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Factors Influencing the Release of Arsenic, Manganese and Iron from Sulfide and Arsenide Minerals to Water Environment

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Abstract

The releasing process of arsenic, manganese and iron from their sulfide/arsenide ores was investigated in an equipment imitating natural conditions. The experiments were carried out in flooding, trickling and pulse mode. The results showed that in flooding mode, the concentration of the studied elements in water phase was very low, but in the trickling or pulse modes it was high enough. The influence of main factors was surveyed and their effects on each element were different and were explained reasonably. The results of this paper may supplement some new data of the very common processes in nature, and they will also contribute to control and management of toxic substances which may be released into the environment.

Keywords: arsenic releasing; arsenide ore weathering

1. Introduction

In aerobic conditions and presence of solar light, water/humidity and others factors, arsenic, manganese and iron are released from their original symbiotic sulfide, arsenide ores or their exploited tails or waste (Can, 2001; Noubactep *et al*., 2008). This weathering progresses slowly, but unbrokenly, and it is under control of natural conditions, chemical reactions and other geo- and physicochemical processes (Thuan, 2000). Oxidation plays a decisive role in the initial process where natural rocks are corroded and in the subsequent processes such dissolution, precipitation, and sorption desorption etc. The results of all mentioned processes decide existing formation of substances in the environment (Meng *et al*., 2002; McArthur *et al*., 2001). The fact is that, in the gold or polymetallic sulfide/arsenide mining exploitation areas, where there are heaps of tail ore and pour – ore – waste, heavy metals and arsenic concentrations in liquid leakage (Ahmad and Carboo, 2000) are extremely high. It heavily impacts on water environment. In order to increase our understanding of the reasons and possibilities of polluting with these toxic species, this study was undertaken to elucidate the releasing process in experiments imitating the natural processes. Factors influencing the release of arsenic, manganese and iron from arsenopyrite and polymetallic sulfide ore into water phase were investigated. We have previously published investigations concerning heavy metals release from rock and soil into water environment (Con *et al*., 2003; Dung *et al*., 2010)

2. Materials and Methods

2.1. Installation of investigation equipment

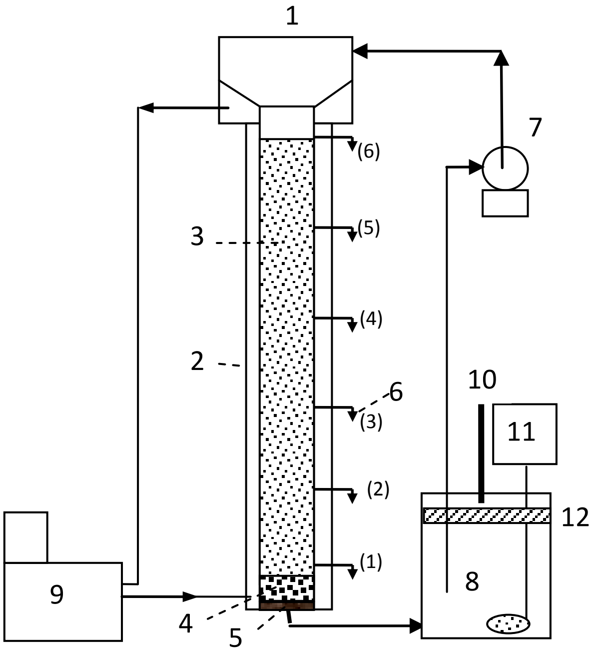
Equipment for the investigation (Fig. 1) includes main components: (1) thermostabilizing column (700 mm in length and 45 mm diameter) containing a mixture of polymetallic sulfide and arsenide ore and clean quartz sand sized 0.5 – 1.0 mm (the proportion of ore to sand was 5/100); (7) peristaltic pump for recycling of water phase, (8) reservoir for water phase which has similar composition to rainwater (table 1); (9) thermostat for stabilization of temperature in the working column, (11) air supplying device and other auxiliary components. The equipment can work in flooding, trickling and pulse conditions.

2.2. Methods for analysis

Analytical methods used for determination of ions in water and solid phase samples are listed in table 2.

