



Characterization of phosphorus leaching from phosphate waste rock in the Xiangxi River watershed, Three Gorges Reservoir, China



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HIGHLIGHTS

- The phosphorus released under acidic conditions exceed that under neutral conditions by an order of magnitude.
- The phosphorus release mechanism of phosphate waste rock is solubility-controlled.
- The phosphorus was released faster during the period when environmental pH turned from weak alkalinity to slight acidity.
- The phosphate waste rocks deposited within the Xiangxi River watershed could threaten the adjacent surface-water environment.

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ABSTRACT

Phosphate mining waste rocks dumped in the Xiangxi River (XXR) bay, which is the largest backwater zone of the Three Gorges Reservoir (TGR), are treated as Type I industry solid wastes by the Chinese government. To evaluate the potential pollution risk of phosphorus leaching from phosphate waste rocks, the phosphorus leaching behaviors of six phosphate waste rock samples with different weathering degrees under both neutral and acidic conditions were investigated using a series of column leaching experiments, following the Method 1314 standard of the US EPA. The results indicate that the phosphorus release mechanism is solubility-controlled. Phosphorus release from waste rocks increases as pH decreases. The phosphorus leaching concentration and cumulative phosphorus released in acidic leaching conditions were found to be one order of magnitude greater than that in neutral leaching conditions. In addition, the phosphorus was released faster during the period when environmental pH turned from weak alkalinity to slight acidity, with this accelerated release period appearing when L/S was in the range of 0.5–2.0 mL/g. In both neutral and acidic conditions, the average values of Total Phosphorus (TP), including orthophosphates, polyphosphates and organic phosphate, leaching concentration exceed the availability by regulatory (0.5 mg/L) in the whole L/S range, suggesting that the phosphate waste rocks stacked within the XXR watershed should be considered as Type II industry solid wastes. Therefore, the phosphate waste rocks deposited within the study area should be considered as phosphorus point pollution sources, which could threaten the adjacent surface-water environment.

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1. Introduction

Water eutrophication in the Three Gorges Reservoir (TGR) has attracted extensive attention in recent years. According to monitoring data provided by the Ministry of Environmental Protection of the People's Republic of China, superabundant nutrients leading to

varying degrees of algae blooms have appeared within backwater areas of all twelve first-level branches of the Yangtze River, especially in the Xiangxi River (XXR) bay, which is the first-level branch nearest to the Three Gorges Dam. During the last decade, varying degrees of algal bloom have appeared in each spring and summer.

Previous research identified the most important eutrophication factors in the XXR bay as the low water flow velocity of the backwater area and the great quantity of nutrients received (Huang et al., 2015; Li et al., 2008). A backwater area of approximately 40 km is formed along the XXR when TGR elevates the impounded

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water level to 172.5 m. The average flow velocity in the backwater area is less than 0.05 m/s. Over the past decade, the annual concentration of Total Nitrogen (TN) and Total Phosphorus (TP) of the XXR was 1.41 mg/L and 0.17 mg/L, respectively. Over 1600 tons TN and 330 tons TP are received by the XXR each year (Shao et al., 2007; Liu et al., 2012; Yang et al., 2015). Most researchers ascribe the substantial amounts of nutrients to the runoff from agriculture and from untreated domestic or industrial sewage (Wang et al., 2011; Li et al., 2012, 2014), but few consider the pollution from phosphate mining activities within the XXR watershed. Abundant phosphate rock resources are deposited within the watershed, and phosphate mining is one of the local pillar industries. More than 200 million tons of raw phosphate rocks have been extracted to date in this region. Approximate 1.4 million tons of raw phosphate rocks are exploited every year, leading to large quantities of solid waste, which is typically dumped as waste rock piles within phosphate mining areas.

There are few studies concerning the phosphorus pollution risk of phosphate mining waste rocks. Some researchers have investigated the heavy metal pollution from phosphate waste rock (Mar and Okazaki, 2012; Sabiha-Javied et al., 2009). In nature, water percolates through phosphate waste rocks in the environment, which contain low grade and/or commercial value phosphate ore body, leaching phosphorus from the waste rock. However, the release of the nutrient TP from phosphate waste rock is poorly understood under field leaching conditions. Nonetheless, the TP contributed by phosphate waste rocks in the XXR watershed should be considered due to the very special geological background and environmental sensitivity of this region.

The primary objective of this research was to investigate the phosphorus release potential of phosphate waste rocks in the environmental conditions of the XXR watershed. Six representative phosphate waste rock piles dumped within the XXR watershed were selected as the objects of the study. Column leaching experiments were implemented based on the Leaching Environmental Assessment Framework (LEAF) methodology recently developed by the US EPA. Insight into the phosphorus leaching behavior under percolation conditions, which are a close match for the conditions found in the environment, is important for pollution risk assessment of phosphate waste rocks. In addition, the results could reveal the release mechanism of phosphorus from phosphate waste rock.

2. Materials and methods

2.1. Study area description

The XXR has three main branches, including the Gaolan River (GLR), the Gufu River (GFR) and the Jiuchong River (JCR). The main stream of the XXR crosses through Xingshan County from the north to south, mingling with GLR at Xiakou Town and emptying into the Yangtze River at Xiangxi Town (Fig. 1). The geographical position of the XXR watershed is in the range of 30°37'–31°34' N and 110°25'–111°06' E. The Shu Kongping mining area, located about 32 km northeast of Xiakou Town, was selected as the investigation region. When the water level of the TGR reaches 147.5 m, Xiakou Town is the end of the backwater zone of the XXR bay. The Shu Kongping mine is one of the major production mines of Hubei Xingfa Chemicals Group Co. Ltd. There are over 120 ha of mining waste rocks dumped within the study area; most of them have been simply reclaimed by being covered with shallow soil. The main extraction phosphate rock strata (Ph_1^{3-3} and Ph_1^{3-2}) deposited in Shu Kongping belongs to the Upper Sinian system of the Doushantuo Formation as well as to the GLR and the JCR watersheds. Consequently, the leaching behavior of waste rocks in the Shu Kongping mining area may be considered as representative of most

phosphate waste rocks within the XXR watershed.

