PRODUCT DEVELOPMENT AND UTILIZATION OF ZIMMER STATION WET FGD BY-PRODUCTS

FINAL REPORT

VOLUME 4: A LABORATORY STUDY CONDUCTED IN FULFILLMENT OF PHASE 2, OBJECTIVE 1 TITLED:

Inhibition of Acid Production in Coal Refuse Amended with Calcium Sulfite and Calcium Sulfate - Containing FGD Solids

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Wooster, OH 44691

Principle Authors: Y. L. Hao, W. A. Dick, R. C. Stehouwer, J. M. Bigham
Ohio Agricultural Research Development Center

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ABSTRACT

Control of SO_2 emission from coal combustion requires desulfurization of coal before its combustion to produce coal refuse. Alternatively, gaseous emissions from coal combustion may be scrubbed to yield flue gas desulfurization (FGD) by-products that include calcium sulfite ($CaSO_3 \cdot 0.5H_2O$ or simply $CaSO_3$). Acid production in coal refuse due to pyrite oxidation and disposal of large amounts of FGD can cause environmental degradation. Addition of $CaSO_3$ and $CaSO_3$-containing FGD to coal refuse may reduce the amounts of oxygen and ferric ion available to oxidize pyrite because the sulfite moiety in $CaSO_3$ is a strong reductant and thus may mitigate acid production in coal refuse. In Chapter 1, it was shown that $CaSO_3$ efficiently scavenged dissolved oxygen and ferric ion in water under the conditions commonly encountered in a coal refuse disposal environment. In the presence of $CaSO_3$, the concentration of dissolved oxygen in water exposed to the atmosphere declined to below 0.01 mg L^{-1} at pH <8.0. In Chapter 2, it was demonstrated that $CaSO_3$ prevented a pH drop in coal refuse slurry when 0.2 g $CaSO_3$ was added to a 2% fresh coal refuse slurry every three days. Calcium sulfite also inhibited acid leaching from fresh coal refuse in bench-scale columns under controlled conditions. During the initial 13 weeks of leaching, the total amounts of titratable acidity, soluble H^+, Fe, and Al from $CaSO_3$-treated refuse (6.4 g in 50 g fresh coal refuse) were only 26%,

10%, 32%, and 39% of those of the control columns, respectively. A combination of $CaSO_3$ with $CaCO_3$ or fly ash enhanced the inhibitory effect of $CaSO_3$ on acid leaching. Calcium sulfite-containing FGD which combined $CaSO_3$, $CaCO_3$, fly ash, and gypsum showed a much stronger inhibitory effect on acid leaching than $CaSO_3$ alone. This combination effect was partially due to the positive interaction of $CaSO_3$ with $CaCO_3$ and fly ash on inhibition of acid leaching. In Chapter 3, $CaSO_3$-containing FGD was found to inhibit acid leaching from both fresh and aged coal refuse in large scale columns under simulated field conditions. During 39 weeks of leaching, the reduction of leachate acidity and Fe concentration and the increase of leachate pH were significant ($p < 0.05$) for the 22% FGD treatment with a linear response to increasing FGD rates (0%, 5.5%, 11%, and 22%). I conclude that $CaSO_3$ and $CaSO_3$-containing FGD have the ability to inhibit acid production in coal refuse and the inhibitory effect shown in this experiment is likely to occur under field conditions. Thus, the research results present a potential new method for mitigation of acid production in coal refuse and another beneficial utilization of FGD by-products.

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INTRODUCTION

Desulfurization of coal and coal combustion flue gas: formation of coal refuse and flue gas desulfurization (FGD) by-products. Coal provides approximately 1/3 of the total energy and 45% of the electric power for the world's population based on recent statistics (Haggin, 1991). In the United States, about one billion tons of coal are now produced each year (Manahan, 1994). With increasingly scarce supplies of oil and natural gas (Schobert, 1987) our needs for coal will increase.

Coal contains organic and inorganic sulfur compounds. The total sulfur content in coal varies normally from 0.4% to 5% with the organic sulfur content ranging from 0.3% to 2% and the pyritic sulfur content from 0.1% to 4% (Meyers, 1977). Other inorganic sulfur sources include sulfate salts and elemental sulfur.

Coal combustion oxidizes the sulfur compounds in coal to sulfur oxides as follows:

$$\text{Organic S} + O_2 \rightarrow SO_2$$

$$2FeS_2 + 5.5O_2 \rightarrow Fe_2O_3 + 4SO_2$$

$$(Fe)_2(SO_4)_3 \rightarrow Fe_2O_3 + 3SO_3$$

$$S + O_2 \rightarrow SO_2$$

$$SO_2 + 0.5O_2 \rightarrow SO_3$$

These coal combustion reactions account for the major part of anthropogenic sulfur oxide emissions.

Sulfur oxides readily dissolve in and acidify the water:

$$SO_2 + H_2O \rightarrow H^+ + HSO_3^-$$

$$SO_3 + H_2O \rightarrow 2H^+ + SO_4^{2-}$$

These reactions are responsible for the formation of acid rain which can have pH values less than 4 resulting in the acidification of air, water, and soil. Environmental acidification adversely affects many kinds of life forms and corrodes various man-made structures. Inhalation of air containing higher than 33 mg L^{-1} SO_2 can cause distress or even death (Ough, 1993). The 1990 amendments to the Clean Air Act mandated a two-stage, 9.07 million Mg reduction in sulfur dioxide emission by the year 2000 (USEPA, 1996).

Reduction of sulfur oxide emission in coal combustion are accomplished by desulfurization of mined coal prior to coal combustion and desulfurization of coal combustion flue gases during and after coal combustion. Various physical, chemical, and microbiological methods have been designed to remove sulfur compounds from mined coal before combustion. Among these methods, only several physical methods are commercialized at present and include gravity separation, froth flotation, oil agglomeration, and electrostatic separation. These physical methods separate pyrite from coal based on differences in density and surface properties between pyrite and coal. The gravity separation method is the main method used and can remove up to 30% of pyrite from coal (IEA Coal Research, 1989). The gravity separation method also removes non-

sulfur inorganic compounds such as aluminosilicates and metal oxides to increase the heating value of coal. The sulfur and non-sulfur minerals removed from raw coal are called coal refuse.

Sulfur oxides can also be scrubbed from coal combustion gases so that sulfur emissions are reduced. Alkaline materials, typically pulverized limestone or hydrated lime, called sorbents, are reacted with sulfur oxides in or downstream from the coal boiler to form non-gaseous sulfur compounds which are retained in liquid or solid from:

$$CaCO_3 + SO_2 \rightarrow CaSO_3 + CO_2$$

$$CaCO_3 + SO_3 \rightarrow CaSO_4 + CO_2$$

The materials produced during the scrubbing process are often called flue gas desulfurization (FGD) by-products.

The processes designed for flue gas desulfurization in the coal boiler itself mainly include lime injection multistage burners (LIMB) and pressurized and atmospheric fluidized bed combustion (PFBC and AFBC). In these processes, the alkaline materials, typically pulverized limestone or hydrated lime are injected into the coal boiler and react with sulfur oxides while coal is being burned. The resulting products are dry and contain unspent sorbent, fly ash, calcium sulfite, and calcium sulfate.

Duct injection, spray dryer, and wet lime slurry scrubbing are the main processes to remove sulfur oxides in the flue gas downstream from the coal boiler. In the first two processes, lime or limestone are injected into the flue gas downstream from the coal boiler and dry reaction products are created that contain a mixture of unspent sorbents, fly

ash, calcium sulfite, and calcium sulfate. Wet lime slurry scrubbing uses slaked lime or limestone to absorb sulfur oxides from the flue gas.

In Ohio, the three largest wet scrubbers use a magnesium enhanced lime that has a small amount of $Mg(OH)_2$ to more efficiently remove SO_2. The $Ca(OH)_2$ regenerates the $Mg(OH)_2$ from $MgSO_3$ forming $CaSO_3$ precipitate. This reaction produces a slurry. Compared to dry FGD, this material is often called wet FGD and contains very little fly ash due to removal of fly ash (usually by means of an electrostatic precipitator) prior to SO_2 scrubbing. The $CaSO_3$ is dewatered by vacuum filtration or centrifugation. Depending on the extent of oxidation in the slurry scrubbing reaction and the amounts of fly ash and lime added back to the dewatered solids to stabilize it for landfilling, the composition of wet FGD varies (FGD at Conesville is about 80% $CaSO_3$ and 20% $CaSO_4$) and can range from pure calcium sulfite, a blend, or pure calcium sulfate. Wet FGD is the major type of FGD by-product.

Environmental degradation: acid production in coal refuse and disposal of FGD. It is obvious that the coal refuse generated by the gravity separation method would contain higher concentrations of inorganic sulfur compounds, mainly pyrite, than the raw coal. Stewart and Daniels (1992) reported the mean total sulfur contents in 27 coarse coal refuse piles was 4.4%. Buttermore et al. (1978) found the total sulfur content of the coarse coal refuse in West Virginia reached 6%. In this research, the coarse coal refuse obtained from the Conesville Coal Preparation Plant of the American Electric Power (Coshocton, OH) contained total sulfur concentrations as high as 10%.

Oxidation of pyrite in coal refuse exposed to O_2 and water in the environment produces acid according to the following reactions:

$$2FeS_2 + 7.5O_2 + H_2O \rightarrow 2Fe^{3+} + 4SO_4^{2-} + 2H^+$$

$$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3 + 3H^+$$

$$FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 16H^+ + 2SO_4^{2-}$$

Under acidic pH conditions, various other elements can be released into the coal refuse solution from aluminosilicates such as anorthite, illite, and kaolinite. These minerals are common in coal refuse (Meyers, 1977; Berkowitz, 1994). The reactions producing increased concentrations of soluble metals include:

$$CaAl_2Si_2O_8 + 8H^+ \rightarrow Ca^{2+} + 2Al^{3+} + 2H_4SiO_4$$

$$K_{0.6}Mg_{0.25}Al_{2.3}Si_{3.5}O_{10}(OH)_2 + 8H^+ + 2H_2O \rightarrow 0.6K^+ + 0.25Mg^{2+} + 2.3Al^{3+} + 3.5H_4SiO_4$$

$$Al_2Si_2O_5(OH)_4 + 6H^+ \rightarrow 2Al^{3+} + H_2O + 2H_4SiO_4$$

$$Fe_2O_3 + 6H^+ \rightarrow 2Fe^{3+} + 3H_2O$$

$$MnO + 2H^+ \rightarrow Mn^{2+} + H_2O$$

$$Al(OH)_3 + H^+ \rightarrow Al^{3+} + 3H_2O$$

In addition, oxidation of metal sulfides other than pyrite in coal also release various metal ions into water:

$$MS + 2.5O_2 + 2H^+ \rightarrow M^{2+} + SO_4^{2-} + H_2O \quad (M = Cu^{2+}, Ni^{2+}, Pb^{2+}, \text{and } Zn^{2+})$$

When precipitation falls on coal refuse, reacts, and is washed (leached) out into the environment, dissolved metal ions such as Fe^{3+}, Al^{3+}, and Mn^{4+} hydrolyze to produce even more acid than what the pH indicates:

$$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3 + 3H^+$$

$$Al^{3+} + 3H_2O \rightarrow Al(OH)_3 + 3H^+$$

$$Mn^{2+} + H_2O \rightarrow Mn(OH)_2 + 2H^+$$

The amount of $CaCO_3$ needed to raise the pH of one liter of solution to 8.3 is called titratable acidity. The common units to express this acidity are mmol H^+ L^{-1} or mg $CaCO_3$ L^{-1}.

The drainage water from coal refuse commonly has low pH, high acidity, and toxic concentrations of various metals. Martin (1974) observed that the effluents of some coal refuse had a pH as low as 2, acidity as high as several thousand milligrams of $CaCO_3$ per liter, and high concentrations of Fe (up to 6000 mg L^{-1}), S (up to 10,000 mg L^{-1}), Al (up to 1000 mg L^{-1}) and several trace elements (Cu, Mn, Ni, Pb, and Zn concentrations were much higher than drinking water standards). Acid production in coal refuse can cause severe environmental degradation (Kelly, 1988; Martin, 1974; Nesler and Bachmann, 1977).

Early in 1939, the first legislation to regulate surface mine reclamation was enacted in West Virginia. Since that time, requirements for the reclamation of mine waste and overburden have become increasingly stringent. In 1977, the Surface Mining Control and Reclamation Act (SMCRA) was passed by the US Congress. This law required the establishment and maintenance of vegetation for five years and achievement of premining water quality without artificial treatment after final reclamation. To reach the requirements set by SMCRA, several feet of soil are often needed to cover the surface of coal refuse. Such treatments are rather expensive and may have a negative impact on the area where soil is removed.

Approximately 10 to 60% of mined coal ends up as coal refuse (Daniels et al., 1995; Falkie et al., 1974; Stewart and Daniels, 1992). In 1989, there were about 156 million Mg of coal refuse produced in the U.S. (Stewart, 1990). With increased mining of coal and the development of coal cleaning processes to produce fuels that will help meet stringent SO_2 emission standards, more coal refuse will be produced. Therefore, inhibition of acid production in coal refuse is important for protection of our environment.

Disposal of FGD through landfills (dry and dewatered FGD) and settling ponds (FGD slurry) causes concerns about groundwater contamination from leachates and elevated concentrations of trace elements in plants and animals surrounding the disposal area (Santhanam et al., 1979). Under anaerobic conditions, sulfite and sulfate in FGD can be reduced to toxic hydrogen sulfide (Adams and Farwell, 1981). Under aerobic conditions, sulfite oxidation can cause O_2 deficiency in surface and ground waters affected by FGD (Santhanam et al., 1979). To control the leaching of excess amounts of elements from FGD disposal sites into the environment, the use of liners is becoming more common (USEPA, 1988), which increases the cost for FGD disposal.

The amount of FGD produced annually in the United States is prodigious. The reason is primarily due to the two-stage, 9.07 million Mg reduction in sulfur dioxide emission by the year 2000 mandated by the 1990 amendments to the Clean Air Act. In the USA, FGD production was approximately 21.7 million Mg in 1996 and may reach more than 45 million Mg by the year 2000 (American Coal Ash Association, 1997). In 1996, only 1.5 million Mg of FGD (7% of total) was utilized with the remainder deposited in

landfills or surface impoundments (American Coal Ash Association, 1997). With increasing scarcity and cost of landfill sites, beneficial utilization of FGD is highly desirable (Bigham et al., 1992).

Property of calcium sulfite and calcium sulfite-containing FGD. Calcium sulfite ($CaSO_3 \cdot 0.5H_2O$ or simply $CaSO_3$) is a weak base. Dissolution of $CaSO_3$ in water forms sulfite (SO_3^{2-}), bisulfite (HSO_3^-), sulfurous acid (H_2SO_3), and metabisulfite ($S_2O_5^{2-}$):

$$CaSO_3 \cdot 0.5H_2O \rightarrow Ca^{2+} + SO_3^{2-} + 0.5H_2O$$

$$SO_3^{2-} - + H_2O \rightarrow HSO_3^- + OH^-$$

$$HSO_3^- + H_2O \rightarrow H_2SO_3 + OH^-$$

$$2HSO_3^- \rightarrow S_2O_5^{2-} + H_2O$$

The relative amounts of these anions in water depend on pH with the dominant anion being sulfite at pH >7.2, sulfurous acid at pH <1.76, and bisulfite at intermediate pH values (Ough, 1993). The water pH in equilibrium with solid $CaSO_3$ at 25^0 C is about 9.7.

The solubility of $CaSO_3$ in water at 25^0 C is 0.054 g L^{-1} (Masson, 1986), which is about 40 times less than that of gypsum ($CaSO_4 \cdot 2H_2O$, 2.1 g L^{-1}). Decreasing temperature increases the solubility of $CaSO_3$ (Masson, 1986). Calcium sulfite solubility is the lowest at pH 8.0 and increases rapidly with decreasing pH and slightly at pHs above 8 (Masson, 1986). The dissolution rate of $CaSO_3$ in water also greatly depends on pH and temperature (Tseng and Rochelle, 1986). At pH 5 and 40^0C, the mass transfer coefficient for dissolution of $CaSO_3$ was found to be 4.5×10^{-5} m s^{-1} in a semi-batch reactor stirred at 1800 rpm (Weisnicht et al., 1980).

Dissolved sulfite, bisulfite, and sulfurous acid are strong chemical reductants for dissolved O_2 and Fe^{3+} ion with sulfite being the strongest (Conklin and Hoffmann, 1988a). The reaction of sulfite with O_2

$$2SO_3^{2-} + O_2 \rightarrow 2SO_4^{2-}$$

has a large equilibrium constant $K = 6.66 \times 10^{40}$ at 25^0C, 1 atm (thermodynamic data from CRC Handbook of Chemistry and Physics, Weast, 1969). The reaction is rapid in the presence of some transition metal ions such as Fe^{2+} (Reddy and Eldik, 1991), Fe^{3+} (Conklin and Hoffmann, 1988b), Cu^{2+} (Conklin and Hoffmann, 1988a; Barron and O'Hern, 1966), Co^{2+} (Bengtsson and Bjerle, 1975), and Mn^{2+} (Pasiuk-Bronikowska et al., 1981). At temperatures of 20 to 50^0C and in the presence of Co^{2+} or Mn^{2+}, the rate constant was reported to be in the range of 23 to 38 s^{-1} (first order) at pH <4 and 8 to 2.1×10^4 M^{-1} s^{-1} (second order) at pH >4 (Pasiuk-Bronikowska and Ziajka, 1985 & 1989).

The reaction of sulfite with Fe^{3+} ion is:

$$SO_3^{2-} + 2Fe^{3+} + H_2O \rightarrow SO_4^{2-} + 2Fe^{2+} + 2H^+$$

and/or

$$2SO_3^{2-} + 2Fe^{3+} \rightarrow S_2O_6^{2-} + 2Fe^{2+}$$

The second reaction may be more important when the source of Fe^{3+} is $Fe(OH)_3$ (Conklin and Hoffmann, 1988b). The equilibrium constants are 2.15×10^{14} for the first reaction and 1.6×10^{21} for the second reaction at 25^0C, 1 atm (thermodynamic data from CRC Handbook of Chemistry and Physics, Weast, 1969, and from Thermodynamic Constants of Inorganic and Organic Compounds, Karapetiants, 1970). The rate constant for the first

reaction is in the range of 0.9-1.5x10^6 M^{-1} s^{-1} at pH <4, 20^{0}C, and under anaerobic conditions (Conklin and Hoffmann, 1988b).

Reynolds (1984) studied the oxidation of $CaSO_3$ in a continuous stirred tank reactor and semi-batch reactor in 0.05 M adipic acid (pH 5) and the presence of Mn^{2+}. The reactors were stirred at 1800 rpm under which limitation of O_2 transfer from gas to liquid was eliminated. The oxidation rates were found to be 0.5-1.0x10^{-5} M s^{-1} at 50^{0}C with 0.01 M initial concentration of $CaSO_3$ which formed a homogeneous solution. Under similar conditions and at 40^{0}C, Weisnicht (1980) measured a rate constant of 85 $M^{-0.5}$ s^{-1} for slurries containing 2000 ppm Mn^{2+} and 0.16 $M^{-0.5}$ s^{-1} for clear solution without Mn^{2+}. The maximum oxidation rate under both conditions was calculated as 2.1x10^{-4} M s^{-1}. At pH 7.3, 20^{0}C to 23^{0}C, and in the presence of Co^{2+}, Pasiuk-Bronlkowska (1992) determined a rate constant of 1.3x10^4 M^{-1} s^{-1} for homogeneous solution and 3.3x10^4 M^{-1} s^{-1} for heterogeneous slurries. His experiment was conducted in a tank stirred at 1175 rpm and impinged with O_2.

Many studies have shown that dissolved sulfite, bisulfite, metabisulfite, and sulfurous acid are toxic to various kinds of microbial cells. These sulfite chemicals can either react with cell components, such as thiamine pyrophosphate and ATP (Ough, 1993), and thus destroy the functions of these components, or form sulfur and O_2 radicals such as $SO_5^{-}\cdot$, $SO_3^{-}\cdot$, $O_2^{-}\cdot$, and $HO_2\cdot$ which can cause various types of damage to cells (Hoffmann et al., 1985; Hurtado et al., 1987). It has been shown that the toxicity of sulfurous acid is greatest among the dissolved sulfite chemicals (Ough, 1993). The toxicity of dissolved sulfite chemicals to yeast increased in the order: sulfite, bisulfite,

and sulfurous acid (Ough, 1993). Hurtado et al. (1987) found that metabisulfite had a stronger inhibition effect on ferrous ion oxidation by *Thiobacillus ferrooxidans* than sulfite and bisulfite. The toxicity of dissolved sulfite chemicals to *Thiobacillus ferrooxidans*, *Thiobacillus thiooxidans*, and *Leptospirillum ferrooxidans*, which are known to be the main bacteria involved in pyrite oxidation, has also been studied (Hirose et al., 1991; Hurtado et al., 1987; Sugio et al., 1994 and 1995; Takeuchi and Suzuki, 1994). These studies showed that sulfite, bisulfite, metabisulfite, and sulfurous acids at concentrations ranging from 0.02 to 2 mM, inhibited sulfur- and iron-oxidation by the above three bacteria.

The composition and properties of $CaSO_3$-containing FGD are determined by coal source, coal combustion conditions, method of flue gas desulfurization, method of FGD disposal, and weathering conditions after disposal. The methods of flue gas desulfurization and FGD disposal determine the relative amounts of $CaSO_3/CaSO_4$, lime materials, and fly ash in the FGD. Leaching of the FGD can remove significant amounts of soluble salts and some trace elements (Aitken and Bell, 1985; Ghodrati et al., 1995). Coal source and the temperature of coal combustion and flue gas desulfurization determine the composition (total amounts of elements and their chemical forms) and morphology (particle size, surface area, and crystallinity) of fly ash.

The dry FGD materials produced by spray dryer and duct injection are essentially coal fly ash diluted with unreacted sorbent and reaction products and commonly contain 20% to 45% $CaSO_3$, 10% to 50% lime ($CaCO_3$ and $Ca(OH)_2$), and 12% to 45% fly ash (Bigham et al., 1992). Although the wet FGD produced by lime slurry scrubbing can be

pure $CaSO_3$, partially $CaSO_4$ or pure $CaSO_4$ depending on the extent of oxidation, lime materials and/or fly ash are commonly added back to stabilize the wet FGD dewatered sludge through pozzolanic reactions (Beeghly et al., 1993). Pozzolanic reactions give the FGD cementitious properties (high compressive strength), thus stabilized FGD may have low permeability coefficients (10^{-5} to 10^{-6} cm s^{-1}, an order of magnitude lower than that of unreacted FGD) (Elnagger et al., 1977).

Fly ash is an important component of FGD and is composed of small, hollow, spherical (<250 μm in diameter), amorphous and crystalline inorganic particles which are mainly aluminosilicate minerals, such as glass, quartz (SiO_2), and mullite ($3Al_2O_3 \cdot 2SiO_2$), together with hematite (Fe_2O_3), and magnetite (Fe_3O_4) (Carlson and Adriano, 1993; Adriano et al., 1980). These particles have a specific surface area of about 3.06 m^2 g^{-1}, a density of 2.1 to 2.6 g cm^{-3}, and high mechanical strength. Fly ash contains almost all naturally occurring elements and many of these elements are more concentrated on the surface of smaller particles (Klein et al., 1975; Volkovic, 1983). The pH of fly ash ranges from 4.5 to 12 (Adriano et al., 1980) depending on the amount of lime materials associated with the coal.

Inhibition of acid production in coal refuse using calcium sulfite and calcium sulfite-containing FGD. Technologies used to inhibit acid production in coal refuse (or coal mine overburden) vary widely and employ physical, chemical, and biological methods. These methods can either prevent acid production before it occurs or treat acid production after it occurs. According to pyrite oxidation reactions, the methods for prevention of acid production must accomplish at least one of the following goals: (1)

removal of O_2, the ultimate oxidant of pyrite; (2) removal of Fe^{3+}, the major direct oxidant of pyrite (Evengelou and Zhang, 1995) and the oxidation product of Fe^{2+} ion by O_2; (3) removal of water, one of the reactants in pyrite oxidation; (4) removal of H^+, the decomposer of associated minerals; and (5) inhibition of pyrite-oxidizing bacterial activity, the catalyst of pyrite oxidation.

Physical methods use various kinds of materials to limit the contact of pyrite with O_2 and/or water. Examples include the formation of cementitious materials created by mixing fly ash and portland cement (Gabr et al., 1994), the use plastic liners (Meek, 1994), and the use of soil caps (Bell et al., 1994; Brundage, 1974; Vinikour et al., 1988). Pyritic materials may also be submerged in water (Fraser and Robertson, 1994) to limit pyrite contact with O_2. Chemical methods use various alkaline materials to neutralize acid and limit Fe^{3+} activity in water. These materials include limestone ($CaCO_3$) (Burt and Carruccio, 1986; Davidson, 1974; Draper et al., 1984; Pietz et al., 1989a, b, and c; Sorrell, 1974; Stokowski and Gilbert, 1988), fly ash (Bhumble et al., 1991; Capp and Gillmore, 1974; Plank and Martens, 1973; Plass and Capp, 1974; Sutton and Dick, 1987; Taylor and Schuman, 1988), FGD (Capp and Gillmore, 1974; Dick et al., 1994; Jastrow et al., 1981; Siddle et al., 1979; Stehouwer et al., 1995a, b, and c), lime kiln dust (Rich and Hutchison, 1990), steel making slags (Skousen and Ziemkiewicz, 1995), and phosphate (Evangelou, 1995). Organic materials such as humic acid and fulvic acid were also studied as chelates for dissolved Fe^{3+} to inhibit pyrite oxidation (Pichtel and Dick, 1991; Pichtel et al., 1994).

Two biological methods have been recognized. One is the development of a vegetative cover on the surface of coal refuse (or coal mine spoil) by addition of organic compost (Hoitink and Watson, 1982; Pichtel et al., 1994; Sopper, 1992), sewage sludge (Joost et al., 1987; Pietz et al., 1989a, b, and c; Sopper, 1992; Webber et al., 1994). Vegetative cover can limit O_2 diffusion from the atmosphere into the coal refuse through root respiration. The cover also decreases surface refuse erosion and intercepts precipitation water through evapotranspiration. The other biological method is to use bactericides such as lauryl sulfate and sodium benzoate to inhibit pyrite-oxidizing bacteria such as *Thiobacillus ferrooxidans* (Dugan and Apel, 1983; Kelley and Tuovinen, 1988; Rastogi, 1996).

Due to a large area of abandoned mine land where acid production occurs and the inefficiency of most prevention methods, the treatment of acid production is often necessary. To reduce the concentrations of protons, sulfate, and metal ions in acid water, various alkaline chemicals such as $Ca(OH)_2$, CaO, $CaCO_3$, $Mg(OH)_2$, NaOH, Na_2CO_3, and ammonia may be added. Wetland treatment of acid water is a combination of chemical and biological processes in which acid neutralization, metal precipitation and adsorption, and sulfate reduction to sulfide are encouraged (Wieder, 1989 and 1994).

The above methods are often applied in combination to increase their effectiveness and to reduce the cost of inhibiting acid production. Calcium sulfite and $CaSO_3$-containing FGD, produced in large quantities and disposed as waste materials, may be utilized alone or in combination with the other methods to inhibit acid production. This is possible because of the chemical properties of the sulfite which serves as a strong

reductant, as a source of alkalinity, and as a toxicant to pyrite-oxidizing bacteria. The strong reducing power of sulfite can be combined with other physical, chemical or biological methods to further limit the quantities of O_2 and Fe^{3+} in coal refuse. The alkalinity of the solution and the presence of $CaSO_3$ suppresses the activity of acidophilic pyrite-oxidizing bacteria and also limits the amount of dissolved Fe^{3+}. The solubility of $CaSO_3$ may also produce sulfite concentrations high enough to be toxic to pyrite-oxidizing bacteria, but low enough not to readily leach into the environment. The oxidation product of $CaSO_3$ by O_2 is gypsum, which can reduce Al toxicity to plants (Farina and Channon, 1988; Korcak, 1988; Shainberg et al., 1989). Appropriate application of $CaSO_3$ or $CaSO_3$-containing FGD has the potential to reduce the negative environmental impact of both acid production and waste disposal.

Applications of $CaSO_3$ to inhibit acid production in coal refuse has not been reported. There are some recent studies using wet FGD to improve the surface and subsurface conditions of coal refuse for plant growth (Stehouwer and Mafi, 1997). In such studies, the content of $CaSO_3$ in the FGD and the improvement of leachate quality were not determined. Thus, the effect of $CaSO_3$ on inhibition of acid production was unknown and the apparent positive effect of the FGD on plant growth was attributed to the alkaline components in the FGD.

Purpose of this study. The main purpose of this research is to study the ability of $CaSO_3$ and $CaSO_3$-containing FGD by-products to inhibit acid production in coal refuse. The coal refuse used in this study contains high amounts of pyrite (up to 8.5%) and has a strong potential to rapidly produce acid. If $CaSO_3$ or the $CaSO_3$-containing FGD can

inhibit acid production in this coal refuse, the inhibition is likely to occur or even to be stronger in coal refuses containing less amounts of pyrite or having less potential for pyrite oxidation.

