

# Stabilization of Mine Waste Using Iron and Steel-Making Slag to Prevent Acid Mine Drainage

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**Abstract.** Mine waste can create environmental pollution through leaching of potentially toxic elements or increased acidity in waterways from acid mine drainage (AMD). Consequently, effective solutions for management of AMD are required. In the present study, the use of slag was investigated for stabilizing AMD. Slag is an industrial byproduct of iron and steel-making, and is an inexpensive material for use in AMD management. When mixed with mine waste in a 10:8 ratio, converter steelmaking slag neutralized the eluate and reduced the concentrations of almost all metals to below Japanese standards for industrial effluents. Among the slags studied, converter steelmaking slag (C-slag) was the most effective slag for inhibition of AMD formation.

**Keywords:** Acid mine drainage, iron and steel making slag, mine waste

## 1. Introduction

Acid mine drainage (AMD) is a problematic environmental pollutant in the mining industry. AMD is formed when pyrite and other sulfide minerals are exposed to air and water. This produces an aqueous solution with a high concentration of dissolved heavy metals and sulfate, and can have a pH as low as 2 [1]-[3]. When discharged to streams and aquifers, AMD can kill all aquatic life, coat river bottoms with layers of rust-like particles, and decrease the pH of the waterway. Therefore, mine drainage needs to be treated before discharge. Typically, this is achieved by a neutralization process with addition of alkaline materials that remove metals as metal hydroxides. However, this method is expensive and the treatment results are not permanent.

Several studies have investigated treatment of mine drainage by reducing the levels of oxygen, which is required for oxidation of pyrite [4], [5]. Other studies have looked at sealing mine tailing storage areas with watertight barriers to prevent infiltration of water. A simple barrier constructed from a layer of impermeable soil (clay, silt or till) could perform better than oxygen reduction, and be less expensive than complex barriers. However, these types of barriers have limited efficiency because of difficulties with maintaining the material at a high degree of saturation and ensure its integrity with intrusion by tree roots and climatic variations (e.g. freeze/thaw, wet/dry). Traditionally, simple barriers have been constructed from natural materials. However, industrial residues could be attractive as barrier materials for economic reasons.

One such material that could be used in barrier construction is slag. Around 26,000,000 tons (1 ton = 1000 kg) of slag are produced in iron- and steelmaking in Japan each year. This slag is widely used for cement production, road construction, and as a concrete aggregate, but the capacity for use of recycled slags in these fields is saturated and new ways for using slag are required [6].

The aim of the present study was to investigate stabilization of mine waste using slag. The effect of slag addition on AMD discharge from mine waste was evaluated, and the underlying chemistry for the addition of slag to mine waste was considered.

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## 2. Materials and Methods

### 2.1. Samples

Waste rock was collected from the Matsuo Mine (Iwate Prefecture, Japan). The rock was crushed and ground by mill. The powder was sieved to collect particles with diameters of less than 500  $\mu\text{m}$ . These particles were air dried. The samples used in this study were oxidized and highly reactive to water.

The chemical composition of the mine waste is given in Table I, and the X-ray diffraction (XRD) pattern of the mine waste is shown in Fig. 1. The mine waste was mainly composed of  $\text{Fe}_2\text{O}_3$ ,  $\text{SO}_3$ , and  $\text{SiO}_2$ , which originate from pyrite, quartz and cristobalite.

Iron- and steelmaking slags used in this study were obtained from a Japanese steelmaking plant. These included a water quenched blast furnace slag (W-slag), slow air-cooled blast furnace slag (S-slag) and converter steelmaking slag (C-slag). Each slag sample was ground to a powder in a ball mill, and sieved to collect particles with diameters of less than 1 mm.

