ORIGINAL ARTICLE

Evaluation of the potential release of phosphorus from phosphate waste rock piles in different environmental scenarios

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Abstract The effect of phosphate waste rocks dumped in the Three Gorges Reservoir Region on water quality has been disregarded. For this reason, the leaching behaviours of six phosphate waste rock piles deposited in Xiangxi River watershed were characterised in this study in accordance with Method 1313 and Method 1316 standards of the Leaching Environmental Assessment Framework to determine the potential release of phosphorus from phosphate waste rocks in different environmental scenarios. Phosphorus leaching characteristics were investigated at pH 2.0–13.0 and at liquid-to-solid ratios ranging from 0.5 mL/g dry material to 10 mL/g dry material. Results indicated that higher amounts of phosphorus were likely released from waste rocks in acidic environments than in neutral or basic environments. Phosphorus released in acidic environment was determined as one or two orders of magnitude greater than that in neutral or basic environment. Although the paste pH of waste rocks was maintained in a weakly basic range (7.5–9.0) by long-term leaching effect, liquid-phase concentrations of phosphorus released by most waste rocks exceeded the availability threshold (0.5 mg/L), as influenced by short- and long-term leaching. In addition, the chemical equilibrium between acid neutralisation capacities of waste rocks and local acid rain could be a dominant factor in phosphorus leachability affected by long-term leaching. Therefore, phosphate waste

rocks deposited in the study areas should be considered as phosphorus point pollution sources, which could threaten adjacent surface water environments. As such, future management practices would be highly effective if water infiltration could be prevented and inner environment pH of waste rock piles could be maintained at paste pH.

Introduction

Water eutrophication commonly occurring in the Three Gorges Reservoir (TGR) has been extensively investigated. The monitoring data promulgated by Ministry of Environmental Protection of the People's Republic of China indicate that varying degrees of algal blooms occur every year in backwater areas of the 12 first-level branches of Yangtze River after TGR impounding was completed; furthermore, algal blooms have seriously affected Xiangxi River (XXR) (Xiong et al. 2013; Zhang et al. 2012; Ye 2006; Shao et al. 2014). For example, algal blooms occurred five times in midstream and/or upstream of XXR in spring and summer 2010 (Zheng et al. 2011; Li et al. 2012). Chen (2013) and Tian et al. (2012) analysed the causes of XXR aquatic ecosystem deterioration after TGR impounding occurs; Chen (2013) and Tian et al. (2012) indicated that the large amount of nutrients contained in XXR water body is a predominant cause of the frequent occurrence of algal blooms. Based on water quality monitoring data, the annual concentrations of total nitrogen (TN) and total phosphorus (TP) of XXR are 1.41 and 0.17 mg/L, respectively. Furthermore, more than 1,600 tons TN and 330 tons TP released from different

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point and/or nonpoint pollution sources enter XXR every year (Song et al. 2013; Li et al. 2008; Qiu et al. 2008). Surface runoff water from fertilised farmlands can generate primary non-point pollution sources, whereas untreated domestic and/or industrial wastewater discharged directly may produce point pollution sources in XXR watershed (Chen et al. 2013; Mei et al. 2012; Tang et al. 2014; Fang et al. 2006). However, few individuals have considered the influence of phosphate mining activities in the watershed on water eutrophication in XXR.

Abundant industrial reserves of phosphate resource are present in Yichang City. Yichang City contains more than 9 billion tons of recoverable phosphate ore deposits, which approximately account for 38 % of the total phosphate ore reserves in Hubei Province (Xia et al. 2011). Most phosphate ore deposits are classified as high-grade phosphate resources, that is, the phosphorus pentoxide content of the ore body is >30 %. The history of phosphate resource exploitation in Yichang City can be traced back to the 1960s. Considering the rapid development of phosphate mining industry in the past few decades, more than 137 phosphate mining areas were established in Yichang City and more than 6 million tons of phosphate ores were produced in 2000 (Li 2000). However, the environment has been disrupted and Yichang phosphate mining areas have been polluted as a consequence of the rapid development of phosphate mining industry because of the lack of exploitation planning and environmental protection regulations. Many phosphate mining areas have exploited high-grade ore bodies. Furthermore, low-grade phosphate rocks are discarded as waste rocks and then casually dumped in mining areas. For example, 74 phosphate waste rock piles were formed in Yiling District in 2012. More than 2.6 million tons of phosphate waste rocks were also stacked directly without any restoration or coverage. Unfortunately, most of these phosphate waste rocks were casually dumped in and/or nearby seasonal rivers (Guo et al. 2012). These phosphate waste rocks may continuously release phosphorus, as affected by short- and long-term leaching triggered by local rainfall; thus, a large amount of point pollution sources may be produced in adjacent surface waters. Therefore, phosphate waste rocks stacked in the watershed should be considered as potential phosphorus discharging sources; moreover, the pollution risk posed by these waste rocks should be evaluated.

This research primarily aimed to investigate the potential release of phosphorus from phosphate waste rocks in different environmental scenarios. Six representative phosphate waste rock piles dumped in the XXR watershed were selected as study objects. A series of parallel batch leaching experiments were conducted in accordance with the Leaching Environmental Assessment Framework (LEAF) methodology recently developed by the United

States Environmental Protection Agency (US EPA). Further insights into phosphorus leaching behaviours in different environmental scenarios should be provided to design risk assessment of phosphate waste rocks. In addition, the results of this study will allow engineers to develop effective remediation techniques and solutions.

