

Adsorption of Heavy Metals Fe and Mn in Acid Mine Drainage from Coal Mining Waste Using Calcium Oxide and Fly Ash

Hendra Pratama^{1*}, Edy Nursanto¹, Rika Ernawati¹, Muhammad Giatman²

¹ Master Program of Mining Engineering, Faculty of Mineral Technology, Pembangunan Nasional “Veteran” University Yogyakarta

Jl. SWK No 104, Condongcatur Yogyakarta, Indonesia-55283

² Department of Civil Engineering, Engineering Faculty, Universitas Negeri Padang

Jl. Prof. Dr. Hamka Kampus UNP, Air Tawar Padang, Indonesia-25131

*Corresponding author: hndra5151@gmail.com

Doi : <https://doi.org/10.24036/invotek.v22i2.1020>

This work is licensed under a Creative Commons Attribution 4.0 International License



Abstract

Acid mine drainage for Fe and Mn metals have a negative impact on the environment. This study studies the use of calcium oxide and fly ash as adsorbents, used to absorb Fe and Mn metals contained in acid mine drainage. This study aims to analyze the effectiveness of Calcium Oxide and fly ash as adsorbents, that an adsorbent of Fe and Mn metals in acid mine drainage. The method used is experimental with a laboratory scale, the test is carried out by adsorption using a batch system. Magnetic stirrer is used as a stirring medium in the adsorption process. Calcium oxide with various doses (0.1; 0.2; 0.3 grams) and fly ash with various doses (10; 14; 17 grams) were mixed with 250 ml acid mine drainage, then stirred at a speed of 150 rpm and (30; 60; 90 minutes) stirring time. The characterization of the adsorbent was carried out by SEM testing. The results show that fly ash adsorbent has a better adsorption effectiveness than calcium oxide. The effectiveness of Fe is 85.35% and Mn 78.14%. While calcium oxide has the effectiveness of Fe 72.91% and Mn 61.81%. SEM testing of holes that increase and enlarge after adsorption, as well as the filling of the cavity by the material indicates the success of the adsorption process.

Keywords: adsorption, calcium oxide, effectiveness, fly ash, SEM

1. Introduction

Human necessity derived from natural resources (minerals, oil, and coal) are increasing along with the development of technology for production, communication, and transportation. The mining industry plays an important role in regional and state economic growth. Opening high exports and promising prices also encourage business actors to invest in the coal mining industry.

In addition to the benefits and positive impacts of the mining industry, there are negative impacts arising from mining waste, namely acid mine drainage formed due to the oxidation of sulfide minerals. The presence of water and oxygen in the air as a source of oxidation. Sulphide minerals are often found in the coal mining industry and ore minerals in which the digging and backfilling activities caused by the exposure of sulfide minerals that were previously below the soil surface [1]. This causes an increasing production in the water body which is characterized by low pH, and dissolved metal concentrations in the receiving water body [2].

Treatment of acid mine drainage generally uses calcium oxide (CaO), which is the result of burning calcium carbonate (CaCO₃). Based on limestone which is formed as a result of a calcination reaction using heating at a temperature of 900 °C, it causes carbon dioxide (CO₂) to come out and leaves calcium oxide (CaO) [3]. The calcium oxide has a high stability which when reacted with water can directly neutralize the acid solution [4], but it is not effective in reducing heavy metals in acid mine drainage [5].

Steam power plants (PLTU) used coal as a fuel source produce residues in the form of bottom ash and fly ash, known as FABA. Physically, fly ash is fine with a size of $<20\ \mu\text{m}$, with a surface area of 300-500 m^2/kg . Some fly ash is acidic with a pH of 3-4, but it is generally alkaline with a pH of 10-12 [6]. In addition, fly ash contains large amounts of unburned carbon, and has a high adsorption capacity [7]. Fly ash is also a great alternative as a conventional adsorbent [8].

With large power plant production, fly ash waste is generally only disposed of around industrial areas. Limitations in the use of fly ash waste, have an impact on the accumulation of waste. This case has the potential to contaminate dissolved heavy metals in the surrounding waters. By blown the wind which will adversely affect breathing [9]. Various efforts have been made to increase the utilization of fly ash waste, including the issuance of fly ash waste from the B3 waste category by the government [10].

Adsorption is a process that can be used for the purpose of reducing heavy metals in acid mine drainage. The adsorption process has several advantages, namely the processing is relatively simple, effective, high efficiency, and does not have a negative impact on the environment [11]. Adsorption is also the process of separating or removing low concentration pollutants from large volumes of wastewater and aqueous solutions [12]. The adsorption process has an influence on contact time, stirring speed, adsorbent mass, and particle area [13].

This research is a development of previous research, where the use of the adsorbent dose is varied and the stirring speed is increased, so that more representative results are obtained. The purpose of this study was to analyze the effectiveness of using calcium oxide and fly ash as adsorbents for the absorption of Fe and Mn metals in acid mine drainage, and comparing the surface structure before and after adsorption using a scanning electron microscope.