The chemical compositions of the slags are shown in Table I, and their XRD patterns are shown in Fig. 2. The W- and S-slag were mainly composed of  $\text{CaO}$ ,  $\text{SiO}_2$ , and  $\text{Al}_2\text{O}_3$  in the form of calcite ( $\text{CaCO}_3$ ), gehlenite ( $\text{Ca}_2\text{Al}_2\text{SiO}_7$ ) and larnite ( $\text{Ca}_2\text{SiO}_4$ ). Other oxides, such as  $\text{MgO}$ ,  $\text{SO}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{K}_2\text{O}$ , and  $\text{MnO}$ , occurred in lesser amounts. The C-slag was composed mainly of  $\text{CaO}$  (60.1 % mass fraction) and  $\text{Fe}_2\text{O}_3$  (21.7 % mass fraction). This slag contained the crystalline phases portlandite, srebrodlskite and calcite. Other oxides, such as  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{MgO}$ ,  $\text{K}_2\text{O}$ ,  $\text{SO}_3$ ,  $\text{TiO}_2$ ,  $\text{P}_2\text{O}_5$ ,  $\text{MnO}$ , and  $\text{SrO}$ , occurred in lesser amounts.

Table I: Chemical compositions of mine waste and different slags

	Mine waste	W-slag	S-slag	C-slag
$\text{Fe}_2\text{O}_3$	23.4	0.6	1.1	20.6
$\text{SO}_3$	27.9	1.1	1.3	0.2
$\text{SiO}_2$	44.4	34.5	33.9	23.8
$\text{Al}_2\text{O}_3$	0.9	13.7	14.2	2.4
$\text{CaO}$	0.6	42.9	41.5	49.3
$\text{MgO}$	0.3	6.1	6.6	8.8
$\text{K}_2\text{O}$	0.3	0.3	0.3	0.0
$\text{TiO}_2$	1.9	0.4	0.6	0.5
$\text{MnO}$		0.3	0.3	2.6
$\text{SrO}$		0.1	0.1	0.1
$\text{P}_2\text{O}_5$			0.1	1.7
$\text{Cr}_2\text{O}_3$				0.1
$\text{V}_2\text{O}_5$				0.1
$\text{Na}_2\text{O}$				0.6

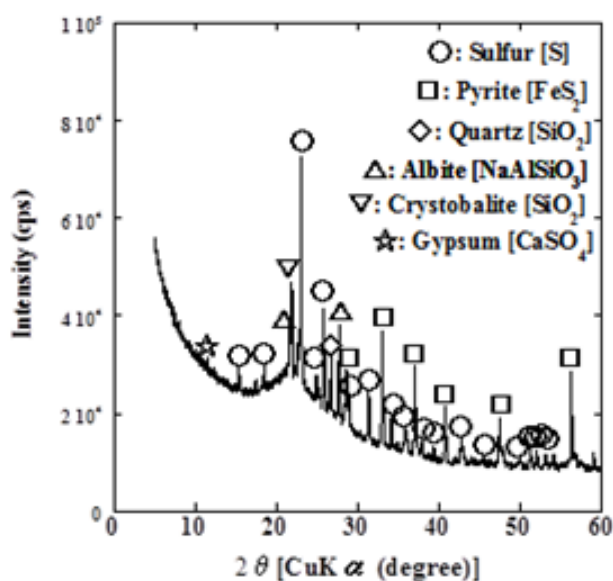


Fig. 1: XRD pattern of mine waste.

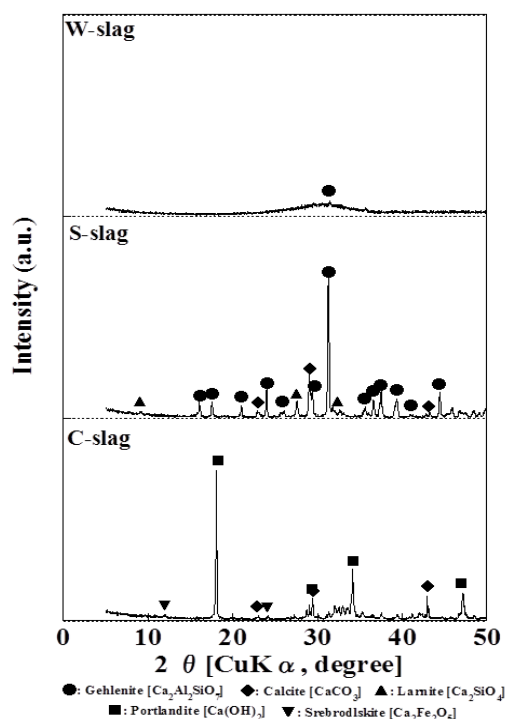


Fig. 2: XRD patterns of different slags.