Materials and methods

Site description and phosphate waste rock sampling

The three branches of XXR are Gaolan River (GLR), Gufu River (GFR) and Jiuchong River (JCR). The main stream of XXR crosses the Xingshan County from north to south, intersects GLR at Xiakou Town and finally empties into Yangtze River in Xiangxi Town (Fig. 1). The total length of the main stream of XXR is approximately 94 km. The geographical position of the XXR watershed is at $30°37'$N–$31°34'$N and $110°25'$E–$111°06'$E and spans 3,000 km^2. The local climate type of the watershed is characterised as subtropical continental monsoon climate. Based on the local statistical precipitation data of the past 20 years (i.e., 1990–2009), the average annual rainfall, evaporation and temperature were approximately 956, 1,344 mm and 17.1 °C, respectively (Zhang et al. 2013).

Field collections of phosphate waste rock samples were conducted in summer 2012. Six phosphate waste rock piles stacked in Shu Kong-ping phosphate mining area were selected as the study objects (Fig. 1). The Shu Kong-ping mining area is operated by Hubei Xingfa Chemicals Group Co., Ltd., which is the largest phosphorus chemical enterprise in Hubei Province. The mining area is located on the border of Xingshan County and Yiling District and is geographically a part of the GLR watershed. Based on previous geological investigations, the phosphate rock stratum (Ph_1^{3-3} and Ph_1^{3-2}) deposited in the area can be classified under the Upper Sinian System, Doushantuo Formation. The lithology of phosphate ores is mainly composed of phosphorite with dolomite and mudstone (Zheng and Dongye 1994; Yang et al. 2008).

Four waste rock piles (WR-A, WR-B, WR-C and WR-E) were dumped in a "valley-filled" mode and two waste rock piles (WR-D and WR-F) were piled in a "hill-slide" mode. These two modes are commonly used to stack waste rock piles in the mining area. The total area of each waste rock pile ranges approximately from 0.4 to 1.4 km^2. Parallel line sampling method was used in field sampling. The sampling lines were set in the field approximately parallel to the top surface of the selected piles. More than four sampling points were randomly selected on each line. At least 2 kg of waste rocks from 5 to 20 cm of the surface were collected at each point. Rocks with a particle size

Fig. 1 Location of Xiangxi River watershed and sampled waste rock piles
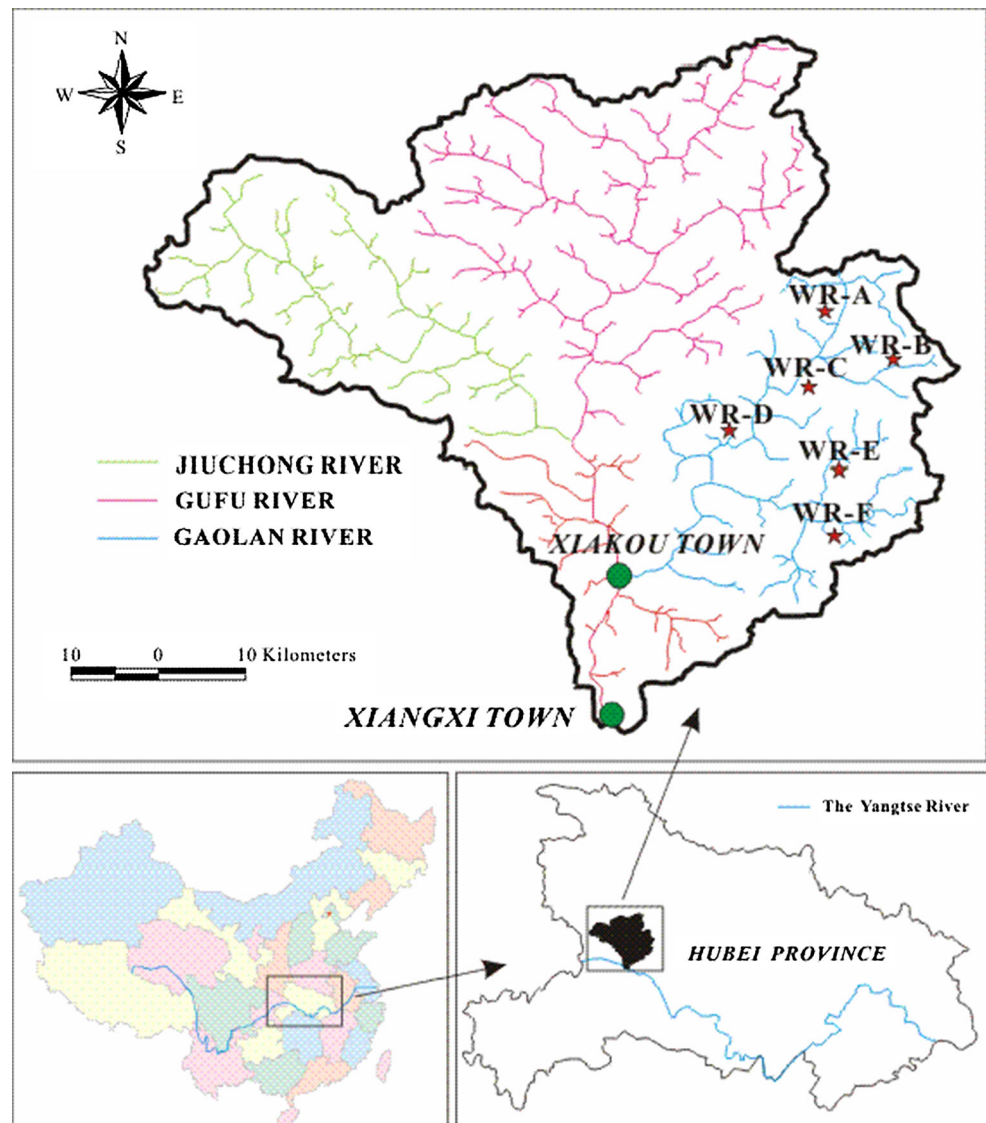
>20 mm were discarded and only small waste rock particles with a particle size <20 mm were collected and labelled as WR-A to WR-F in the field because the particle size of waste rock is heterogeneous (Table 1).

