

SOME CONSIDERATIONS WHEN APPLYING LIMESTONE/ROCK PHOSPHATE MATERIALS ON TO ACID PYRITIC SPOILS

Bill Evangelou
U. M. Sainju
E. Portig

Agronomy Department
University of Kentucky

Published in the 1991
Proceedings of West Virginia Surface Mine Drainage Task Force

ABSTRACT

Armoring of ameliorant agents (e.g. limestone, rock phosphate) employed as means of neutralizing acid pyritic spoils and/or acid drainages, leads to ameliorant inactivity. Although, armoring is visually observed in a field environment, knowledge on the mechanisms and on the quantification of armoring is not available. This knowledge would allow one to estimate accurately the quantity of ameliorant needed for a particular acid pyritic condition as well as predict potential effectiveness of the applied ameliorant. In this study, the mechanisms of armoring of calcite, dolomite and rock phosphate by manganese II (Mn^{2+}) were investigated employing Mn^{2+} adsorption isotherms as a function of ameliorant particle size, and surface Fourier transform infrared spectroscopy (FT-IR). The study reveals that Mn^{2+} adsorption onto limestone particles is an apparent exchange reaction. for every chemical equivalent of Mn^{2+} adsorbed, an equivalent quantity of Ca^{2+} is desorbed. Infrared spectroscopy (FT-IR) reveals that the bonding mechanism of Mn^{2+} onto limestone surfaces involves the formation of a hydroxyl (OH^-) bridge which facilitates Mn^{2+} oxidation and consequently limestone surface armoring. On the other hand, Mn^{2+} adsorption on to rock phosphate surfaces appears to involve an OH^- bridge as well as a strong Mn-Phosphate bridge. The data also demonstrate that the quantity of Mn^{2+} consumed for ameliorant armoring is greatest for rock phosphate followed by calcite and dolomite. However, this Mn^{2+} quantity is inversely related to the size of the ameliorant particle but is independent of the ratio of ameliorant to solution. The latter suggests that ameliorant armoring is independent of reaction kinetics and obeys equilibrium considerations. his strongly implies that magnitude of ameliorant armoring in the field is predictable.



The research leading to this document was supported by the United States Department of the Interior, Office of Surface Mining, under Cooperative Agreement No. HQ5I-GR87-10018, and

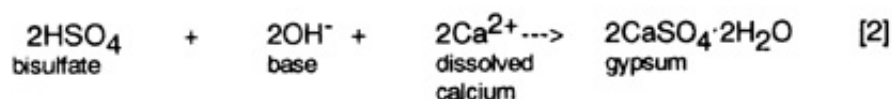
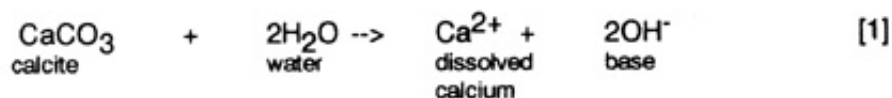
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LIMESTONE REACTIONS

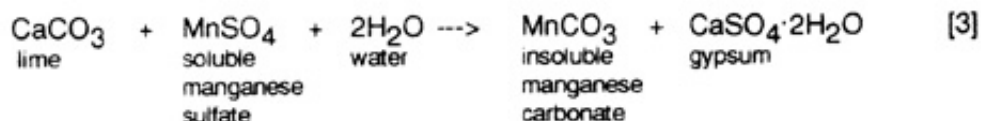
How Limestone Reacts With Acid Solutions And Acid Metals

The mechanism by which limestone is assumed to regulate acidity is by the generation of hydroxyls (OH^-) and/or the release of carbonate ions (CO_3^{2-}). These reactions are demonstrated below:



Reaction [1] shows the production of two hydroxyls (2OH^-) upon introducing limestone (CaCO_3) to water (H_2O). In reaction [2] the hydroxyls produced by reaction [1] are shown to react with bisulfate (HSO_4), a product of pyrite oxidation, leading to the production of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$). Keep in mind that gypsum, a product of acid mine drainage neutralization, by water quality drinking standards is quite polluting. Rain water percolating through a spoil containing free gypsum has the potential of reaching 600 mg/l dissolved calcium (Ca) and up to 1440 mg/l dissolved sulfate (SO_4). The maximum concentration of sulfate for drinking water is set by the US government at 250 mg/l.

