics, while simultaneously reducing emissions by >70%. These results demonstrate that the novel SolarPass process can address diverse challenges with mining-influenced waters and provides an effective solution for passive tailings and process water management and remediation.

**Keywords:** Photocatalysis, Passive Treatment, Tailings, Sulfur, Organics

## Introduction

Globally, vast amounts of mining process-affected water are accumulated in tailings ponds which may have an impact on the local environment, community health, and mine water resources. Typically, treatment of contaminants in mining effluents requires chemical additives or capital-intensive separation technologies. These methods are often operationally complex, energy-intensive, and require a high degree of maintenance oversight to operate successfully. Additionally, fugitive volatile emissions and odours can be released from surface of tailings ponds, affecting the local air quality. Due to the scale of these tailings ponds, the elimination of these emissions and odours is a challenge that is not effectively addressed by conventional technologies.

To this end, H2nanO Inc. has developed SolarPass, a novel self-assembling floating reactive barrier (FRB) comprised of buoyant photocatalyst ceramic beads similar to those studied in Leshuk *et al.*, 2018. SolarPass provides a passive sunlight-activated treatment process to degrade target contaminants while simultaneously acting

as a barrier towards volatile emissions from the mining process-affected water (Figure 1). This in-situ photocatalytic barrier can be deployed and collected in new or existing ponds for continuous oxidative treatment of persistent mining contaminants without the need for chemical or electrical inputs. Furthermore, as the photocatalyst beads are not consumed, they may be recovered from the pond once treatment is complete, for potential re-use elsewhere. This in-pond retrofit provides the ability to quickly and directly intercept and treat volatiles and contaminants without additional land, energy, or operational resources.

Previous work has validated the efficacy of using floating photocatalysts for the treatment of environmentally persistent naphthenic acids in mining process-affected water using natural sunlight UV-radiation at the bench-scale (Leshuk *et al.* 2018). Additionally, literature studies have demonstrated the widespread applicability of photocatalysis to treat mining-related wastewater and tailings including but not limited to the removal of cyanide (Augugliaro *et al.* 1999), arsenic (Lu *et al.* 2019), and selenium (Holmes and Gu

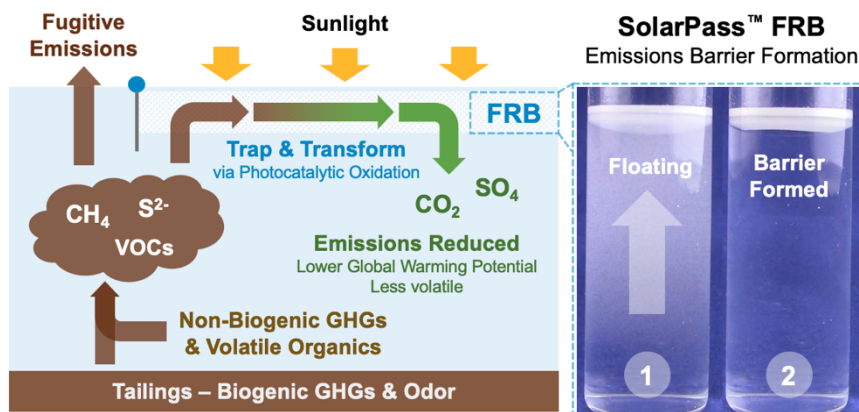


Figure 1 SolarPass™ FRB floats to form a layer at the water surface, blocks emissions and passively transforms compounds by oxidation photocatalytically using sunlight.

2016). Expanding on this prior work, H2nanO recently validated the efficacy of the SolarPass system for in-situ treatment of mining tailings through an outdoor pilot-scale system in Alberta, Canada (June to September, 2020). Under natural sunlight illumination, the efficacy of the SolarPass FRB was investigated for the simultaneous treatment and capture of volatile organic compounds (VOC) and reduced sulfur compounds (RSC). Toluene was investigated as a representative VOC using bench-scale experiments to validate the reaction products, and an open-tank pilot-scale experiment to demonstrate its retention via the SolarPass barrier. Reduced sulfur compound treatment was investigated at the pilot-scale using a closed-cell reactor for accurate quantification of the emission retention efficiency for hydrogen sulfide (H<sub>2</sub>S) gas. Additional experiments were performed and are detailed in forthcoming publications.