Experimental methods

Preprocessing of the samples in the laboratory

Each type of waste rock sample was screened using a 60-mesh sieve and then air-dried at room temperature (20 ± 2 °C). A jaw crusher and a rock grinder were sequentially used to reduce the particle size of oversized samples to ensure that 80 % of the materials passed through the sieve. Afterwards, ground samples were homogeneously mixed and sealed in plastic bags for subsequent tests and analyses.

Moisture content was determined using a procedure based on ASTM D2216-10 (2010). The water contents of the six air-dried waste rocks are listed in Table 1. A Phillips PW 3710-based X-ray diffractometer with a Cu tube anode, generator tension of 40 kV and current of 20 mA was used to analyse the crystal line forms present in WR-A to WR-F samples.

Leaching test methods

Leaching characterisations of phosphate waste rocks were conducted in accordance with the LEAF methodology promulgated by the US EPA. The entire framework of LEAF consists of four leaching methods, including Method 1313 to Method 1316. These methods are based on the chemical equilibrium condition between liquid and solid phases. In this study, Method 1313 and Method 1316 were

Table 1 Description of waste rock samples and their sampling sites

Sample site	Stacking mode	Dump height (m)	Area (km^2)	Number of sample line	Number of sample points	Moister content after air-drying (%)
WR-A	Valley-filled	8.9	0.8	5	20	2.5
WR-B	Valley-filled	10.6	1.4	5	20	0.7
WR-C	Valley-filled	6.5	0.6	4	18	0.7
WR-D	Hill-slide	6.2	0.4	4	16	0.5
WR-E	Valley-filled	9.7	0.8	5	20	3.4
WR-F	Hill-slide	5.5	0.5	4	16	0.9

selected as leaching test protocols because some experimental conditions established in both methods are also required in the Chinese National Standards. Therefore, the results of this study can be used not only to evaluate the potential release of phosphorus in different specific environmental scenarios but also to provide fundamental references for local environmental protection departments to identify whether phosphate waste rocks can form phosphorus pollution sources under specified conditions.

pH-dependent leaching tests (Method 1313)

Method 1313 (liquid–solid partitioning as a function of extract pH by using a parallel batch extraction procedure) consists of nine parallel batch extractions of a particle size-reduced solid material in dilute acid or base solution to achieve final extract pH values at specific target values (pH 13.0, 12.0, 10.5, 9.0, 8.0, natural, 5.5, 4.0 and 2.0). Solid material subsamples equivalent to 20 g of dry mass were separately added to nine 250 mL leak-proof high-density polyethylene (HDPE) bottles. Nine types of reagent water composed of deionised (DI) water and acid or base solution were injected into the bottles at the specified acid/base addition schedule to achieve a final liquid-to-solid (L/S) ratio of 10 mL/g dry material and specific target pH values. The extraction bottles were tumbled in an end-over-end manner at 28 ± 2 rpm for 24 h. At the end of extraction, the bottles were allowed to stand for 15 min and then centrifuged at 4,000 rpm for 15 min. The liquid supernatant was collected and separated by a combination of pressure and vacuum filtration with 0.45 μm polypropylene filter membrane. The filtered samples were acidified to pH <2 using sulphuric acid and stored in an environment at constant temperature (4 °C) until analysis.

The acid/base addition schedule for each type of sample was formulated before regular leaching procedures were conducted. In general, two approaches were used to obtain the acid/base addition schedules for the specific tested samples: (1) prior geochemical knowledge or database of the samples and (2) a group of acid and base pre-titration tests. A set of acid and base pre-titration tests for each type

of phosphate waste rocks was performed for the acid/base addition schedules used in regular leaching tests because of the lack of previous information on phosphate waste rocks deposited in Yichang phosphate mining area. In this study, the acid and base pre-titration tests were conducted on the basis of DIN CEN/TS 14429 (2006), Annex C, which requires a final L/S ratio of 10 mL/g after acid or base is added. Approximately 10 g of dry mass solid samples was separately placed in six 250 mL leak-proof HDPE bottles. DI water was then added to establish an L/S ratio of approximately 9.0 mL/g dry material. Three bottles were used in acid pre-titration tests and the remaining bottles were used in base pre-titration tests. After manual titration with small volumes of acid or base solutions was conducted, the bottles were tumbled for 30 min and then allowed to settle for 10 min; afterwards, the pH values of the eluates without centrifugation and filtration. Titration–agitation measurement was performed continuously until the target pH or low pH values were obtained. The equilibrium condition at the target pH could be calibrated when the distance between the obtained pH values was less than 1.5. If the L/S ratio exceeds 11 mL/g because of high acid or base consumption of the material at the specific pH value, then a stronger acid or base solution should be used to adjust pH. In this study, 1 N NaOH and 1 N HNO_3 were selected for acid and base additions. Based on the extensive range (i.e., pH 2–12) of target pH values required in regular leaching tests, the target pH values in pre-titration tests were set at 2.0, 4.0, 5.5, 10.5, 12.0 and 13.5. Acid and base additions and the obtained pH values were recorded after each titration was conducted. The acid/base titration curve of each sample was evaluated by plotting the final titration target pH value of each eluate as a function of milliequivalents of acid added per gramme of dry solid material (meq/g). Based on the acid/base titration curve, the acid/base addition schedule of a specific sample could be expressed as follows:

