

論文 / 著書情報
Article / Book Information

題目(和文)	
Title(English)	Effects of raw and treated coal fly ash amendment on water retention capacity of soils and sands
著者(和文)	林聖蕾
Author(English)	Shenglei Lin
出典(和文)	学位:博士(工学), 学位授与機関:東京工業大学, 報告番号:甲第10984号, 授与年月日:2018年9月20日, 学位の種別:課程博士, 審査員:高橋 史武,吉川 邦夫,竹下 健二,中崎 清彦,時松 宏治,梶谷 史朗
Citation(English)	Degree:Doctor (Engineering), Conferring organization: Tokyo Institute of Technology, Report number:甲第10984号, Conferred date:2018/9/20, Degree Type:Course doctor, Examiner:,,,,,
学位種別(和文)	博士論文
Type(English)	Doctoral Thesis

Chapter 1

Introduction

1. Introduction

1.1 Coal fly ash

Nowadays, the most popular power generation in the world is coal-fired power generation. Coal-fired power generation meet over 30 % of global energy requirement. (Ram L.C., Masto R.E., 2014). Regardless of incentive promotion of renewable energy, 50% increase of global coal consumption is expected from 2010 to 2040 (U.S. Energy Information Administration, 2013). As by-products, coal fly ash (FA) and bottom ash (BA) are two major solid wastes from the combustion process of coal-fired power generation. Because of the enormous consumption of coal, more than 750 million Mg/yr of FA are produced in the world (Izquierdo and Querol, 2012; Ram L.C., Masto R.E., 2014).

China, United States, India and Australia are the largest coal consumers in the world (Ram L.C., Masto R.E., 2014). For example, China consumes 1439.5 million Mg of bituminous coal per year (International Energy Agency, 2013). About 100 million Mg of coal combustion by-products are produced every year. World average recycle ratio of FA is estimated to be less than 50% (Izquierdo and Querol, 2012) or about 25% (Wang, 2008). Thus, huge amount of FA has been disposed in landfill sites and/or open dumping sites without effective reutilization. Its improper disposal has become an environmental concern according to potential emission of toxic elements contained in FA to the environment (Izquierdo and Querol, 2012; Prasad et al., 1996; Yao et al, 2015). Reutilizing FA has become a sever environmental problem in large coal-consuming countries like China and India.

FA is considered by some researchers as the world's fifth largest raw material resource (Ahmaruzzaman M., 2010). FA utilization as alternative raw material to industrial processes and applications like cement and concrete production, structural fill and cover material, and pavements (Ram L.C., Masto R.E., 2014). Because of physical properties of FA like fine and sphere particles, effective applications of FA are believed feasible. In summary, an application of FA with higher

efficiency and stability is required urgently.

1.1.1 Physical properties of FA

FA consists of fine, powdery particles predominantly spherical in shape, either solid or hollow, and mostly glassy (amorphous) in nature. The particle size distribution of most bituminous coal fly ash is generally similar to that of silt. With the same silt size, sub-bituminous coal fly ash is slightly coarser than bituminous coal fly ash (Ahmaruzzaman, 2010). The specific gravity of fly ash usually ranges from 2.1 to 3.0, while its specific surface area varies from 170 to 1000 m²/kg (Roy et al., 1981; Tolle et al., 1982; Mattigod et al., 1990). Depending on unburned carbon in ash, the color can vary from tan to gray or black.

1.1.2 Chemical properties of FA

The chemical properties of fly ash are influenced by the properties of the coal handled and burned, and it is also sometimes classified according to the type of coal burned (Ahmaruzzaman, 2010). Because of the large amount of production that mentioned just before, the amount of coal waste (fly ash), released by factories and thermal power plants, has become a serious environmental problem.

Coal fly ash is regularly reported to contain various kinds of alkaline metallic oxides, like Al₂O₃, Fe₂O₃, K₂O, MgO, Na₂O, CaO (Tamilselvi Dananjayan et al., 2015; Ukwattage et al., 2015) and pH value is regularly high, FAs also contain nonmetal oxides like SO₃, P₂O₅, SiO₂ (Lieberman et al., 2015). FA is treated as hazardous waste because it contains heavy metals and toxic elements like B, Cr, Cu, Se, As, Cd, Sr, Hg, Pb etc. It might cause pollution to the environment for the contents of heavy metal and toxic elements (mg/kg) exceed soil standard (Lieberman et al., 2015, Lin and Takahashi, 2015).

Contacting FA with water will cause leaching of some elements into water and lead to a secondary environmental pollution. Many important aspects of leaching behavior of FA were reported by a number of researches (Iyer R., 2002; Mohapatra and Rao, 2001; Reijnder L., 2005; Prasad et al., 1996). Leachability of heavy metals from FA is comparatively low and trace metal concentration depends on FA weight/solution, pH, concentration of elements, temperature, pressure, and time. Low pH causes rapid leaching of most of the trace elements (except Cu) from

the surface of ash particles (Prasad et al., 1996).

1.1.3 Utilization of FA

Nowadays most industrial wastes are being used without taking full advantages of their characteristics or disposed rather than used. It is recommended that an economically viable solution to this problem should include utilization of waste materials for new products rather than land disposal. Therefore, it has motivated many researches on FA recycles such as soil amelioration, construction industry, ceramic industry, etc. (Yao et al., 2015; Ahmaruzzaman, 2010; Blissett and Rowson, 2012; Dhadse et al., 2008).

As the world average, the present day utilization of ash on worldwide basis varied widely from a minimum of 3 % to a maximum of 57 % (Ahmaruzzaman, 2010; Joshi and Lothia, 1997). Average FA recycle ratio is estimated to be less than 50% (Izquierdo and Querol, 2012) or about 25% (Wang, 2008). Thus, huge amount of FA has not been used but disposed in controlled landfill sites and/or open dumping sites. Its improper disposal has become an environmental concern according to potential emission of toxic elements contained in FA (Izquierdo and Querol, 2012; Prasad et al., 1996; Yao et al., 2015). The large scale storage of wet fly ash in ponds takes up large valuable land, and will result in severe environmental degradation in the near future (Ahmaruzzaman, 2010).

FA has been reported to improve mechanical properties and durability of concrete, same utilization with ground granulated blast furnace slag (Jalal et al., 2015). Maximum usage of the amount of FA is generally limited to 15-25 % of the total materials while concretes were initially developed to use high volume FA concrete application to reduce the heat of hydration (Jalal et al., 2015; Bilodeau and Malhotra, 2000). A study taken by Bouzoubaa and Lachemi showed that it was possible to replace up to 60 % of self consolidating concrete with Class F FA (Jalal et al., 2015; Bouzoubaa and Lachemi, 2001). About 25 % of fly ash in India is used for cement production (Ahmaruzzaman, 2010), Fly ash also contains different essential elements for planting including both macronutrients P, K, Ca, Mg and Zn, Fe, Cu, Mn, B and Mo (Ahmaruzzaman, 2010). Efforts have been made to reduce SO_x emissions by installing equipment for flue gas desulphurization (FGD) (Ahmaruzzaman, 2010), and it has also been used for adsorbents for NO_x removal from flue gases (Ahmaruzzaman, 2010; Lu and Do, 1991). Apart from flue gas, FA also has been used for removal of mercury-containing air. Although the role of inorganic components

of fly ash is still sometimes unclear, considerable attention has been paid to the capture of mercury by unburned fly ash carbons (Pavlish et al., 2003; Sakulpitaphon et al., 2003; Hower et al., 2000; Hower et al., 2005; Lopez-Anton et al., 2007; Sloss, 1995; Li et al., 2002; Suarez-Ruiz et al., 2007). The concentration of unburned carbons and their respective ability to capture Hg have also been related to their textural properties (Ahmaruzzaman, 2010; Hower et al., 2000; Suarez-Ruiz and Parra et al., 2007; Maroto-Valer et al., 1999; Maroto-Valer et al., 2001). FA has also been used for adsorption of organic gas. It was found that FA product obtained after particle aggregation and thermal activation showed satisfactory adsorption performance for toluene vapours (Rovatti et al., 1988).

Because of its major chemical components, FA has potential application in wastewater treatment. Heavy metals are most serious pollutants, becoming a severe public health problem, and adsorption process may be a simple and effective technique for removal of heavy metals from wastewater. FA has been widely used as a low-cost adsorbent for the removal of heavy metal, like Zn^{2+} , Cd^{2+} , Pb^{2+} , Cu^{2+} , Ni^{2+} , Cr^{3+} , Cr^{6+} , Hg^{2+} , As^{3+} , As^{5+} , etc. (Banerjee et al., 2003; Bayat, 2002a; Bayat, 2002b; Srivastava et al., 2006; Srivastava et al., 2008; Ricou et al., 1999). It was reported that the initial concentration of heavy metal has a strong effect on the adsorption capacity of the fly ash, and pH is also the other factor for the adsorption of heavy metal (Ahmaruzzaman, 2010).

Apart from heavy metal adsorption, inorganic and organic meters also urgently needed to be adsorbed as their harms on human health, inorganic components like phosphate, fluoride, boron, and so on and organic compounds like phenolic compounds, pesticides, lots kind of dyes and other organic compounds.

Because of the physical properties of FA, FA amendment will lead to impact on soil physical properties. Physical characteristics of soil are primarily impacted by the texture of soil. Soil texture is correlated with bulk density (BD), porosity, hydraulic conductivity, void ratio, and water holding capacity, which have a direct impact on plant growth and on the nutrient retention and biological activity of the soil (Ram and Masto, 2014; Campbell et al., 1983; Fulekar and Dave, 1986; Biliski et al., 1995; Fang et al., 2001; Guest et al., 2001; Jayasinghe and Tokashiki, 2012). For the chemical properties of FA, soil pH, soil salinity, soil fertility, soil heavy metals and soil biological/biochemical quality are impacted. Because of the high contents of Si and Ca in FA, it can be helpful in synthesizing zeolite and adsorbing metals on FA based zeolite. For the advantage

of economic saving to the manufacture, FA can also be utilized for lightweight aggregate, road sub-base and mine backfill.

1.2. Desertification in arid and semi-arid areas

Besides FA recycling problem in semi-arid area, desertification of the savanna and agricultural land has become an emerging environmental and social problem in some areas, especially China, Australia, USA where at the same time huge amount of FA are produced by coal-fired power generation (Chen and Tang, 2005; Fredrickson et al., 1998; Xue, 1996). As a typical example, desertification processes in Sahara is affecting 46% of African land, in which 55% is at high or very high risk, and in total about 485 million people are seriously affected (Reich et al., 2004). Although anti-desertification activities need integrated approaches, water retention agent might be an effective method to reclaim degraded soil and sand soil area (Bastida et al., 2007).

China is one of the country that suffering desertification seriously for decades. It has made great efforts to mitigate desertification (Yang et al., 2005). In north China, however, around 175,000 km² of land are still under desertification or extremely severe desertification.

1.3. FA amendment to soil

The fundamental phenomenon of desertification is land degradation and soil moisture loss which are usually caused by continuous and human-made activities. If FA can be recycled as water retention agent after necessary treatment for environmental safety, it will contribute into anti-desertification and FA management at the same time. Many works have been reported on the effect of FA amending on plant growth (Gond et al., 2013; Jayasinghe and Tokashiki, 2012; Lau and Wong, 2001; Wong and Wong, 1989), soil pH (Jankowski et al., 2006; Matsi and Keramidas, 1999; Pathan et al., 2003a), soil toxic elements (Eary et al., 1990; Jankowski et al., 2006; Kukier et al., 1994; Plank and Martens; 1974; Phung et al., 1979), soil salinity (Adriano et al., 2002; Matsi and Keramidas, 1999; Phung et al., 1979), soil fertility (El-Mogazi et al., 1988; Khan and Singh, 2001; Srivastava et al., 2003; Taylor and Schuman, 1988), water holding capacity (WHC) (Adriano and Weber, 2001; Campbell et al., 1983; Chang et al., 1977; Gangloff et al., 2000; Pathan et al., 2003b; Yunusa et al., 2006; Basu M.,

et al., 2009), and soil conductivity (Khan and Khan, 1996). According to previous works cited above, it is usually reported that FA amendment increases soil WHC as well as inorganic or organic amendments with FA (Belyaeva and Haynes, 2009; Jayasinghe et al., 2009; Punshon et al., 2002; Singh et al., 2011; Veeresh et al., 2003). Soil amelioration by FA has been also reported anywhere (Aitken RL., et al., 1984; Sikka and Kansal, 1994; Desmukh A. et al., 2000; Grewal KS., 2001; Nidhi J., 2003; Inam A., 2007a, 2007b). FA as soil ameliorant contains a strong potential to reclaim FA with large amount, numbers of studies point larger potentials to utilize FA to increase soil productivity and ameliorate degraded land, agriculture or re-vegetation (Mishra and Shukla, 1986a, 1986b; Bhumbra et al., 1991; Saxena et al., 1997; Ram et al., 2007; Ram et al., 2008; Srivastava and Ram, 2009, 2010a, 2010b; Chassapis et al., 2010; Sen and Kumar, 2012; Ukwattage et al., 2013). All works done to coal FA are reviewed in Table 1-1.

Table 1-1 References about FA amendment on soil properties

Purpose/Target	Reference
Coal FA producing	AUA, Australia Uranium Association, 2007; Ram L.C., Masto R.E., 2014; U.S. Energy Information Administration, 2013; Izquierdo and Querol, 2012; International Energy Agency, 2013; Ahmaruzzaman M., 2010;
Average recycle ratio of coal FA	Wang, 2008; Anmaruzzaman, 2010; Joshi and Lothia, 1997; Izquierdo and Querol, 2012;
Physical properties of FA	Roy et al., 1981; Tolle et al., 1982; Mattigod et al., 1990;
Chemical properties of FA	R.R.Tamilselvi Dananjayan et al., 2015; Ukwattage et al., 2015; Lieberman et al., 2015; Lin, 2015;
Utilization researches of FA	Yao et al., 2015; Ahmaruzzaman, 2010; Blissett and Rowson, 2012; Dhadse et al., 2008;
As cement replace material	Jalal et al., 2015; Bilodeau and Malhotra, 2000; Ahmaruzzaman, 2010;
As adsorbents for cleaning of flus gas and metals in waste water	Ahmaruzzaman, 2010; Lu and Do, 1991; Pavlish et al., 2003; Sakulpitaphon et al., 2003; Hower et al., 2000; Hower et al., 2005; Lopez-Anton et al., 2007; Sloss, 1995; Li et al., 2002; Suarez-Ruiz et al., 2007; Suarez-Ruiz and Parra et al., 2007; Maroto-Valer et al., 1999; Maroto-Valer et al., 2001; Rovatti et al., 1988;

Removal of toxic metals from wastewater	Banerjee et al., 2003; Bayat, 2002a; Bayat, 2002b; Srivastava et al., 2006; Srivastava et al., 2008; Ricou et al., 1999; Ahmaruzzaman, 2010;
Soil fertility	Gond et al., 2013; Jayasinghe and Tokashiki, 2012; Lau and Wong, 2001; Wong and Wong, 1989; El-Mogazi et al., 1988; Khan and Singh, 2001; Srivastava et al., 2003; Taylor and Schuman, 1988; Ram and Masto, 2014; Campbell et al., 1983; Fulekar and Dave, 1986; Biliski et al., 1995; Fang et al., 2001; Guest et al., 2001; Jayasinghe and Tokashiki, 2012;
Soil pH	Jankowski et al., 2006; Matsi and Keramidas, 1999; Pathan et al., 2003a;
Soil toxic elements	Eary et al., 1990; Jankowski et al., 2006; Kukier et al., 1994; Plank and Martens; 1974; Phung et al., 1979; Lieberman et al., 2015; Lin, 2015; Iyer R., 2002; Mohapatra and Rao, 2001; Reijnder l., 2005; Prasad et al., 1996; Prasad et al., 1996; Izquierdo and Querol, 2012; Prasad et al., 1996; Yao et al, 2015;
Soil salinity	Adriano et al., 2002; Matsi and Keramidas, 1999; Phung et al., 1979;
Soil water holding capacity	Belyaeva and Haynes, 2009; Jayasinghe et al., 2009; Punshon et al., 2002; Singh et al., 2011; Veeresh et al., 2003; Adriano and Weber, 2001; Campbell et al., 1983; Chang et al., 1977; Gangloff et al., 2000; Pathan et al., 2003b; Yunusa et al., 2006; Basu M., et al., 2009; Zheng et al., 2017; Paudel et al., 2015; Van der Sman et al., 2013b; Behrman et al., 2016; Campos et al., 2016; González-Zamora et al., 2016; Hansen et al., 2016; Horne and Scotter, 2016; Li et al., 2016; Liu et al., 2013; Mohamed et al., 2016; Mouazen et al., 2014;
Soil conductivity	Khan and Khan, 1996;
Soil amelioration	Aitken RL., et al., 1984; Sikka R. et al., 1994; Desmukh A. et al., 2000; Grewal KS., 2001; Nidhi J., 2003; Inam A., 2007a, 2007b; Mishra and Shukla, 1986a, 1986b; Bhumbra et al., 1991; Saxena et al., 1997; Ram et al., 2007; Ram et al., 2008; Srivastava and Ram, 2009, 2010a,2010b; Chassapis et al., 2010; Sen and Kumar, 2012; Ukwattage et al., 2013;

1.4 Water content in soil/sand

In natural mechanisms, weathering igneous rocks forms soil and sand. After thousands of years weathering, big rocks are decomposed into gravel (>2 mm), sand ($0.02\sim 2$ mm), silt ($2\sim 20$ μm) and clay (<2 μm).

Plants grow, fade and then left biomass compounds like litters in the soil. Other biomass, like animal discharges, animal bodies and plants are turned into humus by bacteria and microorganism. Humus connects soil particles and form aggregation. Strong particle aggregation will reform soil into stone. Different soil particle size with appropriate soil particle aggregations are very important in plant growth. Even in soil, available air for respiration is important for plants. Void space for air in soil can be also used for water retention. Void space in soil, which are controlled by soil and aggregates size distributions, serves water and air to plants.

Water content in soil is called soil moisture. Soil moisture is identified as hygroscopic water, adhesive water, capillary water and gravitational water (see Figure 1-1). Hygroscopic water is the amount of water absorbed from humid air by dry soil. Hygroscopic water is determined by comparative humid rate of the air and textural properties of soil. High humid air and stickier soil texture increase the amount of hygroscopic water. Because hygroscopic water is strongly sucked by soil particle surface, its pF value is around 4.5 to 7.0. Thus hygroscopic water cannot move nor be absorbed by roots. It is also not influenced by gravity. Hygroscopic water will transfer only when it is evaporated to gas phase. Therefore, it is called tight-bound water.

Adhesive water is the water absorbed by soil particle surface. Its pF value is around 3.8 to 4.5. Thickness of adhesive water layer is dozens or hundreds of water molecules. Adhesive water content will be higher when soil texture is more sticky, soil density is heavier and humus content is higher. Adhesive water is moveable, slowly from thick water layer to thin water layer, and absorbable for root. Because the amount of adhesive water is usually too little compared to capillary water, it will not be used for plant growth.

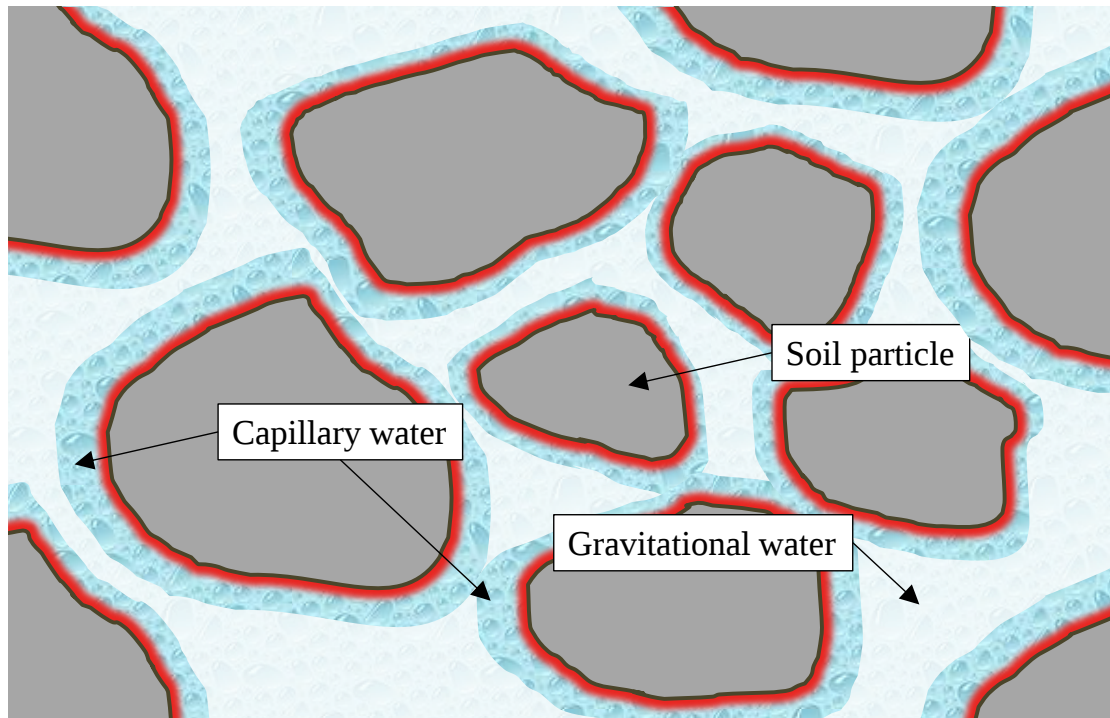


Figure 1-1 Type of moisture in soil system

Capillary water is the water absorbed by capillary attraction inside the soil. Its volume might be the maximum when pore diameter is around or less 0.5 mm. Its pF value is around 2.0. Capillary effect is the strongest when pore diameter is 0.001-0.1 mm. On the other hand, it becomes invalid when pore diameter is smaller than 0.001 mm. Therefore the pF value of capillary water ranges from 2.0-3.8. Capillary water is moveable and suction force of root is stronger than the force that capillary water is held in soil. Therefore, capillary water can be absorbed by plants and nutrients in capillary water will be also absorbed by plant roots. Capillary water is the most important water content in soil in terms of plant growth.

When water content exceeds water holding capacity of soil, free water leaks driven by gravity. This water is called gravitational water. Gravitational water reaches impermeable layer and form groundwater. Therefore, gravitational water is the main source of groundwater. Although gravitational water can also be absorbed by plants, it usually transfers too fast to be utilized by plants.

In summary, water content that can be absorbed by plants in soil is adhesive water, capillary water and gravitational water. Owing to high transfer speed of gravitational water

and small amount of adhesive water, capillary water is the most important for plant growth. Pore-water (free water) is identified as gravitational water, which will be influenced by evaporation and gravity. It will be lost very fast from the soil. Capillary-water (bound water) is strongly stored in capillary among soil particles, which is not influenced by gravity but by evaporation at high temperature. When temperature increased, water in the capillary will move to the surface and then evaporate to the gas phase in soil. Water held in capillary remains relatively longer in soil and will be used for plants via absorption. In this research, adhesive water and hygroscopic water is considered negligible because drying temperature in this research is too low to evaporate.

1.5 Gaps between WHC and water fates in soil system

Water holding capacity (WHC) is a conventional indicator to measure the amount of water in soil under certain conditions. Many research works have been reported anywhere (Zheng *et al.*, 2017; Paudel *et al.*, 2015; Van der Sman *et al.*, 2013; Behrman *et al.*, 2016; Campos *et al.*, 2016; González-Zamora *et al.*, 2016; Hansen *et al.*, 2016; Horne and Scotter, 2016; Li *et al.*, 2016; Liu *et al.*, 2013; Mohamed *et al.*, 2016; Mouazen *et al.*, 2014). Because of FA problem in arid/semi-arid areas, it is promising to recycle FA as water retention agent to increase soil WHC. FA amendment is usually reported to be effective on increasing soil WHC. However, no one uses raw FA for soil amendment. WHC focuses on only water volume held in soil system at certain pressure. WHC does not take water evaporation into consideration although water evaporation is a major pathway of water loss in semi-arid area. This supposes WHC may not be an appropriate indicator to investigate water loss by evaporation from the viewpoint of anti-desertification.

Water in soil/sand system is categorized as gravitational water, capillary water, adhesive water and hygroscopic water. According to background of plant growth, soil from surface to 40 cm depth of soil system is concerned. From the viewpoint of water potential, gravitational water and capillary water is available for plant. As gravitational water losses too fast in soil system, capillary water is the most important water for plant growth and anti-desertification. Major pathways of capillary water loss are surface runoff, evapotranspiration via plants and grasses, and direct evaporation from soil system to the

atmosphere. Remaining more water, especially more capillary water in soil/sand system for longer time, is critical for plant growth in semi-arid area and anti-desertification research.

WHC measured by conventional methods are calculated based on water mass loss by gravity (free water removal) or transpiration under low air pressure conditions. WHC measures maximum amount of water that can be held by soil/sand system. It does not consider the amount of capillary water nor retention time of water in soil at high temperature in arid/semi-arid area. Samples are usually water-saturated when WHC measurement starts. In the real arid/semi-arid environment, however, soil is usually unsaturated even after rainfalls. At the same time, evaporation is driven by temperature, not by unnatural low air pressure. Therefore, WHC does not simulate real water loss in soil of arid/semi-arid areas. These suggest that WHC measurement has a gap with the real situation of water retention in soil/sand system. It is noted again that WHC of soil/sand system is not appropriate for plant growth and for the research from the view point of anti-desertification. WHC measurements also request specific apparatus and rich experiences. In addition, it is difficult for field-scale experiments.

1.6 Water retention capacity (WRC)

In this study, a new and easy measurement method of WHC is tested, called as water retention capacity (WRC) (Lin and Takahashi, 2015). WRC quantifies soil mitigation capacity against water loss by temperature-driven evaporation under ambient pressure. WRC can measure water evaporation rate in samples at room temperature or any high temperature/changeable temperature, which is directly related to retention time of moisture in soil/sand system. In addition, samples utilized in WRC measurement are unsaturated which is the same with the real environment in arid/semi-arid area. By combining WRC with capillary water content measurement, water fate in soil system can be clearly shown.

As referred from a lot studies mentioned in section 1.3, amendment of raw FA is reported as effective to increases soil WHC. In contrast, raw FA amendment decreases soil WRC (Lin and Takahashi, 2015). This suggests that FA amendment might promote water evaporation from soil system and thus pretreatment of FA is necessary to change FA amendment effect on WRC. This fact supposes why raw FA is not utilized as soil amelioration

in reality. WRC drying experiment, a measurement focusing on water retention and retention time of water in soil system for plant growth and anti-desertification, is more appropriate than the conventional WHC. It is the originality of this research.

1.7 Research objective

Purpose of this research is reutilizing FA for soil amelioration, in particular water retention agents from the view point of anti-desertification. This study focuses on apatite-synthesis treatment and several organic treatments of FA (Lin et al., 2018) because some collaborative effects are expected. FA surface modification by apatite synthesis might modify FA surface more hydrophilic and increase the amount of capillary water in soil. At the same time, calcium phosphate mineral, called apatite, is effective to immobilize toxic heavy metals (Mu et al., 2017). So, apatite-synthesis treatment might be promising for FA reutilization. On the other hand, organic treatments of FA might modify textural properties of FA particles, in particular micro-structure on the surface. It might be effective to increase surface hydrophilicity and the amount of capillary water. In addition, soil an FA properties like surface morphology and water repellency are analyzed to find influential factors on WRC.

References

- Adriano, D.C., Weber, J.T. (2001) Influence of fly ash on soil physical properties and turfgrass establishment, *Journal of Environmental Quality*, 30(2), 596-601.
- Adriano, D.C., Weber, J., Bolan, N.S., Paramasivam, S., Koo, B.J., Sajwan, K.S. (2002) Effects of high rates of coal fly ash on soil, turfgrass, and groundwater quality, *Water, Air and Soil Pollution*, 139(1-4), 365-385.
- Ahmaruzzaman, M. (2010) A review on the utilization of fly ash, *Progress in Energy and Combustion Science*, 36, 327–363.
- Aitken, R.L., Campbell, D.J., Bell L.C. (1984) Properties of Australian fly ash relevant to their agronomic utilization, *Aust J Soil Res*, 22, 443–53.
- Banerjee, S.S., Jayaram, R.V., Joshi, M.V. (2003) Removal of nickel(II) and zinc(II) from wastewater using fly ash and impregnated fly ash, *Sep Sci Technol*, 38:1015–32.
- Bastida, F., Moreno, J.L., Garcia, C., Hernandez, T. (2007) Addition of urban waste to semiarid degraded soil: Long-term effect, *Pedosphere*, 17(5), 557-567.
- Basu, M., Pande, M., P.B.S. Bhadoria, S.C. Mahapatra (2009) Potential fly-ash utilization in agriculture: A global review, 19, 1173-1186.
- Bayat, B. (2002a) Combined removal of zinc (II) and cadmium (II) from aqueous solutions by adsorption onto high-calcium Turkish fly ash, *Water Air Soil Pollut*, 136:69–92.
- Bayat, B. (2002b) Comparative study of adsorption properties of Turkish fly ashes. I. The case of nickel(II), copper(II) and zinc(II), *J Hazard Mater*, 95:251–73.
- Behrman K.D., Norfleet M.L., Williams J. (2016): Methods to estimate plant available water for simulation models, *Agricultural Water Management*, 175: 72-77.
- Belyaeva, O.N., Haynes, R.J. (2009) Chemical, microbial and physical properties of manufactured soils produced by co-composting municipal green waste with coal fly ash, *Bioresource Technology*, 100(21), 5203-5209.
- Bhumbla, D.K., Singh, R.N., Keeker, R.F., 1991 Water quality from surface mined land reclaimed with fly ash, Orlando, F.L. (Ed.), Proc. 9th Ash Use Symposium, 57, *American Coal Ash Association: Academic Press*, 1–22.
- Biliski, J.J., Alva, A.K., Sajwan, K.S. (1995) Fly ash. In: Rechcigl, J.E. (Ed.), Soil Amendments and Environmental Quality, *Lewis Publishers*, London, pp. 327–363.
- Bilodeau A., Malhotra V.M., (2000) High-volume fly ash system: concrete solution for sustainable development, *ACI Mater. J.* 97: 41-48.
- Blissett, R.S., Rowson, N.A. (2012) A review of the multi-component utilisation of coal fly ash, *Fuel*, 97, 1-23.
- Campbell, D.J., Fox, W.E., Aitken, R.L., Bell, L.C. (1983) Physical characterization of sands amended with fly ash, *Australian Journal of Soil Research*, 21(2), 147–154.
- Campos I., González-Piqueras J., Carrara A., Villodre J., Calera A. (2016): Estimation of total available water in the soil layer by integrating actual evapotranspiration data in a remote sensing-driven soil water balance. *Journal of Hydrology*, 534: 427-439.
- Chang, A.C., Lund, L. J., Page, A.L., Warneke, J.E. (1977) Physical properties of fly ash amended soils, *Journal of Environmental Quality*, 6, 267–270.
- Chassapis, K., Roulia, M., Vrettou, E., Fili, D., Zervaki, M., 2010 Biofunctional Characteristics of lignite fly ash modified by humates: a new soil conditioner. *Bioinorg. Chem. Appl.* <http://dx.doi.org/10.1155/2010/457964>

- Chen, Y., Tang, H. (2005) Desertification in north China: Background, anthropogenic impacts and failures in combating it, *Land Degradation & Development*, 16(4), 367-376.
- Desmukh, A., Matti, D.B., Bharti, B., (2000) Soil properties as influenced by fly ash application. *J Soils Crops*, 10, 69–71.
- Dhadse, S., Kumari, P., Bhagia, L.J. (2008) Fly ash characterization, utilization and Government initiatives in India - A review, *J. Sci. Ind. Res. India*, 67(1), 11-18.
- Eary, L.E., Rai, D., Mattigod, S.V., Ainsworth, C.C. (1990) Geochemical factors controlling the mobilization of inorganic constituents of fossil fuel combustion residues: II. Review of the minor elements, *Journal of Environmental Quality*, 19, 201–214.
- El-Mogazi, D., Lisk, D.J., Weinstein, L.H. (1988) A review of physical, chemical, and biological properties of fly ash and effects on agricultural ecosystems, *Science of the Total Environment*, 74, 1–37.
- Fang, M., Wong, M.H., Wong, J.W.C. (2001) Digestion activity of thermophilic bacteria isolated from ash amended sewage sludge compost, *Water Air Soil Pollut.* 126, 1–12.
- Fredrickson, E., Havstad, K.M., Estell, R. (1998) Perspectives on desertification: south-western United States, *Journal of Arid Environments*, 39(2), 191-207.
- Fulekar, M.H., Dave, J.M., (1986) Disposal of fly ash-an environmental problem. *Int. J. Environ. Stud.*, 26, 191-215.
- Gangloff, W.J., Ghodrati, M., Sims, J.T., Vasilas, B.L. (2000) Impact of fly ash amendment and incorporation method on hydraulic properties of a sandy soil, *Water Air and Soil Pollution*, 119(1-4), 231-245.
- Gond, D.P., Singh, S., Pal, A., Tewary, B.K. (2013) Growth, yield and metal residues in *Solanum melongena* grown in fly ash amended soils, *Journal of Environmental Biology*, 34(3), 539–544.
- González-Zamora Á., Sánchez N., Martínez-Fernández J., Wagner W. (2016): Root-zone plant available water estimation using the SMOS-derived soil water index. *Advances in Water Resources*, 96: 339-353.
- Grewal KS, Yadav PS, Mehta SC, et al. (2001) Direct and residual effect of fly ash application to soil on crop yield and soil properties. *Crop Res*, 21, 60–5.
- Guest, C.A., Johnston, C.T., King, J.J., Alleman, J.E., Tishmack, J.K., Norton, L.D. (2001) Chemical characterization of synthetic soil from composting coal combustion and pharmaceutical by-product, *J. Environ. Qual.*, 30, 25–246.
- Hansen V., Hauggaard-Nielsen H., Petersen C.T., Nørgaard Mikkelsen T., Müller-Stöver D. (2016): Effects of gasification biochar on plant-available water capacity and plant growth in two contrasting soil types. *Soil & Tillage Research*, 161: 1-9.
- Horne D.J., Scotter D.R. (2016): The available water holding capacity of soils under pasture. *Agricultural Water Management*, 177: 165-171.
- Hower, J.C., Maroto-Valer, M.M., Taulbee, D.N., Sakulpitakphon, T., (2000) Mercury capture by distinct fly ash carbon forms. *Energy Fuel*, 14:224–6
- Hower, J.C., Robl, T.L., Anderson, C., Thomas, G.A., Sakulpitakphon, T., Mardon, S., (2005) Characteristics of coal combustion products (CCP's) from Kentucky power plants, with emphasis on mercury content. *Fuel*, 84:1338–50.
- Inam A. (2007a) Use of fly ash in turnip (*Brassica rapa* L.) cultivation. *Pollut Res*, 26(1), 39–42.
- Inam A. (2007b) Response of methi to nitrogen and fly ash supplemented as a source of nutrients.

- Pollut Res*, 26(1), 43–7.
- International Energy Agency (2013) Statistics: Coal and Peat. <http://www.iea.org/stats/prodresult.asp?PRODUCT=Coal%20and%20Peat> (2013)
- Izquierdo, M., Querol, X.. (2012) Leaching behaviour of elements from coal combustion fly ash: An overview, *International Journal of Coal Geology*, 94, 54-66.
- Iyer, R., (2002) The surface chemistry of leaching coal fly ash. *J Hazard Mater*, 93:321–9.
- Jalal M., Pouladkhan A., Harandi O.F., Jafari D., 2015 Comparative study on effects of Class F fly ash, nano silica and silica fume on properties of high performance self compacting concrete, *Construction and Building Materials*, 94:90-104.
- Jankowski, J., Ward, C.R., French, D., Groves, S. (2006) Mobility of trace elements from selected Australian fly ashes and its potential impact on aquatic ecosystems, *Fuel*, 85, 243–256.
- Jayasinghe, G.Y., Tokashiki, Y., Kitou, M. (2009) Evaluation of Coal Fly Ash-Based Synthetic Aggregates as a Soil Ameliorant for the Low Productive Acidic Red Soil, *Water, Air, and Soil Pollution*, 204(1-4), 29-41.
- Jayasinghe, G.Y., Tokashiki, Y. (2012) Influence of coal fly ash pellet aggregates on the growth and nutrient composition of *Brassica campestris* and physicochemical properties of greysoils in Okinawa, *Journal of Plant Nutrition*, 35(3), 453-470.
- Joshi, R.C., Lothia, R.P., (1997) Fly ash in concrete: production, properties and uses. *Advances in concrete technology*, vol. 2. Gordon and Breach Science Publishers.
- Khan MR, Khan MW (1996) The effect of fly ash on plant growth and yield of tomato, *Environmental Pollution*, 92(2), 105-111.
- Khan, M.R., Singh, W.N. (2001) Effects of soil application of fly ash on the fusarial wilt on tomato cultivars, *International Journal of Pest Management*, 47, 293–297.
- Kukier, U., Sumner, M.E., Miller, W.P. (1994) Boron release from fly ash and its uptake by corn, *Journal of Environmental Quality*, 23, 596–603.
- Lau, S.S.S., Wong, J.W.C. (2001) Toxicity evaluation of weathered coal fly ash amended manure compost, *Water Air Soil Pollution*, 128, 243–254.
- Li D., Gao G., Shao M., Fu B. (2016): Predicting available water of soil from particle-size distribution and bulk density in an oasis–desert transect in northwestern China. *Journal of Hydrology*, 538: 539-550.
- Li, Z., Luo, X., Hwang, J.Y., (2002) Unburned carbons from fly ash for mercury adsorption II: adsorption isotherms and mechanisms. *J Min Mater Cgara En*, 1:79-96.
- Lieberman R.N., Green U., Segev G., Polat M., Mastai Y., Cohen H., (2015) Coal fly ash as a potential fixation reagent for radioactive wastes, *Fuel*, 153:437-444.
- Lin S., Song M., Kuramochi H., Takahashi F. (2018): Raw and apatite-synthesized coal fly ash amendment as soil water retention agent, *Journal of Arid Land Studies*, under review.
- Lin S., Takahashi F. (2015): Raw and Treated Coal Fly Ash Amendment Aiming for Water Holding Capacity Adjustment of Natural Soils, *J. Residuals Sci. Technol.*, 12(2): 73-84.
- Liu Y., Gao M., Wu W., Tanveer S.K., Wen X., Liao Y. (2013): The effects of conservation tillage practices on the soil water-holding capacity of a non-irrigated apple orchard in the Loess Plateau, China, *Soil & Tillage Research*, 130: 7-12.
- Lo ´pez-Anto ´n, M.A., Dı ´az-Somoano, M., Martı ´nez-Tarazona, M.R., (2007) Mercury retention by fly ashes from coal combustion: influence of the unburned coal content, *Ind Eng Chem Res*, 46:927–31.

- Lu, G.Q., Do, D.D., (1991) Adsorption properties of fly ash particles for NO_x removal from flue gases. *Fuel Process Technol*, 27:95–107.
- Maroto-Valer M.M., Taulbee, D.N., Hower, J.C., (1999) Novel separation of the differing forms of unburned carbon present in fly ash using density gradient centrifugation, *Energy Fuel*, 13: 947–53.
- Maroto-Valer, M.M., Taulbee, D.N., Hower, J.C., (2001) Characterization of differing forms of unburned carbon present in fly ash separated by density gradient centrifugation, *Fuel*, 80: 795–800.
- Matsi, T., Keramidas, V.Z. (1999) Fly-ash application on two acid soils and its effect on soil salinity, pH, B, P, and on ryegrass growth and composition, *Environmental Pollution*, 104, 107–112.
- Mattigod, S.V., Dhanpat, R., Eary, L.E., Ainsworth, C.C., (1990) Geochemical factors controlling the mobilization of inorganic constituents from fossil fuel combustion residues: I. Review of the major elements, *Journal of Environmental Quality*, 19:188–201.
- Mishra, L.C., Shukla, K.N., 1986a Effect of fly ash deposition on growth, metabolism and dry matter production of maize and soybean, *Environmental Pollution*, 42, 1–13.
- Mishra, L.C., Shukla, K.N., 1986b Elemental concentration of corn and soybean grown on fly ash amended soil, *Environmental Pollution Series B: Chemical and Physical*, 12, 313–321.
- Mohamed B. A., Ellis N., Kim C., Bi X., Emam A. E. (2016): Engineered biochar from microwave-assisted catalytic pyrolysis of switchgrass for increasing water-holding capacity and fertility of sandy soil, *Science of the Total Environment*, 566-567, 387-397.
- Mohapatra, R., Rao, J.R., (2001) Some aspects of characterisation, utilisation and environmental effects of fly ash, *J Chem Technol Biotechnol*, 76:9–26.
- Mouazen A. M., Alhwaimeel S. A., Kuang B., Waite T., (2014), Multiple on-line soil sensors and data fusion approach for delineation of water holding capacity zones for site specific irrigation. *Soil & Tillage Research*, 143:95-105.
- Mu Y., Saffarzadeh A., Shimaoka T. (2017): Utilization of waste natural fishbone for heavy metal stabilization in municipal solid waste incineration fly ash. *Journal of Cleaner Production*, In press.
- Nidhi J. (2003) Looks the ways to utilize fly ash, *Down Earth*, 12(3), 1–5.
- Pathan, S.M., Aylmore, L.A.G., Colmer, T.D. (2003a) Properties of several fly ash materials in relation to use as soil amendments, *Journal of Environmental Quality*, 32, 687–693.
- Pathan, S.M., Aylmore, L.A.G., Colmer, T.D. (2003b) Soil properties and turf growth on a sandy soil amended with fly ash, *Plant and Soil*, 256(1), 103-114.
- Paudel, E., Boom, R.M., van der Sman, R.G.M., 2015. Change in water-holding capacity in mushroom with temperature analyzed by flory-rehner theory. *Food Bioprocess Technol.*, 8 (5), 960–970.
- Pavlish, J.H., Sondreal, E.A., Mann, M.D., Olson, E.S., Galbreath KICK, Laudal D.L., (2003) Status review of mercury control options for coal-fired power plants. *Fuel Process Technol*, 82:89–165.
- Phung, H.T., Lam, H.V., Page, A.L., Lund, L.J. (1979) The practice of leaching boron and soluble salts from fly ash amended soils, *Water, Air, and Soil Pollution*, 12, 247-254.
- Plank, C.O., Martens, D.C. (1974) Boron availability as influenced by an application of fly ash to soil, *Soil Science Society of America*, Proceedings, 38, 974–977.

- Prasad, B., Banerjee, N.N., Dhar, B.B. (1996) Environmental assessment of coal ash disposal: A review, *Journal of Scientific & Industrial Research*, 55(10), 772-780.
- Punshon, T., Adriano, D.C., Weber, J.T. (2002) Restoration of drastically eroded land using coal fly ash and poultry biosolid, *Science of The Total Environment*, 296(1-3), 209-225.
- Ram, L.C., Masto, R.E., Jha, S.K., Selvi, V.A., Srivastava, N.K., Sinha, A.K., (2007) Reclamation of coal mine spoil using fly ash: a synoptic review, *Proceedings of the 1st International Conference on Managing the Social and Environmental Consequences of Coal Mining in India (MSECCMI)*, 771-801.
- Ram, L.C., Jha, S.K., Tripathi, R.C., Masto, R.E., Selvi, V.A., (2008) Remediation of fly ash landfills through plantation, *Remediation J.*, 18, 71-90.
- Ram, L.C., Masto, R.E. (2014) Fly ash for soil amelioration: A review on the influence of ash blending with inorganic and organic amendments, *Earth-Science Reviews*, 128, 52-74.
- Reich, P.F., Numbem, S.T., Almaraz, R.A., Es-waran, H. (2004) Land resource stresses and desertification in Africa, *Agro-Science*, 2001:2(2), 1-10.
- Reijnders, L., (2005) Disposal, uses and treatments of combustion ashes: a review, *Resour Conserv Recycl*, 43:313-36.
- Ricou, P., Lecuyer, I., Le Cloirec, P., (1999) Removal of Cu²⁺, Zn²⁺ and Pb²⁺ by adsorption onto fly ash and fly ash/lime mixing, *Water Sci Technol*, 39:239-47.
- Rovatti, M., Peloso, A., Ferraiolo, G., (1988) Susceptibility to regeneration of fly ash as an adsorbent material, *Resour Conserv Recycl*, 1:137-43.
- Roy, W.R., Thiery, R.G., Schuller, R.M., Suloway, J.J., (1981) Coal fly ash: a review of the literature and proposed classification system with emphasis on environmental impacts, *Environmental geology notes* 96, Champaign, IL: Illinois State Geological Survey.
- Sakulpitaphon, T., Hower, J.C., Trimble, A.S., Schram, W.H., Thomas, G.A., (2003) Arsenic and mercury partitioning in fly ash at a Kentucky power plant, *Energy Fuel*, 17:1028-33.
- Saxena, M., Ashokan, P., Srimanth, S., Chauhan, A., Mandal, S., 1997, Impact of fly ash on vegetation, *J. Environ. Stud. Policy*, 1, 55-60.
- Sen, S., Kumar, V., 2012 The effect of different soil amendments on growth of Mung bean (*Vigna radiata* L.) in coalmine overburden dumps. *Int. J. Emerg. Technol. Adv. Eng.*, 2, 264-270.
- Sikka R, Kansal BD. (1994) Characterization of thermal powerplant fly ash for agronomic purposes and to identify pollution hazards, *Bioresour Technol*, 50, 269-73.
- Singh, J.S., Pandey, V.C., Singh, D.P. (2011) Coal fly ash and farmyard manure amendments in dry-land paddy agriculture field: Effect on N-dynamics and paddy productivity, *Applied Soil Ecology*, 47(2), 133-140.
- Sloss, L.L., (1995) Mercury emissions and effects-the role of coal, *IEA Coal Research IEAPER*, 19, p. 39.
- Srivastava, N.K., Ram, L.C., Jha, S.K., Tripathi, R.C., Singh, G. (2003) Role of CFRI's fly ash soil amendment technology (FASAT) in improving the socio-economic condition of farmers via improvement in soil fertility and crop productivity, *Journal of Ecophysiology and Occupational Health*, 3, 127-142.
- Srivastava, N.K., Ram, L.C., 2009 Bio-restoration of coal mine spoil with fly ash and biological amendments. In: Chaubey, O.P., Bahadur, Vijay, Shukla, P.K. (Eds.), *Sustainable Rehabilitation of Degraded Ecosystems*. Avishkar Publishers, Distributors, Jaipur (Rajsthan). ISBN: 978-81-7910-288-6, pp. 77-91 (Published by, Chapter-7).

