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Mineralogy of Ferrihydrite and Schwertmannite from the Acid Mine Drainage in the Donghae Coal Mine Area

동해탄광일대의 산성광산배수에서 침전된 페리하이드라이트와 슈워트마나이트에 대한 광물학적 연구

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ABSTRACT : The ochreous precipitates, reddish brown and brownish yellow in color, are precipitated in the stream bottom of acid mine drainage (AMD) in the Donghae coal mine area. X-ray diffraction analysis shows that the reddish brown precipitate consists mainly of ferrihydrite with small amount of goethite, while the brownish yellow precipitate of schwertmannite. Thermal experiments show that ferrihydrite and schwertmannite partially convert to poorly-crystallized hematite at 400 ℃ and to well-crystallized hematite at 700 ℃.

Key words : acid mine drainage, ferrihydrite, schwertmannite, goethite, hematite

요약 : 동해탄광 일대에서 산성광산배수가 유입되는 하천의 바닥에는 적갈색과 황갈색의 침전물이 형성되고 있다. 이 침전물에 대한 X-선 회절분석 결과 적갈색 침전물은 대부분 페리하이드라이트이며 소량의 침철석을 포함하고 있는 반면에 황갈색 침전물은 슈워트마나이트로 구성되어 있다. 열분석과 가열 실험에서 페리하이드라이트와 슈워트마나이트는 약 400 ℃에서 결정도가 낮은 적철석으로 변화하며 700 ℃에서는 결정도가 높은.적철석으로 변화한다.

주요어 : 산성광산배수, 페리하이드라이트, 슈워트마나이트, 침철석, 적철석

Introduction

The Donghae coal mine (long. 128° 56'E, lat. 37° 06'N) located in the eastern part of Taebaeg city, Korea. The mine was closed early 1990s due to economic and industrial reasons by Coal Industry Promotion Board. The altitude of the waste dump is approximately 1,000 m above sea level. Several hundred square meters are covered with waste rocks. The acid mine drainage (AMD) produced from the Donghae coal mine and the leachate through waste dumps enters directly into local streams. The dissolved species in the AMD is precipitated to the ochreous sediments in the stream bottom under control of the chemical conditions of the stream waters (Kim et al., 2002).

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AMD is extremely acidic and enriched in iron, aluminum, sulfate and heavy metals such as lead, mercury, cadmium and manganese (Chapman *et al.*, 1983; Herr and Gray 1995; Schwertmann *et al.*, 1995). AMD, a common type of pollution in mining areas, derives from the oxidation of sulfide minerals in coal or other mining waste and tailings, which generates the free acidity and soluble metal species. In the oxidizing environment of the coal mine, the oxidation of pyrite releases ferrous/ferric irons, sulfur that in turn may be oxidized to sulfate, and H^+.

The production of AMD from metal and coal mining operations typically results in the precipitation of iron oxyhydroxides within implicated stream channels (Chapmen *et al.*, 1983; Ferris *et al.*, 1989; Bowell and Bruce, 1995). The discharge of AMD not only introduces a large quantity of metals that will become associated with sediments, but also results in the formation of ochreous precipitates consisting mainly of Fe and SO_4 (Winland *et al.*, 1991; Yu, 1996; Kim, 2002; Rose and Elliott, 2000).

Ferrihydrite is a common iron oxide mineral in low temperature surface environments such as soils, lake and drainage bottoms, and hot spring deposits (Schwertmann and Taylor, 1989). It is important in environmental geology because of its common occurrence in mine-waste environments and its demonstrated ability to adsorb or form coprecipitates with organic compounds and ions of a wide variety of elements (Jambor, 1994; Jambor and Dutrizac, 1998).

Schwertmannite occurs as an ochreous precipitate from acid, sulfate-rich waters and elsewhere (Bigham *et al.*, 1994; Webster *et al.*, 1998; Carlson, *et al.*, 2002; Kim *et al.*, 2002). Its ideal formula is $Fe_8O_8(OH)_6SO_4$ but may range to $Fe_8O_8(OH)_{4.5}(SO_4)_{1.75}$ depending upon the degree to which tunnel and surface sites are saturated with sulfate (Bigham *et al.*, 1990, 1996).

