Study of rare earth elements potential in acid mine drainage from coal mine: a case study

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Abstract. Acid Mine Drainage (AMD) is one of the crucial impacts of coal mining activities. This issue is becoming increasingly important because acid mine drainage will become a burden in the post-mining period if not appropriately managed. AMD can leach side materials, causing an increase in dissolved heavy metals, including Rare Earth Elements. REE is an essential raw material for applying modern technology whose demand is increasing globally from year to year. Until 2019, 77% of REE production came from China. The combination of scarce supply and high demand has encouraged various studies to evaluate alternative REE resources. In Indonesia, there is few research about the presence of REE in AMD from coal mine. The objective of this study to determine the amount, characteristics and enrichment mechanisms of REE in AMD, moreover this research is a preliminary study on the alternatives of REE resources. Five water samples were subjected to physical tests well as analysis of IC and ICP-MS. The water sample was 5 had a low pH of 2.90 - 3.82. The concentration of Total REE (not include Lu and Tb) from samples ranged from 0.1032 - 0.6174 ppm with an average Total REE of 0.4810 - 3 ppm.

1. Introduction
Acid Mine Drainage (AMD) is a significant environmental impact of coal mining activities. This issue is increasingly important because if AMD not managed correctly, it will become a burden in the post-mining phase, as long as the three elements that makeup AMD are still present.

Rare Earth Elements, including Yttrium (REY), are essential raw material for modern technological applications. Its most important uses include the manufacture of permanent magnets for wind turbines, alloys for rechargeable batteries and jet engines, and phosphorus light-emitting compounds for plasma, liquid crystals, or light-emitting diodes [1].

The current global demand for REE is consistently increased. The increasing demand for REE, which use for the development of advanced technology such as electric vehicles and various applications in material knowledge, has increased REE production economically. Various studies state that at the coal source, REE found with low concentrations in a large quantity [1], making the REE study at AMD is high value and very interesting.

The abundance REEs in coal basins has been widely studied, including studies of REE from coal and coal by-products like in coal ash (fly ash and bottom ash), coal, overburden, and AMD. Coal ash in the world has a total value (ΣREE) ± 404µg/g [2,3], while in Indonesia, namely the coal ash of PLTU Ombilin, it is known that the amount of REE (Ce, Y, La, Nd, Sm) in coal power plant ash is amounting
to 169 ppm in fly ash and 64 ppm in bottom ash [4]. The REE concentration in AMD in the Iberian Pyrite Belt varies between 0.07 - 13 mg/L, with an average total REY of 2.3 mg/L [1]. REE concentrations in AMD from the Sitai coal mine ranged from 0.391 to 68.8 µg/g with an average of 61.2 µg/g [5]. Badhurahan [6] researched at the Bukit Asam Coal Mine, REE concentration in AMD at the Muara Tiga Besar Mine ranged from 5.54 - 261.05 µg/L.

The natural process that produces AMD expected to continue for centuries or thousands of years [1] without investment in energy; therefore this can be considered a renewable resource of REE [1], although efforts to develop the technology and circuits needed to extract them economically have not been sufficient [7].

The objective of this study to determine the number, characteristics, and enrichment mechanisms of REE in AMD. Through this research, can find out the REE enrichment mechanism in AMD, which can then be used for further research if one day REE in AMD from a coal mine can be called the REE resource.

2. Rare earth elements

REE (Rare Earth Elements) or REM (Rare Earth Metals) are a group of metal elements belonging to the transition group or the lanthanide chemical group, namely La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, plus the two elements of group IIIB, namely Sc and Y, because of the similarity of the ionic ratio and ionic charge.

