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TECHNICAL COMMUNICATION

Investigation of Sludge Volume from Abandoned Mine Wastewater Treatment by Layered Double Hydroxides: A Case Study Targeting As and Fe

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Abstract

We treated three samples of wastewater from an abandoned mine using NO_3-type Mg–Al layered double hydroxides with different Mg/Al ratios (denoted LDH-2 and LDH-4) and the conventional neutralizer $Ca(OH)_2$. We determined the optimal condition for each treatment before confirming the residual As and Fe concentrations, pH, and the amount of suspended solids (SS) in the supernatant after treatment under optimal conditions. We then estimated and compared the volume of sludge generated over 8 h in each treatment. We found that when treated under optimal conditions, both As and Fe were removed in compliance with Japan's Uniform National Effluent Standards and that pH and SS met the standard in all cases. The final sludge volume at 8 h was 70 mL when $Ca(OH)_2$ was used; this was twice as much when LDH-2 was used (30 mL) and four times that when LDH-4 was used (15 mL). These results strongly suggest that LDH has a high potential for treating wastewater from mines.

Keywords Mg–Al LDH · $Ca(OH)_2$ · Metal · Water treatment · Optimization

Introduction

Japan used to be a leading mining country; production peaked around World War II. However, the depletion of mineral resources and massive imports of high-quality, low-cost foreign resources led to the closure of nearly 5000 mines in Japan; ≈ 450 of these abandoned mines are still pollution sources (JOGMEC 2018). Since Japan mined mostly sulfide minerals, the minerals remaining after the mines were closed include pyrite (FeS_2), chalcopyrite ($CuFeS_2$), and galena (ZnS); these are exposed to oxygen in the air and groundwater, generating acid mine wastewater containing various harmful metals (JOGMEC 2006). The proper treatment of abandoned mine wastewater is vitally important for the safety of humans and the environment.

Chemical precipitation is widely used to treat mine wastewater. Lime ($Ca(OH)_2$) or caustic soda (NaOH) are often used to precipitate metal hydroxides, which are generally stable and insoluble in alkaline solutions. The process is relatively simple and effective and can also be used for wastewater containing mixed metals. However, the treatment generates large amounts of sludge with a high-water content; its management requires an enormous amount of energy and high costs (Clifford et al. 1986; Rahman et al. 2019). Moreover, a shortage of intermediate waste processing facilities and final disposal sites has become a serious concern. According to the Japanese Ministry of the Environment (MOE 2017), there were 18,680 intermediate waste processing facilities and 1827 final landfill sites for industrial waste throughout Japan in 2014, with only 16 years left before the remaining landfill sites

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were full (remaining capacity: 166.04 million tons, final disposal volume: 10.4 million tons). Therefore, reducing the volume of sludge after treatment is particularly important.

Layered double hydroxides (LDHs) are a group of natural or synthetic materials with the general formula $[M^{2+}{}_{1-x}M^{3+}{}_{x}(OH)_2][(A^{n-})_{x/n}•mH_2O]$, where M^{2+} represents divalent cations like Mg^{2+}, Zn^{2+}, Co^{2+}, or Ni^{2+}; M^{3+} represents trivalent metal cations like Al^{3+} or Fe^{3+}; A^{n-} represents interlayer anions such as $CO_3{}^{2-}$ or Cl^-; and x is the molar ratio of $M^{3+}/(M^{2+}+M^{3+})$ in the range $0.20 \le x \le 0.33$ (Boclair and Braterman 1999). The layers of LDHs have a positive charge due to partial replacement of M^{2+} with M^{3+}; this is balanced by negatively charged interlayer anions and the accommodation of water molecules, which results in a group of hydrogen bonds between layers (Mills et al. 2012). The interlayer anions in LDHs are loosely bound and can thus be exchanged following the sequence $OH^- > F^- > Cl^- > Br^- > NO_3{}^- > I^-$ for monovalent anions and $CO_3{}^{2-} > SO_4{}^{2-}$ for divalent anions (Miyata 1983). This characteristic gives LDH an excellent capability for removing oxide anions such as As (e.g. $AsO_4{}^{3-}$, $HAsO_4{}^{2-}$, $H_2AsO_4{}^-$) and Cr ($HCrO_4{}^{2-}$, $Cr_2O_7{}^{2-}$, $CrO_4{}^{2-}$) (Douglas et al. 2010; Goh et al. 2009). However, cations such as Fe^{2+}, Cu^{2+}, and Zn^{2+} can also be removed by LDHs; this probably occurs through the dissolution of the LDHs, the release of hydroxide ions from its layers, and the resultant precipitation (Rahman et al. 2019). Based on these properties, LDH is considered a promising agent for the simultaneous removal of anions and cations in wastewater. Indeed, an approach in which LDHs are formed in situ to treat acidic mine water has already been successfully field tested and commercialized (Douglas 2014; Douglas et al. 2010; VCL 2020).

