



## ORIGINAL PAPER

## CHEMICAL OXIDATION OF ARSENOPYRITE BY STRONG OXIDIZING AGENTS: FOR OXIDATIVE PRETREATMENT OF REFRACTORY ARSENOPYRITIC GOLD ORES

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## ABSTRACT

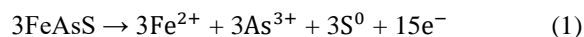
Arsenopyrite (FeAsS) stands as one of the primary host minerals for refractory gold, where the gold is finely disseminated or chemically locked up within the matrix of these raw materials. Therefore, oxidation of this sulfide mineral is necessary for the liberation of gold (Au), and then improving its extraction. This paper aims to study the chemical oxidation of arsenopyrite by four oxidizing agents:  $S_2O_8^{2-}$ ,  $H_2O_2$ ,  $ClO_4^-$  and  $Cr_2O_7^{2-}$ . The objective was to enhance the oxidation efficiency of arsenopyrite through examining the impact of pH, acid type, and reaction time. The findings showed that  $S_2O_8^{2-}$  is the most effective oxidant for arsenopyrite, and the oxidation efficiency varies in the following order:  $S_2O_8^{2-} > H_2O_2 > ClO_4^- > Cr_2O_7^{2-}$ . The optimum pH for all the studied oxidizing agent was pH=2. The effect of acid type experiments revealed that, for each oxidant,  $HClO_4$  was the optimum acid to be used in regulating pH, and the effect of acid type varies in the following order:  $HClO_4 > HNO_3 > HCl > H_2SO_4$ . The highest oxidation rate recorded in this study was in the case of  $S_2O_8^{2-}$  oxidizing agent with pH regulated by  $HClO_4$ , for which the oxidation efficiency achieved 81.90 % for As oxidation, and 63.94 % for Fe oxidation. This study will help to develop an oxidative pretreatment processes for refractory arsenopyritic gold ores.

## 1. INTRODUCTION

With the depletion of free milling gold resources, the extraction of gold from refractory ores gains significant attention. Gold-bearing materials are considered to be refractory when the extraction of gold by conventional cyanidation is low (Rogozhnikov et al., 2021). Some authors have defined refractory ores as those for which gold extraction using conventional cyanide leaching falls below 80 % (Mesa Espitia and Lapidus, 2015). In refractory ores, gold particles frequently exist in an "invisible" state, enclosed within sulfide minerals such as pyrite and arsenopyrite (Cabri et al., 1989; Maddox et al., 1998). Arsenopyrite (FeAsS), is the most widely As-bearing mineral, and it stands as one of the primary host minerals for refractory gold, where the gold is finely disseminated or chemically locked up within the matrix of these raw materials (Rodríguez-Rodríguez et al., 2018). Therefore, improving gold extraction requires an oxidative pretreatment of refractory arsenopyritic gold ores, aiming to break down the crystal lattice of arsenopyrite, and enabling the liberation of the enclosed gold for subsequent step of leaching.

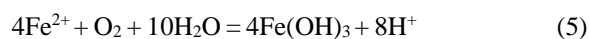
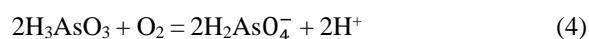
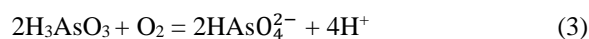
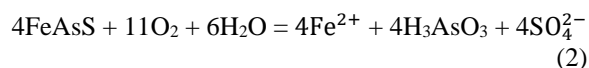
From an electrochemical point of view, and due to its semiconductor behavior (Zhu et al., 2018), arsenopyrite can dissolve preferentially under

oxidizing conditions. Accordingly, the oxidation of arsenopyrite is possible thermodynamically by using oxidizing agents with high oxidation-reduction potential. Based on the measured rest potentials of sulfide minerals, arsenopyrite has a rest potential less than that of pyrite (Guo-hua et al., 2004). In this context, studies have demonstrated that arsenopyrite dissolves 3–4 times faster than pyrite (McKibben et al., 2008). The oxidation of arsenopyrite involves an electrochemical process that unfolds through three stages: anodic reaction, electron transport, and cathodic reaction. The crucial step that determine the reaction rate is the transfer of electrons from the mineral to the oxidant, in other words, the movement of electrons from the anodic site to the cathodic site (Corkhill et al. 2009). Equation 1 shows the anodic oxidation of arsenopyrite:

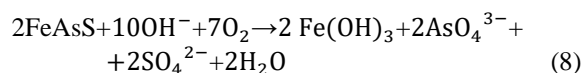
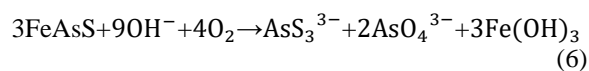


According to the literature, the mechanism and kinetics of arsenopyrite oxidation have been studied mainly in the presence of ferric iron  $Fe^{3+}$  and dissolved  $O_2$ . Walker et al. (2006) outlined a sequence of oxidation reactions involving arsenopyrite in the presence of dissolved oxygen at near-neutral pH. Throughout the oxidation process, both sulfur (S) and

arsenic (As) atoms within arsenopyrite undergo multiple oxidation states, resulting in the diverse array of reaction products. The authors suggested that As(-I) and S(-I) are oxidized first to As(+III) as  $\text{H}_3\text{AsO}_3$  and to S(+VI) as  $\text{SO}_4^{2-}$  respectively (Eq. 2). Subsequently, As(+III) undergoes additional oxidation, resulting in the formation of  $\text{HAsO}_4^{2-}$  (Eq.3) and  $\text{H}_2\text{AsO}_4^-$  (Eq. 4), both present in roughly equivalent concentrations. Additionally, in these conditions, Fe(+II) is oxidized to Fe(+III) in the form of  $\text{Fe}(\text{OH})_3$  (Eq. 5).



