THE EFFECT OF SILICA, pH AND TEMPERATURE ON PYRITE PRECIPITATION

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RESUMO

O efeito da sílica na precipitação da pirita foi investigado visando contribuir na interpretação da gênese das formações ferríferas bandadas. Ensaios de precipitação em sistema batelada foram realizados na ausência e na presença de sílica. Pirita foi sintetizada pela reação entre íons ferrosos e íons sulfetos em solução aquosa. Avaliou-se a influência das variáveis tempo (0 a 500h), pH (6 e 7), temperatura (65 e 80°C) e concentração de sílica presente no sistema (0 a 1000mg/L) na formação do precipitado. Os produtos sólidos foram caracterizados por difração de raios-X, microscopia eletrônica de varredura e determinação do tamanho das partículas. Em pH 6 e 65°C, obteve-se um favorecimento da precipitação da pirita, tanto no sistema puro quanto em presença de sílica. Em pH 7 e 80°C, a presença de 80mg/L de sílica também favoreceu a precipitação da pirita em relação ao sistema puro. No entanto, nessa temperatura e em pH 6, um efeito contrário foi observado. Baseado nas concentrações de enxofre solúvel, observou-se que, em pH 7 e 80°C, elevadas concentrações de sílica (500 e 1000mg/L) podem mascarar o efeito da sílica. Para toda a faixa de concentração de sílica avaliada, não foi observada alteração na morfologia das partículas de pirita formadas.

Palavras-chaves: precipitação, pirita, sílica, formações ferríferas bandadas.

ABSTRACT

The effect of silica on pyrite precipitation was studied in order to contribute to the investigation to the genesis of banded iron formations (BIF). Batch precipitation experiments were carried out in the presence and absence of silica. Pyrite was obtained by the reaction between ferrous and sulfide ions in aqueous solution. The influence of time (0 to 500h), temperature (65 e 80°C) and silica concentration (0 a 1000mg/L) on the amount of solid formed and also on the solids morphology was investigated. The solid reaction product was characterized with respect to the presence of crystalline phases and size. In pH 6 and temperature of 65°C, pyrite formation was favored both in pure system and in the presence of silica. The presence of 80mg/L of silica in pH 7 and temperature of 80°C also favored the pyrite precipitation in comparison of pure system. However, in lower pH, 6, the opposite effect was observed. The sulfur soluble in solution thus indicates that in pH 7 and temperature of 80°C, high silica concentrations (500 e 1000mg/L) could mask the silica effect. For the whole concentration range evaluated, it was not observed change on the morphology of pyrite particles formed.

Keywords: precipitation, pyrite, silica, banded iron formation
1. INTRODUCTION

Pyrite (FeS₂) is an important source of sulfur and iron in the earth’s crust. Pyrite deposits are often explored due to the gold or copper associated with it, FeS₂ itself being a source of sulfur for sulfuric acid and ferrous sulfate production. Synthetic finely divided pyrite finds application in lithium batteries as the active cathodic material. It has also been considered for use as anodic depolarizer in the production of electrolytic hydrogen. Pyrite deposits occur as alternated layers of silica and iron minerals such as magnetite, hematite, siderite and pyrite, and constitute the so-called banded iron formations (BIF). This alternation of layers suggests that BIF would be associated to some cyclic natural phenomenon such as the earth’s rotation (Castro, 1994) or translation (Trendall and Blockley, 1970). These formations derive from the pre-cambrian period, when both hydrosphere and atmosphere were of a reducing character. In order to better elucidate the genesis of BIF, the formation of pyrite in reducing environments has been extensively studied (Brener, 1970, 1983 and Braterman et al, 1983).

For low pressures, temperatures below 100°C and under a reducing environment, hydrogen sulfide and dissolved iron react to form amorphous ferrous monosulfide (mackinawite) with chemical formulae varying between FeS₀.₈₉ to FeS₁.₃. This precursor, in the presence of elemental sulfur or polysulfide ions, transforms into pyrite (Osseo-Asare and Wei, 1996, 1997). For non reducing conditions, i.e. with little oxygen present, amorphous FeS transforms into hexagonal pirrotite (similar to mackinawite in structure and composition), greigite (Fe₃S₄) and finally pyrite. The complete oxidation of amorphous FeS results in the formation of the ferric oxide called lepdocrocite (γ-FeOOH). The conversion of mackinawite to greigite is likely to be promoted in slightly reducing conditions. Apparently, the Ostwald rule of stages applies to the precipitation of iron sulfides, i.e. the first compound formed is thermodynamically the least stable (Morse et al., 1988).

