

PHYSICAL AND CHEMICAL PROPERTIES
OF Palygorskite Mineral

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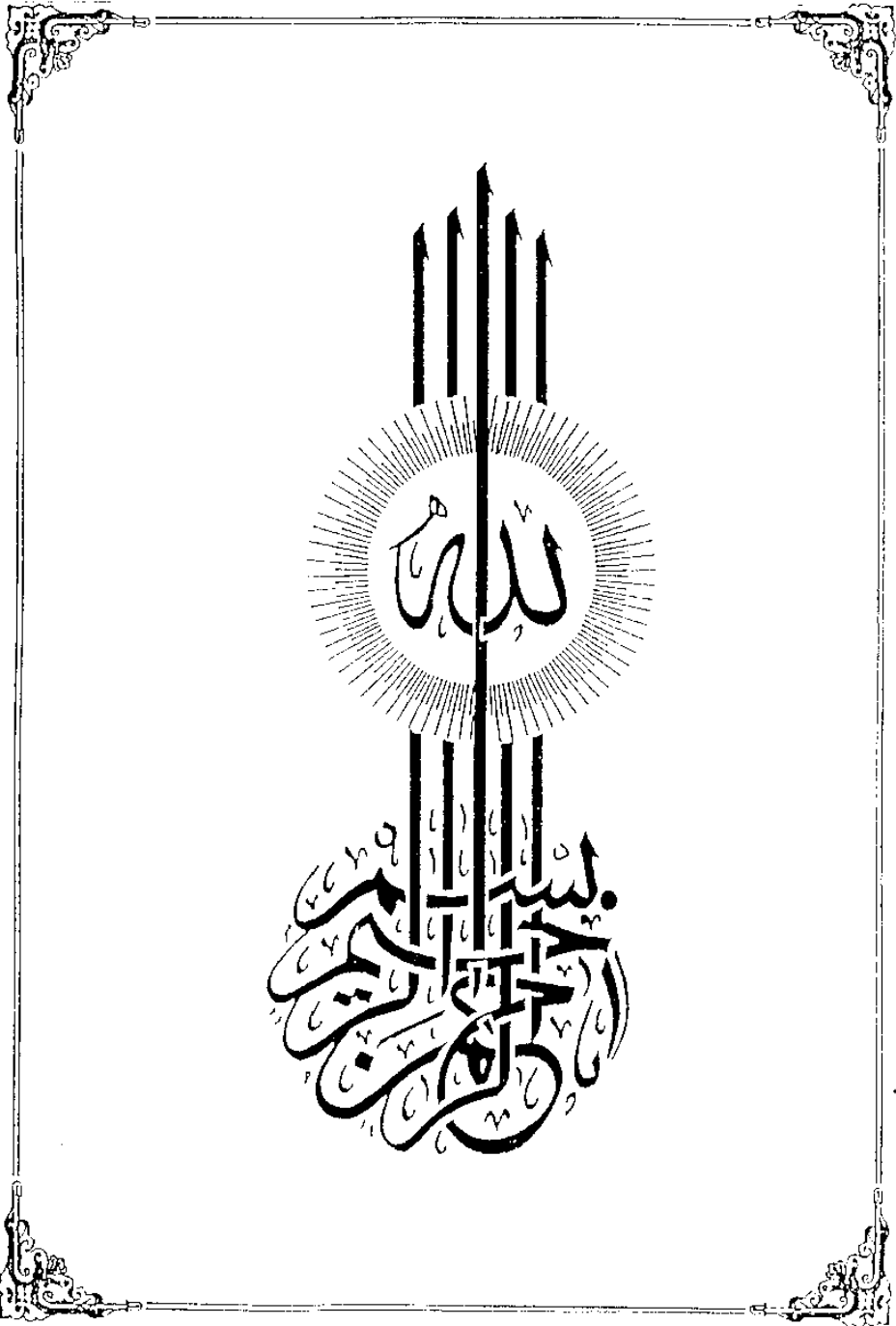
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CONTENTS

	Page
1. Introduction.....	1
2. Review of literature.....	2
3. Materials and methods.....	27
3.1. Influence of cation concentration on its adsorption by palygorskite.....	27
3.2. Influence of complementary anions on cation adsorption by palygorskite.....	28
3.3. Effect of reaction time on cations adsorption by palygorskite.....	28
3.4. Effect of temperature on cations adsorption by palygorskite.....	29
3.5. Effect of heating on cation exchange capacity of palygorskite mineral.....	29
3.6. Preparation of H-clay.....	30
3.7. Titration procedure.....	30
4. Result and discussion.....	31
4.1. Influence of cation concentration on its adsorption by palygorskite.....	31
4.2. Effect of associated anions on cations adsorption.....	49
4.2.1. Effect of associated anions on Na adsorption.....	49