On the other hand, Nan et al. (2014) cited studies by several authors worked on alkaline pretreatment of arsenopyrite-bearing refractory gold ores, and they reported that the main chemical reactions of the mechanism are shown in Eqs. (6-8). However, Corkhill et al. (2009) reported that the oxidation of arsenopyrite is faster in acid solutions than in alkaline solutions.



This study focuses on evaluating the effectiveness of  $\text{S}_2\text{O}_8^{2-}$ ,  $\text{H}_2\text{O}_2$ ,  $\text{ClO}_4^-$  and  $\text{Cr}_2\text{O}_7^{2-}$  oxidizing agents on the oxidation efficiency of arsenopyrite. The chosen path of studying chemical oxidation of arsenopyrite with these specific oxidizing agents was driven by the need to explore and identify highly efficient and practical methods for its oxidation. These agents were selected based on their ability to generate strong oxidizing conditions, with the potential to improve the liberation of gold enclosed in this sulfide mineral. The study further examines the effects of pH, acid type and reaction time, a topic that has not been thoroughly explored in existing literature. The mechanistic insights of the studied oxidizing agents have also been discussed. This research provides practical recommendations for developing more efficient oxidative pretreatment processes for refractory arsenopyritic gold ores.

## 2. MATERIALS AND METHODS

### 2.1. MATERIALS

The experiments were conducted using a crystal specimen of high-purity arsenopyrite (not refractory gold ore, in order to eliminate interference of other

compounds). Oxidizing agents examined include potassium peroxydisulfate ( $\text{K}_2\text{S}_2\text{O}_8$ ), hydrogen peroxide ( $\text{H}_2\text{O}_2$ ), sodium perchlorate ( $\text{NaClO}_4$ ), and potassium dichromate ( $\text{K}_2\text{Cr}_2\text{O}_7$ ). Sulfuric acid ( $\text{H}_2\text{SO}_4$ ), hydrochloric acid ( $\text{HCl}$ ), nitric acid ( $\text{HNO}_3$ ), perchloric acid ( $\text{HClO}_4$ ) and sodium hydroxide ( $\text{NaOH}$ ) were employed to regulate the solution's pH (with monitoring). All reagents utilized were of analytical grade.

### 2.2. METHODS

The arsenopyrite sample was characterized using X-ray diffraction with an Aeris Panalytical diffractometer (Cobalt,  $\text{K}\alpha$  radiation;  $\lambda = 1.724 \text{ \AA}$ ), working at 40 kV/200 mA, with  $2\theta$  ranging from  $10^\circ$  to  $70^\circ$ , using a counting time of 5 s/step and a step size of  $0.07^\circ$  ( $2\theta$ ). The diffractometer was equipped with HighScore Plus software for mineralogical identification. The mineralogical analysis revealed that the major phase existing in the sample is arsenopyrite, with a minor presence of quartz as illustrated in Figure 1. The chemical composition was determined by atomic absorption spectroscopy (AAS) using Agilent 280 FS AA Flame technique for iron and arsenic analysis, and inductively coupled plasma-optical emission spectrometer (ICP-OES) using Agilent 5110 SVDV machine for sulfur and  $\text{SiO}_2$  analysis. The analysis confirms the high purity of the sample, and was as follows: Fe 21.25 wt. %, As 44.23 wt. %, S 31.45 wt. %, and 3.07 wt. %  $\text{SiO}_2$ , compared to Fe 19.69 wt.%, As 46.01 wt.% and S 34.30 wt.% for stoichiometric FeAsS. The sample was ground using a mortar mill, resulting in a particle size distribution of  $D_{80} = 75 \mu\text{m}$ .

The experiments were performed in a 400 mL glass beaker, filled with a 250 mL solution containing 0.1 M of the oxidant. The solution was agitated using a magnetic stirrer at speed of 400 rpm. All experiments were carried out under ambient conditions at a temperature of  $25^\circ\text{C}$ . After the preparation of the solution, 0.5g of arsenopyrite powder was added, initiating the oxidative reaction. The proportion of arsenopyrite reacted over time was measured by extracting seven samples from the solution at intervals of 30 minutes, 1 hour, 1.5 hours, 2 hours, 4 hours, 6 hours, and 24 hours. Iron (Fe) and Arsenic (As) contents in these samples were analyzed using atomic absorption spectroscopy (AAS). The oxidation efficiency of Fe and As in arsenopyrite was calculated based on the provided equations (9) and (10):

Oxidation efficiency of iron (Fe) in arsenopyrite (%)

$$\alpha = \frac{C_{\text{TFe}} \times V \times M(\text{FeAsS})}{m \times M(\text{Fe})} \times 100 \quad (9)$$

Oxidation efficiency of arsenic (As) in arsenopyrite (%)

$$\beta = \frac{C_{\text{TAs}} \times V \times M(\text{FeAsS})}{m \times M(\text{As})} \times 100 \quad (10)$$

Where:

