Multi-Step Passive Treatment Using Limestone, Wood Chips and Concrete Waste Material for Zn and Cd Removal

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Abstract

Japan Organization for Metals and Energy Security (JOGMEC) has conducted research on passive treatment (PT) methods to reduce costs. This study evaluated the use of concrete waste material (CWM) as a neutralizer for the PT of mine water containing Zn and Cd through a multistep process comprising limestone and CWM reactors. During continuous flow tests, the pH remained above 9 for over 200 days when the CWM reactors contained a 1:2 ratio of CWM to woodchips. The dissolved Zn and Cd were decreased by an average of 98.8% and 98.6% during this period without maintenance.

Keywords: Passive Treatment, Concrete Waste Material, Limestone, Acid Mine Drainage, Abandoned Mine

Introduction

Active treatment of mine water is being conducted in approximately 100 abandoned mines in Japan, incurring considerable annual costs. Japan Organization for Metals and Energy Security (JOGMEC) has conducted research on passive treatment (PT) to reduce costs, though there been few domestic examples of PT of mine water. Generally, a process using sulfate-reducing bacteria is employed to realize PT removal of Zn and Cd (Sato *et al*. 2018, Habe *et al*. 2018). However, this process is difficult to apply at sites with low winter temperatures and low sulfate ion concentrations in the mine water; in such cases, the pH must be increased to remove Zn and Cd. Furthermore, limestone, a commonly used neutralizer in PT, is not expected to sufficiently increase the pH. Therefore, a neutralizer with a high pH that is adaptable to PT is essential to realize the removal of Zn and Cd from mine water. This study accordingly evaluated the use of concrete waste material (CWM), generated during the manufacture of concrete products, as a neutralizer for PT (Takaya *et al*. 2022). As CWM contains calcium hydroxide as a major component, it is expected to have a strong pH-raising effect (Adrian Brown. 2022). Therefore, this study evaluated a novel multistep process using limestone and CWM for PT of mine water containing high concentrations of Zn and Cd.

Methods

Mine water profile of the target mine

The water profile of the target mine considered in this study at the experiment site is listed in Table 1.

Materials

A high-purity limestone crystal neutralizer (20-40 mm) supplied by Ookubo Rozai Co., Ltd. was used as the limestone and PAdeCS (5-20 mm) derived from concrete sludge marketed by Nippon Concrete Industries Co., Ltd. was used as the CWM. This PAdeCS not only has a high alkaline content but is less expensive than limestone. The chemical and mineralogical compositions of the limestone and CWM were determined using X-ray

Table 1 Water profile of the target mine

	pH	Temp.	Zn	Cd	Cu	Pb	Fe	SO_4^{2-}
	(-)	(˚C)	(mg L^{-1})	(mg L^{-1})	(mg L^{-1})	(mg L^{-1})	(mg L^{-1})	(mg L^{-1})
Ave.	3.8	10.7	21	0.24	11	0.24	1.8	138
Max.	5.1	13.5	52	0.54	26	4.3	18	300
Min.	3.2	9.1	9.4	0.11	3.6	0.7	0.3	94

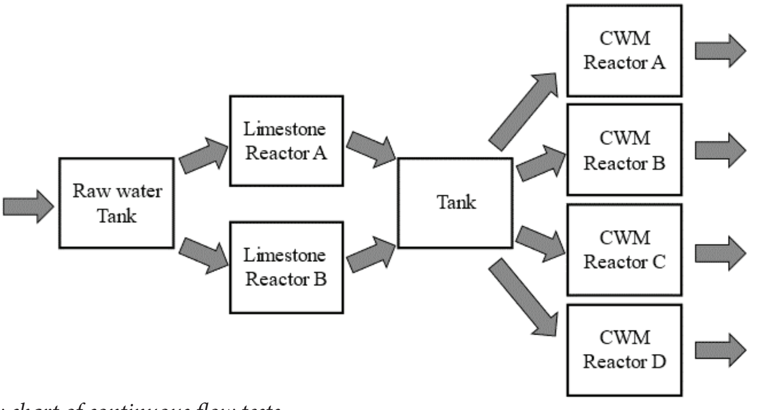

Figure 1 *Flow chart of continuous flow tests*

Figure 2 *Reactors employed in the continuous flow test; limestone reactor (right), CWM reactor (left)*

fluorescence (XRF, ZSX Primus 2, Rigaku, Japan) and X-ray diffraction (XRD, Ultima 4, Rigaku, Japan), shown in Table 2. Finally, woodchips less than 40 mm long, marketed by Mogami Mokushitsu Energy and comprising a mixture of tree species, were also employed in the CWM reactor.