It should be emphasized that severe acid precipitation is common in the study area. According to statistical data from Hubei Province Environmental Status Bulletin, which is published by the Hubei Environmental Protection Bureau, the acid rain frequency of Yichang City was as high as 69% in 2013, and the average pH value of rainwater was 4.86. In 2014, the Yichang Environmental Protection Bureau published the local environmental monitoring data, which indicated that the annual mean pH value of rain water around the Yichang urban area was 4.45 and the frequency of acid precipitation was as high as 98.5%.

2.2. Sampling method in field

The field sampling work was undertaken in the summer of 2013. Six phosphate waste rock piles with different stacking modes, weathering age and utilization were selected as the objects of investigation (shown in Table 1). Two of them (WR-B and WR-F) were dumped in the “valley-filled” method; three of them (WR-A, WR-D and WR-E) were piled in the “cross-valley” method and one of them (WR-C) was stacked in the “land-heap” method. WR-B is planned for residential land use. WR-C was casually dumped. The remaining four piles were reclaimed for vegetation restoration. The longest weathering time was 8 years (WR-B) while the pile with the shortest weathering time was still being dumped during sample work (WR-C). As shown in Fig. 1, waste deposits in field are extremely heterogeneous. The particle size of waste rocks generally shows a wide distribution, ranging from boulders to silt. However, waste deposits with particle size larger than 400 mm were not found in any of the investigated piles.

For solid wastes with heterogeneous mineral and/or chemical properties, it is crucial to take samples representing a statistical average of chemical characteristics. The systematic sampling method specified by the US EPA was selected for sampling operations in field (US EPA, 2002). This sampling approach is attractive because it can be easily implemented in waste rock piles with different geometries, but it has some limitations, such as not being truly random. However, the sampling design can be improved by using random sampling within each grid block (Myers, 1997). For the present work, twelve to fifty-three grid-blocks per pile were established to cover the whole surface based on area and stacking mode, and at least two sampling points were randomly selected in each grid block (see Table 1). The sampling depths varied from 30 to 100 cm, mainly depending on whether the target piles were reclaimed or not. Rocks with particle sizes larger than 200 mm were discarded and only small waste rock particles (i.e., smaller than 200 mm) were selected for laboratory tests. At least 2 kg of waste rocks were collected from each grid block. According to the field investigation, the rocks with particle sizes larger than 200 mm account for approximately 10 percent of all waste rocks. Furthermore, according to the visually identification, the phosphate mineral is not deposited in large particles. In other words, the phosphorus mineral is not concentrated in the large particles relative to the smaller particles. Therefore, the sampling error induced by removing the coarse particles could be acceptable (US EPA, 2002). In total, approximately 350 kg of phosphate waste rocks were collected from the six sites.

2.3. Sample preparations and mineralogical characterization

The phosphate waste rock samples were air-dried in the laboratory at room temperature (23 ± 2 °C). Then they were disaggregated by a mechanical jaw crusher, and shifted to yield 85% of the material passing through a 10 mesh (2 mm) standard sieve. Then the ground samples were homogeneously mixed and

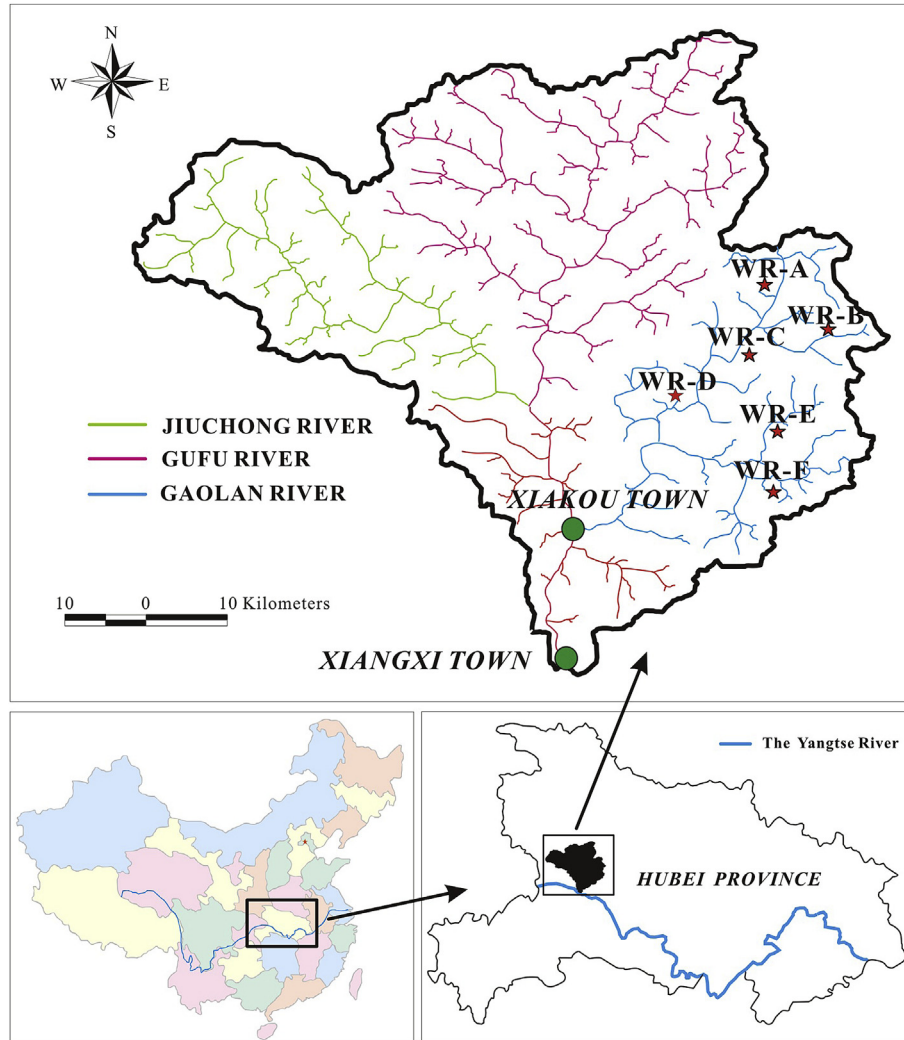


Fig. 1. Location of the XXR watershed and sampled waste rock piles.