A column leaching test is mainly used in these studies because this approach can give a close approximation of field weathering conditions (Stewart et al., 1997; Hood and Oertel, 1984).

Three specific objectives were established and each chapter of this dissertation provides information on research conducted specific to each objective.

Objective 1 (Chapter 1): To test the ability of $CaSO_3$ to scavenge O_2 and Fe^{3+} under the conditions commonly encountered in coal refuse disposal environment.

Objective 2 (Chapter 2): To test the ability of $CaSO_3$ and its combination with other FGD components such as $CaCO_3$ and fly ash to inhibit acid production in finely ground coal refuse in a bench-scale column under controlled leaching conditions.

Objective 3 (Chapter 3): To test the ability of $CaSO_3$-containing FGD to inhibit acid production in coal refuse in a large scale column and under simulated field leaching conditions.

CHAPTER 1

OXIDATION OF CALCIUM SULFITE IN AN AQUEOUS SLURRY BY OXYGEN AND FERRIC ION

ABSTRACT

The oxidation of calcium sulfite ($CaSO_3 \cdot 0.5H_2O$ or simply $CaSO_3$) by O_2 and Fe^{3+} was studied under conditions commonly encountered in a coal refuse disposal environment in order to determine the potential ability of $CaSO_3$ to inhibit pyrite oxidation and thus acid production in coal refuse. The conditions for oxidation of $CaSO_3$ in aqueous slurry by O_2 were: (1) initial $CaSO_3$ concentration (g L^{-1}) of 10, 20, and 40; (2) initial pH of 2.0, 3.5, 5.0, 6.5, and 8.0; (3) temperature (^{0}C) of 5, 15, 25; and (4) O_2 content (%) of 0.2 and 21. The slurry was constantly mixed by reciprocal shaking at 80 rpm. The conditions for oxidation of $CaSO_3$ in aqueous slurry by Fe^{3+} were: (1) initial $CaSO_3$ concentration of 7 mmol L^{-1}; (2) initial Fe^{3+} ($FeNH_4(SO_4)_2 \cdot 12H_2O$) concentration of 15.6 mmol L^{-1}; (3) initial pH of 2.0, 3.0, and 4.0; and (4) an anaerobic system. Constant mixing of the slurry was achieved with a magnetic stirring bar. The oxidation

rate of $CaSO_3$ by O_2 gradually decreased with time and dramatically increased when the initial pH decreased from 6.5 to 5.0 at 25^0C, when temperature increased from 5^0C to 15^0C at an initial pH of 5.0, and when air O_2 content increased from 0.2% to 21% at 25^0C and initial pH of 5.0. The initial concentrations of $CaSO_3$ did not exert a dramatic effect on the oxidation rate. At 25^0C and 21% air O_2, $CaSO_3$ decreased the dissolved O_2 concentration to less than 10 $\mu g\ L^{-1}$ at pH <8.0. At the initial pH of 2.0 and 3.5, 14 to 44% of the initial S was released as SO_2 during 24 h oxidation. The amount of SO_2 released increased with increasing initial concentration of $CaSO_3$ and decreasing initial pH. The oxidation rate of $CaSO_3$ by Fe^{3+} under anaerobic conditions greatly increased when the initial pH decreased from 4.0 to 2.0. As the $CaSO_3$ oxidation reaction proceeded, the slurry pH increased and this was attributed to formation of dithionate ($S_2O_6^{2-}$) based on the ratio of the amount of Fe^{2+} produced to the amount of sulfite oxidized. We concluded that $CaSO_3$ has a strong potential to scavenge O_2 and Fe^{3+} and thus to inhibit pyrite oxidation and acid production in coal refuse. Concerns caused by SO_2 release and sulfite leaching might be reduced by maintaining the pH above 5 so that the dissolution and oxidation rates of $CaSO_3$ will be fast enough to efficiently scavenge dissolved O_2 and Fe^{3+}.

INTRODUCTION

Oxygen and Fe^{3+} are the two main oxidants of pyrite in coal refuse. Ferric ion is produced when Fe^{2+} in pyrite is oxidized by O_2. Minimizing contact of O_2 with coal refuse is a common approach to inhibit pyrite oxidation. Even though several measures have been practiced, they can not completely remove O_2 in coal refuse. Removal of residual O_2 might be accomplished by the addition of readily available strong reductants such as sulfite into coal refuse.

There are several sulfite salts such as Na_2SO_3, K_2SO_3, and $(NH_4)_2SO_3$ which have been used as O_2 scavengers for the preservation of foods and drugs for many years (Modderman, 1985; Schroeter, 1962). These sulfite salts are relatively expensive and only used in small quantities. Calcium sulfite is produced in a large quantity in the desulfurization of coal combustion flue gases and can exist either as a rather pure product or as a component in flue gas desulfurization (FGD) by-products. Calcium sulfite and the FGD containing $CaSO_3$ are commonly disposed of as a landfill waste. However, the use of $CaSO_3$ and a $CaSO_3$-containing FGD may be beneficial if mixed with coal refuse to remove O_2 and Fe^{3+} for inhibiting pyrite oxidation and acid production.

In the past, sulfite oxidation by O_2 and Fe^{3+} has been extensively studied because of their involvement in the preservation of foods and drugs (Ough, 1993) and in the removal of SO_2 from the atmosphere (Clarke and Radojevic, 1987; Kraft and Eldik, 1989) and from coal combustion flue gases (Alper and Abu-Sharkh, 1988; Huss, 1978). In these studies, readily soluble sulfite salts were used instead of $CaSO_3$. Where $CaSO_3$

has been used, oxidation conditions have included high amounts of O_2, trace amounts of Fe^{3+}, and forced oxidation at high temperature by purging O_2 and stirring at high speed, all of which are different from the conditions in a coal refuse disposal environment.

In a coal refuse disposal environment, the oxidation of $CaSO_3$ will mainly occur under heterogeneous solution conditions with high concentrations of $CaSO_3$. The amount of O_2 will vary greatly with location, the amount of Fe^{3+} can reach a high concentration (mmol L^{-1} level), and pH and temperature will vary greatly with time and location. To determine if $CaSO_3$ or a $CaSO_3$-containing FGD can be added to coal refuse to inhibit pyrite oxidation, oxidation rates of $CaSO_3$ by O_2 and Fe^{3+} need to be measured under the broad range of conditions commonly encountered in coal refuse disposal environments.

Because coal refuse has a strong potential to produce acid, the addition of $CaSO_3$ in coal refuse raises concerns about SO_2 release into the atmosphere due to the dissociation of sulfurous acid. Likewise, sulfite leaching into the surrounding environment may occur due to the increasing solubility of $CaSO_3$ with decreasing pH. Determination of the oxidation rates of $CaSO_3$ by O_2 and Fe^{3+} as well as the rate of SO_2 release under different pH regimes would help to select the optimum pH for application of $CaSO_3$, not only to efficiently scavenge O_2 and Fe^{3+} but also to minimize SO_2 release and sulfite leaching.

The purpose of this experiment is to observe the ability of $CaSO_3$ to scavenge O_2 and Fe^{3+} under the broad range of conditions commonly encountered in coal refuse disposal environments.

MATERIALS AND METHODS

Calcium sulfite. Calcium sulfite was synthesized by mixing 6% sulfurous acid with calcium hydroxide. The excess sulfurous acid was removed by heating gradually in a water bath to a temperature not more than 90^0C. The precipitate of $CaSO_3$ was washed with a large quantity of double deionized water and then dried at 60^0C. Thermogravimetric analysis indicated the product contained more than 96% $CaSO_3$ which was also ascertained to be hannebachite ($CaSO_3 \cdot 0.5H_2O$) by X-ray diffraction analysis. The element composition of the synthesized $CaSO_3$ is shown in Table 1.1.

Oxidation of $CaSO_3$ by O_2. A slurry was prepared by mixing $CaSO_3$ with water. One ml of this slurry was placed in each well of a 12-well microplates (Becton Dickinson & Co., Lincoln Park, NJ). To ensure reactions were not catalyzed by bacteria, the slurries were autoclaved at 121^0C for 20 min. and then distributed into each well under a sterile hood. The microplates were shaken on a reciprocal water bath shaker at 80 rpm. The reaction was initiated by adding concentrated H_2SO_4 or 10 M NaOH to the slurries to adjust the pH to the desired values. The experimental conditions were: (1) initial $CaSO_3$ concentrations (g L^{-1}) of 10, 20, and 40; (2) initial pH of 2.0, 3.5, 5.0, 6.5, and 8.0; (3) incubation temperature (^{0}C) of 5, 15, and 25; and (4) air O_2 content of 0.2% and 21%. Under alkaline pH conditions (the experiments last more than one week), sterile double deionized water was added each week to replace that lost by evaporation.

Oxidation of $CaSO_3$ under 0.2% O_2 content was conducted in an anaerobic chamber in which O_2 content in the gas phase was controlled by intermittent flushes of

Element	Concentration		Element	Concentration	
	mg kg^{-1}	mmol kg^{-1}		mg kg^{-1}	mmol kg^{-1}
Al	49.9	1.85	Mg	15.8	0.66
As	62.3	0.84	Mn	0.00	0.00
Ba	5.01	0.04	Mo	7.44	0.08
Ca	312000	7800	Na	0.00	0.00
Co	8.84	0.15	Ni	3.33	0.06
Cu	16.1	0.25	S	250000	7810
Fe	37.4	0.67	Si	11.2	0.40
K	329	8.43	Zn	4.81	0.07

Table 1.1: Element concentrations in synthesized $CaSO_3$.

N_2. Oxygen content in the anaerobic chamber was monitored by injection of a 5 ml gas sample into a gas chromatography (Water Dimension Gas Chromatography, electron capture detector, Tremetrics Inc., Austin, TX) (Mosier and Mack, 1980). Standard concentrations of O_2 gas were prepared by mixing pure O_2 and N_2 gases at various ratios.

Samples were taken by sacrificing triplicate wells. Total $CaSO_3$ (dissolved and non-dissolved) remaining in each well was analyzed by addition of excess 1.0 N iodine solution and then back titrating with 0.1 M sodium thiosulfate solution using starch as an indicator.

Concentration of dissolved O_2 in the $CaSO_3$ slurry. A glass beaker containing 100 ml of double deionized water was put in the anaerobic chamber and a slurry was prepared by adding 1 g of $CaSO_3$. The $CaSO_3$ oxidation reaction was initiated by adjusting the pH to 12 with 10 M NaOH. Dissolved O_2 was immediately determined using YSI 5905 BOD probe and YSI M58 dissolved oxygen meter (Yellow Springs Instrument Co., Inc., Yellow Springs, OH). The pH was then lowered by about one unit by addition of concentrated H_2SO_4 and dissolved O_2 was again determined. Further decrease in pH were made until dissolved O_2 was below the detection limit (0.01 mg L^{-1}).

Release of SO_2 in $CaSO_3$ slurry. At pH 5.0 and below, total S in the slurries was determined by inductively-coupled plasma (ICP) atomic emission spectroscopy at the start and at the end of the reactions. Due to the aerobic condition in this experiment, the differences in total S between the start and the end of the reaction were attributed to SO_2 release. Release of SO_2 was identified by a color change in a solution which contained 5% glycerol, 0.1 M NaOH, and color reagents (formaldehyde and rosaniline) (Urone and

Boggs, 1951). This solution was placed inside a closed bottle containing $CaSO_3$ slurry. For the analysis of total S, $CaSO_3$ was first dissolved by addition of iodine solution to oxidize sulfite to sulfate. Concentrated HNO_3 was added to dissolve the $CaSO_3$ and the resultant solution was then analyzed for total S by ICP spectroscopy.

Oxidation of $CaSO_3$ by Fe^{3+}. Glass bottles were filled with 100 ml of 7.5 g L^{-1} (15.6 mM) $FeNH_4(SO_4)_2 \cdot 12H_2O$ slurry or 100 ml of 10 g L^{-1} (77.5 mM) $CaSO_3$ slurry and then capped with a rubber stopper and sealed with an aluminum ring. Nitrogen gas was bubbled into the glass bottles for 5 minutes to remove oxygen. This was done to ensure oxidation of $CaSO_3$ was strictly due to Fe^{3+} and not dissolved O_2. The pH of both bottles were adjusted by injecting either concentrated H_2SO_4 or 10 M NaOH to achieve the desired initial pHs. The initial pH values were 2.0, 3.0, and 4.0. The reaction was initiated by transferring 10 ml of a 10 g L^{-1} $CaSO_3$ slurry into the 100 ml of $FeNH_4(SO_4)_2 \cdot 12H_2O$ slurry using a syringe. Thus, the initial concentration of $CaSO_3$ in the reaction mixture was about 0.91 g L^{-1} (7.05 mM). Controls consisted of $FeNH_4(SO_4)_2 \cdot 12H_2O$ alone. A magnetic stirring bar was used to provide constant mixing.

Samples were analyzed for total $CaSO_3$ concentration and dissolved Fe^{2+} and Fe^{3+} concentrations. For sulfite analysis, a 1-ml sample was oxidized with excess 1.0 N iodine solution and then back titrated with 0.1 M sodium thiosulfate solution using starch as an indicator. Preliminary experiments verified no interference of titration results by dissolved Fe^{2+} and Fe^{3+} under the experimental conditions.

Dissolved Fe^{2+} and Fe^{3+} were analyzed by a spectrophotometric method using 1,10-phenanthroline as a color reagent (Greenberg et al., 1985). For this analysis, 0.5 ml

samples were transferred into eppendorf centrifuge tubes under a flow of N_2 gas and then centrifuged at 6640 g (10,000 rpm, Beckman Microfuge II) for 15 seconds. Immediately after centrifugation, 50 µl supernatant were transferred into another centrifuge tube which contained 850 µl of 37% formaldehyde and 100 µl of concentrated HCl. The formaldehyde was added to complex sulfite ion so that it could no longer reduce Fe^{3+}. This acidified sample was further diluted 10 times in double deionized water, and a 0.5 ml diluted sample was used to react with the spectrometric reagents. Absorbance was measured at 510 nm. The analysis was completed in less than 1 h. There was no significant reduction of Fe^{3+} ion by formaldehyde in the period of analysis, which was verified by a preliminary experiment. Acidifying samples prevented oxidation of Fe^{2+} by O_2 in formaldehyde solution and in the following dilution process.

RESULTS AND DISCUSSION

Oxidation rate of $CaSO_3$ by O_2. Oxidation rate of $CaSO_3$ under 21% O_2 at 25^0C was greatly affected by the initial pH (Fig. 1.1). There was a dramatic increase in oxidation rate when the initial pH decreased from 6.5 to 5.0 but only a slight change from 8.0 to 6.5 (note different time scales used in Fig. 1.1). At an initial pH of 5.0, the concentration of $CaSO_3$ after 24 h oxidation dropped below 0.5 g L^{-1} regardless of the initial concentrations of $CaSO_3$. At initial pHs of 6.5 and 8.0, the final concentration of $CaSO_3$ after 14 days of oxidation was at least 3 g L^{-1} for an initial 10 g L^{-1} $CaSO_3$, at least 5 g L^{-1} for an initial 20 g L^{-1} $CaSO_3$, and at least 22 g L^{-1} for an initial 40 g L^{-1} $CaSO_3$.

At a pH of 5.0, decreasing temperature from 25 to 15^0C had little effect on oxidation rate of $CaSO_3$ (Fig. 1.2). However, decreasing temperature from 15 to 5^0C greatly decreased the oxidation rate (Fig. 1.2). The concentrations of $CaSO_3$ after 4 days of oxidation at 5^0C and a pH of 5.0 were similar to those at 25^0C and an initial pH of 8.0.

Decreasing O_2 content in air from 21% to 0.2% at 25^0C and an initial pH of 5.0 slowed down the oxidation of $CaSO_3$ (Fig. 1.3). At 0.2% O_2, the concentration of $CaSO_3$ dropped below 0.5 g L^{-1} after 46 h compared to 24 h at 21% O_2.

The oxidation rate of $CaSO_3$ decreased with time under 21% O_2 (Figs. 1.1 and 1.2). For the conditions under which fast oxidation of $CaSO_3$ occurred (15^0C or 25^0C at pH 5.0), oxidation of $CaSO_3$ exhibited a rapid reaction phase followed by a slow reaction phase with most of the $CaSO_3$ being oxidized in the rapid reaction phase (Fig. 1.1 and 1.2). However, for the conditions under which oxidation of $CaSO_3$ was slow (5^0C at pH

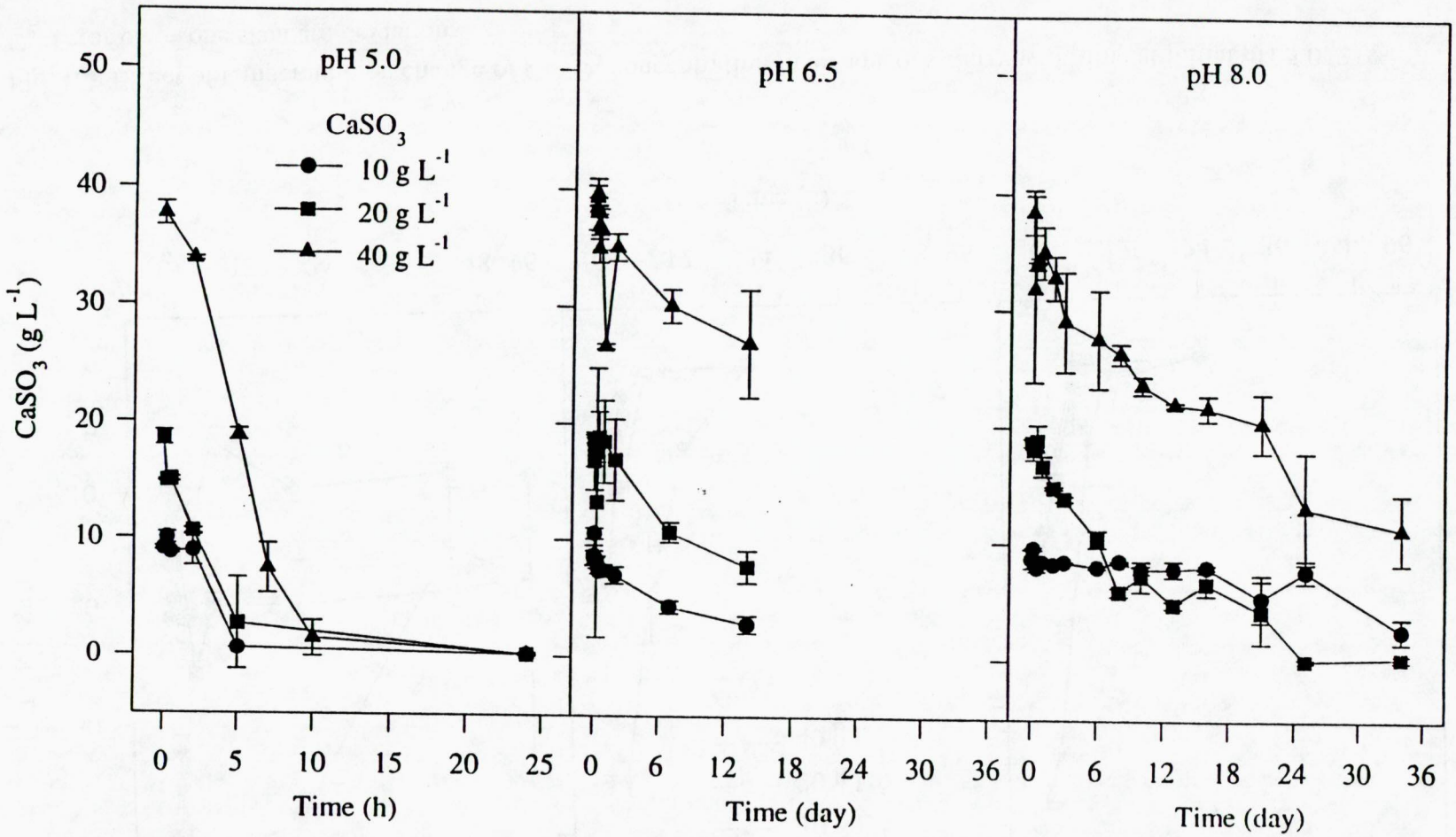

Fig. 1.1: Effect of initial pH on change of $CaSO_3$ concentration in an aqueous slurry with time at 21% O_2, 25^0C. Error bar = one standard deviation.

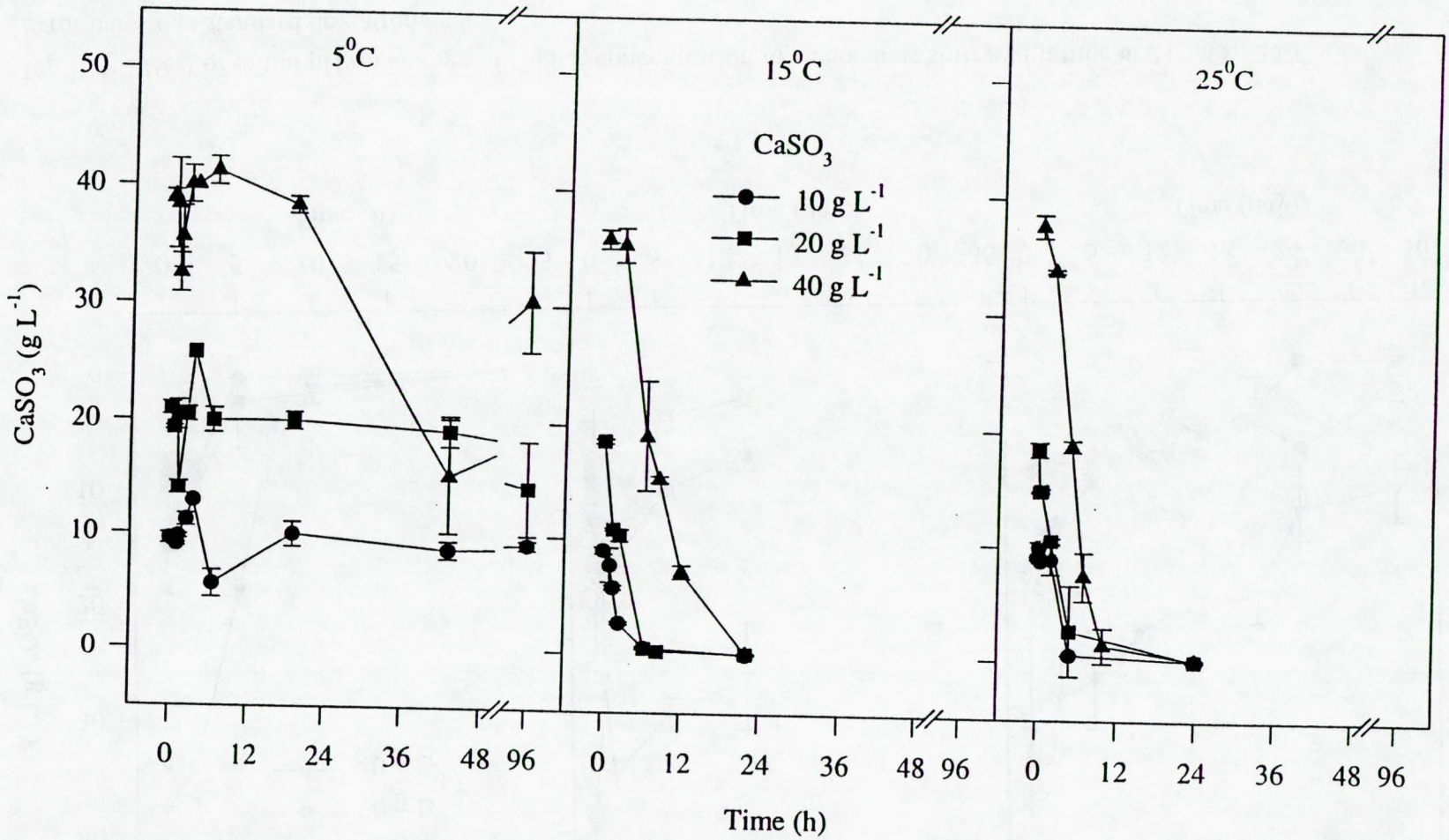

Fig. 1.2: Effect of temperature on change of $CaSO_3$ concentration in an aqueous slurry with time at initial pH 5.0, 21% O_2. Error bar = one standard deviation.

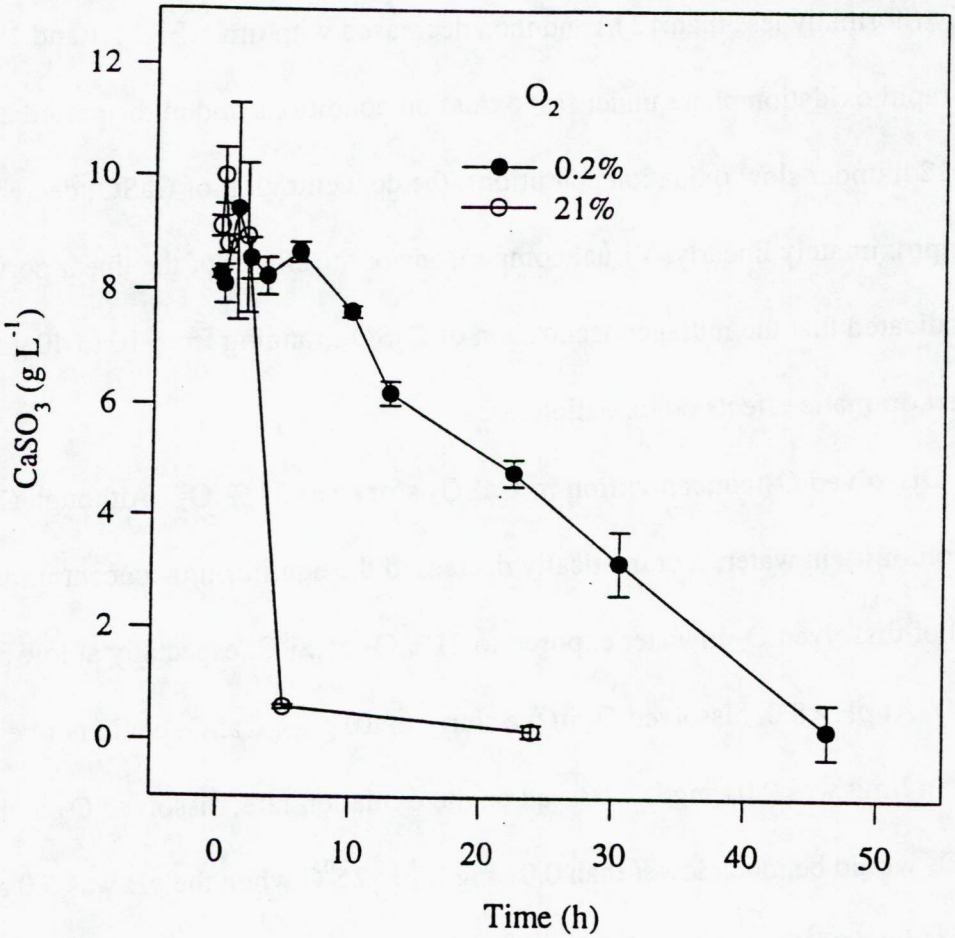

Fig. 1.3: Effect of O_2 content in air on change of $CaSO_3$ concentration in an aqueous slurry with time at initial pH 5.0, 25^0C. Error bar = one standard deviation.

5.0, or 25^{0}C at pH 6.5 or 8.0), the concentration of $CaSO_3$ decreased rapidly or fluctuated initially (normally less than 12 h) and then decreased with time (Fig. 1.1 and 1.2). In the initial rapid oxidation phase under fast oxidation conditions and in the period after the initial 12 h under slow oxidation conditions, the concentration of $CaSO_3$ decreased with time approximately linearly. Visual comparisons of the slopes of the linear portions of the lines indicated that the initial concentration of $CaSO_3$, ranging from 10 to 40 g L^{-1}, did not exert dramatic effects on oxidation rate.

Dissolved O_2 concentration in $CaSO_3$ slurry at 21% O_2. Although $CaSO_3$ has a low solubility in water, it dramatically decreased the equilibrium concentration (about 8 mg L^{-1}) of dissolved O_2 in water exposed to 21% O_2 at 25^{0}C, especially at low pH (Fig.1.4). At pH <8.0, dissolved O_2 in the slurry of 10 g L^{-1} $CaSO_3$ could not be detected (detection limit was 0.01 mg L^{-1}). Based on the oxidation rate, dissolved O_2 in the slurry of $CaSO_3$ would be much lower than 0.01 mg L^{-1} at 25^{0}C when the pH was 5.0 and also would not be detected either at 5^{0}C or 15^{0}C when the pH was 5.0. Compared to 8 mg L^{-1} dissolved O_2 in water saturated with 21% O_2, $CaSO_3$ decreased dissolved O_2 in water at least by 800 times at pH <8.0, which indicated that oxidation of pyrite by O_2 would be significantly slowed by $CaSO_3$.

In the pH range of 8 to 12, dissolved O_2 concentrations in the slurry of $CaSO_3$ at 25^{0}C and 21% O_2 decreased with decreasing pH (Fig. 1.4). This might be due to a faster dissolution rate of $CaSO_3$ at lower pH (Tseng and Rochelle, 1986).