- Srivastava, N.K., Ram, L.C., 2010a Reclamation of mine over-burden and low-lying area with coal fly ash: a sustainable ecological approach. In: Dassisti, Michele, Ghani Olabi, Abdul, De Nicolo, Michele, Chimienti, Michela (Eds.), Proceedings 4th International Conference on “Sustainable Energy & Environmental Protection” (SEEP-2010) ‘Environmental Protection in the New Era’ — Part-2. DIMeG, Politecnico di Bari, BARI — ITALY. ISBN: 978-88-905185-2-2 (<http://seep2010.poliba.it>).
- Srivastava, N.K., Ram, L.C., 2010b Reclamation of coal mine spoil dump through fly ash and biological amendments, *Int. J. Ecol. Dev*, 17 (F10), 17–33
- Srivastava, V.C., Mall, I.D., Mishra, I.M., (2006) Modelling individual and competitive adsorption of cadmium(II) and zinc(II) metal ions from aqueous solution onto bagasse fly ash, *Sep Sci Technol*, 41:2685.
- Srivastava, V.C., Mall, I.D., Mishra, I.M., (2008) Removal of cadmium(II) and zinc(II) metal ions from binary aqueous solution by rice husk ash, *Colloids Surf A: Physicochem Eng Aspects*, 312:172-84.
- Sua íez-Ruiz, I., Hower, J.C., Thomas, G.A., (2007) Hg and Se capture and fly ash carbons from combustion of complex pulverized feed blends mainly of anthracitic coal rank in Spanish power plants, *Energy Fuel*, 21:59–70.
- Sua íez-Ruiz, I., Parra, J.B., (2007) Relationship between the textural properties, fly ash carbons and Hg capture in fly ashes derived from the combustion of anthracitic pulverized feed blends, *Energy Fuel*, 21:1915–23.
- Tamilselvi Dananjayan R.R., Kandasamy P., Andimuthu R., (2015) Direct mineral carbonation of coal fly ash for CO₂ sequestration, *Journal of Cleaner Production* xxx:1-10
- Taylor Jr., E.M., Schuman, G.E. (1988) Fly ash and lime amendment of acidic coal spoil to aid revegetation, *Journal of Environmental Quality*, 17, 120–124.
- Tolle, D.A., Arthur, M.F., Pomeroy, S.E., (1982) Fly ash use for agriculture and land reclamation: a critical literature review and identification of additional research needs. RP-1224-5. Columbus. Ohio: Battelle Columbus Laboratories.
- Ukwattage, N.L., Ranjith, P.G., Bouazza, M., 2013 The use of coal combustion fly ash as a soil amendment in agricultural lands (with comments on its potential to improve food security and sequester carbon), *Fuel*, 109, 400–408.
- Ukwattage, N.L., Ranjith, P.G., Yellishetty, M., Bui, H.H., Xu, T., (2015) A laboratory-scale study of the aqueous mineral carbonation of coal fly ash for CO₂ sequestration, *Journal of Cleaner Production*, 103:665-674.
- U.S. Energy Information Administration (2013) International Energy Outlook 2013, DOE/EIA-0484, 1000 Independence Ave., SW, Washington, DC 20585.
- Van der Sman, R.G.M., Paudel, E., Voda, A., Khalloufi, S., Khallou, S., 2013. Hydration properties of vegetable foods explained by Flory-Rehner theory. *Food Res. Int.*, 54 (1), 804–811.
- Veeresh, H., Tripathy, S., Chaudhuri, D., Ghosh, B.C., Hart, B.R., Powell, M.A. (2003) Changes in physical and chemical properties of three soil types in India as a result of amendment with fly ash and sewage sludge, *Environmental Geology*, 43(5), 513-520.
- Wang, S. (2008) Application of solid ash based catalysts in heterogeneous catalysis, *Environmental Science & Technology*, 42(19), 7055-7063.
- Wong, M.H., Wong, J.W.C. (1989) Germination and seedling growth of vegetable crops in fly

- ash-amended soils, *Agriculture, Ecosystems & Environment*, 26, 23–35.
- Xue, Y.K. (1996) The impact of desertification in the Mongolian and the Inner Mongolian grassland on the regional climate, *Journal of Climate*, 9(9), 2173–2189.
- Yang X., Zhang K., Jia B., Ci L. (2005) Desertification assessment in China: An overview, *Journal of Arid Environments*, 63, 517–531.
- Yao, Z.T., Ji, X.S., Sarker, P.K., Tang, J.H., Ge, L.Q., Xia, M.S., Xi, Y.Q. (2015) A comprehensive review on the applications of coal fly ash, *Earth-Science Reviews*, 141, 105–121.
- Yunusa, I.A.M., Eamus, D., De Silva, D.L., Murray, B.R., Burchett, M.D., Skilbeck, G.C., Heidrich, C. (2006) Fly-ash: an exploitable resource for management of Australian agricultural soils, *Fuel*, 85, 2337–2344.
- Zheng H., Han M., Yang H., Tang C., Xu X., Zhou G. (2017). Application of high pressure to chicken meat batters during heating modifies physicochemical properties, enabling salt reduction for high-quality products. *LWT - Food Science and Technology*, 84, 693–700.

Chapter 2

Experimental materials & methods

2.1 Soils, sands and coal fly ash properties

In this research, two kinds of gardening soils, decomposed granite soil (DGS) and akadama soil (AS), were tested as soil samples. Two kinds of sands, silica sand (SS) and river sand (RS), were also tested as sand samples. By sieving 100 g of each sample and weighing each size fraction, cumulative size distribution was measured. The cumulative size distributions with weight percentage unit are plotted in Figure 2-1. Both soil and sand samples primarily contain sand-size fractions (0.2-2.0 mm). AS has relatively larger particle sizes than DGS. Size distribution of DGS is slightly larger than that of RS. SS has the largest fractions of small particle size than others. Coefficients of Uniformity and Gradation are defined by ASTM international (ASTM D2487) to classify soils for engineering purposes.

Equations are shown below:

$$\text{Coefficients of Uniformity} = \frac{D_{60}}{D_{10}}$$

$$\text{Coefficients of Gradation} = \frac{(D_{30})^2}{(D_{60} \times D_{10})}$$

where, D_{60} is diameter corresponding to 60 % finer in the grain size distribution, D_{30} is diameter corresponding to 30 % finer in the grain size distribution, and D_{10} is diameter corresponding to 10 % finer in the grain size distribution, known as effective size.

Coefficients of Uniformity of RS, SS, DGS and AS are 7.5, 2.3, 10 and 7.7, respectively. Coefficients of Gradation of RS, SS, DGS and AS are 0.64, 0.86, 0.78 and 1.4, respectively. In this research, in order to compare all soil/sand samples at the same particle size level and exclude noise parameters, all soil/sand samples are sieved to under 150 μm . Coal fly ash (FA) was taken from a coal-fired power plant in Japan. Coal fly ashes were classified in silt size (<0.2 mm). Energy Dispersive X-Ray Fluorescence spectrometer was used to analyze elemental content of tested FA. The results are listed in Table 2-1. Major component elements of FA are Si, Al, Fe, and Ca, which are similar compared with other

researches (Belviso et al, 2015; Hot et al, 2016). Surface morphology of soil, sand and FA samples smaller than 150 μm are shown in Figure 2-2. DGS has uniform distribution of particle size, rough surface and grooves on particle surface. AS particle sizes are smaller than that of DGS and less uniform. Its surfaces are rough and have grooves. SS has uniform particle size distribution, smooth surface and no groove observed on particle surface. RS particle size distribution is less uniform than that of SS and has smooth surface without grooves. Coal FA has very wide range of particles size, from nanometer level to micrometer level. FA particles have sphere shape and smooth surface without groove.

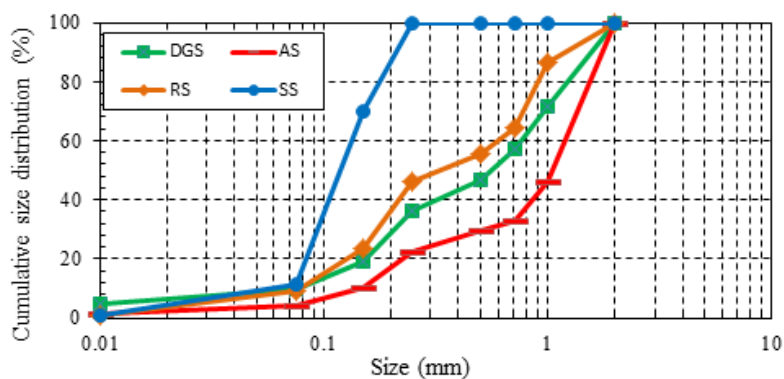


Figure 2-1 Cumulative size distribution of two tested soils (Unit: wt%)
(DGS: Decomposed granite soil, AS: Akadama soil, SS: Silica Sand, RS: River Sand)

Table 2-1 Elemental content of FA utilized

Element	Si	Al	Fe	Ca	Ti	K	Ba	Mg	Sr	S
Content (wt%)	46.9	19.6	15.2	5.86	3.66	3.17	1.44	1.21	0.615	0.504
Element	P	Zr	Mn	Co	Zn	Ni	Cr	Cu	Sn	
Content (wt%)	0.41	0.398	0.186	0.119	0.118	0.10	0.093	0.081	0.060	

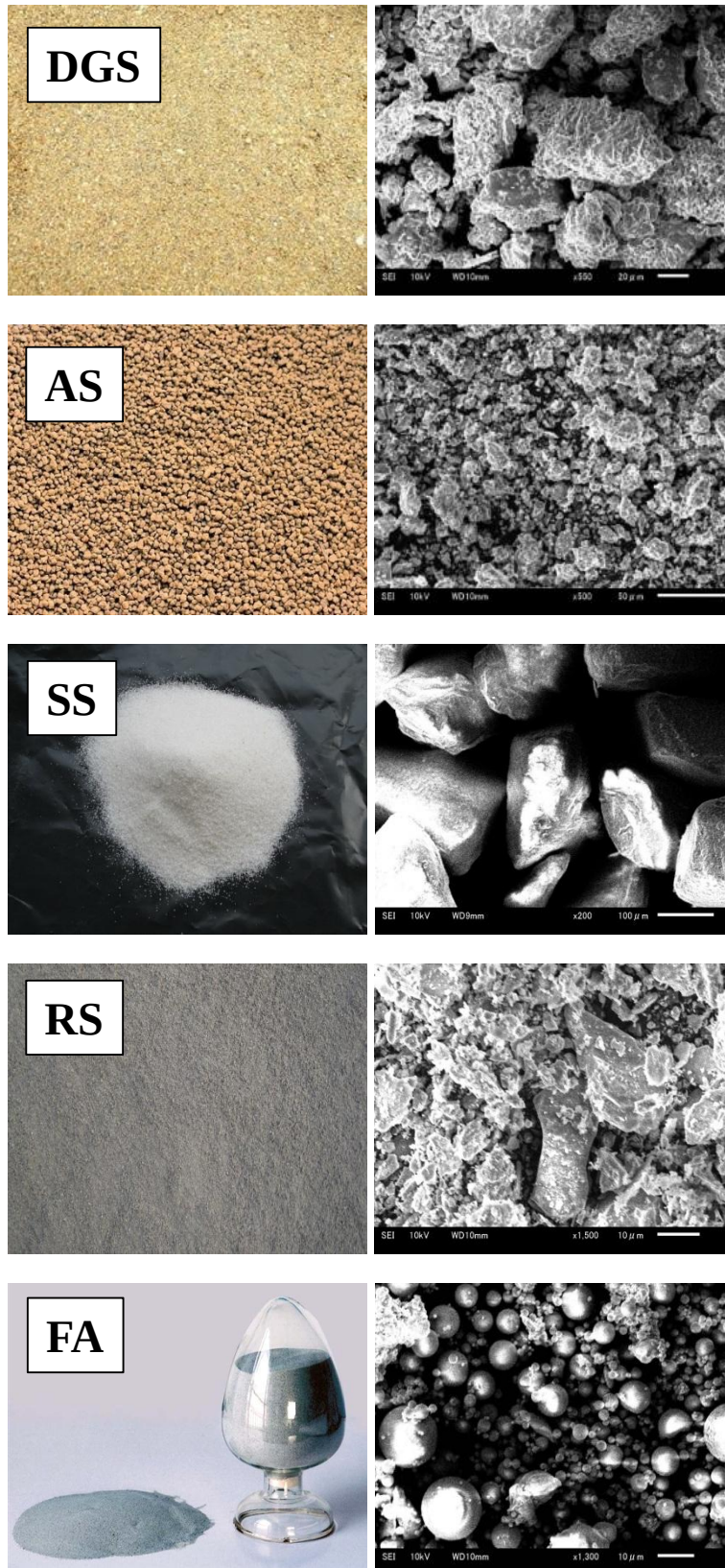


Figure 2-2 Surface morphology of soil/sand and FA

2.2 Water in soil/sand system

In soil and sand matrices, water exists as gravitational water and capillary water. Larger pore size (void spaces) among soil/sand particles will generate higher porosity. It will hold more amount of gravity water in soil/sand system (water holding capacity). When void space in soil system is in “capillary range” more and more, it will hold more amount of capillary water and thus high resistivity against water evaporation will be expected (water retention capacity). When air pressure out of soil/sand system decreased or temperature increased, free water will evaporate first, becomes steam and diffuse inside the soil system (see Figure 2-3). In the case of capillary water, it has higher pF values than gravitational water and strongly adsorbed on soil surfaces. Therefore, capillary water evaporation is slow. When gravitational water and capillary water evaporate at the same time, evaporation rate of more hydrophobic soil is expected to be faster because of lower water potential for hydrophobic soil.

Capillary water evaporation might be influenced by soil surface properties like specific surface area and hydraulic properties like surface hydrophilicity/hydrophobicity and surface water suction (water potential, pF value) to some extents. Therefore, surface modification might be effective to increase capillary water and water retention capacity. Micro-structures on soil surfaces and aggregation of soil particles might also influence WRC.

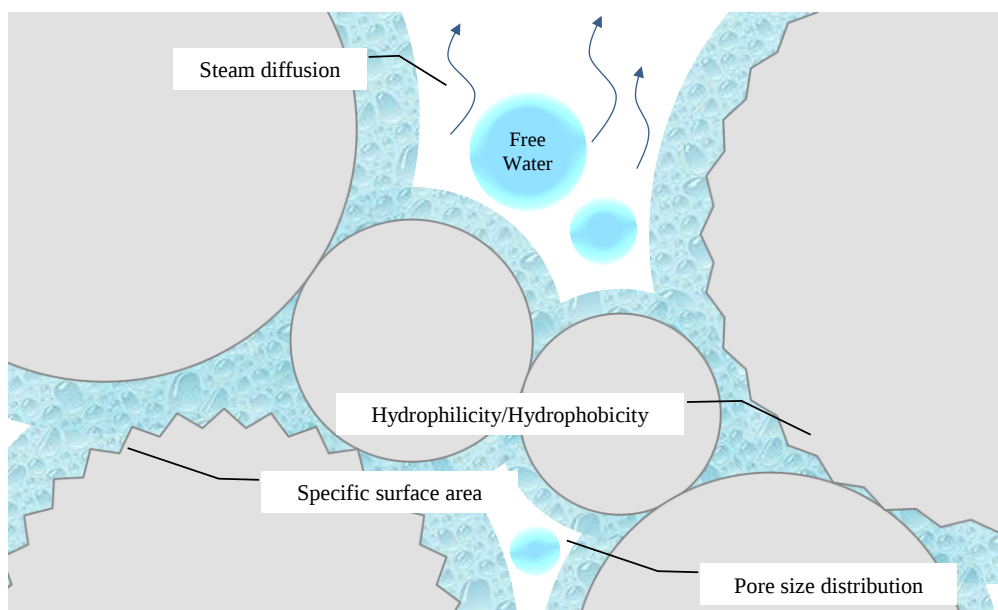


Figure 2-3 Water retention methodology in soil/sand system

2.3 Water Retention Capacity (WRC) measurement

Water retention capacities (WRC) of pure samples (only FA, DGS, AS, RS, and SS) and FA mixed samples (soil/sand amended with FA) were measured by drying experiments (Lin & Takahashi, 2015). Mixing ratios of FA were 10 wt%, 20 wt% and 30 wt% in order to find mixing ratio dependency. Total weight of sample is 17.5 g. When FA is amended to soil/sand, 1.75 g of FA was mixed for 10 wt% mixing ratio, 3.5 g of FA for 20 wt% and 5.25 g of FA for 30 wt%, respectively. To adjust water content of each sample as 30 wt%, 7.5 g of distilled water was added to 25 g of soil/sand/FA-mixture samples. All samples were dried at room temperature (averagely 25 °C in summer and 15 °C in winter) and 40 °C in drying ovens for simulating real situation in arid/semi-arid area (EYELA NDO-420). During drying experiments, water content was monitored for 12 hours in one-hour interval. The weight of samples was measured by electronic weight balance. Based on monitoring data, weight-based relative percentages of remained water in samples were calculated. Water evaporation curves were drawn based on these data. It sets 100 % at the beginning of drying experiment and 0 % means completely dry. When water retention curve has a constant trend, it suggests that pore-water completely evaporated and capillary water starts to evaporate. In order to compare WRC more clearly, area below water retention curve was identified as WRC. The concept of WRC measurement is illustrated in Figure 2-4.

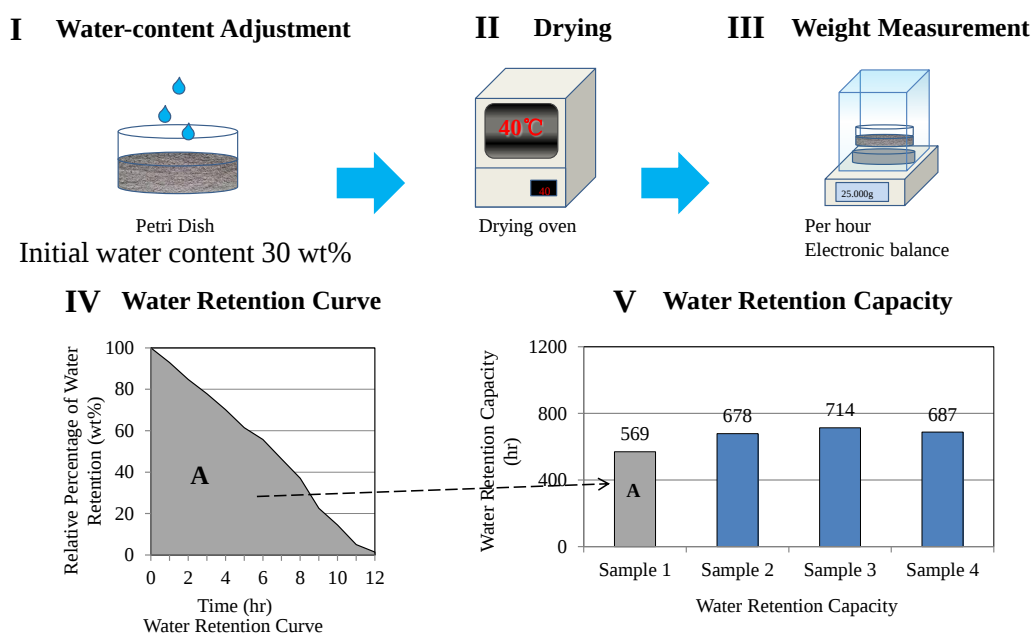


Figure 2-4 Calculation concept of WRC based on water retention curve

2.4 Particle surface morphology and particle size distribution analysis

Microscopic surface conditions of soil/sand, raw FA, and treated FA particles were observed by scanning electron microscope (SEM; JSM-6610LA, JEOL Co.). Samples were put on carbon tape on observation stage and then observed without spattering. Samples were magnified at 500 times, 2000 times, 10000 times and observations were repeated 7 to 10 times. All observation data were utilized for surface characterization. Particle size distributions of raw and treated FA were measured according to SEM images. In every type of FA, about 1000 to 1500 of particles were counted and observed for size measurement.

2.5 Water Drop Penetration Time experiment (WDPT)

Water drop penetration time (WDPT) is a common and simple method to evaluate water repellency of hydrophobic soils, sands and FAs (Leelamanie et al, 2008; Leelamanie, 2016; Chenu et al, 2000). In this study, WDPT was measured to investigate correlation between water repellency of samples (FA, soil/sand, and their mixture) and WRC. Distilled water was dropped onto the surface of each sample. The time that water droplet was completely absorbed into sample surface was monitored over 20 times. Averages of measurement data were used for discussions. If FA amendment changes hydrophobicity of soil/sand and it plays an important role of WRC, strong correlation between WRC and WDPT would be expected.

2.6 Water potential of soil/sand

Water potential of samples in this study was measured by soil water leakage. Measurement apparatus are shown in Figure 2-5. Metal container was filled with sample and set tightly with a filter and sample receiver. It was finally closed tightly by mechanical bolts. In this measurements, degassed water, which was prepared by boiling distilled water for more than 5 minutes, were used. The filter was saturated before measurements by submerging it in degassed water for over 24 hours. The container and receiver were set on the stage with height scale and then connected to the burette with water level scale using plastic tubes. Samples were saturated by degassed water for more than 2 days until no water was absorbed anymore. After the burette was turned upside down, the stage was moved to certain position

to increase suction pressure. When hydraulic suction pressure increased, water would leak out from saturated samples and dropped down to the burette. After monitoring the amount of leaked water, the sample stage was moved to lower position in order to increase suction pressure. After monitoring at maximum suction pressure, the weight of remained sample (w_0) was measured. In addition, the weight of dried sample (w_1) was also measured after complete drying at 105 °C for 24 hours. Water contents of samples at each stage position were calculated using water content of the remained sample and monitoring data of leaked water. When water content curves as a function of pF (suction pressure) is drawn, smaller trend of the curve means stronger suction force of absorbed water. In contrast, larger trend means weaker water suction.

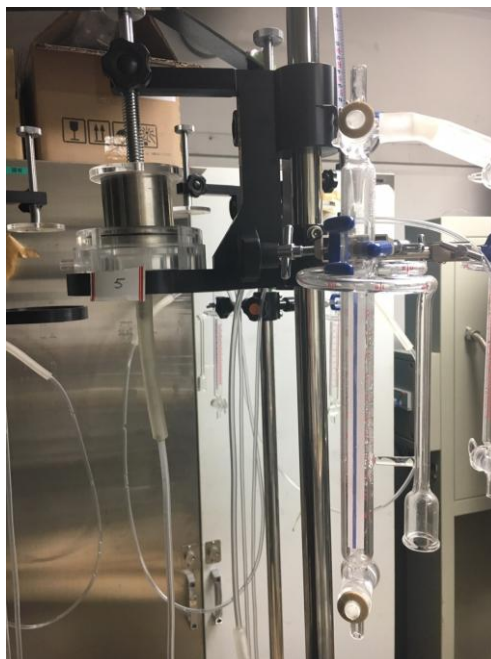
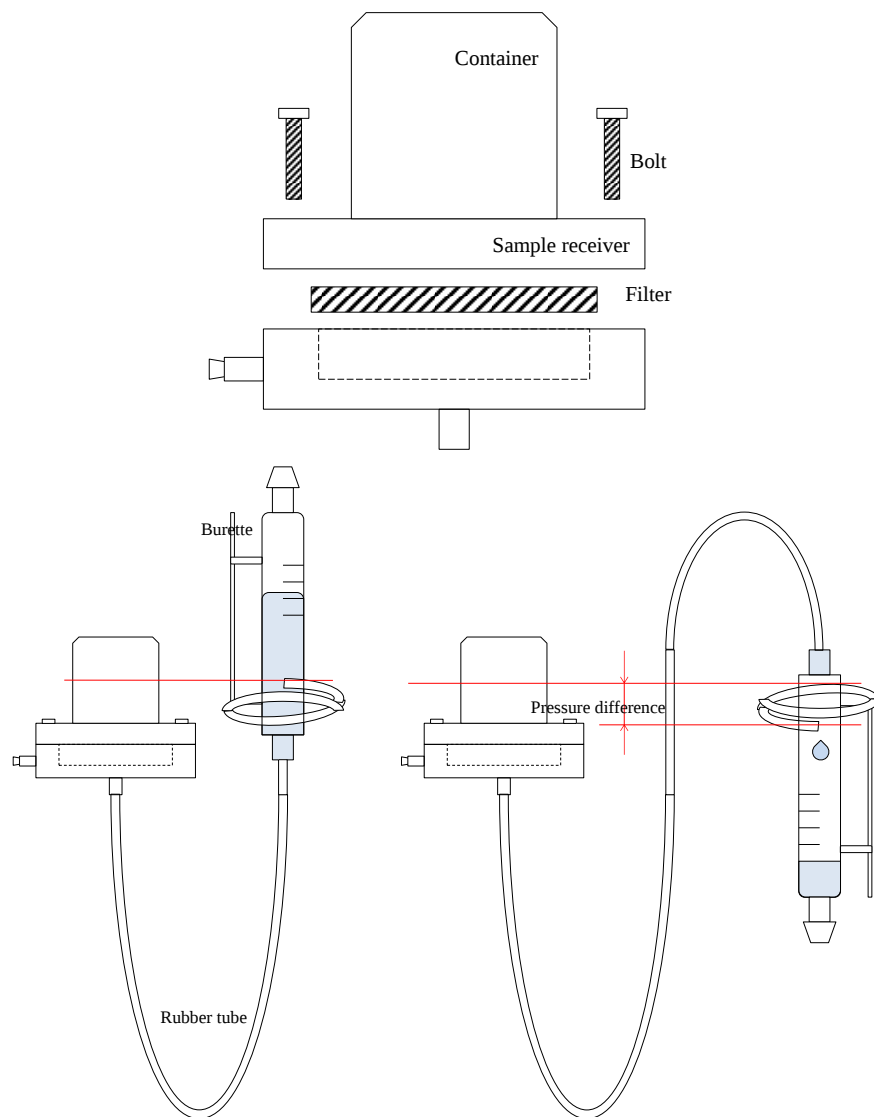


Figure 2-5 Equipment for water potential analysis

2.7 Capillary water content measurement

Capillary water is a part of water contained in soil/sand that is not influenced by gravity. In this study, percentage of capillary water was measured by a simplified method. This method used a cylinder, 45 μm -mesh filter and excess amount of completely dried sand. Measurement apparatus is shown in Figure 2-6. In this method, the weight of samples were measured first under dry condition, and then samples were put into the cylinder. The cylinder was on enough dry sand and the filter was set in-between the cylinder and sand. Excess amount of distilled water was filled into samples and left for over 24 hours. After that weight of sample was measured, percentage of capillary water (adhesive water, hygroscopic water concluded) was calculated by following equation.

$$X = \frac{W_2 - W_1}{W_0} \times 100\%$$

where X is percentage of capillary water (based on weight of dry sample), W_0 is weight of dry sample, W_1 is weight of the container, W_2 is total weight of capillary water, sample and sample container. After measurement, wet sand was dried at 105 $^{\circ}\text{C}$ for over 24 hours and reused for measurement again.

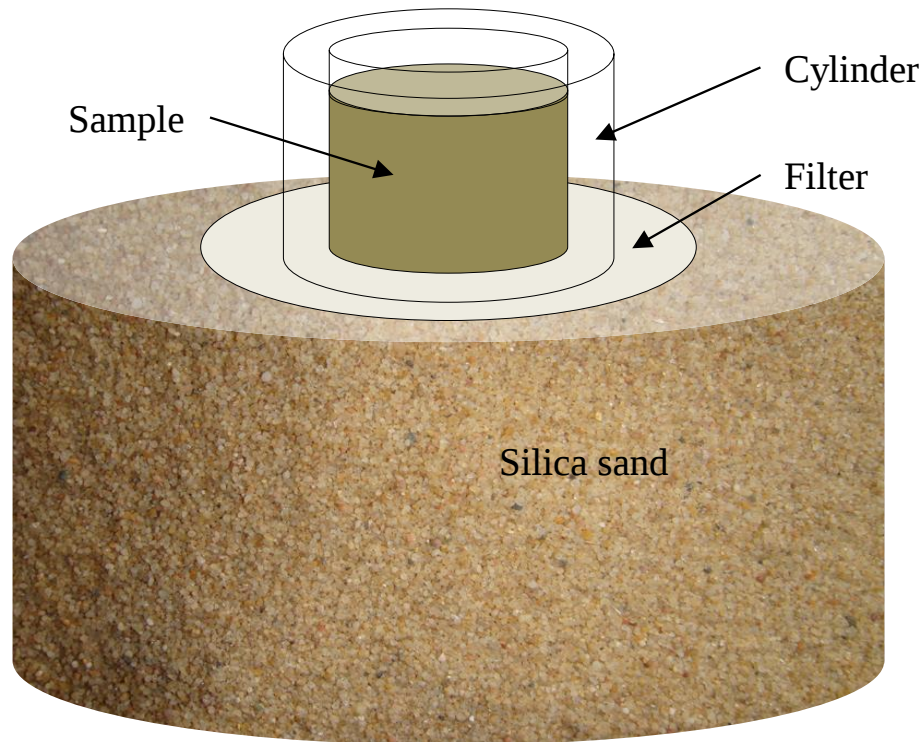


Figure 2-6 Equipment for analyzing capillary water content

2.8 Statistical analysis to evaluate WRC differences beyond experimental errors

In order to assess experimental errors, all experiments were repeated for 3 times or more. Statistical analysis (*Welch's t-test*) was conducted to evaluate the differences of WRC data beyond experimental errors. It means significance test of FA amendment effect on WRC.

Welch's t-test defines statistic t by the following formula:

$$t = \frac{\bar{X}_1 - \bar{X}_2}{\sqrt{\frac{S_1^2}{N_1} + \frac{S_2^2}{N_2}}}$$

Degree of freedom of t is identified by equation below:

$$df = \frac{\left(\frac{S_1^2}{N_1} + \frac{S_2^2}{N_2}\right)^2}{\left(\frac{1}{N_1 - 1} \left(\frac{S_1^2}{N_1}\right)^2 + \frac{1}{N_2 - 1} \left(\frac{S_2^2}{N_2}\right)^2\right)}$$

where $\bar{X}_1$ and $\bar{X}_2$ are the mean of sample 1 and sample 2, S_1^2 and S_2^2 are unbiased variance of sample 1 and sample 2, and N_1 and N_2 are sample size. The degree of freedom of t -distribution is defined by the formula below.

When WRC differences were regarded at 5 % or less than 5 % of significance levels, this study considered that the difference was beyond experimental errors.

2.9 Specific surface area analysis

As described in the previous section, surface area of fly ash particles might be important for WRC because it influences molecule adsorption performance in many ways such as H₂O retention or gas storage (Kim, et al, 2016). Specific surface areas of soil/sand samples, raw FA and apatite-synthesized FA were measured by Brunauer-Emmett-Teller (BET) method (Lowell et al, 2004; Gelb and Gubbins, 1998; Denoyel et al, 1993). After glass tubes with samples were highly vacuumed, they were heated at 200 °C for several hours to evaporate volatile materials. After net weight of sample was measured, nitrogen adsorption and following desorption were monitored. In surface area analysis, multi-point BET plot was utilized. Adsorption amount of nitrogen gas at three points of relative pressure ($P/P_0 = 0.1, 0.2, 0.3$) was used for surface area calculation. Liquid nitrogen used FlowVac®Degasser SI, and Quadrasorb SI (FlowVac®Degasser) of Quantachrome is utilized.

References

- Belviso C., Cavalcante F., Gennaro D. F., Palma A., Ragone P., Fiore S. (2015): Mobility of trace elements in fly ash and in zeolitised coal fly ash. *Fuel*, 144: 369-379.
- Chenu, C., Le Bissonnais, Y., Arrouays, D. (2000): Organic matter influence on clay wettability and soil aggregate stability. *Soil Science Society of America Journal*, 64: 1479-1486.
- Denoyel R., Fernandez-Colinas J., Grillet Y., Rouquerol J. (1993): Assessment of the surface area and microporosity of activated charcoals from immersion calorimetry and nitrogen adsorption data. *Langmuir*, 9(2): 515-518.
- Gelb L.D., Gubbins K.E. (1998): Characterization of porous glasses: Simulation models, adsorption isotherms, and the Brunauer-Emmett-Teller analysis method. *Langmuir*, 14(8): 2097-2111.
- Hot J., Sow M., Tribout C., Martin C. (2016): An investigation of the leaching behavior of trace elements from Spreader Stoker Coal Fly Ashes-based systems. *Construction and Building Materials*, 110: 218-226.
- Kim K., Yoon T., Bae Y. (2016): Applicability of using CO₂ adsorption isotherms to determine BET surface areas of microporous materials. *Microporous and Mesoporous Materials*, 224: 294-301.
- Lin S., Takahashi F. (2015): Raw and Treated Coal Fly Ash Amendment Aiming for Water Holding Capacity Adjustment of Natural Soils. *J. Residuals Sci. Technol.*, 12(2): 73-84.
- Leelamanie D.A.L., Karube J., Yoshida A. (2008): Relative humidity effects on contact angle and water drop penetration time of hydrophobized fine sand. *Soil Sci. Plant Nutr.* 54: 695-700.
- Leelamanie D.A.L. (2016): Occurrence and distribution of water repellency in size fractionated coastal dune sand in Sri Lanka under Casuarina shelterbelt. *Catena*, 142: 206-212.
- Lowell S., Shields J.E., Thomas M.A., Thommes M. (2004): Characterization of Porous Solids and Powders: Surface Area, Pore Size and Density, Springer Netherlands.

Chapter 3

Water retention capacity of soil/sand mixed with/without raw and apatite-synthesized FA

3.1 Background

As mentioned in Chapter 1 and 2, WHC is the amount of water that can be hold by soils. In terms of available water for plants, however, not only moderate water potential but also water retention time are also important because water in soil system will be lost mainly via evaporation with time. In this context, this study suggests a new indicator of water retention which reflects both the amount of remained water and water retention time in soil system. WRC is a parameter that shows water evaporation resistance and calculated from water retention curve. WRC will be also useful to analyze evaporation characteristics of water in soil using simple method and common experimental apparatus.

In this chapter, water retention capacity of soils, sands, raw FA and apatite-synthesized FA would be reported and the effects of FA treatment on WRC of FA would be discussed. Apatite is the mineral that will form on the surface of FA particles. After treatment and crushing, apatite micro-structures should left between FA aggregations or separate micro-structures. Micro-structures create more capillary zone and holding water stronger than raw FA. The initial reason of conducting apatite-synthesis on FA is apatite that covering surface of FA particles can immobilize heavy metals and can be stable for decades of years. At the same time, when apatite is decomposed, phosphate contained compounds can serve as fertilizer for plant growth. After treatment, the effect of FA amendment on WRC of soils and sands would be reported and discussed focusing on water retention curves.

3.2 Apatite-synthesis on fly ash particle surface

Water holding capacity (WHC) of soil depends on organic carbon and soil texture (Ilek et al, 2017; Yang et al, 2014). On the other hand, their impact on water retention capacity (WRC) has been still uncertain. In this chapter, apatite (calcium phosphate hydroxide:

$\text{Ca}_5(\text{PO}_4)_3(\text{OH})_2$) synthesis treatments of FA were tested for its textural modification. Impact of apatite treatment on soil/sand WRC were investigated when apatite-synthesized FA was amended into soil/sand. In apatite treatment, apatite was synthesized on FA particle surface by simple mixing of calcium hydroxide solution with sodium phosphate solution. Solvent utilized in this treatment is distilled water. P and Ca ratio was varied to analyze P/Ca ratio dependency of soil/sand WRC. Tested P/Ca ratios were 3.0, 7.1, 11.7, and 16.0. 200 g of raw FA was mixed with correspondingly changed volumes of 0.19 mol/L Na_3PO_4 solution and saturated $\text{Ca}(\text{OH})_2$ solution in the same manner at other P/Ca ratios. At P/Ca ratio of 3.0, raw FA was mixed with 40 ml of 0.19 mol/L Na_3PO_4 solution first, and then mixed with 10.28 ml of saturated $\text{Ca}(\text{OH})_2$ solution. At P/Ca ratio of 7.1, raw FA was mixed with 30 ml of 0.19 mol/L Na_3PO_4 solution first, and then mixed with 50 ml of saturated $\text{Ca}(\text{OH})_2$ solution. At P/Ca ratio of 11.7, raw FA was mixed with 40 ml of 0.19 mol/L Na_3PO_4 solution first, and then mixed with 40 ml of saturated $\text{Ca}(\text{OH})_2$ solution. At P/Ca ratio of 16.0, raw FA was mixed with 40 ml of 0.19 mol/L Na_3PO_4 solution first, and then mixed with 55 ml of saturated $\text{Ca}(\text{OH})_2$ solution. They are summarized in Table 3-1. Apatite-synthesized FAs were additionally mixed with distilled water for sufficient contacts between calcium phosphate solution and fly ash particles. FA mixture was kept for 24 hours at constant room temperature, and then dried at 105 °C for over 24 hours. After drying, samples were crushed softly and then utilized for WRC experiments.

Table 3-1 Experimental methods for conducting apatite synthesis on FA

P/Ca ratio	Raw FA (g)	$\text{Ca}(\text{OH})_2$ (ml)	Na_3PO_4 (ml)	Rest (hr)	Dry (°C)	Dry time (hr)
3.00	200.00	10.28	40.00	24.00	105.00	24.00
7.10	200.00	50.00	30.00	24.00	105.00	24.00
11.70	200.00	40.00	40.00	24.00	105.00	24.00
16.00	200.00	55.00	40.00	24.00	105.00	24.00

3.3 Results and discussion

3.3.1 WRC of raw/treated FA, soils and sands (single sample cases)

3.3.1.1 WRC of single sample at room temperature

Water retention curves of soils (DGS and AS), sands (SS and RS), raw FA and apatite-synthesized FA at room temperature and 40 °C are shown in Figure 3-1 to 3-4. Error bars in all figures are standard deviation of 3 or more than 3 times repeated measurement data. According to water retention curves, WRC of each sample at each temperature was calculated as described in Chapter 2. WRC of soils, sands, raw FA and apatite-synthesized FA are shown in Figure 3-5. At room temperature, all pure samples have similar WRC with each other. Especially soils, sands, raw FA, and apatite-synthesized FA with P/Ca ratio of 11.7 had almost equal WRC. For example, water evaporation rates of soils and sands were similar and water retention curves were almost the same. After 12 hours, water left around 18 wt% of the whole weight of these samples (see Figure 3-1).

WRC of apatite-synthesized FA with P/Ca ratio of 3.0 and 16.0 are 5 % to 10 % higher than others. The t-test analysis suggests that these differences exceed experimental errors at 5% significance level. In terms of water retention curves, apatite-synthesized FAs with P/Ca ratio of 3.0 and 16.0 have linear trends of water evaporation until 12 hours drying time. On the other hand, raw FA and apatite-synthesized FA with P/Ca ratio of 11.7 have similar water retention curve. Water evaporation rate was smaller until the first 2 hours and it became faster after that. When P/Ca ratio is 7.1, water evaporation rate is constant until the first 10 hours and then it increased (see Figure 3-3).

3.3.1.2 WRC of single sample at 40 °C

When temperature increased, surface condition and size distribution of soil particles will give stronger influence on water holding capacity (WHC) (Elizavet et al, 2017). It might be the same with WRC. At 40 °C, raw and treated FA had different WRC although they are almost equal at room temperature. DGS and AS have the similar WRC (around 800 hr). Correspondingly, water retention curves of both soils at 40 °C are also almost the same. Residual water percentages of both soils after 12 hours drying were around 9 wt%. On the other hand, SS and RS had significantly lower WRC than soils (666 hr and 635 hr). Only 6 wt%

of water left in sand samples after 12 hours drying at 40 °C. Water retention curves of both sands are also the same with each other (see Figure 3-2). Apatite-synthesized FA with P/Ca ratio of 11.7 had the largest WRC (around 947 hr) which is about 1.6 times higher than those of other samples. The t-test suggests this high WRC exceeds experimental errors. Water evaporation rate was very low in apatite-synthesized FA with P/Ca ratio of 11.7 compared to others. Although evaporation rate increased after the first 2 hours, residual water left after 12 hours drying still maintained higher than 40 wt%. This resulted in higher WRC of apatite-synthesized FA with P/Ca ratio of 11.7.

When focusing on water retention curves of other FAs, water evaporation of pure raw FA was very fast. Water content of raw FA decreased to less than 6 wt% at first 8 hours. After 10 hours, water evaporating rate is almost 0. For apatite-synthesized FA with P/Ca ratio of 3.0 and 16.0, water evaporating rates were constant and water retention curves were similar with each other. When P/Ca ratio changes to 7.1, water evaporated fast at first stage. After 5 hours, it evaporated slower until water content dropped to near 0 wt% (see Figure 3-4). According to Figure 3-5, apatite-synthesized FA with P/Ca ratio of 3.0 and 16.0 had comparable WRC with sands (SS and RS) at 40 °C. On the other hand, Figure 3-2 and 3-4 show that water retention curves of these apatite-synthesized FA (P/Ca ratio = 3.0 and 16.0), SS and RS were completely different. Water in these apatite-synthesized FA evaporated constantly at whole drying time. On the other hand, water in sands evaporated slowly at the first 2 hours and 9-12 hours. Evaporation was accelerated from 3 to 9 hours. It suggests that comparable WRC is possible even though water evaporating characteristics are different.

3.3.1.3 WRC comparison between room temperature and 40 °C

WRC of the same sample at room and higher temperatures are also compared. Figure 3-6 shows the comparison of water retention curves of FAs between room temperature and 40 °C. WRC usually decreased at high temperature. Because high temperature accelerated gravitational water and capillary water evaporation and the curve reaches an extremely low water evaporating zone (adhesive water evaporation). When temperature increased, water retention curves shifted down obviously (see Figure 3-6). For example, raw FA had the lowest WRC (around 562 hr) among tested samples when temperature increased, which is 40.6 %

lower than that at room temperature. Water in raw FA evaporated fast and reached adhesive water evaporation zone at 40 °C more quickly than that at room temperature. After that, the water retention curve became stable from 10 to 12 hours.

WRC of apatite-synthesized FA with P/Ca ratio of 3.0 and 16.0 also decreased to about 60-70 % of original WRC at room temperature. Water retention curves of apatite-synthesized FA with P/Ca ratio of 3.0 and 16.0 were also similar with each other (see Figure 3-6). Apatite-synthesized FA with P/Ca ratio of 7.1 has the similar WRC with those of P/Ca ratio of 3.0 and 16.0 while water retention curve of apatite-synthesized FA with P/Ca ratio of 7.1 was different from those of apatite-synthesized FA with P/Ca ratio of 3.0 and 16.0 (see Figure 3-6). In contrast, apatite-synthesized FA with P/Ca ratio of 11.7, which had the largest WRC among tested samples at 40 °C, kept almost the same WRC value with that at room temperature. Experimental results clearly show that apatite-synthesis on FA surface with P/Ca ratio of 11.7 increased evaporation resistivity of moisture at high temperature. As shown in Figure 3-6, water retention curves of apatite-synthesized FA with P/Ca ratio of 11.7 were similar at both room temperature and 40 °C. This means that water evaporation was not accelerated at high temperature by apatite-synthesis treatment of FA with P/Ca ratio of 11.7.