$C_{\text{TFe}}$  and  $C_{\text{TAs}}$  are the total iron concentration and

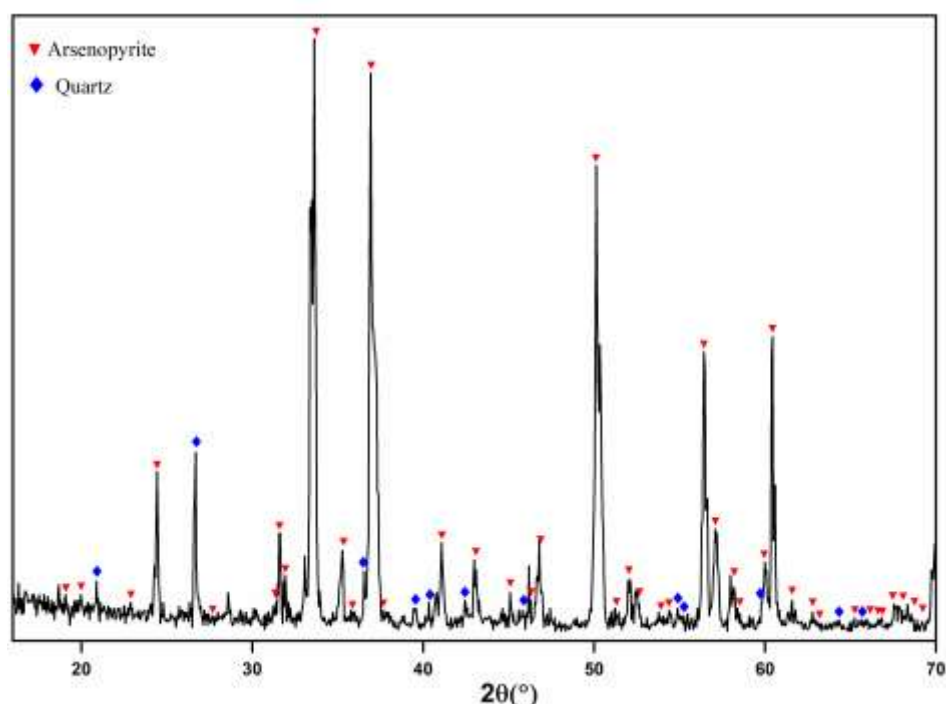


Fig. 1 XRD pattern of the arsenopyrite crystal specimen.

arsenic concentration measured in the solution (g/L) respectively,  $V$  is the volume of the solution (L),  $M(\text{FeAsS})$  is the molecular mass of arsenopyrite (g/mol),  $m$  is the mass of arsenopyrite (g), and  $M(\text{Fe})$  and  $M(\text{As})$  are the molecular mass of iron and arsenic respectively (g/mol).

The characterization of solid residues after the oxidation process was carried out using X-ray diffraction XRD and Scanning Electron Microscopy coupled with Energy-Dispersive X-ray Spectroscopy SEM-EDS (Tescan VEGA 3 equipped with KEVEX detector (Si-Li diode) working in X energy dispersion (X-EDS)). Before SEM-EDS characterization, samples were metallized with carbon. The acceleration voltage was 10 kV, the acquisition time was 120 s, and the angle of the output was  $30^\circ$ .

In order to explain the obtained results, HSC Chemistry 10.2.2.0 software was used to establish the potential-pH diagrams for the different oxidizing agents.

### 3. RESULTS

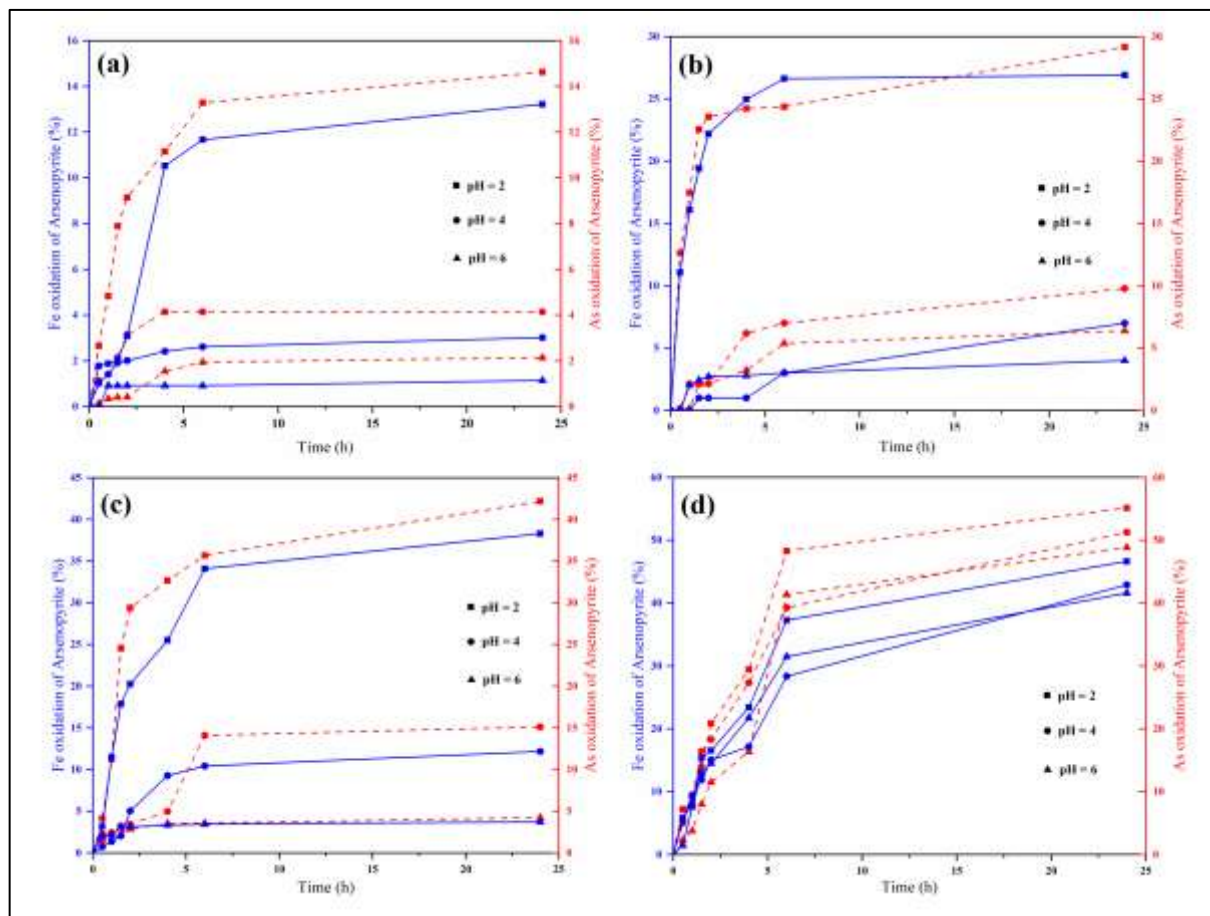
#### 3.1. EFFECT OF PH

The oxidation experiments of arsenopyrite by the studied oxidizing agents have been examined in acidic media at pH values 2, 4 and 6. The pH was adjusted using sulfuric acid  $\text{H}_2\text{SO}_4$  and sodium hydroxide NaOH. Figure 2 describes the effect of pH on the oxidation of arsenopyrite. Interestingly, the findings revealed a prominent trend in oxidation rates. Notably, for  $\text{Cr}_2\text{O}_7^{2-}$  (Fig. 2a)  $\text{ClO}_4^-$  (Fig. 2b) and  $\text{H}_2\text{O}_2$  (Fig. 2c), the highest rates of oxidation were consistently observed at pH 2. However,  $\text{S}_2\text{O}_8^{2-}$  oxidizing agent (Fig. 2d) exhibited a strikingly different behavior,

