Absorption and Desorption of Liquid Water by a Superabsorbent Polymer: Effect of Polymer in the Drying of the Soil and the Quality of Certain Plants

M. BAKASS,[1] A. MOKHLISSE,[1] M. LALLEMANT[2]

[1] Laboratoire de Chimie-Physique, Faculté des Sciences Semlalia, Université Cadi Ayyad, B.P. S 15, Marrakech, Morrocco

[2] Laboratoire de Recherche sur la Réactivité des Solides, URA 23 C.N.R.S., Faculté des Sciences Mirande, Université de Bourgogne, B.P. 138, 21004 Dijon, France

ABSTRACT: In this work, we were interested in the study of the kinetic behavior of the reaction of drying soil representing the Marrakesh region (south of Morocco) in the presence of an superabsorbent polymer. The presence of a polymer in the soil diminished the kinetic drying of the soil, which will have as an application a reduction in water loss in the process of irrigation. The presence of a polymer in the soil enables a complete modification of the kinetic regimes controlling the soil-drying kinetic. We also realized the first study of the behavior of certain selected plants in the melange of a soil and a polymer. © 2002 John Wiley & Sons, Inc. J Appl Polym Sci 83: 234–243, 2002

Key words: polymer; superabsorbent; soil; gel; dryness; plants

INTRODUCTION

The presence of water in soil is essential to vegetation.[1,2] Liquid water ensures the feeding of plants in nutritive elements, which makes it possible to obtain a better growth of plants. It appeared interesting to exploit the existing water potential by reducing the losses of water and also ensuring better living conditions for vegetation. Taking into account the interesting particular characteristics of the adsorption of vapor water[3] and of the absorption of liquid water[4] by a polymer, we studied the possibilities of its application in the agricultural field. The studied polymer can absorb water up to 500 times its weight; we think that its use in the agricultural field can reduce water losses by evaporation and infiltration.

We studied the optimal proportions allowing the best retention of water in the melange of the soil and the polymer to prolong the storage period of water in the soil.[5] We also studied the effect of certain ions and the pH on the capacity for absorption of the polymer. The polyelectrolyte gels swell much less in the presence of monovalent salt and can even collapse in the presence of multivalent ions.[5] These ions can be naturally present in the soil or introduced by the use of manure and pesticides. The presence of a polymer in the soil makes it possible to increase the capacity for absorption of the water the soil, which can, thus, involve a saving in water while decreasing the frequency of irrigation and reducing water losses by the phenomena of evaporation and infiltration. In arid areas, the use of a gel obtained by polycondensation or polyaddition in the sandy soil (macroporous medium), to increase its water-holding capacity, seems to be one of the most significant means to improve the quality of plants.[6,7]

Table I   Physical and Chemical Characteristics of the Ground of the Area of Haouz to 30-cm Depth

Composition of the Soil	Quantity
Clay	11.7%
Silt fine and coarse	49.3%
Sand fine and coarse	38.3%
pH	8.1
N	0.057%
C/N	3.5
K_2O	0.376%
P_2O_5	0.692%
$CaCO_3$	3.9%
Matter organic	0.56
C.E at 25°C mm h cm^{-1}	0.83
Salinity	1.31%
Equivalent humidity	16.35

In this article, we studied the drying of a soil representing the area of Haouz (Marrakesh area, south of Morocco) with or without a polymer. Our objective was to prolong the storage period of water in the soil. We also give the results of the behavior of some selected plants (broad beans and corn) in the melange of the soil and the polymer in various compositions.

EXPERIMENTAL

Polymer

The studied polymer is a superabsorbent polyelectrolyte formed from acrylic acid.[3,8] It is presented in the form of spherical balls (diameters ranging between 10 and 100 μm). These spherical balls are formed by macromolecular chains attached by covalent bonds. The polymer is able to absorb a significant quantity of liquid water (500 times its weight of water). It inflates easily and instantaneously in the presence of liquid water or in salt solutions and gives rise to a transparent and soft gel.[9,10]

Soil

The soil used in this study is representative of the area of Haouz provided by the specialized services of the Regional Office of Agricultural Development of Haouz to Marrakesh. The physicochemical analyses of the soil were carried out in the laboratories of this same office. Table I gives the results of the analysis carried out.

The analysis of these results enables us to conclude that the soil is slightly basic and low in organic matter, presents a good humification (significant report C/N), and is rich in potassium and phosphorus. We carried out a mineralogical study of the pleasure party of the soil by X-ray diffraction.[5] The analysis of this party by X-rays showed the existence of three types of minerals (illite, kaolinite, and vermiculite).

Experimental Technique

The study of the drying kinetics of the gel and soil under controlled pressures and temperatures was carried out using an original assembly in our laboratory. It is formed by two reactional compartments attached by an adapted system of lines and valves.[11] The first compartment allows the regulation of the partial pressure of water vapor in the engine; the second contains the polymer. Each compartment is plunged into a thermostated bath.

