Interaction between physical and chemical weathering of argillaceous rocks and the effects on the occurrence of acid mine drainage (AMD)

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1	Interaction between physical and chemical weathering of argillaceous rocks and
2	the effects on the occurrence of acid mine drainage (AMD)
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13	Interaction between physical and chemical weathering of argillaceous rocks
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17	Abstract: The disintegration of rocks by weathering plays an important role in the
18	occurrence of Acid Mine Drainage (AMD), which is the environmental problem
19	caused by the exposure of sulfide minerals to water and oxygen. The weathering
20	of rocks is, generally, classified into physical or chemical weathering. However,
21	there are few studies that focus on the complex interaction between physical and
22	chemical weathering of rocks and on the effects of the interaction on the
23	occurrence of AMD. This paper elucidates the complex interrelation between
24	physical and chemical weathering of rocks as well as the progress of AMD
25	through leaching test and weathering test with argillaceous rocks taken in
26	open-cast coal mine in Indonesia in addition to sample analysis before and after
27	the wetting and drying cycle: the rock samples were exposed to oxygen and water
28	during the cycle. The results indicated that the argillaceous rocks which consist of
29	sulfide and/or sulfate caused chemical weathering with micro-cracks on the
30	surface of rocks through the dissolution of soluble iron and sulfur during the
31	occurrence of AMD. Additionally, physical weathering of rocks due to clay
32	minerals was accelerated by chemical weathering with the development of cracks
33	with the occurrence of AMD in the argillaceous rocks containing kaolinite and
34	pyrite. Although weathering of rocks also accelerated AMD, it was concluded that

35	the sulfur co	ntent,	the forn	n of sulfur	and iron i	n rocks, an	d the supply	of oxygen
36	significantly	contril	buted to	the occurre	ence of AN	MD.		
37								
38	Keywords:	Acid	Mine	Drainage	(AMD),	physical	weathering,	chemical
39	weathering, a	argillac	ceous ro	cks				
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53 1. INTRODUCTION

Acid Mine Drainage (AMD), which is the environmental problem caused by the 54exposure of sulfide minerals to water and oxygen, has a negative impact on the 55ecosystem in the surrounding area owing to low-pH and heavy metals dissolved with 56the decrease of pH (Jennings et al., 2008). It is mainly caused by the oxidation of pyrite, 57and the main oxidants are O_2 and Fe^{3+} as shown in Eq. (1) and Eq. (3). Firstly, Fe^{2+} is 58dissolved from pyrite (Eq. (1)), and Fe^{2+} is oxidized to Fe^{3+} by O₂ (Eq. (2)). 5960 $\text{FeS}_2 + 7/2 \text{ O}_2 + \text{H}_2\text{ O} \rightarrow \text{Fe}^{2+} + 2\text{SO}_4^{2-} + 2\text{H}^+,$ (1) 61 $Fe^{2+} + 1/4O_2 + H^+ \rightarrow Fe^{3+} + 1/2H_2O_1$ 62 (2) 63 With the reaction progress as presented above, the pH decreases. The oxidation of pyrite 64 is, moreover, accelerated by Fe^{3+} which is strong oxidant (Eq. (3)). Depending on pH, 65Fe³⁺ precipitates as Fe(OH)₃ (Eq. (4)). 66 67 $\text{FeS}_2 + 14\text{Fe}^{3+} + 8\text{H}_2\text{O} \rightarrow 15\text{Fe}^{2+} + 2\text{SO}_4^{2-} + 16\text{H}^+,$ 6869 (3) $Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3 + 3H^+$, 70 (4)