Rahman et al. (2019) investigated the removal efficiency and possible removal mechanism of As and Fe in mine water, using NO_3-type Mg–Al LDHs and $Ca(OH)_2$. When 5 g/L of LDH was used with an Mg/Al ratio of 2:1 and 10 min of shaking, effluent standards for both As and Fe were met, while only Fe was removed to standard when 5 g/L of $Ca(OH)_2$ was used. The sludge volume was 12 mL/L when Mg–Al LDH was used, compared to 100 mL/L when $Ca(OH)_2$ was used.

To further study the use of LDHs for treating mine wastewater, tests were conducted to optimize testing conditions, using water from an abandoned mine containing As and Fe. We first optimized the conditions of each treatment using Mg–Al LDH with a Mg/Al ratio of 2 or 4 or $Ca(OH)_2$ in a 50 mL batch experiment. We then scaled up the experiment and treated 500 mL of mine water under the optimal conditions determined, checked the water quality, and finally estimated and compared sludge volumes to evaluate treatment effectiveness.

Materials and Methods

All reagents were purchased from Kanto Chemical. Co. Inc. and Fujifilm Wako Pure Chemical Corporation without previous purification. Solutions were prepared using deionized water.

The abandoned mine wastewater used in this study was collected from mine A in Hokkaido, Japan. This site had operated as a sulfur and iron sulfide mine since the Meiji Era, but closed in 1973 due to a downturn in the sulfur market caused by the rapid growth of desulfurized crude oil. Acidic water containing a high concentration of As has been flowing out of the mine since it was operational and ≈ 3.77 m^3/min of wastewater is still being discharged (Endou 2013).

Synthesis of Mg–Al Layered Double Hydroxides (LDH)

Two types of Mg–Al LDH intercalated with $NO_3{}^-$, with Mg/Al molar ratios of 2:1 and 4:1 (defined as LDH-2 and LDH-4, respectively, in this paper), were prepared using the following coprecipitation method. Two sets of $Mg(NO_3)_2•6H_2O$ and $Al(NO_3)_3•9H_2O$ mixtures (500 mL each, total concentration $[Mg^{2+}]+[Al^{3+}]=0.50$ mol/L, i.e. for Mg/Al molar ratio of 2:1, $[Mg^{2+}]=0.67$ mol/L, $[Al^{3+}]=0.33$ mol/L; for Mg/Al molar ratio of 4:1, $[Mg^{2+}]=0.40$ mol/L, $[Al^{3+}]=0.10$ mol/L) were prepared and added dropwise to 500 mL of deionized water in a 1 L 5-neck round bottom flask. NaOH solution was then added to adjust the pH of the reaction mixture and keep it at 10.5; the mixture was stirred at 300 rpm and reacted at 30 ℃ over time. The mixture was then purged with N_2 gas to eliminate carbon dioxide as it could have formed $CO_3{}^{2-}$ and thus prevented the intercalation of $NO_3{}^-$ into the LDH layers. The resulting precipitate was separated from the suspension via suction filtration, washed with deionized water, and then dried at 40 °C in a vacuum oven for 40 h. The products, LDH-2 and LDH-4, were ground into fine powder, filled on a glass with a recess for powder, and then characterized by x-ray diffractometer (XRD) using a Rigaku RINT 2200 diffractometer with Cu K_α radiation at 40 kV and 20 mA (scanning rate of 3°/min). A Thermo Scientific iCAP6500DuO inductively coupled plasma-atomic emission spectrometry (ICP-AES) was used to obtain the elemental composition of the synthesized LDHs. All the ICP analyses were run in triplicate with the calibration curve method after solution check. Images of LDHs were captured by a Hitachi-Hightech S-4800 scanning electron microscope (SEM).