The main chemical species involved in an aqueous systems containing Fe and S are summarized in Table I. Reaction mechanisms involving these species have been proposed for the formation of pyrite. Robert et al. (1969) suggested that pyrite formation under sedimentary conditions occurred by a direct reaction between ferrous and disulfide ions, eq. (1). However, the concentration of disulfide ions in natural waters is very low due to the formation of polysulfides S₂⁻, (Murrowchick, 1986), which would preferentially be the sulfur source for pyrite in sedimentary formations (Rickard, 1975; Goldhaber and Kaplan, 1974), eq. (2). More recently, Luther (1991) suggested that not only the species Fe(HS)⁺ as also solid iron monosulfide directly reacts with the polysulfides ions to nucleate pyrite.

Table I. Chemical equilibria in the Fe-S-H₂O system.

<table>
<thead>
<tr>
<th>Reaction</th>
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<tr>
<td>Fe²⁺ + 2HS⁻</td>
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<tr>
<td>Fe³⁺ + HS⁻</td>
</tr>
<tr>
<td>S⁰ + 2HS⁻</td>
</tr>
<tr>
<td>2H₂S⁻</td>
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</table>

The diagram Eh-pH for the system Fe-S-H₂O at 25°C is presented in Figure 1. It can be observed that pyrite is stable under a board range of pH and in reducing conditions. In high values of Eh the oxides/hydroxides predominate.

In this work pyrite precipitation in the presence of silica, a very important component of BIF, has been investigated.
2. EXPERIMENTAL

A ferrous sulfide (FeS) suspension was prepared by first rapidly adding 20 mL of a 0.39 M Na$_2$S.5H$_2$O solution into a beaker containing 20 mL of a 0.1 M FeCl$_2$ solution. Thereafter 1 mL of a 0.1 M NaOH solution and 3mL water were added and the flask was sealed with plastic film. FeS precipitated instantaneously. All solutions had previously been deionized and deaerated by bubbling with nitrogen gas for half an hour. Pyrite precipitation was accomplished by mixing 0.084 g of elemental sulfur, 3 mL of silica solution, 10 mL of a FeS suspension and by filling the flask to 50 mL with KH$_2$PO$_4$ - NaOH buffer solutions with pH values of 6, 6.5 or 7. The reaction was allowed to proceed for 240 h (experiments with pH 6) and for 380 h (pH 7). The silica solutions were prepared with commercial silica in order to obtain the following initial concentrations in the reaction media: 0, 80, 100, 200, 500 and 1000 mg SiO$_2$/L. The flasks were sealed with plastic film and placed in an oven at 60 or 80 °C. The flask contents were manually agitated once a day. The suspension was hot filtered through Millipore 0.22 µm membranes. In the filtrate, the total sulfur concentration in the liquor was determined by a turbidimetric method involving sulfur oxidation to sulfate with water peroxide and subsequent sulfate precipitation with barium chloride solution. The precipitate was washed with water, carbon disulfide (CS$_2$) and acetone and weighed. CS$_2$ was used to remove any non-reacted elemental sulfur. The silica content in the precipitate was determined. The solid product was characterized by X-ray diffraction and scanning electron microscopy (SEM) coupled with energy dispersive spectrometry (EDS). Its size distribution was also determined with a Coulter-Counter. The amount of unreacted FeS in the product was determined by washing the precipitate with a hot 0.6 N HCl solution. Since FeS dissolves, weighing the dry precipitate before and after washing gives the amount of FeS which was originally present in the solid.

3. RESULTS

3.1. System without silica

Precipitation of pyrite at 80°C and pH 6.5 did not proceed substantially after 144 h, since the amount of precipitate formed was constant thereafter (Figure 2). During the reaction, a yellowish color developed, which is characteristic of polysulfides. Soluble sulfur concentration initially decreased and then increased (Figure 2), indicating that the precipitation of pyrite dominated the process in its early stages and that later the formation of polysulfides was dominant. The amount of precipitate formed did not increased, despite it was soluble sulfur present into solution. The
pyrite formed may be deposited on the FeS particles, thus hindering the progress of the reaction. Increasing the pH from 6 to 7 caused a reduction in the amount of precipitate formed (Figure 3) and a corresponding increase in the amount of soluble sulfur (Figure 4). These results are consistent with data obtained by Wilkin et al. (1996b). These authors used polysulfides as pyrite precursor and found for pH 7 a conversion into pyrite of 75 wt% of the iron initially present after 218 h. For pH 8, a conversion of only 10 wt% was obtained by those authors. Robert et al. (1969), as well as Rickard (1975) also found that the precipitation is faster for lower pH values. Figure 3 also shows that a lower temperature favors a larger amount of precipitate.

X-ray diffraction showed that pyrite was the main phase formed in all experiments. Pyrite particles investigated by SEM had frambooidal morphology (Figures 5 and 6). According to Wilkin and Barnes (1996a), the frambooidal formation results from 4 consecutive processes: (i) nucleation and growth of ferrous monosulfide particles; (ii) their transformation into greigite (Fe₃S₄); (iii) the aggregation of uniformly sized greigite microcrystals to give a frambooidal morphology; (iv) transformation of greigite into pyrite. Wilkin and Barnes (1996c) also propose that frambooidal habit is associated to slightly oxidizing conditions and to high supersaturations. Particle sizes were within the range of 2 to 20 μm (Figure 7).