Based on the geochemical classification, REE divided into three groups, namely: light (LREE: La, Ce, Pr, Nd, and Sm), Medium (MREE: Eu, Gd, Tb, Dy, and Y), and heavy (HREE: Ho, Er, Tm, Yb, and Lu). Industrial classification used to evaluate coal as a raw material for REE. Base of this classification is on Dudley Kingsnorth’s (IMCOA) forecast of the relationship between supply and demand for certain types of REE in recent years. According to this classification, REE divided into Critical (Nd, Eu, Tb, Dy, Y), Uncritical (La, Pr, Sm, and Gd), and Excessive (Ce, Ho, Tm, Yb, and Lu) groups [4]. The relationship between two classifications illustrated in Figure 1. The Critical Group is a group that is sought after because it is currently widely used in the use of alternative energy and efficient energy technology, but its supply is minimal. Meanwhile, the Excessive group consists of various elements whose production is greater than the current needs of the industry. Meanwhile, for the elements La, Pr, Sm, and Gd, the value of production and consumption can be said to be balanced so that they categorized as Uncritical groups.

2.1. REE from coal and coal by-products

REE are also known to be found in coal deposits (coal, coal ash, and AMD). Several studies [4] show that several global coal deposits contain REE. In coal, REE is found in mineral matter and the residual ash from coal combustion at the PLTU.

REE found in 2 types of basins, where coal formed, namely basins with weathering of igneous and/or metamorphic rocks and basins formed along with the volcanic activity. REE found in basins with weathering of igneous rock and, or metamorphic rock formed due to the bedrock of the basin exposed to the structure, causing the rock to interact with near-surface water or a Cl-rich solution. Other REE sources formed in basins or depressions resulting from tectonic and volcanic activity, which causes the coal to deposited under active volcanic conditions. The REE enrichment in this type of basin comes from the washing of volcanic ash, acidic or alkaline, then disintegrating and melting together with the accumulated peat (tonstein dissolution). In certain geological conditions, REE in coal seams enriched with concentrations equal to or even higher than the REE content found in weathered igneous/metamorphic rocks [4].

Coal containing REE formed under a variety of different geological conditions. There are four types of REE genesis in coal: terrigenous, tuffaceous, infiltration, and hydrothermal. The terrigenous type influenced by surface water input, the tuffaceous type relates to the dropping and dissolving of acid and alkaline volcanic ash, the infiltration type is strongly influenced by meteoric water. In contrast, the hydrothermal type relates to hot water containing minerals. Terrigenous and tuffaceous types form at
the peat swamp stage; the infiltration type is generally epigenetic; whereas the hydrothermal type can form at various stages of coal basin development. REEs with concentrations in coal found equal to or higher than in crystalline bedrock.

The REE enrichment type can be characterized into L type (from tuffaceous or clastic sediments), M type (from acidic groundwater circulating in coal basins), and type H (carried by alkaline water, or fluid-borne. hydrothermal or volcanic) [4]. REE can be present in coal as autogenic clastics/minerals or organic compounds/iod adsorption. Mineralization in REE Zr-Nb-rich tuff deposits is associated with tonstein, which is alkaline or acidic. Whereas in hydrothermal mineralization, it is rich in REE Fe-Mn oxyhydroxide, and is characterized by mineralization that intersects each other due to fault zones, alteration, and breccias in rocks. Tambaria, 2017 in PPSDMBP, 2019 states that coal from the Air Lay field is dominated by type H, which is influenced by water circulation in the coal basin [4]. Meanwhile, REE enrichment in coal and tonstein Pit Banko shows that almost all coal experiences H-type REE enrichment, and only one sample shows enrichment of the H-M type [8].

2.2. REE from acid mine drainage
Acid mine drainage (AMD) is acidic water in mining or excavation activities (has high acidity). It is a result of oxidation of sulfide minerals accompanied by the presence of water [9]. The source of acidity is oxidizable sulfide minerals. The primary source of oxidation is oxygen in the air. Water is one of the reactants in the formation process of AMD and also as a medium for washing or dissolving oxidation products. The source of water can be in the form of rainwater runoff or groundwater.