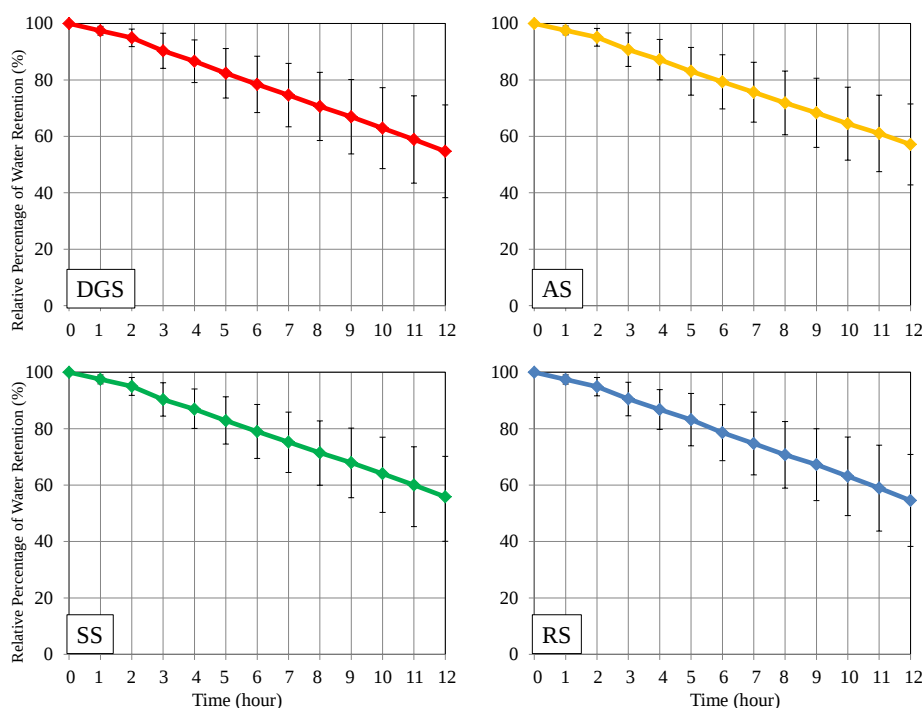


Figure 3-1 Water retention curves of DGS, AS, SS and RS at room temperature

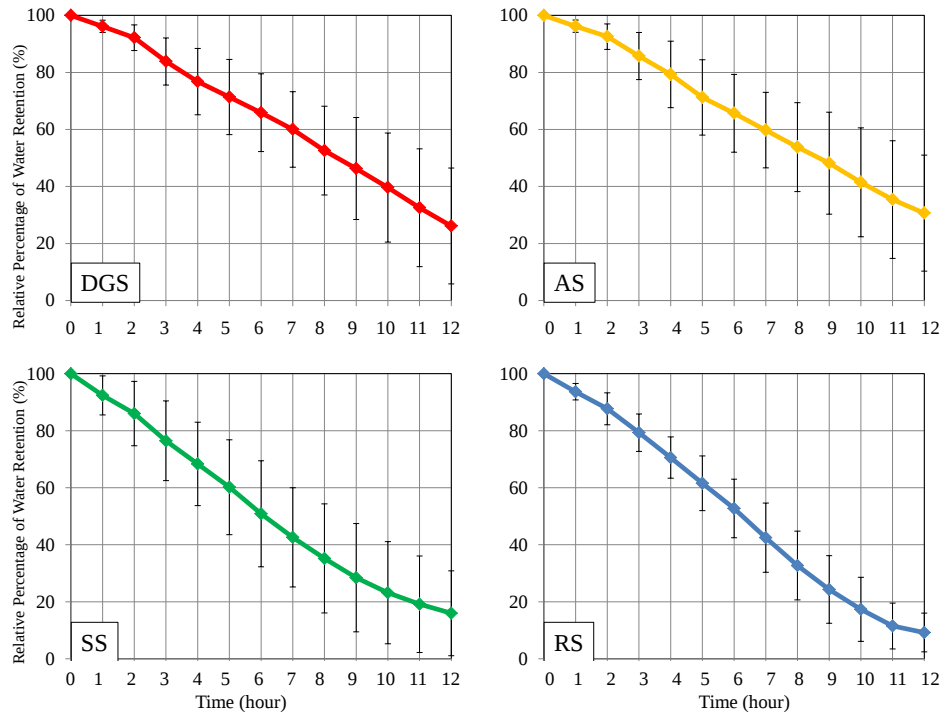


Figure 3-2 Water retention curves of DGS, AS, SS and RS at 40 °C

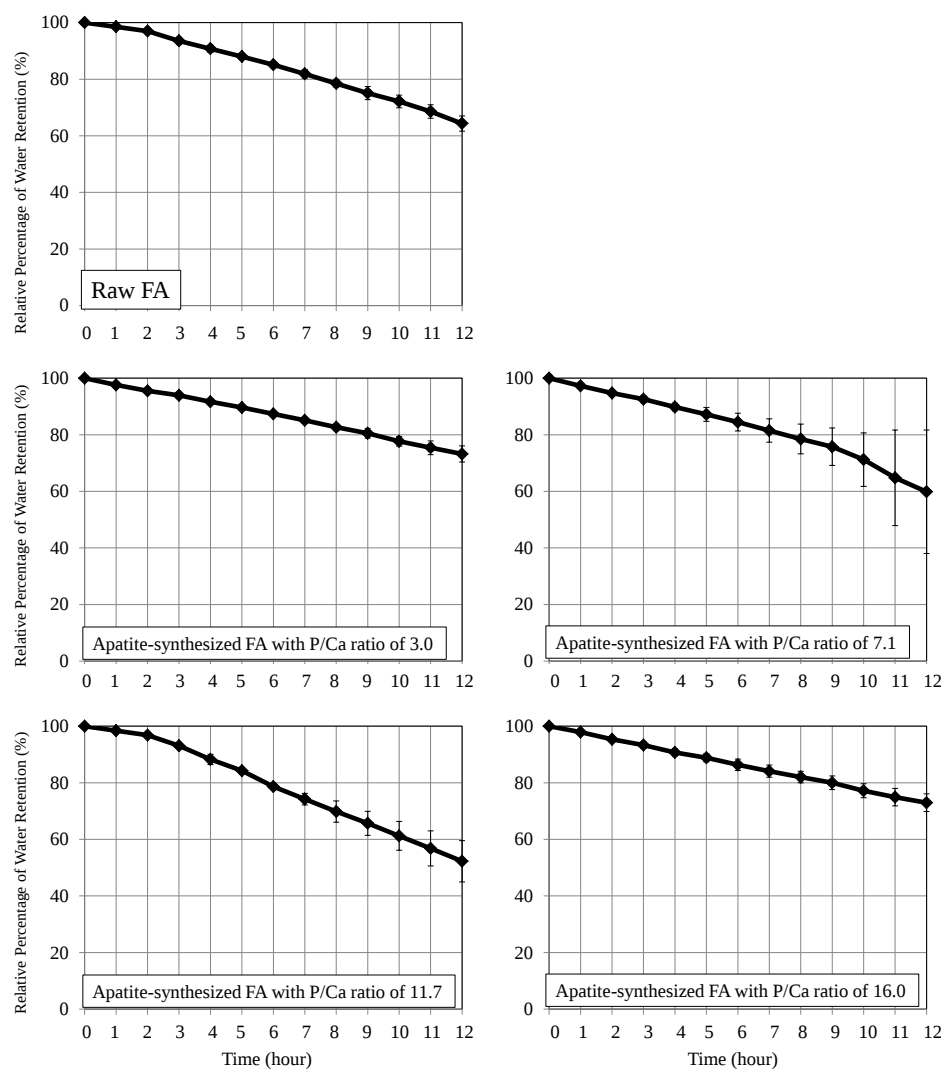


Figure 3-3 Water retention curves of raw FA and apatite-synthesized FA with P/Ca ratio of 3.0, 7.1, 11.7 and 16.0 at room temperature

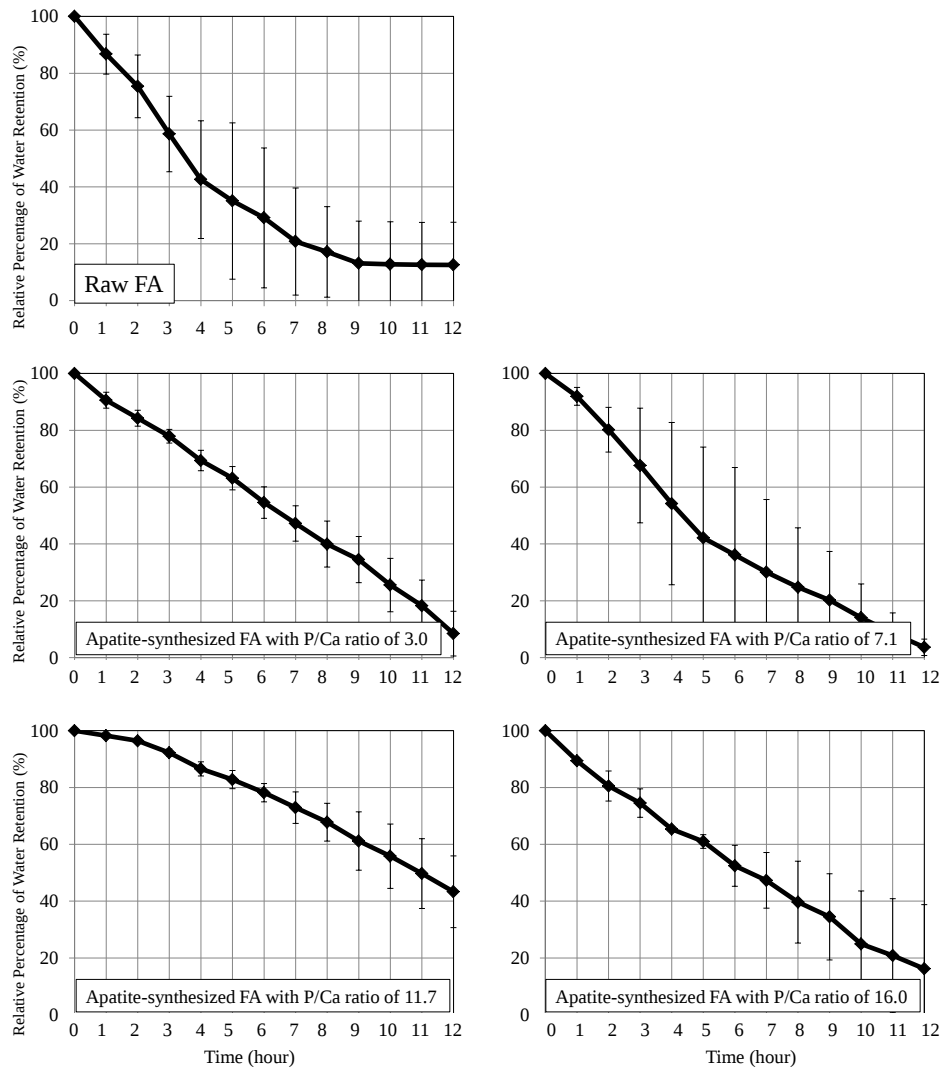


Figure 3-4 Water retention curves of raw FA and apatite-synthesized FA with P/Ca ratio of 3.0, 7.1, 11.7 and 16.0 at 40 °C

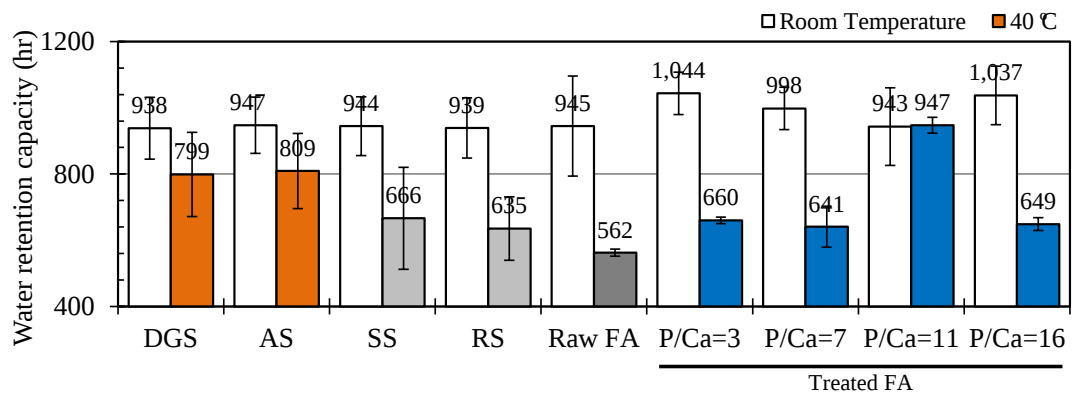


Figure 3-5 WRC of pure soil/sand, raw FA and apatite-synthesized FA

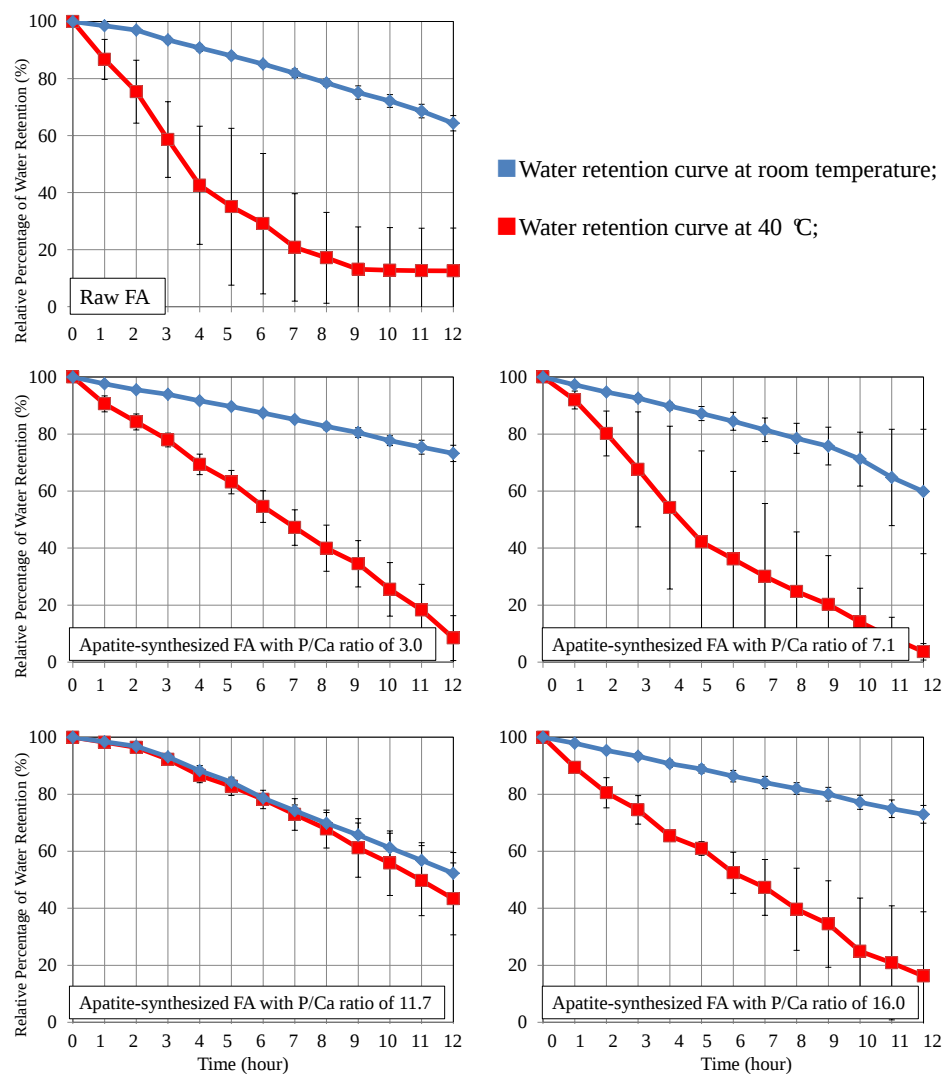


Figure 3-6 Comparison between water retention curves of FAs at room temperature and 40 °C

3.3.2 WRC of FA-amended samples at room temperature

To investigate the impact of raw/treated FA amendment on WRC, soil/sand samples without FA amendment and those amended with raw FA were used as global control and amendment control, respectively. Water retention curves of FA-amended soil/sand samples at room temperature are shown in Figure 3-7 to 3-21. In addition, WRC of these samples are also shown in Figure 3-22 to 3-25 with error bar and summarized in Table 3-3.

Raw FA amendment gave no significant impact on WRC at any mixing ratios. It is the same with expectation because WRC of raw FA are comparable with those of soils and sands at room temperature.

On the other hand, amendment of apatite-synthesized FA with P/Ca ratio of 3.0 increased WRC compared to no amendment and raw FA amendment cases beyond experimental errors, certificated by t-test at 1 % or 5 % significance level (see Figure 3-22). As shown in Figure 3-7 to 3-12, water retention curves of all amended soils and sands were similar at room temperature. Compared to WRC of raw FA amendment cases (soils/sands), the only difference was higher water content left after 12 hours drying when apatite-synthesized FA with P/Ca ratio of 3.0 was mixed into soil/sand. It is also reasonable because WRC of apatite-synthesized FA with P/Ca ratio of 3.0 is significantly higher than that of raw FA at room temperature (see Figure 3-6). On the other hand, increases of WRC by treated FA amendment were constant regardless of mixing ratio from 10 wt% to 30 wt% (see Figure 3-22 to 3-25). It might imply that a 10 % addition is sufficient to modify soil/sand texture and thus change WRC of samples. In terms of water retention curves at room temperature, the mixing ratio does not matter. Water retention curves are similar with each other and percentages of water left after 12 hours drying were also almost the same (around 21%).

When apatite-synthesized FA with P/Ca ratio of 7.1 was amended, WRC of mixture samples were similar with the control (raw FA amendment case). The t-test suggests no significant difference. As shown in Figure 3-7 to 3-9 and 3-13 to 3-15, difference of mixing ratios gave insignificant changes to water retention curves. Water contents of soil/sand with apatite-synthesized FA with P/Ca ratio of 7.1 left after 12 hours drying were smaller than those in raw FA-amended soil/sand. It is reminded that WRC of raw and apatite-synthesized

FA with P/Ca ratio of 7.1 were proved to have no difference by t-test (see Figure 3-22 to 3-25). Although water evaporation rates of soils/sands with apatite-synthesized FA with P/Ca ratio of 7.1 are always lower at any drying time than those of raw-FA-amended soils/sands, it is within experimental errors. On the other hand, water in apatite-synthesized FA (P/Ca = 7.1)-amended soil/sand evaporated faster and less amount of residual water left when compared to that of soil/sand mixed with apatite-synthesized FA with P/Ca ratio of 3.0. WRC slightly decreased at any mixing ratios compared to the previous case (P/Ca ratio of 3.0).

It was the same with the case of P/C ratio of 11.7 (see Figure 3-22 to 3-25). The only difference appeared in water retention curve (Figure 3-16 to 3-18). Water evaporation rate is not constant at whole drying time. At the first 2 hours, water evaporated slower than following 10 hours in both soils and sands mixed with apatite-synthesized FA with P/Ca ratio of 11.7.

When apatite-synthesized FA with P/Ca ratio of 16.0 was amended to soil or sand, WRC increased again to the same level with the first case (P/Ca ratio of 3.0) (see Figure 3-22 to 3-25). Water retention curves were also almost the same with those of soils/sands with apatite-synthesized FA with P/Ca ratio of 3.0. (see Figure 3-19 to 3-21) It is also reasonable results owing to high WRC of apatite-synthesized FA with P/Ca ratio of 16.0, which is similar to that of apatite-synthesized FA with P/Ca ratio of 3.0 (see Figure 3-5).

Experimental results would be summarized as follows (see Table 3-3). Amendment of apatite-synthesized FA with P/Ca ratio of 3.0 and 16.0 are effective to increase WRC at room temperature. They are reasonable owing to higher WRC of these FA samples compared to those of soils, sands, and other treated FA. However, the amendment effect might have to be concluded as limited because increases of WRC by apatite-synthesized FA addition were only 5 % or less. Although the amendment of apatite-synthesized FA with P/Ca ratio of 3.0 and 16.0 was effective for all tested soil/sand, it had no dependency on FA mixing ratio.

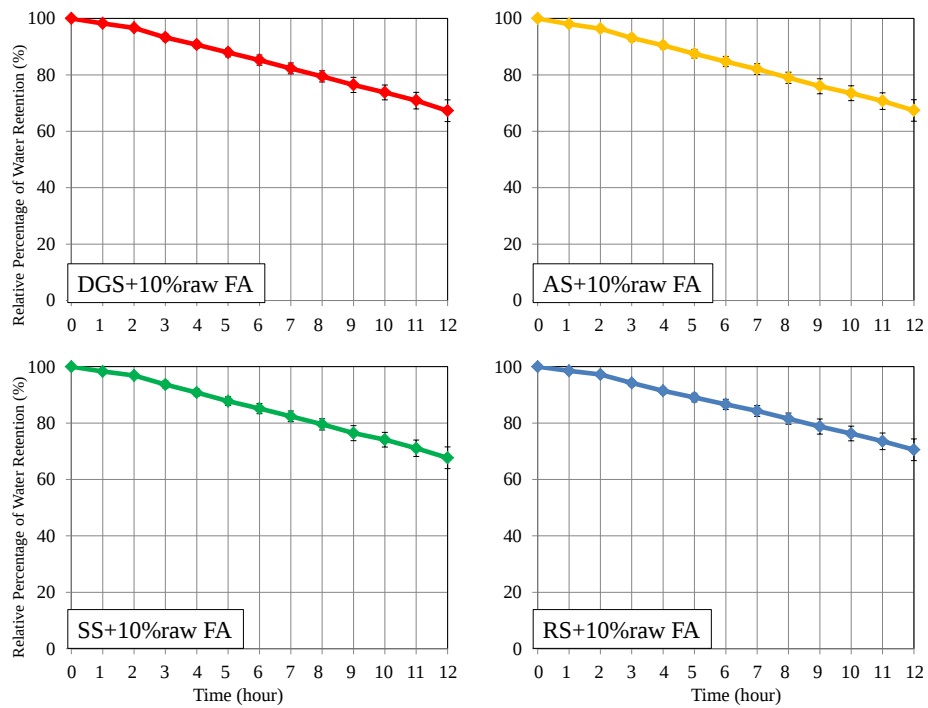


Figure 3-7 Water retention curves of DGS, AS, SS and RS mixed with raw FA at 10 wt% mixing ratio and room temperature

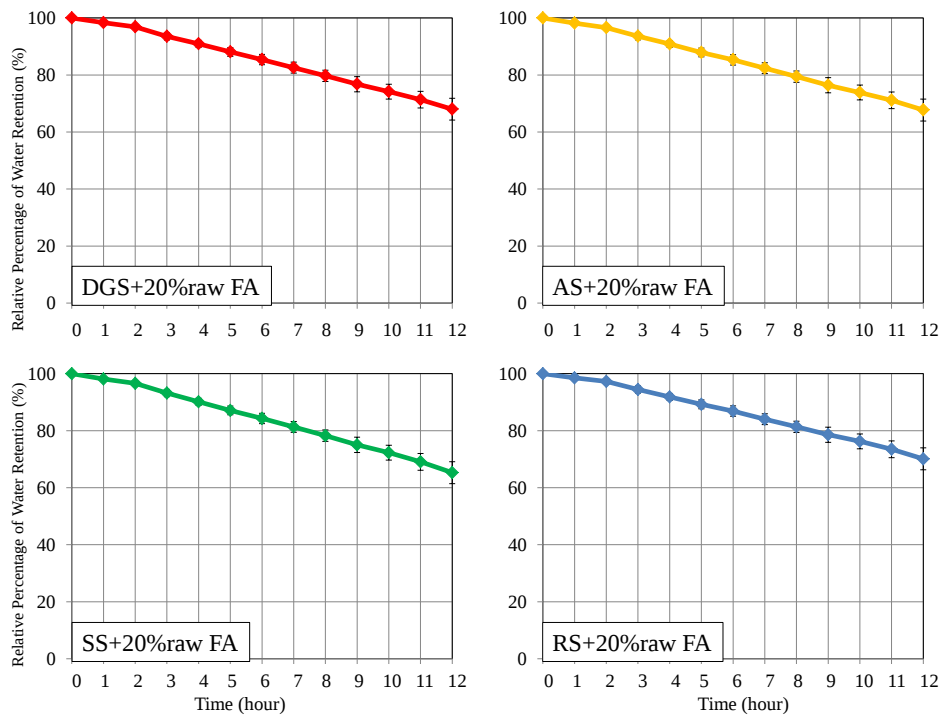


Figure 3-8 Water retention curves of DGS, AS, SS and RS mixed with raw FA at 20 wt% mixing ratio and room temperature

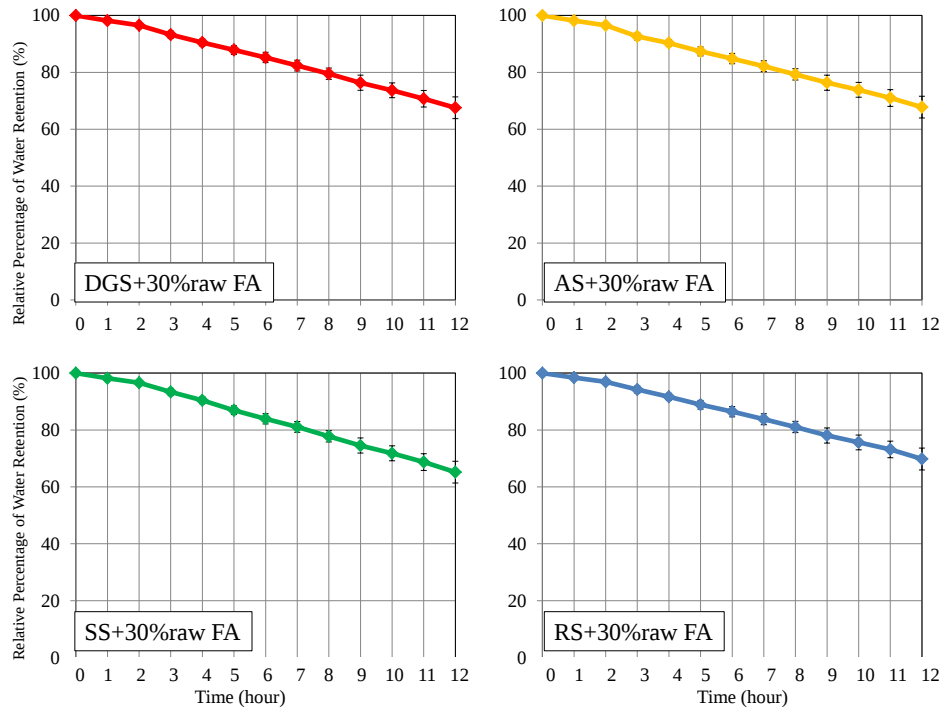


Figure 3-9 Water retention curves of DGS, AS, SS and RS mixed with raw FA at 30 wt% mixing ratio and room temperature

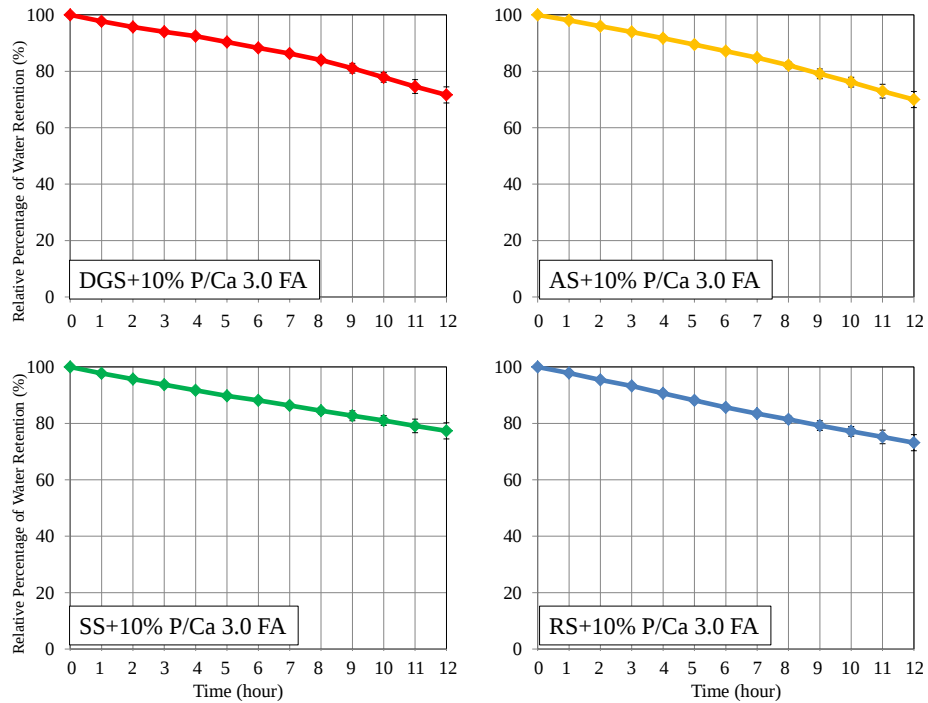


Figure 3-10 Water retention curves of DGS, AS, SS and RS mixed with apatite-synthesized FA with P/Ca ratio of 3.0 at 10 wt% mixing ratio and room temperature

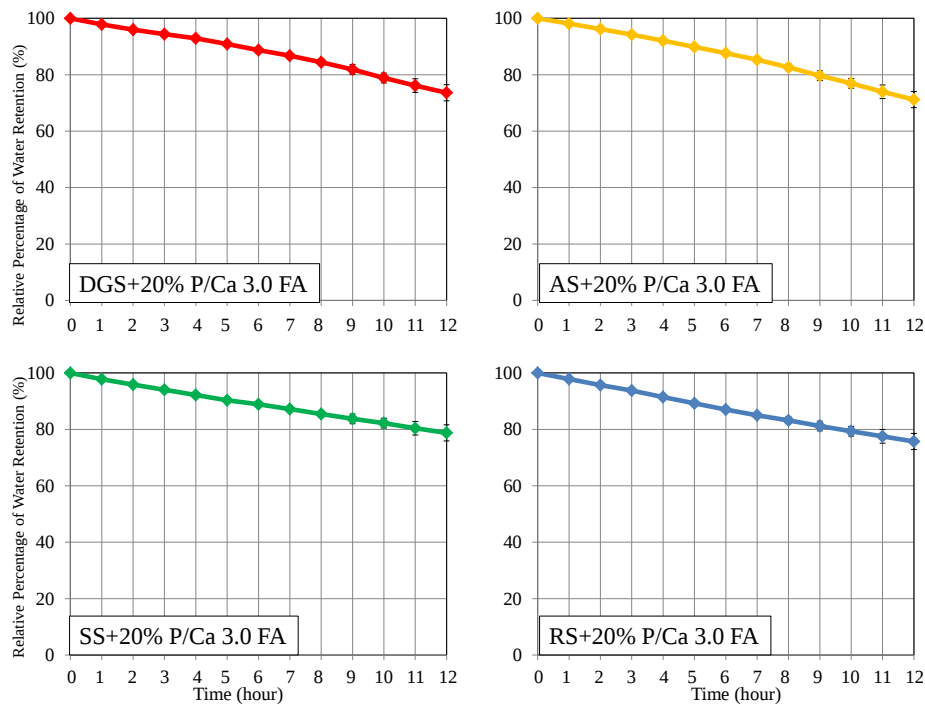


Figure 3-11 Water retention curves of DGS, AS, SS and RS mixed with apatite-synthesized FA with P/Ca ratio of 3.0 at 20 wt% mixing ratio and room temperature

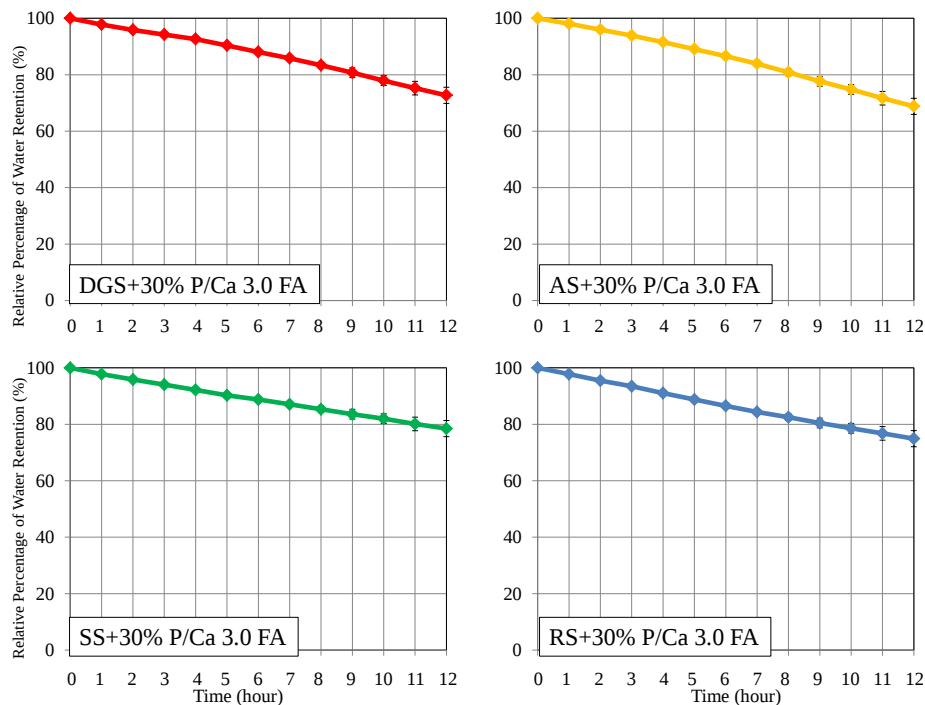


Figure 3-12 Water retention curves of DGS, AS, SS and RS mixed with apatite-synthesized FA with P/Ca ratio of 3.0 at 30 wt% mixing ratio and room temperature

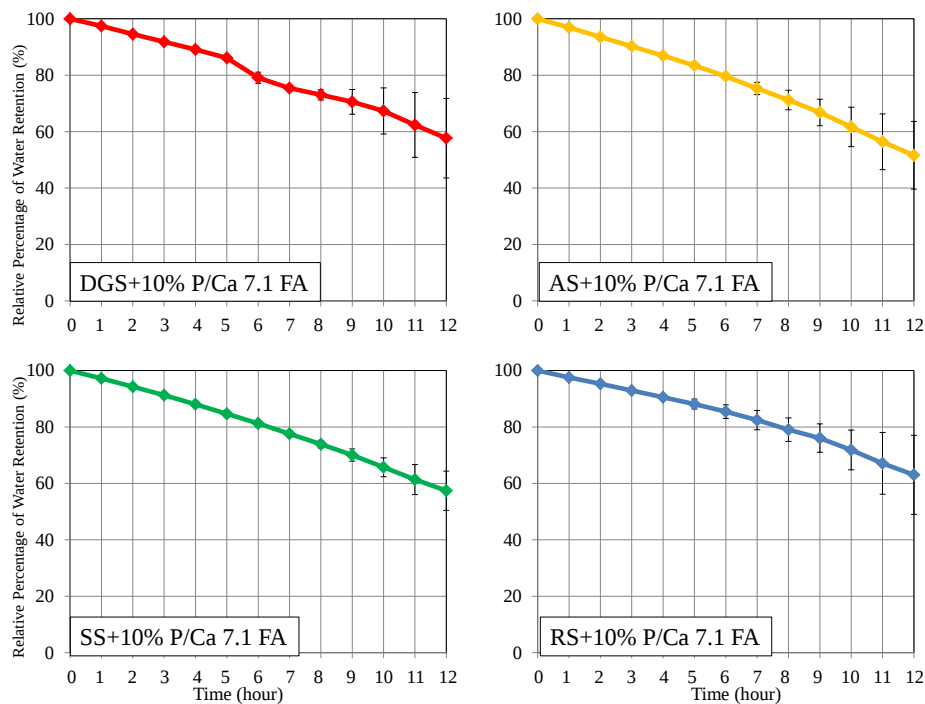


Figure 3-13 Water retention curves of DGS, AS, SS and RS mixed with apatite-synthesized FA with P/Ca ratio of 7.1 at 10 wt% mixing ratio and room temperature

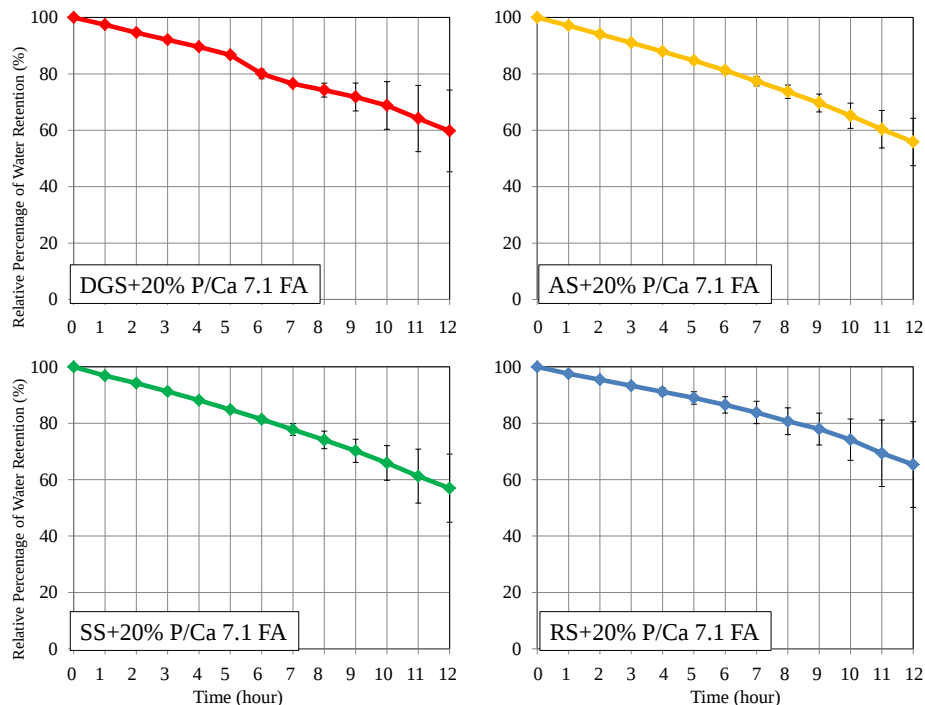


Figure 3-14 Water retention curves of DGS, AS, SS and RS mixed with apatite-synthesized FA with P/Ca ratio of 7.1 at 20 wt% mixing ratio and room temperature

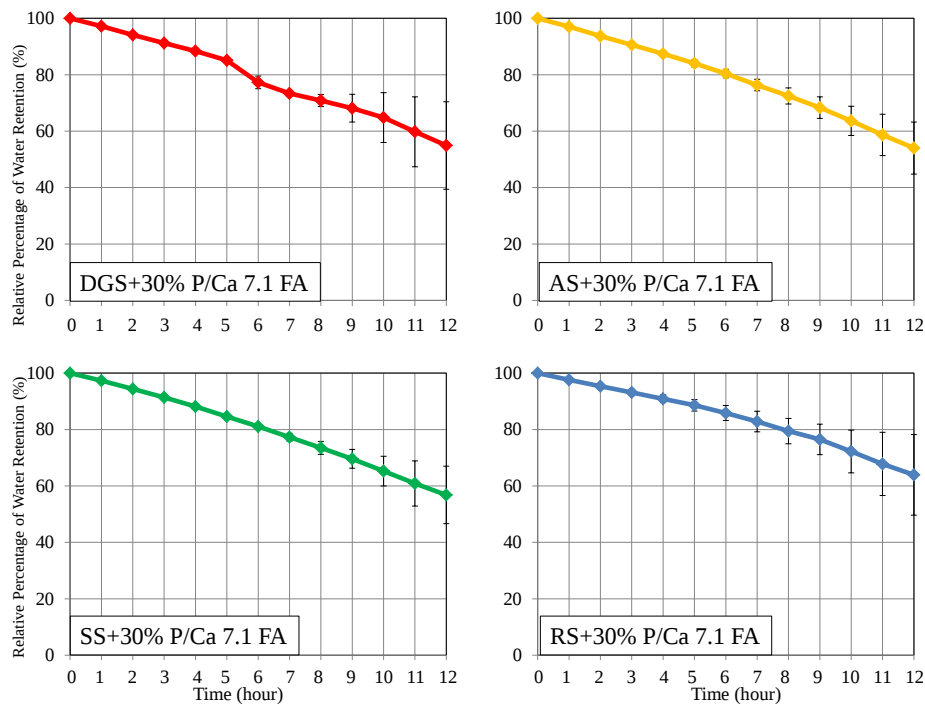


Figure 3-15 Water retention curves of DGS, AS, SS and RS mixed with apatite-synthesized FA with P/Ca ratio of 7.1 at 30 wt% mixing ratio and room temperature

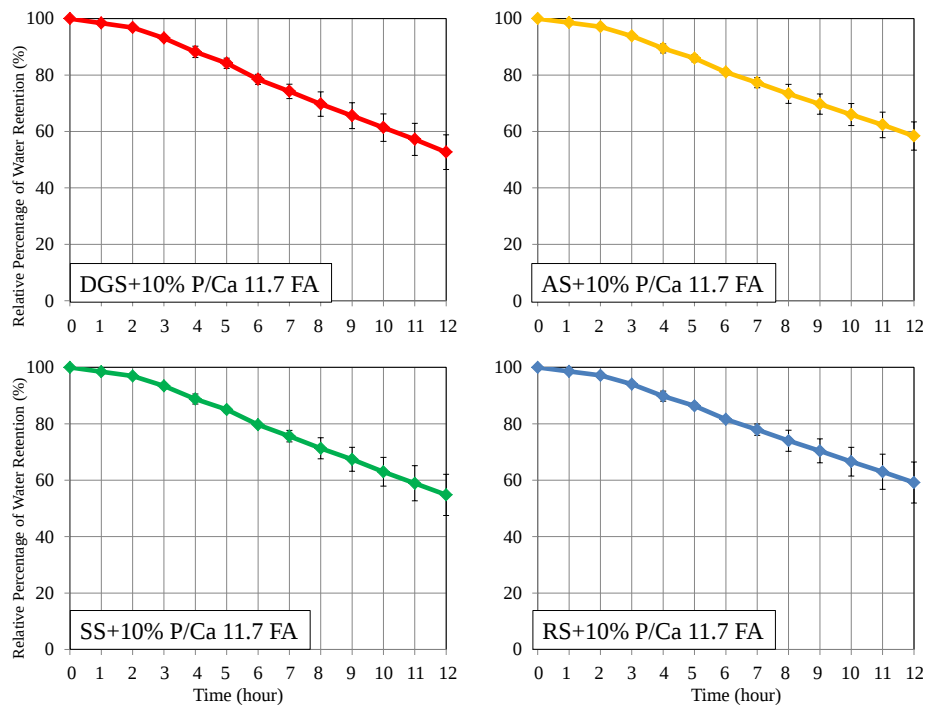


Figure 3-16 Water retention curves of DGS, AS, SS and RS mixed with apatite-synthesized FA with P/Ca ratio of 11.7 at 10 wt% mixing ratio and room temperature

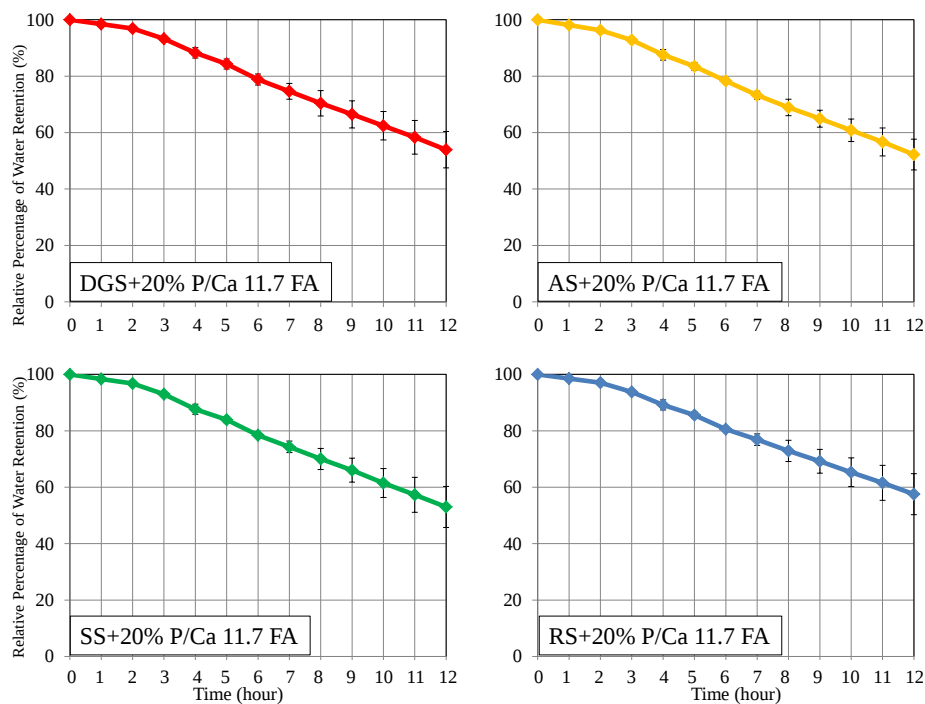


Figure 3-17 Water retention curves of DGS, AS, SS and RS mixed with apatite-synthesized FA with P/Ca ratio of 11.7 at 20 wt% mixing ratio and room temperature

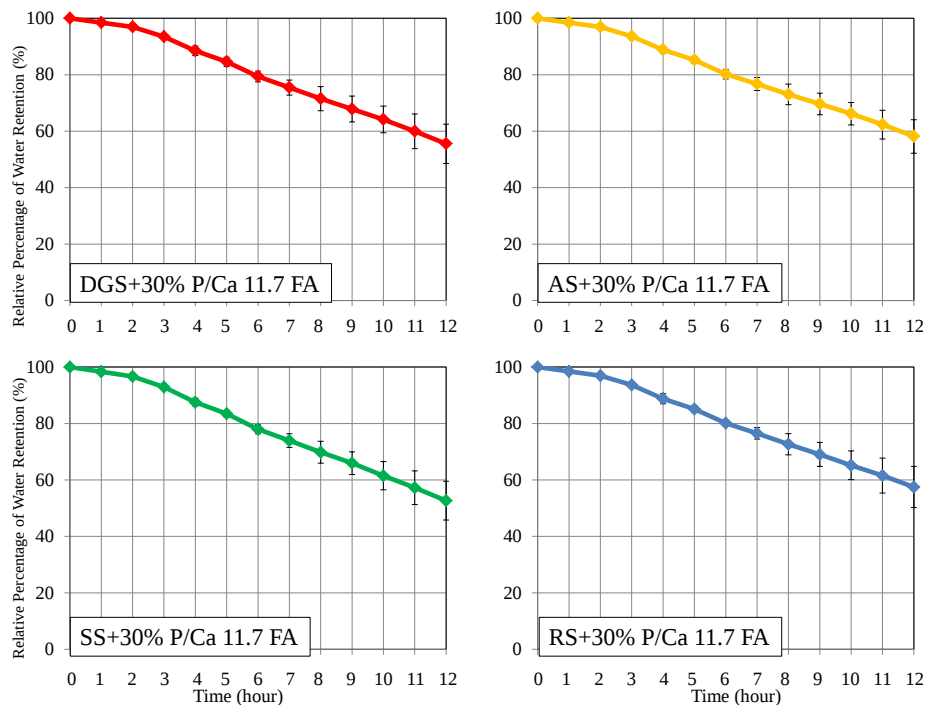


Figure 3-18 Water retention curves of DGS, AS, SS and RS mixed with apatite-synthesized FA with P/Ca ratio of 11.7 at 30 wt% mixing ratio and room temperature

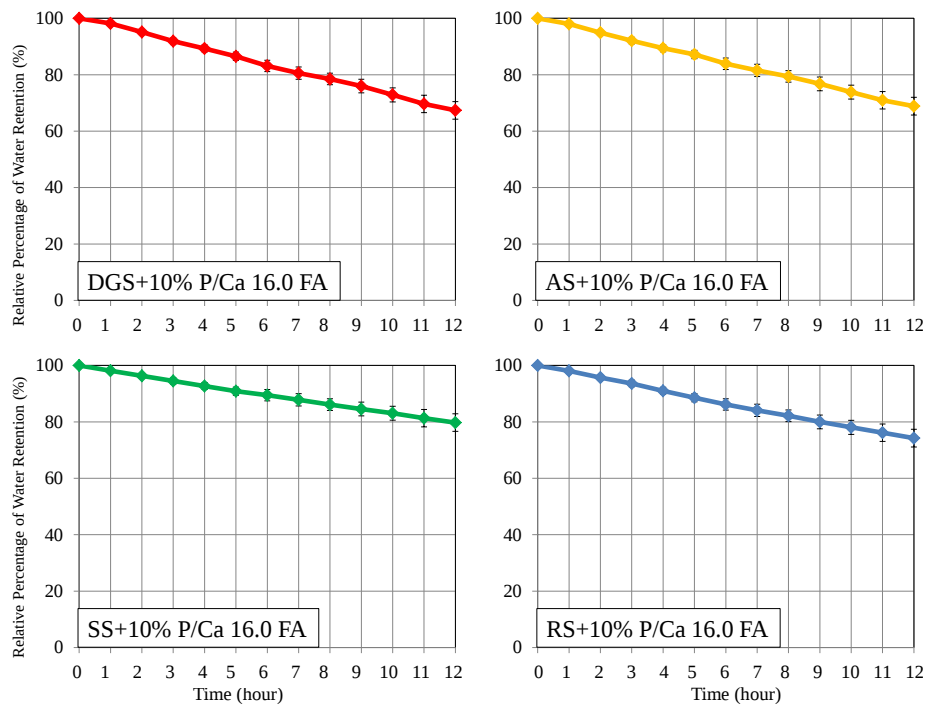


Figure 3-19 Water retention curves of DGS, AS, SS and RS mixed with apatite-synthesized FA with P/Ca ratio of 16.0 at 10 wt% mixing ratio and room temperature

