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KINETICS OF HYDROMETALLURGICAL EXTRACTION OF SULFUR FROM EGYPTIAN EL-MAGHARA COAL DEPOSITS

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Tests were carried out to determine pyrite dissolution, present in coal, in aqueous sulfuric acid and oxygen as an oxidant. The main objective is the evaluation of oxidative treatment in acidic media focused on the elimination of pyrite from coal. The influence of several parameters such as temperature, acid, and oxygen pressure concentrations were investigated. It was found that the dissolution curves for pyritic sulfur follow the kinetic model of the shrinking core model, with diffusion through the solid product of the reaction as the controlling stage. Additional tests show a preferential release of iron from pyrite leaving a “polysulfide” or “metal deficient” layer. Results also indicate that in aqueous solutions of 0.5 M of H₂SO₄ at 150°C and with increase in the oxygen pressure, pyrite dissolution increases around 50%.

keywords: kinetics, extraction, sulfur, coal, Egypt

1. INTRODUCTION

Coal is a complex and heterogeneous material incorporating a variety of minerals in different forms, where silicates and carbonates constitute the major ash-forming minerals. The principal sulfur-bearing minerals in coal are pyrite and marcasite. Other sulfide minerals, elemental sulfur and calcium as well as iron sulfates are found as minor constituents, while a considerable portion of the sulfur content may be organic in the form of alkyl and aryl thiols. Organic sulfur level ranges commonly from about

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0.3 to 2.0%, whereas the pyritic sulfur content may be from about 0.8 to 6%. Pyrite may be present in a wide variety of forms ranging from large grains to micron size crystallites (Wheelock and Markuszewski, 1981). When coal is burned, various sulfur forms are converted to gaseous oxides which are emitted to the atmosphere. Sulfur oxides upon reacting with atmospheric water form sulfuric acid which eventually causes acid rain. Coal is also used in the manufacture of steel, where the presence of high sulfur content is also deleterious in steel making. Therefore, coal desulfurization is important for protection of the environment and for producing metallurgical quality coals.

The conventional coal cleaning techniques are usually used for removal of coarsely liberated pyritic sulfur. However, since pyrite in most coals exists in fine sizes, advanced coal cleaning technology is required to effectively separate pyritic sulfur from coal. Removal of sulfur and ash by coal preparation methods is more economical than removing the ash and sulfur from boiler products. Desulfurization of coal is carried out through chemical processing using different leachants (iron and copper sulfate) and oxidizing agents such as H_2O_2 and O_2 (Mixon and Vermeulen 1981; Prasassarakich and Pecharanond, 1992; Yaman et al., 1995; Prayuenyong, 2002). Flotation and microbial beneficiation have been considered the most potential techniques for desulfurizing coal (Nikitin et al., 1981; Mistrik et al., 1982; Petukhov et al., 1988; Ichinose et al., 1988; Sen et al., 1991; Setfanova et al., 1991; Choudhry and Aplan, 1992; Dogan and Celedk; 1992). Both flotation and microbial beneficiation partially separate pyritic sulfur from coal, while organic sulfur, which is chemically bound to the organic structure, can be removed only through chemical reaction. Additional problems of separation by flotation result from similarity in the surface properties of unweathered coal and fresh coal pyrite. An efficient sulfur removal is difficult to be reached since both materials are hydrophobic. Chemical desulfurization is a promising technique for removal of both inorganic and organic sulfur. In this investigation desulfurization of Maghara coal is achieved through leaching with diluted sulfuric acid under oxygen pressure to convert pyrite into water-soluble sulfate form. The effect of temperature, sulfuric acid concentration, and oxygen partial pressure upon leaching of pyritic sulfur as well as kinetics of the leaching process have been studied.

2. EXPERIMENTAL

2.1. MATERIALS AND APARATUS

Maghara coal deposits are considered as the largest and the only economical coal deposits in Egypt (Al Far, 1966; Adindani, 1970; Nakhala, 1990; Said, 1991). The average results of proximate analysis on the dry basis of the studied representative coal samples are given in Table 1.

