



Evaluation of arsenic immobilization in red mud by CO₂ or waste acid acidification combined ferrous (Fe²⁺) treatment

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ABSTRACT

Arsenic was detected in a red mud (RM) produced during alumina production from bauxite known as the Bayer process. The transporting RM was a mixture of RM solid phase (RMs_f) and RM liquid phase (RM_l_f). The mass content of RMs_f in RM is about 30–40%. The alkalinities concentrations in the RM_l_f were in a range of 37.2×10^3 mg/l to 51.5×10^3 mg/l. Acidification by CO₂ or waste acid (WA) combined with ferrous (Fe²⁺) treatment was evaluated for arsenic immobilization in the RM. The aqueous arsenic concentration in the RM_l_f decreased from 6.1 mg/l to 0.5 mg/l and 0.06 mg/l with the addition of CO₂ and WA, respectively. Ferrous was then added to decrease the aqueous arsenic concentration to be lower than 0.05 mg/l. The cost-effective dosages of CO₂ or WA were 80.1 g/l or 26.7 g/l, and the corresponding dosages of ferrous were both 6 g/l. A 2³ full factorial design was employed to evaluate the importance of chemical components of the RM in the cost of arsenic immobilization. High concentrations of arsenic and alkalinities in the RM will increase the cost while the effects of alumina contents varied during the different acidifications. Dissolvable arsenic in the RMs_f was 8.2% and 9.5% after the CO₂ and WA combined ferrous treatments, respectively.

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1. Introduction

Each year, about 120 million tons of alumina are produced all over the world [1]. Generally, 1–1.5 tons of red mud (RM) will be produced with each ton of alumina produced. RM has accumulated over the years and caused serious environmental problem because of its high alkalinity and large amount [2]. Although researches have focused on the reutilization of RM [3–5], large amounts of RM are still disposed during alumina production.

RM is usually transported to the RM disposal area in the form of a mixture of solid phase (RMs_f) and liquid phase (RM_l_f). The transporting RM has a solid content of 30–40%. The RMs_f is disposed in the RM disposal area and the RM_l_f is recycled or discharged after treatment. The chemical compositions of the RM were affected by bauxites and additives in alumina production. Arsenic was detected as a harmful component in the RM, which is a neurotoxic material which poses great threat to human health. It was reported that arsenic was contained in the RM (110 mg/kg dry mass) and unleashed by the spill during Hungarian reservoir wall cracks in 2010 [6]. Mobilized arsenic in the RM posed a risk for environment and human health.

Therefore, arsenic immobilization is significant in the RM disposal. There were numerous studies that focused on aqueous arsenic removal or immobilization [7–9]. Up to now, many approaches such as coagulation/precipitation, adsorption, membrane treatment and biological methods were increasingly being used for aqueous arsenic removal or immobilization. Coagulation/precipitation was widely used for its simplicity and low-cost nature, especially in developing countries [10].

It was reported that a high concentration of carbonate inhibited aqueous arsenic removal by coagulation/precipitation [11,12]. The complex chemical composition of the RM, especially the high concentration of alkalinities, could affect the arsenic immobilization efficiency. Therefore, a cost effective technology with high arsenic immobilization efficiency is significant for the RM treatment.

Aqueous arsenic immobilization in the RM has not been reported previously. The main objective of this work was to investigate a cost effective technology for arsenic immobilization in the RM. Carbon dioxide (CO₂) is produced from sintering process for alumina production in the No. 1 factory of Shandong Branch, Aluminum Corporation of China. Industrial waste acid (WA) is a low-cost byproduct. Therefore, CO₂ and WA were used as the cost-effective acidifier in this work. The arsenic contained RM samples were collected from the No. 2 factory of Shandong Branch, Aluminum Corporation of China. The effects and costs of arsenic immobilization technologies in treating RM were evaluated.

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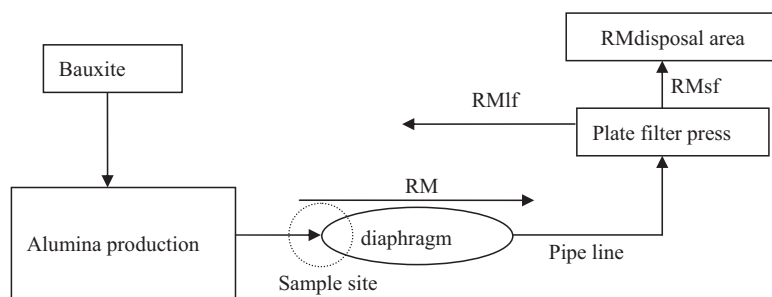


Fig. 1. Schematic explanation of the fate of RM slurry after alumina production.

