Need for Solution or Exchangeable Calcium and/or Critical EC Level for Flocculation of Clay by Polyacrylamides

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It is generally accepted that low EC (electrical conductance) is not conducive to flocculation of clay with anionic water-soluble polyacrylamide (WS-PAM) *(Aly and Letey 1988, Ben-Hur and Letey 1989, Letey et al. 1992)*, that calcium from gypsum and other sources serves as a bridging agent between clay and anionic WS-PAM *(Shainberg et al. 1990)*, and that electrolytes, even without WS-PAM, can contribute to water stability of soil aggregates *(Shainberg and Letey 1984, Shainberg et al. 1989, Sumner and Miller 1992)*.

Even if calcium is required as a bridging agent with anionic WS-PAM, its absolute requirement really is not very large. If irrigation water contained 10 mg/l of WS-PAM with 20% negative charges, and if the molecular weight of the WS-PAM were 15 million Daltons, we calculate that the requirement for calcium ions, if there is a 1:1 relationship, would be 2.86×10^{-5} molar. This is equivalent to an EC of about 0.003 dS/m. If a 10-fold excess were needed for rapid reaction, the EC need for calcium would be only 0.03 dS/m.

In our landscape work with WS-PAM where we use a 20% anion-charged molecule, we have encountered many situations where the polymers did not result in good flocculation of the soil unless gypsum was also applied. Calcium, which is contained in gypsum, is considered to be the bridging agent between the anionic polymer and the negative charges on the clay *(Aly and Letey 1988)*. This could be one reason why WS-PAM can fail to function in some situations.

One situation poorly responsive to WS-PAM was a soil with pH of about 8.5 and highly sodic and calcareous. The EC was not low, but the soluble calcium was. With simultaneous application of gypsum, response to WS-PAM was pronounced (transplanted trees grew four times more in the first four months than did control trees) *(Unpublished Newsletter, June 1987)*.

Much of the irrigation water used in the California San Joaquin Valley is low in EC (less than 0.2 dS/m at 25° C) because the water is mostly snow melt coming from mountains having volcanic rock. This water results in poor infiltration into soil with associated irrigation and crop yield problems *(Wildman et al. 1988)*. A whole industry has been developing to help growers cope with the problem. Devices have been built to inject solution-grade gypsum into irrigation systems *(Traynor 1986)*. Some, but not all, mined gypsum is of sufficient purity and solubility that, when ground to appropriate particle sizes, can be engineered to flow into irrigation systems.

When 50 kg solution-grade gypsum is applied to a hectare of land in 2.5 cm of irrigation water, the concentration of calcium in the water is about 44 mg/l assuming that the gypsum were 95% pure. This would also add about 0.2 EC in dS/m to the irrigation water. The range of calcium addition to the irrigation water is usually 40 to 100 mg/l. This has a considerably favorable effect on maintaining permeability of the soil *(Shainberg et al. 1989)*. It could be important also for enhancing the value of WS-PAM.

Calcium from gypsum or from other sources does have the capacity to flocculate clays so gypsum alone at effective concentrations should prevent soil erosion at least to a degree. Actually, a higher EC with cations other than calcium can flocculate soil also *(Shainberg and Letey 1984)*. A hypothesis for testing then can be that gypsum combined with WS-PAM could more effectively control erosion in irrigation furrows than could WS-PAM or gypsum alone, especially if the irrigation water were low in EC or if the combination of irrigation water EC and soil solution EC were low.

Several other workers have found that a high EC within limits enhances the ability of WS-PAM to control erosion *(Levy et al. 1992; Shainberg and Levy 1994)*. WS-PAM of the anionic type (about 20%) has been reported to be extremely effective in the control of erosion in furrow irrigation and in other ways *(Lentz et al. 1995; McCutchan et al. 1993; and Sojka and Lentz 1994)*.

