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Polymer Hydrogel–Humic Compositions for Retaining Moisture in Sulphate-Crusted Rainfed Desert Soils of The Navoi Region At 30–50 °C

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Abstract

Rainfed desert rangelands of the Navoi region (Uzbekistan) receive less than 100 mm of precipitation a year, and spring rain moisture evaporates before the ephemeral vegetation sets seed. Soils of the Karmana, Navbahor and Konimex districts were characterised by X-ray diffraction, and moisture retention by locally produced polyacrylamide gel (PAM), sodium carboxymethylcellulose (CMC), humic substances from Angren brown coal (HS) and their compositions was measured gravimetrically at 30–50 °C. Salt minerals accumulated in the 0.2–0.5 cm surface crust and were of the sulphate type (22.5–39.5 wt.% sulphate minerals, mainly thenardite and astrakhanite; chlorides 0.4–0.8 wt.%). A comparison of a wet (2016) and a dry (2021) year identified April–May as the critical period of moisture deficit. The optimal concentrations were 3 g/L for PAM and 2 g/L for CMC. When untreated soil reached its minimum moisture (0.92–1.20 %), the compositions CMC 2 g/L + HS 3 g/L and PAM 3 g/L + HS 3 g/L still held 3.0–4.7 %, and their first-order drying constants were 1.5–3.1 times lower than that of the control. The combined effect of hydrogel and HS was not consistently synergistic (additivity index 67–227 %).

Keywords: Rainfed rangeland, soil moisture, polyacrylamide, carboxymethylcellulose, humic substances, salt crust, drying kinetics.

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1. Introduction

Land degradation affects up to 40 % of the global land area, and more than 833 million hectares of soils are salt-affected, mostly in arid and semi-arid regions [1], [2]. Drylands already cover about 41 % of the land surface, or up to 45 % by a recent estimate [3], and are projected to expand under climate warming [4]. Central Asia is among the regions most exposed to increasing aridity [5], and over 1979–2011 it warmed by about 0.36–0.42 °C per decade, with the strongest warming in spring [6]. Spring is exactly the season in which the ephemeral and ephemeroid vegetation of desert rangelands forms its biomass.

In Uzbekistan the rainfed desert rangelands adjoining the

Kyzylkum are the main forage base for karakul sheep [7]. In the Karmana, Navbahor and Konimex districts of the Navoi region annual precipitation is below 100 mm, evaporation exceeds precipitation several times, summer air temperature reaches 45–50 °C, and the soils are salinised. Under these conditions, retaining spring rain moisture in the topsoil for a few additional weeks would allow the vegetation to complete its cycle and protect the surface from crusting and deflation.

2. Related Work

Superabsorbent hydrogels increase the water-holding capacity of soil, reduce evaporation and deep percolation and improve seedling survival under drought [8]–[11]. Polyacrylamide is the most widely used synthetic polymer for soil conditioning [12], whereas polysaccharide-based hydrogels such as carboxymethylcellulose are biodegradable alternatives [13]. The swelling of polyelectrolyte hydrogels decreases in saline solutions, especially in the presence of multivalent cations [8], [9], and anionic polyacrylamide is adsorbed on clay surfaces through cation bridges [14]. Humic substances improve aggregate stability [15] and act as plant biostimulants [16], and humic products can be obtained from oxidised Angren brown coal [17]. The environmental fate of polyacrylamide is governed by slow degradation of the polymer and by the toxicity of the residual acrylamide monomer, while anionic formulations show low toxicity [12], [18], [19]. Most hydrogel studies, however, were carried out on non-saline soils at moderate temperatures. The behaviour of hydrogel–humic compositions in sulphate-salinised desert soils at the 40–50 °C typical of a Kyzylkum summer has not been reported.

3. Scope of Research

The aim of this work was (i) to determine the type of salinisation of rainfed soils in three districts of the Navoi region from their mineral composition, (ii) to identify the critical period of moisture deficit from meteorological data, (iii) to select the optimal concentrations of local PAM and CMC, and (iv) to evaluate the moisture retention of hydrogel–humic compositions at 30, 35, 40, 45 and 50 °C.