Table 1. Average results of proximate analysis on dry basis in wt. percent of studied coal samples

Constituents	Proximate chemical analysis wt. %
Volatiles	53.80
Ash	9.20
Fixed carbon	36.00
Calculated	100.00

Table 1 indicates that the Maghara coal is of a high-volatile bituminous rank with low to medium grade.

All pressure oxidation tests were conducted in a 2 dm³ autoclave with titanium internal parts to resist acid corrosion. The experimental setup and procedure were similar to those described previously (Papangelakis et al., 1991; Amer, 2001). The acidity was fixed at 0.5 M H₂SO₄ throughout the experiments and the temperature range investigated was from 120 to 160°C. The partial pressures of O₂ varied from 0.5 to 2.0 MPa. Pyrite dissolution was followed by iron analysis with atomic absorption spectrophotometer. For the calculation of the pyrite conversion, correction factors were applied to account for the volume and mass losses due to sampling, so the following formula was used:

$$X = \frac{(C_1 V_1 + A_1) 10^{-6} \cdot M_{\text{FeS}_2}}{m \cdot M_{\text{Fe}}} \quad (1)$$

where X denotes conversion of FeS₂, C_1 iron concentration (kg m⁻³), V_1 volume of leaching solution prior to its sampling (m³), A_1 total amount of iron withdrawn with previous samples (kg), M_{FeS_2} molecular mass of pyrite (g mol⁻¹), M_{Fe} molecular mass of iron (g mol⁻¹), M mass of charged coal (kg).

3. RESULT AND DISCUSSION

3.1. PETROGRAPHIC STUDY

A petrographic examination of the polished section of the studied coal samples revealed the following:

- Maghara coal samples are rich in liptinite maceral group mainly in the form of thick and/or thin walled cuticles. Pyrite grains are well observed by its yellowish colour and isotropism as euhedral to subhedral crystals and/or aggregate of fine grained framboidal pyrite associated with coal forming microlithotypes,
- study of ash by transmitted light revealed that iron oxides, mainly in the form of reddish to brownish hematite, are observed as fine to coarse grains.

3.2. X-RAY DIFFRACTION STUDY

From X-ray diffraction of the Maghara coal ash (Fig. 1) it is evident that the diagnostic peaks of hematite at "d" values 0.269 nm and 0.252 nm have maximum intensities. This ascertains a high percentage of pyrite in the Maghara coal. It is worth to mention that the presence of hematite in the Maghara coal ash is due to mainly complete combustion of pyrite associated with its coal forming lithotyes (Gaigher, 1983).

3.3. INFRA-RED SPECTRAL ANALYSIS

The infra-red (IR) absorption spectrum is a useful and quick method that can be used for analysis of most organic compounds, including coal and kerogen-rich shales. The interpretation of IR spectra (Griddle et al., 1980), displayed in Fig. 2, has revealed the following results:

- organic groups comprise free (OH) at $3660\text{--}3420\text{ cm}^{-1}$, H-bonded (OH) at $3530\text{--}3480\text{ cm}^{-1}$,
- inorganic ions include the groups of silicates mainly as kaolinite at $1050\text{--}1035\text{ cm}^{-1}$ and 930 cm^{-1} , carbonates, such as calcite or dolomite, at $1460\text{--}1445\text{ cm}^{-1}$, 790 cm^{-1} and 690 cm^{-1} , and oxides in the form of hematite at 530 cm^{-1} , and quartz at 465 cm^{-1} .

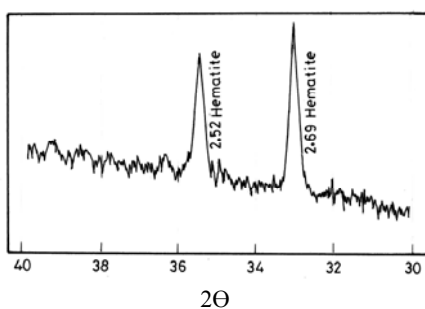


Fig. 1. X-ray diffraction of studied coal ashes showing characteristic hematite peaks

