Towards Improved Application of Super Absorbent Polymers in Agriculture and Hydrology: A Cross-Disciplinary Approach

by

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Abstract

Fresh water is the essential and key component to support life on this planet. It constitutes about 0.01% of world's total water. Though freshwater is renewable, it is finite. In recent years, the demand for fresh water increased due to increase in population and industrial growth and it is projected to increase further. To meet the food demand for the growing population more land is brought under agriculture with the aid of irrigation. Irrigated agriculture is the largest consumer of water for human consumption – 67% of current global water withdrawal and 87% of consumptive water use. It is beneficial to look for possible avenues to mitigate water consumption in this particular field. One such possible means is to alter the water holding capacity of the soils by changing the hydraulic conductivity. Hydraulic conductivity is the measure of ability of the soil to transmit water. The hydraulic conductivity of the soil could be altered by amending the soils with Super Absorbent Polymers (SAPs).

SAPs are long chain, slightly cross-linked polymers capable of absorbing large quantities of water and retaining it within them. They were initially developed for agricultural usage to improve water holding capacity of soils and promote germination of seeds, but they have found extensive application in disposable pads, towels used in surgery and various other products. The water absorbing property of the SAPs can be altered by various means. Further, SAPs also undergo controllable volume changes when the ambient environment is altered. Non availability of SAPs with identical chemical and physical properties leads to preparation of poly (acrylic acid-co-acrylamide) with three different cross link ratios and particle sizes using acrylic acid

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(AA) and acrylamide (AAm) monomers. The SAPs thus prepared were characterized using spectroscopic methods. The water absorbing property of the SAPs was measured using deionized water and 9000 ppm sodium chloride solution. Mechanical strength increased and porosity decreased with increase in AAm content. The water absorbing capacity of the SAPs increased with decreasing AAm content and particle size. Also, the water absorbing capacity of SAPs decreases drastically in sodium chloride solution. The SAPs released the absorbed water when the ambient pressure is reduced. Further, the water absorbing capacity of the SAPs did not decrease drastically when reused.

Earlier studies do not offer clarity on changes in hydraulic conductivity due to SAP amendment in soils. The effect of SAPs on hydraulic conductivity of soils is a function of the soils to expand. The effect of overburdened pressure in soils has not been accounted in the previous studies. Three different soils – Sandy Loam, Clay Loam and Sandy Clay Loam are amended with SAPs of three different water absorbing capacities and particle sizes. The application rates of SAPs in soils are 0.05%, 0.15% and 0.25%. Sandy Loam soil was further studied for effect of variable overlying pressure on the soil-SAP mixture with an application rate of 0.25%. The overlying pressures used were 0, 0.05, 0.11, 0.18 and 0.23 Pa. The free swelling conditions simulate amendment of SAPs near surface whereas restricted swelling conditions simulate that of amendment at subsurface of soil. In sandy loam soil, under free swelling condition, the hydraulic conductivity increases with increase in application rate. In clay loam and sandy clay loam soils, there is no significant change in hydraulic conductivity on amendment of SAPs. Further under free swelling conditions, the expansion of soil increases with increase in application rates of SAPs for all the three soils. The hydraulic conductivity of all SAP amended soils under restricted swelling conditions decreased drastically compared to free swelling

conditions. In restricted swelling conditions, only the sandy loam showed increase in expansion with application rate, whereas clay loam and sandy clay loam soils showed mixed response. For sandy loam soil under varying overlying pressure the hydraulic conductivity of the soil-SAP mixture decreases with increase in overlying pressure. The soil amended with smallest SAPs particles has the lowest hydraulic conductivity and soil expansion compared to other SAP particle sizes. It can be concluded that, the hydraulic conductivity of the SAP amended soil increases under free swelling conditions and decreases under restricted swelling conditions.

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List of Abbreviations

SAP	Super Absorbent Polymer
AA	Acrylic Acid
AAm	Acrylamide
KPS	Potassium Peroxydisulfate
KMB	Potassium Metabisulfate
L	SAP of particle size -10+18
М	SAP of particle size -35+60
S	SAP of particle size – 140+270
FT-IR	Fourier Transform Infra-Red Spectroscopy
SEM	Scanning Electron Microscopy
ASTM	American Society for Testing and Materials
HL	Head Land Soil
TN1	Tennessee Soil 1
TN2	Tennessee Soil 2
Eqn.	equation

I. Literature Review

Introduction

Water is an essential and a key component of this planet and supports all life that exists on it. Of all the global water, fresh water is the most important to support life on this planet. Freshwater constitutes about 0.01% of world's water and are held in aquifers, soil pores, lakes, swamps and rivers (Postel et al., 1996).

Fresh water from its resources is renewable but it is finite (Postel 2000). Consumption of fresh water in United States of America (USA) as well as across the world has increased tremendously due to population explosion and economic growth during the nineteenth and twentieth centuries (Brown 2000; Gleick 2003b). World's population has increased from 1.7 billion in 1910 to 6.9 billion in 2010 and it is forecasted to reach 9 billion in 2050 (Jackson et al. 2001; United Nations 2010). Arnell (2004) discusses that according to UN Comprehensive Assessment of the Freshwater Resources of the World estimates that in 2025 up to two-thirds of the world's population would be living in water stressed countries.

Irrigated agricultural land constitutes about 17% of global cropland and 40% of world's food comes from irrigated land (Döll 2002; Postel 2000). Irrigated agriculture is the single largest consumer of water for human consumption - 67% of current global water withdrawal and 87% of the consumptive water use (Döll, 2002; Fereres and Soriano, 2007). Since 1975, global irrigated land has increased by approximately 70% (Foley et al. 2005). By 2050, the global grain demand was projected to double (Tilman et al., 2002).

With a projected increase in water stress in the future due to population growth and climatic changes and environmental factors related to irrigation, it would be beneficial to look for possible avenues to mitigate consumption of water through a combination of good

management practices, environment-friendly and efficient technologies. Some of the good management practices are usage of drought resistant crops (Parry et al., 1998), crop rotation (Huang et al., 2003; Tennakoon and Hulugalle, 2006), better water management practices in urban areas (Gleick 2003a) and efficient water delivery systems in irrigated agriculture (Clothier and Green, 1994; Fereres and Soriano, 2007; Howell, 2001; Wallace, 2000).

An alternative method for better water management in agriculture and other allied applications is by altering the water holding property of the soils so that they could be used to optimize the use of irrigation water for agricultural operations and recreational activities (such as golf courses) while maintaining sustainability of water resources. The irrigation pattern for the same plant could be altered for soils with different water retention properties (Grimes and Dickens, 1974). Increase in water-retention of the soils has shown increase in plant yield in sandy soils (Ahmed et al., 2000). The hydraulic conductivity of the soil can be affected by altering the water retention properties that is relation between matric potential and water content (van Genuchten, 1980). Thus change in hydraulic conductivity of the soil affects the infiltration rates and surface runoffs. A possible means by which water holding capacity and water retention in soils could be altered is to mix the soil with hydrophilic superabsorbent polymers (SAPs) that are capable of swelling and retaining water 400 - 1600 times their own weight (Buchholz and Graham, 1997; Kazanskii and Dubrovskii, 1992).

Super Absorbing Polymers (SAPs)

Superabsorbent polymers are cross-linked polymers, which can absorb large volumes of liquid and retain it with them. This is realized by increase in volume of the polymer (Buchholz and Graham, 1997; Kazanskii and Dubrovskii, 1992). Superabsorbent polymers were first developed by USDA in 1970s for applications in agriculture to improve the water holding

capacity of soils to promote seed germination and plant growth and now finds extensive application in disposable pads and sheets, towels used in surgery, adult incontinence and female hygiene products (Liu and Guo, 2001). Superabsorbent polymers can be classified into two types: based on charge – nonionic and ionic (Buchholz and Graham, 1997) and based on its affinity towards water – hydrophobic (Atta et al., 2005; Jang and Kim, 2000) and hydrophilic. Ionic SAPs are further classified into cationic and anionic (Buchholz and Graham, 1997).

Chemical Structure of Super Absorbent Polymers

SAPs contain long polymeric chains which are slightly cross-linked (Liu and Guo, 2001). Superlative water absorbing property of SAPs arises from electrostatic repulsion between charges on the polymer chains and osmotic imbalance between the interior and exterior of the polymer (Ono et al., 2007). Besides, certain functional groups in the polymeric chain also forms hydrogen bonding with water molecules (Xie et al., 2007). The swelling of the polymer is limited as the polymer chains are cross-linked (Liu and Guo, 2001) and this cross-linking makes these polymers insoluble in water (Buchholz and Graham, 1997).

SAPs are prepared by two principal processes – bulk solution polymerization and suspension polymerization (Buchholz and Graham, 1997). SAPs are quantified for practical features using the following methods – water absorption capacity, swelling rate, swollen gel strength, wicking capacity, sol fraction, residual monomer and ionic sensitivity (Zohuriaan-Mehr and Kabiri, 2008).