The purpose of this study is the characterization of mineralogy of ferrihydrite and schwertmannite precipitated at AMD in Donghae coal mine.

Materials and Methods

Sampling

The sediment on the stream bottom of the acid mine drainage in the Donghae coal mine area were very fine and reddish brown and brownish yellow in color with variable amounts of detrital materials. They are generally less than 1 mm in thickness. Ochreous precipitates were sieved in laboratory using the 63 μm plastic sieve to remove large detrital materials, concentrated by gravity settling, and dried at room temperature for experiments.

Analytical Methods

For identification of mineral constituents of precipitates, X-ray diffraction analyses were conducted using Co$K\alpha$ radiation with automatic horizontal goniometer equipped with a scintillation counter, and graphite monochromator and a 1° DS, 0.6 mm RS, 1° SS slit conditions. All specimens were step scanned in step interval $0.05^\circ/2\theta$ and with 10 sec scanning time. Differential thermal analysis (DTA) and thermogravimetry (TG) were run on representative samples of ferrihydrite and schwertmannite using Setaram LABTGA at a heating rate of 10 ℃/min. Weight loss was determined for 20~35 mg samples in alumina crucibles at temperatures ranging from 50 to 1200 ℃. Chemical compositions of precipitates were analyzed using a JSX-3200 energy dispersive X-ray fluorescence spectrometer (ED-XRF) at 30 kV and scanning time for 600 sec.

Results and Discussion

Ferrihydrite

Table 1 shows that reddish brown precipitate consists approximately of 75~79% Fe and 17~20% H_2O with small amounts of 0.6~1.3% Al_2O_3, 0.7~1.1% SiO_2 and 0.7~0.8% CaO.

XRD analysis shows that the reddish brown

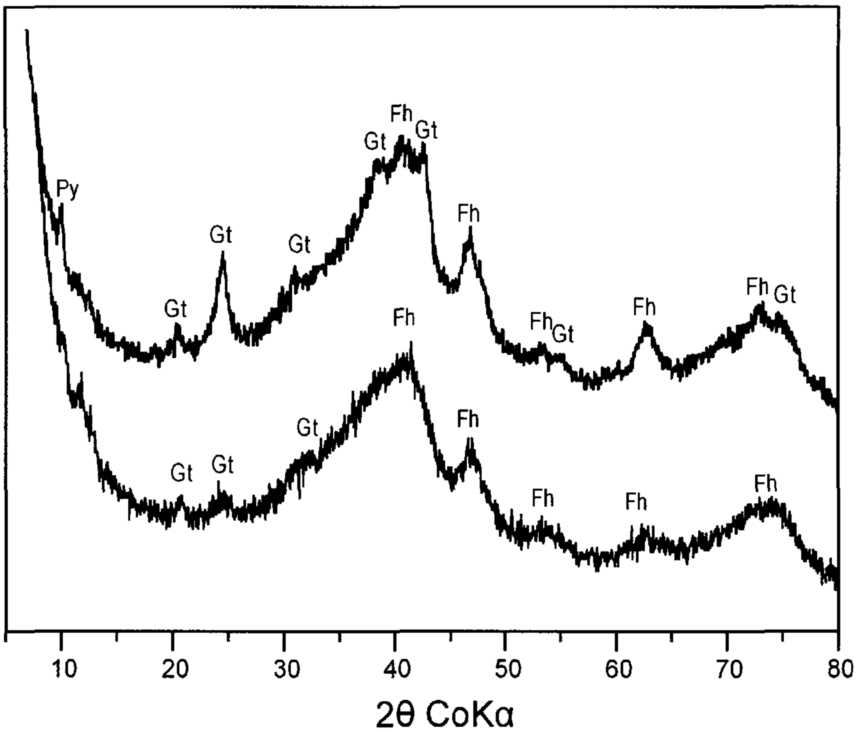

Fig. 1. XRD patterns of reddish brown precipitates from stream bottom in the study area. (Gt: goethite, Fh: ferrihydrite, Py: pyrophyllite)