Table 1

Description of waste rock samples and their sampling information.

Sample site	Stacking mode	Weathering age (year)	Dump height (m)	Area (km ²)	Land utilization	Grid number	Sample point number	Moister content (%)	Total sample mass (kg)	Total phosphorus in solid phase (mg/kg)
WR-A	CV	2–3	8.9	0.03	VR	24	78	2.5	50	1679
WR-B	VF	7–8	10.6	0.08	RL	53	160	0.7	110	1768
WR-C	LH	<1	6.5	0.04	–	25	80	0.7	50	1654
WR-D	CV	3–4	6.2	0.02	VR	12	36	0.5	30	1385
WR-E	CV	3–4	9.7	0.05	VR	26	82	3.4	60	1288
WR-F	VF	5–7	5.5	0.03	VR	20	63	0.9	45	1510

CV: cross-valley; VF: valley-filled; LH: land-heap; VR: vegetation restoration; RL: residential land.

separately sealed in moisture-barrier bags as the “as-tested” materials. From each waste rock site, at least 5 kg of “as-tested” material were prepared for the leaching tests. The moisture content of each type of “as-tested” material (shown in Table 1) was determined based on ASTM D2216 (ASTM, 1992).

The mineralogical composition of the six waste rock samples was determined by X-ray diffraction (XRD) in the laboratory of the Institute of Rock and Soil Mechanics, Chinese Academy of Science. A Phillips PW 3710 was used to analyze the crystal line forms present in samples WR-A to WR-F with a Cu tube anode, a generator tension of 40 kV, and a current of 20 mA. Table 2 summarizes the mineral composition as determined by X-ray diffraction. The predominant

phases detected by X-ray diffraction in all samples were carbonate minerals, including dolomite (16.5–27.1 wt%) and calcite (7.9–12.8 wt%). The total phosphorus content in solid phase of each sample was tested following the method outlined by Ostrofsky (2012), and the results are listed in Table 1.

2.4. Column leaching test

Column leaching tests approximate natural conditions closer than any other laboratory test and at the same time yield more robust results than batch tests (Kalbe et al., 2007; Grathwohl and Susset, 2009; Grathwohl, 2014). The column leaching test is

Table 2
Mineralogical analysis (XRD) of the waste phosphate rocks used in percolation experiments.

Minerals	Formula	Percentage by weight (%)					
		WR-A	WR-B	WR-C	WR-D	WR-E	WR-F
Quartz	SiO ₂	34.5	28.2	37.3	35.8	20.1	28.7
Fluorapatite	Ca ₁₀ (PO ₄) ₆ F ₂	16.2	18.2	16.4	14.7	11.7	15.8
Dolomite	CaMg(CO ₃) ₂	20.6	16.5	18.4	21.3	20.5	27.1
Calcite	CaCO ₃	9.3	9.7	7.9	8.2	12.8	9.6
Illite	(K,H ₃ O)(Al,Mg,Fe) ₂ (Si,Al) ₄ O ₁₀ [(OH) ₂ (H ₂ O)]	6.5	5.3	N/A	4.5	3.7	11.4
Albite	NaAlSi ₃ O ₈	5.4	3.4	N/A	7.4	15.2	N/A
Clinocllore	(Mg,Fe) ₃ (Si,Al) ₄ O ₁₀ (OH) ₂ ·(Mg,Fe) ₃ (OH) ₆	1.5	N/A	12.7	N/A	13.7	N/A
Pyrite	FeS ₂	0.4	0.7	0.4	0.8	0.5	0.3
Others		5.5	17.9	6.86	7.6	1.7	7.4

designed to provide the liquid solid partitioning (LSP) of constituents in a granular solid material as a function of Liquid-to-Solid ratio (L/S) under percolation conditions. In the present work, the standard of US EPA Method 1314 (US EPA 2013) was used as the reference test protocol. A 50-cm straight cylinder column with an inner diameter of 5 cm, constructed of Plexiglass fitted with polypropylene (PP) end cap adapters, was used as the main column apparatus. A thin layer of acid-washed silica sand with particle size less than 0.5 mm was placed at the bottom of the column. The “as-tested” materials were then added in successive layers (20–30 mm each) and gently compacted with a rammer. The total packed height of materials in each column was about 480 mm. Another layer of acid-washed sand was added at the top of the column. This packing manner was designed to support the materials and prevent material losses from the column, as well as for distribution of the incoming water solution to the column. It should be emphasized that there is no explicit packing manner mentioned in US EPA Method 1314, while the standard of CEN/TS 14405 (CEN/TS, 2004) recommends that the test portion of the column should be filled with tested materials in at least five consecutive layers, and each layer should be introduced into column in three sub-layers and leveled separately. Following the packing method recommended by CEN/TS 14405, a rammer with a weight of 125 g was used as the tamping device, and was dropped three times on each layer from a height of approximately 20 cm. In total, approximately 1855 g of “as-tested” materials were packed into each column (see Table 3).

