Investigations on the interaction between iron monosulfide and nitrate

Research article

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Abstract:

The interaction between iron monosulfide (FeS) and nitrate anion (NO_3^-) was analyzed by quantum calculations and by FTIR analysis of the FeS reacted with aqueous solutions of NO_3^- with two different concentrations (0.125 M and 0.5 M). The reaction conditions were as follows: temperature of 25 °C, neutral pH, and the contact time between FeS and NO_3^- solution was one month. It was found that at a low concentration of NO_3^- (0.125 M) the oxidized surface of FeS is poorer in elemental sulfur than that of FeS oxidized at a high concentration of nitrate (0.5 M). The charges of the atoms and the E_{LUMO}-E_{HOMO} difference (0.11 Hartree) for the NO_3^- were evaluated by quantum calculations.
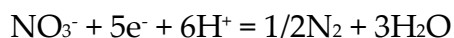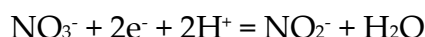
1. INTRODUCTION

Due to their high reactivity, iron monosulfides (pyrrhotite, troilite, etc.) can have harmful effects on the environment, for example through the formation of acid mine drainage (AMD) [1-5]. The AMD generating reactions associated to FeS phases are:

$$FeS + 4H_2O = Fe^{2+} + SO_4^{2-} + 8H^+ + 8e^-$$
$$Fe^{2+} = Fe^{3+} + e^-$$
$$Fe^{3+} + H_2O = Fe(OH)_3 + 3H^+$$
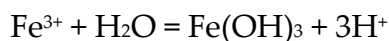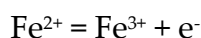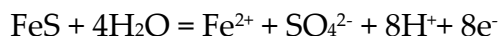
The most common oxidants are dissolved O_2 and Fe^{3+} [3,4]. The corresponding oxidation reactions are intensively studied because there is much uncertainty about their mechanism and reaction products.

In addition to the aforementioned oxidants, the role of FeS oxidant can also be played by the nitrate anion (NO_3^-). The reactions that occur when FeS and NO_3^- interact can be:

$$S^{2-} + 4H_2O = SO_4^{2-} + 8H^+ + 8e^-$$
$$NO_3^- + 2e^- + 2H^+ = NO_2^- + H_2O$$
$$NO_3^- + 5e^- + 6H^+ = 1/2N_2 + 3H_2O$$
$$NO_3^- + 8e^- + 9H^+ = NH_3 + 3H_2O$$

If we take into account the higher toxicity of NO_3^- than that of the pyrite oxidation product, sulfate (SO_4^{2-}), then the oxidation of FeS with nitrate can be beneficial for the environment [6,7]. Hence the objective of our study is the investigation of the interactions between FeS and nitrate anion by quantum calculations and by Fourier Transform Infrared (FTIR) analysis of the FeS reacted with aqueous solutions of NO_3^-. The reaction conditions were as follows: temperature of 25°C, neutral pH, and the contact time between the iron monosulfide and the oxidant solution was one month.

2. MATERIALS AND METHODS

For the experiments, it was used synthetic FeS and reagent grade $NaNO_3$. The solutions were prepared with distilled water. The concentrations of the nitrate solutions were 0.125 M and 0.5 M.

The interaction between FeS and nitrate anion (NO_3^-) occurred at a temperature of 25 °C and a neutral pH. The contact time between FeS and NO_3^- was of one month. At the ending of the experiments the reacted FeS samples were separated from the liquid and dried in the desiccator.

The analysis of the reacted FeS samples was performed by Fourier Transform Infrared (FTIR) spectroscopy.

Density Functional Theory (DFT) analysis of NO_3^- and iron monosulfide was performed by Amsterdam Density Functional 2016 (ADF2016). The Local Density Approximation (LDA) was used for the DFT study. The electronic configuration was described by a DZ basis set.

3. RESULTS AND DISCUSSION

3.1. FTIR results

The FTIR spectra obtained for the two reacted FeS samples are shown in Figure 1. The peaks at 484 and 559 cm^{-1} can be assigned to S_2^{2-}, S_n^{2-} and S^0 [3,4]. The signals at 1016 and 1153 cm^{-1} can be ascribed to $S_2O_3^{2-}$ and SO_4^{2-} species [3]. The peak at 1625 cm^{-1} is due to H_2O [4]. The bands centered to 3195 and 3434 cm^{-1} can be ascribed to H_2O and Fe(III) oxyhydroxides [3,4,8]. The peak observed at 737 cm^{-1} can be due to the NO_3^- [9] adsorbed on the reacted FeS.

The weak signals at 1625, 3195 and 3434 cm^{-1} observed for the FeS sample oxidized with 0,5 M NO_3^- (Figure 1) indicate a hydrophobic surface of the sample. The hydrophobicity of FeS sample oxidized in solution with 0.5 M NO_3^- can be explained by the preferential formation of elemental sulfur on its surface [3]:

$$S^{2-} = S^0 + 2e^-$$
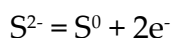
For the FeS sample oxidized in solution with 0.125 M NO_3^- we can observe a strong signal at 1016 cm^{-1} (assigned to SO_4^{2-}) which indicate as the major reaction the formation of sulfate [3,4]:
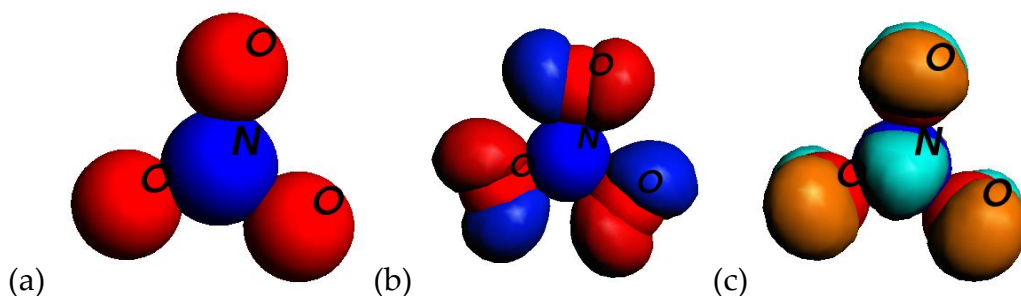
$$S^{2-} + 4H_2O = SO_4^{2-} + 8H^+ + 8e^-$$
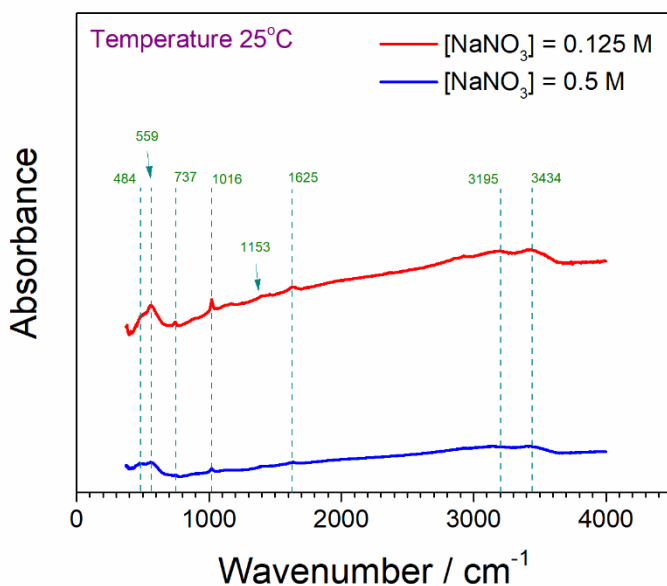
**Figure 1.** FTIR spectra of the reacted FeS samples.

3.2. DFT study for NO3- and FeS

The arrangement of N and O atoms for the case NO_3^- is presented in Figure 2a. In Figure 2b are presented the HOMO (highest occupied molecular orbital) orbitals of NO_3^-, and in Figure 2c are presented LUMO (lowest unoccupied molecular orbital) orbitals of NO_3^-.

(a)   (b)   (c)

Figure 2. (a) Optimized structure of NO_3^-; (b) HOMO orbitals of NO_3^-, and (c) LUMO orbitals of NO_3^-.

The energy difference between the LUMO and HOMO orbitals is 0.11 Hartrees (E_{LUMO}-E_{HOMO}=-0.11 Hartree). This high value indicates that covalent adsorption of NO_3^- on the FeS surface is unlikely [10].

The arrangement of Fe and S atoms for the 001 surface of FeS is shown in Figure 3. As is natural, quantum calculations have shown that iron atoms have positive charges, and sulfur atoms have negative charges.
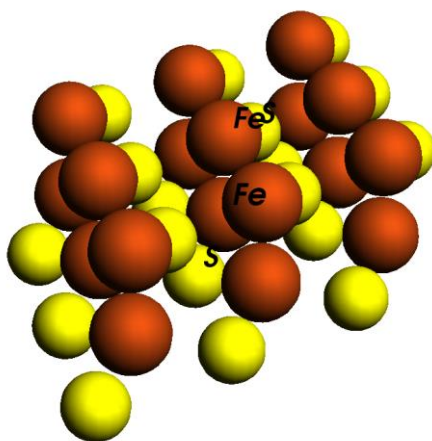
Figure 3. The positions of Fe and S atoms for the 001 surface of FeS

If we consider the large energy difference between the LUMO and HOMO orbitals, it results that the adsorption of NO_3^- on the FeS surface is controlled by the charge distribution of the atoms in NO_3^- (Figure 4) and FeS. Most probable, the adsorption process will occur as a result of electrostatic attraction between the oppositely charged atoms in FeS and NO_3^-, i.e. Fe – O and/or S – N.
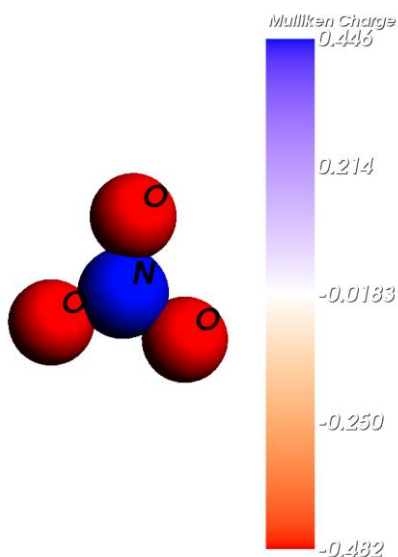
Figure 4. Nitrogen and oxygen charges in NO_3^-

4. CONCLUSION

Analysis of the interaction of iron monosulfide with NO_3^- at 25 °C leads to the following conclusions:

• At low NO_3^- concentration (0.125M $NaNO_3$) the oxidized FeS surface is more hydrophilic than that of FeS oxidized at high concentration of NO_3^- (0.5M $NaNO_3$).

• The difference between E_{LUMO} and E_{HOMO} evaluated for NO_3^- by quantum calculation is 0.11 Hartree.

• Due to the large difference between E_{HOMO} and E_{LUMO}, the interaction between FeS and NO_3^- is most likely achieved by electrostatic attraction between ions of opposite sign, i.e. Fe – O and/or S – N.

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