2. Research Methodology

The tests were carried out using experimental methods on a laboratory scale. The adsorption process is carried out using a batch system, namely adsorption by immersion in a solution containing heavy metals, which will then be absorbed and observed quality changes at certain intervals. The material used is acid mine drainage from the coal mining sump location of PT X. Acid mine drainage uses a purposive sampling method and refers to the wastewater sampling method [14]. Furthermore, calcium oxide was taken at the location of the people's mining industry in the Padang Panjang area, while the fly ash sample came from the PLTU which was taken at the TPS location. Dry oven, analytical balance, watch glass, beaker, stirring bar, magnetic stirrer, elenmeyer, glass funnel, filter paper, mortal and pestle are tools used in adsorption testing. This research was conducted in an accredited and standardized laboratory.

2.1 Characterization of adsorbent

Characterization of calcium oxide and fly ash samples was carried out using a scanning electron microscope (SEM). The test was carried out to determine the surface structure of the adsorbent before adsorption, then carried out again after the adsorption experiment. The test was carried out aimed at knowing the differences and changes in the structure of the calcium oxide and fly ash adsorbents. The following is the SEM testing process which can be seen in Figure 1.

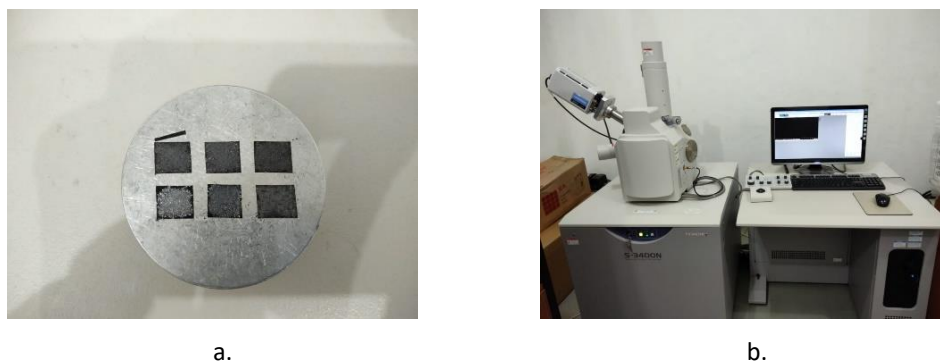


Figure 1 a. The adsorbent sample is placed in the holder, b. The sample is loaded into the SEM Hitachi S-3400N tool

2.2 Fe and Mn metal content in acid mine drainage

Measurement of the metal content of Fe and Mn in acid mine drainage was carried out with atomic absorption spectrophotometry (AAS) before and after the adsorption experiment. Water quality testing refers to the Indonesian Nasional Standard on Water and Wastewater Quality, the AAS method of iron (Fe) testing [15] and the AAS method of manganese (Mn) testing [16]. Based on the quality standard of coal mining waste [17], the maximum concentration for Fe metal is 7 mg/l and Mn metal is 4 mg/l.

2.3 The process of adsorption uses calcium oxide and fly ash

The process of adsorption was carried out on a laboratory scale with a magnetic stirrer as a media stirrer. Before used, the adsorbent must be heated in an dry oven to remove the water content of the adsorbent. Furthermore, the adsorbent dose was weighed according to the predetermined dose, using an analytical balance which was measured on a watch glass. Then, the dose is mixed into a beaker glass, with acid mine drainage with a volume of 250 ml. Then a stirring bar is inserted as a magnet to stir in the magnetic stirrer. After that, stirring was carried out by adjusting the stirring speed at 150 rpm, and the stirring time was in accordance with the design of adsorption. Adsorption using adsorbents in the form of calcium oxide and fly ash can be seen more clearly in Table 1.

Table 1. Adsorption of Experiment Design

Variations of Calcium Oxide	C1 (0,1 gram), C2 (0,2 gram), C3 (0,3 gram)				
Variations of Fly Ash	F1 (10 gram), F2 (14 gram), F3 (17 gram)				
Stirring Speed	S1 (150 rpm)				
Stirring Time	T1 (30 min), T2 (60 min), T3 (90 min)				
C1S1T1	C2S1T1	C3S1T1	C1S1T2	C2S1T2	C3S1T2
C1S1T3	C2S1T3	C3S1T3	F1S1T1	F2S1T1	F3S1T1
F1S1T2	F2S1T2	F3S1T2	F1S1T3	F2S1T3	F3S1T3

The next sample is poured into an erlenmeyer after the stirring process is complete, and filtered using filter paper placed on a glass funnel. The filtering results in the form of water are then put into a PET bottle, so AAS analysis is carried out to determine the remaining content of Fe and Mn metals. The results of the AAS analysis are calculated the effectiveness of the adsorption of Fe and Mn metals. The effectiveness of heavy metal reduction uses the following equation formula:

$$1 - \left(\frac{C_t}{C_o}\right) \times 100\% \tag{1}$$

Where Co is the initial metal concentration (mg/l), and Ct is the final concentration (mg/l). The results of the effectiveness is the form of a percentage level (%) of the decrease in Fe and Mn metals. Meanwhile, the sedimentation sample on filter paper was dried to remove the moisture content using a dry oven, then ground using a mortar and pestle. Furthermore, on the sedimentation sample that has

been dry and smooth, SEM testing is carried out to see the surface morphology and pore structure after adsorption.

