REACTIONS AND MECHANISMS CONTROLLING WATER QUALITY IN SURFACE-MINED SPOILS[1]

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ABSTRACT

Water quality degradation is often associated with the surface mining of coal. This review article addresses the parameters constituting water quality and the means by which these parameters are measured. More importantly the article focuses on the reactions and mechanisms controlling release or immobilization of water quality determining ions such as Ca, Mg, Na, K, Fe, Mn, Al and SO_4 in surface and subsurface water flow. Solid-solution phase interactions influencing water quality are also examined with respect to the amount and the type of ions dissolved or precipitated, and the role of pH, solution speciation and ionic strength on mineral stability equilibria. Furthermore, kinetic aspects of mineral solubility in terms of carbonates, sulfides, sulfates, and aluminosilicates are studied to determine how they influence water quality in runoff and subsurface water transportability. A discussion pertaining to the role of the soil's or spoil's exchange phase in controlling water quality through qualitative and quantitative modifications of ion exchange properties occurring during the course of solution-solid phase interactions is also included. Finally, the importance of understanding these reactions and how this information can be utilized to project and consequently minimize adverse effects on water supplies is emphasized.

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INTRODUCTION

Water quality can be viewed in terms of many properties. These properties include types and levels of dissolved organic and inorganic constituents, levels of dispersed solids, degree of oxygenation and levels and types of bacteria and/or viruses.

In the last two decades surface mining of metallic and/or nonmetallic ores has been of concern in the U.S. and worldwide, in terms of its effect on water quality. Degradation of water quality due to surface mining activities occurs primarily through enriching the surface and subsurface water with metals and sulfates and lowering the pH.

Although a great deal of field data have been gathered from mine spoil reclamation studies on these water quality parameters, most of the experiments have been conducted on a trial and error basis. More importantly, the majority of these studies are site specific and attempts have not been made for interpreting this data through basic physicochemical reactions modelling natural soil or spoil systems. Therefore, before interpretations and extrapolations can be made from the existing field data there is a need for a close qualitative and quantitative evaluation of the physicochemical parameters involved and the processes controlling water quality. A better understanding of these processes would allow one to utilize the most effective reclamation practices and make long term quality predictions.

This paper defines the parameters dictating water quality on surface coal mine sites and discusses the physicochemical reactions and processes that control their behavior and magnitude. It also examines the role of surface and subsurface flow in modifying water quality; specific reactions and mechanisms controlling Fe, Mn and Al solubility; the effect of lime and

N-fertilizers on water quality and how the above relationships can be utilized in selecting management practices that will maintain, predict or improve water quality.

I. WATER QUALITY

The most important factor in preserving water quality is understanding it. Table 1 shows the components of water that must be measured by coal mine operators and the maximum concentrations of what is allowed by law. The acid metals Fe and Mn are most commonly found in acid coal mining environments of the midwestern and eastern U.S. coal fields. Table 4 shows water quality parameters most often encountered in western U.S. coal fields. These waters are sodium enriched and their equilibria is mainly that of a $Na - HCO_3 - CO_3$ system. Such water is often utilized for irrigation purposes. Tables 2 and 3 show general parameters that dictate water quality for human consumption.

Alkalinity and Acidity

Two terms that are often discussed in regards to surface mine water quality in the eastern coal fields are acidity and alkalinity. These two terms are often misunderstood because the chemistry of surface mine runoff is complex, especially in the presence of sediments.

Acidity and alkalinity are determined by titration. This involves the addition of a known amount of base or acid to a water sample and calculation of acidity or alkalinity by the amount of acid or base needed to bring the pH to a certain specified level. The specified pH level is 4.2 for alkalinity determination and 7 or 8.2 for acidity determination. Titration values, however, can be misleading, especially in the presence of transition metals (Fe, Mn) where the rate of acid or base addition and the presence or absence of gaseous oxygen (O_2) can drastically alter the results (1).

In order to understand what constitutes acidity or alkalinity, the concept of electroneutrality needs to be defined. Electroneutrality is described by the equation:

$$\Sigma zc_i - \Sigma za_i = 0 \qquad [1]$$

where Σ denotes sum, z is the valence of ions involved, c and a are concentrations of cations and anions, respectively, expressed as moles per liter and the subscript i indicates the type of cations and anions. For a water sample from a mining site with no transition or acid metals the electroneutrality equation would be:

$$[2(Ca^{2+}) + 2(Mg^{2+}) + (Na^{+}) + (K^{+}) + (H^{+})] - \qquad [2]$$
$$[2(SO_4^{2-}) + (Cl^{-}) + (NO_3^{-}) + (OH^{-}) + 2(CO_3^{2-}) + (HCO_3^{-})] = 0.$$

Equation [2] can be used to calculate alkalinity from the following relationships:

$$\text{alkalinity} = 2(CO_3^{2-}) + (HCO_3^{-}) + (OH^{-}) - (H^{+}),\ \text{or} \qquad [3]$$

$$\text{alkalinity} = [2(Ca^{2+}) + 2(Mg^{2+}) + (Na^{+}) + (K^{+})] -$$
$$[2(SO_4^{2-}) + (Cl^{-}) + (NO_3^{-})]. \qquad [4]$$

Assuming that the ions shown in equation [2] do not satisfy electroneutrality ($\Sigma zc_i - \Sigma za_i \neq 0$), then if $\Sigma zc_i \ll \Sigma za_i$, the difference is assumed to be made up by Al, Mn, Zn, Cu or Fe ions which constitute the acidity of the water. This relationship holds well down to a pH of at least 3.5. Below this pH level the anion bisulfate (HSO_4^{-}) is formed, especially in the presence of very high concentrations of sulfate (SO_4^{2-}) encountered in coal surface mining environments, thereby contributing to the total acidity along with the acid metal cations Al, Mn, Zn, Cu and Fe. In pH ranges between 5 and 9 the contribution of H^+ and OH^- is negligible and both ions can be omitted.

The concept of electroneutrality has some direct practical implications in troubleshooting general water quality problems. For example, an electroneutrality test in a water sample can provide information about the presence or absence of additional ions not included in the original analysis. The same concept can also be used to determine whether or not the analysis has been carried out accurately by the laboratory.

