

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

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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 were 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 $\sim 5 \text{ mg L}^{-1}$, 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 ($\sim 20\%$ 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.

Keywords: Metal release; Polluted waters; Red mud; Removal kinetics; Sulfide

Introduction

Sulfide is an important pollutant in a wide range of industrial wastewaters (e.g. petrochemical, tannery, paper mill and mineral waste), 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, 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

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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 H₂S 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 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 1800°C, Shanghai, China) at temperatures of 800°C and 1100°C. These sintered RM 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 (XRF), and specific surface area or pore size distribution measurements (Micro Structure Analysing and Testing Lab of Peking University, Beijing, China). Standard Errors are lower than 0.25. Total trace metals in the RM were determined by ICP-MS analysis (ELAN DRC II, PerkinElmer Ltd., Hong Kong) following digestion in HCl-HNO₃-HF-HClO₄.

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 1000 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 $\sim 25^{\circ}\text{C}$. They were allowed to settle (2h), and then concentrations of metals in upper clarified solutions were measured to investigate the metals leaching from different RMs 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, $\sim 5\text{mg L}^{-1}$ (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 1000 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, 1000 and 2000 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 $\sim 25^{\circ}\text{C}$. They were allowed to settle (2h), 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 (6 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 ion Chromatography (Dionex ICS3000, DIONEX, USA). All metal analysis were finished automatically by 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, Mg; and trace quantities of S, K and P. This is reflected in the mineralogy of the raw RM, with calcite (75%, Table S1, supporting information) and perovskite (16%) the dominant crystalline phases identified. Aragonite and magnetite were detected by XRD analysis in the raw red mud. After sintering at 800 °C the calcite originally present is converted to perovskite (from 16% to 28%). At 1100 °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 (Table S2, supporting information). The average pore size however shows the opposite trend upon sintering. Scanning electron microscope (SEM) photomicrographs collected for the three red mud types (Fig. S1, supporting information) shows 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 table S3, 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 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 red mud (Burke et al., 2012, 2013; Lehoux et al., 2013; Mišík et al., 2014).

Leaching of metals under different pH values

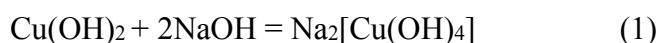
In order to assess the potential risk of metal release from RMs as an adsorbent in aqueous system under different pH values, metal leaching capacity with different RM dosage was investigated. The concentrations of different metals leached from the different RM loading are listed in metal release Table 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 (Table S3, supporting information). For Zn, release decreases with increasing pH, and the concentrations reach similar values after 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 max value (RM-1100 is ~ 6 µg L⁻¹), but at still higher pH the release

decreases (at pH 12: RM-1100 is $\sim 0.2 \mu\text{g L}^{-1}$). 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, 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 were enhanced after sintering process. These results indicate that sintering may change the form of Cr and V, resulting in more soluble Cr and V.

Table 1 Concentrations of metals leached from RM loading (Unit: $\mu\text{g L}^{-1}$)

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
1000 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

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:



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)₄²⁻ 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 Fig. 2, 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 Fe₂O₃, α -FeOOH and CaSO₄ • 2H₂O, with a minor presence of CaCO₃, CaC₂O₄ • H₂O 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, 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 (Fe₃O₄) appears at 900 °C (Li et al., 2010). Because Fe₃O₄ is much less reactive with sulfide (half-live for the reductive dissolution is 72 days, Poulton et al., 2004) compared to α -FeOOH and Fe₂O₃, 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 Fe²⁺ 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 are 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 Fe²⁺ 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 (Fig. 2), so the raw RM should be selected as adsorbent for

sulfide removal in aqueous systems.

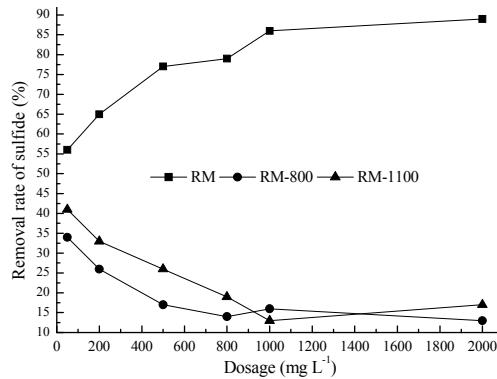


Fig. 2 Variations of sulfide removal rate by different RM samples (RM, RM-800 and RM-1100) in aqueous system (4.66 mg L⁻¹ sulfide solution)

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 (Fig. 2). Raw RM has high specific surface area and mineral reactivity. It can be seen from Fig. 1 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 and 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%, Fig. 1), which is consistent with previous studies of competitive adsorption during the reaction of dissolved sulfide with ferrihydrite (Poulton, 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 500mg/l 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, Fe₃O₄) (Poulton et al., 2003, 2004) and high pH. In Table 5, for any dosage (50-2000mgL⁻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 (section 3.3), most metal decreased with pH increase (Table S1) in sintered RM solutions except for Cu and Al. Although sulfide will readily react with Cu²⁺/Cu⁺, such ions were transferred to Cu(OH)₄²⁻ in strong alkaline condition (pH ~10), so sulfide cannot be removed by CuS/Cu₂S. 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.

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.

Table 2 Leachability of metals in different RM sulfide solutions (Unit: $\mu\text{g L}^{-1}$)

Sample	RM added (mg L^{-1})	50	200	500	800	1000	2000	Squirt – reference levels
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	-

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 (Table 5). For metal release, the concentrations of Pb, Mo, Cu, Zn and Cd leached from RM, RM-800 and RM-1100 in solutions all were 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 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 section 3.3. 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 surface 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 2000 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,

Table 5), so chronic exposure risk would be difficult to avoid during discharge as an effluent, so the sintered RM is probably unsuitable for use in polluted water remediation.

4. Conclusions

The highest sulfide removal rate (89% of the original 4.66 mg L^{-1} 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, overall consideration, pH of solutions should be controlled between 7 and 8.5 to prevent metal release while us RM as an absorbent.

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