

Alkalinity Production and Neutralization Potential of Used Limestone Retrieved from Anoxic Reactors

Young Wook Cheong¹, Gil Jae Yim¹, Hyun Sung Park²

¹Geologic Environment Division, Korea Institute of Geoscience and Mineral Resources, South Korea
ywc@kigam.re.kr, gjyim@kigam.re.kr

²Mine Reclamation Corporation, South Korea, hspark@mireco.or.kr

Abstract A study was carried out to evaluate the remaining alkalinity producing capacities and reuse potential of the used limestone from successive alkalinity producing systems when limestone would be excavated to ameliorate. With two reactors having limestone and cow manure as substrates and mine waters as reacting medium reduced environment was created in the laboratory. The limestone from the reduced reactor with higher acidic mine water produced about a 300mg/L CaCO₃ of alkalinity while the one less acidic produced around a 130mg/L CaCO₃. After washing both the limestone samples, it was observed that these still produced alkalinity of about 100mg/L CaCO₃, though less than the 130 mg/L CaCO₃ of the fresh limestone.

Key Words Acid mine drainage, Amelioration of SAPS, Reuse of limestone, Neutralization

Introduction

Acid mine drainage (AMD) with less pollution load has been treated using passive treatment systems at some countries such as USA, UK and South Korea. Among the systems are SAPS, Anoxic Limestone Drain (ALD), Oxidic Limestone Drain (OLD) and man-made wetland. In case of mine drainage with a high acidity, acidity could be eliminated by the SAPS (Gazea *et al.*, 1996; PIRAMID, 2003). When the limestone contact with AMD with dissolved iron and then is coated with the iron hydroxide at oxidation condition, neutralization effect is reportedly only 2~ 62% compared to the fresh limestone at early stage (Ziemkiewicz *et al.*, 1997) Such limestone surface comprise a multiple layers and Simon *et al.*, (2004) found that inner layer closer to the limestone was Al-concentrated Basaluminite and the intermediate layer was Fe-concentrated Schwertmannite or Jarosite and the outer layer of gypsum. These coating compounds prevent limestone to be dissolved and thus fail to produce alkalinity.

On the other hand, metal sulfide is deposited organic substrates and limestone layer even though iron hydroxide is deposited on the top of organic substrates in SAPS. As operation periods are extended, considerable amount of precipitates is formed on organic layer and inside the limestone layer and finally make AMD overflow due to reduced permeability. That is, it is necessary to refurbish the SAPS to improve the capacity. There are many reports on coatings and alkalinity production of limestone exposed oxidation environment as previously mentioned. However, few report on evaluating the alkalinity producing capacity of the limestone placed in SAPS. This study was aimed at evaluating the anoxic used limestone's capability of creating the alkalinity and reuse while repairing SAPS.

Methods

To obtain limestone from a the reduced environment, crushed limestone (55.97 % CaO) with a grain size of 9.52mm ~ 35mm was placed into plastic containers (42cm × 23cm × 30cm) with cow manure wrapped in cotton cloth. Cow manure was used as the sulfate reducing bacteria source (Reisman, *et al.*, 2003). A 4mm (ID) sampling tube was installed at the bottom of each container that extended into the sample. Then, 10L of mine drainage from the Seokbong coal mine was poured into each container and stored for one month.

The limestone retrieved from the containers was combined with AMD or distilled water (1kg : 500mL) in 1 L bottles as described in Table 1. The bottles were completely sealed except case 1–2 (table 1). Water samples were taken with a syringe and filtered (0.45µm) at 3, 6, 12 and 24-hour intervals. pH, oxidation-reduction potential (Toa Eh meter, Japan), electrical conductivity (EC) (Orion 130 Conductivity meter, USA) and dissolved oxygen (DO) (Hach HQ40D LDO101, USA) were measured. Bicarbonate ion concentration was determined by titration. Water samples were also analyzed for Fe_{Total}, Al, Mn, Ca and Mg using ICP-AES (Inductively Coupled Plasma Atomic Emission Spectrophotometer; Jobin Yvon 38).

Result and discussion

Reactors used to produce used limestone

In case of reactor (container) H, Eh was significantly reduced to -66mV in a day which maintained -300mV or less in 4 days or longer (Fig 1). pH was 3.25 at early stage which was drastically increased up to 6 in a day. DO was maintained at 1mg/L level (Fig 1).

Reactor L also showed very similar changes as reactor H. Limestone in two reactors were covered

Table 1 Treatment combinations of limestone and mine water by case.