Continuous flow tests

Two vertical downflow limestone reactors (400 mm wide, 300 mm long, and 610 mm deep) and four vertical downflow CWM reactors (543 mm wide, 340 mm long, and 295 mm deep) were installed in series, as

Table 2 *The characterisation of limestone and CWM*

		Limestone	CWM (PAdeCS)
			
Particle Size (mm)		20 - 40	5 - 20
Mineral Components		$CaCO_3$	$CaCO_3$ $Ca(OH)_2$
Elements (mass%)	Ca	70.1	43.5
	Mg	0.39	0.7
	Si	0.18	9.87
	Al	0.02	3.16

Table 3 *The contents and HRTs for the CWM reactors*

	Limestone/CWM/woodchips volume ratio	Limestone Volume (L)	CWM Volume (L)	Woodchips Volume (L)	HRT (h)
CWM reactor A	0/1/0	-	9	-	3 ※4
CWM reactor B	1/1/0	9	9	-	3 ※4
CWM reactor C	0/1/1	-	9	9	3 ※4
CMW reactor D	0/1/2	-	6	12	3

※ After 169 days of water flow, HRT was changed from 3 to 4 hours.

illustrated in the flow chart in Figure 1, in a tunnel at the mine site, as shown in Figure 2. Mine water was introduced at the top of each reactor from the preceding tank using an electric pump. The headspace of each reactor was open, and the CWM reactors were designed to drain from the bottom. Each limestone reactor was filled with a 300 mm thick layer of limestone and the water level was set at 50 mm above the top of this layer. The hydraulic retention time (HRT) in the limestone reactors was set to 2 – 4 h. Each CWM reactor was filled with a 300 mm thick layer comprising different volume ratios of limestone, CWM, and woodchips, and the water level was set at 40 mm above top of this layer. The HRT in the CWM reactors was set to 3–4 h and the contents and HRTs for the four CWM reactors are summarized in Table 3. This reactor configuration has been employed in an ongoing continuous flow test that was begun in June 2022.

Monitoring parameters and analytical methods

Water temperature and pH were monitored at the mine site at all times, and water samples of the effluent from each reactor were regularly collected to determine the concentrations of total Zn, Cd, Cu, Pb, and Fe using inductively coupled plasma optical emission spectrometry (ICP-OES; Agilent 5110 ICP-OES, Agilent Technologies Inc., USA). A membrane filter with a pore size of 0.45 μm was used to filter the suspended metals from the water sample and thereby determine the contents of soluble Zn, Cd, Cu, Pb, and Fe within.

Results and Discussion

The water temperature in each CWM reactor increased during the summer and decreased only slightly during the winter. The effluent from the limestone reactors had a pH of approximately 6. The measured pH changes in each CWM reactor are shown in Figure 3, which indicates that Reactors A, B, and C maintained a stable pH above 9 for approximately 60 d after water began to flow at an HRT of 3 h. This stability was a result of the dissolution of calcium hydroxide, a major component of CWM, providing hydroxide. The effluent from the reactors containing CWM mixed with limestone or woodchips exhibited a higher pH than that from the CWM-only reactor. This indicates that CWM has a strong pH-raising effect and is effective as a neutralizer, and that its effectiveness is enhanced when it is mixed with limestone or woodchips. However, approximately 60 d after water flow began, the pH in these reactors decreased and became unstable. Flushing, in which the water and precipitation in the reactor are drained vigorously out of the reactor by opening a cock installed at the bottom of the reactor, was subsequently performed to prevent the pH from decreasing further, causing the pH to recover for approximately 20 d. However, the pH again became unstable, and the pH recovery effect was reduced following a second flushing. The HRT was subsequently increased from 3 to 4 h, causing the pH of the effluent to stabilize and largely remained above 9 thereafter. In contrast, Reactor D maintained a stable pH above 9 for over 200 d at an HRT of 3 h without maintenance. These results indicate that the effluent from a reactor containing CWM and woodchips will remain stable at a higher pH than that from a reactor containing CWM alone or CWM with limestone, and that a CWM-to-woodchip volume ratio of 1:2 is optimal.