Two types of eluent, deionized (DI) water and acid solution, were selected for the column leaching test. DI water was used to reveal the phosphorus leaching behavior under neutral conditions (i.e., without regard to chemical properties of percolating water). A dilute sulfuric acid solution with a pH of 4.5 was selected to reflecting the phosphorus leaching behavior under local acid rainfall conditions. The eluent was introduced to each column by a

peristaltic pump in up-flow percolating mode to minimize air entrainment and flow channeling effect. Eluent was pumped into each column as a constant flow rate for pre-saturation. When the sample in the column was completely wetted and the eluent was just beginning to be seen through the effluent tubing at the top of the column apparatus, the pump was stopped. The column was rested for 24 h to allow it reach chemical equilibrium, then the saturated mass of the sample was recorded. After that, the flow rate of the peristaltic pump was adjusted to provide an eluate production rate of 0.75 ± 0.25 L/S/day according to the average dry mass of the “as-tested” materials in the columns. The peristaltic pump rate for each column was initially set as 1335 mL/day with consideration of pump inefficiencies, back pressure, and dead-volume lag times. Eluates were collected over nine fractions at pre-determined cumulative L/S of 0.2, 0.5, 1.0, 1.5, 2.0, 4.5, 5.0, 9.5, and 10 mL/gdry. Different size (100 mL–1000 mL) PP bottles equipped with air-lock devices were used as eluate collection bottles. All columns were maintained under laboratory temperatures (23 ± 2 °C) and humidity (45–55%). In total, twelve column leaching tests were conducted, and one hundred and eight analytical liquid samples were prepared. Table 3 provides the basic information of each column leaching test.

For integrated evaluating the inorganic constituent leaching from wastes and secondary materials, the Leaching Environmental Assessment Framework (LEAF) was developed to assess leaching for a wide variety of solid materials, including process wastes, construction materials and mining wastes (Garrabrants et al., 2010). Under this assessment, four leaching tests (i.e., Method 1313 to 1316) to evaluate the equilibrium between a solid matrix and a liquid phase typically consist of either batch equilibrium or column tests. Method 1313 is a parallel batch extraction test which providing the LSP of constituents as a function of eluate pH while Method 1314 is an up-flow column leaching test which establishing

Table 3
Basic parameters of each column leaching test.

Test material	Eluent type	H	V	M _{wet}	M _{dry}	M _{sat}	V _{pore}	n	r _{out}	L/S
		cm	(cm ³)	(g)	(g)	(g)	(cm ³)	(–)	mL/d	(L/S)/d
WR-A	DI	46.2	907.1	1810.0	1683.3	263.4	263	0.29	1352	0.80
	ACID	46.0	903.2	1823.2	1695.6	293.1	293	0.32	1468	0.87
WR-B	DI	45.6	895.4	1805.5	1661.1	290.6	291	0.32	1150	0.69
	ACID	45.8	899.3	1832.6	1686.0	296.5	297	0.33	1250	0.74
WR-C	DI	45.2	887.5	1822.2	1712.9	285.6	286	0.32	1386	0.81
	ACID	45.5	893.4	1863.7	1751.9	291.5	292	0.33	1188	0.68
WR-D	DI	46.2	907.1	1855.1	1688.1	289.8	290	0.32	1503	0.89
	ACID	46.5	913.0	1872.9	1704.3	303.1	303	0.33	1423	0.83
WR-E	DI	46.8	918.9	1903.6	1751.3	293.3	293	0.32	1533	0.88
	ACID	46.0	903.2	1863.6	1714.5	284.5	285	0.31	1231	0.72
WR-F	DI	46.2	907.1	1894.2	1799.5	291.3	291	0.32	1216	0.68
	ACID	46.5	913.0	1914.7	1819.0	302.5	303	0.33	1315	0.72

the LSP of constituents as a function of L/S. Although not specifically written into the LEAF, it is reasonable to assume that the LSP data for Method 1314 is related to the LSP data collected for eluate concentration in the Method 1313 (Garrabrants et al., 2011).

The characterization of the phosphorus leaching behaviors under a wide range of pH (2.0–13.0) conditions according to Method 1313 can be found elsewhere (Jiang et al., 2015). Except for the particle size, all the “as-tested” materials used in former and present works have the same chemical and mineral compositions. Therefore, the experimental results derived from Method 1313 would be introduced for integration analysis in the following discussions.

2.5. Chemical analysis

A laboratory pH meter (SC210, glass composite electrode, STARTER 2100/3C Pro, OHAUS) was used for pH measurement of all eluates following DIN ISO 10390 (2005) (three-point calibration using standard pH buffer solutions at 4.00, 7.00, and 10.00 as the zero points). The concentration of total phosphate (TP) was measured using an ultraviolet–visible spectrophotometer (DR 5000, HACH) in accordance with the methods of PhosVer 3 with acid persulfate digestion, TestN Tube procedure. This method is equivalent to US EPA Method 365.2, Standard Method 4500-PB5, and PE, particularly for reporting wastewater analysis, and is accepted by the US EPA. All of the chemical agents used in the TP concentration test were obtained from the prefabricated reagent set supplied by HACH Company (Reagent Set 2742645 for low-range TP of 0.06–3.5 mg/L PO_4^{3-} and Reagent Set 27672-45 for high-range TP of 0.06–100 mg/L PO_4^{3-}). When more than two eluate collection bottles were used for large L/S fractions, the volume weight method specified in US EPA Method 1314 was used for composite analytical samples.

3. Results and discussion

3.1. Leaching environment pH of phosphate waste rocks

3.1.1. Neutral conditions

The relationship between the pH values of the eluates extracted by DI water from different phosphate waste rocks (WR-A ~ WR-F) and their cumulative L/S ratios is presented in Fig. 2a. The results indicate that eluate pH was maintained in the range of neutral and/or weakly alkaline (i.e., 7.0–9.0) under neutral conditions. Phosphate waste rock is a typical salt type mineral system, and the leaching environment pH of phosphate waste rocks could be either acidic or basic, depending on the mineralogical composition of the saturated solution (Somasundaran et al., 1985). According to the numerical simulations and experimental results stated in other literature (Inskeep and Bloom, 1985; Königsberger et al., 1989; House, 1990; Somasundaran and Wang, 2006), under equilibrium conditions, the pH of solutions of calcite and dolomite, which are the main gangue minerals of phosphate waste rock, are both above 9.0, while the pH of apatite-saturated solution is near 7.4. Therefore, the pH of heterogeneous mineral systems found in phosphate waste rock should behave as weakly alkaline. Furthermore, eluate pH increased slightly as L/S increased, indicating that the inner leaching environment of phosphate waste rock piles would not be easily affected by L/S under neutral conditions.

