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Development and modelling of a steel slag filter effluent neutralization process with CO_2-enriched air from an upstream bioprocess

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Abstract

The main objective of this project was to develop a steel slag filter effluent neutralization process by acidification with CO_2-enriched air coming from a bioprocess. Sub-objectives were to evaluate the neutralization capacity of different configurations of neutralization units in lab-scale conditions and to propose a design model of steel slag effluent neutralization. Two lab-scale column neutralization units fed with two different types of influent were operated at hydraulic retention time of 10 hours. Tested variables were mode of flow (saturated or percolating), type of media (none, gravel, Bionest and AnoxKaldnes K3), type of air (ambient or CO_2-enriched) and airflow rate. One neutralization field test (saturated and no media, 2000 to 5000 ppm CO_2, sequential feeding, hydraulic retention time of 7.8 hours) was conducted for 7 days. Lab-scale and field-scale tests resulted in effluent pH of 7.5 to 9.5 when the aeration rate was sufficiently high. A model was implemented in the PHREEQC software and was based on the carbonate system, CO_2 transfer and calcite precipitation; and was calibrated on ambient air lab tests. The model was validated with CO_2-enriched air lab and field tests, providing satisfactory validation results over a wide range of CO_2 concentrations. The flow mode had a major impact on CO_2 transfer and hydraulic efficiency, while the type of media had little influence. The flow mode also had a major impact on the calcite surface concentration in the reactor: it was constant in saturated mode and was increasing in percolating mode. Predictions could be made for different steel slag effluent pH and different operation conditions (hydraulic retention time, CO_2 concentration, media and mode of flow). The pH of the steel slag filter effluent and the CO_2 concentration of the enriched air were factors that influenced most the effluent pH of the neutralization process. An increased concentration in CO_2 in the enriched air reduced calcite precipitation and clogging risks. Stoichiometric calculations showed that a typical domestic septic tank effluent with 300 mg/L of biodegradable COD provides enough biological CO_2 for neutralization of a steel slag effluent with pH of 10.5 to 11.5. A saturated neutralization reactor with no media operated at hydraulic retention time of 10 h and a concentration of 2000 ppm in CO_2 enriched air is recommended for full-scale applications.

Keywords: Steel slag filter; Neutralization; Gas transfer; Wastewater; CO2; Modelling

1 Introduction

Phosphorus removal is required for wastewater effluents discharged into sensitive environments such as lakes or upstream of a lake in the province of Quebec, Canada. For residential systems with a point discharge, a tertiary treatment criteria for total phosphorus (TP) is set at 1 mg TP/L (MDDELCC, 2017). Slag filters are efficient and economical for phosphorus removal and they could be used in isolated dwellings tertiary treatment. However, effluent pH of 11 makes its application difficult (Barca et al., 2012). These values exceed the pH discharge criteria between 6.0 and 9.5 applied for water resource recovery facilities (LégisQuébec, 2017).

This project is carried out as part of a larger project to develop a slag filter phosphorus treatment system for onsite and decentralized treatment of domestic wastewater. The main objective of this project was to develop a steel slag filter effluent neutralization process by using passive CO_2 acidification. Secondary objectives of this project were to evaluate the neutralization capacity of different configurations of neutralization units in laboratory conditions and to propose a design model of steel slag effluent neutralization. The variables tested were the aeration rate, the media used (none, Bionest, AnoxKaldnes K3 and gravel), the type of flow (saturated or percolating) and the CO_2 air concentration. A model for CO_2 transfer and calcite precipitation was developed, calibrated and validated with lab and field tests.

Two approaches were previously used for phosphorus removal from wastewater using reactive alkaline filters: treatment of a primary or of a secondary effluent. Nilsson et al. (2013a) used reactive filters with a high recirculation rate for the treatment of a primary effluent for 90 days, resulting in 40-80% phosphate removal. Claveau-Mallet et al. (2015) used a slag filter in a recirculation line within a septic tank, which increased the phosphorus removal of the septic tank. Karabelnik et al. (2012) fed primary effluent to a percolating filter followed by a horizontal saturated filter both filled by oil shale fly ash. They achieved combined removal of organic matter, nitrogen and phosphorus. It was shown that a high organic matter concentration reduced the phosphorus removal efficiency of a slag filter (Nilsson et al. 2013b), enlightening the need for a secondary treatment prior to the reactive filter for increased longevity.

Reactive alkaline filters as tertiary treatment (fed with secondary effluent) has been tested by several research teams. Slag filters have been tested as tertiary units following an aerated bed (Kõiv et al., 2016) or constructed wetlands (Barca et al., 2013). While past studies on phosphorus removal are focused on phosphorus removal efficiency and filter longevity, little attention has been given to process design of the high-pH effluent neutralization.

The originality of this project resides in the evaluation of the neutralization capacity of different configurations of neutralization units in laboratory conditions and the proposal of a mechanistic model of steel slag effluent neutralisation. The original neutralization strategy is to use CO_2 enriched air coming from a biological wastewater treatment process (Boutet et al., 2017), which is more passive and economical than using CO_2 from gas cylinders. Confined secondary treatment processes typically used in decentralized applications are expected to provide CO_2 enriched air with a concentration between 1000 and 5000 ppm.

The pH of alkaline reactive filters effluents for P removal using steel slag (Claveau-Mallet et al., 2013; Penn et al., 2016) or hydrated oil shale ash (Kõiv et al., 2010) is typically between pH 11 and 12 at the beginning of operation, and it drops progressively to 9 or less. Calcite precipitation in alkaline reactive filter neutralization is expected because of typical high calcium concentration in such effluents (Vohla et al., 2011).