4. Materials and Methodology

Soil samples were taken according to GOST 17.4.3.01-83 and GOST 28168-89 in Karmana (Hazora village, oasis margin, 24 km from Navoi), Navbahor (Shorkishlok village, oasis–desert boundary, 22 km) and Konimex (rainfed rangeland, 28 km). In Karmana and Navbahor three horizons were sampled (surface crust 0.2–0.5 cm, 2–10 cm and 10–30 cm), and in Konimex the normal soil and the salt crust; soil from the Navoi city campus served as the control (Fig. 1). One profile was described per district. The mineral composition was determined on a Panalytical Empyrean diffractometer (2θ = 4–80°, step 0.01°) and quantified by the Rietveld method in Profex/BGMN [20]; the standard error of the phase contents was 0.1–0.5 wt.%. The type of salinisation was assessed from the sum of sulphate and chloride salt minerals; calcite and dolomite were treated separately as lithogenic carbonates.

Monthly air temperature and relative humidity (RH) of a wet year (2016) and a dry year (2021) for the Navoi region [meteorological station and data source to be specified] were compared. To separate the effect of temperature from that of the air water-vapour content, the RH expected at constant vapour pressure was calculated as $RH2 = RH1 \cdot e°(T1)/e°(T2)$, where $e°(T) = 0.6108 \cdot \exp[17.27T/(T + 237.3)]$ kPa [21].

PAM (granular, “Navoiyazot” JSC), sodium CMC and HS obtained from Angren brown coal were used. To select hydrogel concentrations, normal and saline soils were saturated with 0.5–5 g/L PAM or CMC solutions. In the main experiment, 500 g portions of moderately saline soil (sieved to 1.0 mm, dried at 50 °C) were saturated with 100 mL of water (control), CMC 2 g/L, PAM 3 g/L, HS 3 g/L, CMC 2 g/L + HS 3 g/L or PAM 3 g/L + HS 3 g/L and kept in a thermostat at 30, 35, 40, 45 or 50 °C [number of replicates to be stated]. The samples were weighed daily until the control fell to about 1 % moisture. Gravimetric moisture K was calculated relative to the soil mass dried at 50 °C.

The following indicators were calculated from the daily K values: the drying constant k from the first-order model $\ln K = \ln K'0 - kt$ (least squares); the moisture half-life t0.5, the day on which K fell to half of its day-1 value (linear interpolation between days); the moisture retention ratio Rn = Kvariant/Kcontrol on the day the control reached its minimum; and the additivity index $A = \Delta K_{gel+HS}/(\Delta K_{gel} + \Delta K_{HS}) \cdot 100$ %, where $\Delta K = K_{variant} - K_{control}$ on that day.

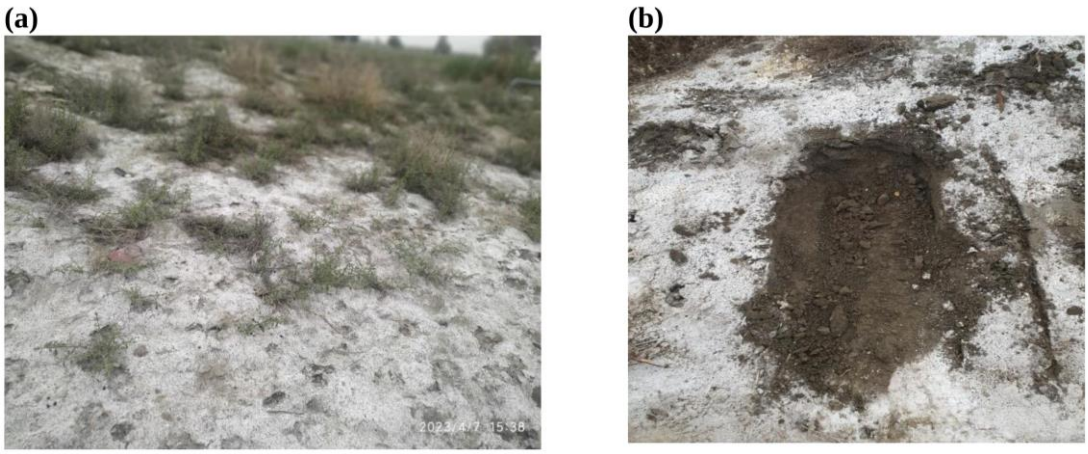


Fig. 1. White salt crust formed on rainfed soil of the study area under strong spring insolation: (a) crust surface with sparse vegetation; (b) crust and the underlying soil in a test pit.