We studied the effect of the polymer over the life span of certain plants (corn and broad) after their watering. The tests were carried out in plastic pots (30 × 40 cm) containing the soil and polymer (melange: polymer/soil) with various percentages of the polymer. The polymer was distributed on the surface of the soil. For each studied plant, we tested the effect of the polymer in 50 pots (each pot comprises two seeds), treated in the same manner. We examined four polymer rates (0.1, 0.3, 0.5, and 1.0%). The soil mass used in each pot was 10 kg (without the use of manure). The experiments were carried out in the gardens of the Faculty of Science of Marrakesh.

RESULTS

Drying of Gel

We studied the influence of the partial pressure of vapor water at a fixed temperature (and the temperature at constant pressure) on the drying kinetics of the gel in the presence of air. The study was carried out under different conditions of pressure and temperature. Figure 1 shows the evolution of the advance rate according to the time for various partial pressures of vapor water at T = 328 K. The advance rate α is defined as being

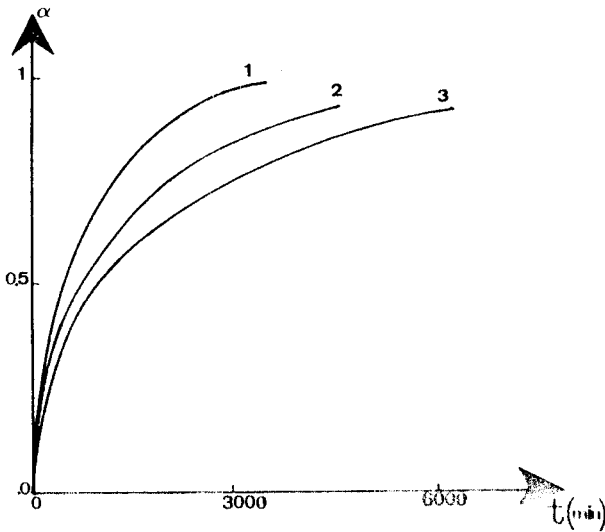$$\alpha = (m_0 - m_t)/(m_0 - m_e)$$

Figure 1 Advance curves of gel drying at $T = 328$ K: (1) $P = 286.5$ Pa; (2) $P = 2337.7$ Pa; (3) $P = 5030.0$ Pa.

where m_0 is the initial mass of the gel; m_t, the mass of the gel at moment t; and m_e, the final mass of the gel.

From the advance curves $\alpha{:}f(t)$ obtained from the kinetic study of the drying reaction to constant pressure and various temperatures of the gel, we could draw the curves in Figure 2 which represent the variation of the initial speed of drying according to the temperature:
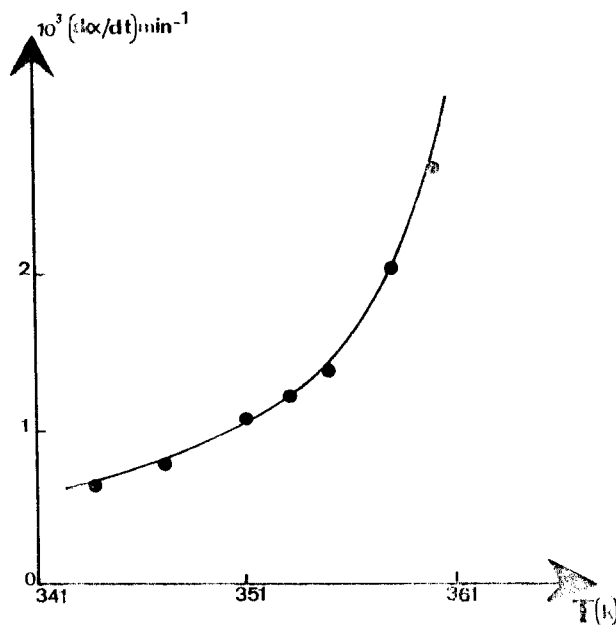

Figure 2 Variation of the reaction speed of gel drying with the temperature at $P = 5.6 \times 10^3$ Pa.
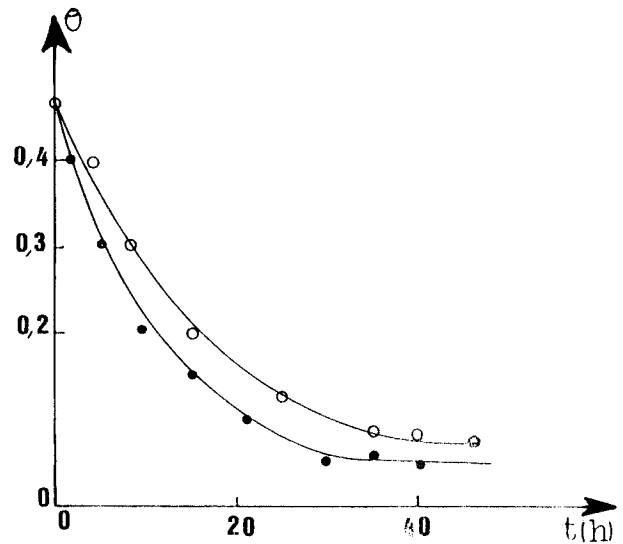

Figure 3 Evolution of the absorption rate according to time for two different samples from the wet soil and dried under the same conditions ($T = 323$ K and $P = 1.4 \times 10^3$ Pa).