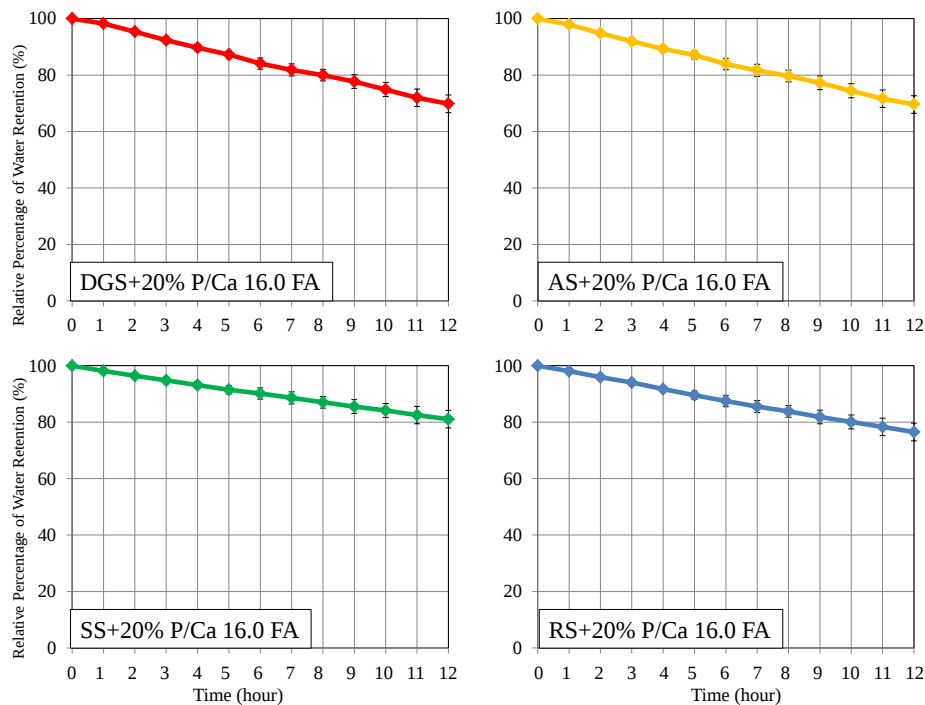


Figure 3-20 Water retention curves of DGS, AS, SS and RS mixed with apatite-synthesized FA with P/Ca ratio of 16.0 at 20 wt% mixing ratio and room temperature

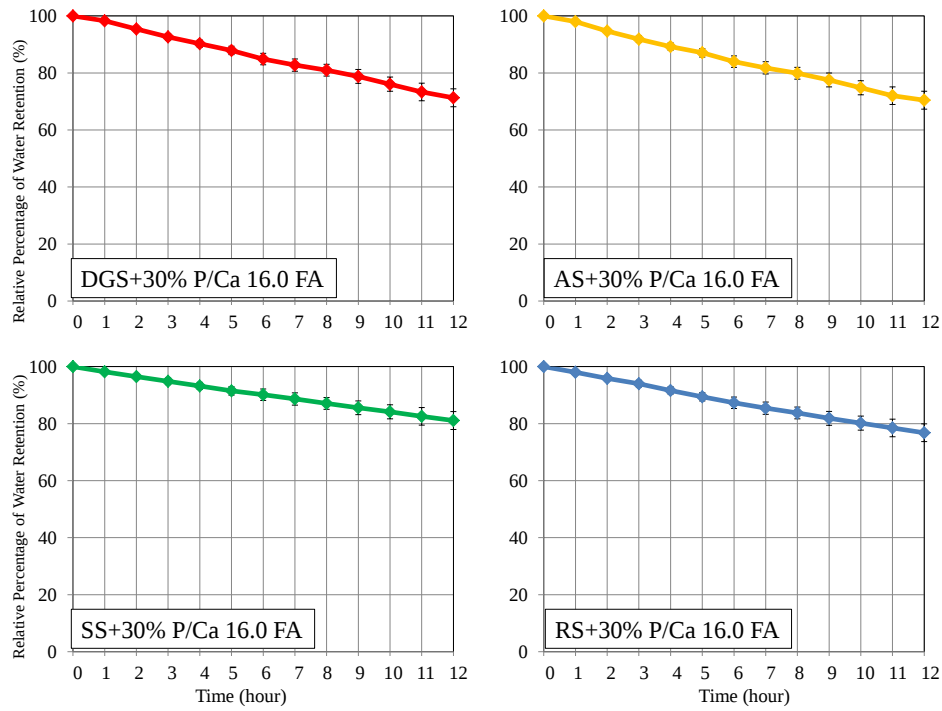


Figure 3-21 Water retention curves of DGS, AS, SS and RS mixed with apatite-synthesized FA with P/Ca ratio of 16.0 at 30 wt% mixing ratio and room temperature

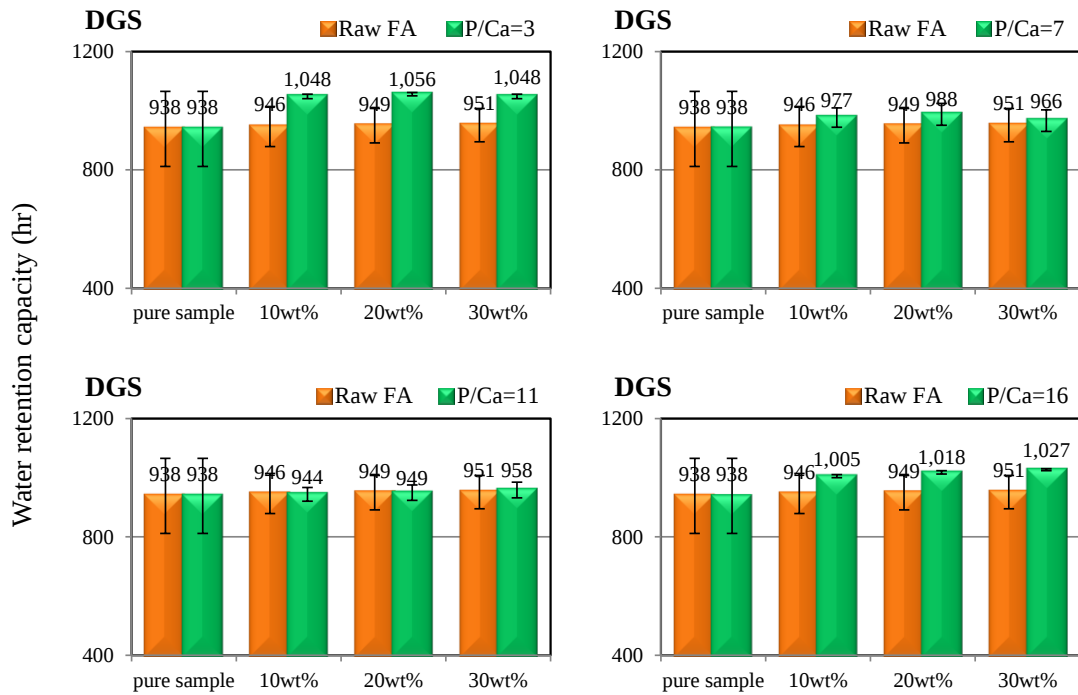


Figure 3-22 WRC of DGS mixed with raw FA or apatite-synthesized FA with P/Ca ratio of 3.0, 7.1, 11.7 and 16.0 at room temperature

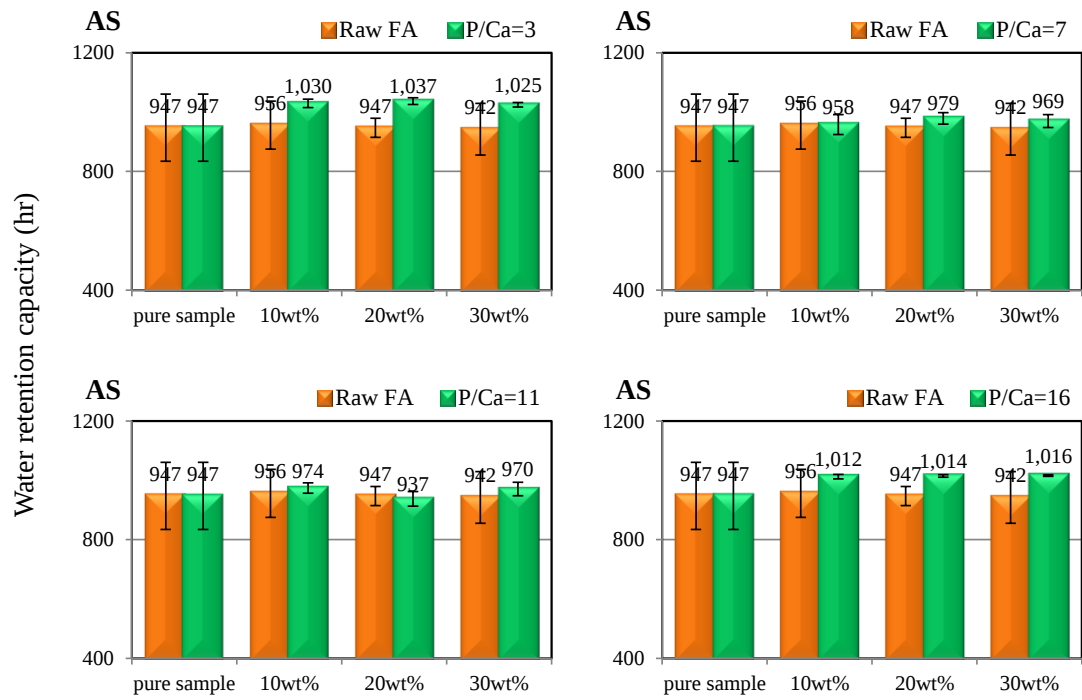


Figure 3-23 WRC of AS mixed with raw FA or apatite-synthesized FA with P/Ca ratio of 3.0, 7.1, 11.7 and 16.0 at room temperature

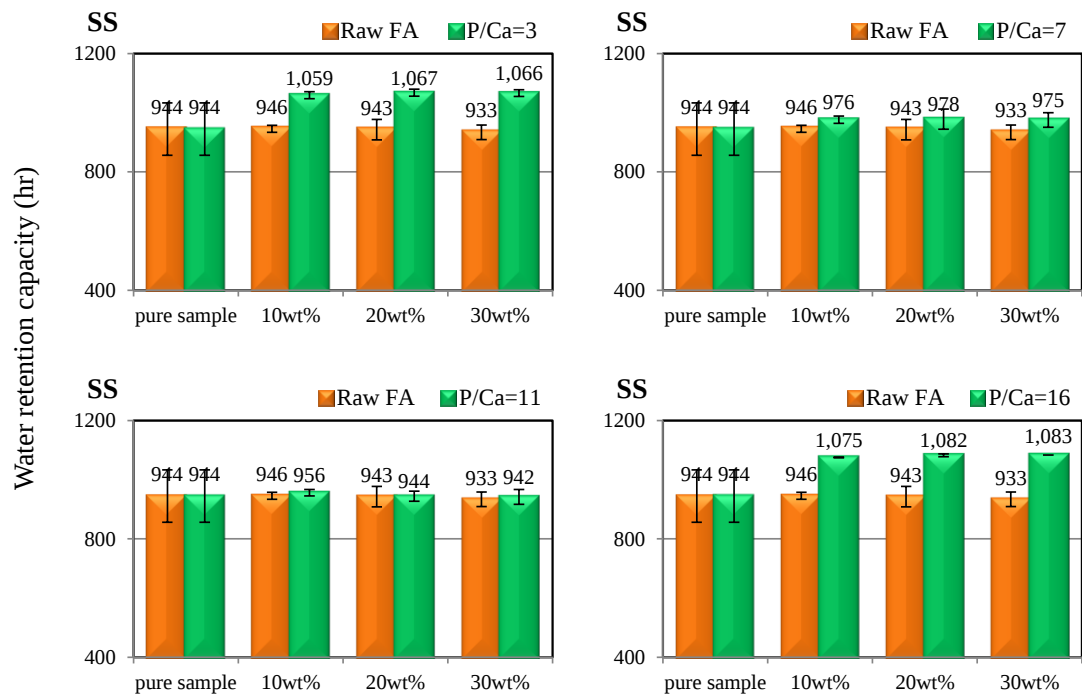


Figure 3-24 WRC of SS mixed with raw FA or apatite-synthesized FA with P/Ca ratio of 3.0, 7.1, 11.7 and 16.0 at room temperature

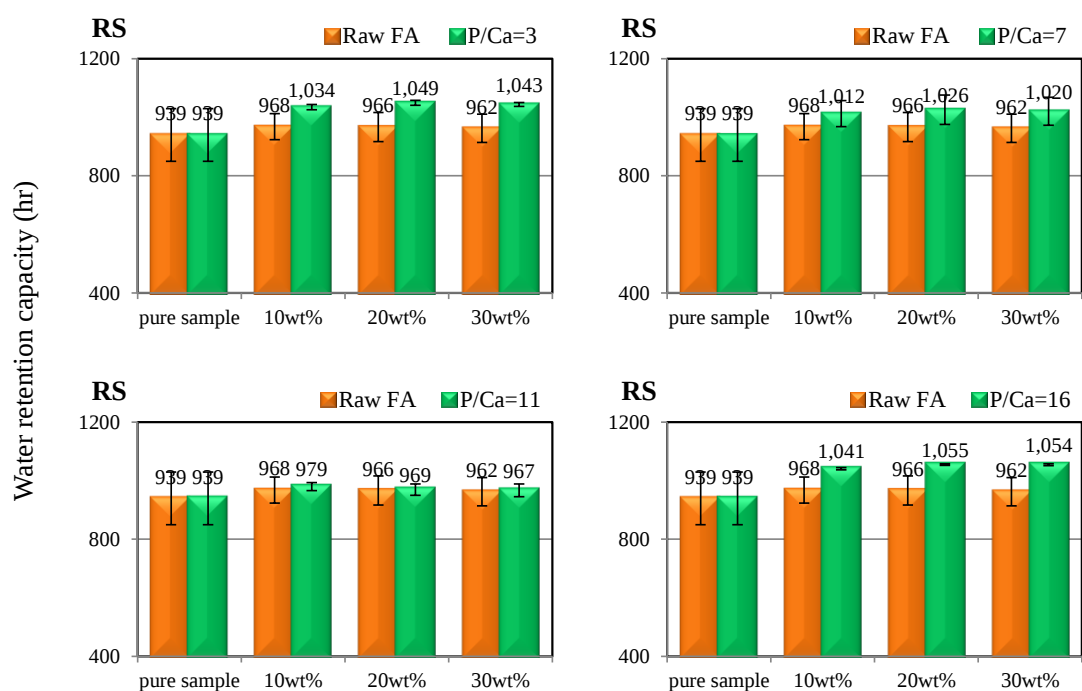


Figure 3-25 WRC of RS mixed with raw FA or apatite-synthesized FA with P/Ca ratio of 3.0, 7.1, 11.7 and 16.0 at room temperature

Table 3-3 Summary of WRC of soil/sand mixed with raw/apatite-synthesized FAs at room temperature

Flay ash		Room temperature			
		DGS	AS	SS	RS
Raw FA		—	—	—	—
Apatite-synthesized FA	P/Ca = 3.0	+12.6%*	+9.5%*	+13.0%*	+11.7%*
	P/Ca = 7.1	—	—	—	+9.3%*
	P/Ca = 11.7	—	—	—	—
	P/Ca = 16.0	+9.5%*	+7.3%*	+14.7%*	+12.4%*

All data was conducted by t-test, and “*” stand to “p value < 0.05”, “**” stand to “p value < 0.01” of t-test.

3.3.3 WRC of FA-amended samples at 40 °C

3.3.3.1 Categorization of water retention curves

If WRC of FA itself controls WRC of FA-amended samples, it would be suggested that amendment of raw FA and apatite-synthesized FA excluding P/Ca ratio of 11.7 is negatively effective and decrease WRC of mixture samples, in particular soil samples (DGS and AS) at 40 °C because WRC of pure FA samples are significantly lower than those of pure soils and sands at 40 °C. Water retention curves of FA-amended soil/sand samples at 40 °C are shown in Figure 3-29 to 3-43. In addition, WRC of FA-amended samples at 40 °C are shown in Figure 3-44 to 3-47 with error bar. In this section, water retention curve of soil/sand are categorized as shown in Figure 3-26 to 3-28 to easily understand water evaporation characteristics. When water evaporates linearly with drying time, it is categorized as type C. Type C would be further categorized based on change of residual water after 12 hours drying by FA amendment. When FA amendment gives no change of residual water, it is type C_c. When FA amendment accelerates water evaporation and residual water decreases compared to no FA amendment case, it is type C_d. When FA amendment decreases water evaporation and residual water increases compared to no FA amendment case, it is type C_u. In type S, water evaporation is slow at the first drying stage, becomes faster at the middle stage, and finally decreased again. Type S is also further categorized based on change of residual water after 12 hours drying by FA amendment. When residual water increases compared to that of no FA amendment case, it is type S_u. On the other hand, they are type S_c when residual water is not changed. Type S_d means S type water retention curve with residual water reduction by FA amendment. In type L, water evaporation is faster at the first drying stage and become slow at middle or final stage. When residual water increases, not changes, and decreases compared to those of no FA amendment case, they are type L_u, L_C and L_d, respectively. The types of water retention curves are summarized in Table 3-2 only when change of WRC by FA amendment is statistically significant.

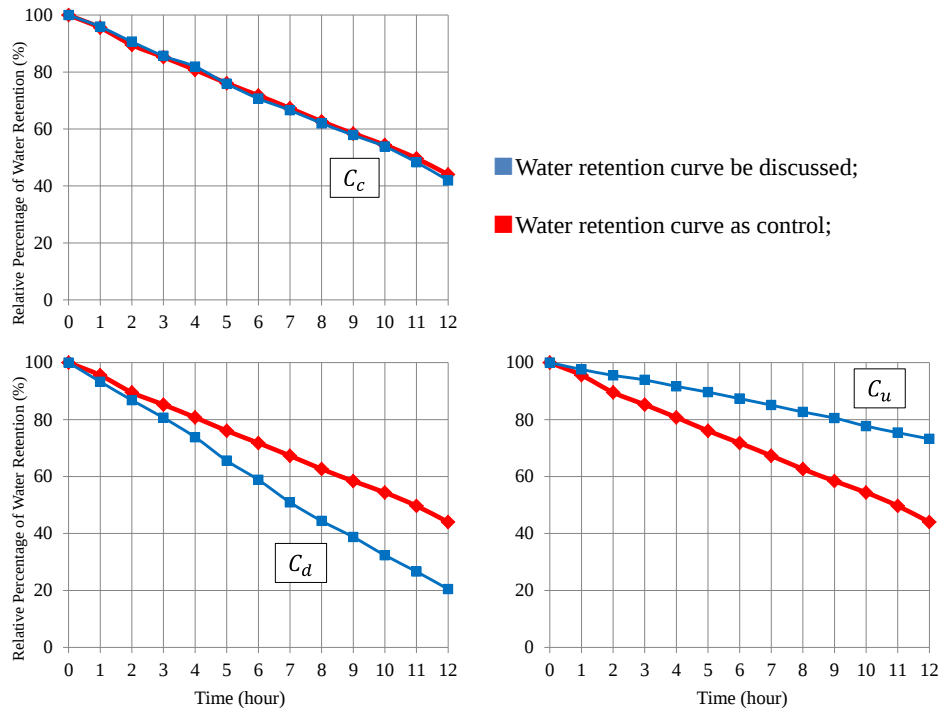


Figure 3-26 Example of water retention curve that categorized as type C

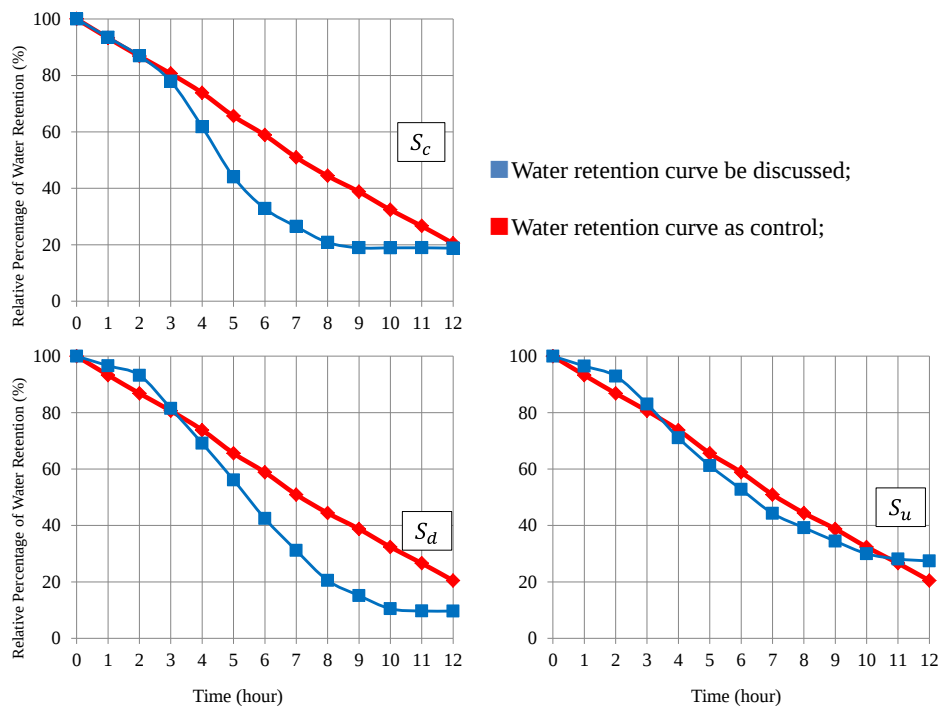


Figure 3-27 Example of water retention curve that categorized as type S

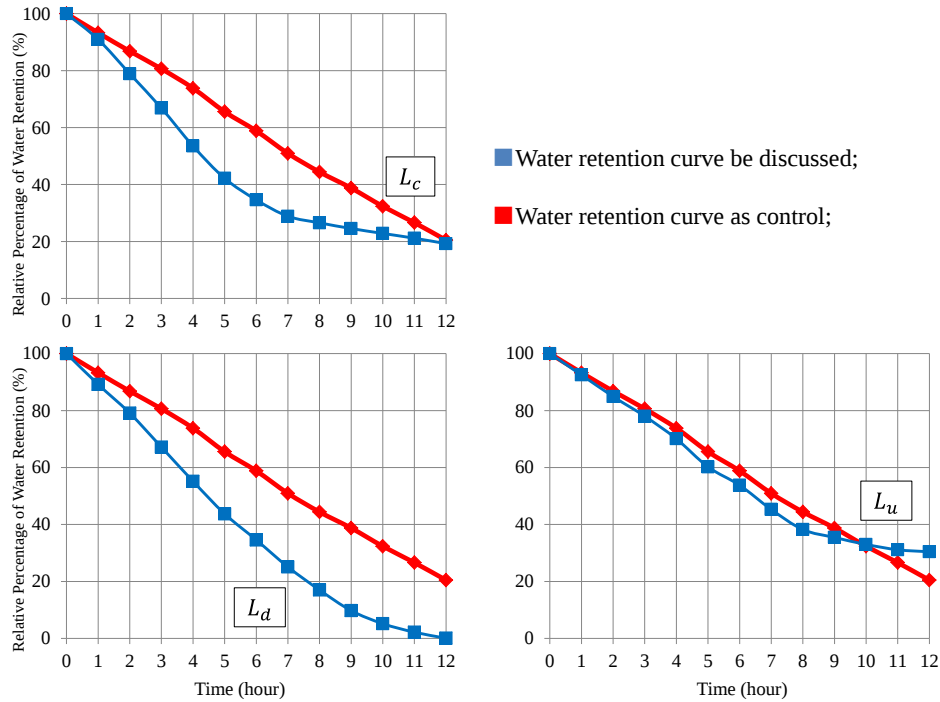


Figure 3-28 Example of water retention curve that categorized as type L

3.3.3.2 WRC of soils and sands amended with raw FA at 40 °C

Raw FA amendment decreased WRC of soil/sand obviously compared to pure soil/sand at 40 °C (certified by t-test at 5 % significant level), as shown in Figure 3-44 to 3-47. When soil/sand were mixed with raw FA, WRC of DGS was decreased by 11.1 %, WRC of AS was decreased by 10.4 % and WRC of SS was decreased by 5.3 %, respectively. The t-test suggests these reductions exceed experimental errors. On the other hand, WRC of RS was also decreased by raw FA amendment but its changes were insignificant according to t-test. As shown in Figure 3-29 to 3-31, water retention curves of soil/sand at different mixing ratios were similar. However, percentages of water in soil/sand left after 12 hours drying decreased a lot when they are compared to those at room temperature. Especially in the cases of SS and RS mixed with raw FA, residual water of SS at 12 hours decreased by about 60 % and residual water of RS decreased by about 50 % at 40 °C, respectively. Gravitational and capillary water of raw FA-mixed soil/sand evaporated very fast and reached adhesive water zone around 10 hours at high temperature. Figure 3-48 compared water retention curves between pure soil/sand and 20 wt% raw FA-mixed soil/sand. For soils and SS, water retention curves are similar with each other. However, percentages of water left after 12 hours drying

are smaller than those without raw FA amendment. Water retention curves of raw FA-amended soils are type C_d for DGS, type S_d for raw FA-amended AS, respectively. Water retention curves of raw FA-amended sands are type L_d for raw FA-amended SS. This means that raw FA amendment accelerated water evaporation of DGS from 4 hours drying time and decreased residual water at 12 hours. It is the same when raw FA was amended to AS. However, water evaporation was accelerated from 2 hours drying time. Raw FA amendment promoted water evaporation of SS at whole drying time and decreased residual water.

No negative effect was found for raw FA-mixed RS at any FA mixing ratios. In Figure 3-49, water retention curves of RS mixed with 10 to 30 wt% of raw FA were compared to pure RS. In raw FA-mixed RS, water evaporated faster than pure RS at initial drying stage while water evaporation rate became slower at the last 3-4 hours than that of RS. Water retention curves of raw FA-mixed RS finally became higher than that of RS. Water retention curve of RS mixed with 10 wt% of raw FA is type L_u , the same with RS mixed with 20 wt% of raw FA. But for RS mixed with 30 wt% of raw FA, it is type L_c . Because changes of water evaporation rates were balanced, WRC difference between RS and raw FA-mixed RS were negligible.

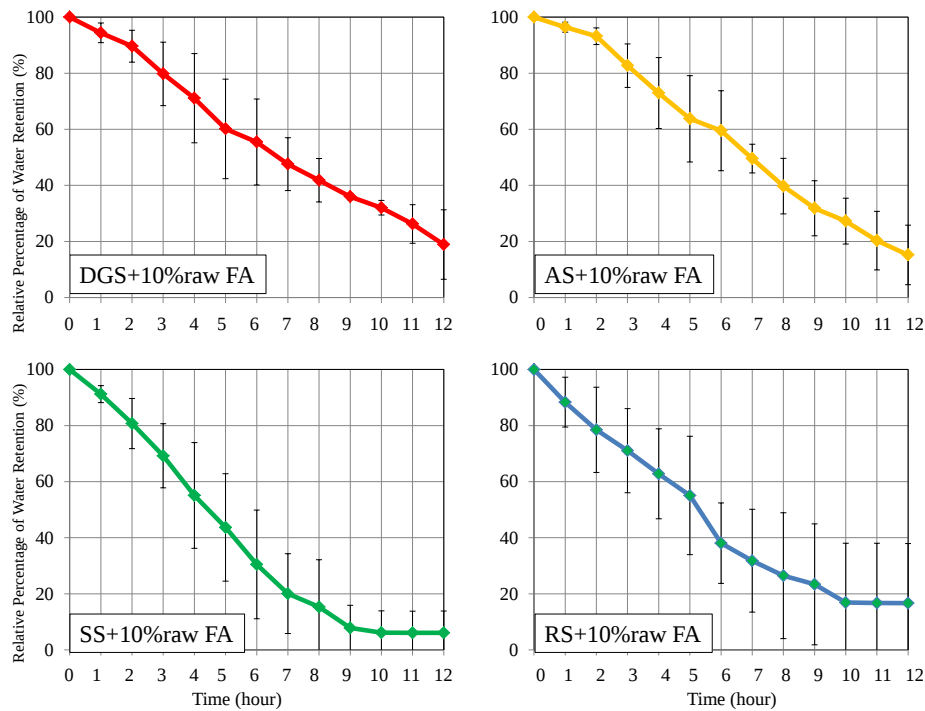


Figure 3-29 Water retention curves of DGs, AS, SS and RS mixed with raw FA at 10 wt% mixing ratio and 40 °C

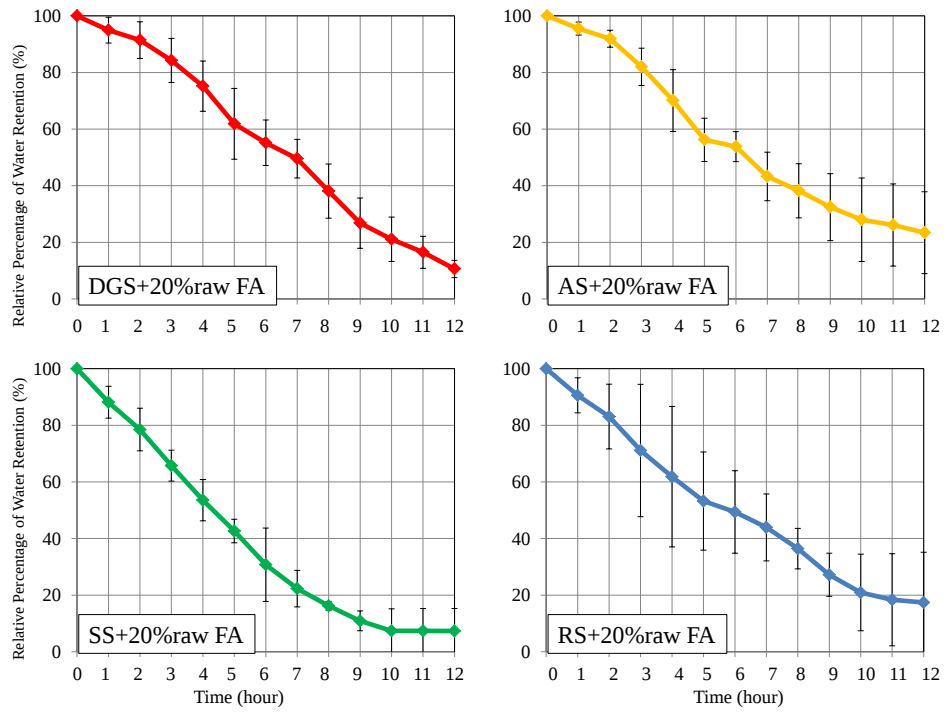


Figure 3-30 Water retention curve of DGS, AS, SS and RS mixed with raw FA at 20 wt% mixing ratio and 40 °C

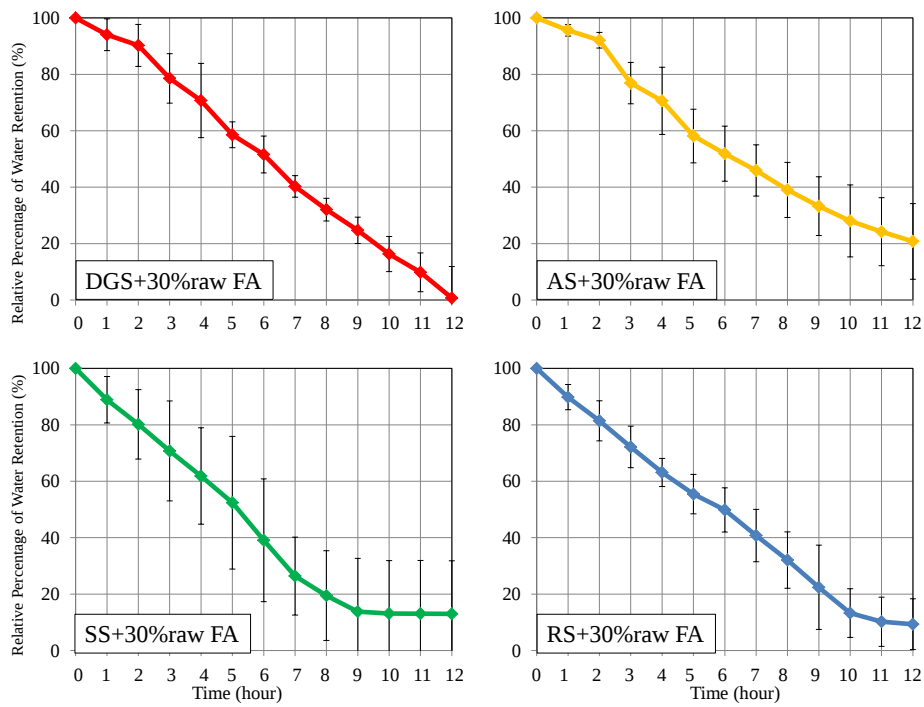


Figure 3-31 Water retention curve of DGS, AS, SS and RS mixed with raw FA at 30 wt% mixing ratio and 40 °C

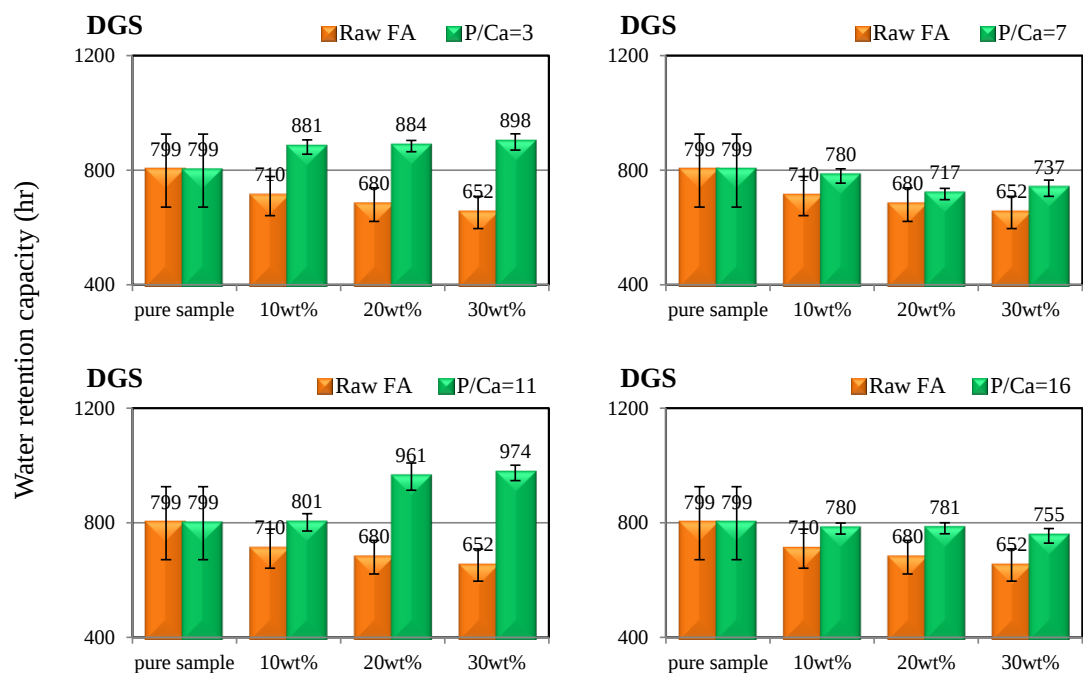


Figure 3-44 WRC of DGS mixed with raw FA or apatite-synthesized FA with P/Ca ratio of 3.0, 7.1, 11.7 and 16.0 at 40 °C

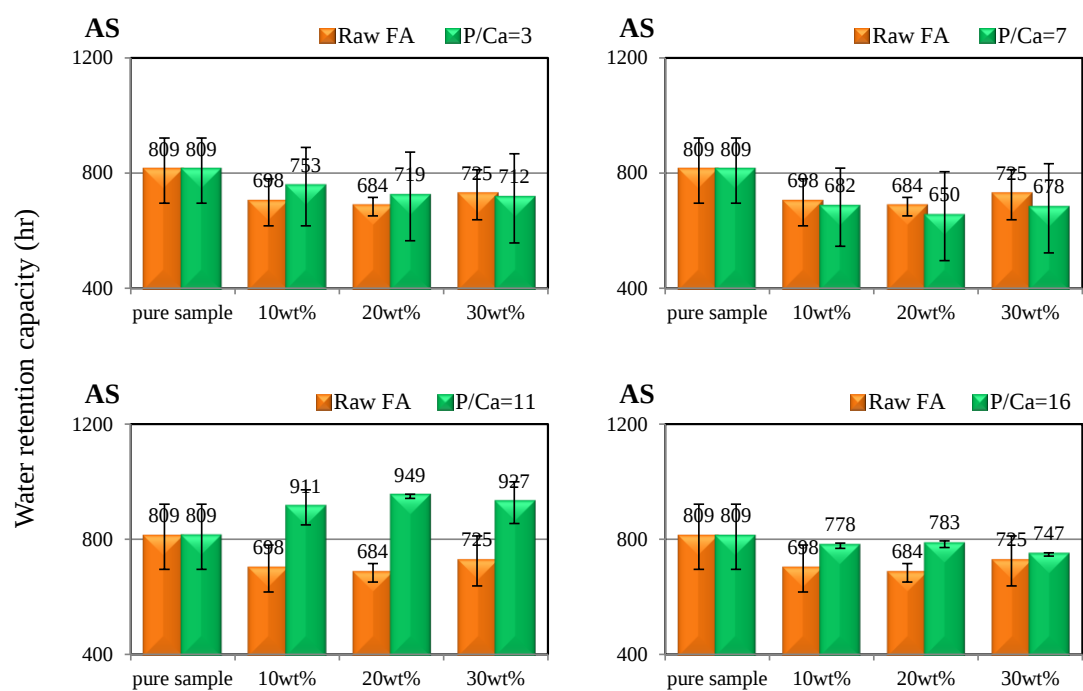


Figure 3-45 WRC of AS mixed with raw FA or apatite-synthesized FA with P/Ca ratio of 3.0, 7.1, 11.7 and 16.0 at 40 °C

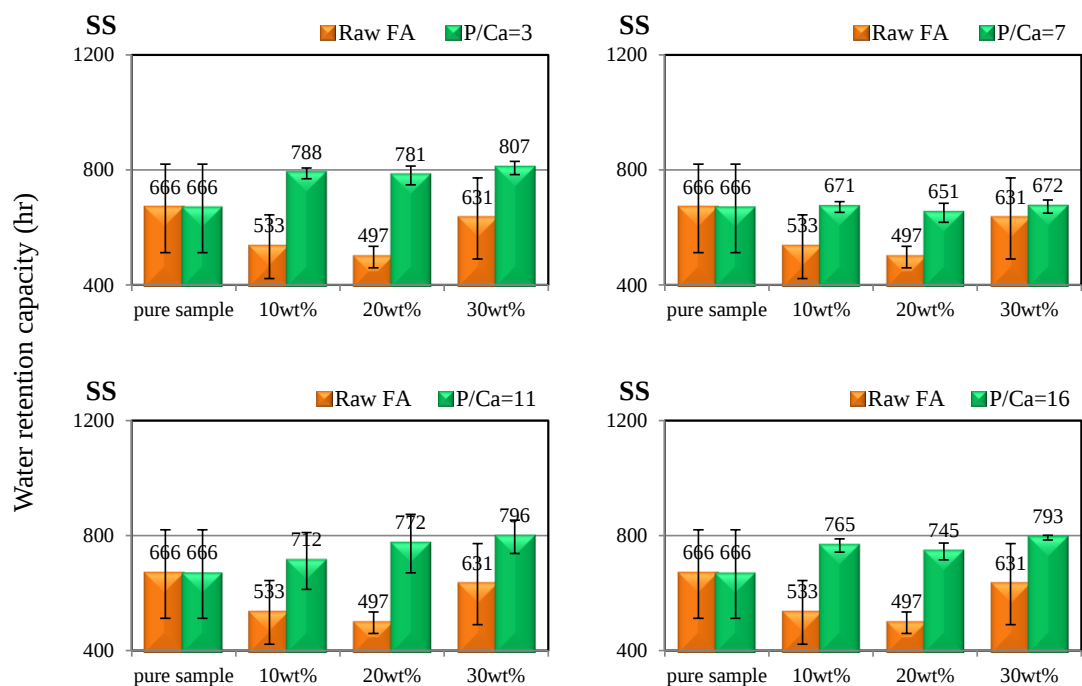


Figure 3-46 WRC of SS mixed with raw FA or apatite-synthesized FA with P/Ca ratio of 3.0, 7.1, 11.7 and 16.0 at 40 °C

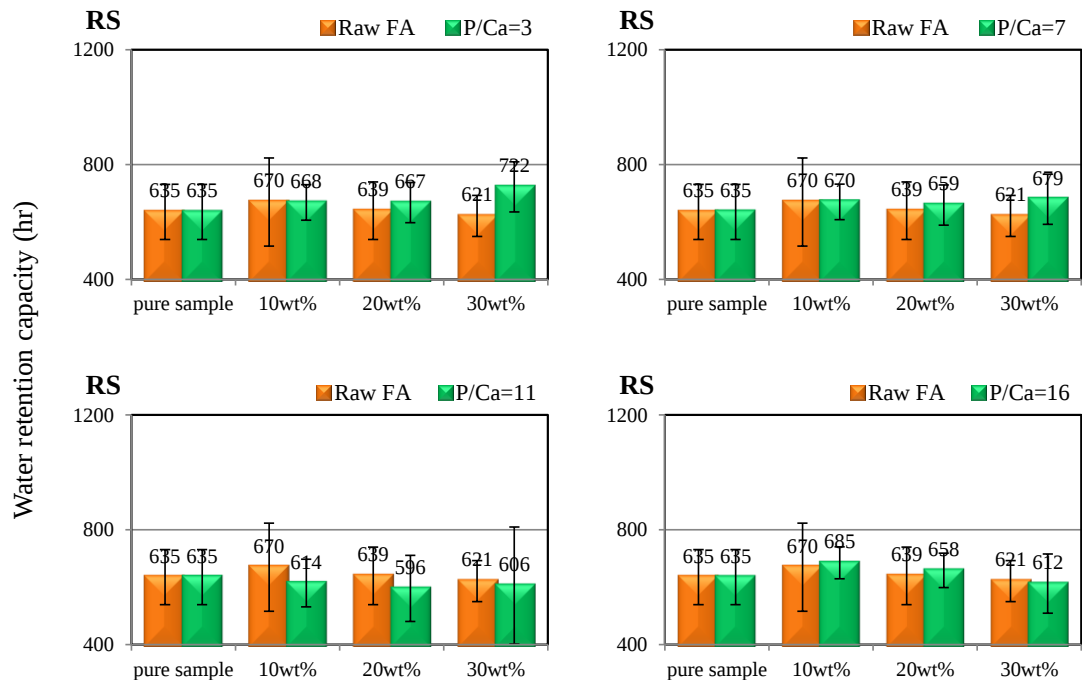


Figure 3-47 WRC of RS mixed with raw FA or apatite-synthesized FA with P/Ca ratio of 3.0, 7.1, 11.7 and 16.0 at 40 °C

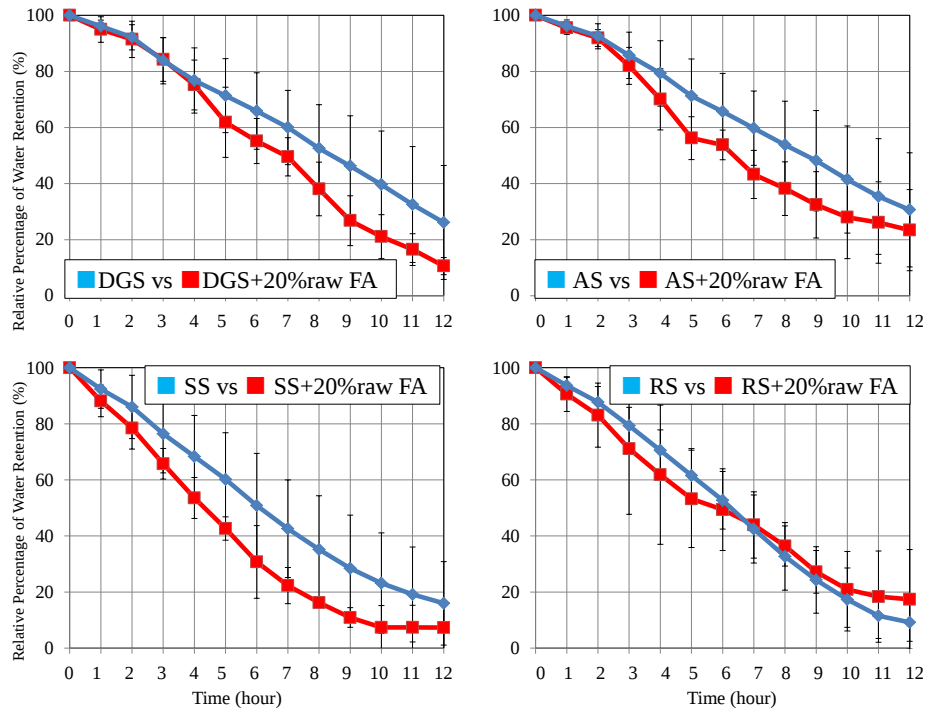


Figure 3-48 comparison between water retention curves of soil/sand and soil/sand mixed with raw FA at 20 wt% of mixing ratio

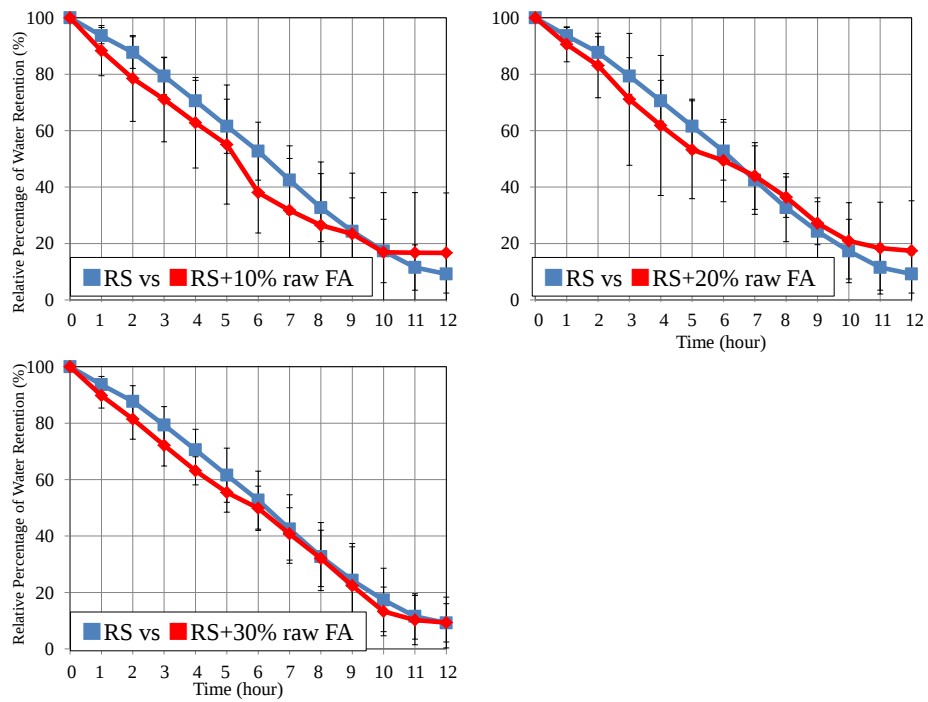


Figure 3-49 Comparison between water retention curves of RS and RS mixed with raw FA at 10 wt%, 20 wt% and 30 wt% of mixing ratio

3.3.3.3 WRC of soils and sands amended with apatite-synthesized FA (P/Ca = 3.0) at 40 °C

In contrast to the expectation described in the previous sub-section, amendment of treated FA with P/Ca ratio of 3.0 increased WRC of DGS and SS beyond experimental errors at 5 % significance level. The water in DGS and SS mixed with apatite-synthesized FA with P/Ca ratio of 3.0 left more after 12 hours drying, as shown by water retention curves in Figure 3-32 to 3-34. All water retention curves of soil/sand mixed with apatite-synthesized FA with P/Ca ratio of 3.0 are identified as type C and water evaporated constantly. As shown in Figure 3-50 which is the comparison between water retention curves of pure soil/sand and soil/sand mixed with apatite-synthesized FA with P/Ca ratio of 3.0, water retention curve of DGS changed from type C to C_u after amendment, and that of SS changed from type S to type C_u . This means that water evaporation of DGS and SS at whole drying process was inhibited and the evaporation rate became constant. On the other hand, it decreased WRC of AS as expected. It was observed from Figure 3-32 to 3-34 and Figure 3-2 that when AS was mixed with apatite-synthesized FA with P/Ca ratio of 3.0, water content after 12 hours drying was higher than that in pure AS at 40 °C. However, the positive effect of apatite-synthesized FA (P/Ca = 3.0) on WRC of AS was proved to be negligible by t-test.