displaying its highest oxidation rate across all tested pH levels, with a little increase at pH = 2. The findings indicate also that the reaction exhibits greater oxidation rate within the initial six hours, whereas extended periods resulted in a slight increase oxidation rate. Moreover, it can be seen from the oxidation curves that, for the four oxidizing agents studied, As oxidation occurs more rapidly than Fe oxidation at all pH values.

The oxidant  $\text{Cr}_2\text{O}_7^{2-}$  demonstrated the lowest oxidation rate compared to the other oxidizing agents. After 24 hours of reaction, the oxidation efficiencies were recorded at 14.62 %, 4.14 %, and 2.14 % for arsenic, and 13.21 %, 3.01 %, and 1.14 % for iron, at pH levels 2, 4, and 6 respectively. In contrast,  $\text{S}_2\text{O}_8^{2-}$  oxidant showcased the highest efficacy, recording oxidation efficiencies of 55.11 %, 51.25 %, and 48.84 % for arsenic, and 46.62 %, 42.89 %, and 41.59 % for iron at pH levels 2, 4, and 6, respectively. These findings demonstrate the superior performance of  $\text{S}_2\text{O}_8^{2-}$ , which consistently exhibited the highest oxidation rates across all pH levels tested, thereby highlighting its potential as a highly effective oxidizing agent for arsenopyrite oxidation processes.

On the other hand,  $\text{ClO}_4^-$  and  $\text{H}_2\text{O}_2$  exhibited intermediate oxidation rates between those of  $\text{Cr}_2\text{O}_7^{2-}$  and  $\text{S}_2\text{O}_8^{2-}$ . For  $\text{H}_2\text{O}_2$ , the oxidation efficiency after 24 hours of reaction reached at pH values 2, 4 and 6, 42.17 %, 15.11 %, 4.24 % for As, and 38.29 %, 12.18 %, 3.73 % for Fe respectively. While, the oxidation efficiency recorded for  $\text{ClO}_4^-$  were 29.16 %, 9.78 %, and 6.39 % for arsenic, and 26.91 %, 7.01 %, and 4.01 % for iron at pH levels 2, 4 and 6, respectively.



**Fig. 2** Effect of pH on the oxidation efficiency of arsenopyrite: (a)  $\text{Cr}_2\text{O}_7^{2-}$ ; (b)  $\text{ClO}_4^-$ ; (c)  $\text{H}_2\text{O}_2$ ; (d)  $\text{S}_2\text{O}_8^{2-}$ .

### 3.2. EFFECT OF ACID TYPE

The oxidation tests assessing the pH effect revealed that the optimum pH for all the studied oxidizing agents was pH 2. Consequently, subsequent oxidation experiments were conducted at this pH level using various type of acids. Four inorganic acids were subjected to testing:  $\text{H}_2\text{SO}_4$ ,  $\text{HCl}$ ,  $\text{HNO}_3$ , and  $\text{HClO}_4$ . The results, illustrated in Figure 3, revealed a strong correlation between the oxidation rate of As and Fe within arsenopyrite and the type of acid employed.

For each different oxidizing agent tested,  $\text{HClO}_4$  acid was found to be the most effective acid for oxidizing both As and Fe within arsenopyrite, followed by  $\text{HNO}_3$ ,  $\text{HCl}$ , and  $\text{H}_2\text{SO}_4$ , respectively. Additionally, the findings highlighted that, generally, As exhibited a faster oxidation rate than Fe under any given condition.