2. Materials and methods

2.1. RM samples

The RM samples were provided by the No. 2 factory of Shandong Branch, Aluminum Corporation of China. Two samples were collected at the sample site (before diaphragm) in February and October 2010, as shown in Fig. 1

The RMSf contents in these two samples were about 30–40% (w/w). The chemical compositions of RMSf and RMlf were evaluated after solid–liquid separation. The RM was centrifuged at 8000 rpm for 20 min; after that, RMlf and RMSf were collected. The RMlf were filtered through 0.45 μm PVDF membrane filters, and the chemical compositions were evaluated. The RMSf were washed with deionized water three times and then dried at 75°C. An X-ray diffractometer (ShimadzuXRD-6000) operated at 40 kV and 30 mA. Cu K α ($\lambda = 0.15418$ nm) radiation over the range of 2 θ from 10 to 80° was used to identify the crystal structure and crystallinity. The main mineral phases of the RM were hematite, anatase, quartz, CaCO₃ and $\alpha\text{-Al}(\text{OH})_3$.

2.2. WA pre-acidification

Industrial waste acid (WA, mainly hydrochloric acid) was provided by Zibo City Economic and Trade Co., Ltd. The free H⁺ concentration in WA was 5.9 M. WA was quantitatively added to a 1000 ml RM, which was placed in a plastic jar. The mixture was mixed with a stirrer at 300 rpm for 20 min and the pH was measured. A 20 ml volume of RM was collected after WA pre-acidification. The collected RM was centrifuged at 8000 rpm for 20 min. The RMlf were filtered through a Type HA filter (0.45 μm , Millipore) and the chemical compositions of elements were measured. The RMSf were 24 h continuous freeze drying to preserve the original structure of the mineral phase.

2.3. CO₂ pre-acidification

A schematic diagram of the aeration equipment is shown in Fig. 2. Carbon dioxide was provided by a high-pressure gas cylinder and the aeration rate of 100 ml/min was controlled by a rotameter. The aeration time and flow rate were used to calculate the amount of carbon dioxide. 1000 ml of the RM was placed in the plastic beaker, which was mixed with carbon dioxide by a stirrer at 500 rpm. A plastic cover was placed on top of the jar to improve the gas utilization efficiency. The pH detector was placed in the jar, and the results were measured during CO₂ added. Meanwhile, a 20 ml volume of RM was collected. The collected samples were centrifuged at 8000 rpm for 5 min. The supernatant was filtered through a Type HA filter (0.45 μm , Millipore) and the chemical compositions of elements were measured. The residue was freeze dried for 24 h to preserve the original structures of the RMSf.

2.4. Iron precipitation

Ferrous stock solution was prepared by quantitatively dissolving FeSO₄·6H₂O (analytical grade) in deionized water. Ferrous was added in the RM followed by 300 rpm mixing for 30 min using a multiple stirrer apparatus. Collected samples were treated by the method previously described. Supernatants and residues were separated by a centrifuge (LD5-2A, Beijing Lab Centrifuge Co., Ltd.). A leachability test was conducted to evaluate the mobility of arsenic in the RMSf.

2.5. Cost evaluation

The cost for arsenic immobilization in the RM was evaluated. Total cost consisted of acidification and ferrous treatment. The costs for RM transportation, gas purging, and mixing are only a small proportion in the total cost. CO₂ is produced and emitted directly in No. 1 factory of Shandong Branch, Aluminum Corporation of China, and the cost was not considered in the evaluation. Ferrous and WA were about 23.3 US dollar/t and 6.2 US dollar/t, respectively. The exchange rate of the RMB against the US dollar was about 1–6.5 in 2010. Furthermore, a 2³ full factorial design was employed to evaluate the importance of chemicals content in the RM on the cost of arsenic immobilization. The different alumina, arsenic and alkalinity concentrations were artificially prepared with analytical-grade chemicals added to the RM samples.

2.6. Leachability test of arsenic in the RMSf by water elution

Because of the base condition and buffer ability of RM, the leachability test did not follow the standard TCLP test. A four-stage water elution test [13] was carried out to determine the arsenic retention in the RMSf. Briefly, after freeze-drying, 1 g of

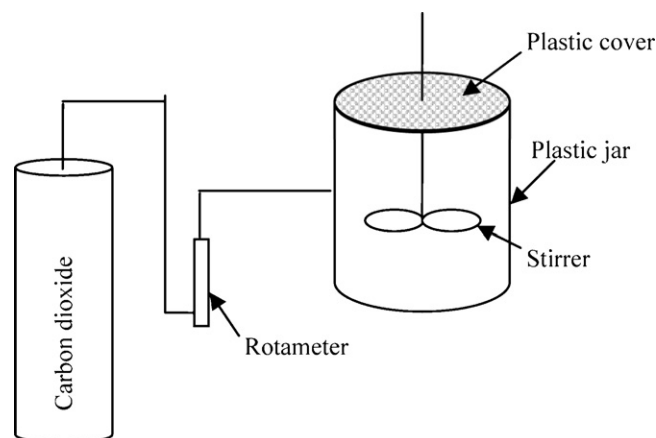


Fig. 2. Schematic explanation of carbon dioxide aeration system.

the RMSf was suspended in 10 ml of deionized water. The suspensions were shaken at 120 rpm for 1 h. After that, suspensions were centrifuged at 8000 rpm for 20 min, and the supernatants were collected. The precipitates of the first elution were re-suspended in 10 ml of deionized water and eluted again. Equal parts of all four supernatants were mixed and filtered by a Type HA filter (0.45 μm , Millipore), and the mixture was analyzed for mobile soluble arsenic in the RMSf.