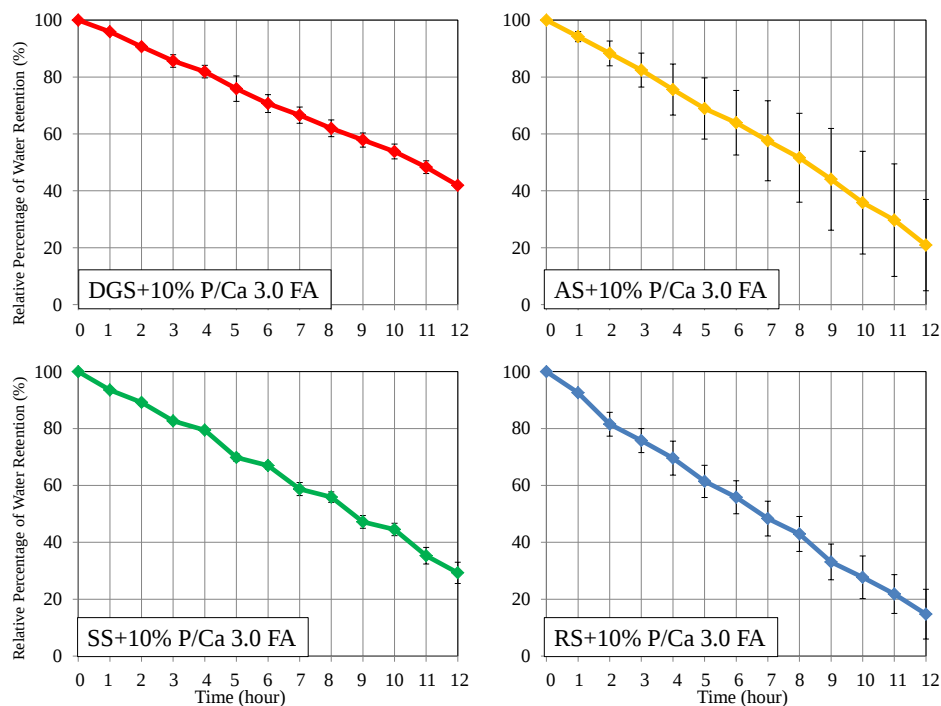


Figure 3-32 Water retention curve of DGS, AS, SS and RS mixed with apatite-synthesized FA with P/Ca ratio of 3.0 at 10 wt% mixing ratio and 40 °C

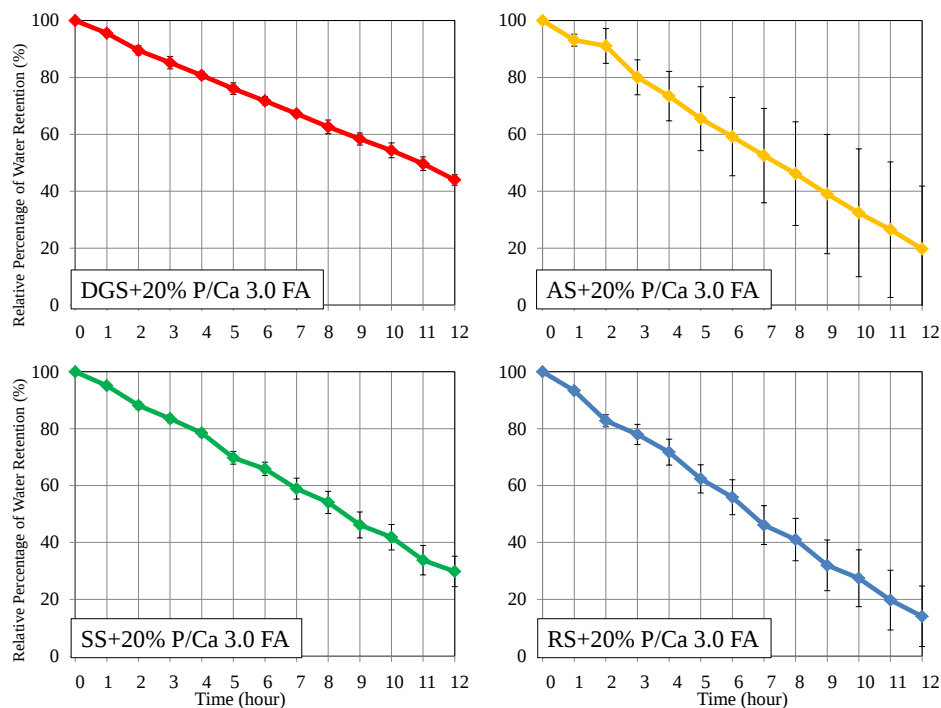


Figure 3-33 Water retention curve of DGS, AS, SS and RS mixed with apatite-synthesized FA with P/Ca ratio of 3.0 at 20 wt% mixing ratio and 40 °C

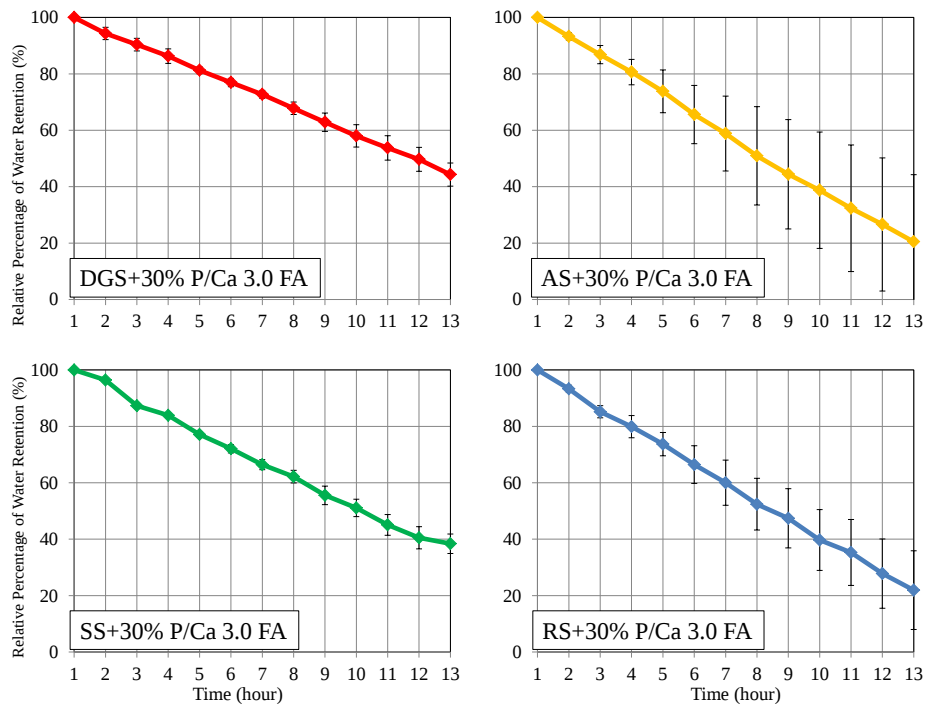


Figure 3-34 Water retention curve of DGS, AS, SS and RS mixed with apatite-synthesized FA with P/Ca ratio of 3.0 at 30 wt% mixing ratio and 40 °C

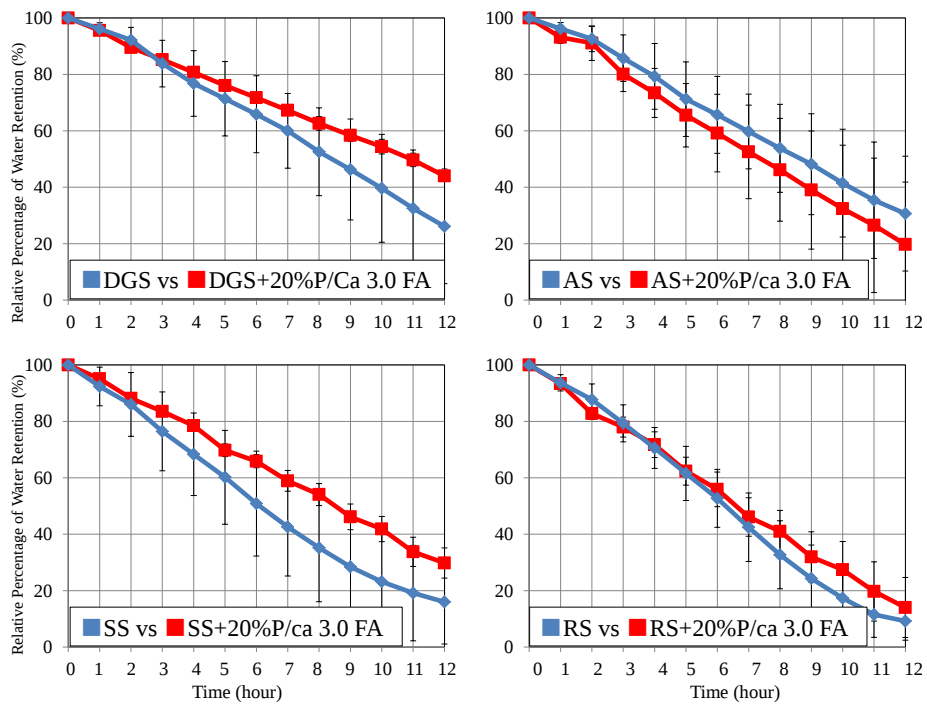


Figure 3-50 Comparison between water retention curves of soil/sand and soil/sand mixed with apatite-synthesized FA with P/Ca ratio of 3.0 at 20 wt% of mixing ratio

3.3.3.4 WRC of soils and sands amended with apatite-synthesized FA (P/Ca = 7.1) at 40 °C

Amendment of apatite-synthesized FA with P/Ca ratio of 7.1 generated different results compared to the previous case (P/Ca = 3.0). Treated-FA amendment gave no impact on WRC of all soil/sand mixtures although apparently large reduction of WRC by treated FA with P/Ca ratio of 7.1 was measured for AS (about 15.7% decrease). The t-test suggests that this reduction is within experimental errors. Figure 3-51 shows the comparison between water retention curves of pure soil/sand and soil/sand mixed with apatite-synthesized FA (P/Ca = 7.1) at 20 wt% of mixing ratio. Water retention curves varied slightly between pure soil/sand and soil/sand mixed with apatite-synthesized FA with P/ca ratio of 7.1. Thus apatite-synthesized FA with P/Ca ratio of 7.1 gives almost no effect on WRC of all soil/sand at 40 °C.

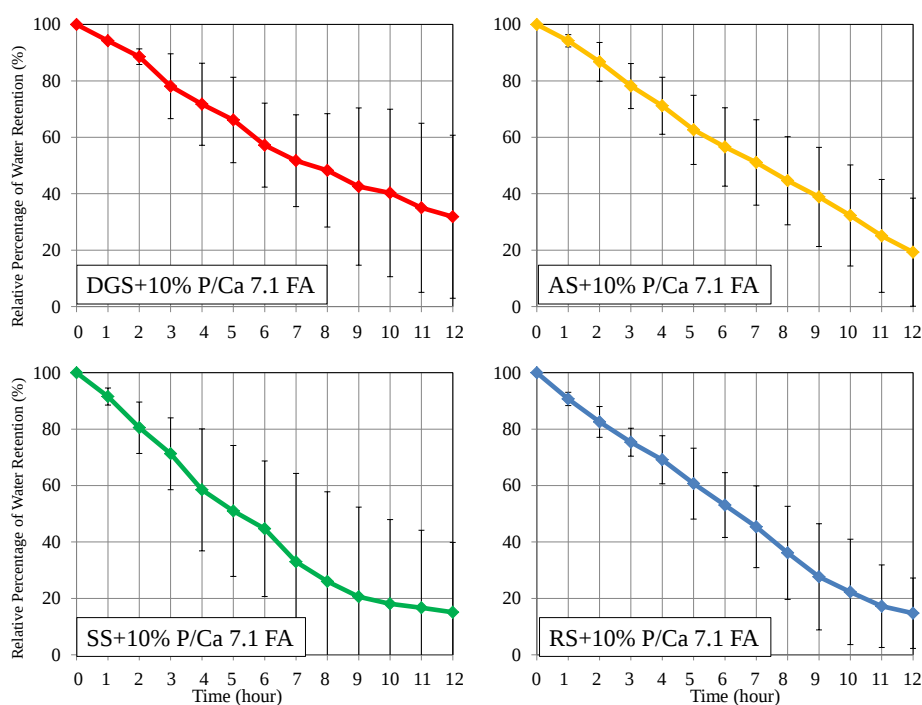


Figure 3-35 Water retention curve of DGS, AS, SS and RS mixed with apatite-synthesized FA with P/Ca ratio of 7.1 at 10 wt% mixing ratio and 40 °C

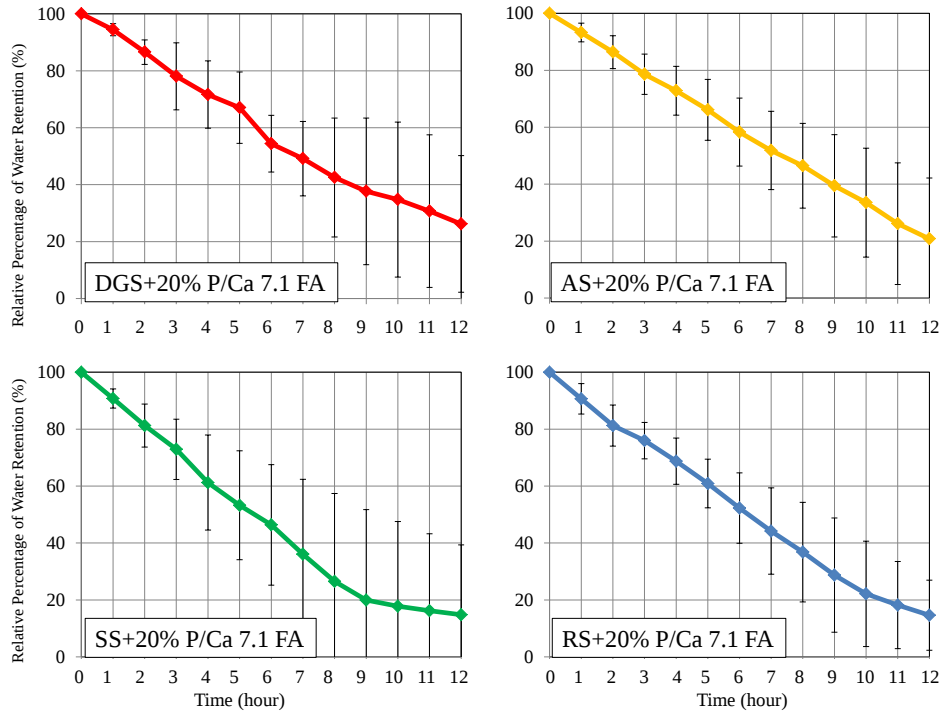


Figure 3-36 Water retention curve of DGS, AS, SS and RS mixed with apatite-synthesized FA with P/Ca ratio of 7.1 at 20 wt% mixing ratio and 40 °C

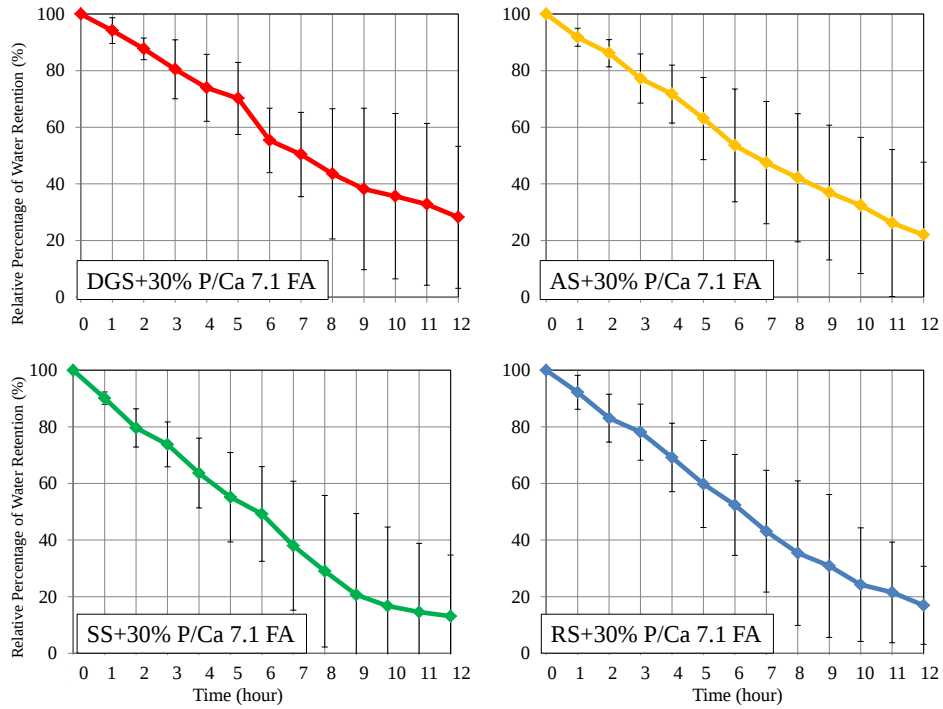


Figure 3-37 Water retention curve of DGS, AS, SS and RS mixed with apatite-synthesized FA with P/Ca ratio of 7.1 at 30 wt% mixing ratio and 40 °C

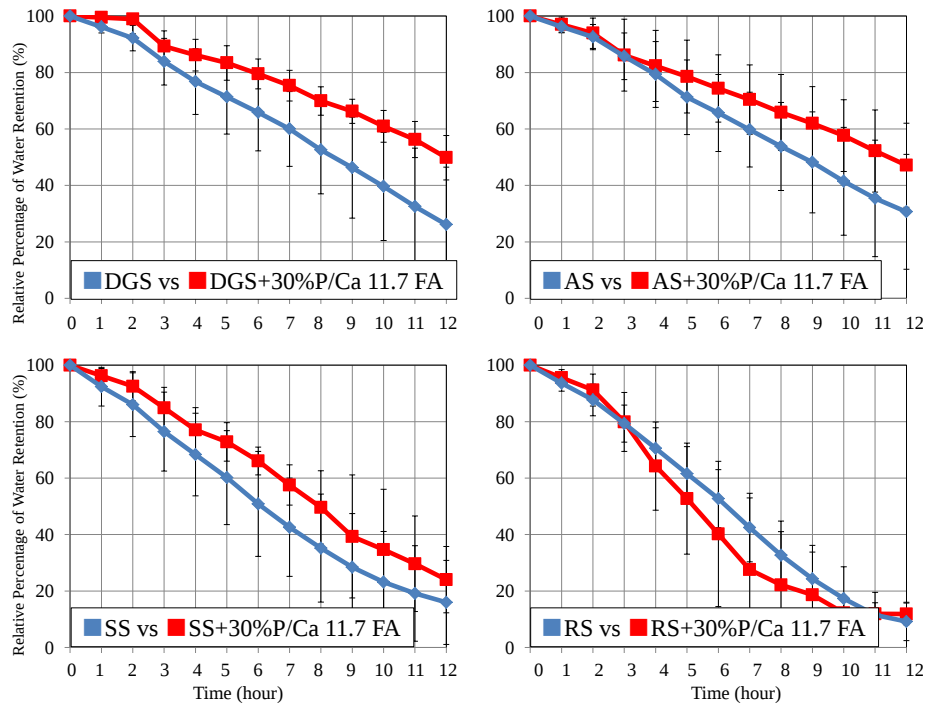


Figure 3-51 Comparison between water retention curves of soil/sand and soil/sand mixed with apatite-synthesized FA with P/Ca ratio of 7.1 at 20 wt% of mixing ratio

3.3.3.5 WRC of soils and sands amended with apatite-synthesized FA (P/Ca = 11.7) at 40 °C

As shown in Figure 3-5, apatite-synthesized FA with P/Ca ratio of 11.7 had specifically higher WRC at 40 °C compared to other samples. Apatite-synthesized FA amendment increased WRC of soils (DGS and AS) and SS beyond experimental errors when FA mixing was higher than 10 %. As shown in Figure 3-38 to 3-40 for comparison of water retention curves to those of other amended soil/sand, water evaporated slower than other FA-amended soils and FA-amended SS. Besides, mixing apatite-synthesized FA with P/Ca ratio of 11.7 increased residual water content that left in soils and SS after 12 hours drying. According to Figure 3-52, the water retention curves of FA-mixture samples were categorized type C_u for soils (DGS and AS) and type S_u for SS, respectively. This means that water evaporation was inhibited at the whole drying process and increased residual water at 12 hours. Thus it resulted in higher WRC of soils and SS mixed with apatite-synthesized FA with P/Ca ratio of 11.7.

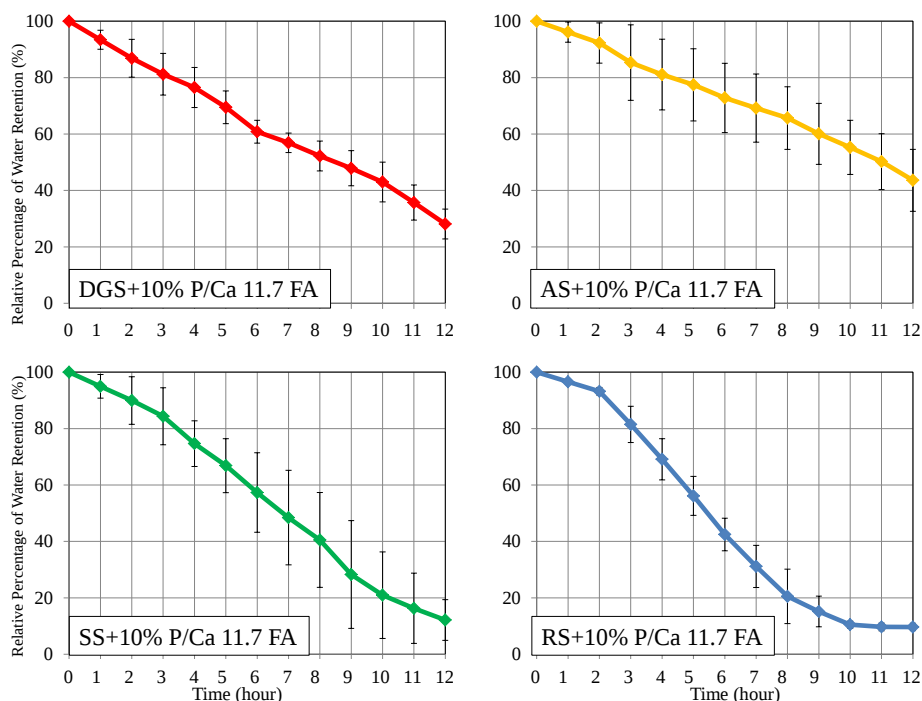


Figure 3-38 Water retention curve of DGS, AS, SS and RS mixed with apatite-synthesized FA with P/Ca ratio of 11.7 at 10 wt% mixing ratio and 40 °C

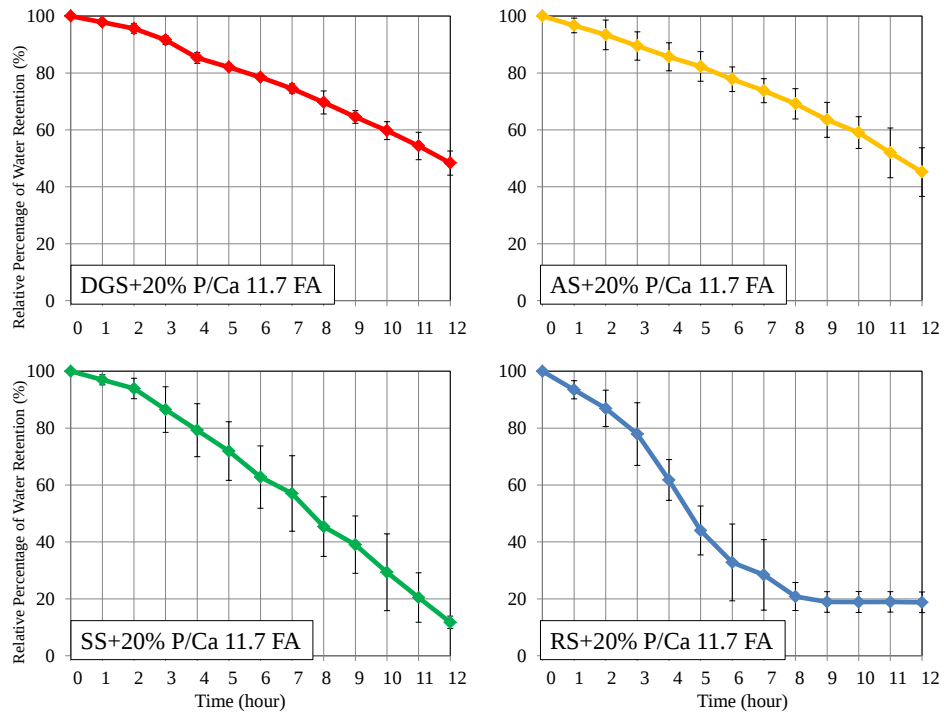


Figure 3-39 Water retention curve of DGS, AS, SS and RS mixed with apatite-synthesized FA with P/Ca ratio of 11.7 at 20 wt% mixing ratio and 40 °C

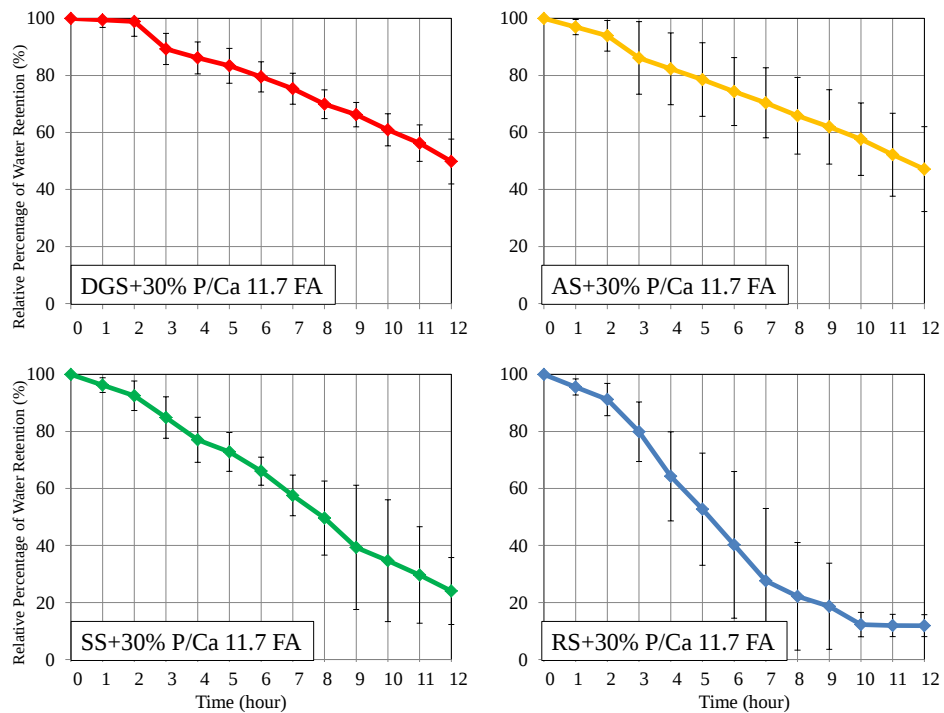


Figure 3-40 Water retention curve of DGS, AS, SS and RS mixed with apatite-synthesized FA with P/Ca ratio of 11.7 at 30 wt% mixing ratio and 40 °C

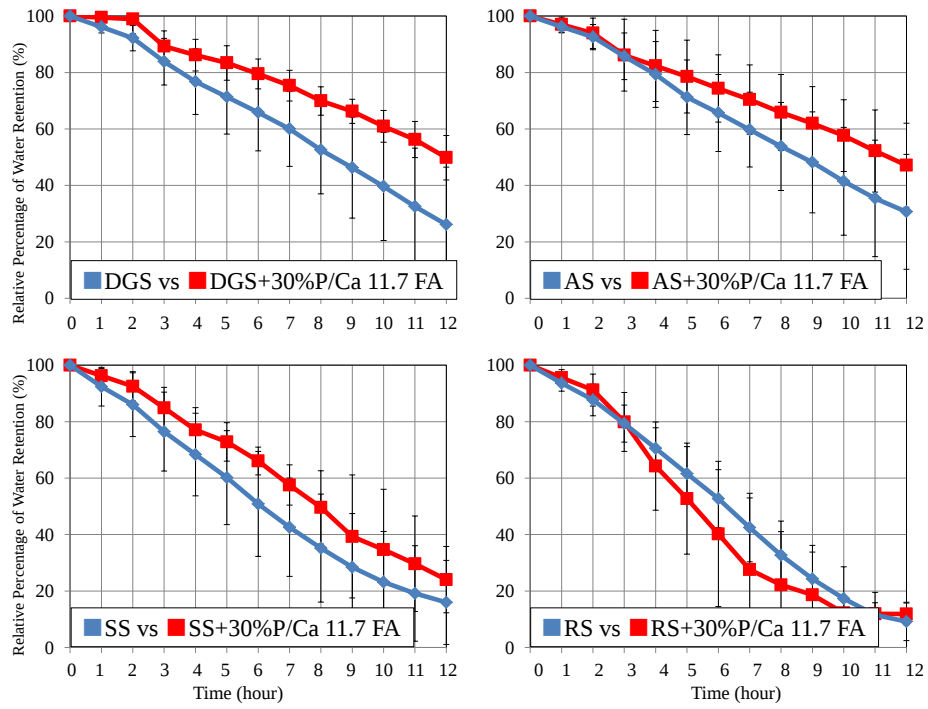


Figure 3-52 Comparison between water retention curves of soil/sand and soil/sand mixed with apatite-synthesized FA with P/Ca ratio of 11.7 at 30 wt% of mixing ratio

3.3.3.6 WRC of soils and sands amended with apatite-synthesized FA (P/Ca = 16.0) at 40 °C

Amendment of treated FA with P/Ca ratio of 16.0 significantly increased WRC of SS as well as the case of P/Ca ratio of 3.0. It is supported by water retention curves of SS with apatite-synthesized FA with P/Ca ratio of 16.0. The water content of FA-amended SS left after 12 hours drying was higher than that of pure SS (see Figure 3-41 to 3-43 and Figure 3-2). By the amendment of apatite-synthesized FA with P/Ca ratio of 16.0, water retention curve of SS changed from type S to type C_u. This means water evaporation of SS was inhibited and the rate became constant after amendment (see Figure 3-53). On the other hand, amendment of apatite-synthesized FA with P/Ca ratios of 16.0 apparently decreased WRC of AS. However, the t-test suggests that it is within experimental errors. As shown in Figure 3-2 and 3-41 to 3-43, water retention curves of both pure AS and AS with apatite-synthesized FA with P/Ca ratio of 16.0 decreased linearly with drying time.

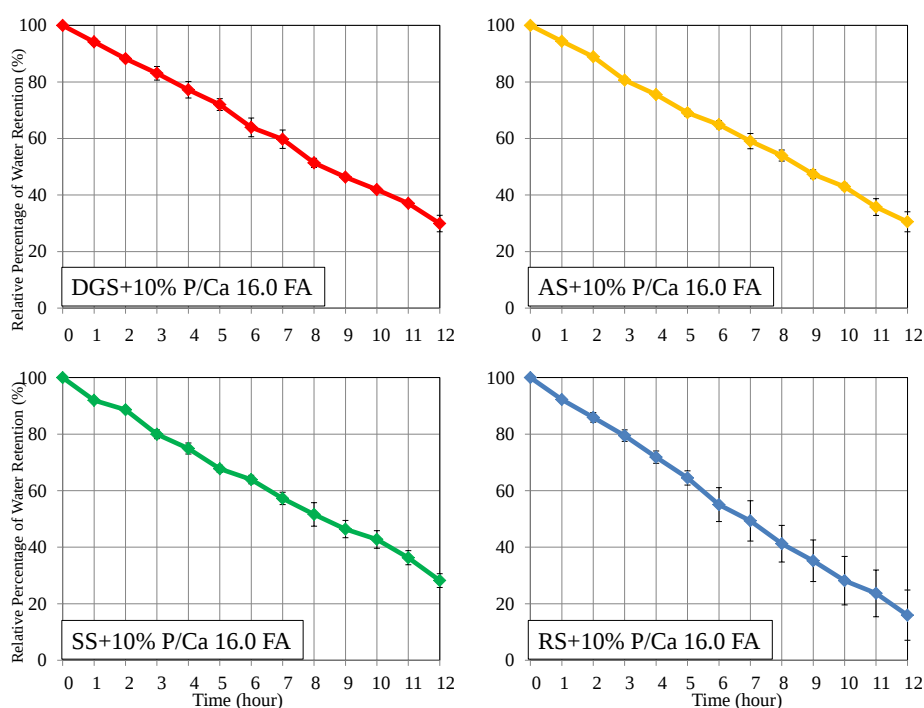


Figure 3-41 Water retention curve of DGS, AS, SS and RS mixed with apatite-synthesized FA with P/Ca ratio of 16.0 at 10 wt% mixing ratio and 40 °C

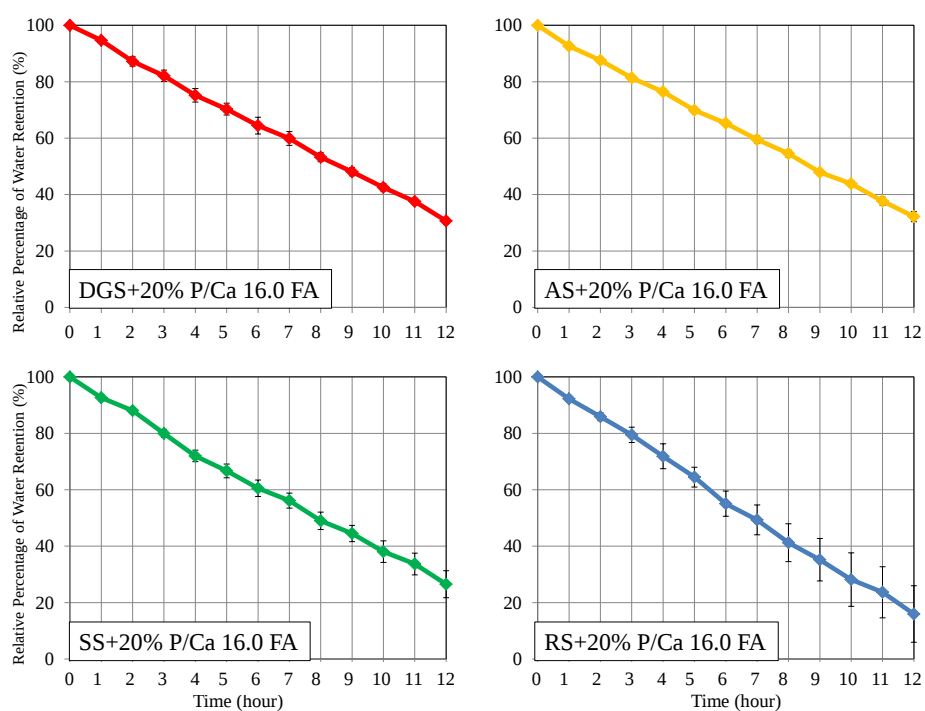


Figure 3-42 Water retention curve of DGS, AS, SS and RS mixed with apatite-synthesized FA with P/Ca ratio of 16.0 at 20 wt% mixing ratio and 40 °C

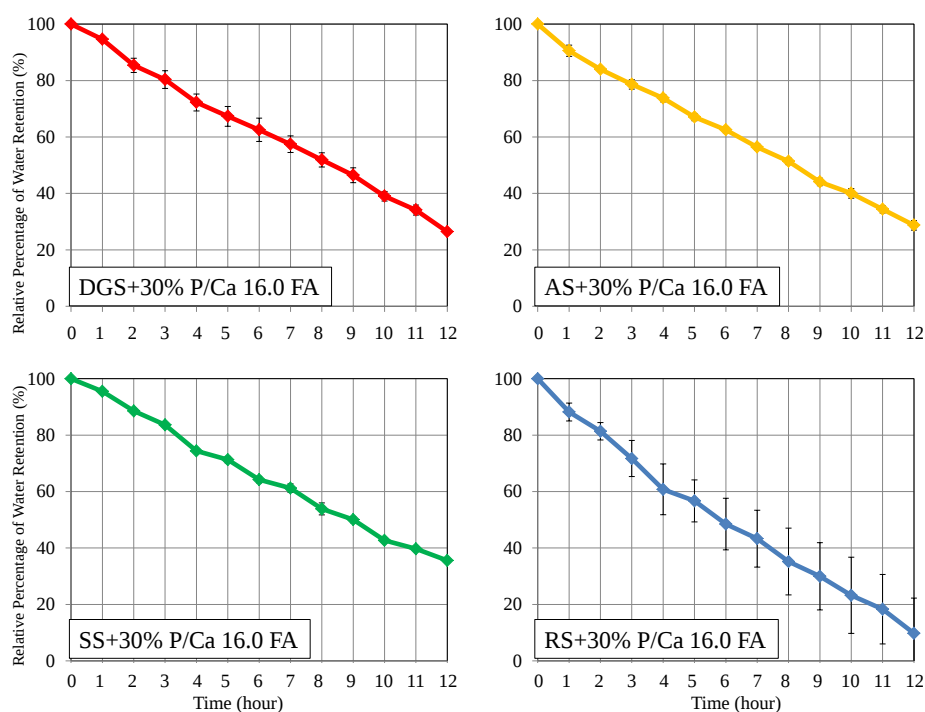


Figure 3-43 Water retention curve of DGS, AS, SS and RS mixed with apatite-synthesized FA with P/Ca ratio of 16.0 at 30 wt% mixing ratio and 40 °C

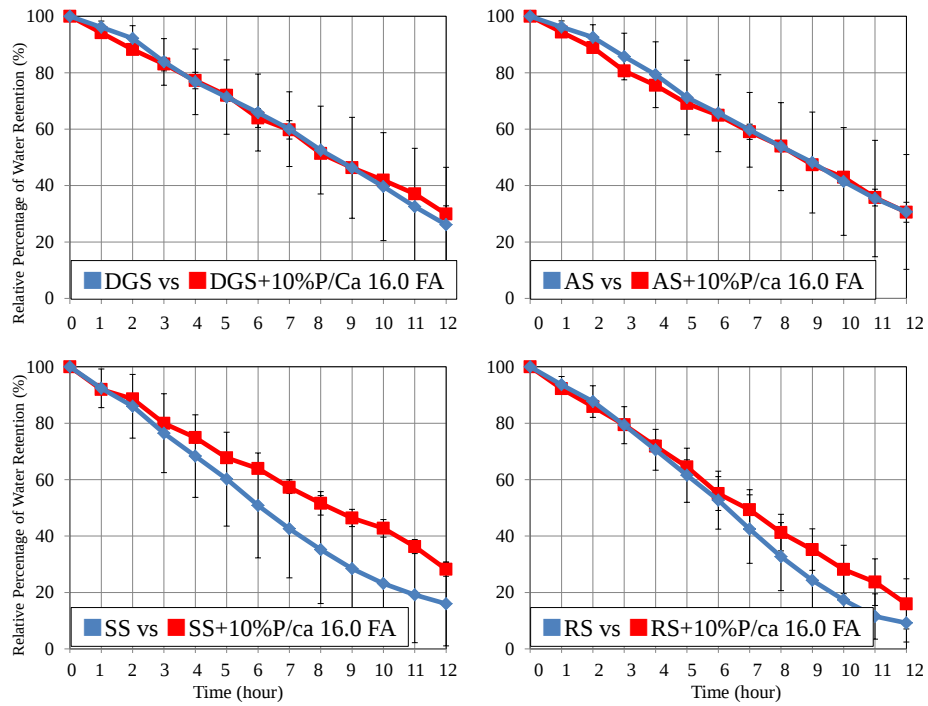


Figure 3-53 Comparison between water retention curves of soil/sand and soil/sand mixed with apatite-synthesized FA with P/Ca ratio of 16.0 at 30 wt% of mixing ratio

Table 3-2 Summary for type change of water retention curves of soil/sand mixed with apatite-synthesized FA from room temperature to 40 °C

Flay ash		Room temperature → 40 °C			
		DGS	AS	SS	RS
Raw FA		C	C	S	—
Apatite-synthesized FA	P/Ca = 3.0	C→C _u	—	S→C _u	—
	P/Ca = 7.1	—	—	—	—
	P/Ca = 11.7	C→C _u	C→C _u	S→S _u	—
	P/Ca = 16.0	C→C _u	—	S→C _u	—

3.3.3.7 Negligible impact of FA amendment on WRC of RS at 40 °C

WRC of RS received no impact from any apatite-synthesized FA. According to comparison of water retention curves shown in Figure 3-54, all FA-mixed RS had similar water retention curves with that of pure RS except for amendment of apatite-synthesized FA with P/Ca ratio of 11.7. Water evaporating rate of RS amended by apatite-synthesized FA with P/Ca ratio of 11.7 is also similar with that of pure RS at the first 3-4 hours. However, water evaporated faster than pure RS in the next 5 hours. After 10 hours drying, adhesive water in RS amended by apatite-synthesized FA with P/Ca ratio of 11.7 likely started to evaporate and water evaporating rate was near 0. Finally, residual water content of RS amended by apatite-synthesized FA with P/Ca ratio of 11.7 after 12 hours drying was higher than that of pure RS. Although water retention characteristic of pure RS and RS with apatite-synthesized FA with P/Ca ratio of 11.7 are different, their WRC were almost the same.