The measured changes in the total concentrations of Zn and Cd in the raw water, limestone reactor effluent, and effluent from each CWM reactor are shown in Figures 4 and 5, respectively. Soluble Zn and Cd in the effluent from all four CWM reactors were removed by an average of over 99.1% and 96.4%, respectively, over the first ≈60 d after water flow began. Furthermore, the correlation between the Cd concentration and pH shown in Fig. 6 shows that soluble Cd concentrations in the effluent from each CWM reactor were less than theoretically predicted at the given pH for removal of Cd as a hydroxide. During treatment, the mine water passed through the limestone reactor and then the CWM reactor, where it was supplied with hydroxide and carbonate, facilitating the removal of Zn and Cd, respectively. However, approximately 60 d after water flow began, as the pH decreased,

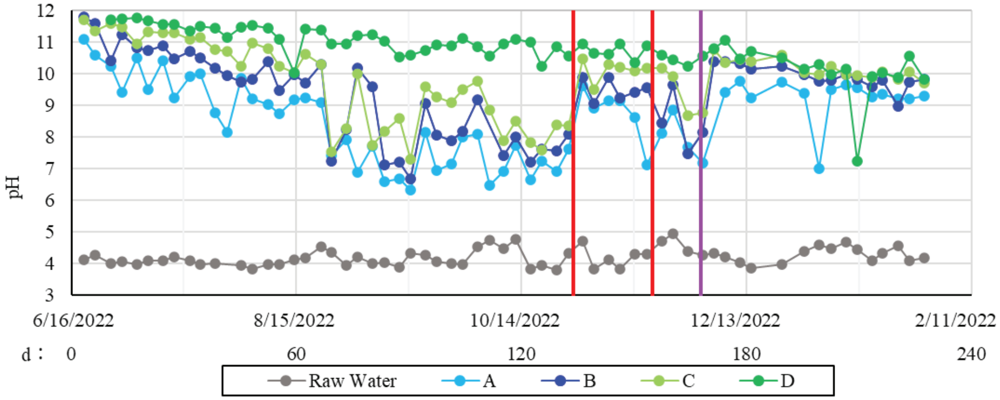

Figure 3 *Changes in CWM reactor pH over time; Flushing in CWM reactor A, B and C (red line), HRT changed 3 h to 4 h in CWM reactor A, B and C (purple line)*