2.7. Analytical method

The total arsenic was analyzed with an Atomic Fluorescence Spectrometer (AF-610A, Rayleigh Analytical Instrument Corp., China). The method of As(III) detection was using a method by Hug [14]. Briefly, a pH5 citrate buffer (0.5 M disodium hydrogencitrate) was used instead of HCl, and only As(III) (and no As(V)) is converted to AsH_3 under these conditions. Carbonate, bicarbonate and hydroxyl were measured by acid–base titration; phenolphthalein and methyl orange were used as indicators. Chlorine and sulfate radical anions were measured by ion chromatography (861, Metrohm). Alumina, iron, calcium, magnesium and silicon concentrations in the RMf were analyzed on Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES, Prodigy). Chemical compositions of RMSf were also measured by ICP-AES. To prepare the RMSf samples for ICP-AES analysis, the dried solid samples were digested [Aqua regia (3 + 1 HCl–HNO₃)] by a microwave oven (MARS, CEM).

Most experiments were performed in duplicate and the mean values were considered. The control experiments showed no detectable arsenic, alumina or iron adsorbed on the walls of the glass beaker or plastic centrifugal tube. In order to ascertain the reproducibility of results, a group of experiments was repeated twice and the results were found to vary within 5%.

3. Results and discussions

3.1. Chemical compositions of RMSf and RMf

The main chemical compositions of the RMf were as follows: 1.5×10^3 – 3.1×10^3 mg/l Al, 4.0–11.3 mg/l As, 30.1×10^3 – 63.2×10^3 mg/l Na, and the total alkalinity TA, $\text{CO}_3^{2-} + \text{HCO}_3^- + \text{OH}^-$ ranged from 37.2×10^3 to 51.5×10^3 mg/l. Other components such as Ca, Mg, Si, and SO_4^{2-} were detected at less than 3 mg/l. Pentavalent arsenic was the main species and the content of trivalent arsenic was less than 0.05 mg/l.

The chemical compositions of the RMSf are shown in Table 1. A high content of Na_2O lead to a high alkalinity of RM. There was little arsenic detected in the washed RM.

3.2. Pre-acidification treatment

Kinetic studies of pre-acidification treatment were conducted. The pH, alkalinity and alumina contents in the RMf showed little discrepancy in the first 24 h after CO_2 or WA was added.

The main alkaline anions buffering the RM are $\text{HCO}_3^-/\text{CO}_3^{2-}$, $\text{Al}(\text{OH})_4^-$ and OH^- . There may be a small amount of $\text{H}_2\text{SiO}_4^{2-}/\text{H}_3\text{SiO}_4^-/\text{H}_4\text{SiO}_4$, $\text{PO}_4^{3-}/\text{HPO}_4^{2-}/\text{H}_2\text{PO}_4^-$ and $\text{VO}_4^{3-}/\text{HVO}_4^{2-}$ in RM. Acid–base neutralization reactions were the main chemical processes after CO_2 or WA were added in the RM.

As the results of Fig. 3, after CO_2 was added in the RM, the CO_3^{2-} concentration decreased and the HCO_3^- concentration increased. The concentrations of CO_3^{2-} and HCO_3^- decreased when WA was added. The concentration of aqueous Al decreased when CO_2 or WA was added.

The concentrations of alkalinity in the RMf varied when WA or CO_2 was added during pre-acidification. Pre-acidification could

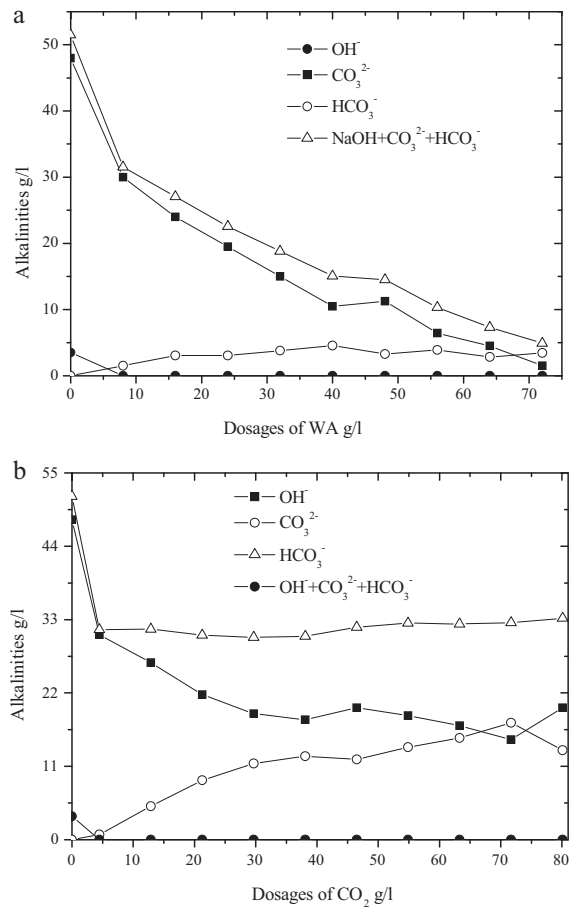


Fig. 3. Variations of alkalinity in the RMf during acidification treatment. (a) With CO_2 added, (b) with WA added.

be divided into three stages with the gradual addition of CO_2 or WA, the results are shown in Figs. 3 and 4. The similar stages of RM acidification were reported before [15]. Free alkaline ions such as OH^- , CO_3^{2-} and AlO_2^- in the RMf are mobile and accessible, they were neutralized first after acidifier added during stage 1. After that, buffer ions, mainly HCO_3^- , and ionized surface hydroxyl groups on the RMSf may slow down the decrease of pH during stage 2. The pH sharply decreased with acidifier added after buffer ions and surface groups of RMSf were neutralized in stage 3.

