



Shahrood University of  
Technology



Iranian Society of  
Mining Engineering  
(IRSM)

## Comparison of Efficiencies of Neutralizing Agents for Heavy Metal Removal from Acid Mine Drainage

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### Article Info

Received 9 July 2022

Received in Revised form 31 August 2022

Accepted 14 September 2022

Published online 14 September 2022

DOI:10.22044/jme.2022.12090.2205

### Keywords

Heavy metals

Active treatment

Flocculation

Soda ash

Caustic soda

### Abstract

The treatment of acid mine drainages is usually based on two basic technologies, active and passive treatment technologies. Whichever acid mine drainage (AMD) treatment method is employed, a neutralizing procedure that raises the water's pH over 7.0 using alkaline agents is required prior to discharge. A comparison of eight different agents ( $\text{BaCO}_3$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{NaOH}$ ,  $\text{KOH}$ ,  $\text{K}_2\text{CO}_3$ ,  $\text{MgO}$ ,  $\text{CaCO}_3$ , and  $\text{Ba}(\text{OH})_2$ ) was performed in order to choose the most effective neutralizing agent for acid mine drainage treatment. The experiments were performed using a multi-component synthetic aqueous solution with an initial concentration of 10 mg/L of the Cu, Mn, Zn, Fe, and Pb ions and an initial pH value of 1.9. According to the research, the most effective neutralizing agent for the removal of heavy metals from a multi-component aqueous solution is  $\text{MgO}$ , while the least effective agent was  $\text{Na}_2\text{CO}_3$ . The obtained series of effective neutralizing agents for the removal of heavy metals from a multi-component aqueous solution are presented in the work. The effect of the studied concentration of neutralizing agents depends on the neutralizing agents and heavy metals that are used. The percentage of heavy metals removed from aqueous solutions increases along with rising pH values. The consumption of the neutralizing agent decreases as the concentration of the neutralizing agent is increased. In addition, the time taken to achieve pH depends on the agent concentration. In particular, as the concentration of the neutralizing agent increases, the time to reach the pH decreases.

### 1. Introduction

Mining activities expose a significant amount of mineral deposits containing pyrite, sphalerite, galena or other sulfide minerals deposited in the layers of rock beneath the earth's surface, where there is little or no oxygen. Mining activities bring these deposits to the surface, where they are crushed to liberate precious minerals such as lead, copper, zinc, gold, nickel, and other metals, with the tailings remaining at the mine site. Thus large amounts of sulfide minerals become exposed to surface conditions, i.e. air and water that will assist in the oxidation of the sulfide minerals to produce acid mine drainage [1].

Pyrite is recognized as a major source of acid mine drainage due to its abundance in the environment [2] but there are other metals

commonly found in acid mine drainage such as aluminium, copper, lead, nickel, and zinc because they are present in the sediments, ore deposits, mineralized veins, hydrothermally altered rocks, and soils with pyrite [3, 4].

Acid mine drainage (AMD) is one of the most serious environmental issues associated with mining, mineral processing, and other large-scale excavations around the world [5, 6]. The oxidative dissolution of sulfide minerals in the presence of water and oxygen gives rise to these acidic, metal-laden waters. As the oxidation process occurs, acidic water interacts with rocks containing various minerals and dissolves toxic metals along the way [7]. The high acidity of AMD and the large amounts of dissolved heavy metals such as copper,

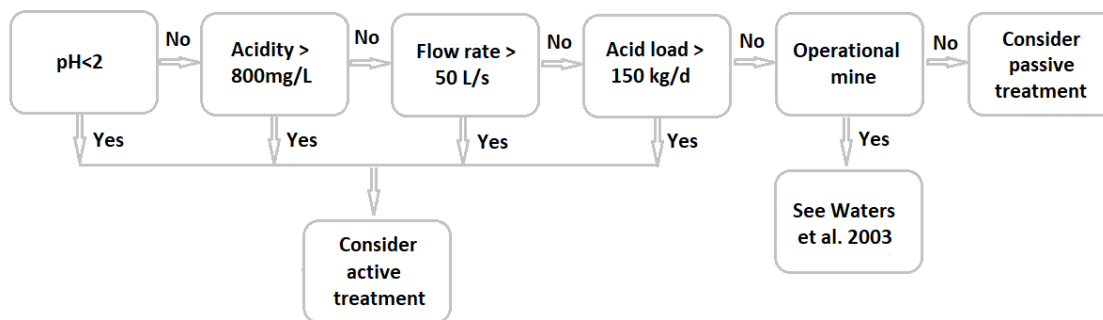
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zinc, manganese, iron, arsenic, and lead generally make AMD extremely toxic to most living organisms [8].

The treatment of mine drainages is usually based on two basic technologies, i.e. active and passive treatment technologies. The main difference between these technologies is that active treatment systems (as the name implies) require constant

system maintenance, while passive treatment systems require less maintenance (or no maintenance) [9].

In Figure 1, a flow chart is given for making the choice between active and passive treatment for acid mine drainage [10, 20]. Acid load is calculated as acidity (mg CaCO<sub>3</sub>/L) x flow rate (L/s) x 0.0864.





**Figure 1. Flow chart for making a choice between active and passive treatment for acid mine drainage (modified from Waters et al. 2003) [10, 20].**










Active treatment is the most common method of treating acid mine drainage, which involves the addition of alkaline minerals-neutralizing agents [11] in order to precipitate metals, for adsorption, ion exchange, and membrane technology, among others [12]. These methods are typically used to treat AMD with very high levels of acidity, while being capable of adjusting to the varying geochemical properties. However, active treatment is limited by its cost and sludge generation, making it unsustainable in the long run [13]. In comparison, passive treatments are considered to be more cost-effective to use in a closed and abandoned mine site due to the stable chemistry at these mine sites as well as the accessible land for remediation systems [14, 15].

Regardless of which AMD treatment process is used, a neutralization process must be used to raise the water’s pH above 7.0, using alkaline reagents, before discharge. The materials that are often used to generate alkalinity are limestone (CaCO<sub>3</sub>), hydrated lime (Ca(OH)<sub>2</sub>), lime (CaO), quicklime (CaO), magnesite (MgCO<sub>3</sub>), periclase (MgO), brucite (Mg(OH)<sub>2</sub>), dolomite (CaMg(CO<sub>3</sub>)<sub>2</sub>), fly ash, soda ash (Na<sub>2</sub>CO<sub>3</sub>), caustic soda (NaOH), and ammonia (NH<sub>3</sub>) [7, 22, 23] (Table 1). Also waste by-products were used as an alkalinity-generating material such as eggshell waste [16], wood ash [17], phosphatic waste rock [18], concrete aggregate [19], and serpentinite found in mining waste rock that belongs to the serpentine group of minerals considered as alkaline-rich [7].