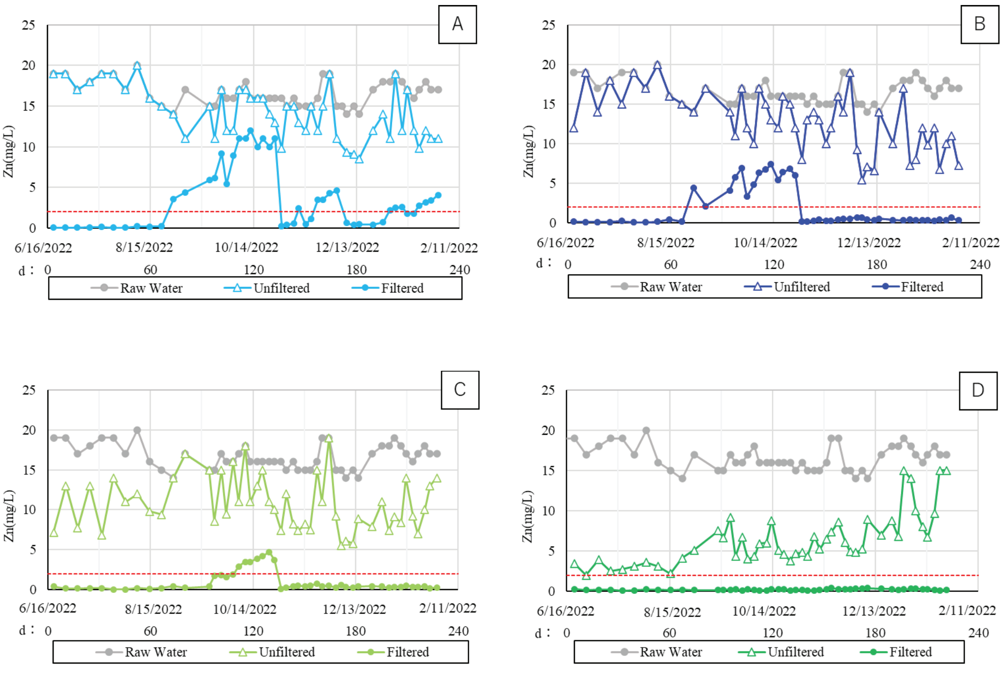

***Figure 4** Zn concentrations in CWM reactor effluent over time (the dashed line indicates the maximum allowed by the domestic discharge standard)*

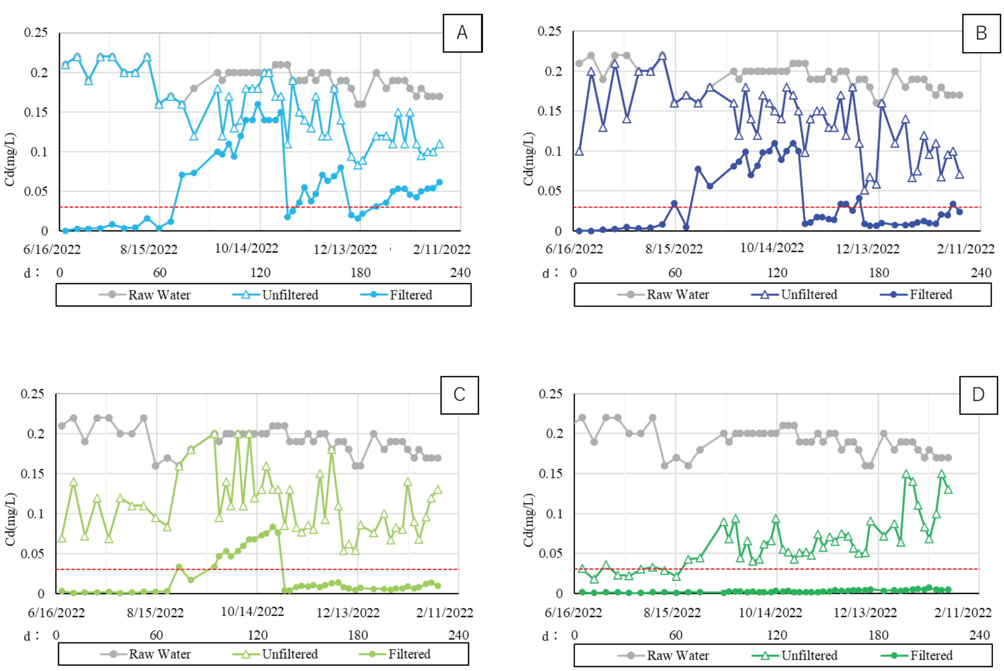

***Figure 5** Cd concentrations in CWM reactor effluent over time (the dashed line indicates the maximum allowed by the domestic discharge standard)*

