REE Enrichment Pattern in Acid Mine Drainage and Overburden from Coal Mine in Indonesia

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Abstract

Acid mine drainage (AMD) is one of main negative environmental impact from mining activities. AMD is resulted from reaction between sulfide mineral, mainly pyrite, with oxygen and water. AMD characterized as high-acidic water with elevated sulfate, iron and other dissolved metals concentration, including rare earth elements (REE). REE is used as an indicator in water-rock interaction and pollution of AMD and as a source of REE. Studies show that North American Shale Composite (NASC) normalized REE concentration in AMD has pattern or enrichment, i.e. medium rare earth elements enrichment (MREE) or light rare earth elements (LREE), despite the processes controlling this enrichment are still unknown and unclear whether related to sources or aqueous process.

This study is conducted in PT Bukit Asam coal mine in Indonesia, which consist of 3 main coal mines namely Banko Barat, Tambang Air Laya and Muara Tiga Besar. Those mines show varieties in geochemical characteristics of water and overburden. Previous studies showed that there is indication of REE-enrichments in AMD from PT Bukit Asam, Indonesia. This study aims to characterize REE enrichment in AMD and overburden samples from PT Bukit Asam coal mine, Indonesia.

Geochemical characteristics of REE in AMD and overburden from PT Bukit Asam coal mine, Indonesia were investigated by determining concentration of dissolved REE and other geochemical parameters of 11 AMD samples and concentration of REE from 24 overburden samples. The REE concentration is normalized using) to determine the enrichment pattern of REE of both type of sample. Those samples are representing 3 main mines in PT Bukit Asam coal mine. AMD samples have varying pH value, dissolved Fe and dissolved Mn of 2.74 – 5.91, 0.11 – 29,78 mg/L and 2.83 – 16.35 mg/L, respectively. AMD samples shows elevated dissolved ΣREE concentration varying from 5.54 – 261.05 µg/L. The overburden samples have varying ΣREE concentration from 14.95 mg/kg to 106.95 mg/kg. NASC-normalized REE concentration of all AMD samples shows distinctive MREE (medium rare earth elements) enrichment pattern. In the other hand, overburden samples show variety of enrichment pattern, mostly MREE.

Similarity between enrichment type of AMD and overburden samples shows that processes controlling REE enrichment in AMD is somewhat relate to the source of REE. Further study on the mechanism of REE enrichment from overburden to AMD to determine whether the mechanism is controlled by the source of REE or the geochemical characteristics of AMD is needed to obtain more information of processes of REE enrichment in AMD.

Keywords: acid mine drainage (AMD), overburden, rare earth elements (REE), enrichment

Introduction

Mining activities potentially cause substantial environmental impacts. Excavation and dumping activities might expose sulfide minerals that previously confined in rocks beneath the surface to the open air. Contact between oxygen, sulfide and water minerals will lead to oxidation reactions that produce acid mine drainage (AMD). AMD is an acidic water formed by oxidation of sulphide minerals and characterised by a low pH or below pH value of 5 (Gautama 2014).

Acid mine drainage due to its characteristic, is able to leach hard metals (including REE) from rocks. Research on the leaching process and accumulation of hard rocks are widely available, but leaching process and accumulation of REE by AMD especially which of that related to coal mine is still scarce. This study aims to demonstrate the REE enrichment patterns in water and overburden samples from PTBA which served as an initial indication of REE-enrichment process from overburden to water in coal mine.

General Information

This study is conducted in PT Bukit Asam (PTBA) coal mine in Indonesia PTBA is one of major coal producers, located at Tanjung Enim, South Sumatra Province. There are 3 main mining sites that are still active, namely Muara Tiga Besar (MTB), Bangko Barat (BB) and Tambang Air Laya (TAL). Previous work by Gautama (1994) and Gautama and Hartaji (2004) has shown that acid mine drainage is an important issue at the Tanjung Enim mine. Gautama and Hartaji (2004) demonstrated that the source of the AMD is predominantly from the overburden and inter-seam rocks (interburden) and they were able to differentiate between potentially acid forming (PAF) and non-acid forming (NAF) rocks by the application of both static and kinetic testing procedures. The PTBA pits yield different mine water quality, as reported by Gautama (2018), due to different geochemical characteristic of rocks, spatially and stratigraphically. It is evident also that there is elevated concentration of Fe and Mn, as well as REE, which also varying for each pit (Gautama 2018).

