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Article

Estimation of Alkali Overdosing in a Lime Neutralization Process for Acid Mine Drainage

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Abstract

Lime has been used for the neutralization of acidic waste because it is cheap and available in large quantities. The resulting sludge often contains a considerable amount of unreacted lime due to alkali overdosing, even during automatic neutralization processes, which mainly arises from the poor solubility of lime. The sludge cake from lime neutralization of Ilkwang Mine also contained high percentages of calcium and magnesium. The elemental content of the sludge cake was compared with those obtained from a simulation of the lime neutralization facility installed at Ilkwang Mine. A Goldsim® model estimated the degree of lime overdosing to be 19.1% based on the fractions of ferrous oxide. The analysis suggests that resolubilization of aluminum hydroxide could occur in the settling basin, in which pH exceeded 10 due to the continued dissolution of the overdosed lime. The present study demonstrated that chemical analysis of sludge combined with process simulation could provide a reasonable estimate of mass balance and chemistry in a neutralization facility for acid mine drainage.

***Keywords**: Alkali overdosing, Lime neutralization, GoldSim, Metal hydroxide*

1. Introduction

Dissolved metals in acidic effluents are usually removed by precipitation as insoluble hydroxides after neutralization[1]. Neutralization of acid mine drainage (AMD) can be performed simply in a pond with a large footprint, but also in a neutralization reactor within a small footprint[2]. Continuous stirred tank reactors are also used for AMD neutralization, in which pH is automatically controlled by the addition of alkali[3]. Lime is the most economically favorable alkaline reagent to use for acid neutralization, but it is insoluble, and, thus, difficult to handle in a continuous process[1]. An automatic pH control can be a more challenging problem, especially when lime is used as an alkali agent[4]. Because of poor solubility of aqueous slurry of hydrated lime, neutralization velocity is very much dependent on the total surface area, porosity, and shape of solid particles[5]. When lime slurries are used as neutralization reagents, a sufficient residence time should be allowed for dissolution in a neutralization tank. Thus, process optimization is required to reduce operating costs, volume of sludge generated, and metal release to the environments[6]. In addition, overdosing of lime can lead to the wastewater reaching pH 12[7]. Although sophisticated pH control and optimization methods were employed at semi-active processes to deal with the effect of process delays caused by lime dissolution, excessive alkali consumption often observed as in the passive process such as lime ponds for AMD treatment. A significant variation of AMD flow rate caused by summer monsoon rains is also an inevitable factor of disturbance in pH control.

In this study, we investigated the possibility of excessive alkali consumption in the semi-active AMD treatment process of Ilkwang Mine in Korea. Ilkwang process was chosen since the quality and color of the neutralized stream varies significantly from white to red. Thus, the chemical compositions of sludge obtained from the settling process were analyzed and compared to those of theoretical simulation results of neutralization process. Simulation of the neutralization process was performed using GoldSim® under varying lime overdosing conditions. Process analysis and estimation of lime excess in Ilkwang process could be a useful tool for operation improvement and the development of a more efficient lime neutralization process for AMD treatment.

2. Materials and Methods

2.1. Neutralization process

The semi-active process employed by Ilkwang Mine at Kijang-gun of Busan, South Korea, operates to neutralize up to 700 m^3/day of AMD from an adit of the abandoned Cu-Zn metal mine. The design capacity was determined by the considerations of seasonal variation of AMD flow rate. The AMD discharges usually above the rate of 100 m^3/day but purges more than 700 m^3/day for a short period after the monsoon season in summer. The acidic drainage from the adit located at a lower level of the underground mine system is directed to holding basin (58 m^3) and then two 4.87 m^3 neutralization tanks. Non-settling 20%(w/v) lime slurry (calciumhydroxide, > 98%) is used to bring pH