Water absorbing capacity or swelling of the polymer can be controlled by two methods type and degree of cross linking between polymeric chains and morphology of the SAP. Xie et al. (2009) discusses that the water absorbing property of the SAPs can be greatly affected by type of cross-linking agent used. Also the cross linking agent varies the polymeric chain length –

longer polymer chains have more network space and thus increases water absorbing capacity (Buchholz and Graham, 1997). Besides, the length of polymeric chain also affects its water absorption capacity – smaller polymer chains have more polymer ends which do not contribute to water absorption (Liu and Rempel, 1997).

Morphological property like porosity also affects water absorption of SAPs (Isik and Kis, 2004; Kabiri and Zohuriaan-Mehr, 2004; Turan and Çaykara, 2007). Another morphological property - particle size, also affects water absorption of SAP. Bharadwaj et al. (2007) discusses that smaller the average grain sizes of SAP, larger the water absorption. Also SAPs undergo controllable volume changes in response to small environmental conditions such as temperature, pH and ionic strength (Beltran et al., 1991; Gudeman and Peppas, 1995; Liu et al., 1995).

Uses of Super Absorbent Polymers in Agriculture

The ability of SAPs to absorb large volumes of water and retain it within them has many practical applications in agriculture. The saturated hydraulic conductivity of the soil decreases significantly with increase in mixing ratio and swelling property of the SAP (Andry et al. 2009). Abedi-Koupai et al. (2008) found that as when SAPs swell, it reduces the largest pores in the soil especially in the sandy soils. But Bhardwaj et al. (2007) in their finding states that the hydraulic conductivity of soil initially increases and then decreases. Andry et al. (2009) further states that, the expansion of soil-SAP mixture increases with increase in mixing ratio and swelling property of SAP.

Also the application of SAPs to the soil increases both saturated and residual water content, water holding capacity and available water content (Abedi-Koupai et al., 2008; Andry et al., 2009; Dorraji et al., 2010; Sivapalan, 2006). Buchholz and Graham (1997) also suggest that

the SAPs can be used in the same way as mulch, to help the soil to retain more moisture and also for longer.

Amendment of SAPs also affects other properties of soil like infiltration rates, bulk density, soil structure, compaction, soil texture, aggregate stability, crust hardness and evaporation rates (Abedi-Koupai and Asadkazemi, 2006).

The bulk density of the soil decreases with increase in application rates of SAPs (Bai et al., 2010). Application of SAPs to soil also reduces infiltration and thus avoids potential loss to deep percolation. Further, the infiltration reduction produced did not decline with decreasing treated soil layer thickness (Hüttermann et al., 2009; Lentz, 2007). The expansion and contraction of SAPs in soil during the cycle of water absorption and evaporation helps to improve air content in the soils, especially in clayey soils (Buchholz and Graham, 1997).

SAPs application in soils greatly reduces irrigation induced erosion and soil water seepage and further increases the uniformity of furrow water applications (Dorraji et al., 2010; Geesing and Schmidhalter, 2004; Ingram and Yeager, 1987; Lentz and Sojka, 1994; Lentz et al., 1992; Lentz and Sojka, 2009). Another advantage of amendment of SAP is that it greatly reduces the irrigation frequency particularly in coarse-textured soils. This property could be best utilized for water management practices in arid and semi-arid regions (Abedi-Koupai et al., 2008; Chatzoudis and Rigas, 1999; Sivapalan, 2006).

The SAPs are also biodegradable and further their products do not harm the microbial community present in the soil (Hüttermann et al., 2009).

Dorraji (2010) states that SAP amendment increases yield and water use efficiency of plants that is increase in plant biomass. SAP amendment aides plant growth by increase in plant available water, induce faster growth of plants and also prolong survival of plants under water

stress and drought conditions (Beniwal et al., 2010; Buchholz and Graham, 1997; Hüttermann et al., 2009).

El-Rehim et al. (2004) evaluated corn growth in SAP amended soil and have reported that the corn grown on SAP amended soil is better than on control soil. Similar results have been reported in corn and bean crop by Lentz and Sojka. (2009). Burke et al. (2010) have also stated that SAP amended soil has increased the biomass of rye grass by 30, 140 and 300% in normal, semi-arid and arid conditions respectively. Dorraji (2010) in his report also found that corn plant have greater water use efficiency in SAP amended soil and suggests that SAP amendment would help irrigation projects in arid and semi-arid regions. Sivapalan (2006) also observed similar results with soybeans. Other plants like tomatoes, lettuce, barley, wheat, chick pea and some tree species have also shown similar results in SAP amended soil (Hüttermann et al., 2009).

Soils amended with SAP have been used for establishment of tree seedlings and transplanted trees in arid regions of Africa and Australia to increase plant survival (Abedi-Koupai and Asadkazemi, 2006). It is also been reported that SAPs have been used in soils in barren lands of Uganda and China for successful establishment of certain trees (Hüttermann et al., 2009). Also, they have been amended to soil for grass restoration in arid regions where regular irrigation is a constraint (Lucero et al., 2010). The survival rate of plants in the SAP amended soil doubles in the absence of irrigation and deficit irrigation (Abedi-Koupai et al., 2008). Rowe et al. (2005) also supports this argument that the survival of trees in the waste land was more in the soil amended with SAPs.

The success rate of SAP amendment in soils in semi-arid and arid regions could be explained by Andry (2009). When the surrounding temperature of the swollen SAP increases, it releases the absorbed water, which could then be used by plants for their survival.

SAP amendment in soil alters certain properties of soil which do aid plant growth. SAP amendment reduces the negative effect of soil salinity on plants (Dorraji et al., 2010). Also SAPs have certain metal chelating groups which tend to bind heavy metals and thus reducing their bioavailability for plants (Hüttermann et al., 2009). Further SAPs can be used as a source of slow release of nutrients (Liu et al., 2006; Teodorescu et al., 2009).

The cost of SAP amendment can be recovered by increase in production of crops, decrease in irrigation rate and increase in plant survival rate (Hüttermann et al., 2009; Lentz and Sojka, 2009).

Limitations of Super Absorbent Polymers in Agriculture

Though the SAP amendment in soil has many beneficial uses, there are some limitations to its applications in soil. SAPs are quite fragile and tend to break apart easily thereby losing their water retention property. Further SAPs can also dehydrate rapidly in a matter of hours thus losing their absorbed water (Kim and Nadarajah, 2008). The water absorption of SAPs greatly reduces in the soils as SAPs are under pressure and unable to swell and take in water (Bhardwaj et al., 2009). The water absorption of SAPs in soils further decreases due to formation of additional crosslinks with certain ions like Ca²⁺ and Al³⁺ present in the soil (Chatzoudis and Rigas, 1999). The water absorption of the SAP also decreases with increase in salinity of irrigation water (Lentz and Sojka, 2009; Taban and Naeini, 2006). The SAPs in soils releases water with increase in temperature and this water could be potentially lost to deep percolation (Andry et al. 2009). Furthermore from Geesing and Schmidhalter (2004) work, it could be inferred that the effectiveness of SAP decreased on rewetting and can affect the hydraulic properties of soil only if applied in higher application rates. Also the efficacy of the SAP decreases over a period of time and to compensate for these loses, higher application rates are

required (Al-Harbi et al., 1999). This factor affects the economic value of crops grown on fields amended with SAP.

SAP amendment also has negative effect on plant growth. For example, Ingram and Yeager (1987) have found that the height of wheat plant grown in SAP amended soil is shorter than on control. Also the height of plant decreased with increase in SAP amendment percentage in soil. In certain cases it have been reported that the wilting point of the plants was not affected significantly (Chatzoudis and Rigas, 1999). Sarvaš et al. (2007) also reported that higher application rate of SAPs may lead to plant mortality.

For water soluble fertilizer, quantity of potassium leached increases with increase in water absorption capacity of polymers. The presence of hydrogels increased dissolution of controlled-release fertilizer. SAPs amendment increases water content which in turn increases dissolution of fertilizers and potentially leached to deeper depths (Chatzoudis and Rigas, 1998).

Frantz et al. (2005) discusses that the potential benefit of SAP amendment may be realized only in early stages of plant production and little or no benefit later in production and in post-production. Our reviews indicate that there is a mixed response of applications of SAPs in agriculture. SAPs of identical and physical properties were not used to compare the results. Further it can be inferred that there is clear lack of communication between research groups working exclusively on SAPs and its application in soils. A detailed cross disciplinary approach is required. The goal of this thesis is to have a cross disciplinary approach for preparation of SAPs exclusively for applications in soil and study their effects on their hydraulic properties.

This thesis is organized into three chapters including the literature review chapter. In the second chapter we discuss about the synthesis and characterization of SAPs for application in

soils. In third chapter we discuss about the effect of SAPs on the hydraulic conductivity of soil under free swelling and restricted swelling conditions for the three south eastern USA soils.