**Table 1. Materials that generate alkalinity.**

| Name                              | Figure  | Formula             | Max pH at 25 °C | Comment  |
|-----------------------------------|---|---------------------|-----------------|--|
| Calcium hydroxide (hydrated lime) |  | Ca(OH) <sub>2</sub> | 12.45           | Most commonly used alkaline reagent. Cost effective reagent, requires mixing.  |
| Calcium oxide (pebble quicklime)  |  | CaO                 | 12.45           | In terms of the gram-equivalent weight, CaO is economically advantageous over Ca(OH) <sub>2</sub> . Very reactive, needs metering equipment. |

Continue of Table 1. Materials that generate alkalinity.

|  |   |                          |      |  |
|--|---|--------------------------|------|--|
| Calcium carbonate (limestone, calcite) |    | $\text{CaCO}_3$          | 7    | Resulting slurry has good sedimentation and dehydration characteristics. However, pH cannot increase beyond 7. Used in anoxic limestone drains and open limestone channels.  |
| Sodium hydroxide, (caustic soda)       |    | $\text{NaOH}$            | 14   | Very soluble, can be in solid or liquid form. Expensive but cheaper in liquid form. Extremely fast-acting to complete neutralization.  |
| Magnesium oxide (magnesia)             |    | $\text{MgO}$             | 10   | No Gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) formation-less amount of sludge. Resulting slurry has excellent settling/dewatering characteristics. Long reaction time is required due to low solubility. |
| Barium carbonate                       |    | $\text{BaCO}_3$          | 7.5  | It is insoluble in water and soluble in most acids, with the exception of sulfuric acid.   |
| Sodium carbonate (soda ash)            |   | $\text{Na}_2\text{CO}_3$ | < 11 | Recommended for low flow and low amounts of acidity and metals. Moderately fast-acting to complete neutralization. System for remote locations, but expensive.   |
| Potassium carbonate                    |  | $\text{K}_2\text{CO}_3$  | < 11 | Similar to soda ash. Rarely used.  |
| Magnesium hydroxide                    |  | $\text{Mg}(\text{OH})_2$ | 10.6 | Similar to hydrated lime. Fairly slow-acting to 95% complete neutralization  |
| Barium hydroxide                       |  | $\text{Ba}(\text{OH})_2$ | 12   | Used for sulphate removal with combination with other neutralizing agents.   |
| Potassium hydroxide                    |  | $\text{KOH}$             | 12   | Similar to caustic.  |

Generally, metals can be removed from AMD by precipitation and sorption. Fe precipitate as hydroxides, whereas manganese (Mn) is removed by a combination of oxidation and precipitation. Some divalent metals (e.g. Fe, Zn, Pb) can be removed by precipitation as sulfide minerals. Sorption, coprecipitation, and exchange to precipitated Fe and Mn, organic materials, and soil-like materials are additional mechanisms for metal removal. Sorption to organic materials is important for Al and divalent transition metals and Pb, while sorption to precipitated Fe and Mn and even limestone surfaces can contribute to trace metal removal [25].

The main goal of this work was to investigate the efficiencies of the neutralizing agents such as  $\text{BaCO}_3$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{NaOH}$ ,  $\text{KOH}$ ,  $\text{K}_2\text{CO}_3$ ,  $\text{MgO}$ ,  $\text{CaCO}_3$ , and  $\text{Ba(OH)}_2$  in order to remove heavy metals (Cu, Fe, Mn, Pb, and Zn) from a multi-component synthetic acidic aqueous solution and the possibility of their application in acid mine drainage treatment. Using neutralizing agents for heavy metal removal from AMD has been studied by some authors [25-27, 30] but only a few studies have been conducted to compare the effectiveness of neutralizing agents under the same conditions [28, 29]. Precisely because of that, experiments were carried out to investigate the effectiveness of the neutralizing agents under the same conditions using the most commonly used neutralizing agent as well as some of the less commonly used. The comparison of the speed at which pH is achieved, the highest value of the pH that can be achieved, and the consumption of the neutralization agents is also discussed.

## 2. Materials and methods

The multi-component synthetic acidic aqueous solution with concentration of 10 mg/L of Cu, Mn, Zn, Fe, and Pb ions were prepared in the laboratory conditions using distilled water and standard certified solutions from Perkin Elmer in the form of nitrates of copper, iron, manganese, zinc, and lead. Due to the content of 2% nitric acid in the standard certified solutions, the initial pH value of the multi-component synthetic aqueous solution was 1.90. To control and monitor the pH value, a pH 1000L VWR was used and combined with electrode pH enomenal 221 (ecn: 662-1161). Measurement of metal concentration was performed using atomic absorption spectroscopy. The instrumental technique used was an AAnalyst 400 Perkin Elmer atomic absorber.

The neutralizing agents prepared in concentrations of 0.025, 0.050, and 0.075 mol/L were added with a 10 mL A class pipette in a 100 mL of the multi-component synthetic aqueous solution using a 300 mL glass. The neutralizing agents were loaded continuously, adding 10 mL at a time until a constant pH was achieved in the multi-component synthetic aqueous solution. The solution was mixed using a magnetic stirrer, model: As One HS-4DC /1-262-01 Battery Operated Starler. The neutralizing agents used in the experiments were  $\text{BaCO}_3$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{NaOH}$ ,  $\text{KOH}$ ,  $\text{K}_2\text{CO}_3$ ,  $\text{MgO}$ ,  $\text{CaCO}_3$ , and  $\text{Ba(OH)}_2$ .

An organic flocculant with the commercial name PRAESTOL 2515 was used for flocculation, which is a copolymer of acrylamide and sodium acrylate. The flocculation time was 3 hours.

All experiments were performed twice, and the average value was presented in this work. The standard deviation was in range of 0.01-1.6 for pH, up to 30 s for the time, and 0.02, 0.01, 0.05, 0.02, and 0.03 mg/L for Cu, Fe, Mn, Zn, and Pb, respectively.

## 3. Results and Discussion

The efficiency of neutralizing agents for acid mine drainage treatment was compared using eight different agents including  $\text{BaCO}_3$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{NaOH}$ ,  $\text{KOH}$ ,  $\text{K}_2\text{CO}_3$ ,  $\text{MgO}$ ,  $\text{CaCO}_3$ , and  $\text{Ba(OH)}_2$ . The experiments were performed using a multi-component synthetic aqueous solution with an initial concentration of 10 mg/L of the Cu, Mn, Zn, Fe, and Pb ions and the initial pH value of 1.9.