Sample Information

11 samples of AMD samples are sampled from various pit sumps otherwise from detention pond if not accessible. 24 samples of overburden are taken from various lithology and stratigraphy from all three mining sites.

Methods

Measurements of pH is conducted in the field using Lutron WA-2017 SD. AMD samples are filtered with 45 µm filter disc and stored in 2 different bottles for each sample. One bottle of sample is acidified using HNO3 for measurements of cation and REE. Cation (Fe and Mn) are measured using Perkin Elmer Atomic Absorption Spectrometer (AAS) analyst 400S and REE concentration is measured using Inductively Coupled Plasma Mass Spectrometer (ICP-MS) Agilent 7000. All instruments are calibrated prior measurements. Overburden samples are pulverized into size less than 75 µm, measured ±500 mg and digested using ultrapure concentrated acid (HF + aqua regia) in Teflon digestion crucibles at 180 °C. After cooling, the vessel contents centrifuged then discharging, diluted to volume of 10 mL. REE concentration then is measured using Inductively-Coupled Plasma Mass Spectrometer (ICP-MS) Agilent 7000. Standard and blanks are also measured alongside the AMD and overburden samples. REE concentration of water and overburden samples are then normalized using North American Shale Composites (NASC) value (McLennan et al., 1980) to determine the REE enrichment pattern of those samples.

Results

The result of REE concentration and water geochemical characteristic (pH, Total Fe and Mn) for water samples are shown in Table 1. REE concentration for overburden samples are shown in Table 2, Table 3 and Table 4. (on the next page).

REE enrichment pattern

REE enrichment parameters are calculated to determine the enrichment pattern of REE concentration in water and overburden samples. There are mainly 3 types of REE-enrichment patterns, i.e. LREE/Light REE, MREE/Medium REE and HREE/heavy REE. Common calculations used in determining enrichment pattern of REE are shown in Table 5. The calculation result of REE enrichment pattern parameter for water samples and overburden samples is shown in Table 6.

AMD samples have varying pH value, dissolved Fe and dissolved Mn of 2.74 – 5.91, 0.11 – 29,78 mg/L and 2.83 – 16.35 mg/L, respectively. AMD samples shows elevated dissolved ΣREE concentration varying from 5.54 – 261.05 µg/L. In the other hand, overburden samples have varying ΣREE concentration from 14.95 mg/kg to 106.95 mg/kg.

***Table 1** REE Concentration in Water Samples (Sample ID SW1 – SW8).*

Sample ID	SW1	SW2	SW3	SW4	SW5	SW6	SW7	SW8	SW9	SW10	SW11
Mining Site	BB	BB	TAL	TAL	BB	MTB	TAL	TAL	BB	TAL	TAL
pH	2.74	2.84	5.23	4.85	3.05	4.05	5.82	5.18	3.87	4.05	5.91
ΣFe (mg/L)	0.76	1.07	0.00	0.01	0.13	0.01	0.01	0.04	0.01	0.01	0.00
Mn (mg/L)	0.40	0.39	0.22	0.10	0.27	0.25	0.37	0.60	0.36	0.39	0.22
					concentration in µg/L						
La	42.09	37.14	1.54	6.91	24.40	7.77	1.82	9.25	13.96	11.71	1.17
Ce	96.34	67.11	2.68	11.55	47.77	16.55	1.96	16.64	21.29	28.31	1.81
Pr	11.69	6.71	0.20	1.26	5.59	1.84	0.18	1.81	2.57	3.20	0.18
Nd	47.24	24.46	0.75	4.50	22.49	7.22	0.69	7.12	9.73	13.22	0.71
Sm	12.15	4.73	0.17	0.89	5.80	1.70	0.14	1.69	2.16	3.61	0.15
Eu	3.24	1.18	0.05	0.27	1.54	0.47	0.05	0.46	0.55	1.01	0.05
Gd	14.81	5.67	0.23	1.19	7.07	2.22	0.27	2.30	2.62	4.90	0.23
Tb	2.34	0.83	0.04	0.17	1.12	0.34	0.04	0.32	0.38	0.79	0.03
Dy	13.94	4.63	0.20	0.93	6.60	2.01	0.19	1.92	2.30	4.76	0.20
Ho	2.68	0.94	0.05	0.19	1.25	0.39	0.04	0.38	0.45	0.95	0.04
Er	7.15	2.50	0.11	0.49	3.25	1.03	0.10	0.95	1.20	2.53	0.11
Tm	0.95	0.33	0.02	0.06	0.42	0.13	0.01	0.12	0.14	0.33	0.01
Yb	5.61	1.80	0.08	0.32	2.49	0.78	0.05	0.70	0.87	1.89	0.07
Lu	0.82	0.27	0.02	0.05	0.35	0.11	0.01	0.11	0.13	0.27	0.01
ΣREE	261.05	158.28	6.14	28.79	130.16	42.56	5.54	43.78	58.33	77.48	4.78