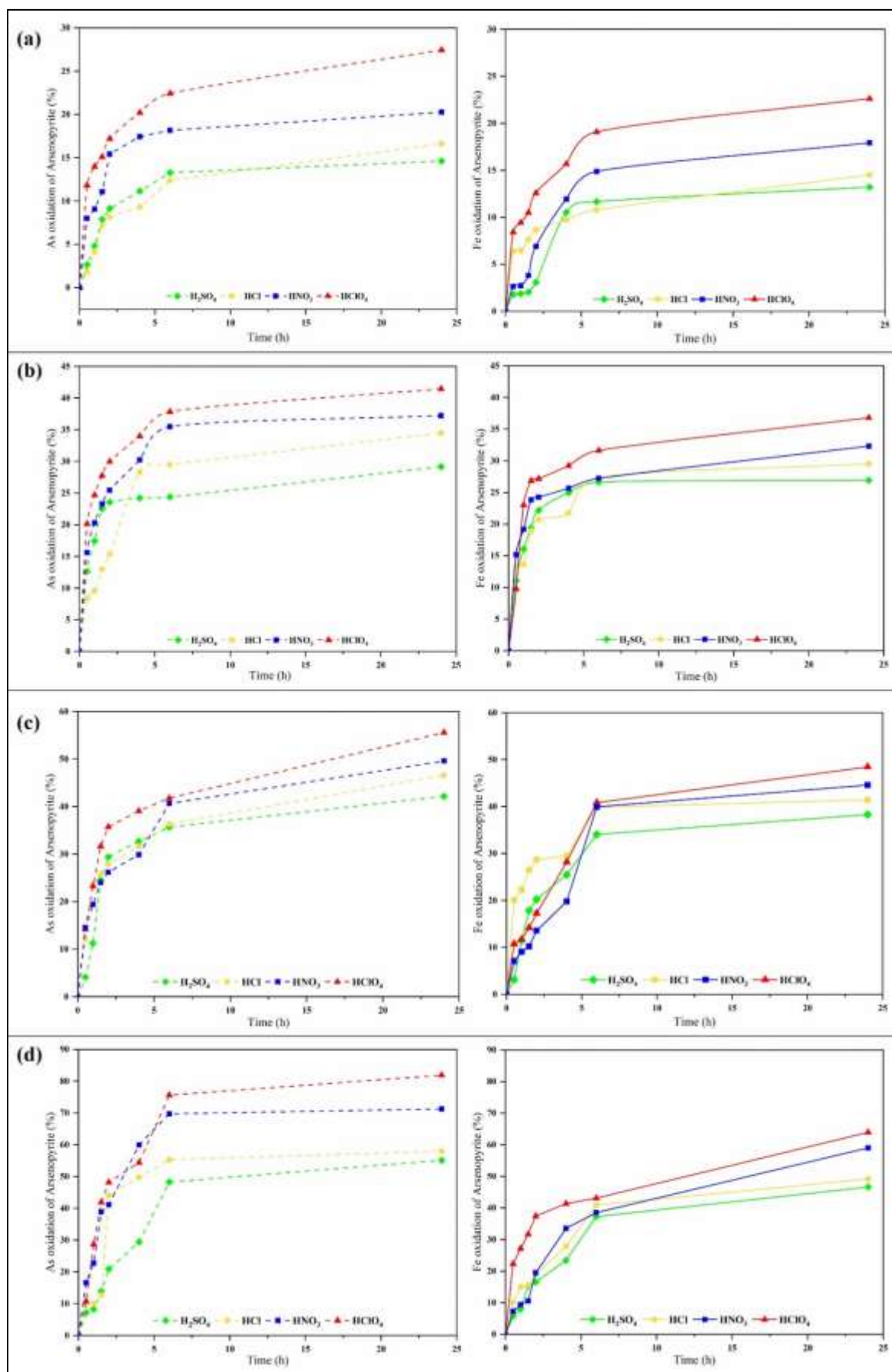
A notably high oxidation rate of arsenopyrite was observed when using the  $\text{S}_2\text{O}_8^{2-}$  oxidizing agent with pH regulated by  $\text{HClO}_4$ . After 24 hours of reaction, the achieved oxidation efficiencies were 81.90 %, 71.23 %, 57.95 %, and 55.11 % for As oxidation, and 63.94 %, 59.02 %, 49.15 %, and 46.62 % for Fe oxidation, for  $\text{HClO}_4$ ,  $\text{HNO}_3$ ,  $\text{HCl}$ , and  $\text{H}_2\text{SO}_4$  respectively.

## 4. DISCUSSION

### 4.1. EFFECT OF OXIDIZING AGENT TYPE

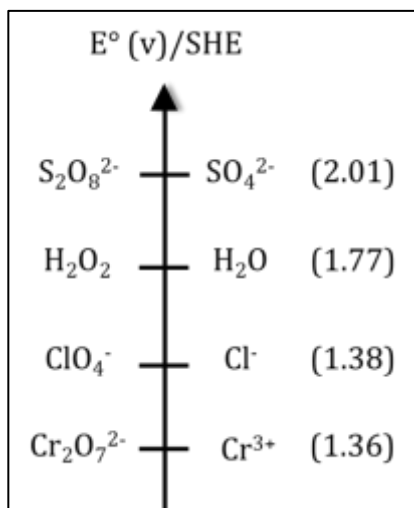
The findings revealed that among oxidants tested,  $\text{S}_2\text{O}_8^{2-}$  proved to be the most efficient in oxidizing arsenic (As) and iron (Fe) present in arsenopyrite. For each different pH, the oxidation efficiency varies in the following order:  $\text{S}_2\text{O}_8^{2-} > \text{H}_2\text{O}_2 > \text{ClO}_4^- > \text{Cr}_2\text{O}_7^{2-}$ . Interestingly, this order coincides perfectly with the electrochemical standard potential of these oxidizing agents (Fig. 4). The theoretical perspective reinforces this correlation, pointing out that a higher  $E^\circ$  value signifies a greater strength of the oxidant.

In addition, various reasons could contribute to the diverse performance observed in arsenopyrite oxidation. The slow oxidation rate seen in arsenopyrite when oxidized by  $\text{Cr}_2\text{O}_7^{2-}$  might be due to the chemisorption of chromium (VI) on the surface of arsenopyrite. Antonijevic et al. (1993) suggest that, in the case of pyrite, the chromium (VI) within  $\text{Cr}_2\text{O}_7^{2-}$  may saturate the pyrite surface, potentially affecting the oxidation process. Similarly, chromium might also be adsorbed onto the arsenopyrite surface, leading to inhibition of the galvanic interaction between  $\text{Cr}_2\text{O}_7^{2-}$  and arsenopyrite.



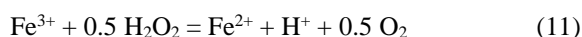
**Fig. 3** Effect of acid type on As (---) and Fe (—) oxidation of arsenopyrite: (a)  $Cr_2O_7^{2-}$ ; (b)  $ClO_4^-$ ; (c)  $H_2O_2$ ; (d)  $S_2O_8^{2-}$ .