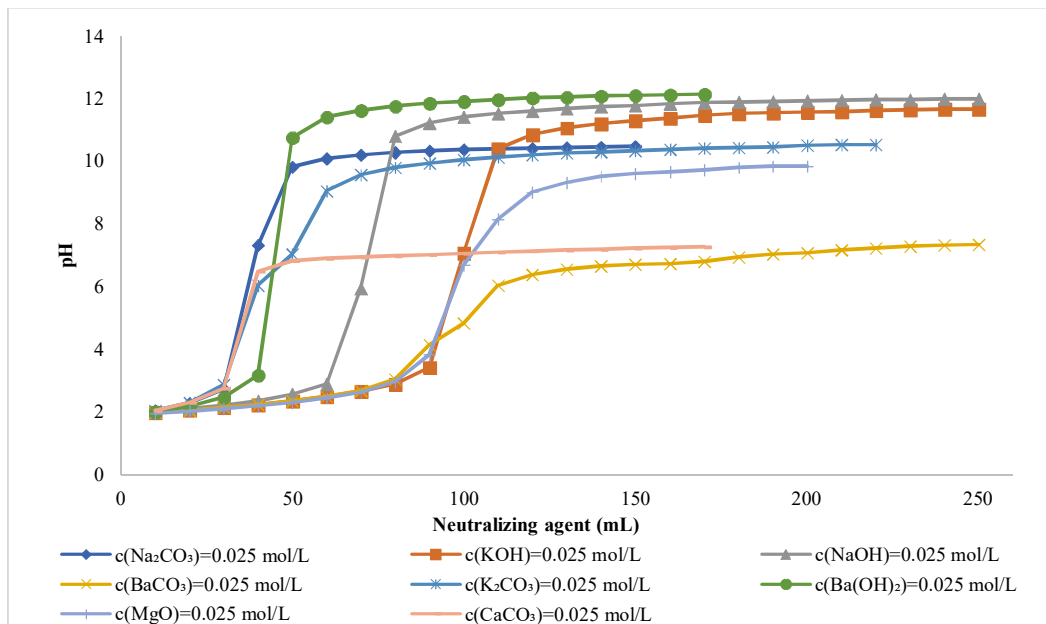
### 3.1. Effect of pH on neutralizing agent consumption

The effect of pH on the neutralizing agent consumption was studied using three different concentrations of each neutralizing agent such as 0.025, 0.050, and 0.075 mol/L. Normally, the neutralizing agent consumption increased as the pH increased. The same trend was obtained by Loza *et al.* [21]. As expected, for most studied agents, as the concentration of the neutralizing agent increased, the pH value also increased, and its consumption decreased, except for  $\text{Na}_2\text{CO}_3$ , where maximum pH and minimum consumption were achieved at a neutralizing agent concentration of 0.050 mol/L.

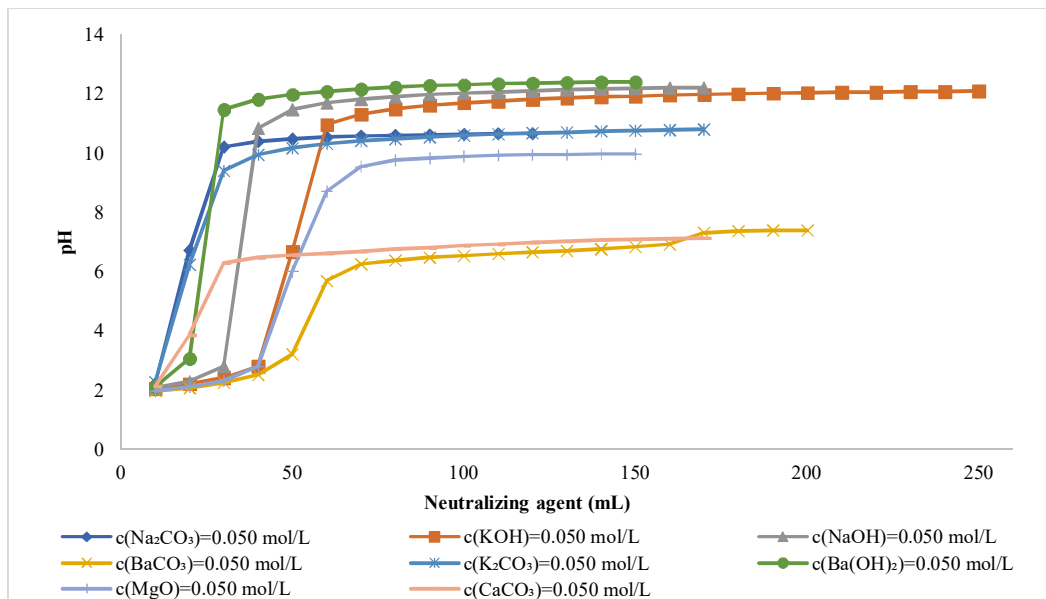
From the obtained results (Figure 2), it can be concluded that the studied neutralizing agents according to the achieved pH value and consumption of the agents can be grouped in three groups. The hydroxide agents  $\text{Ba(OH)}_2$ ,  $\text{NaOH}$ ,

and KOH achieved pH 12, and as the concentration of the neutralizing agents increased, their consumption significantly decreased. The second group, carbonate agents  $\text{Na}_2\text{CO}_3$ , and  $\text{K}_2\text{CO}_3$  as well as MgO achieved a pH value around 10 and agent consumption varied with concentration but

the differences were not significant. The third group of  $\text{BaCO}_3$  and  $\text{CaCO}_3$  achieved a pH value around 7, and as the concentration of the agents increased, the consumption significantly decreased.

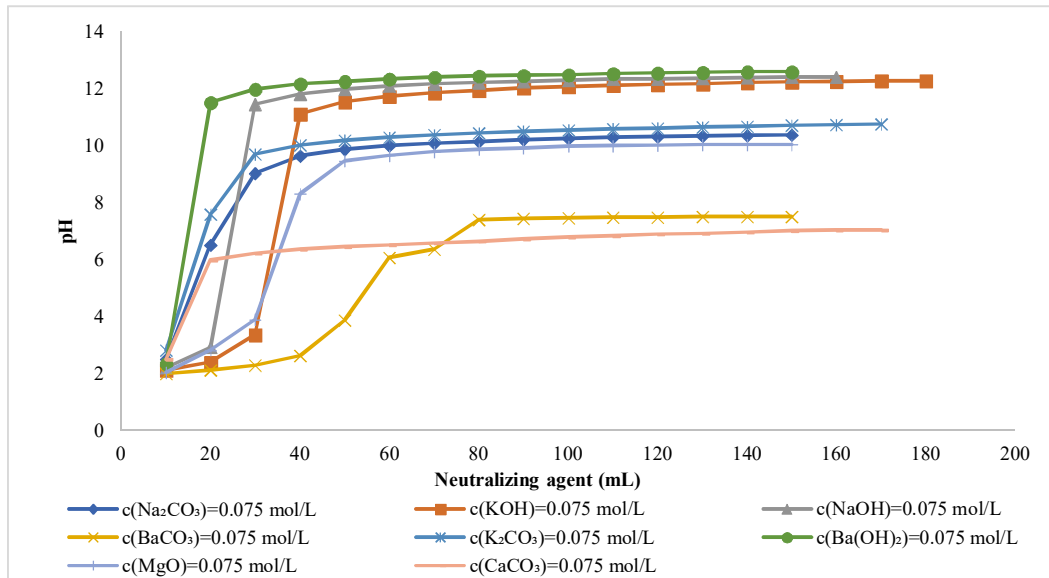


(a)



(b)

Figure 2. Neutralizing agent consumption vs. pH. a). Concentration of neutralizing agent of 0.025 mol/L b). Concentration of neutralizing agent of 0.050 mol/L c). Concentration of neutralizing agent of 0.075 mol/L.