3. Result and Discussion

3.1 The test results of SEM

Based on the SEM test before the experiment on calcium oxide and fly ash, it showed that there were few pores and a hollow surface. After the experiment the changes in the pores were getting more and more visible and became denser. The surface morphology of calcium oxide and fly ash before and after adsorption can be seen in Figure 2 and Figure 3.

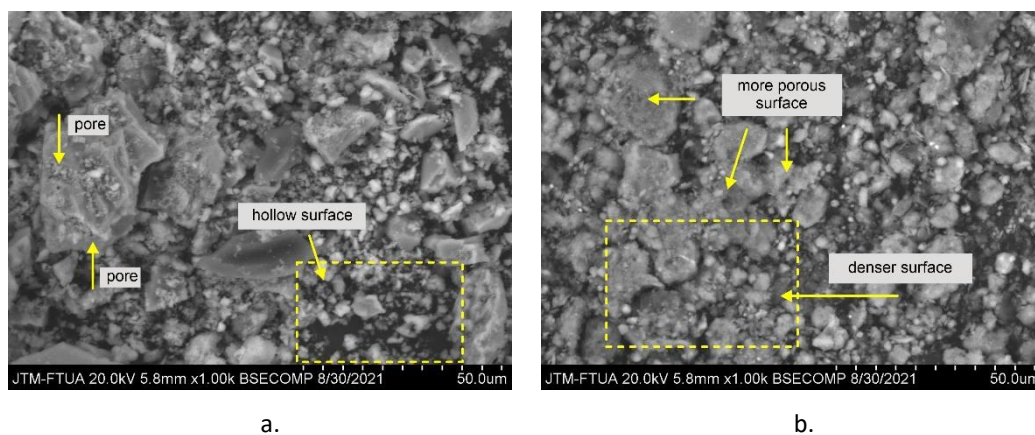


Figure 2a. Surface morphology of calcium oxide before adsorption, b. Surface morphology of calcium oxide after adsorption

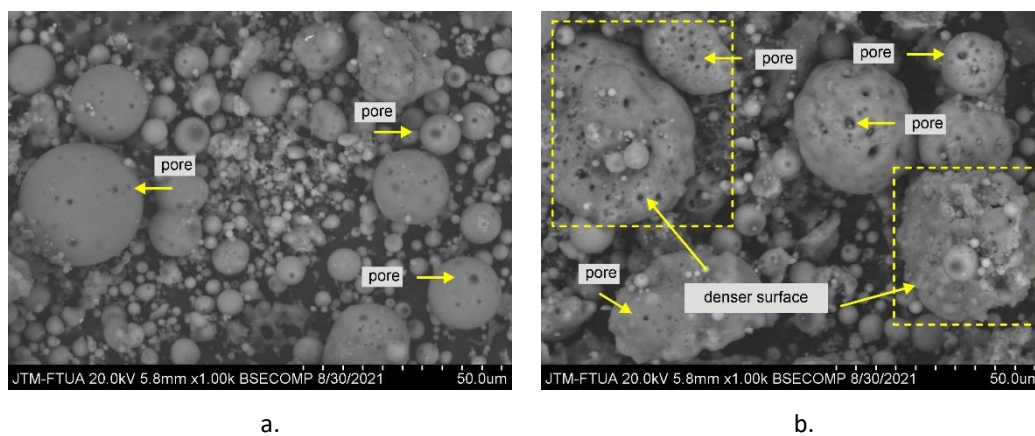


Figure 3a. Surface morphology of fly ash before adsorption, b. Surface morphology of fly ash after adsorption

In Figure 2 and Figure 3, it can be seen that the pores increase and enlarge which indicates an increase in the surface area of the adsorbent. The presence of small pores that are getting bigger after the experiment, shows that acid mine drainage has acidic properties that can damage the surface of calcium oxide and fly ash. Silica and alumina are porous media which presence is indicated by white color, as well as active groups that have the potential as adsorbents for metal ions. As active groups, silica and alumina will come out to the surface if there is damage to the surface layer, so that they can adsorb heavy metals Fe and Mn.

In addition to the increasing number of pores, a significant thing shows that the adsorbent has adsorbed Fe and Mn metals on the pore surface. The pore surface in question is the surface of the adsorbent which was previously hollow which looks denser because the cavity is filled with material. This shows that the material enters and adheres to the surface of the adsorbent, then the voids are seen to be less than before the experiment. So it can be concluded that calcium oxide and fly ash adsorbents successfully absorb heavy metals from acid mine drainage.