1.1 Use of CO_2 for alkaline wastewater neutralization

CO_2 acidification has already been used to neutralize various wastewater streams such as ash-pond effluents, cooling water or others (Wine & Morrison, 1986). For example, a pilot-scale basic oxygen furnace slag filter effluent with pH between 11.5 and 12.0 was successfully neutralized using pure CO_2 during 2 years (Hussain et al., 2014). This filter treated lake water with phosphate concentrations between 0.25 and 0.49 mg/L. In their study, 0.01 moles of CO_2/L liquid effluent were used to reduce effluent pH between 6.5 and 8.5. The need of CO_2 was higher in the first days of operation, when the slag filter effluent pH was higher. In another study (Mayes et al., 2006), a 1500 m^2 pond of alkaline (pH>10) leachate from a steel slag storage pile was documented. Natural attenuation by ambient air CO_2 and biological activity from the wetland was observed in this pond. Calcite precipitation rate downstream of steel slag leachate was highest when the carbonate ion was a dominant constituent of alkalinity (at pH > 9.5). Estimates of calcite precipitation was made using the limestone tablet method (Mayes et al., 2006), which consists in monitoring calcite precipitation on a limestone tablet with weight measurements of the tablet at the beginning and end of the experiment. CO_2 neutralization was also reported as part of intensive industrial synergy processes. A landfill gas was purified from its CO_2 while being used for neutralization of an alkaline wastewater (Gaur et al., 2009). Also, neutralization of alkaline metalworking wastewater and carbonation of slag, in a steel making plant, was performed using CO_2, which insured efficient wastewater neutralization, CO_2 capture and improvement of slag stability (Pan et al., 2013).

2 Material and Methods

The project included three parts, first, neutralization column tests in which the effect of media and mode of flow were tested, then a neutralization field test and finally, modelling of experimental results to propose design criteria.

2.1 Column Tests

Two parallel streams of an upflow steel slag filters followed by a clear polyvinyl chloride (PVC) neutralization columns were installed. Electric arc furnace (EAF) slag from Arcelor Mittal (Contrecoeur, QC) was used. Its particle size was 5-10 mm and its grain density was 3.6 g/cm^3. The chemical composition of the slag was 33% Fe_2O_3, 30% CaO, 16% SiO_2 and 12% MgO (Claveau-Mallet et al., 2014). Each steel slag column had a diameter of 10 cm and a length of 159 cm and was run at a hydraulic retention time of voids (HRT_V) of 13.9 h for column 1 and 13.7 h for column 2. EAF slag from steel slag filter 2 was changed for new media after a year of use. A different synthetic influent solution was used for each stream and it was continuously pumped through the steel slag filter then to the neutralization column (Table 1). Solution 1 contained analytical grade KH_2PO_4, K_2HPO_4, $NaHCO_3$ and $CaCl_2$ in tap water. Solution 2 contained analytical grade CH_3COOH

and CH_3COONa in tap water. The solution composition was fixed in a previous project in which the slag filter behavior was studied (Claveau-Mallet et al., 2017 for column 1 and results not yet published for column 2).

Table 1 : Mean chemical composition of synthetic solutions and steel slag effluents

		Synthetic solutions		Steel slag effluent	
		Solution 1	Solution 2	Column 1	Column 2
Parameter	**Units**	**Concentration**			
COD	mg/L	0	320	0	310
TOC	mg C/L	0	121	0	121
pH	-	7.8	7.3	11.0	11.2
TP	mg P/L	11.5	0	0.15	0
o-PO_4	mg P/L	8.9	0	0.020	0
Ca	mg/L	61.6	37.1	45.7	65.3
Na	mg/L	28.3	114	NA	NA
DIC	mg C/L	21.9	21.9	3.4	3.6
Alkalinity	mg $CaCO_3$/L	102	215	85	269

The neutralization columns were run with an empty bed HRT of about 10 h. Each neutralization column had a diameter of 63 mm by 1520 mm in length with 1300 mm of water level. Percolating tests were fed downflow and saturated tests were fed upflow. Ambient air or CO_2 enriched air was injected at the bottom of the neutralization columns through a fine-bubble air stone. Air was enriched by combining it with CO_2 from a gas cylinder in a sealed container in which there was a CO_2 probe. Mixing of pure CO_2 and ambient air was done in a sand layer located in the sealed container. The variables tested in the neutralization units (see Table 2) were air flow rate, type of air and CO_2 concentration (ambient or enriched), type of media (none, Bionest, AnoxKaldnes K3, gravel) and flow mode (saturated or percolating). The Bionest media is composed of an unattached elongated thin plastic film with a nest-like configuration and is normally used as support in fixed film biological processes (Bionest, 2011). The AnoxKaldnes K3 carriers are composed of polyethylene of high density, several cavities of alveolar shape are present in the carrier that is generally used as suspended biofilm growing support (Brosseau, 2015). For example, an experiment identified as SEN would have had operating conditions of Saturated flow, CO_2 Enriched air and No media (Table 2). The neutralization columns were packed with media up to their water level. The effluent from each neutralization column was sampled three times a week for dissolved inorganic carbon (DIC) and for pH, and once a week for alkalinity and calcium concentration. The flow was measured before sampling three times a week.

Table 2 : Column test operating conditions (listed in chronological order of testing)