Sulfur dioxide release in $CaSO_3$ slurry. At an initial pH of 5.0, the amount of SO_2 released from the slurry of $CaSO_3$ in 24 h was significant only at an initial $CaSO_3$

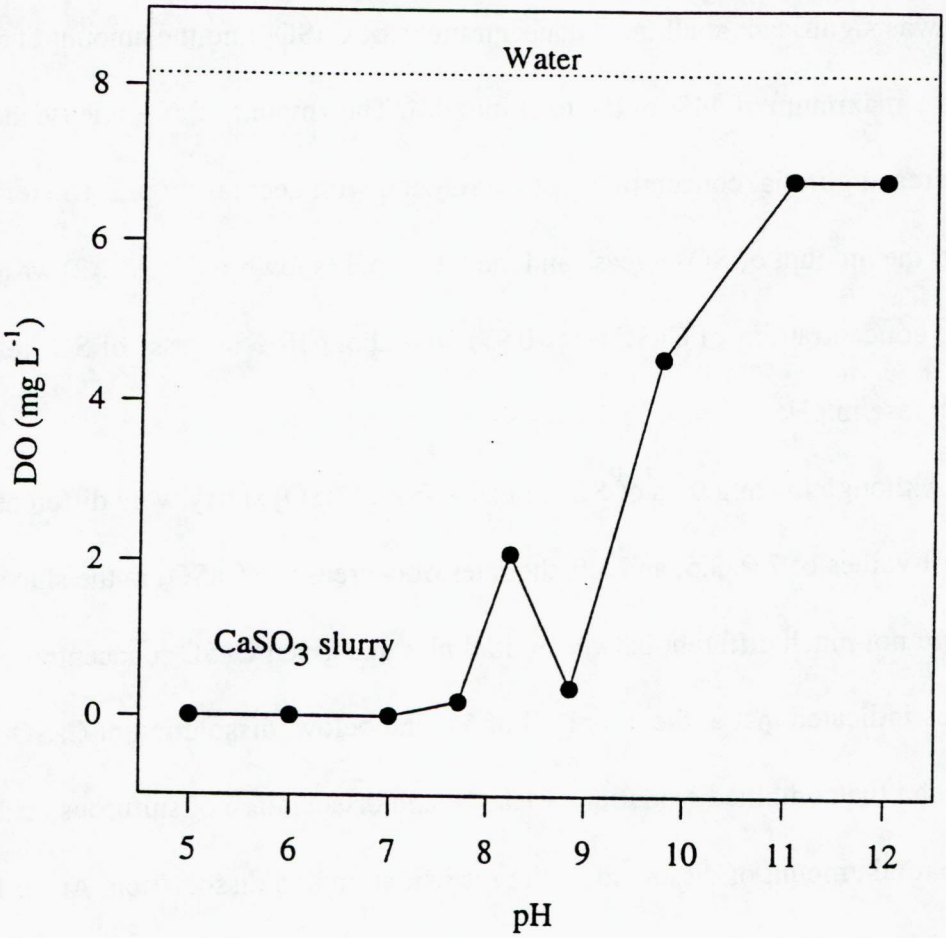

Fig. 1.4: Effect of pH on dissolved O_2 (DO) concentration in 10 g L^{-1} $CaSO_3$ slurry at 21% O_2, 25^0C.

concentration of 40 g L^{-1} (Table 1.2). At initial pHs of 2.0 and 3.5, the amount of SO_2 release was significant at all three concentrations of $CaSO_3$ and the amount of S loss reached a maximum of 44% of the total initial S. The amount of SO_2 release increased with increasing initial concentration of $CaSO_3$ and with decreasing pH. The relationship between the amount of SO_2 release and the initial pH (shown in Table 1.2) was linear at all three concentrations of $CaSO_3$ (r^2 >0.97) with about 10% increase of SO_2 release per unit decrease in pH.

Although the amounts of SO_2 released from $CaSO_3$ slurry were different at the initial pH values of 2.0, 3.5, and 5.0, the rates of decrease of $CaSO_3$ in the slurry with time were not much different between initial pHs at a given $CaSO_3$ concentrations (Fig. 1.5). This indicated that at the initial pH of 5.0 and below, dissolution of $CaSO_3$ may be slower than the combined oxidation of $CaSO_3$ and dissociation of sulfurous acid and thus limit the total amount of dissolved sulfite for oxidation and dissociation. At the lowest initial pH, more dissolved sulfite dissociated into SO_2 instead of being oxidized to sulfate but the total amount of sulfite decrease was similar to that at the higher initial pH.

Oxidation rate of $CaSO_3$ (dissolved and non-dissolved) by Fe^{3+}. The oxidation rate of $CaSO_3$ by Fe^{3+} was dramatically increased by decreasing the initial pH due not only to the increased activity of dissolved $CaSO_3$ but also to the increased activity of Fe^{3+} in solution (Fig. 1.6). The time period for the initial 7 mmol L^{-1} of $CaSO_3$ concentration to decrease to or below 1 mmol L^{-1} was 17 days for the initial pH of 4.0, 19 h for the initial pH of 3.0, and only 3 h for the initial pH of 2.0.

Initial pH	Initial $CaSO_3$ concentration ($g\ L^{-1}$)	Gaseous S release[a] (% of initial S)
2.0	10	33.1
3.5	10	14.1
5.0	10	1.4
2.0	20	34.9
3.5	20	21.0
5.0	20	-0.2
2.0	40	43.9
3.5	40	21.7
5.0	40	9.3

[a], Calculated as (A-B)*100/A where A and B are the initial and final S concentrations, respectively.

Table 1.2: Effects of initial pH and initial $CaSO_3$ concentrations on the amounts of gaseous S release from aqueous $CaSO_3$ slurry during 24 h oxidation at 21% O_2, 25^0C.

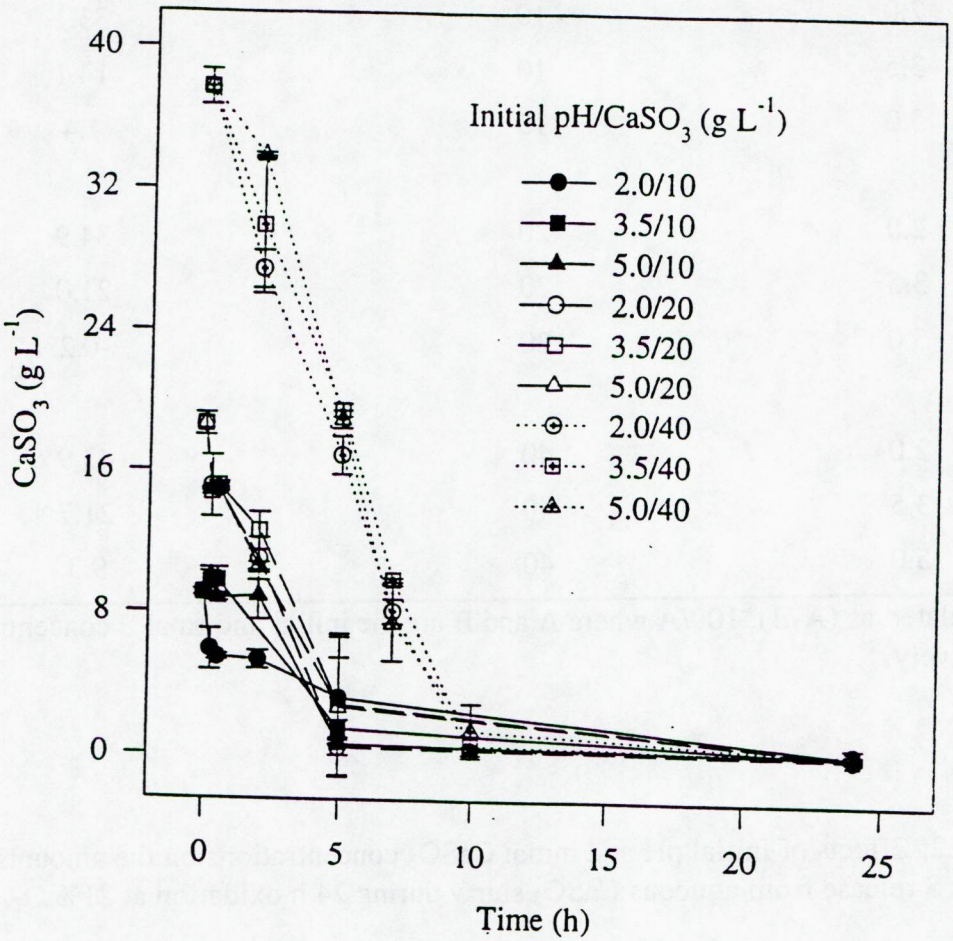

Fig. 1.5: Change of $CaSO_3$ concentration in an queous slurry with time at initial pH 5.0 and below where SO_2 release is significant. 25^0C. 21% O_2. Error bar = one standard deviation.

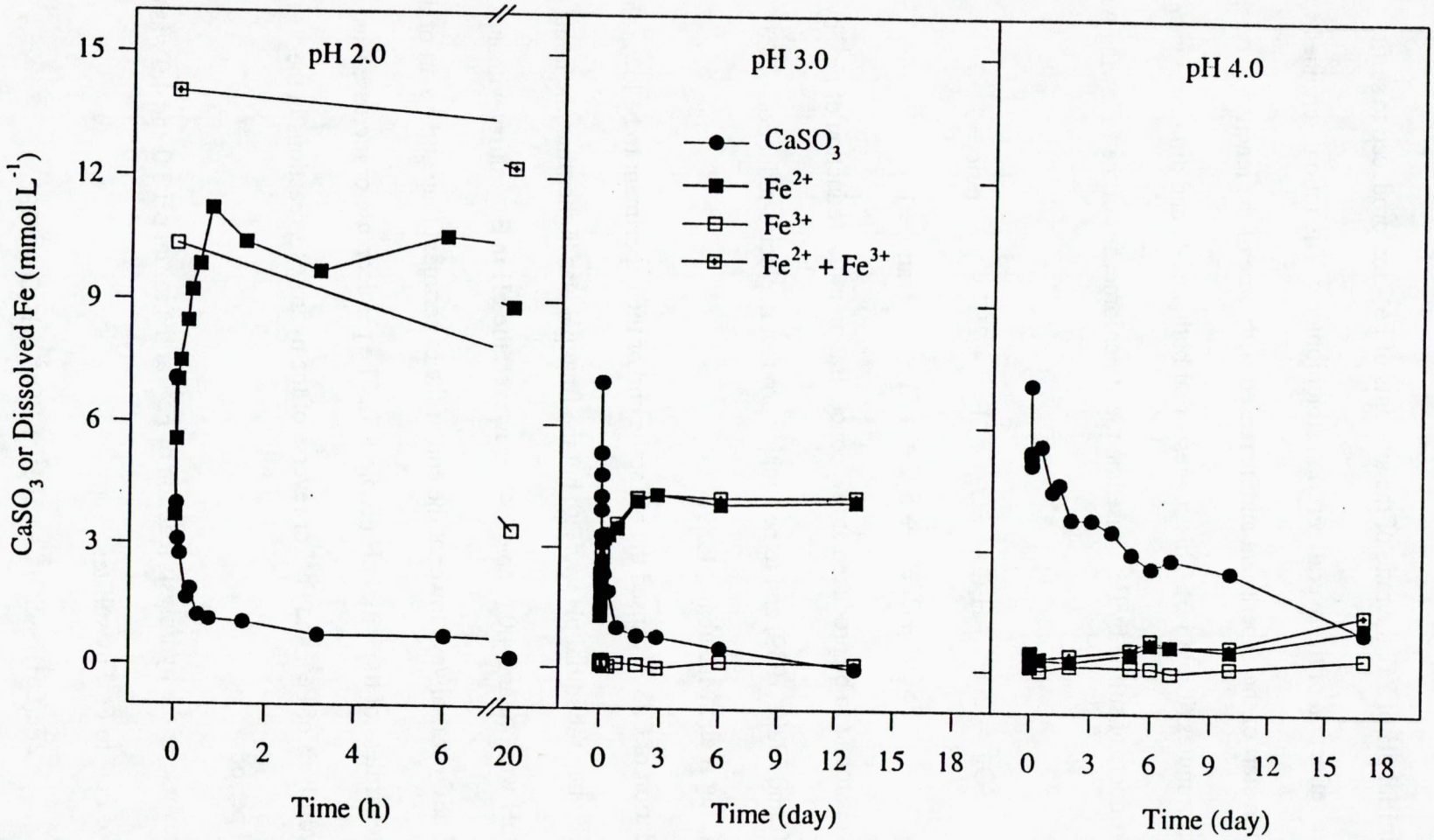

Fig. 1.6: Oxidation of $CaSO_3$ by $FeNH_4(SO_4)_2$ in an aqueous slurry under anaerobic conditions at 25^0C as affected by the initial pH.

At initial pH of 2.0, the ratio of the amounts of Fe^{2+} ion produced to sulfite oxidized is a reflection of the overall reaction stoichiometry. The ratio determined was near 1.0 at the start of the experiment and increased with time of the reaction to reach 1.57 after 45 minutes (Table 1.3). This suggests that both sulfate and dithionate were the oxidation products of sulfite by Fe^{3+} based on the stoichiometries of the following two reactions:

$$SO_3^{2-} + 2Fe^{3+} + H_2O \rightarrow SO_4^{2-} + 2Fe^{2+} + 2H^+ \qquad \text{ratio} = 2$$

$$2SO_3^{2-} + 2Fe^{3+} \rightarrow S_2O_6^{2-} + 2Fe^{2+} \qquad \text{ratio} = 1$$

Dithionate was found to be produced at low concentration in the reduction of Fe^{3+} by sulfite (Kraft and Eldik, 1989) and to be a major product in electro-reduction of Cu^{2+} ion by sulfite (Katagiri and Matsubara, 1989).

Oxidation of $CaSO_3$ caused the pH at the end of the experiment to be lower than the initial pH when the initial pH was 2.0, but the final pH was higher than the initial pH if the initial pH was 3.0 and 4.0 (Table 1.4). However, the pH in Fe^{3+} slurry without addition of $CaSO_3$ was always lower at the end of the experiment than at the start of the experiment regardless of the initial pH (Table 1.5). The pH decrease or increase was caused by hydrolysis of Fe^{3+} and Fe^{2+} or reverse of the hydrolysis reactions in the experimental period.

The reverse of the hydrolysis reaction of Fe^{3+} at the initial pH 3.0 and 4.0 was due to reduction of Fe^{3+} to Fe^{2+} by sulfite:

$$2Fe(OH)_3 + SO_3^{2-} \rightarrow 2Fe^{2+} + SO_4^{2-} + H_2O + 4OH^-$$

$$2Fe(OH)_3 + 2SO_3^{2-} \rightarrow 2Fe^{2+} + S_2O_6^{2-} + 6OH^-$$

Time (min)	Fe^{2+} ion produced (mmol)	Sulfite oxidized (mmol)	Ratio
1	1.88	1.83	1.03
3	3.33	2.72	1.22
6	3.80	3.08	1.23
15	4.78	4.18	1.14
20	5.52	3.96	1.39
30	6.15	4.61	1.33
45	7.52	4.78	1.57

Table 1.3: The ratio of the amount of Fe^{2+} ion produced to the amount of sulfite oxidized in 110 ml reaction slurry during the initial 45 minutes of the reaction at initial pH 2.0.

Treatment	Oxidation period	pH		
		Initial	Final	Final - Initial
Control	24 h	2.01	1.87	-0.14
	14 days	2.92	2.57	-0.35
	17 days	4.07	2.91	-1.16
Experiment	24 h	2.01	1.91	-0.10
	14 days	2.92	3.55	0.63
	17 days	4.07	4.45	0.38

Table 1.4: Change of pH during oxidation of $CaSO_3$ by Fe^{3+}. Controls contained $FeNH_4(SO_4)_2 \cdot 12H_2O$ but no $CaSO_3$.

in which 4 or 6 hydroxyl ions were produced. Because four H^+ are produced in formation of $Fe(OH)_3$ in the following reaction:

$$2Fe^{2+} \text{ (in pyrite)} + 0.5O_2 + 5H_2O \rightarrow 2Fe(OH)_3 + 4H^+$$

in which Fe^{2+} in pyrite is oxidized to Fe^{3+} and then Fe^{3+} hydrolyzes, oxidation of $CaSO_3$ by Fe^{3+} in coal refuse would not decrease pH if sulfate is formed and would increase pH if dithionate is formed.

CONCLUSIONS

The oxidation rate of $CaSO_3$ by O_2 was studied under the conditions commonly encountered in a coal refuse disposal environment. In a 10 g L^{-1} $CaSO_3$ slurry, dissolved O_2 concentration was below 10 μg L^{-1} at pH <8. At initial pHs of 2.0 and 3.5, 14 to 44% of the initial S was released as SO_2 during a 24 h oxidation period and the amount of SO_2 released increased with increasing initial concentration of $CaSO_3$ and decreasing initial pH. Oxidation rate of $CaSO_3$ by Fe^{3+} ion increased when the initial pH decreased from 4.0 to 2.0.

The above experimental results indicate that although $CaSO_3$ is only slightly soluble in water, it can efficiently scavenge dissolved O_2 and Fe^{3+} under coal refuse disposal environmental conditions and thus has a potential to inhibit pyrite oxidation and acid production in coal refuse. Concerns about SO_2 release into the atmosphere and sulfite leaching into surrounding environments when $CaSO_3$ is added to coal refuse can be reduced by maintaining a pH >5 under which $CaSO_3$ can efficiently scavenge dissolved O_2 and Fe^{3+}. Maintaining pH >5 might be accomplished by using a FGD which also contains $CaCO_3$.

CHAPTER 2

EFFECTS OF CALCIUM SULFITE ALONE AND IN COMBINATION WITH CALCIUM CARBONATE AND FLY ASH ON INHIBITION OF ACID PRODUCTION IN COAL REFUSE

ABSTRACT

The abilities of calcium sulfite alone ($CaSO_3 \cdot 0.5H_2O$ or simply $CaSO_3$) and in combination with $CaCO_3$ and fly ash to inhibit acid production in pyritic coal refuse was tested in a slurry experiment (only for $CaSO_3$) and in a column leaching experiment. Addition of 0.1 g $CaSO_3$ at 1% air O_2 or 0.2 g $CaSO_3$ at 21% air O_2 to the coal refuse slurry (2 g fresh coal refuse in 100 ml water) every 3 days prevented a pH drop below the initial pH for 33 days. In the column leaching experiment, $CaSO_3$ (6.4 g in 50 g coal refuse) inhibited acid leaching in the coal refuse columns for 27 weeks. In the initial 13 weeks, the total amounts of acidity, H^+, Fe, and Al produced by the $CaSO_3$ treatment were only 26%, 10%, 32%, and 39% of those of the control. In the last 14 weeks, the inhibitory effect of $CaSO_3$ on acid leaching was less than that in the initial 13 weeks.

Calcium sulfite may inhibit pyrite oxidation by increasing pH and decreasing the redox potential of the solution phase in coal refuse. A combination of $CaSO_3$ with both $CaCO_3$ and fly ash enhanced the inhibitory effect of $CaSO_3$ on acid production in coal refuse. A calcium sulfite-containing FGD by-product which combined $CaSO_3$ (64%) with $CaCO_3$ (10%), fly ash (17%), and $CaSO_4 \cdot 2H_2O$ (9%), had a much stronger inhibitory effect on acid leaching than $CaSO_3$ alone. The above combination effect was at least partially produced by the positive interaction of $CaSO_3$ with $CaCO_3$ and fly ash. We conclude that it is reasonable to further test the ability of $CaSO_3$ or $CaSO_3$-containing FGD to inhibit acid production in coal refuse on a larger scale.

INTRODUCTION

Calcium sulfite is an efficient scavenger of dissolved O_2 and Fe^{3+} under the conditions commonly encountered in coal refuse disposal environments (Chapter 1). At pH <8, the concentration of dissolved O_2 in water exposed to the atmosphere was below 10 $\mu g\ L^{-1}$ in the presence of 10 g L^{-1} $CaSO_3$. Therefore, addition of $CaSO_3$ in coal refuse may decrease the amounts of dissolved O_2 and Fe^{3+} available to oxidize pyrite.

There is little published information on the use of $CaSO_3$ to inhibit acid production in coal refuse. In the past few years, however, various FGD by-products have been evaluated as materials to reclaim mine spoil and coal refuse and have been found to inhibit acid production and stimulate plant growth (see introduction). These studies did not differentiate the effects of $CaSO_3$ from those of $CaCO_3$, fly ash, and calcium sulfate contained in the FGD, thus, the ability of $CaSO_3$ to inhibit acid production in coal refuse is unknown and should be determined.

The dissolution and oxidation of $CaSO_3$ depends greatly on pH and O_2 diffusion rate. Concentrations of metal ions, $CaCO_3$ and fly ash contained in FGD may also affect the reactions and, thus, the ability of FGD to inhibit acid production in coal refuse. The pH of water in equilibrium with $CaCO_3$ is about 8.5. At this pH, dissolution and oxidation of $CaSO_3$ is fast enough to maintain dissolved O_2 around 10 $\mu g\ L^{-1}$ (Chapter 1) under which the oxidation of pyrite would be significantly slowed. Fly ash is characterized by small particles (<0.05 mm) which produce a relatively large surface area (>1 $m^2\ g^{-1}$). Small particles can fill the pore space of coarse coal refuse and thus retard O_2

diffusion from the atmosphere into the coal refuse. Pozzolanic reactions between $CaSO_3$, $CaCO_3$, and fly ash can occur and create a material with reduced rates of water percolation. A determination of interactions of $CaSO_3$ with $CaCO_3$ and fly ash should be useful for enhancing the inhibitory effect of $CaSO_3$ on acid production in coal refuse.

In this study, we conducted both a slurry experiment and a bench-scale column leaching experiment using a coal refuse that contained a high percentage of pyrite and had a strong potential to rapidly produce acid. The inhibitory effects observed in this study should, therefore, be more likely to occur in coal refuses which have less potential to produce acid. Our objectives were to determine the abilities of $CaSO_3$ and $CaSO_3$-containing FGD to inhibit acid production in coal refuse and observe possible interactions of $CaSO_3$ with $CaCO_3$ and fly ash in inhibition of acid leaching. The results will be useful to predict the outcome of applying $CaSO_3$ or $CaSO_3$-containing FGD to inhibit acid production in coal refuse under field conditions.

MATERIALS AND METHODS

Coal refuse. Unweathered (fresh) coal refuse was obtained from the American Electric Power Plant (Coshocton, Ohio). The coal refuse was coarse (36% 1-10 mm and 64% >10 mm) and was produced by a gravity separation method. It was sieved through 1.25 cm openings, air-dried, and ground into particles less than 2 mm. Total S content in the coal refuse was 3600 mmol kg^{-1} as determined by an aqua-regia-HF digestion and inductively-coupled plasma (ICP) emission spectroscopy (Table 2.1) (Bigham et al., 1992). The amounts of other elements in the coal refuse were also determined by an aqua-regia-HF digestion and ICP (Table 1). X-ray diffraction analysis indicated that the fresh coal refuse contained gypsum, kaolinite, marcasite, pyrite, and quartz. The detailed procedure for X-ray diffraction pattern analysis can be found in Bigham et al. (1992). Pyrite content of the coal refuse was analyzed by the method of Begheijn et al. (1978) and was approximately 1525 mmol kg^{-1} which was equivalent to 3050 mmol S kg^{-1} (85% of total S).

Amendments. Calcium sulfite was synthesized by mixing 6% sulfurous acid with reagent grade calcium hydroxide. The excess sulfurous acid was removed by gradually increasing the temperature to 90^0C in a water bath. The calcium sulfite precipitate was washed with a large quantity of double deionized water and then dried at 60^0C. Thermogravimetric analysis (Bigham et al., 1992) indicated that the product contained more than 96% $CaSO_3$ which was also ascertained to be hannebachite by X-ray diffraction analysis. Total element concentrations in the synthesized $CaSO_3$ were

Sample	pH	TNP [a]	Al	Ca	Fe	K	Mg	Na	S	Si
			.....			mmol kg^{-1}			.....	
$CaSO_3$	9.7	3	1.85	7790	0.67	8.44	0.66	0.00	7810	0.40
Fly ash	3.9	0	4530	466	3120	319	215	205	145	6890
FGD	10.6	11	2090	4480	1200	127	283	176	2270	3690
Coal refuse	4.2	ND	1300	91	1860	116	89	161	3560	3210

[a], TNP = total neutralization potential calculated as an equivalent amount of $CaCO_3$ contained in the samples. ND = not determined.

Table 2.1: Chemical composition of the amendments and coal refuse used in the column leaching experiment.

analyzed by ICP following acid digestion (Table 2.1) (Isaac and Johnson, 1985). The calcium carbonate used was a reagent grade chemical.

Fly ash and FGD were obtained from the American Electric Power plant at Coshocton, Ohio. The fly ash was collected in an electrostatic precipitator. The FGD by-product was produced in the power plant by mixing filter cake ($CaSO_3$), fly ash (collected in electrostatic precipitator), and calcium oxide and was weathered for several weeks on the landfill site near the power plant. Before use, the FGD was dried at 105^0C. Particle sizes of fly ash and FGD were less than 0.5 mm. Thermogravimetric analysis (Bigham et al., 1992) indicated that the FGD contained 64% $CaSO_3$, 10% $CaCO_3$, 9% gypsum ($CaSO_4\ 2H_2O$), and 17% fly ash. The chemical compositions of the fly ash and FGD are shown in table 2.1. Total neutralization potential (TNP) was determined by the following procedure: samples were oxidized with 30% H_2O_2 for 30 min, acidified with 0.2 M HCl, heated for 30 min and then cooled before back-titrating with 0.5 M NaOH to pH 7.0.

Coal refuse slurry experiment. Coal refuse slurry, formed by adding 2 g of the coal refuse (<2 mm) to 100 ml double deionized water, was placed in 250 ml Erlenmyer flasks and shaken at 180 rpm in a rotary shaker. Calcium sulfite was added to the coal refuse slurry at the start of the experiment and every 3 days. Before each addition of $CaSO_3$, double deionized water was added to supplement water evaporation (calculated by weighing the flasks). The pH was determined (glass electrode and Accumet model 50 electric pH meter) every 3 days after addition of water but before addition of $CaSO_3$. The experiment last for 33 days.

The experiment was conducted at 21% and 1% O_2 content in air. At 21% O_2, three amounts of $CaSO_3$ (0 g, 0.1 g and 0.2 g) were added to the slurry. At 1% O_2, two amounts of $CaSO_3$ (0 and 0.1 g) were added to the slurry. Triplicate flasks were set up for each experimental condition and the experimental temperature was 25^0C. The experiment at 1% O_2 was set up in an anaerobic chamber in which air was replaced by nitrogen gas and O_2 content in the gas phase was monitored by gas chromatography (see Chapter 1).

Leaching of coal refuse columns. Plastic syringes (2.5 cm inside diameter and 13 cm long) were used as columns. Fifty grams of coal refuse (particle size <2 mm) were thoroughly mixed with different amendments and then placed in the columns. Glass wool was applied at the bottom (1 g) and the top (0.2 g) of the syringes to facilitate water movement through the columns. The amount of FGD added to coal refuse was 10 g (20% rate, w/w).

Seven treatments were investigated and included: $CaSO_3$, $CaCO_3$, fly ash, combination of $CaSO_3$ with $CaCO_3$, combination of $CaSO_3$ with fly ash, FGD, and an untreated control. The amounts of $CaSO_3$ (6.4 g, 12.8%), $CaCO_3$ (1 g, 2%), and fly ash (1.7 g, 3.4%) were equal to the amounts contained in 10 g FGD. Each treatment was replicated three times. The experimental design was a randomized complete block.

To obtain the same water potential for all the columns before regular leaching started, 25 ml double deionized water was added and the columns were extracted until no water came out. Three days later, leaching was started. The columns were leached weekly for the first 13 weeks and biweekly for the last 14 weeks (total 27 weeks). For each leaching, 20 ml of double deionized water was added to the columns. The leaching speed

was 1 ml per hour and was controlled by a mechanical extractor (Model 24-01, Centurion International Inc., Lincoln, NC). Leaching lasted for approximately 36 hours to ensure 20 ml water go through the columns of all treatments.

Leachates were analyzed for pH (glass electrode), redox potential (platinum Ag/AgCl combination electrode M13-620-82, Fisher Scientific Co., Pittsburgh, PA), titratable acidity, and concentrations of S, Fe, and Al. For the acidity determination, 0.5 to 1 ml leachate was titrated with 0.1 M NaOH using an automatic titrator. The pH end point was 8.3. For determination of S, Fe, and Al, 5 ml leachate was filtered through 0.45 μm filter paper, the filtrates were acidified by addition of 0.1 ml concentrated HNO_3, and the acidified filtrates were analyzed for S, Fe, and Al by ICP.

Statistics. For the coal refuse slurry experiment, the activity of H^+ was calculated from pH and summed for all pH values measured in 33 days to get total H^+ activity. The total H^+ was the total H^+ activity multiplied by the volume of the slurry (100 ml) and is simply referred to as total H^+ in the following description. The total H^+ was used for statistical analysis. The interaction between $CaSO_3$ addition (0 g and 0.1 g) and the O_2 content in air (21% and 1%) on the total H^+ was tested.