2.3. Investigation in flooding mode

For flooding condition, the ore containing layer in the working column was sunk under water level and water current flowed circularly from the column reservoir (top to bottom) and back at a rate of 1.5 cm per min (near the flow rate of natural water leaching through common tail ore layer). Air was supplied continuously to the water reservoir in order to keep dissolved oxygen



Note
1. Working column
2. Thermstabilizing cover
3. Sand-ore mixture layer
4. Gravel layer
5. Supporting bottom filter
6. (1 – 6) Sampling valve
7. Peristaltic pump
8. Water phase reservoir
9. Thermostat
10. Air venting tube
11. Air supplying device
12. Sol blocking device

Figure 1. Experimental equipment

Table 1. The water phase composition

Component	As (T) (ppb)	SO_4^{2-} (ppm)	NO_3^- (ppm)	Fe (T) (ppm)	NH_4^+ (ppm)	HCO_3^- (ppm)
Concentration	0.8	11.6	8.2	0.087	4.14	50

Table 2. The methods for analysis (APHA, AWWA, WEF, 1999)

Ions	*Analysis methods*
Total Fe and Mn	F - AAS method
Total Arsenic	AAS - HVG method
NH_4^+	Phenate method
NO_3^-	Cadmium reduction method
SO_4^{2-}	Methylthymol blue method
Phosphate	Stannous chloride method
Silicate	Molybdosilicate method

concentration stable at approximately 8.0 mg/L (measured in the reservoir). Samples were taken from valve (1) in the bottom of the column at 2-day intervals. pH was measured immediately after sampling and total concentrations of As, Mn, Fe were analyzed. In the case of pH influencing investigation, the exterior injection of pH changing reagent was used.

2.4. Investigation in trickling and pulse modes

The operating procedure for this investigation was similar with section 2.3. The difference was only that, the operation started with dried column material and opened head cover and opened recycling valve in column bottom. Water trickling flow rate was approximately 25 ml/min. For the case of pulse investigation, the operation started with wet column material and the pulse of water phase was 250 ml after every 2 days.

2.5. Investigation of influencing factors

Influencing factors, such as phosphate, silicate, bicarbonate, on the releasing process were controlled by exterior injection of the corresponding ion solution into the water phase; actual concentration were measured in samples taken from bottom valve. The temperature and the hydraulic rate were operated at 25, 35 and 45^{o}C and 1.0; 3.0 and 6.0 cm per min, respectively.

3. Results and discussion

3.1. Variation of pH and concentration of As, Mn and Fe in flooding mode

The experiment was running in flooding mode as described in section 2.3 for 23 days at 30 ± 1^{o}C. The variation of pH and concentrations of surveying elements are presented in Fig. 2. With increasing running times the pH was marginally decreased and concentration of Mn and Fe was increased at an average rate of 0.010 and 0.015 mg/day, respectively. Meanwhile, the arsenic concentration remained very low and almost unchanged. The decrease of pH was probably caused first by the of dissolution of CO_2, then by dissociation of carbonic acid species followed by oxidation of Fe(II), Mn(II), and then hydrolysis of Fe^{3+} and Mn^{4+} into $Fe(OH)_3$ and MnO_2 respectively. The general reaction of these processes could be as below:

$2FeAsS + 4H_2O + 6O_2 + (h\nu) \rightarrow 2Fe^{2+} + 2SO_4^{2-} + 2AsO_4^{3-} + 8H^+$,

$2Fe^{2+} + 1/2O_2 + 2H^+ \rightarrow 2Fe^{3+} + H_2O$,

$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3 + 3H^+$,

$MnS + 2O_2 + (h\nu) \rightarrow Mn^{2+} + SO_4^{2-}$,

$Mn^{2+} + 1/2O_2 + H_2O \rightarrow MnO_2 + 2H^+$,

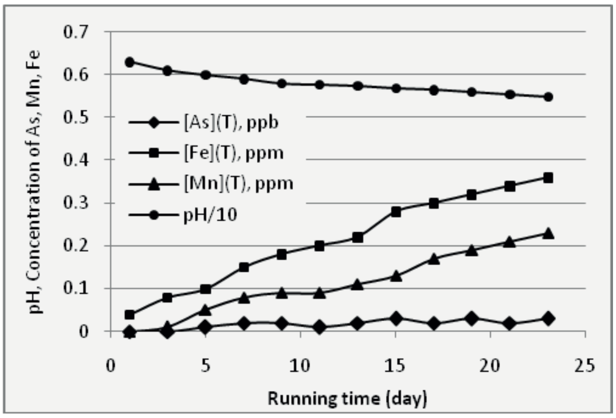


Figure 2. Variation of pH and concentration of surveying elements in flooding condition

Despite the significant amounts of H^+ ion generated from these above reactions, the decrease of pH value was negligible (from nearly 6.4 to 5.6). This may be due to the large volume of the water phase, and because the bicarbonate – carbonic buffer system.