Code	Col No	Flow mode	Air type	Media	Media concentration in reactor		Duration	pH of the steel slag filter effluent	Air flow rate range*	CO_2 conc. range
		(S/P)	(A/E)	(N/G/B/K)	m^2/m^3	kg/m^3	d	-	mL/min	ppm
SAN	1	Saturated	Ambient	None	-	-	44	11.27±0.15	700-3000	400
SEN	1	Saturated	Enriched	None	-	-	51	11.08±0.16	65-1800	400-22500
PAG	1	Percolating	Ambient	Gravel	229	1440	12	10.97±0.04	0-1200	400
PEG	1	Percolating	Enriched	Gravel	229	1440	21	10.99±0.05	150-2400	460-7700
SAG	1	Saturated	Ambient	Gravel	229	1440	19	10.96±0.06	250-2000	400
SEG	1	Saturated	Enriched	Gravel	229	1440	42	10.79±0.09	90-2100	2000-9200
SAB	2	Saturated	Ambient	Bionest	162	16	35	11.28±0.16	480-1400	400
SEB	2	Saturated	Enriched	Bionest	162	16	38	11.26±0.15	80-1000	400-24000
PAB	2	Percolating	Ambient	Bionest	805	80	12	10.90±0.06	0-2300	400
PEB	2	Percolating	Enriched	Bionest	805	80	21	10.84±0.10	190-3000	500-7700
SAK	2	Saturated	Ambient	K3	500	80	17	11.03±0.16	100-2200	400
Change slag media for fresh slag in column 2										
SEK	2	Saturated	Enriched	K3	500	80	14	11.47±0.10	200-200	2000-9200
PEK	2	Percolating	Enriched	K3	500	80	19	11.32±0.05	160-2400	2000-8700
PAK	2	Percolating	Ambient	K3	500	80	13	11.40±0.05	0-3500	400

* Standard conditions 1 atm and 20°C

2.1.1 Description of tracer test method

Tracer experiments were carried out for each neutralization condition. An amount of 0.1 mg of fluorescein was injected to the column in one pulse. Equal volumes of effluent were collected periodically from each column and were tested for absorbance using a spectrofluorophotometer (model RF-1501 from Shimadzu).

2.2 Field Test

The field test was composed of a typical onsite domestic wastewater treatment system including a septic tank followed by a Bionest secondary treatment unit (MDDELCC, 2017). The Bionest unit effluent was sent to a steel slag filter, and the steel slag filter effluent was sent to a neutralization unit. Wastewater from the Grandes-Piles village (Quebec, Canada) was used as the influent to the system. The wastewater flowrate was 1350 L/d in a sequential feeding mode (feeding during 3 hours in the morning, 3 hours at noon and 3 hours in the evening). The composition of the Bionest effluent was pH = 7.2, alkalinity = 20-50 mg $CaCO_3$/L, TP = 3.1 mg P/L, o-PO_4 = 3.0 mg P/L, COD = 43 mg/L, TSS = 6 mg/L and NH_4 = 10 mg N/L, while that of the slag filter effluent was pH = 10.5, TP = 0.7 mg P/L and o-PO_4 = 0.6 mg P/L.

The slag filter and neutralization unit were combined in a modified septic tank reactor. The first compartment was filled with slag and was operated in an upflow mode using a low-pressure distribution system typically used for infiltration beds. The slag filter effluent was overflowing through sealed pipes going to the bottom of the second compartment in which neutralization occurred. The slag filter HRT_V was 15.4 h and the neutralization unit HRT was 7.8 h. In the neutralization compartment, air was injected at the bottom of the reactor using a fine bubble diffuser at 64 L/min. Neutralization air was pumped from the Bionest biological reactor, resulting in CO_2 enriched air at 3500 to 5500 ppm CO_2 concentration. The CO_2 concentration was 5000-5500 in feeding sequences and it decreased slowly to 3500 ppm at the end of rest periods. The slag filter and neutralization units were completely confined, except for two capped manholes. pH in the neutralization unit water and CO_2 concentration in the gas headspace of the neutralization unit were continuously monitored with probes for 7 days.

2.3 Analytical Determinations

The pH determinations were carried out using a pH-meter XL15 from Fisher Scientific and a VWR 89231-596 refillable 3M KCl electrode according to Standard Method 4500-H+ (APHA et al., 2012). The electrode was 3-point calibrated using pH 7, 10 and 12 standards. DIC and TOC were measured using a Dohrman Rosemount DC-190 instrument according to Standard Method 5310-B High temperature Combustion method, on 0.45 µm filtered samples for DIC (APHA et al., 2012). Water samples were filtered at 0.45 µm and acidified with H_2SO_4 5N or HNO_3 6N prior to sodium and calcium analyses. Analyse of calcium and sodium were conducted with an AAnalyst 200 flame atomic absorption apparatus, using a standard mass spectrometry method (MDDEP, 2006). Alkalinity was determined using a Mettler Toledo DL28 Titrator according to Standard Methods 2320B (APHA et al., 2012). Samples were capped with parafilm just after sampling and were analyzed within 1 hour following sampling, to limit contact with ambient air CO_2. CO_2 concentrations were measured using Scion 456-GC apparatus with TCD (Thermal Conductivity Detector) and gas vector hydrogen-argon for configurations SEN and SEB and with the probe Wöhler CDL 210 in the headspace of the container. Samples for GC were taken from the air inlet pipe with a three-way valve into a gas vial.

2.4 Model Description and Numerical Simulations

The model included CO_2 transfer (Lizarralde et al., 2015) and the PWP model for calcite precipitation (Plummer et al., 1978), as seen in Table 3. In the model equations, K_{H_CO2} is the Henry's law constant for CO_2 (M/atm), K_{spCAL} is the calcite solubility product (M^2), k_{CO2} is the CO_2 transfer coefficient (s^{-1}), a_{CAL} is the concentration of calcite surface on which precipitation occurs (cm^2/L), T is temperature (K) and $\{CO_2\}$, $\{Ca^{2+}\}$ and $\{{CO_3}^{2-}\}$ are species activity (M).