- For a fixed gel temperature (Fig. 1), increase in the pressure causes a reduction of the reaction speed. The experimental curves are characterized by a first common rectilinear part for all the partial pressures of vapor water and a significant final part. The end time of the reaction increases as the pressure imposed on the reactional system increases.
- For a fixed partial pressure of vapor water (Fig. 2), the evolution of the drying speed of the gel presents an increasing exponential form with the temperature, showing that the reaction kinetics is strongly influenced by the temperature.

Drying of the Recomposed Soil

The recomposed soil is formed from three types of minerals (clay 11.7%, silt 49.3%, and sand 38.3%).[5] Before each drying reaction, the recomposed soil is wet by adding to it the distilled water until its saturation rate is reached, defined as

θ = mass of absorptive water

by soil/mass of the anhydrous soil

We studied the drying kinetics of recomposed soil starting from its saturation rate according to the temperature and the partial pressure of the vapor water. Figure 3 shows the variation of the absorp-
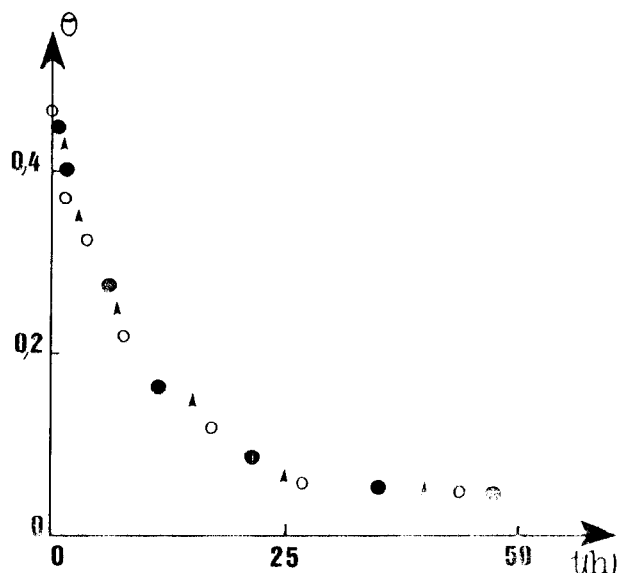
Figure 4 Influence of cycle number on the drying kinetics of the same sample of soil at $T = 323$ K and $P = 1.4 \times 10^3$ Pa: (●) first cycle; (○) second cycle; (△) third cycle.
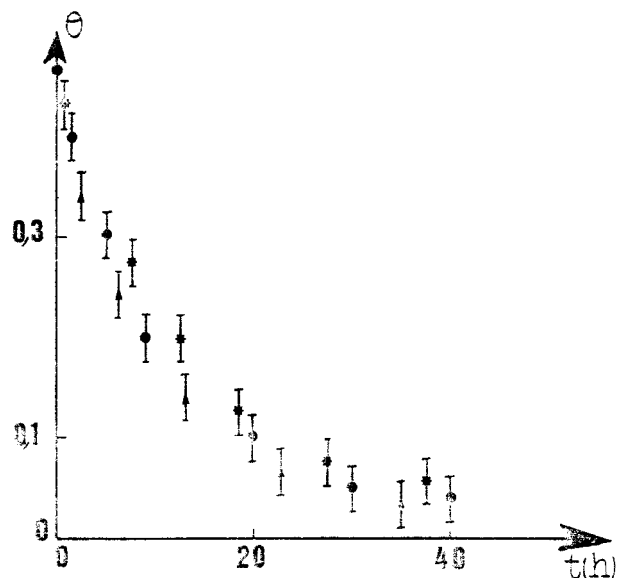

Figure 5 Effect of the pressure on the drying kinetics of the wet soil at $T = 323$ K: (●) $P = 6.0 \times 10^2$ Pa; (△)$P = 1.4 \times 10^3$ Pa; (*) $P = 2.3 \times 10^3$ Pa.

tion rate according to time for two samples of soil dried under the same conditions (partial pressure of vapor water and temperature). These two drying curves of soil were obtained for the same mass of soil (7 g). These curves do not coincide even if they correspond to the same thermodynamic conditions. This can be due to the difference in composition between the samples of the prepared soil. The difference between the two curves becomes very significant when it is about an original soil.

Figure 4 presents the evolution of the absorption rate in relation to the time of drying for three different cycles. The obtained curves correspond to the drying reactions carried out on the same sample of reconstituted soil and under the same conditions of pressure and temperature. The obtained curves for repeated drying reactions are superimposed. This result shows that when it is about the same sample, the drying reactions of recomposed soil are perfectly reproducible. This result was also noted for a rough soil.

The same results were obtained for the sandy and muddy fractions. For the argillaceous part, we noted that, for the same or different samples, the drying curves are superimposed and the experimental points coincide perfectly during drying the same mass of the sample under the same conditions. During sifting, argillaceous particles, whose diameters are the smallest (smaller than 2 μm), were obtained only. Sandy or muddy parti-

cles were always obtained in the presence of certain argillaceous particles, which remain, in fact, stuck on the grains of sand and silt.