	Page
4.2.2. Effect of associated anions on K adsorption...	52
4.2.3. Effect of associated anions on NH ₄ adsorption..	55
4.2.4. Effect of associated anions on Ca adsorption..	57
4.2.5. Effect of associated anions on Mg adsorption..	58
4.3. Effect of reaction time on cations adsorption by palygorskite.....	61
4.3.1. Effect of reaction time on Na adsorption.....	66
4.3.2. Effect of reaction time on K adsorption.....	66
4.3.3. Effect of reaction time on NH ₄ adsorption.....	67
4.3.4. Effect of reaction time on Ca adsorption.....	68
4.3.5. Effect of reaction time on Mg adsorption.....	69
4.4. Effect of temperature on cations adsorption by palygorskite.....	70
4.4.1. Effect of temperature on Na adsorption.....	70
4.4.2. Effect of temperature on K adsorption.....	72
4.4.3. Effect of temperature on NH ₄ adsorption.....	74
4.4.4. Effect of temperature on Ca adsorption.....	76
4.4.5. Effect of temperature on Mg adsorption.....	77
4.5. Effect of heating on cation exchange property of palygorskite.....	79
4.6. Titration curves of palygorskite mineral	83
5. Summary.....	89
References.....	
Arabic summary.....	

INTRODUCTION

The occurrence of palygorskite in the calcareous sediments of the World is now well known. Its presence as one of the dominant clay minerals in the calcareous soils of Egypt is also assured, thus it is expected to influence most, if not all, soil properties. Reviewing the previous literature on palygorskite declared that its properties are not fully investigated. Therefore, one cannot predict what the presence of this mineral may exert to soil properties.

The aim of the present study is to shed light on the physical and chemical properties of palygorskite in an attempt to add more information on such mineral. Special emphasis is given to ion exchange phenomenon and factors involved in such phenomenon.

II- REVIEW OF LITERATURE

Due to the lack of information concerning the physical and chemical properties of palygorskite mineral, the review is mainly concerned with the occurrence of palygorskite in the soil environment. Besides, data on some physical and chemical properties that the mineral imparts to soil systems are also provided. In general, this mineral is characterized by the rare occurrence in solon (A&B horizons) and its occurrence is generally limited to soils with a high pH or where acid weathering has been negligible. Zelazny and Calhoun (1977). The limited occurrence of this mineral has resulted in a recent knowledge of its properties. Therefore, available data are herein reviewed.

Palygorskite, attapulgite and sepiolite are designated as true phyllosilicates since they contain continuous true two-dimensional tetrahedral sheets in which individual tetrahedra are linked with neighbouring tetrahedra by sharing three corners each, Bailey et al.(1971a). The 1967's IMA Nomenclature Committee recommended that the name "attapulgite" be relegated to the synonymy, as the

name "Palygorskite" is Judged to have priority, Baile et al.(1971b). Therefore, the name palygorskite is used to refer to literature citations including both names, attapulgite and palygorskite.

The ideal structural formula of palygorskite is provided by Bradley (1940) as; $(OH_2)_4 (OH)_2 Mg_5 Si_8 O_{20} 4H_2O$. Recent studies by Henin and Caillere (1975) revealed that palygorskite contains eight tetrahedral positions and five octahedral positions per unit cell, of which 4 to 4.25 of the latter positions are filled. They added that aluminum occupies 1.13 to 2.34 of these five sites or between 28 to 59% of the occupied sites. Tetrahedrally-coordinated Al ranges from 0.01 to 0.69 per eight possible positions, Weaver and Pollard (1973).

Structurally, attapulgite which is also widely known by an earlier name palygorskite was first applied by Fersman (1913), to a family of fibrous hydrous siliceous minerals forming an isomorphous series between two end-members, an aluminum end-member called para-montmorillonite because of its resemblance to montmorillonite in all ways except the fibrous character, and a magnesium end-member called sepiolite. The term palygorskite has been used, in a more specific sense, for specimens

thought to be like sepiolite except for some replacement of magnesium by aluminum. Nigeon (1936), Caillere (1936) and Longchambon (1937) were the first to suggest that the palygorskite - sepiolite minerals have an amphibole - like structure composed of double chains of silica tetrahedron, whereas Delapparent (1938) believed them to have micaceous similarities. The structure of the palygorskite-sepiolite minerals, as pointed out earlier by Bradley (1940), is now generally accepted. According to this structure, palygorskite consists of double amphibole silica chains running parallel to the C axis with the chains linked together through oxygen at their longitudinal edges. The apices of the tetrahedrons in successive chains point in opposite directions. The linked chains, therefore, form a kind of double-ribbed sheet, with two rows of tetrahedral apices at alternate intervals in the top and bottom of the sheets. The ribbed sheets are arranged so that the **apices** of successive sheets point together, and the sheets are held together by Al and/or Mg in octahedral coordination between the apex oxygens successive sheets. The octahedral layer is continuous in only one direction. This layer is completed by

central OH groups and by hydroxyls at the open sides. The mineral has good cleavage parallel to (110) caused by the weak link through O of the Silica chains in the ribbed layer. Chains of water molecules running parallel to C fill the interstices between the amphibole chains. The cavities accommodate four molecules of water per unit cell, and this water would account for the dehydration loss at low temperatures. Moreover, the ideal end-member formula, given by Bradley (1940), has protons attached to OH groups along the channel edges. The $4\text{H}_2\text{O}$ groups occur in the channels. Substitution of 2Al^{3+} for 3Mg^{2+} in the octahedral position is possible. Usually some excess negative charge gives rise to exchangeable cations in the channels. Cleavage is through the channels along the planes of the shaved basal oxygens, giving sheets having optical properties similar to those of montmorillonite.