The pH of the RM decreased from an approximately value 14–11 during stage 1 of acidification. About 12.9 g/l CO_2 or 16 g/l WA was added during this stage. About 3.5×10^3 mg/l OH^- remained in the RM. Alkalinity ($\text{OH}^- + \text{HCO}_3^- + \text{CO}_3^{2-}$) decreased significantly by 40–45% in stage 1 of acidification. Meanwhile, about 63–72% AlO_2^- , precipitated in this stage. Aqueous arsenic concentration were 34.6% and 26.6% decreased after WA and CO_2 were added, respectively.

The total alkalinity fluctuated slightly during stage 2 of CO_2 acidification from 31.6×10^3 mg/l to 32.4×10^3 mg/l. The CO_3^{2-} concentration decreased from 26.6×10^3 mg/l to 17.1×10^3 mg/l, mean while, the HCO_3^- concentration increased from 5.0×10^3 mg/l to 15.3×10^3 mg/l. The total alkalinity decreased from 51.5×10^3 mg/l to 27.1×10^3 mg/l in stage 2 of WA acidification. In the stage 2, aqueous arsenic concentration in the RMf was 0.94 mg/l and 0.54 mg/l after 56.0 g/l WA and 63.3 g/l CO_2 added, respectively. 98.2% and 97.1% alumina precipitated in the stage 2 of WA and CO_2 acidification, respectively. It was reported that aqueous arsenic may be effectively removed by alumina precipitation. Removal of the soluble fraction was due to surface

Table 1
Chemical compositions of the RMSf.

	SiO ₂ (%)	Fe ₂ O ₃ (%)	Al ₂ O ₃ (%)	CaO (%)	TiO ₂ (%)	Na ₂ O (%)	K ₂ O (%)	Ignition loss (%)
RM residues	21.24	29.79	22.96	2.03	1.83	8.93	0.03	12.19

interactions between the arsenic and the aluminium flocs [16]. The results of aqueous arsenic removal during RM acidification were in accordance with the work reported by Altundogan et al. [17]. Precipitation of alumina in the RM played an important role in aqueous arsenic treatment. Meanwhile, the adsorption of arsenic by alumina oxide and the RMSf were also of importance in arsenic removal.

The pH, arsenic, alumina and alkalinities in the RMlf remained unchanged in stage 3 of CO₂ acidification. Relatively, the pH decreased from 9.4 to 6.6 with a greater addition of WA in the stage3. The CO₃²⁻ concentration decreased to less than 10 g/l after 72.0 g/l of WA was added. Aqueous arsenic concentrations were 0.06 mg/l and 0.52 mg/l after WA and CO₂ acidification, respectively. The RMSf was an effective adsorbent for aqueous arsenic removal especially in neutral or acid circumstance [18–20]. Adsorption of arsenic by alumina flocs and RMSf could play an important role in stage 3 of WA acidification when the pH is less than 9.5 [17].

Aqueous arsenic concentration in the RMlf failed to meet the China Environmental quality standard for surface water (0.05 mg/l, GB3838-2002) after CO₂ or WA acidification. Further treatment was considered after acidification treatment.

3.3. Arsenic removal by ferrous added

The kinetic studies of arsenic removal by ferrous precipitation were previously investigated [21]. The arsenic adsorption equilibrium by iron oxide may not be reached in this experiment. However, the designed location to add the ferrous was before the solid–liquid separator in the RM disposal area. The interaction of iron oxide and arsenic was limited. Therefore stirring a mixture of ferrous and the RM for 30 min was considered to be proper and practical.

In order to meet the standard of GB3838-2002, the required ferrous dosage was affected by the acidification process. Arsenic removal efficiencies by ferrous were evaluated after acidification, and the results are shown in Fig. 5. The initial arsenic concentration in ferrous treatment was determined by the amount of acidifier added.