precipitate is composed mainly of ferrihydrite with small amount of goethite (Fig.1). XRD pattern of ferrihydrite consists of six diffraction bands. The gradual development of hematite from ferrihydrite is seen from the XRD patterns resulting from heating experiment (Fig. 2). X-ray diffraction analyses of heated ferrihydrite show that it is partially converted to poorly crystallized hematite at 400 ℃ and transformed to well crystallize hematite at 700 ℃.

Thermal decomposition of ferrihydrite from acid mine drainage precipitates produces a low-temperature endotherm in 120 ℃ (Fig. 3). The endothermic reaction is associated with a weight loss of approximately 18.89% that probably derives from the vaporization of a layer of chemisorbed H_2O as well as structural OH/H_2O. After vaporization of structural OH/H_2O, ferrihydrite is completely converted to hematite at approximately 400 ℃. A final weight loss of approximately 21.18% at 850 ℃ is attributed to decomposition of ferrihydrite to hematite. Saleh and Jones (1984) and Eggleton and Fitzpatrick (1988) found a weight loss of 22.4% for a synthetic 6-line ferrihydrite and of 19.65% for 6- and 2-line ferrihydrite, respectively.

Schwertmannite

The brownish yellow precipitates on the stream bottom contain approximately 58~61% Fe, 15% SO_3, 19~21% H_2O and 0.8~3.4% Al_2O_3, 1.0~3.9% SiO_2 and 0.8~3.5% CaO (Table 1). The Fe:S ratios are ranges from 3.77 to 4.12. Though Fe:S ratio for ideal schwertmannite, $Fe_8O_8(OH)_6SO_4$, is 8, the lower values (ranging to <5) are usually found and are attributed to adsorption of excess sulfate on the schwertmannite surface (Ghiorse and Ehrlich, 1992; Schwertmann *et al.*, 1995).

XRD analysis shows that the brownish yellow precipitate is composed mainly of schwertmannite

