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New Water-Keeping Soil Additives

Alim Asamatdinov*

Department of Surface-active Substances, Institute of General and Inorganic Chemistry, Academy of Sciences of Uzbekistan, Tashkent, Russia

***Corresponding author:** Alim Asamatdinov, Department of Surface-active Substances, Institute of General and Inorganic Chemistry, Academy of Sciences of Uzbekistan, Tashkent, Russia, Tel: 3712625660; E-mail: asamatdinov@mail.ru

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Abstract

Superabsorbent polymer hydrogels can swell to absorb huge volumes of water or aqueous solutions. This property has led to many practical applications of these new materials, particularly in agriculture for improving the water retention of soils and the water supply of plants. This article reviews the methods of polymeric hydrogels, measurements and treatments of their properties, as well as their effects in soil and on plant growth. The thermodynamic approach used to describe the swelling behaviour of polymer networks proves to be quite helpful in modelling the hydrogel efficiency of water-absorbing additives. The paper presents the results of a study of the physical and chemical properties of hydrogels based on of the production of "Nitron" (Polyacrylonitrile) wastes fibre and salts of the 3rd transition metals and formalin. The developed hydrogels HG-Al, HG and HG-Cr have been tested for water holding capacity of sand. Such conclusion was also confirmed by data from the method of determining the wilting point by vegetative thumbnails. In the entering process using a dose of 0.1% of the swelling polymeric hydrogel in sand with a culture of barley the difference between the wilting point in comparison with the control was negligible. This indicates that the moisture which was contained in the hydrogel is involved in moisture availability for plant growth, to the same extent as that in the capillaries.

Keywords: Soil; Sand; Polymer; Hydrogel; Swelling; Metal; Plant growth; Moisture; Additives

Introduction

Human life is entirely connected to food, food depends highly on agriculture, and agriculture is absolutely indebted to water. Taking into account the water imbibing characteristics of swelling polymer materials, the potential of their applications in agricultural fields has increasingly been investigated to alleviate certain agricultural problems. In such applications, the water absorbency and retention are essential. For example, the use of swelling hydrogels in sandy soil, to increase its water-holding capacity in arid areas, seems to be one of the most important means to improve the quality of plants [1]. The super absorbent polymer (SAP) particles may be considered as "miniature water reservoirs" in soil. Water will be removed from the reservoirs upon the root demand through the osmotic pressure difference. The SAP use for agricultural applications has shown encouraging results. The certain advantages of SAP use in this direction can generally be listed as follows [2,3]:

- reducing irrigation water consumption and the death rate of plants.
- increasing the available water in the soil which enables the plants to survive longer under water stress.
- reducing the evapotranspiration rate of the plants.
- inducing a much higher growth rate.
- reducing compaction tendency and increasing the soil aeration and microbial activity.
- preventing erosion and water runoff.
- improving fertilizer retention in the soil and thus increasing the fertilizer efficiency as well as preventing the contamination of the underwater sources.
- binding heavy metals and mitigating their action on plants.
- mitigating the effects of salinity.
- water-retaining materials in the form of seed additives (to aid in germination and in seedling establishment), seed coatings, and root dips, etc.

The SAP's are not yet affordable to be used on vast cultivation areas of strategic plants such as wheat and corn. However, their high costs are going to be overshadowed progressively by the benefits of the SAP improvement of soils. There are many reports available on the SAP synthesis for agricultural purposes. In an earlier publication, Kazanskii and Dubrovskii (1992) reviewed the methods of superabsorbent gel synthesis, measurements and treatment of their properties, as well as their effects on the soil and on the plant growth [4]. Preservation of water and soil reconditioning are two of the main tasks of the effort to solve the human problems that have originated mainly from imbalanced illogical human activities, causing water shortage and the desertification which are extremely serious in many regions of the world (30% of the total solid land). Ecological restoration of these lands is a major challenge for the mankind since they are the only option left for increasing the area of arable land and producing food for the ever-growing worldwide population. One common feature of these degraded lands is the fact that their organic soil matter is degraded as well. One solution for the restoration of these lands could be the application of SAP's to these soils. Since SAP's are hydrophilic and contain carboxylic groups, they can be used as artificial humus. This enables them to bind cations and water; and thus, they have the following advantages for the restoration of degraded lands.