The formation of iron hydroxide after ferrous addition consists two steps: (1) green rusts (general formula: Fe₄(II)Fe₂(III)(OH)₁₂SO₄·3H₂O, Fe₄(II)Fe₂(III)(OH)₁₂CO₃·3H₂O, etc.) were first produced because of the partial oxidation of ferrous. (2) Hydrous ferric oxides were produced after complete

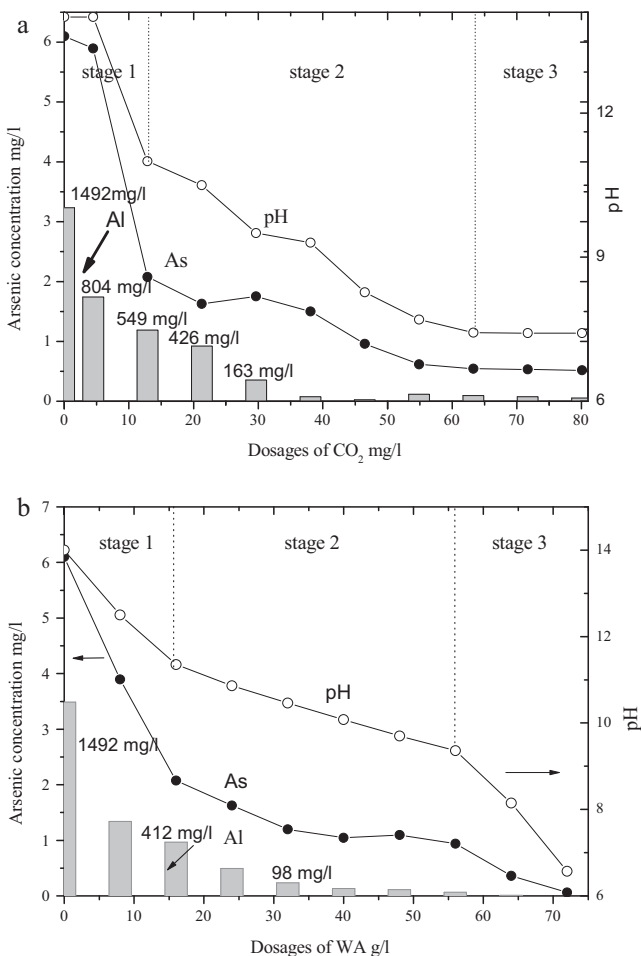


Fig. 4. Variations of alumina, arsenic and pH in RMlf during acidification treatment. (a) With CO₂ added, (b) with WA added.

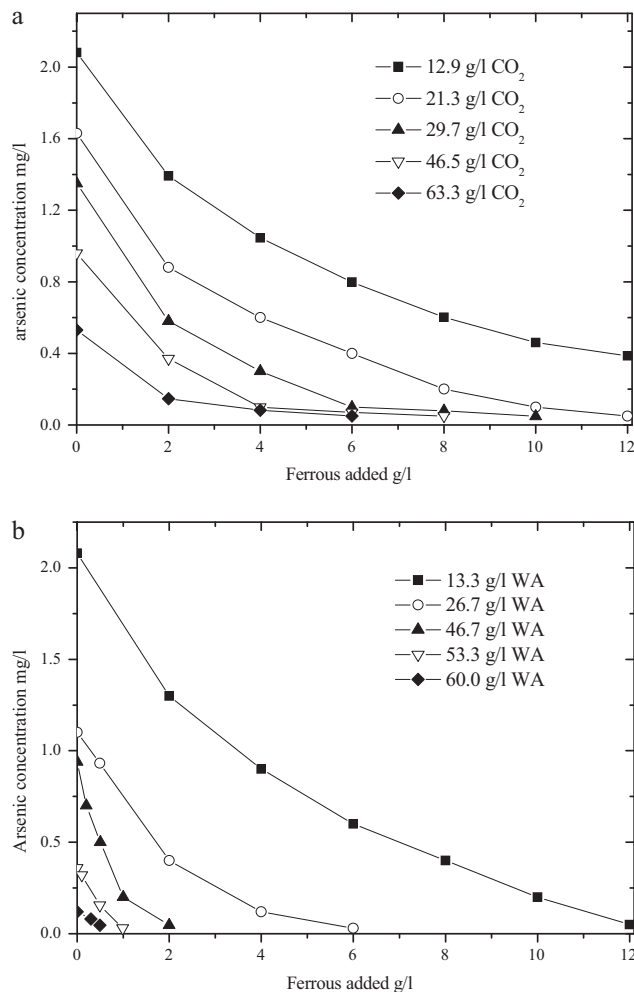


Fig. 5. Efficiency of aqueous arsenic removal from the RMlf by ferrous after different acidification treatment. (a) CO₂-ferrous treatment, (b) WA-ferrous treatment.

Table 2
Chemical compositions of the RMlf.

	Concentration in supernatants (mg/l)								
	As	Al	Ca	Fe	Si	OH ⁻	SO ₄ ²⁻	Cl ⁻	CO ₃ ²⁻ + HCO ₃ ⁻
Original	6.1	1.5 × 10 ³	1.4	<0.1	0.8	3.5 × 10 ³	0.8 × 10 ³	2.3	64.0 × 10 ³
WA treatment (pH < 8.0)	0.1	2.8	6.9	<0.1	6.0	N/A	0.4 × 10 ³	1.5 × 10 ³	9.7 × 10 ³
WA + ferrous treatment	N/A	2.5	5.2	<0.1	9.4	N/A	1.3 × 10 ³	1.5 × 10 ³	9.6 × 10 ³
CO ₂ treatment (pH < 8.0)	0.5	1.5	10.3	0.1	0.8	N/A	0.7 × 10 ³	19.1	33.2 × 10 ³
CO ₂ + ferrous treatment	<0.05	1.2	9.1	0.3	0.5	N/A	7.2 × 10 ³	25.3	32.4 × 10 ³

oxidation of green rusts [22,23]. The rate of Fe(II) oxidation is extremely slow at a pH lower than 6 and it rises sharply above this pH [24]. Meanwhile, it was also reported that green rusts and hydrous ferric oxides were effective in arsenic adsorption [25]. The mechanisms of iron–arsenic combination should be surface complexation and surface precipitation [26].