All eluates showed a relatively low pH during the initial leaching time (i.e., $L/S \leq 1.0$). The eluates of WR-A, WR-E, and WR-F even behaved as acids. The reason for this phenomenon is not clear from the experiments of this study. The same result could also be found in the previous work (Jiang et al., 2015). As shown in Table 2, there is a small fraction of the sulphide mineral (i.e., pyrite) present in the

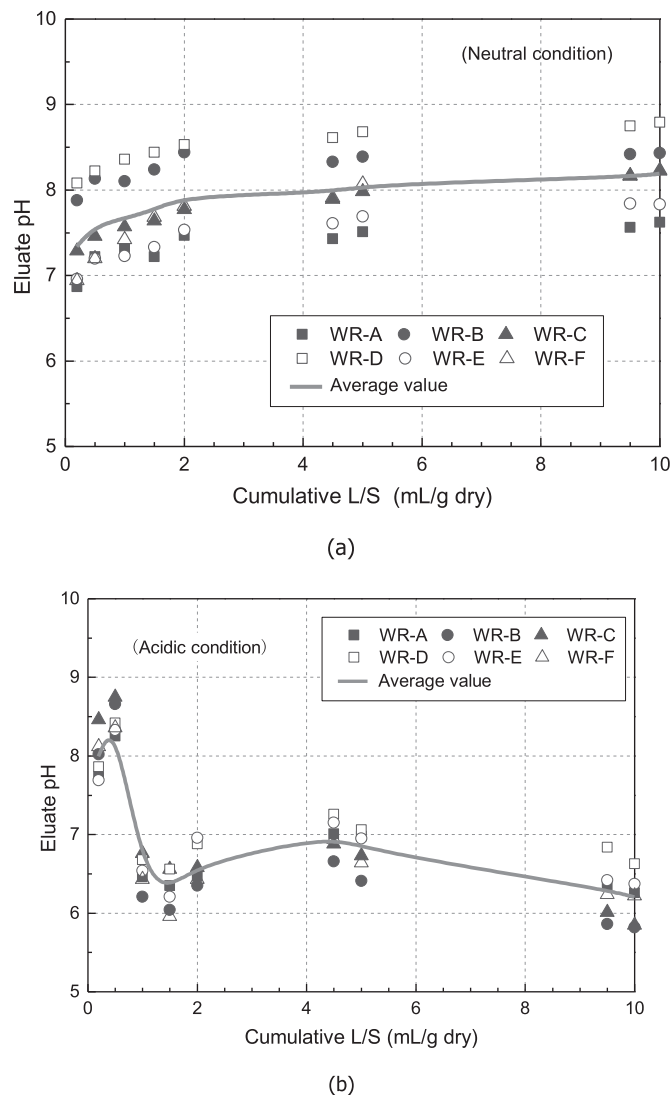


Fig. 2. Eluates' pH of phosphate waste rocks as a function of L/S under different leaching conditions (a) Neutral condition; (b) Acidic condition.

waste rocks. These pyrites may be oxidized and then release hydrogen ions. However, due to the total content of the carbonate minerals is 10 times larger than the sulphide level in sample materials, any acid would be buffered by the abundantly carbonate minerals immediately. Further testing may be required to explain this behavior.

3.1.2. Acidic condition

The pH of eluates leached by acidic eluent varied with cumulative L/S of different phosphate waste rocks, as shown in Fig. 2b. Compared with the results under neutral conditions, the pH of eluates under acidic conditions were quite different. The variation of the mean value (solid line) indicates that the eluates' pH remained in the weakly alkaline range (pH = 7.5–8.5) during the initial leaching period ($L/S \leq 0.5$), the same as under neutral conditions, then sharply descended to 6.5 when $L/S = 1.0-2.0$. After a small increase (approximately 0.5 pH per unit) around $L/S = 5.0$, the eluates' pH decreased to 6.5 again when $L/S = 9.0-10.0$. The initial basic environment may be due to the acid-neutralizing effect of carbonate minerals present in waste rocks. The sharp decline of eluate pH may result from the wash-out effect formed by eluent

advection through the column (Romero et al., 2013; Pantini et al., 2015; Kalbe et al., 2014). It should be noted that the final eluate pH values did not equilibrate with the eluent pH value (4.5), suggesting that the neutralizing effect from carbonate minerals could remain for a long period. Consequently, local acid precipitation would form a slightly acidic inner environment in phosphate waste rocks over both short and long leaching periods.

3.2. Phosphorus leaching behaviors of phosphate waste rocks

The Chinese government classifies general industrial solid wastes in two types, Type I and Type II, according to the environmental sensitivity of the deposition region. As far as the study watershed is concerned, if TP leaching concentration of phosphate waste rock eluates is higher than 0.5 mg/L, then the waste rocks in the watershed should be regarded as Type II solid wastes. It is important to note that an impervious layer and a capping layer must be set in both bottom and top of the waste disposal site if it has been identified as Type II.