## 2.2. Elution Test

We determined the effect of slag addition on AMD from mine waste by an elution test. The elution test was performed as follows. A sample of slag weighing 0–10 g was mixed with 10 g of mine waste, and then added to 100 mL of distilled water in a 200 mL Erlenmeyer flask. The flask was placed in an incubator at 60 °C, shaken for 6 h, and then filtered. The pH of the filtrate was measured using a pH meter (MA-130, Horiba, Kyoto, Japan). Major and trace elements in the filtrate were determined using inductively coupled plasma atomic emission spectroscopy (SPS5510, SII Nanotechnology, Hitachi High Technologies, Tokyo, Japan). Solid samples, including the mine waste, slag, and residues remaining after the elution test, were analyzed by XRD (RINT-2500, Rigaku, Tokyo, Japan) and X-ray fluorescence spectrometry (XRF-1700, Shimadzu, Kyoto, Japan).

## 3. Results and Discussion

The effect of slag addition on the inhibition of AMD from mine waste was investigated. Fig. 3 shows the pH of the solution eluted from the mine waste with addition of each of the three slags. The horizontal axis indicates the mass of slag added per 100 mL of elution solution, which contained 10 g of mine waste. Without addition of slag, the pH of the solution was acidic (around pH 2). As the mass of slag added to the solution was increased, the pH gradually increased. The solution was neutral (pH 6–8) when 4 g of slag was added per 100 mL of elution solution. The C-slag was the most effective at increasing the pH, followed by the S-slag, and then the W-slag.

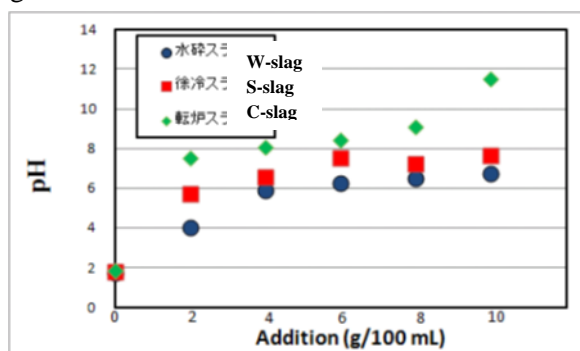


Fig. 3: The pH of the solutions obtained from elution tests using different slags.

Fig. 4 shows the concentrations of a number of metals in the eluate obtained from the mine waste with and without slag addition. For raw mine waste, large quantities of all of the metals were present in the eluate, and the concentrations of Fe, As, Pb, Cu and Ni were above Japanese standards for industrial effluents. When slag was added, the concentrations of the metals decreased, and higher decreases in metal concentrations were observed with higher slag additions. The concentrations that were above Japanese standards for industrial effluents decreased to below the standards. Ca and Si did not elute from the mine waste without slag addition, but did from slag in the mixture. The C-slag was most effective at reducing the metal concentrations, followed by the S-slag, and then the W-slag. Compared to the other slags, the C-slag was especially effectively at inhibiting elution of Ni from the mine waste.