References

- Abedi-Koupai, J., F. Sohrab and G. Swarbrick. 2008. "Evaluation of Hydrogel Application on Soil Water Retention Characteristics." *Journal of Plant Nutrition* 31: 317-331.
- Abedi-Koupai, J. and J. Asadkazemi. 2006. "Effects of a Hydrophilic Polymer on the Field Performance of an Ornamental Plant (Cupressus arizonica) under Reduced Irrigation Regimes." *Iranian Polymer Journal* 15(9): 715-725.
- Ahmed, M. M., J. H. Sanders and W. T. Nell. 2000. "New sorghum and millet cultivar introduction in Sub-Saharan Africa: impacts and research agenda." *Agricultural Systems* 64: 55-65.
- Al-Harbi, A.R., A.M. Al-Omran, A.A. Shalaby and M.I. Choudhary. 1999. "Efficacy of a Hydrophilic Polymer Declines with Time in Greenhouse Experiments." *HortScience* 34(2): 223-224.
- Andry, H., T. Yamamoto, T. Irie, S. Moritani, M. Inoue and H. Fujiyama. 2009. "Water retention, hydraulic conductivity of hydrophilic polymers in sandy soil as affected by temperature and water quality." *Journal of Hydrology* 373: 177-183.
- Arnell, N.W. 2004. "Climate change and global water resources: SRES emissions and socioeconomic scenarios." *Global Environmental Change* 14(1): 31-52.
- Atta, A.M., R.A. El-Ghazawy, R.K. Farag, A.F. El-Kafrawy and A.A. Abdel-Azim. 2005. "Crosslinked cinnamoyloxyethyl methacrylate and isooctyl acrylate copolymers as oil sorbers." *Polymer International* 54: 1088-1096.

- Bai, W., H. Zhang, B. Liu, Y. Wu and J. Song. 2010. "Effects of super-absorbent polymers on the physical and chemical properties of soil following different wetting and drying cycles." *Soil Use and Management* 26: 253-260.
- Beltran, S., J.P. Baker, H.H. Hooper, H.W. Blanch and J.M. Prausnitz. 1991. "Swelling Equilibria for Weakly Ionizable, Temperature-Sensitive Hydrogels." *Macromolecular Materials and Engineering* 24(2): 549-551.
- Beniwal, R.S., R. Langenfeld-Heyser and A. Polle. 2010. "Ectomycorrhiza and hydrogel protect hybrid poplar from water deficit and unravel plastic responses of xylem anatomy." *Environmental and Experimental Botany* 69: 189-197.
- Bhardwaj, A. K., R. A. McLaughlin, I. Shainberg and G. J. Levy. 2009. "Hydraulic Characteristics of Depositional Seals as Affected by Exchangeable Cations, Clay Mineralogy, and Polyacrylamide." *Soil Science Society of America Journal* 73: 910 918.
- Bhardwaj, A. K., I. Shainberg, D. Goldstein, D. N. Warrington and G.J. Levy. 2007. "Water Retention and Hydraulic Conductivity of Cross-Linked Polyacrylamides in Sandy Soils." *Soil Science Society of America Journal* 71: 406 - 412.
- Brown, T. C. 2000. "Projecting U . S . freshwater withdrawals." *Journal of Water Resources Research* 36(3): 769-780.
- Buchholz, F.L. and A.T. Graham. 1997. "Modern Superabsorbent Polymer Technology." In *John Wiley & Sons Inc.*,.

- Burke, D. R., G. Akay and P. E. Bilsborrow. 2010. "Development of Novel Polymeric Materials for Agroprocess Intensification." *Journal of Applied Polymer Science* 118: 3292 - 3299.
- Chatzoudis, G. K. and F. Rigas. 1998. "Macroreticular Hydrogel Effects on Dissolution Rate of Controlled-Release Fertilizers." *Journal of Agricultural and Food Chemistry* 46: 2830-2833.
- Chatzoudis, G. K. and F. Rigas. 1999. "Soil Salts Reduce Hydration of Polymeric Gels and Affect Moisture Characteristics of Soil." *Communications in Soil Science and Plant Analysis* 30 (17 and 18): 2465-2474.
- Clothier, B.E. and S.R. Green. 1994. "Rootzone Processes and the efficient use of irrigation water." *Agricultural Water Management* 25: 1-12.
- Dorraji, S.S., A. Golchin and S. Ahmadi. 2010. "The Effects of Hydrophilic Polymer and Soil Salinity on Corn Growth in Sandy and Loamy Soils." *Clean Soil, Air, Water* 38 (7): 584 591.
- Döll, P. 2002. "Impact of Climate Change and Variability on Irrigation Requirements : A Global Perspective." *Climatic Change* 54: 269–293.
- El-Rehim, H.A.A., E.A. Hegazy and H.L.A. El-Mohdy. 2004. "Radiation synthesis of hydrogels to enhance sandy soils water retention and increase plant performance." *Journal of Applied Polymer Science* 93: 1360-1371.

- Fereres, E. and M.A. Soriano. 2007. "Deficit irrigation for reducing agricultural water use." *Journal of Experimental Botany* 58 (2): 147 - 159.
- Foley, J.A., R. DeFries, G.P. Asner, C. Barford, G. Bonan, S.R. Carpenter, F.S. Chapin, M.T.
 Coe, G.C. Daily, H.K. Gibbs, J.H. Helkowski, T. Holloway, E.A. Howard, C.J. Kucharik,
 C. Monfreda, J.A. Patz, I.C. Prentice, N. Ramankutty and P.K. Snyder. 2005. "Global
 Consequences of Land Use." *Science* 309: 570-574.
- Frantz, J.M., J.C. Locke, D.S. Pitchay and C.R. Krause. 2005. "Actual Performance versus Theoretical Advantages of Polyacrylamide Hydrogel throughout Bedding Plant Production." *HortScience* 40(7): 2040-2046.
- Geesing, D., and U. Schmidhalter. 2004. "Influence of sodium polyacrylate on the water-holding capacity of three different soils and effects on growth of wheat." *Soil Use and Management* 20: 207-209.
- Gleick, P.H. 2003a. "Global Freshwater Resources: Soft-Path Solutions for the 21st Century." *Science* 302: 1524 1528.

Gleick, P.H. 2003b. "Water Use." Annual Review of Environment and Resources 28: 275-314.

- Grimes, D. W. and W. L. Dickens. 1974. "Dating Termination of Cotton Irrigation from Soil Water-Retention Characteristics." *Agronomy Journal* 66: 403 404.
- Gudeman, L.F. and N.A. Peppas. 1995. "pH-Sensitive membranes from poly (vinyl alcohol)/ poly (acrylic acid) interpenetrating networks." *Journal of Membrane Science* 107(3): 239-248.

- Howell, T.A. 2001. "Enhancing Water Use Efficiency in Irrigated Agriculture." *Agronomy Journal* 93: 281 - 289.
- Huang, M., M. Shao, L. Zhang and Y. Li. 2003. "Water use efficiency and sustainability of different long-term crop rotation systems in the Loess Plateau of China." *Soil and Tillage Research* 72: 95 - 104.
- Hüttermann, A., L.J. B. Orikiriza and H. Agaba. 2009. "Application of Superabsorbent Polymers for Improving the Ecological Chemistry of Degraded or Polluted Lands." *Clean* 37(7): 517-526.
- Ingram, D. L., and T.H. Yeager. 1987. "Effects of Irrigation Frequency and A Water-Absorbing Polymer Amendment on Ligustrum Growth and Moisture Retention by a Container Medium." *Journal of Environmental Horticulture* 5(1): 19 - 21.
- Isık, B. and M. Kıs. 2004. "Preparation and determination of swelling behavior of poly(acrylamide-co-acrylic acid) hydrogels in water." *Journal of Applied Polymer Science* 94: 1526-1531.
- Jackson, R.B., S.R. Carpenter, C.N. Dahm, D.M. McKnight, R.J. Naiman, S.L. Postel and S.W. Running. 2001. "Water in a Changing World." *Ecological Applications* 11(4): 1027-1045.
- Jang, J. and B. Kim. 2000. "Studies of Crosslinked Styrene-Alkyl Acrylate Copolymers for Oil Absorbency Application. II. Effects of Polymerization Conditions on Oil Absorbency." *Journal of Applied Polymer Science* 77: 914-920.