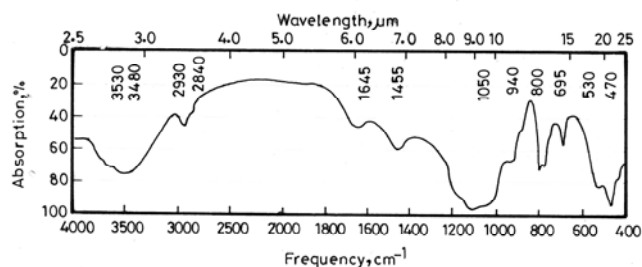
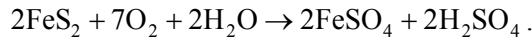
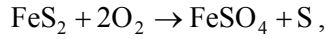


Fig. 2. Infrared absorption spectra of Maghara coals

3.4. PRESSURE OXIDATION OF PYRITE

The oxidation of pyrite may be represented by two main reactions:



An examination was made to study the effect of the following variables on the kinetics of oxidation of pyrite present in studied coal and on the distribution of products: temperature 120-160°C, oxygen partial pressure 0.5-2.0 MPa, initial acid concentration 0.1-0.6 M, pulp density 2-8% solids.

3.5. EFFECT OF TEMPERATURE

Rate for oxidation experiments at temperature from 120-160°C are shown in Fig. 3. The temperature coefficient of the rate corresponds to an activation energy of 55.9 kJ/mol. This value is consistent with 46.2 9 kJ/mol determined by Mckey and Halpern (1958) for the rate of oxidation of pyrite. The rate law for the oxidation of pyrite can be represented by

$$\frac{-d[\text{FeS}_2]}{dt} = K \cdot A_{\text{FeS}_2} \cdot P_{\text{O}_2} , \tag{1}$$

where $[\text{FeS}_2]$ is the concentration of pyrite (kg m^{-3}), A_{FeS_2} surface area of coal (m^2), P_{O_2} oxygen partial pressure in MPa.

The experimental data lead to the following expression for k

$$k = 0.125 \exp[-13.300/RT] . \tag{2}$$

Varying temperature has a marked effect on the distribution of sulfur oxidation products. With increasing temperature the formation of sulfuric acid was favored at the expense of elemental sulfur.

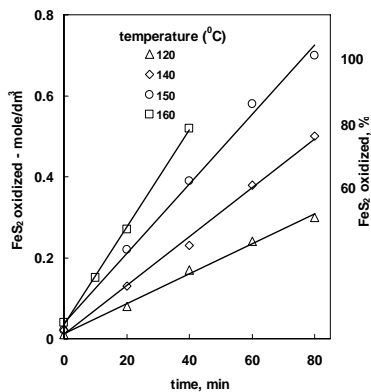


Fig. 3. Oxidation of coal pyrite in 0.5 M H₂SO₄ at 1 MPa of O₂ at various temperatures

3.6. EFFECT OF OXYGEN PARTIAL PRESSURE

Rate plots of a series of experiments in which the oxygen partial pressure was varied from 0.5 to 2.0 MPa are shown in Fig. 4. The slopes of these plots were found to be directly proportional to the oxygen partial pressure (Fig. 5).

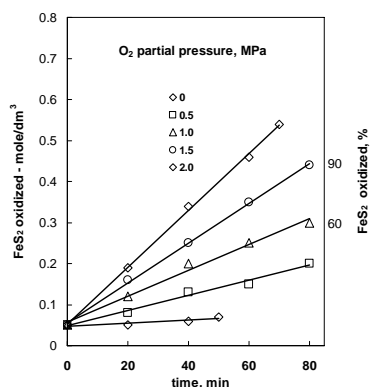


Fig. 4. Oxidation of coal pyrite at 0.5 M H_2SO_4 , 150°C at various O_2 pressure partial pressure

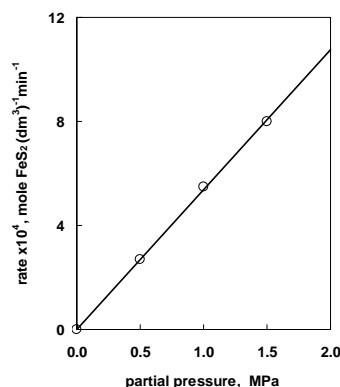


Fig. 5. Dependence of oxidation rate of coal pyrite at 150°C on O_2 pressure

3.7. EFFECT OF INITIAL ACID CONCENTRATION

The results of experiments made with solutions containing different initial concentrations of H_2SO_4 ranging from 0 to 0.6 M are shown in Fig. 6. The most marked effect of this variation is on the distribution of sulfur products. With increasing acid concentration all sulfur in the pyrite and organic forms is oxidized to sulfate, which appears as ferrous and ferric sulfates and sulfuric acid.

