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Understanding a passive treatment mechanism of manganese and zinc at a legacy mine in northern Japan

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Contents

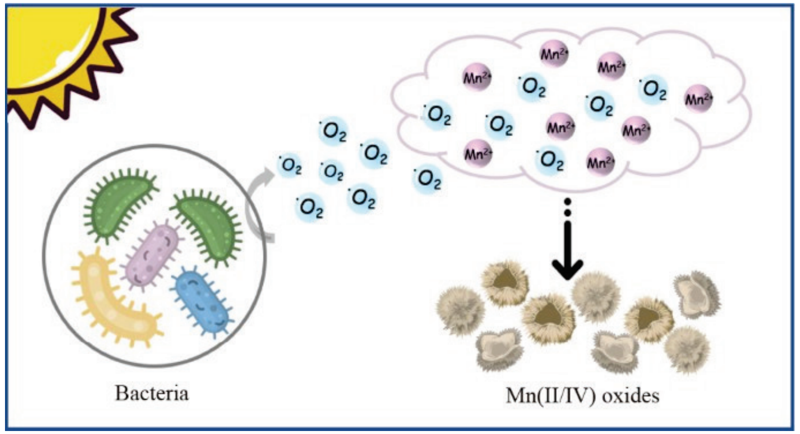
Introduction

Study area

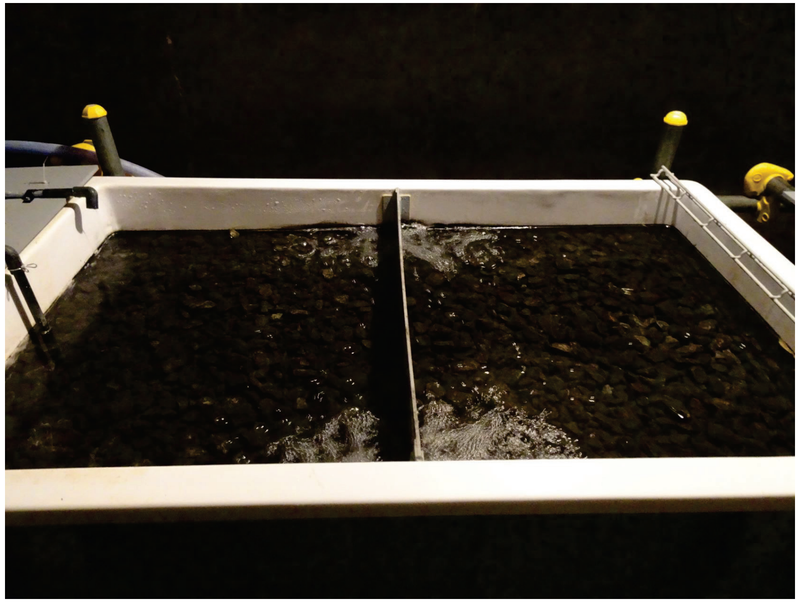
- The mine drainage of legacy mine X in the northern Japan riches in Mn and Zn concentration.
- The huge amount of fund have been spent on the active treatment of mine drainage at mine X, even the mine activities was closed since 1979.

The pilot-scale passive treatment

- The pilot-scale passive treatment (PT) was conducted to investigate the possibility of passive treatment of Mn and Zn.
- Mn concentration was reported to have been successfully treated in the pilot-scale passive treatment due to the formation of bio-birnessite (Miyata et al., 2022).
- Even thought, the treatment mechanisms of Mn and Zn in the pilot-scale PT, as well as the optimal hydraulic retention time (HRT), have not yet been finalized.



Mn oxidation under the present of Mn-oxidizing bacteria (Yang et al., 2022)



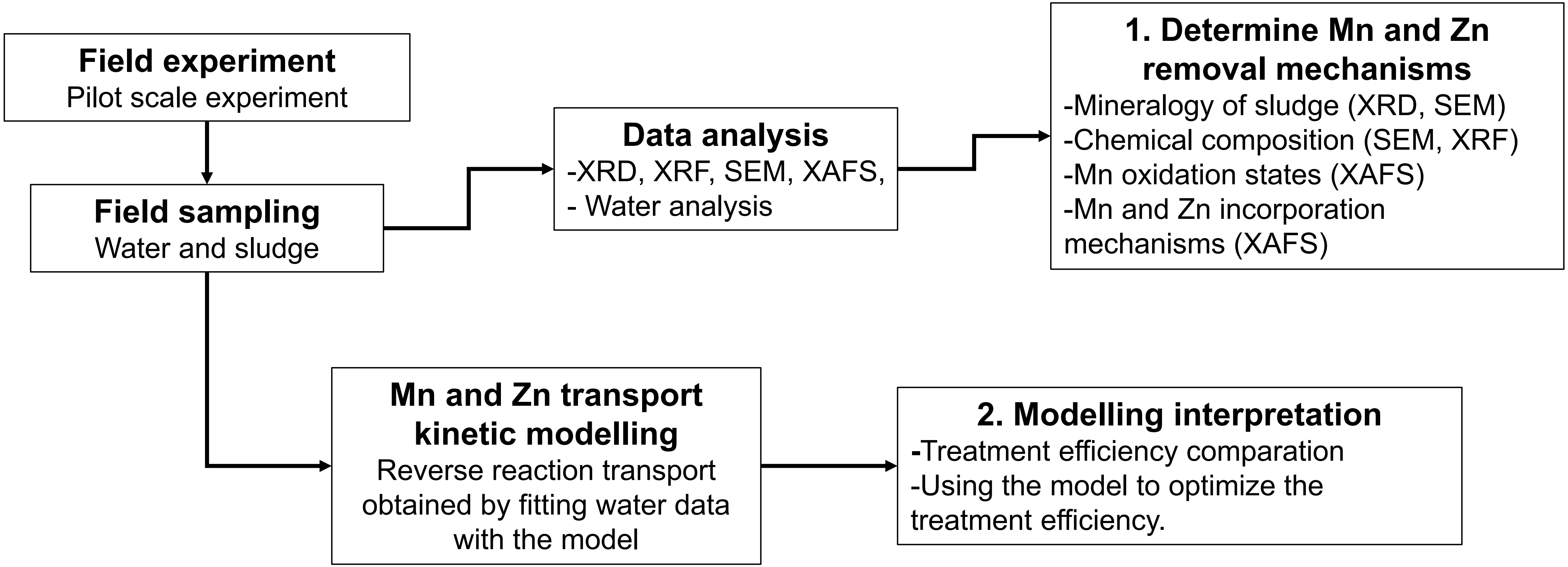
The pilot-scale passive treatment at mine X

