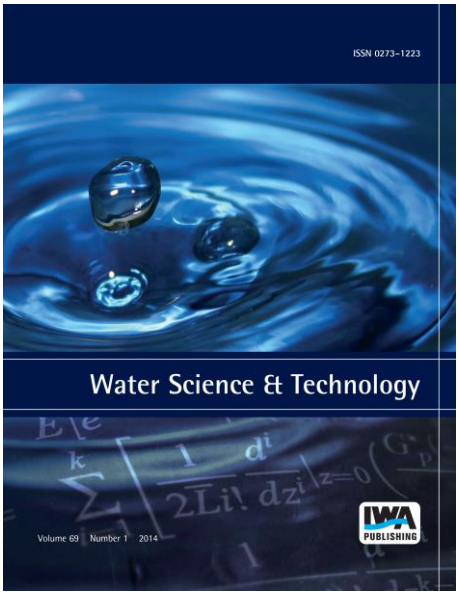

Use of bauxite residue (red mud) as a low cost sorbent for sulfide removal in polluted water remediation

Yanqing Sheng, Qiyao Sun, Ruichuan Sun, Ian T. Burke and Robert J. G. Mortimer

ABSTRACT

Sulfide is an important pollutant in aqueous systems. Sulfide removal from polluted waters is required prior to discharge. Red mud (RM) is a solid waste of bauxite processing that is rich in reactive iron oxides and consequently has the potential to be used to remove sulfide from aqueous systems. A series of experiments was undertaken using raw and sintered RM to remove sulfide from waters. RM was highly efficient at sulfide removal (average 75% sulfide removal at initial concentration of ~5 mg L^{-1}, with 500 mg L^{-1} RM addition) due to both physical adsorption (high specific area) and chemical reaction (with amorphous Fe). Sintered RM, which has a lower surface area and lower mineral reactivity, was much less efficient at removing sulfide (~20% removal under equivalent experimental conditions). Furthermore, concomitant metal release from raw RM was lower than for sintered RM during the sulfide removal process. The results showed that raw RM is a potentially suitable material for sulfide removal from polluted waters and consequently could be used as a low cost alternative treatment in certain engineering applications.

Key words | metal release, polluted waters, red mud, removal kinetics, sulfide

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INTRODUCTION

Sulfide is an important pollutant in a wide range of industrial wastewaters (e.g. petrochemical, tannery, paper mill and mineral waste) and sewage, and also occurs in natural water bodies. When present in water, even at negligible levels, sulfides are distinctly perceptible and give rise to a noxious taste and smell. Such sulfidic water cannot be used for municipal or industrial purposes (Jacukowicz-Sobala *et al.* 2015). Sulfide is unstable in aqueous systems and it is toxic, corrosive, odorous and highly toxic to humans and aquatic life and needs to be removed from wastewater before it is discharged into waterways (Dutta *et al.* 2010; Tsang *et al.* 2015). Therefore, it is important to find effective methods for the removal of sulfide from wastewater streams or other polluted aqueous systems. There are many methods for the removal of sulfide in wastewater, including adsorption (Stepova *et al.* 2009), oxidation (Talei *et al.* 2015), chemical and biological technologies (Wang *et al.* 2016) and electrochemical methods (Dutta *et al.* 2010). For the adsorption methods, the selection of absorbents is crucial to the removal efficiency.

Red mud (RM) is a solid waste by-product of bauxite processing via the Bayer process, and is a highly saline and alkaline waste material. RM typically comprises residual iron oxides, quartz, sodium aluminosilicates, titanium dioxide, calcium carbonate/aluminate and sodium hydroxide which raises the pH up to 13 (Burke *et al.* 2012; Lehoux *et al.* 2013). Its disposal remains an important issue, with significant environmental concerns due to its high alkalinity, toxic metal content, and large storage volume. Based on the characteristics of RM, e.g. high component of iron oxides, it is expected that it can be used as an absorbent for the removal of sulfide in aqueous systems. Although RM was found to be a good absorbent for the removal of H_2S in waste gas (Sahu *et al.* 2011), the use of RM for dissolved sulfide removal in aqueous system is not well understood. Furthermore, no studies have assessed

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the environmental risk of RM application in sulfide pollution control.

This study therefore had the following specific objectives: (1) to characterize the raw RM and the sintered RM used as absorbent; (2) to determine if RM has the potential to remove sulfide from polluted waters; (3) to determine if RM addition to remove sulfide from aqueous systems causes any associated deleterious effects.