Generally speaking, water with high alkalinity dominated by HCO_3^- and CO_3^{2-} is expected to emanate from western U.S. mining environments, especially from spoils high in sodium content. A mechanistic explanation is shown below:

$$ExNa_2 + CaCO_3 \longrightarrow ExCa + CO_3^{2-} + 2Na^+ \qquad [5]$$

where Ex denotes "exchangeable" . On the other hand, water with high acidity is expected to emanate from pyritic coal spoils of the eastern U.S. mine fields following the reaction:

$$FeS_2 + 7/_2O_2 + H_2O \longrightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+ \qquad [6]$$

Alkaline water is not commonly found in eastern U.S. coal fields. A few instances of water alkalinity in this region are the result of $CaCO_3$ dissolution from limestone and the interaction between $CaCO_3$ and the clay exchange phase.

$$ExMg + CaCO_3 \longrightarrow ExCa + Mg^{2+} + CO_3^{2-} \qquad [7]$$

Equation [7] explains how the alkalinity in waters of the eastern U.S. coal fields can go beyond the concentrations dictated by the solubility of $CaCO_3$ in water and the partial pressure of CO_2. The effect of carbonate dissolution on water alkalinity is shown in Fig. 1. When the P_{CO_2} increases so does the concentration of Ca^{2+} and HCO_3^- while the absolute decrease in the CO_3^{2-} and OH^- concentration is almost negligible. There is approximately an 18-fold increase in the concentration of calcium when P_{CO_2} increases from 3.1x 10^{-4} to nearly one atmosphere (3). A study reported by Dickens et al (2) in coal mines of Tennessee showed that alkalinity of subsurface waters varied from 144.8 to 303.4 mgL^{-1} expressed as equivalent $CaCO_3$. These values exceeded those justified by water dissolution of $CaCO_3$ under a P_{CO_2} of 3.32×10^{-3} atm encountered in soils [3]. A second approach to explaining high water alkalinity in both eastern and western U.S. coal fields is the exposure of geologic strata containing sodium silicates. Under these conditions, the following reaction may take place:

$$\text{Na-silicate} + CO_2 + H_2O \longrightarrow H_4SiO_4 + Na^+ + CO_3^{2-} \qquad [8]$$

Dissolved Solids

Another parameter used for water quality evaluation is the amount of dissolved solids. The concentration of dissolved solids can be estimated by taking the electrical conductivity (EC) of the water sample, and by utilizing empirical relationships between EC vs dissolved solids.

In choosing an established empirical relationship between EC and dissolved solids, pH and the presence or absence of SO_4^{2-} and Cl^- should be considered. At pH values above 3.5, it is necessary to know whether the water sample represents a SO_4^{2-} or a Cl^- system. Presently, no empirical relationship exists for Cl^- or SO_4^{2-}

systems at pH values <3.5. Existing equations that best fit data for Cl^- and SO_4^{2-} systems are shown in Fig. 2. Most coal mine spoils are SO_4^{2-} dominated systems. However, a relationship such as the one shown in Fig. 2 cannot have universal use because organic- and aluminum-sulfate complexes may introduce variabilities.

II. IMPLICATIONS OF SURFACE AND SUBSURFACE FLOWS ON WATER QUALITY

Surface and subsurface water quality is also a function of water flow rate, erosion, mineral solubility, kinetics of mineral dissolution, chemical properties of rainwater, interactions of the dissolved ions, and physicochemical properties of spoil or soil material. During a runoff event on a disturbed site, the sediment exchange phase and the solution phase approach an equilibrium state (4), (5). However, the only chemical constituents that could be quantified within an acceptable degree of accuracy in such reactions are mainly Ca, Mg, Na, K, Cl and SO_4. From these ions, SO_4 is by far the dominant anion in spoil leachates (6).

Subsurface water flow has a large influence on the water quality of underground water reservoirs (7). Two of the most important factors influencing water quality in subsurface flows are saturated macropore flow and micropore flow. Macropore flow at saturation does not allow the water to approach a true equilibrium with the solid phase, therefore water chemistry under such flow is not representative of the chemistry of the spoil. Well developed soils that are not disturbed to a large extent usually conduct water through macropores, and to a lesser degree through micropores. Micropore flow is relatively slow and allows the percolating water to reach equilibrium with the exchange phase, and possibly approach a near equilibrium condition with the mineral and solution phases of the system (6), (9).

Exchange Reactions

Exchange reactions involving eroding coal mine spoils and cation-anion solution phase interactions have been described with some detail by Evangelou (6). A typical reaction describing the exchange phenomenon between two cations of the same valency e.g., Ca^{2+} and Mg^{2+} is:

$$ExCa + Mg^{2+} \longrightarrow ExMg + Ca^{2+}. \qquad [9]$$

At equilibrium,

$$K_{Ca}^{Mg} = \frac{[ExMg]\ [Ca^{2+}]}{[ExCa]\ [Mg^{2+}]} \qquad [10]$$

where, K_{Ca}^{Mg} is the selectivity coefficient for equation [9], ExCa and ExMg denote exchangeable Ca and Mg in meq per 100 g of clay, and [Ca] and [Mg] denote solution concentrations of Ca^{2+} and Mg^{2+} in moles per liter. Values of K_{Ca}^{Mg} for coal mine spoils have been found to vary from 0.71 to 0.14 (6). The magnitude of the K_{Ca}^{Mg} value can be used as a preference index of the spoil exchange phase for Ca^{2+} over Mg^{2+}. Values less than 1 indicate preference for Ca^{2+} over Mg^{2+}, and values greater than 1 indicate preference for Mg^{2+} over Ca^{2+}. Equation [10] can be used to predict Ca^{2+} and Mg^{2+} concentrations in runoff, if the initial concentrations of constituents in the spoil solution and exchange phase, cation exchange capacity, and spoil:water ratio of runoff are known. Such modeling can be applied to eastern U.S. coal fields that are dominated by gypsum and magnesium sulfate salts (6), (10), (11).

Equation [10] also allows certain qualitative predictions. It is normally considered that the K_{Ca}^{Mg} value is less than 1, especially for spoils with high Al and Fe oxide content (6). This suggests that Mg would be leached faster than Ca from a spoil assuming that the spoil has equal quantities of Ca and Mg. Columns of spoil material leached for a period of 4 months in the laboratory showed an initial Mg leachate concentration of 231 meq L^{-1} and a final concentration of 3.4 meqL^{-1}. On the other hand, Ca concentration was reduced only to 18.4 meq L^{-1} from the original gypsum saturated state of 30 meq L^{-1} (10). In terms of water quality, dominance of magnesium would create nutrient imbalances to plants grown on soils that accept such runoff water. In terms of spoil reclamation, the faster the leaching of Mg from the spoil, the more suitable the spoil is for plant growth.

For sodic spoils such as those encountered in the western U.S. coal fields, the Gapon equation is commonly used to predict water composition (6). For a Na-Ca-Mg spoil system the Gapon equation can be written as follows:

$$\frac{\mathrm{ExNa}}{\mathrm{CEC} - \mathrm{ExNa}} = K_G \frac{[\mathrm{Na}^+]}{[\mathrm{Ca}^{2+} + \mathrm{Mg}^{2+}]^{\frac{1}{2}}} \qquad [11]$$

where, exchangeable ions are expressed in meq/100 g and solution concentrations in mmoles L^{-1}. In this equation K_{Ca}^{Mg} has a value of 1 and therefore Mg^{2+} and Ca^{2+} are treated as one ion. By setting:

$$\mathrm{SAR} = \frac{[\mathrm{Na}^+]}{[\mathrm{Ca}^{2+} + \mathrm{Mg}^{2+}]^{\frac{1}{2}}}, \text{ and} \qquad [12]$$

$$\mathrm{ESR} = \frac{[\mathrm{ExNa}]}{[\mathrm{CEC} - \mathrm{ExNa}]} \qquad [13]$$

where, SAR = sodium adsorption ratio, ESR = exchangeable sodium ratio, and CEC = cation exchange capacity, the relationship ESR = K_G(SAR) is derived.