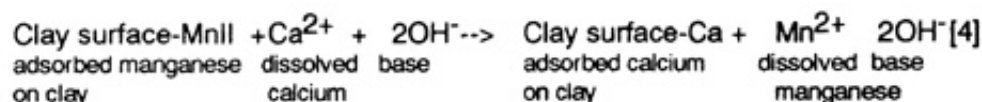
An additional mechanism of acid neutralization in mining environments is the precipitation of metals such as iron (Fe^{2+}) and manganese (Mn^{2+}) as iron carbonate (FeCO_3) and manganese carbonate (MnCO_3), respectively. The two metal carbonate minerals are quite water insoluble and acid resistant. The reaction is shown below:



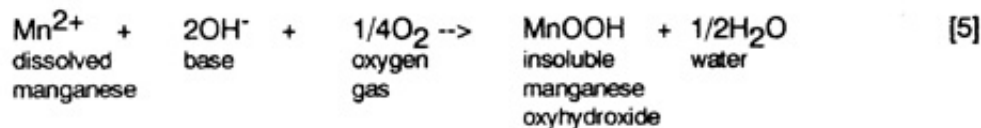
To what extent reaction [3] is taking place in spoils it is not known and it is hard to predict because of its dependency on spoil variables such as pH, partial pressure of carbon dioxide and spoil solution ionic composition.

A second set of reactions of the hydroxyls (OH^-) produced by CaCO_3 are those involving

adsorbed metals, e.g manganese (MnII), aluminum (AlII), iron (FeII) etc by clays and other solid surfaces. These reactions are shown below:



and



Reaction [4] shows how reduced or soluble manganese (MnII) adsorbed on to a clay surface reacts with soluble calcium derived from CaCO_3 . The process shows that MnII becomes soluble by being displaced from the clay surface by calcium (Ca^{2+}). The dissolved MnII according to reaction [5], reacts with hydroxyls and atmospheric oxygen (O_2) to produce an insoluble manganese oxyhydroxide. A similar reaction can be written for reduced or soluble iron (FeII).

In order for the above reactions to proceed one has to assume that limestone when applied to pyritic spoils remains intact and continues to dissolve until all of it is consumed. However, anyone who has applied limestone on pyritic mine spoils or on acid mine drainages or in sediments ponds has observed a process known as limestone coating or limestone armoring. The process involves the adsorption and oxidation of FeII and/or MnII on to the limestone surfaces. This renders the limestone nonreactive. The knowledge in predicting these limestone surface reactions is not available at this time, however, such reactions are expected to predominate in pyritic spoils that have remained exposed to the atmosphere and their solution has been enriched with dissolved iron (FeII) and manganese (MnII) (Table 1) or similarly limestone applied to drainages or sedimentation pond water enriched with dissolved iron and manganese. Evidence that such reactions are taking place in these environments is the discoloration of limestone particles when exposed to such environments. Additional evidence that such reactions are taking place when limestone is applied to pyritic spoils is the observation that limestone does not always control acid mine drainage production in the field.

Surface Manganese Adsorption Potential of Limestone Particles

In this article I will be presenting results from recent studies that we have completed. These studies deal with the evaluation of limestone, namely calcium carbonate (CaCO_3), dolomite ($\text{CaMg}(\text{CO}_3)_2$) and rock phosphate. We were particularly interested to demonstrate the capacity of these rocks to adsorb manganese (MnII). Based on field observations limestone applied to mine drainage waters containing high concentrations of manganese (MnII) and/or iron (FeII) or coal spoils containing high concentrations of manganese (MnII) and/or iron (FeII) in their solution (spoil solution is defined as the solution entrapped in the spoil material; see Table 1) reacts for the most part as a surface. In other words, the dissolved metals manganese (MnII) and iron (FeII) are precipitated (removed from water) not by lime

dissolution but rather by metal adsorption on to the lime's or rock phosphate's surface. The end result of this reaction is the coating or armoring of the lime/rock phosphate particles which renders these acid ameliorants ineffective. The data shown in Fig. 1a through Fig. 1d presents the results of these studies.

Table 1. Values of pH, electrical conductivity (EC) and concentration of various cations of the spoil saturation extracts.