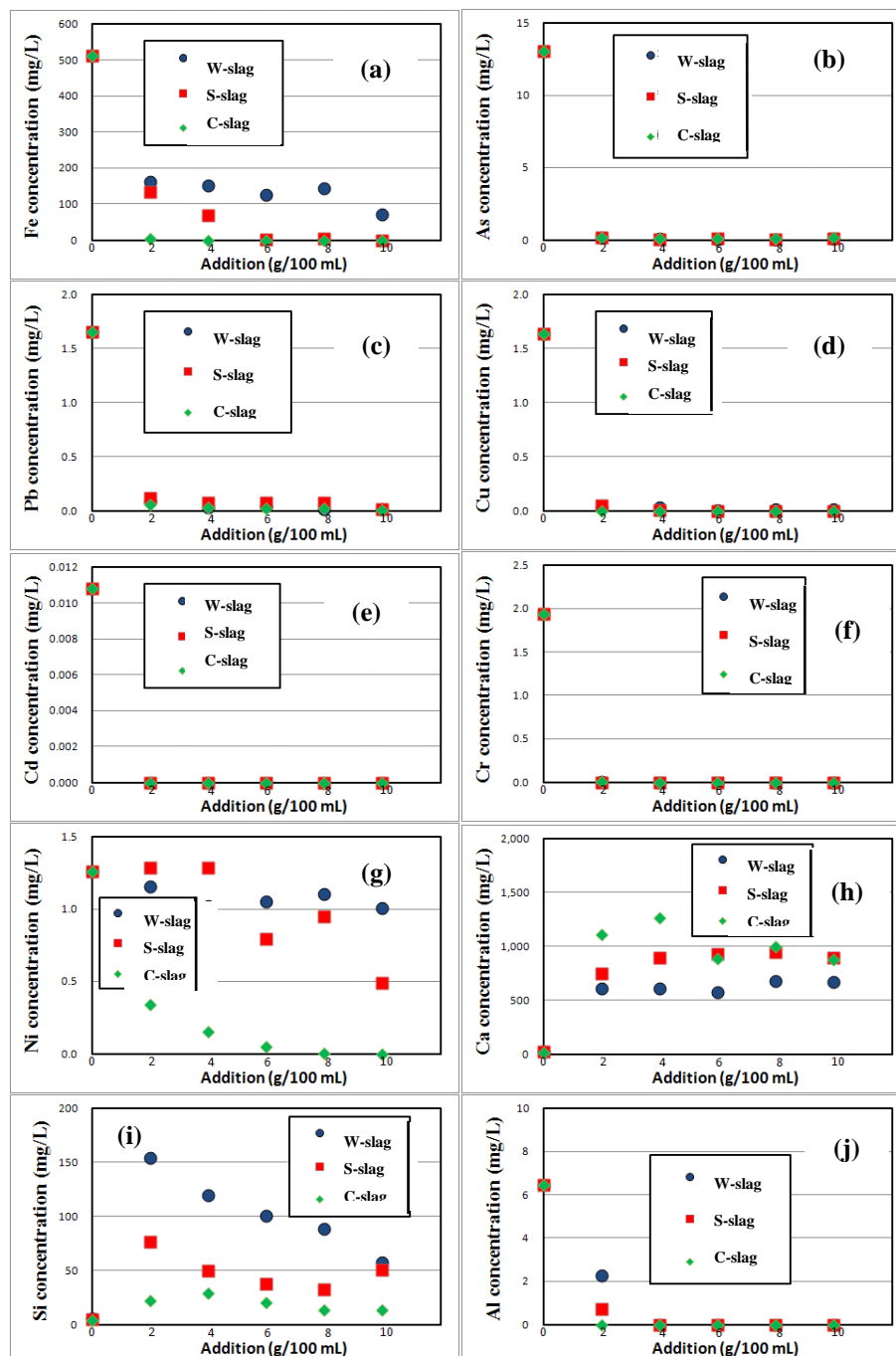


Fig. 4: Concentrations of various elements in the mine waste eluates obtained with and without different slags.

These results indicate that mixing mine waste with C-slag at a mass ratio of mine waste to slag of 10:8 will result in a neutral eluate and metal concentrations below Japanese standards for industrial effluents.

Fig. 5 shows the XRD patterns for the mixtures obtained after the elution tests with the different slags. The crystalline phases in the mine wastes were similar, gehlenite was present in S-slag and calcite was present in C-slag, and gypsum formed in all slags.

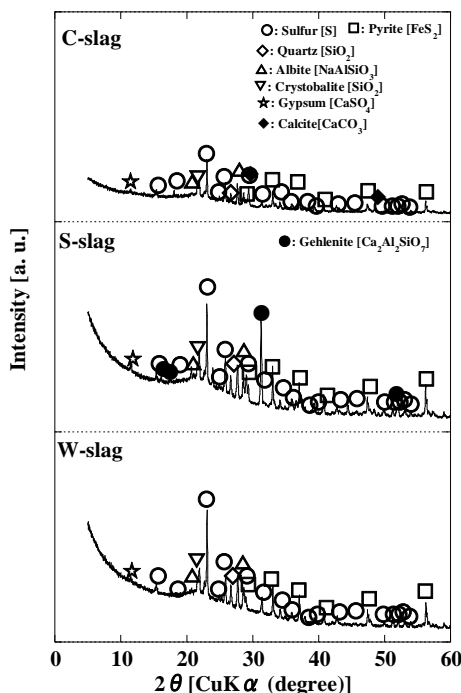
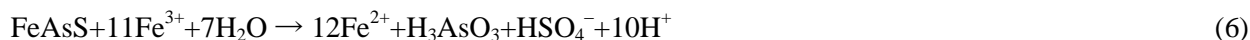
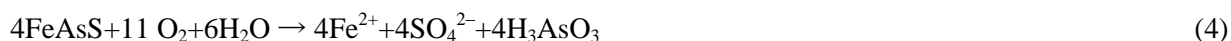


Fig. 5: XRD patterns of the residues remaining after elution tests with different slags.