METHOD AND MATERIALS

RM preparation and content analysis

The raw RM used in this study was collected from the bauxite residue storage area of the Shandong Aluminium Industry Corporation Ltd (Zibo, China). The raw RM was dried (~80 °C) to constant weight and homogenized using a pestle and mortar (approximately 150 μm). In order to investigate its adsorption capacity for sulfide removal compared to the raw material, a sintering treatment of RM was performed using a muffle furnace (ZWF 1,800 °C, Shanghai, China) at temperatures of 800 °C and 1,100 °C. These sintered RMs were named RM-800 and RM-1100, respectively. The physico-chemical characteristics of the raw and sintered RM were measured using atomic force microscopy (MultiMode 8, USA), X-ray diffraction (XRD), X-ray fluorescence, and specific surface area or pore size distribution measurements (Micro Structure Analysing and Testing Laboratory of Peking University, Beijing, China). Standard errors are lower than 0.25. Total trace metals in the RM were determined by inductively coupled plasma mass spectrometry (ICP-MS) analysis (ELAN DRC II, PerkinElmer Ltd, Hong Kong) following digestion in HCl-HNO_3-HF-$HClO_4$.

Influence of pH on metals leaching from RM

Three groups of experiments were set up to investigate metal leaching under different alkaline conditions by raw and sintered RMs with an addition concentration of RM of 50, 500 and 1,000 mg L^{-1}, respectively. For each group, RM was added to beakers containing 300 mL of Milli-Q water, and then HCl and/or NaOH used to give a final pH of ~6, 7, 8, 9, 10 and 12. The solutions were then stirred for 1 hour at ~25 °C. They were allowed to settle (2 h), and then concentrations of metals in upper clarified solutions were measured to investigate the metals leaching from different RM types and loadings.

Test of sulfide removal by RM and sintered RM

Based on the sulfide concentrations in conventional industrial wastewaters and polluted surface water bodies, ~5 mg L^{-1} (calculated as S) solution of sodium sulfide (Na_2S) was prepared with deoxygenated Milli-Q water in an anaerobic glove box (with N_2 used as carrier gas to avoid oxidation risk). The corresponding accurate concentration of 4.66 mg L^{-1} was calibrated by APHA standard methods (APHA 1998). Three groups of experiments were set up to determine the removal efficiency by raw and sintered RMs and their optimal addition concentration: eighteen 1,000 mL beakers were divided into three groups of six beakers. For each group, 800 mL Na_2S solution (4.66 mg L^{-1}) was added to these beakers and then different RM powder (raw RM, RM-800 and RM-1100) added to give final concentrations of 50, 200, 500, 800, 1,000 and 2,000 mg L^{-1}, respectively (these particular concentrations used were based on the results of preliminary experiments). The beakers were then stirred (200 rpm) for 1 h at ~25 °C. They were allowed to settle (2 h), and then concentrations of sulfide in upper clarified solutions were measured to determine the sulfide removal efficiency of the different RM treatments. Two duplicates were conducted in each group (six samples); standard deviations were lower than 5%. A control test without RM addition was set to assess sulfide loss during the experiment (evaporation as H_2S or oxidation by residual dissolved oxygen in solution) and calculate the concentration of metals (e.g. Na concentration calculation).

Heavy metals leaching from RM in sulfide removal process

In addition to sampling the upper clarified solutions from the experiments for sulfide, they were sampled to determine leachability of metals from the RMs. Heavy metals in solutions were analyzed by ICP-MS analysis. Al, Na and Mo in solutions were analyzed by the ion Chromatography (Dionex ICS3000, DIONEX, USA). All metal analyses were finished automatically by the corresponding detector through three duplicates; the standard deviations were much lower than 2.5%. At the same time, corresponding pH and conductivity values of each solution were measured to investigate the influence of pH on heavy metal release. Conductivity was measured using a YSI Professional Plus (TechTrend International Limited, USA). The pH was measured using a PHS-3CT pH meter (Hengci Co. Ltd, Shanghai, China).

Data processing

All analytical data were subject to strict quality control. All data generated in the study were obtained through three replicate trials and the average values used for data analysis. The concentration of Na in solutions was calculated by the difference between actual concentration (sulfide solution with RMs addition) and control concentration (standard sulfide solution). The purity level of all chemical reagents used in the analysis was analytical grade or better.