Objectives and research framework

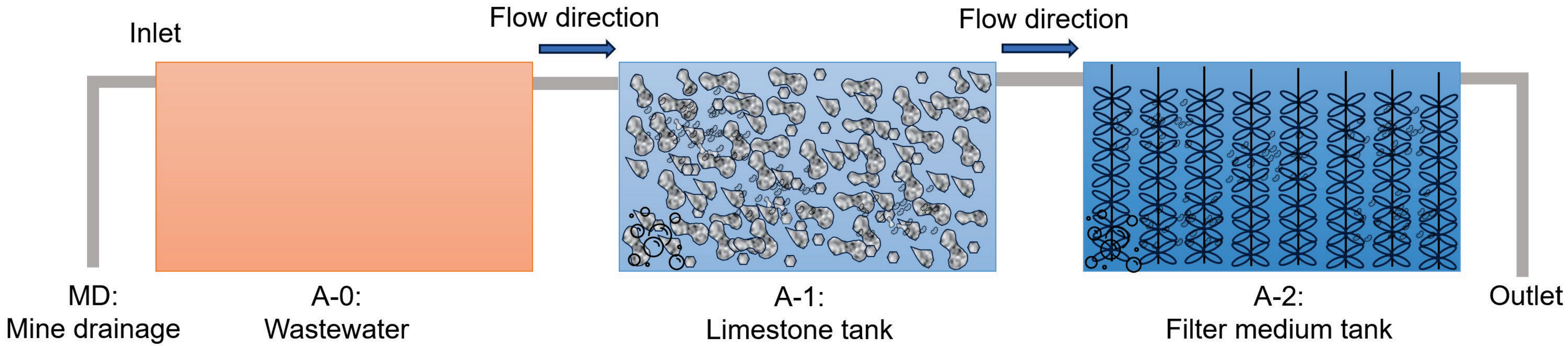
Therefore, objectives in this study were:

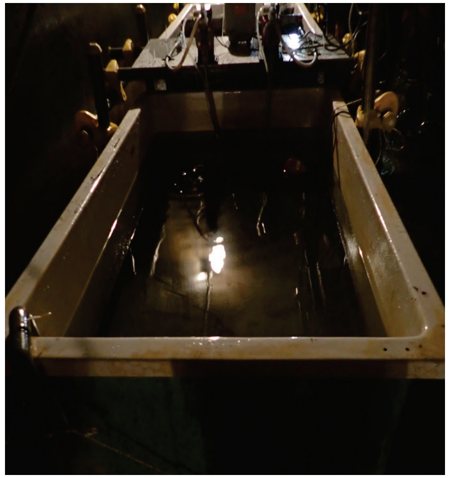
(1) to determine the treatment mechanisms of Mn and Zn in the pilot-scale passive treatment

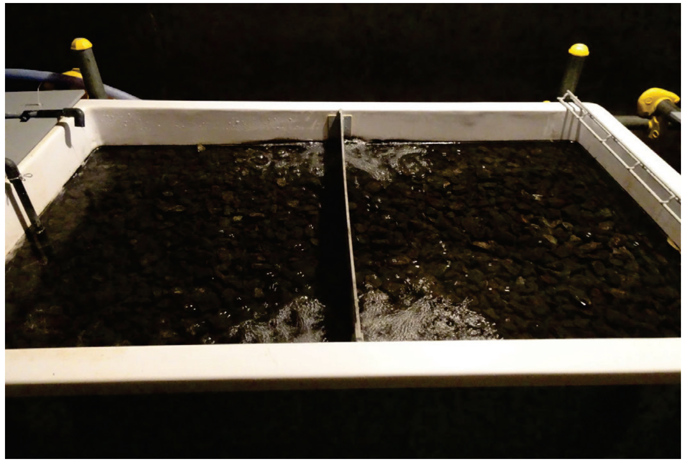
(2) To employ geochemical modeling to comprehensively understand the role of hydraulic retention time (HRT) in the long-term implications of passive treatment.



Pilot-scale passive installation







- Tank size: 160 cm(W) × 97 cm(D) × 74.5 cm(H)
- Tank volume =600 L, Limestone: 800 Kg,
- Porosity A-1=48%; A-2=92%
- Duration of experiment: 152 days
- Total Hydraulic retention time (HRT) : 6 days, 1.5 days, and 1 days.