The main components of AMD are sulfide minerals, air, and water. The source of AMD formation is sulfide minerals contained in rocks. Excavation and stockpiling activities allow sulfide minerals confined in the rock below the surface to exposed in the open air. Contact between oxygen and sulfide minerals and water will cause an oxidation reaction that produces ferrous ions and sulfuric acid. The Ferro ion can be further oxidized to produce a compound iron hydroxide, which gives it a reddish-brown or yellowish color known as "yellow boy" and produces even more acidity. The presence of water, apart from being one of the reactants, will also dissolve the products of oxidation, especially sulfuric acid, increasing in water acidity and produce AMD, which is corrosive and cannot support a variety of aquatic life, if the flow of AMD contacts or through rocks containing metal minerals, AMD will dissolve metal ions contained in these rocks and cause an increase in metal levels in the water.

The presence of REE in AMD is mainly due to the dissolution of REE-carrying species under acidic conditions created by the natural oxidation of sulfide minerals, mainly pyrite. When exposed to nature, oxidized pyrite undergoes the following reactions:

\[
\begin{align*}
\text{FeS}_2(s) + \frac{7}{2}O_2(aq) + H_2O(l) & \rightarrow Fe^{2+}(aq) + 2SO_4^{2-}(aq) + 2H^+(aq) \\
\text{FeS}_2(s) + 14Fe^{3+}(aq) + 18H_2O(l) & \rightarrow 15Fe^{2+}(aq) + 2SO_4^{2-}(aq) + 16H^+(aq) \\
Fe^{2+}(aq) + \frac{1}{4}O_2 + H^+(aq) & \rightarrow Fe^{3+}(aq) + \frac{1}{2}H_2O(l) \\
Fe^{2+} + \frac{1}{4}O_2 + \frac{5}{2}H_2O & \rightarrow Fe(OH)_{3(s)} + 2H^+
\end{align*}
\]

Many studies on REE characterization in AMD [5, 10, 11] found that REE concentrations increase exponentially with decreasing pH. Verplanck et al. (2004) explained that REE behaves conservatively in two acid streams at pH below 5.1, and partitioning into a solid phase at a pH between 5.1 and 6.1. The REE speciation in AMD indicate as complex sulfate REE (LnSO_4^{2-}) with a composition of more than 60%, making it the main form of dissolved REE. At the same time the rest are free metal cation species (Ln^{3+}) with a composition of 20% - 40% [5].

3. Method
The sample of sump water was taken directly from the sump Arutmin Site Asam Asam as many as 5 sample points, then a physical test of pH, temperature, Total Dissolve Solid (TDS), and Electric Conductivity (EC) was carried out on the spot. The physical test results are shown in Table 1. Then the
water sample was prepared by filtering using 4.5 µm filter paper and placed in a polyethylene bottle, which rinse with distilled water. All samples were stored at temperatures less than 4°C until laboratory analysis were conducted. Ion Chromatography performed to determine the number of ions in the sample. HNO₃ was added to the sample bottles then analyzed for REE by ICP-MS at the Hydrogeology and Hydrogeochemical Laboratory of FTTM, ITB.

4. Results and discussion

Statistical results of physical and chemical parameters measurement are shown in Table 1. The pH value of the sample has a high acidity in the range of 2.9 - 3.82 (average 3.31), with the lowest pH at S-3. Electrical Conductivity, TDS varies between 1065-1998 mS/cm and 532-994 ppm. The concentration of SO₄²⁻ is in the range between 998-1496 mg/L. The highest EC value from S-5, as well as the highest TDS. The dominant major cations in all samples were Mg (101-175.56 mg/L), followed by Ca (79-168 mg/L), and K (5-14.37 mg/L). SO₄²⁻ concentrations are very high (998-1496 mg/L) compared to SO₄²⁻ standards for drinking water (250 mg/L). The range is wide enough for the concentration of Cl⁻ and NH₄ between S-1 and S-2 - S-5, where the Cl⁻ in the S-1 sample is very high 52.3 mg/L, while in the other sample, the Cl⁻ value is between 0.27 - 5.12 mg/L as well as NH₄ in the S-1, sample was very high at 33.36 mg/L while in the other samples it only ranged between 0.42 - 1.7 mg/L. Fe concentration was very high at S-1 and S-5, namely, 128.49 mg/L and 169.4 mg/L, while those at S-3 and S-4 were 57.11 mg/L and 48.93 mg/L. The lowest concentrations of Fe and Mn were at S-1 with values of 6.43 mg/L and 4.72 mg. The high SO₄²⁻ concentration comes from the oxidation of pyrite from coal mines, while Na and Al come from the weathering of aluminosilicates.