Sample	pH	Ca	Mg	Fe	Mn	Al	SO ₄
I.D.	-----mg/liter-----						
1	2.36	503	194	89.0	107	808	6,644
2	2.74	446	151	10.6	59	386	3,864
3	2.08	437	215	16.40	245	234	43,015
4	2.65	424	232	181.5	180	1211	9,030
5	2.57	438	216	57.8	171	324	4,041

The data in Fig. 1 a and 1 b show that rock phosphate adsorbs more manganese II than either calcite or dolomite. The second important point shown in Fig 1 a and Fig. 1 b that the amount of manganese adsorbed by a mineral is particle size dependent. The smaller the particle the greater the quantity of manganese II adsorbed on to the surface. For example, when the average diameter of the rock phosphate particles is 1.5 millimeters one kilogram of rock phosphate adsorbs 300 milligrams of manganese at an approximate concentration of dissolved manganese of 2 ppm. On the other hand, rock phosphate with an average particle diameter of .025 millimeters adsorbs approximately 1,000 milligrams of manganese per kilogram weight with an average manganese concentration in solution of 2 ppm. The data in all five figures show that for every chemical equivalent of manganese adsorbed by any one of three ameliorants; an equivalent quantity of calcium or calcium plus magnesium (in the case of dolomite) is desorbed. This demonstrates that limestone armoring is accompanied with dissolution. However, the quantity of limestone dissolving is very small to take care of the acidity present.