Material and methods (1) :

Sampling

- MD：Suspended sediment of natural sample
- A-1 and A-2：Sludge in the passive treatment

Analytical methods of sludge:

- X-ray diffraction: mineralogical composition
- SEM-EDS: minerals and chemical composition
- XAFS analysis using Athena software for data interpretation XANES and EXAFS

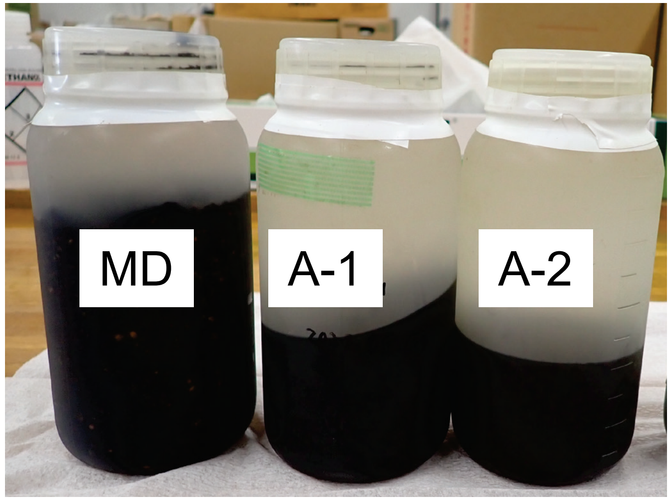
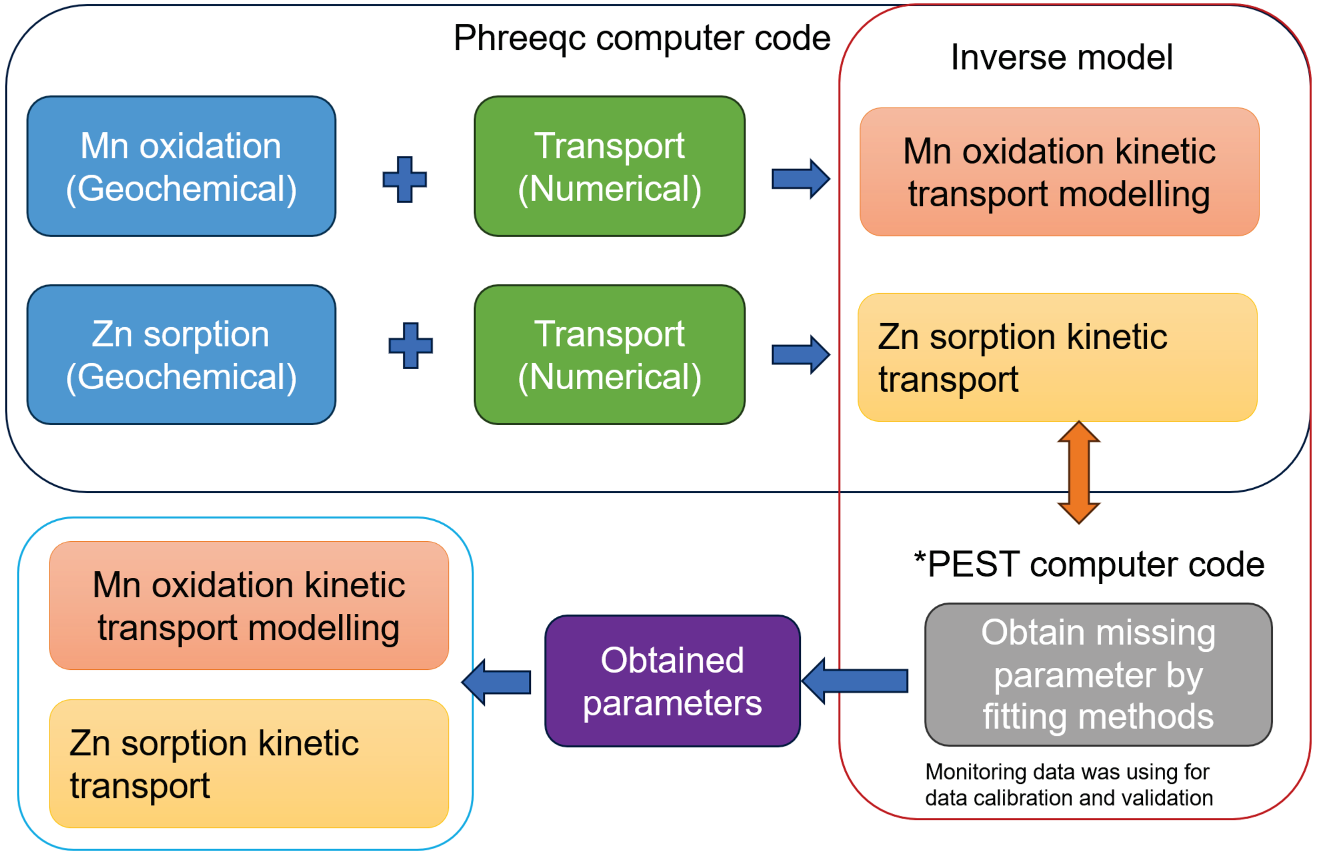


Fig1. Suspended solid and sludge collected from MD, A-1, A-2



Geochemical modelling:

Couple of geochemical and numerical transport modeling:

- Mn^{2+} oxidation kinetics transport
- Zn^{2+} sorption kinetics transport
- Computer software: Phreeqc and GWB