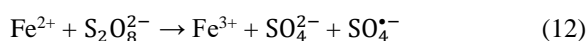


**Fig. 4** Standard potential of the studied oxidizing agents.

Moreover, the effectiveness of perchlorate  $\text{ClO}_4^-$  and hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) in oxidizing arsenic (As) and iron (Fe) within arsenopyrite is relatively limited. According to Urbansky (2002) perchlorate exhibits slow kinetics and requires the presence of highly concentrated acid to be reduced. However, in the presence of ferrous iron ( $\text{Fe}^{2+}$ ), which is released from arsenopyrite (Eq. 1), even in the presence of high acid concentration, perchlorate remains unreactive and is not reduced by  $\text{Fe}^{2+}$  ions. Differently, other influencing factors impact the behavior of  $\text{H}_2\text{O}_2$ . According to Chirita (2009), Marzzacco (1999) and Salas-Martell et al. (2020),  $\text{Fe}^{3+}$  ions, which could be formed by the oxidation of  $\text{Fe}^{2+}$ , react with  $\text{H}_2\text{O}_2$ , causing its decomposition (Eq. 11). Consequently, this reaction leads to a considerable loss of  $\text{H}_2\text{O}_2$ , which limits the oxidation of arsenopyrite.



On the other hand, the high efficiency of arsenopyrite oxidation by  $\text{S}_2\text{O}_8^{2-}$  could be attributed to further oxidation of arsenopyrite by sulfate radicals, which could be formed under the conditions of the experiment. Ferrous iron  $\text{Fe}^{2+}$  released from arsenopyrite (Eq. 1), contributes significantly to this process, and serves as an effective activator for  $\text{S}_2\text{O}_8^{2-}$  to produce sulfate radicals (Eq. 12) (Karim et al., 2021; Matzek and Carter, 2016; Xie et al., 2023). Sulfate radical ( $\text{SO}_4^{\bullet-}$ ) is well known for its strong capacity in oxidizing any oxidizable agents, possessing a notably high oxidizing potential ( $E^\circ = 2.6 \text{ V}$  vs. NHE) (Duan et al., 2022; Li et al., 2022; Xie et al., 2023). Therefore, the oxidation efficiency increases as arsenopyrite undergoes further oxidation due to generation of these radicals.



Furthermore, the results of all the oxidation experiments showed that, As exhibited a faster oxidation rate than Fe whatever the conditions. Our findings agree with several researchers, who studied and compared the oxidation rates of Fe and As elements within arsenopyrite. McKibben et al. (2008) showed that, As is the faster element dissolved in the oxidation process of arsenopyrite. Corkhill et al. (2009) reported that, the biological oxidation of arsenopyrite with *Leptospirillum ferrooxidans* bacteria showed a highest rate of oxidation for arsenic compared to iron. Also, Nesbiit et al. (1995) showed in their results that, when arsenopyrite is oxidized in air or in water, the oxidation of As occurs more rapidly than that of Fe.

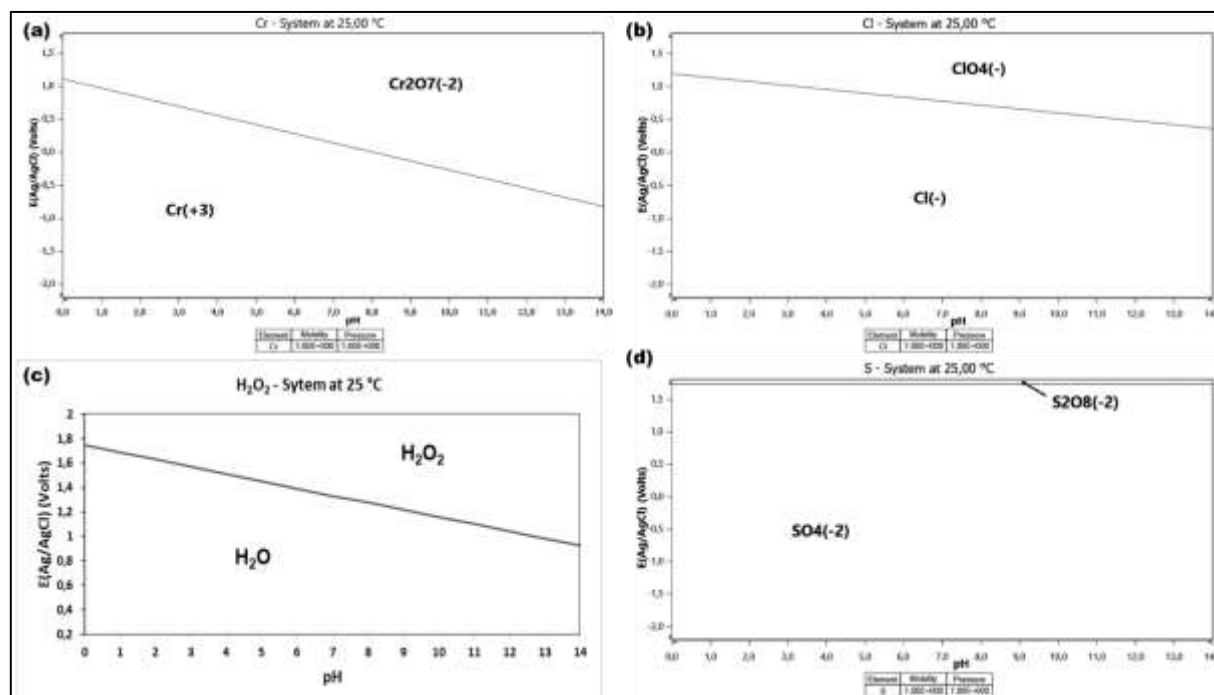
Overall, the difference in the oxidation rate between As and Fe within arsenopyrite could be explained by the galvanic interactions phenomena.  $\text{Fe}^{3+}/\text{Fe}^{2+}$  couple has a higher standard potential ( $E^\circ = 0.77 \text{ V}$  vs NHE) compared to all forms couples of arsenic. Consequently, arsenic has a higher tendency to undergo oxidation by galvanic effect due to its lower standard potential  $E^\circ$ .