RESULTS AND DISCUSSION

Characterization of the RM and sintered RM

The chemical and mineralogical composition of the three RM types is given in Table 1. The chemistry of all RM types was dominated by Ca, Si and Fe, with minor amounts of Al, Na, Ti, and Mg and trace quantities of S, K and P. This is reflected in the mineralogy of the raw RM, with calcite (75%, Supplementary Table S1, supporting information, available with the online version of this paper) and perovskite (16%) the dominant crystalline phases identified. Aragonite and magnetite were detected by XRD analysis in the raw RM. After sintering at 800 °C the calcite originally present is converted to perovskite (from 16% to 28%). At 1,100 °C, the calcite is converted to perovskite (36%), gehlenite (33%), larnite (25%) and magnetite (6%), and carbonate phases are decomposed completely. Another consequence of sintering is that Fe- and Si-containing phases that are possibly amorphous in the raw RM are replaced by more crystalline phases (i.e. magnetite and gehlenite, respectively). This change in mineralogy is also accompanied by a large reduction in specific surface area and overall pore volume (Supplementary Table S2, supporting information, available online). The average pore size, however, shows the opposite trend upon sintering. Scanning electron microscope photomicrographs collected for the three RM types (Supplementary Figure S1, supporting information, available online) show how sintering results in removal of fine and platy particles and the production of large blocky particles, consistent with the change in surface area, pore volume and pore sizes.

Comparison of total heavy metals in RM and relevant environmental standards

Minor and trace element concentrations found in the raw RM are shown in Supplementary Table S3 (available online), along with values for the marine sediment standard for China (GB 18668-2002, China State Bureau of Quality and Technical Supervision (CSBTS)), sediment quality guidelines (SQGs) of the United States Environmental Protection Agency, and Dutch Target and Intervention standards. Mo, Cu, Pb and Cr were below detection. As

Table 1 | Concentrations of metals leached from RM loading (unit: μg L^{-1})

RM	pH	Pb	Ni	Cu	Cr	Zn	Cd	As	Mo	Al	V
50 mg L^{-1}	6.01	0.014	0.426	0.018	0.002	1.01	0.007	0.047	0.04	0.106	0.088
	7	0.019	0.472	0.043	0.159	0.498	0.005	0.046	0.027	0.176	0.695
	8.08	0.025	0.462	0.049	0.138	0.497	0.008	0.061	0.024	0.164	0.639
	8.99	0.023	0.563	0.269	0.102	2.314	0.005	0.074	0.07	9.349	0.611
	10.05	0.022	0.477	0.062	0.592	0.003	0.003	0.069	0.016	4.234	1.143
	11.99	0.011	0.188	1.887	25.93	0.188	0.002	0.068	0.055	19.834	2.881
500 mg L^{-1}	6.06	0.012	4.294	0.059	3.124	2.047	0.026	0.2	0.044	1.015	2.563
	7.01	0.01	4.193	0.047	3.123	0.525	0.005	0.223	0.027	3.397	2.701
	8	0.01	4.115	0.048	3.045	0.104	0.004	0.193	0.03	25.214	3.157
	9.03	0.006	4.326	0.042	2.38	0.224	0.004	0.159	0.024	15.172	4.688
	10.01	0.006	3.756	0.073	2.438	0.079	0.003	0.137	0.022	14.589	7.414
	12	0.006	0.979	2.152	15.595	0.072	0.001	0.069	0.032	112.702	22.456
1,000 mg L^{-1}	6.02	0.018	8.556	0.063	6.077	3.2	0.007	0.431	0.055	1.801	3.566
	7	0.016	8.165	0.102	5.949	1.039	0.003	0.336	0.052	6	3.495
	8.02	0.01	7.645	0.053	4.548	0.238	0.004	0.277	0.039	26.548	3.616
	8.99	0.007	6.979	0.034	2.895	0.2	0.004	0.138	0.024	13.927	4.193
	10.04	0.008	7.068	0.09	2.78	0.626	0.003	0.108	0.037	12.128	8.952
	11.99	0.005	4.02	1.6	3.475	0.049	0.001	0.067	0.075	179.881	37.335

and Cd were both present at concentrations close to or below the guideline values considered. Zn was present at concentrations just above the CSBTS and SQG levels. Although there are no CSBTS and SQG levels for V, it is present at concentrations well above the Dutch intervention standards. This is of particular concern due to the noted mobility of V in waters in contact with RM (Burke *et al.* 2012, 2013; Lehoux *et al.* 2013; Mišík *et al.* 2014).