| Parameter | S-1  | S-2  | S-3  | S-4  | S-5  | Average |
|-----------|------|------|------|------|------|---------|
| pH        | 3.82 | 3.05 | 2.9  | 3.62 | 3.16 | 3.31    |
| EC (mS/cm)| 1065 | 1864 | 1605 | 1339 | 1998 | 1574.2  |
| TDS (ppm) | 532  | 933  | 802  | 670  | 994  | 786.2   |
| SO₄²⁻ (mg/L) | 1496 | 998.9 | 1044.86 | 1328.46 | 1356.14 | 1244.87 |
| F (mg/L)  | 0.23 | 0.34 | 0.27 | 0.44 | 0.91 | 0.44    |
| Cl⁻ (mg/L)| 52.03| 5.12 | 0.27 | 0.44 | 0.91 | 11.75   |
| NO₃⁻ (mg/L)| 2.51 | 2.66 | 2.14 | 2.23 | 2.23 | 2.35    |
| Na (mg/L) | 5.13 | 7.36 | 4.14 | 2.34 | 3.14 | 4.42    |
| NH₄ (mg/L)| 33.36| 1.29 | 0.42 | 1.7  | 1.49 | 7.65    |
| K (mg/L)  | 12.49| 14.37| 5.42 | 9.74 | 14.8 | 11.36   |
| Ca (mg/L) | 168.71| 90.98| 79.93| 108.26| 112.76| 112.13  |
| Mg (mg/L) | 175.56| 142.7| 101.43| 169.03| 149.81| 147.71  |
| Li (mg/L) | 0.12 | 0.06 | 0.11 | 0.11 | 0.09 | 0.1     |
| Al (mg/L) | 10.03| 4.43 | 25.97| 14.72| 5.29 | 12.09   |
| Mn (mg/L) | 19.02| 4.72 | 11.43| 25.12| 17.88| 15.63   |
| ΣFe (mg/L)| 128.49| 6.43 | 57.11| 48.93| 169.4| 82.07   |

Water species were analyzed using piper diagrams/tertiary diagrams, using water quality test data that convert into meq/L units. Piper diagram for determining aquatic species/water types. The plot of major cations and anions on the piper diagram shows that the anions are of the SO₄²⁻ type for all samples, and the cations are dominated by the Mg type for all samples. Then the water samples facies are entire of sulfate-Ca-Cl type and are strong acids. This condition is similar to the Bukit Asam sump water sample. All the water samples have a sulfate type with a little carbonate/bicarbonate content so that the aqueous system for the anions is different from the type of cation and the water system. The cation types
of all Bukit Asam samples varied (Mg, Ca, Na + K), while the water samples were \( \text{H}_2\text{O} - \text{SO}_4^{2-} - \text{CO}_3^{2-} \). Water-Sulfate-Carbonate System. The percentage of REE fractionation in Bukit Asam's water samples was dominated by \( \text{REE}^{3+} \) species, which form complex ions with sulfates in the form of \( \text{REE(SO}_4)^{2-} \) and \( \text{REE(SO}_4)^{2-} \) compared to \( \text{REE}^{3+} \) free ion species. In water samples SW-01 - SW-11, REE-Sulfate species varied between 66.80% - 82.30%, while REE species in the form of free ions, varied between 17.70% - 33.20%. Other species, namely REE-hydroxy and REE-oxy and REE-carbonate ions are generally below 0.25% except for SW-07 samples with REE-Carbonate and REE Oxohydroxy 1.58% species [6].