#### 4.2. EFFECT OF PH

The oxidation efficiency of As and Fe using  $\text{Cr}_2\text{O}_7^{2-}$ ,  $\text{ClO}_4^-$ , and  $\text{H}_2\text{O}_2$  oxidizing agents, decreases by increasing pH, as described in Figure 2. This could be attributed to the stability of these oxidants. According to E-pH diagrams (Fig. 5), these oxidizing agents exhibit stability across a wide pH range. However, as the pH value increases, there is a decrease in the electrochemical potential, suggesting that oxidation appears to be more effective in acidic environments. However, as can be seen from Figure 5d,  $\text{S}_2\text{O}_8^{2-}$  is stable in all the range of pH, which explain its highest oxidation rate across all tested pH levels.

#### 4.3. EFFECT OF ACID TYPE

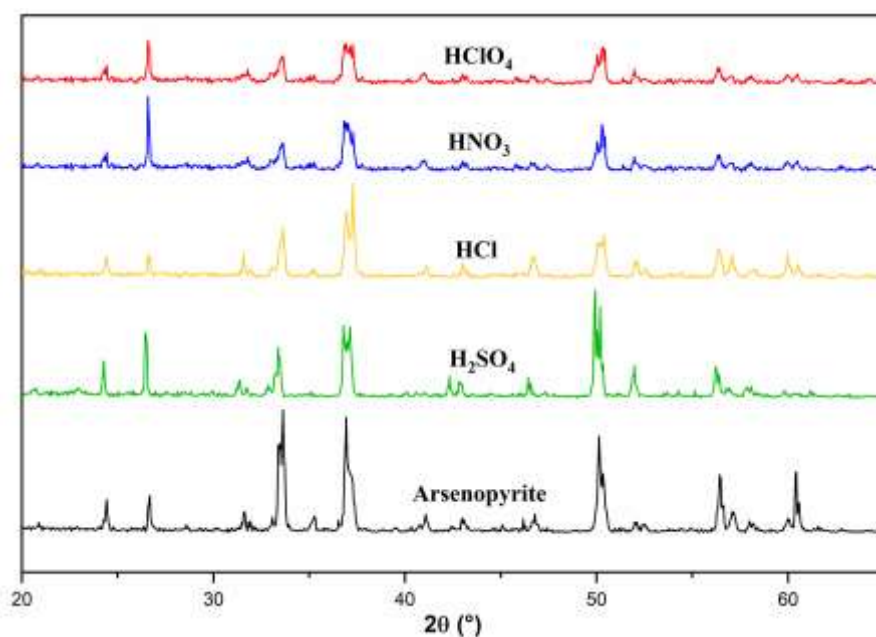
The effect of acid type experiments (Fig. 3) revealed that  $\text{HClO}_4$  was the optimum acid to be used in regulating pH for arsenopyrite oxidation by each oxidant. The effect of acid type varies in the following order:  $\text{HClO}_4 > \text{HNO}_3 > \text{HCl} > \text{H}_2\text{SO}_4$ . Antonijevic et al. (2005) mentioned the same results in their investigation of the anodic oxidation of pyrite mineral. Their results showed that the current density observed during the electrochemical measurements was higher for  $\text{HClO}_4$ , followed by  $\text{HCl}$  and  $\text{H}_2\text{SO}_4$  respectively. High current density signifies a higher rate of electron flow through the specific area of the particles. This explains the increased reaction rates observed for  $\text{HClO}_4$ . The above order of acids could be explained also by the impact of acid anions on the oxidation rate. In their studies on pyrite oxidation, Antonijevic et al. (1997) and Dimitrijevic et al. (1999) showed that  $\text{SO}_4^{2-}$  and  $\text{Cl}^-$  anions have an inhibiting effect on the oxidation. The reason of this inhibition effect was attributed to the adsorption of these anions on the



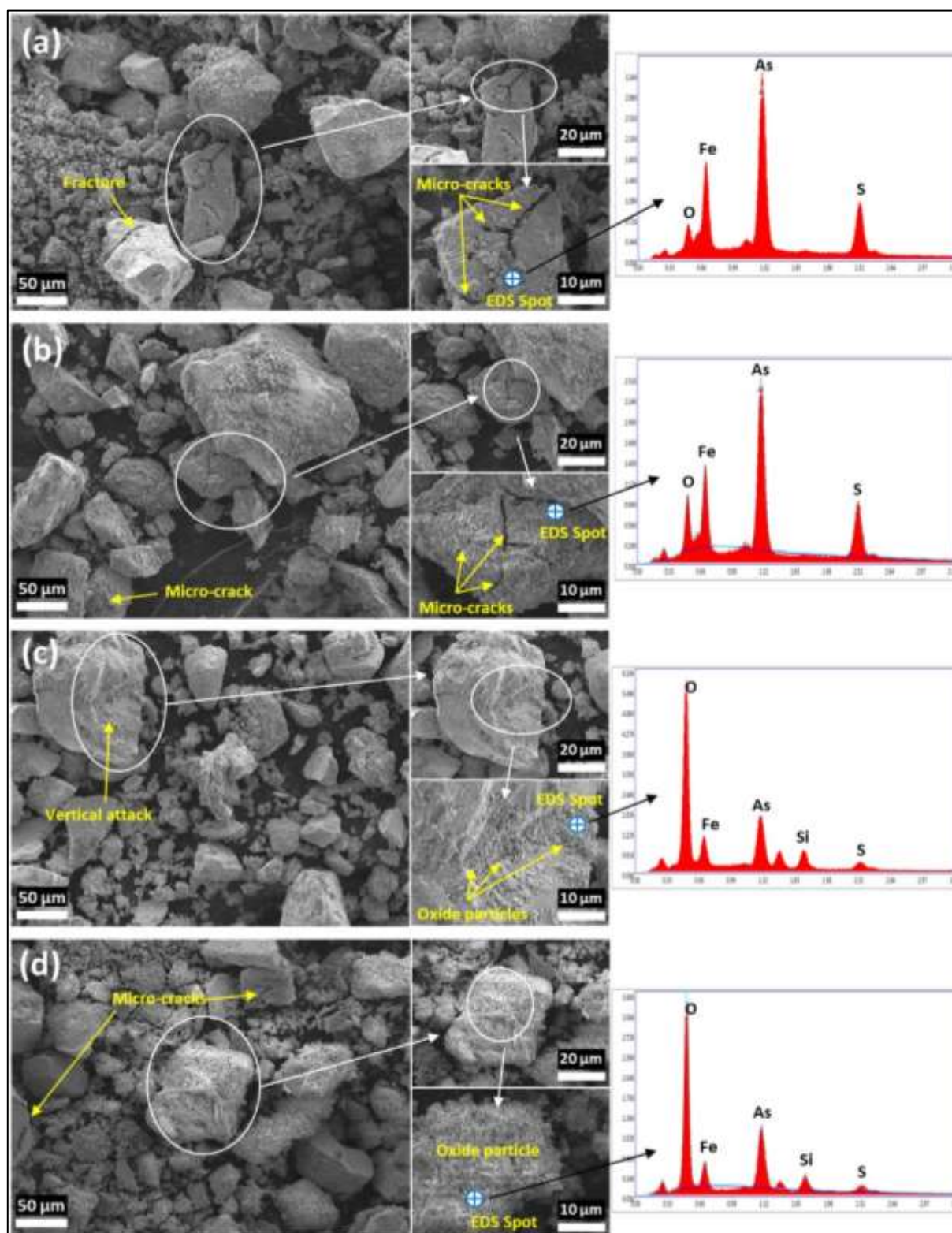
**Fig. 5** Potential-pH equilibrium diagram of: (a)  $\text{Cr}_2\text{O}_7^{2-}$ ; (b)  $\text{ClO}_4^-$ ; (c)  $\text{H}_2\text{O}_2$ ; (d)  $\text{S}_2\text{O}_8^{2-}$ ; Figures (a), (b) and (d). Constructed by HSC Chemistry 10.2.2.0 software.