Materials and Methods

Three soils were used in laboratory studies. The soils have been used in previous studies and described in some detail. One soil has pH of over 8 and an EC of about 3.5 dS/m in the saturation extract *(Mitchell 1986, Wallace and Nelson 1989)*. Another has a pH of about 4 and an EC of about 0.15 dS/m in the saturation extract *(Wallace 1989)*. The third soil is of pH about 6 *(Wallace and Nelson 1986)* and an EC of about 0.25 dS/m. Samples of the soils were leached with deionized water (EC = 0.005 dS/m) to equilibration which was about 0.09 dS/m for the pH 8 soil, 0.027 dS/m for the pH 4 soil and 0.04 dS/m for the other. The equilibrium EC of the pH 8 soil was limited by solubility of components in the soil, probably all as $CaCO_3$. The three soils are designated as Holtville (pH 8), Tilson (pH 4), and Yolo (pH 6).

For some tests the pH 4 soil was neutralized to pH 7 by either $Ca(OH)_2$ or KOH. The EC of test suspensions was varied with gypsum and NaCl. Polymers tested were polyacrylamides of 5 to 15 million Daltons and representing 0, 20 and 40% anionic charge which resulted from copolymerization with acrylate where necessary.

Five gram samples of each soil were used in test tubes with 10 ml of appropriate solution representing various EC (corrected to 25° C) and various salts. Soils were of near uniform particle size to facilitate easy suspension when shaken. Stock solutions were prepared of the WS-PAM for a 0, 20 and 40% charge density at the concentration of 100 mg/liter. Increments of the WS-PAM were pipeted into the test tubes with agitation for each increment. Flocculation was determined as the appearance of a very clear solution. In some cases, where the result was indicated as biphasic, flocculation did occur, but a fraction of fine clay was not easily flocculated. Multiple determinations were made for each condition. Tests were also made with unleached Tilson soil.

Results

The results are summarized in Tables 1 to 4. No soil flocculated well with any WS-PAM in solutions with very low EC (less than 0.1 dS/m). As EC was increased with gypsum and with NaCl, amounts of PAM needed for flocculation generally decreased. A leveling-off effect was observed. Generally, maximum flocculation was achieved with EC between 1 and 2 dS/m although at slightly lower EC, flocculation was often satisfactory.

With the pH 4 soil, the 0 charge WS-PAM was somewhat more effective than the 20 and 40% negative charge WS-PAM. Iron and aluminum possibly denatured the negative charged WS-PAM with this soil. The reverse charge density effect was observed for the pH 8 soil. The latter soil does contain some smectite. Another possibility is increasing charge repulsion as the anionic charge was increased. This factor should obtain at all pH values but was not general.

The poor flocculation effects with low EC seemed to be a biphasic reaction. This means that there was flocculation of the larger particles in suspension in the presence of low EC, but the finer particles actually sometimes never did flocculate. The concentration of non-flocculated fines was around 2 to 5 g/l.

The rationale for study of the very acidic soil together with WS-PAM of variable charge was that the procedure perhaps could be a vehicle for identifying some of the relationships between bridging and electrical conductivity on flocculation of soil. It was reasoned that if there was a dif-

Table 1. Amounts of WS-PAM of different charge density needed to flocculate a leached acid soil with and without neutralizing with Ca(OH)2 and at different EC values (mg per liter with 5 g soil in 10 ml solution).*

pH of soil	Negative charge density		
	0	20	40
		EC less than 0.04 dS/m	
4	45	40	50
7	22	20	45
		EC around 0.4 dS/m	
4	8	10	13
7	10	11	14
		EC near 2 dS/m	
4	10	13	22
7	3	5	17

* *The EC was varied with gypsum*

ference in the amount of WS-PAM needed for flocculation of the pH 4 soil compared with the same soil after being neutralized to pH 7 with $Ca(OH)_2$ it may be possible to determine the importance of the bridging mechanism. Both pH 4 and pH 7 soil suspensions would have the same electrical conductivity at the low-EC level. Also in the case of 0 charge, the aluminum and iron available in the pH 4 soil would not denature the WS-PAM. Further, neutralizing the soil with KOH would not be beneficial if bridging were the mechanism.

