**Spontaneous combustion tendency of iron sulfide corrosion: oxidation characterization and thermostability**

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**Abstract**

The oxidation characterization and thermostability was studied using X-ray diffraction, Raman analysis and thermo gravimetric–differential scanning calorimetric analysis (TG-DSC). Controlled oxidation experiments were conducted for 30 mins, 1 hour and 4 hours. S-species were characterized and qualified on the surface of corrosion particle combine XRD with Raman analysis. Mackinawite FeS transforms into greigite Fe$_3$S$_4$ readily with additional S$_8$ under air atmosphere. Amorphous mackinawite is the initial phase during crystallization and its stability is poor. The thermal behavior of the corrosion is studied in heat rating 10 °C/min between ambient and 1000 °C using TG-DSC. The mass loss is mainly caused by the release of SO$_2$ between 23 and 397 °C. The maximum exothermic intensity occurs between 200 and 400 °C. Oxidation of mackiwite /greigite releases abundance of heat, which served as a trigger for spontaneously self-ignited.

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**Keywords:** iron sulfide; spontaneous combustion; Raman spectrum; TG-DSC; XRD

**1. Introduction**

It is widespread that sulfur corrosion exists in the production and transportation facilities for sour oil and gas fields. The iron sulfide film in internal carbon steel is mainly caused by corrosive media (H$_2$S /CO$_2$ and Cl$^-$ in liquid water). It could start an intense exothermic reaction only when the corrosion is exposed in air. Self-heating, and even spontaneous combustion, has imposed a serious problem in oil and gas fields. The first recognition about sulfur
corrosion of carbon steel dated from the 1940s and numerous works were devoted to the investigation of spontaneous combustion tendency in recent twenty years [1].

The conversion of iron sulfide is a complex physical and chemical process. It is reported that mackinawite transforms to other phases over a wide range of temperature or pH via various oxidative pathways. The ageing experiments indicate that mackinawite is unstable unless in reducing atmosphere. Oxidant, other than H₂S, can induce the conversion to more stable phase (pyrite or marcasite) [2,3]. Oxidation process of iron sulfide can be divided into three stages: surface layer self-heating period, incubative period and accelerative oxidation period [4]. Fe₂O₃, Fe₃O₄ and Fe(OH)₃ react with H₂S was investigated by differential thermal analysis and thermogravimetric analysis. The initial oxidation temperature of product is 233.13 °C, 308.14 °C and 287.167 °C orderly [5].

Crystalline parameters are estimated by conventional powder X-ray diffraction. Because sample is extremely sensitive to oxidation, the final product is only identified as Fe₂O₃ and Fe₃O₄ [6]. Intermediate phases are not fully understood. Furthermore, XRD is not available for poorly crystalline phase. Hence, Raman analysis is involved in studying oxidation pathway combining with XRD. Thermo gravimetric-differential scanning calorimetric analysis (TG–DSC) is used widely in thermal analysis under air atmospheres. Different heating rates are taken in account. It is reported that the oxidation reaction of purity mackianwite and greirite is endothermic [7]. But the kinetic model of complexity iron sulfide phases is carried out to obtain. Various experiments study on synthesis of iron sulfide via several pathways in laboratory [8,9]. The kinetics models of oxidation reaction are proposed. However, spontaneously self-ignited of mechanism was not illustrated in detail [10–12]. Moreover, limited studies are investigated using thermo gravimetric analysis for the kinetics of iron sulfide corrosion.

In this study, the corrosion was obtained from the facility in gas factory in order to investigate the spontaneously ignited mechanism in accordance with actual working conditions. XRD was used to identify the species and evaluate quantity for corrosion. The species changes of corrosion on sample surface were studied in ambient temperature by Raman analysis. The thermal behavior of corrosion and heat release were analyzed ranging 1000 °C from ambient under air atmosphere.

2. Experimental methods

2.1. Material

The corrosion sample was extracted from the second gas production plant of Petro China Chang-Qing Oil-field Company, Shanxi province. The sample location is at the internal surface of facility which is a part of temperature control system. According to measurement on the condition of running status, the concentration of CO₂ gas is 140±10 mg/L and H₂S gas is 39±5 mg/L.