3.2 Adsorption of Fe and Mn metals

Based on the results of the analysis before the adsorption experiment using atomic absorption spectrophotometry, it is known that the Fe and Mn metals contained in the acid mine drainage are Fe 8.8605 mg/l and Mn 7.0375 mg/l. After the adsorption experiment, there was a decrease in the concentration of Fe and Mn in acid mine drainage. The results of using calcium oxide to decrease Fe and Mn concentrations can be seen in Figure 4 and Figure 5.

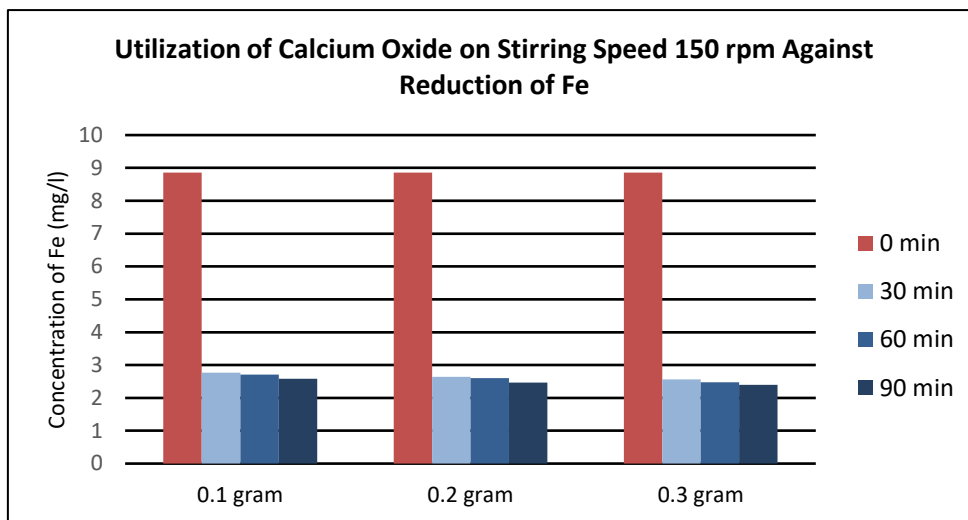


Figure 4. Utilization of Calcium Oxide Against Reduction of Fe

In Figure 4 above, it is shown the results of decreasing the concentration of Fe metal using calcium oxide as an adsorbent. The decrease occurred from the original concentration of Fe, which was 8.8605 mg/l to 2.4002 mg/l. Mixing the 0.1 gram dose, Fe decreased to 2.77 mg/l in 30 minutes, then decreased in 60 minutes to 2.7119 and 2.5816 in 90 minutes. At a dose of 0.2 gram it decreased in 30 minutes to 2.6421 mg/l, and decreased slightly to 2.6049 mg/l in 60 minutes, then at 90 minutes it became 2.4653 mg/l. The use of a dose of 0.3 gram decreased to 2.5584 mg/l in 30 minutes, at 60 minutes it decreased to 2.477 mg/l and the highest decrease occurred at 90 minutes to 2.4002 mg/l.

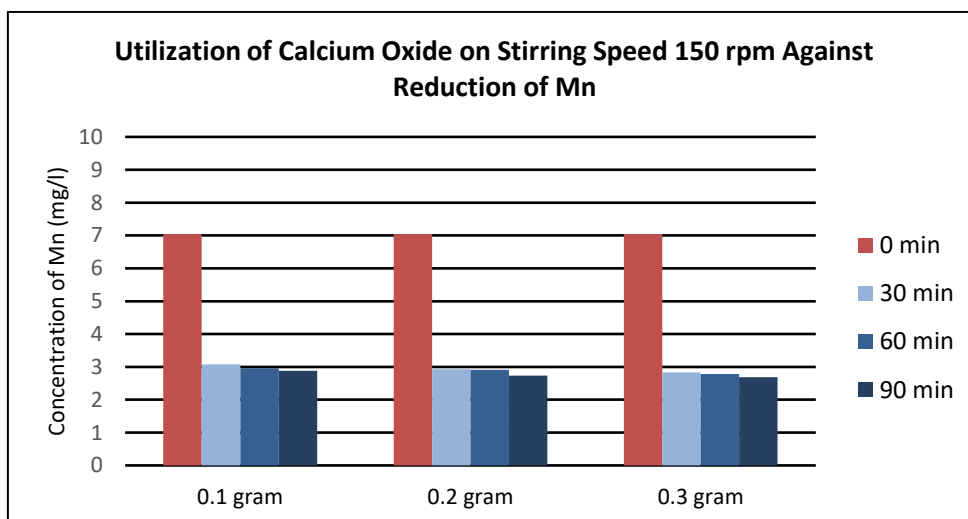


Figure 5. Utilization of Calcium Oxide Against Reduction of Mn

Figure 5 shows of decreasing the concentration of Mn using of calcium oxide. Concentration of Mn decreased from the initial 7.0375 mg/l to 2.6875 mg/l. For the use of a dose of 0.1 gram, decreasing in Mn at 30 minutes reached 3.072 mg/l, after that it decreased slightly to 2.9606 mg/l at 60 minutes and 2.8841 mg/l at 90 minutes. At using a dose of 0.2 gram there was a decrease to 2.9278 mg/l at 30 minutes, then to 2.9103 mg/l at 60 minutes and 90 minutes back down to 2.7312 mg/l. Giving a dose of 0.3 gram,