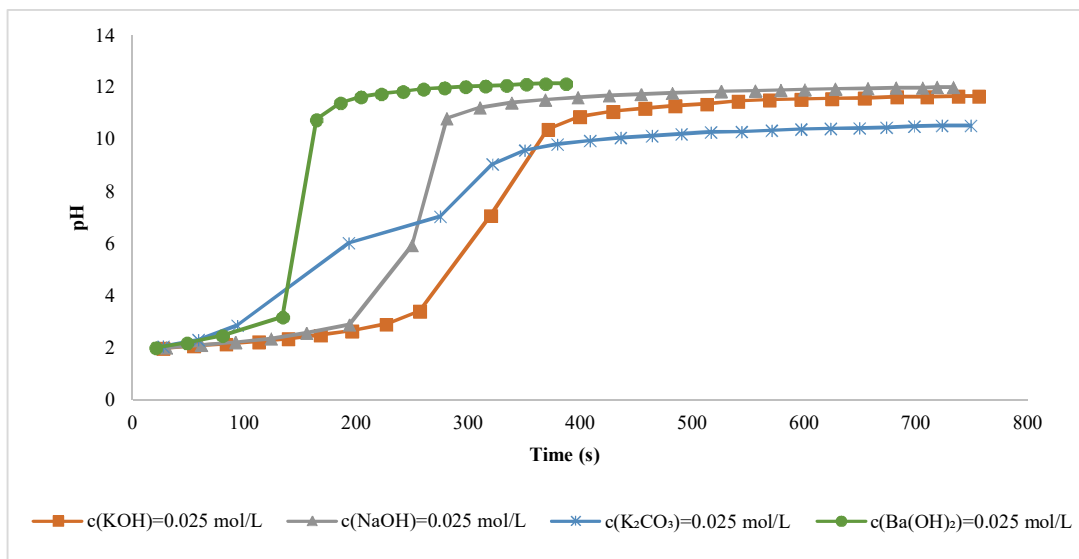
(c)

Continue of Figure 2.

**3.2. Kinetics of pH**

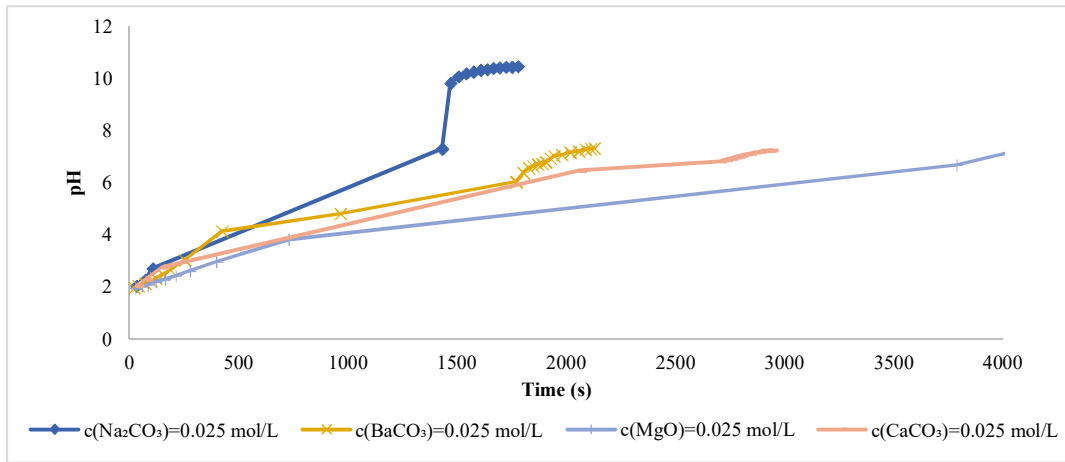
In continuation of the previous examination, the time taken to achieve a pH value was also measured in order to determine the kinetics of pH. The obtained results are shown in Figure 3, and it can be concluded that the time taken to achieve a pH depend on the agent concentration. In particular, as the concentration of the neutralizing agent increased, the time to reach the pH decreased.

The rate of the achieved pH value is in the following order:  $Ba(OH)_2 > NaOH > KOH > K_2CO_3 > Na_2CO_3 > BaCO_3 > CaCO_3 > MgO$ , and this pattern is observed in all neutralizing agent concentrations that were studied. According to Masindi *et al.*, [29] using pH as an indicator, the neutralisation efficiencies varied as follows: caustic soda  $\geq$  hydrated lime  $\geq$  lime  $\geq$  cryptocrystalline magnesite  $\geq$  periclase  $\geq$  soda ash  $\geq$  brucite  $\geq$  limestone.

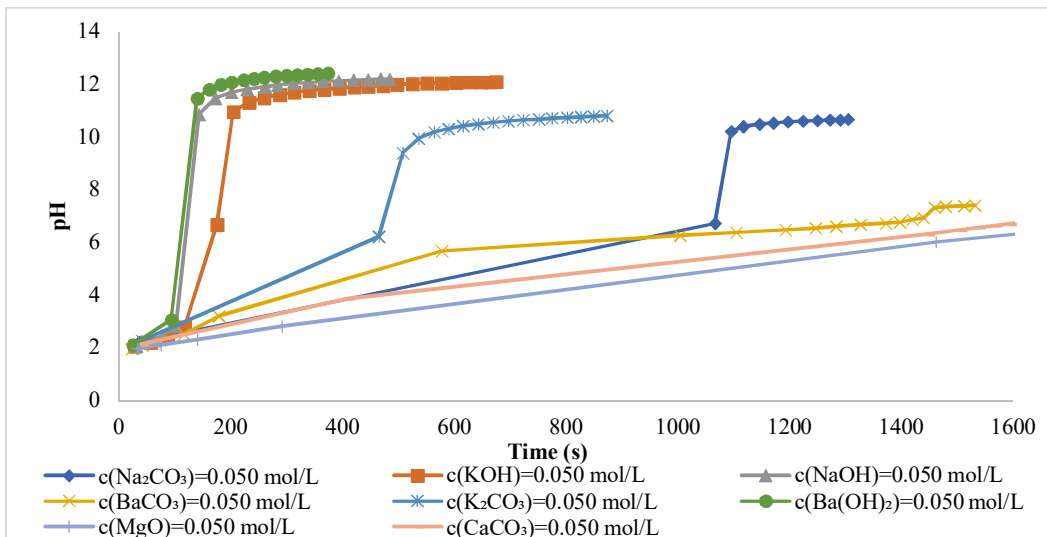


(a)