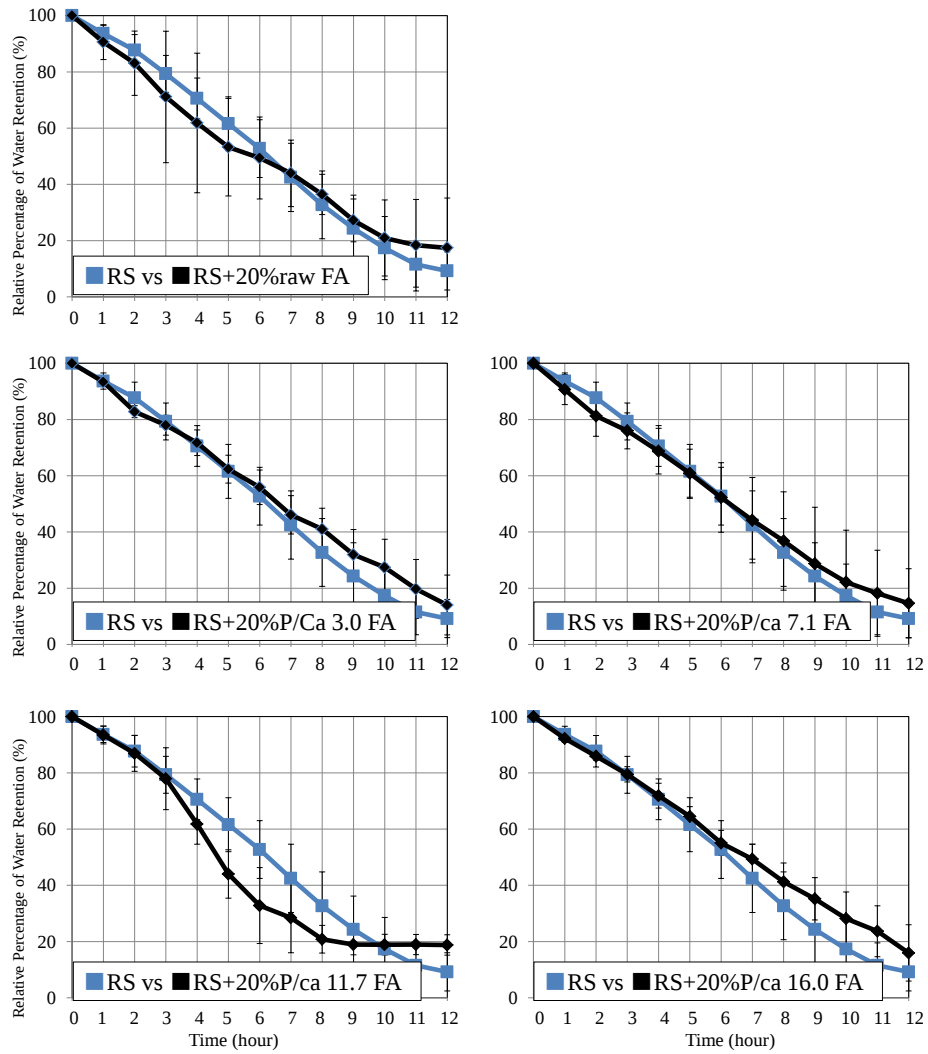


Figure 3-54 Comparison between water retention curves of RS and RS mixed with raw/apatite-synthesized FA at 20 wt% of mixing ratio

3.3.3.8 Summary of FA amendment on WRC of soils and sands at 40 °C

Effects of amending raw FA or apatite-synthesized FA on WRC of soil/sand are summarized in Table 3-4. As listed in the tables, effects of amending apatite-synthesized FA on soil/sand WRC are not the same with each other. Raw FA amendment decreased WRC of soils (DGS and AS) and SS. Raw FA amendment accelerated water evaporation of DGS, AS, and SS. It also decreased residual water at 12 hours. On the other hand, no effect was found for RS. The effect of apatite-synthesized FA amendment at 40 °C is very complicated. It depends on not only P/Ca ratio of apatite synthesis treatment but also soil/sand type. FA mixing ratio is less important than P/Ca ratio and soil/sand type. In addition, water evaporation characteristics were sometimes changed by FA amendment even when no significant change of WRC was found after FA amendment. It is noted that amendment of apatite-synthesized FA with P/Ca ratio of 3.0 increased WRC of DGS and SS beyond experimental errors. Apatite-synthesized FA (P/Ca = 3.0) amendment inhibited water evaporation at whole drying time and increased residual water at 12 hours. Amendment of apatite-synthesized FA with P/Ca ratio of 11.7 is more effective to increase WRC of DGS, AS and SS beyond experimental errors. It also inhibited water evaporation at whole drying time and increased residual water. In Chapter 4, some factors which seem to influence the effect of raw/treated FA amendment on soil/sand WRC would be discussed. The results of WRC measurement of apatite-synthesized FA amendment cases make discussion more difficult and also implies complicated mechanisms that control WRC of FA-soil/sand mixture system.

Table 3-4 Summary of WRC of soil/sand mixed with raw/apatite-synthesized FAs at 40 °C

Flay ash		40 °C			
		DGS	AS	SS	RS
Raw FA		-11.1%**	-10.4%**	-5.3%**	—
Apatite-synthesized FA	P/Ca = 3.0	+12.4%*	—	+21.2%**	—
	P/Ca = 7.1	—	—	—	—
	P/Ca = 11.7	+21.9%*	+17.3%**	+19.5%**	—
	P/Ca = 16.0	-2.3%*	—	+19.1%**	—

All data was conducted by t-test, and “*” stand to “p value < 0.05”, “**” stand to “p value < 0.01” of t-test.

3.3.4 Comparison of FA amendment effects on WRC at between room and high temperatures

Effects of amending FA on soil/sand WRC at room temperature and 40 °C are compared in this section. Results are shown in Table 3-5. The ratios of WRC change at room temperature by FA amendment to that at 40 °C are summarized in Table 3-4. When the ratio is larger than 1, it means that FA amendment effect on soil/sand WRC at 40 °C is larger than that at room temperature. It should be noted that these ratios were calculated using WRC changes which were regarded as within experimental errors by t-test. Therefore, discussions in this section might include some uncertainties. The effect of raw FA amendment on WRC at 40 °C is larger than that at room temperature. As described in the previous section, raw FA amendment at high temperature clearly decreased WRC of soils and SS. Higher effects on WRC at 40 °C are also found for apatite-synthesized FA with P/Ca ratio of 3.0 and 11.7. In particular, treated FA with P/Ca ratio of 11.7 gives stronger effect at high temperature. In contrast to raw FA, amendment of these treated FA increase WRC of DGS and SS at both room and high temperature. On the other hand, the effects of amending apatite-synthesized FA with P/Ca ratio of 7.1 and 16.0 on WRC at high temperature are weaker than those at room temperature except for AS with treated FA (P/Ca=7.1) and SS with treated FA (P/Ca=16.0). As summary, it can be emphasized that the effects of raw FA amendment and treated FA amendment (especially P/Ca=11.7) on WRC are stronger at high temperature. Raw FA amendment decreases WRC but treated FA (P/Ca=11.7) increased WRC compared to those of pure soils/sands. In addition, these results clearly show temperature dependency of FA amendment effect on WRC. This temperature dependency also depends on soil/sand type and P/Ca ratio of FA treatment. It also suggests complex mechanisms of WRC in soil/sand system with raw/treated FA.

Table 3-5 Comparison between effects of soil/sand mixed with apatite-synthesized FA at room temperature and 40 °C

Flay ash		40 °C/Room temperature			
		DGS	AS	SS	RS
Raw FA		-7.93	-10.40	-26.50	-0.71
Apatite-synthesized FA	P/Ca = 3.0	0.98	-0.73	1.63	1.17
	P/Ca = 7.1	0.45	-4.62	0.25	0.74
	P/Ca = 11.7	10.43	5.97	15.00	-0.77
	P/Ca = 16.0	-0.24	-0.44	1.30	0.64

3.4 Conclusion of Chapter 3

Effects of amending raw FA or apatite-synthesized FA on WRC of soil/sand are summarized in Table 3-3 and 3-5. At room temperature, amendment of raw and apatite-synthesized FA (P/Ca = 7.1 and 11.7) is not effective on WRC of soils and sands, except for RS with treated FA (P/Ca = 7.1). On the other hand, apatite-synthesized FA (P/Ca = 3.0 and 16.0) increased WRC of all samples. At 40 °C, FA amendment effects were different greatly. Raw FA amendment decreased WRC of soils (DGS and AS) and SS. Raw FA amendment accelerated water evaporation of DGS, AS, and SS. It also decreased residual water at 12 hours. Amendment of apatite-synthesized FA with P/Ca ratio of 3.0 increased WRC of DGS and SS beyond experimental errors. Its amendment inhibited water evaporation at whole drying time and increased residual water at 12 hours. Amendment of apatite-synthesized FA with P/Ca ratio of 11.7 is more effective to increase WRC of DGS, AS and SS beyond experimental errors. It also inhibited water evaporation at whole drying time and increased residual water. On the other hand, no effect was always found for RS at any FA amendment at 40 °C. The effect of apatite-synthesized FA amendment at 40 °C is very complicated. It depends on not only P/Ca ratio of apatite synthesis treatment but also soil/sand type. FA mixing ratio is less important than P/Ca ratio and soil/sand type. In addition, water evaporation characteristics were sometimes changed by FA amendment even when no significant change of WRC was found after FA amendment. The results of WRC measurement implies complicated mechanisms that control WRC of FA-soil/sand mixture system.

References

- Elizavet Ya. Gatapova, Irina A. Graur, Oleg A. Kabov, Vladimir M. Aniskin, Maxim A. Filipenko, Felix Sharipov, Lounès Tadrist, 2017, The temperature jump at water – air interface during evaporation, *International Journal of Heat and Mass Transfer* 104 (2017) 800-812
- Ilek A., Kucza J., Szostek M. (2017): The effect of the bulk density and the decomposition index of organic matter on the water storage capacity of the surface layers of forest soils, *Geoderm.* 285: 27-34.
- Yang F., Zhang G., Yang J., Li D, Zhao Y., Liu F., Yang R., Yang F. (2014): Organic matter controls of soil water retention in an alpine grassland and its significance for hydrological processes. *Journal of Hydrology*, 519: 3086-3093

Chapter 4

Impacts of physical and hydraulic properties on water retention capacity

4.1 Background

In the previous chapter, water retention curves and WRC of soil/sand, raw FA, apatite-synthesized FA and FA amended soil/sand samples at room temperature and 40 °C were reported. The effects of FA amendment on WRC of soil/sand have complicated dependency like temperature, P/Ca ratio of apatite-synthesis treatments. In this chapter, some parameters that likely control WRC would be discussed. This study focuses on capillary water content, water repellency, surface morphology, specific surface area, and size distribution of apatite-synthesized FAs.

4.2 Expected mechanisms which control WRC

Conventional water holding capacity (WHC) is measured based on physical water loss by gravity or certain suction pressure. WHC shows the amount of water remained in soil system at given pressure. Therefore, void volume (pore volume) of the soil system and hydraulic affinity of soil particle surface are important for WHC. Pore volume of the soil system regulates physically available space for water retention. On the other hand, hydraulic affinity of soil particle surface controls necessary dehydration pressure from soil particle surface. It means necessary energy to convert bound water to free water. Hydraulic affinity of soil particle can be evaluated directly by pF measurement.

Water retention capacity (WRC), suggested in this study, measures resistivity of the soil system against water evaporation which is driven by temperature, not suction pressure. Not only liquid water transfer but also gaseous water transfer in the soil system are important for WRC. Pore volume of the soil system and hydraulic affinity of soil particle are also important for WRC as well as WHC. In addition to pore volume, pore size distribution is also important because it likely controls gas permeability in the soil system. Only evaporated

water emission from sample surface is the water loss pathway during WRC measurement. Therefore, gas permeability, which controls transfer of evaporated water in the soil system, might control WRC. Evaporated water transfer would be driven by physical diffusion and convection. Both diffusion and convection will depend on not only pore size distribution but also temperature. When pore size is small, it decreases gas (evaporated water) flux and might be sealed by liquid water. Slow transfer of evaporated water in pores will increase WRC to some extent. High temperature promotes diffusion and might generate larger temperature degradation in the soil system between the outside and the inside. It will promote convection of evaporated water. Liquid water behaviors are still important for WRC. When hydraulic affinity of soil particle is larger, evaporation of bound water on soil particle surface will require larger energy. Therefore, pF might control WRC strongly. This study focuses on not only pF but also one more indicator of soil surface hydraulic affinity. It is water repellency of the soil system. In contrast to pF, water repellency shows hydrophobicity of soil particle surface. It should be noted that pF and water repellency might be partially or strongly controlled by pore size distribution of the soil system when capillary water are concerned. Appropriate range of pore size makes inner water bound continuously from various sides and make it “capillary water”. Water repellency and pF also seem to be controlled by physical and chemical characteristics of soil particle surface. As is expected naturally, hydrophilic organic/inorganic substances on the soil particle surface will contribute to stronger hydraulic affinity of the surface. Inorganic minerals like apatite and some of organic compounds might change surface hydrophilicity/hydrophobicity and thus change water repellency of the soil system. When soil particle has coarse and rough surface, such as micro-structure on the surface, might give larger surface area in the micro-scale to water and thus make surface water bound strongly. In this sense, morphology of soil/sand/FA particles might be one of important factors for WRC. Surface area is also suggested as a potentially important factor of WRC. When surface area is larger, it might increase capillary water and adhesive water in the soil system. Because evaporation of capillary water and adhesive water requires high temperature and long drying time, larger surface area might increase WRC. Expected mechanisms of WRC described above is illustrated in Figure 4-1.

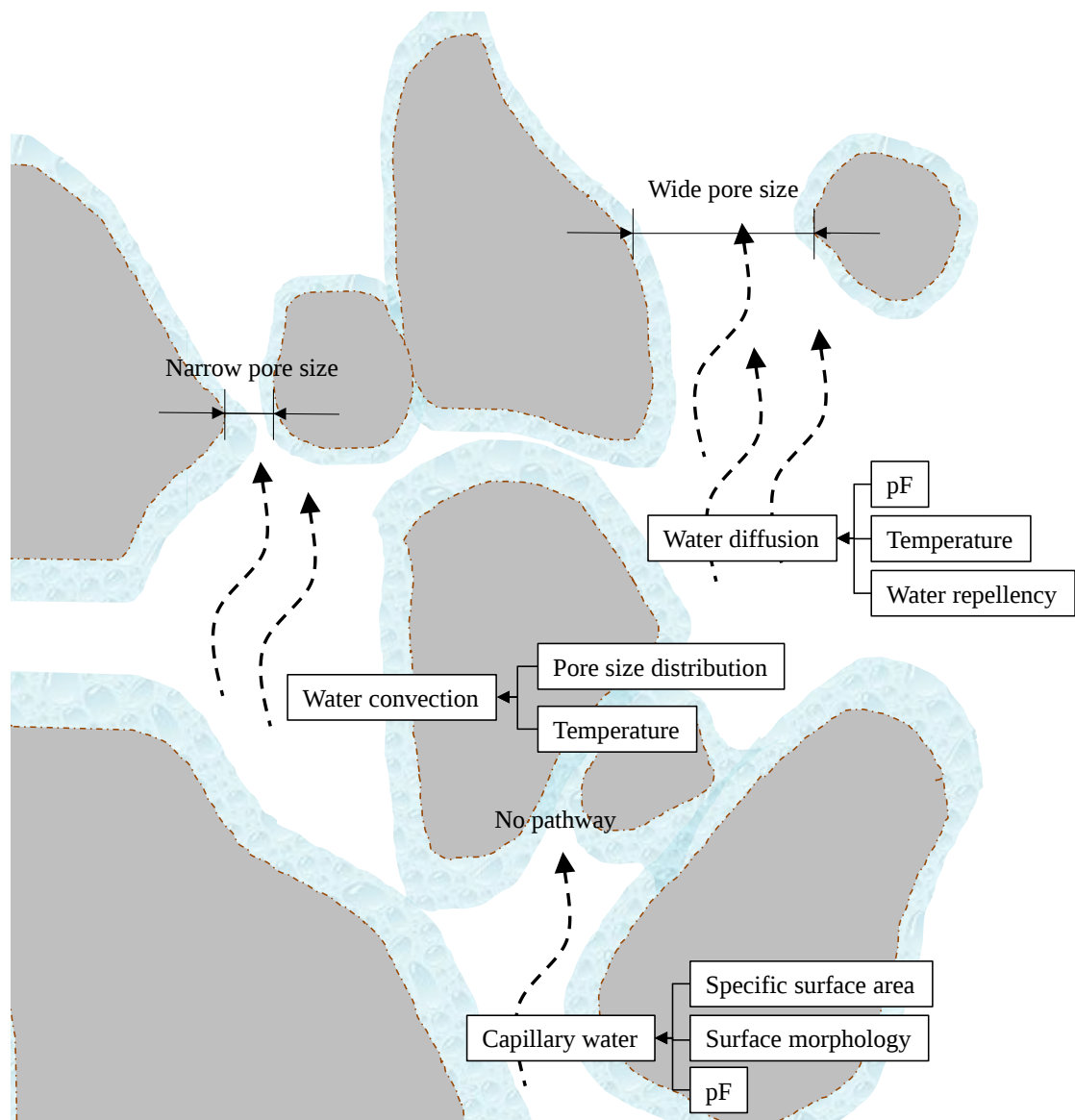


Figure 4-1 Expected mechanisms which control WRC

4.3 Potential controlling factors of WRC

4.3.1 Particle surface morphology

Soil texture, pore-size distribution and soil particle distribution are complicatedly correlated and they give large impacts on WHC (Dinga et al, 2016). WRC might be also controlled by complex mechanisms depending on many physical and hydraulic properties. It would be discussed below.

Surface morphology of apatite-synthesized FA is shown in Figure 4-2. Morphology of apatite-synthesized FA is compared to raw FA. Particle surface of raw FA is smooth with sphere shape. They look like hard surface without grooves. Apatite-synthesized FA with P/Ca ratio of 3.0 also has smooth surface as well as raw FA. Obvious micro-structure of apatite was not observed on the FA surfaces. Most of FA particles are still sphere. On the other hand, some aggregates of small particles were also found. It might change pore size distribution in soil/sand system and increase capillary water compared to that with raw FA. When P/Ca ratio of apatite-synthesis treatment increased to 7.1 or more, FA surface became rougher and more obvious micro-structure of apatite was observed on the FA surfaces. It is reminded that amendment of apatite-synthesized FA with P/Ca ratio of 3.0 and 11.7 increased WRC of DGS and SS at 40 °C. When the surfaces of apatite-synthesized FA with P/Ca ratio of 7.0, 11.7 and 16.0 were compared with each other, bigger-sized aggregations of FA particles were sometimes found in treated FA with P/Ca ratio of 7.1. On the other hand, there was no clear difference of apatite micro-structures among these apatite-synthesized FA. As listed in Table 3-5, apatite-synthesized FA with P/Ca ratio of 7.1 gave no effect on WRC of soil/sand at 40 °C. In contrast, treated FA with P/Ca ratio of 11.7 is the most effective on increasing WRC of soil/sand. Although SEM observations were limited, it is concluded that there was no obvious difference of surface morphology among apatite-synthesized FA with different P/Ca ratios. In contrast to expectation, apatite-synthesis treatment changed surface morphology of FA very limitedly. It is noted again that Raw FA amendment decreased WRC of soils and SS at 40 °C and the effects of apatite-synthesized FA amendment on WRC of soils and sands depend on P/Ca ratio. The results of SEM observations suggest that surface morphology observed in micro-meter scale and its limited changes by apatite-synthesis treatment do not explain FA amendment effects on WRC. Although surface observation in nano-meter scale

might find clear difference of morphology with/without apatite-synthesis treatment, it is a further study.

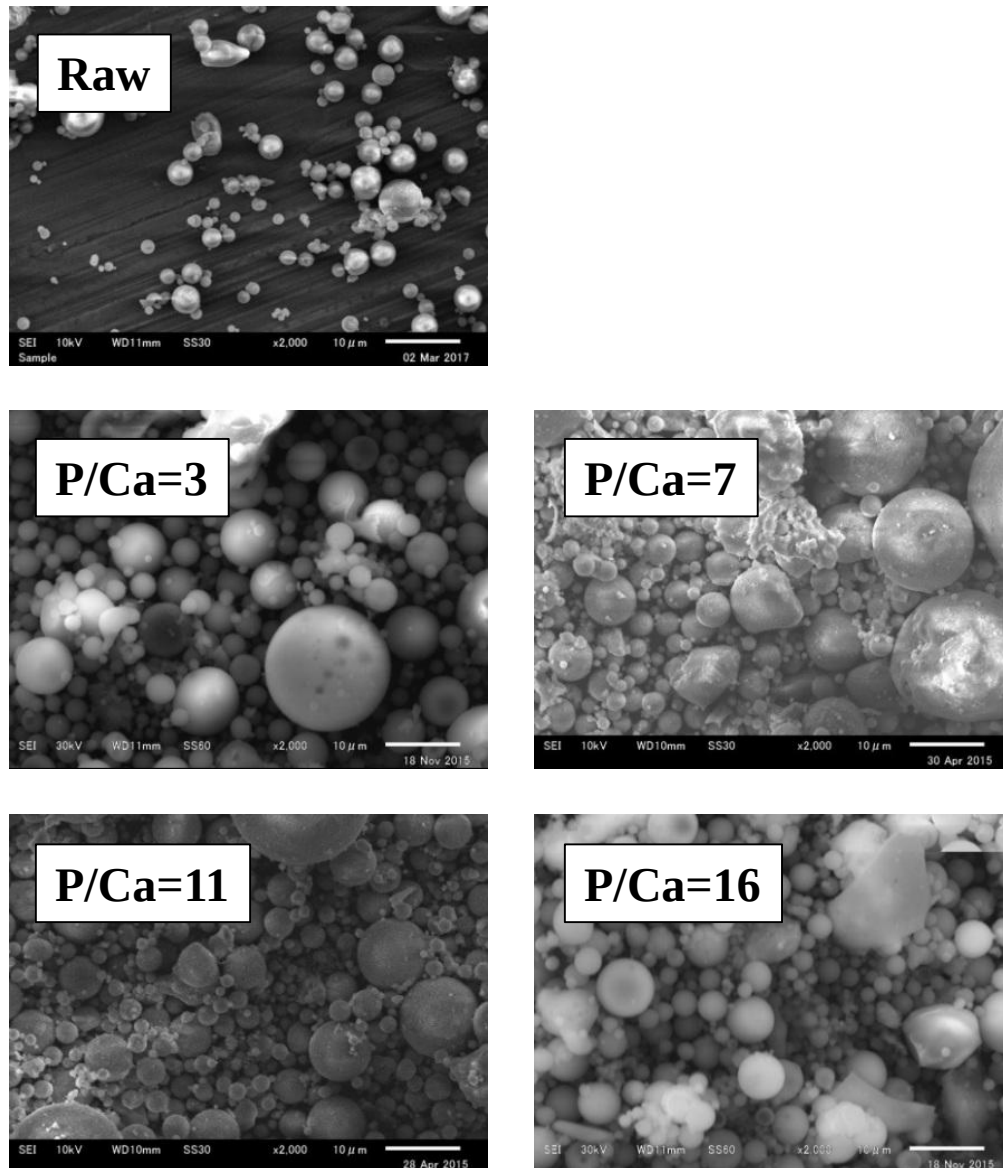


Figure 4-2 Surface morphology of apatite-synthesized FA with P/Ca ratio of 3.0, 7.1, 11.7 and 16.0

4.3.2 Particle size distributions of FAs

As described in section 4.2, pore size distribution of the soil system is likely related to evaporated water transfer and capillary water generation. It might control WRC dominantly. However, experimental measurement of pore size distribution of soil/sands with/without FA amendment is difficult. Its scale is too large to measure it using BET method. Therefore, this study focuses on particle size distribution rather than pore size distribution because pore size distribution would be controlled by particle size distribution of FA-amended soil/sand. Significant changes of FA particle size distribution might explain the effect of FA amendment on WRC of soil/sand.

Particle size distributions of raw and apatite-synthesized FA are shown in Figure 4-3. It should be noted that this measurement was based on SEM observation data, not by conventional methods like dynamic light scattering method nor laser diffraction/scattering method. Therefore, non-negligible uncertainty should be taken into account compared to conventional methods. Figure 4-3 shows no significant difference of size distribution between raw and treated FA. P/Ca ratio of apatite synthesis also produced negligible differences. Because slight difference of size distribution seems not to generate non-negligible difference of pore size distribution in FA-soil/sand mixture system, particle size is not sufficient to explain the effect of treated FA amendment on WRC.

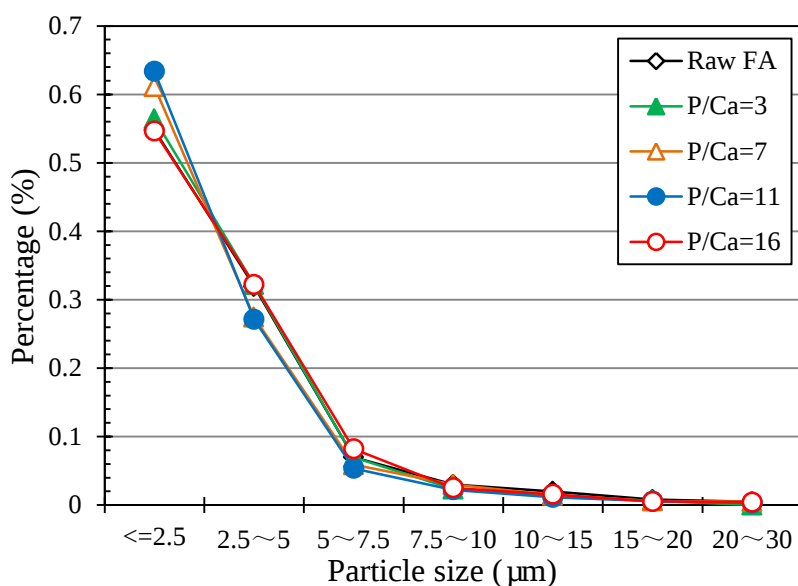


Figure 4-3 Size distribution of raw FA and apatite synthesized FA

4.3.3 Specific surface areas of soils, sands and FA

Surface area of soils (DGS and AS), sands (SS and RS), raw and apatite-synthesized FA are compared in Figure 4-4. AS has the biggest surface area (about 136.9 m²/g) which is much bigger than the other samples. If larger surface area is effective to increase capillary water, it might make water evaporation rate lower. DGS also has relatively larger surface area (15.6 m²/g) than RS (4.7 m²/g) and SS (1.7 m²/g). Apatite synthesis on FA surface increased surface area higher than raw FA. As described above, large surface area is expected as effective on increase of capillary water in FA-amended soil/sand system. Owing to the highest WRC of treated FA with P/Ca ratio of 11.7 at 40 °C among treated FA, this treated FA should have the largest surface area if surface area controls WRC independently. However, measurement results are contrast to the expectation. Treated FA with P/Ca ratio of 11.7 had the smallest surface area than the other treated FA and it is close to that of raw FA. This clearly suggests that surface area of amended FA does not dominantly control WRC of FA-soil/sand mixture system. When surface area is compared to WRC, no correlation is obviously confirmed at both temperatures (see Figure 4-4). It is concluded that surface areas of soil, sand, raw/treated FA does not control WRC of FA-soil/sand mixture system directly. This conclusion also suggests the necessity to verify expected mechanism among surface area, capillary water, and WRC. Although larger surface area was expected to increase capillary water in FA-soil/sand mixture system, it might give negligible impact on capillary water. Capillary water generation might be controlled by pore size distribution and/or surface hydraulic characteristics rather than surface area. The other mechanism to be verified is the impact of capillary water on WRC. Because capillary water is strongly bound on the surface and requires more energy for evaporation, larger amount of capillary water is expected to increase WRC. However, it might be negligible. These would be also discussed in following sections.

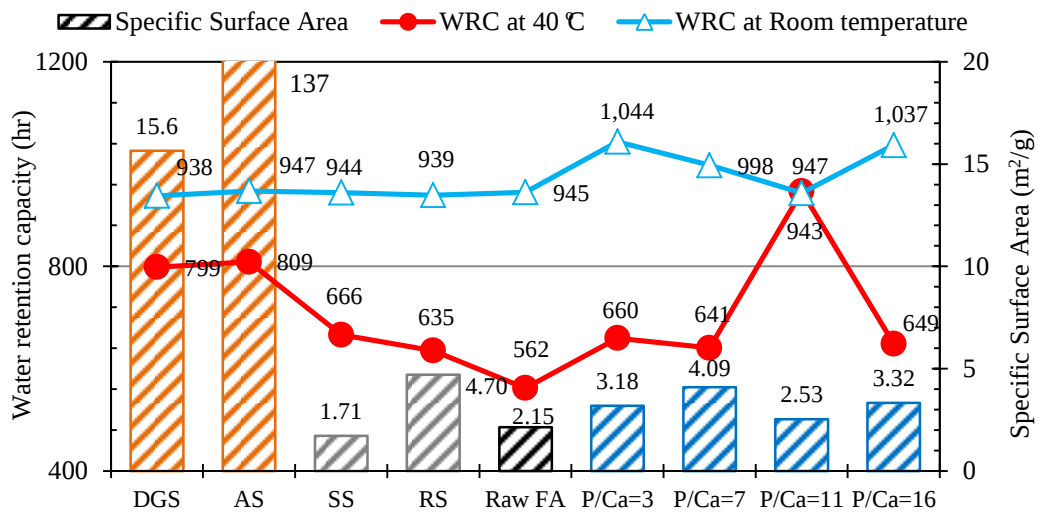


Figure 4-4 Correlation between specific surface area and WRC at 40 °C and natural condition of pure soil/sand, raw FA and apatite synthesized FA

4.3.4 Water repellency of soil/sand, raw/treated FA and amended soil/sand

As mentioned in section 4.2, if hydrophilicity or hydrophobicity of FA surface give significant impacts on soil moisture evaporation, it controls WRC of FA-soil/sand mixture system. Therefore, water repellency of FA-soil/sand mixture samples should be correlated to evaporation rates of capillary water. Water drop penetration time (WDPT), which represents water repellency, and WRC of all samples are plotted in Figure 4-5. SS has the lowest WDPT around 0.21 s. DGS has 1.26 s for WDPT. RS has 4.09 s for WDPT and AS has the highest WDPT, which is 6.05 s. This means that water repellency of SS is weaker than those of DGS, AS and RS. AS has the strongest water repellency among pure soil/sand. This suggests water evaporation rate in SS should be the lowest and that of AS should be the highest among soils and sands. As described in section 3.3.1.2, however, WRC of SS at 40 °C was the lowest among all soils and sands. This means water evaporation rate of SS was the highest. AS had the highest WRC, which means evaporation rate of AS was the lowest. These results show that water evaporation rate of single soil/sand were opposite to the expectation from the results of water repellency. Water repellency does not influence WRC of single soil/sand directly.

When focusing on WDPT of apatite synthesized FAs, WDPT results of all

apatite-synthesized FA were similar with each other. WDPT of apatite-synthesized FA with P/Ca ratio of 3.0 was 1.44 s and that of apatite-synthesized FA with P/Ca ratio of 7.1 was 1.11 s. Treated FA with P/Ca ratio of 11.7 and 16.0 have 1.40 s and 1.64 s of WDPT, respectively. Water evaporation rates of apatite-synthesized FAs should also be similar if water repellency controls water evaporation independently. According to WRCs in section 3.3.3, WRC of apatite-synthesized FA with P/Ca ratio of 3.0, 7.1 and 16.0 at 40 °C were similar. However, WRC of apatite-synthesized FA with P/Ca ratio of 11.7 was extremely higher than those of other apatite-synthesized FAs. Owing to exceptionally high WRC with comparable WDPT of apatite-synthesized FA with P/Ca ratio of 11.7, it is concluded that water repellency does not dominantly influence WRC of apatite-synthesized FAs.

When mixing raw FA or apatite-synthesized FAs into soil/sand, WDPTs of soil/sand were varied and water evaporation rate also changed. Correlations between WRC and WDPT of FA-amended soil/sand would be discussed here. When raw FA was amended, it increased WDPT of all soil/sand samples. Raw FA has WDPT of 5.40 s, which is higher than WDPT of DGS, SS and RS, and lower than that of AS. Because raw FA amendment filled void spaces of DGS and sands system, it might make FA-soil/sand mixture system more hydrophobic. According to Table 4-1, WDPT of DGS was increased by 111.3 %. WDPT of SS was increased by 471.4 %, and WDPT of RS was increased by 61.8 %. For AS, although raw FA has the lower WDPT than AS, mixing raw FA increased WDPT of the mixture by 28.3 % and is suggested as significant by t-test. According to WRC of soil/sand mixed with raw FA at 40 °C (see section 3.3.3.2), WRC of soil/sand were all decreased (except for WRC of raw FA mixed RS, which was regarded as insignificant by t-test). This means that water evaporation rate of soils and SS were fasten when mixed with raw FA. In the case of soil/sand amended with raw FA at 40 °C, water repellency and water evaporation rate have a consistent relation as was expected.

In contrast, amendment of apatite-synthesized FA gave complicated impacts on WDPT which depend on mixing ratio, P/Ca ratio of apatite synthesis and also soil/sand type. They are summarized in Table 4-1.

Effect of mixing apatite-synthesized FAs on WDPT (water repellency) of soil/sand showed obvious soil/sand type dependency. WDPT of DGS increased by about 25.1 % to

38.3 % when apatite-synthesized FAs were mixed. For AS, the trends were different from that of DGS. WDPT of AS was decreased by 10.7 % to 23.6 % when mixing with apatite-synthesized FAs. WDPT of SS amended with apatite-synthesized FAs was increased significantly by about 180.9 % to 261.9 % and WDPT of RS was increased by 47.6 % to 68.5 % after mixture. It is summarized that WDPT (water evaporation) of samples depends on soil and sand type clearly.

On the other hand, when compared to WRC of soil/sand mixed with apatite-synthesized FAs, the correlation became complicated. WDPT of DGS amended with apatite-synthesized FA with P/Ca ratio of 3.0, 7.1, 11.7 and 16.0 were increased by 25.1 %, 22.1 %, 33.5 % and 38.3 %, respectively. Although WRC of DGS with apatite-synthesized FA with P/Ca ratio of 3.0 and 11.7 increased by 12.4 % and 21.9 %, amendment of apatite-synthesized FA with P/Ca ratio of 7.1 did not change WRC of DGS and addition of apatite-synthesized FA with P/Ca ratio of 16.0 decreased WRC of DGS by 2.3 %. All results are regarded as significant by statistical test. If WDPT controls WRC of DGS at 40 °C, variation of WDPT should be related to variation of WRC. Because WRC variations of DGS with apatite-synthesized FAs are different from each other, correlation between WDPT and WRC of DGS mixed with apatite-synthesized FAs is correspondingly small.

The same comparison was conducted between WDPT and WRC of AS, SS and RS amended with apatite-synthesized FAs at 40 °C. For apatite-synthesized FA-mixed AS, WDPTs of amended AS were all decreased. However, WRC of amended AS was not influenced by mixing apatite-synthesized FA with P/Ca ratio of 3.0, 7.1 and 16.0, and increased by mixing apatite-synthesized FA with P/Ca ratio of 11.7. There is no clear correlation between WDPT and WRC for AS with apatite-synthesized FA as well as DGS. WDPT of SS with apatite-synthesized FAs increased by about 200 %, and their WRC also increased by about 20 % except for one case. Only when SS was amended with apatite-synthesized FA with P/Ca ratio of 7.1, WRC change was suggested to be insignificant by t-test. A relation between WDPT and WRC of amended SS is contrast to the expectation, in which longer WDPT (high water repellency) promotes water evaporation and thus decrease WRC. In the case of RS amended with apatite-synthesized FAs, WDPTs of RS were increased by around 60 %, except for apatite-synthesized FA with P/Ca ratio of 3.0 (suggested to be

insignificant by t-test). On the other hand, WRCs of RS with apatite-synthesized FAs have no significant difference with that of pure RS at 40 °C. There is no correlation between WDPT and WRC in RS amended with apatite-synthesized FAs.

These results are summarized as follows. Correlations between WDPT and WRC have dependency to soil/sand type and FA type (raw or apatite-synthesized). In the case of raw FA amendment to soil/sand, it increased WDPT of all soil/sand and decreased WRC except for RS. It agrees with expected mechanism. On the other hand, amendment of apatite-synthesized FAs increased WDPT of all soil/sand except for AS. It did not decrease WRC of DGS, SS and RS but increased WRC of DGS and SS. No impact was found on WRC of RS. Although amendment of apatite-synthesized FAs decreased WDPT of AS, it gave no impact on WRC of AS or increased when P/Ca ratio of apatite-synthesis treatment was 11.7. Owing to complicated and inconsistent relations between WDPT and WRC for FA-amended soil/sand, it is concluded that water repellency does not control WRC independently. These complicated correlations suggest that there are some unconsidered mechanisms between WRC and water repellency.

Table 4-1 Summary on effect of apatite-synthesized FA on WDPT of soil/sand

WDPT(s)	DGS	AS	SS	RS
Raw FA	+111.3%**	+28.3%**	+471.4%**	+61.8%**
Apatite synthesized FA with P/Ca ratio 3.0	+25.1%**	-10.7%*	+261.9%**	—
Apatite synthesized FA with P/Ca ratio 7.1	+22.1%**	-23.6%**	+252.4%**	+68.5%**
Apatite synthesized FA with P/Ca ratio 11.7	+33.5%**	-21.3%**	+180.9%**	+56.8%**
Apatite synthesized FA with P/Ca ratio 16.0	+38.3%**	-23.3%**	+233.3%**	+47.6%**

All data was conducted by t-test, and “*” stand to “p value < 0.05”, “**” stand to “p value < 0.01” of t-test.

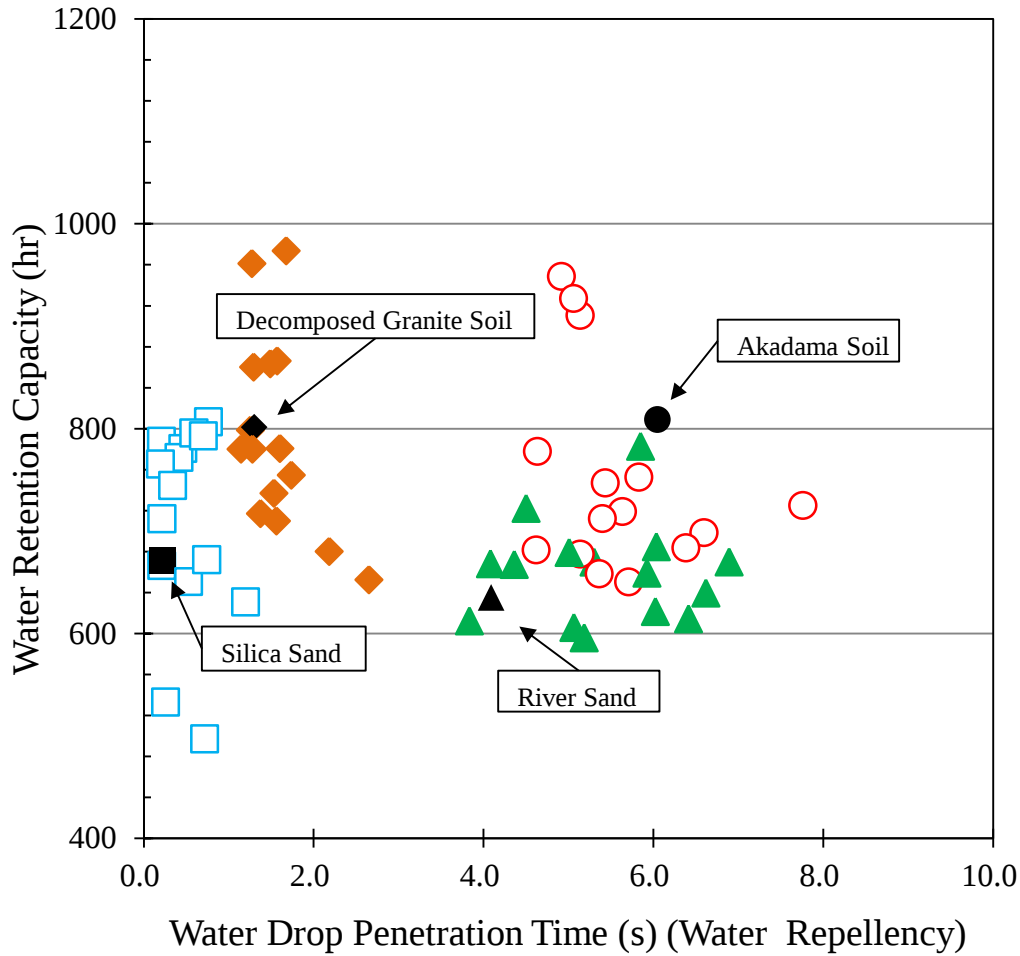


Figure 4-5 Correlation between WDPT and WRC at 40 °C of raw FA, apatite synthesized FA

4.3.5 Capillary water content of soil/sand, raw FA and FA amended soil/sand

Capillary water content in soil system is important for plant growth, as mentioned in chapter 1. In soil system, stronger water suction force leads to higher content of adhesive water and capillary water. Therefore, it should lead to higher water holding capacity and also stronger water evaporation resistivity. In this section, capillary water and adhesive water contents are considered together because adhesive water content is usually low. Capillary water content of soil/sand, raw FA and FA-amended soil/sand are summarized in Table 4-2.

Capillary water content of SS is about 5.6 wt%, which is the smallest among all soils and sands. AS has the highest capillary water content (63.1 wt%) and DGS has the second highest capillary water content (31.9 wt%). RS has 26.0 wt% of capillary water content. Capillary water content of DGS and AS were higher than 30 wt%, which is the initial water content of water drying experiment in this research. This means that almost all of water

in DGS and AS at 40 °C was capillary water during WRC measurements. It means that WRC of DGS and AS was evaporation resistivity of capillary water. RS samples include 87 % of capillary water and 13 % of gravitational water when WRC measurement started. Although WRC of RS was mainly derived from evaporation resistivity of capillary water, it was also partially derived from gravitational water. Water in SS samples consists of 19 % of capillary water and 81 % of gravitational water at the start time of WRC measurement.

If capillary water content controls WRC directly, WRC of DGS and AS should have similar WRC and WRC of RS should be a little lower than those of DGS and AS. SS should have the lowest WRC. According to section 3.3.1.2, WRC of AS is 809 hr, which is the highest among all soils and sands. As was expected, DGS has similar WRC around 799 hr, slightly lower than that of AS. WRC of SS was 666 hr, which is much lower than those of DGS and AS. In contrast to the expectation, WRC of RS was 635 hr, which is slightly lower than that of SS and much lower than those of DGS and AS. Even if capillary water controls WRC the most, the results of RS suggests that some other factors originated from hydraulic properties of soil/sand system can also control WRC partially or strongly.

When focusing on capillary water content of raw FA and apatite-synthesized FAs, raw FA has 42.5 wt% of capillary water content and it was similar with those of apatite-synthesized FAs. Apatite-synthesized FA with P/Ca ratio of 3.0 and 7.1 have 43.6 wt% and 43.3 wt%, respectively. When P/Ca ratio was changed into 11.7, capillary water content increased a little to 46.4 wt%. For apatite-synthesized FA with P/Ca ratio of 16.0, capillary water content is lower than other treated FA, but still maintains at 40.3 wt%. If capillary water in FAs controls WRC directly, WRC of all FAs should be similar. As described in section 3.3.1.2, however, WRC of raw FA at 40 °C was 562 hr, the lowest among raw and apatite-synthesized FAs. On the other hand, apatite-synthesized FA with P/Ca ratio of 3.0, 7.1 and 16.0 had similar WRC. Apatite-synthesized FA with P/Ca ratio of 11.7 had the highest WRC (947 hr). Difference of WRC between raw and apatite-synthesized FAs were so obvious that capillary water contents of FA did not directly control WRC of raw and apatite-synthesized FAs.

After mixing raw FA or apatite-synthesized FAs into soil/sand, capillary water content of soils and sands changed as follows. It should be noted that all results of capillary

water contents of FA-mixed soils/sands were only 20 wt% mixing ratio owing to limited available samples. Mixing raw FA into DGS decreased capillary water content of DGS to 25.1 wt% (by about 6.8 wt% reduction). Because DGS with raw FA has capillary water content lower than 30 wt%, which is initial water content of WRC measurement, WRC of DGS with raw FA is evaporation resistivity of not only capillary water but also gravitational water. For apatite-synthesized FA mixture, capillary water content of DGS stayed constant or increased slightly depending on P/Ca ratios of treated FAs. In all cases, capillary water contents of DGS with apatite-synthesized FA were higher than 30 wt%. Therefore, WRC of DGS with apatite-synthesized FA means evaporation resistivity of only capillary water. If capillary water controls WRC, DGS with raw FA should have smaller WRC than original DGS owing to decrease of capillary water content. The results of WRC agree with this expectation. On the other hand, DGS amended with apatite-synthesized FA should have comparable WRC with each other owing to similar amount of capillary water. However, DGS with apatite-synthesized FA (P/Ca = 11.7) has significantly larger WRC than those of DGS with other apatite-synthesized FA.

For AS, capillary water contents decreased when raw FA and apatite-synthesized FA were mixed. Decreasing rate was around 10 %. AS with raw and apatite-synthesized FA still have higher than 30 wt% of capillary water content. WRC of AS with raw/treated FA also means evaporation resistivity of capillary water as well as DGS. However, raw FA amendment decreased WRC of AS and apatite-synthesized FA amendment gave no or positive impact on WRC. Treated FA with P/Ca ratio of 11.7 increased WRC of AS. No clear correlation was found between capillary water and WRC in this case.

When SS was concerned, capillary water content increased obviously when raw and apatite-synthesized FA were mixed. Increasing rates were over 150 % for all FA-mixed SS. Capillary water content of SS with raw and apatite-synthesized FA ranges from 13.3 wt% to 17.8 wt%. This means that evaporation resistivity of gravitational water and capillary water were monitored during WRC measurement of SS with raw and apatite-synthesized FA. Because raw/treated FA amendment increased capillary water contents of SS, WRC should increase in all cases of FA amendment if capillary water controls WRC directly. However, raw FA amendment decreased WRC of SS significantly. On the other hand, apatite-synthesized FA

amendment increased WRC of SS as the same with the expectation.

For RS, the effects of FA amendment on capillary water content are complicated. Raw and apatite-synthesized FA with P/Ca ratio of 11.7 and 16.0 increased capillary water contents. On the other hand, apatite-synthesized FA with P/Ca ratio of 3.0 and 7.1 decreased it. WRC received no significant impacts by raw/treated FA amendment.

Comparison between capillary water content and WRC suggests that capillary water does not control WRC dominantly. Even when capillary water, which should have smaller evaporation rate than gravitational water owing to higher water potential, was increased by raw/apatite-synthesized FA amendment, WRC changes complicatedly depending on soil/sand type and P/Ca ratio of apatite-synthesis treatment. This suggests that evaporation of capillary water is influenced by some other factors like adsorption strength and/or suction pressure of capillary water onto soil/sand particle surfaces. The pF value and its relation to WRC would be discussed in the next section.