decreasing in 30 minutes has reached 2.836 mg/l and at 60 minutes it has decreased to 2.7858 mg/l, then at 90 minutes it has reached 2.6875 mg/l which is the highest decrease for Mn. Furthermore, the results of the use of fly ash adsorbent on decreasing Fe and Mn concentrations can be seen in Figure 6 and Figure 7.

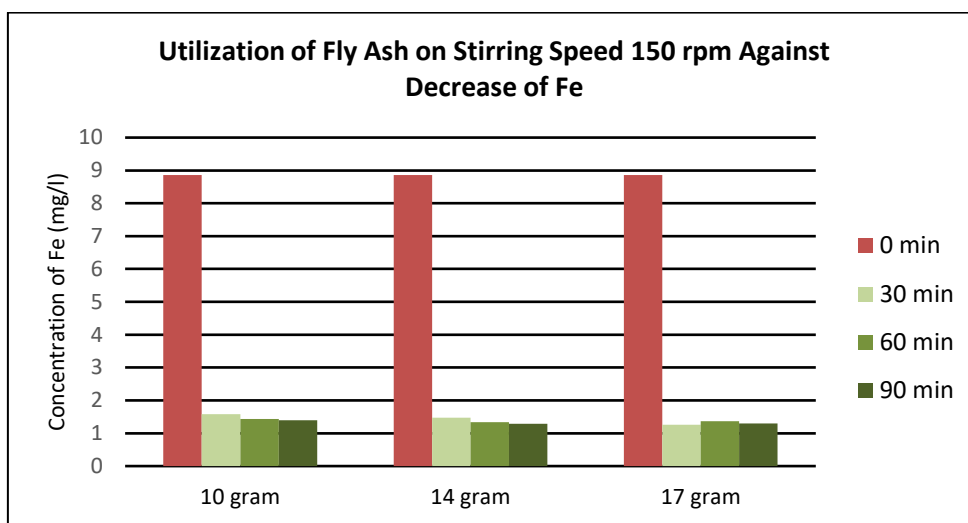


Figure 6. Utilization of Fly Ash Against Reduction of Fe

Based on Figure 6, there was a decreasing in the concentration of Fe metal with fly ash as adsorbent. The concentration of Fe was originally 8.8605 mg/l decreased to 1.2559 mg/l. In the use of a dose of 10 grams there has been a decrease in Fe in 30 minutes to 1.5815 mg/l, after that it decreased to 1.4304 mg/l in 60 minutes and 1.3931 mg/l in 90 minutes. Mixing dose of 14 grams decreased to 1.4722 mg/l at 30 minutes, then decreased to 1.3373 mg/l in 60 minutes and again decreased to 1.2862 mg/l at 90 minutes. Using a dose of 17 grams, the highest decrease at 30 minutes reached 1.2559 mg/l, then increased by 1.3629 mg/l in 60 minutes and then fell again in 90 minutes to 1.3024 mg/l.