Optimizing the Treatment of Wastewater from an Abandoned Mine

As and Fe concentrations in the abandoned mine wastewater were measured using ICP-AES. In contrast to previous studies using powdered LDH and $Ca(OH)_2$ (Rahman et al. 2017, 2019), we prepared a suspension of $Ca(OH)_2$ and synthesized LDH in 10 g/L for use as the reagent based on the actual treatment processes. Different amounts of these suspensions were added to 50 mL wastewater and reacted by stirring at 300 rpm at 10 °C, which is a common reaction temperature for wastewater from an abandoned mine, soon after the water was collected. The reacting suspension was sampled at 1, 5, 15, and 30 min and immediately filtered through a 0.45 µm membrane. Residual As and Fe concentrations in the supernatant were analyzed using ICP-AES. In all cases, the pH of the reacting suspension was measured until it stabilized. The amount of $Ca(OH)_2$, LDH-2, and LDH-4 suspensions at which residual As and Fe concentrations and pH met the Japanese Uniform National Effluent Standards [i.e. As and its compounds < 0.1 mg/L, dissolved Fe < 10.0 mg/L, pH 5.8–8.6 (MOE 2015)] was defined as the optimal amount of each reagent. The time at which the pH stabilized was determined as the optimal reaction time.

Treating Wastewater from the Abandoned Mine under Optimal Conditions

Three sets of treatments using 500 mL of mine wastewater were conducted in a 1 L 3-neck round bottom flask; each treatment used $Ca(OH)_2$, LDH-2, and LDH-4 at the previously determined optimal conditions. The mixtures produced by the reactions were immediately transferred into a 1 L cylinder and sedimentation behavior and sludge volumes were assessed for 8 h. Subsequently, 100 mL of supernatant was collected and filtered three times and the quantity of suspended solids (SS) was calculated from the increase in the weight of the filter paper. Residual As and Fe concentrations and pH were measured to confirm the effectiveness of the treatment. The precipitates were then filtered and dried at 40 ℃ in a vacuum oven for 48 h and then observed using XRD and SEM.

Results and Discussion

Characterization of Mg–Al LDHs

The XRD patterns of the synthesized LDH-2 and LDH-4 are shown in Supplemental Fig. S-1. The XRD patterns and d_{003} values were ascribed to hydrotalcite (JCPDS card 22-700), which represents the hydroxyl carbonate of Mg and Al with the formula $Mg_6Al_2(OH)_{16}CO_3{\cdot}4H_2O$. The sharp symmetric peaks at lower angles and the broad weak peaks at higher angles demonstrate the layered structure of the LDHs (Bagherifam et al. 2014). In comparisons of LDH-2 and LDH-4, the diffraction peaks of LDH-2 shifted towards lower angles and the d_{003} interval was larger. This is because a lower Mg/Al molar ratio results in a higher positively charged density; thus, more nitrate ions were intercalated into the LDH layers to maintain electrostatic balance, which led to the formation of thicker layers.

Table 1 shows the elemental composition of the two prepared LDHs. Though the Mg/Al molar ratio of LDH-4 was overestimated slightly, probably due to the formation of $Mg(OH)_2$ during synthesis (i.e. not all Mg^{2+} was incorporated into the layers), the results suggested that the LDHs were basically prepared in the planned ratio. Figure 1 shows SEM images of the prepared LDHs. Stacked sheet-like particles can be seen in both LDH-2 and LDH-4, which means that the layered structure of the LDHs was formed successfully.