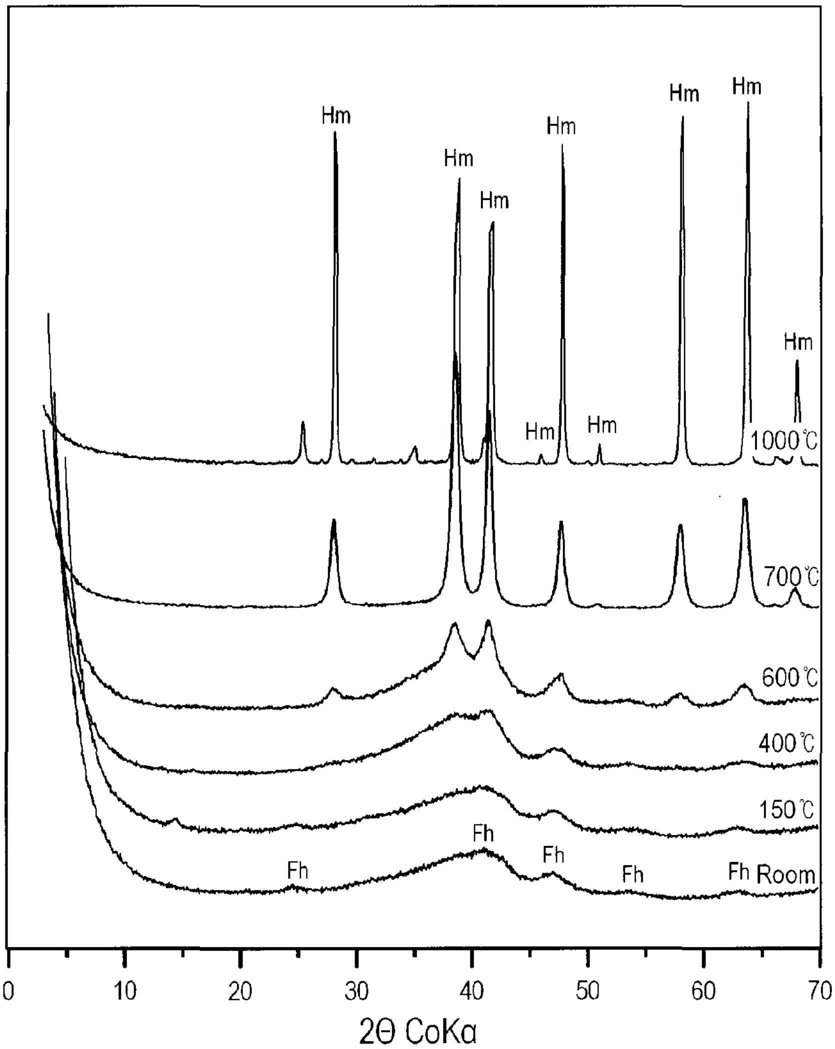

Fig. 2. XRD patterns of ferrihydrite heated for 3 hours. (Fh: ferrihydrite, Hm: hematite)

with small amounts of quartz, pyrophyllite and illite (Fig. 4). The XRD pattern of schwertmannite consists of eight broad peaks with superimposed sharp peaks due primarily to detrital materials. The broad diffraction peaks of schwertmannite indicate poor crystallinity, limiting the use of conventional XRD analysis, but the mineral has a unique XRD profile that can be readily distinguished from those of associated minerals if specimens are reasonably pure. The XRD pattern of schwertmannite consists of eight broad peaks and is perhaps most easily confused with that of well crystallized ferrihydrite. The strongest peak for both minerals occurs at about 2.54 Å, but that of schwertmannite is characteristically more symmetrical. The detection of schwertmannite in mixed assemblage with other minerals may be difficult because of its poor crystallinity.

XRD analyses of schwertmannie samples heat-treated at 400 ℃ show that it is at least partially convert to poorly crystallized hematite (Fig. 5). Schwertmannite converts to well crystallize hematite at about 700 ℃.

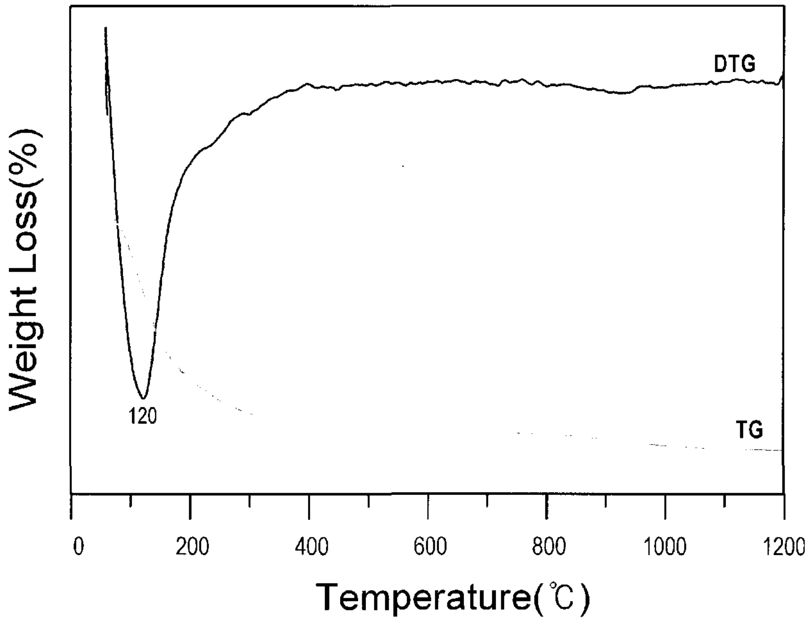

Fig. 3. DTG and TG curves of ferrihydrite from stream bottom of AMD in the study area. Total initial sample weight: 26.49 mg.