$$V_{a/b} = \frac{Eq_{a/b}}{N_{a/b}} \times M_{tested},$$

where $V_{a/b}$ is the volume of acid or base to be added in the regular extraction procedure (mL); $Eq_{a/b}$ is the equivalent

of the acid or base selected for the target pH value, as determined from the pretest titration curve (meq/g); $N_{a/b}$ is the normality of the acid or base solution (meq/mL); and M_{tested} is the equivalent mass of the dry material used for the regular extraction procedure (g).

L/S ratio-dependent leaching tests (Method 1316)

Method 1316 (liquid–solid partitioning as a function of liquid-to-solid ratio in solid materials using a parallel batch procedure) consists of five parallel batch extractions at a range of L/S ratios (i.e., 0.5, 1, 2, 5 and 10 mL/g dry material). The eluent with a constant volume of 200 mL used in each test portion was composed of sample moisture and DI water. The equivalent masses of the dry material used in the tests were 400, 200, 100, 50 and 20 g to preserve the L/S ratio at specified values. Extraction procedure, contact time, experimental temperature, liquid–solid separation methods and preservation specified in Method 1316 were similar to those indicated in Method 1313. Extraction using the waste rock samples was not conducted at L/S of 10 mL/g in this study because the same leaching results under "natural condition" in Method 1313 were obtained using Method 1316.

A total of 96 leaching experiments, including 72 extractions based on Method 1313 and 24 extractions based on Method 1316, were conducted.

Eluate pH values were measured using a laboratory pH meter (SC210, glass composite electrode, STARTER 2100/3C Pro, Ohaus). The concentration of total phosphate (TP) was measured using an ultraviolet–visible spectrophotometer (DR 5000, HACH) in accordance with the procedures of PhosVer 3 with acid persulfate digestion, Test'N Tube. 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 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-}).

Results and discussion

X-ray diffraction for mineral characterisation

The mineralogy characteristics of the six types of phosphate waste rock samples are presented in Table 2. The variable content of fluorapatite detected in all of the tested samples indicates that some phosphate ores are commonly present in waste rock piles. These phosphate ores may originate from ore sorting or discarded phosphate ore layers with low exploitation values. Calcite and dolomite as main gangue minerals with different content values were also present in all of the samples. The mineralogical difference between different samples could possibly be related to variable degrees of weathering in waste rock piles with different ages.

Pre-titration curve of phosphate waste rocks

The acid and base neutralisation behaviours of different phosphate waste rocks are shown in Fig. 2. The green solid circle dots represent the pre-titration results of each type of phosphate waste rock sample. Base equivalents are presented as the opposite sign of acid equivalents. The blue solid up-triangle dots represent the final pH values in regular extractions. The final pH values of each type of sample obtained in regular extractions satisfied the target pH value with available deviation (±0.5 pH unit; Fig. 2). All of the waste rock samples generally showed acid-buffering capacities at approximately pH 5.5. The acid addition (corresponding to 0.5 meq/g) caused a significant decrease in pH to approximately 5.5 units, at which a plateau was observed in each sample. The results could be probably explained by the equivalence pH point of

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

Minerals	Formula	Percentage by weight (%)					
		WR-A	WR-B	WR-C	WR-D	WR-E	WR-F
Quartz	SiO_2	34.46	28.23	37.28	42.84	20.05	38.73
Fluorapatite	$Ca_{10}(PO_4)_6F_2$	6.22	18.20	16.44	14.73	11.72	5.81
Dolomite	$CaMg(CO_3)_2$	20.63	16.54	18.43	16.28	20.49	17.09
Calcite	$CaCO_3$	19.29	6.73	7.04	16.11	12.84	9.61
Illite	$(K,H_3O)(Al,Mg,Fe)_2(Si,Al)_4O_{10}[(OH)_2,(H_2O)]$	6.48	5.28	N/A	0.98	N/A	11.37
Albite	$NaAlSi_3O_8$	5.44	2.98	N/A	N/A	16.46	N/A
Clinochlore	$(Mg,Fe)_3(Si,Al)_4O_{10}(OH)_2·(Mg,Fe)_3(OH)_6$	N/A	N/A	12.69	4.09	13.72	N/A
Others		7.48	22.03	7.58	4.97	4.68	17.38

Fig. 2 Titration *curves* produced by adding acid/base to 10.00 g-dry waste rocks, L/S 10 mL/g-dry material