For the coal refuse column leaching experiment, the amounts of acidity, H^+, Fe, and Al in the leachates were calculated by multiplication of their concentrations with leachate volume (20 ml). The total acidity, H^+, Fe, and Al were calculated for weekly leaching periods (weeks 1 to 13, 13 leachates), biweekly leaching periods (weeks 13 to 27, 8 leachates), and total leaching period (weeks 1 to 27, 20 leachates). A t test was performed to compare the effects of the two treatments on total acidity, H^+, Al, and Fe in

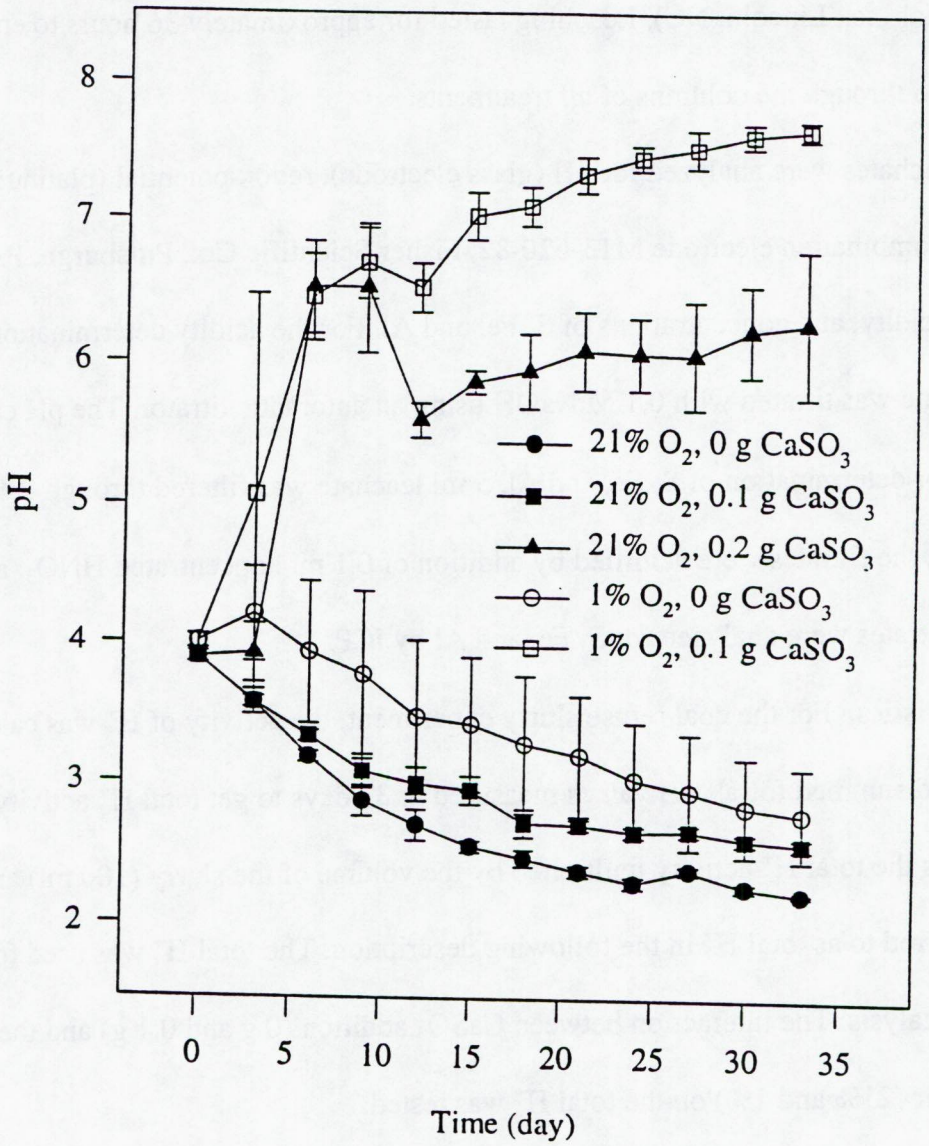

Fig. 2.1: Change of coal refuse slurry pH with time as affected by the amounts of $CaSO_3$ addition and O_2 content in air. Error bar = one standard deviation.

$CaSO_3$, the pH of the coal refuse slurry continuously decreased with time due to pyrite oxidation (not to dissolution of acidic precipitates on the surface of coal refuse particles because the pH after 33 days (4.85) was higher than the initial pH (about 4.0) if the coal refuse slurry was incubated under anaerobic conditions).

Inhibitory effect of calcium sulfite on acid leaching from coal refuse columns. The coal refuse had a strong potential to rapidly produce acid. During the initial 4 weeks, the leachate acidity of the control columns increased from 160 to 680 $mmol_c\ L^{-1}$ and the leachate pH dropped from 2.61 to 1.12 (Fig. 2.2). However, the leachate acidity of the $CaSO_3$-treated columns was below 30 $mmol_c\ L^{-1}$ over the initial 4 weeks and the leachate pH increased from 2.82 to 3.93 during the initial 2 weeks and maintained a pH higher than the initial pH (2.82) for the first 4 weeks. For the first 13 weeks, $CaSO_3$ significantly ($p < 0.0017$) reduced leachate acidity compared to the control (Fig. 2.2) (at least 130 $mmol_c\ L^{-1}$ lower than that of the control for each leachate and only 26% of the total acidity of the control) (Table 2.2). Results obtained for pH, Fe, and Al leaching during the initial 13 weeks (Fig. 2.2 and 2.3, Table 2.2) corroborated the acidity observations and further indicated the inhibitory effects of $CaSO_3$ on acid leaching from the coal refuse columns. For the initial 13 weeks, the total amounts of H^+, Fe, and Al produced in the $CaSO_3$ treatment were only 10%, 32%, and 39% of those of the control.

During the last 14 weeks, the inhibitory effect of $CaSO_3$ on acid leaching in the coal refuse columns was much less effective than during the initial 13 weeks. Although the acidities of the last seven leachates for $CaSO_3$ treatment were always lower than those for the control (Fig. 2.2), the differences were not significant at $p < 0.05$. The leachate

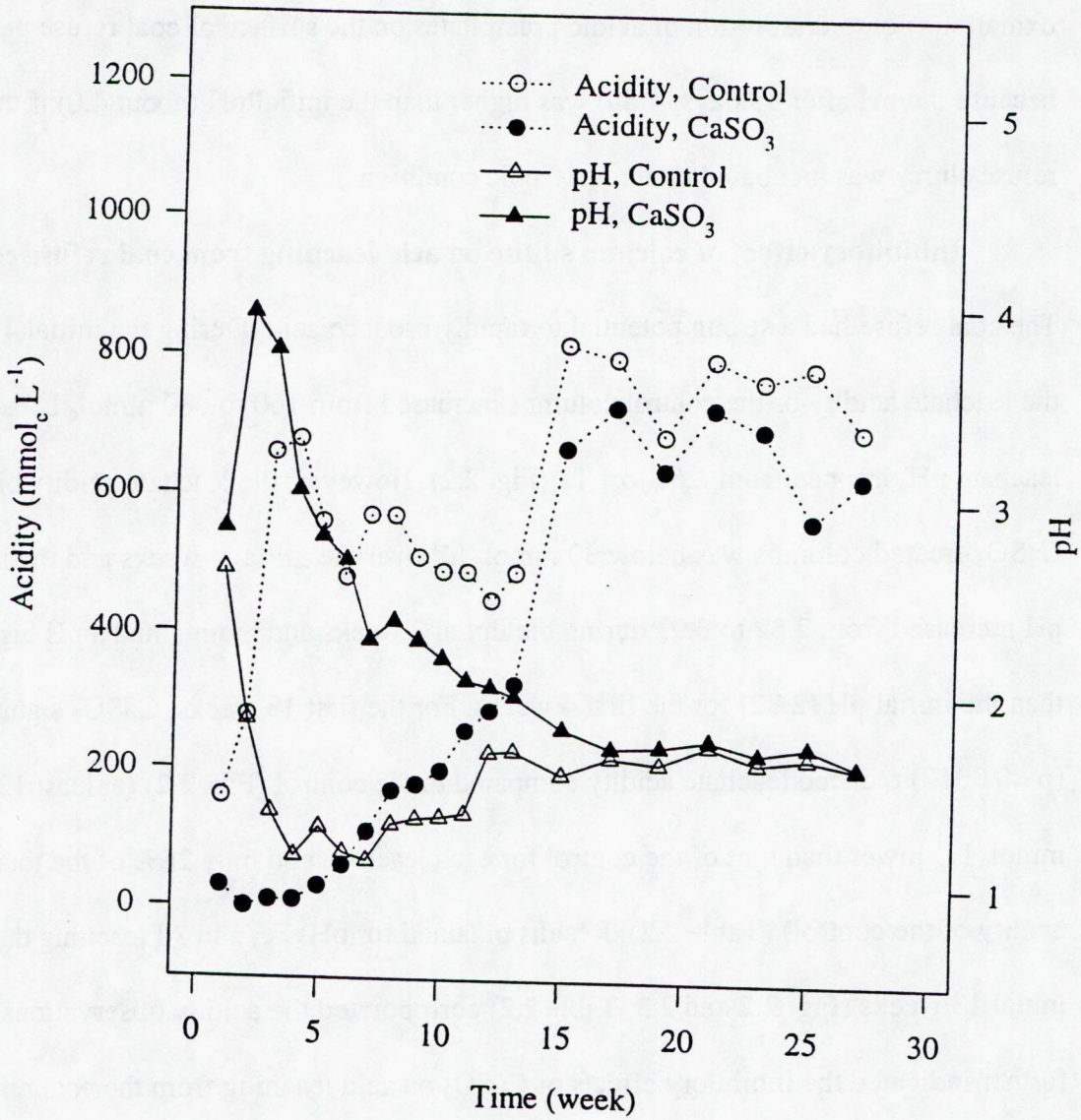

Fig. 2.2: Change of leachate acidity and pH with time for the coal refuse columns amended with and without $CaSO_3$.

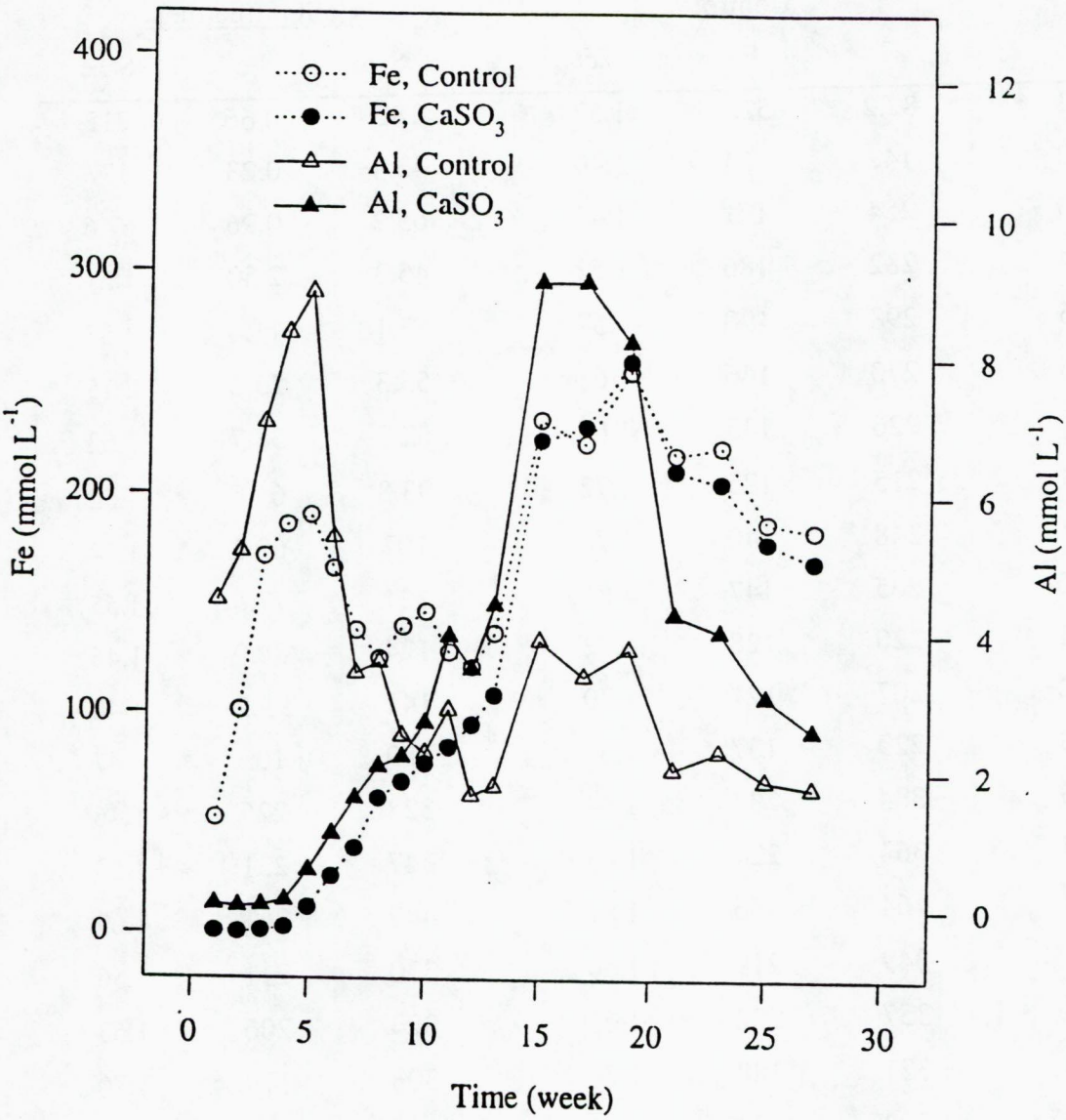

Fig. 2.3: Change of leachate concentrations of Fe and Al with time for the coal refuse columns amended with or without $CaSO_3$.

Time (week)	Concentrations of S and Fe (mmol L^{-1}) and their ratio					
	Control			$CaSO_3$ treatment		
	S	Fe	S/Fe	S	Fe	S/Fe
1	82.2	52.5	1.57	142	0.66	215
2	142	101	1.40	43.4	0.23	187
3	254	171	1.49	65.2	0.96	67.6
4	282	186	1.52	45.3	2.50	18.1
5	298	190	1.57	52.1	11.4	4.57
6	270	166	1.63	55.3	25.8	2.15
7	226	138	1.64	62.7	38.7	1.62
8	215	125	1.72	93.8	61.6	1.52
9	248	140	1.78	107	69.3	1.54
10	265	147	1.81	121	77.6	1.55
11	220	128	1.72	124	84.9	1.46
12	207	121	1.70	141	95.2	1.48
13	229	137	1.67	159	109	1.47
15	384	234	1.64	328	225	1.46
17	364	224	1.63	347	231	1.50
19	464	256	1.81	442	261	1.69
21	349	219	1.60	330	211	1.56
23	357	222	1.61	324	206	1.57
25	321	188	1.71	303	179	1.70
27	302	184	1.64	275	170	1.62

Table 2.4: S and Fe concentrations and their ratio in leachate from coal refuse columns treated with or without $CaSO_3$.

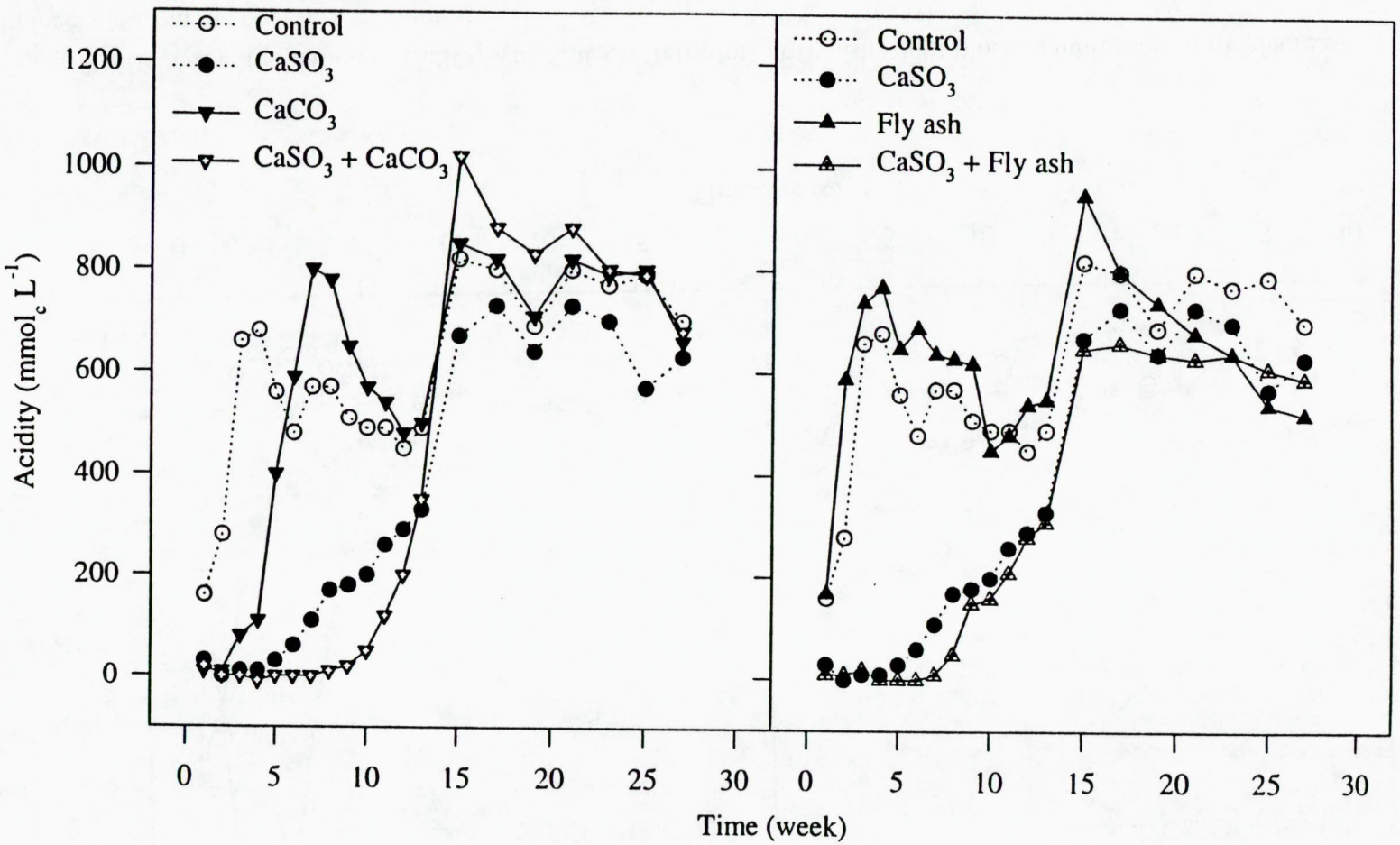

Fig. 2.4: Effect of combination of $CaSO_3$ with $CaCO_3$ (left plot) or fly ash (right plot) on inhibition of acidity increase in leachate from the coal refuse columns.

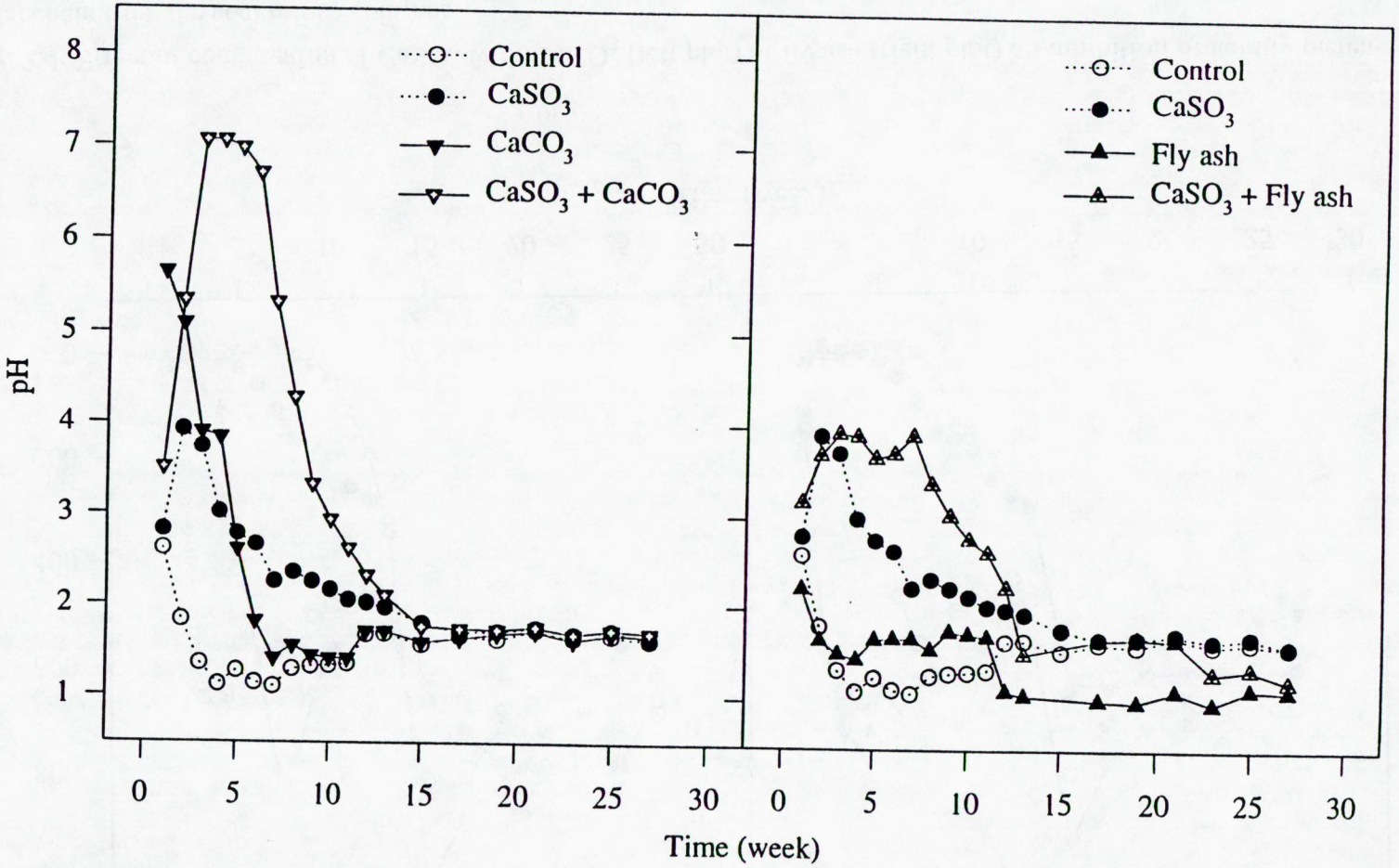

Fig. 2.5: Effect of combination of $CaSO_3$ with $CaCO_3$ (left plot) or fly ash (right plot) on inhibition of pH decrease in leachate from the coal refuse columns.

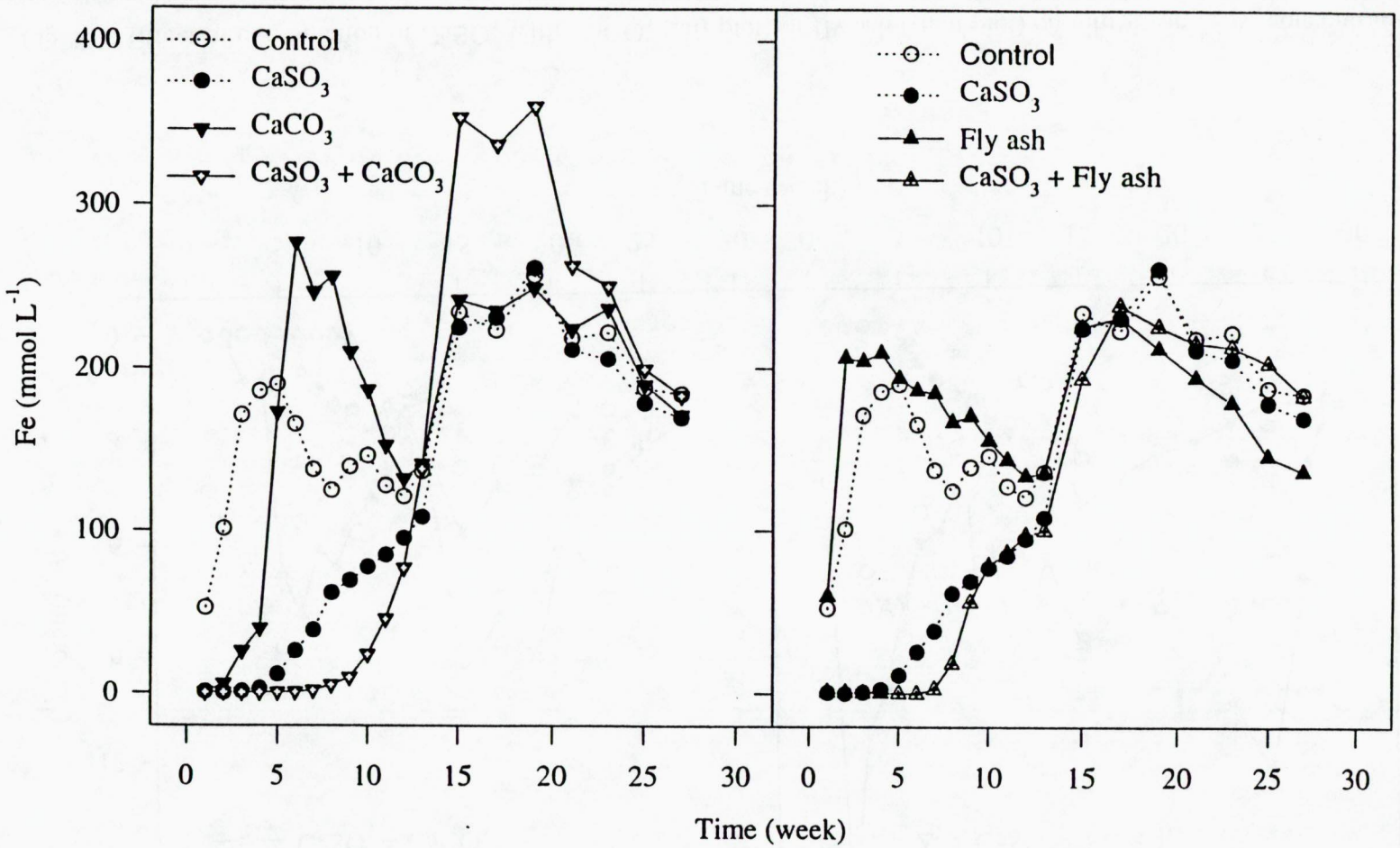

Fig. 2.6: Effect of combination of $CaSO_3$ with $CaCO_3$ (left plot) or fly ash (right plot) on inhibition of Fe concentration increase in leachate from the coal refuse columns.

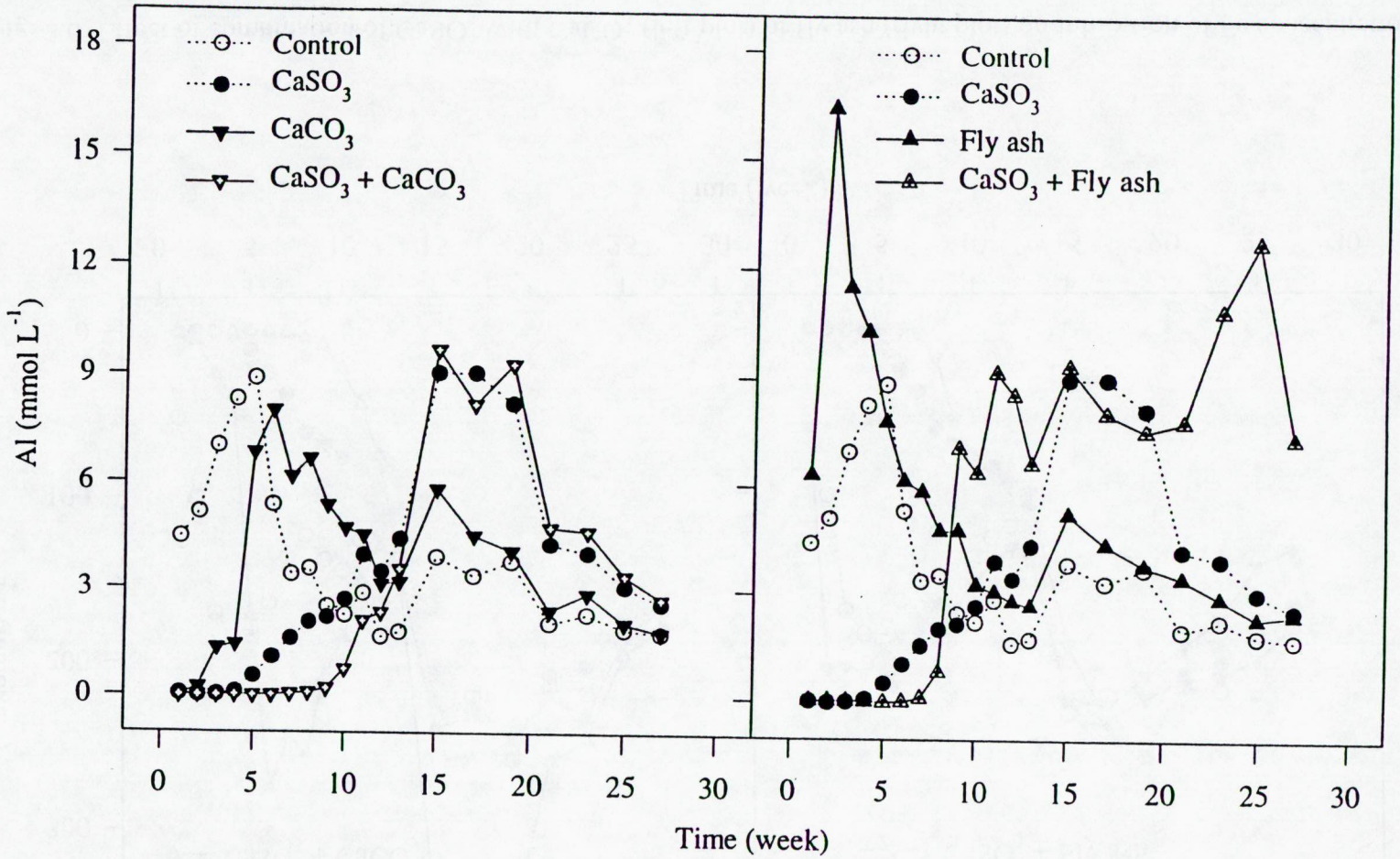

Fig. 2.7: Effect of combination of $CaSO_3$ with $CaCO_3$ (left plot) or fly ash (right plot) on inhibition of Al concentration increase in leachate from the coal refuse columns.

