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ETTRINGITE FORMATION FOLLOWING CHEMICAL NEUTRALIZATION TREATMENT OF ACIDIC COAL MINE DRAINAGE

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ABSTRACT

This paper reports an unusual occurrence of the rare mineral ettringite, which formed as a result of acid mine drainage treatment at a surface coal mine in northern West Virginia, USA. Ettringite, a hydrated basic sulfate of calcium and aluminum [$Ca_6Al_2(SO_4)_3OH_{12}$ $26H_2O$], forms in high pH environments under oxidizing conditions where sufficient dissolved calcium, aluminum, and sulfate are present. When viewed in relation to the overall goal of mine drainage treatment, namely to produce an effluent that is less detrimental to aquatic biota, ettringite formation documents severe overtreatment of acidic mine waters to the point of producing a highly alkaline effluent that may have adverse effects upon aquatic life.

INTRODUCTION

Ettringite, a hydrated basic sulfate of calcium and aluminum [$Ca_6Al_2(SO_4)_3(OH)_{12}$ $26H_2O$], was originally identified in cavities of metamorphosed limestone inclusions in a leucite-nepheline-tephrite near Ettringen, Germany, in the 1870s [1]. Other reported occurrences of this relatively rare mineral include County Antrim, Ireland, in a contact zone between limestone and dolerite [2]; near Tombstone, Arizona, USA, as an alteration product of calcium and aluminum silicates; at Franklin, New Jersey, USA [3], and at Crestmore, California, USA [4,5]. Ettringite is also a hydration product of Portland and supersulfated cements, a common product of concrete alteration, and is used in "satin white" for paper coatings [6]. Ettringite is frequently associated with thaumasite [$Ca_6H_4(SiO_4)_2(SO_4)_2(CO_3)_2$ $26H_2O$], which is similar in physical properties and unit cell dimensions [7], and may be associated with several other related minerals [8].

This paper records an unusual occurrence of ettringite in a settling pond at a coal strip mine in northern West Virginia, USA. Detailed sampling and analysis of sediments at this retention pond were undertaken as part of a study examining the distribution and mobility of selected transition metals in such sediments. Predictive equations for extractable metals in retention pond sediments (based on data from 19 surface coal mines in the Eastern and Midwestern U.S.) were discussed previously [9].

METHODS

The retention pond examined was located approximately 16 km southwest of Kingwood, West Virginia. The mine drainage, most of which was contributed from abandoned underground mine operations in the area, was acidic (pH about 2.0), contained high levels of sulfate and aluminum, and required treatment with a neutralizing reagent before discharge in order to comply with U.S. government standards for pH, iron, and manganese. The pond was constructed to trap both transported sediment and newly formed precipitates resulting from the neutralization treatment. Treatment was usually accomplished by adding a solution of 20% sodium hydroxide (NaOH) to the drainage stream through a flow-proportional dispensing system. After treatment, the mine drainage flowed approximately 224 m through an open channel to the settling pond. During times of high flow, the NaOH system was by-passed, and the pond was sprayed with a aqueous suspension of hydrated lime, or $Ca(OH)_2$. Water depth was approximately 1 m. The pond drained through a perforated standpipe; during major rainfalls, the pond also drained through an emergency spillway. The general configuration of the pond and associated inlet/outlet structures are shown in Figure 1.