Table 3: Model equations for CO_2 transfer and calcite precipitation

Process	Formula	Rate	Solubility constant
CO_2 transfer	CO_2	$r_{CO2} = -k_{CO2} \times \left(K_{H\_CO2}\, p_{CO2} - \{CO_2\}\right)$	$K_{H\_CO2} = 10^{-1.468}\, {}^{M}\!/_{atm}$
Calcite precipitation	$CaCO_3$	$r_{CAL} = 0.001r\left(1 - \left(\frac{\{Ca^{2+}\}\{CO_3{}^{2-}\}}{K_{spCAL}}\right)^{2/3}\right)$ $r = a_{CAL}\left(k_1\{H^+\} + k_2\{CO_{2(aq)}\} + k_3\{H_2O\}\right)$ $k_1 = 10^{\left(0.198-\frac{444}{T}\right)}$ $k_2 = 10^{\left(2.84-\frac{2177}{T}\right)}$ $k_3 = 10^{\left(-5.86-\frac{317}{T}\right)}$	$K_{spCAL} = 10^{-8.48}M^2$

The model was implemented in the PHREEQC software using a MATLAB interface via IPHREEQC modules (Charlton & Parkhurst, 2011). Model equations were written in the RATES and KINETICS datablock; while reactor hydraulic was written in MIX or TRANSPORT datablocks (Table 4). For hybrid reactors, the effective volume fraction n_e, immobile volume fraction n_{im}, dispersivity D* and diffusion coefficient D_n needed for the dual porosity feature (Parkhurst & Appelo, 1999) were calibrated with experimental tracer tests. All column test conditions were considered hybrid following calibration with tracer tests. Field test data was divided into individual segments; completely mixed (feeding phase); batch (feeding just stopped); and equilibrium (no feeding and equilibrium reached). The feeding phase was assumed to be completely mixed without having conducted tracer tests.

Table 4: Modeling methodology for hydraulic

Type of reactor	PHREEQC datablock
Batch (no inflow)	KINETICS only, no datablock for flow
Completely mixed	succession of MIX; 1% influent with 99% from reactor
Hybrid (between CM and plug flow)	TRANSPORT with first order dual porosity

For column tests, the influent was simulated using the REACTION datablock in which $CaCl_2$ and $NaHCO_3$ (col 1) or CH_3COOH, CH_3COONa and $NaHCO_3$ (col 2) were added to pure water to reproduce experimental concentrations. NaOH was added to reproduce the exact pH of the experimental slag filter effluent, using the Newton method. The influent calibration was refined by changing added $NaHCO_3$ until the slag filter alkalinity was accurately reproduced. The influent was calibrated at each neutralization configuration. For field test, the influent was simulated using the same methodology with salts KH_2PO_4, K_2HPO_4, $NaHCO_3$, $CaCl_2$, NH_4Cl, $NaNO_2$, $NaNO_3$ and NaOH. The influent calibration was refined at each completely mixed test by changing $NaHCO_3$ concentration until pH at the end of the preceding rest period was properly reproduced (equilibrium was assumed to be reached).

The model constants k_{CO2} and a_{CAL} were determined by calibration of column tests with ambient air. pH and DIC grab sample data were accurately reproduced while calcium was used as validation. The model was validated by reproducing both column tests with CO_2 enriched air and field test using calibrated k_{CO2} and a_{CAL}.

3 Results and discussion

Calibration of the model with ambient air column tests results are presented in a first section that is followed by model validation with CO_2 enriched air column tests and a full scale field test. Simulations for process design and full-scale recommendation are presented in the two last sections.

3.1 Model calibration

Ambient air neutralization resulted in effluent pH values shown in Figure 1. In saturation mode (black symbols), pH was above 8.3 for all media and Q_G/Q_W generally influenced pH decrease until Q_G/Q_W reached 100-150. Saturated conditions with media provided only a slight decrease of pH compared to conditions without media. Under saturated conditions, the Bionest media showed the best result (lowest effluent pH) at Q_G/Q_W under 170. Percolating conditions were not as efficient as saturated conditions for the Bionest and Kaldnes K3 media but were more efficient for gravel, attaining an effluent pH value of 8.3 or less at Q_G/Q_W of higher than 100. PAB pH decreased until Q_G/Q_W >200 at pH around 9.2 but PAK pH was not stable following Q_G/Q_W. The poor performance of PAK can be explained by high influent pH as slag was renewed prior to this test (Table 2), leading to random pH at the neutralization process effluent.

The decrease in Ca concentration in the effluent was observed in all ambient air tests and indicated the precipitation of calcite. A white precipitate assumed to be calcite was observed on the porous diffuser and reactor sides upon dismantling.

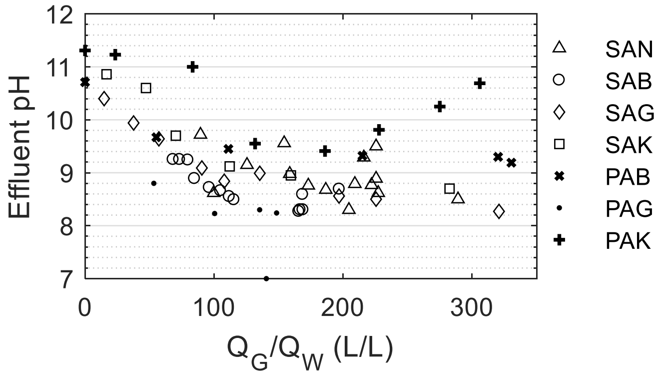

Figure 1 : Effect of Q_{gas}/Q_{water} ratio on the effluent pH using ambient air in columns (standard conditions of 20˚C and 1 atm for Q_{gas}).

Tracer test results are presented in Figure 2 and % tracer recovery and displacement efficiency E_D are presented in Table 5, where $E_D = t_m/HRT$ (t_m is the average retention time or mass center of the tracer curve). The % tracer recovery obtained was between 82 and 107%, indicating valid tracer results. All saturated configurations resulted in satisfactory E_D (0.75 and over), indicating that the whole reactor volume was used for the process. The gravel percolating configuration also showed an efficient hydraulic behavior (E_D = 1.33). The hydraulic behavior of other percolating configurations, however, was poorer, with E_D of 0.21 and 0.40 for Bionest and K3 media, respectively. The Bionest media was the media that showed the poorest hydraulic behavior in percolating mode.