The marginal increased concentration of iron could be caused by dissolution of precipitated iron hydroxide as a consequence of a decreasing of pH and formation of soluble bicarbonate species.

$Fe(OH)_3 + H^+ \Leftrightarrow Fe(OH)_2+ + H_2O$

$Fe(OH)_3 + 3H_2CO_3^- \Leftrightarrow Fe^{3+} + 3HCO_3^- + 3H_2O$

For manganese the main reason could be an oxidation reaction of Mn^{2+} to form MnO_2 by air oxygen. This reaction occurs in near neutral or alkaline conditions, but would be insignificant during acidic conditions.

In the case of arsenic, the fresh formation of manganese dioxide, especially iron(III) hydroxide were strong adsorbents of arsenate anion and in any case, the actual amount of iron and manganese was generally thousands time higher than arsenic. So, in flooding conditions, arsenic concentration in the water phase was always negligible.

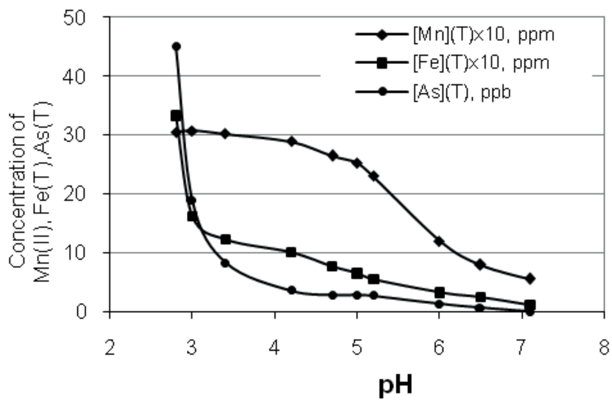


Figure 3. Influence of pH on concentration of iron, manganese and arsenic in water phase

In order to have a clearly sight of mentioned phenomena, in the next experiment the influence of pH reduction in the water phase was investigated. In order to gradually reduce pH, small amounts of acid solution were injected into column. The result is shown in Fig. 3. It was clear that at pH ≥ 7 all surveying elements were almost insoluble. For manganese, when pH ≤ 4, there was no oxidation and precipitation reaction; almost all manganese ions remained in the water phase. In the case of iron and arsenic, when pH decreased from 6.5 to 3.0, their concentrations increased nearly linearly. At pH < 3 the concentrations of both elements significantly increased. This was a consequence of dissolution of almost iron precipitate and dissociation of all adsorbed arsenate.

3.2. Variation of pH, ROP and concentration of As, Mn, Fe in trickling and pulse mode

Both experiment modes were running for 30 days at temperature 30 ± 1°C. Sampling and analysis were carried our as described at section 2.4. The results were similar. Fig. 4 presents a view of the variation of surveying parameters during the trickling mode experiment. From the results we can see that in the first 22 days, the pH value decreased regularly, concentration of arsenic and iron increased nearly linearly at a rate of 0.40 μg and 0.25 mg per day, respectively. After day 25 when pH decreased to value ≤ 3.0, the concentration of both elements sharply increased. The reason is presumably similar to those happening in flooding mode. Meanwhile, the variation of manganese was different. In the interval from beginning to day 16, the pH of the water phase still was higher than 4, the concentration of manganese increased regularly with the rate about 0.16 mg per day. From day 18, when pH decreased down to values lower than 4, the concentration of manganese was almost unchanged. This means at that pH, the oxidation of wet manganese sulfide by oxygen could not happen, despite ROP value exceeding 100 mV.

It is possible to infer a similar situation in the heavy metals exploitation areas from mentioned presented results.

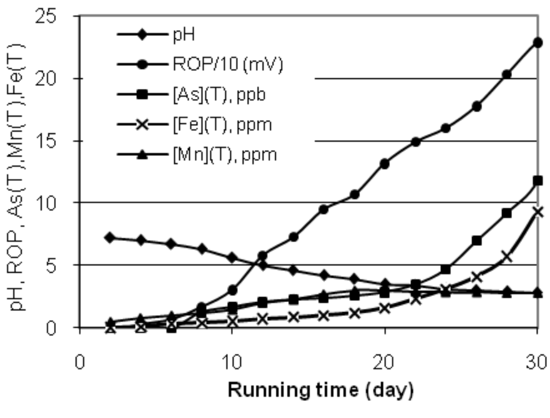


Figure 4. Variation of pH, ROP and concentration of As, Fe and Mn in trickling mode experiment

3.3. Influence of silicate and phosphate on arsenic releasing possibility

According to the results presented in section 3.1, the arsenic concentration was very low due to its adsorption on fresh precipitate of iron hydroxide and manganese oxide. A number of previous published works have discussed sorption competition of arsenate with phosphate and silicate present in the environment. In this paper, especially in flooding condition, the influence of silicate and phosphate on arsenic releasing was surveyed. The phosphate or silicate was injected to water phase and experiments carried out at 25 ± 1°C, pH 6.5 ± 0.1 and working procedure was according to section 2.5. The influence of phosphate and silicate concentration is shown in Figs. 5-6, respectively.