3.2.1. Phosphorus leaching behaviors under neutral conditions

The results of the column leaching test can be shown as a function of L/S for element leaching concentrations in eluate (mg/L) and cumulative release on the basis of the total amount included in

the solid sample (mg/kg). The relationship between TP leaching concentrations of different phosphate waste rock samples and cumulative L/S with DI water as eluent is shown in Fig. 3a and Fig. 4a respectively. As shown in Fig. 3a, after the initial relatively higher values, TP leaching concentrations remained constant with cumulative L/S and decreased slightly at the end of the experiments. Compared with the eluate pH under neutral conditions (Fig. 2a), the results indicate that the TP leaching concentration decreased as eluate pH increased, suggesting that the leaching behavior of phosphate waste rock with different weathering ages is solubility-controlled under neutral percolating conditions. In other words, TP leaching concentrations of eluates would be mainly dependent on the pH of the liquid phase which contacting with the phosphate waste rocks. The cumulative phosphorus released from the unit mass of waste rock (mg/kg) over the entire L/S range was plotted in Fig. 4a. As shown in the figure, the cumulative phosphorus release curves of different phosphate waste rocks all followed a slope 1 curve (black solid line). Kosson et al. (2002) pointed out that the results of column leaching experiments could be used to reveal the release mechanism of the species. They concluded that both a constant concentration (mg/L) measured at each time interval and a 1:1 slope in a cumulative leaching curve is indicative of solubility control. Therefore, according to the results of the presented work, the phosphorus release mechanism of the phosphate waste rock is

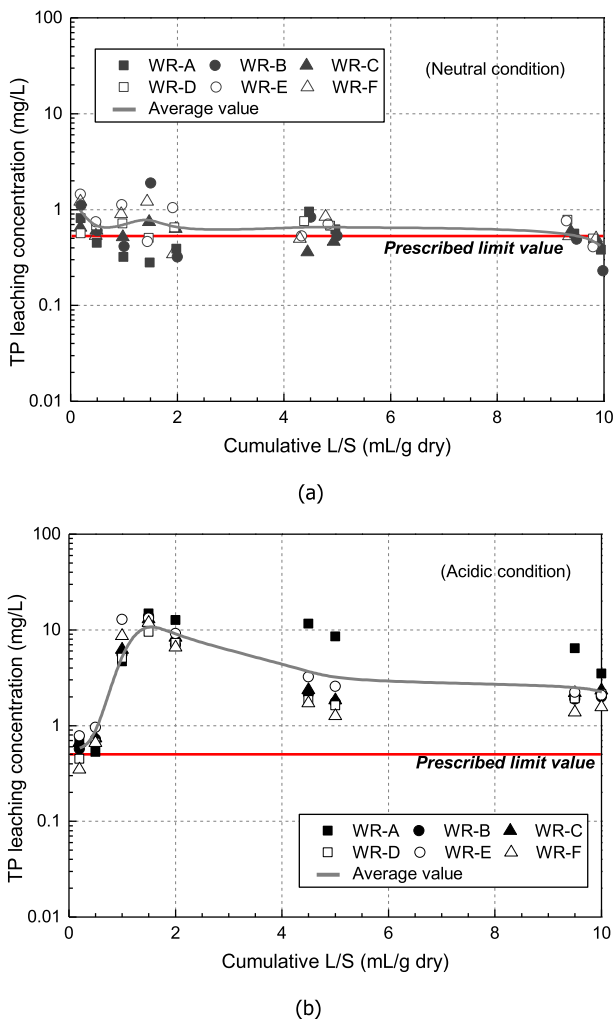


Fig. 3. TP leaching concentration (mg/L) as a function of L/S (a) Neutral condition; (b) Acidic condition.

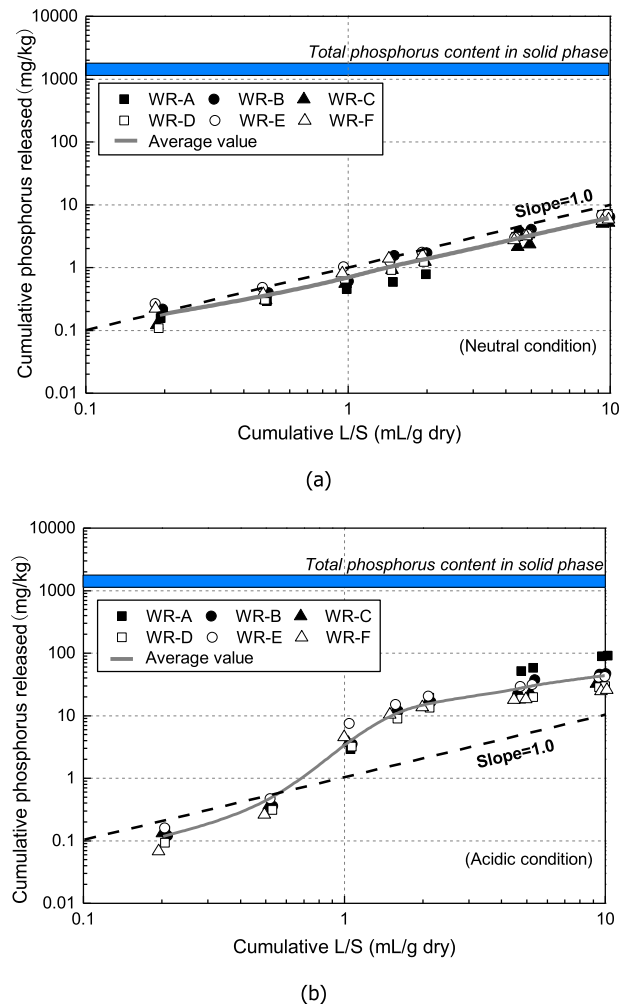


Fig. 4. TP cumulative released (mg/kg) as a function of L/S (a) Neutral condition; (b) Acidic condition.

solubility controlled under neutral conditions, which indicates that the phosphorus would be released from apatite remaining in waste rocks at a constant rate over a long-term leaching period under neutral conditions (i.e., pH = 7.0–9.0).