However, combinations of $CaSO_3$ with $CaCO_3$ or fly ash enhanced the inhibitory effect of $CaSO_3$ on acid leaching from the coal refuse columns during the first 13 weeks. The changes of acidity, pH, Fe, and Al (Fig. 2.4 to 2.7, respectively) with time all showed that the combination of both $CaCO_3$ (left plot) and fly ash (right plot) with $CaSO_3$ prolonged the periods before the acidity and concentrations of Fe and Al started to increase or before the pH dropped below the initial pH. Combination of $CaSO_3$ with $CaCO_3$ increased the leachate pH to about 7 and maintained the pH above 5 for 6 weeks compared to a maximum pH around 4 with $CaSO_3$ alone. Combination of $CaSO_3$ with fly ash maintained the leachate pH around 4 for 6 weeks compared to only 1 week with $CaSO_3$ alone.

Both $CaCO_3$ and combination of $CaCO_3$ with $CaSO_3$ produced higher leachate acidity and Fe than the control after certain time periods (Figs. 2.4 and 2.6). This may have been due to the initial high pH with $CaCO_3$ addition. This initial high pH caused precipitation of Fe resulting in a decreased amount of Fe in the leachate during the first few weeks of the experiment compared to the control. As oxidation of the pyrite proceeded and pH dropped, this Fe, along with any new Fe produced by pyrite oxidation, would become soluble. As a result, the amount of soluble Fe and acidity would be increased in the $CaCO_3$ treated refuse compared to the untreated refuse (control). It is also possible that CO_3^{2-} catalyzed pyrite oxidation at the early stage of the experiment when the pH was near neutral (Evangelou and Zhang, 1995).

Calcium sulfite-containing FGD which combined $CaSO_3$ (64%) with $CaCO_3$ (10%), fly ash (17%), and $CaSO_4 \cdot 2H_2O$ (9%) showed much stronger inhibitory effects on

acid leaching from the coal refuse columns than $CaSO_3$ alone (Figs. 2.8 and 2.9). During the initial 13 weeks, the leachate acidity of the FGD treatment was near zero from weeks 2 to 10 (Fig. 2.8). The total acidity of the FGD treatment during this period was only 1.8% that of the $CaSO_3$ treatment (Table 2.2). The leachate pH of the FGD treatment reached a maximum of 8.14 in the sixth week and remained above 5.35 for the entire initial 13 weeks. This was at least 2.5 units higher than the leachate pH of the $CaSO_3$ treatment (Fig. 2.8). The total amount of H^+ produced by the FGD treatment in the initial 13 weeks was only 0.014% that of the $CaSO_3$ treatment (Table 2.2). The total amounts of soluble Fe and Al from the FGD treatment were also much lower than those of the $CaSO_3$ treatment (Table 2.2). During the last 14 weeks, the difference in inhibitory effect on acid leaching between the FGD treatment and $CaSO_3$ treatment was less than that during the initial 13 weeks (Table 2.2. Figs. 2.8 and 2.9).

The enhancement of the inhibitory effect of $CaSO_3$ on acid production in the coal refuse by the other FGD components must be due either to additive effects of these components to the effect of $CaSO_3$ or to their positive interactions with $CaSO_3$. Based on the above observations, the enhancement of the inhibitory effect of $CaSO_3$ on acid leaching by $CaCO_3$ may be either additive or interactive. By contrast, the enhancement by fly ash seemed to be primarily interactive. Statistical analysis indicated that for the first 13 weeks, there were significant interactions of $CaSO_3$ with $CaCO_3$ and fly ash on reduction of the total amounts of H^+ and Al but not on reduction of the total amounts of acidity and Fe (Fig. 2.10).

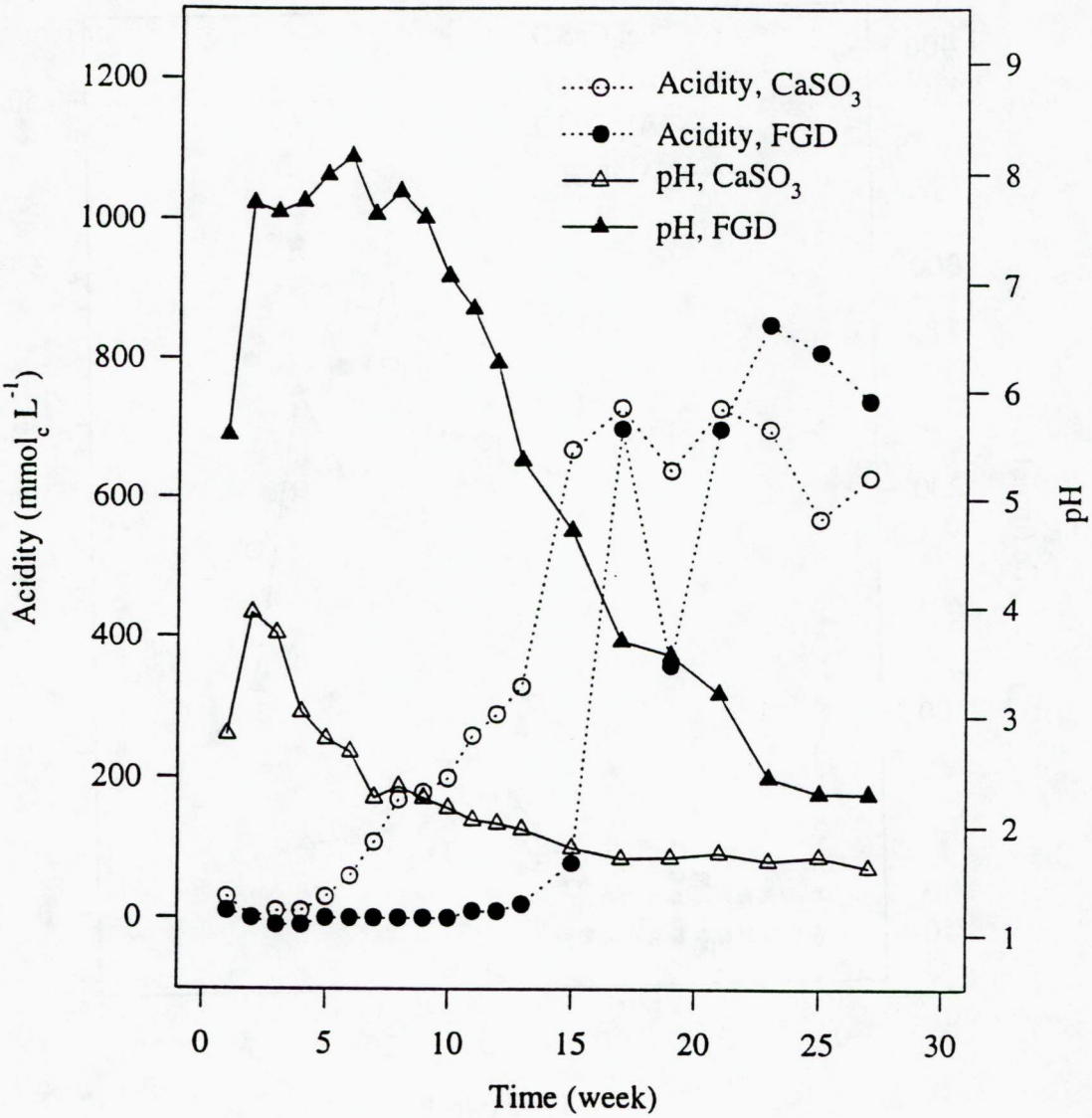

Fig. 2.8: Change of leachate acidity and pH with time for the coal refuse columns amended with $CaSO_3$ or FGD.

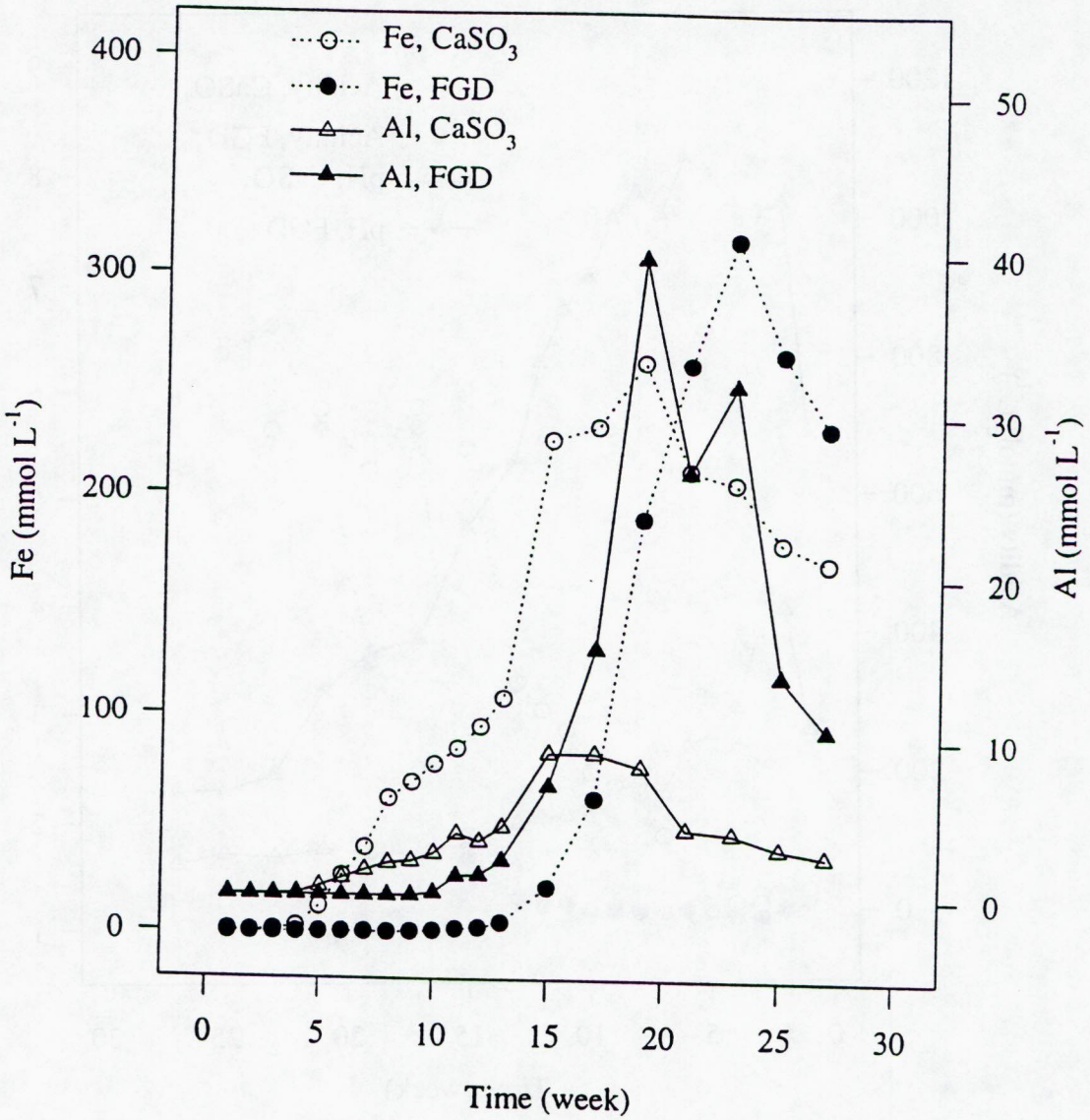

Fig. 2.9: Change of leachate concentrations of Fe and Al with time for the coal refuse columns amended with $CaSO_3$ or FGD.

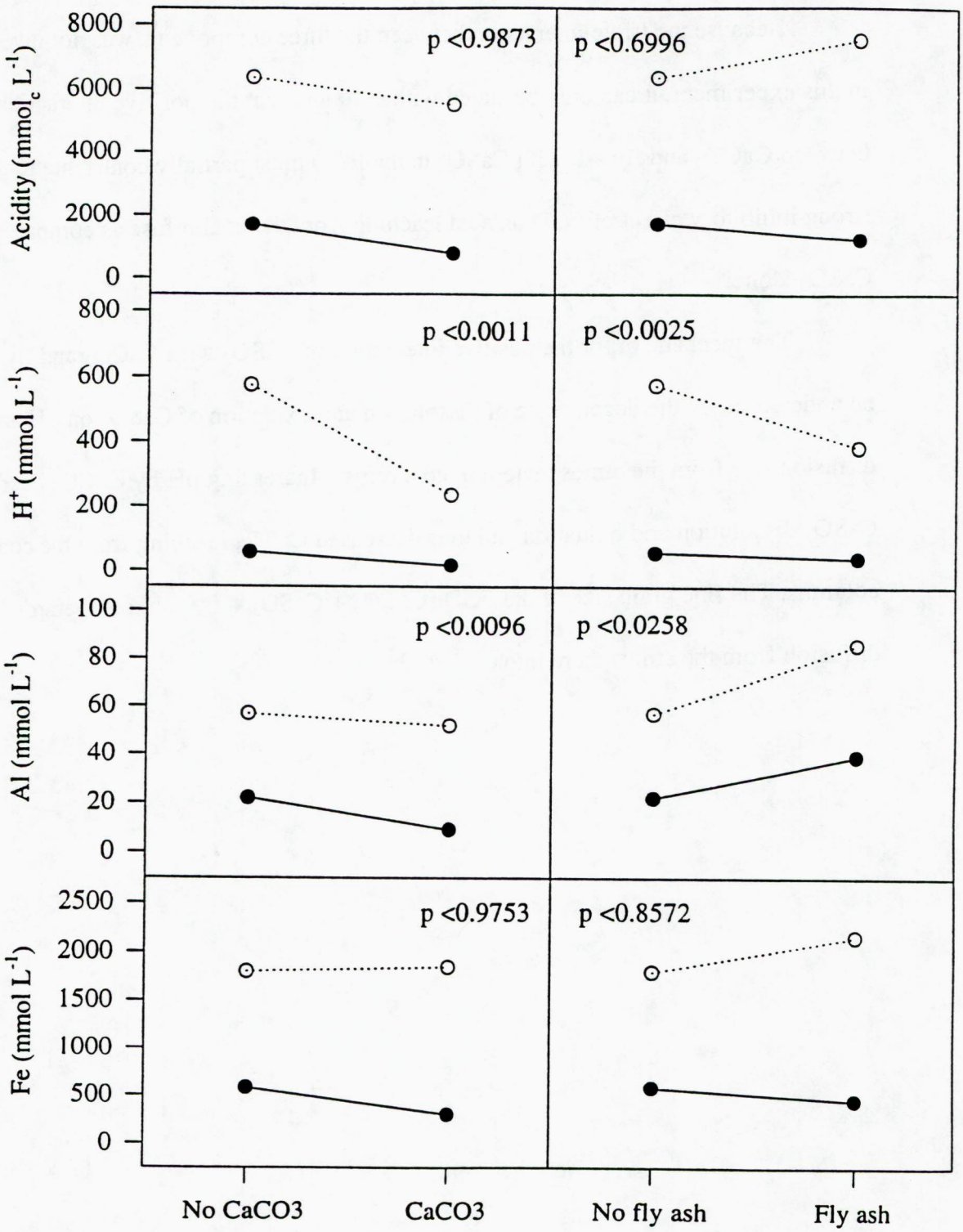

Fig. 2.10: Effect of interaction of $CaSO_3$ with $CaCO_3$ and fly ash on total amounts of acidity, H^+, Fe, and Al in leachate from coal refuse columns during the initial 13 weeks. Hollow circle = no $CaSO_3$ and filled circle = $CaSO_3$ treatment.

Because the triple interaction between the three components was not investigated in this experiment, it can only be stated with certainty that the positive interactions between $CaCO_3$ and fly ash with $CaSO_3$ in the FGD must partially contribute to the strong inhibitory effect of FGD on acid leaching from the coal refuse as compared to $CaSO_3$ alone.

The mechanism for the positive interaction of $CaSO_3$ with $CaCO_3$ and fly ash can be understood by the dependence of dissolution and oxidation of $CaSO_3$ on pH and O_2 diffusion rate from the atmosphere into coal refuse. Increasing pH by $CaCO_3$ decreased $CaSO_3$ dissolution and oxidation and thus decreased $CaSO_3$ leaching from the coal refuse columns. The fine grain size of the FGD ($CaCO_3$ + $CaSO_3$ + fly ash) also retarded O_2 diffusion from the atmosphere into coal refuse.

CONCLUSIONS

Calcium sulfite inhibited pyrite oxidation and pH decrease in the coal refuse slurry. In a column leaching experiment, the total amounts of acidity, H^+, Fe, and Al produced by the $CaSO_3$ treatment were only 26%, 10%, 32%, and 39% those of the control, respectively. The inhibitory effect of $CaSO_3$ on acid leaching was stronger in the initial 13 weeks than in the final 14 weeks. Calcium sulfite may have inhibited pyrite oxidation in the coal refuse columns by decreasing redox potential and increasing pH. By increasing pH, $CaSO_3$ would also inhibit acid leaching of Fe and Al by increasing precipitation of various mineral species.

Combinations of $CaSO_3$ with both $CaCO_3$ and fly ash enhanced the inhibitory effect of $CaSO_3$ on acid leaching in coal refuse. There were significant interactions of $CaSO_3$ with $CaCO_3$ or fly ash on reduction of the total amounts of H^+ and Al leaching but not on the total amounts of acidity and Fe during the initial 13 weeks. Calcium sulfite-containing FGD had a much stronger inhibitory effect on acid leaching from the coal refuse columns than $CaSO_3$ alone. The experimental results indicate the potential of $CaSO_3$ and $CaSO_3$-containing FGD to inhibit acid production in coal refuse. Further tests on a larger scale should be conducted.

CHAPTER 3

ACID REDUCTION IN COAL REFUSE BY CALCIUM SULFITE-CONTAINING FLUE GAS DESULFURIZATION BY-PRODUCT

ABSTRACT

Flue gas desulfurization (FGD) by-product containing calcium sulfite ($CaSO_3 \cdot 0.5H_2O$ or simply $CaSO_3$) used in Chapter 2 was applied in the top 15 cm of two 50 cm coal refuse layers to inhibit acid production under simulated field conditions. The coal refuse included both fresh (described in Chapter 2) and aged material. The refuse was packed into large columns (30 cm inside diameter and 120 cm long) with one layer applied 2 weeks after the other to simulate field operations. There were four FGD rates (%, w/w): 0/0, 5.5/1.25, 11/2.5, and 22/5.0 with the first numbers being in the upper layer and the second numbers being in the lower layer. Treatments are referred to by amendment rates in the upper layer. The columns were leached with water weekly from weeks 1 to 13, biweekly from weeks 13 to 27, and monthly from weeks 27 to 39. Analysis of leachate, interstitial water in the coal refuse, and the coal refuse itself at the

end of the experiment showed that the FGD inhibited acid production in both the fresh and the aged materials. This was indicated by a decrease in acidity and in concentrations of Fe and Al and by an increase in pH. The decrease in leachate acidity and Fe concentration and the increase in leachate pH was generally significant ($p < 0.05$) for the 22% FGD treatment and was linear with increasing FGD rates. After the third week, the leachate acidity of the 22% FGD treatment was at least 500 and 470 mmol L^{-1} lower than that of the control for the fresh and aged coal refuse, respectively. The coal refuse amended with 22% FGD had higher pH and lower concentrations of Fe and Al than that not amended with FGD. The inhibitory effect of the FGD on acid production was greater for leachates than for interstitial waters and greater for the fresh than for the aged coal refuse. Calcium sulfite as a base and strong reductant was thought to be the main contributor to the inhibitory effect of the FGD on acid production in the coal refuse. Similar results are likely to occur under field conditions.

INTRODUCTION

Calcium sulfite is an efficient scavenger of dissolved O_2 and Fe^{3+} in water and inhibits acid production in coal refuse (Chapter 1 and II of this dissertation). However, in the small column leaching experiment (Chapter 2), the coarse coal refuse with particle size larger than 1 cm was ground to < 2 mm, which dramatically changed the kinetics of pyrite oxidation. Small particles have larger surface area which would stimulate pyrite oxidation. However, small particles decrease pore space which retards oxygen diffusion from the atmosphere into the coal refuse, thus inhibiting pyrite oxidation. In addition, small particles can promote homogeneous mixing of coal refuse with $CaSO_3$ or the FGD which would also inhibit pyrite oxidation. Furthermore, grinding coal refuse would change the path and distribution of water flow in coal refuse and affect leachate chemistry. Therefore, the inhibitory effect of $CaSO_3$ and $CaSO_3$-containing FGD on acid production in coal refuse under more natural weathering conditions needs to be examined.

Stehouwer and Mafi (1997) applied 20% and 50% (w/w) wet FGD to acidic coal refuse. These treatments improved surface and subsurface conditions in the coal refuse and enhanced plant growth. However, in these studies, the content of $CaSO_3$ in the FGD was not determined and the effect of the FGD on drainage water chemistry was not described. In a study conducted in our lab (data not published), dry FGD containing about 35% $CaSO_3$ was mixed into the top 15 cm of the aged coal mine spoil at rates of 0%,10%, 20%, and 40% (w/w). The spoil materials in large columns were placed in the

field and exposed to natural weathering conditions for about 5 yrs and improved drainage water chemistry with the FGD treatment was found. However, the mine spoil used in this study had weathered for many years prior to treatment and did not exhibit a strong potential to produce acid compared to the most freshly produced coal refuse materials.

In the present study, large columns (30 cm inside diameter and 120 cm long) were filled with coarse coal refuse and leached with water under simulated natural weathering conditions. To simulate landfilling of coal refuse, a $CaSO_3$-containing wet FGD (described in Chapter 2) was mixed into the top 15 cm of two 50 cm coal refuse layers which were packed separately two weeks apart. Due to large amounts of abandoned coal refuse piles, aged coal refuse was also used to compare with the fresh material.

The purpose of this study was to determine the ability of $CaSO_3$-containing FGD to inhibit acid production in coal refuse under simulated field conditions. The results can be used to predict inhibitory effects of FGD on acid production in the coal refuse at landfill sites.

MATERIALS AND METHODS

Coal refuse and flue gas desulfurization (FGD) by-product. Both fresh and aged coal refuse were used in this experiment. The fresh coal refuse was the same as used in the small column leaching experiment in Chapter 2 but was not ground and dried in this experiment (only particles larger than 10 cm were excluded). Both the fresh and aged coal refuse were obtained from the American Electric Power Plant in Coshocton, OH, and were generated by a gravity separation method. The coal refuse contained 64% (w/w) particles larger than 10 mm and 36% particles between 1 to 10 mm. Water content was 12% (fresh) or 8% (aged) as determined by weighing the coal refuse before and after drying at 105^0C (Table 3.1). The fresh coal refuse was transported from the coal washing plant to the greenhouse on the day it was produced. It was then placed into the columns within 3 days. The aged coal refuse was obtained from the top 15 cm of a coal refuse pile that had weathered for 4 to 5 months at the landfill site near the power plant. The aged coal refuse was transported from the landfill site to the greenhouse 3 days before packing the columns.

The flue gas desulfurization by-product was the same as used in the small column leaching experiment (Chapter 2) but was used without drying. The FGD was also obtained from the American Electric Power Plant at Coshocton, OH, and was generated by mixing filter cake ($CaSO_3$), fly ash (collected in an electrostatic precipitator), and calcium oxide. This product weathered for several weeks before being transported from the American Electric Power Plant to the greenhouse. It was stored at -5^0C and used

Sample	Moisture	pH	TNP[a]	Al	Ca	Fe	K	Mg	Na	S	Si
	%		%, $CaCO_3$	.....		mmol kg^{-1} dry material				.....	
Fresh	10.5	3.81	ND	1300	91	1860	116	89	161	3560	3210
Aged	8.8	3.21	ND	1470	126	1830	69	97	220	3250	3920
FGD	38.7	10.63	11	2090	4480	1200	127	283	176	2270	3690

[a], TNP = total neutralization potential calculated as an equivalent amount of $CaCO_3$ contained in the samples. ND = not determined.

Table 3.1: Characterization of the fresh coal refuse, the aged coal refuse, and the FGD.

within 1 month. Large chunks formed in the weathering process and these were broken by hand to pass through a 1-cm sieve before mixing the FGD with the coal refuse.

The pH, chemical and mineral composition of the coal refuse and FGD, and total neutralization potential (TNP) of the FGD were determined as previously described for the small column leaching experiment (Chapter 2). The results are listed in Table 3.1. Gypsum, kaolinite, marcasite, pyrite, and quartz were the main minerals in the fresh coal refuse. Pyrite content of the fresh coal refuse was analyzed by the method of Begheijn et al. (1978) and was approximately 1525 mmol kg^{-1}. This is equivalent to 3050 mmol S kg^{-1} which accounted for 85% of the total S concentration (3600 mmol kg^{-1}, Table 3.1). Mineralogical composition and pyrite content were not determined for the aged coal refuse. Mineral composition of the FGD was 64% $CaSO_3$, 10% $CaCO_3$, 17% fly ash, and 9% gypsum ($CaSO_4 \cdot 2H_2O$).

Set-up of columns. Coal refuse was packed into PVC columns (30 x 120 cm, Fig. 3.1) during July 25 to 30, 1996 and a second packing of additional coal refuse was made two weeks later during August 14 to 16, 1996. Both packings included a 35 cm layer of coal refuse (30 kg based on dry weight) topped with an additional 15 to 25 cm layer mixture of coal refuse (13 kg based on dry weight) and FGD. Therefore, in each column, the treatments created four layers (Fig. 3.1): a top layer (FGD-amended except for the control), upper middle layer (no FGD), lower middle layer (FGD-amended except for the control), and bottom layer (no FGD). After column packing was completed, ceramic lysimeters (Soil Moisture Equipment, Santa Barbara, CA) were inserted into the upper and lower middle layers (Fig. 3.1). Silicone flour was used to facilitate connection

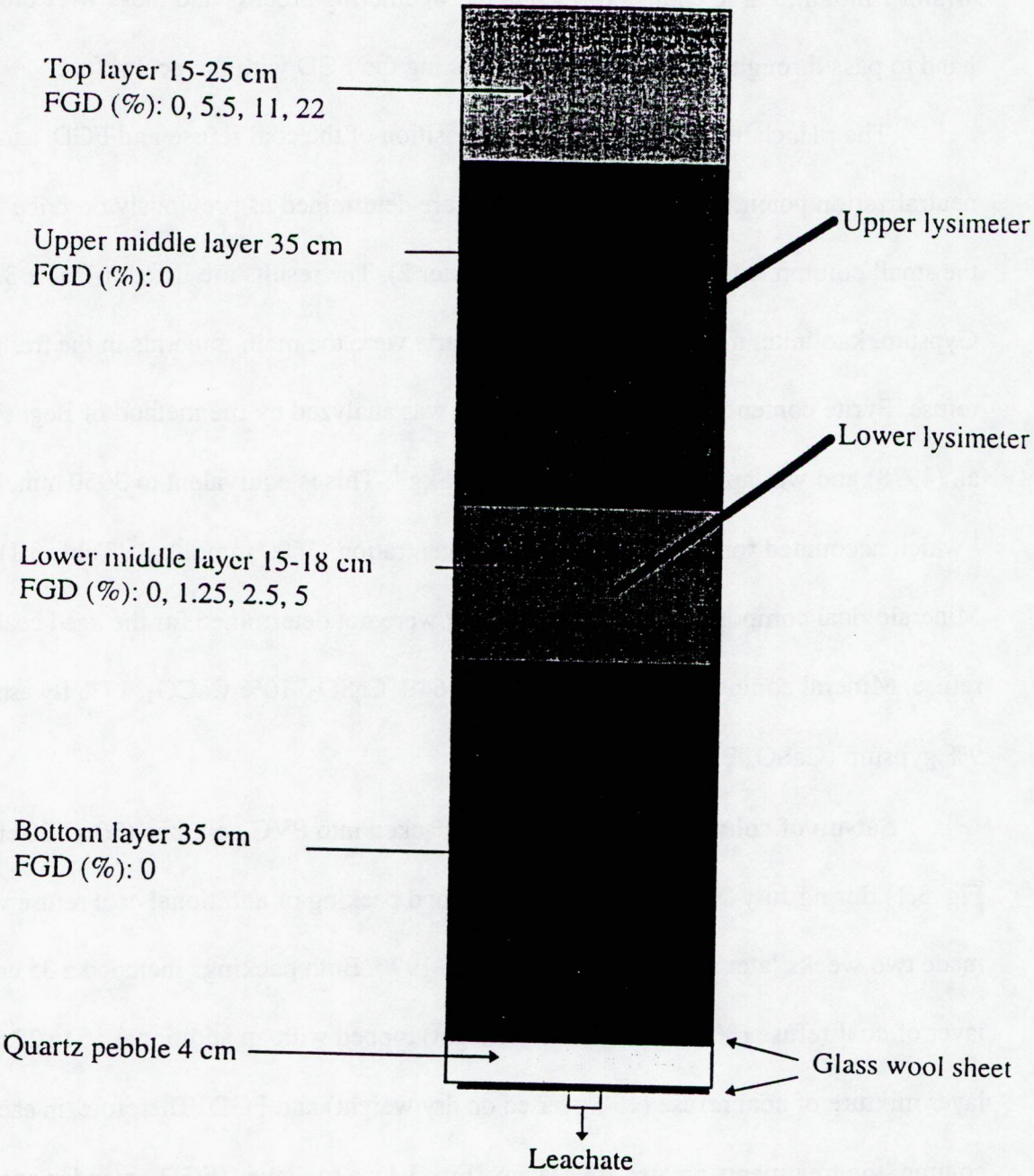

Fig. 3.1: Greenhouse column (30 x 120 cm) containing four layers of coal refuse (fresh or aged) for leaching experiment.

between the lysimeter walls and the coal refuse. The open areas between the lysimeters and column walls were sealed with silicone sealant (Dow Corning, Midland, MI).