Table 4-2 Summary on effect of apatite-synthesized FA on capillary water content of soil/sand

Capillary water content (wt%)	FA	DGS	AS	SS	RS
Pure sample	—	31.9(—)	63.1(—)	5.6(—)	26.0(—)
Raw FA	42.5	25.1(6.8↓)	56.8(6.3↓)	17.8(12.2↑)	27.8(1.8↑)
Apatite-synthesized FA with P/Ca ratio of 3.0	43.6	31.9(—)	53.8(9.3↓)	13.3(7.7↑)	25.3(0.7↓)
Apatite-synthesized FA with P/Ca ratio of 7.1	43.3	34.5(2.6↑)	56.8(6.3↓)	15.9(10.3↑)	24.7(1.3↓)
Apatite-synthesized FA with P/Ca ratio of 11.7	46.4	32.0(0.1↑)	54.4(8.7↓)	15.1(9.5↑)	26.5(0.5↑)
Apatite-synthesized FA with P/Ca ratio of 16.0	40.3	34.1(2.2↑)	55.6(7.5↓)	14.2(8.6↑)	26.4(0.4↑)

4.3.6 pF of DGS and SS amended with raw and apatite-synthesized FA

Capillary water content is influenced by water adsorption strength/water suction pressure on surface of soil/sand particles in soil system. It is known that higher water adsorption strength will lead to higher contents of adhesive (negligible) and capillary water in soil/sand system. Water suction pressure of DGS mixed with 20 wt% of raw FA, apatite-synthesized FAs with P/Ca ratio of 3.0, 7.1 and 11.7 are shown in Figure 4-6, respectively. Those of SS are also shown in Figure 4-7. Because of the height limitation of experimental equipment, pF value of samples mentioned above were only measured ranging from 0.3 to 2.0. In this range of pF, water in the samples were all gravitational water. When pF value ranges 2.0 to 3.8, water in the sample will be capillary water. The results are compared to WRC of DGS and SS with raw/apatite-synthesized FA at mixing ratio of 20 wt% at 40 °C. When pF value changed from 0.3 to 2.0, water will be desorbed from the sample by suction pressure and water content of the sample will decrease. If water suction pressure influences WRC directly, the sample with higher water content at high pF should have higher WRC.

As shown in Figure 4-6, water content of pure DGS at 0.3 of pF was 54.8 %. When pF value increased to 2.0, at which gravitational water will be sucked out, water content was decreased to 39.3 %. It suggests that 15.5 % of total water contained in pure DGS at 0.3 of pF was gravitational water. For DGS mixed with raw FA, the final water content at pF value of 2.0 was 33.7 %. 17.3 % of total water at 0.3 of pF is gravitational water. For DGS mixed with apatite-synthesized FA with P/Ca ratio of 3.0, 7.1, and 11.7, water contents of DGS with treated FA were 41.7 %, 34.4 %, 41.7 % at 2.0 of pF, respectively. Therefore, gravitational water contained in these samples at 0.3 of pF were 12.5 %, 11.1 % and 9.5 %, respectively. It should be noted that water contents of all DGS samples at 2.0 of pF were higher than 30 wt%, which was the initial water content in WRC measurements. Therefore, water contents of DGS with/without FA amendment as a function of pF, measured in this study, cannot be directly used to discuss relations between WRC and pF. However, measurement data clearly shows that amendment of raw FA and apatite-synthesized FA with P/Ca ratio of 7.1 decreased water contents at any pF from 0.3 to 2.0 compared to DGS. On the other hand, amendment of apatite-synthesized FA with P/Ca ratio of 3.0 and 11.7 increased water content at pF higher

than 1.3. Because water retention with larger volume results in larger WRC, the effects of FA amendment on water content at pF higher than 1.3 agrees with their effects on WRC.

In the cases of SS and SS mixed with raw/apatite-synthesized FA, according to Figure 4-7, final water contents at pF value 2.0 were 11.3 % for SS, 19.9 % for SS with raw FA, 18.9 % for SS with treated FA (P/Ca = 3.0), 19.9 % for SS with treated FA (P/Ca = 7.1), and 18.0 % for SS with treated FA (P/Ca = 11.7), respectively. Percentages of gravitational water in these samples at 0.3 of pF were 16.9 % for SS, 9.3 % for SS with raw FA, and 8.6 %, 7.8 %, 10.1 % for SS with apatite-synthesized FA with P/Ca ratio of 3.0, 7.1, 11.7, respectively. In these cases, all water contents at each pF were below 30 wt % and can be used for discussion on WRC and pF. If pF controls WRC dominantly, it is expected that WRC of SS is the lowest and SS mixed with raw and apatite-synthesized FA would have similar WRC with each other, which are higher than that of pure SS. According to section 3.3.3, however, WRC of SS mixed with raw FA was the lowest and that of SS mixed with apatite-synthesized FA with P/Ca ratio of 3.0 was the highest. The effect of mixing apatite-synthesized FA with P/Ca ratio of 7.1 on WRC was negligible by t-test. Therefore, it is concluded that water suction pressure is not sufficient to explain WRC changes of SS by FA amendment at 40 °C.

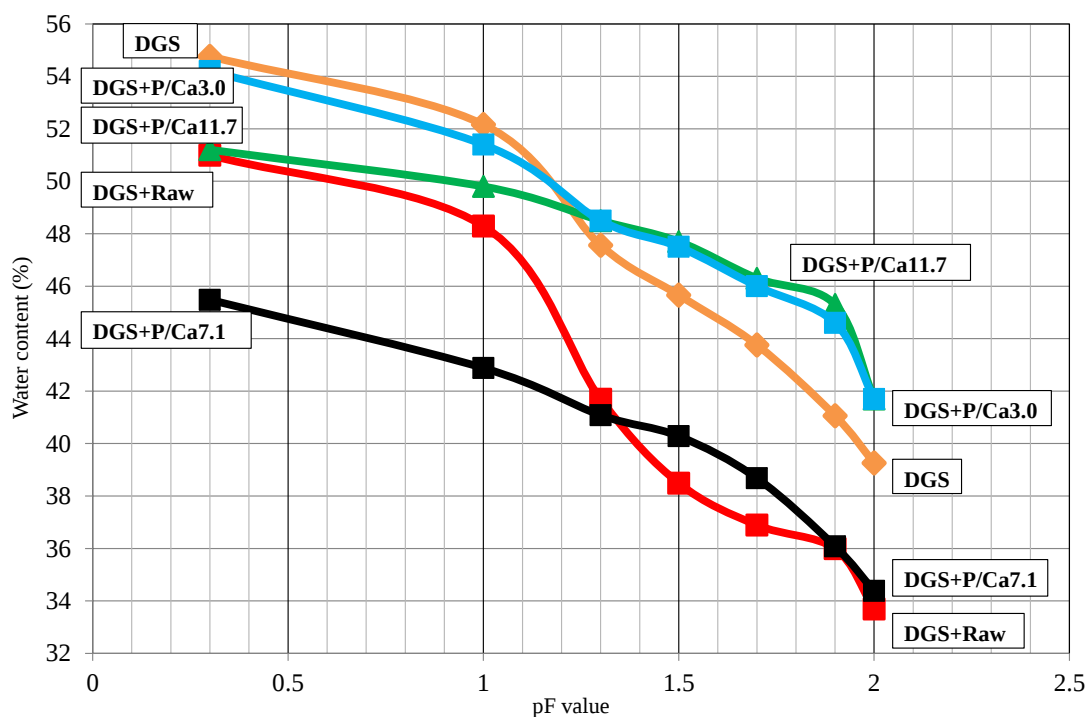


Figure 4-6 pF-water content curve of DGS and DGS mixed with raw FA and apatite-synthesized FA with P/Ca ratio of 3.0, 7.1 and 11.7

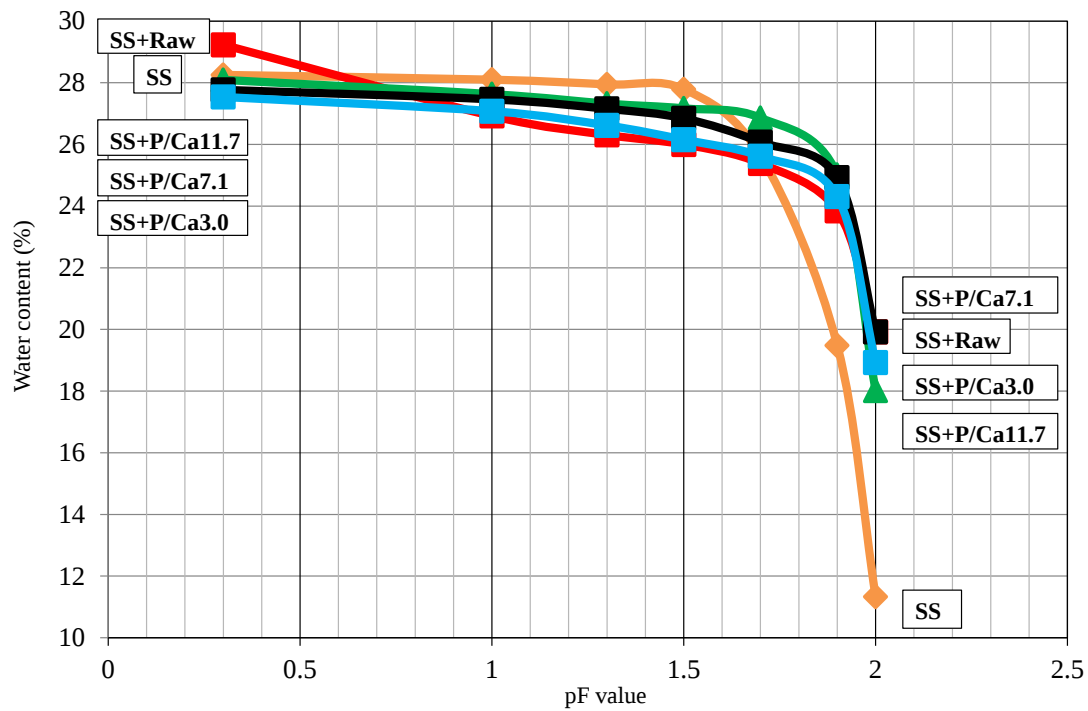


Figure 4-7 pF-water content curve of SS and SS mixed with raw FA and apatite-synthesized FA with P/Ca ratio of 3.0, 7.1 and 11.7

4.3.7 Multi-regression analysis on WRC and potentially controlling factors

In previous sections, correlation between WRC and surface morphology, particle size distribution, specific surface area, water repellency, capillary water content and pF of soil/sand, raw FA and FA-amended soil/sand were investigated individually. It is concluded that these parameters were not the dominantly controlling factor of WRC, but might be somehow interactively related to WRC. Some other unknown parameters are always found to be more effective than the parameters that investigated in previous sections. In this section, correlation between specific surface area, water repellency, capillary water content and WRC of samples will be investigated together and their combining effect will be analyzed by multi-regression analysis. If there is a specific correlation between these parameters and WRC, there will be a reliable regress-equation found from analysis. It should be noted that all data utilized in multi-regression analysis are variation of parameter, not the value of parameter, in order to figure out priority of effect of parameter changes on WRC.

The results are shown in Table 4-3 to 4-8. All data utilized was WRC of DGS, AS, SS and RS mixed with raw, apatite-synthesized FA with P/Ca ratio of 3.0, 7.1, 11.7, and 16.0 by 20 wt%

at 40 °C because of limitation data of capillary water content analysis. It should be noted that though all data was analyzed by statistical analysis, some of the significant data variation might be caused by experimental equipment replacement and weather changing. Equation of correlation between water repellency, surface area, capillary water content and WRC is as follows:

$$\text{WRC variation} = a_1 \times w + a_2 \times s + a_3 \times c + k$$

where WRC variation is variation percentage of WRC (%), w is variation percentage of water repellency (%), s is variation percentage of specific surface area (%), and c is variation percentage of capillary water content in sample (%). k is the constant.

At first, all soil/sand mixed with FAs by 20 wt% data were considered without concerning significance, results were shown in Table 4-3 (without constant) and 4-4 (with constant). In Table 4-3, effect of water repellency on WRC was suggested to be negative and effects from other parameters on WRC were suggested to be positive, all these are the same with expectation. However, P value of this equation was higher than 0.05, which is identified as unreliable. When concerning constant in analysis, in Table 4-4, effect from water repellency on WR was suggested as negative effect and effects from surface area, capillary water content on WRC were suggested to be positive, which were the same with expectation. In addition, surface area was supposed to be most strong in controlling WRC at 40 °C. At last, the equation about WRC, water repellency, surface area and capillary water content can be summarized as follows:

$$\text{WRC variation} = -0.163 \times w + 0.768 \times s + 0.008 \times c + 0.111$$

where P value of the equation was 0.019, and supposes the equation was reliable. Besides, constant was 0.111, appeared to be bigger than capillary water content value, this means there are some other parameters also influence WRC significantly at the same time.

As all data were soil/sand mixed with raw/apatite-synthesized FAs at 20 wt%, some data were identified as insignificant by t-test, in order to purchase reliability of multi-regression analysis, only significant data of the samples were analyzed. Results were shown in Table 4-5 (without constant) and 4-6 (with constant). Results in Table 4-5 suggests that specific surface area is negative on WRC, however in the expectation, higher specific surface area leads to higher WRC. In addition, P value of equation was bigger than 0.05 and showed this equation is not reliable. When constant was concerned in Table 4-6, effect of water repellency was supposed to be negative

on WRC and effects of surface area, capillary water content were supposed to be positive on WRC. Specific surface area in soil system was suggested to be the most positive factor on adjusting WRC at 40 °C. In previous analysis correlation between specific surface area and WRC was checked and no clear correlation was found. In multi-regression analysis, variation of specific surface area was compared to variation of WRC, and in this case, specific surface area was suggested to be important on WRC. P value of analysis is quite low and reliable.

Multi-regression analysis was at last broken down to be conducted on soil/sand separately on soil/sand with/without constant, and results were shown in Table 4-7 (without constant) and 4-8 (with constant), respectively. In the analysis without constant (see Table 4-7), effect of specific surface area was suggested to be negative on WRC of DGS, effect of water repellency was suggested to be positive on WRC of RS and effect of capillary water content was suggested to be negative on WRC of RS. All these were opposite to expectation and P value of the equation was too big to be reliable. In the analysis with constant (see Table 4-8), for DGS, AS and RS, specific surface area appeared to be very important on WRC. However, effects of surface area on WRC of soils and SS were opposite to expectation. At the same time, effect of capillary water content appeared to be negative on WRC of FA-amended SS. In addition, constant were very big, means some other unknown parameters appeared to be more powerful on WRC, and P values of all equations were over 0.05 and equations were suggested to be unreliable.

It was shown that for all WRC of soil/sand samples mixed with raw/apatite-synthesized FAs by 20 wt% at 40 °C, a reliable correlation was appeared to be found between WRC and water repellency, surface area, capillary water content. Specific surface area is supposed to be most powerful on WRC and capillary water content to be the weakest. There are some strong factors (for example, organic matters) that control WRC variation should be investigated in future works. However, when breaking the analysis down on only significant data or data that separated by soil/sand type, equations became unreliable.

Table 4-3 Multi-regression analysis on all data of WRC of soil/sand mixed with apatite-synthesized FA at 20 wt% of mixing ratio at 40 °C without constant term

Variation of WRC (%)		
	Variation (%)	P value
Water repellency (s)	-0.138	0.088
Specific surface area (m ² /g)	0.171	0.413
Capillary water content (wt%)	0.100	0.200
Correlation coefficient R	0.540	
P value	0.111	

Table 4-4 Multi-regression analysis on all data of WRC of soil/sand mixed with apatite-synthesized FA at 20 wt% of mixing ratio at 40 °C with constant term

Variation of WRC (%)		
	Variation (%)	P value
Water repellency (s)	-0.163	0.032
Specific surface area (m ² /g)	0.768	0.030
Capillary water content (wt%)	0.008	0.924
Constant	0.111	0.040
Correlation coefficient R	0.673	
P value	0.019	

Table 4-5 Multi-regression analysis on only significant data of WRC of soil/sand mixed with apatite-synthesized FA at 20 wt% of mixing ratio at 40 °C without constant term

Variation of WRC (%)		
	Variation (%)	P value
Water repellency (s)	-0.261	0.239
Specific surface area (m ² /g)	-0.099	0.844
Capillary water content (wt%)	0.220	0.361
Correlation coefficient R	0.647	
P value	0.494	

Table 4-6 Multi-regression analysis on only significant data of WRC of soil/sand mixed with apatite-synthesized FA at 20 wt% of mixing ratio at 40 °C with constant term

	Variation of WRC (%)	
	Variation (%)	P value
Water repellency (s)	-0.269	0.146
Specific surface area (m ² /g)	1.196	0.188
Capillary water content (wt%)	0.033	0.867
Constant	0.249	0.125
Correlation coefficient R	0.8738	
P value	0.181	

Table 4-7 Multi-regression analysis on WRC of soil/sand mixed with apatite-synthesized FA at 20 wt% of mixing ratio at 40 °C without constant term

	Variation of WRC of DGS (%)		Variation of WRC of AS (%)		Variation of WRC of SS (%)		Variation of WRC of RS (%)	
	Variation (%)	P value	Variation (%)	P value	Variation (%)	P value	Variation (%)	P value
Water repellency (s)	-0.251	0.532	-1.125	0.295	-0.259	0.270	0.056	0.702
Specific surface area (m ² /g)	-0.166	0.798	1.113	0.646	0.359	0.708	0.073	0.925
Capillary water content (wt%)	-0.159	0.859	-0.688	0.866	0.179	0.433	-0.522	0.533
Correlation coefficient R	0.697		0.855		0.818		0.543	
P value	0.662		0.375		0.454		0.840	

Table 4-8 Multi-regression analysis on WRC of soil/sand mixed with apatite-synthesized FA at 20 wt% of mixing ratio at 40 °C with constant term

	WRC of DGS (hr) at 40 °C		WRC of AS (hr) at 40 °C		WRC of SS (hr) at 40 °C		WRC of RS (hr) at 40 °C	
	°C		°C		°C		°C	
	Variation (%)	P value	Variation (%)	P value	Variation (%)	P value	Variation (%)	P value
Water repellency (s)	-0.135	0.839	-1.270	0.339	-0.124	0.501	-0.048	0.871
Specific surface area (m ² /g)	-5.94	0.749	-58.976	0.457	-0.190	0.797	1.736	0.659
Capillary water content (wt%)	0.469	0.843	0.084	0.984	-0.333	0.435	0.754	0.799
Constant	-0.955	0.755	-11.666	0.451	0.810	0.286	0.148	0.659
Correlation coefficient R	0.679		0.927		0.967		0.647	
P value	0.843		0.468		0.322		0.866	

4.4 Conclusion of Chapter 4

In this chapter, factors that control variation of WRC of soil/sand mixed with raw FA and apatite-synthesized FA with P/Ca ratio of 3.0, 7.1, 11.7 and 16.0 at 40 °C were analyzed.

Particle aggregation and surface modification might change size distribution and porosity of apatite-synthesized FA and thus influence WRC when treated FAs were mixed into soil/sand. However, micro-meter scale observation is not enough for confirming correlation between surface modification and WRC variation. Particle size distribution of apatite-synthesized FAs was also analyzed, but it was suggested to be not sufficient to explain the effect of apatite-synthesized FA amendment on WRC of soil/sand at 40 °C. Specific surface area seems somehow positively related to WRC variation and also related to amount of capillary water content in soil system. Water repellency is believed to be an important factor for WRC, and higher water repellency should lead to faster water evaporation, then lead to a lower WRC. Water repellency has the soil/sand dependency, when soil/sand mixed with apatite-synthesized FAs were concerned, effect of water repellency on WRC became complicated, suggested that there are some other unconsidered mechanisms influences WRC at the same time. Capillary water of samples was proved to have soil/sand dependency, too. However, effect from capillary water on WRC was suggested as not directly when treated FA amendment cases were considered. pF value shows water suction force of particle surface

thus stronger water suction pressure is believed to have the higher WRC. This expectation was proved in DGS cases but showed to be uncertain in SS cases. When considering effects of water repellency, surface area and capillary water content on WRC together, multi-regression analysis was conducted. Reliable combined correlation was appeared to be found on all data between WRC and water repellency, specific surface area and capillary water content. However, when breaking the analysis down on only significant data or data that separated by soil/sand type, no reliable equation was found.

References

Dianyuan Dinga, Ying Zhaoa, Hao Fenga, Xinhua Peng, Bingcheng Si, 2016, Using the double-exponential water retention equation to determine how soil pore-size distribution is linked to soil texture, *Soil & Tillage Research*, 156 (2016) 119-130

Chapter 5

Water retention capacity of soil/sand mixed with/without organic-treated FA

5.1 Background

In the previous section, the effects of amending raw/apatite-synthesized FA with P/Ca ratio of 3.0, 7.1, 11.7 and 16.0 on WRC of soil/sand at room temperature/40 °C were considered. Factors that seemed to control WRC like surface morphology, particle size distribution, specific surface area, water repellency, capillary water content, and pF were analyzed. Although it still includes uncertainty, large impact of specific surface area, negligible impact of capillary water content, smaller and comparable impacts of water repellency and other unconsidered factors were suggested by multi-regression analysis.

On the other hand, organic matters have been reported as important for WHC (Bauer and Black, 1992; Hudson, 1994). Organic matters might be also important for WRC and one of unconsidered factors, suggested by multi-regression analysis, might be organic matters. In this chapter, 3 kinds of organic-added FA modification were tested. They are organic-treatment, organic-apatite treatment and organic-added thermal treatment.

The reason for utilizing organic-treatments like chitosan, sodium alginate and guanidine hydrochloride is all organic solutions are sticky and after drying organic-FA mixtures at 105 °C, more obvious organic structures, more FA-organic aggregation was expected.

Organic-apatite treatments were proposed for combined effect of apatite-synthesis with P/Ca ratio of 11.7 and organic treatments. Effect of mixing apatite-synthesized FA with P/Ca ratio of 11.7 is very promising on WRC of soil/sand. Combined treatments might lead to obvious change on surface morphology and have unexpected effect.

Further, in order to confirm effect of obvious porous organic structures on WRC, thermal treatments were conducted. Cellulose, starch and sucrose were utilized for building organic binding and for porous structure by high temperature thermal treatment. Effects of

these organic-added modifications on WRC would be discussed in this chapter. Surface morphology, water repellency, and capillary water content would be also investigated in terms of their effect on WRC.

5.2 Experimental conduction and analysis

5.2.1 Surface modification of FA by organic treatment

Organic treatments using chitosan, sodium alginate and guanidine hydrochloride were tested for FA. 200 g of FA were mixed with 80 ml of 2 wt% of chitosan solution (chitosan treatment), 1 wt% of sodium alginate (alginate treatment), or 61 mL of 3.87 wt% of guanidine hydrochloride (guanidine treatment), respectively. Organic solutions were simply mixed with raw FA. Distilled water was also mixed in order to keep the mixture constantly wet. After 24 hours, the mixture samples were dried at 105 °C for 24 hours to increase organic content on FA surface. After drying, samples were crushed softly and then utilized for WRC experiments.

5.2.2 Surface modification of FA by organic-apatite treatment

Organic-apatite treatments were tested for comparison with organic treatments. In organic-apatite treatments, saturated calcium hydroxide solution and sodium phosphate solution were used with 2 wt% chitosan solution, 1 wt% sodium alginate solution, or 3.87 wt% guanidine hydrochloride solution. 80 ml of chitosan/alginate solution or 61 ml of guanidine solution, 40 ml of calcium hydroxide solution and sodium phosphate solution were mixed with 200 g of FA at first. Distilled water was mixed in order to keep the mixture wet. All treated FA were kept for 24 hours at constant room temperature and then dried at 105 °C for over 24 hours. After drying, samples were crushed softly and then utilized for WRC experiments.

5.2.3 Surface modification of FA by organic-added thermal treatment

In order to build micro-pore structure on FA surface and modify surface properties of FA, organic-added thermal treatment was tried. Cellulose, starch and sucrose were tested as organic additives and sodium bicarbonate was used to form micro-pore structure during thermal treatment. The modification was conducted under 3 different conditions. The first

experimental set used 10 g of organic compounds (cellulose, sucrose, or starch) and 17.5 g of FA. After mixing them with pure water, the mixture was heated at 300 °C for 3 hours. In the second set, organic reagent was decreased to 1.75 g. Organic compounds used in this set were 17.5 g and the mixtures were heated at 300 °C for 1 hour. In the third set, 1.75 g of sodium bicarbonate and organic compounds were added into 17.5 g of FA and heated under the same condition with the second set. All treated FA were crushed softly before WRC measurement.

Details of experimental methods for conducting organic-added FA modification were shown in Table 5-1.

Table 5-1 Experimental methods for conducting organic-added FA modification

Treatments	Raw FA (g)	Organic (g)	Organic (ml)	Ca(OH) ₂ (ml)	Na ₃ PO ₄ (ml)	Rest (hr)	Dry (°C)	Dry time (hr)
Chitosan-treatment	200.00	—	80.00	—	—	24.00	105.00	24.00
Alginate-treatment	200.00	—	80.00	—	—	24.00	105.00	24.00
Guanidine-treatment	200.00	—	61.00	—	—	24.00	105.00	24.00
Chitosan-apatite treatment	200.00	—	80.00	40.00	40.00	24.00	105.00	24.00
Alginate-apatite treatment	200.00	—	80.00	40.00	40.00	24.00	105.00	24.00
Guanidine-apatite treatment	200.00	—	61.00	40.00	40.00	24.00	105.00	24.00
Organic-added thermal treated FA of set I	200.00	114.29	—	—	—	—	300.00	3.00
Organic-added thermal treated FA of set II	200.00	20.00	—	—	—	—	300.00	1.00
Organic-added thermal treated FA of set III	200.00	20.00	—	—	—	—	300.00	1.00

5.3 Results and discussion

5.3.1 Organic-treated FA

5.3.1.1 WRC of organic-treated FA

Water retention curves of organic-treated FA at room temperature and 40 °C are shown in Figure 5-1 and 5-2. WRC of soil/sand, raw FA and organic-treated FA at room temperature and 40 °C are shown in Figure 5-3 with error bars. At room temperature, similar with that in previous chapter, WRC of all samples, excluding guanidine-treated FA, at low temperature are similar because of low evaporation rate. On the other hand, guanidine-treated FA had WRC around 812 hr, which is about 15 % lower than others. Water retention curves shown in Figure 5-1 and 5-2 indicate that water evaporation rates of chitosan-treated FA was constant whole drying time. On the other hand, water evaporation rates of alginate-treated FA and guanidine-treated FA were relatively slower in the first 2 hours drying time and then constant. Water content left after 12 hours drying of guanidine-treated FA was lower than other organic-treated FA. It eventually caused lower WRC of guanidine-treated FA than those of other organic-treated FA.

At 40 °C, organic-treatments kept WRC of FA higher than those of DGS and AS. They are 886 hr for chitosan-treated FA, 917 hr for alginate-treated FA and 948 hr for guanidine-treated FA, respectively. WRC of guanidine-treated FA became higher than that at room temperature, unexpectedly. WRC of organic-treated FA are similar to the WRC of apatite-synthesized FA with P/Ca ratio of 11.7 at 40 °C. Water retention curves of organic-treated FA at room temperature and 40 °C were compared in Figure 5-1 and 5-2. Water retention curves of organic-treated FA were still identified as C type. On the other hand, water contents left after 12 hours drying of chitosan- and alginate-treated FA were lower than those at room temperature. It leads to lower WRC of chitosan- and alginate-treated FA at 40 °C than those at room temperature. Water content left after 12 hours drying of guanidine-treated FA was about 50 wt% and about 15 wt% higher than that at room temperature. It makes WRC of guanidine-treated FA at 40 °C higher than that at room temperature. As the same with apatite-synthesized FA with P/Ca of 11.7, mixing organic-treated FA into soil/sand is expected to increase WRC of soil/sand.

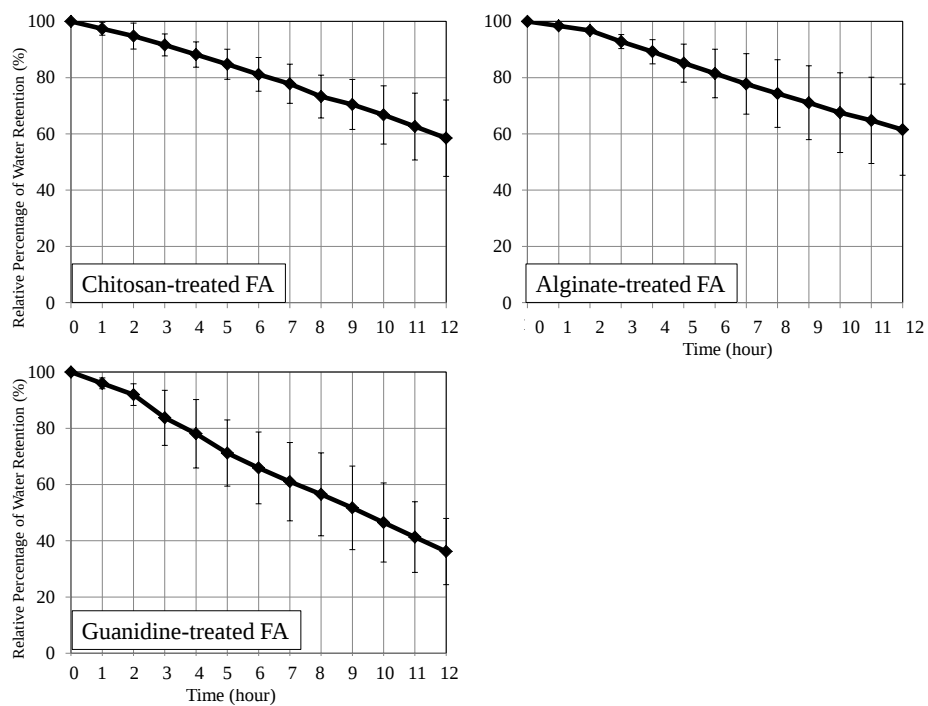


Figure 5-1 Water retention curves of organic-treated FA at room temperature

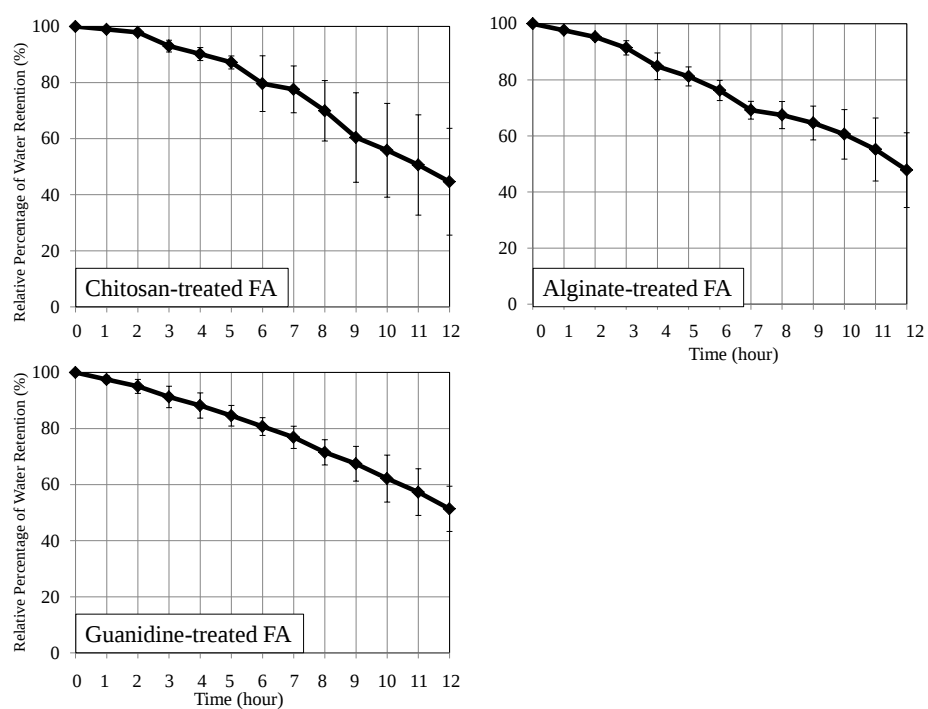


Figure 5-2 Water retention curves of organic-treated FA at 40 °C

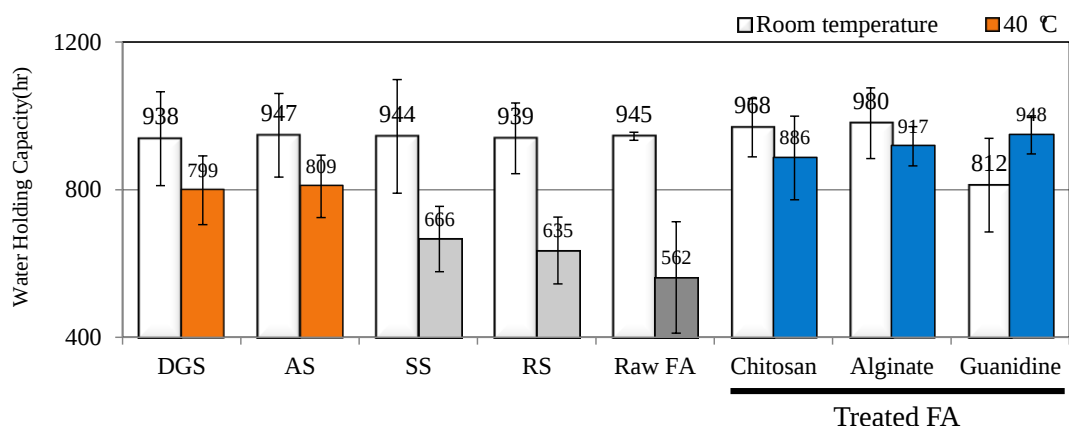


Figure 5-3 WRC of pure soil/sand, raw FA and organic treated FA

5.3.1.2 WRC of soil/sand amended with organic-treated FA at room temperature

Water retention curves of soil/sand mixed with organic-treated FA at room temperature are shown in Figure 5-4 to 5-12. WRC of soil/sand mixed with organic-treated FA at room temperature are shown in Figure 5-13 to 5-16 with error bars and summarized in Table 5-2. When mixing soil/sand with chitosan-treated FA, WRC of soil/sand increased slightly. Increase of WRC were 5.0 % for DGS, 3.8 % for AS, 3.6 % for SS and 4.9 % for RS, respectively. However, statistical analysis suggests that their increases are insignificant within experimental errors. According to water retention curves in Figure 5-4 to 5-6, all water retention curves were identified as type C and water evaporated at constant rates. When comparing them to water retention curves of soil/sand at room temperature (see Figure 3-1), all water retention curves were quite similar and residual water content after 12 hours drying time were almost the same. This supports that chitosan-treated FA has no effect on WRC of soil/sand at room temperature.

Alginate-treated FA also apparently increase WRC of soil/sand. WRC increases are 5.8 % for DGS, 6.4 % for AS, 3.9 % for SS and 6.4 % for RS, respectively. However, these WRC changes were still regarded to be insignificant. According to Figure 5-7 to 5-9, water evaporation rates of soil/sand mixed with alginate-treated FA were constant. Water retention curves of soil/sand mixed with alginate-treated FA were identified as type C. When comparing water retention curves of soil/sand mixed with alginate-treated FA to those of pure soil/sand (see Figure 3-1), all water retention curves were quite similar and residual water

content left in soil system after 12 hours drying were almost the same. This resulted in insignificant effect of amending alginate-treated FA on WRC of soil/sand at room temperature.

Guanidine-treated FA decreased WRC of soil/sand at room temperature. WRC decreases are 16.0 % for DGS, 18.3 % for AS, 17.5 % for SS and 12.7 % for RS, respectively. However, these WRC variations were also regarded as insignificant again (except for WRC of SS mixed with guanidine-treated FA). According to water retention curves of soil/sand mixed with guanidine-treated FA (see Figure 5-10 to 5-12), all water retention curves were similar with each other. Water evaporation rates of soil/sand mixed with guanidine-treated FA were constant. In addition, water contents after 12 hours drying were all around 12 wt%. However, residual water contents of soil/sand mixed with guanidine-treated FA were obviously lower than those of pure soil/sand at room temperature (see Figure 3-1).

As summarized in Table 5-2, no significant effect was found for mixing chitosan- and alginate-treated FA on WRC of soil/sand at room temperature. Although amendment of guanidine-treated FA is also regarded to be insignificant on WRC of DGS, AS and RS, it significantly decreased WRC of SS by promoting water evaporation rate whole drying time.

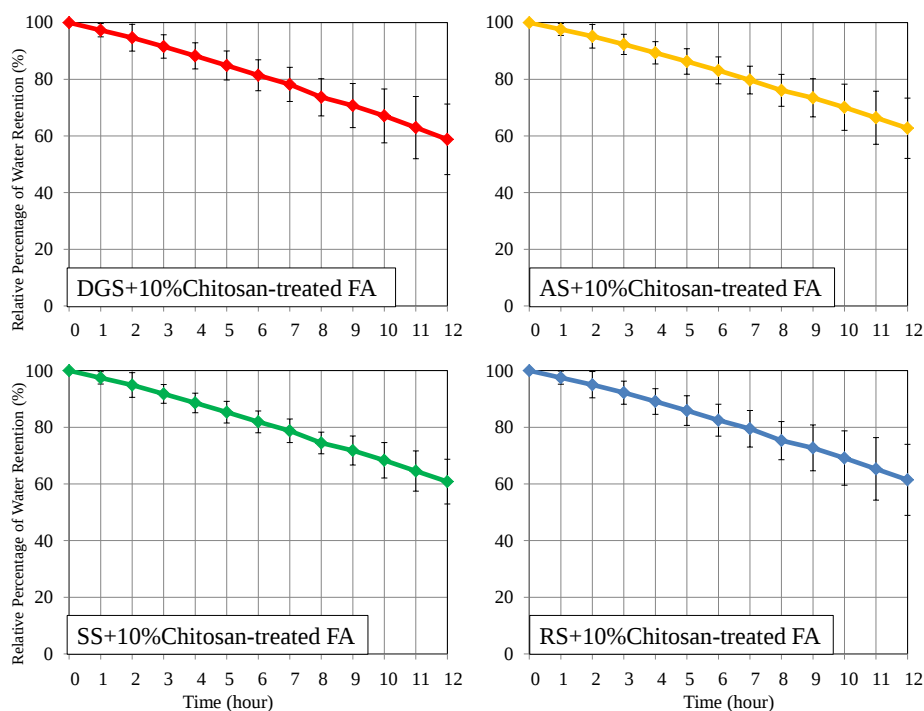


Figure 5-4 Water retention curves of DGS, AS, SS and RS mixed with chitosan-treated FA at 10 wt% mixing ratio and room temperature

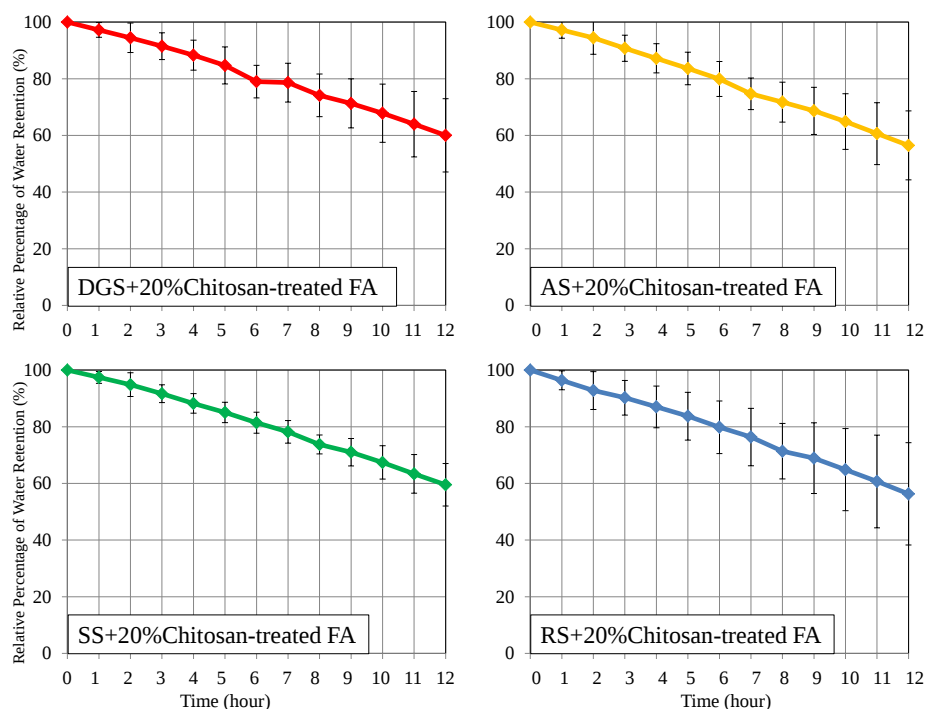


Figure 5-5 Water retention curves of DGS, AS, SS and RS mixed with chitosan-treated FA at 20 wt% mixing ratio and room temperature

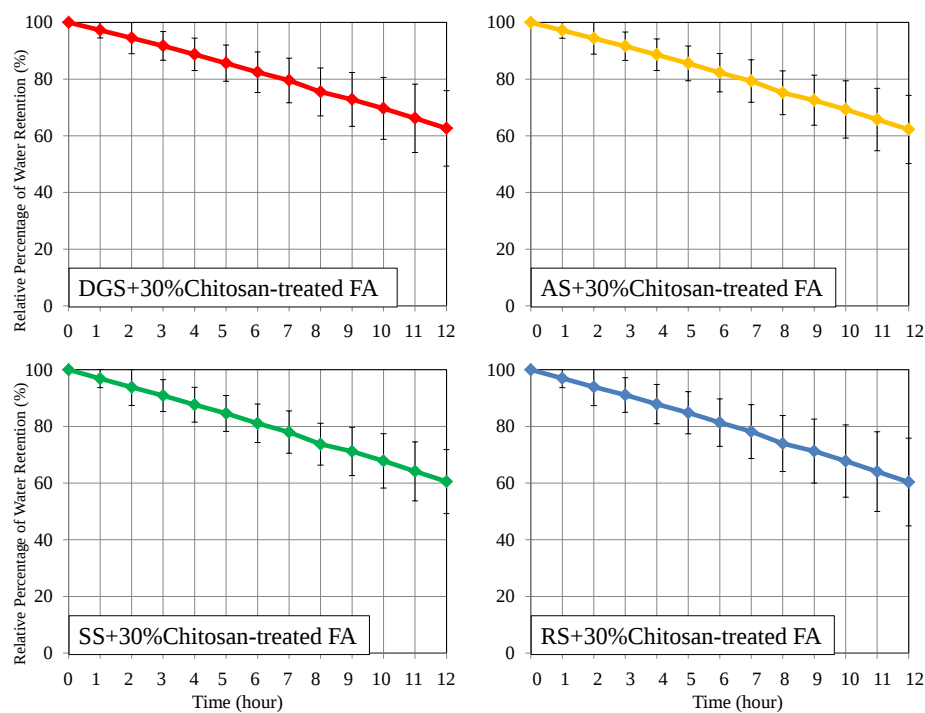


Figure 5-6 Water retention curves of DGS, AS, SS and RS mixed with chitosan-treated FA at 30 wt% mixing ratio and room temperature

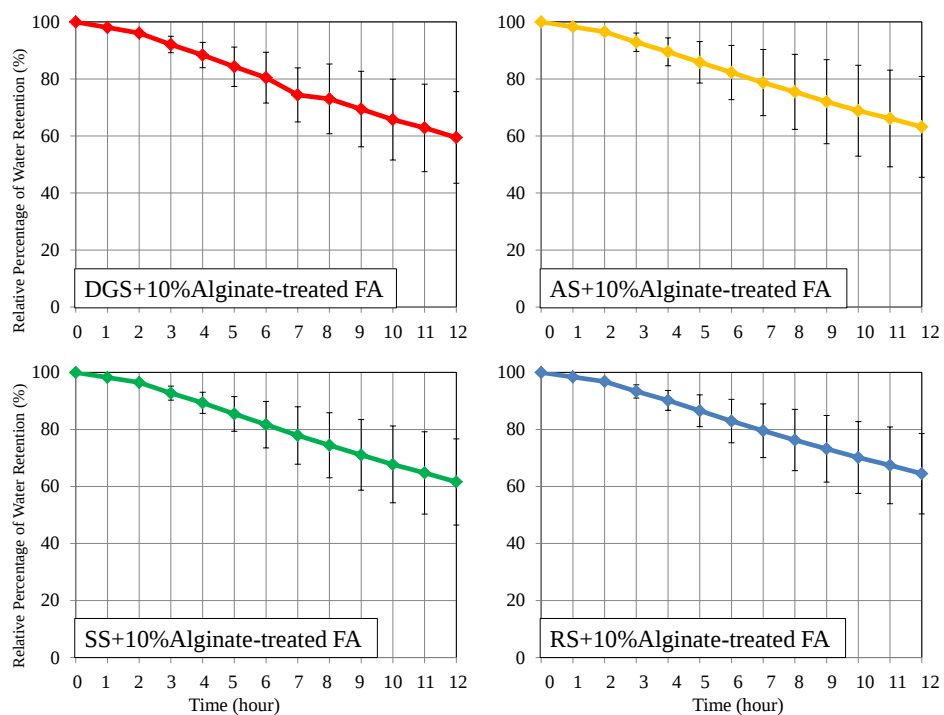


Figure 5-7 Water retention curves of DGS, AS, SS and RS mixed with alginate-treated FA at 10 wt% mixing ratio and room temperature

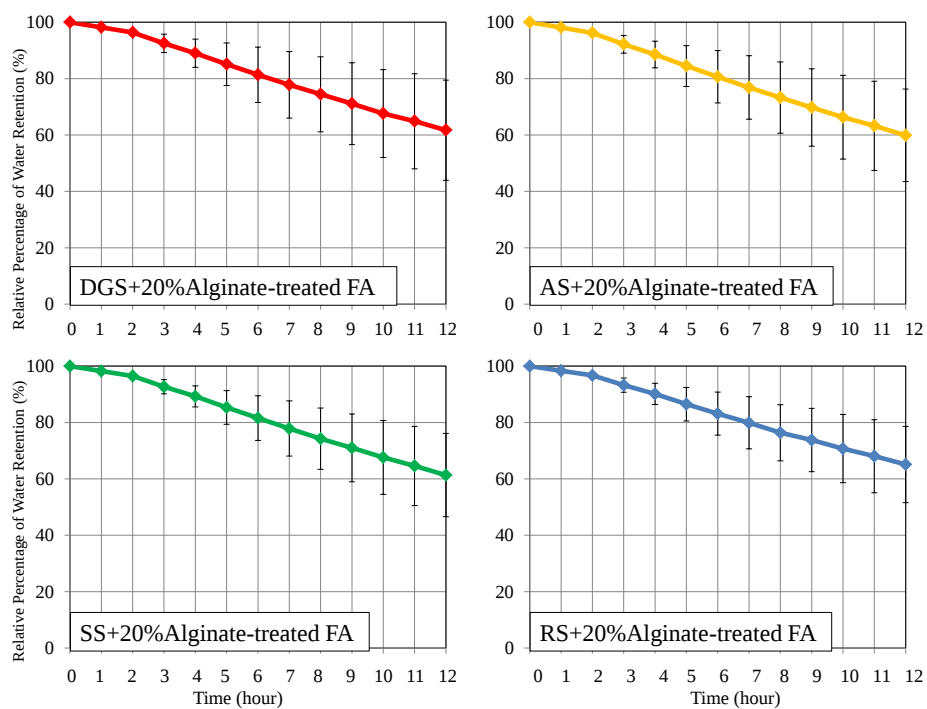


Figure 5-8 Water retention curves of DGS, AS, SS and RS mixed with alginate-treated FA at 20 wt% mixing ratio and room temperature