72	To carry out effective measures against AMD, it is necessary to elucidate the
73	mechanism and the cause of AMD. The weathering of rocks is one of the key factors for
74	understanding the progress of AMD in nature since the weathering of rocks easily
75	occurs under acid conditions, and it causes the release of most of the elements (Jennings
76	et al., 2008; Dold et al., 2013). The weathering of rocks is classified into physical or
77	chemical weathering by the types of the cause of the weathering such as rain, snow,
78	wind and temperature, resulting in a complex mechanism of the progress of the
79	weathering of rocks (Lobb and Femmer, 2007; Moon and Jayawardane, 2004). Since
80	the weathering of rocks can affect the occurrence of AMD through the increase of
81	reactive area of rocks with the disintegration, the progress of AMD has to be
82	investigated in terms of physical and chemical weathering of rocks. However, there are
83	few studies that focus on the complex interaction between physical and chemical
84	weathering of rocks and the effects of the interaction on the occurrence of AMD.
85	In this study, leaching test and weathering test were conducted with argillaceous rock

which is a sedimentary rock formed by clay and taken in open-cast coal mine in Indonesia in addition to sample analysis before and after the wetting and drying cycle: the rock samples were exposed to oxygen and water during the cycle. On the basis of the results, we examined the interaction between physical and chemical weathering of
rocks as well as the effect of the interaction on AMD.

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92 2. MATERIALS AND METHODS

93 2.1. Rock Samples and Analytical Methods

Rock samples were collected in pit in the coal mine in Indonesia where the 94 weathering of rocks and the occurrence of AMD have been reported owing to heavy 95 rain and high temperature in the tropical climate. Four samples which were not exposed 96 97 to the atmosphere were taken from the wall in pit, followed by sample analysis in a laboratory. All samples were categorized as argillaceous rock according to geological 98data in the mine. They were named as sample A, B, C, and D, respectively. These 99 samples were dried at 50°C in a nitrogen atmosphere for 24 hours to supply for X-ray 100Diffraction (XRD) and X-ray Fluorescence (XRF) analysis. Major minerals in the 101samples were analyzed using the X-ray diffractometer (Rigaku, Ultima IV, Japan) under 102 the following condition: radiation CuKa, operating voltage 40 kV, current 26 mA, 103divergence slid 1 deg, anti-scatter 1 deg, receiving slit 0.3 mm, step scanning 0.050°, 104105scan speed 2.000°/min, scan range 2.000-65.000°. In addition, quartz index (QI) was calculated based on the results of XRD analysis in order to compare the mineral content 106

of the samples. QI was calculated by dividing the maximum intensity (I_m) of the target 107 mineral in the sample by X-ray intensity of 100 wt% of standard quartz (Ip) which was 108 measured under the same conditions as follows (Okawara et al., 1996): 109 $QI = I_m/I_p \times 100$ 110 Whereas QI is affected by the effect of X-ray mass-absorption coefficient and the 111 difference of reflected intensity at the bottom of minerals, it can be used to compare the 112mineral content relative to the same type of mineral in other samples (Okawara et al., 1131996). 114

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116 **2.2. Leaching Test**

Leaching test was performed with sample A, B, C and D so as to understand the acid 117generating potential of the samples. After sieving the samples into 1.5-2.0 mm, they 118 were packed into a glass column (40.4 mm diameter × 58.9 mm height). 10 mm 119120 thickness of a supporting layer was installed by setting paper filter, 0.5-1.0 mm of glass beads, and sieves at the bottom of the column to support the samples. In order to unify 121122the reactive area of the samples in each column, the porosity was calculated using the density of the samples and the volume of filling the samples and set at 60%. 100 ml of 123distilled water was poured into the column and the leachate was sampled from the 124

125	bottom of the column for the measurement of pH, followed by the drying process by
126	using an artificial light for 24 hours. The weight of the samples after pouring distilled
127	water was confirmed to decrease to the initial weight of the samples at the end of the
128	drying process. After the wetting and drying cycle was repeated until 10 times, 14 days
129	of the drying process was prepared without an artificial light. The step of 10 times of the
130	wetting and drying cycle with 14 days of the drying process was, furthermore, repeated
131	until 3 times. The total number of the supply of 100 ml of distilled water was 30 times
132	in this study on the assumption of annual rainfall in the mine area in Indonesia. Thus,
133	the wetting and drying cycle was attributed to the supply of distilled water and the heat
134	of the artificial light in this experiment. Additionally, 20.6% of O ₂ was measured with
135	oxygen meter (Toray, LC-450F, Japan) at the top and the bottom of the column at the
136	end of every drying process, indicating that same amount of oxygen was supplied to the
137	samples in each column during the drying process. At the end of the leaching test, grain
138	size analysis was, besides, conducted so that the progress of the weathering of rocks
139	with the occurrence of AMD during the leaching test was examined.
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143	2.3. Slaking	Index (SI)) Test <mark>t</mark>	to Understand Ph	ysical Weathering	g of Rocks

