



The effects of palygorskite on chemical and physico-chemical properties of soils: a review

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Abstract

Very little was known about how palygorskite affects soil properties when it constitutes a significant component of the soil clay fraction. This constituted a serious impediment for the proper management of palygorskite-containing soils under irrigated agriculture. The present review is intended to summarize studies on the effects of palygorskite on chemical and physico-chemical properties of soils carried out in recent years, and to discuss future research required in this area. When palygorskite-containing soils are involved in irrigation practices, release of Mg from palygorskite into the soil solution will occur. Magnesium as an exchangeable cation, in turn, is known to decrease aggregate stability and to enhance the dispersivity of the soil clay fractions. On the other hand, magnesium as a dissolved cation is known to improve phosphorus availability in arid soils. Knowledge of factors affecting rheological properties of soil clay suspensions is essential for understanding of mechanisms of water and solid particle transfer through the soil profile. The rheological behavior of soil clay suspensions is, however, complex and cannot be predicted from that of suspensions of standard clays. Although the flocculation value of palygorskite at near neutral pH is significantly lower than that of smectite, the presence of palygorskite in the soil clay fraction will not affect the flocculation value of the soil clay since smectite, which is always present in the clay fraction of palygorskite-containing soils, has a dispersive effect on palygorskite. Palygorskite has the strongest disaggregation potential and the highest ability to migrate in the soil among common phyllosilicates such as smectite and kaolinite. Palygorskite particles are thus likely to move preferentially over smectite and kaolinite downward in the soil profile, and eventually to clog soil pores. Disaggregation and migration of palygorskite from the surface-soil during rainfall and/or irrigation may have an effect on the degree of erosion as well. Palycretes (duripans in which the cementing material is dominantly composed of palygorskite) can be formed in some landscapes. Where palycretes occur close to the surface, plant growth is severely impeded. Palycretes also reduce water permeability of the soils, creating water-logged conditions that necessitate drainage installation.

Although some progress has been made recently in understanding the effects of palygorskite on chemical and physico-chemical properties of soils, much research remains to be done. Performing some additional studies on disaggregation potential and migration ability of palygorskite under conditions close to those in the field is strongly desirable. Scanning electron microscopy observations on possible changes in aggregation of palygorskite in soils following intensive irrigation might be useful. Studies of the rheological behavior of soil clays with different mineralogical composition, and

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palygorskite-containing soil clays in particular, are strongly encouraged. There is a need as well to study interactions of various contaminants (both organic and inorganic) with palygorskite-containing soil clays.

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1. Introduction

Palygorskite is a clay mineral characterized by a microfibrillar morphology, low surface charge, high magnesium content and high specific surface area. Palygorskite-containing soils occur almost exclusively in arid and semiarid areas of the world. Palygorskite-containing soils can be cultivated profitably only by using irrigation, where management practices have to take account on the effects of flowing water on soil properties.

Singer (2002) reviewed the basic mineral characteristics of palygorskite, as well as the means of its identification, and discussed its origin, as well as its environmental significance. The author emphasized, however, that very little is known about how palygorskite affects soil properties when it constitutes a significant component of the soil clay fraction. This constitutes a serious impediment for the proper management of palygorskite-containing soils under irrigated agriculture.

Following the above-mentioned review, some studies have been performed and progress has been made in understanding the effects of palygorskite on chemical and physico-chemical properties of soils. The present review is intended to summarize these recent studies as well as to discuss future research required in this area.

2. Mg-chemistry of palygorskite-containing soils

Palygorskite has been shown to be rather unstable in humid areas of the world. According to Paquet and Millot (1973), palygorskite weathers into smectite when the mean annual rainfall exceeds 300 mm. According to Singer and Norrish (1974), palygorskite is stable only at relatively high Si and Mg activities and alkaline pH. Palygorskite is the most magnesium-rich among the common clay minerals (Weaver and

Pollard, 1973; Singer, 2002). Although sepiolite contains more Mg than palygorskite, sepiolite in soils has been reported from only a few locations (Singer, 2002). Based on acid leaching experiments of palygorskite, Mg appears to be preferentially released into solution over Fe and Al (Singer, 1977; Corma et al., 1987, 1990). The aggressive environment created by acids, however, can hardly serve as a model for the soil medium in which palygorskite occurs.