### Table 2 REE Concentrations and REE NASC Normalized

| Sample ID | La  | Ce  | Pr  | Nd  | Sm  | Eu  | Gd  | Dy  | Ho  | Er  | Tm  | Yb  | ΣREE |
|-----------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-------|
|           | S-1 | S-2 | S-3 | S-4 | S-5 | S-1 | S-2 | S-3 | S-4 | S-5 | S-4 | S-5 |       |
| Concentration in µg/L | 54.1 | 15.6 | 94.8 | 86.4 | 31.6 | 1.74E-03 | 5.02E-04 | 3.05E-03 | 2.78E-03 | 1.02E-03 |       |
|          | Ce  | 140.4 | 41.1 | 256.9 | 244.3 | 79.7 | 2.10E-03 | 6.16E-04 | 3.85E-03 | 3.66E-03 | 1.19E-03 |       |
|          | Pr  | 15.5 | 4.8 | 29.6 | 28.5 | 8.7 | 2.01E-03 | 6.23E-04 | 3.84E-03 | 3.70E-03 | 1.13E-03 |       |
|          | Nd  | 66.9 | 20.1 | 128.8 | 121.4 | 36.9 | 2.44E-03 | 7.34E-04 | 4.70E-03 | 4.43E-03 | 1.35E-03 |       |
|          | Sm  | 16.6 | 5 | 31.4 | 32.1 | 86 | 2.97E-03 | 8.94E-04 | 5.62E-03 | 5.74E-03 | 1.54E-03 |       |
|          | Eu  | 4.8 | 1.4 | 9.1 | 8.4 | 2.4 | 4.07E-03 | 1.19E-03 | 7.71E-03 | 7.12E-03 | 2.03E-03 |       |
|          | Gd  | 18.2 | 5.7 | 31.8 | 35.2 | 10.7 | 3.71E-03 | 1.16E-03 | 6.49E-03 | 7.18E-03 | 2.18E-03 |       |
|          | Dy  | 14.9 | 4.6 | 2.51 | 29.7 | 9.1 | 3.57E-03 | 1.10E-03 | 6.02E-03 | 7.12E-03 | 2.18E-03 |       |
|          | Ho  | 2.8 | 0.8 | 4.7 | 5.6 | 1.8 | 2.75E-03 | 7.84E-04 | 4.61E-03 | 5.49E-03 | 1.76E-03 |       |
|          | Er  | 7.1 | 2.3 | 11.6 | 14.3 | 3.6 | 2.50E-03 | 8.10E-04 | 4.08E-03 | 5.04E-03 | 1.62E-03 |       |
|          | Tm  | 0.9 | 0.3 | 1.5 | 1.7 | 0.6 | 1.88E-03 | 6.25E-04 | 3.13E-03 | 3.54E-03 | 1.25E-03 |       |
|          | Yb  | 4.9 | 1.5 | 8.6 | 9.8 | 3.1 | 1.60E-03 | 4.90E-04 | 2.81E-03 | 3.20E-03 | 1.01E-03 |       |
| ΣREE     | 347.1 | 103 | 611.3 | 617.4 | 274 | | | | | | | |