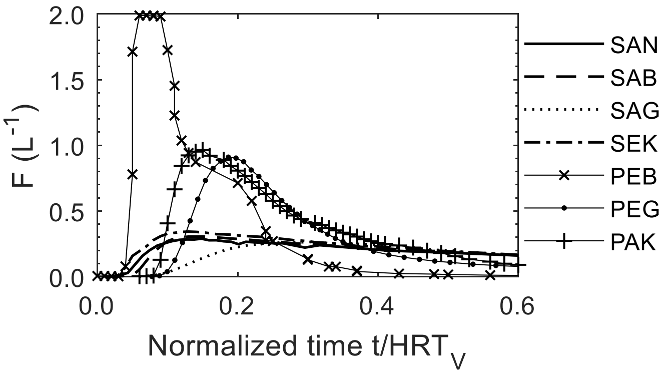

Figure 2 : Tracer test results for each operating condition tested. F: normalized concentration C / total mass (L^{-1})

Table 5 : Column tracer test results

Code	Column No	Recovery (%)	E_D
SAN	1	102	0.90
PEG	1	94	1.33
SAG	1	102	1.32
SAB	2	89	0.93
PEB	2	82	0.21
SEK	2	97	0.75

PAK	2	107	0.40

Results of gas transfer coefficient k_{CO2} calibration are shown in Figure 3A. The gas transfer constant k_{CO2} was higher for percolating conditions (mean 0.014 s^{-1} [1210 d^{-1}]) than for saturated conditions (mean 0.00285 s^{-1} [250 d^{-1}]), indicating that the mass transfer was better under percolating conditions. In saturated mode, k_{CO2} was slightly higher for SAN and SAB than for SAG and SAK (according to t-tests with $p \leq 0.05$). k_{CO2} for percolating conditions was significantly higher for PAB and PAK (reaching 0.018 s^{-1}) than for PAG (reaching 0.010 s^{-1}), meaning that the high specific surface of the Bionest and K3 media were useful to reduce water drop size and improve gas transfer. Percolating conditions required a high ventilation rate (Q_G/Q_w) near 200 before reaching the maximum k_{CO2} compared to saturated conditions which were less affected by the ventilation rate.

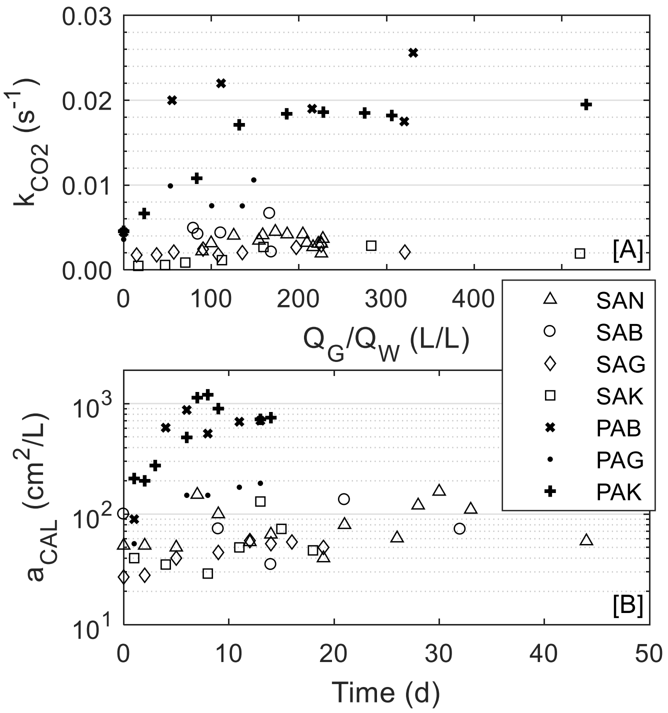

Figure 3 : Effect of media and feeding mode on ambient air calibration (standard conditions of 20˚C and 1 atm for Q_{gas}) of CO_2 transfer coefficient (A) and calcite surface concentration calibration (B). Each data point was collected after reaching steady state in the reactor at fixed Q_G/Q_w.

Even though media type had a minor influence on k_{CO2}, the feeding mode (saturated or percolating) was the factor that had the greatest influence on the k_{CO2} transfer constant. It was initially thought that adding a media to a saturated reactor would increase gas transfer but this expected improvement was not observed. This result is not consistent with previous studies in which media improved oxygen transfer by fractionation of coarse bubbles (Dias et al., 2017). In the present study, the media may have been inefficient for bubble fractionation because a fine diffuser was used. In saturated mode, the observed minor effect of media on k_{CO2} may not be relevant because the aeration rate was not the same for different tests. The minor effect of media may also be attributed to the slowly and gradually decreasing pH of the steel slag filter effluent resulting in media not being tested under identical steel slag effluent pH, and pH uncertainty is greater with higher pH.

Results of calcite surface concentration (a_{CAL}) calibration are shown in Figure 3B. In saturated mode, a_{CAL} was not affected by the media and had a mean value of 68 cm^2/L. a_{CAL} slightly increased over time, meaning that newly formed crystal precipitates were mostly evacuated from the reactor under steady state conditions. In percolating mode, a_{CAL} increased markedly over time, meaning that precipitates were accumulating on the media surface and progressively increasing the precipitation rate. In percolating mode, media with high specific surface (Bionest and K3) resulted in higher a_{CAL} increase rate (up to 1000 cm^2/L) while gravel only resulted in a_{CAL} increasing up to 200 cm^2/L. These findings have important consequence on maintenance aspects. While calcite precipitation takes place under both saturated and percolating mode (Table 6), saturated mode may be less affected by clogging as calcite is constantly evacuated from the reactor. In percolating mode, calcite is expected to accumulate and result in gradual media clogging.