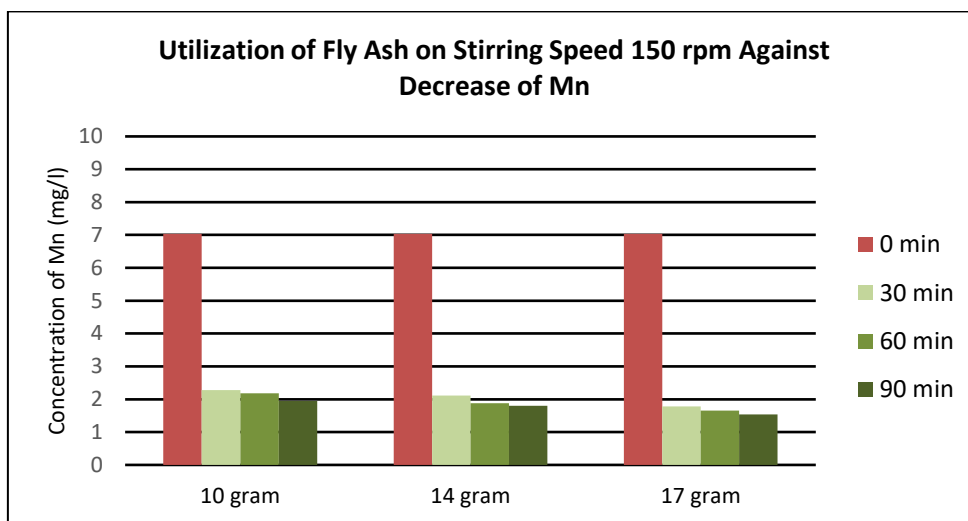


Figure 7. Utilization of Fly Ash Against Reduction of Mn

Figure 7 shows Utilization of fly ash resulted decreasing in the concentration of Mn. Decreasing concentration of Mn from 7.0375 mg/l to 1.5382 mg/l. For giving dose of 10 grams was decreased to 2.2745 mg/l in 30 minutes, then decreased at 60 minutes to 2.1827 mg/l and 1.9511 mg/l in 90 minutes. Utilization of dose in 14 grams decreased at 30 minutes to 2.1098 mg/l and 1.8834 mg/l at 60 minutes, and fell again at 90 minutes to 1.796 mg/l. On mixing 17 grams it has become 1.7851 mg/l in 30 minutes, then decreases in 60 minutes to 1.6562 mg/l and the highest decrease in 90 minutes becomes 1.5382 mg/l.

3.3 The effectiveness of Fe and Mn metal adsorption

Based on decreasing in Fe and Mn metals, the effectiveness of the adsorption ability of calcium oxide and fly ash is calculated as shown in Table 2 and Table 3.

Table 2. Effectiveness of Calcium Oxide

Effectiveness of Adsorption Using Adsorbent of Calcium Oxide						
Dose	Fe			Mn		
	30 min	60 min	90 min	30 min	60 min	90 min
0.1 gram	68.74%	69.39%	70.86%	56.35%	57.93%	59.02%
0.2 gram	70.18%	70.60%	72.18%	58.40%	58.65%	61.19%
0.3 gram	71.13%	72.04%	72.91%	59.70%	60.41%	61.81%

Table 2 shows the effectiveness of adsorption by using calcium oxide as an adsorbent. In Fe metal, the lowest adsorption effectiveness was 68.74%, namely the administration of a dose of 0.1 gram with 30 minutes of stirring, while the highest effectiveness was with 90 minutes of stirring time and a dose of 0.3 gram reaching 72.91%. Furthermore, on Mn metal, the lowest adsorption effectiveness was also at a dose of 0.1 gram and 30 minutes of stirring time with an effectiveness of 56.35%. The highest effectiveness of Mn was recorded at 61.81% at a dose of 0.3 grams and 90 minutes of stirring time.

Table 3. Effectiveness of Fly Ash

Effectiveness of Adsorption Using Adsorbent of Fly Ash						
Dose	Fe			Mn		
	30 min	60 min	90 min	30 min	60 min	90 min
10 gram	82.15%	83.86%	84.28%	67.68%	68.98%	72.28%
14 gram	83.38%	84.91%	85.48%	70.02%	73.24%	74.48%
17 gram	85.83%	84.62%	85.30%	74.63%	76.47%	78.14%

Table 3 describes the effectiveness of adsorption by using fly ash as an adsorbent. The lowest adsorption effectiveness of Fe metal reached 82.15% with 30 minutes of stirring time and 10 grams of fly ash dose, while the highest adsorption occurred at a dose of 17 grams and 30 minutes of stirring time. In Mn metal, the lowest effectiveness was 67.68% for a dose of 10 grams and 30 minutes of stirring time. While the highest effectiveness was at 90 minutes of stirring time and 17 grams of fly ash dose. Furthermore, the average effectiveness of the adsorption of each dose of Fe and Mn is calculated, calculations by comparing calcium oxide and fly ash can be seen in Figure 8 and Figure 9.

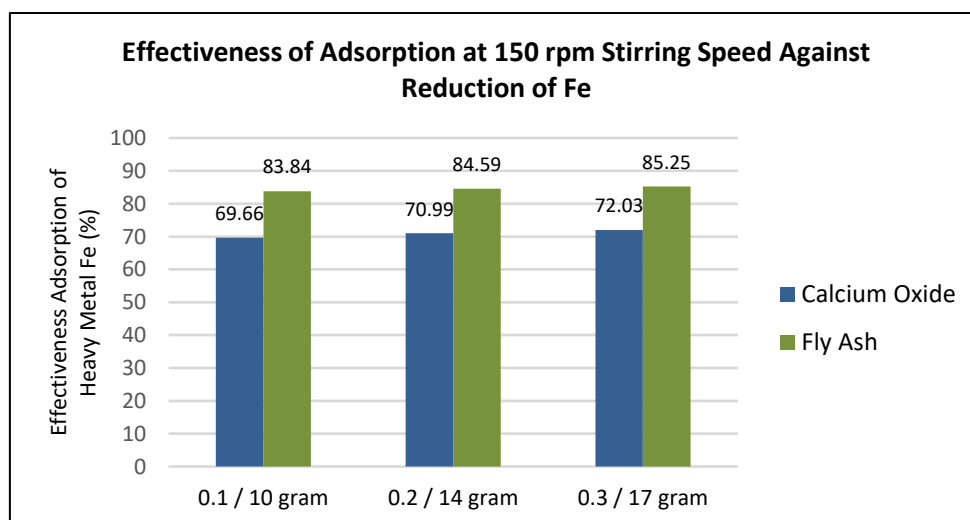


Figure 8. Effectiveness average of Metal Fe Adsorption

Based on Figure 8, the average comparison of the effectiveness of adsorption on the adsorption of Fe metal is shown. The average effectiveness of calcium oxide at each dose of 0.1 gram reached 69.66%, a dose of 0.2 gram reached 70.99%, and a dose of 0.3 gram reached 72.03%. While on fly ash the average effectiveness at each dose of 10 grams reached 83.84%, the dose of 14 grams reached 84.59%, and the dose of 17 grams reached 85.25%.