The results with this acid soil did indicate that with EC around 0.04 dS/m and with 0 charge WS-PAM, less WS-PAM was needed for flocculation at pH 7 than at pH 4 (Table 1). Neutralizing to pH 7 with KOH with no change in EC did not result in a decrease of WS-PAM needed for flocculation as did neutralizing with $Ca(OH)_2$. Both results, at least mildly, indicate need for bridging. There are even possible bridges between amide groups and clay.

Increasing the EC to 0.4 dS/m with gypsum decreased the amount of WS-PAM of 0 charge needed for flocculation at both pH 4 and pH 7 (Table 1). The critical need for minimum EC for effective flocculation is therefore substantiated.

Even higher EC (1.6 dS/m and higher) resulted in less WS-PAM needed for flocculation, especially at the 0 charge.

It was further reasoned that if calcium bridging were of major importance in flocculation that it would be very pronounced in the amount of WS-PAM needed for flocculation as the anionic charge of the WS-PAM were increased. This was not generally seen. Aluminum and iron denaturing the anionic WS-PAM at pH 4 had to be considered as a possibility, however.

There was some indication of denaturing of the WS-PAM of 20 and 40% anionic charge at low soil pH (Table 1). There was also little effect of soil pH on the amount of anionic WS-PAM needed for flocculation at any EC, but there was some effect for the 0 charge where decreases were noted for both increasing pH and increasing EC to about 2 dS/m.

Much less WS-PAM was needed for flocculation of the unleached soil

Table 2. Amounts of WS-PAM of different charge density needed to flocculate an unleached acid soil with and without neutralizing with Ca(OH)2 and at different EC values (mg per liter with 5 g soil in 10 ml solution).*

pH of soil	Negative charge density 0	20	40
	EC less than 0.08 dS/m		
4	15	10	11
7	10	6	12
	EC around 0.6 dS/m		
4	6	7	6
7	3	3	6
	EC near 1.6 dS/m		
4	3	4	5
7	3	4	5

**The EC was varied with gypsum.*

Table 3. Amounts of WS-PAM of different charge density needed to flocculate two different soils leached to remove salts and at different EC values (mg per liter with 5 g soil in 10 ml solution).*

Soil	Negative charge density 0	20	40
	EC less than 0.1 dS/m		
pH 8 (Holtville)	60	38	25
pH 6 (Yolo)	7	18	24
	EC around 0.4 dS/m		
pH 8 (Holtville)	20	13	13
pH 6 (Yolo)	3	2	1
	EC near 2 dS/m		
pH 8 (Holtville)	8	8	8
pH 6 (Yolo)	1	1	0.5

**The EC was varied with gypsum.*

than the leached soil (Table 2) even though the EC values were almost the same. Again there was more indication of calcium bridging for the 0 charge WS-PAM than the 40% negatively charged WS-PAM. The reason why leaching causes a loss of flocculation ability other than decreasing the EC is not known.

The Holtville (pH 8) and Tilson (pH 4) soils do contain some smectite minerals. They may have more of a bridging requirement than soils that do not contain smectites. They had need for higher EC for flocculation than the Yolo soil of pH 6 (Tables 1-3).

When leached, the Holtville and Yolo soils did not easily flocculate at EC values less than 0.1 dS/m (Table 3). The high negative charge density was of less effect with the Holtville soil than the 0 charge WS-PAM, but was more important with the Yolo soil where increasing charge density resulted in less WS-PAM needed for flocculation except at low EC. The 0 charge was less effective for Yolo than high charge. The critical EC for flocculation leveled off at around 2 dS/m, and the most effective EC was between 0.5 and 2 dS/m, but will vary with soil types.