Table 6 : Calcium concentration in influent and effluent of neutralization units

Code	Column	Mean Ca inf (mg/L)	Mean Ca eff (mg/L)	% Ca in effluent
SAN	1	62.6	30.0	48%
SEN	1	47.2	49.9	106%
PAG	1	42.5	23.7	56%
PEG	1	42.9	37.0	86%
SAG	1	41.0	27.0	66%
SEG	1	38.7	46.1	119%
SAB	2	66.7	31.4	47%
SEB	2	59.3	62.9	106%
PAB	2	39.1	20.1	51%
PEB	2	39.9	29.6	74%
SAK	2	48.1	33.9	71%
Change slag media for fresh slag in steel slag column 2				
SEK	2	89.9	62.1	69%
PEK	2	99.2	68.2	69%
PAK	2	80.4	37.1	46%

The effect of feeding mode on evolution of a_{CAL} also influences current practice in wastewater treatment modelling. Recent modelling approaches consider a calcite precipitation rate increase as a result of surface increase following accumulation of calcite (Lizarralde et al., 2015; Mbamba, Batstone, et al., 2015; Mbamba, Tait, et al., 2015). In particular conditions, the calcite precipitation rate is constant and does not increase following calcite accumulation possibly due to aeration inducing enough turbulence for the steady state evacuation of calcite seeds, as indicated by results from this study. Conducting more research related to calcite precipitation mechanisms (occurrence of homogeneous precipitation with constant precipitation rate or heterogeneous precipitation with precipitation rate related to surface increase) could improve modelling tools. Factors that may influence precipitation behavior are aeration and mixing (Jung et al., 2010), seeding surfaces and presence/absence of catalyzers or inhibitors (Feng et al., 2007).

3.2 Model Validation

The calibrated model was used to reproduce data from CO_2 enriched air column tests and from a field test as validation step. For the column tests, mean values of k_{CO2} and a_{CAL} were used for each condition (mode of flow and type of media). Mean values of $k_{CO2} = 0.00285\ s^{-1}$ and $a_{CAL} = 68\ cm^2/L$ from saturated conditions were used for the field test. For the field test, two additional simulations with $k_{CO2} = 0.0015\ s^{-1}$ (mean value minus standard deviation) and $k_{CO2} = 0.0042\ s^{-1}$ (mean value plus standard deviation) from calibration of saturated conditions were realized. Simulated and experimental data are compared in Figures 4 and 5.

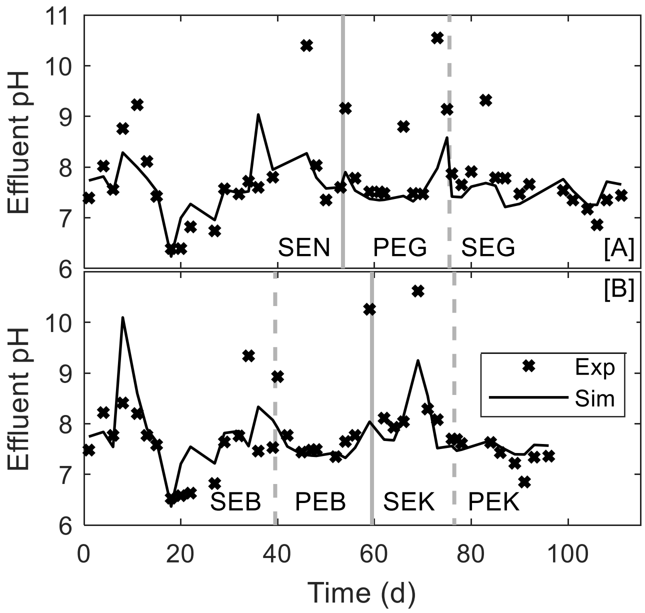

Figure 4 : Lab-scale model validation for the effluent pH from the neutralization reactor effluent of columns 1 (A) and 2 (B). Changes in type of flow mode (dashed lines) or media (full lines) are indicated by vertical gray lines.

In the validation step using CO_2 enriched air conditions lab data (Figure 4), good prediction was obtained for pH values between 6.5 and 8.5 for all medias used in both columns, under a wide range of CO_2 enriched air concentration (400 to 24 000 ppm). Predictions were less accurate at higher pH values: this reduced accuracy can be explained by the high pH sensitivity to any CO_2 input if pH is greater than 8.5, and higher experimental uncertainty on pH measurement at high pH. In addition, some inconsistency can be explained by the CO_2 concentration measurement method that was not optimized for the first CO_2 enriched air tests (SEN & SEB).

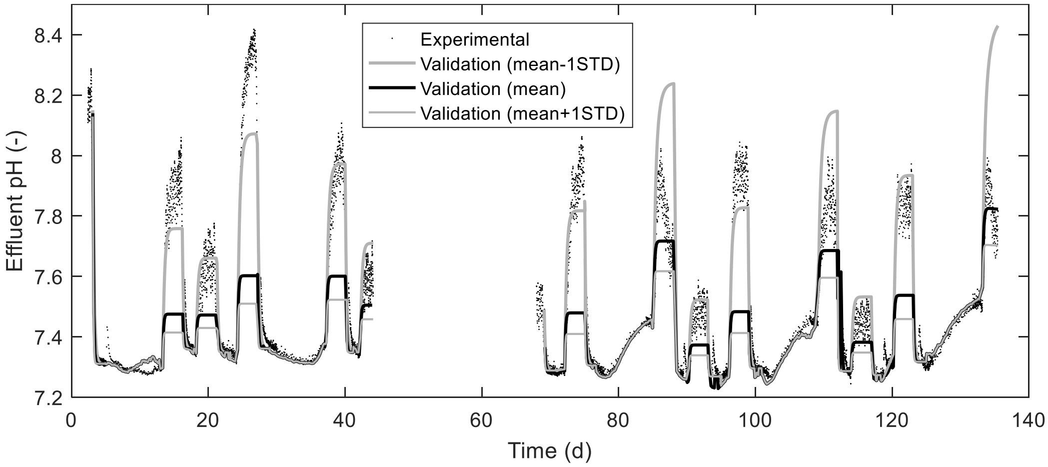

Figure 5: Field-scale model validation for the neutralization reactor effluent pH (STD = standard deviation)

Validation using field test data lead to good prediction with pH being slightly underestimated (Figure 5, mean validation). The simulation with k_{CO2} of 0.0015 s^{-1} (mean minus 1 standard deviation) improved the validation quality. This smaller k_{CO2} may be attributed to the reduced transfer efficiency in real wastewater compared to synthetic wastewater, or to incertitude considering the high result variability of the k_{CO2} calibration.