Case	Treatment Combination	Case	Treatment Combination
1	ULS + DIW	7	HLS-Dry+MW
2	ULS + MW	8	LLS-Dry + MW
3	HLS + DIW	9	Washed sample ¹⁾ from case2 + MW
4	HLS + MW	10	Washed sample ¹⁾ from case4 + MW
5	LLS + DIW	11	Washed sample ¹⁾ from case6 + MW
6	LLS + MW	1-2	ULS+DIW, opened to the air

Note: 1) Washed vigorously by hand under flowing tap water. ULS: unused limestone, DIW: distilled water, HLS: used limestone from H reactor, LLS: used limestone from L reactor, Mine water: MW

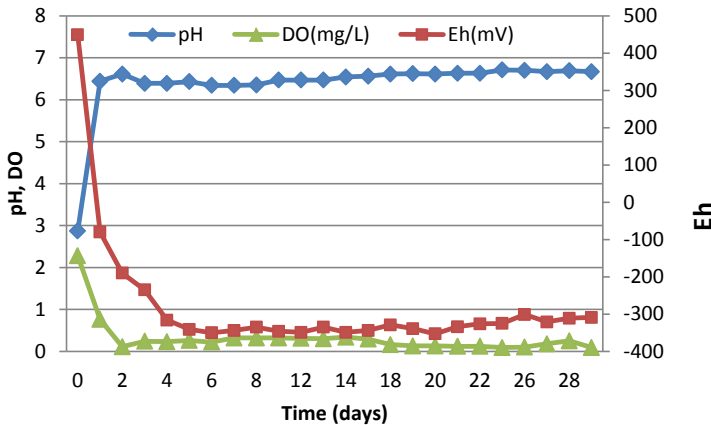


Figure 1 Changes in water parameters at the H reactor over time.

with black precipitates. Though it could be not definitely described, it seemed to be a metal sulfide caused by sulfate reduction with metals such as Fe in AMD. The limestones were taken after 30 days to use for evaluating the alkalinity and neutralization characteristics.

Alkalinity and metal concentration

The used limestone in L reactor was filled with the higher pollution load than one in the reactor H. Al-

kalinities of distilled water was increased from 0.84 mg/L CaCO₃ to about 30 mg/L CaCO₃, while the alkalinity of AMD was increased from 0 mg/L CaCO₃ to 135 mg/L CaCO₃ (Fig. 2). While the used limestone from reactor L (Case 5) indicated the alkalinity of 300mg/L CaCO₃, the limestone from reactor (case 3) showed 130mg/L CaCO₃. Comparing to the alkalinity of 9 mg/L CaCO₃ (Case1) with the distilled water, the alkalinity was almost 15 to 30 times and was even higher than Case 2. This result

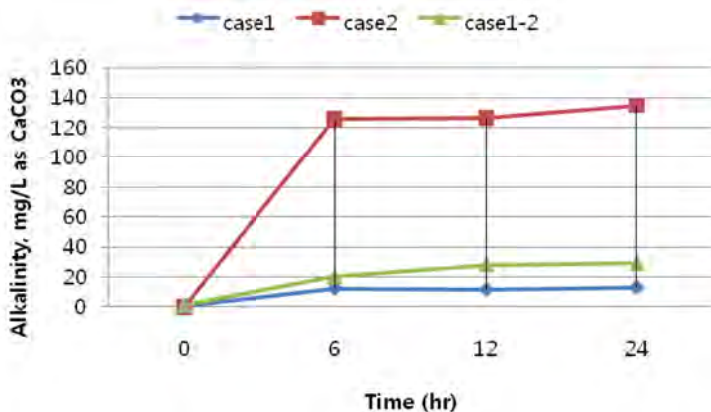


Figure 2 Effect of different waters chemistry (pH) on alkalinity production over time

indicated the alkalinity production from limestone itself as well as the existence of bicarbonate source in substrate. In case 3 and 5, used limestone with the precipitates in black were intactly put into together just after removing the moisture on it and such material seemed to create the alkalinity too. When unused limestone reacted with the distilled water, Ca which is the main component of the limestone was increased from 160mg/L to 412mg/L.

Al and Fe were reduced by increased pH but Mn still remained unchanged (Fig. 3) When used limestone reacted with AMD (Case 4), Ca concentration reached to 292mg/L but Al and Fe decreased due to pH elevation caused by limestone dissolution. This result indicated the possibility of reusing the use limestone in SAPS which were in reduced environment.

Effect of washing and drying on alkalinity production

The precipitate was washed out to find difference between before and after alkalinity. Alkalinity decreased in around 100 mg/L CaCO₃ (Fig. 4) after removing the black precipitate. Electric conductivities after washing also were reduced to

2600 μS/cm or less after washing. Such result implied that precipitates on used limestone were soluble compounds containing bicarbonate ion. Used limestone before and after washing increased pH of AMD to 6 or more, indicating unused limestone still have inherent similar neutralization characteristics of fresh limestone. When repairing SAPS on site, the limestone excavated from SAPS is exposed to the air for extended time. It is questioned whether the alkalinity of limestone varies. To identify the effect of dryness of precipitates, alkalinity of the dried limestone was compared (Fig. 5). Case 4 showed the alkalinity around 150 mg/L CaCO₃ and Case 6 showed 120 mg/L CaCO₃. When the case 4 and 6 were dried (Case 7 and 8), the alkalinity was reduced by about 20 ≈ 30 mg/L CaCO₃.