The physical mixture of native cassava starch and PAN was hydrolyzed by NaOH solution to yield starch-poly (sodium acrylate-co-acrylamide) superabsorbent hydrogel. The agricultural performance of the hydrogel–soil mixture samples in which maize seedlings have been planted were measured as a function of hydrogel loading and compared with the values obtained in the control to which hydrogel was not added. The results of the soil-hydrogel analyses at monthly intervals showed that there was a significant increase in the ability of the soil to retain moisture and also an increase in the growth performance of the maize seedlings compared to the control [5].

Water swelling hydrogels are slightly cross-linked three dimensional hydrophilic polymers that are capable of absorbing large quantities of water or other biological fluids without disintegrating. They have found extensive applications in various areas such as medicines/ pharmaceuticals, chemical engineering, agriculture and other environmental fields [6-11]. In the design and development of new superabsorbent hydrogels, high swelling capacity, fast swelling rate and good gel strength were especially desired. Among these properties, the swelling rate is important because it determines the application properties of superabsorbent hydrogel in almost every field. Recently, many efforts have been made to improve the swelling rate of the superabsorbent hydrogel for improving its applicability [12,13]. In principle, the initial swelling rate of a superabsorbent is primarily due to the penetration of water molecules into the polymeric network through diffusion and capillarity [14]. Higher porosity in the superabsorbents can increase the contact area between polymeric network and external solution that facilitate the speeding up of the diffusion rate. Thus, the swelling rate of superabsorbent hydrogels can be enhanced through the creation of a porosity structure. Various methods, such as the phase inversion technique, freeze-drying and hydration technique, the water-soluble porogens and the foam technique [15-18], have been used to create the porous structure of hydrogels. However, a contradiction between the controllable porosity and the convenience of the pore-forming technique still exists in the hydrogel polymerization.

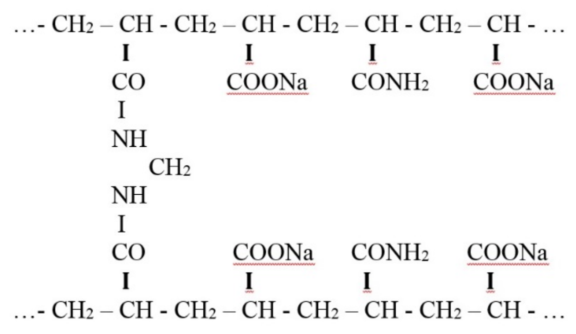
In arid regions the low moisture capacity of sand is the reason, why vegetation cannot use an even relatively small amount of precipitation completely, as much of the moisture (100-150 mm) extends beyond the root layer. The hydrogel amendments may improve the seedling growth and establishment by increasing the water retention capacity of soils and regulating the water supplies available to the plants, particularly under arid environments. The effects of different levels of a locally prepared hydrogel were studied on the moisture properties of sandy loam and loam soils and on the growth response of three plant species: barley (*Hordeum vulgare L.*), wheat (*Triticum aestivum L.*) and chickpea (*Cicer arietinum L.*). Water absorption by gel was rapid and highest in distilled water and was inhibited by an increase in water salinity [19].

To increase the moisture capacity of sands it is proposed to enter the heavy granulometric soil composition by deep loosening of the sandy layer with explosions in order to increase the capacity of the root layer and other techniques [20]. One of the new ways of moisture retention can be attributed to the application of the swellable polymer hydrogels, different types of which are tested and used to increase the moisture capacity of sandy soils in arid regions for the agricultural crops under irrigation [21]. The important directions of application are also the objects of silviculture on quartz sands in arid areas. The solution of the problem of conservation of water balance in southern areas requires the necessary procedures and the most important are the soil-improving methods, directed to increase the efficiency of irrigation and agriculture of rainfed lands, to develop methods to control water and wind erosion, desertification, and other negative phenomena.