144	Slaking of rocks which is caused by the swelling pressure of clay minerals through
145	the wetting and drying cycle is classified into physical weathering of rocks
146	(Karathanasis et al., 2014). In this study, Slaking Index (SI) test was performed to
147	understand the slaking behavior of the rock samples (Sadisun et al., 2003). Less than 2
148	mm of the samples was removed by sieving and the weight of more than 2 mm of the
149	samples was measured after the wetting and drying cycle in SI test. SI was calculated as
150	the indicator of slaking using the change of the weight of the samples until 5 times.
151	
152	2.4. Acid Extraction Test to Understand Chemical Weathering of Rocks
153	Acid extraction test was carried out by reference to the analysis conducted by Sasaki
154	et al. (2002) to elucidate the form of sulfur and iron in the rock samples since the
155	dissolution rate of elements depends on the form of minerals (Sasaki et al., 2002).
156	Minerals can be extracted with acids at each stage of the extraction (Huerta-Diaz and
157	Morse, 1990). 2.5 g of dried sample was dissolved with 20 ml of 1 mol/dm ³
158	hydrochloric acid (HCl), 60 ml of 46% hydrogen fluoride (HF), and 10 ml of conc.
159	nitric acid (HNO ₃) in line with the method in the past research (Sasaki et al., 2002).
160	Sasaki et al. (2002) mentioned that soluble minerals were extracted with HCl, and

161	silicate minerals were extracted with HF, and refractory minerals such as sulfide
162	minerals were extracted with HNO ₃ . In this study, the time of shaking of the mixture at
163	HNO ₃ step was changed from 2 hours in the past research to 6 hours in order to dissolve
164	sulfide minerals completely. The proportion of each form of sulfur and iron composing
165	pyrite was calculated based on the amount of extracted sulfur and iron (mg/g) from rock
166	samples.
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168	2.5. Simple Dissolution Test and Scanning Electron Microscopy (SEM)
169	Observation
170	Simple dissolution test was conducted by reference to the standard of the pH _{1:2} test of
171	AMIRA in addition to the acid extraction test so as to observe the chemical weathering
172	of rocks: the ratio of solid to liquid was 1:2 (AMIRA, 2002). The size of samples was
173	changed from -75 μm in the standard to 1.0 mm in order to clearly observe the change
174	of surface conditions of the samples before and after the simple dissolution test using
175	Scanning Electron Microscopy (SEM). The sample which underwent the wetting and
176	drying cycle was used to compare the amount of extracted iron and sulfur with HCl in
177	the acid extraction test and the amount of dissolved sulfur and iron in the leachate in the
178	simple dissolution test. The leachate was supplied to Inductively Coupled

179	Plasma-Atomic Emission Spectrometry (ICP-AES) to measure the concentration of
180	sulfur and iron soon after the simple dissolution test in order not to accelerate the
181	reaction of the samples with oxygen and water. The results were calculated using the
182	unit of mg/g to compare the results of the simple dissolution test and the acid extraction
183	test. Besides, the samples after the simple dissolution test were dried by lyophilizer
184	filled with nitrogen gas to prevent the oxidation of the samples before the observation
185	using SEM. The progress of chemical weathering of rocks was investigated based on
186	the change of surface conditions of the rock samples before and after the simple
187	dissolution test.