3.3 Using simulations for process design

The treatment system considered for simulations consists of a septic tank, a biological treatment process, a slag filter and a neutralization unit. The model was used to simulate different operating conditions of a saturated neutralization unit without media using CO_2 enriched air with Q_G/Q_w = 100 (SEN; Figure 6). In this figure, the neutralization capacity of the SEN configuration is shown for different steel slag effluent pH, secondary effluent (slag filter influent) alkalinity and CO_2 enriched air concentration. Simulations were divided in two operation scenarios which are neutralization at the beginning of the slag filter operation (critical conditions with high pH at the slag filter effluent, Figure 6A) and neutralization once the pH of the slag filter has slightly decreased (pH of 11.0, Figure 6B). The initial operation of the neutralization unit represents critical conditions because CO_2 needs are much higher with fresh slag and may require a longer HRT or a higher addition of CO_2. At high slag filter effluent pH, small changes in pH represent large variations in CO_2 needs. For example, increasing the slag effluent pH from 11.4 to only 11.5 represents a 15-20% increase in CO_2 needs. A pH of 11.5 was chosen as representative of initial operation of slag based on this study's results and also from previous works using the same type of slag (Claveau-Mallet et al., 2017; Claveau-Mallet et al., 2015; Kõiv et al., 2016). The alkalinity range was chosen following possible alkalinity met in onsite domestic cases for which groundwater is often the source of drinking water.

Low alkalinity and filter slag effluent pH requires a shorter reactor HRT to provide sufficient neutralization. The CO_2 enriched air concentration had a major effect on neutralization result. While ambient air conditions (400 ppm) resulted in sufficient neutralization at HRT of at least 16 h, complete neutralization was properly achieved at HRT of only 6 h with the use of 2000 ppm CO_2 enriched air. A higher concentration of CO_2 would also reduce clogging risks by reducing calcite precipitation. Simulations results indicated an increase in the effluent calcium concentration following an increase in CO_2 concentration. Simulation results corresponded well with experimental observations: more clogging occurred (accumulation of calcite suspension on the diffuser and lower calcium concentration at effluent, Table 6) under ambient air conditions than under CO_2 enriched air conditions.

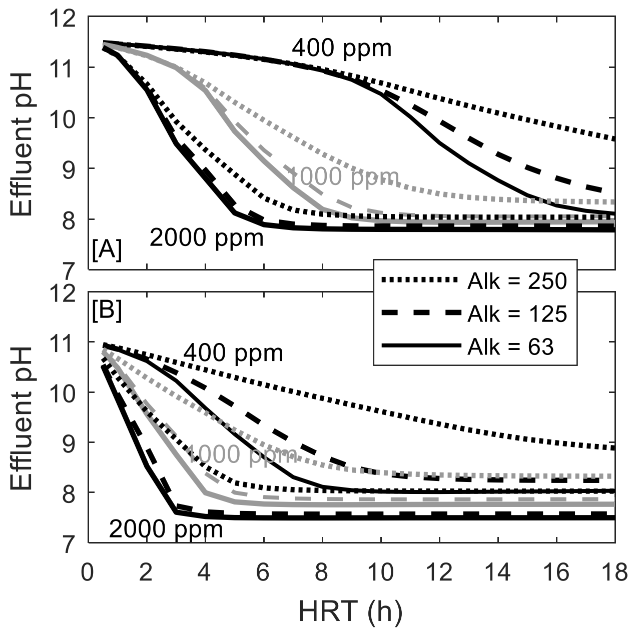

Figure 6: Simulated effluent pH of SEN neutralization unit under different CO_2 concentration and HRT at the beginning of slag operation (pH slag effluent = 11.5, panel A) and after the initial period of slag operation (pH slag effluent = 11.0, panel B). Alkalinity of slag filter influent is indicated in the legend (units mg $CaCO_3$/L)

Simulations for all configurations tested at the lab are shown in Figure 7 (set conditions for influent alkalinity, slag filter pH and CO_2 enriched air concentration). All modes of flow and types of media resulted in similar decreasing curves, with minimum operation HRT being between 6 and 10 h. For percolating conditions, the combination of higher k_{CO2} but poorer hydraulic efficiency resulted in neutralization efficiency similar to saturated conditions. The performance of the percolating conditions could be improved by optimising flow distribution and media packing to improve hydraulic efficiency. Considering uncertainties on the model calibration and experimental measurement (discussed in previous sections), Figure 7 was not used for comparison of media but was only used for evaluating effluent pH ranges from model predictions. Using this conservatory approach, an HRT of 10 h was selected for design of saturated conditions.

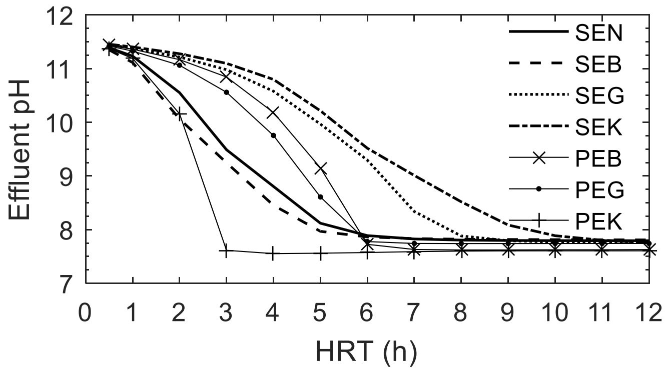

Figure 7: Simulated effluent pH of various neutralization units under fixed conditions (Influent alkalinity = 63 mg $CaCO_3$/L; pH at slag filter effluent = 11.5; enriched air concentration = 2000 ppm CO_2)

3.4 Recommendations and full-scale considerations

Based on experimental and simulations conducted in this study, it is recommended to use a saturated reactor without media operated at an HRT of 10 h and using CO_2 enriched air at concentration of 2000 ppm. The saturated mode was chosen for simplicity and robustness for onsite applications (essentially no head loss and lower risks of poor hydraulics and clogging) while the absence of media was chosen considering the minimal performance improvement resulting from adding media. The HRT of 10 h was chosen to provide a sufficiently long HRT under critical conditions (initial period of slag filter operation, Figure 7). As the critical period is expected to be at the beginning of the slag filter operation, design of the neutralization unit should be done according to this period and not to the expected mean pH value which will be lower. A minimum of 2000 ppm was recommended to ensure fast neutralization and reduced calcite precipitation.