The main chemical components of the RMlf are shown in Table 2. The concentration of calcium increased after WA or CO₂ acidification. It was possible that part of calcium dissolved from the RMSf after acidifier was added. The sulfate concentration showed little changes during acidification and significantly increased after ferrous treatment. The chlorine concentration increased due to the WA acidification. It was generally considered that the most effective competitive anions for arsenic adsorption were phosphate and silicate. The concentration of phosphate was below detection limit, and the concentration of silicate was lower than 10 mg/l in the RMlf. The carbonates concentrations in the RMlf were 1.5 × 10³ mg/l and 19.8 × 10³ mg/l after 72.0 g/l WA and 80.1 g/l CO₂ were added, respectively. Compared with the huge amount of (bi)carbonates, phosphate and silicon should not be the main factors that control aqueous arsenic removal in the RM.

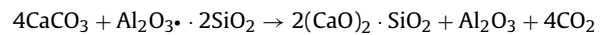
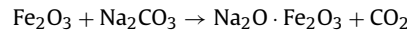
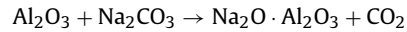
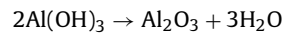
The (bi)carbonates concentrations decreased with WA added. Meanwhile, the arsenic removal efficiency by ferrous improved with more WA added. The results were consistent with former studies that high (bi)carbonates concentrations inhibited the aqueous arsenic removal by iron [27]. The pH was another important factor that affected arsenic adsorption or co-precipitation with iron. Arsenic removal efficiency by ferrous was advantaged in neutral or acid conditions. Also, arsenic removal by precipitated alumina could be increased by adding more acidifier [17]. More acidifier could reduce the ferrous needed for arsenic removal in the RMlf.

3.4. Cost evaluation

Fig. 6 showed the relationship between ferrous and acidifier. Less ferrous was required in the fully acidified RM. The pH of the RM was about 9.5 when 29.7 g/l CO₂ was purged during acidification. In order to meet the 0.05 mg/l arsenic standard, the required ferrous dosages should be about 10 g/l. When a greater amount of CO₂ was purged, the required ferrous dosages was decreased. Similar results were also shown in WA acidification when an increase in WA dosages would decrease the required ferrous.

The lime-soda sinter process was used in the No. 1 factory of Shandong Branch, Aluminum Corporation of China. The sintering

process during alumina production produces CO₂, which can be described by the following reactions:



The generated CO₂ in sintering process of alumina production was discharged directly to the atmosphere. Therefore, the cost of CO₂ acidification in this work was mainly the capital investment, such as air pump, aeration device and gas pipeline for short distance. The estimated cost of transporting and purging CO₂ could be less than 0.001 dollar/m³ considering the life circle of the equipment. Therefore, the cost of CO₂ was neglected in this work. The costs of arsenic treatment were mainly consisted of the costs of WA and ferrous. The costs of WA and ferrous were about 6.15 and 23.3 US dollar per ton respectively. The total costs of acidification combined ferrous treatment are shown in Fig. 6. An amount of 26.7 g/l WA combined with 6.0 g/l ferrous was cost-effective in the arsenic treatment. In this condition, the pH of the RM was about 10.5. Sufficient CO₂ combined with 6.0 g/l ferrous was the optimal condition for arsenic treatment, and the pH of the RM was about 7.5.

The ingredients in the RM varied in alumina production. The contents of alumina, arsenic and alkalinities in RM were the main factors that influenced the required acidifier and ferrous dosages. The cost for arsenic treatment for different RM samples were shown in Table 3. The cost of WA-ferrous treatment was higher than CO₂-ferrous treatment. The cost of WA-ferrous treatment increased with more WA added when the pH of the RM was lower than 10.5. More WA added will reduce the required ferrous thus decrease the amount of solid wastes.

A 2³ full factorial design was employed to evaluate the importance of alumina, arsenic and alkalinities on the cost of the RM treatment, the results are shown in Table 4. The response variable is total cost of the RM treatment. The factors were determined by determining the chemical components of the RM at different times. The matrix of three variables is varied at two levels (+1, -1). The effects were designed as shown in Table 4. This table shows the values of the factors selected in this study. Analytical grades alumina, arsenic and hydrochloric acid were added in the RM to obtain the target concentrations of the orthogonal test.

Table 3
Costs evaluation of arsenic immobilization in two RM samples.