Optimizing the Treatment of Wastewater from an Abandoned Mine

The concentrations of As and Fe measured in this wastewater, which had an initial pH of 1.93, were: As (V) = 8.86 mg/L, Fe (II) = 301 mg/L. Figure 2 shows the concentration of As and Fe and equilibration pH at each addition amount of each treatment. When 8 mL of $Ca(OH)_2$ was added to the suspension (Fig. 2a), both As and Fe removal was below effluent standards (As < 0.1 mg/L, Fe < 10.0 mg/L). The pH of the reaction mixture reached 6.5 and remained stable at that value after 1 h, meeting the effluent standards (pH 5.8–8.6). In this case, the $Ca(OH)_2$ acted as the precipitating agent and Fe was precipitated as $Fe(OH)_3$, which led to the coprecipitation of As. Tiwari and Pandey (2013) noted that when As concentrations were low and Fe concentrations were high, the As and ferrihydrite will co-precipitate; this is an effective method to remove dissolved As. Extended x-ray absorption fine structure studies have shown that various inner-sphere monodentate or bidentate complexes are formed when As (V) is absorbed onto ferrihydrite (Tiwari and Pandey 2013).

When 30 mL of LDH-2 was used in the suspension (Fig. 2b), As and Fe concentrations dropped below effluent

Table 1 Elemental composition of prepared layered double hydroxides

Initial Mg/Al molar ratio	Wt (%)		Actual Mg/Al molar ratio
	Mg^{2+}	Al^{3+}	
2:1	18.9	10.3	2.04
4:1	23.1	5.77	4.47

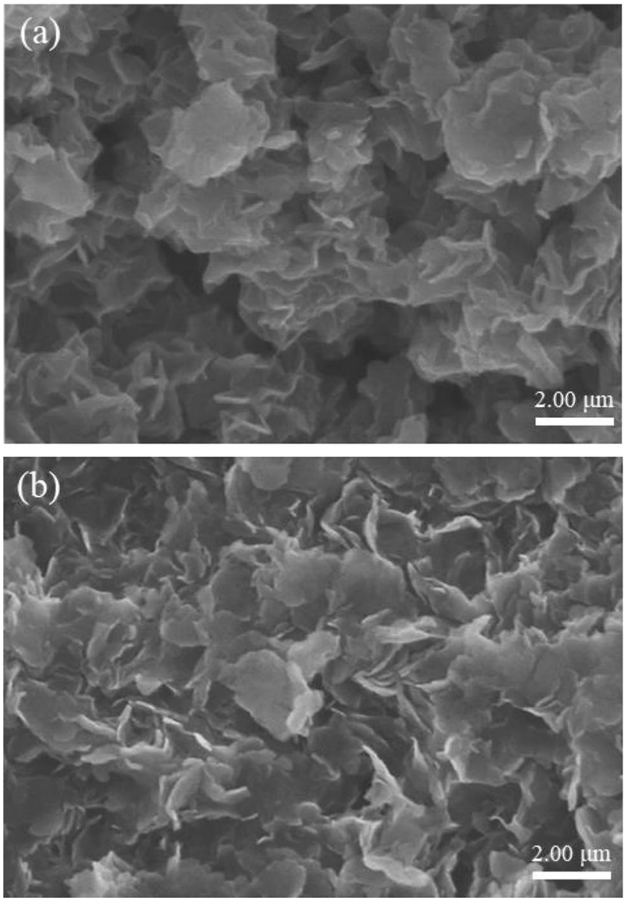

Fig. 1 Scanning electron microscopy images of prepared layered double hydroxides (LDHs): **a** LDH-2: Mg/Al molar ratio 2:1, **b** LDH-4: Mg/Al molar ratio 4:1