Neaman and Singer (2000a) conducted batch experiments with dilute salt solutions under neutral conditions in the presence of cationic resin to study the kinetics of clay dissolution. The presence of the cationic resin was intended to prevent equilibrium being attained, and dilute salt solutions were considered to be a better approximation to soil solution than deionised water.

The rates of mineral dissolution differed significantly among five standard¹ palygorskite samples of different origin with different chemical compositions used in the study. Rates of Mg release were in the range from 2.0×10^{-15} to 1.6×10^{-14} mol Mg/(m² s). The differences in release rate of Mg among the palygorskite samples were due to differences in chemical composition: release rate of Mg increased with Mg content in the clays.

Since smectite is always present in the clay fraction of palygorskite-containing soils and may also release Mg into soil solution, the authors examined the dissolution of saponite and Mg-rich montmorillonite as well. The release rate of Mg from Mg-rich montmorillonite (1.9×10^{-15} mol Mg/(m² s)) was lower than that from palygorskites. The release rate of Mg

¹ Herein and below, “standard palygorskite (or smectite or montmorillonite or kaolinite or illite) clays” are defined as clays obtained from deposits, in which palygorskite (or smectite or montmorillonite or kaolinite or illite, respectively) is the major mineral phase, and differ from “soil clays”, which contain a mixture of minerals.

from saponite (7.5×10^{-15} mol Mg/(m² s)) did not exceed that from palygorskites.

Magnesium release from some palygorskite–smectite–kaolinite-containing soil clays (from which carbonates, iron oxides and organic matter had been removed) under neutral conditions was studied as well (Neaman and Singer, 2000b). Palygorskite was suggested to be the only significant source of Mg released from the soil clays studied. The release rate of Mg from soil clays (2.2×10^{-15} to 7.5×10^{-15} mol Mg/(m² s)) was similar to that from standard palygorskites. Thus, the models suggested for dissolution of standard palygorskite clays were applicable for Mg release from palygorskite-containing soil clays.

These data suggest that, when palygorskite-containing soils are involved in irrigation practices, release of Mg from palygorskite into soil solution will occur. Magnesium as an exchangeable cation, in turn, is known to decrease aggregate stability and to enhance the dispersivity of the soil clay fractions (Shainberg et al., 1988; Keren, 1991), which is not desirable for soil management under irrigation. On the other hand, magnesium as a dissolved cation is known to reduce phosphorus fixation on calcite, increase desorption of phosphorus sorbed on calcite and inhibit formation of Ca-phosphates (Shariatmadari and Mermut, 1999). Thus, the presence of palygorskite as a slow release source of Mg can improve P availability in arid soils.

3. Flocculation of palygorskite-containing clays

Flocculation of clays has received much attention because of its effect on the physical behavior of soil. Flocculation value (FV) is the minimum electrolyte concentration necessary to flocculate a given colloid dispersion in a given time (van Olphen, 1977).

Neaman and Singer (1999) investigated flocculation of standard palygorskites, palygorskite–montmorillonite mixtures and palygorskite-containing soil clays. The flocculation of the clays was determined visually by settling after 24 h of standing in a series of test tubes. The FV of Na-saturated palygorskites at near neutral pH was found to be significantly lower than that of Na-saturated montmorillonite from Wyoming. The FVs of four standard palygorskites of different origins were in the range from 0.2 to 2.5

meq/l NaCl and the FV of Na-montmorillonite was 13.3 meq/l NaCl at near neutral pH values. The authors related low FV of palygorskite to its low rate of isomorphic substitution and to its low negative surface charge. Flocculation values of palygorskite–montmorillonite mixtures at near neutral pH values increased with montmorillonite percentage in the mixture. At a specific concentration of montmorillonite in the mixture (in the range of 40–60%), the FV of the system attains the FV of pure montmorillonite and does not change with further montmorillonite addition. FVs of three palygorskite–smectite–kaolinite-containing soil clays (from which carbonates, iron oxides and organic matter had been removed) at near neutral pH values were the same as FV of standard montmorillonite.