Pilot-scale passive treatment efficiency

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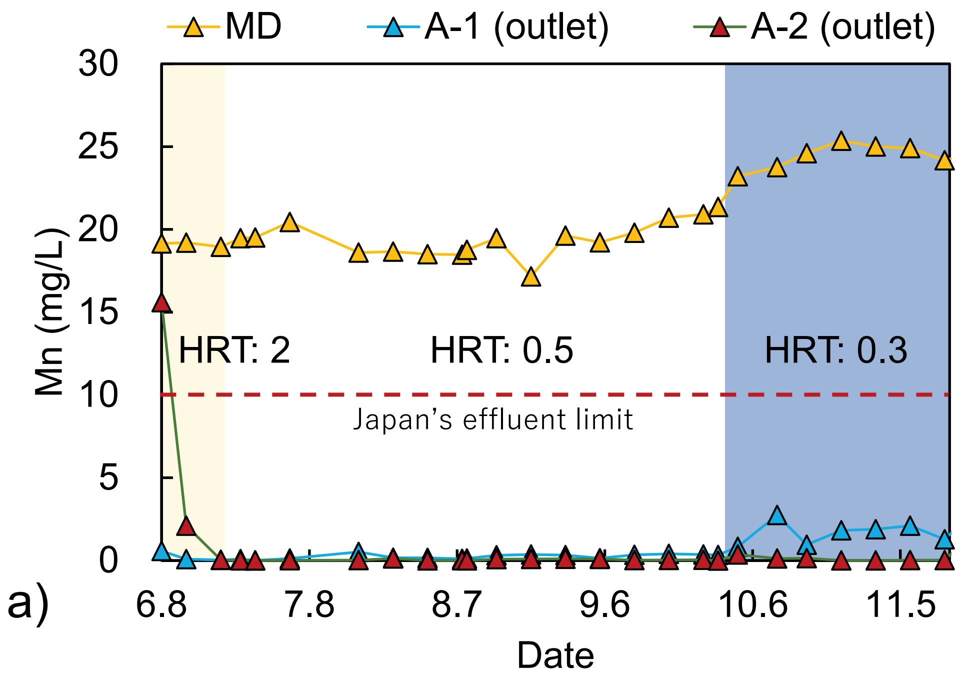

Fig.a) Monitoring data of Mn in the pilot-scale passive treatment

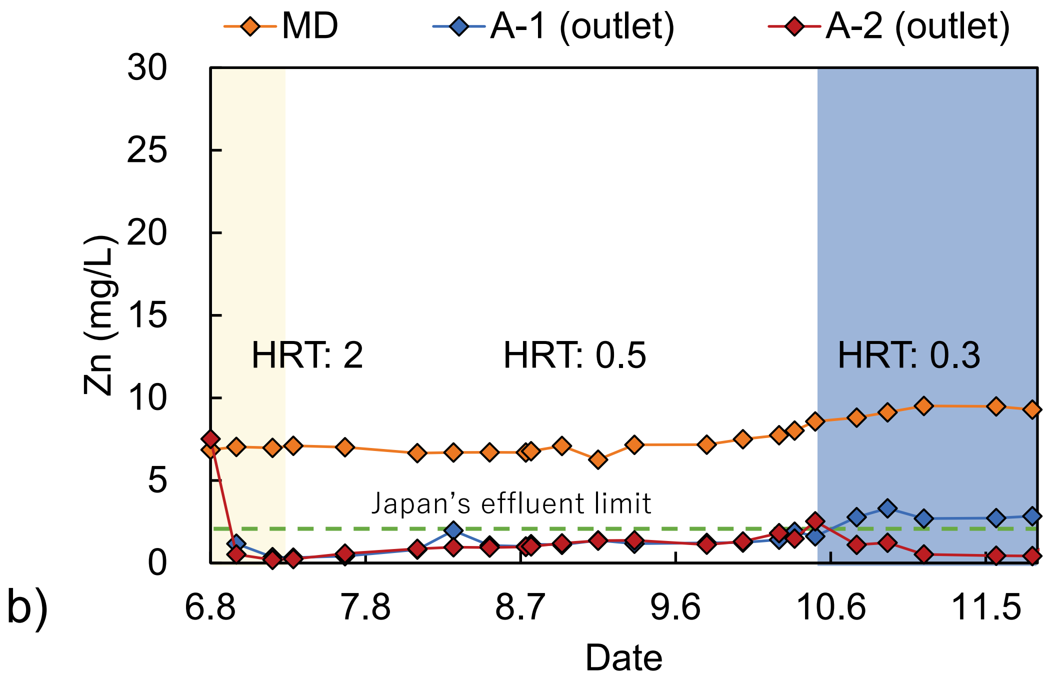

Fig.b) Monitoring data of Zn in the pilot-scale passive treatment

Table.1. Water quality at the pilot-scale passive treatment

Tanks	ORP mV	DO mg/L	pH	EC (μS/cm)
MD	138	5.02	6.72	1135
A-1	161	9.18	7.12	1101
A-2	177	9.48	7.04	1096

- Mn in A-1 and A-2 was less than effluent limit in all different time steps
- Mn and Zn was successfully treated up 97% and 89% respectively with the HRT more than 0.5 days.
- The HRT of 0.3 days was not able to remove Zn to less than effluent limit