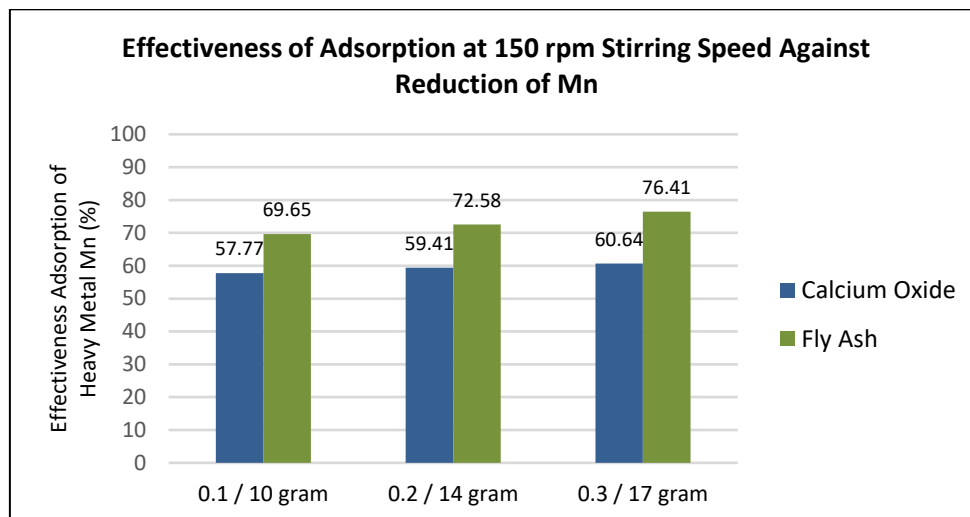


Figure 9. Effectiveness average of Metal Mn Adsorption

Figure 9 shows the comparison of the average adsorption effectiveness with the adsorption of Mn metal. Calcium oxide has an average effectiveness at a dose of 0.1 gram reaching 57.77%, a dose of 0.2 gram reaching 59.41%, and a dose of 0.3 gram reaching 60.64%. In fly ash the average effectiveness at a dose of 10 grams reached 69.65%, for a dose of 14 grams it reached 72.58%, and a dose of 17 grams reached 76.41%.

From the analysis between Fe and Mn metals, there is a difference that shows the adsorption of Fe metal better than the adsorption of Mn metal. This happens because the electronegativity of Fe is greater than Mn. The order of the ability to absorb ions in water due to the presence of ion selectivity towards the adsorbent, namely $Fe^{3+} > Al^{3+} > Pb^{2+} > Ba^{2+} > Sr^{2+} > Zn^{2+} > Cu^{2+} > Fe^{2+} > Mn^{2+} > Ca^{2+} > Mg^{2+} > K^+ > NH_4^+ > H^+ > Li^+$ [18]. In addition, it is also influenced by the acidity of the acid mine drainage, where the adsorption of Mn in a solution goes well at high pH, whereas if the pH is below 8 the adsorption will be slow [19].

4. Conclusion

Calcium oxide and fly ash are good adsorbents for the adsorption of Fe and Mn metals in acid mine drainage, experiments with various variations succeeded in reducing Fe and Mn metals to below the specified quality standards. The SEM test shows the pores increasing and getting bigger, due to the acidic nature of the water which damages the surface of the adsorbent, which results in an increase in the surface area of the adsorbent. In addition, the previous hollow surface has been filled with material, which indicates the adsorbent has successfully adsorbed Fe and Mn metals. The effectiveness of calcium oxide on the adsorption of Fe metal is 72.91% and Mn is 61.81%, where the effectiveness occurs at the same dose and time, namely 0.3 grams and 90 minutes. Better effectiveness occurred in fly ash with Fe metal adsorption of 85.83% at a dose of 17 grams and 30 minutes, while Mn metal was 78.14% at a dose of 17 grams and 90 minutes. Fly ash is an alternative that can be used in acid mine drainage treatment, because of the abundant availability of fly ash and its not yet maximized utilization. The use of fly ash is also more economical than calcium oxide, because fly ash is a residue from the combustion of steam power plants, so there is no need to spend money to get it.