## Methods

A preliminary investigation of toluene treatment via the SolarPass FRB process was performed at the bench-scale using the apparatus illustrated in Figure 2. A solution of 1.5 L of 3.5 mg/L toluene in DI water and premeasured amount of catalyst were added to a glass closed-cell reactor (2.5 L total volume). To control the extent of UV exposure, the sides of the reactor were covered with aluminum foil such that the only opening for UV light was a round quartz glass

window (8.7 cm diameter) in the stainless-steel reactor lid. Prior to treatment the catalyst beads coalesced for 3h, forming a floating layer at the water surface (0.2-1 cm thick), after which the headspace volume was purged tenfold with compressed air. Pre-treatment of the purge gas was performed using a drying trap to remove moisture (the activated carbon trap is sensitive to humidity), an activated carbon trap to remove trace hydrocarbons, and a 1% w/v. sodium hydroxide scrubber to re-humidify the air while simultaneously removing any carbon dioxide (CO<sub>2</sub>). Initial and final samples of the headspace were taken using a thermal decomposition tube (ATD tube) and foil gas bag (1 L). Initial and final liquid samples of 110 mL were also taken. Aqueous samples were analysed for toluene and alkalinity (bicarbonate as CaCO<sub>3</sub>) and the headspace samples were analysed for toluene and CO<sub>2</sub> (gas). Analysis was performed by ALS Environmental (Waterloo, ON), a CALA certified laboratory.

An open tank reactor (30 m<sup>2</sup> open surface area) with direct exposure to the local environmental conditions was used to obtain the pilot-scale toluene treatment results (Figure 3). A solution of 15 m<sup>3</sup> of tailings pond water (water depth of 60 cm) dosed with 750 mL of toluene was added to the reactor and SolarPass catalyst was added to achieve an FRB layer thickness of 0.2-1 cm. The toluene flux was determined by the concentration in the beam length using open

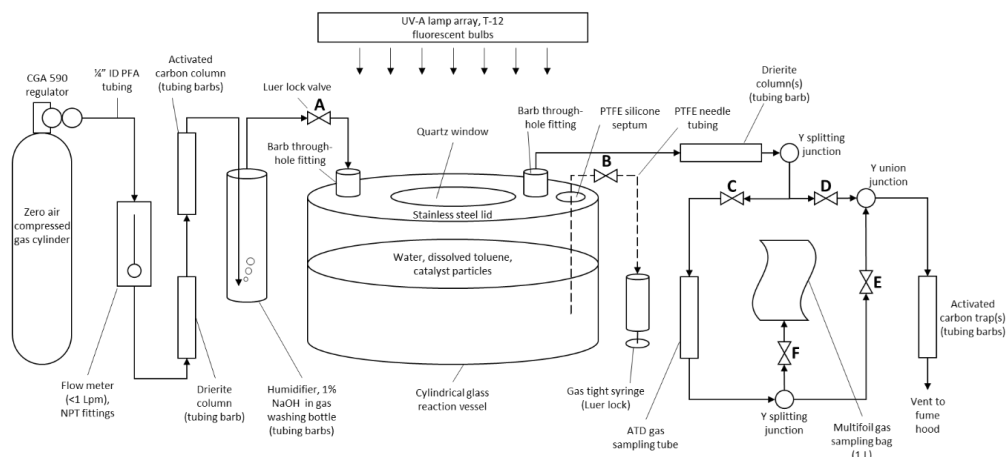


Figure 2 Bench-scale apparatus for preliminary toluene treatment study.