Relationships of this type have been developed for various mine spoil areas, and as expected, they vary with soil or spoil clay mineral composition. For a number of shale samples from Colorado (4) this relationship was ESR = $-0.0362 + 0.042$(SAR) with $r^2=0.906$. This equation compares with ESR = $-0.0126 + 0.0147$(SAR) and an $r^2 = 0.852$, given by the U.S. Salinity Lab (12) for a number of western U.S. soils. Similar equations reported by Harron et al (133) for Canadian geologic materials are: ESR = $0.0076 + 0.0058$(SAR) and ESR = $-0.080 + 0.0173$(SAR) with $r^2 = 0.902$.

The important consideration about these equations is that the K_G (slope of the line) represents affinity of the soil or spoil exchange phase for sodium ions. The greater the affinity, the higher the value of the K_G. Usually, soils or spoils with high CEC have low K_G values and vice versa. Exchangeable Sodium Ratio-SAR equations can also be used to evaluate the quality of water emanating from sodic spoils during runoff events. Such an evaluation can be done by incorporating chemistry predicting equations into sediment erosion predicting models.

Kinetics

Ion release into subsurface water flow is dependent upon contact time between the solids and water. This contact time is dependent on the type of flow predominating in the soil or spoil system.

For a number of Kentucky soils, it has been shown that macropore and micropore flows are taking place simultaneously, as would be expected, but for some soils, macropore flow dominates (14). The data in Table 5 demonstrate that the value of C/Co for Cl^- at breakthrough is a function of the soil type and water flux. For soil types and water fluxes with C/Co values approaching 1, macropore flow is dominant. The effect of macropore vs micropore flow in reconstructed acid coal spoil profiles is demonstrated in Fig. 3. Macropore flow increases water flux and water quality is greatly improved, as compared to micropore flow where water flux is slow and the water of poor quality. The effect of water flux on water quality during reclamation of sodic geologic material is demonstrated in Table 6. The data show that, with increasing gypsum rates, the solution percolating through the material approaches the gypsum saturation point. However, as the water flux increases, a greater shift in calcium concentration is observed at the lower gypsum rates. Since coal mine spoils with potential to contaminate underground water have slow water fluxes, ranging from near zero to about 1 cm hr^{-1} (15), (16), (17), (18), saturated water flow through reconstructed coal mine spoil profiles can accurately be described as Darcian. Such flow is characterized by maximum chromatographic column effects (salt pulses) (15), (16). Because of extremely low water fluxes occurring in many spoil materials chemical equilibria concepts can be used to approximately describe the quality of water fluxing through such systems, especially those containing significant amounts of gypsum and Na or Mg sulfate salts.

III. REACTIONS AND MECHANISMS CONTROLLING IRON, MANGANESE AND ALUMINUM

The number of mineral components that control the release of Fe, Mn, and Al in coal mine spoils are multiple and often difficult to determine under field conditions due to differential kinetic dissolution of the minerals involved. Generally, two of the most important components in controlling Fe and Mn concentrations in the soil or spoil solution are pH and Eh. Furthermore, the kinetics of oxidation of the reduced Fe and Mn forms are an important consideration in maintaining Fe^{2+} and Mn^{2+} in solution. The data in Tables 7 and 8 demonstrate that the rate of oxidation of Fe^{2+} and Mn^{2+} at P_{O_2} of 0.2 is highly pH dependent. Furthermore, the data point out that the rate of oxidation of Mn^{2+} is slower than that of the Fe^{2+} and takes place at higher pH values. The main sources of Fe^{2+} and Mn^{2+} in the spoil solution and water of sediment ponds of eastern U.S. coal fields is known to be pyrite and manganese oxides. During pyrite oxidation Fe^{2+} and SO_4^{2-} ions released into solution interact with the overburden materials. During the course of this interaction, protons are largely inactivated by ion exchange and weathering reactions. This buffering action results in a pH increase and formation of various ferrous iron sulfates. Depending on pH and Eh of the system part or all of the remaining Fe^{2+} is further oxidized to Fe^{3+}, precipitating ferric hydroxide ($Fe(OH)_3$), goethite (FeOOH) and basic iron sulfates. This oxidation process is partially catalyzed by the presence of iron oxidizing bacteria. Although relatively soluble iron sulfates may control the solubility and release of iron in waters flowing in the vicinity of sulfide surfaces, the most effective mineral limiting the release of iron in runoff or sediment pond water is $Fe(OH)_3$. Other important minerals contributing significant iron levels in water emanating from mine spoils include ferrus hydroxide [$Fe(OH)_2$] , siderite [$FeCO_3$] and jarosite [$K\ Fe_3(OH)_6(SO_4)_2$]. On the other hand, the most effective mineral controlling Mn solubility in runoff or sediment pond water is MnO_2, with limited contributions from $MnCO_3$ and/or $Mn(OH)_2$ depending on Eh-pH conditions.

During runoff events on well oxidized spoils, Fe and Mn concentrations approach values of near zero, even under slightly acid conditions (19). However, reducing conditions in sediment ponds often cause release of these two metals in the water. Bucek (20) has reported dissolved Fe and Mn values in sediment pond water approaching 6 and 10 mg L^{-1}, respectively, even at pH values greater than 9.

A very important factor in understanding Fe and Mn release in surface and underground water reservoirs is the interrelationship between the two ions. In the presence of MnO_2, low pH and Fe^{2+}, Mn reduction occurs according to the following equation (6), (21):

$$MnO_2 + 4H^+ + 2Fe^{2+} \longrightarrow Mn^{2+} + Fe^{3+} + 2H_2O \qquad [14]$$

Under such conditions in Kentucky the authors observed Mn concentrations approaching 1000 mg L^{-1} (unpublished data).

Recently, great emphasis has been put on understanding Al solubility in coal mine environments mainly because Al has been linked to human and animal health. Its toxicity effects to plants are well documented. In acid soils with low buffering capacity, excess Al in infiltrating solutions may be complexed by organic colloids, polymerized into hydroxy-oxide forms, or immobilized in interlayer mineral positions.

Although the low solubility of aluminum hydroxides $[Al_x(OH)_{3x}]$ and aluminosilicates generally dictate the Al concentration in natural soil and geologic systems, more soluble basic aluminum sulfate minerals, weathering products of exposed pyritic shales and other overburden materials, control the amount of Al in waters of disturbed by surface mining watersheds (22). These Al-sulfates are the result of adjustments that the common soil minerals have to undergo under the new Al-rich environment, as opposed to their previous low Al environment controlled by the low solubility of the Al-silicates (23). Adjustments of the soil minerals to the shift in equilibrium will involve alteration or dissolution of the most weatherable minerals and reprecipitation in a more stable form (24). Figure 4 shows a system initially in equilibrium with gibbsite, kaolinite, hydroxyinterlayered vermiculite, (HIV), and mica minerals which are commonly found in natural soil and geologic systems. The upper limit for the activity of Al^{3+}, maintained by these minerals in natural waters with pH values between 4 and 6 ranges from $10^{-3.5}$ to $10^{-6.0}$M and the lower limit ranges between $10^{-9.5}$ to 10^{-12}M. Gibbsite is the mineral that supports the highest Al levels in solution.