- Kabiri, K. and M.J. Zohuriaan-Mehr. 2004. "Porous Superabsorbent Hydrogel Composites: Synthesis, Morphology and Swelling Rate." *Macromolecular Materials and Engineering* 289:653-661
- Kazanskii, K.S. and S.A. Dubrovskii. 1992. "Chemistry and Physics of 'Agricultural' Hydrogels." *Advances in Polymer Science* 104: 97 - 133.
- Kim, S. and A.Nadarajah. 2008. "Development of Double-Layer Hydrogels for Agricultural Applications." In *AIChE Annual Meeting 2008*.
- Lentz, R.D., I. Shainberg, R.E. Sojka and D.L. Carter. 1992. "Preventing Irrigation Furrow Erosion with Small Applications of Polymers." *Soil Science Society of America Journal* 56(6): 1926-1932.
- Lentz, R.D. and R.E. Sojka. 1994. "Field results using polyacrylamide to manage furrow erosion and infiltration." *Soil Science* 158(4): 274-282.
- Lentz, R.D. 2007. "Inhibiting Water Infiltration into Soils with Cross-linked Polyacrylamide:
 Seepage Reduction for Irrigated Agriculture." *Soil Science Society of America Journal* 71: 1352 1362.
- Lentz, R.D. and R.E. Sojka. 2009. "Long-Term Polyacrylamide Formulation Effects on Soil Erosion, Water Infiltration, and Yields of Furrow-Irrigated Crops." *Agronomy Journal* 101(2): 305 - 314.
- Liu, M. and T. Guo. 2001. "Preparation and Swelling Properties of Crosslinked Sodium Polyacrylate." *Journal of Applied Polymer Science* 82: 1515-1520.

- Liu, X., Z. Tong and O. Hu. 1995. "Swelling Equilibria of Hydrogels with Sulfonate Groups in Water and in Aqueous Salt Solutions." *Macromolecules* 28: 3813-3817.
- Liu, Z. S. and G. L. Rempel. 1997. "Preparation of Superabsorbent Polymers by Crosslinking Acrylic Acid and Acrylamide Copolymers." *Journal of Applied Polymer Science* 64: 1345-1353.
- Liu, M., R. Liang, F. Zhan, Z. Liu and A. Niu. 2006. "Synthesis of a slow-release and superabsorbent nitrogen fertilizer and its properties." *Polmers for Advanced Technologies* 17: 430-438
- Lucero, M.E., D.R. Dreesen and D.M. VanLeeuwen. 2010. "Using hydrogel filled, embedded tubes to sustain grass transplants for arid land restoration." *Journal of Arid Environments* 74: 987-990.
- van Genuchten, M.T. 1980. "A Closed-form Equation for Predicting the Hydraulic Conductivity of Unsaturated Soils." *Soil Science Society of America Journal1* 44: 892 898.
- Ono, T., T. Sugimoto, S. Shinkai and K. Sada. 2007. "Lipophilic polyelectrolyte gels as superabsorbent polymers for nonpolar organic solvents." *Nature materials* 6: 429 - 433.
- Parry, M., N. Arnell, M. Hulme, R. Nicholls and M. Livermore. 1998. "Adapting to the inevitable." *Nature* 395: 741.
- Postel, S. L. 2000. "Entering an Era of Water Scarcity: The Challenges Ahead." *Ecological Applications* 10(4): 941-948.

- Postel, S. L., G.C. Daily, and P.R. Ehrlich. 1996. "Human Appropriation of Renewable Fresh Water." *Science* 271(5250): 785-788.
- Rowe, E. C., J. C. Williamson, D. L. Jones, P. Holliman and J. R. Healey. 2005. "Initial Tree Establishment on Blocky Quarry Waste Ameliorated with Hydrogel or Slate Processing fines." *Journal of Environmental Quality* 34: 994-1003.
- Sarvaš, M., P. Pavlenda, and E. Takáovčá. 2007. "Effect of hydrogel application on survival and growth of pine seedlings in reclamations." *Journal of Forest Science* 53(5): 204-209.
- Sivapalan, S. 2006. "Benefits of treating a sandy soil with a crosslinked-type polyacrylamide." *Australian Journal of Experimental Agriculture* 46: 579 - 584.
- Taban, M. and S. A. R. M. Naeini. 2006. "Effect of Aquasorb and Organic Compost Amendments on Soil Water Retention and Evaporation with Different Evaporation Potentials and Soil Textures." *Communications in Soil Science and Plant Analysis* 37: 2031-2055.
- Tennakoon, S. B., and N. R. Hulugalle. 2006. "Impact of crop rotation and minimum tillage on water use efficiency of irrigated cotton in a Vertisol." *Irrigation Science* 25: 45 52.
- Teodorescu, M., A. Lungu, P.O. Stanescu and C. Neamţu. 2009. "Preparation and Properties of Novel Slow-Release NPK Agrochemical Formulations Based on Poly(acrylic acid)
 Hydrogels and Liquid Fertilizers." *Industrial & Engineering Chemistry Research* 48: 6527-6534.

- Tilman, D., K.G. Cassman, P.A. Matson, R. Naylor and S. Polasky. 2002. "Agricultural sustainability and intensive production practices." *Nature* 418: 671 677.
- Turan, E. and T. Çaykara. 2007. "Swelling and Network Parameters of pH-Sensitive Poly (acrylamide-co-acrylic acid) Hydrogels." *Journal of Applied Polymer Science* 106: 2000 -2007.
- United Nations. 2010. "World Population Prospects, the 2010 Revision." http://esa.un.org/unpd/wpp/unpp/p2k0data.asp.
- Wallace, J.S. 2000. "Increasing agricultural water use efficiency to meet future food production." *Agriculture, Ecosystems & Environment* 82: 105–119.
- Xie, J., X. Liu, J. Liang and Y. Luo. 2009. "Swelling Properties of Superabsorbent Poly (acrylic acid-co-acrylamide) with Different Crosslinkers." *Journal of Applied Polymer Science* 112: 602 608.
- Xie, J., X. Liu and J. Liang. 2007. "Absorbency and Adsorption of Poly (acrylic acid-coacrylamide) Hydrogel." *Journal of Applied Polymer Science* 106: 1606 - 1613.
- Zohuriaan-Mehr, M.J. and K. Kabiri. 2008. "Superabsorbent Polymer Materials: A Review." *Iranian Polymer Journal* 17(6): 451-477.

II. Synthesis and Characterization of Super Absorbent Polymers for Agricultural Purposes Abstract

Super Absorbent Polymers are long chain, slightly cross-linked polymers capable of absorbing large quantities of water and retaining it within them. They were initially developed for agricultural usage to improve water holding capacity of soils and promote germination of seeds but finds extensive application in disposable pads, towels used in surgery and various other products. The water absorbing property of the SAPs can be altered by various means. Further the SAPs also undergo controllable volume changes when the ambient environment is altered. The ability of SAPs to absorb water has many practical applications in agriculture. One such property could be affected by amendment of SAPs in soils is hydraulic conductivity. Non availability of SAPs with identical chemical and physical properties leads to preparation of poly (acrylic acidco-acrylamide) with three different cross link ratios and particle sizes using acrylic acid (AA) and acrylamide (AAm) monomers. The SAPs thus prepared were characterized using spectroscopic methods. The water absorbing property of the SAPs was measured using deionized water and 9000 ppm sodium chloride solution. The mechanical strength increases and porosity decreases with increase in AAm content. The water absorbing capacity of the SAPs increases with decrease in AAm content and particle size. Also, the water absorbing capacity of SAPs decreases drastically in sodium chloride solution. The SAPs release the absorbed water when the ambient pressure is reduced. Further, the water absorbing capacity of the SAPs does not decrease drastically when reused.

Introduction

In our daily life, cotton, paper and sponges are commonly used to absorb water. These materials absorb only a few times their weight of water and have rather poor properties with respect to water retention (Liu and Rempel, 1997). However, some types of polymers and copolymers do function as high water absorbents, having very good water retention properties and high affinity towards water. These polymers are termed as Super Absorbent Polymers (SAPs). High water absorption of SAPs is realized by increase in their volume (Buchholz and Graham, 1997; Kazanskii and Dubrovskii, 1992). The SAPs were first developed by group of researchers at Northern Regional Research Laboratory of U. S. Department of Agriculture in 1970s for applications in agriculture to improve water holding capacity of soils to promote germination of seeds and plant growth, but finds extensive applications in disposable pads and sheets, towels used in surgery, adult incontinence and female hygiene products (Liu and Guo, 2001).

SAPs contain long polymeric chains which are slightly cross-linked (Liu and Guo, 2001). Superlative water absorbing property of SAPs arises from electrostatic repulsion between charges on the polymer chains and osmotic imbalance between the interior and exterior of the SAPs (Ono et al., 2007). Besides, certain functional groups in the polymeric chain forms hydrogen bonding with water molecules (Xie et al., 2007). The swelling of the SAP is limited as the polymer chains are cross-linked (Liu and Guo, 2001) and this cross-linking makes these SAPs insoluble in water (Buchholz and Graham, 1997). Water absorbing properties of the SAPs are controlled by two methods – type and degree of cross linking between polymeric chains (Buchholz and Graham, 1997; Liu and Rempel, 1997; Xie et al., 2009) and morphology of SAP particles (Isik and Kis, 2004; Kabiri and Zohuriaan-Mehr, 2004; Turan and Çaykara, 2007).

SAPs also undergo controllable volume changes in response to small environmental conditions such as temperature, pH and ionic strength (Beltran et al., 1991; Gudeman and Peppas, 1995; Liu et al., 1995).