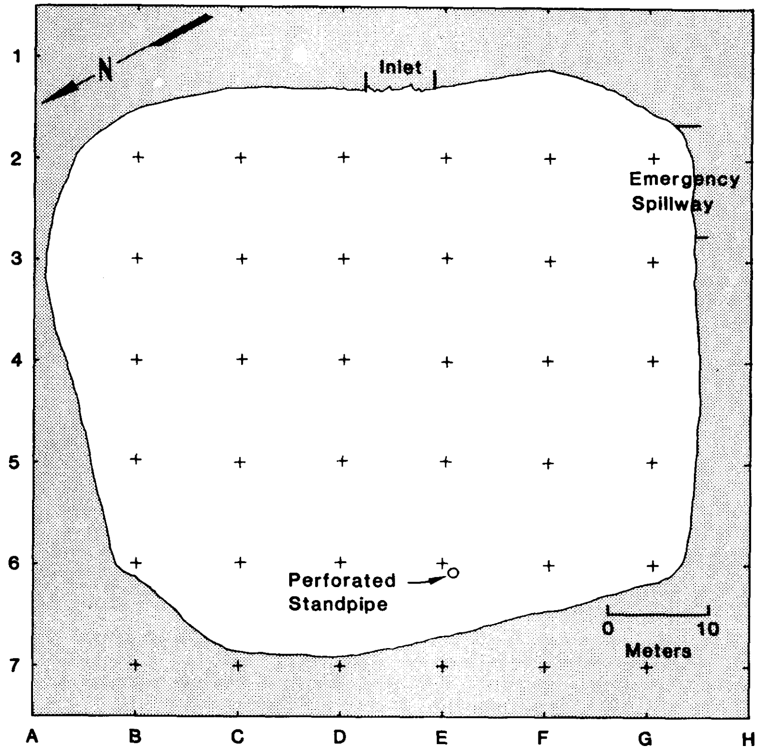

Fig. 1. Base map of settling pond, showing grid system used to determine sample locations.

Field procedures pertinent to this paper included (a) establishing a 10-m grid system for the pond and a limited area of pond perimeter; (b) sampling water at each of the established grid points in the pond; (c) taking instantaneous measurements of water pH at the pond surface and immediately above the sediment/water interface; (d) sampling sediment at each grid point; and (e) immediately measuring pH of each sediment sample collected from the pond bottom. All sediment samples were grab samples. All sampling was done on May 29, 1980.

Laboratory procedures included chemical analysis and use of optical and x-ray diffraction techniques for mineralogical identification. Scanning electron microscopy (SEM) provided a direct view of the ettringite formed. Chemical analysis included (a) analysis of pond water for major and minor constituents and selected trace metals, and (b) analyses of digested air-dried sediment samples for sulfur fractions and selected total and extractable metals. All metals analyses were done in triplicate on a Perkin-Elmer 603 Atomic Absorption Spectrophotometer. Sulfur analyses on pond sediment were done by LECO furnace. X-ray diffraction of random mount powdered samples, using nickel-filtered CuK_a x-radiation was completed for all sediment samples. Refractive indices were measured by standard optical techniques.

RESULTS

Physically, the pond sediment consisted of a green to red/brown gelatinous precipitate with varying amounts of detrital material. X-ray diffraction indicated the presence of ettringite in sample D5 (Figure 1); the ettringite was associated with less than 5% a-quartz and calcite. In other sediment samples, crystalline components that were identified included gypsum, a-quartz, kaolinite, calcite, and dolomite. The sum of these minerals was frequently a small percentage by weight of the total; accordingly, large quantities of amorphous or poorly crystalline material was present. The chemical extraction data (not reported here) indicated that this material consisted mainly of iron oxyhydroxides and other metal hydroxides.

A comparison was made of X-ray diffraction data for pond sample D5 to published powder-diffraction data [10] and to a synthetic ettringite sample obtained from the Portland Cement Association, Skokie, IL, USA (See note 1). Strong reflections at 9.70, 5.60, 3.88, 3.46, 2.77, and 2.56 / confirmed the identification of ettringite in sample D5. Reflections of weak intensity on the reference sample of ettringite could not be distinguished from background radiation on sample D5. Taking the reference sample

Fig. 2. Scanning electron micrograph of sample D5, showing characteristic needlelike crystals of ettringite. Scale is 10 µm.

obtained from the Portland Cement Association as approximately 100% pure ettringite and comparing peak heights, the pond sample was approximately 67% ettringite. Since ettringite and thaumasite may be closely associated, a comparison was made between the three most intense peaks of sample D5 and the three most intense peaks of thaumasite, which are 9.66, 3.79, and 4.58 Å with I/I' of 100 75, and 65, respectively [11]. This comparison confirmed that the three most intense peaks of sample D5 coincided more closely with those of ettringite than with those of thaumasite. A repetition of the diffraction analysis for sample D5 approximately six months after the initial identification showed no change in the diffraction patterns.