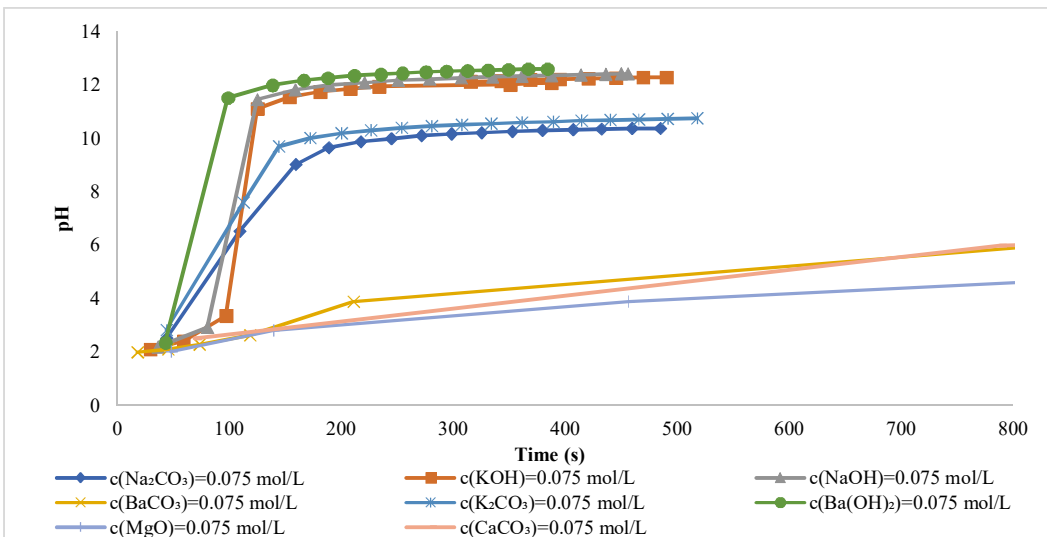
Figure 3. Kinetics of pH. a.) Concentration of neutralizing agent of 0.025 mol/L b.) Concentration of neutralizing agent of 0.050 mol/L c.) Concentration of neutralizing agent of 0.075 mol/L.



(a)



(b)



(c)

Continue of Figure 3. Kinetics of pH. a). Concentration of neutralizing agent of 0.025 mol/L b). Concentration of neutralizing agent of 0.050 mol/L c.) Concentration of neutralizing agent of 0.075 mol/L.



The slowest pH reached was through the use of MgO. Using MgO with a concentration of 0.025, 0.050, and 0.075 mol/L, a maximum pH value of 9.84 was obtained for 88 minutes (Figure 3a), pH 9.98 for 64 minutes (Figure 3b), and pH 10 for 57 minutes (Figure 3c), respectively. Due to the greater clarity of the graphs, these values are not shown in Figure 3. CaCO<sub>3</sub> was also a slower neutralizing agent, and some data is not shown on the graphs. Using concentrations of 0.050 and 0.075 mol/L, a maximum pH 7 for 30 minutes (Figure 3b) and pH 7 for 1500 seconds (Figure 3c) were obtained, respectively.

### 3.3 Removal of heavy metals

The investigation of the effectiveness of neutralizing agents to remove heavy metals from a

multi-component synthetic acidic aqueous solution was done using BaCO<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub>, NaOH, KOH, K<sub>2</sub>CO<sub>3</sub>, MgO, CaCO<sub>3</sub>, and Ba(OH)<sub>2</sub> with concentrations of 0.025, 0.050, and 0.075 mol/L. The experiments were performed using a multi-component synthetic aqueous solution with initial concentrations of 10 mg/L of Cu, Mn, Zn, Fe, and Pb ions and an initial pH value of 1.9.

The results presented in this section were before the use of the flocculant because the effectiveness of the removal of heavy metals after flocculation was almost 97-100% for each studied agent and metal ion. The exception was with the experiments with Mn and Zn using BaCO<sub>3</sub>, Zn and Pb using Ba(OH)<sub>2</sub> and Mn and Zn using CaCO<sub>3</sub>. These results are presented in Tables 1S-8S (supplement material).

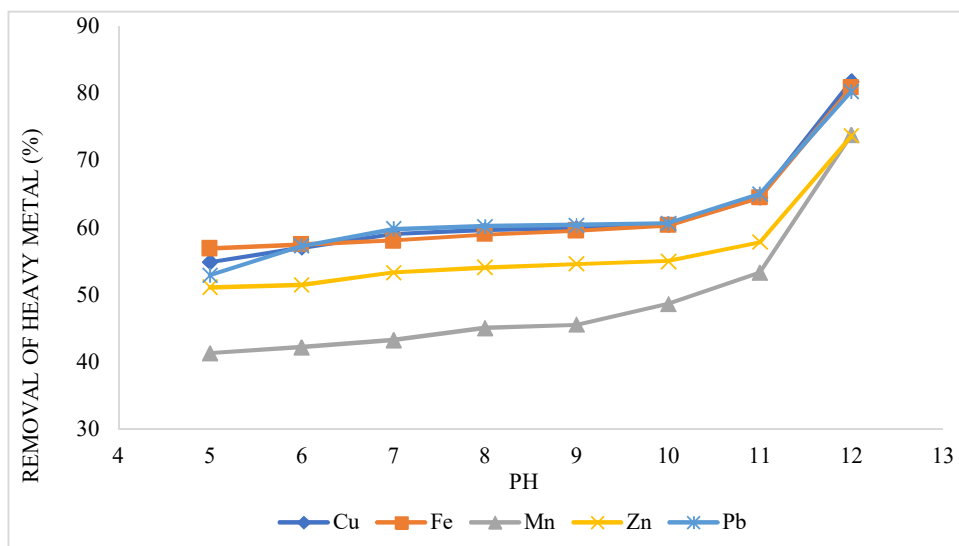


Figure 4. pH ranges for metal precipitation with KOH.

In order to remove heavy metals from aqueous solutions as efficiently as possible, the optimal pH value was found (Figure 4). Almost 80-82% of Pb, Zn, and Cu were precipitated at pH 12, while almost 74% of Zn and Mn were precipitated at pH 12. Additionally, it is clear from Figure 4 that the percentage of heavy metals removed increases along with rising pH values.

The obtained results are inconsistent with those reported by Skousen *et al.* [24]. According to them, the types and amounts of metals in the water heavily influence the selection of an AMD treatment system because the pH required to precipitate most metals from water ranges from pH 6 to 9 (except Fe<sup>+3</sup>, which precipitates at pH > 3.5) [24]. Ferrous iron converts to a solid bluish-green Fe(OH)<sub>2</sub> at pH > 8.5. In the presence of oxygen, Fe<sup>+2</sup> oxidizes to Fe<sup>+3</sup>, and Fe(OH)<sub>3</sub> forms a

yellowish-orange solid (commonly called yellow boy), which precipitates at pH > 3.5. In oxygen-poor AMD, where Fe is primarily in the Fe<sup>+2</sup> form, enough alkalinity must be added to raise the solution pH to 8.5 before Fe(OH)<sub>2</sub> precipitates [24].

Manganese precipitation is variable due to its many oxidation states but will generally precipitate at a pH of 9.0 to 9.5. Interactions among metals also influence the rate and degree to which metals precipitate. For example, Fe precipitation will largely remove Mn from the water at pH 8 due to co-precipitation but only if the Fe concentration in the water is much greater than the Mn content (about 4 times more or greater). If the Fe:Mn ratio is less than 4, Mn is not removed by co-precipitation, and a solution pH of > 9 is necessary to remove it from solution [24].