The ceramic lysimeter was 18 cm long and allowed the column center to be sampled. It included two parts: a ceramic cup (9 cm long, 0.32 cm wall thickness, and 2.2 cm outer diameter) and a PVC extension (12 cm long and 2.5 cm outer diameter) glued to the outer surface of the ceramic cup (3 cm overlapping length). The ceramic cup was fitted with a rubber stopper through which two, 0.3-cm diameter polypropylene tubes were inserted. One tube was inserted to a distance of 1 cm inside the ceramic cup for vacuum suction. The other tube was inserted to a distance of 8 cm inside the ceramic cup for sampling solution. Both tubes were fitted with Luerlock stopcocks (Baxter, Valencia, CA) at their external ends. The outer end of PVC extension was sealed with silicone sealant. Before inserting into the columns, the ceramic cups were soaked and washed with distilled water.

At the bottom of the columns, two glass wool mats separated by a 4 cm layer of quartz pebbles were placed to facilitate water movement to the drainage holes (1 cm in diameter, Fig. 3.1). The quartz pebbles were larger than 1 cm and washed with tap water, soapy water, distilled water, 1:10 HCl, and distilled water (neutral pH). One piece of sponge (1 cm thick) was layered on the surface of each column to help water evenly percolate through the columns. The temperature in the greenhouse was maintained at approximately 25^0C.

There were eight treatments (two types of coal refuse and four FGD application levels) and each treatment was replicated three times yielding a total of 24 columns. The

experimental design was a randomized complete block. The weight percentages of FGD in the upper layer (first number) and in the lower layer (second number) for each treatment were: 0/0, 5.5/1.25, 11/2.5, and 22/5.0. These FGD rates yielded paste pH values of the mixtures of coal refuse and FGD (1:1, water): 3.81/3.29, 7.88/5.19, 7.99/5.97, and 9.17/5.60 for the fresh coal refuse; and 3.21/2.44, 4.09/3.28, 6.31/4.81, and 5.81/5.27 for the aged coal refuse.

Leaching and sampling of columns. The first leaching was initiated one day after the first packing of the coal refuse was completed and is referred to as the week zero leaching. All subsequent leachings were made on the last day of the week and were designated by their week numbers. The second packing of the coal refuse was made between the week 2 and week 3 leaching. The columns were leached for three consecutive periods: weekly from weeks 0 to 13, biweekly from weeks 13 to 27, and monthly from weeks 27 to 39 (Fig. 3.2). This yielded a total of 24 leaching events. From weeks 0 to 5, the leachings were conducted by adding 250 to 500 ml distilled water to the columns during a one to two day period so that the total volume of water added ranged from 1000 to 2500 ml. This amount of water was required to fully moisten the coal refuse and to obtain a sufficient volume of leachate for analysis. From weeks 6 to 39, two, 500-ml doses of distilled water were added two hours apart to the top of each column (total 1000 ml).

Gravity flow leachate was collected for 24 h in plastic bottles (550 ml) placed under the columns. The leachate volumes obtained generally ranged from 25 to 500 ml. If a leachate volume from a column was insufficient for chemical analysis, suction was

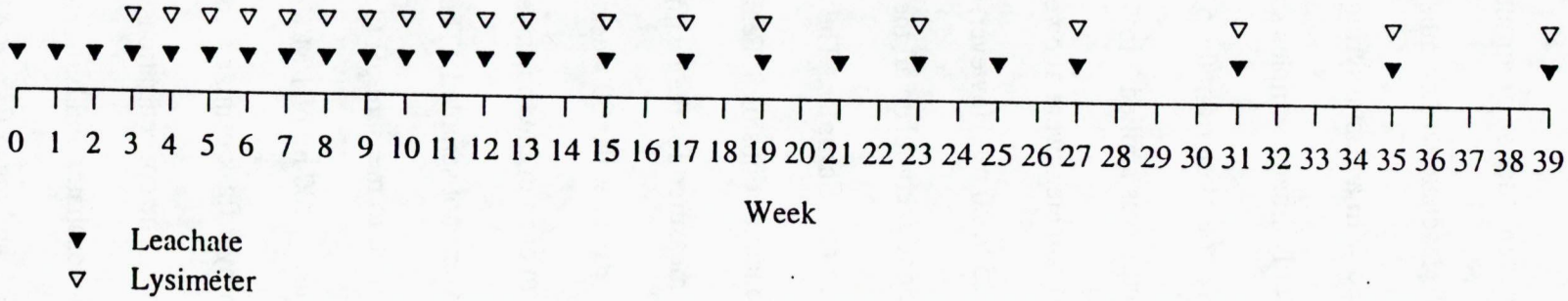

Fig. 3.2: Time schedule for sampling leachate and lysimeter samples from the coal refuse columns.

applied at the bottom of columns. To prevent suction of air into the columns, the vacuum was kept minimal and, in some cases, no leachate was obtained even with suction.

Lysimeter samples were collected with a plastic syringe (20 ml) at the completion of the 24 h leaching period. Collection of lysimeter samples started at week 3 and was not made on weeks 21 and 25. Samples were not taken from the 5.5% and 11% FGD treatments of the aged coal refuse. Vacuum was applied 3 to 4 h after the last addition of water to the top of the columns and the lysimeters were allowed to refill. The lysimeter sample volumes generally ranged from 15 to 20 ml. However, in some cases, the lysimeter sample volumes were insufficient to complete all the chemical analysis.

Analysis of Leachates and Lysimeter Samples. The methods for measuring pH, redox potential, titratable acidity, and concentrations of S, Fe, and Al were as described previously (Chapter 2). Acidity was not measured for the lysimeter samples until week 8.

Sampling and analysis of coal refuse. After 39 weeks of leaching, a core sample (5 cm in diameter) was taken from each of the four layers (the 5.5% and 11% FGD treatments of the aged coal refuse were not sampled). The samples were sieved (1 cm opening) and the sieved sample was used to measure pH (1:1, water). The amounts of extractable S, Fe, and Al were obtained using 100 ml of 1 M KCl solution added to 10 g coal refuse and shaken in a 250 ml Erlenmyer flask using a wrist-action shaker (Burell Scientific, Inc., Pittsburgh, PA) for 30 min. The concentrations of S, Fe, and Al in the slurry were measured as described for the leachates and lysimeter samples.

Statistics. Mean acidity, mean pH, and mean Fe and Al concentrations were calculated for the four leaching periods: weekly leaching period (weeks 0 to 13), biweekly

leaching period (weeks 13 to 27), monthly leaching period (weeks 27 to 39), and total leaching period (weeks 0 to 39). These mean values were used to compare results as affected by FGD rates and fresh *vs* aged coal refuse. Least significance difference (LSD) and t tests were performed using the SAS program (SAS Institute, 1988). Linear and quadratic contrasts were also conducted to determine the response of acid leaching to increasing FGD rates.

For the leached coal refuse materials, the differences in pH and the amounts of KCl-extracted Fe and Al as affected by FGD rates were analyzed by LSD, t tests, and linear and quadratic contrasts. All significant judgments were based on 95% confidence (p value <0.05).

RESULTS AND DISCUSSION

Inhibition of acid leaching from fresh coal refuse by FGD. The fresh coal refuse without FGD amendment rapidly produced a large amount of acid. In the initial 4 weeks, leachate acidity increased from 90 to 1000 $mmol_c\ L^{-1}$, [Fe] from 5 to 400 mmol L^{-1}, [Al] from 1 to 36 mmol L^{-1}, and leachate pH decreased from 3.05 to 2.11. Addition of the FGD into the coal refuse significantly decreased leachate acidity and [Fe] and significantly increased leachate pH for all four leaching periods compared to the control (Table 3.2 to 3.4, Figs. 3.3 to 3.5). The decrease of acidity and [Fe] and the increase of pH responded linearly to the increasing FGD rates. Starting from week 3 (after completing the second addition of coal refuse to the columns), the acidity of the 22% FGD treatment was at least 500 mmol L^{-1} less than that of the control (Fig. 3.3). Although the FGD treatment did not increase the initial leachate pH (about 3.0) compared to the control, the leachate pH of the 22% FGD treatment was at least 0.5 unit higher than that of the control after week 3 and at least one unit higher than that of the control during the biweekly leaching period (Fig. 3.4).

The leachate [Al] was significantly reduced compared to the control by the FGD during weekly leaching period and by the 22% FGD treatment during all but monthly leaching periods (Table 3.5. Fig. 3.6). During the monthly leaching period, leachate [Al] in the 5.5% and 11% FGD treatments was higher than those of the control. Less effect of the FGD on reduction of leachate [Al] than on reduction of leachate acidity and [Fe] was

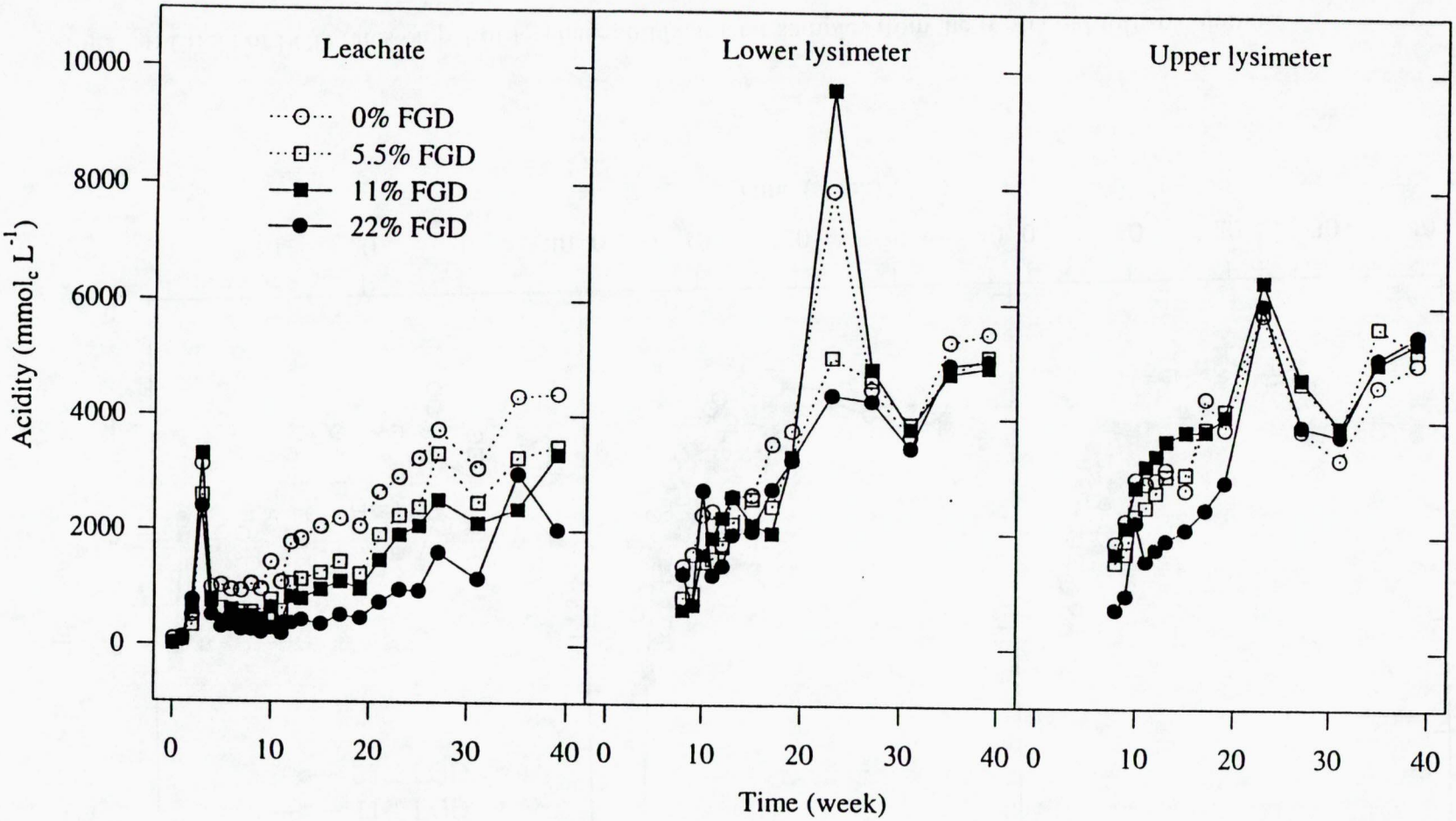

Fig. 3.3: Effect of FGD rates on acidity of leachate and lysimeter samples from the fresh coal refuse columns.

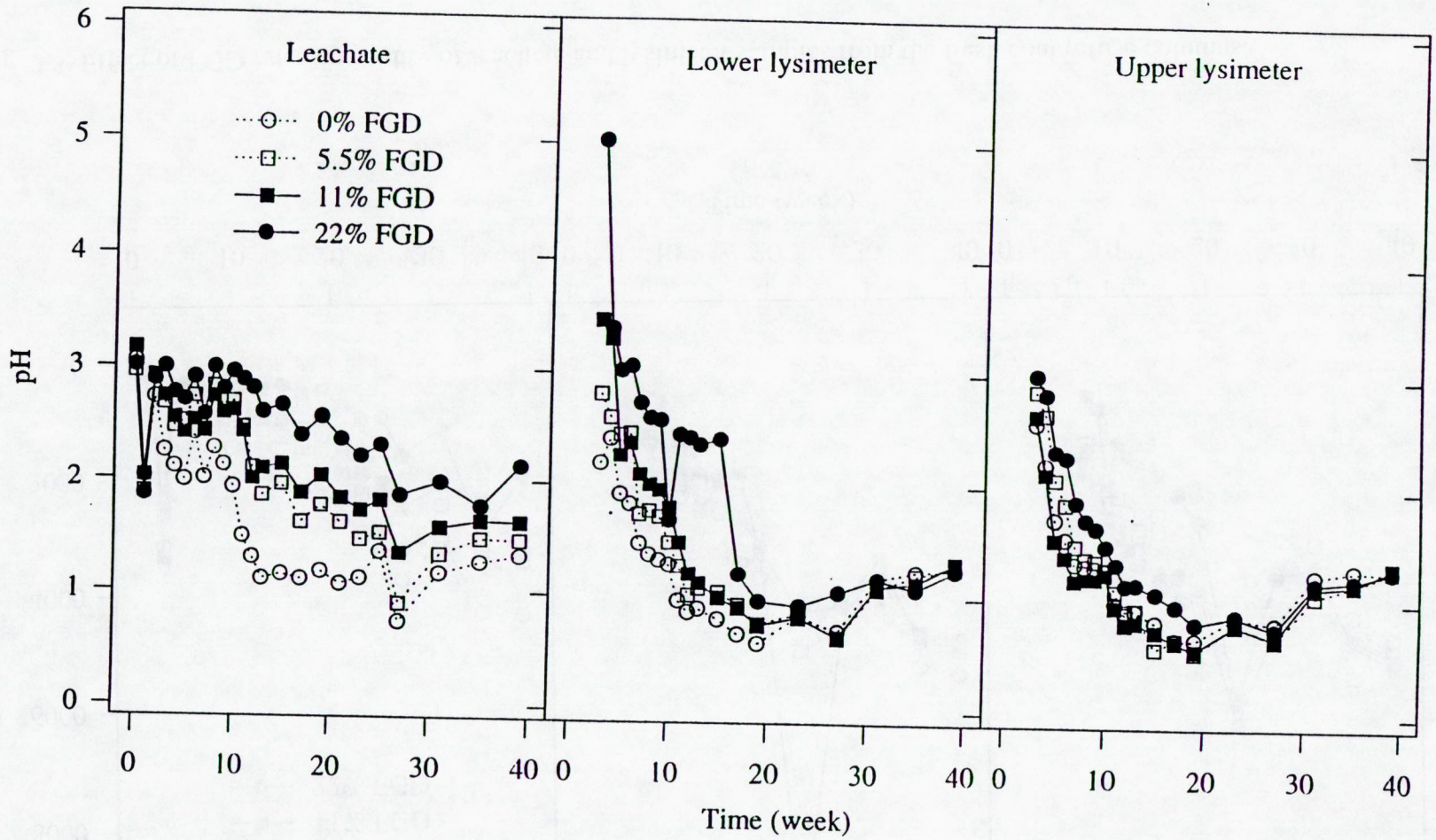

Fig. 3.4: Effect of FGD rates on pH of leachate and lysimeter samples from the fresh coal refuse columns.

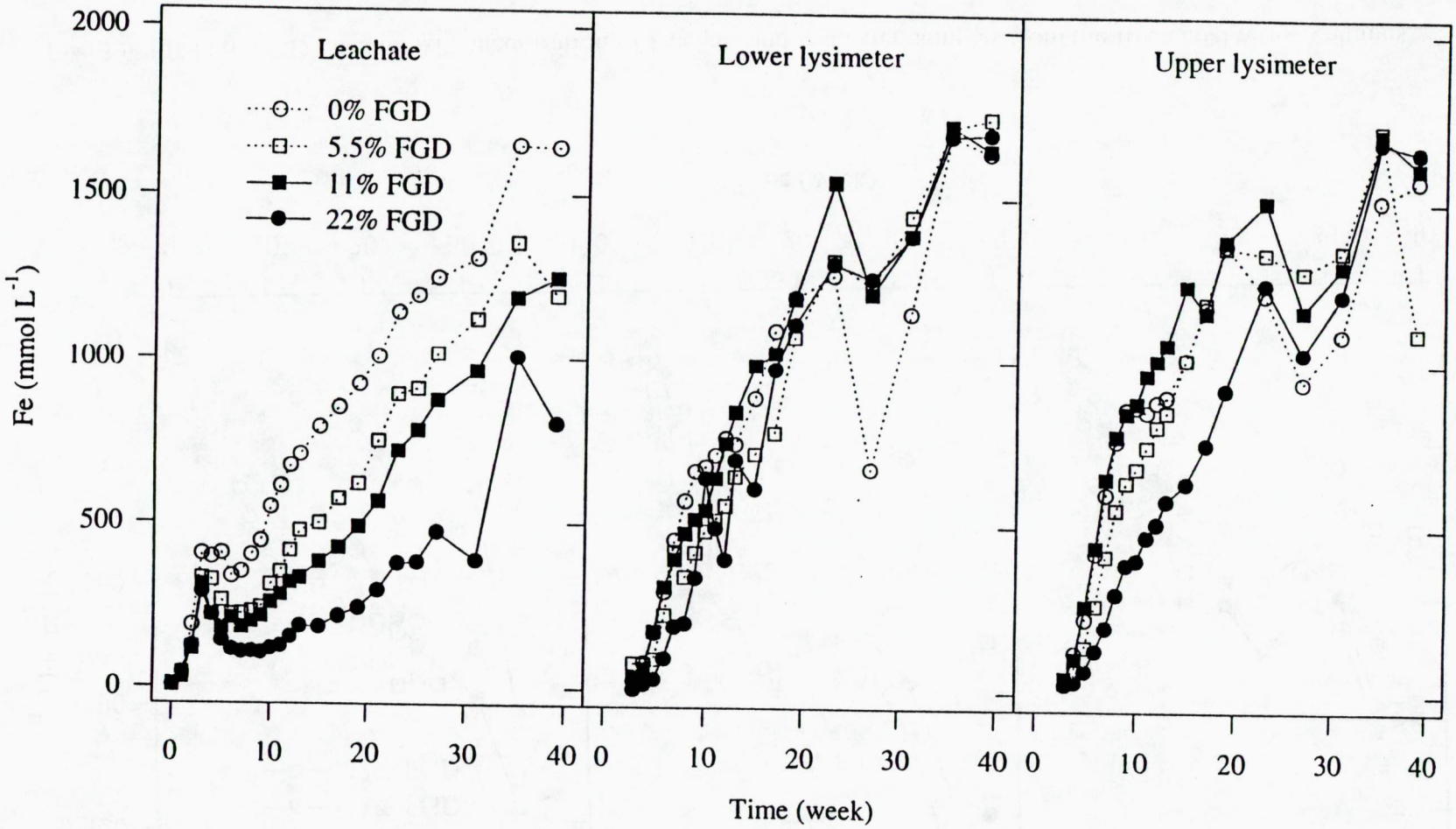

Fig. 3.5: Effect of FGD rates on Fe concentration of leachate and lysimeter samples from the fresh coal refuse columns.

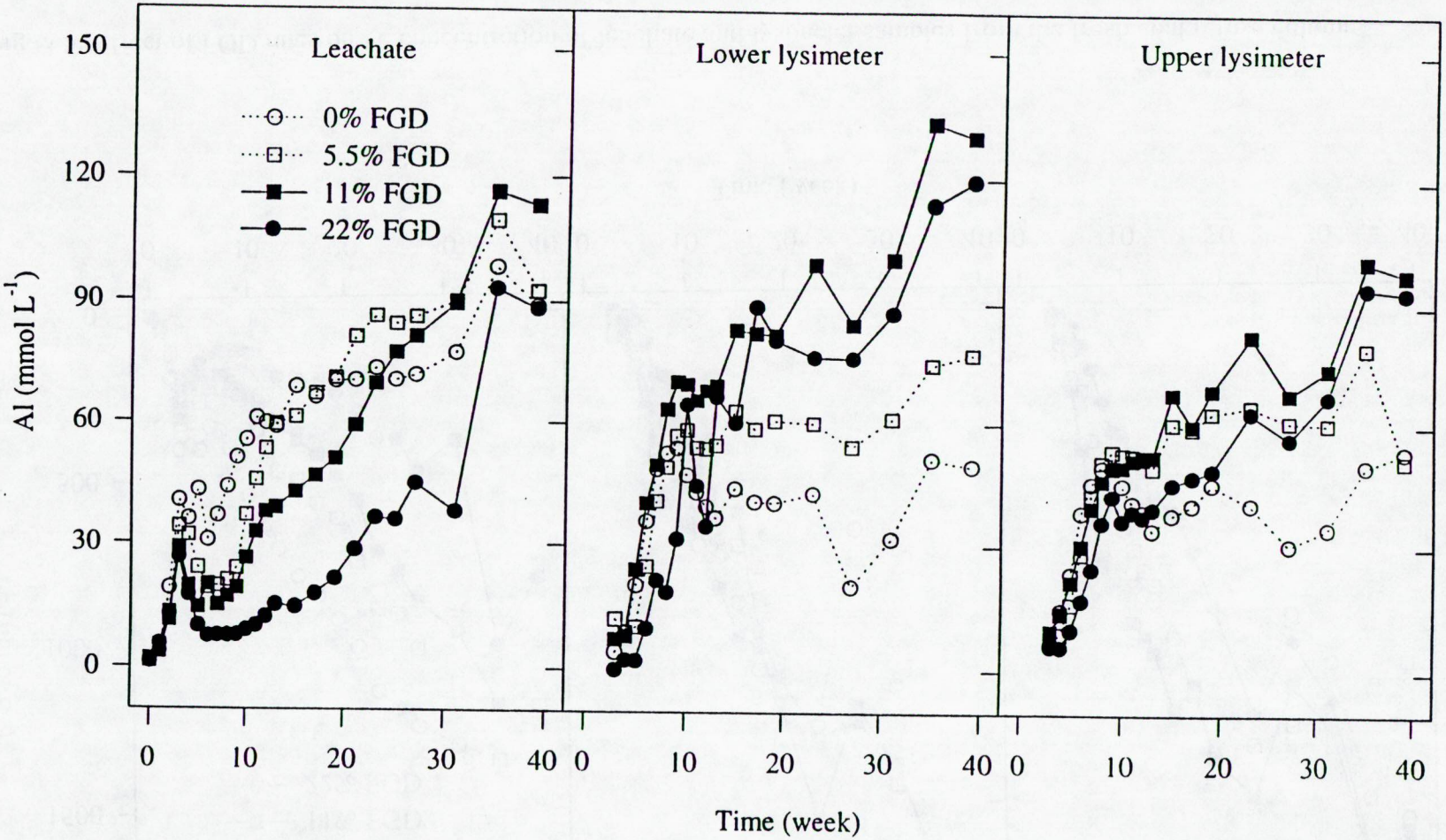

Fig. 3.6: Effect of FGD rates on Al concentration of leachate and lysimeter samples from the fresh coal refuse columns.

FGD rate	Mean acidity[a] ($mmol_c\ L^{-1}$)			
	Weeks 0-13	Weeks 13-27	Weeks 27-39	Weeks 0-39
		Leachate		
0%	1140a	2600a	3890a	1950a
5.5%	745b	1880b	3140b	1400b
11%	719b	1490c	2590c	1210b
22%	472c	763d	1950d	768c
$LSD_{0.05}$	200	377	541	199
p value[b]	0.0004	0.0001	0.0002	0.0001
Linear	0.0001	0.0001	0.0001	0.0001
Quadratic	0.0666	0.1103	0.1138	0.0193
		Lower lysimeter sample		
0%	2020a	4180a	4760a	3510a
5.5%	1460a	3380ab	4620a	2910ab
11%	1640a	4100a	4590a	3240ab
22%	1570a	3120b	4440a	2830b
$LSD_{0.05}$	795	1450	1053	1470
p value	0.2062	0.0971	0.1804	0.0850
Linear	0.1208	0.0559	0.0496	0.0293
Quadratic	0.5780	0.3095	0.6924	0.4937
		Upper lysimeter sample		
0%	2700a	3990b	4200b	3560a
5.5%	2320b	4130ab	4850a	3600a
11%	2830a	4420a	4760a	3870a
22%	1530c	3230c	4570ab	2930b
$LSD_{0.05}$	367	397	477	294
p value	0.0001	0.0011	0.0427	0.0009
Linear	0.0001	0.0035	0.1855	0.0017
Quadratic	0.0047	0.0010	0.0250	0.0015

[a], The numbers containing the same letters are not significantly different based on $LSD_{0.05}$ values.

[b], The p value is for F test of one-way analysis of variance. When $p < 0.05$, significant differences of LSD test are more meaningful.

Table 3.2: Mean acidities of leachate and lysimeter samples from the fresh coal refuse during the four leaching periods as affected by the FGD rates. The results of F test of one way analysis of variance, LSD test, and linear and quadratic regressions are shown.

FGD rate	pH[a]			
	Weeks 0-13	Weeks 13-27	Weeks 27-39	Weeks 0-39
		Leachate		
0%	2.05b	1.1c	1.12b	1.67c
5.5%	2.51a	1.59bc	1.29b	2.09bc
11%	2.52a	1.86ab	1.55ab	2.2ab
22%	2.77a	2.37ab	1.94a	2.54a
$LSD_{0.05}$	0.33	0.73	0.51	0.43
p value[b]	0.0068	0.0227	0.0246	0.0102
Linear	0.0017	0.0037	0.0038	0.0018
Quadratic	0.1548	0.5684	0.9394	0.3821
		Lower lysimeter sample		
0%	1.5c	0.75a	1.09a	1.25b
5.5%	1.86bc	0.89a	1.05a	1.48b
11%	2.1ab	0.88a	1.05a	1.62ab
22%	2.85a	1.49a	1.13a	2.18a
$LSD_{0.05}$	0.66	1.38	0.26	0.86
p value	0.0046	0.2276	0.4189	0.0221
Linear	0.0006	0.0662	0.3546	0.0034
Quadratic	0.7782	0.3924	0.1610	0.9905
		Upper lysimeter sample		
0%	1.47b	0.8ab	1.16a	1.25b
5.5%	1.63ab	0.71b	1.05b	1.31b
11%	1.38b	0.72b	1.08ab	1.17b
22%	1.9a	0.94a	1.11ab	1.53a
$LSD_{0.05}$	0.31	0.20	0.14	0.18
p value	0.0170	0.0895	0.1891	0.0100
Linear	0.0135	0.0760	0.7914	0.0065
Quadratic	0.1391	0.0533	0.0928	0.0515

[a], The numbers containing the same letters are not significantly different based on $LSD_{0.05}$ values.