189 **3. RESULTS AND DISCUSSION**

190	In order to clarify each experiment and the purpose, the experimental scheme is
191	presented in Table 1.
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194	Table 1.
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197 **3.1. Acid Generating Potential of Rock Samples**

The XRD patterns of the rock samples are shown in Figure 1. The peaks of quartz 198 and kaolinite were found in all samples. The peaks of pyrite were clearly observed in 199 sample B and D, indicating that the content of pyrite was high in sample B and D. The 200 peaks of albite were clearly seen in only sample A, B, and C, while it was not found in 201sample D. Additionally, only sample A contained siderite based on the result in Figure 1. 202 203Table 2 shows QI which was calculated using the intensity of each mineral in Figure 1, and Figure 2 shows the chemical component of the samples: others in sample B and D 204 205were mostly composed of water. Although QI of quartz was quite low in sample D, similar values of QI of kaolinite were obtained in all samples. Besides, QI of albite was 206 slightly higher in sample C. The content of silica in each sample in Figure 2 was 207supported by QI of quartz in Table 2. Moreover, a large amount of iron and sulfur in 208 sample B and D in Figure 2 was well correlated with the peaks of pyrite in the samples 209 in Figure 1. Pyrite was not observed in sample A and C in Figure 1; however, the sulfur 210content was 0.83% and 0.03% in sample A and C, respectively. This suggested that 211sample A and C may contain small amount of sulfide causing AMD. 212

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217	Fig. 1.
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220	Table 2.
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223	Fig. 2.
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226	Figure 3 shows the change of pH in the leaching test. The change of pH can be
227	classified into two groups. The pH in sample B and D remained at pH 2.0-3.0, while
228	sample C showed a rapid increase in pH at the early step of leaching, followed by a
229	gradual increase at pH 7.0-8.0. Furthermore, sample A showed a gradual increase in pH
230	overall. As the content of pyrite was high in sample B and D, the pH in sample B and D
231	remained at low-pH with the dissolution of pyrite in the leaching test. On the other hand,
232	the pH gradually increased in sample A and C because of the low content of sulfur.

233	During the drying process in the leaching test, the same amount of oxygen was supplied
234	to the samples: 20.6% of oxygen was measured with oxygen meter at the top and the
235	bottom of the column at the end of drying process. In sample B and D in which the
236	content of pyrite was high, acidic water, therefore, occurred at the rate comparable to
237	the amount of oxygen supply, resulting in similar pH at each step of leaching.
238	Meanwhile, sample A and C showed a gradual increase in pH since only residual sulfide
239	caused acidic water by reacting with the oxygen supply at each step of leaching. The
240	decrease of the amount of sulfide in sample A and C with the step of leaching resulted
241	in the gradual increase in pH. Thus, it was found that the change of pH was dependent
242	on the sulfur content in rocks and the amount of oxygen supply. There was, moreover, a
243	sharp drop in pH after 14 days of the drying process in all samples, especially in sample
244	A, B, and D, as indicated by means of arrows in Figure 3. This suggested that the
245	amount of oxygen supply during the drying process played an important role in the
246	progress of AMD. Consequently, the wetting and drying cycle attributed to the supply
247	of deionized water and the heat of the artificial light accelerated the deterioration in the
248	water quality with the dissolution of sulfide in the leaching test. The sulfur content in
249	rocks and the amount of oxygen supply, especially, played an important role in the
250	change of pH on the basis of the results in this study.

252**Fig. 3**. 2532542553.2. Physical Weathering of Rocks 256257The change of slaking index (SI) of the samples is displayed in Figure 4. The particle size distribution after the leaching test is described in Figure 5. There was a rapid 258259increase in SI at the first step in sample A, B, and C, followed by a slight increase until the fifth step, whereas SI gradually increased overall in sample D in Figure 4. This 260

result indicated that sample A, B, and C easily disintegrated through the wetting and 261drying cycle, which is called as a rapid slaking (Tanaka et al., 1997). In contrast, sample 262D gradually disintegrated through the wetting and drying cycle. The particle size of the 263rock samples in the columns was set at 1.5-2.0 mm before beginning the leaching test as 264shown by a straight line in Figure 5. More than 50% of the rock samples consisted of 265266 less than 0.25 mm of small particles in sample A, B, and C after the leaching test as indicated by a circle in Figure 5. The rate of decline of particle size was consistent with 267 the change of slaking index in Figure 4, indicating that rapid slaking caused a 268