(a) WR-A

(b) WR-B

(c) WR-C

(d) WR-D

(e) WR-E

(f) WR-F
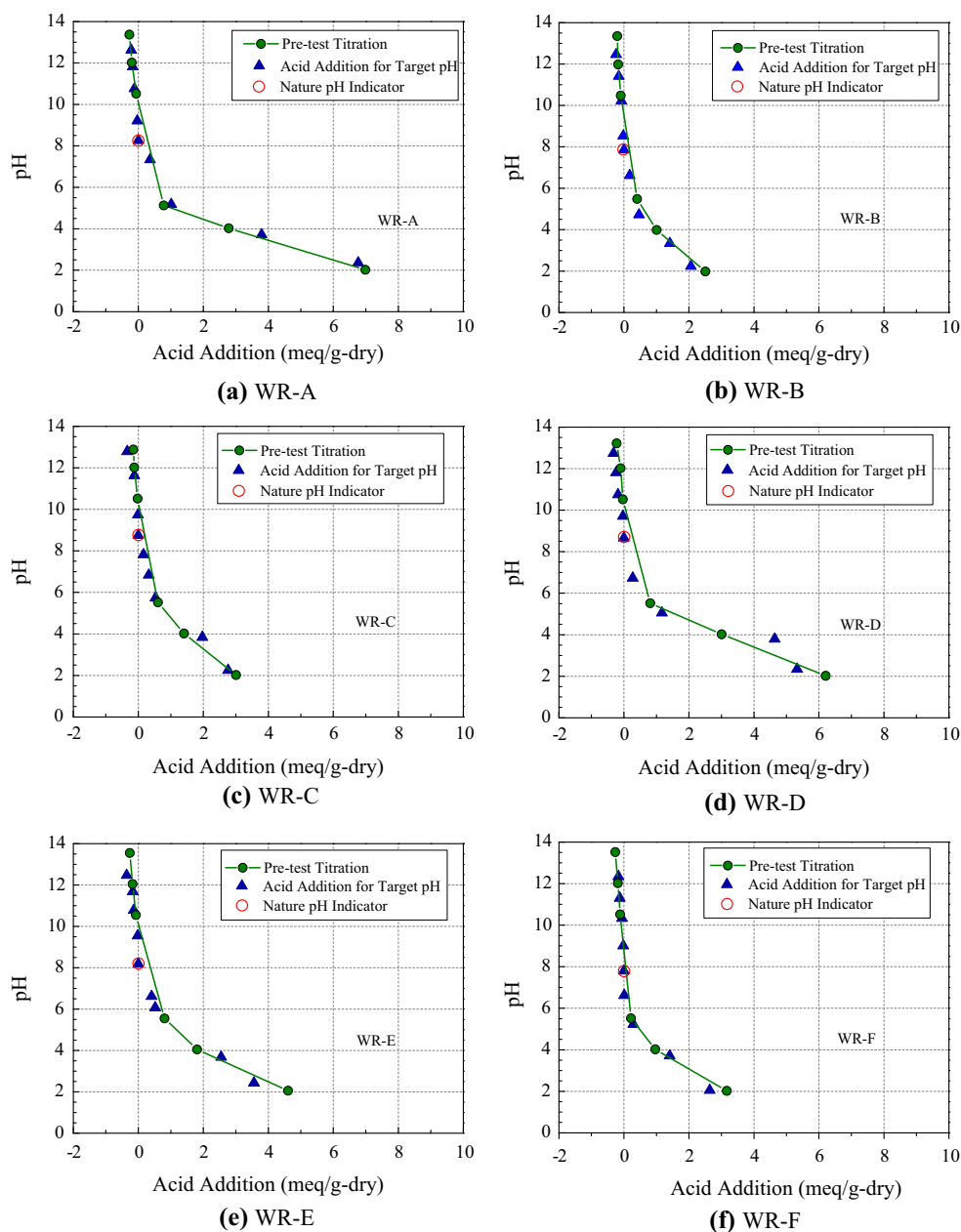
carbonate/bicarbonate minerals at approximately pH 5.5 (Baciocchi et al. 2008; Wahlström et al. 2009; Galvín et al. 2014). The acid-buffering capacities at approximately pH 5.5 of WR-A and WR-D were stronger than those of other samples because of numerous calcite and dolomite contained in WR-A and WR-D (Table 2).

Influence of pH on leaching behaviours

Figure 3 shows the leaching behaviours of different phosphate waste rocks, and leached phosphorus is depicted as eluate total phosphorus (TP) concentration (mg/L) as a function of pH conditions. The results indicated that the acidic environment could influence phosphorus release more significantly than neutral and basic environments. The phosphorus released under acidic conditions was one or two magnitudes greater than that under neutral and basic conditions. The highest TP concentration in different waste rock eluates varied from 139.00 mg/L (WR-F) to 161.50 mg/L (WR-C) at the lowest specified pH (pH 2.0 ± 0.5). Hattaway et al. (2013), Du et al. (2012) and Thorneloe et al. (2014) indicated that the constituent of potential concern (COPC) concentration at approximately pH 2 can be used as an indicator to estimate the total or
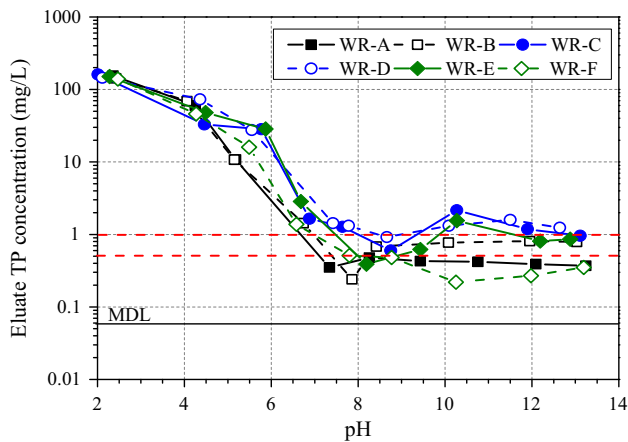
Fig. 3 Comparison of leaching as a function of pH for different phosphate waste rocks