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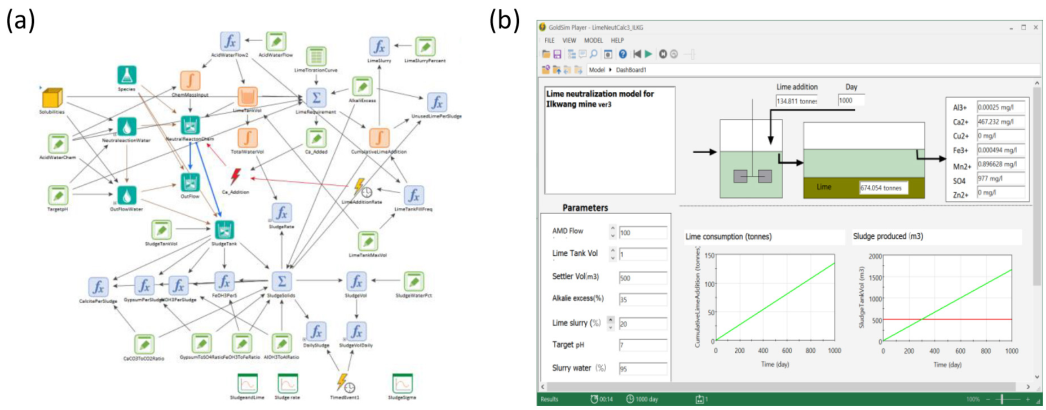

Figure 1. Structure of process elements of Ilkwang facility simulation (a) and result display.

to a set-point of 7.0 by an automated control system. The neutralized flow is directed to two settling basins (1,023 m^3/each). At the end, mine water flows through an aerobic wetland (91 m^2) with cattle. Thus, the corresponding residence time varies from 1.17 to 0.17 h at each neutralization tank, and the apparent residence of flow in the settling basin also varies from 10.3 to 1.5 days. When the settling basin is filled with sludge with high content of water, sludge is sucked in with a pump, and dewatered with a filter press on the ground, and stored as a cake.

2.2. Water Quality and Sludge Analysis

Measurement of pH and electrical conductivity in situ was conducted at the mine water discharge point. Sampling sites were set at the holding basin and discharge point of the Ilkwang facility. The sludge specimen was taken from the settling basin in the Ilkwang Mine and cake was sampled from storage bags for cake from filter press. The sludge and cake samples were dried at 105 °C using a drying furnace, and then disaggregated. X-Ray Fluorescence Spectrometers (MXF-2400, Shimadzu, Japan) was used for determination of ten major components: N_2O, MgO, Al_2O_3, SiO_2, P_2O_3, K_2O, CaO, TiO_2, MnO, and Fe_2O_3. Sulfur content was measured separately by wet chemistry. Dried sludge powder was dissolved with nitric acid, hydrochloric acid, perchloric acid, and hydrochloric acid. After silicate removal and iron (III) masking, $BaSO_4$ was precipitated by addition of 10% $BaCl_2$ solution. The weight of barium sulfate was measured after heating at 800 °C to obtain the sulfur content.

2.3. Simulation of lime neutralization of acid mine drainage using GoldSim®

GoldSim® (GoldSim Technology Group, Redmond, WA, USA) is a simulation package that frequently used in modeling of water balances for mine sites and water resource management[8]. A compartment GoldSim® model was developed using GoldSim® software ver. 12.1 to simulate the Ilkwang facility for lime neutralization. The model was modified from an example (ARD_WaterTreatment.gsp) provided by the manufacturer[9]. The model is comprised of lookup tables of metal hydroxide solubility and the lime requirements for neutralizing Ilkwang AMD. Modification was also made to include a variable of alkali overdose and to calculate the composition of metal hydroxide, Ca/Mg oxide, and other insoluble salts. The GoldSim® model was constructed was constructed by connecting processing elements that keep track of inflows, outflows, and precipitations based on lookup tables of solubility of components in the AMD of Ilkwang Mine at different pH levels as shown in Figure 1(a). Quantitative predictions calculated for the neutralization reaction at the given pH along with the operation time were presented in a user-friendly interface (Figure 1b). The system was designed to estimate lime consumption, effluent water quality, and lime sludge production and composition.

3. Results and Discussion

3.1. Element analysis of sludge from AMD neutralization process using lime

Lime slurry has been used for the neutralization of AMD in the treatment facility of Ilkwang Mine. The resulting metal hydroxides agglomerate and precipitate into sludge in the subsequent settling basin. The sludge is further concentrated and dehydrated into dry cakes. It has been observed that the effluent from neutralization tank changes its color from red to white from time to time. This prompted us to analyze the chemical composition of the dry cake and the red and white-colored effluent samples using XRF (Table 1).