Under the acidic conditions encountered during chemical weathering by acid shale drainage waters, there is a tendency for the excess Al and SO_4 in solution to precipitate as basic aluminum sulfates. The driving force for the transformation of common clay minerals like mica, kaolinite and gibbsite to form basic aluminum sulfates depends greatly on pH and SO_4^{2-} activity. At SO_4^{2-} level of 10^{-4}M any pH below 4.5 is sufficient to precipitate a stable or metastable basic aluminum sulfate that may persist for long periods of time. The more soluble of these aluminum sulfates (alunogen, jurbanite) can dramatically increase the solubility of Al in water reservoirs of watersheds contaminated by acid shale drainage (22). Figure 5 shows that Al^{3+} activity in solution maintained by some of these aluminum sulfates can be up to 10^{10} greater than that supported by gibbsite at different SO_4^{2-} activity levels. An unknown basic aluminum-sulfate with the stoichiometric composition $AlOHSO_4$ and a Ksp of 17.2 was assumed to control the upper limit of Al^{3+} (22) (Fig. 5) in acid sulfate soils and mine spoils according to the following equilibrium reaction:

$$AlOHSO_4 = Al^{3+} + OH^- + SO_4^{2-} \qquad [15]$$

Direct proof for this reaction and the nature of this compound, however, is lacking. It is more likely that a combination of solubility mechanisms involving basic aluminum sulfates, gibbsite and certain other soil minerals will dictate upper limits of dissolved Al in solutions contacting soils contaminated by acid shale drainage (26), (27).

Under continued acid drainage infiltration, and depending on the amount of moisture and the pH of the water flux in the soil zone, basic aluminum sulfates will form a storage sink for and a source of sulfates which will redissolve and reprecipitate in a cyclic pattern. It is also likely that a significant increase in pH, caused by water table fluctuation, may completely dissolve some of the Al-sulfates and cause them to revert to Al-hydroxide forms, following the reaction (25), (26):

$$\text{Al-sulfate} + 3OH^- = Al(OH)_3 + SO_4^{2-} \qquad [16]$$

The literature cited in this paper provides sufficient evidence that the aqueous geochemistry of Al is significantly modified by the presence of sulfate, which dominates acid shale drainages contaminating water reservoirs of surface mined watersheds. Under these conditions, gibbsite and kaolinite become unstable and the solubility of Al is controlled by newly precipitated Al-sulfate minerals formed from weathering products of the least stable minerals. The nature and solubility of these Al-sulfates, however, varies with soil pH and the physicochemical and mineralogical soil characteristics, which are also altered by the interaction between acid drainage and the soil system.

IV. EFFECT OF LIME AND NITROGEN ON WATER QUALITY

The role of lime in assessing water quality goes beyond its ability to increase the pH of soils and spoils. With increasing pH, CEC and specific adsorption of metals increases while anion adsorption decreases (28). Adsorption and desorption processes as a function of liming are demonstrated in Table 9. These data point out that as the pH increases, the potential leachate increases in Ca, Cl and NO_3, and decreases in Mg, Na and K. Similar trends have been observed by Grove and Evangelou in coal spoils of sulfate nature (29). In addition to quantitative changes in ion release from limed spoils, there are also qualitative changes. The data in Table 10 illustrate that during the first stage of pH increase in an acid spoil after liming, the ability of a spoil exchange complex to adsorb Al-hydroxy species increases. Because of this, an effective drop in CEC and an increase in Mg concentration in the leachate is observed. However, at further increasing pH levels, the Al-hydroxy-species precipitate as amorphous aluminum hydroxides, thus, effectively increasing the CEC. This increase causes removal of Mg from the leachate.

Application of fertilizers in disturbed lands is also expected to have significant effects on the quality of water emanating from such sites, but data is not readily available. The phenomenon of metal release from soils through fertilizer acidification is well documented. This is shown in Table 11 where metal concentrations in the leachate increase by applying ammonium nitrate, an acid producing fertilizer commonly used in soils. Yearly fluctuations in the quality of water emanating from disturbed sites can be also associated with the so called "spring flush". During early spring, oxidation of NH_4^+ to NO_3^- leads to a build-up of acidity in the soil or spoil and increases metals in the leachate.

CONCLUSIONS

The quality of waters emanating from coal mining environments is controlled by a variety of factors such as the composition (including pH and Eh) of the water percolating the spoil and/or soil system, the chemical and mineralogical constituents present in the overburden materials, the solubility of such constituents, rates of soil erosion, rates of water infiltration into the soil or overburden material, and interactions occurring between exchange and solution phase ions.

The above processes are taking place in disturbed mining environments as well as in established soil systems. The difference in the quality of water emanating from established soils vs geologic strata, aside from geomorphological differences, is the nature of the depositional environment. Understanding the chemistry of such strata and the reactions and mechanisms involved in the ion release would allow one to predict the type of water quality problems expected and means of correction.

Soils in the eastern U.S. are relatively more weathered and oxidized systems, having been depleted from the most readily water soluble constituents dominating the western U.S. coal mine fields. However, some geologic strata in the same region may have been the site of soluble constituent accumulation and/or formation of sulfides due to reducing conditions present in the depositional stage. Although different constituents may control the quality of water in these regions, basic physicochemical relationships can be used to predict acidity, alkalinity, high levels of dissolved and dispersed solids and select the most appropriate management.

In applying certain management practices for spoil reclamation, knowledge of carbonate equilibria will help in understanding buffering capacities of the overburden materials and the importance of vegetation to improve spoil and water quality. Knowledge of the type of ion-solid interactions (ion exchange, dissolution, adsorption, desorption) occurring in the spoil zone is also of great importance in selecting spoil amendments and rates of application. Applications of lime and mulches for example, can have immediate and long term effects on water quality. Knowing the effect of lime and mulch on the surface negative charge of colloids it would be possible to predict pH increase and metal ion immobilization. On the other hand, nitrogen fertilizer application in the form of NH_4^+ would, upon NH_4^+ oxidation, lead to spoil acidification, negative charge reduction of the colloidal phases and water enrichment in NO_3 and metals.

Finally, kinetic relationships of water infiltration through macropores and micropores are essential for predicting surface and subsurface water quality. The faster the infiltration rate the lesser the potential for water contamination by the chemistry of the spoil. Therefore, ripping, deep incorporation of organic material and use of equipment causing little compaction can drastically affect water quality by modifying macropore and micropore flow.