Fig. 4 Eluates pH as a function of L/S for different phosphate waste rocks

available content of COPC in a solid matrix. Hence, the phosphorus content in the solid phase of different waste rocks could be estimated at a range of 1.39–1.62 g/kg.

Apatite dissolution is a complex chemical reaction. The hypothetical reaction resulting in the release of $H_2PO_4^-$ and Ca^{2+} is expressed as follows:

$$Ca_{10}(PO_4)_6F_2 + 12H^+ \rightarrow 10Ca^{2+} + 6H_2PO_4^- + 2F^-. \tag{1}$$
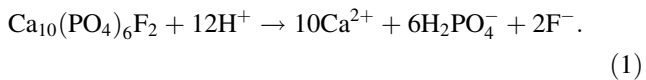
The chemical reaction implies that fluorapatite dissolution can be enhanced by increasing the supply of protons (H^+) (Somasundaran 1968; Khasawneh and Doll 1978; Chander and Fuerstenau 1982; Somasundaran and Wang 1984). A decreased pH value indicates that apatite comes in contact with an increased concentration of hydrogen ions, thereby transferring more phosphorus into the liquid phase, as indicated by the leaching method based on EPA Method 1313 that aims to achieve constituent equilibrium liquid–solid partitioning under specified static pH conditions. Studies focusing on direct long-term application of phosphate rocks in acidic soils for crops have concluded that acidic environments can enhance phosphorus release (Le Mare 1991; Akande et al. 2005; Uwumarongie-llori et al. 2012). On the basis of dissolution kinetics, Guidry and Machkenzie (2003) also reported that the release rates of fluorapatite soluble components (calcium, phosphorus and fluoride) likely increase by decreasing pH under acidic conditions.

Phosphate waste rock is considered as a heterogeneous mineral system because of the presence of abundant calcite and dolomite (Table 2). The eluate chemical compositions of phosphate waste rocks were possibly dominated by chemical equilibrium states of the calcite–apatite–dolomite system under different pH conditions. Somasundaran et al. (1985) discussed the chemical equilibrium states of the calcite–apatite–dolomite system under closed and open
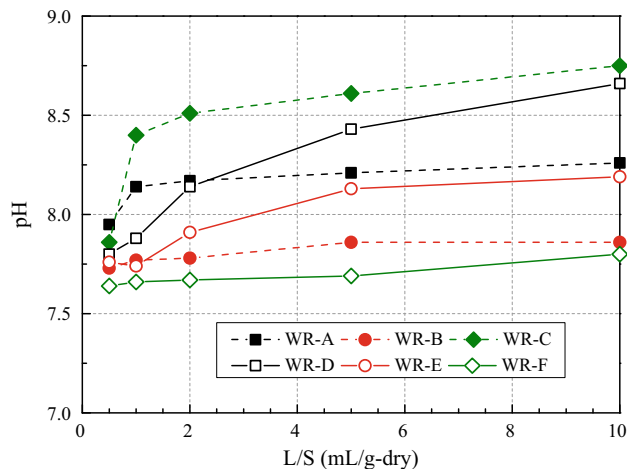
conditions. Their conclusions indicate that dolomite is more stable than apatite at pH >9.2 under closed (10^{-3} - kmol m^{-3} carbonate) conditions; by contrast, apatite is most stable in a pH range of 8.2–9.2. The variation of apatite equilibrium states at approximately pH 9.2 could explain the apparent increase in TP concentrations of WR-B, WR-C and WR-E with pH >9.0 (Fig. 3). In fact, mineral systems would be open to the atmosphere under field conditions. Therefore, the equilibrium states of the calcite–apatite–dolomite system are unlikely influenced by carbon dioxide partial pressure. In this situation, apatite is more unstable than calcite and dolomite at pH >9.0 (Somasundaran et al. 1985). Therefore, higher amounts of phosphorus would be released under field conditions than under laboratory conditions.

Iron and calcium are among the most abundant metals found in gangue minerals of the phosphate rocks in Yichang mining area (Luo 2007). Although Fe oxide (Fe_2O_3) represents potential sorption sites for phosphorus, the ability of Fe_2O_3 to retain phosphorus is reduced at increased pH because of ion exchange of phosphate with hydroxide ions (Hartikainen et al. 1996; Stumm and Morgan 1995; Batziaka et al. 2008). However, the calcium content in eluates probably binds phosphorus as $Ca_3(PO_4)_2$, and increased $CaCO_3$ precipitation can lead to co-precipitation or adsorption of phosphates under basic conditions. The two reactions (ion exchange and precipitation with Ca) act antagonistically, and the result depends on the degree of participation of each reaction.