References

- [1] R. S. Gautama, *Pembentukan, Pengendalian dan Pengelolaan Air Asam Tambang*, II. Bandung: ITB Press, 2019.
- [2] M. S. Abfertiawan, "Model Transpor Air Asam Tambang Melalui Pendekatan Daerah Tangkapan Air," Institut Teknologi Bandung, 2016.
- [3] J. Collie dan S. Stephen, *Literature in The Language Classroom: A Resource book of Ideas and Activity*. Cambridge University Press, 2008.
- [4] I. T. N. Siregar, "Analisis Netralisasi Air Asam Tambang Menggunakan CaO dan Fly Ash Pada PT. Alamjaya Bara Pratama Kabupaten Kutai Kartanegara, Provinsi Kalimantan Timur," Universitas Pembangunan Nasional "Veteran" Yogyakarta, 2019.
- [5] A. P. Gobel, E. Nursanto, dan W. D. Ratminah, "Efektifitas Pemanfaatan Fly Ash Batubara Sebagai Adsorben Dalam Menetralsir Air Asam Tambang pada Settling Pond Penambangan Banko PT. Bukit Asam (Persero), Tbk," *J. Miner. Energi dan Lingkung.*, vol. 2, no. 1, hal. 1–11, 2018, doi: 10.31315/jmel.v2i1.2113.
- [6] B. Arifin, "Penggunaan Abu Batu Bara PLTU MPANAU Sebagai Bahan Stabilisasi Tanah Lempung," *SMARTek*, vol. 7, no. 4, hal. 219–228, 2009.
- [7] Z. T. Yao et al., "A comprehensive review on the applications of coal fly ash," *Earth-Science Rev.*, vol. 141, hal. 105–121, 2015, [Daring]. Tersedia pada: <http://linkinghub.elsevier.com/retrieve/pii/S0012825214002219>.
- [8] S. J. Kulkarni, S. R. Dhokpande, dan J. P. Kaware, "Studies On Flyash As An Adsorbent For Removal Of Various Pollutants From Wastewater," *Int. J. Eng. Res. Technol.*, vol. 2, no. 5, hal. 1190–1195, 2013, [Daring]. Tersedia pada: <https://www.ijert.org/research/studies-on-flyash-as-an-adsorbent-for-removal-of-various-pollutants-from-wastewater-IJERTV2IS50668.pdf>.
- [9] E. R. Aida, S. Y. Lisha, dan Y. Puty, "Pemanfaatan Limbah Abu Terbang Batubara (Fly Ash) Di Pltu Ombilin Sebagai Bahan Koagulan," *J. Pendidik. Teknol. Kejuru.*, vol. 1, no. 3, hal. 125–131, 2018, doi: 10.24036/jptk.v1i3.2223.
- [10] Peraturan Pemerintah Republik Indonesia, "Peraturan Pemerintah Republik Indonesia Nomor 22 Tahun 2021 tentang Penyelenggaraan Perlindungan dan Pengelolaan Lingkungan Hidup." 2021.
- [11] M. A. Hossain, H. H. Ngo, W. S. Guo, dan T. V. Nguyen, "Removal of copper from water by adsorption onto banana peel as bioadsorbent," *Int. J. GEOMATE*, vol. 2, no. 2, hal. 227–234, 2012, doi: 10.21660/2012.4.3c.
- [12] C. Nwodika dan O. D. Onukwuli, "Adsorption Study of Kinetics and Equilibrium of Basic Dye on Kola Nut Pod Carbon," *Gazi Univ. J. Sci.*, vol. 30, no. 4, hal. 86–102, 2017.
- [13] R. Delarozza, "Adsorpsi logam berat menggunakan adsorben alami pada air limbah industri," Universitas Trisakti Jakarta, 2018.
- [14] Badan Standardisasi Nasional, "SNI 6989.59:2008 Metoda Pengambilan Contoh Air Limbah." 2008.
- [15] Badan Standardisasi Nasional, "SNI 6989.4:2009 Cara Uji Besi (Fe) Secara Spektrofotometri Serapan Atom (SSA)." 2009.
- [16] Badan Standardisasi Nasional, "SNI 6989.5:2009 Cara Uji Mangan (Mn) Secara Spektrofotometri Serapan Atom (SSA)." 2009.
- [17] Keputusan Menteri Negara Lingkungan Hidup, "Keputusan Menteri Negara Lingkungan Hidup Nomor 113 Tahun 2003 tentang Baku Mutu Air Limbah Bagi Usaha dan atau Kegiatan Pertambangan Batubara." 2003.
- [18] M. Paradise, "Adsorpsi Logam Berat Besi (Fe) dan Mangan (Mn) Menggunakan Komposit Claystone, Zeolit, dan Arang Aktif Tempurung Kelapa pada Sampel Air Asam Tambang Batubara," Universitas Pembangunan Nasional "Veteran" Yogyakarta, 2021.
- [19] W. Stumm dan J. J. Morgan, *Aquatic chemistry: chemical equilibria and rates in natural waters*, 126 ed. John Wiley & Sons, 2012.