We found that both anions have a significant influence on arsenic release from its insoluble species

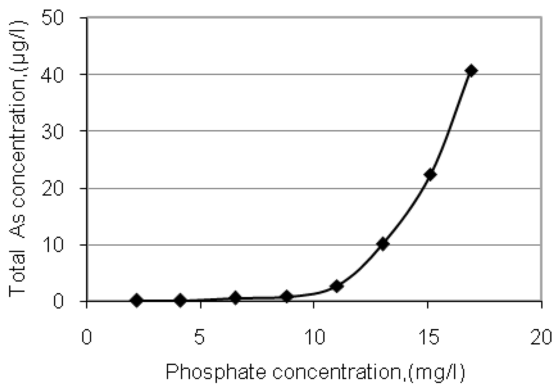


Figure 5. Influence of phosphate concentration

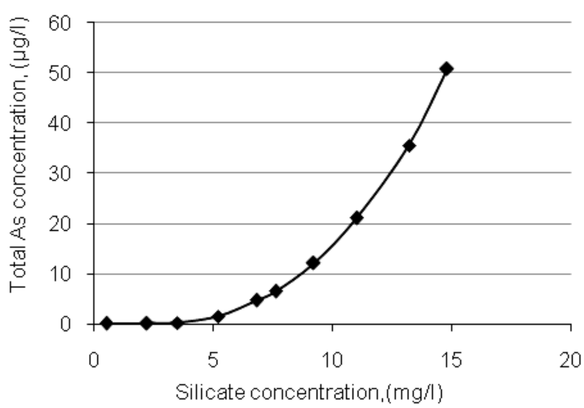


Figure 6. Influence of silicate concentration

created during the oxidation process of arsenide ore. However, in the competition of silicate with arsenate for adsorption – precipitation was stronger than that of phosphate. While the influence of silicate appeared at concentration about 5 mg/L (equal approximately 0.05 mM), that of phosphate occurred at a concentration near 10 mg/L (equal approximately 0.10 mM).

3.4. Influence of water flow rate and temperature

For this investigation, the trickling mode of experiments was applied. Increasing of water flow rate caused more intensive supply of oxygen; slowed down decreasing rate of pH, and caused a higher dilution of ions in the water phase. Experimental results showed that, in general, the concentration of the surveyed elements was decreased with increasing flow rate of the water phase. However, the decreasing rate of each element was different. This means that the influence of the factors consequent upon the increasing of water flow rate on each element was different (see Fig. 7).

The experimental results also showed that influence of temperature on releasing rate of surveying elements was directly proportion to the increasing temperature. Increasing temperature caused an increase of the oxidation process and shortening of ore decomposition period.

4. Conclusion

The releasing possibility of arsenic, iron and manganese from their sulfide/arsenide ore was affected by many factors. Main factors of them were oxidation, precipitation, sorption - desorption process, water flow rate, temperature, pH and competitive ions in the environment. While the oxidation process, water flow rate and temperature mainly affected the decomposition of the ore; the pH and competitive ions affected sorption-desorption process and existing formation of the elements. The experimental running mode also influenced existing formation of the elements. This means, in different actual situation (flooding, trickling or pulse condition), that the risk of toxic elements' pollution in the concerning areas was different. Our results may supplement some new data of very common processes in nature and they may also contribute to the control and management of toxic substances possibly released to environment.

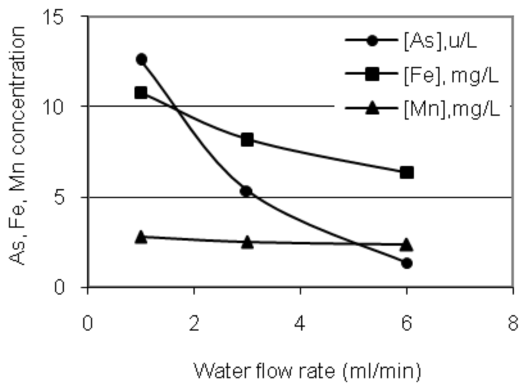


Figure 7. Influence of water flow rate

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