Comparing the LSP data and identifying species under solubility control or highly soluble species in the eluates of the L/S-based test could be performed by plotting both Method 1314 eluate concentration as a function of pH against analogous results derived from Method 1313 (Garrabrants et al., 2011). TP leaching concentrations from Method 1314 plotted as a function of eluate pH against the statistics data from Method 1313 is shown in Fig. 5a. The statistics data derived from Method 1313 include the mean of the collected values (blue solid squares) and the interval about the mean representing the overall standard deviation interval (blue dash lines). As shown in the figure, TP leaching concentrations from Method 1314 fall along the pH-dependence curve while independent of L/S. Almost all of the data derived from different L/S coverage in the overall standard deviation interval of results under neutral conditions (i.e., pH = 7.0–9.0). Consequently, the comparing results confirm the fact that the solubility of the phosphorus provided by the dissolution of the phosphate mineral (i.e., fluorapatite) present in waste rocks controls the TP leaching concentration through

solid–liquid equilibrium with a saturated solution under neutral condition.

Although the TP leaching concentrations of some individual waste rock samples were lower than the prescribed limit (0.5 mg/L) during part of the column leaching test, the average TP leaching concentrations were higher than 0.5 mg/L over the entire L/S range up to L/S = 10 mL/g. It should be pointed out that the testing method prescribed by Chinese National Standard (CNS, 1999), which is used for classifying solid wastes by type, consists of tumbling a suspension of solid sample and DI water in end-over-end manner at L/S = 10 mL/g. Compared with the TP leaching concentrations shown in Fig. 3a, the results obtained from Chinese National Standard may underestimate the risk of phosphorus contamination. As the largest backwater zone of the TGR, the water of the XXR bay is particularly susceptible to contamination from local industrial solid wastes. Therefore, considering the environmental sensitivity of the study area, the phosphate waste rocks should be regarded as Type II industrial solid waste.

3.2.2. Phosphorus leaching behaviors under acidic conditions

The variations of TP leaching concentration (mg/L) and cumulative phosphorus released (mg/kg) with cumulative L/S under synthetic acidic conditions are presented in Fig. 3b and Fig. 4b respectively. Compared with the eluate pH under acidic conditions (Fig. 2b), the results indicate that the TP leaching concentration increased as eluate pH decreased. The average value of TP leaching concentration reached the maximum value (approximately 12.7 mg/L) at cumulative L/S = 1.5 mL/g, then decreased and maintained in the range of 2–3 mg/L until the end of the experiments. Compared with the results under neutral condition (Fig. 3a), the acidic leaching environment apparently increases the TP leaching concentration. Long-term leaching (i.e., L/S > 5.0 mg/L) under acidic conditions would make the TP leaching concentration increase 4 times (2.6 mg/L), which is more than the prescribed limit value of 2.5 times (0.5 mg/L).

TP leaching concentration in the eluates of the L/S-based test as a function of pH against analogous results derived from pH-dependent leaching tests (i.e., Method 1313) is shown in Fig. 5b. Owing to more eluate pH values under acidic percolating condition distributed in weakly acidic range (Fig. 2b) and the pH-dependent release curve varied sharply from acidic to neutral condition, TP leaching concentration data from Method 1314 behaved more distinct partitioning along the pH-dependent release curve. The result indicates that the leaching concentration of TP is pH-dependent. In other words, phosphorus release from the phosphate waste rock would be dominated by the solubility of phosphate mineral under specified liquid phase pH. Consequently, combining the results of neutral percolating condition, a conclusion that the phosphorus release from phosphate waste rock is solubility controlled could be confirmed unambiguously.

The dissolution characteristics of phosphate rock under acidic conditions are widely discussed, owing to phosphate rock decomposition by sulfuric acid remaining the most widely used method for phosphoric acid production. Over 90% phosphoric acid produced worldwide is manufactured by digestion of phosphate rocks with sulfuric acid (Tekin, 2002; Sinirkaya et al., 2014; Lassus et al., 2015). Direct application of low-grade phosphate rocks is widely used for acidic soil texture improvement, contaminated soil amendment and acid mine drainage restoration, because phosphorus is easily released in an acidic environment (Stiller et al., 1989; Hakkou et al., 2009; Sima et al., 2015).

Phosphorus mineral dissolution is a complex chemical reaction. Taking fluorapatite as an example, the hypothetical reaction resulting in the release of phosphorus (H_2PO_4^-) is expressed as follows (Kanabo and Gilkes, 1987):

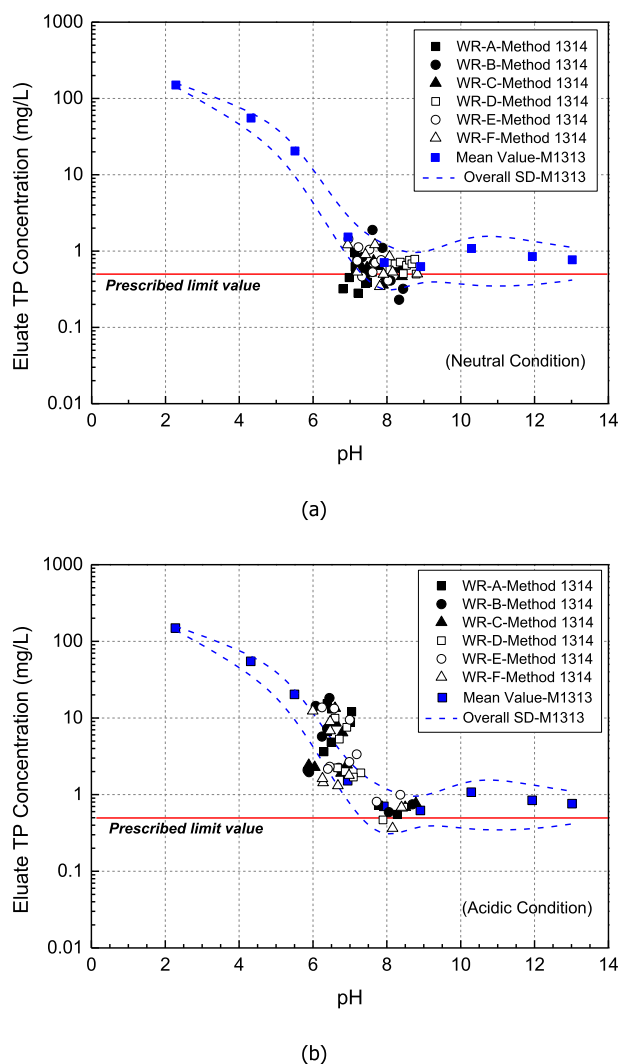
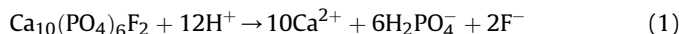


Fig. 5. Consistency check between Method 1314 data and LSP statistics from Method 1313. a. under neutral condition; b. under acidic condition.