Influence of the L/S ratio on leaching behaviours

Figure 4 shows the paste pH evolutions of different phosphate waste rock samples as a function of the L/S ratio after chemical equilibrium is achieved under natural conditions.
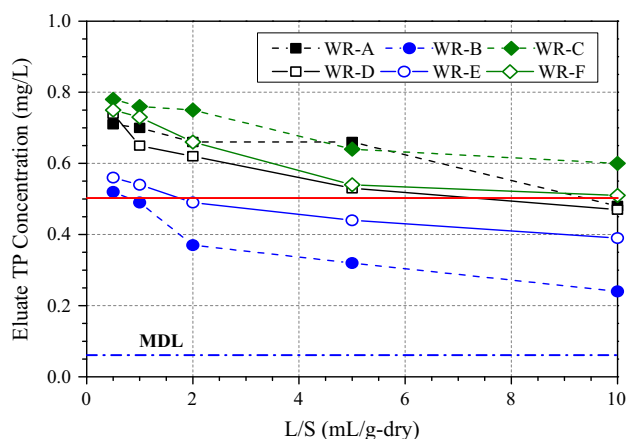
Fig. 5 Comparison of phosphorus LSP *curves* as a function of L/S for different phosphate waste rocks
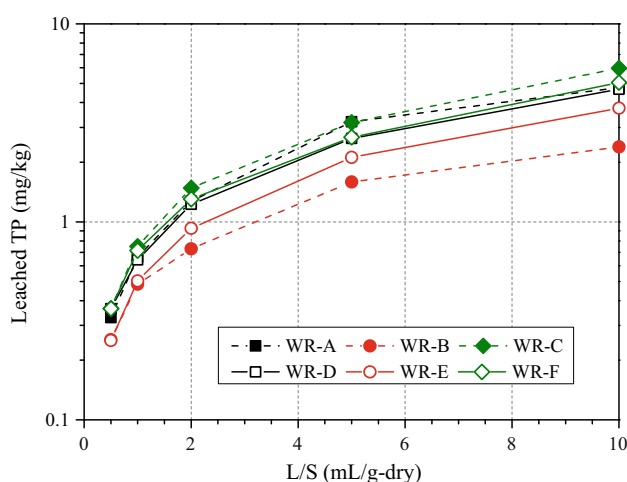

Fig. 6 Comparison of leached phosphorus as a function of L/S for different phosphate waste rocks

The paste pH of the waste rock samples was generally present as weakly basic varying from 7.5 to 9.0; furthermore, the paste pH increases slightly as L/S ratio increased, indicating that natural paste pH values of different waste rocks would not be easily affected by L/S ratio. The saturation pH value of the fluorapatite solution was 7.40 under closed conditions, and this value is less than the experimental results (Larsen and Jensen 1986; Larsen 1986). The discrepancy is probably due to the dissolution of alkaline gangue minerals (i.e., calcite and dolomite), which are characterised by equilibrium solution pH values >9.73 under closed conditions (Pokrovsky et al. 2005).

Figures 5 and 6 illustrate the released phosphorus from different phosphate waste rocks under different L/S ratio conditions. Phosphorus leachability was presented as liquid phase concentration (mg/L) and leached amount from per unit mass of solid materials (mg/kg). TP concentrations in the liquid phase of the phosphate waste rocks decreased as

L/S ratio increased (Fig. 5). For solid waste materials leaching under natural conditions, L/S ratio is defined as the ratio between the volume of eluant and the mass of solid material, which represents the cumulative volume of rainwater that infiltrated the wastes during a specific period. Thus, different L/S ratios can correspond to the leaching duration of a specific waste storage body under field conditions (Walek et al. 2008; Eldyasti et al. 2010). Garrabrants et al. (2010) proposed that an L/S ratio of 5 mL/g can be considered as the cutoff point of short-term and long-term leaching behaviours of solid materials. For instance, the eluate chemical composition obtained at less than 5 mL/g can indicate the short-term leaching behaviour of solid materials. Concentrations at an L/S ratio ≥5 mL/g may correspond to the long-term leaching behaviour of solid materials. The experimental results of this study showed that eluate TP concentrations of WR-A, WR-C, WR-D and WR-G samples were greater than 0.5 mg/L at an L/S ratio of <5 mL/g; this result indicated that phosphorus released by short-term leaching may threaten the surface water body near phosphate waste rock piles. Long-term leaching (L/S ratio >5 mL/g) could reduce the eluate TP concentrations of the waste rock samples to varying degrees. The eluate TP concentrations of WR-A and WR-D at an L/S ratio of 10 mL/g were less than but almost close to the cutoff value of 0.5 mg/L (0.48 mg/L for WR-A and 0.47 mg/L for WR-D).

The leached amounts of phosphorus from phosphate waste rocks increased as L/S ratio increased, in contrast to the variation tendency of eluate TP concentration (Fig. 6). This finding indicated that higher amounts of infiltrated water would enhance the dissolution of apatite existing in the waste rocks. The eluate of phosphate waste rock is considered as a heterogeneous mineral system because abundant calcite and dolomite are present. Therefore, the chemical equilibrium state of the calcite–apatite–dolomite system could determine the eluate compositions of different phosphate waste rocks; this chemical equilibrium state could also dominate dissolution/precipitation geochemical processes on the surface of solid particles. Somasundaran et al. (1985) also demonstrated that the chemical stabilities of the main gangue minerals of phosphate waste rocks (calcite, apatite and dolomite) likely depend on system pH value. In this study, the eluate pH values of different phosphate waste rocks were in the range of 7.5–9.0 under the closed experimental condition (Fig. 4). Under this condition, apatite was the most stable mineral of the system, indicating that the surface of the apatite particle would be converted to calcite and/or dolomite and possibly formed a precipitation film. Studies have confirmed the presence of this surface precipitation film and established a "shrinking core model" to demonstrate the diffusion-controlled mechanism of phosphorus released from apatite

(Ashraf et al. 2005; Kandil et al. 2010; Heydarpour et al. 2011). Thus, high amounts of water-containing phosphate waste rocks at L/S ratios could enhance the turbulent flow of the liquid phase and release high amounts of phosphorus into the liquid phase.