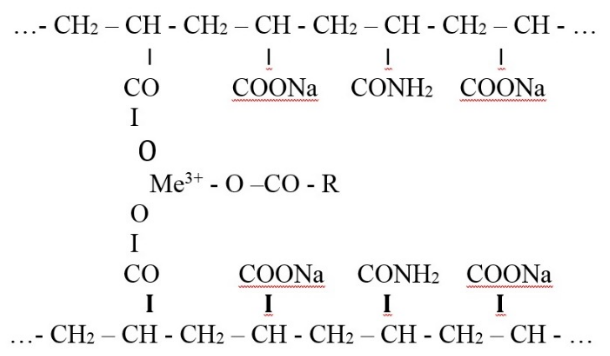
What are the general principles of hydrogels on water regime of soil and moisture availability of plants?

While swelling or absorption capacity of general hydrogels in water is less than 100% (1 g/g), the SAP's can imbibe as much water as about 1,000-100,000% (10-1,000 g/g) [22]. Entering into the root layer, for example, a uniform distribution of the substrate hydrogel particles is located in pores and when they receive moisture they swell, thus providing an increase in the moisture content compared to untreated soil and favorable conditions for plant growth. Obviously, this method in general, can be effective and economically justified if the hydrogels are capable to accumulate a considerable amount of water and transfer it into plants. This study is focused on the possibilities analysis of the practically acceptable hydrogels, their physical and chemical characteristics, particular qualities of actions in the system soil-moisture-plant and the prospects for their use [23-25].

An important method of creating hydrogels is by cross-linking of the hydrolyzed product which is made from the "Nitron" fibre in the presence of crosslinking agents. Thus, up to 95-99% of the product can be converted into a cross-linked state and this cross-linked polymer can swell up and adsorb water in an amount of 700-1000 ml/g. After drying the cross-linked polymer it formed a vitreous mass and this mass was crushed into required particle size. The "Nitron" wastes of fibre production were chosen in order to obtain polyelectrolytes, from which cross linked hydrogels have been derived. To crosslink the macromolecules in the hydrolysis products from the "Nitron" waste fibre crosslinkers were polyvalent metals (Al^{3+}, Cr^{3+}) and formaline. Distilled water was used as a solvent. When studying the kinetics of hydrolysis in aqueous alkaline NaOH under a certain conditions state, a water soluble polymer, conventionally called product K-30 was obtained [26]. Then, based on the "Nitron" hydrolyzed fibre K-30 and salts of 3-d transition metals swelling polymer hydrogels complex HG-Al and HG-Cr were synthesized, and based on of 37% formalin hydrogel HG-F was made (Schemes 1 and 2).



Scheme 1: Scheme of the crosslinked structure with formalin.



Scheme 2: Scheme of the crosslinked structure with polyvalent metals.

For modeling the impacts of salts on water adsorption of hydrogels Knop's solution was chosen, reflecting the composition of soil solution [27]. Research on the dependence of the hydrogels characteristics on the conditions of synthesis and composition can open possibilities for optimizing the method.

Materials and Methods

Apparatus and reagents

The objects of the study were the waste of the "Nitron" fibre production used for obtaining polyelectrolytes which are crosslinked and result in hydrogels, solvents and reaction products.

For crosslinking of the macromolecules in the hydrolysis products of the wastes of the "Nitron" fibre production the crosslinking agents used were the polyvalent metals (Al^{3+}, Cr^{3+}), and formaldehyde. Distilled water was used as the solvent.

Used waste fibre production "Nitron" brand "B", TC 63-08-95, waste production of polyacrylonitrile fibre TC Uz 6.1-66-98, yarn PAN TC Uz 6.1.70.98. As the dispersion system the Rybatskiy gulf sands of the Aral region have been studied (Table 1).