Measurement of the refractive indices for sample D5 coincided closely with reported refractive indices for ettringite, ω = 1.4655 and ε = 1.4618 [12]. In addition, scanning electron microscopy (SEM), as shown in Fig. 2, indicated the characteristic needlelike habit of ettringite in sample D5 sediment.

Selected chemical data and a generalized consideration of pond geochemistry support the identification of ettringite in sample D5 in the downstream portion of the pond. Most of the pond sediment was characterized by gypsum rather than ettringite; the gypsum ranged from a trace to approximately 10% by weight of the sediment. Figure 3a, a contour plot of sediment pH, indicates that the occurrence of ettringite in the pond coincided with the region of highest pH values (in excess of 11.0), a condition necessary for ettringite formation. In the area of sample D5, pockets of unreacted hydrated lime were also noted in the sediment. Figure 3b, a contour plot of pond water pH immediately above the sediment/water interface, shows pH in excess of 10.0 at the point of ettringite occurrence. Correspondingly, plots of percent total sulfur in sediment and calcium concentration in pond water (Figures 3c and 3d) also indicate high values at location D5. Total aluminum in D5 sediment is approximately 4%. In all four plots (Figures 3a through 3D), strong concentration gradients exist from the pond inlet to the area around the standpipe.

CONCLUSIONS AND ENVIRONMENTAL IMPLICATIONS

Ettringite formed in the retention pond under study as a result of treatment of low pH, high sulfate water with sodium hydroxide and hydrated lime. Chemical evidence favoring ettringite formation included high pH conditions and high concentrations of sulfur and calcium at the location of ettringite occurrence (D5 on reference grid). The overall purpose of acid mine drainage treatment is to reduce high levels of dissolved metals and acidity in order to produce an effluent that is less detrimental to aquatic biota in

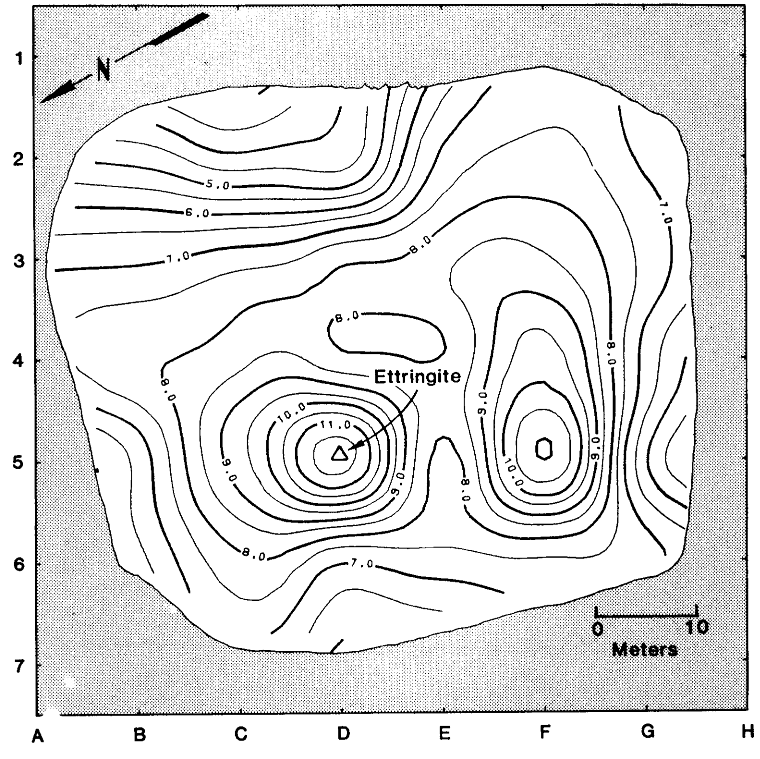

Fig. 3a. Contour plot of sediment pH.