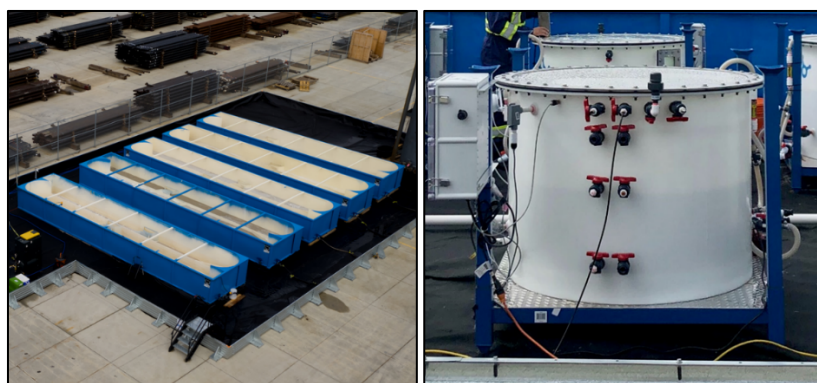


Figure 3 Open tank (left) and closed reactor (right) used for the pilot-scale treatability studies of toluene and sulfur compounds.

path Fourier transform infrared (OP-FTIR) spectrometry and applied to the open surface area of the reactors.

For the pilot-scale volatile sulfur compound experiments, a polypropylene closed-cell reactor (650 L total volume), equipped with a UV-transparent acrylic lid (Figure 3), was filled with 530 L of tailings pond water (water depth of 60 cm) and dosed with sodium sulfide ( $\text{Na}_2\text{S}$ ) to achieve an initial sulfide concentration 84-130 mg/L sulfide ( $\text{S}^{2-}$ ). The initial pH of the solution was adjusted to 8.5-9 an initial  $\text{H}_2\text{S}$  signal of 500 ppmv would be present in the reactor headspace. A SolarPass catalyst loading was used to obtain a layer of 0.2-1 cm thick. Headspace  $\text{H}_2\text{S}$  concentrations were measured using a Ventis

MX4 handheld gas meter. Aqueous sulfide concentrations were analysed according to the standard method for total dissolved sulfides (SM 4500D). Aqueous sulfite was measured according to a colorimetric test referenced from established protocols in literature (Dasgupta *et al.* 1980). Sulfate was analysed using the standard turbidimetric method (SM 4500E). Total sulfur was determined using a two-part analysis following pre-treatment with 0.1 mL of 1 M zinc acetate solution and centrifugation (5 min at 15,000 rpm) to separate the sulfide species (as zinc sulfide precipitate) from the remaining aqueous sulfur. The precipitated zinc sulfide was quantified using the SM 4500D method, and the total sulfur content of the supernatant

(excluding sulfide) was analysed using inductively coupled plasma optical emission spectrometry (ICP-OES) (Whaley-Martin *et al.* 2020).

## Results

Prior to quantifying the emission mitigation efficacy of the SolarPass FRB for volatile organic carbon species, bench-scale experiments were performed to validate the photocatalytic treatment of toluene and determine the oxidation reaction products. At the lab-scale, aqueous toluene ( $3120 \pm 13 \mu\text{g/L}$ ) was passively oxidized via photocatalysis to below detection limits ( $<0.5 \mu\text{g/L}$ ) after 2 weeks of UVA exposure (simulated sunlight). Notably, there was no statistically significant change in the gas-phase toluene concentration ( $13.7 \pm 3.8 \mu\text{g/m}^3$  initial and  $22 \pm 7.4 \mu\text{g/m}^3$  final) and  $>99.9\%$  of the toluene remained in the aqueous phase, demonstrating at a lab-scale the VOC emission retention efficacy of the SolarPass FRB. Of the toluene that remained in the aqueous phase,  $>50\%$  was fully oxidized to  $\text{HCO}_3^-$  and  $\text{CO}_2$ , illustrated below in Figure 4. Any unaccounted-for carbon is assumed to be a non- $\text{CO}_2$  organic oxidation intermediate that remained in the aqueous phase.

Following the validation of the SolarPass FRB for VOC emission retention and treatment at the bench-scale, a pilot-scale study

was performed to validate the emission blocking efficacy in an open-tank system under natural sunlight and weather conditions. At elevated aqueous toluene levels 100-450x (to enable detection using the OP-FTIR apparatus), the SolarPass FRB decreased the toluene gas flux by 72% (Figure 5) when compared to a catalyst-free control. These results, combined with the lab-scale treatment study, demonstrate that the SolarPass FRB is a suitable solution for passive VOC emission containment and treatment in tailings ponds.