Studies by Goldberg and Glaubig (1987) for kaolinite–montmorillonite mixtures as well as the above-mentioned results of Neaman and Singer (1999) indicate that smectite has a dispersive effect on both kaolinite and palygorskite. Thus, presence of palygorskite in the clay fraction of soils that contain also smectite does not influence the FV of the soil clay.

Industrial experience, indicating a relatively low rheological susceptibility to salts of palygorskite muds compared with smectite muds (e.g., Galán, 1996), suggests that the FV of palygorskite is higher than that of smectite. Above-mentioned data indicate, however, that the FV of palygorskite at near neutral pH is significantly lower than that of montmorillonite. This apparent contradiction can be explained as follows.

Electrolyte addition to concentrated suspension of palygorskite used for industrial applications causes coagulation of the fibers, which, in turn, increases viscosity of the suspension. The influence of electrolyte addition on the viscosity of palygorskite suspensions is slight, because the initial magnitude of the surface charge is low and electrostatic repulsion is weak (Neaman and Singer, 2000c).

Neaman and Singer (1999) indicated that only very diluted suspensions (<0.1% w/v) can be used for FV measurements of palygorskite using flocculation series tests. Two parts of the flocculation process can be distinguished: (1) association between the individual particles and formation of flocculi (coagulation) and (2) settling of flocculi formed, under gravitation. Although coagulation occurs in relatively concentrated (>0.5% w/v) palygorskite suspension with salt addi-

tion, the flocculi formed cannot settle down under gravitation due to formation of a three-dimensional network structure or “scaffolding structure” (van Olphen, 1977) throughout the mass of the suspension at large clay concentrations.

Dixon and Golden (1990) described the problem of dewatering and sedimentation of palygorskite–smectite suspensions that are waste products produced in the phosphate mining areas in Florida. The sedimentation of these clays proceeds at a very slow pace even in saline environments due, most probably, to formation of a three-dimensional network structure throughout the mass of the suspension, preventing the settling of flocculi.

Thus, low FVs of dilute palygorskite suspensions and low rheological susceptibility of concentrated palygorskite suspensions to salts known from industrial experience as well as low sedimentation rates of concentrated palygorskite suspensions in saline environments are not contradictory. The apparent contradiction can be explained by differences in clay concentrations used for FV measurements and in industrial applications.

4. Rheology of palygorskite-containing suspensions

Clay dispersion occurs when the electrolyte concentration in the percolating solution in soil is below the flocculation value of the clay. Under such conditions, water flow in the soil changes from flow of solution to flow of clay suspension (e.g., Pupisky and Shainberg, 1979). The presence of clay particles in the percolating solution may increase significantly the viscosity of the flowing suspension and, therefore, may decrease its fluidity (which is the reciprocal of viscosity). This, in turn, would decrease soil hydraulic conductivity. When particle–particle interactions occur, causing non-Newtonian flow, soil hydraulic conductivity decreases even further (Hillel, 1998).

Knowledge of factors affecting rheological properties of soil clay suspensions is essential for understanding of mechanisms of water and solid particle transfer through the soil profile. The rheological parameters of clay suspensions can be used to evaluate particle–particle interactions. Although there have been many studies on the rheological behavior of suspensions of standard clays, studies on the rheology

of suspensions of mixed clays and soil clays remain limited. The rheological properties of mixed clay and soil clay suspensions are, therefore, not yet fully understood and appreciated.

Neaman and Singer (2000c) investigated the rheology of aqueous suspensions of six standard palygorskites of different origin with different particle morphologies as a function of clay concentration, adsorbed ion, pH and electrolyte concentration. It was found that some rheological properties of palygorskite were similar to those of platy clay minerals such as kaolinite and montmorillonite, while other rheological properties deviated considerably. The models developed to explain the rheological behavior of platy clay minerals did not always account for the behavior of palygorskite, because of differences in particle morphology and surface structure. The authors suggested some new models.