The ability of SAPs to absorb water and retain it within them has many practical applications in agriculture. This thesis focuses on how the amendment of SAPs in soil affects one of the properties of soil - the hydraulic conductivity. To study the effects of amendment of SAPs in soil, SAPs with identical physical and chemical properties are required. Due to unavailability of SAPs with above criteria, poly(acrylic acid – co – acrylamide) SAPs are prepared with different cross-link ratio and particle size and their effect on water absorption are studied. Further for agricultural purposes, the SAPs have to release the absorbed water and should be reusable. These aspects of the SAPs are also investigated.

Materials and Methods

Materials

Acrylic acid (AA) (99%), Acrylamide (AAm) (98%), Formaldehyde (37% solution in water, v/v), Potassium Peroxydisulfate (KPS) (99%), Potassium Metabisulfite (KMB) (95%) were supplied by Alfa Aesar (USA). Sodium hydroxide (98.1%) supplied by Fischer-Scientific (USA) was used to prepare 333333ppm solution using de-ionized water. All the above chemicals were used as such in SAP preparation. Ethanol (98%) was used to precipitate polymer from its solution.

Preparation of SAP

The SAPs are prepared as mentioned in Liu and Rempel (1997). 0.1 g of KPS and 0.042g of KMB and 185 ml of water are mixed in a three necked round bottom flask to form the redox initiator and heated to 65°C in a water bath such that temperature is maintained. A pre-

determined amount of AA and AAm (table 1) are mixed in 32 ml of water and then added in drop-wise fashion into the redox system at 65°C over a period of 10 minutes. The solution is then mixed for 10 minutes and neutralized with sodium hydroxide solution to a pH of 4.5. The pH of the solution is measured using a pH meter. The solution is then heated at 70°C for 2 hours. The solution mixture is then cooled to 45°C. 6.25 ml of formaldehyde solution is added and mixed for 30 minutes. The solution mixture is then heated at 70°C for 3 hours. The polymer thus formed is dewatered using ethanol and dried at 80°C to a constant weight. The polymer thus formed is cross linked poly(acrylic acid - co acrylamide) super absorbing polymer (SAP).

Classification to different particle size

The polymer in its newly formed state is shaped as one mass. The SAPs thus obtained are crushed under mortar and pestle and sieved to obtain the necessary particle sizes. In this study, we form three distinct particle sizes as shown in Table 2. These particle sizes are selected because they represent the soil particle sizes for very coarse sand, medium sand and very fine sand respectively.

Fourier Transform Infra-Red Spectroscopy

In Fourier Transform Infra-Red Spectroscopy, Infra-Red (IR) radiation is passed through a sample. A part of the IR radiation is absorbed and a part of it is transmitted through the sample. The resulting spectrum represents the molecular absorption and transmission, creating a molecular fingerprint of the sample. Like a fingerprint no two molecular structures have the same infrared spectrum. Thermo Fischer Scientific NICOLET 6700 FT-IR instrument is used for analysis. The sample holder and probe in the spectrometer are cleaned. The spectrometer is scanned to collect the spectrum of the background. This is done to nullify the effect of chemicals other than the sample present in the spectrometer environment (background IR spectrum). The

SAP sample is then placed in the sample holder and pressed against the diamond in the sample holder using the probe. Care should be taken not to damage the diamond in the sample holder. The FT-IR spectrometer is then turned on to scan the sample. The sample was scanned for wavenumbers 4000 to 400 cm⁻¹. The output from the detector is fed to the computer, which removes the background spectrum to give the IR spectrum of the sample.

Scanning Electron Microscopy (SEM)

The SAP sample is analyzed in Scanning Electron microscope to study its morphological features. Scanning electron microscope Zeiss EVO50 is used for SEM analysis. The SAP samples are non-conductors, so before SEM analysis the samples are sputter coated with gold as a sample preparation step to make them conductive.

Water Absorbing Capacity

Determination of water absorbing capacity by the SAP was carried out according to Liu and Rempel (1997). About 0.2 g (W_2) of SAP of particle size L is taken and soaked in 200 ml of de-ionized water for 30 minutes. The swollen SAP is filtered through the mesh and weighed (W_1). Water absorbing capacity (WA) of the SAP is measured by using eqn. [2.1].

$$WA = \frac{W_1 - W_2}{W_2} \qquad \dots \qquad [2.1]$$

The water absorbency of the SAPs of particle size M and S are measured using the above procedure. Water absorbing capacity of SAPs can also be defined as the ability of per unit mass of SAP to retain water.

Electrolyte Absorbing Capacity

About 0.2 g (W_B) of SAP of particle size L is taken and soaked in 200 ml of 9000 ppm sodium chloride solution for 30 minutes. The swollen SAP is filtered through the mesh and

weighed (W_A). Electrolyte Absorbing Capacity (WA_E) of the SAP is measured by using eqn. [2.2].

$$WA_E = \frac{W_A - W_B}{W_B} \qquad \dots \qquad [2.2]$$

The electrolyte absorbency of the SAPs of particle size M and S are measured using above procedure

Water absorption kinetics

1 g of SAP of particle size L is taken in a nylon mesh bag. The bag is then immersed in de-ionized water for certain pre-determined time. The SAP along with the nylon bag is then removed from water and allowed to drain in air for 5 minutes. The weight of the swollen SAP in air is then noted. Water absorbing capacity of the SAP is measured using eqn. [2.1]. The assumption in this water absorption kinetics approach is that when lifted above water, water absorption by the SAP ceases and the water that is not absorbed drains. This procedure is carried out till the weight of SAP in air reaches a steady state. The same procedure is used to study the water absorption kinetics of SAPs of particle size M and S.

Desorption

The SAP of particle size L is soaked in de-ionized water for 30 minutes. The swollen SAP is filtered through an appropriate mesh. Water absorption of SAP is measured using eqn. [2.1]. A funnel fitted with Whatmann filter paper Number 40 is used and about 25 g of the swollen SAP is weighed and placed in the funnel. Rearranging eqn. [2.1], the initial dry weight (W₂) of SAP can be calculated using eqn. [2.3], where W₁ is weight of swollen polymer and WA is the water absorbing capacity of the SAP.

$$W_2 = \frac{W_1}{WA+1}$$
 [2.3]

The funnel is then placed in a vacuum chamber and negative pressure is applied in a step wise fashion for every 24 hours. Weight of swollen SAP before each pressure increase step is measured. From the initial dry weight of SAP (W_2) and the weight of swollen SAP measured before each pressure increase, water absorbing capacity of SAP is calculated using eqn. [2.1]. The same procedure is repeated for other SAP particle sizes Medium and Small.

Reswelling

About 200 mg (W_2) of dry SAP of particle size L is taken in a nylon bag. The bag is soaked in de-ionized water for 30 minutes. The bag is then suspended in air for 5 minutes to drain the water unabsorbed by the SAP. The weight of swollen polymer is measured as W_1 . Water absorbing capacity of SAP is calculated using eqn. [I2.1]. The bag is then placed in an oven at 105°C. The bag is kept in the oven until the weight of bag reaches steady state. The weight of nylon bag with the SAP is noted and again soaked in de-ionized water and the same procedure is repeated for six times. The above procedure for reswelling is carried out for other SAP particle sizes M and S.

Results and Discussion

FTIR

The infra-red spectra of SAP A, B and C are given in figure 2.2. The characteristic peak at wave number 1033.4 cm⁻¹ arises from the ether group -O- providing evidence of a crosslinking reaction.

Scanning Electron Microscopy (SEM)

The SEM images of the SAPs are given in figure 2.3. The pore size increases with increase in AAm content. Also the quantity of pores decreases with increase in AAm content in the polymer. The pores in the polymers are formed when ethanol evaporates from the polymer
during the drying process. The difference in pore size and quantity is caused by the cross-linking density. Increase in AAm increases cross-linking density and this forms a tight network structure in the polymer. In the preparation process, when ethanol vaporizes from within the polymer system, enough pressure has to be created to break the tight polymer structure. So for SAP A more vapors are required to create enough pressure to break the tight network structure and escape from the system whereas in SAP C less amount of vapors are enough to create pressure to break the network structure.

Water Absorbing Capacity

The water absorbing capacities of the SAPs are given in figure 2.4. Water absorbing capacity of the SAP increases with decrease in AAm content. Besides, it also increases with decrease in particle size of SAPs. The increase in water absorbing capacity with decrease in AAm content could be explained as follows. The copolymer is divided into non-ionic and ionic part. The ionic part in SAP is acrylic acid and non-ionic part is acrylamide. Acrylic acid component in the polymer chain has charges in the molecule. These charges are responsible for the osmotic pressure in the SAP. When the SAPs are soaked in water, the chains become mobile. Due to repelling of the chains, the polymer chains expand and absorb more water. Further higher is the charge difference between the polymer and the solution, more is the osmotic pressure (Liu et al., 1995). So increase in acrylic acid content increases the water absorbing capacity of SAPs.