[b], The p value is for F test of one-way analysis of variance. When $p < 0.05$, significant differences of LSD test are more meaningful.

Table 3.3: Mean pH of leachate and lysimeter samples from the fresh coal refuse during the four leaching periods as affected by the FGD rates. The results of F test of one-way analysis of variance, LSD test, and linear and quadratic regressions are shown.

FGD rate	Fe[a] (mmol L^{-1})			
	Weeks 0-13	Weeks 13-27	Weeks 27-39	Weeks 0-39
		Leachate		
0%	392a	984a	1460a	719a
5.5%	254b	717b	1170b	520b
11%	205c	571c	1070b	438c
22%	132d	295d	668c	259d
$LSD_{0.05}$	42	112	226	73
p value[b]	0.0001	0.0001	0.0005	0.0001
Linear	0.0001	0.0001	0.0001	0.0001
Quadratic	0.0015	0.0632	0.5182	0.0269
		Lower lysimeter sample		
0%	472a	978a	1290a	778a
5.5%	353ab	962a	1530a	732a
11%	435ab	1140a	1490a	816a
22%	285b	994a	1510a	693a
$LSD_{0.05}$	230	455	540	461
p value	0.0928	0.4215	0.4256	0.1402
Linear	0.0294	0.2748	0.1837	0.0585
Quadratic	0.6816	0.3822	0.2962	0.4664
		Upper lysimeter sample		
0%	596a	1110b	1280b	866ab
5.5%	476b	1180ab	1360a	822b
11%	643a	1250a	1450ab	955a
22%	287c	864c	1400ab	647c
$LSD_{0.05}$	96	144	194	100
p value	0.0001	0.0014	0.1267	0.0005
Linear	0.0001	0.0028	0.4557	0.0008
Quadratic	0.0038	0.0013	0.0564	0.0024

[a], The numbers containing the same letters are not significantly different based on $LSD_{0.05}$ values.

[b], The p value is for F test of one-way analysis of variance. When $p < 0.05$, significant differences of LSD test are more meaningful.

Table 3.4: Mean Fe concentrations in leachate and lysimeter samples from the fresh coal refuse during the four leaching periods as affected by the FGD rates. The results of F test of one-way analysis of variance, LSD test, and linear and quadratic regressions are shown.

FGD rate	Al[a] (mmol L^{-1})			
	Weeks 0-13	Weeks 13-27	Weeks 27-39	Weeks 0-39
		Leachate		
0%	38a	68a	84ab	54a
5.5%	27b	74a	94a	50a
11%	20c	58a	100a	43b
22%	10d	26b	66b	23c
$LSD_{0.05}$	6	17	22	8
p value[b]	0.0001	0.0009	0.0814	0.0001
Linear	0.0001	0.0002	0.1660	0.0001
Quadratic	0.0634	0.0461	0.0269	0.1288
		Lower lysimeter sample		
0%	35ab	37c	38b	37ab
5.5%	38ab	58bc	67b	49ab
11%	48a	83a	112a	70a
22%	27b	75ab	99a	52b
$LSD_{0.05}$	21	18	24	32
p value	0.0913	0.0065	0.0025	0.1392
Linear	0.0846	0.0070	0.0024	0.5990
Quadratic	0.0811	0.0078	0.0042	0.0460
		Upper lysimeter sample		
0%	35a	38c	42c	38b
5.5%	37a	59a	63b	48a
11%	38a	66a	85a	54a
22%	26b	50b	78ab	42b
$LSD_{0.05}$	5	8	14	6
p value	0.0038	0.0002	0.0005	0.0016
Linear	0.0024	0.0392	0.0005	0.4048
Quadratic	0.0089	0.0001	0.0008	0.0002

[a], The numbers containing the same letters are not significantly different based on $LSD_{0.05}$ values.

[b], The p value is for F test of one-way analysis of variance. When $p < 0.05$, significant differences of LSD test are more meaningful.

Table 3.5: Mean Al concentrations in leachate and lysimeter samples from the fresh coal refuse during the four leaching periods as affected by the FGD rates. The results of F test of one-way analysis of variance, LSD test, and linear and quadratic regressions are shown.

probably because the FGD contained a significant amount of Al and Ca salts. Dissolution of Ca salts could mobilize Al through cation exchange reaction.

For both lysimeter samples, decrease of acidity and [Fe] and increase of pH by the FGD were often insignificant during any of the four leaching periods compared to the control (Table 3.2 to 3.4). However, the 22% FGD treatment always yielded lower acidity, lower [Fe], and higher pH than the control for both lysimeter samples before week 23 (Figs. 3.3 to 3.5). The pH of the lower lysimeter sample in the 22% FGD treatment started almost two units higher than the pH of the control and was at least one unit higher during weeks 0 to 13 except in week 10. Compared to the control, the [Al] of both lysimeter samples was decreased by the 22% FGD treatment before week 10 but increased by all FGD treatments during the biweekly and monthly leaching periods (Fig. 3.6).

Although acidity, [Fe], and [Al] in the leachate and lysimeter samples increased with time and the pH decreased with time for all treatments during the weekly and biweekly leaching periods, the reduction of acid leaching in the leachate and lysimeter samples by the FGD treatments (especially the 22% FGD treatment) compared to the control increased with time during this period (Figs. 3.3 to 3.6). During the monthly leaching period, acidity, [Fe], and [Al] of leachate fluctuated but the pH of the leachate slightly increased or stabilized with time. This time trend also occurred with the lysimeter samples but started at week 20 when lysimeter sampling frequency changed from biweekly to monthly (no lysimeter samples taken on weeks 21 and 25). The peak that occurred in week 3 in acid leaching of leachate might be due to the second packing of

coal refuse (increased amounts of coal refuse and FGD) and/or a more frequent and longer period of leaching (water added to columns five times in 2 days). The peak that occurred in week 23 in acid leaching of lysimeter samples was not understood and might be due to the change of leaching frequency.

Inhibition of acid leaching from aged coal refuse by FGD. Because of the extensive pyrite oxidation that occurred in the aged coal refuse during its weathering prior to sampling from the landfill site, initial values of acidity, [Fe], and [Al] reached 1290 $mmol_c\ L^{-1}$, 658 $mmol\ L^{-1}$, and 86 $mmol\ L^{-1}$, respectively, as compared to 90 $mmol_c\ L^{-1}$, 5 $mmol\ L^{-1}$, and 1 $mmol\ L^{-1}$ in the week zero leaching of the fresh coal refuse. In the week zero leachate, the pH of the aged coal refuse (1.99) was one unit lower than the pH of the fresh coal refuse (3.05).

Despite the large amount of acid produced in the aged coal refuse before it was amended with FGD, the 22% FGD treatment still significantly reduced leachate acidity and [Fe] and increased leachate pH compared to the control for all the leaching periods (Table 3.6). Starting from week 3, the leachate acidity and [Fe] of the 22% FGD treatment were at least 470 $mmol_c\ L^{-1}$ and 115 $mmol\ L^{-1}$ lower than those of the control, respectively, and the leachate pH at least 0.5 units higher than that of the control. The 5.5% and 11% FGD treatments always had lower leachate acidity and [Fe] and higher leachate pH than the control from weeks 3 to 21 (Figs. 3.7 to 3.9), although such effect was often insignificant during the four leaching periods (significant for the fresh coal refuse). Compared to the control, the 22% FGD treatment did not significantly reduce leachate [Al] for any of the four leaching periods (significant for the fresh coal refuse

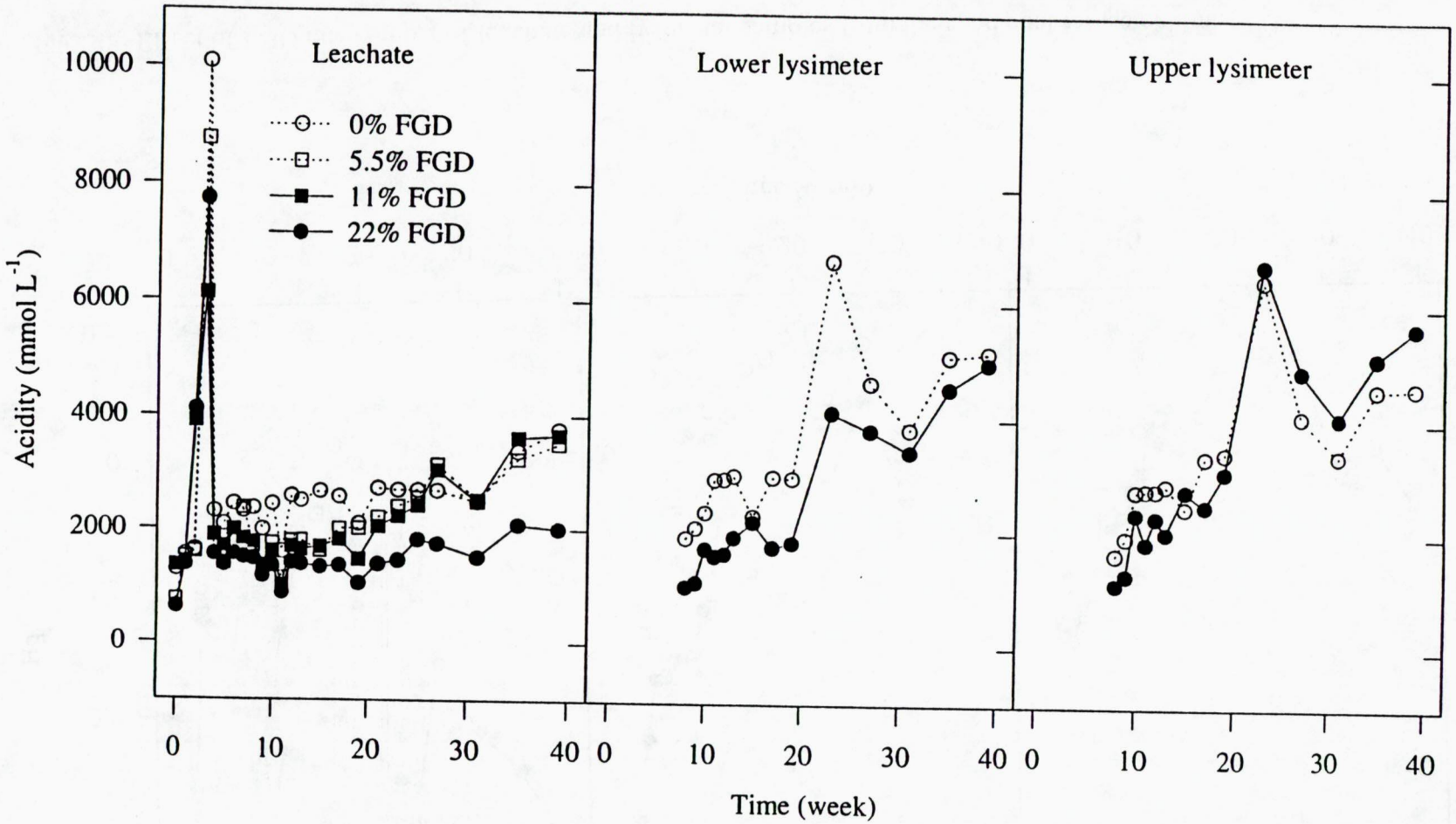

Fig. 3.7: Effect of FGD rates on acidity of leachate and lysimeter samples from the aged coal refuse columns.

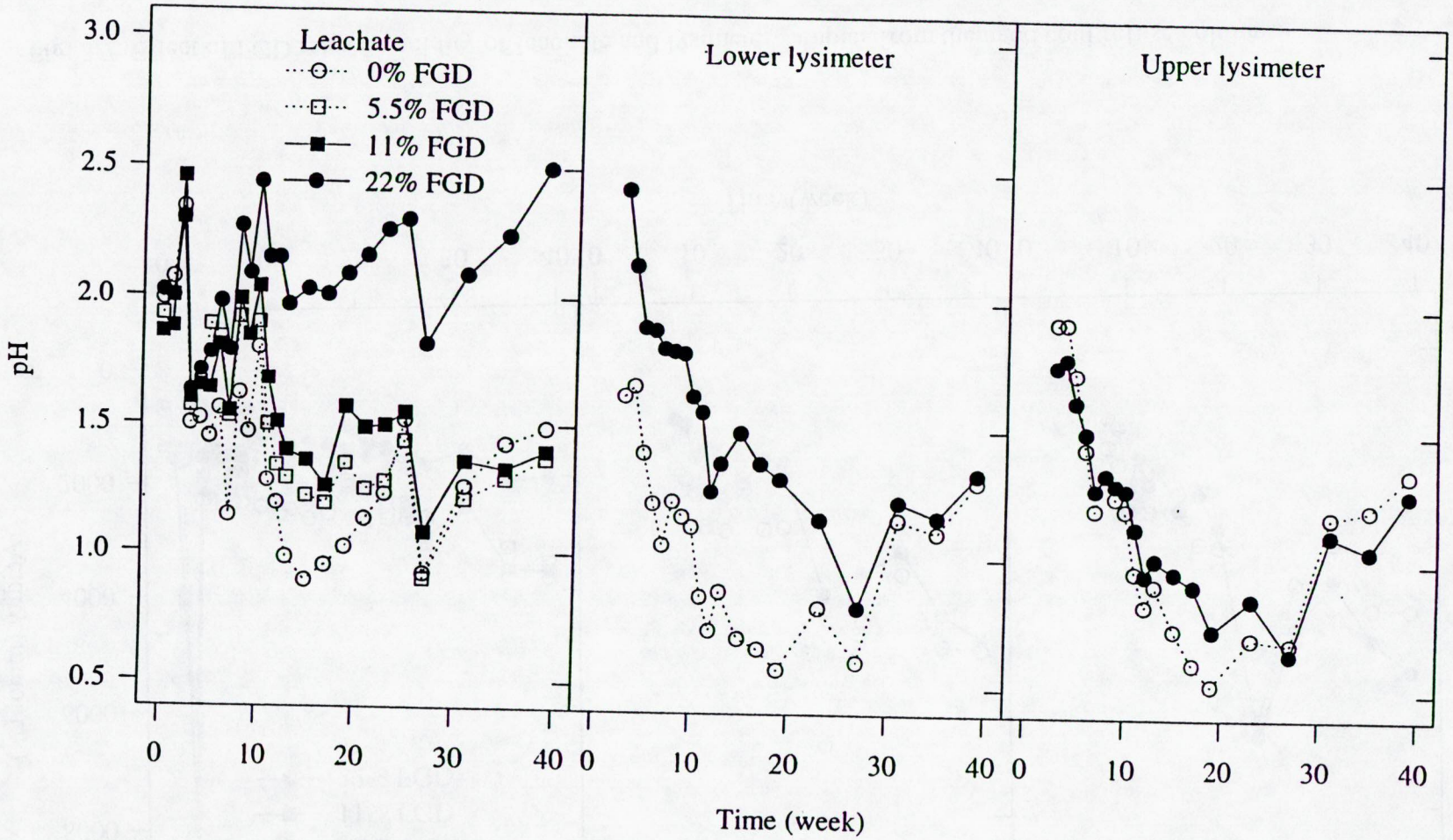

Fig. 3.8: Effect of FGD rates on pH of leachate and lysimeter samples from the aged coal refuse columns.

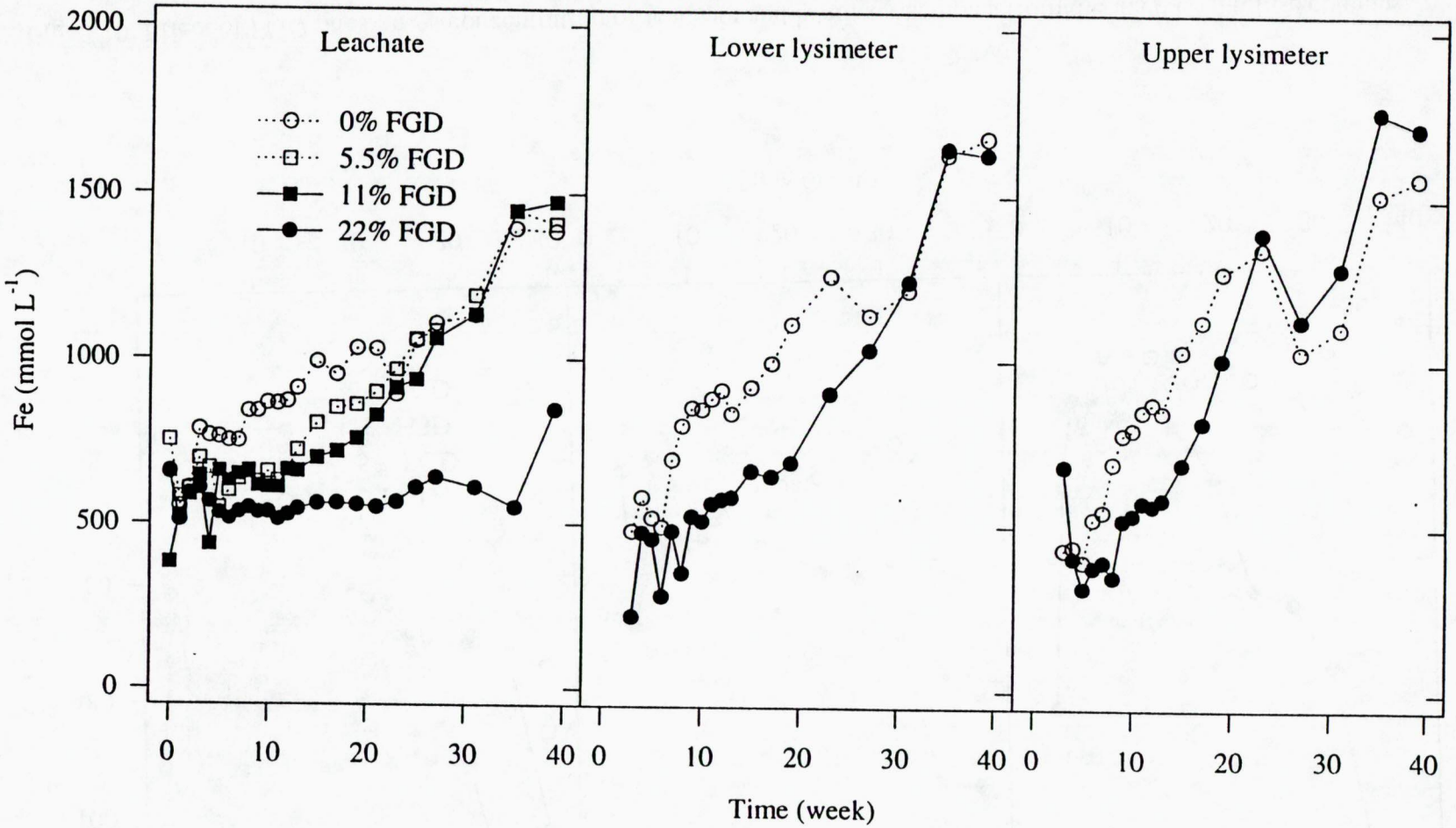

Fig. 3.9: Effect of FGD rates on Fe concentration of leachate and lysimeter samples from the aged coal refuse columns.

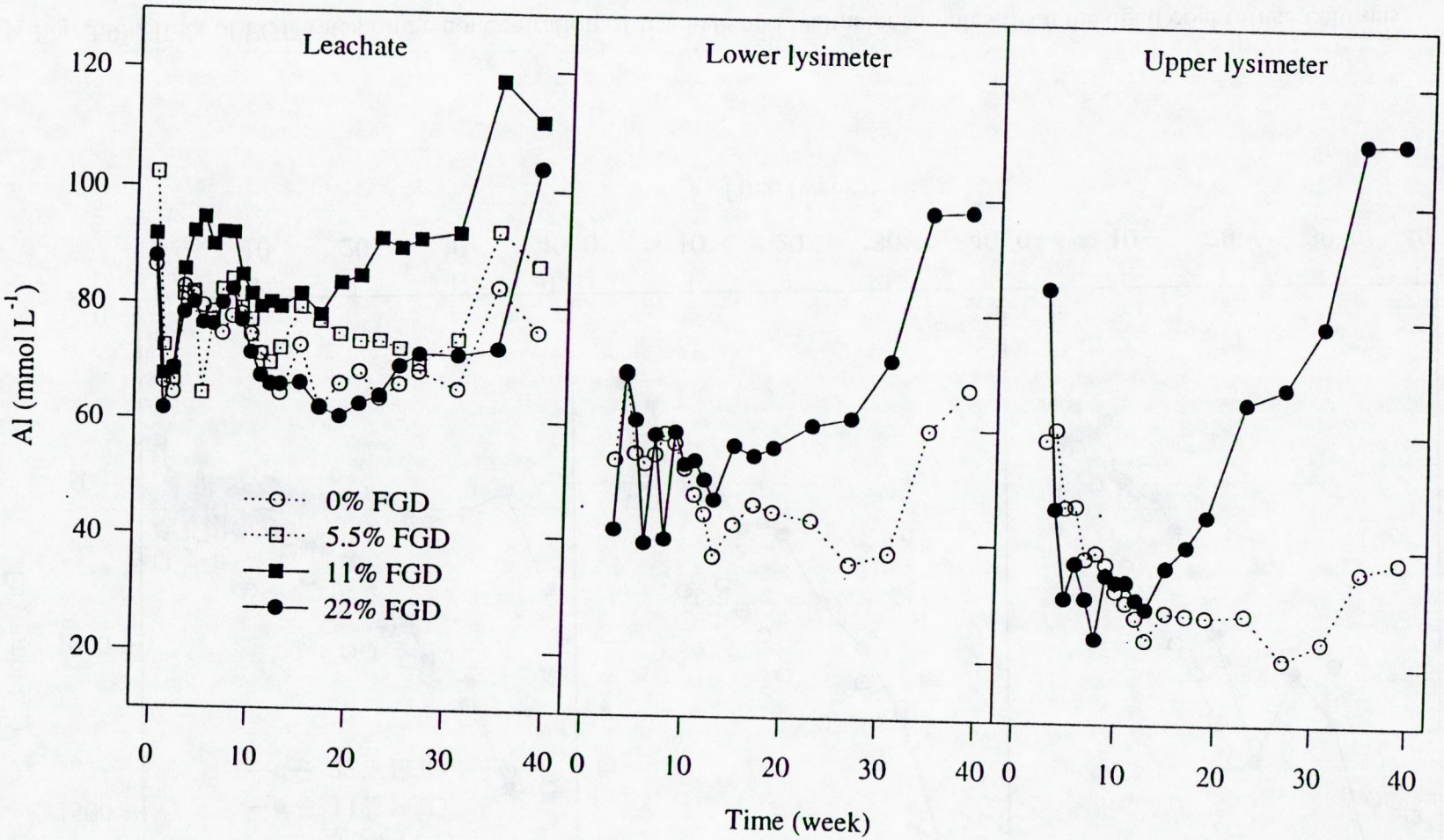

Fig. 3.10: Effect of FGD rates on Al concentration of leachate and lysimeter samples from the aged coal refuse columns.

Period	Leachate								Lower lysimeter			Upper lysimeter		
	0%	5.5%	11%	22%	$LSD_{0.05}$	p value[b]	Linear	Quadratic	0%	22%	p value	0%	22%	p value
								Acidity ($mmol_c\ L^{-1}$)						
Weekly	2660a[a]	2140ab	2100ab	1970b	675	0.1746	0.0690	0.2584	2540	1510	0.0714	2490	1860	0.1410
Biweekly	2590a	2230a	2050ab	1450b	698	0.0320	0.0051	0.9961	3780	2600	0.3498	3810	3690	0.5256
Monthly	3090a	3120a	3210a	1840b	601	0.0022	0.0009	0.0124	4680	4190	0.0539	4190	4940	0.0195
Total	2710a	2300ab	2250ab	1810b	512	0.0241	0.0043	0.6817	3500	2550	0.3523	3390	3290	0.5772
								pH						
Weekly	1.56c	1.75b	1.78b	2.02a	0.16	0.0016	0.0002	0.7561	1.17	1.78	0.0360	1.34	1.36	0.9169
Biweekly	1.08c	1.24bc	1.40bc	2.08a	0.30	0.0003	0.0001	0.1584	0.70	1.25	0.0588	0.70	0.86	0.2493
Monthly	1.27b	1.19b	1.29b	2.16a	0.26	0.0001	0.0001	0.0016	1.04	1.13	0.2006	1.11	1.02	0.0946
Total	1.40c	1.54bc	1.61b	2.07a	0.19	0.0002	0.0001	0.1598	1.04	1.55	0.0364	1.14	1.18	0.7641
								Fe ($mmol\ L^{-1}$)						
Weekly	773a	646b	595b	550b	112	0.0089	0.0021	0.0910	720	459	0.0624	653	484	0.0236
Biweekly	997a	907a	822a	574b	222	0.0120	0.0017	0.6869	1040	755	0.0099	1111	939	0.1812
Monthly	1260a	1290a	1280a	662b	242	0.0014	0.0005	0.0113	1410	1390	0.4845	1310	1470	0.0828
Total	908a	818ab	763b	573c	120	0.0015	0.0002	0.8201	940	711	0.0373	905	796	0.1928
								Al ($mmol\ L^{-1}$)						
Weekly	74a	77a	84a	74a	13	0.2837	0.9264	0.0916	53	52	0.763	40	38	0.7872
Biweekly	66b	74b	85a	65b	10	0.0079	0.7312	0.0015	42	56	0.3434	27	48	0.0872
Monthly	73b	81b	103a	79b	16	0.0128	0.0646	0.0084	50	82	0.1766	30	92	0.0344
Total	72b	77b	87a	72b	8	0.0072	0.6958	0.0017	51	60	0.308	36	51	0.0989

[a], The numbers containing the same letters are not significantly different based on $LSD_{0.05}$ values.

[b], The p value is for F test of one-way analysis of variance. When $p < 0.05$, significant differences of LSD test are more meaningful.

Table 3.6: Effect of FGD rates on mean acidity, mean pH, and mean concentrations of Fe and Al of leachate and lysimeter samples from the aged coal refuse during the four leaching periods.

except during monthly leaching period) and the 5.5% and 11% FGD treatments always yielded higher leachate [Al] except after the weeks 5 and 6 (lower for the fresh coal refuse in weekly leaching period) (Table 3.6, Fig. 3.10).The effect of the 22% FGD treatment on acidity, [Fe], [Al], and pH of both lysimeter samples of the aged coal refuse was almost the same as occurred in the fresh coal refuse and was weaker than the effect on leachate (Figs. 3.7 to 3.10).

For the aged coal refuse, the amounts of acid in the leachate and lysimeter samples changed with time to a lesser extent than what was shown for the fresh coal refuse (Fig. 3.11 for acidity, figures for pH, [Fe], and [Al] not shown). With time, the acidity, [H^+] (instead of pH for simplification), [Fe], and [Al] of leachate and lysimeter samples of the aged coal refuse gradually changed from higher than those of the fresh coal refuse to lower than or close to those of the fresh coal refuse for the control and the 22% FGD treatment. Unlike the leachate pH of the fresh coal refuse which decreased with time, the leachate pH of the aged coal refuse fluctuated with time for the control and the 5.5% and 11% FGD treatments and slightly increased with time for the 22% FGD treatment (Fig. 3.8). The Al leaching from the control of the aged coal refuse also decreased with time in weeks 0 to 13 (Fig. 3.10).

Less increase of acid leaching with time from the aged coal refuse as compared to the fresh coal refuse may indicate a slower pyrite oxidation rate in the aged coal refuse than in the fresh coal refuse. The faster pyrite oxidation rate in the earlier stage of weathering of the coal refuse emphasizes that it would be more beneficial to apply the FGD in the coal refuse as early as possible.