Sample	п.п.п.	SiO_2	Al_2O_3	Fe_2O_3	SO_3	CaO	MgO	K_2O	Na_2O	Σ
Rybatskiy gulf sand										
Site 1	16,10	40,55	10,11	13,29	1,43	10,76	3,59	1,99	3,32	101,14
Site 2	12,88	46,38	8,27	13,60	2,27	10,71	2,72	1,82	1,89	100,54
Site 3	14,39	43,48	10,92	0,88	10,69	12,05	3,67	0,88	3,24	100,20
Site 4	13,04	46,21	8,90	2,64	7,29	15,10	0,93	2,46	3,67	100,24

Table 1: Data of chemical analysis samples of soil and sand the dried bottom of the Aral Sea, %.

In the experiments using the medium-, and fine-grained sand and soils of the Rybatskiy gulf. Its granulometric composition (by sieve analysis) was as follows: particle diameter of >1 mm - 4.8%; 1.0-0.5 mm 6.2%; 0.50-0.25 mm 56.1%; <0.25 mm 32.9%.

Determining the hydrogel swelling degree

0.2 g of the gel was weighed and placed in distilled water for equilibrium swelling. The swollen gel was separated from the water in the funnel with a glass filter. The swollen gel sample was sequentially treated 3 times with acetone and three times with ether, and then dried in a vacuum oven to a constant weight for 48 hours. The swelling coefficient is given by:

$$\alpha = \frac{m_2 - m_1}{m_1}$$

m_1: mass of the dry gel, g;

m_2: mass of the swollen gel, g.

The determination of the dry remainder: Drying of the polymer to a constant weight at 50-55°C or at room temperature under vacuum, in a desiccator over $CaCl_2$. A solid content (%) was calculated using the formula:

$$X = \frac{(m - m).100}{(m_1 - m_2)}$$

m: mass of beaker with lid and linkage sample after drying, g;

m_1: mass of beaker with lid, g;

m_2: mass of beaker with lid and sample before drying, g.

Polyelectrolyte properties of the polymers were determined by measuring the electrical conductivity and viscosity of aqueous solutions. Conductivity measurements were carried out on the setting-up in the bridge system. The source voltage used sound generator brand 3G-6M. The output voltage of 6 V. Conductivity measurements were carried out at a frequency of 1000 Hz. Electric cell made of glass 50 ml with vertical platinum electrodes. Temperature control of the cell was carried out in the water thermostat. The cell constant (K) at 289 K is 0.37.

Conductivity was calculated using the formula:

$$æ = \frac{K_{KCl}}{R}$$

where R: resistance, Ohm (77). Determination of the viscosity (76) dilutions carried out in a capillary viscometer Ostwald with an inner diameter of 0.4-0.5 mm, the expiration time of water ~95.

Relative, specific and reduced viscosity was calculated for each solution, then the viscosity of the polymer solution concentration plotted. On the chart we find the value of the intrinsic viscosity (η), by extrapolating the curve of this dependence to zero concentration, that is infinite dilution.

$$[\eta] = \frac{\eta_{y\partial}}{C}; \eta_{np} = \frac{\eta_{y\partial}}{C}; \eta_{y\partial} = \frac{\tau - \tau_0}{\tau_0} = \eta_{ohm} - 1;$$

Ʈ: solution viscosity of the investigating polymer;

$Ʈ_0$: viscosity of the solvent.

On the abscissa axis there are delayed values of the concentration of polymer solutions containing 0.01-10 kg/m^3 on the vertical axis - the value of the reduced viscosity. Dependence η_s/C of C in set-up range is characterized by increasing concentration of the line. The segment shutting of this line on the axis of the η_s/C is a characteristic viscosity (η) investigating polymer. In determining the characteristic viscosity neutral salt-KCl is added for the suppression of the polyelectrolyte effect in the solution.