In table 4 are amounts of WS-PAM needed for flocculation of the leached three soils at one level of NaCl (EC of around 3 dS/m). The NaCl was a very effective source of EC and flocculation was comparable with that obtained from gypsum. NaCl itself can flocculate soil *(Shainberg and Letey 1984).* The 40% anionic WS-PAM resulted in more polymer needed for flocculation in the pH 4 soil than for less charged WS-PAM which could indicate a need for bridging with calcium or partial denaturing of WS-PAM or could indicate the effect of repulsion of negative charges.

The 20% anionic charged WS-PAM of high molecular weight is generally preferred and used as a soil conditioner. The results here tend to imply that at least in some circumstances, the 0 charge and the 40% charge can also be managed to function satisfactorily. Results and logic suggest that cation bridging would be of some importance for the 20% charge and even more so for the 40% charge and be of little or no importance for the 0 charge WS-PAM. This may be only partially correct.

The relationships among EC, degree of negative charge of the WS-PAM, types of soil and types of salt so far are not completely clear. Although more studies are indicated, there are some trends worth noting.

Table 4. Amounts of WS-PAM of different charge density needed to flocculate the three different after leaching to reduce EC levels followed by treatment with NaCl to provide a solute concentration of near 3 dS m-1 (mg per liter with 5 g soil in 10 ml solution).

Soil*	Negative charge density 0	20	40
pH 4	2	5	10
pH 6	2	1.5	1.5
pH 8	9	7	9

The three soils were described in text.

Discussion

Several important points are suggested by the data and the literature:

1. Both EC and calcium are variously needed in the flocculation process with anionic WS-PAM, but EC may be the most important. EC and calcium may also be important in flocculation with 0 charge WS-PAM.
2. The amide groups as well as anionic groups participate in binding to clay and to other surfaces.
3. Very low pH can be detrimental to flocculation of anionic WS-PAM with clay partly because iron and aluminum tend to denature the WS-PAM, but this can be circumvented with increasing soil pH.
4. Gypsum and even NaCl alone without WS-PAM can flocculate soil, but both may be more effective when combined with WS-PAM.
5. Non-anionic WS-PAM can, in some situations, be more effective than anionic PAM for flocculation (results may be different for stability of the flocculated soil).
6. NaCl used to increase with EC was effective in promoting flocculation together with WS-PAM but gypsum may be more effective.
7. Soils do vary considerably in the amount of WS-PAM needed for flocculation of soil.

Where gypsum machines are used to put gypsum into irrigation water, simultaneous addition of WS-PAM may be worthwhile when erosion control and even more water infiltration are needed. This assures a source of calcium and also an adequate EC for full function of the WS-PAM. Both calcium and EC independently add to the flocculation effect. The gypsum and the WS-PAM, may need to be applied separately, however.

It may be of interest that in our studies of zeolites and similar materials with high cation-exchange capacity, less WS-PAM of 0 charge is needed for flocculation than with 20 and 40% negatively charged WS-PAM. But EC is important there also. Mechanisms may not be easy to define because WS-PAM of varying charge also flocculates such items as elemental sulfur and lime.

Summary

We have frequently observed in our field work that coapplication of gypsum with polyacrylamide leads to increased flocculation of soil. Various techniques have been used in the laboratory to evaluate the possible importance of either or both calcium bridging and solute concentration (EC) on the flocculation process. For study a calcareous soil of pH over 8 and slightly saline was leached with deionized water to an EC of 0.08 dS/m in the leachate. An acid clay soil of pH near 4 was leached to 0.027 dS/m and was studied with and without neutralization with Ca(OH)2 and KOH. Non-leached samples were also studied. A third soil of pH near 6 was leached to 0.04 dS/m. The EC in the systems was varied with gypsum and NaCl. Polyacrylamides used had around near 0, 20, 40% anionic charges. Full flocculation was exceedingly difficult to achieve in the very low solute soils. There may be a two-component effect. Neutralization of the acid soil with $Ca(OH)_2$ dramatically increased flocculation, but neutralization with KOH did not. Both gypsum and NaCl were effective in enhancing the flocculation.