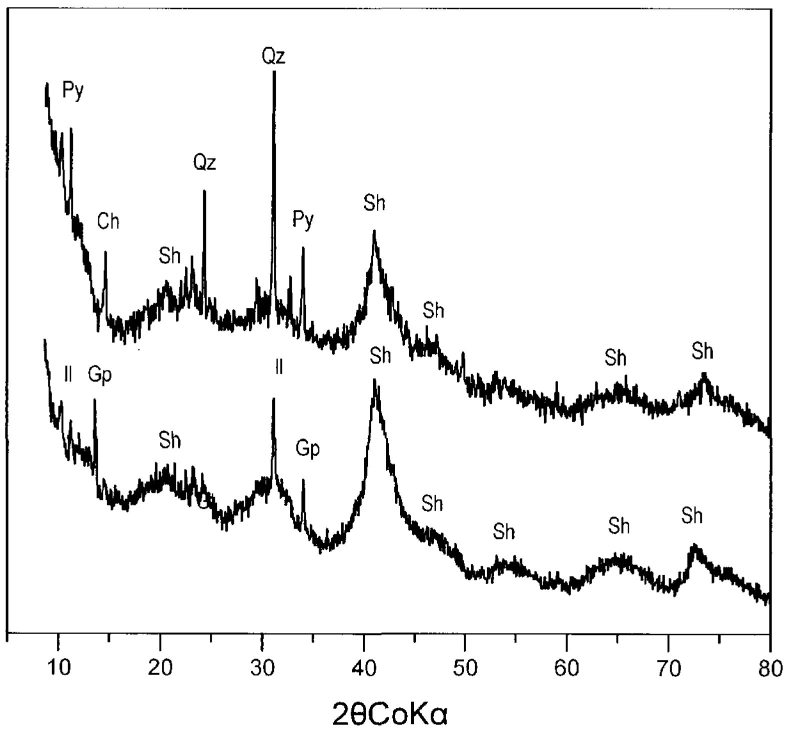

Fig. 4. XRD patterns of brownish yellow precipitates from stream bottom in the study area. (Gp: gypsum, Qz: quartz, Gt: goethite, Il: illite, Py: pyrophyllite, Ch: chlorite, Sh: schwertmannite)

Table 1. Chemical compositions of ferrihydrite and schwertmannite analyzed by ED-XRF

Samples	Al_2O_3	SiO_2	P_2O_5	SO_3	CaO	Fe_2O_3	H_2O	Total
reddish brown	0.63	1.11	0.01	0.63	0.77	74.89	20.12	98.16
(ferrihydrite)	1.25	0.67	0.01	0.58	0.67	78.82	16.86	98.84
brownish yellow	0.86	1.02	0.39	14.74	0.57	60.76	20.54	98.87
(schwertmannite)	3.35	3.87	0.07	15.34	1.73	57.78	18.66	100.80