Also as seen from the polymer reaction equation, increase in acrylamide content increases cross linking density of the SAPs with resists the swelling and decreases its water absorbing capacity. Besides, porosity of the SAPs decreases with increase in AAm content as shown in the SEM images in figure 2.3.

Electrolyte Absorbing Capacity

When 9000 ppm of sodium chloride solution was used, water absorbing capacity of the SAPs decreases drastically. The difference in charge within the polymer and the electrolyte solution decreases due to presence of ions in electrolyte (Liu et al., 1995). This causes decrease in osmotic pressure - the primary driving force for superlative water absorbing capacity in the SAP. SAP A has the lower charge and thus decrease in absorbing capacity is lower compared to that of SAP C which has a higher charge due to presence of more AA content. The particle size has negligible effect on absorbing capacity of SAPs.

Water Absorption Kinetics

The water absorption kinetics of SAPs is given in figure 2.5. The particle sizes of the SAPs have negligible effect on water absorption of the polymer. SAP A attains steady state faster than SAP B and C.

Desorption

Desorption of water from SAPs under application of negative pressure or vacuum is given in figure 2.6. The water absorbing capacity of SAPs decreases with increase in applied negative pressure. Further, the SAPs also release all the absorbed water at 800 cm of pressure. Comparatively, SAP C releases more water at low negative pressures compared to SAPs A and B.

Reswelling

Reswelling of all three SAPs is given in figure 2.7. The water absorbing capacity of the SAPs do not decrease drastically even after repeated swelling for six times. This property of the SAPs enables them to be reused in applications where their properties can be best utilized.

Conclusion

Super Absorbing Polymers with different water absorbing capacities and particle sizes were prepared. As the AAm content in the SAP increases, the mechanical strength increases and porosity decreases. Water absorbing capacity of the SAPs increases with decrease in AAm content, particle size and electrolyte concentration. Further, water absorption by SAP is reversible as it releases the absorbed water when subjected to negative pressures. Also, the reswelling ability of the SAPs makes it reusable in many fields especially in agriculture were it can be applied. The ability of the SAPs to absorb water and retain under normal conditions has many possible applications in agriculture. One such application is amendment of soil with SAPs to alter the hydraulic properties of the soil. Further research is required to explore the possible applications of SAPs in agriculture.

SAP Type	AA:AAm	Weight of AA (g)	Weight of AAm (g)			
Α	97:3	24.25	0.75			
В	98:2	24.5	0.5			
С	98.75:1.25	24.69	0.31			

Table 1: Composition of Super Absorbent Polymers

Table 2: Particle size classification of Super Absorbent Polymers

Туре	Particle Size		Representative soil		
	ASTM Mesh Number	Mm	classification		
Large (L)	-10 + 18	1 – 2	Very coarse sand		
Medium (M)	-35 + 60	0.25 - 0.5	Medium sand		
Small (S)	-140 + 270	0.053 - 0.106	Very fine sand		

$$\begin{array}{c} & & & \\ & & & & \\ & & & \\ & & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ &$$





Figure 2.1: Polymerization reaction



Figure 2.2: FT-IR Spectrum of Super Absorbent Polymers







Scale 10 µm

Figure 2.3: SEM images of Super Absorbent Polymers. Clockwise - (a) - SAP A, (b) - SAP B, (c) - SAP C



Figure 2.4: Comparison of Water and Electrolyte Absorbing Capacity of Super Absorbent Polymers



Figure 2.5: Water Absorption Kinetics of Super Absorbent Polymers



Figure 2.6: Desorption of water by Super Absorbent Polymers under negative pressure



Figure 2.7: Reswelling of Super Absorbent Polymers

References

- Beltran, S., J.P. Baker, H.H. Hooper, H.W. Blanch and J.M. Prausnitz. 1991. "Swelling Equilibria for Weakly Ionizable, Temperature-Sensitive Hydrogels." *Macromolecular Materials and Engineering* 24: 549-551.
- Buchholz, F. L. and A.T. Graham. 1997. "Modern Superabsorbent Polymer Technology." *John Wiley & Sons Inc.*
- Gudeman, L. F. and N.A. Peppas. 1995." pH-Sensitive membranes from poly (vinyl alcohol) / poly (acrylic acid) interpenetrating networks." *Journal of Membrane Science 107:* 239-248.
- Isık, B. and M. Kıs. 2004. "Preparation and determination of swelling behavior of poly(acrylamide-co-acrylic acid) hydrogels in water." *Journal of Applied Polymer Science* 94: 1526-1531.
- Kabiri, K. and M.J. Zohuriaan-Mehr. 2004. "Porous Superabsorbent Hydrogel Composites: Synthesis, Morphology and Swelling Rate." *Macromolecular Materials and Engineering* 289: 653-661.
- Kazanskii, K. S. and S.A. Dubrovskii. 1992. "Chemistry and Physics of 'Agricultural' Hydrogels. Advances in Polymer Science 104: 97-133.
- Liu, M. and T. Guo. 2001. "Preparation and Swelling Properties of Crosslinked Sodium Polyacrylate." *Journal of Applied Polymer Science* 82: 1515-1520.

- Liu, X., Z. Tong and O. Hu. 1995. "Swelling Equilibria of Hydrogels with Sulfonate Groups in Water and in Aqueous Salt Solutions." *Macromolecules* 28: 3813-3817.
- Liu, Z. S. and G.L. Rempel. 1997. "Preparation of Superabsorbent Polymers by Crosslinking Acrylic Acid and Acrylamide Copolymers." *Journal of Applied Polymer Science* 64: 1345-1353.
- Ono, T., T. Sugimoto, S. Shinkai and K. Sada. 2007. "Lipophilic polyelectrolyte gels as superabsorbent polymers for nonpolar organic solvents." *Nature materials 6:* 429-433.
- Turan, E. and T. Çaykara. 2007. "Swelling and Network Parameters of pH-Sensitive Poly (acrylamide-co-acrylic acid) Hydrogels." *Journal of Applied Polymer Science 106:* 2000-2007.
- Xie, J., X. Liu and J. Liang. 2007. "Absorbency and Adsorption of Poly (acrylic acid-coacrylamide) Hydrogel." *Journal of Applied Polymer Science 106:* 1606-1613.
- Xie, J., X. Liu, J. Liang and Y.Luo. 2009. "Swelling Properties of Superabsorbent Poly (acrylic acid-co-acrylamide) with Different Crosslinkers." *Journal of Applied Polymer Science 112:* 602-608.

III. Hydraulic Conductivity of SAP amended Soil under Free Swelling and Restricted Swelling Conditions

Abstract

Hydraulic conductivity of soil is a measure of ability of soil to transmit water. The hydraulic conductivity of the soil could be altered by amending the soils with super absorbent polymers (SAPs). Previous studies do not offer clarity on changes in hydraulic conductivity due to SAP amendment in soils. The effect of SAP on hydraulic conductivity of soils is a function of the soils to expand. The effect of overburdened pressure in soils has not been accounted in the previous studies. Three different soils – Sandy Loam, Clay Loam and Sandy Clay Loam are amended with SAPs of three different water absorbing capacities and particle sizes. The application rates of SAPs in soils are 0.05%, 0.15% and 0.25%. Sandy Loam soil was further studied for effect of variable overlying pressure on the soil-SAP mixture with an application rate of 0.25%. The overlying pressures used were 0, 0.05, 0.11, 0.18 and 0.23 Pa. The free swelling conditions simulate amendment of SAP near surface whereas restricted swelling conditions simulate that of amendment at subsurface of soil. In Sandy Loam soil, under free swelling condition, the hydraulic conductivity increases with increase in application rate. In Clay Loam and Sandy Clay Loam soils, there is no significant change in hydraulic conductivity on amendment of SAPs. Further under free swelling conditions, the expansion of soil increases with increase in application rates of SAPs for all the three soils. The hydraulic conductivity of all SAP amended soil under restricted swelling conditions decreased drastically compared to free swelling conditions. In restricted swelling condition, only the Sandy Loam showed increase in expansion with application rate, whereas Clay Loam and Sandy Clay Loam soils showed mixed

response. For Sandy Loam soil under varying overlying pressure the hydraulic conductivity of the soil-SAP mixture decreases with increase in overlying pressure. The soil amended with smallest SAPs particles has the lowest hydraulic conductivity and soil expansion compared to other SAP particle sizes. It can be concluded that, the hydraulic conductivity of the SAP amended soil increases under free swelling conditions and decreases under restricted swelling conditions.

Introduction

The rate of movement of water through soils is of considerable importance in many aspects of agricultural and hydrology. Some of the important situations where rate of movement of water through soils play an important role are entry of water into soil, movement of water to plant roots, flow of water to drains and wells and evaporation of water from the soil surface (Klute and Dirksen, 1986). The physical factors that determine the flow of water through soils are hydraulic conductivity and water retention characteristics. Hydraulic conductivity of soil is the measure of ability of soil to transmit water, whereas water retention characteristics are an expression of its ability to store water. These two properties are often discussed as hydraulic properties of soil.