According to Eq. (1), the dissolution of phosphate minerals can be increased by increasing the supply of protons (H^+) and by the continuous removed of the dissolved products (i.e., calcium (Ca), fluoride (F) and phosphorus (P)) from the zone of dissolution (Kirk and Nye, 1986). Owing to the calcium and fluoride released from phosphate minerals are not the direct reasons leaching to the eutrophication of the XXR, the TP leaching concentrations were only focused during the tests. A decreased eluate pH indicates that the phosphate mineral comes in contact with an increased concentration of hydrogen ions, thereby transferring more phosphorus into the liquid phase. It should be noted that the reaction between phosphate rocks and acids depends on several factors, including the chemical and mineralogical composition of the phosphate rocks, specific surface area, and the type of acid solution (Calamnovici and Giulietti, 1990). Several studies on phosphate rock dissolution by nitric acid shows that the solubility is very high, and this process avoids the formation of a calcium-rich layer (i.e., phosphogypsum) (Abdel-Aal and Amer, 1995; Olanipekun, 2003). In addition, the calcium and fluoride concentration in the liquid phase can also affect the phosphorus release from the solid matrix (Wong et al., 1987). However, owing to the objective of the present work being phosphorus pollution risk evaluation of phosphate waste rocks under field conditions, the calcium and fluoride leaching concentrations are not analyzed and the influences of these ions on phosphorus dissolution are not discussed here. From Table 2 and Fig. 3b, we can conclude that the TP leaching concentrations are independent of the phosphate mineral mass fraction of the tested samples. The same conclusion can also be found in Rajan et al. (1996). They concluded that the solubility of phosphorus is related closely to the $\text{CO}_3:\text{PO}_4$ ratio of apatite but not to the total P_2O_5 content.

From the relationship between cumulative released TP (mg/kg) and cumulative L/S, the leaching rate of phosphorus is seen to remain a constant value, with a slope approximately equal to 1.0, when $L/S < 0.5$ and $L/S > 4.5$. The phosphorus is released significantly more quickly when L/S in the range of 0.5 and 1.5, which gives a slope greater than 1.0. Compared with the evolution pattern of the eluates' pH (Fig. 2b), the accelerated release period of the phosphorus corresponds to the stage when the eluates' pH turns from weak alkalinity to slight acidity. At the end of the leaching tests, cumulative released phosphorus under acidic conditions exceeded that under neutral conditions by an order of magnitude. Some research points out that acid precipitation in the field has a negligible effect on the inner environment of solid waste landfill sites (Astrup, 2004; Astrup et al., 2006). As mentioned above, the final eluate pH decreased 2 pH units under acidic conditions. However, due to the solubility of phosphate minerals being very sensitive to liquid pH, neglecting the role of field acid precipitation would lead to underestimation of the pollution risk of the phosphate waste rocks dumped in the study area.

4. Conclusions

As a result of excessive nutrients, including phosphorus, in the water, algal blooms emerge frequently in the XXR bay. Since there are abundant phosphate ores deposits within the XXR watershed, the phosphate waste rocks stacked within the watershed and their potential environmental pollution risks should be carefully evaluated. Based on the Method 1314 standard of the Leaching Environmental Assessment Framework (LEAF), this paper investigated the phosphorus leaching characteristics of selected phosphate waste rocks under different percolating conditions. Our results are

summarized as follows:

- (1) The eluate pH analyses showed that the pH of the inner environment of phosphate waste rocks was neutral and/or weakly alkaline (7.0–9.0) in the whole L/S range under neutral conditions. This quickly decreased to a slightly acidic range (6.0–7.0) when $L/S > 1.0$ mL/g under synthetic acid rain percolation conditions, owing to the neutralization of carbonate minerals.
- (2) Compared with neutral conditions, the acidic leaching environment formed by field acid precipitation would lead to higher TP leaching concentration and cumulative phosphorus released. The phosphorus is released faster during the period of eluate pH turning from weak alkalinity to slight acidity. The accelerated release period appeared when the cumulative L/S was approximately in the range of 0.5–2.0 mL/g.
- (3) The results of leaching concentration and cumulative phosphorus released indicated that the phosphorus release mechanism is solubility-controlled. More percolating water does not lead to a dilution effect, while the solubility of phosphate minerals under specific pH conditions determines the phosphorus release. The TP leaching concentration and the cumulative phosphorus released under acidic conditions exceed that under neutral conditions by an order of magnitude.
- (4) In summary, both in neutral and acidic conditions, the average values of TP leaching concentration exceed the prescribed limit (0.5 mg/L) in the whole L/S range, suggesting that the phosphate waste rocks stacked within the XXR watershed could form point phosphorus pollution sources in the XXR water body so they should be considered as Type II industry solid wastes. For the abundant and dispersed existing phosphate waste rock dumps, the in-situ treatment would be an economical approach for preventing phosphorus pollution. Based on the further understanding of the release controlling processes, it can be concluded that covering a capping layer which can prevent acidic water percolation and maintain the weakly alkaline inner-environment pH of waste piles would be an effective treatment method.

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