Physical-chemical characteristics of hydrogels

The most important properties of hydrogels for their use as soil moisture-absorbers, refer to swelling which depends on the structure of the hydrogel and on the external conditions. Due to the nature of polyelectrolytes the structure of most hydrogels can be characterized by a thermodynamic interaction parameter of the polymer with water, density of mesh points, proportion of ionic groups and their degree of dissociation. The value of the equilibrium degree swelling of hydrogels is defined by the zero swelling pressure of hydrogel, which in turn consists of osmotic forces, elasticity of mesh and availability of the related ions [28]. The process of swelling experimentally investigated by the methods from optical measurement of geometric dimensions visualized correct form samples (cylinders, spheres) automatic registration volume of liquid that remains after its absorption by the sample [23].

Influence of hydrogels on water holding capacity of sands

For assessing application prospects of hydrogels as soil moisture absorber the energy characteristics of moisture state are important. To estimate this, experiments were conducted by methods of Richards membrane press and by Dolgov capillarimeter.

Hydrogels have the potential to have a large number of benefits for the landscape. They have proven to be an aid in decreasing erosion, thus reducing nutrient and sediment losses in sensitive environments, and adsorbing nutrients for slow release. Hydrogels have also, in most circumstances, aided in the establishment of plants, mycorrhizae, and bacteria. However, the most important aspect concerning hydrogels is that responses associated with them are site-specific variables (i.e., soil structure, salt and fertilizer concentration) and often species-specific variables (i.e., what conditions the plant normally grows under). Given the adverse side effects potentially associated with the hydrophilic polymers, care should be taken in determining what the ultimate objectives of the project are (i.e., temporary plant establishment or permanent, irrigated or unirrigated, etc.). Therefore, each used field must be carefully analyzed for organism responses expected due to the wide range of results possible when using these products.

Results and Discussion

Researchers have reported that the use of hydrogels increases the amount of available moisture in the root zone, thus implying longer intervals between irrigations [29,30]. It must be pointed out that the polymers do not reduce the amount of water used by plants. The water-holding capacity depends on the texture of the soil, the type of hydrogel and particle size (powder or granules), the salinity of the soil solution and the presence of ions. Cross-linked polyacrylamides hold up to 400 times their weight in water and release 95% of the water retained within the granule to growing plants. In general, a high degree of cross-linkage results in the material having a relatively low water-retention capacity. However, the water-holding capacity drops significantly at sites where the source of irrigation water contains high levels of dissolved salts (e.g., effluent water) or in the presence of fertilizer salts [31]. The amount of water retained is also adversely affected by chemicals or ions (Mg^{2+}, Ca^{2+}, Fe^{2+}) present in the water [32]. James and Richards suggested that these divalent cations develop strong interactions with the polymer gels and are able to displace water molecules trapped within the polymer [33]. Even though monovalent cations (Na^+) can also replace water molecules, the effect is not as pronounced as with the divalent counterparts as the process is fully reversible by repeated soaking with deionised water.

Typical dependence of degree swelling of hydrogels from pH and from time presented in Figure 1 [34]. This behavior is typical for the majority of the currently known products of hydrogels, because the high degree of swelling can be obtained only by cross-linking of macromolecules. Thus, it is necessary to point out two important aspects. On the one hand the curves in Figure 1 allow to predict the moisture capacity of hydrogels under concrete conditions. On the other hand, the values of the total lower limit of hydrogel swelling testify to completely eliminate the influence of the charged mesh, which opens the possibility to determine the crosslink density with using classical relations for polymer networks.

Such assessment indicates an extremely low degree of crosslinking hydrogels. To main indicators of hydrogels should be attributed time for swelling and dehydration in a result of syneresis. Obviously, these values must be consistent with frequency and intensity of moisture into soil with additives of the hydrogel. Direct measurements show that the time of swelling is proportional to the square of particle size, which is common for most diffusion processes.

Synergic of moisture due to small potential difference of water in the hydrogel and in a pure liquid happens almost at the same rate as that from the surface of water and is limited by diffusion. This has been confirmed experimentally.