Theory

For one dimensional flow conditions, flow of water can be defined by Darcy's law which may be written as follows

where *q* is the volume flux density, Darcy velocity, or apparent velocity (i.e., the volume of liquid phase passing through unit cross-sectional area of soil in unit time), $\partial H/\partial z$ is the gradient of hydraulic head *H* and K(θ) is the hydraulic conductivity. The driving force is expressed as the negative gradient of the hydraulic head composed of the gravitational head *z* and the pressure head *h* which may be written as follows

$$H = h + z \qquad [3.2]$$

The hydraulic conductivity of saturated soils is measured in laboratory by applying the Darcy's equation to a saturated soil column of uniform cross-sectional area. A hydraulic head

difference is imposed on the soil column and the resulting flux of water is measured. The hydraulic conductivity is given by

$$K_s = \frac{VL}{At(H_2 - H_1)}$$
 [3.3]

where *V* is the volume of water that flows through the sample of cross-sectional area *A* for time *t* and (H_2-H_1) is the hydraulic head difference imposed across the sample of length *L*. The hydraulic conductivity of saturated layered soils in series (figure 3.1) is measured in laboratory by applying eqn. [3.4] which is written as follows

$$K_{eff(s)} = \frac{L}{\sum_{i=1}^{n} \frac{l_i}{K_{si}}} \quad \dots \dots \quad [3.4]$$

where $K_{eff(s)}$ is the effective hydraulic conductivity of the layered soil system in series of total length *L*. K_{si} is the hydraulic conductivity of individual soil layer of length l_i and n is the number of soil layers of different hydraulic conductivity in the soil core.

Eqn. [3.4] can be derived as follows. In layered soils, the Darcian velocity q remains constant across all the layers. Applying Darcy's law for each soil layer

$$q = K_{s1} \frac{(H_2 - H_1)}{l_1} = K_{s2} \frac{(H_3 - H_2)}{l_2} = K_{s3} \frac{(H_4 - H_3)}{l_3} = K_{s4} \frac{(H_5 - H_4)}{l_4} \quad \dots \quad [3.5]$$

where $(H_{i+1} - H_i)$ is the hydraulic head across the soil layer of length l_i . Also

$$q = K_{eff(s)} \frac{(H_5 - H_1)}{L} \qquad [3.6]$$

Rearranging

$$(H_5 - H_1) = \frac{qL}{K_{eff(s)}}$$
[3.7]

and

$$(H_5 - H_1) = (H_2 - H_1) + (H_3 - H_2) + (H_4 - H_3) + (H_5 - H_4)$$

$$(3.8]$$

From eqn. [3.5] and [3.6]

$$(H_2 - H_1) = \frac{ql_1}{\kappa_1} \qquad \dots \qquad [3.9]$$

Similarly

$$(H_3 - H_2) = \frac{ql_2}{K_2}$$
 [3.10]

$$(H_4 - H_3) = \frac{ql_3}{K_3}$$
 [3.11]

$$(H_5 - H_4) = \frac{ql_4}{K_4}$$
 [3.12]

Substituting eqn. [3.7] and [3.9] to [3.12] in [3.8]

$$\frac{qL}{K_{eff(s)}} = \frac{ql_1}{K_1} + \frac{ql_2}{K_2} + \frac{ql_3}{K_3} + \frac{ql_4}{K_4} \qquad [3.13]$$

Rearranging

$$K_{eff(s)} = \frac{L}{\frac{l_1}{K_1} + \frac{l_2}{K_2} + \frac{l_3}{K_3} + \frac{l_4}{K_4}}$$
(3.14)

Rewriting gives eqn [3.4]

$$K_{eff(s)} = \frac{L}{\sum_{i=1}^{n} \frac{l_i}{K_{si}}}$$

$$(3.4)$$

Hydraulic Conductivity and SAPs

A possible means by which hydraulic conductivity of soil could be altered is to mix the soil with hydrophilic superabsorbent polymers (SAPs) that are capable of swelling and retaining water 400 – 1600 times their own weight (Buchholz and Graham, 1997). Andry (2009) states

that the hydraulic conductivity of soil decreases significantly with increase in mixing ratio and swelling properties of SAPs. This phenomenon is due to the fact as the SAP swells, it reduces the largest pores in the soil especially in the sandy soils. (Abedi-Koupai et al, 2008). Also, SAP amended soils expand when the SAPs swell and the expansion increases with increase in mixing ratio and swelling property of SAPs (Andry et al. 2009). Some of the other properties which are affected by SAPs amendment in soils are infiltration rates, bulk density, soil structure, compaction, soil texture, aggregate stability, crust hardness and evaporation rates (Abedi-Koupai and Asadkazemi, 2006). It is clear that SAPs amendment alters the texture and structure of the soil which are the primary determinants of geometry of soil pores, one of the physical factors that determine the hydraulic conductivity. In this research, hydraulic conductivity of SAP amended soil is studied under free swelling and restricted swelling conditions. This study would give valuable information regarding the effect of SAPs on hydraulic conductivity of soils when applied near surface and at subsurface.

Materials and Methods

Materials

Three different soils from Southeastern US are used for analysis. Each soil - Sandy Loam, Clay Loam and Sandy Clay Loam are designated as HL, TN1 and TN2 respectively . Sandy Loam soil was collected from Wiregrass Research Station located in Headland, AL, USA. Soils Clay Loam and Sandy Clay Loam were obtained from Sevier County near Knoxville, TN, USA. The details of the soils are given in table 3.1. Super absorbent polymers (SAPs) A, B and C are used as amendment for the above mentioned soils. The particle sizes of SAPs used are Large (1-2 mm), Medium (0.25-0.5 mm) and Small (0.053-0.106 mm). Metal columns made of either stainless steel or brass of dimension 5.36 cm diameter and length 6 cm are used to pack the soil. Industrial sand of particle size F75 bought from F & S Abrasives Co., Inc. (Birmingham, AL, USA) is used for restricted swelling experiment. Flat circular rings are used as dead weight to apply pressure on soil. A wooden rack with a trough and able to hold eight soil columns is used to measure saturated hydraulic conductivity using constant head method (figure 3.2).

Sample preparation

Oven dried soil enough to pack the desired number of soil cores are placed in a plastic bag. A known quantity of SAP is added to achieve the required application rate and mixed well. The application rates of SAPs used in soils are 0.05%, 0.15% and 0.25%. For our measurements, we use a metal column of 12 cm length to pack the soil. One end of the metal column is covered with cheese cloth and a base plate is inserted (figure 3.3). About 130 g of soil-SAP mixture is then packed into each metal column to the required bulk densities. The required bulk densities for HL, TN1 and TN2 soils are 1.79, 1.25 and 1.33 g/cm³ respectively.

For restricted swelling condition samples, soil-SAP mixture is packed into the metal columns similar to free-swelling condition. The top of the soil is covered with a small cheese cloth. About 70 g of industrial sand of particle size F75 is carefully packed over the cheese cloth. The sand is covered with double layer cheese cloth and sufficient overburdened pressure is added to avoid the soil from swelling. The overburdened pressure was applied using heavy circular rings such that the water flow in to the soil column is not impeded (figure 3.4). The industrial sand and the flat circular rings together apply a pressure of 0.23 Pa uniformly over the soil-SAP mixture.

The HL soil is further studied for variable overlying pressure. SAPs A, B and C of particle sizes L, M and S are used. The application rate of SAPs is 0.25% and the overlying

pressures are 0, 0.05, 0.11, 0.18 and 0.23 Pa. The sample preparation is same as mentioned for restricted swelling condition.

The metal columns with soil-SAP mixtures are then placed in a trough containing water to saturate them from bottom. Such a procedure assures minimum air entrapment. The samples were allowed to saturate with water for 12 hours or until water level within the metal columns are above the top layer of the soil-SAP mixture.

Experimental setup – Constant head method

The saturated soil columns were connected to a constant head of water at the top and allowed to drain from the bottom. The volume of water *V* that passes through the sample for time *t* was measured. Substituting the hydraulic head driving the flow, (H_2-H_1) , *V* and *t* in to eq. [3.3], the saturated hydraulic conductivity of the soil column was estimated. For restricted swelling and variable overlying pressure conditions, eq. [3.3] gives effective saturated hydraulic conductivity of entire soil column with sand. The hydraulic conductivity of the soil-SAP mixture is given by substituting values in eq. [3.4].