The sample is sensitive to O₂ atmosphere. When sampling, it was immediately placed in vacuum box to reserve in order to avoid oxidation. Subsequently, the sample was dried in vacuum oven at 55 °C for 10 hours. It was grinded and screened with particle size 44-74 nm in a glove box under O₂-free nitrogen.

2.2. Controlled oxidation experiments

Oxidation was designed for texting changes in species and reaction mechanism of fresh sample evolution. The corrosion powder was weighted for three heaps about 5 g using the electronic scale. The sample was put in conical flask under a continuous gas flow, which was switched to a N₂/O₂ gas mixture (10%O₂ in N₂). The inside temperature of flask was maintain in 30 °C. The sample was opened to the low concentration oxygen atmosphere allowing slow oxidation to take place for 30 min. Other two samples in this experiment followed the same steps as described above for 1 and 4 hours separately.

2.3. Characterization

2.3.1. X-ray diffraction

The sample was estimated by X-Pert PRO powder X-ray diffraction with Cu(λ=1.54178Å) irradiation at the
scanning rate of 10°C/min in the 2θ range of 20-80°, operating at 40kV and 40mA. Before analysis, the sample was sheltered by coating with glycerol to prevent air atmosphere.

2.3.2. Raman spectra

Raman spectra was carried out with a Renishaw-2000 Spectrometer equipped with coupled to a confocal microscope. It equipped with the excitation source of 632.8 nm at a low energy level (2mW), the spectra wavenumber range from 200-2000 cm⁻¹.

2.3.3. Thermo gravimetric–differential scanning calorimetric analysis (TG–DSC)

Thermo gravimetric–differential scanning calorimetric analysis (TG–DSC) was also performed using a simultaneous differential thermal analyzer, Mettler-Toledo DSC 1/1600. The sample was measured under air atmosphere. Sample had a mass of about 14±0.1 mg. It was placed in a platinum crucible and heated at a linear heating rate of 20 °C/min with temperature range from ambient temperature to 1000 °C.

3. Result and discussion

3.1. XRD analysis

XRD is used to identify the species and evaluate quantity for corrosion derived from gas facility. The XRD pattern of the initial sample before oxidation is shown in Fig. 1, which indicates that corrosion involves several species. Because of H₂S gas as the only S-source, the formation of iron sulfide corrosion is mainly caused by the acid gas H₂S. Iron sulfide is identified as main S-species corrosion products of steel in dissolved-CO₂ and H₂S solution. The formation of pyrite is accelerated in water film of carbon steel surface, which contained chlorine ion and dissolved H₂S/CO₂. The equimolar amounts of pyrite and siderite products were consistent with the stoichiometry associated. The formation of pyrite is accelerated with the presence of CO₂. A broad hump is located at 21.32° with d-spacing (110) of 0.42nm, which is consistent with the well crystalline goethite FeO(OH). Another sharper peak at 31.53° with d-spacing (104) of 0.279 nm is confirmed as siderite FeCO₃. The formation can be illustrated following reaction below.

\[
\begin{align*}
4\text{Fe(OH)}_2 + \text{O}_2(aq) + 4\text{H}_2\text{O} & \rightarrow 4\text{FeO(OH)} + 2\text{H}_2\text{O} + 4\text{H}_2 \\
2\text{Fe}^{3+} + 2\text{S}^{2-} + \text{CO}_3^{2-} & \rightarrow \text{FeS}_2 + \text{FeCO}_3
\end{align*}
\]

Fig. 1. Diffraction patterns of corrosion by XRD.
It is the dominant mechanism for the formation of the first generation of pyrite [12]. A broad hump is located at 21.32° with d-spacing$\sigma_{(110)}$ of 0.42 nm, which is consistent with the well crystalline goethite FeO(OH). Another sharper peak at 31.53° with d-spacing$\sigma_{(104)}$ of 0.279 nm is confirmed as siderite FeCO$_3$.

The XRD pattern of sample after 4 h ours oxidation as shown in Fig. 2. Three board humps were observed at about 25.98°, 36.34° and 52.36°, which were attributed as greigite. It is reported that mackinawite is enriched on the outer layer surface of sample and subsequently transfer into greigite [13]. However, there phases is poorly crystalline which is induced by surface nucleation. The transformation could be discussed in Raman analysis.