***Table 2** REE Concentration in Overburden Samples (Sample ID S1 – S8).*

Sample ID	S1	S2	S3	S4	S5	S6	S7	S8
Mining Site	BB	MTB	BB	BB	TAL	TAL	TAL	TAL
			concentration in mg/kg					
La	17.53	15.51	17.85	18.05	3.3	4.37	1.51	21.16
Ce	33.67	37.18	34.37	43.83	8.03	10	4.32	46.81
Pr	3.43	4.15	3.52	4.74	1.01	1.27	0.64	5.01
Nd	12.06	16.54	12.16	18.69	4.14	5.06	3.18	17.92
Sm	2.45	3.71	2.55	4.15	1.02	1.2	1.17	3.72
Eu	0.22	0.9	0.21	1.02	0.26	0.31	0.33	0.47
Gd	2.52	3.47	2.47	3.92	1.05	1.18	1.59	3.28
Tb	0.42	0.52	0.42	0.59	0.17	0.17	0.24	0.46
Dy	2.69	2.98	2.59	3.31	1	0.95	1.13	2.27
Ho	0.57	0.57	0.54	0.63	0.21	0.18	0.18	0.36
Er	1.73	1.58	1.56	1.66	0.62	0.49	0.37	0.85
Tm	0.26	0.22	0.22	0.23	0.09	0.06	0.04	0.1
Yb	1.75	1.35	1.43	1.44	0.57	0.35	0.22	0.63
Lu	0.28	0.2	0.22	0.21	0.09	0.05	0.03	0.09
ΣREE	79.59	88.89	80.11	102.46	21.56	25.65	14.95	103.13

From Table 6. it is evident that all water samples showed Medium-REE/MREE enrichment pattern, with value of (MREE/MREE*) NASC more than 1 (ranged from 1.18 to 1.57). 5 samples are also exhibit LREE-enrichment pattern (Sample SW-1, SW-2, SW-4, SW-7 and SW-9), but generally enrichment patterns for all water samples are categorized as MREE-Enrichment.

REE enrichment in overburden samples show more varying result. 15 samples show MREE-enrichment with (MREE/MREE)NASC (Sm/Yb)NASC dan (Sm/La)NASC value more than 1.20, 6 samples show LREE-enrichment pattern and only 3 samples, i.e. S-1; S-5;-S16 show HREE-enrichment.