### 3.2. System with silica

In all experiments, pyrite was the only phase detected with X-ray diffraction. SEM with EDS revealed that silica was associated with iron and sulfur and that no individual crystalline silica particles were present. The co-precipitated silica was amorphous. The amount of precipitate formed increased only slightly with the silica concentration in the liquid phase for values up to 500 ppm When 1000 ppm silica was present, however, the amount of precipitate formed was four times higher (Figure 8). Correspondingly, the concentration of soluble sulfur decreased slightly for liquid phase silica concentrations up to 500 ppm and showed a marked drop for 1000 ppm.

Chemical analysis revealed that silica incorporation in the precipitate increased with silica concentration in the liquid phase (Table II). The solubility of amorphous silica is, approximately, 350 p.p.m at 65°C, 420 ppm at and is practically independent of pH in the range of interest here (Iler, 1957; Baumann, 1957). Therefore, in the experiments with 500 ppm and 1000 ppm of silica was co-precipitation possible. The increase in Si content in the precipitate from 4.2wt% to
24 wt% and the increased mass of precipitate formed in these conditions indicate that co-precipitation indeed took place. For all other concentration values, Si was most likely adsorbed on the surface of pyrite particles.

Pyrite particle sizes increased substantially with Si content in the reacting. The mean particle size $D_{50}$ for the pure system and for 500 ppm Si were respectively 3.8 and 7.0 μm. For 1000 ppm Si, $D_{50}$ was 9.8 μm, but this measurement represented not only pyrite, but also included co-precipitated silica particles (Figure 7). It has been reported (Schenck, 1967) that monomeric silica promotes the oxidation of ferrous ions to ferric ions in oxidizing media for the pH range of 6.5 to 7. Ferric ions react promptly to form pyrite (Osseo-Asare and Wei, 1996) according to the reaction:

$$2Fe^{3+}_{(aq)} + 2S^{2-}_{(aq)} \rightarrow Fe^{2+}_{(aq)} + S_2(aq)$$ \hspace{1cm} (3)

Although ferric ions would eventually lead to the formation of oxidized phases such as FeOOH, in environments with reducing conditions, where sulfides are the predominant species, these iron oxihydroxides would be consumed to form ferrous ions again (Wilkin and Barnes, 1996c):

$$4 FeOOH + 1/2H_2S + 7H^+ \rightarrow 4Fe^{2+} + 1/2SO_2^{-4} + 6H_2O$$ \hspace{1cm} (4)

![Figure 3- The effect of pH on the amount of precipitate formed.](image-url)
Figure 4 - The effect of temperature and pH on sulfur concentration (pH 6, 240 h and pH 7, 384 h).

Figure 5 - Precipitate formed at pure system (pH 6.0) and temperature of (a) 65°C and (b) 80°C (reaction time of 240 h)

Figure 6 - Precipitate formed at pure system at pH 7.0 and temperature of 65°C (Reaction time of 384 h)
Figure 7- The effect of pH and temperature on the precipitate size distribution in absence of silica.

Figure 7- The effect of silica concentration on the amount of precipitate formed at pH 6.

Table II- Silica content of the precipitate formed at pH 6.5 and 80°C, after 240 h of reaction.

<table>
<thead>
<tr>
<th>Dissolved silica concentration (mg/L)</th>
<th>Silica content in the precipitate (mass %)</th>
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<tbody>
<tr>
<td>80</td>
<td>&lt; 0.1</td>
</tr>
<tr>
<td>100</td>
<td>0.4</td>
</tr>
<tr>
<td>500</td>
<td>4.2</td>
</tr>
<tr>
<td>1000</td>
<td>24.5</td>
</tr>
</tbody>
</table>
CONCLUSIONS

Pyrite synthesis from ferrous ions, elementary sulfur and sulfide ions is feasible and may be easily implemented. The extent of conversion of pyrite from ferrous monosulfate is higher at low pH values in the range 6 to 7 as well as at low temperatures in the range of 65 °C to 80°C, both in the absence and in the presence of silica in the reacting media. Precipitation is complete after 144 h for a pH of 6.5 and 80°C. Soluble silica present during pyrite precipitation incorporates in the product. For liquid phase Si concentrations in the range 80 to 500 ppm incorporation is likely to follow a surface adsorption mechanism. The Si content in the product increases with liquid phase concentration from <0.1 to 4.2 wt%. For 1000 ppm Si in the liquid phase, substantial co-precipitation of amorphous silica took place. The conversion of ferrous sulfide to pyrite was substantially enhanced in the presence of silica.

REFERENCES