Figures 5 and 6 show, respectively, evolutions of the absorption rate according to time for various partial pressures of vapor water at a constant
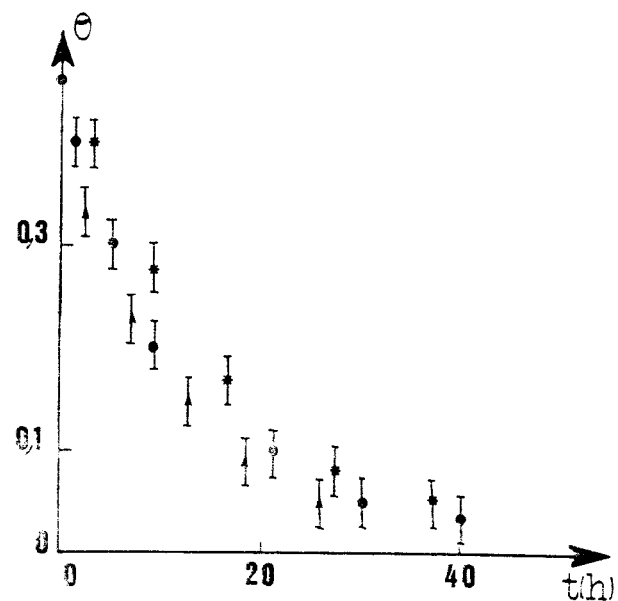

Figure 6 Effect of the temperature on the drying kinetics of the wet soil at $P = 1.4 \times 10^3$ Pa: (●) $T = 313$ K; (▲) $T = 323$ K; (*) $T = 333$ K.
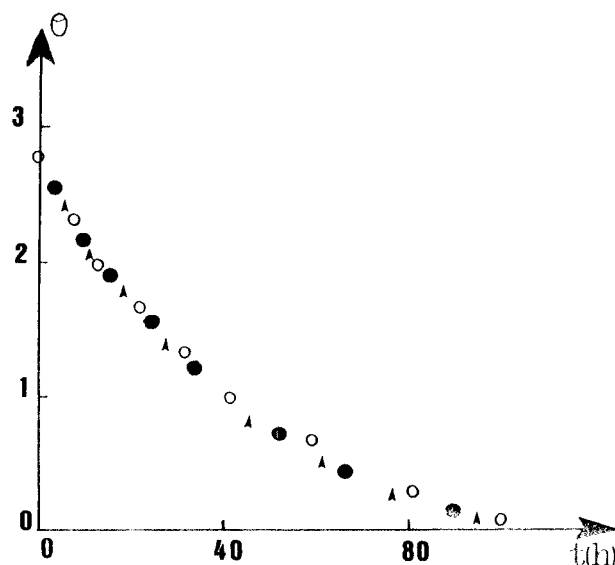
Figure 7 Evolution of the absorption rate according to time for three different samples of polymer/soil dried under the same conditions (T = 323 K and P = 1.4 $\times$ 10^3 Pa).

temperature and for various temperatures of the sample under a fixed partial pressure of vapor water. We noted the following points:

- The curves present the same decreasing form.
- For the absorption rates ranging between the initial value and 0.2, the curves took a quasilinear form.
- For absorption rates lower than 0.2, the curves curve took a decreasing parabolic form.

Drying of the Melange (Soil and Polymer)

Figure 7 shows the evolution of the absorption rate according to the time of a polymer/soil melange containing 1.0% of the polymer for three different samples dried under the same thermodynamic conditions. The drying reactions in the presence of the polymer on the surface of the soil are perfectly reproducible and the experimental points coincide perfectly between them. This result is different from that obtained during drying of the soil without the polymer. The great quantity of absorptive water by the melange is absorbed by the polymer and the drying kinetics of the gel is reproducible.[4]

We followed the evolution of the drying kinetics of the melange (polymer/soil) for various polymer

percentages 0.1, 0.3, 0.5, and 1.0%. Figure 8 shows the variation of the absorption rate according to the time for various polymer percentages in the soil under the same conditions of pressure, temperature, and sample mass. The curves obtained with the addition of the polymer do not have the same form as that of those corresponding to the soil. They present the same decreasing parabolic form and only one kinetic phenomenon controlling the reaction. Contrary to the drying reactions of the soil (Figs. 3–6) where there are two water types in it (capillary water and absorbed water), two mechanisms limiting the reaction can be induced. The end time of the reaction increases with the polymer percentage in the soil.

Tests on Some Plants

For corn, two series of experimentation were carried out: The first experimentation was carried out starting on April 12, 1994, and the second, on April 18, 1995. For each experimentation series, we followed the life span of plants after watering was stopped according to the percentage of the polymer in the soil. For the first series, watering was stopped on June 12, 1994. The average size of the plant was about 65 cm. For the second series, we stopped watering on June 27, 1995. The average size of the plant was 69 cm.

Figure 9 shows the curves of the evolution of the average life span of the plant in relation to the polymer percentage in the soil for two experiments series. The life span of plants is defined as being the day when all the sheets of the plant become senescent during a normal senescence. The life span of plants after the stopping of watering increases as the polymer rate in the soil increases. The life span of plants passes from 16 days for a soil without the polymer to 24 days for a polymer percentage of 1.0% for the first series and 15–22 days for the second series.