***Table 3** REE Concentration in Overburden Samples (Sample ID S9 – S16).*

Sample ID	S9	S10	S11	S12	S13	S14	S15	S16
Mining Site	TAL	TAL	BB	MTB	MTB	TAL	BB	MTB
	REE concentration in mg/kg							
La	7.3	5.82	18.08	7.49	22.35	11.01	8.2	11.69
Ce	18.44	16.05	33.72	15.51	45.37	29.43	26.95	27.77
Pr	2.21	1.94	3.35	1.5	4.52	3.29	3.22	3.01
Nd	9.43	8.37	11.04	4.93	14.78	13.65	13.37	12.1
Sm	2.39	2.19	2.21	0.94	2.83	3.15	3.09	2.7
Eu	0.63	0.56	0.29	0.12	0.26	0.79	0.74	0.72
Gd	2.58	2.32	2.14	0.81	2.5	3.17	2.86	2.98
Tb	0.4	0.36	0.37	0.13	0.41	0.46	0.44	0.48
Dy	2.34	2.1	2.39	0.84	2.53	2.49	2.52	3.08
Ho	0.46	0.41	0.49	0.17	0.52	0.45	0.49	0.67
Er	1.27	1.15	1.49	0.52	1.57	1.19	1.35	2.09
Tm	0.18	0.16	0.23	0.08	0.25	0.15	0.19	0.3
Yb	1.08	0.99	1.52	0.55	1.79	0.92	1.23	1.96
Lu	0.16	0.15	0.23	0.09	0.29	0.13	0.19	0.31
ΣREE	48.87	42.56	77.55	33.68	99.97	70.28	64.83	69.86

***Table 4** REE Concentration in Overburden Samples (Sample ID S17 – S24).*

Sample ID	S17	S18	S19	S20	S21	S22	S23	S24
Mining Site	MTB	BB	BB	BB	BB	BB	BB	MTB
	REE concentration in mg/kg							
La	18.39	12.15	12.75	8.6	6.72	9.7	7.31	5.85
Ce	45.2	32.42	33.58	23.92	18.18	25.82	20.31	15.76
Pr	5	3.5	3.7	2.77	2.13	3.04	2.28	1.8
Nd	20.05	13.87	14.65	11.31	8.86	12.6	9.33	7.18
Sm	4.4	3.08	3.22	2.7	2.16	3.03	2.18	1.6
Eu	1.07	0.74	0.77	0.7	0.55	0.76	0.53	0.4
Gd	4.09	2.81	2.91	2.67	2.18	2.93	2	1.52
Tb	0.62	0.41	0.43	0.4	0.33	0.43	0.28	0.21
Dy	3.52	2.27	2.24	2.3	1.86	2.44	1.52	1.18
Ho	0.66	0.41	0.39	0.43	0.34	0.44	0.27	0.21
Er	1.82	1.06	0.98	1.15	0.93	1.2	0.7	0.51
Tm	0.26	0.14	0.12	0.15	0.12	0.16	0.09	0.06
Yb	1.64	0.8	0.73	0.91	0.75	1.01	0.54	0.34
Lu	0.24	0.11	0.1	0.13	0.1	0.16	0.08	0.05
ΣREE	106.95	73.75	76.57	58.15	45.22	63.73	47.42	36.67

***Table 5** Equation for Enrichment Pattern Parameter of REE.*

Enrichment Parameter	Calculation used
LREE enrichment relative to HREE	$=(La/Yb)_{NASC}$
LREE enrichment relative to MREE	$=(La/Sm)_{NASC}$
MREE enrichment relative to LREE	$=(Sm/\mathrm{La})_{NASC}$
MREE enrichment relative to HREE	$=(Sm/Yb)_{NASC}$
HREE enrichment relative to LREE	$=(\mathrm{Yb}/\mathrm{La})_{NASC}$
HREE enrichment relative to MREE	$=(\mathrm{Yb}/\mathrm{Sm})_{NASC}$
MREE Enrichment Relative to LREE and HREE	$(MREE/MREE^{*})_{NASC} = \frac{\overline{MREE_{NASC}}}{\sqrt{\overline{\overline{LREE_{NASC} \times HREE_{NASC}}}}}$

Table 6 *Calculation for Enrichment Pattern Parameter of REE in Water and Overburden Samples.*