The XRD pattern was refined by MDI Jade and the composition of corrosion was estimated, as presented in Table 1. Oxidation promotes changes in composition of iron sulfide. It can be concluded that makinawite is main reactant in oxidation. Pyrite is formed as primary products by surface nucleation mechanism in acid dissolved- H$_2$S/CO$_2$ film. The formation of marcasite, allotrope of pyrite, is caused by the low concentration of acid film.

Table 1. The composition of corrosion derived from gas facility.

<table>
<thead>
<tr>
<th>mineral</th>
<th>Pyrite</th>
<th>Greigeite</th>
<th>Iron sulfate</th>
<th>Marcasite</th>
<th>Mackinawite</th>
</tr>
</thead>
<tbody>
<tr>
<td>formula</td>
<td>FeS$_2$</td>
<td>Fe$_3$S$_4$</td>
<td>FeSO$_3$</td>
<td>FeS$_2$</td>
<td>FeS</td>
</tr>
<tr>
<td>mineral/%</td>
<td>before oxidation</td>
<td>9.3</td>
<td>3.1</td>
<td>5.9</td>
<td>-</td>
</tr>
<tr>
<td>mineral/%</td>
<td>after oxidation</td>
<td>12.7</td>
<td>4.8</td>
<td>2.1</td>
<td>0.4</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>mineral</th>
<th>Goethite</th>
<th>Siderite</th>
<th>Magnetite</th>
<th>Iron oxide</th>
<th>Hematite</th>
</tr>
</thead>
<tbody>
<tr>
<td>formula</td>
<td>FeO(OH)</td>
<td>Fe(CO$_3$)</td>
<td>Fe$_3$O$_4$</td>
<td>$\gamma$ -Fe$_2$O$_3$</td>
<td>Fe$_2$O$_3$</td>
</tr>
<tr>
<td>mineral/%</td>
<td>before oxidation</td>
<td>32.5</td>
<td>12.8</td>
<td>9.3</td>
<td>-</td>
</tr>
<tr>
<td>mineral/%</td>
<td>after oxidation</td>
<td>43.4</td>
<td>15.7</td>
<td>2.1</td>
<td>2.1</td>
</tr>
</tbody>
</table>

3.2. Raman analysis

Raman spectrometry was deemed as an efficacious means to identify the species on the surface of sample, especially non-crystalline substance. In order to verify species transformation in the surface of corrosion, Raman analysis was carried out.

The sample for 30mins oxidation was set on glass slide. Dark brown zone on the surface of sample was chosen by confocal microscope, because oxidized iron sulfide species probably existed. The Raman spectrum of corrosion after 30mins oxidation is shown in Fig. 2. The two peaks of related Raman spectrum is observed at 208 and 371 cm$^{-1}$. The band at 208 cm$^{-1}$ corresponded to a lattice mode of mackinawite. It is attributed as amorphous mackinawite in related studies [14,15]. Hence, amorphous mackinawite is the initial phase during crystallization. The bond at 371 cm$^{-1}$ is assigned to pyrite, which was the first generation of pyrite on greigite surface [16]. Greigite is formed as an intermediate on the pathway from mackinawite to pyrite. Subsequently, the sample is exposed in low-O$_2$ gas after 1 hour and chartered in the similar zone. The detected spectrums are distinguished at 211 and 371 cm$^{-1}$ with additional small peaks in Fig. 3. Two small peaks at 330 and 353 cm$^{-1}$ are evaluated as $\alpha$-FeO(OH) and $\beta$-FeO(OH) corresponded with literature data [15]. The shift from 282 to 298 cm$^{-1}$ corresponds to crystallization. It is indicated that amorphous mackinawite start converting to greigite in the early oxidation stage. The molecule structure of amorphous mackinawite is in the metastable state. Oxidation reactivity of iron sulfide occurs on the surface initiatively strengthens the Fe-S bond. Hence, the initial heat release can be assumed to the crystallization of amorphous mackinawite.