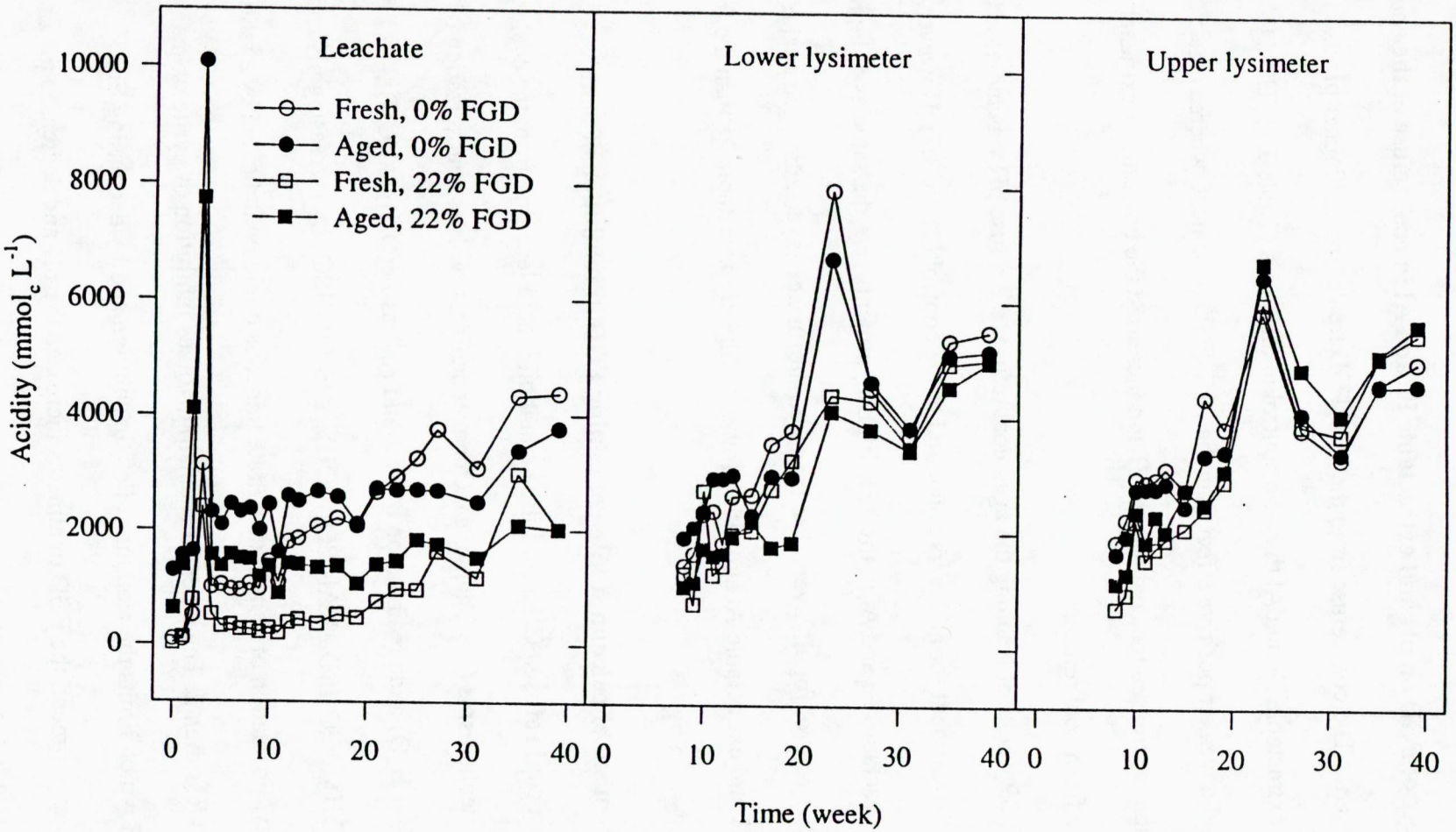

Fig. 3.11: Acidity comparison between the fresh and aged coal refuse amended with or without 22% FGD.

Effect of FGD on pH and extractable Fe and Al in coal refuse at the end of the experiment. The coal refuse from the 22% FGD treatment had higher pH and lower amounts of extractable Fe and Al than the control in all layers (Table 3.7). The 11% FGD treatment had a weaker positive effect than the 22% FGD treatment, whereas the 5.5% FGD treatment decreased the coal refuse pH and increased the amounts of extractable Fe and Al in the fresh coal refuse.

After 39 weeks of leaching the aged coal refuse, the refuse pH was increased by the 22% FGD treatment for all layers compared to the control (Table 3.7). However, the amount of extractable Fe and Al in the 22% FGD treatment were the same as or higher than that of the control for all layers. For the three subsurface layers, the aged coal refuse had lower pH and extractable Al and either lower or higher extractable Fe than the fresh coal refuse (Table 3.7).

Mechanism of calcium sulfite-containing FGD in inhibition of acid production in coal refuse. Calcium sulfite can inhibit acid leaching from the coal refuse through two mechanisms (see Chapter 2). One mechanism involves neutralization of H^+ ($SO_3^{2-} + 2H^+ \rightarrow H_2O$) and precipitation of Fe^{3+} and Al^{3+} as $Fe(OH)_3$, $Al(OH)_3$, $KFe_3(SO_4)_2(OH)_6$, $FeOHSO_4$, $KAl_3(SO_4)_2(OH)_6$, and $AlOHSO_4$ by increasing pH and sulfate activity. Formation of aluminum sulfate minerals could be indicated by a ratio of S to Fe that was less than 2. The other mechanism involves inhibition of pyrite oxidation by increasing pH which limits the amount of Fe^{3+} in solution and by decreasing Eh.

In this experiment, the FGD treatments increased the pH and decreased the Eh (Fig. 3.12) of both leachate and lysimeter samples (except for the lysimeter samples of the

Layer	Fresh coal refuse							Aged coal refuse		
	0%	5.5%	11%	22%	$LSD_{0.05}$	Linear	Quadratic	0%	22%	p value[a]
						pH				
Top	1.56	1.55	1.86	2.32	0.25	0.0001	0.1510	1.49	2.06	0.0068
Upper middle	1.77	1.51	1.70	1.93	0.20	0.0165	0.0128	1.47	1.68	0.1126
Lower middle	1.57	1.42	1.74	2.17	0.17	0.0001	0.0085	1.41	1.72	0.0255
Bottom	1.64	1.64	1.88	2.49	0.18	0.0001	0.0105	1.50	2.02	0.0005
$LSD_{0.05}$	0.21	0.21	0.20	0.19				0.16	0.26	
						Fe (mmol kg^{-1})				
Top	313	316	304	248	94	0.0161	0.0046	264	265	0.2613
Upper middle	259	240	222	212	39	0.0132	0.5653	242	246	0.9815
Lower middle	220	230	225	194	33	0.0197	0.0105	196	192	0.3077
Bottom	171	150	163	162	29	0.0001	0.0838	200	180	0.0627
$LSD_{0.05}$	50	73	63	20				21	92	
						Al (mmol kg^{-1})				
Top	40	51	33	23	16	0.0049	0.3362	9	29	0.0075
Upper middle	14	16	13	14	8	0.7288	0.7811	7	10	0.0207
Lower middle	14	17	15	13	5	0.0021	0.3435	9	10	0.0560
Bottom	14	15	14	12	4	0.0012	0.2203	10	11	0.0448
$LSD_{0.05}$	9	7	10	11				1	15	

[a], The p value is for F test of one-way analysis of variance.

Table 3.7: The pH and the amounts of 1 M KCl extractable Fe and Al in the four layers of coal refuse columns after 39 weeks of leaching. The effects of the FGD rates on pH and the amounts of extractable Fe and Al were analyzed by F test of one-way analysis of variance, LSD test, and linear and quadratic regressions. The effects of the layers on pH and the amounts of extractable Fe and Al were analyzed by LSD test.

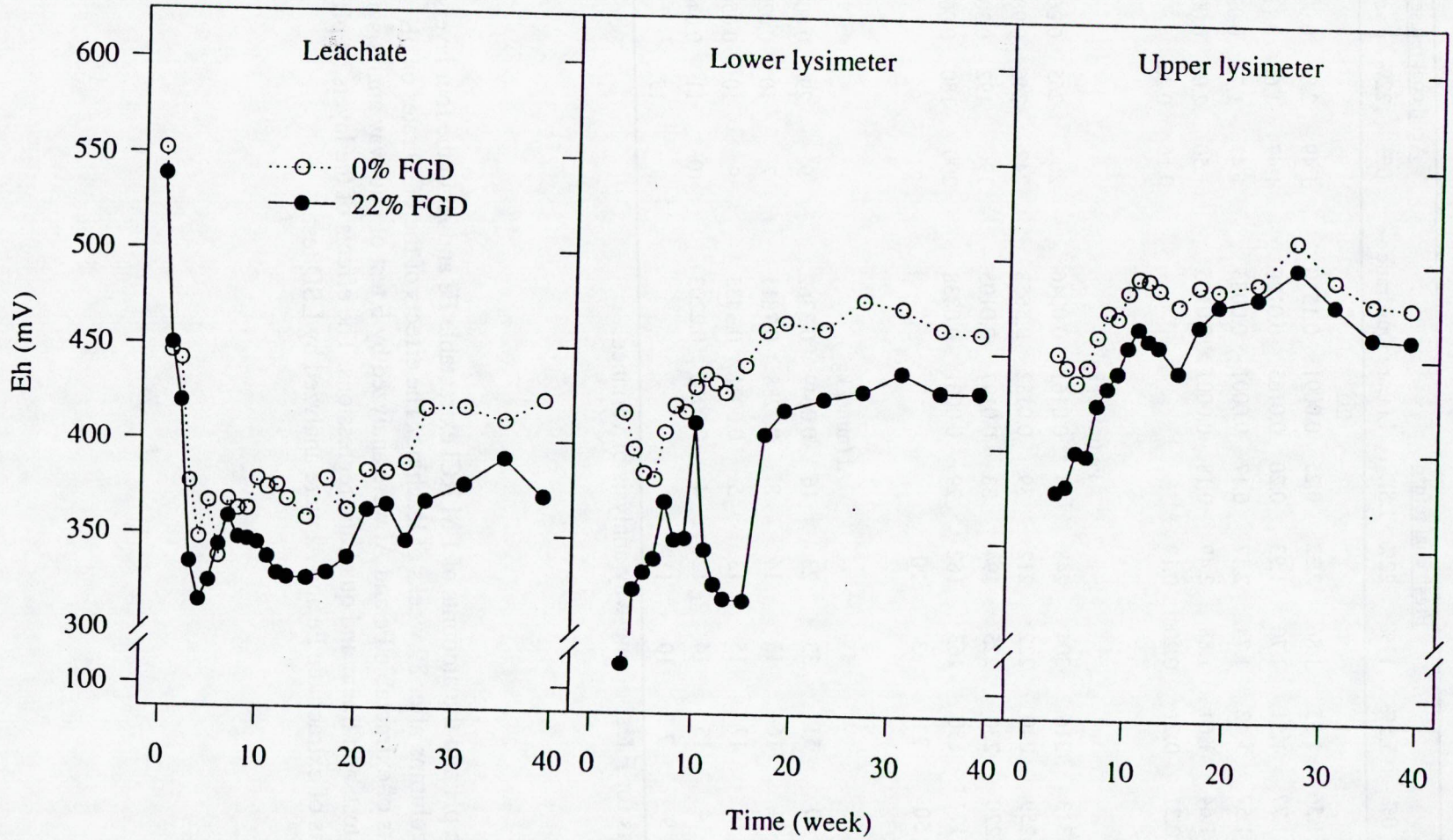

Fig. 3.12: Effect of FGD rates on redox potential (Eh) of leachate and lysimeter samples from the fresh coal refuse columns.

aged coal refuse in weeks 27 to 39). The ratio of S to Fe in leachate and lysimeter samples was less than 2 except for the initial several weeks (Table 3.8). For the coal refuse samples taken after the last leaching, the ratio of S to Fe was close to or higher than 2 for the layers amended with FGD and less than 2 for the layers not amended with FGD. However, X-ray analysis of the leached fresh coal refuse of the 0% and 22% FGD treatments in the upper middle and bottom layers did not detect aluminum sulfate minerals. Gypsum was detected in the fresh coal refuse samples both before and after leaching.

The inhibitory effect of $CaSO_3$ contained in the FGD on acid production in the coal refuse may also be indicated by the following phenomena. Leachates normally exhibited lower acidity and [Fe] and higher pH than the two lysimeter samples in the coal refuse (Fig. 3.13 for acidity leached from the fresh coal refuse). Higher pH and lower amounts of extractable Fe were found in the bottom layer as compared to the two middle layers for both fresh and aged coal refuse (Table 3.7). These data indicate that $CaSO_3$ in FGD might have inhibited pyrite oxidation in the bottom layer by moving downward from the lower middle layer due to its dissolution at low pH (<5.0 in the lower middle layer). Such movement combined with the depth of the bottom layer may cause much lower concentrations of dissolved O_2 and Fe^{3+} in the bottom layer. This would result in less acid formation, and therefore, less acid leaching compared to the lysimeter samples.

Downward movement of $CaSO_3$ would also explain why increasing FGD rates led to even less acid in the leachate than in lysimeter samples but did not lead to less acid in the lower lysimeter sample compared to the upper lysimeter sample (Table 3.9). This was

Time (week)	Leachate				Lower lysimeter		Upper lysimeter	
	0%	5.5%	11%	22%	0%	22%	0%	22%
				Fresh coal refuse				
0	8.05	8.70	4.83	6.31	ND	ND	ND	ND
1	2.74	2.44	2.76	2.39	ND	ND	ND	ND
3	1.39	1.41	1.43	1.36	1.94	7.34	2.61	2.42
5	1.37	1.38	1.41	1.40	1.51	2.20	1.53	1.81
7	1.35	1.32	1.42	1.41	1.39	1.48	1.44	1.57
11	1.30	1.34	1.36	1.44	1.65	1.53	1.68	1.73
15	1.26	1.26	1.32	1.36	1.42	1.30	1.47	1.49
23	1.26	1.23	1.28	1.29	1.40	1.31	1.42	1.44
31	1.32	1.26	1.28	1.31	1.49	1.38	1.51	1.50
39	1.28	1.23	1.23	1.26	1.41	1.31	1.42	1.42
				Aged coal refuse				
0	1.44	1.44	1.48	1.45	ND	ND	ND	ND
1	1.48	1.47	1.49	1.53	ND	ND	ND	ND
3	1.35	1.37	1.41	1.36	1.42	1.55	1.44	1.35
5	1.36	1.33	1.37	1.38	1.47	1.41	1.49	1.56
7	1.36	1.33	1.33	1.35	1.44	1.37	1.46	1.52
11	1.33	1.30	1.33	1.31	1.65	1.50	1.64	1.71
15	1.31	1.25	1.27	1.27	1.40	1.30	1.40	1.49
23	1.20	1.22	1.21	1.23	1.40	1.34	1.36	1.43
31	1.28	1.28	1.26	1.28	1.46	1.40	1.44	1.51
39	1.26	1.23	1.21	1.23	1.42	1.34	1.36	1.43

Table 3.8: Molar ratio of S to Fe in leachate and lysimeter samples.

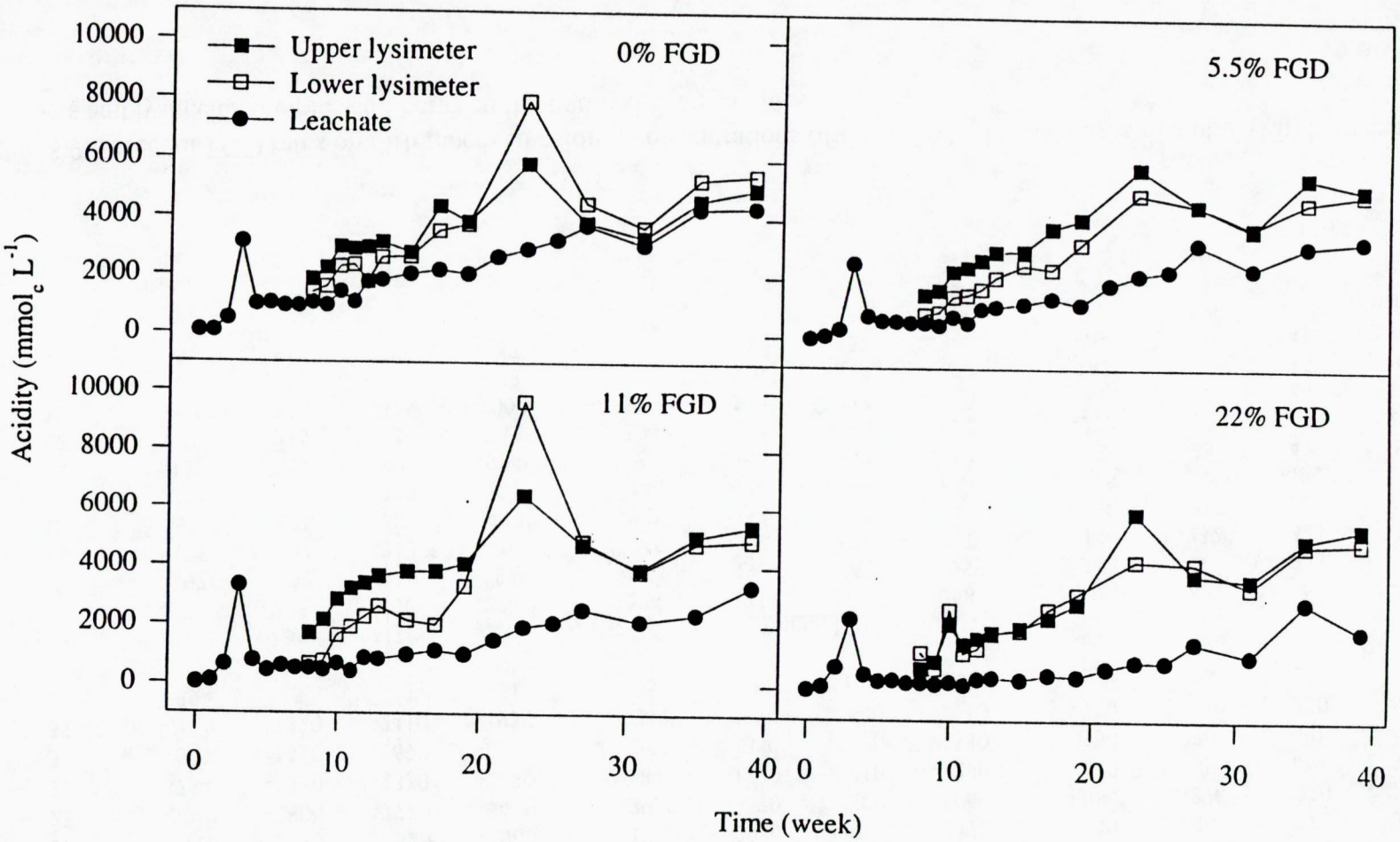

Fig. 3.13: Acidity comparison between leachate and lysimeter samples from the fresh coal refuse columns amended with the four FGD rates.

Time (week)	Leachate - Lower lysimeter				Leachate - Upper lysimeter				Lower lysimeter - Upper lysimeter			
	0%	5.5%	11%	22%	0%	5.5%	11%	22%	0%	5.5%	11%	22%
						Acidity ($mmol_c\ L^{-1}$)						
11	-1280	-948	-1500	-1060	-1830	-1900	-2810	-1370	-550	-950	-1310	-310
15	-599	-1330	-1180	-1660	-739	-1820	-2840	-1740	-140	-490	-1660	-80
19	-1710	-2090	-2320	-2800	-1790	-2950	-3090	-2470	-80	-860	-770	330
23	-5010	-2800	-7720	-3430	-2930	-3670	-4500	-5060	2080	-870	3220	-1630
27	-754	-1330	-2330	-2680	-84	-1330	-2210	-2290	670	0	120	390
31	-603	-1410	-1690	-2320	-253	-1340	-1770	-2580	350	70	-80	-260
35	-1010	-1520	-2410	-1950	-287	-2370	-2640	-2110	720	-850	-230	-160
39	39	15	-17	-31	35	41	15	-5	-4	26	32	26
						Fe ($mmol\ L^{-1}$)						
3	374	248	266	284	374	294	260	258	0	46	-6	-26
7	-107	-198	-215	-87	-253	-193	-468	-95	-146	5	-253	-8
11	-105	-167	-363	-367	-245	-399	-686	-350	-140	-232	-323	17
15	-97	-221	-607	-429	-225	-518	-862	-454	-128	-297	-255	-25
19	-274	-458	-705	-874	-449	-746	-895	-681	-175	-288	-190	194
23	-121	-419	-829	-924	-73	-452	-782	-871	48	-33	47	53
27	576	-215	-334	-783	304	-272	-292	-562	-272	-57	41	221
31	158	-323	-425	-1000	213	-230	-342	-829	55	93	84	171
35	-42	-355	-528	-678	140	-356	-513	-672	182	-1	15	6
39	5	-545	-398	-888	75	95	-357	-846	70	639	41	42

continued,

Table 3.9: Effect of FGD rates on differences in acidity, concentrations of Fe and Al, pH, and redox potential (Eh) between leachates and lysimeter samples and between the two lysimeter samples.

Table 3.9 (continued),

Time (week)	Leachate - Lower lysimeter				Leachate - Upper lysimeter				Lower lysimeter - Upper lysimeter			
	0%	5.5%	11%	22%	0%	5.5%	11%	22%	0%	5.5%	11%	22%
						Al (mmol L^{-1})						
3	36	22	21	27	34	27	19	20	-2	5	-2	-6
7	-12	-21	-35	-14	-9	-23	-25	-17	3	-2	10	-3
11	18	-9	-33	-35	20	-7	-19	-29	2	2	14	6
15	25	-2	-41	-46	31	1	-25	-31	6	3	15	15
19	30	10	-31	-60	25	7	-18	-28	-5	-2	13	32
23	30	26	-30	-40	33	21	-13	-27	2	-5	17	13
27	51	32	-4	-31	41	25	13	-12	-11	-7	17	20
31	45	29	-11	-50	42	29	15	-29	-3	1	26	20
35	47	35	-17	-21	48	30	15	-1	1	-5	32	19
39	39	15	-17	-31	35	41	15	-5	-4	26	32	26
						pH						
3	0.05	-0.14	-0.73	-2.03	-0.34	-0.20	0.08	-0.02	-0.39	-0.06	0.81	2.01
7	0.53	0.70	0.33	-0.16	0.67	0.94	1.24	0.69	0.14	0.24	0.91	0.85
11	0.52	1.19	0.94	0.43	0.50	1.37	1.47	1.55	-0.02	0.18	0.53	1.12
15	0.34	0.91	1.14	0.25	0.32	1.36	1.39	1.59	-0.02	0.45	0.25	1.34
19	0.58	1.00	1.28	1.60	0.50	1.20	1.45	1.75	-0.08	0.20	0.17	0.15
23	0.28	0.61	0.90	1.29	0.24	0.65	0.92	1.33	-0.04	0.04	0.02	0.04
27	0.03	0.25	0.69	0.82	-0.08	0.22	0.66	1.10	-0.11	-0.03	-0.03	0.28
31	0.00	0.26	0.48	0.82	-0.08	0.27	0.44	0.81	-0.08	0.01	-0.04	-0.01
35	0.03	0.27	0.50	0.69	-0.03	0.31	0.47	0.56	-0.06	0.04	-0.03	-0.13
39	0.07	0.20	0.31	0.89	0.04	0.17	0.30	0.85	-0.03	-0.03	-0.01	-0.04

continued,

Table 3.9 (continued),

Time (week)	Leachate - Lower lysimeter				Leachate - Upper lysimeter				Lower lysimeter - Upper lysimeter			
	0%	5.5%	11%	22%	0%	5.5%	11%	22%	0%	5.5%	11%	22%
						Eh (mV)						
3	-40	-18	-6	180	-74	-48	-99	-43	-34	-30	-93	-223
7	-39	-75	-21	-11	-92	-115	-116	-65	-53	-40	-95	-54
11	-63	-97	-82	-7	-116	-162	-136	-127	-53	-65	-55	-120
15	-84	-89	-83	9	-118	-153	-120	-115	-35	-64	-37	-123
19	-102	-117	-91	-81	-122	-140	-123	-139	-20	-23	-32	-58
23	-79	-107	-71	-59	-106	-104	-93	-115	-27	3	-22	-56
27	-60	-88	-85	-61	-95	-91	-108	-129	-35	-3	-23	-68
31	-55	-89	-60	-62	-73	-99	-88	-101	-18	-10	-28	-39
35	-51	-67	-52	-38	-68	-73	-81	-70	-17	-6	-29	-32
39	-38	-56	-50	-58	-55	-71	-78	-89	-17	-15	-28	-31

shown most obviously by the fact that increasing FGD rates changed the leachate [Al] from below to above the lysimeter sample [Al].

However, reduced acidity, [Fe], [Al], and increased pH of the leachate compared to the lysimeter samples as FGD rates were increased may be also partially explained by the different sampling mechanisms. Leachate was collected through gravity flow of water and its residence time in the coal refuse was limited. The lysimeter samples were collected through vacuum suction and contained water that had remained in the coal refuse for longer time periods before being removed by vacuum suction. Furthermore, as indicated by lower leachate volumes with higher FGD rates (data not shown), increasing FGD rates slowed down leaching water movement through the columns due to a higher water retention ability of FGD compared to the coal refuse and thus increased the chance to refill lysimeters before the most recent leaching water passed through.

CONCLUSIONS

The $CaSO_3$-containing FGD inhibited acid production in both the fresh and aged coal refuse which contained a large amount of pyrite. The decrease of leachate acidity and Fe concentration and the increase of leachate pH responded linearly to the increasing FGD rates and were generally significant for the 22% FGD treatment. Because the FGD contained a large amount of Al and Ca salts, whose dissolution can mobilize Al, the reduction of leachate Al by FGD was not as great as the reduction in acidity and Fe. Inhibition of acid production in the coal refuse was also indicated by analysis of lysimeter samples and the leached coal refuse. The inhibition of acid production in the coal refuse by FGD may be caused by neutralization of H^+ by SO_3^{2-}, precipitation of minerals by SO_4^{2-} (oxidation product of SO_3^{2-}) and increased pH (SO_3^{2-} and CO_3^{2-}), and inhibition of pyrite oxidation at lower Eh (SO_3^{2-} reductant).

Because coal refuse from the plant was directly packed into columns and was leached, which simulated field conditions, the inhibitory effect of FGD on acid production in the coal refuse is likely to occur under field conditions. Therefore, the experimental results present a potential new method for mitigation of acid production in coal refuse and for beneficial use of $CaSO_3$-containing FGD.

CHAPTER 4

SUMMARY AND CONCLUSIONS

Although $CaSO_3$ is only slightly soluble in water, it can efficiently scavenge O_2 and Fe^{3+} under the conditions commonly encountered in coal refuse disposal environments and decrease the amounts of O_2 and Fe^{3+} available to oxidize pyrite in coal refuse. In the presence of $CaSO_3$, the concentration of dissolved O_2 in water exposed to the atmosphere was below 0.01 mg L^{-1} at pH <8.0.

When 0.2 g $CaSO_3$ was added to a 2% fresh coal refuse slurry every 3 days, the slurry pH never decreased to below the initial pH. Addition of 6.4 g $CaSO_3$ to bench-scale columns containing 50 g fresh coal refuse inhibited acid leaching from the columns under controlled conditions for 27 weeks. During the initial 13 weeks, total amounts of leachate acidity, H^+, Fe, and Al from the $CaSO_3$ treatments were only 26%, 10%, 32%, and 39% of those of the control, respectively. Combinations of $CaSO_3$ with $CaCO_3$ or fly ash enhanced the inhibitory effect of $CaSO_3$ on acid leaching. Calcium sulfite-containing FGD, which combines $CaSO_3$, $CaCO_3$, fly ash, and gypsum, had a much stronger inhibitory effect on acid leaching than $CaSO_3$ alone. This combination effect was partly due to the positive interaction of $CaSO_3$ with $CaCO_3$ or fly ash.

Calcium sulfite-containing FGD inhibited acid leaching from both fresh and aged coal refuse in large scale columns under simulated field conditions. During 39 weeks of leaching, reductions of leachate acidity and Fe concentration and increase of leachate pH were significant ($p < 0.05$) for the 22% FGD treatment and responded linearly to increasing FGD rates (0%, 5.5%, 11%, and 22%).

Two concerns related to application of $CaSO_3$ or $CaSO_3$-containing FGD in coal refuse for inhibition of acid production were also considered although only in preliminary experiments. One is SO_2 release to the atmosphere through dissociation of sulfurous acid at low pH. At the initial pH of 2.0 and 3.5, 14 to 44% of the initial S was released as SO_2 from $CaSO_3$ slurries during 24 h oxidation as shown in Chapter 1. In the column leaching experiments, SO_2 release was not determined. The other concern is sulfite leaching and movement into the surrounding environment at low pH. Because sulfite was rapidly oxidized under low pH, sulfite leaching was expected to be significant only under acidic, anaerobic conditions. Under aerobic conditions in the large column leaching experiment (Chapter 3), sulfite leaching from the coal refuse columns was not determined. To fully appreciate utilization of $CaSO_3$ and $CaSO_3$-containing FGD to inhibit acid production in coal refuse, SO_2 release and sulfite leaching should be further addressed.

As an O_2 scavenger, $CaSO_3$ and $CaSO_3$-containing FGD would be more effective in inhibition of acid production in coal refuse when used under environments with limited amounts of O_2. Combination of $CaSO_3$ and $CaSO_3$-containing FGD with other physical, chemical, and biological methods which can limit contact of coal refuse with the

atmosphere or application of $CaSO_3$ and $CaSO_3$-containing FGD with deep burial of coal refuse are possible ways to increase their inhibitory effectiveness.

The experimental results indicated that $CaSO_3$ and $CaSO_3$-containing FGD have an ability to inhibit acid production in coal refuse. The inhibitory effects shown in this experiment are likely to occur under field conditions and demonstrate a potential new method for mitigation of acid production in coal refuse and another beneficial utilization of $CaSO_3$ and $CaSO_3$-containing FGD.

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