XRF analysis revealed that the composition of sludge cake was 2.77% of Al_2O_3, 38.43% of Fe_2O_3, 15.28% of CaO, 4.71% of MgO, 1.0% of MnO, 3.4% of sulfur and minor compounds. These components sum up to 92.12 % including the loss on ignition. The molar ratio of CaO was 2.73-fold higher than that of sulfur, suggesting that the slurry contained a significant portion of unreacted lime. XRF analysis showed that the white effluent contained a markedly higher CaO composition (35.5%), suggesting that lime overdosing occurred during automatic pH control in lime neutralization tank. The white-colored effluent contained higher sulfur content (5.06%) than either the sludge cake or the red-colored effluent. The chemical composition of red-colored effluent was similar to those of sludge cake, suggesting that the sludge cake was mostly formed by precipitation of insoluble components of

Table 1. XRF Results of Sludge and Sludge Cake (%)

Components	Sludge cake	Neutralized effluent (red)	Neutralized effluent (white)
SiO_2	4.04 ± 0.04	5.25	2.26
Al_2O_3	6.31 ± 0.08	6.09	2.77
Fe_2O_3	38.43 ± 0.17	35.18	13.96
CaO	15.28 ± 0.22	16.36	35.57
MgO	4.71 ± 0.06	5.75	4.67
K_2O	0.06 ± 0.06	0.09	0.05
Na_2O	0.61 ± 0.01	0.64	0.28
TiO_2	0.06 ± 0.06	0.07	0.04
MnO	1.04 ± 0.01	1.13	0.46
P_2O_5	0.05 ± 0.06	0.05	0.04
S[1)]	3.4 ± 0.12	3.43	5.06
Ig.Loss[2)]	18.17 ± 0.21	18.77	27.22

[1)] Sulfur content measured separately by wet chemistry. [2)] lg.Loss: Loss on ignition. mean ± S.D. (n = 4).

Table 2. Elemental Composition of AMD and Sludge Cake

Elemental composition of sludge cake			Ilkwang mine drainage		
	wt % (exclude O, Ti, Si, and Ig.Loss)	Relative wt% of major components (> 1%)		Influent (pH 2.6)	Effluent (pH 7.0)
Fe	26.88	61.12	Fe^{+3}	202	1.67
Ca	10.92	24.83	Ca^{+2}	106	442
Al	3.34	7.59	Al^{+3}	32.8	<0.5
Mg	2.84	6.46	Mg^{+2}	17.5	19.6
Mn	0.77		Mn^{+2}	6.76	5.86
Na	0.23		Na^{+}	12.5	13.3
K	0.05		K^{+}	< 0.5	< 0.5
P	0.01		PO^{-3}	< 1.0	< 1.0
S*	3.4		SO_4^{-2}	977	1000

* Sulfur was measured separately by wet chemistry.

red-colored effluents.

Thus, elemental components of the sludge were recalculated and compared with the chemical compositions between affluent and effluent of Ilkwang AMD process (Table. 2). Higher percentages of element iron and aluminum in the sludge comply with the decrease of iron and aluminum ions after neutralization. Lime neutralization caused a significant increase in calcium, from 106 ppm in AMD to 442 ppm, in the effluent. Major elements (> 1%) in the sludge were used to compare with the element composition of a simulation result. The relative percentages of iron, calcium, aluminum and magnesium were 61.12%, 24.83%, 7.59% and 6.46%, respectively.

3.2. The effect of alkali overdosing on lime consumption and sludge composition

The metal hydroxides in AMD precipitate upon neutralization and dominate the chemical composition of the resulting sludge cake. XRF analysis revealed that Ilkwang sludge contained a significant amount of calcium and magnesium, indicating a significantly degree of lime overdosing. Thus, lime overdosing in the neutralization facility was simulated using the GoldSim model of this study (Figure 2). With the increasing lime overdosing from 0 to 40%, the iron content in the sludge cake gradually decreased from 86.0 to 46.5%. Aluminum content also decreased from 14.0 to 7.5% with respect to the increasing calcium and magnesium content. At 40% lime overdosing, the resulting calcium content in the sludge increased up to 46.5%.

The ferric ions in AMD hydroxylated and eventually transformed into small particles of hematite at neutral pH[10]. Its solubility (approximately 10^{-10} M) is markedly lower than those of calcium and Aluminum. Thus, iron content was chosen as the basis of comparison between the simulation result and the XRF analysis. According to the XRF analysis results, the iron content in the sludge was 61.12%, which corresponds to the simulated iron content at 19.1% of lime overdosing (arrow in Figure 2). Under the lime overdosing conditions, the simulated content of calcium and magnesium (29.0%) was slightly smaller than the sum of calcium (24.83%) and magnesium (6.46%) of XRF analysis. However, aluminum has more discrepancy between simulated estimation (9.9%) and XRF analysis (7.59%).