### Table 3 The REE concentrations (µg/L) in mine drainage water samples in this study and other location

| Location | Asam Asam Coal Mine, Indonesia | Bukit Asam, Indonesia | Jaintia Coalfields, India | Sitai Coal Mine, China |
|----------|---------------------------------|-----------------------|--------------------------|------------------------|
|          | Min | Max | Avg | Avg | Avg | Avg | Avg | Avg |
| La       | 15.6 | 94.8 | 56.50 | 14.34 | 91.85 | 7.77 |
| Ce       | 41.10 | 256.90 | 152.48 | 28.36 | 284.91 | 19.35 |
| Pr       | 4.80 | 29.60 | 17.42 | 3.20 | 38.42 | 2.78 |
| Nd       | 20.10 | 128.80 | 74.82 | 12.56 | 121.02 | 12.98 |
| Sm       | 5.00 | 86.00 | 34.22 | 3.02 | 38.45 | 2.98 |
| Eu       | 1.40 | 9.10 | 5.22 | 0.81 | 9.12 | 0.87 |
| Gd       | 5.70 | 35.20 | 20.32 | 3.77 | 44.2 | 3.78 |
| Tb       | nd* | nd | nd | 0.58 | 7.34 | 0.70 |
| Dy       | 2.51 | 29.70 | 12.16 | 3.43 | 34.42 | 4.00 |
| Ho       | 0.80 | 5.60 | 3.14 | 0.67 | 8.87 | 0.87 |
| Er       | 2.30 | 14.30 | 7.78 | 1.77 | 15.79 | 2.43 |
| Tm       | 0.30 | 1.70 | 1.00 | 0.23 | 3.63 | 0.34 |
| Yb       | 1.50 | 9.80 | 5.58 | 1.33 | 13.26 | 1.99 |
| Lu       | nd | nd | nd | 0.20 | 3.45 | 0.31 |
| ΣREE     | 489.00 | 74.26 | 714.73 | 61.5 | | | | |

nd: not define, Lu and Tb could not tested because they used as internal standards at the ITB Hydrogeology and Hydrogeochemical Laboratory

The REE concentrations at the study location and the NASC normalized REE in Table 2. The REE value at AMD for research locations in Indonesia, compared to other studies in India and China in Table 3. Total REE concentrations in the AMD sample range between 103,200 µg/L to 633,900 µg/L. The lowest total REE is at S-2, and the highest is on S-3. The concentration of Total REE on AMD from Asam Asam was higher compared to Total REE on AMD from Bukit Asam (4.78 µg/L - 261.05 µg/L).
The average concentration of total REE in the study location is known to be higher than that of other locations in Indonesia, where the Asam Asam location is 489.00 µg/L. In comparison, Bukit Asam is 74.26 µg/L. Meanwhile, the average total REE concentration in Jaintia Coalfield, India was 714.73 µg/L, and Sitai Coal Mine, China was 61.50 µg/L.

4.1. Correlation between parameters on AMD
Water quality parameter relationships are calculated to see the relationship between parameters. The correlation used is the Pearson correlation (Pearson Correlation Coefficient), which shows how significant the linear correlation is between water quality parameters. Table 4 shows the correlation values between pH values, major cations, major anions, Fe, and Mn.

The EC value has a strong negative correlation with a pH value of 0.81; the EC is higher in water conditions with low pH. Furthermore, EC has a strong correlation with TDS, Cl, and NH4, which indicates conductivity can indicate of the degree of contamination. The high acidity (low pH) values observed in AMD indicate a lack of carbonate to neutralize acidity during pyrite oxidation. Then, the pH value is closely related to SO4²⁻, Ca, Mg, and Mn.

The correlation of pH and REE on AMD in Asam Asam and Bukit Asam was different. The plots of pH against ΣREE in Bukit Asam showed a strong negative correlation between the pH value and the ΣREE in the water (R = 0.87). It is because the solubility of REE increases with increasing acidity in the solution. The correlation between the REE fractionation component and the pH value decreased with the addition of REE mass, but it was not much different (R pH-LREE> R pH-MRRR> R pH-HREE, namely 0.88> 0.81> 0.79). The correlation between the REE fractionation component and the pH value decreased with the addition of REE mass, but it was not much different (R pH-LREE> R pH-MRRR> R pH-HREE, namely 0.88> 0.81> 0.79). Meanwhile, the REE relationship with iron, manganese, aluminium, and sulfate is 0.646; 0.097; 0.884; 0.211 [6]. However, Total REE at AMD in Asam Asam did not show a strong correlation between pH and Total REE, namely R 0.14, as well as the correlation between the fractionation components of REE and pH, correlation of pH-LREE 0.09, pH-MREE 0.48, and pH-HREE 0.08.