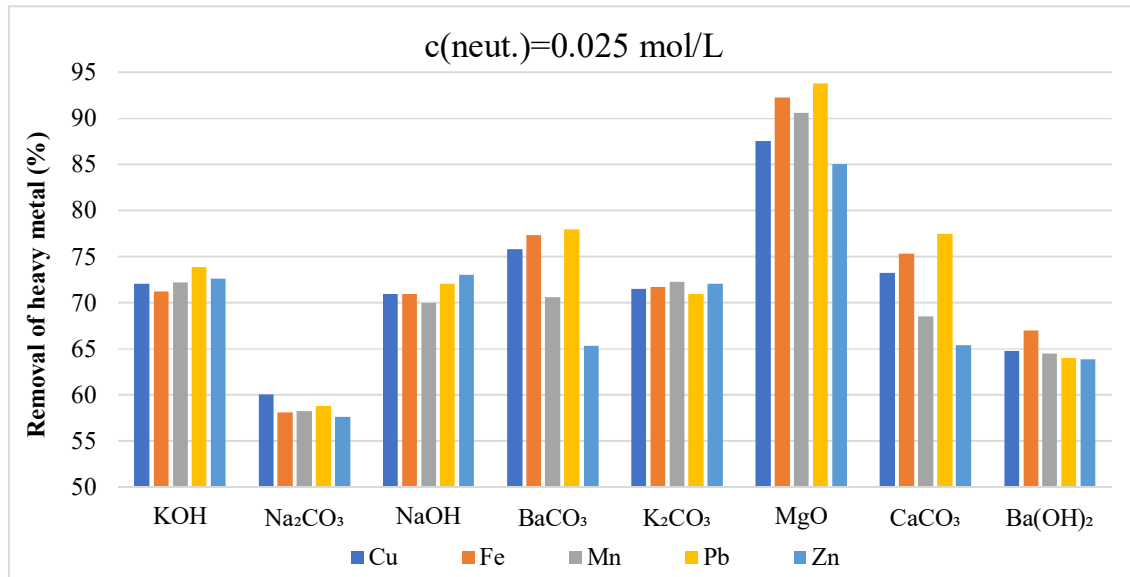


Figure 5. Comparison of studied neutralizing agents for heavy metals removal at lowest neutralizing concentration.

The following experiments were conducted with the greatest pH value that could be achieved in accordance with the neutralizing agent utilized because the maximum removal of heavy metals was obtained at the highest pH value. Comparison of the studied neutralizing agents for heavy metal

removal from aqueous solutions is shown in Figure 5. From the results, it can be concluded that the most effective neutralizing agent for heavy metal removal from multi-component aqueous solution is MgO, while the lowest efficiency is obtained with Na<sub>2</sub>CO<sub>3</sub> (Table 2).

Table 2. Series of effective neutralizing agents for heavy metal removal from multi-component aqueous solution.

| Heavy metal | Series of effective neutralizing agents   |
|-------------|---|
| Cu          | MgO > BaCO <sub>3</sub> > CaCO <sub>3</sub> > KOH > K <sub>2</sub> CO <sub>3</sub> > NaOH > Ba(OH) <sub>2</sub> > Na <sub>2</sub> CO <sub>3</sub> |
| Fe          | MgO > BaCO <sub>3</sub> > CaCO <sub>3</sub> > K <sub>2</sub> CO <sub>3</sub> > KOH > NaOH > Ba(OH) <sub>2</sub> > Na <sub>2</sub> CO <sub>3</sub> |
| Mn          | MgO > K <sub>2</sub> CO <sub>3</sub> > KOH > BaCO <sub>3</sub> > NaOH > CaCO <sub>3</sub> > Ba(OH) <sub>2</sub> > Na <sub>2</sub> CO <sub>3</sub> |
| Zn          | MgO > NaOH > KOH > K <sub>2</sub> CO <sub>3</sub> > CaCO <sub>3</sub> > BaCO <sub>3</sub> > Ba(OH) <sub>2</sub> > Na <sub>2</sub> CO <sub>3</sub> |
| Pb          | MgO > BaCO <sub>3</sub> > CaCO <sub>3</sub> > KOH > NaOH > K <sub>2</sub> CO <sub>3</sub> > Ba(OH) <sub>2</sub> > Na <sub>2</sub> CO <sub>3</sub> |

According to Skousen *et al.* [24], caustic soda (NaOH) is often used if Mn concentrations in AMD are high but according to the results obtained in this work, the precipitation of Mn was more effective using MgO, K<sub>2</sub>CO<sub>3</sub>, KOH, and BaCO<sub>3</sub> than NaOH. A similar comparative study was published by Masindi *et al.* [28], and their results showed that hydrated lime, periclase, magnesite, and caustic soda achieved pH ≥ 9, and ≥ 99% metals removal, whereas the use of soda ash, limestone, lime, and brucite yielded pH ≥ 6, Al and Fe removal ≥ 99%, and Mn ≥ 60%.

From the results shown in Figure 6, it can also be concluded that at lower agents' concentration, the removal of heavy metals is more effective using the neutralizing agents KOH, NaOH, BaCO<sub>3</sub>, and K<sub>2</sub>CO<sub>3</sub>. The fact that at lower agents' concentration, the removal of heavy metals is higher may be due to the slower pH achieved and the heavy metals' longer time for precipitation.

Using Na<sub>2</sub>CO<sub>3</sub> and MgO, more effective results are obtained with higher agents' concentration, while using CaCO<sub>3</sub> and Ba(OH)<sub>2</sub>, the efficiency depends on the concentration of the neutralizing agents for each metal separately.