269	significant decrease of particle size in sample A, B, and C through the wetting and
270	drying cycle during the leaching test. However, the particle size of approximately 30%
271	of sample A was more than 1 mm after the leaching test, while that of more than 90% of
272	sample B, C, and D were less than 1 mm. This was attributed to the prevention of
273	slaking in sample A due to the compacted layer formed in the surface layer as shown in
274	Figure 6. Approximately 1 mm of small particles were observed under the compacted
275	layer at the end of the leaching test in sample A. For these results, the compacted layer
276	prevented the progress of slaking in sample A, leading to the middle size of the residue
277	in the column after the leaching test. Although some of the particles in sample A were
278	not slaked owing to the compacted layer, the decrease of particle size after the leaching
279	test was observed in all samples.
280	In general, clay minerals cause the disintegration of rocks by slaking with swelling
281	pressure while swelling and shrinking with the wetting and drying cycle (Karathanasis
282	et al., 2014). This is considered physical weathering of rocks since the swelling pressure
283	causes the disintegration of rocks. The clay minerals which have a large specific surface
284	area compared with other clay minerals, such as kaolinite, montmorillonite, and illite,
285	significantly contribute to the progress of slaking (Pusch, 1983; Ruiz-Vera and Wu,
286	2006; Emerson, 1964). In regard to the facts and the result of XRD, kaolinite caused

287	disintegration of rocks by slaking through the wetting and drying cycle in this study.
288	Albite also causes slaking of rocks through the hydrolysis of albite according to the past
289	research, but it is very minor effect (Wen et al., 2014). Other clay minerals causing
290	slaking were not observed in all samples in this study. Therefore, the disintegration of
291	rocks by physical weathering was mainly caused by kaolinite during the leaching test
292	and SI test. In spite of the similar content of kaolinite in all samples, the change of SI of
293	sample D in Figure 4, however, differed from that of the other samples, indicating that
294	the change of SI was affected by other factors in this study. Additionally, the
295	disintegration of rocks can accelerate AMD through the increase of the reactive area of
296	rocks, but the pH remained at low-pH overall in sample B and D with the wetting and
297	drying cycle in Figure 3 even if the rock samples disintegrated due to physical
298	weathering during the leaching test. This also suggested that the change of pH depended
299	on the sulfur content and the amount of oxygen supply more than the effect of physical
300	weathering of rocks.
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Fig. 4.

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307	Fig. 5.
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310	Fig. 6.
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313	3.3. Chemical Weathering of Rocks
314	The proportion of the extracted sulfur and iron in the acid extraction test is described
315	by each step of the extraction in Figure 7. The solubility of the elements depends on the
316	existing form of minerals in rocks: sulfate, generally, dissolve in leachate more easily
317	than sulfide (Turkdogan et al., 1974). Thereby, the minerals extracted with HCl affect
318	the water quality in a short time for the high solubility compared with that with HNO ₃ ,
319	whereas the minerals extracted with HNO ₃ contribute to the water quality for a long
320	time owing to the low solubility. In Figure 7, iron and sulfur existed in different form of
321	minerals in the rock samples according to the results: minerals extracted at HCl step, at
322	HF step, and at HNO ₃ step. Considering that sulfate can be extracted with HCl and

323	sulfide can be extracted with HNO3 in the acid extraction test, more than 81% of sulfur
324	and iron existed as sulfide in sample D, and approximately 35% of iron and 60% of
325	sulfur were extracted as sulfide in sample B. Since the high content of sulfide in sample
326	B and D caused acidic water for a long term, the pH remained at low-pH overall in
327	sample B and D in Figure 3. Approximately 0-12% of iron and 42-50% of sulfur were
328	extracted as sulfide, and the sulfur content was 0.83% and 0.03% in sample A and C,
329	respectively. The ratio of sulfate was, moreover, higher in sample A and C than that in
330	sample B and D. Hence, most of the soluble sulfates dissolved in the leachate at the
331	early stage of leaching in sample A and C, leading to a gradual increase of pH in Figure
332	3. It can, furthermore, be seen that high content of siderite resulted in the highest ratio
333	of iron extracted with HCl in sample A. In short, the existence form of sulfur and iron in
334	rocks played an important role in the change of the water quality: this result was
335	consistent with that of the previous study (Matsumoto et al., 2015).
336	Figure 8 shows the comparison between the amount of extracted iron and sulfur with
337	HCl and HNO ₃ before and after the wetting and drying cycle. While the amount of
338	extracted iron and sulfur with HNO3 was higher before the wetting and drying cycle,
339	that with HCl was higher after the wetting and drying cycle in the figure. In terms of the
340	formation of precipitation and/or sulfate with the occurrence of AMD, they were formed