| pH | EC | TDS | F  | Cl  | NO3 | SO4 | Na  | NH4 | K   | Ca  | Mg  | ΣFe | ΣMn |
|----|----|-----|----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
|    |    |     |    |     |     |     |     |     |     |     |     |     |     |
| pH | -0.81 |     |     |     |     |     |     |     |     |     |     |     |     |
| EC | -0.81 | 1.00 |     |     |     |     |     |     |     |     |     |     |     |
| TDS|     | 0.19 | 0.65 | 0.64 |     |     |     |     |     |     |     |     |     |
| F  |     | 0.71 | -0.73 | -0.73 | -0.43 |     |     |     |     |     |     |     |     |
| Cl |     | 0.20 | -0.07 | -0.06 | -0.34 | 0.45 |     |     |     |     |     |     |     |
| NO3|     | 0.84 | -0.55 | -0.55 | 0.25 | 0.63 | -0.08 |     |     |     |     |     |     |
| SO4|     | 0.75 | -0.75 | -0.75 | -0.41 | 1.00 | 0.33 | 0.67 | 0.19 |     |     |     |     |
| Na |     | 0.20 | 0.35 | 0.33 | 0.49 | 0.19 | 0.63 | 0.30 | 0.34 | 0.19 |     |     |     |
| K  |     | 0.86 | -0.67 | -0.67 | -0.11 | 0.92 | 0.33 | 0.87 | -0.02 | 0.93 | 0.38 |     |     |
| Ca |     | 0.89 | -0.48 | -0.48 | 0.11 | 0.53 | -0.71 | 0.78 | -0.13 | 0.56 | 0.58 | 0.77 |     |
| Mg |     | 0.29 | -0.02 | -0.03 | 0.59 | 0.37 | -0.29 | 0.75 | -0.44 | 0.40 | 0.32 | 0.58 | 0.30 |
| ΣFe|     | 0.73 | -0.53 | -0.54 | -0.36 | 0.20 | -0.48 | 0.81 | -0.84 | 0.26 | -0.10 | 0.49 | 0.60 |
| ΣMn|     | 0.14 | -0.52 | -0.51 | -0.36 | -0.12 | -0.71 | 0.04 | -0.62 | -0.09 | -0.91 | -0.16 | -0.24 | -0.17 | 0.49 |
4.2. REE enrichment pattern
The REE enrichment pattern at AMD in Bukit Asam is similar to the enrichment pattern at Arutmin. Badhurahman [6] states that the REE enrichment pattern in AMD generally shows a convex pattern, which indicates MREE-Enrichments are visible in all samples (SW-01 to SW-12), as shown graphically in Figure 1 for samples SW-01 to SW-06 and Figure 6 for samples SW-07 to SW-11. This indicate by an NASC (MREE / MREE) value of more than 1 (range 1.18 - 1.57). Likewise, the REE enrichment pattern at Asam Asam has the same pattern for all samples, and the NASC (La/Sm) value <1, which ranges from 0.48 to 0.66.

The REE enrichment mechanism in AMD is influenced by the chemical conditions of water, namely pH, water redox, the solubility of certain metal ions, the presence of anions and their concentrations, especially sulfates, chlorides, hydroxides, phosphates, carbonates/bicarbonates and the possibility of complex or complex ligand/ion formation or complexation with other ions and the possibility of co-precipitation and adsorption on colloid clay, oxyhydroxy iron, aluminium, and manganese [6].

(a)

(b)
5. Conclusions

Based on the results presented, AMD has high acidity with high metal concentrations of $\text{SO}_4^{2-}$, Fe, and Mn. REE on AMD in Asam Asam was higher (103.20 µg/L - 617.40 µg/L) compared to REE on AMD in Bukit Asam (4.78 µg/L - 261.05 µg/L). The concentration of Total REE in Asam Asam has a strong negative correlation with the concentrations of $\text{NO}_3^-$, K, and Ca. In contrast, in Bukit Asam, it has a strong positive correlation with pH, Fe, and $\text{SO}_4^{2-}$. REE at AMD in Asam Asam also shows the type of MREE enrichment for all samples, as is the pattern of REE enrichment at AMD at Bukit Asam.

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