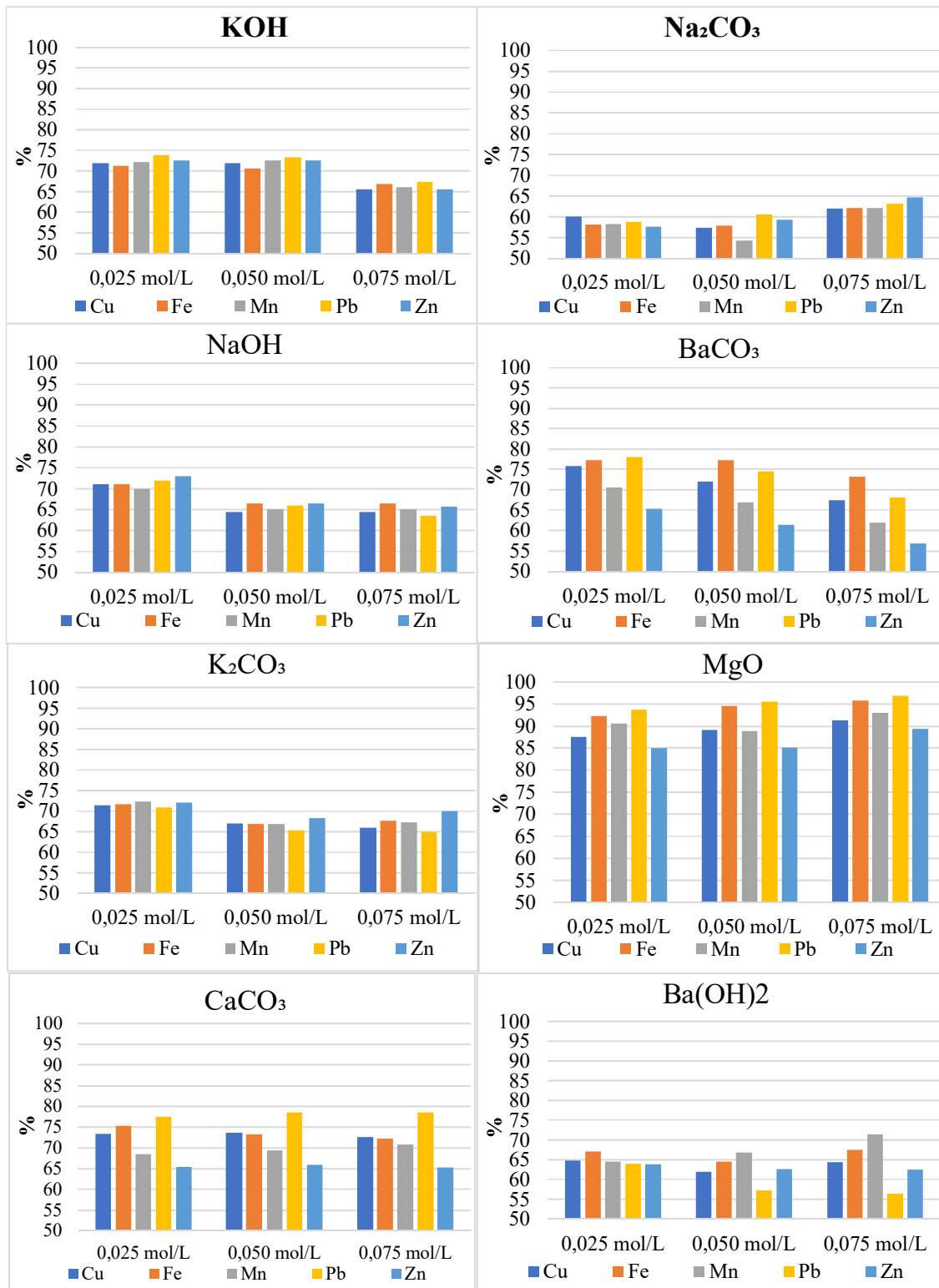


Figure 6. Removal of heavy metals by neutralization.

#### 4. Conclusions

The efficiency of neutralizing agents for acid mine drainage treatment was compared using eight different agents including BaCO<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub>, NaOH, KOH, K<sub>2</sub>CO<sub>3</sub>, MgO, CaCO<sub>3</sub>, and Ba(OH)<sub>2</sub>. The experiments were performed using a multi-component synthetic aqueous solution with an initial concentration of 10 mg/L of Cu, Mn, Zn, Fe, and Pb ions and an initial pH value of 1.9.

The results of this extensive research work showed that the consumption of the neutralizing agent decreased as the concentration of the neutralizing agent increased. Also the time taken to achieve a pH value depended on the agent concentration. In particular, as the concentration of the neutralizing agent increased, the time to reach the pH decreased.

The percentage of heavy metals removed from aqueous solutions increased along with rising pH values. The optimal pH value was pH 12 for all studied heavy metals, and were obtained almost 80-82% removed of Pb, Fe, and Cu, while almost 74% of Zn and Mn.

The comparison of the studied neutralizing agents for the removal of heavy metals showed that the most effective neutralizing agent for the removal of heavy metals from a multi-component aqueous solution is MgO, while the lowest efficiency was obtained with Na<sub>2</sub>CO<sub>3</sub>.

The effect of the concentration of the neutralizing agents was shown to depend on the neutralizing agents and heavy metals used.

The choice of the most effective neutralizing agent for acid mine drainage treatment can be made depending on several things such as consumption, speed of pH achievement, and removal of heavy metals from AMD.

#### References

[1]. Jenkins, D.A., Johnson, D.B., and Freeman, C. (2000). Mynydd Parys Cu-Pb-Zn mines: mineralogy, microbiology and acid mine drainage. In: Cotter-Howells, J.D., Campbell, L.S., Valsami-Jones, E., and Batchelder, M. (Editors.) *Environmental mineralogy: microbial interactions, anthropogenic influences, contaminated land and waste management*. The Mineralogy Society Series No. 9. Mineralogical Society, London, UK, 161-180.

[2]. Evangelou, V.P. (1998). Pyrite chemistry: the key for abatement of acid mine drainage. In: Geller, A., Klapper, H., and Salomons, W., Editors. *Acidic Mining Lakes: Acid Mine Drainage, Limnology and Reclamation*. Berlin: Springer; 197– 222.

[3]. Motsi, T. (2010). Remediation of acid mine drainage using natural zeolite, Doctotal thesis, United Kingdom: School of Chemical Engineering, The University of Birmingham.

[4]. Huyen, D., Tabelin, C., Thuan, H., Dang, D., Truong, P., Vonghuthone, B., Kobayashi, M., and Igarashi, T. (2019). The solid-phase partitioning of arsenic in unconsolidated sediments of the Mekong Delta, Vietnam and its modes of release under various conditions. *Chemosphere* 233, 512–523.

[5]. Igarashi, T., Herrera, P., Uchiyama, H., Miyamae, H., Iyatomi, N., Hashimoto, K., and Tabelin, C. (2020). The two-step neutralization ferrite-formation process for sustainable acid mine drainage treatment: Removal of copper, zinc and arsenic, and the influence of coexisting ions on ferritization. *Sci. Total Environ.* 715, 136877.

[6]. Skousen, J., Ziemkiewicz, P., and McDonald, L. (2019). Acid mine drainage formation, control and treatment: Approaches and strategies. *Extr. Ind. Soc.* 6, 241–249.

[7]. Turingan, C.O.A., Singson, G.B., Melchor, B.T., Alorro, R.D., Beltran, A.B., and Orbecido, A.H. (2020). Evaluation of Efficiencies of Locally Available Neutralizing Agents for Passive Treatment of Acid Mine Drainage. *Minerals*, 10, 845. <https://doi.org/10.3390/min10100845>

[8]. Penreath, R.J. (1994). The discharge of waters from active and abandoned mines. In: Hester, R.E. and Harrison, R.M. (Editors.) *Mining and its environmental impact. Issues in Environmental Science and Technology* No. 1. Royal Society of Chemistry, Herts, UK, 121-132.

[9]. Golomeova, M., Zendelska, A., Krstev, B., Golomeov, B., and Krstev, A. (2012) Mine drainage treatment. In: 4th Congress of ecologists of the Republic of Macedonia with international participation, 12-15 Oct. 2012, Ohrid, Macedonia.

[10]. Waters J.C., Santomartino S., Cramer M., Murphy N., and Taylor J.R. (2003). Acid rock drainage treatment technologies—identifying appropriate solutions. *Proceedings, 6th International Conference on Acid Rock Drainage*. 12–18 July, Cairns, Queensland, Australia. 831 843.

[11]. Coulton, R., Bullen, C., and Hallet, C. (2003). The design and optimization of active mine water treatment plants. *Land Contamination and Reclamation*, 11, 273–279.

[12]. Kefeni, K., Msagati, T., and Mamba, B. (2017). Acid mine drainage: Prevention, treatment options, and resource recovery: A review. *J. Clean. Prod.*

[13]. Park, I., Tabelin, C., Jeon, S., Li, X., Seno, K., Ito, M., and Hiroyoshi, N. (2019). A review of recent strategies for acid mine drainage prevention and mine tailings recycling. *Chemosphere* 219, 588–606.