This paper was not aimed at covering all aspects of the basic science describing water quality. It is rather an attempt to discuss some of the major parameters and processes controlling the quality of water in disturbed by surface coal mining lands. Furthermore, the point being made is that treatment effects are a function of parameters that are often ignored and for this reason data extrapolation to sites with seemingly similar problems is limited.

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Table 1: Summary of current EPA effluent limitations for the coal mining point source category.

Type of operation	Total Fe	Total Mn	Total solids TSS	Suspended settleable solids SS	pH	Category
	mgL^{-1}			$ml\ 1^{-1}$		
Coal preparation plant associated areas	6.0/3.0	4.0/2.0	70/35	-	6-9	NSPS
Coal preparation plants and associated areas	7.0/3.5[2]	4.0/2.0[3]	70/35	-	6-9	BPT
<u>Active mining</u>						
Surface disturbance and underground workings	6.0/3.0	4.0/2.0[4]	70/35	-	6-9	NSPS
Surface disturbance and underground workings	7.0/3.5	4.0/2.0[4]	70/35	-	6-9	BPT
<u>Post-mining (reclamation)</u>						
Surface disturbance	-	-	-	0.5	6-9	NSPS, BPT
Underground workings	6.0/3.0	4.0/2.0[4]	70/35	-	6-9	NSPS
Underground workings	7.0/3.5	4.0/2.0[4]	70/35	-	6-9	BPT
<u>Applicable time period</u>						
Discharge resulting from precipitation $\geq$10-year, 24-hour storm						
All operations except underground workings	-	-	-	0.5	6-9	NSPS, BPT
Discharge resulting from precipitation >10 year, 24 hour storm						
All operations except underground workings	-	-	-		6-9	NSPS, BPT

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[1] NSPS: New Source Performance Standards; BPT: Best Practicable Control Technology Currently Available; BAT: Best Available Technology Economically Achievable; BCT: Best Conventional Pollutant Control Technology) Effluent Limitations are not contained in this table.

[2] 7.0-maxiumum concentration for one day; 3.5-average concentration for 30 consecutive days.

[3] Manganese applicable only if the pH is normally less than 6.0 in untreated discharge.

[4] Manganese applicable only if the pH is normally less than 6.0 or iron is normally equal to or greater than 10 mg/l.

Table 2. Water hardness classification.*

Quality	Hardness as $CaCO_3$ Milligrams Per Liter	Grains Per Gallon
Soft	0 to 60 mg/L	0 to 3½ gpg
Moderate	61 to 120	3½ to 7
Hard	121 to 180	7 to 10½
Very hard	more than 180	more than 10½

Table 3. Chemical concentrations that cause odor and/or taste.*

Chemical	Concentration mg/L	Chemical	Concentration mg/L
Chlorides	100-250	Hydrogen sulfide	0.1-0.2
Total dissolved solids	500-1000	Iron	1.0-2.0
		Zinc	5
Copper	1	ABS (detergent)	0.5
		Phenols	0.001

Table 4. Guidelines for interpreting water quality for agricultural uses in the arid regions of the United States (Recommended by the University of California).

	Water Quality Guidelines		
Problem and Related Constituent	No Problem	Increasing Problems	Severe Problems
<u>Salinity</u>			
EC of irrigation water, in millimhos/cm	<0.75	0.75-3.0	>3.0
<u>Permeability</u>			
EC of irrigation water, in mmhos/cm	>0.5	<0.5	<0.2
SAR	<6.0	6.0-9.0	>9.0
<u>Specific Ion Toxicity</u>			
Soil Solution Sodium adsorption ratio (SAR)	<3	3.0-9.0	>9.0
Chloride (mg/l or ppm)	<142	142-355	>355
Boron (mg/l or ppm)	<0.5	0.5-2.0	2.0-10.0
<u>Irrigation water</u>			
Sodium (mg/l or ppm)	<69	>69	-
Chlorides (mg/l or ppm)	<106	>106	-
<u>Miscellaneous</u>			
HCO_3 (mg/l or ppm) (only with overhead sprinklers)	<90	90-520	>520
pH	normal range = 6.5 - 8.4		

Table 5. Effects of macropore water flow at different velocities on Cl^- breakthrough curves on several well structured Kentucky soils (14).

Soil	Water flux ($cmhr^{-1}$) 4.0	 2.0	 1.0	 0.5
	C /Co			
Maury	0.12	0.10	0.01	0.02
Grider	0.48	0.32	-	0.11
Lanton	0.68	0.38	0.28	-
Huntington	-	0.73	-	0.32

Table 6. Dissolution rate of soil applied gypsum ($CaSO_4 \cdot 2H_2O$) as a function of water flux (9).

Water flux cm hr^{-1}	Gypsum rate (ton ha^{-1}) 6	 17.9	 35.8
	Ca (mmol L^{-1})		
1.2	9.2	14.2	15.8*
5.0	3.3	11.0	14.1
10	1.8	9.23	12.9
15	1.0	8.1	12.6
30	-	6.8	11.0

*Gypsum solubility in equilibrium with water.

Table 7. Effect of pH on rates of Fe^{2+} oxidation at a PO_2 of 0.2 and 25°C (1)

	pH		
Time (minutes)	6.6	6.9	7.2
	Fe^2/Fe_o^{2+}*		
5	1	0.8	0.15
10	0.9	0.6	0.03
30	0.9	0.2	--
40	0.8	0.1	--
50	0.7	0.05	--

*Ratio of remaining iron Fe^{2+} concentration over initial Fe^2 concentration (Fe_o^{2+}).

Table 8. Effect of pH on rates of Mn^{2+} oxidation at PO_2 of 0.2 and 25°C (1).

	pH		
Time (minutes)	9.0	9.3	9.5
	Mn^{2+}/Mn_o^{2+}		
20	0.89	0.83	0.50
40	0.85	0.56	0.20
80	0.80	0.06	--
120	0.63	--	--
160	0.56	--	--

Table 9. Effect of lime on composition of soil solution (potential leachate) (30).

Treatment	pH	Ca	Mg	Na	K	Al	Fe	Mn	Cl	NO_3	HCO_3	OM*	EC
		---------- mgL^{-1} ----------											mmhos cm^{-1}
Unlimed	4.7	147.5	25.7	24.9	21.6	0.5	0.02	0.07	33.3	654.6	--	0.10	1.17
½ Lime requirement	7.2	217.9	18.5	17.2	10.9	0.02	0.01	0.002	41.2	716.9	30.5	0.32	1.45
Lime requirement	7.7	253.3	17.4	15.6	10.2	0.01	0.01	0.001	38.2	756.6	100.7	0.54	1.50

*Absorbance values measured at 260 nm using 1-cm cell.

Table 10: Average chemical composition of spoil leachate after and 8-month reaction period (6).