For the broad bean, we also carried out two experimental series: The first was carried out from November 2, 1993, and the second, from November 5, 1994. Eighty days after the seeding of grains, the average size of the plants was 31 cm for the first series and 29 cm for the second experiment series. The stop day of watering was arbitrarily selected (80 days). We also followed the life span of broad bean stems according to the polymer quantity placed in the soil before the watering stop.

Figure 10 shows the results obtained for the two series. It is also noted, as in the case of the
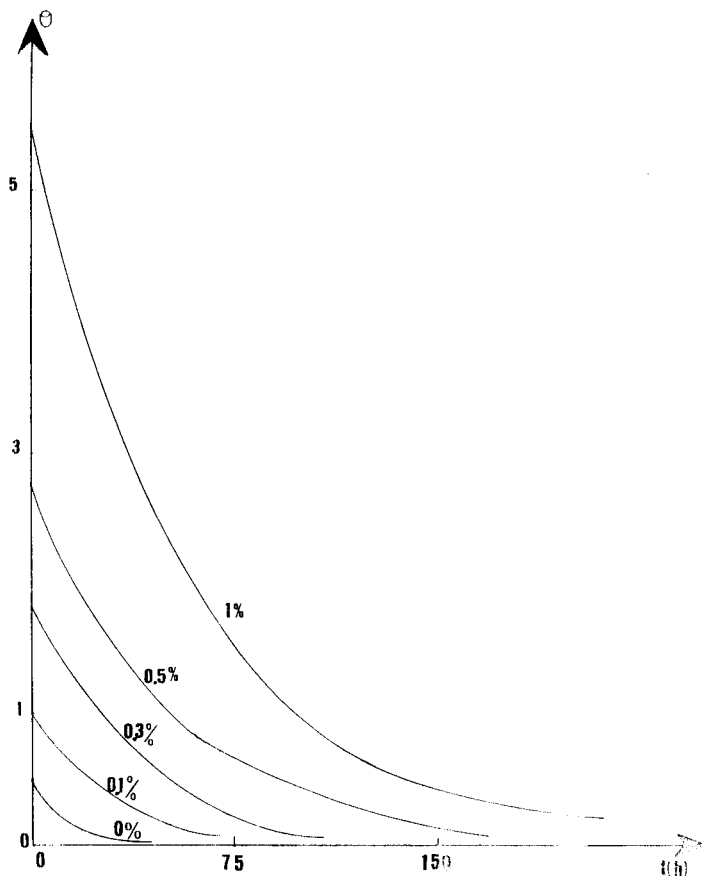
Figure 8 Variation of the absorption rate in relation to time for various polymer percentages in the soil.

corn plant, that the presence of the polymer in the soil increases the life span of the plants. The life span of the plant was 34 days for the first series and 36 days for the second, for a polymer percentage of 1.0%, whereas it was only 26 days for the first series and 25 days for the second for a soil without the polymer.

DISCUSSION

Drying of Gel

We expressed the advance rate with the reduced time. The reduced curve for various partial pressures of vapor water (Fig. 11) coincided with the curve describing a process limited by a three-dimensional diffusion.[12] During the absorption of water by the polymer, it inflates quickly and fixed the molecule of water between the charged polymeric chain.[13–15] During the drying phase, water molecules will pass be-
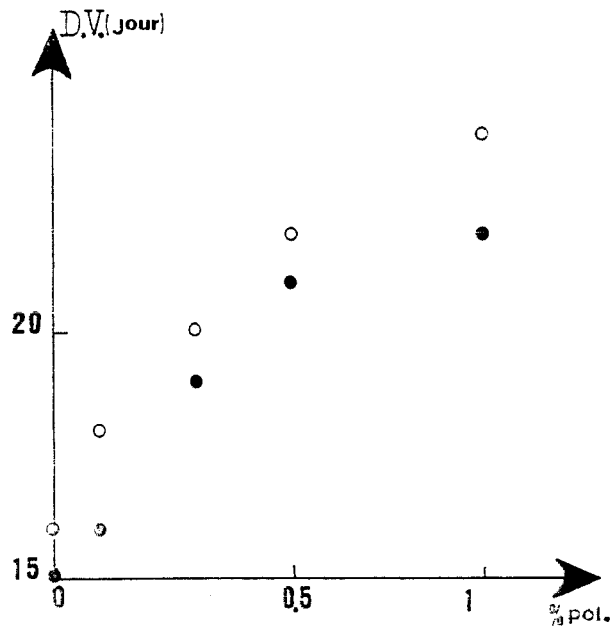