The main stream and the branches of XXR are classified as a Type II water body in accordance with the Chinese National Standards (GB 3838-2002 2002). As such, the eluate phosphorus concentrations (expressed as TP concentration) of phosphate waste rocks located in the XXR watershed should not be higher than 0.5 mg/L. Furthermore, if the TP concentration of phosphate waste rock eluate exceeds 0.5 mg/L, then the phosphate waste rock should be considered as "Class II" solid wastes, and surface coverage layers and/or bottom impermeable layers should be constructed as storage fields to prevent environmental pollution in accordance with the Chinese National Standards (GB 18599-2001 2001 and GB 8978-1996 1996). In addition, the solid waste extraction method specified in the Chinese National Standards is the same as Method 1316. Solid waste is extracted at an L/S ratio of 10 mL/g. The experimental result obtained at this L/S ratio represents the long-term leaching effect of solid wastes. All TP concentrations of eluates except WR-C and WR-G were less than 0.5 mg/L at an L/S ratio of 10 mL/g (Fig. 5). However, the TP concentrations of the tested sample eluates except WR-B and WR-E were higher than 0.5 mg/L at L/S ratio of <10 mL/g. These observations indicated that the leaching results based on Chinese National Standards may underestimate the environmental pollution risk of phosphate waste rocks. Therefore, most phosphate waste rocks stored in the XXR watershed should be considered "Class II" industrial solid wastes, which may release a large amount of phosphorus by short- and long-term leaching. Specific prevention and control treatments of phosphate waste rocks should be conducted to reduce environmental pollution risk.

Severe acid rain in Yichang City should be emphasised. Based on environmental monitoring data published by the Hubei Environmental Protection Bureau, the frequency of acid rain in Yichang City was as high as 69 % in 2012, and the average rain pH value was 4.86. Although acid rain-buffering effects could be generated because of the alkaline minerals present in waste rocks (Table 1), the acid neutralisation capacities of the tested samples did not show strong acid-buffering effects at approximately pH 6.0. The pre-titration curves of the waste rocks indicated that the acid equivalent requirements to maintain the eluate pH in the range of 5.0–6.0 were less than 1 meq/g dry material (Fig. 2); this result indicated that local acid rain would change a weakly basic environment of waste rock piles to a weakly acidic environment in a short time (David 1997; Hakkou et al. 2009; Quina et al. 2009). The variations in TP concentrations are sensitive to acidic environments (Fig. 3). Thus, if the inner environment of phosphate waste rock piles becomes acidic, then a large amount of phosphorus would be released from solid phase to liquid phase, thereby causing severe phosphorus pollution. The total phosphorus concentrations of all samples, which correspond to the allowable maximum concentration of total phosphorus that can be emitted for any type of water body (GB 3838-2002 2002), were even higher than 1.0 mg/L at approximately pH 6.0. Therefore, pH of water infiltration should be adjusted and neutralised to effectively control the phosphorus content of phosphate waste rocks subjected to dissolution or transportation.

Conclusions

As a consequence of excessive nutrient amounts contained in a water body, algal blooms occur frequently in XXR after TGR impounding is completed. As such, large amounts of phosphate waste rocks stacked in watersheds and potential environmental pollution risks should be carefully evaluated because of abundant phosphate ores deposited in the XXR watershed. In this study, the leaching characteristics of phosphorus from selected phosphate waste rocks in different environmental scenarios were investigated in accordance with Method 1313 and Method 1316 standards of the LEAF methodology. The results revealed that phosphorus released from waste rocks was quite sensitive to environmental pH. Phosphorus released in acidic environments increased as pH decreased. The TP concentrations of eluates in acidic environments were one or two orders of magnitude greater than those in neutral or basic environments. Regardless of the effect of environmental pH, the paste pH of phosphate waste rocks was maintained in a weakly basic range (7.5–9.0) and was not easily affected by leaching duration because of relatively high contents of carbonate gangue minerals. In general, the TP concentrations of eluates decreased; by contrast, phosphorus leachability of waste rocks increased as leaching duration was prolonged. The waste rocks also showed acid-buffering capacities at approximately pH 5.5. Acid neutralisation capacities likely increased as carbonate mineral contents of the waste rocks increased. These results indicated that the leaching test method specified by the Chinese National Standards underestimated the environmental pollution risk of phosphate waste rocks. The phosphorus extract concentrations of most waste rocks exceeded the availability threshold (0.5 mg/L), as influenced by short- and long-term leaching. In addition, all of the phosphate waste rocks deposited in the study areas should be considered as phosphorus point pollution sources, which could threaten the adjacent surface water

environment. Therefore, future management practices would be highly effective if these practices involve the prevention of water infiltration and the maintenance of inner environment pH of waste rock piles at paste pH.

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