Type of Spoil	Lime* treatment	pH After a 4-month period	pH After an 8-month period	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	Al^{3+}	Mn^{2+}	Fe^{2+}	SO_4^{2-}
	mt/ha			meq/liter							
Black Shale	0	1.8	1.8	29.66	337.76	5.41	0.21	201.91	42.66	1166.18	2304.02
"	125	4.0	2.2	26.05	508.88	6.28	0.98	41.54	16.40	80.39	734.31
"	250	7.0	4.2	24.19	350.50	7.18	1.77	0.47	4.30	0.09	398.85

*Limed rate represents the total measured acidity in the sample.

Table 11. Effect of ammonium nitrate addition on soil solution (potential leachate).

Treatment	pH	Ca	Mg	Na	K	NO_3	EC mmhos cm^{-1}
	----------------	mg L^{-1}				----------------	
Control	7.2	63	4.3	48	24.9	22	0.48
300 Kg ha^{-1} N (NH_4NO_3)	5.6	366	23.6	242	62.9	286	2.42

(Evangelou and Karathanasis - unpublished data).

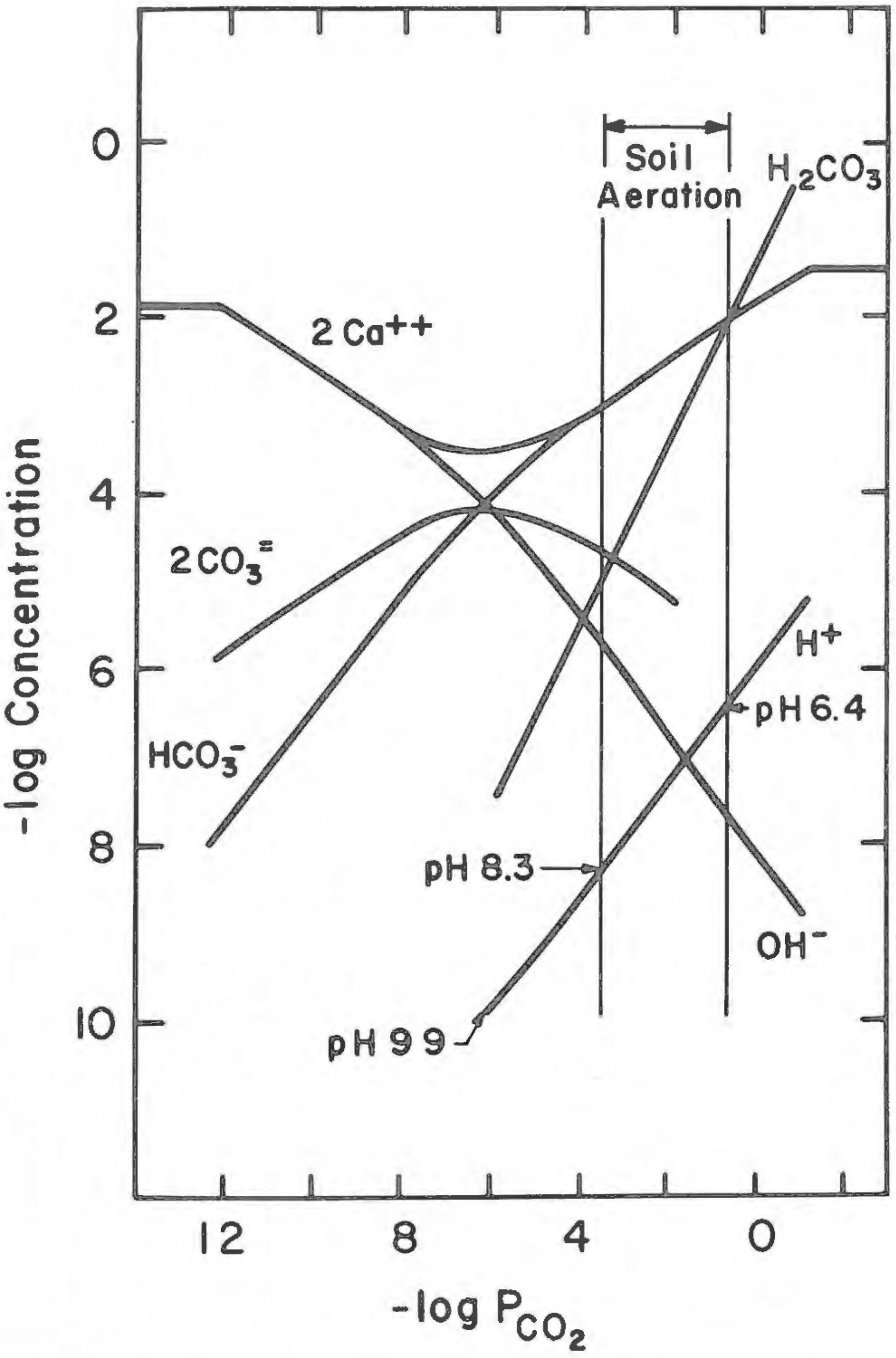

Fig. 1. Stability diagram of calcium carbonate ($CaCO_3$) and carbonate (CO_3) species.