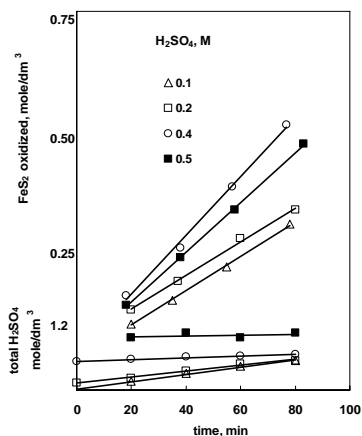


Fig. 6. Effect of initial H_2SO_4 concentration on oxidation of coal pyrite at 150°C and 1 MPa of O_2

3.8. EFFECT OF SURFACE AREA AND PULP DENSITY

The effect of specific surface area and pulp density of the studied coal are shown by the linear rate plots in Figs. 7 and 8. The rate of the reaction between pyrite present in coal with H_2SO_4 in the presence of oxygen appears to be determined by heterogeneous process on the pyrite surface. The distribution of sulfur oxidation products appears to be substantially the same for all the experiments. On the other hand the Fe(III) to Fe(II) ratio is independent of the specific surface area of coal and increases with the pulp density used. This can be explained by the fact that the rate of oxidation of Fe(II) to Fe(III) is of second order. Thus, higher coal concentration favor the formation of Fe(III). It might be expected that the resulting reduction in the size of the coal particles would be accompanied by an increase in surface area which would lead to progressive reduction in the rate as the reaction proceeded. The simplest explanation of this is that leaching is accompanied by an increase in surface roughness which compensates for the reduction in surface area. Microscopic examination of some pyrite crystals present in coal subjected to desulfurization revealed degree of surface etching which provides a support for this interpretation.

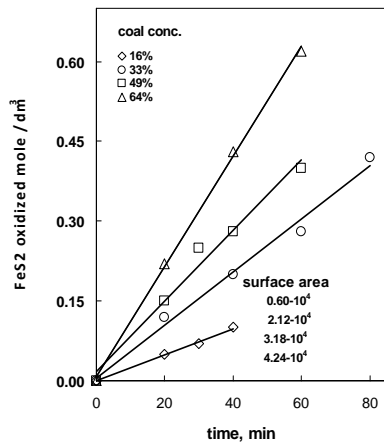


Fig. 7. Effect of pulp density and surface area on oxidation vs. leaching time of coal pyrite at 0.5 M H_2SO_4 , 150°C and 1 MPa of O_2

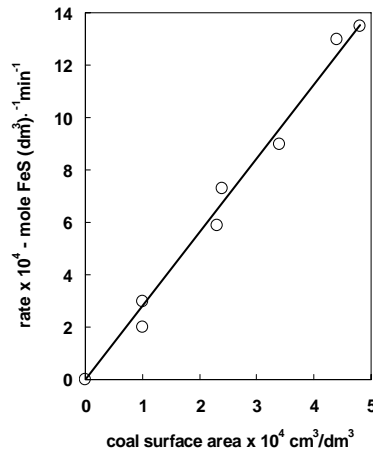
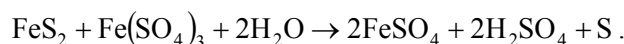


Fig. 8. Dependence of rate of oxidation at 150°C and 1 MPa of O_2 on coal surface area

3.9. EFFECT OF ADDITION OF Fe(II) AND Fe(III) SULFATES

Since ferrous and ferric sulfate accumulate in the solution during leaching of pyrite, it was considered to examine their possible effect on the reaction. It is seen that after leaching time of about 50 min Fe(II) was completely reduced while some FeS_2 was oxidized and leached. The reaction involved in oxidation of pyrite by ferric

sulfate is presumably represented by:



It might be expected that addition of FeSO_4 or $\text{Fe}(\text{SO}_4)_3$ to the solution accelerates oxidation of pyrite by O_2 .