Neaman and Singer (2000d) studied the rheology of mixed palygorskite–montmorillonite suspensions. Addition of montmorillonite to palygorskite suspensions did affect the rheological behavior of the system. The degree of interaction between palygorskite and montmorillonite particles depended on the montmorillonite concentration in the mixture. Small (up to 10% w/v) montmorillonite additions increased the rheological parameters (plastic viscosity and Bingham yield value). Increased additions (10–20% w/v) of montmorillonite, however, decreased the rheological parameters. At even larger montmorillonite additions, in the range of 20–40% w/v, the suspensions showed nearly Newtonian flow, with a plastic viscosity equal to the initial value of pure palygorskite suspension. Thus, at montmorillonite concentrations of 20–40% w/v in the mixture, the interactions between palygorskite and montmorillonite particles were negligible, possibly because palygorskite and montmorillonite prevent each other from forming a three-dimensional network structure in the suspension. Additions of montmorillonite over 40% w/v increase sharply the rheological parameters of the suspensions.

The rheology of some palygorskite–smectite–kaolinite-containing clays of soils from the Jordan Valley (Israel) was studied (Neaman, 2000). Although soil clays differ considerably from each other in clay particle morphology and predominant clay mineral composition, no significant differences were found in the rheological behavior of the suspensions among

the clays. All suspensions exhibited Newtonian flow even at high (10% w/v) suspension concentrations suggesting that the number of linkages between clay particles was negligible. These results suggest that a three-dimensional network structure does not form in suspensions of soil clays, possibly because different clay minerals prevent each other in doing it, analogous to palygorskite–montmorillonite mixtures. The presence of primary minerals (such as quartz and feldspar) in the clay fraction of the soil may also play some role in preventing of the network structure formation in the suspension.

Zhao et al. (1991) reported that the particle arrangement in three suspensions of soil clays, in which kaolinite, montmorillonite and illite were predominant clay minerals, was similar to that in suspensions of standard kaolinite, montmorillonite and illite, respectively. Above-mentioned results for clays from the Jordan Valley soils show, however, that the rheological behavior of soil clay suspensions is complex and cannot be predicted from that of suspensions of standard clays that appear in the soil clay fraction.

In the particular case of the Jordan Valley soils, the flow of clay suspensions in the soil profile is not expected to affect significantly the hydraulic conductivity of the soils, since the clay suspensions have low viscosity and exhibit Newtonian flow even at high (10% w/v) solid concentrations in the suspension.

5. Effect of palygorskite on disaggregation and colloid migration in soils

The forces leading to particle disruption can be of a physical and/or chemical nature. The resistance of aggregates to mechanical stress depends on the intensity of the forces between the particles. Mechanical action will release soil components that are aggregated by very loose bonds only or not at all. Chemical dispersion, on the other hand, will disrupt firm bonds. For chemical dispersion to be effective, the exchangeable sodium percentage (ESP) value should exceed 5, and the electrolyte concentration of the solution should be lower than the flocculation value of the clays (e.g., Sumner, 1993). Disaggregation is defined as the separation of an individual particle from an aggregate and its lack of re-aggregation within a short time-interval. Disaggregation, accordingly, is a re-

sponse to a predominantly physical disruptive process and differs from dispersion, which arises predominantly from chemical factors (Bühmann et al., 1996).

Neaman et al. (1999) examined the influence of clay mineralogy on disaggregation in some palygorskite–smectite–kaolinite-containing soils of the Jordan and Bet-She’an Valleys, Israel. The soils used in that study had low ESP values (<5). The disaggregation potential of different minerals in the soil clay fraction was investigated by determining the differences in the mineral suite between the bulk and the disaggregated clay fractions. By shaking the soil with deionised water, calcite, dolomite, feldspar and palygorskite were disaggregated preferentially. Palygorskite was found to be the most strongly disaggregated mineral among the phyllosilicates that appear in the soil clay fraction.

The differences in the disaggregation potential between various clay minerals was explained in terms of the degree of clay aggregation in soils and the intensity of the binding forces between different clays. Smectite and kaolinite, when saturated with Ca, are known to form aggregates (e.g., Banin and Lahav, 1968; Dixon, 1977), which are stable to mechanical action, at least at ESP levels <5. Scanning electron microscopy observations in the study of Neaman et al. (1999) indicated that palygorskite fibers did not associate into aggregates in soils and suspensions, even when saturated with Ca ions. As a consequence, palygorskite was easily disaggregated following mechanical stress.