Conclusion

The limestone was taken from the reduced reactors with pH 6, anaerobic and Eh 300mV to compare alkalinity production between fresh and anoxic used limestone. The anoxic used limestone was cover with black precipitates which were soluble and washable with flowing tap water and had alkalinity as well. Alkalinity without wash-

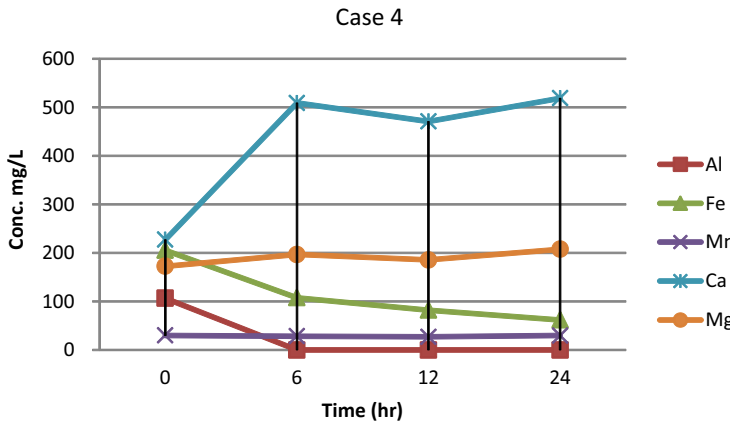


Figure 3 Changes in some metal concentrations in mine water reacted with used limestone over time.

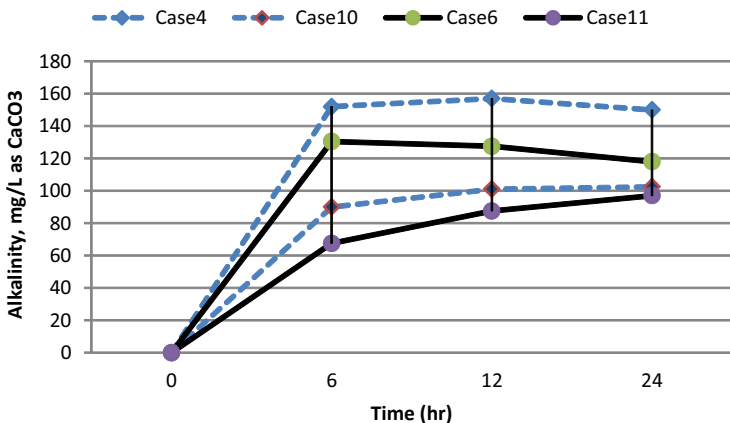


Figure 4 Changes in alkalinities before and after washing two used limestones.

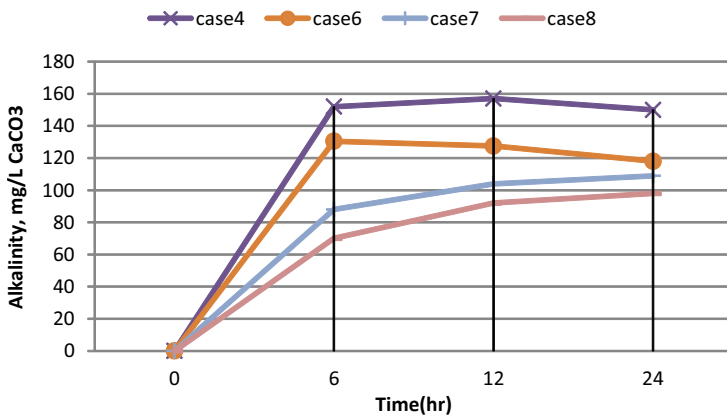


Figure 5 Comparison of alkalinities before and after drying used limestones over time.

ing the precipitates was also able to increase pH by neutralization remove Fe and Al. Alkalinity after washing precipitates on used limestone was similar with one of the fresh limestone, indicating the high possibility of reusing when SAPS would be repaired. Though the precipitates appeared not to prevent production of alkalinity, it probably reduces the hydraulic conductivity of SAPS when reusing the limestone and thus it should be necessary to wash the limestone before reusing.

References

Gazea, B., Adam, K and Kontopoulos, A. (1996) A review of passive systems for the treatment of acid mine drainage, Minerals engineering 9(1):23–42

PIRAMID consortium (2003) Engineering guidelines for the passive remediation of acidic and/or metalliferous mine drainage and similar wastewaters, University of Newcastle Upon Tyne, UK, p 55–79
 Simon, M., Martin, F., Garcia, I., Bouza, P., Dorronsoro, C. and Aguilar, J. (2004) Interaction of limestone grains and acidic solutions from the oxidation of pyrite tailings, Environmental pollution 135: 65–72
 Ziemkiewicz, P.F., Skousen, J. and Brant, D.L., Sterner, P.L. and Lovett, R.J. (1997) Acid Mine Drainage treatment with armored Limestone in open limestone channels, J. Environ. Qual. 26: 1017–1024