standards. The pH of the reaction mixture increased gradually and stabilized at 6.5 after 21 h; this also satisfied the standards. Because the mine wastewater used in this study was so acidic (pH = 1.93), The As was present as $H_2AsO_3^-$ ions and was removed by anion exchange, in which NO_3^- ions was exchanged between the layers of the LDH (Rahman et al. 2016, 2017), along with coprecipitation with Fe. The increase in pH was slower than when $Ca(OH)_2$ was used. This is probably due to the fact that the $Mg(OH)_2$ that made up the layers of the LDH is less soluble than $Ca(OH)_2$ ($Ca(OH)_2$ solubility = 1.54×10^{-4} mol/L, $Mg(OH)_2$ solubility = 2.11×10^{-3} mol/L), which led the dissolution and subsequent reactions to be slow. When 16 mL of LDH-4 was used in the suspension (Fig. 3c), both As and Fe concentrations met the effluent standards. The pH of the solution stabilized at 6.7 after 20 h of reaction. The removal mechanism was considered the same as when using LDH-2. Based on these results, we determined the optimal amount of each reagent and the reaction time for each treatment for 50 mL of wastewater: 8 mL $Ca(OH)_2$, 1 h; 30 mL LDH-2, 21 h; using LDH-4: 16 mL, 20 h.

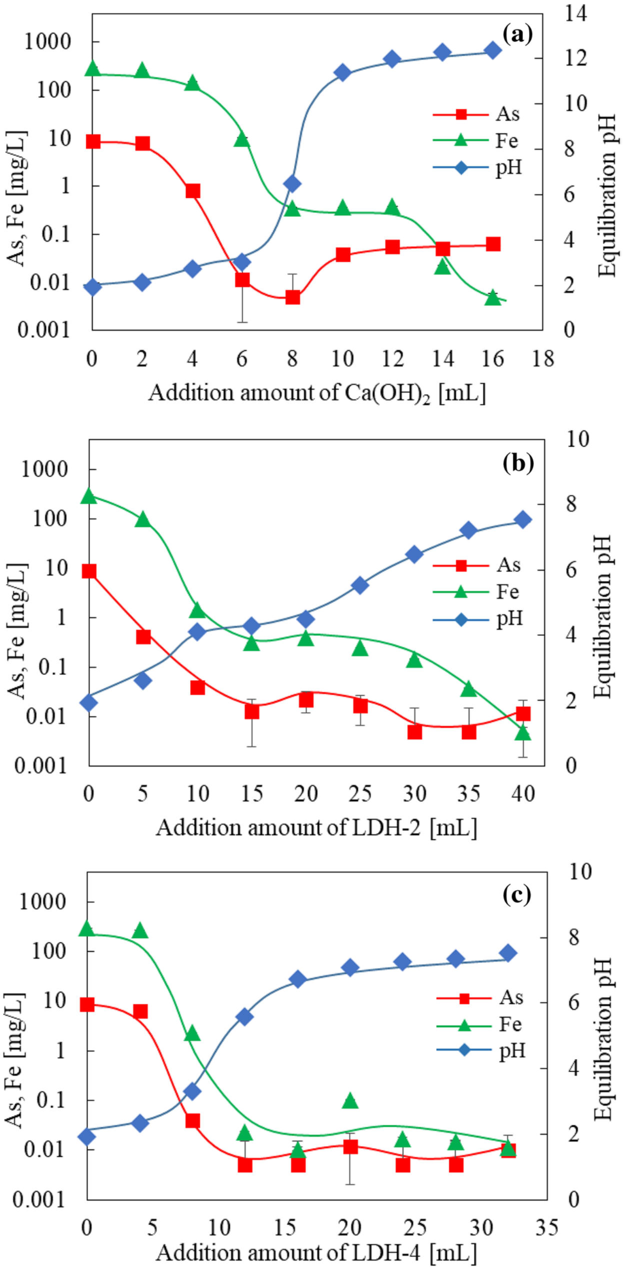

Fig. 2 Arsenic, Fe concentrations, and equilibrium pH at each addition amount: **a** using $Ca(OH)_2$, **b** using LDH-2, **c** using LDH-4

Treating Wastewater from an Abandoned Mine under Optimal Conditions

Post-treatment water quality indicators, including concentrations of residual As and Fe, supernatant pH, and the amount of SS, are shown in Table 2. No residual As or Fe was detected in the treated supernatant in all cases. The amounts of SS after treatment were 18.0 mg/L, 17.3 mg/L, and 16.3 mg/L (not significantly different), easily meeting Japan's Uniform National Effluent