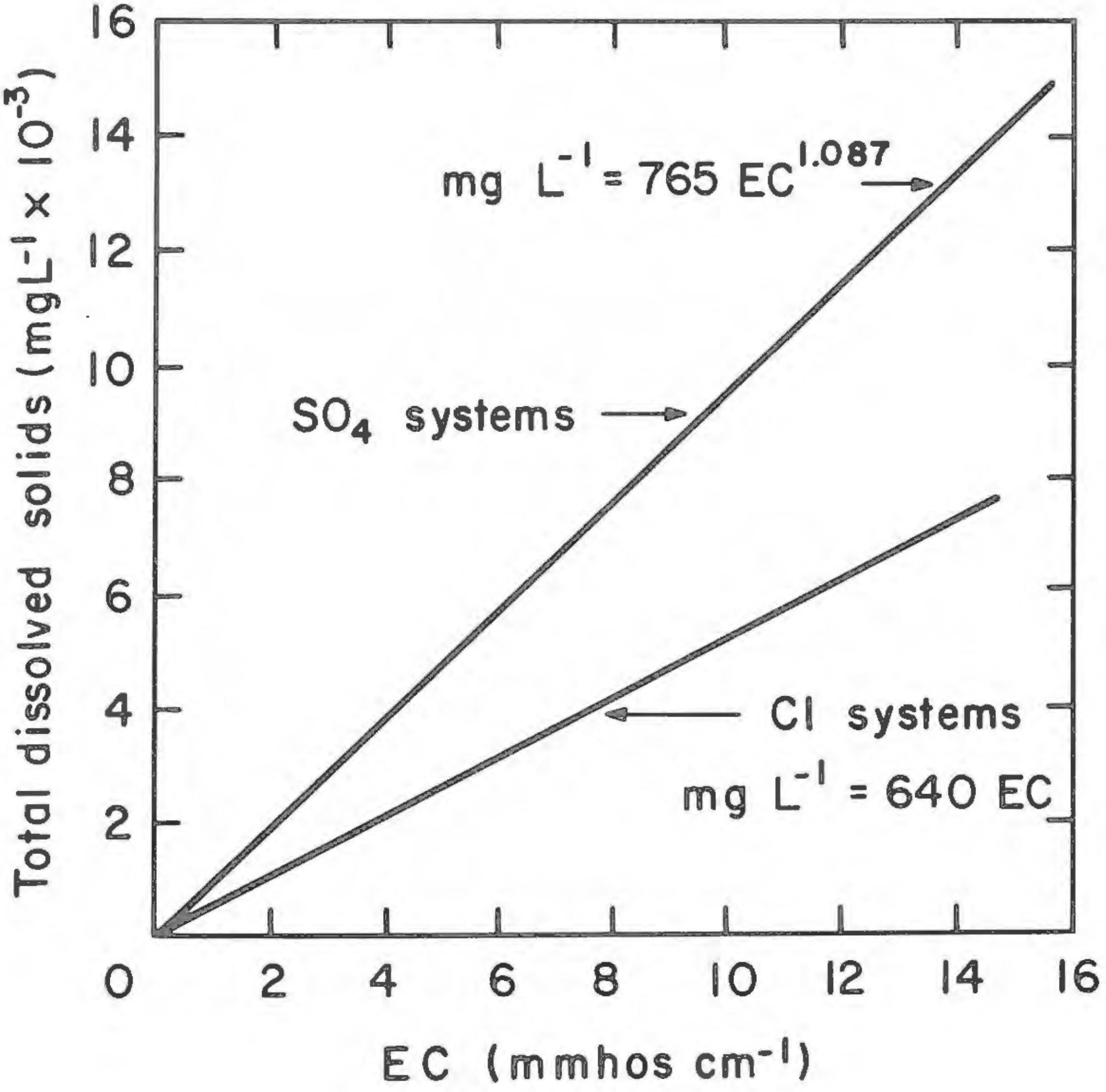

Fig. 2. Relationship between EC and total dissolved solids (12), (31).

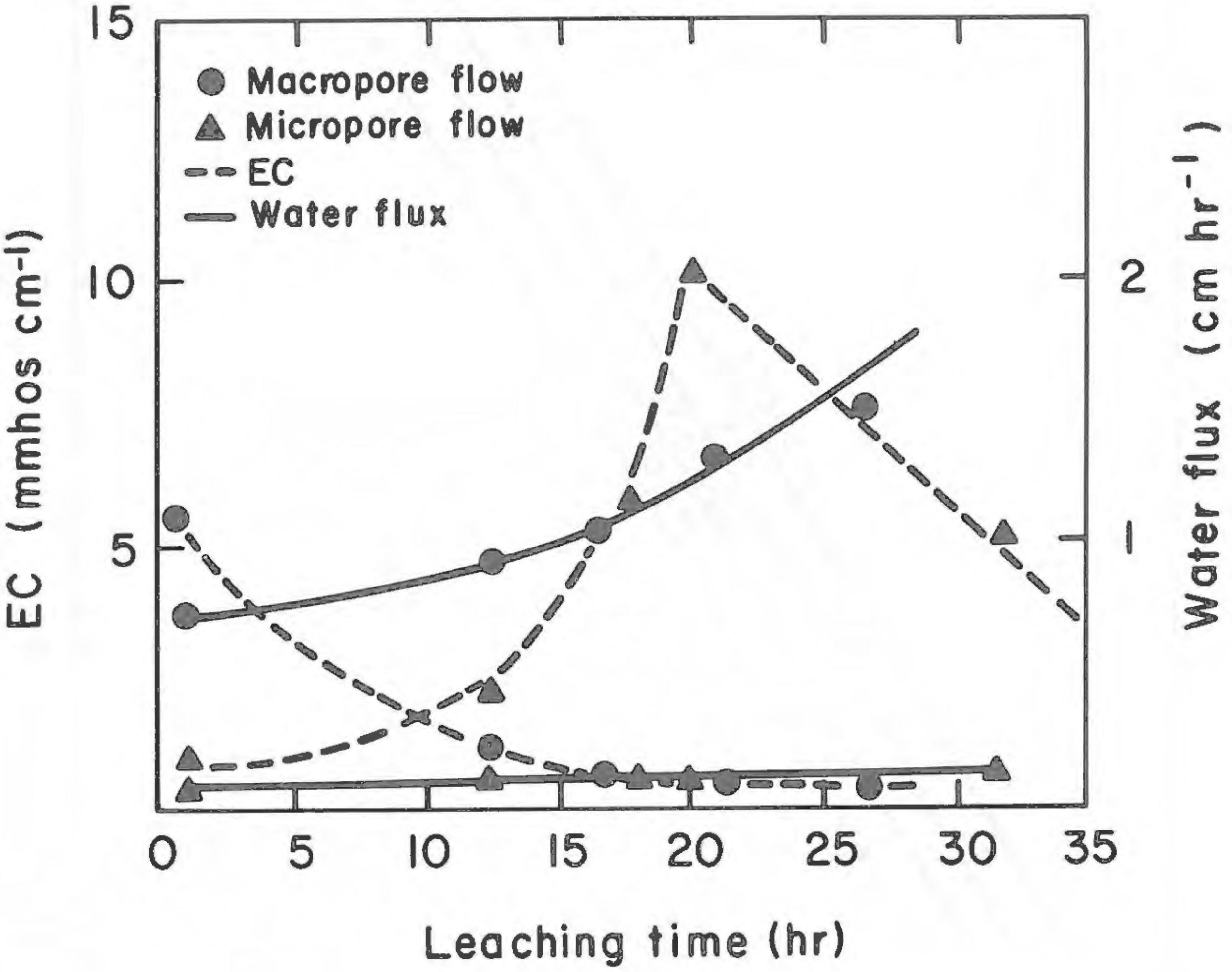

Fig. 3. Effect of macropore and micropore flow on water quality in laboratory simulated coal spoil profiles (15).