The absolute need for calcium as a bridging agent was not proved in the tests, but there were strong indications of the need for minimal EC to obtain most effective flocculation as indicated in much of the literature. Only small differences were noted for the polymers of variable charge indicating the importance and function of the amide groups in flocculation through binding with clay. Calcium bridging with anionic groups is not the main factor in flocculation with 20 and 40% anionic charged polyacrylamide; binding of the amide groups is perhaps more important. Frequently observed higher requirements of polyacrylamide for flocculation as the anion charge was increased may be related either to denaturing of the polyacrylamide with soluble iron and aluminum at low pH or to repulsion of anionic charges.

References Cited

Aly, S.M., and J. Letey. 1988. Polymer and water quality effects on flocculation of montmorillonite. Soil Sci. Soc. Am. J. 52:1453-1458.

Ben-Hur, M., and J. Letey. 1989. Effect of polysaccharides, clay dispersion, and impact energy on water infiltration. Soil Sci. Soc. Am. J. 53:233-238.

Lentz, R.D., T.D. Stieber, and R.E. Sojka. 1995. Applying polyacrylamide (PAM) to reduce erosion and increase infiltration under furrow irrigation. Proceedings 1995 Idaho Winter Community Schools:In Press.

Levy, G.J., and M. Agassi. 1995. Polymer molecular weight and degree of drying effects on infiltration and erosion of three different soils. Aust. J. Soil Res. 33:1007-1018.

Levy, G.J., J. Levin, M. Gal, M. Ben-Hur, and I. Shainberg. 1992. Polymer's effects on infiltration and soil erosion during consecutive simulated sprinkler irrigations. Soil Sci. Soc. Am. J. 56:902-907.

McCutchan, H., P. Osterli, and J. Letey. 1993. Polymers check furrow erosion, help river life. Calif. Agric. 47(5):10-11.

Mitchell, A.R. 1986. Polyacrylamide application in irrigation water to increase infiltration. Soil Sci. 141:353-358.

Miller, W.P. 1995. Environmental considerations in land application of by-product gypsum. Agricultural Utilization of Urban and Industrial By-Products, ASA Special Pub. No. 58, Chapter 9, pp. 183-208.

Shainberg, I., and J. Letey. 1984. Response of soils to sodic and saline conditions. Hilgardia 52(2):1-57.

Shainberg, I., and G.J. Levy. 1994. Organic polymers and soil sealing in cultivated soils. Soil Sci. 158:267-273.

Shainberg, I., M.E. Sumner, W.P. Miller, M.P.W. Farina, M.A. Pavan, and M.V. Fey. 1989. Use of gypsum on soils: A review. Advances in Soil Sci. 9:1-111.

Shainberg, I., D. Warrington, and P. Rengasamy. 1990. Effect of PAM and gypsum application on rain infiltration and runoff. Soil Sci. 149:301-307.

Sojka, R.E., and R.D. Lentz. 1994. Time for another look at soil conditioners. Soil Sci. 158:233-234.

Sumner, M.E., and W.P. Miller. 1992. Soil crusting in relation to global soil degradation. Am. J. Altern. Agr. 7:56-62.

Traynor, J. 1986. Coping with low calcium water. Fruit Grower November:16-A.

Wallace, A. 1989. Mineral composition for nineteen elements in young corn (Zea mays) plants grown in an acid soil with various treatments to overcome infertility of acid soils. Soil Sci. 147:451-453.

Wallace, A., and S.D. Nelson. 1986. Special issue on soil conditioners. Soil Sci. 141:311-397.

Wildman, W.E., W.L. Peacock, and A.M. Wildman. 1988. Effect of amendments on water penetration from drip irrigation, pp. 481-490. IN: Yu-Si Fok, Ed., Infiltration Principles and Practices, Proc. In'l Conf. on Infiltration Development and Application, Water Resources Res. Center, U. of Hawaii, Honolulu.