Samples	Al	As	Alkalinities	Outlet pH = 10.5	Costs	Outlet pH = 6.5	Costs	Outlet pH = 7.5	Costs
				WA + iron	(dollar/m ³)	WA + iron	(dollar/m ³)	CO ₂ + iron	(dollar/m ³)
1#	3.1 × 10 ⁶	6.1	51.5 × 10 ³	26.7 g/l (WA)	\$ 0.32	72.0 g/l (WA)	\$ 0.45	80.1 g/l (CO ₂)	\$ 0.07
				6.0 g/l (FeSO ₄)		0.5 g/l (FeSO ₄)		3.0 g/l (FeSO ₄)	
2#	1.5 × 10 ³	1.3	37.2 × 10 ³	18.7 g/l (WA)	\$ 0.28	48.6 g/l (WA)	\$ 0.31	56.2 g/l (CO ₂)	\$ 0.14
				7.0 g/l (FeSO ₄)		0.5 g/l (FeSO ₄)		6.0 g/l (FeSO ₄)	

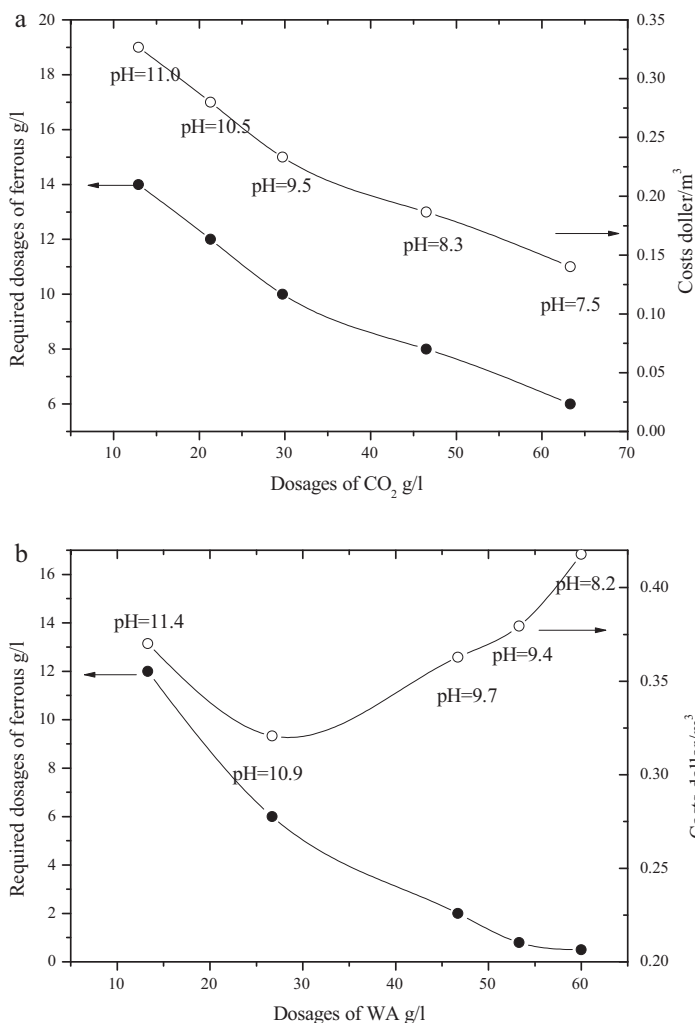


Fig. 6. Relationship of acidifier, ferrous and costs for controlling aqueous arsenic concentration in the RMlf lower than 0.05 mg/l. (a) CO₂-ferrous treatment, (b) WA-ferrous treatment.

Table 4 Factors and levels used in the 2³ factorial design study.

Factor	Low level (-1)	High level (+1)
Alumina, mg/l (A)	1.5 × 10 ³	3.1 × 10 ³
Arsenic, mg/l (B)	6.1	11.3
Alkalinities, mg/l (C)	37.2 × 10 ³	51.5 × 10 ³

The costs of arsenic treatment (Y) were measured for each of these tests as shown in Table 5. A first-order model (Eq. (1)) was chosen to fit the experimental data in Table 5:

$$Y = b_0 + b_1A + b_2B + b_3C \tag{1}$$

Table 5 Experimental design matrix and results for the costs evaluation.

Run number	Factor			Y (CO ₂)	Y (WA)
	A	B	C		
1	-1	-1	-1	0.14	0.26
2	1	-1	-1	0.05	0.27
3	-1	1	-1	0.18	0.28
4	1	1	-1	0.07	0.29
5	-1	-1	1	0.14	0.29
6	1	-1	1	0.05	0.32
7	-1	1	1	0.21	0.32
8	1	1	1	0.07	0.33

A: alumina, B: arsenic, C: alkalinities.

where Y=cost of arsenic treatment, b₁ = coefficients, A= alumina concentration, mg/l, B=arsenic concentration, mg/l, and C=alkalinities concentration, mg/l. A regression analysis was performed to fit the response function with the experimental data (Table 5).

The results calculated from the trial runs are incorporated in regression Eqs. (2) and (3) that can be shown as:

$$Y = 0.114 - 0.054A + 0.019B + 0.004C \tag{2}$$

$$Y = 0.008 - 0.010A + 0.033B + 0.295C \tag{3}$$

These equations revealed the effect of individual variables on the cost of the RM treatment. As seen from Eq. (2), arsenic and alkalinities had positive effects on the cost of the RM treatment in CO₂ acidification. Meanwhile, more alumina contained in RM will reduce the cost. However, as seen from Eq. (3), alumina had positive effect on the cost in WA acidification. A possible reason is that more amount of WA was required for alumina precipitation in the acidification process.