Leaching of metals under different pH values

In order to assess the potential risk of metal release from RMs as an adsorbent in aqueous system under different pH values, metal leaching capacity with different RM dosage was investigated. The concentrations of different metals leached from the different RM loadings are listed in Table 1. Overall, different metals have different trends with pH, which has implications for using RM as an adsorbent since it may cause deleterious effects on water quality. For Pb, release is generally very low, with little or no pH effect, although release from RM-1100 is an order of magnitude higher than raw RM and RM-800 (Supplementary Table S4, supporting information, available online). For Zn, release decreases with increasing pH, and the concentrations reach similar values at pH ≥ 7. Thus, pH control is a significant factor while using RM as adsorbent, and acidic conditions should be avoided. Cadmium (Cd) shows low level release throughout the variations of pH and RM loading. Arsenic (As) release increases with RM loading, and the release trend is RM-1100 > RM-800 > raw RM at the same RM dosage. This result indicates that the sintering process enhances the release of As from RM. At pH of 9, the release of As reaches a maximum value (RM-1100 is ~6 μg L^{-1}), but at still higher pH the release decreases (at pH 12: RM-1100 is ~0.2 μg L^{-1}). This phenomenon indicates that As release to solution was highly dependent on pH. Therefore, some pH control should be adopted to prevent As release, but setting of the desired pH needs to take into account the potential release of other metals. Low release of Mo from raw RM was observed with different pH values (6–12), while release from sintered RM increases with loading. Overall, the release of Pb, Cd, As, and Mo from RMs was not obviously controlled by pH (at pH values > 6). However, for Ni, its release increased with RM loading but decreased with pH increase. Lowest Ni release occurred at pH 12, decreasing by 90% at pH 7. This phenomenon may relate to the production of $Ni(OH)_2$, reducing the concentration of Ni ion in solution. Chromium (Cr) and vanadium (V) release increased with RM loading, and the release was enhanced after the sintering process. These results indicate that sintering may change the form of Cr and V, resulting in more soluble Cr and V.

For Cu and Al released from all RMs, concentrations were similar at pH values of 6–10, but above pH 10 Cu and Al concentrations increased by 30 times and 8 times respectively in contrast to pH 10 in 500 mg L^{-1} raw RM solution. These results indicate that the release of Cu and Al only happens under strongly alkaline conditions. These phenomena can be explained by the following reactions:

$$Cu(OH)_2 + 2NaOH = Na_2[Cu(OH)_4] \quad (1)$$

$$Al(OH)_3 + NaOH = Na[Al(OH)_4] \quad (2)$$

At pH values between 6 and 10, relatively insoluble solids such as $Cu(OH)_2$ and $Al(OH)_3$ will be produced with NaOH addition, producing relatively low solution concentration of these metals. At pH 12, the concentration of Cu and Al both increase due to the formation of soluble $Al(OH)_4^-$ and $Cu(OH)_4^{2-}$ species.

Overall, comparing results for metal release for each RM type used, sintered RM generally produced higher aqueous metal concentration (e.g. Cr, As, Mo, Al, V) compared to raw RM. Furthermore, pH and RM loading also play a role in the release of different metals to solution. In order to prevent metal release as much as possible, pH should be strictly controlled to between 7 and 9.

Sulfide removal of RM in aqueous system

In order to investigate the removal efficiency of sulfide by RM in aqueous systems, 4.66 mg L^{-1} sulfide (after calibration) solution was prepared as simulated wastewater. As shown in Figure 1, the raw RM exhibited the highest sulfide removal rates (highest value 89%, average 75%) compared to the sintered RMs (RM-800 and RM-1100) with sulfide removal rates of ~20%. The lowest sulfide concentration was 0.51 mg L^{-1} with the highest sulfide removal rate (89%) at the raw RM concentration of 800 mg L^{-1}. So the raw RM achieved 5.2 mgS g^{-1} removal (sulfide sorption or reaction capacity) from solution. Usually, RM contains many residual minerals from bauxite, such as Fe_2O_3, α-FeOOH and $CaSO_4 \cdot 2H_2O$, with a minor presence of $CaCO_3$, $CaC_2O_4 \cdot H_2O$ and $Al(OH)_3$ (Wang *et al.* 2008). Such components in RM are available for reaction with sulfide, especially α-FeOOH and hydrous ferric oxide because of their short half-life (5 min) for reductive dissolution by sulfide (Poulton *et al.* 2003,