Geochemical model and analytical result of Mn and Zn treatment mechanisms

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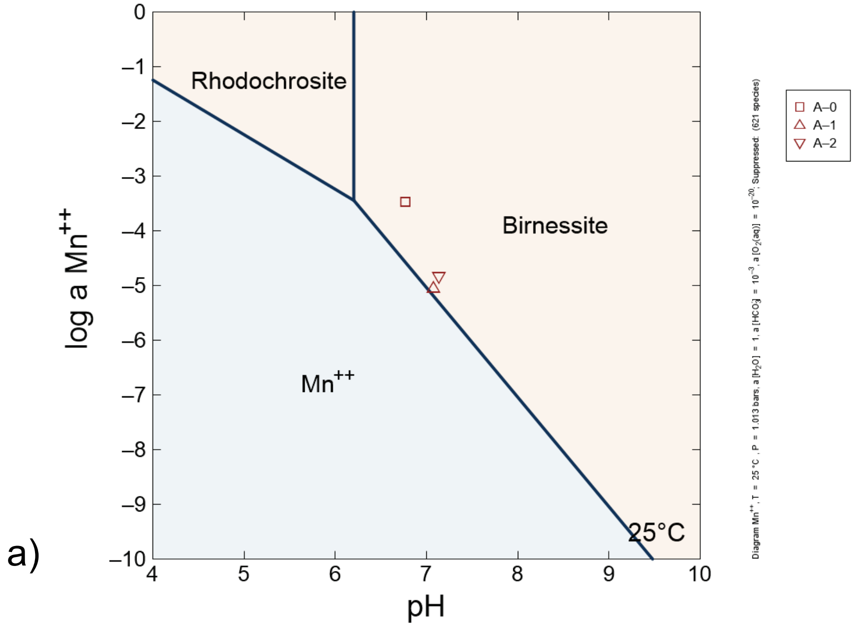
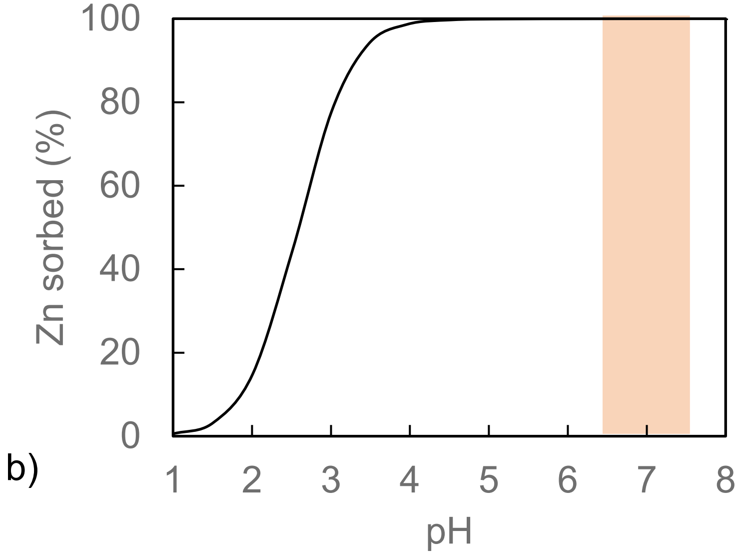


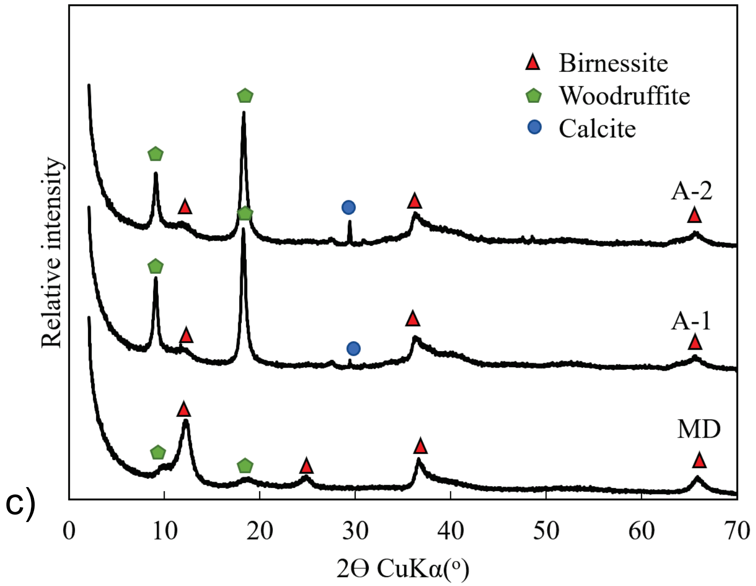
The geochemical modeling in the equilibrium condition shows:

- The solubility field of Mn show that birnessite forms in the system (Fig. a).
- Zn adsorption on birnessite may occur in the system as shown in the surface complexation model

The analytical model shows:

- Minerals precipitated in sludge (Fig.c) are calcite, birnessite (MnO_2), woodruffite ($ZnMn_3O_7 \cdot 2H_2O$).





- The geochemical was able to predict the only the formation of birnessite, as the equilibrium constant (Ks) of woodruffite is unknown.
- The model was consistent with mineral characterization and Mn and Zn concentration trend from the monitoring data.

Fig. .a). The solubility of field Mn species in water systems, b). Zn adsorption capacity (%) using surface complexation model using the database from Tonkin et al. (2003), c). X-diffraction (XRD) patterns of MD and sludge sample in A-1