In these conditions the observed reduction of physical evaporation from the soil with additives of hydrogel is due to moisture conductivity features of the substrate, modified with additives of hydrogel. Studies of hydrogels with methods adopted in physical chemistry of polymers, enable us to formulate basis of their effectiveness as a moisture absorber, as confirmed in the transition to the conditions of modeling of the soil.

Figure 2 shows the results of potentiometric titration of gels (curves 1-3), obtained there from depending on 1/β from 1/α OH, where,

B: number of NaOH g/eq, absorbed by 1 gram equivalents of hydrogels;

α OH: activity of OH ions in the solution after establish equilibrium.

From the figure we can see that in the field of titration COOH carboxyl groups (pH 4-8) observed a linear dependence of 1/β from 1/α OH in this case maximum number of groups bonding OH- ions according to the law of independent adsorbtion is ~85%. It can be assumed that these groups of gels are the carboxyl groups included in defective area- the "hinges".

Thereby, the complex of hydrogels HG-Al, HG-Cr and HG-F represents a three-dimensional reticulate system in which the chain connects ionic bonds, and the number of these connections can vary up to ≈ 65% in neutral media, as well as in concentrated mixtures of low molecular weight salts.

We know that at pH>9 the number of interchain salt bonds in alkaline media decreases. In the acidic environment-a gel, despite the destruction of salt bonds is considerably more resistant. This is due to the stabilizing influence of hydrogen bonds, formed between the carboxyl groups included in the loop.

Figure 3 shows equilibrium values of swelling, corresponding to various values of pressure. If we consider as available moisture to plants its value located between 10 and 100 kPa, then we can conclude that almost all the moisture of hydrogels is in this range. This conclusion is also confirmed by data on the wilting point, obtained by the vegetation thumbnails by Dolgov's. Thus, when using hydrogels at the rate of 0.1 wt. % in the sand culture of barley the wilting point difference compared to the control is not registered, the moisture contained in the hydrogel, supports the plant growth as well as the capillaries.

At higher doses of hydrogels (around 0.25%) the density of sand is reduced from 1.8 up to 1.15-1.06 g/cm^3, which creates additional porosity and therefore increases the moisture capacity up to 41.7-43.5% versus 23.8% in the control group; inflated value in the control group due to inability to completely exclude the influence of the capillary fringe in the laboratory. Such high dosage is economically hardly justified, but the results illustrate the potential effect of the range of hydrogels for the moisture content in sandy soils (Tables 2 and 3).

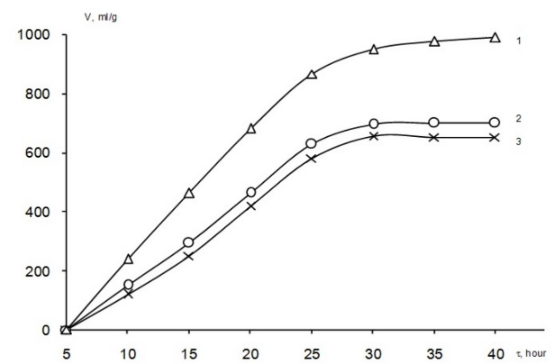


Figure 1: Dependence of degree hydrogels swelling HG-F (1), HG-Cr (2) and HG-Al (3) from time.

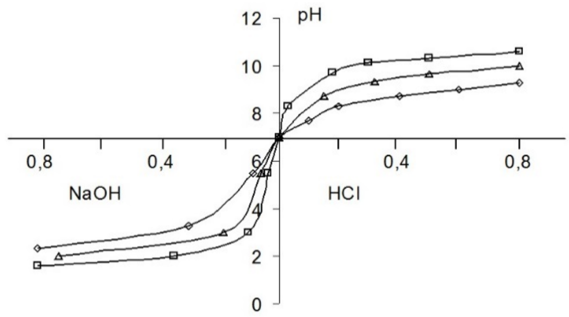


Figure 2: Potentiometric titration curves of hydrogels HG-F (1), HG-Cr (2) and HG-Al (3).