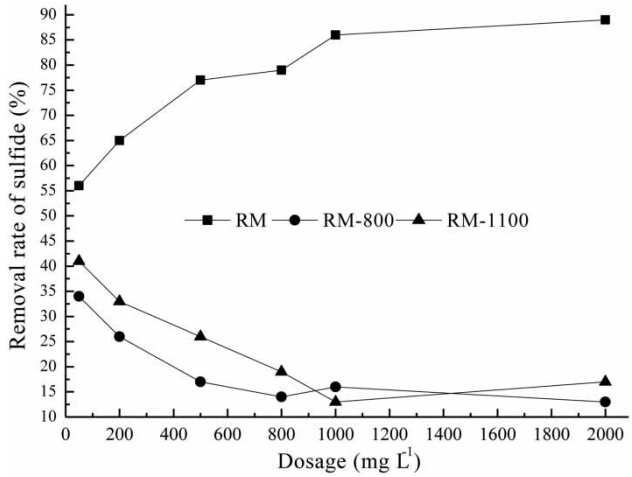

Figure 1 | Variations of sulfide removal rate by different RM samples (RM, RM-800 and RM-1100) in aqueous system (4.66 mg L^{-1} sulfide solution).

2004; Sahu *et al.* 2011). For the sintered RM, previous studies indicate that the RM particles became more refined and the apertures became smaller after sintering, the amorphous iron oxides become converted to crystalline ones, and magnetite (Fe_3O_4) appears at 900 °C (Li *et al.* 2010). Because Fe_3O_4 is much less reactive with sulfide (half-life for the reductive dissolution is 72 days, Poulton *et al.* 2004) compared to α-FeOOH and Fe_2O_3, the raw RM led to the highest sulfide removal rates compared to the sintered RMs in aqueous systems. Furthermore, after raw RM was added, the color of the solution changed quickly from orange-yellow to slightly green, then to grey (black precipitates produced). During this process, physical adsorption and chemical reactions will occur synchronously. For example, sulfide is initially oxidized to elemental sulfur by the ferrihydrite then adsorbed by RM particles, and Fe^{2+} is subsequently released to solution, reacting with additional dissolved sulfide to form solid phase iron monosulphide (Poulton *et al.* 2003). The observed color change are consistent with the transformation of hydrous iron(III) oxides (orange or yellow) in the RM to aqueous iron(II) (green) by sulfide, which is then further transformed to black iron monosulphide (FeS; grey or black). Thus FeS forms as the end product of a sequence of reactions which includes a transitory dissolved Fe^{2+} phase, which does not persist in the presence of excess dissolved sulfide (Poulton *et al.* 2004). However, we did not find the same phenomenon for sintered RMs. Therefore, highly reactive iron in raw RM along with high specific surface area and total pore volume (Table 2) results in higher sulfide removal rates compared to the sintered material (Figure 1), so the raw RM should be selected as adsorbent for sulfide removal in aqueous systems.

Theoretically sulfide removal rate will increase with RM dosage due to the presence of more reactive Fe(III) in RM solutions. However, in the sintered experiments, low RM addition results in moderate removal of sulfide, but increased dosage of RM actually decreases the sulfide removal rate (Figure 1). Raw RM has high specific surface area and mineral reactivity. It can be seen from Supplementary Figure S1 that raw RM consists of dispersed fine particles or microaggregates with high specific surface area and micropores, but the surface of sintered RM is different, consisting of aggregates of larger, more crystalline particles. Previous studies of the reaction of Fe (oxyhydr)oxides with dissolved sulfide suggest that the mineral reactivity is largely controlled by surface area (Morse & Wang 1997). In this work, there are many Fe (oxyhydr)oxides in the raw RM, associated with a high surface area (Table 2), resulting in high sulfide removal rate (average 75%, Figure 1), which is consistent with previous studies of competitive adsorption during the reaction of dissolved sulfide with ferrihydrite (Poulton *et al.* 2003). Furthermore, the reduction of subsurface Fe(III) could occur due to diffusion of sulfide into micropores, then sulfide complexation at the oxide surface reaching fast pre-equilibrium, enhancing mineral reactivity (Poulton *et al.* 2004). So the sulfide removal rate increased with RM dosage. For optimum sulfide removal a raw RM dosage of 500 mg L^{-1} and a pH of 8.4 should be used.