Mineralogy

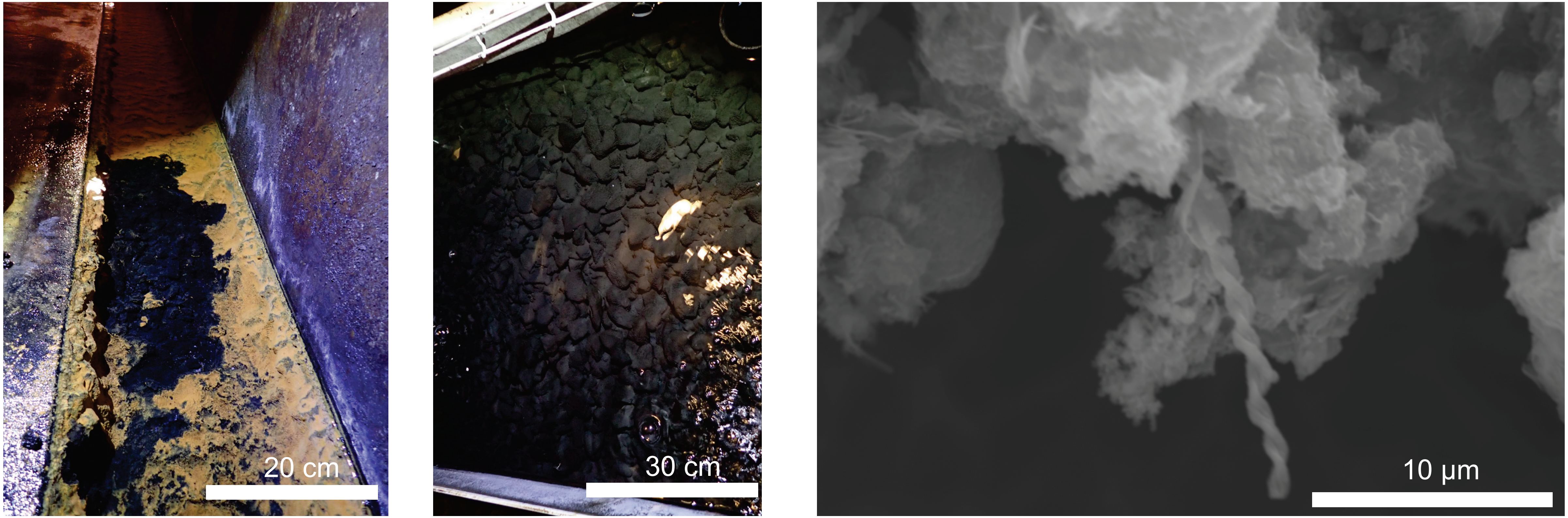


Fig. a. Natural formation suspended sediment from the mine drainage, b. birnessite coated on the limestone, c. SEM image of the natural sediment of the mine drainage.

Besides the formation of birnessite and woodruffite, there was also formation of Fe oxyhydroxide twisted stalks organo-mineral in mixture (Fig.c) as a result of iron-oxidizing bacteria.

Mn oxidation state and Zn incorporation mechanisms

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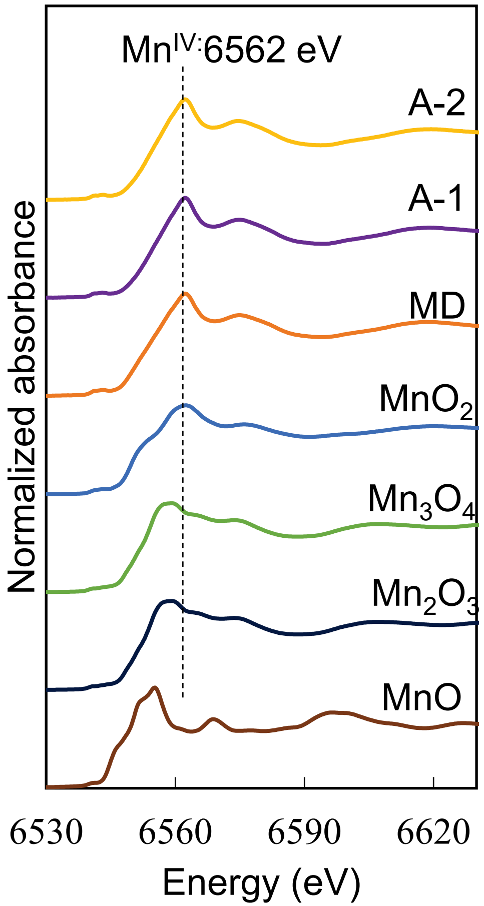
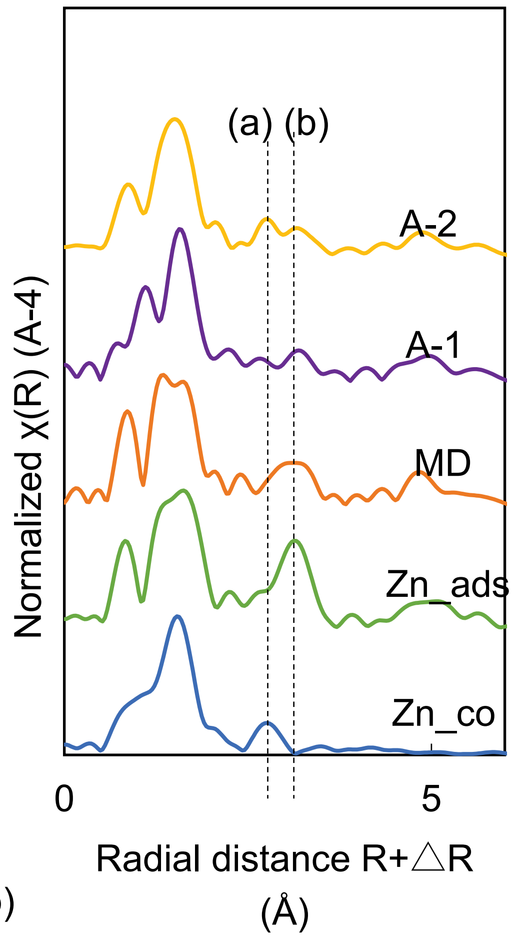


a)



b)

Fig. a). Mn K-edge XANES of the reference material b) Radial distribution function obtained from Fourier transform of Zn K-edge EXAFS spectra (a) Zn_co: coprecipitation, R+△R (Å) = ~2.7 Å, (b) Zn_ads: adsorption; R+△R (Å) = ~3.1 Å

- Mn K-edge XANES spectra shows: Mn^{IV} are dominant species in sludge 97%, and $Mn^{(II,III)}$ was 3.5% in A-1.

$$Mn^{2+} + 1/2\ O_{2aq} + H_2O \rightarrow MnO_2 + 2H^+ \quad (1)$$

- The dominated birnessite that formed in circumneutral condition indicates that Mn^{II} oxidation of reaction (1) is major Mn removal mechanisms.
- Zn removal mechanisms in the pilot-scale treatment is dependent to birnessite by: coprecipitation (60%) and adsorption (40%)

- Zn removal quantity by adsorption and coprecipitation mechanisms were almost the same.
- Therefore, a simplify Zn sorption kinetic model will be used to predict Zn behaviors in the treatment plan.