Recent studies by Millet (1970) clarified that palygorskite is an aluminomagnesian silicate with about equal proportions of Al and Mg. The mineral is intermediate between a dioctahedral and a trioctahedral subgroup, which may be responsible for its fibrous morphology. The fibrous

morphology results from bands elongated parallel to the C - axis and consist of alternating ribbons with a 2:1 type structure, Zelazny and Calhoun (1977). The ribbons consist of five octahedral positions, Bradley (1940) and these appear as the juxtaposition of two pyroxenic chains. Although the tetrahedral sheets are continuous, the apices in adjacent bands point in opposite directions. This structure results in a continuous plane of atoms with (i) tetrahedral positions primarily filled with Si atoms, and (ii) octahedral positions primarily filled with Mg or Al atoms alternating to form open channels.

The previous information about the structure of the palygorskite mineral facilitates its identification by several methods such as X-ray, D.F.A. and electron microscopy. According to Grim (1953) the X-ray diffraction patterns of the mineral have a very strong diffraction intensity at a spacing ranged from 10.2 \AA to 10.5 \AA .

Further confirmation concerning X-ray analysis was provided by Zelazny and Calhoun (1977) who showed that the main X-ray diffraction maxima of palygorskite are a strong

reflection at 10.5 Å, and moderate reflections at 6.44, 5.42, 4.50, 3.68, 3.24 and 2.15. They added that X - ray diffraction maxima do not vary with changes in relative humidity or the addition of organic polar molecules. Heating palygorskite at 200° (483 K) for one hour decreased the intensity of the reflections at 10.50, 4.50 and 3.23 Å, but the 3.68 Å reflection increased in intensity, Hayashi et al. (1969). New reflection also appeared at 9.2 and 4.7 Å. Heating to 600 ° (873 K) completely eliminated the 10.5 Å reflection, while the 9.2 Å reflection increased in intensity. Peak enhancement from rehydrating palygorskite was evident after heating at 350 ° (623K); but was lost after heating above 540° (813k).

As to the differential thermal analysis, Heller(1961) pointed out that the curves obtained for samples of palygorskite mineral show three endothermic peaks, beginning at about 90, 240 and 450° respectively. These D.T.A. curves are quite different from those reported by Hayashi et al. (1969) who showed that palygorskite displayed four endotherms at 80-210°C (353 - 483k), 210 - 325 ° (483 - 598 k), 350 - 450° (623 - 813K), and 690 - 770° (963 - 1043 k)

with an exotherm at about 925°C (1198K).

Thermobalance curves indicate that all these three curves are associated with some loss of water. In view of the temperature range, Heller(1961) attributed the first peak to the loss of zeolitic and sorbed water, and the third to dehydroxylation, but no structural interpretation has yet been published for the second. Zeolitic water is at least partly reabsorbed on cooling at room temperature.

Thermogravimetric analysis of palygorskite shows dehydration proceeding in four distinct steps, Hayashi et al. (1969). These steps may be associated with the loss of (i) hygroscopic water, (ii) Zeolitic water in structure channels; (iii) structural water bound on edges of octahedral sheets, and (iv) hydroxyl groups associated with octahedral sheets. They also mentioned that thermogravimetric analysis indicates an initial rapid loss in weight. With increased temperature, palygorskite loses more weight at lower temperatures than sepiolite. These findings are in harmony with El-Damerdashe et al. (1976).

Also in at least some sepiolites, there is little or no indication of So-Called zeolitic water, which in palygorskite is that coordinated with the magnesiums. According to Longchambon (1936,1938), the loss of water up to about 400°C is not accompanied by any structural changes. At about 400°C , there is a rapid contraction of the crystal lattice normal to the length of the fiber. The modified structure persists to about 775°C when the structure is destroyed and further shrinkage takes place..

Under the electron microscope the palygorskite appears in needle shapes and it is typically about $1\ \mu$ in length and approximately $0.01\ \mu$ across, Haden (1963).

As to the properties of palygorskite, Haden (1963) in his comprehensive study on the properties and uses of such mineral was able to distinguish its properties into four main topics namely; (i) structure of a needle, (ii) structure of a particle; (iii) non-colloidal characteristics, and (iv) colloidal characteristics. A brief account on these properties is given as follows.