5. Experimental Results and Discussion

A. Mineral composition and salinisation type. All soils had a common quartz–mica–feldspar–carbonate matrix; the control soil contained 37.3 % quartz, 19.4 % muscovite, 15.3 % albite, 11.2 % calcite and 7.3 % chlorite, and only 1.0 % salt minerals. In the three districts the salt minerals were concentrated in the 0.2–0.5 cm surface crust (Fig. 1, Fig. 2a). The sum of sulphate minerals in the crust was 39.5 % in Navbahor (thenardite Na2SO4 34.3 %), 35.5 % in Konimex (thenardite 31.9 %) and 22.5 % in Karmana (astrakhanite Na2Mg(SO4)2·4H2O 18.8 %), whereas chloride minerals (halite, sylvite) did not exceed 0.4–0.8 %. In the deeper horizons the salt minerals amounted to 0.7–9.6 %. Calcite and dolomite (10.1–18.8 % in all horizons) occur in the control as well and are of lithogenic origin. The salinisation is therefore of the sulphate type and increases from the oasis-adjacent Karmana towards the oasis–desert boundary (Navbahor) and the rainfed rangeland (Konimex). Thenardite crusts are prone to powdering through the mirabilite–thenardite cycle, so they can be regarded as a potential source of salt dust.

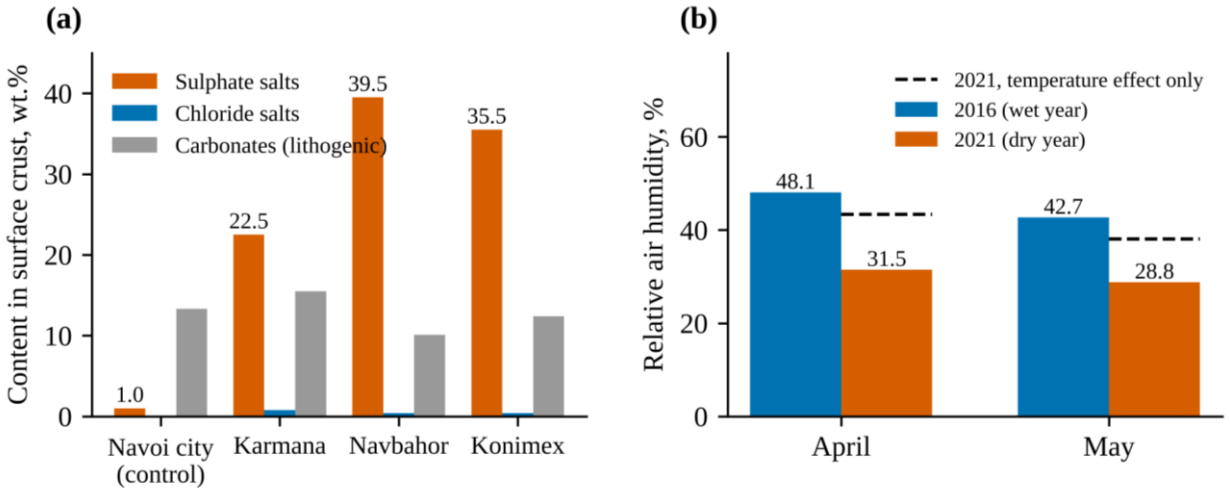


Fig. 2. (a) Sum of sulphate salt, chloride salt and carbonate minerals in the surface crust (0.2–0.5 cm) by Rietveld XRD; (b) mean relative air humidity in April and May of the wet (2016) and dry (2021) years; the dashed line is the 2021 value expected from the temperature difference alone at constant vapour pressure.