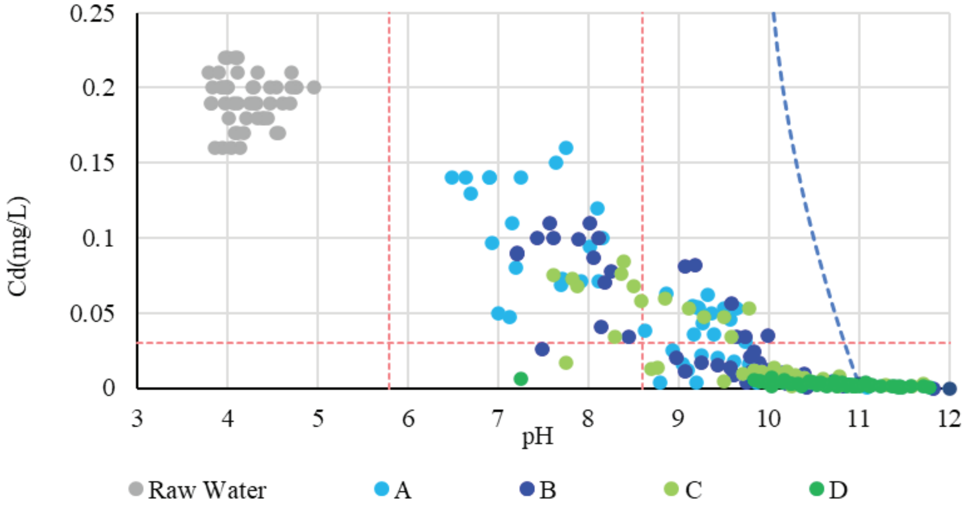

Figure 6 *Correlation between pH and Cd concentration in CWM reactor effluent; the pH and the maximum concentrations allowed by the domestic discharge standard (red dashed lines), Cd concentrations at theoretical pH for removal as hydroxide (Blue dashed line)*

the soluble Zn and Cd concentrations in the effluent from CWM Reactors A, B, and C increased, whereas soluble Zn and Cd in the effluent from CWM Reactor D were decreased uniformly by an average of 98.8% and 98.6% for over 200 d. This confirms that CWM is effective in the PT of mine water containing Zn and Cd, and that a 1:2 volumetric ratio of CWM to woodchips provides optimal treatment. However, the total Zn and Cd in the effluent from the CWM reactors exceeded the domestic discharge standard because they were partially present as suspended particles which were not completely removed by the current process. Therefore, a settling reactor will be placed in series with the CWM reactors in the future.

Conclusions

Continuous flow tests were conducted to treat mine water containing Zn and Cd at a mine site in Japan using a multistep process comprising limestone reactors with an HRT of 2–4 h in series with different CWM reactors with an HRT of 3–4 h. The pH values of the CWM reactor effluents remained above 9 for approximately 60 d for CWM reactors containing CWM only, a 1:1 ratio of limestone to CWM, and 1:1 ratio of CWM to woodchips. The pH remained above 9 for over 200 d for the CWM reactor containing a 1:2 ratio of CWM to woodchips, during which time the soluble Zn and Cd in the effluent were decreased by an average of 98.8% and 98.6% without maintenance. In particular, soluble Cd concentrations were found to be less than the Cd concentrations at theoretical pH for removal as Cd hydroxide. These results can be attributed to the supply of carbonate in the limestone reactor and the increase of the pH in CWM reactor, which removed Zn and Cd as hydroxide as well as carbonate. This result suggests that CWM is applicable as a neutralizer for the PT of mine water containing Zn and Cd, and that a multi-step process comprising limestone and CWM reactors represents a more effective configuration than a CWM-only reactor in terms of the pH requirement and long-term neutralization. Tests will continue to be conducted to remove Zn and Cd suspensions and to clarify of the effects of woodchips and the long-term effectiveness of the proposed PT system.

References

Sato Y, Hamai T, Hori T, Habe H, Kobayashi M and Sakata T (2018) Year-round Performance of a Passive Sulfate-reducing Bioreactor Using Rice Bran as an Organic Carbon Source for Treating Acid Mine Drainage.Mine Water Environ 37 ,586-594

Habe H, Sato Y, Aoyagi T, Inaba T, Hori T, Hamai T, Hayashi K, Kobayashi M, Sakata T and Sato N(2020) Design, application, and microbiome of sulfate-reducing bioreactors for treatment of mining-influenced water. Appl Microbiol Biotechnol 104, 6893–6903.

Takaya Y, Fuchida S, Hamai T, Horiuchi K, Masaki Y, Tokoro C (2022) Prediction of Acid Mine Drainage Treatment by Open Limestone-Alkaline Material Channel and Implications for the Large Scale Implementation of Passive Treatment. Proceedings of The Mining and Materials Processing Institute of Japan. Minato-ku,Tokyo,Japan. 7-9 March 2022 (Online)

Brown, Adrian(2018): Passive Metal Mining and Mine Water Treatment Using Crushed Concrete. – In: Wolkersdorfer, Ch.; Sartz, L.; Weber, A.; Burgess, J. & Tremblay, G.: Mine Water – Risk to Opportunity (Vol II). – p. 1029 – 1036; Pretoria, South Africa (Tshwane University of Technology).