3.10. EFFECT OF COPPER SULPHATE

An addition of copper sulfate to the leaching solution was found to have very little effect on the rate of pyrite oxidation and on the distribution of the sulfur oxidation products. However, a definite trend could be noted in direction of an increased Fe(III) to Fe(II) ratio as the CuSO_4 concentration is increased (Fig. 9). It is also of interest to note that CuSO_4 does not catalyze the direct oxidation of FeS_2 by O_2 . It previously had been suggested that such catalysis might result from the mechanism involving the replacement of CuSO_4 by FeS_2 as follows:

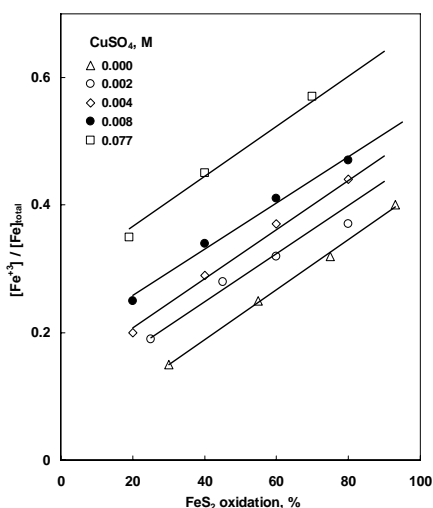
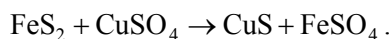


Fig. 9. Effect of CuSO_4 on FeS_2 oxidation at 0.5 M H_2SO_4 , 150°C and 1 MPa of O_2 partial pressure

3. CONCLUSIONS

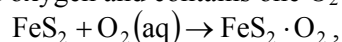
A number of conclusions concerning the mechanism of the Maghara coal desulfurization may be derived from the foregoing results:

- rate-determining step in the oxidation of pyritic sulfur is apparently a heterogeneous process on the pyrite surface,
- desulfurization of coal increases with increasing temperature and oxygen partial pressure where 96% of sulfur present in coal is removed at 150°C in 0.5 M after

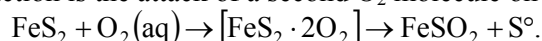
60 min of leaching,

- a plausible mechanism for coal desulfurization is consistent with the observed kinetics, and might involve a sequence of steps:

1) fast, O₂ is chemisorbed rapidly on the pyrite surface which is always covered by a monolayer of oxygen and contains one O₂ molecule at each FeS₂ site



2) slow, the reaction is the attack of a second O₂ molecule on an O₂ covered site



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Przeprowadzono badania w celu określenia rozpuszczalności pirytu obecnego w węglu. Roztworzenie prowadzono za pomocą kwasu siarkowego oraz tlenu jako utleniacza. Głównym celem badań była ocena procesu utleniania pirytu w roztworach kwaśnych w celu usunięcia go z węgla. Badano wpływ temperatury oraz stężenia kwasu, a także ciśnienia tlenu. Stwierdzono, że rozpuszczanie siarki pirytowej zachodzi według modelu "shrinking core" z dyfuzją przez ciało stałe jako reakcją kontrolującą. Dodatkowe badania wykazały, że uprzywilejowane uwalnianie się jonów żelaza z pirytu pozostawia warstwę polysiarczku lub warstwę zubożonej w metal. Otrzymane wyniki wskazują, że w wodnych roztworach 0.5 M H₂SO₄ w temperaturze 160°C i ze wzrostem ciśnienia tlenu rozpuszczanie pirytu wzrasta około 50%, oraz że zachodzi "degradacja" tlenu z powodu obecności jonów żelaza w strukturze węgla.

słowa kluczowe: kinetyka, ekstrakcja, siarka, węgiel, Egipt