In addition to VOC's, the efficacy of the SolarPass technology was demonstrated for the retention and treatment of odorous sulfur compound emissions from tailings ponds. At the pilot-scale,  $\text{Na}_2\text{S}$  was added to the closed reactor ( $84\text{-}130 \text{ mg/L S}^{2-}$ ) and the pH was adjusted to 8.5-9 such that the amount of sulfate expected to be produced by the treatment would be distinguishable above the background sulfate levels naturally already present in the water. Figure 6 highlights the sulfur balances during the photocatalytic process using the SolarPass FRB (left) and a photolysis control (solar illumination without catalyst). Within the timeframe of the experiment, the photocatalytic oxidation process converted 76% of the aqueous sulfide to non-volatile sulfate. Sulfite was also

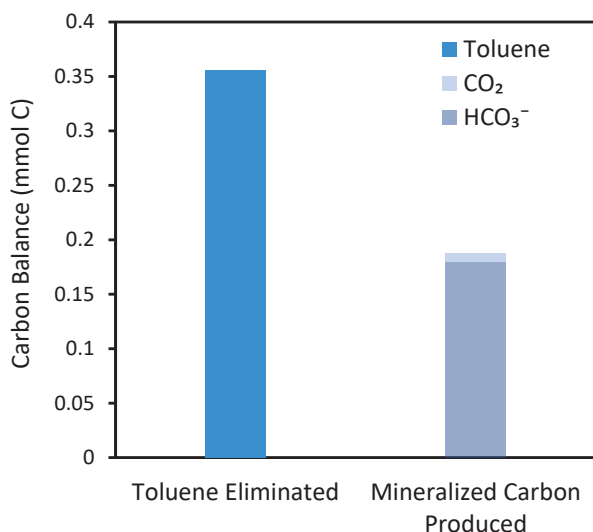


Figure 4 Carbon balance for the photocatalytic oxidation of toluene via the SolarPass FRB.

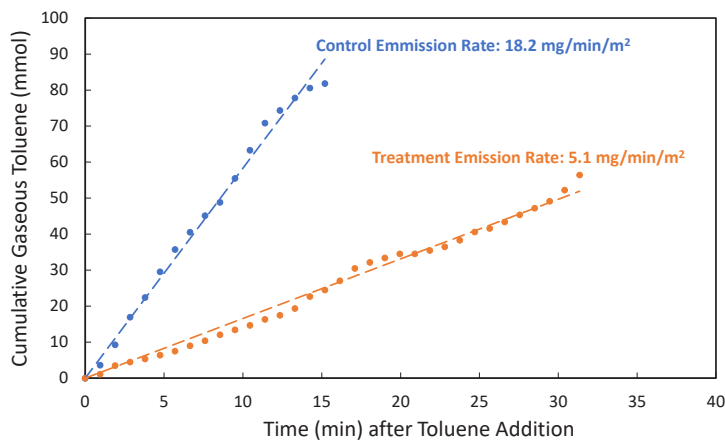


Figure 5 Emission mitigation efficacy of the SolarPass FRB for toluene.