Results

Free Swelling Condition

Changes in hydraulic conductivity of soil-SAP mixture for all three soils under free swelling conditions are given in figures 3.5 to 3.7. Significant changes in hydraulic conductivity with increase in application rate of SAPs in soils are observed in HL soil. Whereas in TN1 and TN2 soils, little or insignificant changes in hydraulic conductivity with amendment of SAPs in soils were observed. In HL soil, increase in particle size of SAPs greatly affects the hydraulic conductivity. In TN1 and TN2 soil, variation in particle size has no significant effect on hydraulic conductivity. Further it can also be observed, the variation in water absorbing capacity

of SAPs have negligible influence on hydraulic conductivity of all three soils. Percentage increase in volume of soil-SAP mixtures upon saturation with water are given in figures 3.9 to 3.11. For all three soils, the volume increases with increase in application rate. The particle size and water absorbing capacity of SAPs have little or no effect on expansion of soil columns.

Restricted Swelling Condition

Changes in hydraulic conductivity of HL, TN1 and TN2 soils under restricted swelling conditions are given in figures 3.5 to 3.7. The hydraulic conductivity of the soil-SAP mixture under restricted swelling conditions decreases significantly compared to free swelling conditions. There is mixed response of particle size, water absorbing capacity and application rate of SAPs effect on hydraulic conductivity. Percentage increase in volume of soil-SAP mixtures upon saturation with water are given in figure 3.8 to 3.10. In HL soil, the volume increases with increase in application rate. The particle size and water absorbing capacity of the SAP has little effect on hydraulic conductivity of soil. In TN1 and TN2 soils, the volume change has mixed response for application rate, particle size and water absorbing capacity of SAPs.

Changes in hydraulic conductivity of soil-SAP mixture of HL soil under variable overlying load are given in figure 3.11. The hydraulic conductivity of the soil decreases with increase in overlying pressure. When there is no overlying pressure, the soil amended with SAP particles of size L has the highest hydraulic conductivity. SAP C amendment in soil shows the lowest hydraulic conductivity for all the overlying pressures. Besides, amendment of soil with SAP particles of size S, have the lowest hydraulic conductivity for all the overlying pressures. Percentage increase in volume of soil-SAP mixture of HL soil upon saturation with water is given in figure 3.12. The expansion of soil-SAP mixture decreases with increase in overlying pressure. SAP C amendment causes the lowest expansion in soils for all the overlying pressure

compared to SAP A and B. Further, the soil amended with SAP particles of size S have the lowest expansion compared to other particle sizes L and M within SAPs of same water absorbing capacities.

Discussion

In free swelling conditions, increase in hydraulic conductivity of SAP amended HL soil could be explained as follows. When the soil-SAP mixture is saturated with water, the SAP particles in soil absorb water and swell. This swelling of SAP exerts pressure on soil particles surrounding it and causes expansion. The expansion of soil column creates large and new soil pores and thus increases the hydraulic conductivity of soil. In TN1 and TN2 soils, the pressure exerted by the SAPs is not sufficient enough to cause expansion and thus reduces the creation of new soil pores. This is evident by comparing the percentage increase in volume of soil-SAP mixtures of all the three soils. Since the SAP particles are restricted to swell, the swelling pressure of the SAP tends to squeeze it into the soil pores thus further blocking them. Further compared to HL soil, the clay content in TN1 and TN2 soils are higher (table 3). The clay particles in present in these soils may interfere with the swelling of the SAPs. It can also be assumed from increase in volume, the bulk density of the soil-SAP mixture decreases when the soil core is saturated with water.

In restricted swelling conditions, decrease in hydraulic conductivity of control soil could be explained as follows. The control soil expands 5-8%. But under restricted swelling conditions the swelling of soils is restricted due to the pressure exerted by the overlying load. When the soil under load is saturated with water, the soil column collapses (Barden et al., 1973). The collapse of soil column causes reduction in soil volume and reduces the number of soil pores and eventually decreases the hydraulic conductivity of the soil. The decrease in hydraulic

conductivity of soil-SAP mixture can be explained as follows. When the soil-SAP mixture is saturated with water, the SAP particles in soil absorb water and swell. This swelling of SAP exerts pressure on soil particles surrounding it and tends to cause expansion. The expansion of soil column is restricted due to the overlying load. The internal pressure within the SAP created due to swelling squeezes it into the soil pores available after collapse, thus further reducing the soil pores available for water movement.

In HL soil under variable overlying pressure conditions, the hydraulic conductivity decreases with increase in overlying pressure. As explained above, the geometry of soil pores are affected due to overlying pressure and clogging of pores due to squeezing of polymers into them. The hydraulic conductivity under overlying pressure for the HL soil amended with SAP C has the lowest value for all the three particle sizes compared to other SAPs. This could be explained as follows. As discussed in chapter 2, SAP C has the lowest mechanical strength and highest water absorption capacity compared to SAPs A and B. The swelling pressure created by SAP C is not adequate to cause expansion and thus SAP C squeezes itself into the soil pores blocking them and thus reducing the hydraulic conductivity.

Conclusion

The hydraulic conductivity of HL soil under free swelling conditions is greatly affected by amendment with SAP. In TN1 and TN2 soils, amendment of SAPs has mixed response. Amendment of SAP causes expansion of soil which eventually causes decrease in bulk density of the soil. Also, the hydraulic conductivity of the soil decreases with increase in overlying pressure for both control and SAP amended soil. The expansion of the soil-SAP mixture decreases with increase in overlying pressure. The properties of the SAP – particle size, mechanical strength and

water absorption capacity also affects the hydraulic conductivity and expansion of soil to certain extent.

It can be concluded from hydraulic conductivity experiments under free swelling and restricted swelling conditions, that when soil is amended with SAP at near surfaces increases hydraulic conductivity in sandy soils. Whereas when SAP is amended to soil at a certain depth, reduces the hydraulic conductivity of the soil greatly. The latter property of SAP amendment in soils could be potentially used in land-fills for clay linings to reduce the flow of percolate beyond the confining layer in case of any damage to it.

Table 3: Classification of Soils	
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Туре	Soil Name	Location	Family Description	Order	рН	% OM	% Sand	% Silt	% Clay	Soil Texture	Bulk Density (g/cm ³)	Particle Density (g/cm ³)
Soil 1	HL	Henry County, AL	Plinthic Kandiudults	Ultisol	5.4	1.5	69	12	19	Sandy Loam	1.79	2.61
Soil 2	TN1	Sevier County, TN	Cumulic Hapdudolls	Mollisol	4.3	4.3	40	32	28	Clay Loam	1.25	2.37
Soil 3	TN3	Sevier County, TN	Typic Eutrodept	Inceptisol	6.6	4.1	52	22	27	Sandy Clay Loam	1.33	2.46



Figure 3.1: Flow of water through soils in series



Figure 3.2: Measurement of Hydraulic Conductivity - Constant Head Method



Figure 3.3: Sample Setup - Free Swelling Condition





Figure 3.5: Comparison of Hydraulic Conductivity under Free Swelling and Restricted Swelling Conditions in HL Soil



Figure 3.6: Comparison of Hydraulic Conductivity under Free Swelling and Restricted Swelling Conditions in TN1 Soil



Figure 3.7: Comparison of Hydraulic Conductivity under Free Swelling and Restricted Swelling Conditions in TN2 Soil



Figure 3.8: Comparison of Volume Change under Free Swelling and Restricted Swelling Conditions in HL Soil



Figure 3.9: Comparison of Volume Change under Free Swelling and Restricted Swelling Conditions in TN1 Soil



Figure 3.10: Comparison of Volume Change under Free Swelling and Restricted Swelling Conditions in TN2 Soil


Figure 3.11: Effect of Varying Overlying Pressure, Water Absorbing Capacity and Particle Size of SAPs on Hydraulic Conductivity of HL Soil



Figure 3.12: Effect of Overlying Pressure, Water Absorbing Capacity and Particle Size of SAP on Expansion of HL Soil

References

- Abedi-Koupai, J., F. Sohrab, and G. Swarbrick. 2008. "Evaluation of Hydrogel Application on Soil Water Retention Characteristics." *Journal of Plant Nutrition 31:* 317-331.
- Abedi-Koupai, J. and J. Asadkazemi. 2006. "Effects of a Hydrophilic Polymer on the Field Performance of an Ornamental Plant (Cupressus arizonica) under Reduced Irrigation Regimes." *Iranian Polymer Journal 15*(9): 715-725.
- Andry, H., T. Yamamoto, T.Irie, S. Moritani, M. Inoue and H. Fujiyama. 2009. "Water retention, hydraulic conductivity of hydrophilic polymers in sandy soil as affected by temperature and water quality." *Journal of Hydrology 373*: 177-183.
- Barden, L., A. McGown and K. Collins. 1973. "The Collapse Mechanism in Partly Saturated Soil." *Engineering Geology* 7: 49-60.
- Buchholz, F. L. and A.T. Graham. 1997. Modern Superabsorbent Polymer Technology. *John Wiley & Sons Inc.*
- Klute, A. and C. Dirksen. 1986. "Hydraulic Conductivity and Diffusivity: Laboratory Methods. *Methods of Soil Analysis Part 1: Physical and Mineralogical Methods* (pp. 687 - 734).