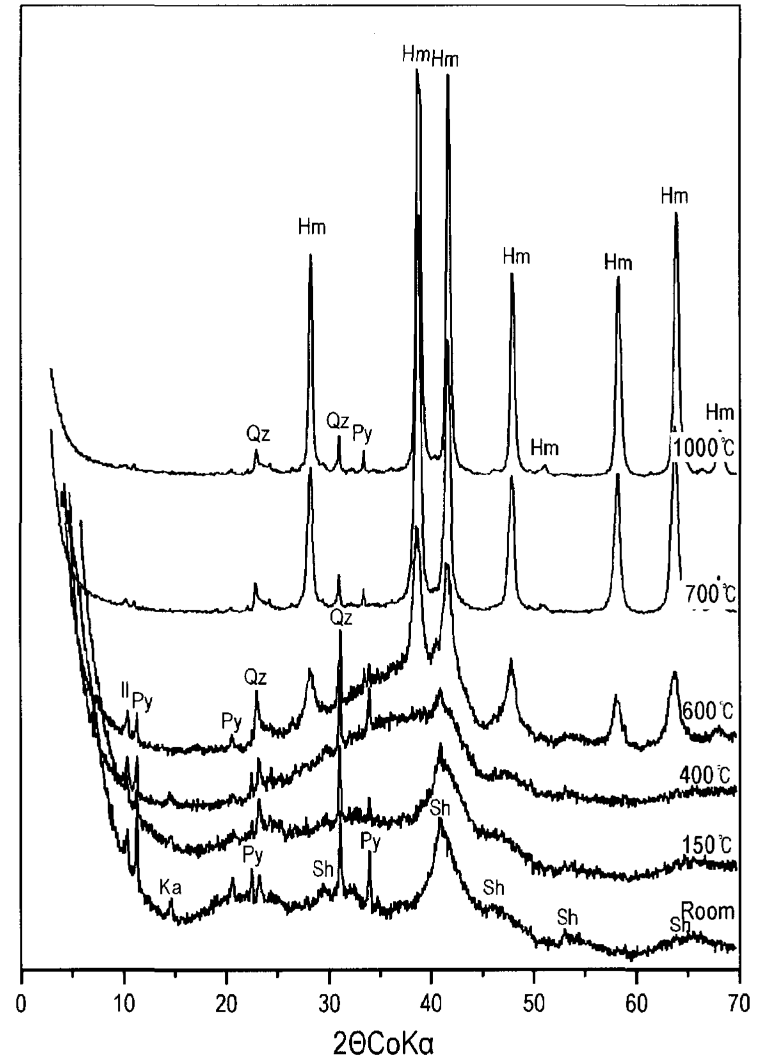

Fig. 5. XRD patterns of schwertmannite heated for 3 hours. (Sh: schwertmannite, Il: illite, Py: pyrophyllite, Qz: quartz, Hm: hematite)

The thermal decomposition of schwertmannite yields a low-temperature endotherm between 100 and 300 ℃ followed by an exotherm at 437 ℃ associated with a weight loss of 15 to 20% by vaporization of sorbed water as well as structural OH/H_2O (Fig. 6). The final endotherm at 634 ℃ is attributed to the decomposition of $Fe_2(SO_4)_3$ to hematite and SO_3 resulting in a weight loss of 5

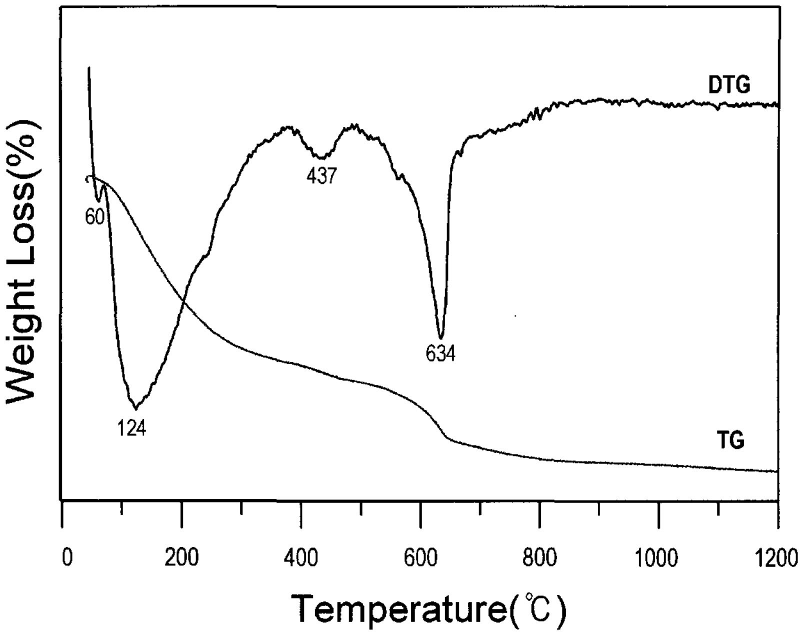

Fig. 6. DTG and TG curves of schwertmannite from stream bottom of AMD in the study area. Total initial sample weight: 32.12 mg.

to 10%.

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