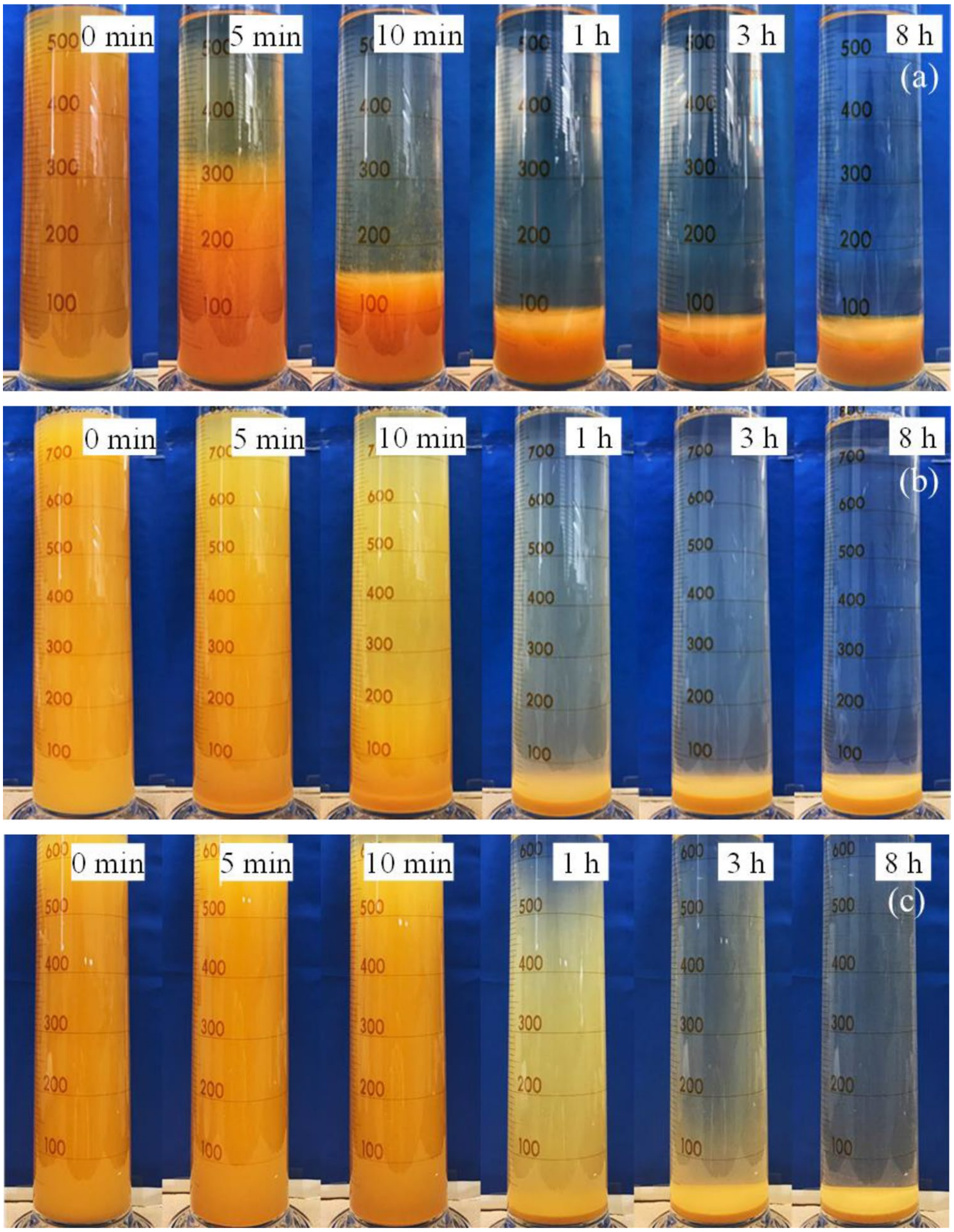

Fig. 3 Estimates of sludge volume over time of each treatment: **a** using $Ca(OH)_2$, **b** using LDH-2, **c** using LDH-4

Table 2 Quality of abandoned mine wastewater (500 mL) after treatment

		Using $Ca(OH)_2$	Using LDH-2	Using LDH-4
Concentration (mg/L)	As	n.d	n.d	n.d
	Fe	n.d	n.d	n.d
Amount of SS (mg/L)	1st	25	16	17
	2nd	16	19	14
	3rd	13	17	18
	Average	18.0	17.3	16.3
pH		7.76	6.01	6.08

Standard of < 200 mg/L (MOE 2015). The final pH values (7.76, 6.01, and 6.08) also all fell within the standard range of 5.8–8.6.