B. Critical period of moisture deficit. The annual means of the wet and dry years were close (16.7 and 16.9 °C; RH 45.0 and 39.2 %), whereas the spring months differed sharply (Fig. 2b). In April 2021 the air was 1.6 °C

warmer than in April 2016 (17.3 vs 15.7 °C), but RH fell from 48.1 to 31.5 %; in May the corresponding values were 25.3 vs 23.4 °C and 28.8 vs 42.7 %. At constant vapour pressure the temperature difference alone would have lowered RH only to 43.4 % in April and to 38.1 % in May. Most of the decrease was therefore caused by drier air rather than by warming. April–May, when the ephemerals form seeds, is the critical period, and a moisture-retaining treatment has to be effective precisely then.

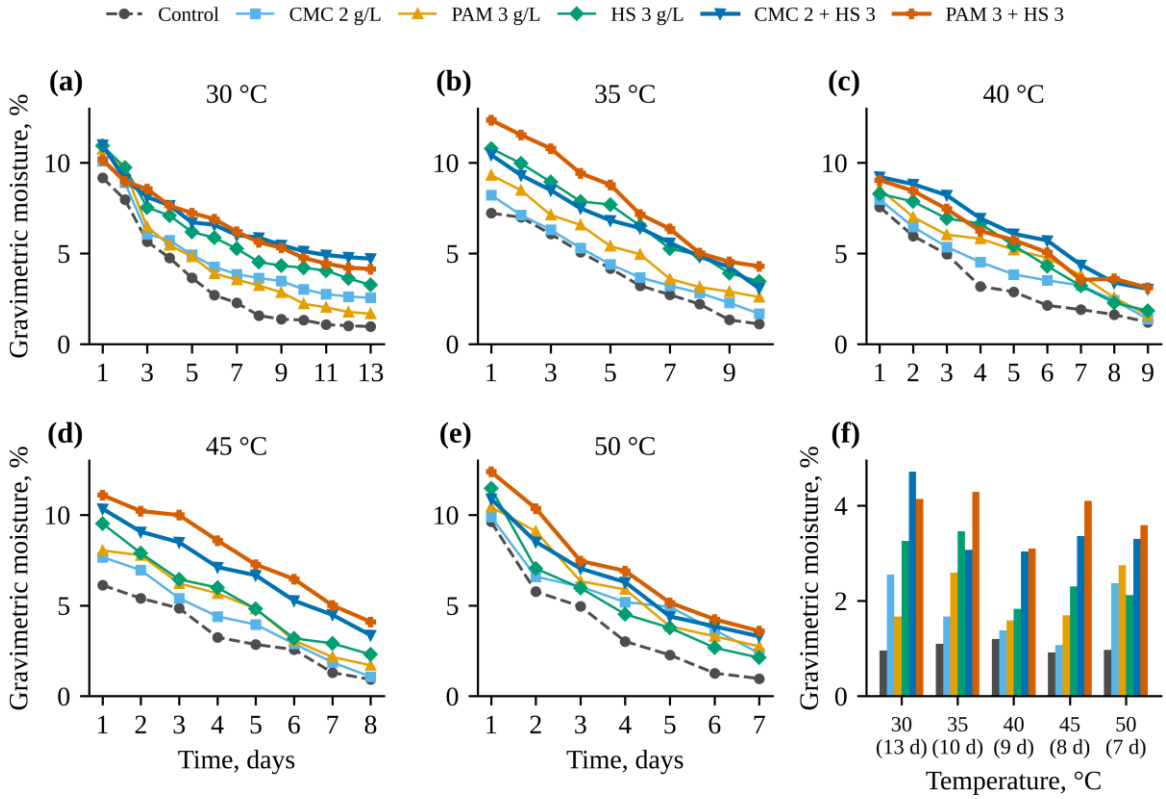


Fig. 3. Gravimetric moisture of saline soil treated with hydrogels, humic substances and their compositions:

(a)–(e) drying curves at 30, 35, 40, 45 and 50 °C; (f) moisture of all variants on the day the control reached its minimum (day number in brackets). HS – humic substances.