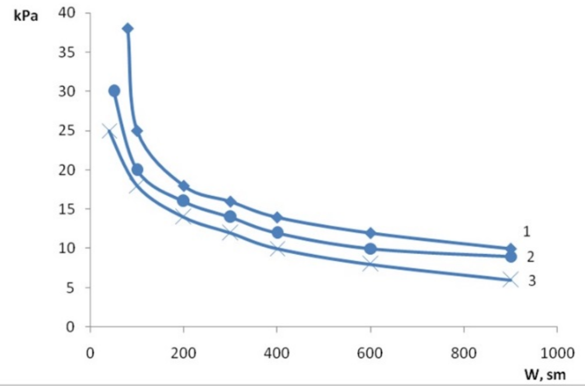


Figure 3: Influence of pressure (soil press) for swelling hydrogels HG-F (1), HG-Cr (2) and HG-Al (3).

Variant	Dose%	Capillary moisture capacity		Total moisture capacity		Water retention	
		Moisture,%	w, cm3/g	Moisture,%	w, cm^3/g	Moisture,%	w, cm^3/g
Control	-	22.4	-	23.9	-	21.5	-
HG-F	0.1	29.5	53	34.8	86	29.7	59
HG-Cr	0.03	25.9	47	29.1	83	26	29

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HG-Al	0.03	26.2	48	29.5	85	26.4	29

Table 2: Water-physical characteristics of sand and its mixtures with hydrogels.

Swelling g/l	100 kg/ha	0.00%	200 kg/ha	0.00%	500 kg/ha	0.01%	1 t/ha	0.02%	2 t/ha	0.04%
	%	mm	%	mm	%	mm	%	mm	%	mm
100	0.2	1	0.4	2	1	5	2	10	4	20
150	0.3	1.5	0.6	3	1.5	7.5	3	15	6	30
200	0.4	2	0.8	4	2	10	4	20	8	40
300	0.6	3	1.2	6	3	15	6	30	12	60
400	0.8	4	1.6	8	4	20	8	40	16	80
500	1	5	2	10	5	25	10	50	20	100

Table 3: Calculated moisture increase in soil with hydrogel* additives.

Conclusion

The beneficial effects of both water-soluble soil conditioners and hydrogels on the soil physical properties is a well-established fact. Numerous publications describe the increase in the yield of various plants as a result of better soil conditions. A lot of research effort has also been geared towards lowering the rate of application of the polymers. However, in most cases these studies have not been extended to large scale agriculture and application rates for most economical yields are not as yet defined. This implies still more research work to be conducted on a crop by crop basis.

Such conclusion is also confirmed by data from method of determining the wilting point by vegetative thumbnails [35]. In entering process in a dose 0,1% of swelling polymeric hydrogel into sand with a culture of barley the difference between the wilting point in comparison with the control was negligible. It means that the moisture contained in hydrogel is involved in moisture availability for plant growth to the same extent, as a capillary. An absolute moisture retention tested hydrogels under soil conditions much inferior for their free swelling in plenty of water; some of data are given in Table 1. This is characteristically for finely dispersed the desert sand, that experimentally shown in work [36]. First of all, such "oppression" of the hydrogel in soil due to pressure of soil layer, which gel can't overcome, without losing the swelling. Such suppression, quite consistent with the obtained data about effect of pressure for degree of swelling of the hydrogel (Figure 3).

The results indicate that there is an improvement in the ability of the soil to hold water by reason of the introduction of the hydrogel, thus, this could become cost effective in irrigation of farmlands in Africa. These results are of interest for the development of hydrogel-based technologies for solving the problem of agriculture and water conservation management in sub-Saharan Africa.

In addition to physical and chemical causes, such as the destruction of the gel swelling under pressure early in the cycle, this factor will depend on the climate and microbiological stability of the hydrogel, and its migration from layer flow of moisture. All these problems are currently not clear and are waiting attention of specialists.

Thus, the use of hydrogels has good prospects in the complex of agricultural technology and irrigation, although it requires additional significant research and development.

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