341	from sulfide during the wetting and drying cycle and dissolved by HCl. Thus, soluble
342	minerals are formed with the occurrence of AMD during the wetting and drying cycle.
343	The amount of sulfur and iron extracted with HCl after the wetting and drying cycle
344	is compared with the amount of dissolved sulfur and iron in the leachate in the simple
345	dissolution test in Figure 9. It suggested that soluble sulfate extracted with HCl was
346	easily dissolved in leachate when they were exposed to water. The amount of dissolved
347	elements was not in good agreement with the amount of extracted iron and sulfur with
348	HCl in sample A and C; however, similar values were obtained in sample B and D.
349	Considering the small amount of sulfur and iron content in sample A and C in Figure 2,
350	the difference was attributed to the heterogeneous distribution of sulfur and iron in
351	rocks. Consequently, the elements which were extracted with HCl easily dissolved in
352	the leachate, leading to AMD in a short time.
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355	Fig. 7.
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361	Fig. 8.
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364	Fig. 9.
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Figure 10 shows the surface conditions of the rock samples after the wetting and 367 drying cycle and the simple dissolution test. While the products which are thought of as 368 oxidative products and/or precipitations were observed on the surface of the samples 369 after the wetting and drying cycle in Figures 10a1, b1, c1, and d1, they were not observed 370 after the simple dissolution test in Figures 10a₂, b₂, c₂, and d₂. The changes were clearly 371372 observed in sample B and D which contained a large amount of iron and sulfur compared to that in sample A and C. In addition, micro-cracks were observed on the 373 surface of the rock samples after the simple dissolution test as presented by white 374circles in Figure 10a₃, b₃, c₃, and d₃. Considering that the elements extracted with HCl 375 dissolved in the simple dissolution test, the micro-cracks were developed at the voids 376

377	which were formed after the dissolution of soluble minerals. According to the previous
378	research, the dissolution of soluble minerals can lead to the decrease of the strength of
379	rocks (Tran et al., 2011; Ciantia et al., 2015). The strength decreased and the
380	micro-cracks occurred as the result of the formation of void after the dissolution of
381	soluble minerals. This phenomenon was considered chemical weathering of rocks in
382	this study since the dissolution of soluble sulfur and iron led to the development of
383	micro-cracks on the surface of rocks. Therefore, chemical weathering of rocks and the
384	occurrence of AMD progressed simultaneously through the wetting and drying cycle
385	with the acidification of rocks. Although the chemical weathering caused by dissolution
386	of soluble iron and sulfur occurred in the leaching test, it can be said that the change of
387	pH was mainly affected by sulfur content, the existence form of sulfur and iron in rocks,
388	and the amount of oxygen supply more than the effect of the chemical weathering in
389	this study.
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392	Fig. 10.
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396	On the basis of the results as shown above, chemical and physical weathering of
397	rocks progressed simultaneously with the occurrence of AMD during the wetting and
398	drying cycle in the argillaceous rocks which contained sulfide and clay minerals related
399	to slaking. In view of the fact that the physical weathering of rocks causes cracks by
400	swelling of clay minerals and the chemical weathering causes micro-cracks with the
401	dissolution of soluble sulfur and iron, physical weathering can be accelerated by
402	chemical weathering with the development of cracks from micro-cracks as shown in
403	Figure 11. Physical weathering of rocks by slaking due to swelling of kaolinite and the
404	hydrolysis of albite and chemical weathering with micro-cracks on the surface of rocks
405	caused by the dissolution of soluble sulfur and iron occurred with the progress of AMD
406	during the leaching test and SI test in this study. Given that the proportion of soluble
407	iron and sulfur in sample A, B, and C was higher than that in sample D by
408	approximately 30% in the ratio, the occurrence of the micro-cracks on the surface of
409	rocks with the dissolution of soluble sulfur and iron significantly accelerated the
410	disintegration of rocks caused by slaking of kaolinite, resulting in the rapid increase of
411	SI in sample A, B, and C in SI test in spite of the similar amount of kaolinite in all