The characterization of sample after 4 hours oxidation show that three Raman bands are observed at 150, 220 and 475 cm$^{-1}$ in Fig. 4. Compared with Raman literature data, it could be confirmed to elemental sulfur S$_8$. Crystalline mackinawite is characterized by two small peaks at 208 and 283 cm$^{-1}$. According to the basis of bonding energy, the bond of iron sulfide crystals broken and abundances of S-species were produced [17,18]. It is assumed that oxidation action induces greigite formation with additional sulphur S$_8$ formed and greigite serves as precursor on the polysulfide pathway to pyrite. It is indicated that the presence of elemental sulfur has been shown to be a significant product of initial oxidation.
3.3. Thermal analysis

To investigate the thermal behavior of the corrosion, the thermo gravimetric–differential scanning calorimetric analysis (TG–DSC) is utilized. The TG–DSC curves of sample were shown in Fig. 5(a). The mass transfer is demonstrated that the mass loss occurred below 400°C and mass increase happened between 398 and 961°C. Because exothermic reaction in low temperature stage (below 400°C) severed as trigger to spontaneous combustion, the curves of this stage is illustrated the thermal behavior in detail, as shown in Fig. 5(b).

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There are three mass losses in TG curve. In the first stage, there is a slightly mass increase stage below -140°C. It is attributed to the effect of physical absorbed O₂. Meanwhile, absorbed water which is physically and chemically
bonded in mackinawite/greigite bulk is removed. The endothermic reaction should be illustrated as DSC curve presented in this stage. It is attributed to exothermic oxidation of amorphous mackinawite contributes to evaporation of absorbed water, which induces the fracture of iron sulfide surface. The first loss is assigned to the conversation of mackinawite to greigite with releasing SO$_2$ gas. It is observed the first peak at 212.5 °C in corresponding with DSC curve, which is assigned that the formation of greigite release heat. Compared with the pyrolysis of sample in nitrogen, crystal phase transforms from mackinawite to greigite at 217.7 °C as shown in Fig. 6. It is concluded that this crystal transform is controlled by the temperature condition rather than oxidizing medium. The existence of S$_8$ at greigite and pyrite surface has been confirmed in Raman analysis above. With the evolution of SO$_2$, mass loss is about 1.1%. The second mass loss of 0.7% is assigned to the formation of pyrite between 228.7 and 333.2 °C. The broad peak, located at 317.5°C in DSC curve, is attributed to transformation from greigite to pyrite. It is observed the first peak at 228.7 °C and second peak at 317.5 °C in DSC curve. The first peak at 317.5 °C in DSC curve is assigned that the formation of greigite release heat. It is reported that pyrite formation is exothermic reaction [19,20]. It suggests that this transformation promote heat release. The third mass loss is about 0.3%. The thermal process is attributed pyrite transform to pyrrhotite. However, there exists three troughs at 445, 524 and 554 °C in DSC as shown in Fig. 5a, which conforms to three endothermic peaks of pyrite oxidation pyrolysis at 450-480 °C, 530-570 °C and 630-690 °C [21]. It is assigned to the pyrolysis effect of pyrite. It could be inferred that the spontaneous combustion tendency would be inhibited by endothermic effect of pyrite. The mass increase at 400 and 1000 °C is due to the chemisorbed O$_2$ of FeO(OH) with the formation of Fe$_2$O$_3$ as pyrolysis products.

![Fig. 5. (a) TG-DSC curve between 25 and 1000 °C; (b) TG-DSC curve between 25 and 1000 °C.](image)

![Fig. 6. TG-DSC curve between 25 and 1000 °C under N$_2$ atmosphere.](image)
4. Conclusions

Controlled oxidation experiment conducted at 30 °C, showed that mackiwite is poorly crystal existing in corrosion sample. In addition, the presence of sulphur implies the beginning point for greigite formation. The presence of CO2 inhibits spontaneous combustion tendency of corrosion. It can be observed from the Raman spectra that the species vary on surface of corrosion particle. The mass loss is mainly caused by the release of SO2 between 23 and 397°C. The maximum exothermic intensity occur between 200 and 400°C. Oxidation of mackiwite/greigite releases abundance of heat, which served as a trigger for spontaneously self-ignited. The heat accumulation is inhibited by the endothermic effect of pyrite and goethite oxidation.

Acknowledgments

The authors gratefully acknowledge the financial support provided by the National Natural Science Foundation of China (NO. 51306164).

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