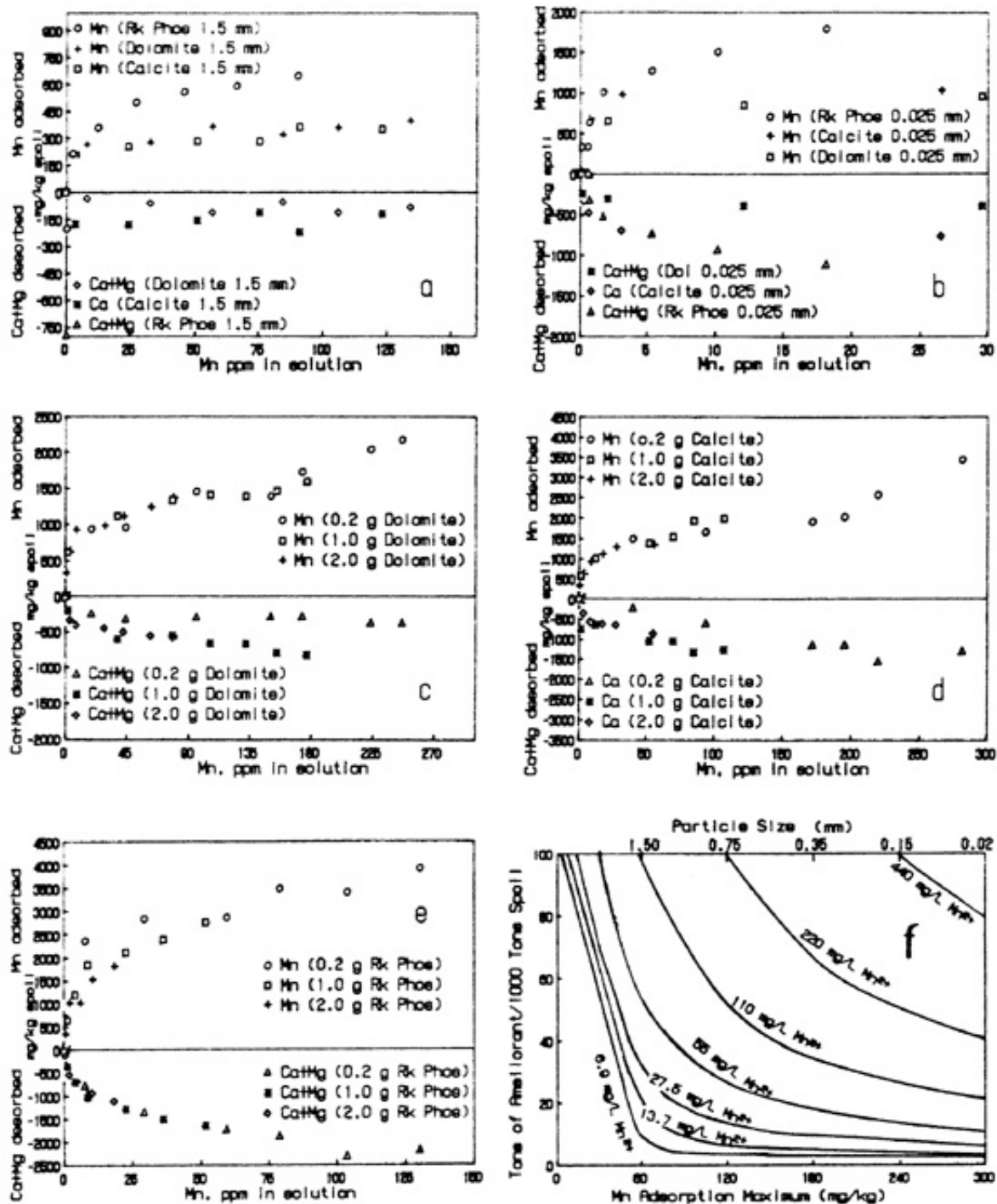


Figure 1. Plots showing the relationships between manganese II adsorbed by calcite, dolomite, and rock phosphate under various particle sizes and solid to solution ratios and manganese II dissolved in the solution (for more detail see text).

The data in Figs. 1 c, 1 d and 1 e show that the adsorption of manganese II by all three ameliorants (calcite, dolomite, rock phosphate) is independent of solid to solution ratio. This implies that the adsorption of manganese II on to solid surfaces is quite predictable.

Figure 1f shows the relationship between quantity of ameliorants and the maximum manganese II adsorption potential for various manganese II levels in the spoil solution. Note that it takes a small quantity of manganese II in solution to armor a large quantity of

limestone or rock phosphate. Assuming that precipitation of manganese II is carried out by ameliorant dissolution instead of surface adsorption then the amount of ameliorant needed would be a small fraction of that needed to remove an equivalent quantity of manganese II by surface adsorption. For example, assuming a calcium carbonate sample, in a granulated form, with a surface manganese adsorption potential of 250 milligrams per kilogram is incorporated into a spoil with approximately 100 ppm of manganese II in the spoil solution, it will require approximately 20 tons of limestone per acre, six inches deep to neutralize this manganese. On the other hand, if we assume that limestone would react through dissolution with dissolved manganese II in order to neutralize the same amount of manganese II as above (100 mg/l) it would only take approximately 1000 lbs of lime per acre, six inches deep.

Note that much of what it is said about manganese also applies to iron. The chemistry of these two metals is fairly similar when it concerns their removal from water. We chose to investigate manganese because it is a little harder to remove from water than is to remove iron.

SUMMARY

The main points that are to be made from the findings in this study is that when reclaiming pyritic spoils that have been exposed to the elements of nature for a number of years then a significant quantity of manganese II and iron II are in the dissolved form. This can be determined by obtaining a fresh composite sample of the spoil from various spoil depths and submitting it to a laboratory for a saturation extract test. If the dissolved manganese II plus iron II are in a quantity greater than 10 mg/l then the limestone should be split in two applications. The first application should be no more than a one third of the total lime needed. This first lime application it would react with dissolved metals by adsorbing them on its surface, The second application should be done after a month or two from the first application. Ideally some wetting (rainfall) and drying should have taken place during the period between the first and second lime or any ameliorant application. This will ensure that the ameliorant applied in the first application has reacted and removed the dissolved metals (manganese and iron) from the soil solution. This in turn will ensure that the ameliorant of the second application won't be armored and rendered chemically inactive. Ideally, when one deals with pyritic spoils with solution highly enriched with dissolved manganese and/or iron (iron and/or manganese greater than 50 mg/l in the saturation extract) then before the second ameliorant application the dissolved iron and manganese should be checked by a saturation extract. Dissolved iron and manganese should be near zero before proceeding with the second application. A similar approach should be taken when one neutralizes acid drainages enriched with dissolved iron and manganese.

This study also shows the reason for the importance of using fine particle limestone in pyritic spoils. Mine operators often make it a practice in using limestone rejects rather than agricultural limestone which is regulated by law.