A possible reaction mechanism for the slags with the mine waste is discussed below. Eluted elements, such as Fe and As, mainly come from sulfide minerals, pyrite and arsenopyrite. In the presence of oxygen and water, the oxidation of pyrite can be represented by the following reaction:



The reaction shown in Eq. (2) is promoted by bacteria, and increases the contents of  $\text{Fe}^{3+}$ ,  $\text{SO}_4^{2-}$ , and  $\text{H}^+$ . The oxidation of arsenopyrite occurs as follows:



The reaction shown in Eq. (5) is also promoted by bacteria, and increases the contents of  $\text{Fe}^{3+}$ ,  $\text{SO}_4^{2-}$ ,  $\text{H}_3\text{AsO}_3$  and  $\text{H}^+$ . The dissolution of pyrite and arsenopyrite supplies  $\text{Fe}^{3+}$  to the solution according to Eqs. (2) and (5), and promotes dissolution of pyrite and arsenopyrite according to Eqs. (3) and (6). At the same time, there occurred a similar oxidation reaction of other sulfide minerals, such as chalcopyrite, wurtzite, sphalerite, alabandite, and galena. The pH of the solution was acidic (around 2), and the concentrations of eluted elements were high. It should be noted that Fe and As in the solution will mostly be present as  $\text{Fe}^{3+}$  and  $\text{As}^{5+}$ , respectively, because of oxidation of  $\text{As}^{3+}$  to  $\text{As}^{5+}$  [7], [8].

With addition of slag, the concentrations of Si and Ca increased because of dissolution of the slag. Dissolved silicates and calcium compounds can neutralize acid by consuming protons ( $\text{H}^+$ ), but their dissolution rate is slow in the neutral pH range. These minerals dissolve more rapidly as the pH decreases, which results in greater acid neutralization under acidic conditions. The mine waste easily dissolved the elements into the solution, and became strongly acidic. With addition of the slags, amorphous silicates and calcium compounds in the slags dissolved into the strongly acidic solution and neutralized it, and this reduced the quantity of the slag remaining after the elution test (Fig. 5).

As the pH of the solution increased with dissolution of the slag, the concentrations of Fe and As in the eluate gradually decreased to below Japanese effluent standards (Fig. 4a and b). The concentrations of Al and Si also decreased (Fig. 4i and j). Metal hydroxides (e.g. Fe, Cu, Pb, Al, Cd, Ni) decrease in solubility with increasing pH, and become hydroxylated and precipitate in neutral solutions [9], [10]. Earlier research has shown that Fe precipitates as a hydroxide, and other anionic metals (As, Cr, Si) in solution coprecipitate with the Fe [11], [12]. Among the slags studied in the present research, C-slag has the highest alkalinity and contains more Fe. Therefore, C-slag is the most effective slag for inhibition of AMD formation. Furthermore, when the pH increases to neutral, catalytic bacterial activity is reduced or stopped, and this reduces the rate of biological oxidation of sulfur present in the mining residues [13]. By contrast, with increasing solution pH, the concentration of Ca remained constant at approximately 500–1000 mg/L (Fig. 4h). A large quantity of  $\text{Ca}^{2+}$  would dissolve from the slags, and some of this would react with  $\text{SO}_4^{2-}$  to form gypsum.

## 4. Conclusion

Remediation of mine waste was investigated using slag. Mixing mine waste with slag neutralized the eluate and reduced the concentrations of most metals below Japanese standards for industrial effluents. C-slag was the most effective slag for inhibition of AMD formation. These results suggest that slags could be used for remediation of mine waste sites.

## 5. Acknowledgements

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## 6. References

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