Figure 9 Evolution of the life span of corn according to the percentage of polymer in soil: (○) first series; (●) second series.
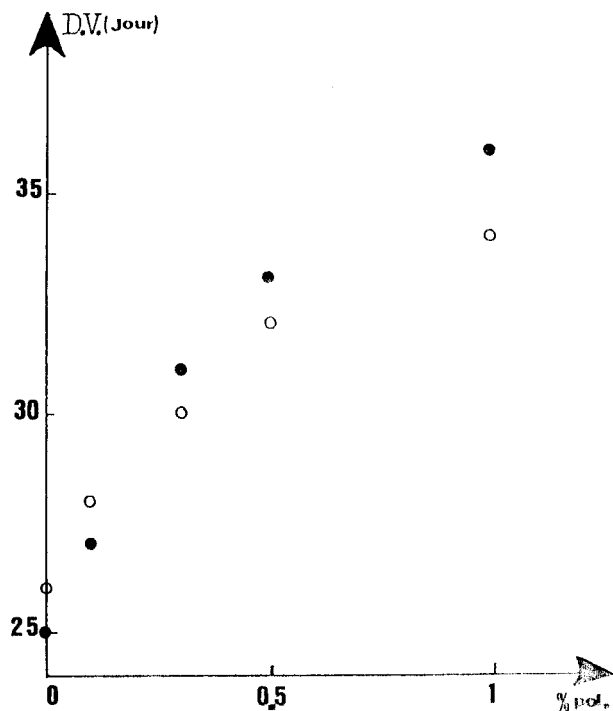
Figure 10 Evolution of the life span of broad bean according to the polymer percentage in soil: (○) first series; (●) second series.

tween the chains inside a sphere and between the spheres. The diffusion of the water molecule can be due to a diffusion in the spherical poly-

meric grain as in the case of a gel drying under a reduced vapor water pressure.[4]

Drying of the Reconstituted Soil (Without Polymer)

The kinetic study of recomposed soil drying starting from its saturation rate started with an evaporation phenomenon; the curves obtained (Figs. 3–5) for absorption rates higher than 0.2 are practically lines (elimination of the interstitial water). For absorption rates lower than value 0.2 (Fig. 12), the reactional mechanism limiting the phenomenon changes and becomes diffusional; it corresponds to the elimination of a second water type: dependent water.

Drying of the Polymer/Soil Mixtures

The experimental results for drying the polymer/soil mixtures are perfectly reproducible. The reproducibility is obtained for the same and different samples at the same mass. This result is different from that obtained for recomposed soil when it is dried without the polymer. For each drying reaction, the gel dried initially, and the soil, near the end of the reaction. Figure 13 is relative to various types of melange of the polymer and the soil at the rate of 1.0%. The curves obtained are superimposed and the evolution of the absorption rate with time is same whatever the type of product (recomposed soil, clay, silt, or
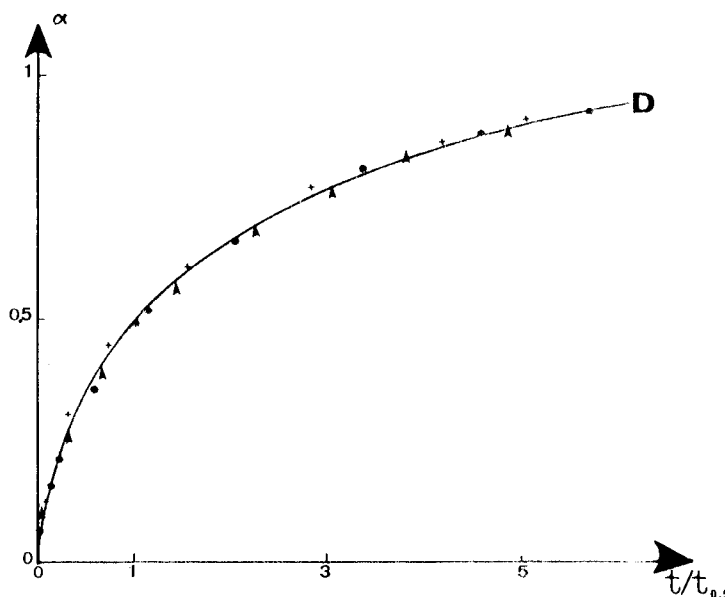

Figure 11 Comparison of the theoretical reduced curve of three-dimensional diffusion with those obtained for the gel drying at $T = 328$ K: (●) $P = 1321.2$ Pa; (+) $P = 2337.7$ Pa; (▲) $P = 5030.0$ Pa.
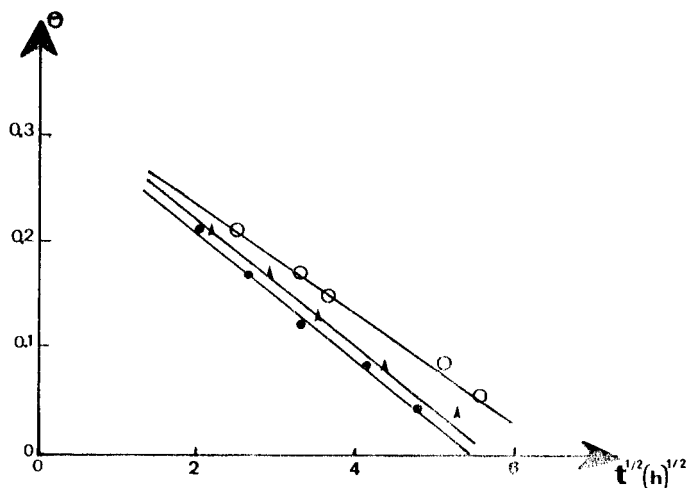
Figure 12   Curves $\theta f(t^{1/2})$ of soil without the polymer when the absorption rate is lower than 0.2: (●) $T = 333$ K; (▲) $T = 323$ K; (○) $T = 313$ K.

sand). The gel dries first, and the product, at the end of the reaction.