- [14]. Skousen, J.G., Sexstone, A., and Ziemkiewicz, P. (2000). Acid mine drainage control and treatment. Reclam. Drastically Disturb. Lands.
- [15]. Skousen, J. and Ziemkiewicz, P. (2005). Performance of 116 passive treatment systems for acid mine drainage. In Proceedings of the 2005 National Meeting of the American Society of Mining and Reclamation, Breckenridge, CO, USA, 19–23 June 2005.
- [16]. Muliwa, A. and Leswif, T. (2018). Performance evaluation of eggshell waste material for remediation of acid mine drainage from coal dump leachate. *Miner. Eng.* 122, 241–250.
- [17]. Heviánková, S. and Bestová, I. (2014). The application of wood ash as a reagent in acid mine drainage treatment. *Miner. Eng.* 56, 109–111.
- [18]. Ouakibi, O. and Hakkou, R. (2014). Phosphate carbonated wastes used as drains for acidic mine drainage passive treatment. *Procedia Eng.* 83, 407–414.
- [19]. Kamal, N.M. and Sulaiman, S.K. (2014). Bench-Scale study of acid mine drainage treatment using local neutralisation agents. *Malays. J. Fundam. Appl. Sci.* 10, 150–153.
- [20]. Trumm, D. (2010). Selection of active and passive treatment systems for AMD—flow charts for New Zealand conditions, *New Zealand Journal of Geology and Geophysics*, 53:2-3, 195-210, DOI: 10.1080/00288306.2010.500715
- [21]. Loza, N. and Aduvire, O. Acid Mine Drainage Treatment Process Optimization for Manganese Content Reduction by Sequential Neutralization. Available at: <https://www.srk.com/en/publications/acid-mine-drainage-treatment-process-optimization-for-manganese-content-reduction-by-sequential-neut>
- [22]. Kapil, N. and Bhattacharyya, K.G. (2017). A comparison of neutralization efficiency of chemicals with respect to acidic Kopili River water, *Appl Water Sci* (2017) 7:2209–2214, DOI 10.1007/s13201-016-0391-6
- [23]. Turingan, C., Singson, G., Melchor, B., Alorro, R., Beltran, A., and Orbecido, A. (2020). A comparison of the acid mine drainage (AMD) neutralization potential of low grade nickel laterite and other alkaline generating materials, *IOP Conf. Series: Materials Science and Engineering* 778, doi:10.1088/1757-899X/778/1/012142
- [24]. Skousen, J.G. Sexstone, A., and Ziemkiewicz, P.F. (2000). Acid mine drainage control and treatment, Chapter 6. Reclamation of Drastically Disturbed Lands, American Society of Agronomy and American Society for Surface Mining and Reclamation. Volume No. 41. <https://doi.org/10.2134/agronmonogr41.c6>
- [25]. Skousen, J., Zipper, C.E., Rose, A., Ziemkiewicz, P.F., Nairn, R., McDonald, L.M., and Kleinmann R.L. (2017). Review of Passive Systems for Acid Mine Drainage Treatment, *Mine Water Environ* (2017) 36:133–153, DOI 10.1007/s10230-016-0417-1
- [26]. Bologo, V., Maree, J.P., and Carlsson, F. (2012). Application of magnesium hydroxide and barium hydroxide for the removal of metals and sulphate from mine water, *Water SA* Vol. 38 No. 1, <http://dx.doi.org/10.4314/wsa.v38i1.4>
- [27]. Maila, M.D., Maree, J.P., and Cele, L.M. (2014). Acid mine water neutralisation with ammonium hydroxide and desalination with barium hydroxide, *Water SA* Vol. 40 No. 3, <http://dx.doi.org/10.4314/wsa.v40i3.16>
- [28]. Masindi V., Akinwekomi V., Philippus M.J., and Lilit M.K. (2017). Efficiencies of different alkaline generating agents for the treatment of acid mine drainage: A comparative study and techno-economic appraisals, *Mine Water and Circular Economy*, Lappeenranta, Finland.
- [29]. Masindi V., Akinwekomi V., Maree J.P., and Muedi K.L. (2017). Comparison of mine water neutralisation efficiencies of different alkaline generating agents, *Journal of Environmental Chemical Engineering*, Vol 5 (4), 3903-3913, <https://doi.org/10.1016/j.jece.2017.07.062>.
- [30]. Potgieter-Vermaak S.S., Potgieter J.H., Monama P., and Van Grieken R. (2006). Comparison of limestone, dolomite and fly ash as pre-treatment agents for acid mine drainage, *Minerals Engineering*, Vol. 19 (5), 454-462, <https://doi.org/10.1016/j.mineng.2005.07.009>.

## مقایسه کارایی عوامل خنثی کننده برای حذف فلزات سنگین از زهاب اسیدی معدن

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ارسال ۲۰۲۲/۰۷/۰۹، پذیرش ۲۰۲۲/۰۹/۱۴

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### چکیده:

تصفیه زهاب اسیدی معدن معمولاً با استفاده از دو فناوری اساسی فن آوری تصفیه فعال و غیرفعال انجام می شود. هر کدام از روش های تصفیه زهاب اسیدی معدن (AMD) استفاده شود، یک روش خنثی سازی که pH آب را با استفاده از عوامل قلیایی بیش از ۷ افزایش می دهد، قبل از تخلیه مورد نیاز است. مقایسه هشت عامل مختلف ( $\text{Ba}(\text{OH})_2$ ،  $\text{CaCO}_3$ ،  $\text{MgO}$ ،  $\text{K}_2\text{CO}_3$ ،  $\text{KOH}$ ،  $\text{NaOH}$ ،  $\text{Na}_2\text{CO}_3$ ،  $\text{BaCO}_3$ ) به منظور انتخاب موثرترین عامل خنثی کننده برای تصفیه زهاب اسیدی معدن انجام شد. آزمایش ها با استفاده از محلول آبی مصنوعی چند جزئی با غلظت اولیه ۱۰ میلی گرم در لیتر یون های مس، منگنز، روی، آهن و سرب و pH اولیه ۱/۹ انجام شد. بر اساس این تحقیقات، موثرترین عامل خنثی کننده برای حذف فلزات سنگین از محلول آبی چند جزئی،  $\text{MgO}$  و کم اثرترین عامل  $\text{Na}_2\text{CO}_3$  بود. سری به دست آمده از عوامل خنثی کننده موثر برای حذف فلزات سنگین از محلول آبی چند جزئی در کار ارائه شده اند. اثر غلظت مورد مطالعه عوامل خنثی کننده به نوع خنثی کننده و فلزات سنگین مورد استفاده بستگی دارد. در صد فلزات سنگین حذف شده از محلول های آبی همراه با افزایش مقادیر pH افزایش می یابد. با افزایش غلظت عامل خنثی کننده، مصرف عامل خنثی کننده کاهش می یابد. علاوه بر این، زمان لازم برای رسیدن به pH به غلظت عامل بستگی دارد. به طور خاص، با افزایش غلظت عامل خنثی کننده، زمان رسیدن به pH کاهش می یابد.

**کلمات کلیدی:** فلزات سنگین، تصفیه فعال، لخته سازی، خاکستر سودا، سود سوزآور.