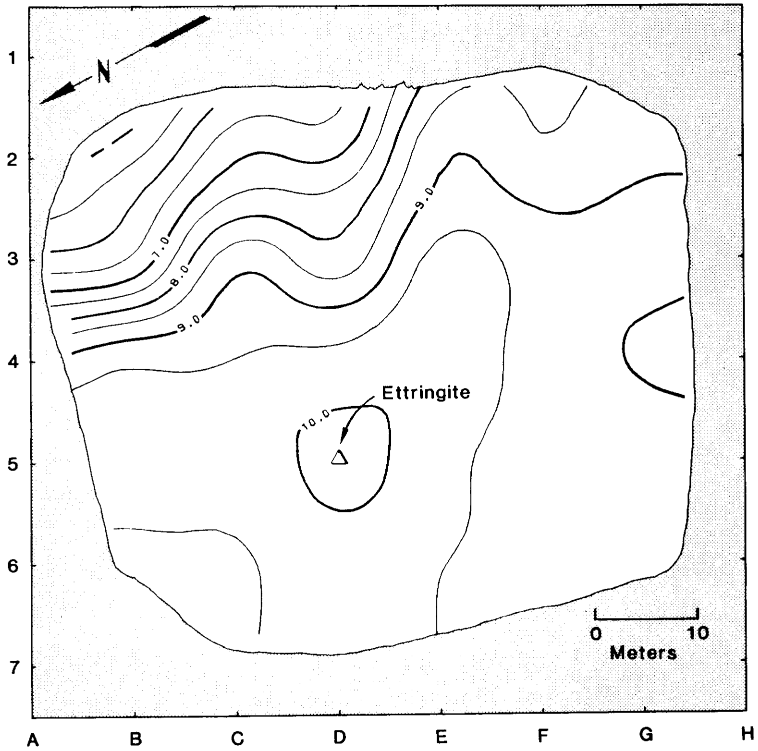

Fig. 3b. Contour plot of pH of pond water at sediment/water interface.

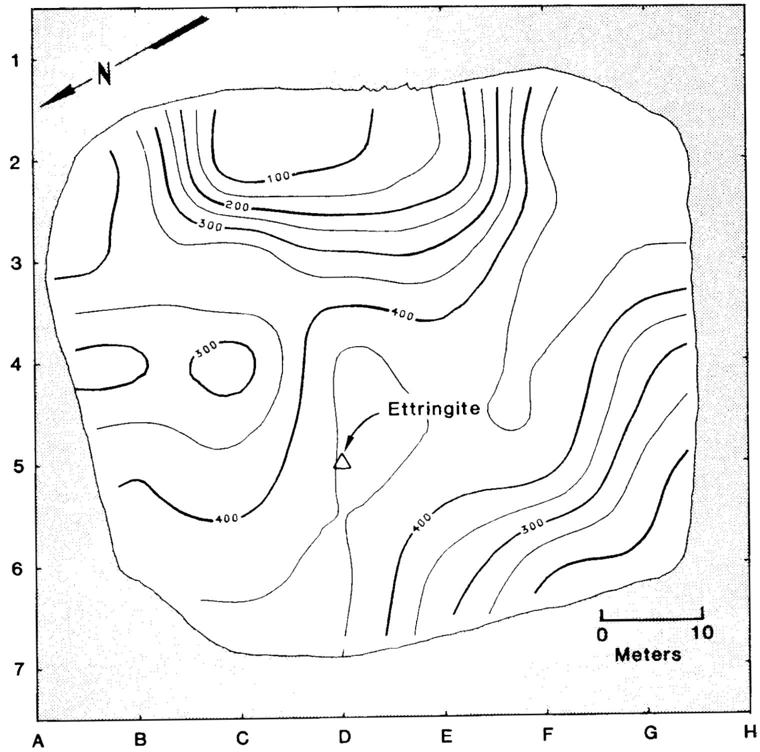

Fig. 3c. Contour plot of calcium concentrations (mg/L) in pond water.