Material and methods (2)

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- **Mn^{2+} oxidation kinetics R_{Mn}(Morgan, 2005)**

$$R_{Mn} = \frac{-d[Mn^{2+}]}{dt} = k_1[Mn^{2+}] + k_2[MnO_x][Mn^{2+}] \quad (1)$$

$$R_{Mn} = \frac{-d[Mn^{2+}]}{dt} = k_1[Mn^{2+}] \quad (2)$$

- **k_1** is the pseudo-first-order reaction rate constant by dissolved Mn^{2+} disappearance from the solution
- **k_2** is the autocatalytic reaction rate constant due to the mineral surface

=> **k_1** is determined by inverse Mn kinetic transport model calibrated with Mn concentration using PEST. **k_2** is neglected due to low autocatalytic effect.

- **Zn sorption kinetic reaction (R_{Zn})** (Tebes-Stevens and Valocchi, 1998) that included the sorption mechanisms:

$$R_{Zn} = -k_m\left(c_{Zn} - \frac{s_{Zn}}{K_d}\right)$$

- S_{Zn}: mass of sorbed concentration (mol/g)
- k_m: mass transfer coefficient (s^{-1})
- K_d: distribution coefficient (L/g)
- c_{Zn}: Concentration of Zn (mol/L)

=> fitting method was used to obtained **k_m and K_d** using Zn concentration from the monitoring data.

=> The obtained **k_1, k_m and K_d** will be used to estimate the suitable HTR in the pilot passive treatment in mine X

Mn oxidation kinetic and transport

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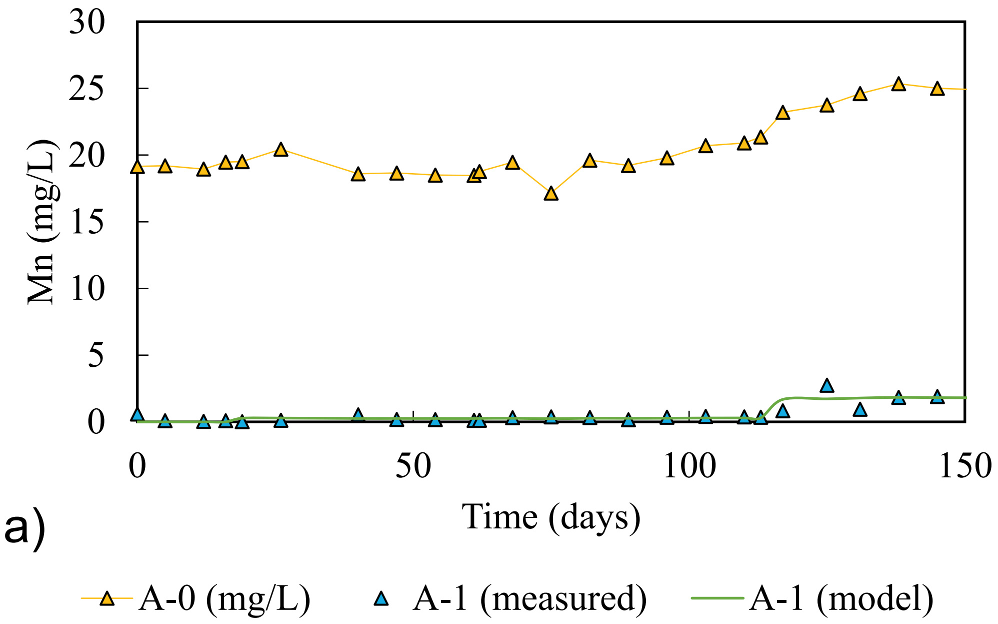
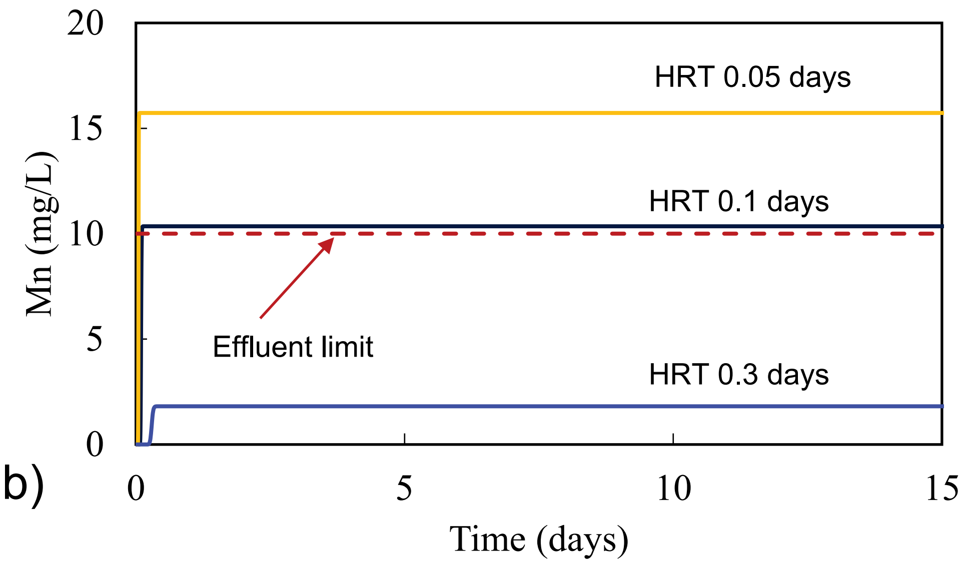


a)



b)