In contrast, for sintered RM, the sulfide removal rate is commonly low (~20%) mainly due to the lower surface area and low reactivity of minerals (i.e. magnetite) (Poulton *et al.* 2003, 2004) and high pH. In Table 2, for any dosage (50–2,000 mgL^{-1}) of sintered RM (RM-800, RM-1100) solutions, the pH was high (8.5–10.9), and increased with sintered RM dosage. But with the sintered RM dosage increase, the sulfide removal rate decreased. From the results of metal release under different pH values ('Leaching of metals under different pH values' selection), most metal decreased with pH increase (Supplementary Table S4) in sintered RM solutions except for Cu and Al. Although sulfide will readily react with Cu^{2+}/Cu^{+}, such ions were transferred to $Cu(OH)_4^{2-}$ in strong alkaline condition (pH ~10), so sulfide cannot be removed by CuS/Cu_2S. Furthermore, under strong alkaline conditions, most heavy metals will be transferred to hydroxides prior to producing metallic sulfide, even including $Fe(OH)_3$ or $[Fe(OH)_4]^-$, resulting in low sulfide removal rate. So the increased dosage of sintered RM actually decreases the sulfide removal rate because more sintered RM leads to more alkaline pH and hence progressively less available metals for reacting with sulfide.

Table 2 | Leachability of metals in different RM sulfide solutions (unit: μg L^{-1})

Sample	Metal	RM added (mg L^{-1})						SQuiRTs reference levels[a]
		50	200	500	800	1,000	2,000	
RM	Pb	0.02	0.02	0.03	0.02	0.02	0.02	2.5
	Cr	1.52	1.10	1.15	2.05	1.85	1.56	11 (as Cr(VI))
	Ni	0.82	1.80	3.70	5.65	6.43	11.94	52
	Cu	0.23	0.23	0.22	0.24	0.26	0.25	9
	Al	13.75	45.58	59.76	62.71	69.31	69.72	87
	As	0.15	0.20	0.22	0.24	0.25	0.30	3.1 (as As(V))
	Na	114.38	433.65	491.38	700.59	687.06	3779.81	–
	Mo	0.17	0.38	0.39	0.47	0.44	0.78	34
	V	1.74	4.97	6.78	8.05	8.64	11.25	19
	pH	6.49	8.31	8.42	8.58	8.62	8.67	–
RM-800	Pb	0.02	0.03	0.02	0.02	0.02	0.02	2.5
	Cr	1.31	9.36	34.81	61.81	69.05	117.51	11 (as Cr(VI))
	Ni	0.82	1.92	3.77	5.02	5.41	6.52	52
	Cu	0.21	0.22	0.21	0.22	0.22	0.22	9
	Al	36.81	42.57	56.84	63.75	110.65	99.40	87
	As	0.18	0.52	1.08	1.29	1.31	0.99	3.1 (as As(V))
	Na	619.54	790.33	787.66	891.76	846.34	1005.17	–
	Mo	0.37	0.57	0.70	0.65	0.64	0.74	34
	V	8.96	43.64	108.96	156.59	181.58	274.76	19
	pH	8.46	9.52	10.19	10.47	10.59	10.92	–
RM-1100	Pb	0.03	0.03	0.02	0.02	0.02	0.03	2.5
	Cr	1.17	1.61	7.56	20.72	28.61	42.69	11 (as Cr(VI))
	Ni	0.48	1.03	1.56	2.19	2.41	3.32	52
	Cu	0.21	0.20	0.20	0.20	0.21	0.22	9
	Al	60.79	72.92	50.22	88.44	71.27	101.02	87
	As	0.12	0.46	1.23	1.76	2.01	2.05	3.1 (as As(V))
	Na	58.57	245.22	259.16	310.27	975.20	905.22	–
	Mo	0.22	0.41	0.50	0.56	0.58	0.65	34
	V	5.36	42.10	86.42	134.19	159.44	232.05	19
	pH	8.57	9.57	10.25	10.46	10.64	10.77	–

[a]SQuiRTs: Screening Quick Reference Tables (http://response.restoration.noaa.gov/cpr/sediment/squirt/squirt.html).

Metal leaching during sulfide removal process in aqueous solutions

The concentration variations of different heavy metals leached from the different RM samples in sulfide-containing water bodies (4.66 mg L^{-1} sulfide solution) are shown in Table 2.