surface of pyrite, thereby preventing the contact between the mineral and the oxidant. Likewise, same effect is probably occurred in the case of arsenopyrite. On the other hand, Dimitrijević et al. (1996) showed that  $\text{ClO}_4^-$  anions have no effect on pyrite oxidation, and the reason behind this phenomenon is due to the strong stability exhibited by these anions in aqueous solutions.

For the four-acid tested, the solid residues of arsenopyrite after the oxidation with of  $\text{S}_2\text{O}_8^{2-}$  oxidizing agent, have been characterized by XRD (Fig. 6) and scanning electron microscope coupled with energy-dispersive X-ray spectroscopy SEM-EDS (Fig. 7). XRD results indicate that the arsenopyrite remained unchanged and no new phases or compounds were formed after the oxidation process.



**Fig. 6** XRD pattern of arsenopyrite residues after the oxidation with  $\text{S}_2\text{O}_8^{2-}$  at pH =2.



**Fig. 7** SEM images and the corresponding EDS spectrum of arsenopyrite after the oxidation by  $S_2O_8^{2-}$  at pH = 2: (a)  $HClO_4$ , (b)  $HNO_3$ , (c)  $HCl$  and (d)  $H_2SO_4$ .



Rogozhnikov et al. (2021) mentioned that, elemental sulfur could be formed under oxidizing conditions. However, according to Flatt et al. (1995) and Miller et al. (2016), elemental sulfur  $S^0$  acts as a cyanide-consuming agent, potentially preventing gold cyanidation through excessive cyanide consumption to produce thiocyanate (Eq. 13)



Hence, the use  $S_2O_8^{2-}$  as oxidizing agent for the oxidative pretreatment of refractory arsenopyritic gold ores, will have no negative effect on the cyanidation process, since elemental sulfur is not produced after the oxidation tests.

Additionally, SEM characterization of the same residues (Fig. 7) showed the presence of fractures and micro-cracks resulting from the aggressive attack of  $S_2O_8^{2-}$  oxidant, particularly evident when exposed to  $HClO_4$  and  $HNO_3$  acids. Elemental composition analysis conducted using the EDS technique indicated the presence of a significant proportion of oxygen, which suggest the formation of oxide particles. In acidic media, iron oxides are generally not stable and are unlikely to be formed, as iron typically remains in solution as  $Fe^{2+}$  or  $Fe^{3+}$  ions (according to E-pH diagram of iron) (Mikali et al., 2023). Therefore, based on the EDS results, arsenic trioxide  $As_2O_3$  is the likely solid oxide that could be formed.

## 5. CONCLUSION

In this study, the chemical oxidation of arsenopyrite using four oxidizing agents has been investigated. Experimental results showed that peroxydisulfate  $S_2O_8^{2-}$  is the most effective oxidant for arsenopyrite, and the oxidation efficiency varies in the following order:  $S_2O_8^{2-} > H_2O_2 > ClO_4^- > Cr_2O_7^{2-}$ . The effect of pH revealed that, for all the studied oxidants, the oxidation efficiency of arsenopyrite decreases by increasing pH from pH = 2 to pH = 6. The effect of acid type experiments revealed a strong correlation between the oxidation rate of As and Fe within arsenopyrite and the type of acid employed.  $HClO_4$  acid was the optimum acid to be used in regulating pH for arsenopyrite oxidation, and the effect of acid type varies in the following order:  $HClO_4 > HNO_3 > HCl > H_2SO_4$ . The oxidation of arsenopyrite with  $S_2O_8^{2-}$  at pH = 2 regulated by  $HClO_4$ , showcased the highest oxidation in this study, with an oxidation efficiency of 81.90 % for As oxidation, and 63.94 % for Fe oxidation. Characterization of the solid residues by XRD in the case of  $S_2O_8^{2-}$  oxidant showed that, no new phases or compounds have been formed after the oxidation process. SEM-EDS of the same residues showed the presence of micro-cracks and the formation of arsenic trioxide particles. The findings of this study suggest that  $S_2O_8^{2-}$  is a promising oxidizing agent for the oxidative pretreatment of refractory arsenopyritic gold ores.

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