3.5. Leachability test of arsenic in the RMSf

The concentrations of dissolved arsenic in the water eluates of the ferrous treated RMSf were tested by four fold water elution. The water elutes of four steps were collected and the arsenic

Table 6
Arsenic concentrations in the RMlf, RMSf and leachability test.

	Ferrous added, g/l				
	0	0.5	2.0	4.0	6.0
As in RMlf, mg/l (WA, pH = 10.5)	1.20		0.41	0.12	0.03
As in RMSf, mg/g (WA, pH = 10.5)	0.8×10^{-2}		0.9×10^{-2}	1.0×10^{-2}	1.0×10^{-2}
Dissolvable As in RMSf, % (WA, pH = 10.5)	23.5		18.2	13.8	8.2
As in RMlf, mg/l (WA, pH = 7.5)	0.06	0.03	0.01		
As in RMSf, mg/g (WA, pH = 7.5)	1.0×10^{-2}	1.0×10^{-2}	1.0×10^{-2}		
Dissolvable As in RMSf, % (WA, pH = 7.5)	43.1	17.8	6.5		
As in RMlf, mg/l (CO ₂ , pH = 7.5)	0.53		0.15	0.08	0.05
As in RMSf, mg/g (CO ₂ , pH = 7.5)	0.9×10^{-2}		1.0×10^{-2}	1.0×10^{-2}	1.0×10^{-2}
Dissolvable As in RMSf, % (CO ₂ , pH = 7.5)	21.3		17.0	12.4	9.5

concentrations are shown in Table 3. Arsenic concentrations in the RMSf were calculated by Eq. (4):

$$c_s = \frac{(6.1 - c_l) \times v_l}{m_s} \quad (4)$$

where c_s is the arsenic contented in the RMSf, mg/g. c_l is the arsenic concentration in supernatant of the RMSf, mg/l. v_l is the volume of supernatant of RM, l. m_s is the content of RMSf in RM, g/l. There were about 0.7 l RMlf and 420 g RMSf in a 1 l RM sample. Therefore, the following equation was obtained:

$$c_s = \frac{(6.1 - c_l) \times 0.7}{420} \quad (5)$$

Arsenic gradually transported from RMlf to RMSf with the addition of ferrous. The arsenic concentration in the RMSf was calculated by Eq. (5) and the results are also shown in Table 6.

To evaluate arsenic leachability in the RMSf, the percent of dissolvable arsenic in the RMSf was calculated as Eq. (6):

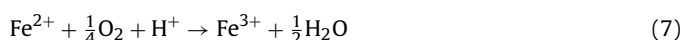
$$p = \frac{0.04 \times c_w}{c_s} \times 100\% \quad (6)$$

where p is the percent of dissolvable arsenic in the RMSf, %. c_w is the aqueous arsenic concentration after 4-fold water elution, mg/l.

The amount of dissolvable arsenic in the RMSf is shown in Table 6. Aqueous arsenic in the RMlf decreased after ferrous was added. It was shown that about 23.5% and 43.1% arsenic dissolved from the RMSf after 26.7 g/l and 72.0 g/l WA added, respectively. There was about 21.3% dissolvable arsenic in the RMSf after 80 g/l CO₂ was purged. The percent of dissolvable arsenic decreased from more than 20% to less than 10% after ferrous treatment. The pH of the RM was independent of the ferrous dosages because of the high content of (bi)carbonates.

The specific surface of red mud could be affected by the acidification process [28], which may influence the arsenic adsorption capacity of red mud. Some mineral phase mainly calcite, sodalite, and quartz were soluble in acidic environment, and the specific surface area of red mud increased after acidification by CO₂ or acid chlorine. Meanwhile, the arsenic adsorption capacity of RM increased significantly after acidification [19,20,28]. Therefore, the acidification process was advantaged for arsenic immobilization in red mud sludge.

It was reported that ferrous sulfate applied in contaminated soil can effectively reduce As mobility and phytoavailability. [29]. Oxidation of Fe(II) to Fe(III) by dissolved oxygen occurred and described by Eq. (7), this reaction rate was fast in neutral or alkaline circumstance [21]. Hydrolysis and precipitation of Fe(III)-hydroxides resulted in the release of H⁺ as described in Eq. (8). Higher concentration of H⁺ decrease the concentrations of alkalinities and thus increase the arsenic adsorption capacity of iron or alumina oxide.



4. Conclusion

The efficiency of arsenic immobilization in the RM by the WA or CO₂ combined ferrous treatment was evaluated. Aqueous arsenic concentration in the RMlf was reduced to less than 0.05 mg/l after acidification in the combined ferrous treatment. The CO₂-ferrous treatment was more cost-effective than WA-ferrous treatment. The required ferrous decreased as more acidifier added during acidification. The amount of dissolvable arsenic in the acidified RMSf decreased with an increased addition of ferrous. Alumina content in the RM increased the cost of WA-ferrous treatment.

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