Observations in the above-mentioned study of Neaman et al. (1999) can be applied to rain-fed agriculture or irrigation with high quality water, which has a low sodium adsorption ratio (SAR). In most cases, however, water used for irrigation in arid areas has relatively high SAR. For this reason, Neaman et al. (2000) have investigated the migration of fine particle within columns of Na-saturated soil-sand mixtures (containing 10% or 20% w/v of soil). Topsoil and subsoil horizons of the investigated soils differed considerably from each other with regards to migration of phyllosilicates. In topsoil horizons, palygorskite was found to be the most mobile mineral among the phyllosilicates. In subsoil horizons, on the other hand, kaolinite was preferentially mobilized. This difference was explained by the different nature of carbonates in the topsoil and subsoil horizons as discussed below.

Experimental results indicated that palygorskite was preferentially occluded within the soil carbonates

of lacustrine origin over smectite and kaolinite. These carbonates were present mainly in the subsoil horizons. In topsoil horizons, on the other hand, carbonates were of pedogenic origin and/or from dust deposition. As a consequence, the presence of carbonates of lacustrine origin in the subsoil horizons decreased the migration of palygorskite mainly, without significant effect on migration of kaolinite and smectite.

The observation that palygorskite has the strongest disaggregation potential and the highest ability to migrate within the soil among the phyllosilicates suggests that palygorskite particles are likely to move preferentially over smectite and kaolinite downward in the soil profile, and eventually to clog soil pores. [Khademi and Mermut \(1999\)](#) also reported the eluviation of palygorskite from topsoil and its entrapment by the pedogenic carbonate in the subsurface horizons. Disaggregation and migration of palygorskite from the surface-soil during rainfall and/or irrigation may have an effect on the degree of erosion as well.

6. Palygorskite-cemented crusts (palycretes)

Duripan ([Soil Survey Staff, 1999](#)) is among the most common surface phenomena that affected ancient and modern landscapes. Essentially, duripans are composed of coarse-grained mineral material cemented together by matrix materials such as carbonates, silicates or iron oxides. Common duripans in dry areas are calcretes and silcretes. Duripans, in which the cementing material was dominantly composed of palygorskite, have been described recently by [Meyer and Pena dos Reis \(1985\)](#), [Rodas et al. \(1994\)](#) and [Stahr et al. \(2000\)](#). These duripans were tentatively named palycretes.

[Stahr et al. \(2000\)](#) suggested that palycretes were formed under a semi-arid, seasonal climate, where strong evaporative processes were active. The authors reported that palygorskite has been eliminated from modern soils developed on the palycrete, indicating that conditions favourable for palygorskite stability had been mainly confined in time when the palycrete had been formed.

Palycretes act the way other duripans do in negatively effecting agricultural cultivation practices. Where palycretes occur close to the surface, plant

growth, particularly that of trees, is severely impeded. Palycretes also reduce water permeability of the soils, creating conditions of waterlogging that necessitate drainage installation.

7. Research needs

Although some progress has been made recently in understanding the effects of palygorskite on chemical and physico-chemical properties of soils, much research remains to be done.

Performing some additional studies on disaggregation potential and migration ability of palygorskite under conditions close to those in the field (e.g., soil monoliths with undisturbed structure, using a rain simulator) is strongly desirable. Scanning electron microscopy observations on possible changes in aggregation of palygorskite in soils following intensive irrigation might be useful. Studies of the rheological behavior of soil clays with different mineralogical composition, and palygorskite-containing soil clays in particular, are strongly encouraged. These studies are expected to be beneficial for improving the understanding of the behavior of palygorskite in a porous soil environment under irrigated agriculture.

The sorption of various organic molecules has been studied on monomineralic and homoionic palygorskite specimens (e.g., [Shariatmadari et al., 1999](#) and references therein) and important information on the sorptive properties of palygorskite has been obtained from these studies ([Singer, 2002](#) and references therein). However, little information is available, as to how the sorptive-behavior of palygorskite translates into soil properties, when palygorskite constitutes a significant component of soil clay fraction. Therefore, there is a need to study interactions of various contaminants (both organic and inorganic) with palygorskite-containing soil clays. Such studies might be helpful for improving the understanding of the fate of contaminants in palygorskite-containing soils.

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