C. Optimal hydrogel concentrations. During the first 3–6 days of the concentration series all solutions retained moisture in proportion to their concentration. On day 7 the soil treated with PAM 3 g/L contained 5.6 % moisture against about 0.8 % in the control, and the soil treated with CMC 2 g/L contained 5.1 % against 0.6 %. Higher concentrations (4–5 g/L) gave no further gain, so 3 g/L PAM and 2 g/L CMC were used in the compositions.

D. Moisture dynamics at 30–50 °C. The drying curves (Fig. 3a–e) show that both hydrogel–humic compositions stayed above the control and, in most cases, above the single components throughout the experiment. The control reached its minimum moisture (0.92–1.20 %) on day 13 at 30 °C, day 10 at 35 °C, day 9 at 40 °C, day 8 at 45 °C and day 7 at 50 °C. On those days the compositions retained 3.04–4.71 % moisture (Fig. 3f), i.e. Rn = 2.5–4.9. At 30 °C the best result was given by CMC 2 g/L + HS 3 g/L (4.71 % against 0.96 %), while at 45 and 50 °C PAM 3 g/L + HS 3 g/L was somewhat better (4.10 and 3.59 % against 0.92 and 0.97 %). Among single components HS was more effective than either hydrogel at 30–45 °C (for example, 3.26 % against 2.55 % for CMC and 1.67 % for PAM at 30 °C). Because day-1 moisture of the control differed between series (6.12–9.62 %), absolute values are compared within a series, and temperature effects are assessed with k and t0.5.

E. Drying kinetics. The first-order model described all curves satisfactorily (R2 = 0.89–0.99). For the control, k increased from 0.203 day−1 at 30 °C to 0.382 day−1 at 50 °C (Fig. 4a). The compositions lowered k to 0.066–0.077 day−1 at 30 °C, i.e. 2.6–3.1 times, and by 1.5–1.9 times at 35–50 °C (0.201–0.210 day−1 at 50 °C). The

half-life t0.5 at 30 °C rose from 4.2 days in the control to 8.9–9.4 days in the compositions, and over the whole range it was 1.3–2.2 times longer than in the control (Fig. 4b). The complete drying time of the control decreased linearly with temperature, D = −0.28T + 20.6 (R2 = 0.92, five points) (Fig. 4d), which can be used to time the treatment.

The additivity index (Fig. 4c) depended on temperature: the effect of the compositions was smaller than the sum of the single-component effects at 35 °C (A = 67–83 %), close to it at 30 and 50 °C (89–106 %) and larger at 40–45 °C (147–227 %). A consistent synergy, and hence the formation of a polymer–humic complex, is not confirmed by these data. The interaction of PAM and CMC with clay minerals and Ca2+/Mg2+ ions [14] was not measured directly and remains a hypothesis.