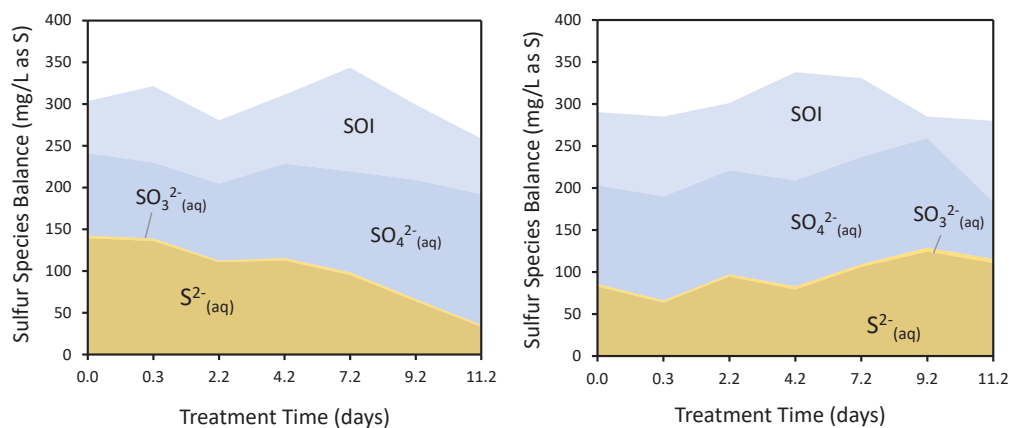


Figure 6 Sulfur balance comparison between the photocatalytic oxidation of aqueous sulfide via the SolarPass FRB (left) and a photolysis control (right).  $S^{2-}$  represents the total dissolved sulfide concentration including  $S^{2-}$ ,  $HS^-$ , and  $H_2S_{(aq)}$ .

present as an oxidation reaction intermediate and the concentration decreased throughout treatment. Due to the complexity of aqueous sulfur chemistry, the unaccounted for sulfur was proposed to be a mixture of uncharacterized sulfur oxidation intermediates (SOI) (Whaley-Martin *et al.* 2020). Negligible sulfur losses from the aqueous phase were observed as the total sulfur remained constant at  $320 \pm 25$  mg/L, indicating a closed mass balance.

Comparing the headspace  $H_2S$  concentration in both the SolarPass treatment reactor and the photolysis control, there was an average decrease in  $H_2S$  emissions of 88% when using the SolarPass FRB (Figure 7).

Notably, there is a substantial decrease in the  $H_2S$  headspace concentration for both the control and the treatment reactor by 263 h. This is likely due to the added oxygen from sampling and humid environment in the closed headspace resulting in some gas-phase oxidation of  $H_2S$  or  $H_2S$  re-absorption by condensation droplets formed inside the reactor slow release of the  $H_2S$  through the lid-sealing interfaces. Coupled with the aqueous sulfide treatment results above, simultaneous photocatalytic treatment and emissions containment of volatile reduced sulfur compounds for tailings ponds was achieved at the pilot-scale.

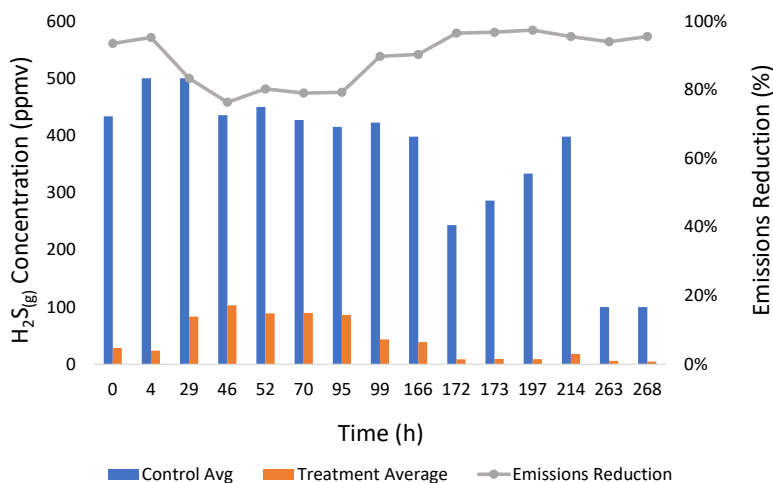


Figure 7 Emission Mitigation Efficacy of the SolarPass FRB for  $H_2S$  Compared to a Photolysis Control.

## Conclusions

As a standalone process or part of a larger treatment system, SolarPass shows promise as a low-cost platform for photocatalytic treatment of mine water contaminants. Using toluene as a representative VOC, >99.9% was oxidized using SolarPass at the bench-scale (>50% mineralization) and the gas flux was reduced by >70% in an open-tank pilot study. Additionally, using SolarPass at the pilot-scale, >75% of aqueous sulfide was oxidized while on average 88% of  $H_2S$  emissions were prevented. The results of this work, and those of literature, demonstrate that the novel SolarPass process can address diverse challenges related to mining impacted waters and provides an effective solution for overall remediation, tailings water emissions reduction, and passive tailings management.

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