Following the recommended HRT of 10 h, a neutralization column providing 130 cm of water level and 66 cm of diameter (volume 450 L) with an aeration air flow of 32 L/min (1.14 SCFM) are required for a two-bedroom home onsite treatment system (design influent flowrate of 1080 L/d). Aeration needs were determined according to the minimum aeration rate observed in this study to reach the maximum CO_2 transfer constant in ambient and CO_2-enriched air (injection of 0.10 g CO_2/L).

It is recommended to run additional field tests with the PEK condition to validate the good neutralization potential observed in this study. It is also recommended to assess the effect of mixing on k_{CO2} for all the configurations.

Neutralization predictions presented in this section assume that CO_2 concentration is controlled and fixed (infinite source of CO_2) which is not the case in practice as CO_2 concentration in the CO_2 enriched-air is the result of a finite input from the biological reactor. Consequently, applicability of this design approach must be validated by stoichiometric calculations of CO_2 needs and CO_2 availability from influent COD. Assuming that all influent biodegradable COD is oxidized with an observed yield of 0.24 g VSS/g bCOD (low value because of high sludge retention time in the Bionest reactor), it is possible to calculate COD needs for providing sufficient CO_2 for neutralization (Table 7). In this table, CO_2 needs were determined using PHREEQC under batch conditions as described previously. Assuming a typical biodegradable COD of 300 mg/L for domestic wastewater septic tank effluents (Bernier, 2001; Metcalf & Eddy et al., 2014), Table 7 indicates that the available influent CO_2 from such a wastewater is sufficient to provide CO_2 enrichment by the secondary treatment process for an efficient neutralization. CO_2 in ambient air would also contribute to pH neutralization, thus reducing CO_2 needs from biological sources.

Table 7 : CO_2 and corresponding influent biodegradable COD needs for neutralization of slag filter effluent with various pH (slag filter influent alkalinity = 156 mg $CaCO_3$/L)

Slag filter effluent pH	CO_2 needs for pH 8.0 neutralization (mmol/L)	Biodegradable COD needed to provide the required CO_2 (mg/L)
11.5	4.85	235
11.0	2.72	132
10.5	2.07	100

The main limitation of the proposed neutralization process is the need of a confined biological process. As shown in Figure 6, neutralization using ambient air does not result in a sufficiently low pH in the effluent, which highlights the need for a CO_2 enriched-air source. The neutralization process could fail if wastewater were diluted, thus limiting CO_2 input for neutralization. Large-scale biological processes as activated sludge could not be used as enriched-air source as there is typically no air confinement. The application potential in decentralized treatment remains interesting because secondary treatment units are generally confined underground.

4 Conclusions

The main objective of this project was to develop a steel slag filter effluent neutralization process by acidifying with CO_2 enriched air produced by a confined biological process. Different configurations of steel slag effluent neutralization units in laboratory and field conditions were tested and provided satisfactory neutralization performance. Best results were obtained with CO_2 enriched air containing at least 2000 ppm in CO_2. A model of slag filter effluent neutralization based on the carbonate system, CO_2 transfer and calcite precipitation was developed, calibrated and validated with lab and field tests over a wide range of CO_2 concentration. The model calibrated in lab-scale conditions provided satisfactory validation at lab scale and field scale conditions.

The mode of flow had an important impact on CO_2 transfer (k_{CO2}) and hydraulic efficiency. A percolating mode had a high k_{CO2} (mean 0.014 s^{-1}) and a poor hydraulic efficiency, while a saturated mode had a low k_{CO2} (mean 0.0029 s^{-1}) and an efficient hydraulic flow. The type of media (none, gravel, Bionest or AnoxKaldnes K3) had little influence on k_{CO2}. In saturated mode, hydraulics was more related to aeration than media, while in percolating mode, media affected the hydraulic flow efficiency.

The mode of flow had an important effect on calcite surface concentration (a_{CAL}) in the reactor. In saturated mode, newly formed calcite precipitates were constantly evacuated, resulting in a fairly constant calcite surface concentration. In percolating mode, calcite a_{CAL} progressively increased following precipitation. The type of media influenced the increase rate of a_{CAL} with media having a higher specific surface (Bionest and K3) resulted in higher increase compared to gravel.

Predictions could be made for different steel slag effluent pH (11.5 and 11.0) and influent alkalinity (50 to 250 mg $CaCO_3$/L) and different operation conditions for the neutralization process (HRT of 4 to 18 h, CO_2 concentration of 400 to 2000 ppm and mode of flow). pH of the steel slag filter effluent and CO_2 concentration of the enriched air were factors that influenced most the effluent pH of the neutralization process, while influent alkalinity and mode of flow had a lower influence. An increased concentration of CO_2 in the enriched air reduced calcite precipitation and clogging risks. Stochiometric calculations showed that a typical domestic septic tank effluent containing 300 mg/L of biodegradable COD provided enough biological CO_2 for neutralization of a steel slag effluent with pH of 10.5 to 11.5. A saturated neutralization reactor with no media operated at HRT of 10 h and a concentration of 2000 ppm in CO_2 enriched air was recommended for full-scale onsite applications.

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