Use of RM-800 and RM-1100 in sulfide removal experiments resulted in high pH values (8.5–10.9) compared to raw RM (6.5–8.7) at the same dosage. This observed pH increase associated with sintered RM addition may be due to some alkaline compounds (e.g. calcite decomposing to CaO (Nath *et al.* 2015)) produced during the sintering process. In experiments using raw RM, conductivity increased from 0.22 to 1.39 mS/cm as a function of dosage. But for RM-800 and RM-1100, the highest value of conductivity was lower than for corresponding RM additions. For metal release, the concentrations of Pb, Mo, Cu, Zn and Cd leached from RM, RM-800 and RM-1100 in solutions were all at relatively low concentrations (with respect to relevant Chinese quality standards) or below detection. These results indicate that the leachability of Pb, Mo, Cu, Cd and Zn in RM samples was low. Furthermore, excess sulfide in solution might react with some metals (e.g. Zn, Cu) to produce precipitation of metallic sulfides, which can explain the low concentrations of such metals because the corresponding concentration of metals in sulfide solutions are lower than those in simple water at the same RM dosage, in contrast to the results in tests of pH effects without sulfide addition, in 'Leaching of metals under different pH values' selection. Ni concentration shows a clear increase with RM dosage. This phenomenon perhaps indicates that production of NiS often needs special conditions, such as catalysis, strong alkalinity and no oxygen. Concentrations of As also increase with RM dosage because arsenate does not react with dissolved sulfide. Ghosh *et al.* (2011) found that

the total extractable metal by microwave digestion decreased due to sintering, and in this study Cr concentrations increased after sintering. This increased Cr release may be related to oxidation of Cr(III) present in RMs to more soluble Cr(VI) during sintering. In addition, excess sulfide in solution might react with some of the metals present (e.g. Zn, Cu) to produce precipitation of metallic sulfides, which would also lead to low solution concentrations.

However, for Al, Na, V and Cr, the concentrations increased with RM dosage (NB: solution pH also increased with dosage). Previous work indicates that Al, As and V are all predicted to be present as soluble oxyanions (as aluminate, arsenate and vanadate), which are poorly adsorbed by mineral surfaces under alkaline conditions (i.e. when pH > 10, Burke *et al.* 2012), resulting in higher solution concentrations (Burke *et al.* 2013). In RM suspensions solution concentrations of Al and As are highest above ~pH 10, but at pH values below 10, formation of insoluble Al oxyhydroxide phases and enhanced adsorption of arsenate to mineral surfaces reduce solution concentrations (Burke *et al.* 2012). However, sorption of vanadate to surfaces is less efficient at pH values between 8 and 10; therefore V can persist in solution at lower pH (Burke *et al.* 2013). The release of Al, As and V can therefore be related to the solution pH during treatment, and control of treatment pH to values < 8.5 is recommended to prevent trace metal release (optimum pH 8.4).

Overall, because the Environmental Quality Standard for Surface Water guideline values (GB 3838-2002, China) for the aqueous concentration of most heavy metals in surface water were quite high, the concentrations of metals released from RM were below the lowest standard (Level V), even for RM dosages of 2,000 mg L^{-1}. However, for RM-800 and RM-1100, the risk of Cr release might be of concern. It is also worth noting that Qu *et al.* (2013) used *Aspergillus niger* as leaching fungus to test the toxicity characteristic leaching procedure of RM, and results showed that the leaching toxicity of the bioleaching residue was far below the levels of relevant regulations. However, in sintered RM solutions, the concentrations of Cr, Al and V were higher than chronic toxicity concentrations (~10-fold); so chronic exposure risk would be difficult to avoid during discharge as an effluent and the sintered RM is probably unsuitable for use in polluted water remediation.

CONCLUSIONS

The highest sulfide removal rate (89% of the original 4.66 mg L^{-1} was removed, leaving just 0.51 mg L^{-1}) was obtained by dosing with 800 mg L^{-1} RM. This corresponds to a removal of 5.2 mg S/g RM. Based on sulfide removal efficiency, low heavy metal release and potentially low engineering operation cost (since RM is a waste material), raw RM could potentially be used as an absorbent in sulfide pollution control. However, other risks such as pH increase need to be taken into account because increased pH will enhance release of some metals. Therefore, in overall consideration, pH of solutions should be controlled between 7 and 8.5 to prevent metal release while using RM as an absorbent.

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