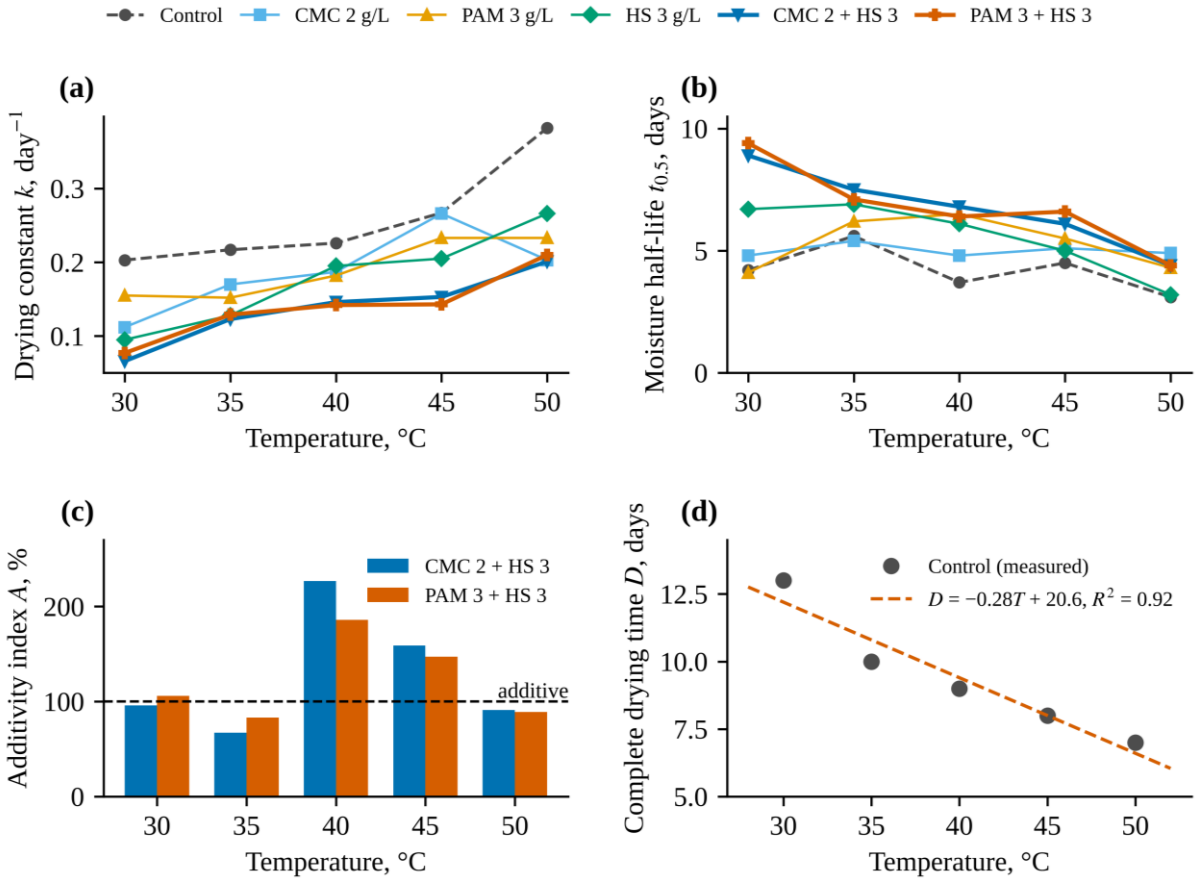


Fig. 4. Calculated indicators of moisture loss:

(a) first-order drying constant k; (b) moisture half-life t0.5; (c) additivity index A of the hydrogel–humic compositions (dashed line – additive effect); (d) complete drying time of the control soil and its linear fit.

F. Practical implications. The results suggest spraying a suspension of CMC 2 g/L + HS 3 g/L on the soil surface in late March – early April, so that it is saturated by the last effective spring rains before the April–May critical period; PAM 3 g/L + HS 3 g/L may be preferred where 45–50 °C is regular. The CMC variant is biodegradable, whereas PAM degrades slowly and should be used only as a certified product with a residual acrylamide content not exceeding 0.05 %. Sulphate-crusted sites of the Navbahor and Konimex type are the first candidates. The study has limitations: only temperature was varied (wind and air humidity were excluded), the soil was dried at 50 °C rather than 105 °C, and the field dose per hectare, the availability of the retained water to plants and the effect on biomass still have to be established in vegetation and field trials.

6. Conclusion

In rainfed soils of the Karmana, Navbahor and Konimex districts the salt minerals are concentrated in the 0.2–0.5 cm surface crust and salinisation is of the sulphate type (22.5–39.5 % sulphate minerals). April–May is the

critical period of moisture deficit, and the drop in RH in a dry year is caused mainly by lower absolute air humidity. The optimal concentrations of local PAM and CMC are 3 and 2 g/L. At 30–50 °C the compositions CMC 2 g/L + HS 3 g/L and PAM 3 g/L + HS 3 g/L retained 3.0–4.7 % moisture when the control had dried to 0.92–1.20 %, reduced the drying constant 1.5–3.1 times and extended the moisture half-life 1.3–2.2 times. The combined effect is additive or temperature-dependent rather than consistently synergistic. These compositions are candidates for field testing as a means of retaining spring rain moisture on degraded rainfed rangelands.

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