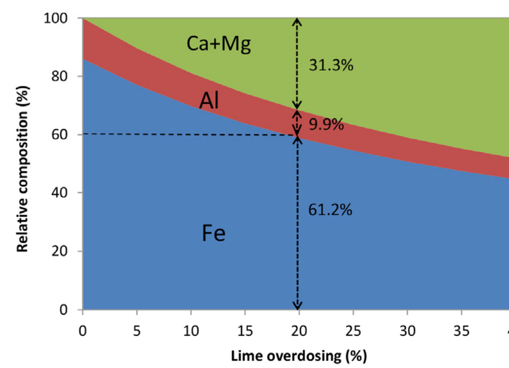

Figure 2. Relative composition of Fe, Al and Ca+Mg at varying lime overdosing.

Aluminum hydroxide is scarcely soluble in a neutral aqueous solution, but resolubilize in the form of $Al(OH)_4^-$ under alkaline conditions[11]. The settling basin of Ilkwang facility remains under alkaline conditions because of sustained dissolution of overdosed lime from the neutralization tank. Thus, the pH of clarified surface water of the settling basin was measured to be higher than pH 10. The GoldSim® model was also used to evaluate the effect of continued dissolution of overdosed lime on the aluminum content in the sludge cake. The aluminum contents were predicted using the GoldSim® model of Ilkwang facility to be varying pH from 7 to 12 and under different alkali overdosing conditions (Figure 3). The aluminum content decreases with the increasing pH of the settling basin, which explains why the aluminum content determined by XRF can be lower than that of the simulation result.

The approach of this study enabled us to understand how lime overdosing could vary the elemental composition of sludge precipitate. It was also useful to elucidate that aluminum content could decrease due

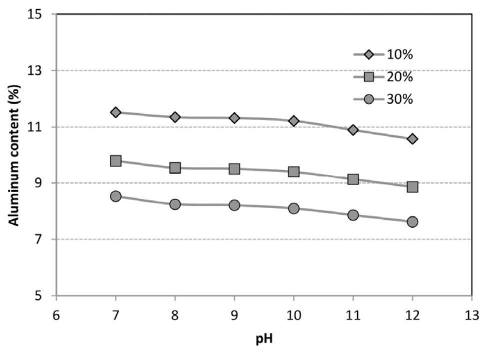

Figure 3. The effect of settling basin pH on the aluminum content in the sludge.

to resolubilization in the alkaline settling basin. The GoldSim® model of this study was used to decipher the XRF results of the effluents and the sludge cake. This is because that the performance of lime neutralization process could be fossilized in the sediment. The simulation model is based on empirical lookup tables of titration and solubilities rather than theoretical calculations. The dissolution of gibbsite particulates may differ from aluminum solubility because of hydrostatic pressure in the settling basin and other components of the sludge, since AMD titration was performed in laboratory not on site. The solubility of aluminum hydroxide is known to vary by the presence of other ionic components[12]. Thus, it cannot be excluded that the decreased aluminum content was influenced by other factors.

The sulfur content of Ilkwang Mine sludge was 3.4% (Table 1), suggesting that gypsum was formed and precipitated in the sludge. However, sulfate concentration was 997 ppm in Ilkwang AMD, which was not high enough to form calcium sulfate and to precipitate as gypsum. Gypsum formation can be attributed to a temporal local elevation of calcium ion concentration on the surface of lime particulates. However, the possibility remains to be further explored.

The present approach made it possible to estimate the degree of lime overdosing. Lime usage can be reduced by improving the efficiency of lime neutralization process. Thus, it would be necessary to simulate the AMD neutralization process for an efficient operation of an existing facility with a decreased lime consumption and for designing a more efficient facility.

4. Conclusions

XRF analysis revealed that high levels of calcium (24.8%) and magnesium (6.46%) were contained in the lime neutralization sludge of Ilkwang AMD. A GoldSim® software model was developed to simulate the lime neutralization facility and to predict the chemical composition of sludge under varying lime overdosing conditions. Comparison to the XRF analysis revealed that lime overdosing can be 19.1% in the lime neutralization in Ilkwang Mine. The simulation also shows that aluminum content discrepancy can be attributed to resolubilization in the alkaline settling basin. This study demonstrated that sludge analysis and simulation comparison can provide a better understanding for an existing semi-active neutralization facility.

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