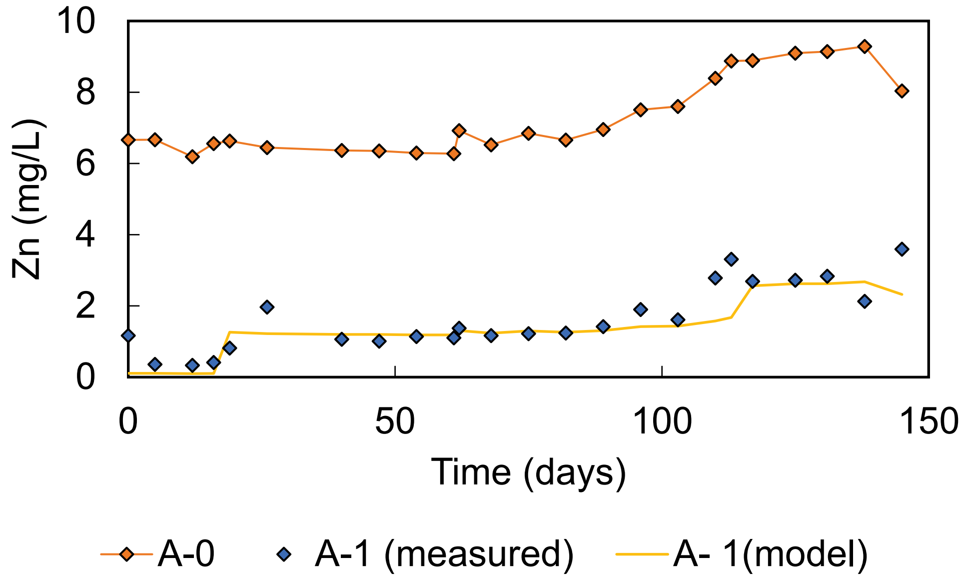
The fitting model (Fig.a) provided:

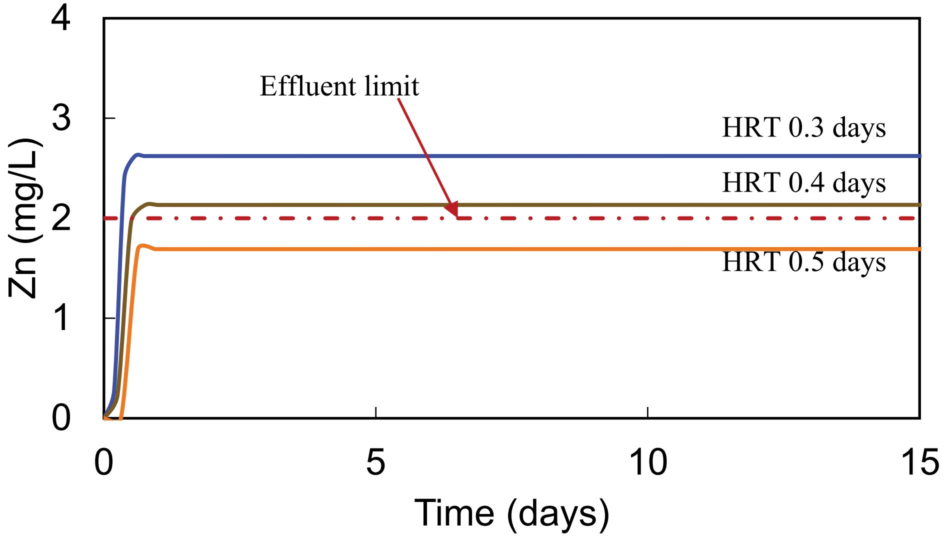
- $k_1 = 8.52\times 10^{-5}\ s^{-1}$
- The predictive model root mean square error is ± 0.36 mg/L (above 5% of uncertainty).

- The pilot experiment have not yet determined the optimum the HRT for Mn and Zn yet.
- So, k_1 is applied to the model back to determine optimum HRT for Mn removal
- The model (Fig.b) shows that when Mn= 25 mg/L at the mine drainage, the HRT > 0.1 days is should be maintained in the pilot treatment to removal Mn.

Fig. a). Mn concentrations in the treatment tank at pilot-scale passive treatment system for 152 days and the predictive Mn oxidation kinetic of birnessite modelling, b). The predictive model of Mn concentration in relation to HRT.

Zn sorption kinetic and transport





The fitting model (Fig.1a) provided;

- k_m= 4.51× 10^{-5} s^{-1}
- K_d =27.63 L/g

The predictive model root mean square error is ± 0.59 mg/L (above 5% of uncertainty)

- 9.5 mg/L Zn, k_m and K_d from fitting model were used as the input of the sorption kinetic transport model.
- The Fig.1b shows the HRT 0.5 days is the optimal HRT for Zn removal from the pilot treatment
- Zn is the rate limiting in the pilot-scale passive treatment

Fig. a). Zn concentrations in the treatment tank at pilot-scale passive treatment system for 152 days and the predictive Zn sorption kinetic on birnessite modelling, b). The predictive model of Zn concentration in relation to HRT.

Conclusion

- The dominated birnessite that formed in circumneutral condition indicates that Mn^{II} oxidation reaction rather than autocatalysis mechanisms.
- Zn was primarily removed from the pilot-scale passive treatment through co-precipitation with MnO_2 (60%), and adsorption (~40%) on the bio-birnessite surface.
- The utilization of inverse Mn^{2+} oxidation kinetics and transport model and Zn sorption and transport model was able to obtained **k_1 , k_m and K_d** .
- The obtained parameters from the monitoring could be to estimate the suitable HTR in the pilot passive treatment in mine X.
- Our findings suggest that an HRT of at least 0.5 days is suggested for successful Mn and Zn treatment in the pilot scale treatment.

Future plan:

- The obtained parameters **k_1 , k_m and K_d** will be used to apply in the scale up passive-treatment in mine X.

Thank you for your attention!

ありがとうございます。