Sample ID	$(La/Yb)_{NASC}$	$(La/Sm)_{NASC}$	$(Sm/Yb)_{NASC}$	$(Sm/La)_{NASC}$	$(Yb/La)_{NASC}$	$(Yb/Sm)_{NASC}$	(MREE/ MREE*)NASC
Water Samples							
SW1	0.74	0.62	1.19	1.61	1.35	0.84	1.53
SW2	2.03	1.41	1.44	0.71	0.49	0.69	1.18
SW3	1.85	1.65	1.12	0.61	0.54	0.89	1.19
SW4	2.12	1.4	1.52	0.72	0.47	0.66	1.32
SW5	0.96	0.76	1.27	1.32	1.04	0.78	1.55
SW6	0.98	0.82	1.19	1.21	1.02	0.84	1.47
SW7	3.32	2.3	1.44	0.43	0.3	0.69	1.36
SW8	1.29	0.98	1.31	1.02	0.77	0.76	1.47
SW9	1.57	1.16	1.35	0.86	0.64	0.74	1.34
SW10	0.61	0.58	1.05	1.72	1.64	0.96	1.57
SW11	1.72	1.44	1.2	0.7	0.58	0.83	1.32
Overburden Samples							
S1	0.98	1.28	0.77	0.78	1.02	1.31	0.86
S2	1.13	0.75	1.50	1.33	0.89	0.67	1.34
S3	1.23	1.26	0.98	0.80	0.82	1.03	0.91
S4	1.23	0.78	1.58	1.28	0.81	0.63	1.34
S5	0.56	0.58	0.97	1.72	1.77	1.03	1.30
S6	1.23	0.65	1.88	1.54	0.82	0.53	1.54
S7	0.68	0.23	2.93	4.29	1.46	0.34	2.98
S8	3.31	1.02	3.24	0.98	0.30	0.31	1.22
S9	0.67	0.55	1.21	1.82	1.50	0.83	1.48
S10	0.58	0.48	1.21	2.09	1.73	0.83	1.50
S11	1.17	1.47	0.80	0.68	0.85	1.25	0.86
S12	1.35	1.44	0.94	0.70	0.74	1.07	0.81
S12	1.35	1.44	0.94	0.70	0.74	1.07	0.81
S13	1.23	1.42	0.87	0.71	0.81	1.15	0.78
S14	1.18	0.63	1.88	1.59	0.85	0.53	1.54
S15	0.66	0.48	1.38	2.09	1.52	0.73	1.40
S16	0.59	0.78	0.76	1.29	1.70	1.32	1.12
S17	1.10	0.75	1.47	1.33	0.91	0.68	1.32
S18	1.49	0.71	2.10	1.41	0.67	0.48	1.44
S19	1.72	0.71	2.42	1.41	0.58	0.41	1.49
S20	0.93	0.57	1.62	1.75	1.08	0.62	1.52
S21	0.88	0.56	1.57	1.79	1.14	0.64	1.55
S22	0.95	0.58	1.64	1.74	1.06	0.61	1.51
S23	1.35	0.60	2.23	1.66	0.74	0.45	1.55
S24	1.71	0.72	2.61	1.52	0.58	0.38	2.64

Discussion

Convex pattern in NASC-normalized REE concentration, which indicated medium-REE/MREE enrichment is one of signature of REE-enrichment in acid mine drainage/AMD (Cao et al. 2019; Zhao et al. 2007), despite other study showed that Light REE/LREE enrichment pattern in acid mine drainage (Bozau et al. 2004) Several studies also showed the same pattern of REE-enrichment from water samples and sediment samples which indicates the possibility of REE enrichment in water from its source (Zhao et al. 2007).

This study results that 15 of 24 samples of overburden samples show MREE enrichment pattern (15 out of 24 samples) and all water samples show MREE enrichment pattern which indicates the possibility of enrichment in water samples is controlled by enrichment of its source.

Conclusions

Similarity between enrichment type of AMD and overburden samples shows that processes controlling REE enrichment in AMD is somewhat relate to the source of REE, in this study the overburden. Further study on the mechanism of REE enrichment from overburden to AMD to determine whether the mechanism is controlled by the source of REE or the geochemical characteristics of AMD is needed to obtain more information of processes of REE enrichment in AMD.

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