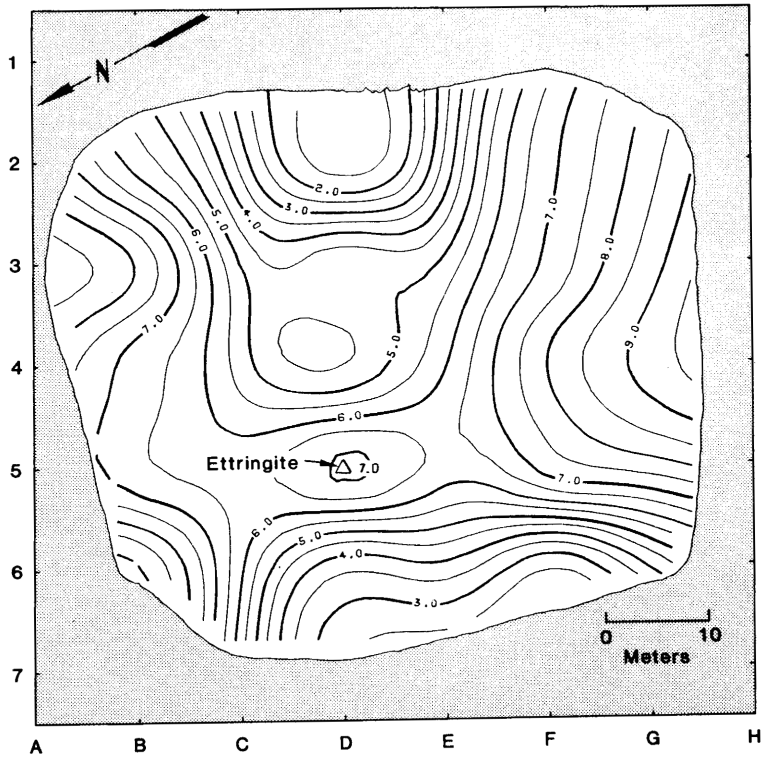

Fig. 3d. Contour plot of total sulfur (%) in pond sediments.

the waterway which receives the mine drainage. Chemical neutralization treatment of acid mine drainage at surface coal mines in the U.S. is usually accomplished by adding a slurry of hydrated lime [$Ca(OH)_2$], soda ash [Na_2CO_3], or a solution of sodium hydroxide [NaOH] to the acid water. The treated drainage is channeled to a settling pond where treatment precipitates and transported sediments are retained. The extreme range of sediment pH in the pond under study (4.0 to 11.0) suggests that discharge water may also have a wide pH range depending on treatment maintenance and rainfall events. The presence of ettringite over the point of effluent discharge indicates that discharge water is often highly alkaline (pH > 9.0) and may be as toxic to aquatic species as the untreated drainage. The formation of stable ettringite is thus a useful indicator of consistently high pH conditions in the downstream portion of the retention pond under study.

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Notes:

1. The synthetic ettringite sample was prepared by firing a mixture of AL_2O_3 and $CaCO_3$ to produce $CA_3Al_2O_6$, which was then ground, and hydrated with pulverized gypsum in the presence of excess water. After agitation, the suspension was filtered and dried over a super-saturated solution of $CaCl_2$ to produce ettringite [13]. Based on differential thermal analysis and thermogravimetric analysis by the Portland Cement Association, the reference was essentially 100% ettringite.

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