Analysis of the curves (Fig. 14) of the polymer/soil mixture drying to various polymer percentages and various conditions of the partial pressure of water vapor and temperature show that the drying reaction is controlled by only one limiting kinetic phenomenon: Figure 14 shows that the kinetics of the reaction is described by a law of type

$$\theta = kt^{1/2}$$

This law characterizes and describes a process controlled by a diffusion reaction of vapor water through the bed of the sample. The reaction of soil drying in the presence of the polymer starts with
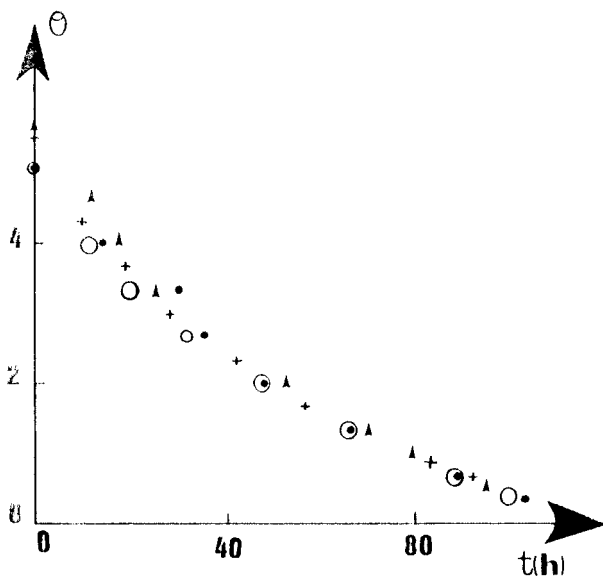

Figure 13   Variation of the absorption rate according to time for various mixtures at a polymer rate of 1.0% ($T = 323$ K and $P = 1.4 \times 10^3$ Pa): (+) polymer/silt; (▲) polymer/sand; (●) polymer/soil; (○) polymer/clay.
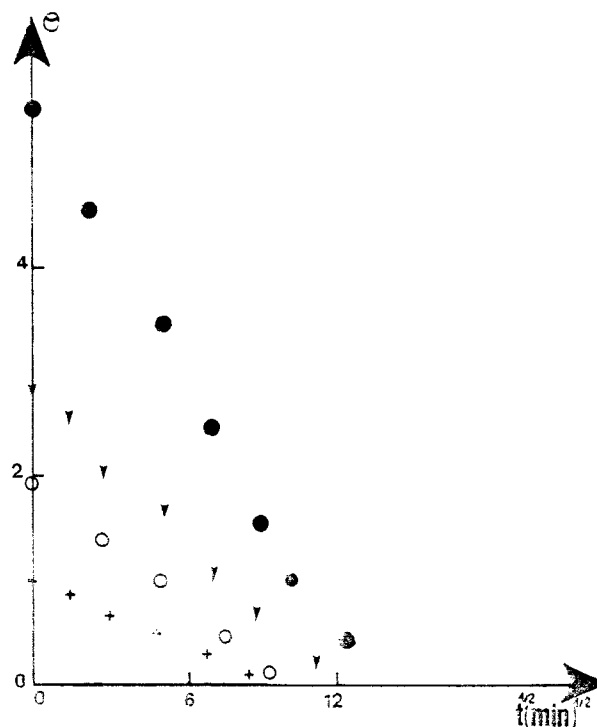

Figure 14   Curves $\theta f(t^{1/2})$ for various polymer rates in the soil at $T = 323$ K and $P = 1.4 \times 10^3$ Pa: (+) 0.1%; (○) 0.3%; (▲) 0.5%; (●) 1,0%.

the drainage of the water trapped by the macro-molecular chains and ends with water related to the microcrystals constituting the soil. At the beginning the reaction, the quantity of water absorbed by the polymer is two to 10 times higher than that absorptive absorbed by the soil; in consequence and also by its position, the gel dries first. If the soil dries first, we would have a reaction limited at the beginning by evaporation (Figs. 3–5). At the end of the reaction, the absorption rates of the polymer and soil are close; they dry together. This result shows that water related to the microcrystals constituting soil is more dependent on the water surrounded by the macro-molecular chains.

The end time of the reaction increases as the polymer quantity in the soil increases; it passes from 100 h for a polymer rate of 0.1% to 250 h for a rate of 1.0% (Fig. 8). But even if the drying kinetics of the wet polymer is faster than that of the soil, the presence of the polymer in the soil makes it possible to preserve water longer than with a soil without the polymer (10 days instead of 2 days). The presence of the polymer in the soil makes it possible to avoid the evaporation phenomenon observed just at the beginning of the drying reaction of the soil; this makes it possible to increase the water quantity retained by the soil in relation to the time which can involve a reduction of water losses by infiltration and evaporation. Woodhousse and Johnson[7] followed the water losses by plants (per evaporation) in pots containing various rates of polyacrylamide gels in the soil. The analysis of the results after the irrigation operation showed that at the end of 4 days the soil without the gel was completely dry; when we added a gel at a rate 2 g per kg of soil, it was after 10 days.