Figure 3 shows estimates of sludge volume over time. When $Ca(OH)_2$ was used (Fig. 3a), the volume of sludge was initially 580 mL; the final sludge volume (at 8 h) was

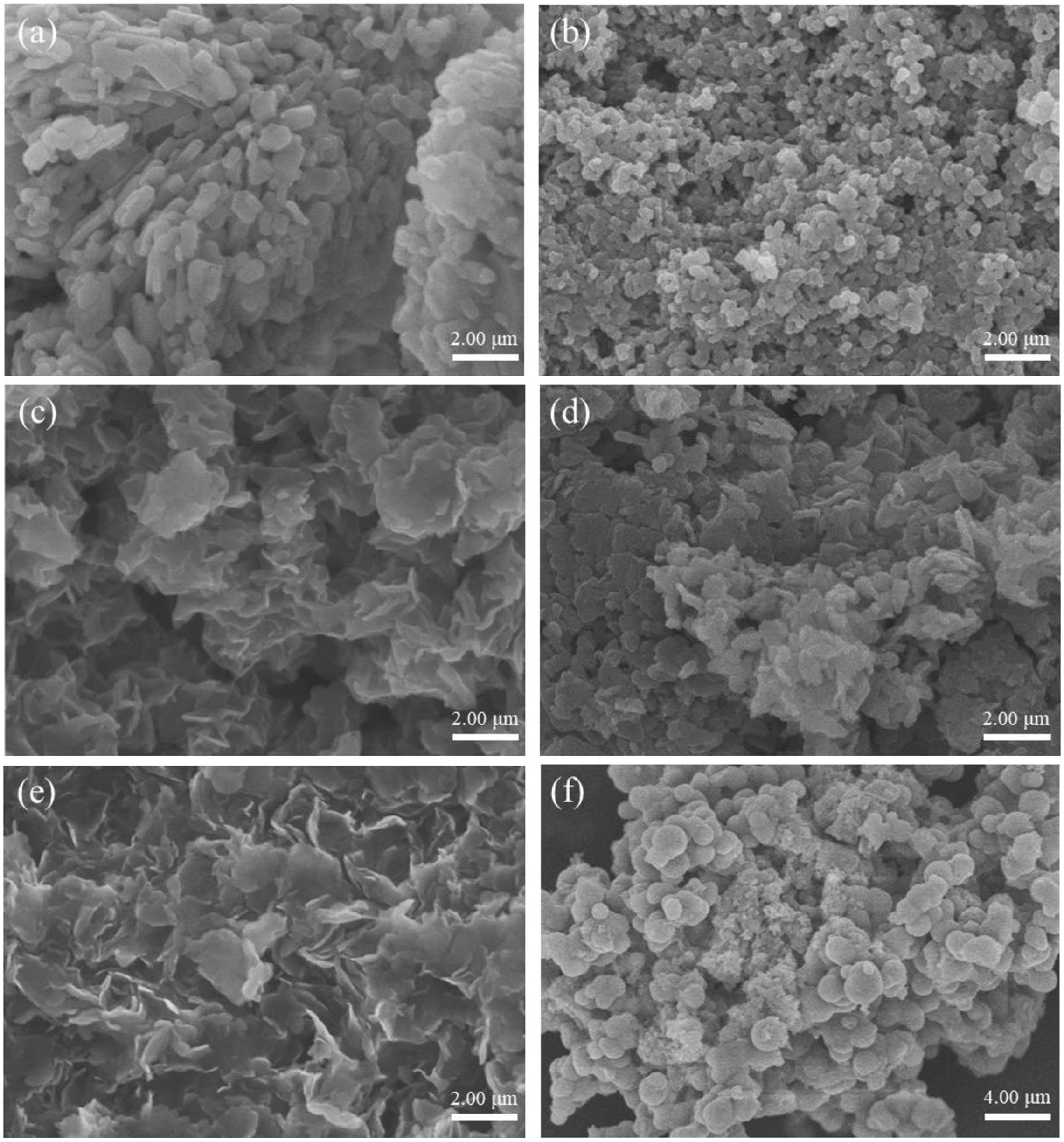

Fig. 4 Scanning electron microscopy images of each reagent and the solids produced after treatment: **a** $Ca(OH)_2$, **b** after-treated $Ca(OH)_2$, **c** LDH-2, **d** after-treated LDH-2, **e** LDH-4, **f** after-treated LDH-4

70 mL after gravitational sedimentation. The SS concentration was high because they settled in a mass, leading to a clear separation between the supernatant and the sludge. When LDH-2 was used (Fig. 3b), the initial sludge volume was 800 mL; this decreased to 30 mL at 8 h. Sedimentation behavior was very different when $Ca(OH)_2$ was used; a sludge layer formed quickly while the settling of the suspended particles was slow in comparison. This is probably due to the interference between particles in the suspension, which might have caused some of them to settle earlier and form the sludge layer while others interfered with each other and settled slowly. When LDH-4 was used (Fig. 3c), the initial sludge volume of 660 mL was reduced to 15 mL at 8 h; this was the lowest volume achieved among the three kinds of treatment.

Supplemental Fig. S-2 and Fig. 4 show the XRD patterns and SEM images of each original agent and the solid produced after treatment. The XRD patterns from when $Ca(OH)_2$ was used show that the typical $Ca(OH)_2$ diffraction peak (JCPDS card 4-733) disappeared on treatment, suggesting dissolution of $Ca(OH)_2$ or an inherent change in its structure. The SEM images (Fig. 4a, b) show that the particles changed from being ≈ 0.2 μm thick and 1 μm long plate-like particles to smaller granular particles. This was due to the Fe and As precipitation reactions, as noted earlier. When LDH-2 was used, similar XRD patterns were observed for the treated solid and original agent, indicating