3.4. Interaction of Physical Weathering and Chemical Weathering of Rocks

412 samples. It was, however, found that the sulfur content, the existence form of sulfur and

413	iron in rocks, and the amount of oxygen supply significantly affected the change of the
414	water quality although the physical and chemical weathering of rocks could affect the
415	progress of AMD with the increase of specific surface area through disintegration of
416	rocks.
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419	Fig. 11.
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422	4. CONCLUSIONS
423	The interaction between physical and chemical weathering of rocks as well as the
424	effect of the interaction on AMD were investigated by performing the leaching test,
425	slaking index (SI) test, and acid extraction test with sample analysis before and after the
426	wetting and drying cycle. The conclusions are summarized as follows:
427	I. The argillaceous rock which contained sulfide caused chemical weathering
428	with micro-cracks on the surface of rocks through the dissolution of soluble
429	iron and sulfur along with the occurrence of AMD.

430	II.	The chemical and physical weathering of rocks by swelling of clay minerals
431		progressed simultaneously with the wetting and drying cycle. Furthermore,
432		chemical weathering accelerated physical weathering of rocks with the
433		occurrence of micro-cracks on the surface of rocks after the dissolution of
434		soluble sulfur and iron.

III. Although the disintegration of rocks by physical and chemical weathering
could affect the progress of AMD, the change of the water quality by AMD
over time was significantly affected by the amount of oxygen supply, the
sulfur content, and the existence form of sulfur and iron in rocks more than
the effect of rock weathering.

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509	Figure Captions
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511	Table 1. Summary of experiment and the purpose in this study.
512	Table 2. Quartz Index (QI) calculated based on the intensity in the result of XRD,
513	Fig. 1. X-ray diffraction (XRD) patterns of sample A, B, C, and D. Qz, Ka, Al, Si, and
514	Py represent quartz, kaolinite, albite, siderite, and pyrite, respectively.

- **Fig. 2.** Chemical composition of sample A, B, C, and D.
- **Fig. 3.** Change of pH in sample A, B, C, and D in the leaching test.

- 517 **Fig. 4.** Change of slaking index (SI) in sample A, B, C, and D.
- 518 Fig. 5. Change of particle size distribution before and after the leaching test: initial size
- of the samples was set at 1.5-2.0 mm.
- 520 Fig. 6. Physical conditions of sample A after the leaching test. (a) Physical conditions of
- 521 the surface layer in the column from side view. (b) Middle-size particles under the
- 522 compacted layer after the leaching test from top view.
- 523 Fig. 7. Proportion of extracted iron and sulfur at each step of the acid extraction. (a)
- 524 Proportion of extracted iron. (b) Proportion of extracted sulfur.
- 525 Fig. 8. Comparison of the amount of extracted iron and sulfur with HCl and HNO₃
- 526 before and after the wetting and drying cycle. (a) Comparison of the amount of
- 527 extracted iron. (b) Comparison of the amount of extracted sulfur.
- 528 Fig. 9. Comparison of the amount of extracted iron and sulfur with HCl in the acid
- 529 extraction test and that of dissolved iron and sulfur in the simple dissolution test. (a)
- 530 Comparison of the amount of soluble iron. (b) Comparison of the amount of soluble531 sulfur.
- 532 Fig. 10. Surface conditions of sample A, B, C, and D. Symbol of "a, b, c, d" represents
- 533 sample A, B, C, and D, respectively. (1) After the wetting and drying cycle. (2) After

- the simple dissolution test. (3) Micro-crack on the surface of rocks after the simple
 dissolution test.
- **Fig. 11.** Interaction between physical and chemical weathering of rocks.