Test on the Corn and the Broad Bean

The test carried out on the corn and the broad bean showed that the presence of the polymer in the soil makes it possible to increase the life span of the plant (8–10 days for a polymer percentage of 1.0% according to the plant) and to preserve the water in the soil for more time (8 days for a percentage of 1.0%).

When the polymer is in the soil, it absorbs a very significant quantity of liquid water, and during drying, the gel dries first before the soil. The water molecules trapped by the polymer are related to the sites charged by weak connections and can involve a good exchange of water between the polymer and the soil.

It is necessary to distinguish between marketed gel (ready for employment) and gel polyelectrolytes obtained from the polymer superabsorbents. The gel which is generally applied in the soil is obtained by polycondensation or polyaddition of two monomers in the presence of a solvent.[16] This gel is completely different from gel polyelectrolytes obtained when the polymer superabsorbents are with liquid water. The gel obtained by polycondensation or polyaddition presents a very slow absorption kinetics of water and also releases water more slowly than does the wet soil.[10,17,18] The superabsorbent polymer, in the presence of water, collects quickly and spontaneously the water and forms a transparent gel.[10,15,19] The application of polymers in soil increase the absorption capacity of the soil[5] and diminish the water losses by evaporation.[20–22]

CONCLUSIONS

In the case of the polymer/soil mixtures, the experimental results were perfectly reproducible. During drying of this type of mixture, the gel dried first and the drying of the soil takes place at the end of the reaction. The soil preserves water longer than does a soil without the polymer. The presence of the polymer preserves water in the soil for 8 days more than did the soil without the polymer. It also modified the kinetic modes controlling the drying kinetics of the soil. The process of drying the soil is controlled by an evaporation phenomenon of water (the drainage of interstitial water) followed by a diffusive process (the drainage of dependent water). The drying kinetics of polymer/soil mixtures is controlled by only one phenomenon: the diffusion of water through the sample bed.

We can say that the polymer under consideration in this study is interesting, having certain applications in the agricultural field:

- Increase of the water-absorption capacity of soil.[5]
- Preserve water in soil longer. Indeed, even if the drying kinetics of gel is faster than that of soil, the presence of a polymer in the soil makes it possible to increase the duration of the presence of water in the soil.
- It is possible to save water by reducing the water losses by infiltration and evaporation

and to improve the life span and quality of plants.

REFERENCES

1. Pearsall, W. H. J Soil Sci 1952, 3, 41.
2. Swartzen-Allen, S. L.; Matijevic, E. Chem Rev 1974, 74, 125.
3. Bakass, M.; Mokhlisse, A.; Lallemant, M. Thermochim Acta 1992, 206, 309.
4. Bakass, M.; Mokhlisse, A.; Lallemant, M. Thermochim Acta 2000, 356, 159.
5. Bakass, M.; Mokhlisse, A.; Lallemant, M. J Appl Polym, in press.
6. Johnson, M. S. J Sci Food Agric 1984, 35, 1196.
7. Woodhousse, J. M.; Johnson, M. S. J Arid Environ 1991, 20, 375.
8. Bakass, M.; Mokhlisse, A.; Lallemant, M. Thermochim Acta 1993, 223, 271.
9. Nisato, G.; Skouri, R.; Schossler, F.; Munch, J. P.; Candau, S. J. Faraday Discuss 1995, 101, 133.
10. Champetier, G.; Sebille, B. Chimie Macromoléculaire; Hermann: New York, 1972; Vol. 2, p 319.
11. Bakass, M.; Mokhlisse, A.; Lallemant, M. Thermochim Acta 1997, 290, 227.
12. Scharp, J. H.; Brindley, G. W.; Narhari, B.; Char, A. J Am Ceram Soc 1966, 49, 379.
13. Ilman, F.; Candau, S. J. Macromol Chem Macromol Symp 1989, 30, 119.
14. Ilman, F; Candau, S. J. Prog Colloid Polym Sci 1989, 79, 172.
15. Moussaid, A.; Munch, J. P.; Schossler, F.; Candau, S. J. J Phys II 1991, 1, 637.
16. Babaoui, A. Thesis of Doctorate, Casabanca, 1993.
17. Ilman, F. Thesis of Doctorate, Strasbourg, 1993.
18. Zagrouba, F. Thesis of Doctorate, Nancy, 1993.
19. Najeh, M. Thesis of Doctorate, Strasbourg, 1992.
20. Fry, J. D.; Butler, J. D. Hort Sci 1989, 24, 79.
21. Magalhaes, J. R. Commun Soil Sci Plant Anal 1987, 18, 1469.
22. Baasir, M.; Ryan, J.; Muchjeik, M.; Harik, S. N. Commun Soil Sci Plant Anal 1986, 17, 573.