that the LDH structure was maintained. However, the decrease in intensity and sharpness indicated less crystallinity. This was supported by the SEM images (Fig. 4c, d), which show a sheet-like layered structure before and after treatment, although the latter was inhomogeneous and had smaller layers. When LDH-4 was used, no XRD peak characteristic of LDH or any other compound was found in the solid post-treatment. The SEM images (Fig. 4e, f) showed that while the LDH structure was sheet-like before treatment, there were massive particles, around 2 µm in size, after treatment, causing significant clotting. This explains why treatment using LDH-4 had the lowest sludge volume: the particles were highly flocculated.

Conclusions

In this study, we treated mine water containing As and Fe using NO_3-type Mg–Al layered double hydroxides (NO_3 Mg–Al LDH) with Mg/Al ratios of 2 and 4, along with conventional treatment using $Ca(OH)_2$. Our aim was to compare the sludge volumes associated using optimal amounts of LDH and $Ca(OH)_2$. First, the optimal conditions (the amount of reagent required and the reaction time) were defined by a series of experiments using 50 mL of wastewater from an abandoned mine: $Ca(OH)_2$: 8 mL, 1 h; LDH-2: 30 mL, 21 h; and LDH-4: 16 mL, 20 h. Then, their respective effectiveness at treating 500 mL of wastewater under these optimal conditions was confirmed by measuring the water quality of each supernatant post-treatment. In all cases, As, Fe, pH, and SS were all in compliance with Japan's Uniform National Effluent Standards. However, there was a noticeable difference in sludge volume: when LDH-4, LDH-2, and $Ca(OH)_2$ were used, the total amounts of sludge present after treatment were 15, 30, and 70 mL, respectively, for 500 mL of wastewater. These results show that LDH should definitely be considered for treating wastewaters from abandoned mines.

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