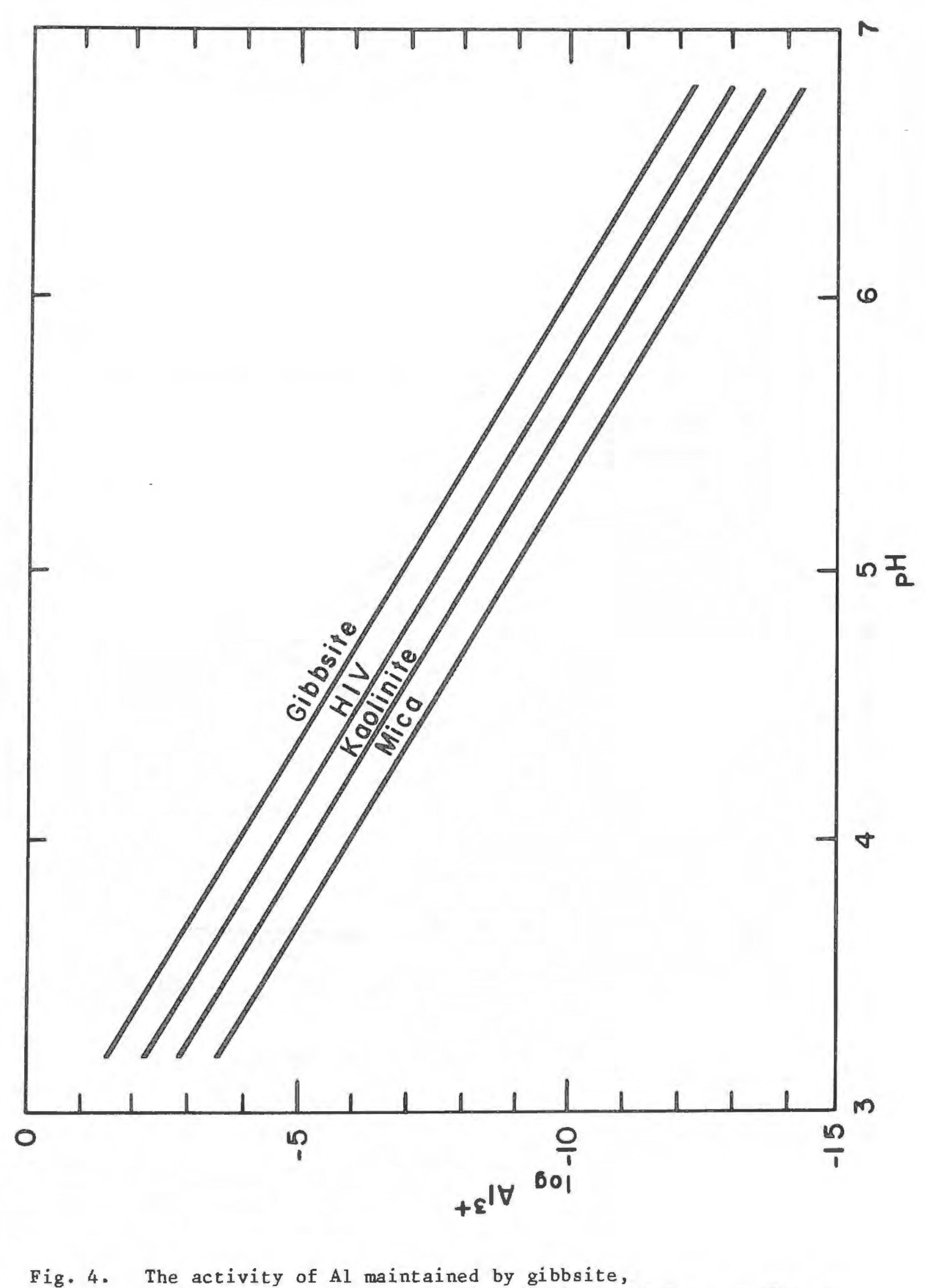

Fig. 4. The activity of Al maintained by gibbsite, hydroxyinterlayered vermiculite (HIV), kaolinite and mica as a function of pH at $pH_4SiO_4 = 3.1$.

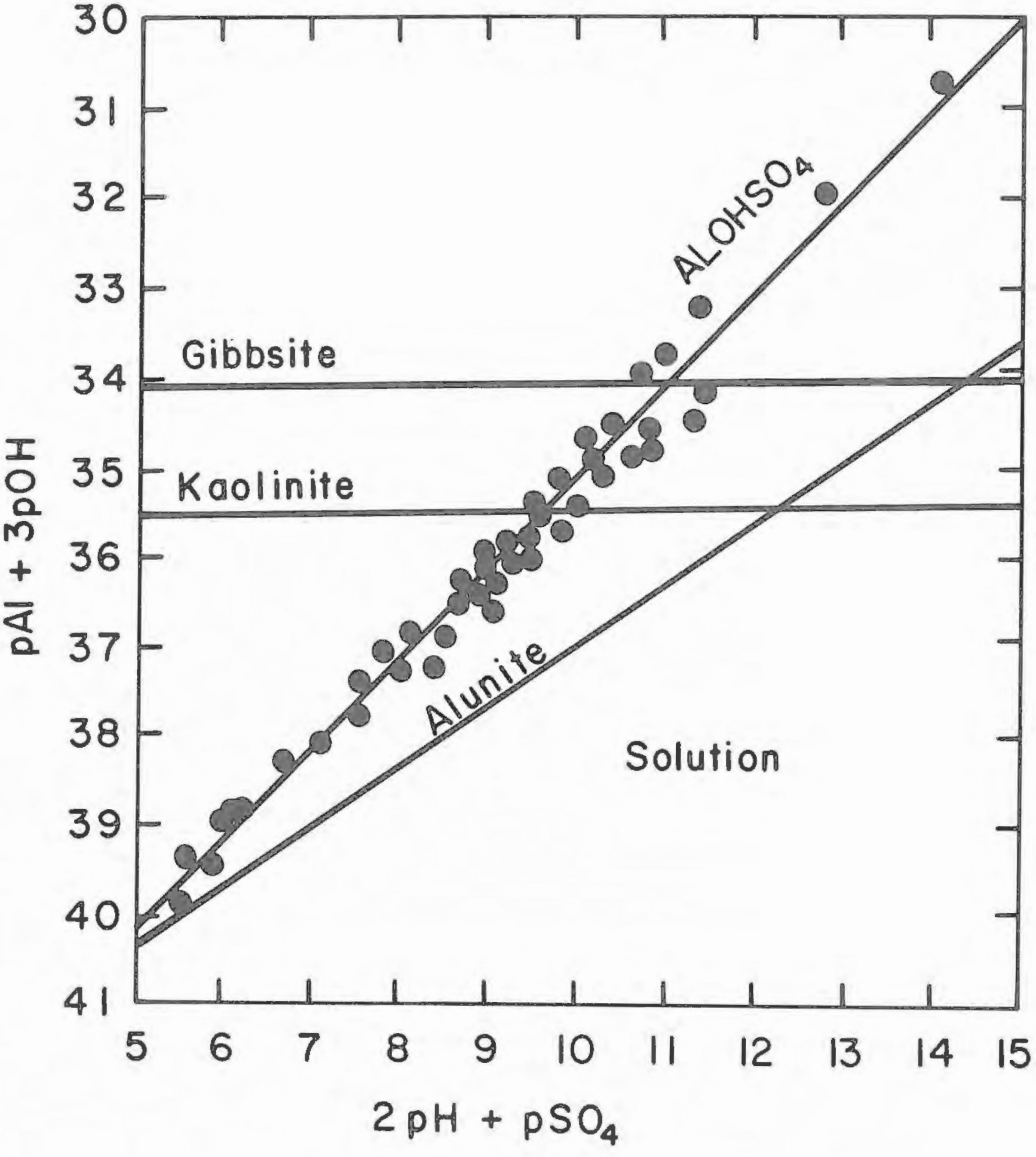

Fig. 5. Solubility diagram for gibbsite, alunite, kaolinite and $AlOHSO_4$. (Plotted symbols represent ground waters from Thailand and Sarawak, along with acid mine waters from Kentucky and Pennsylvania. (25).