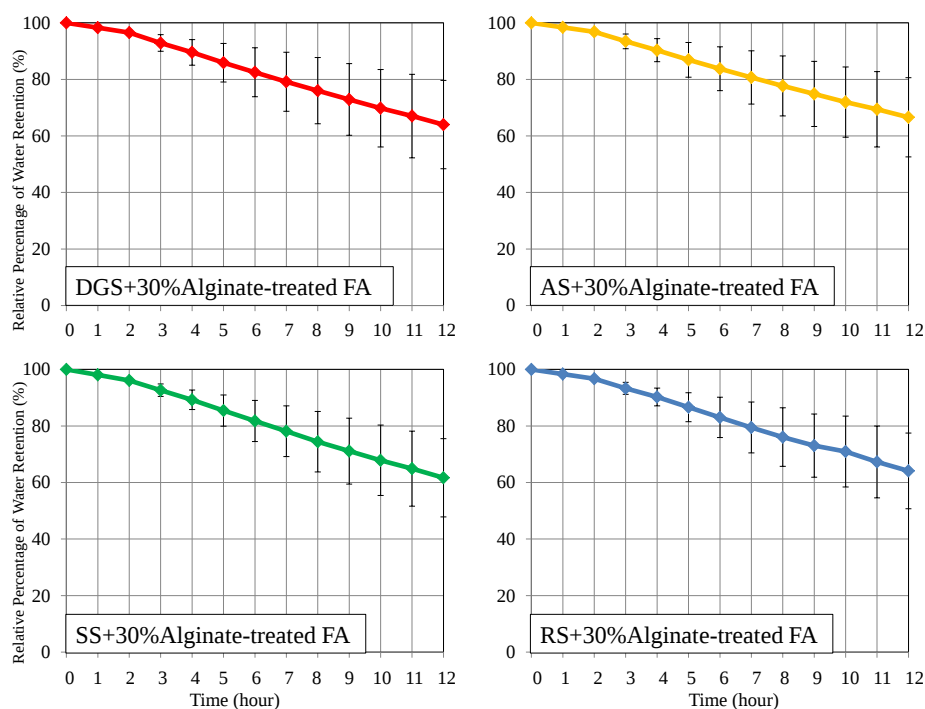


Figure 5-9 Water retention curves of DGS, AS, SS and RS mixed with alginate-treated FA at 30 wt% mixing ratio and room temperature

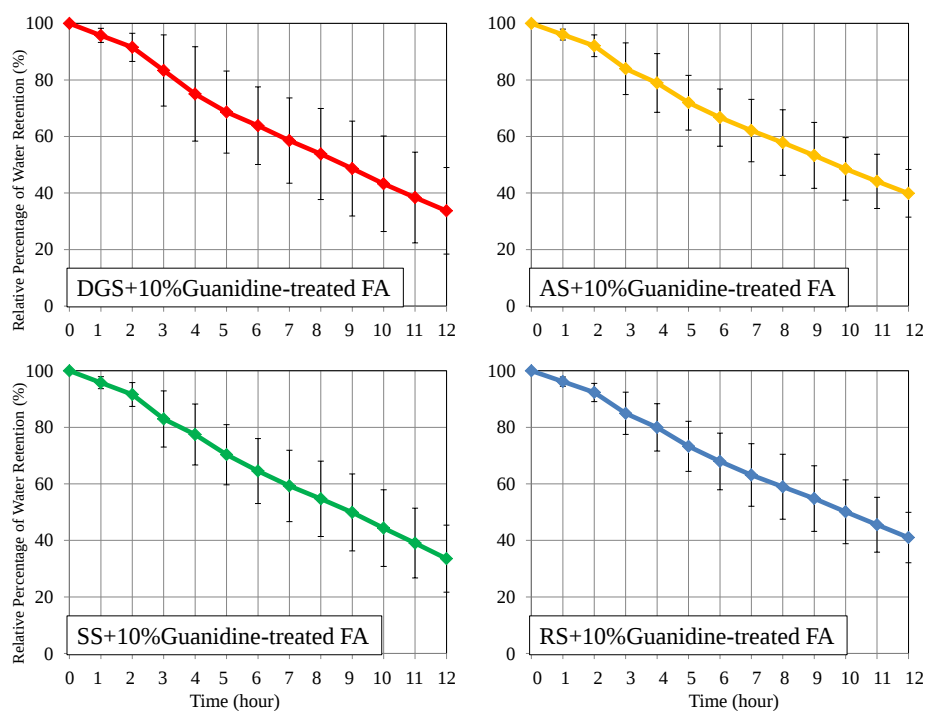


Figure 5-10 Water retention curves of DGS, AS, SS and RS mixed with guanidine-treated FA at 10 wt% mixing ratio and room temperature

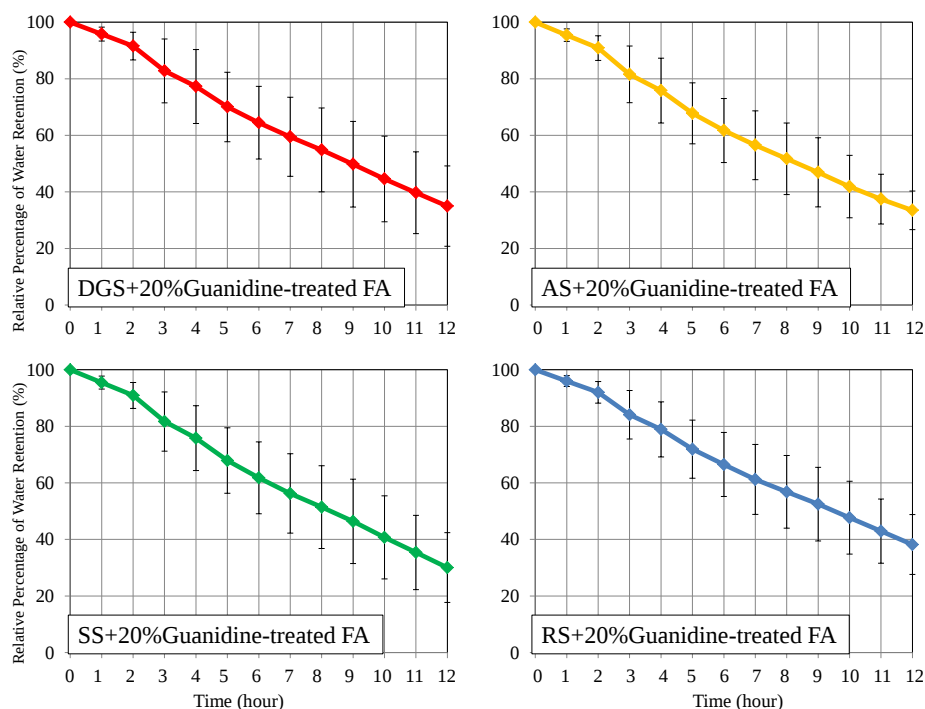


Figure 5-11 Water retention curves of DGS, AS, SS and RS mixed with guanidine-treated FA at 20 wt% mixing ratio and room temperature

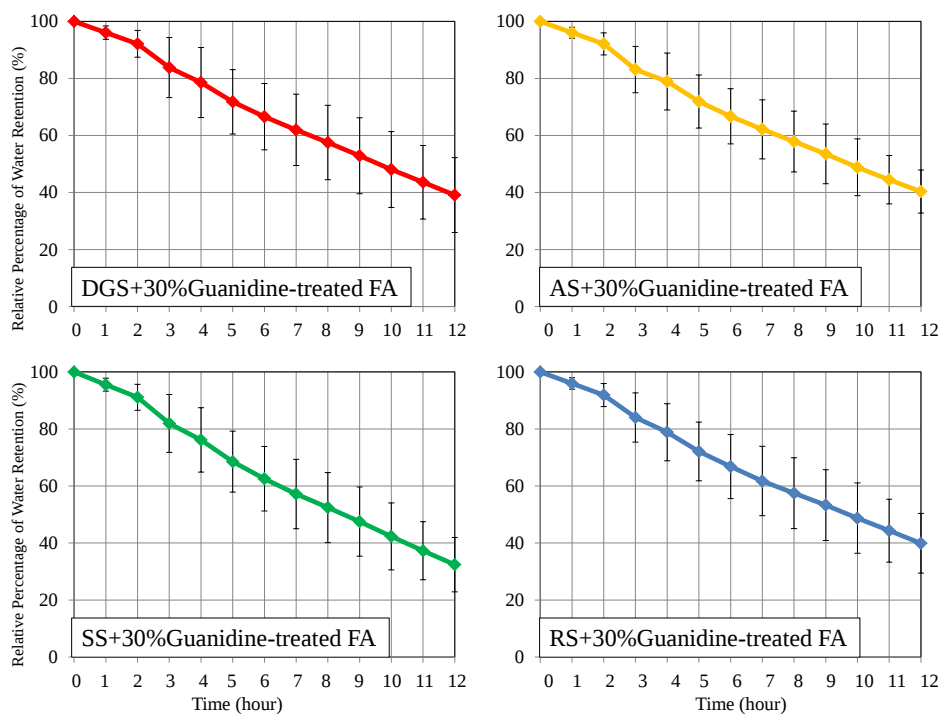


Figure 5-12 Water retention curves of DGS, AS, SS and RS mixed with guanidine-treated FA at 30 wt% mixing ratio and room temperature

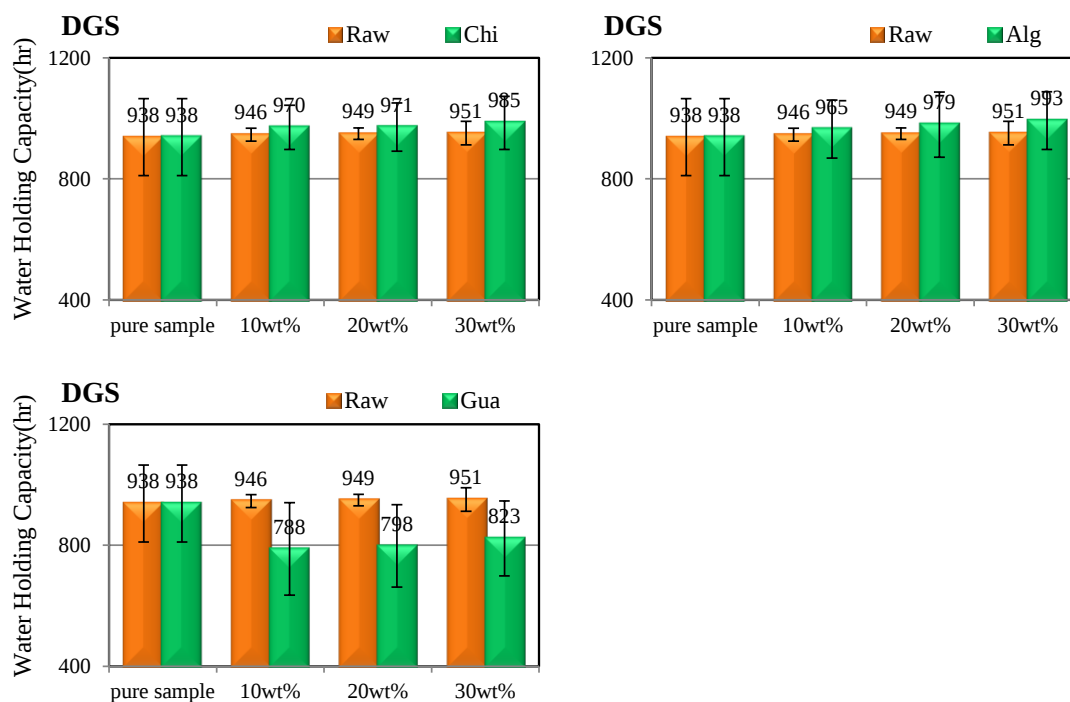


Figure 5-13 WRC of DGS mixed with raw FA or organic treated FA at room temperature

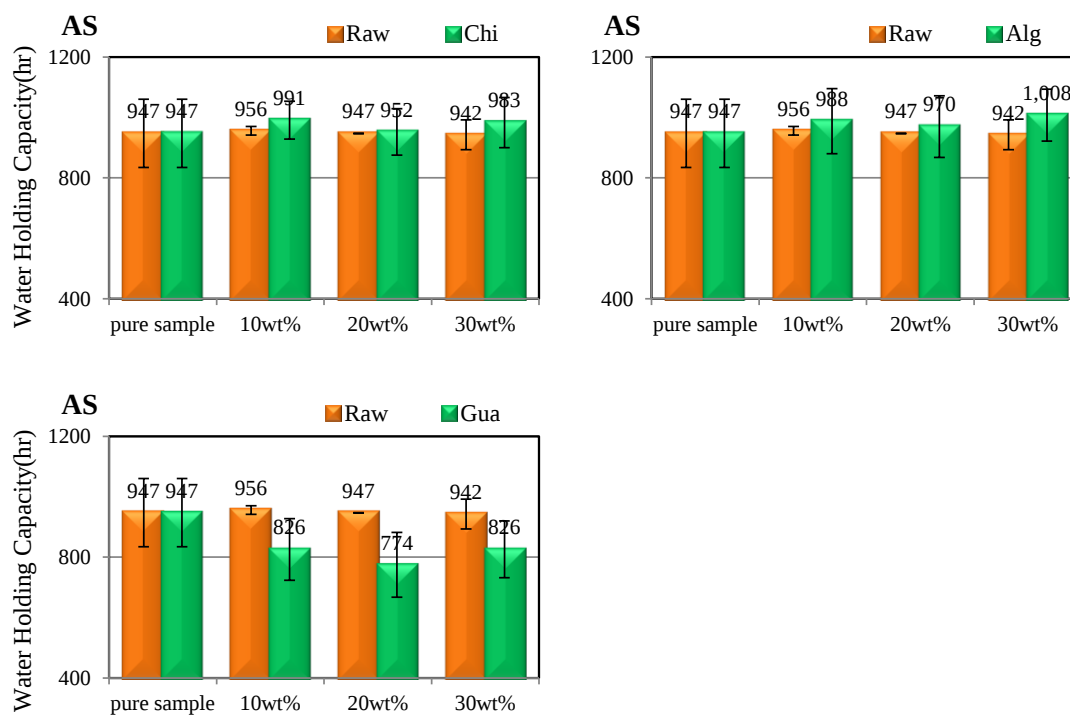


Figure 5-14 WRC of AS mixed with raw FA or organic treated FA at room temperature

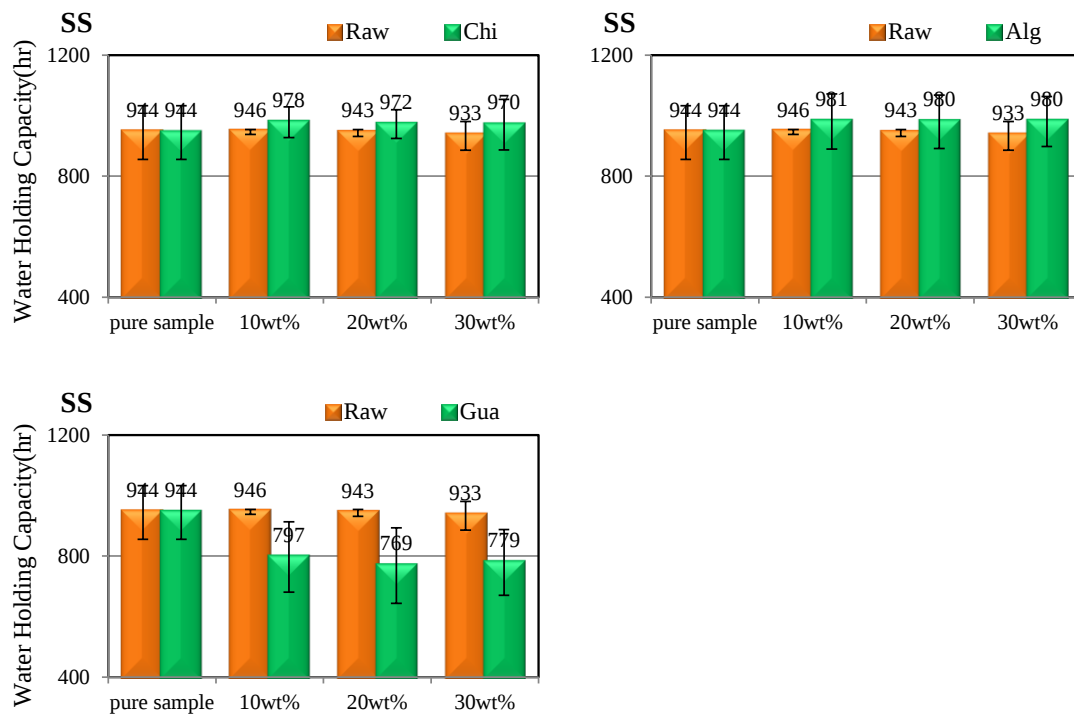


Figure 5-15 WRC of SS mixed with raw FA or organic treated FA at room temperature

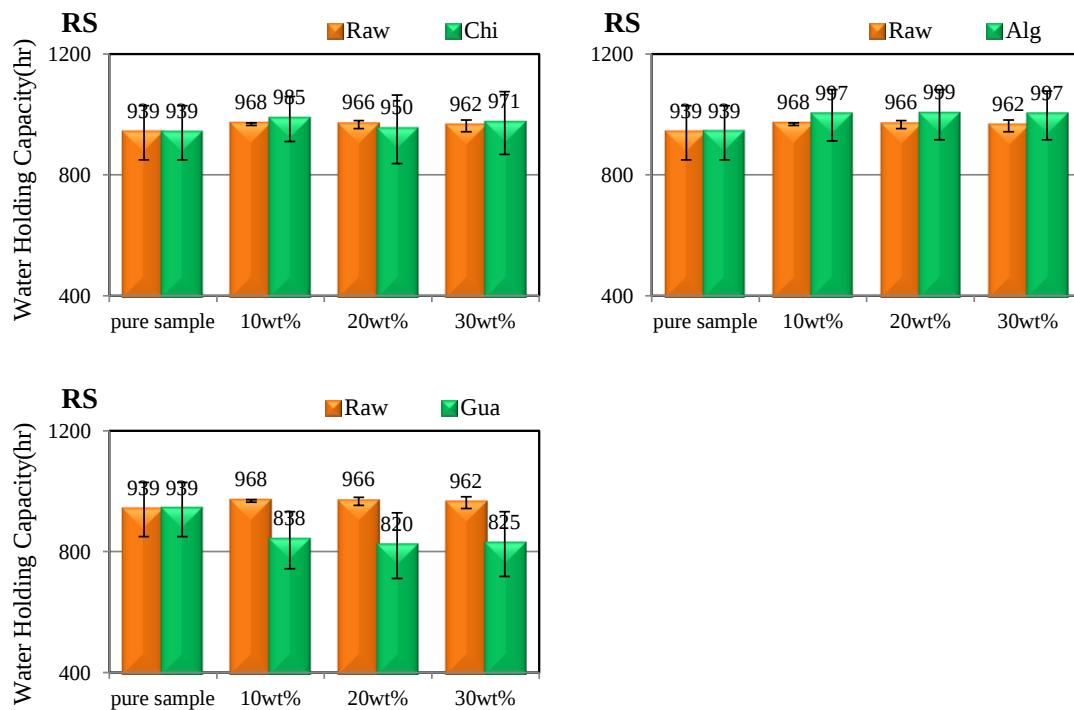


Figure 5-16 WRC of RS mixed with raw FA or organic treated FA at room temperature

Table 5-2 Summary of WRC of soil/sand mixed with organic-treated FA at room temperature

Flay ash		Room temperature			
		DGS	AS	SS	RS
Raw FA		—	—	—	—
Organic-treatment	Chitosan	—	—	—	—
	Alginate	—	—	—	—
	Guanidine	—	—	-17.5%*	—

All data was conducted by t-test, and “*” stand to “p value < 0.05”, “**” stand to “p value < 0.01” of t-test.

5.3.1.3 WRC of organic-treated FA-amended samples at 40 °C

Water retention curves of soil/sand mixed with organic-treated FA at 40 °C are shown in Figure 5-17 to 5-25. WRC of soil/sand mixed with organic-treated FA at 40 °C are shown in Figure 5-26 to 5-29 with error bars and summarized in Table 5-3.

At 40 °C, WRC of DGS and AS increased by 10.6 % and 6.9 %, respectively when chitosan-treated FA is mixed. WRC of SS and RS decreased by 5.3 % and 2.5 %, respectively. As shown in Figure 5-17 to 5-19, water retention curves of soil/sand mixed with chitosan-treated FA changed a lot from that of pure soil/sand at 40 °C. This means that water evaporation properties of soil/sand were changed by mixing chitosan-treated FA. Water retention curves of soil/sand mixed with chitosan-treated FA between different mixing ratios were quite similar. This suggests that mixing ratio dependency is not clear. Figure 5-30 shows the comparison between water retention curves of pure soil/sand and soil/sand mixed with chitosan-treated FA at 30 wt% mixing ratio and 40 °C. It is obvious that water retention curves of DGS and AS with chitosan-treated FA are higher than those of pure DGS and AS, respectively. Water retention curves of soils with chitosan-treated FA are categorized as type C_u. Water content left after 12 hours drying were also higher than those of pure DGS and AS. Although mixing chitosan-treated FA apparently increased WRC of DGS and AS, it was regarded as insignificant by t-test. In the case of SS, water retention curve of SS with chitosan-treated FA is lower than that of SS in the whole water evaporation process, in particular from 4 to 10 hours. Water retention curves of SS with chitosan-treated FA are categorized as type S_C. This suggests that chitosan-treated FA amendment promoted water evaporation especially from 4 to 10 hours drying time and thus decreased WRC of SS beyond

experimental errors. In the case of RS, water evaporated as the same with pure RS until 8 hours drying time when chitosan-treated FA was amended. Water evaporation in RS with chitosan-treated FA suddenly became slower than that of RS. Residual water content left after 12 hours of FA-amended RS was higher than that of pure RS. Water retention curves of RS with chitosan-treated FA are categorized as type S_u . This suggests that amendment of chitosan-treated FA inhibit water evaporation at late drying stage and thus decreased WRC of RS beyond experimental errors.

When mixing alginate-treated FA into soil/sand at 40 °C, WRC of soils were increased and WRC of sands were decreased (see Figure 5-26 to 5-29). All variations of WRC were regarded as significant (except for WRC of AS mixed with alginate-treated FA). According to Figure 5-20 to 5-22 and 5-31, water evaporation rate of DGS mixed with alginate-treated FA was higher than that of pure DGS at 40 °C in all evaporating process and the residual water content was higher than that of pure DGS. Water retention curves of DGS with alginate-treated FA is categorized as type C_u . This means that mixing alginate-treated FA inhibited water evaporation whole drying time and thus increased WRC of DGS beyond experimental errors. For AS mixed with alginate-treated FA, both water evaporation rate and water content left after 12 hours were slightly higher than that of pure AS (see Figure 5-20 to 5-22 and Figure 3-2). Water retention curves of AS with alginate-treated FA is also categorized as type C_u . However, WRC of AS was not significantly influenced by mixing alginate-treated FA. For SS and RS mixed with alginate-treated FA, water evaporation was not changed with/without alginate-treated FA amendment until the first 3 hours. However, it became faster than those in pure SS and RS. Water content reached to adhesive water zone at around 6 hours and evaporation rate was almost 0. Water retention curves of SS and RS with alginate-treated FA are categorized as type S_u . Amendment of alginate-treated FA promoted water evaporation at middle drying stage (3 to 9 hours) and thus decreased WRC of SS and RS at 40 °C beyond experimental errors.

For guanidine-treated FA, its amendment effects on WRC of DGS and AS are insignificant. On the other hand, it significantly decreased WRC of SS and RS by 18.3 % and 25.7 %, respectively (see Figure 5-26 to 5-29). Water retention curves of soil/sand mixed with guanidine-treated FA were shown in Figure 5-23 to 5-25 and 5-32. For DGS mixed with

guanidine-treated FA, water retention curves were similar with those of DGS mixed with chitosan- and alginate-treated FA at 40 °C. This supposes that WRC of soils should be increased by guanidine-treated FA. However, t-test suggested that those effects were insignificant owing to large experimental errors. For water retention curves of sands mixed with guanidine-treated FA, water evaporated faster than pure sands until 8 hours at 40 °C. Water content left after 12 hours drying of SS with guanidine-treated FA was almost the same with that of pure SS. On the other hand, residual water content of RS with guanidine-treated FA was higher than that of pure RS. Water retention curves of SS with guanidine-treated FA and RS with guanidine-treated FA are categorized as type L_c and L_u , respectively. Amendment of guanidine-treated FA promoted water evaporation until 8 hours and makes capillary water evaporated out. It decreased WRC of SS and RS significantly at 40 °C.

As summarized in Table 5-3, organic-treated FA amendments are insignificant on WRC of soils at 40 °C except for positive effect of alginate-treated FA on WRC of DGS. In contrast, organic-treated FA amendments promoted water evaporation and thus decreased WRC of sands beyond experimental errors.

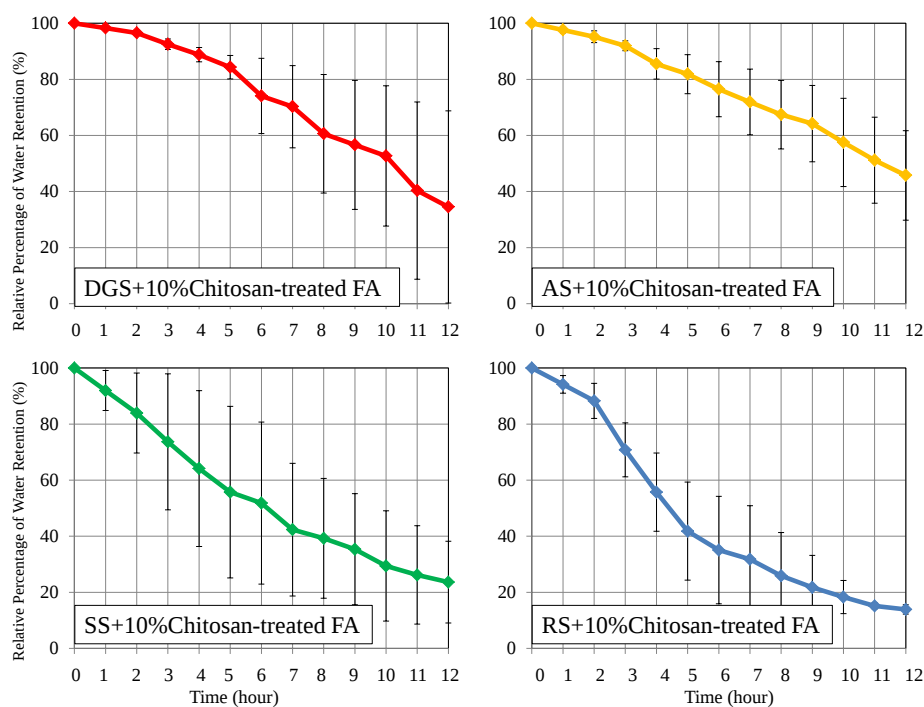


Figure 5-17 Water retention curves of DGS, AS, SS and RS mixed with chitosan-treated FA at 10 wt% mixing ratio and 40 °C

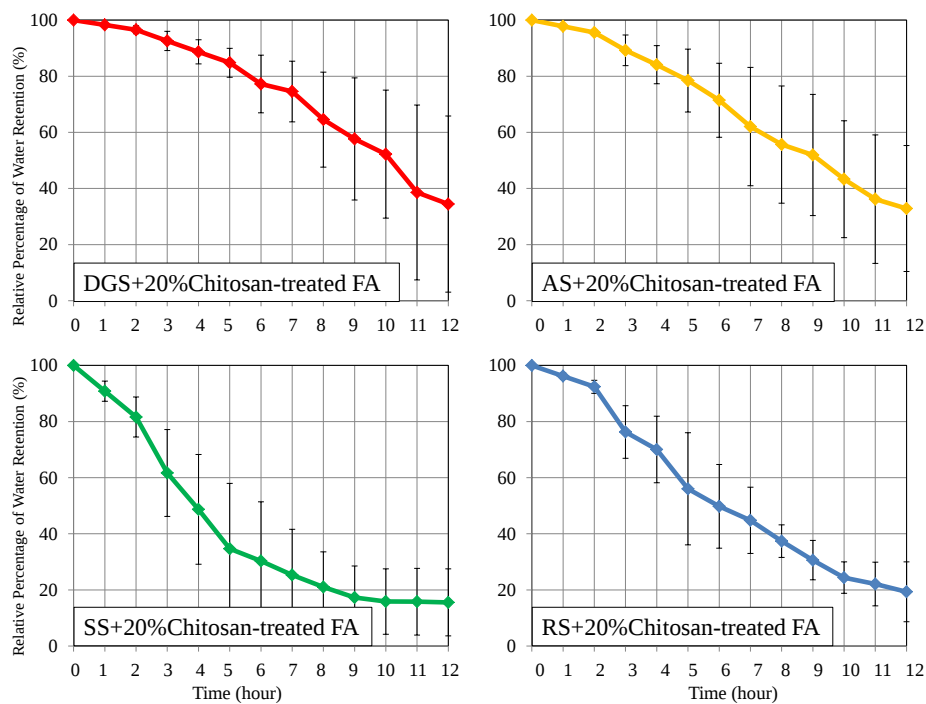


Figure 5-18 Water retention curves of DGS, AS, SS and RS mixed with chitosan-treated FA at 20 wt% mixing ratio and 40 °C

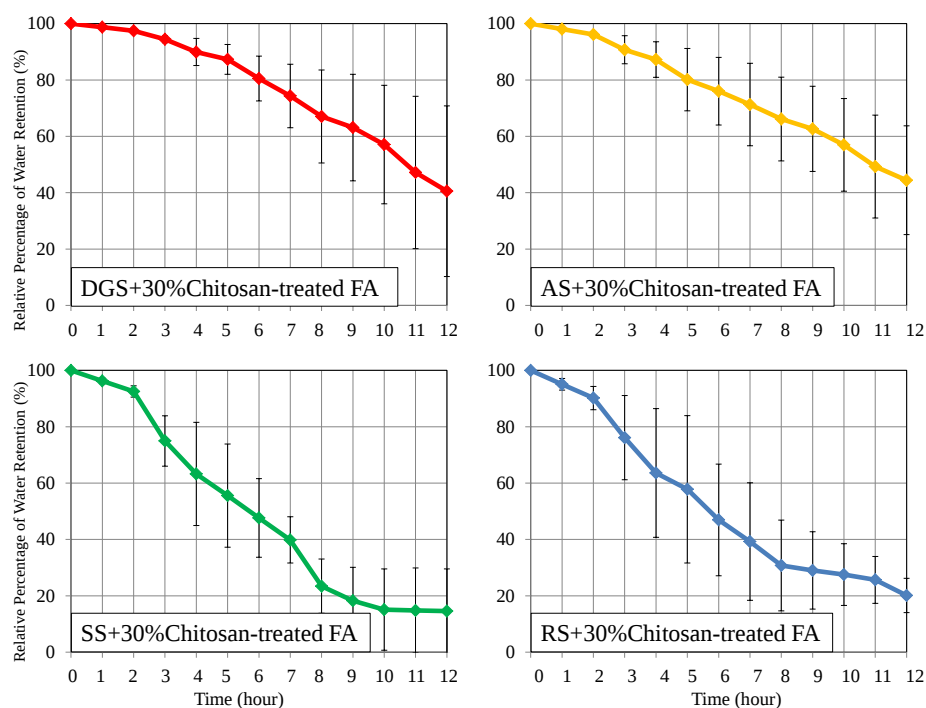


Figure 5-19 Water retention curves of DGS, AS, SS and RS mixed with chitosan-treated FA at 30 wt% mixing ratio and 40 °C

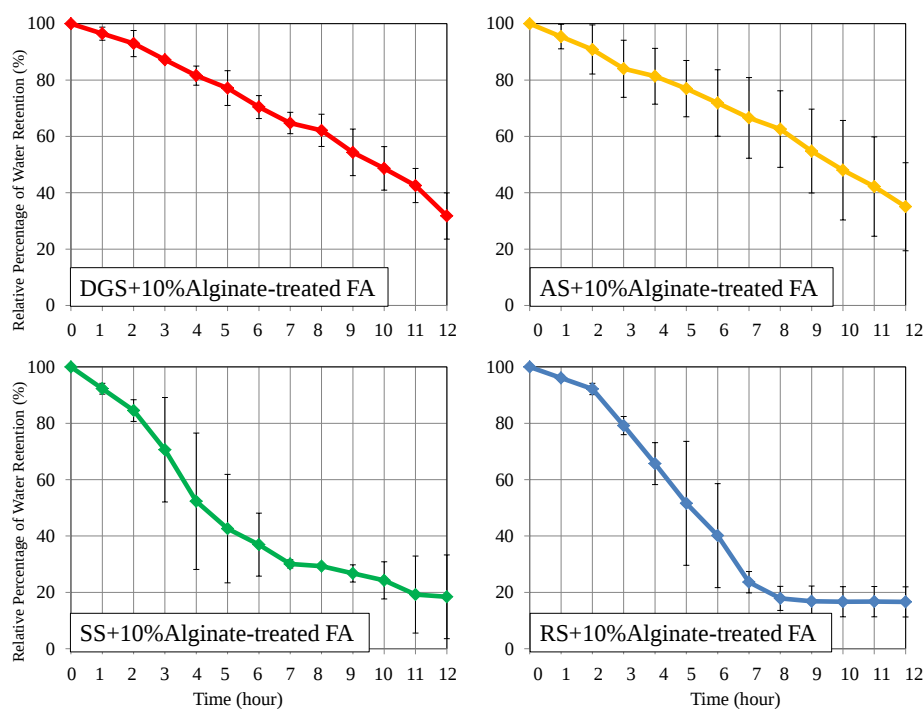


Figure 5-20 Water retention curves of DGS, AS, SS and RS mixed with alginate-treated FA at 10 wt% mixing ratio and 40 °C

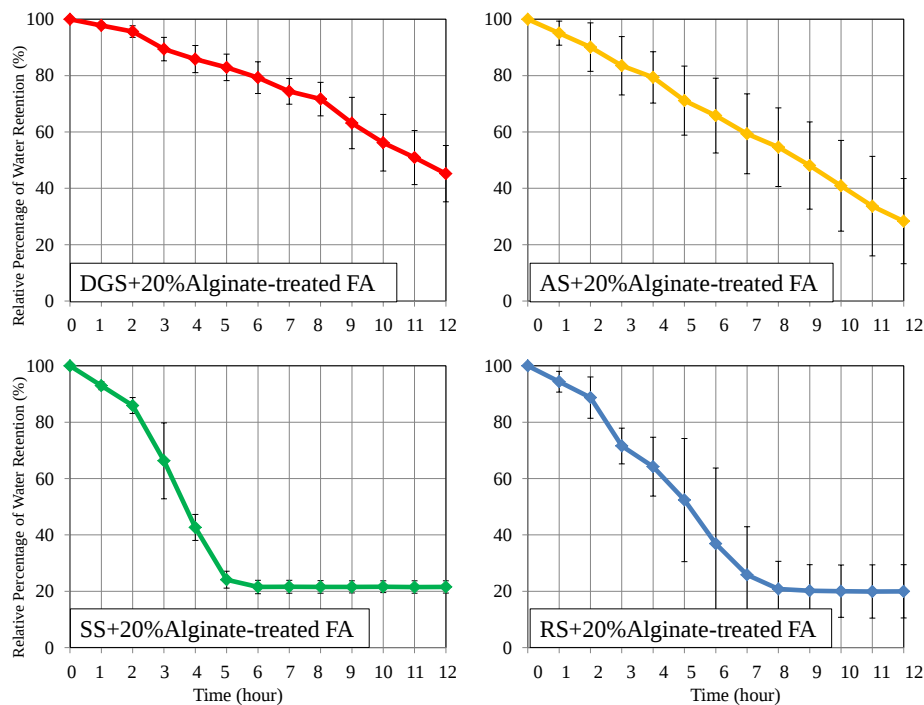


Figure 5-21 Water retention curves of DGS, AS, SS and RS mixed with alginate-treated FA at 20 wt% mixing ratio and 40 °C

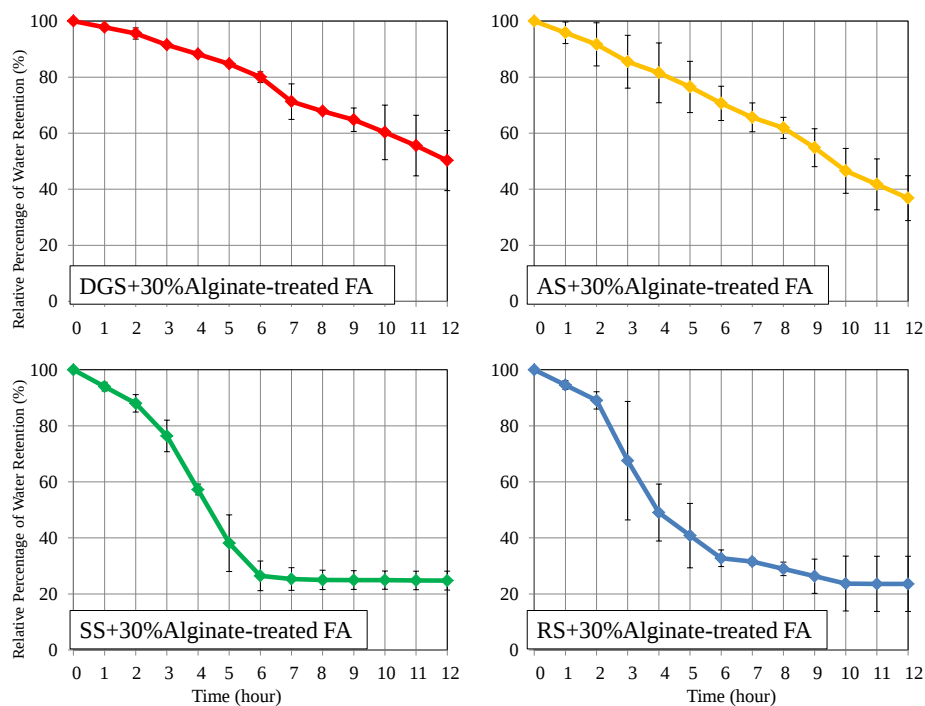


Figure 5-22 Water retention curves of DGS, AS, SS and RS mixed with alginate-treated FA at 30 wt% mixing ratio and 40 °C

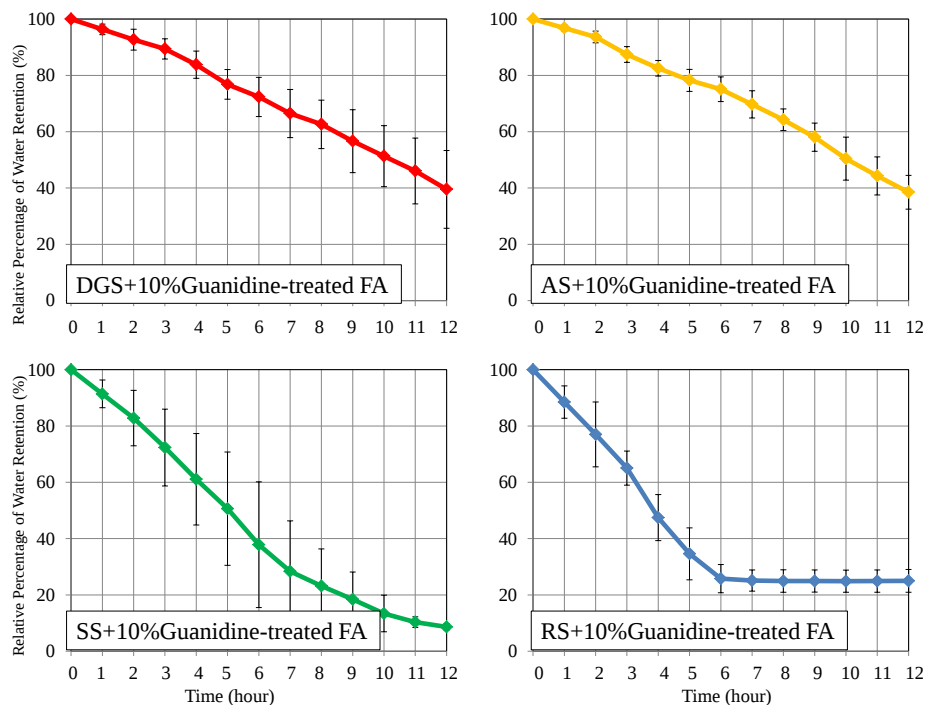


Figure 5-23 Water retention curves of DGS, AS, SS and RS mixed with guanidine-treated FA at 10 wt% mixing ratio and 40 °C

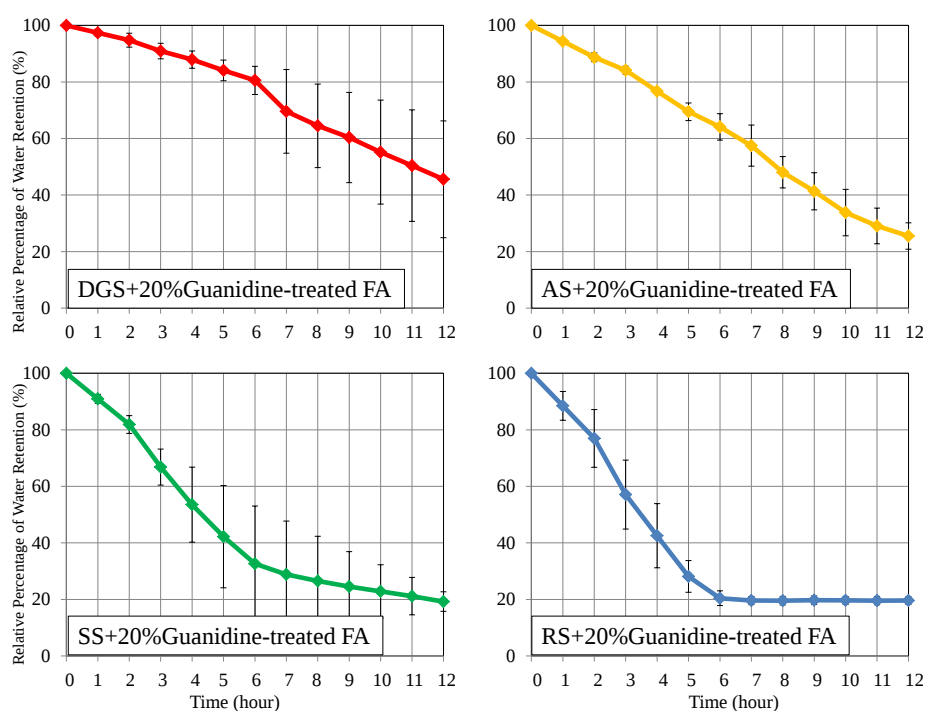


Figure 5-24 Water retention curves of DGS, AS, SS and RS mixed with guanidine-treated FA at 20 wt% mixing ratio and 40 °C

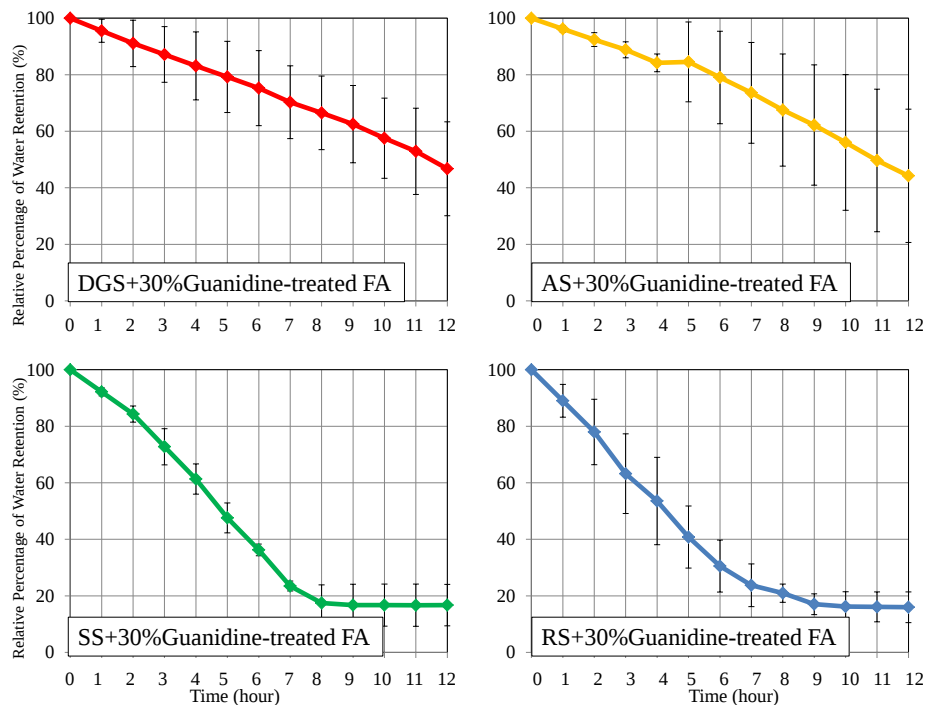


Figure 5-25 Water retention curves of DGS, AS, SS and RS mixed with guanidine-treated FA at 30 wt% mixing ratio and 40 °C

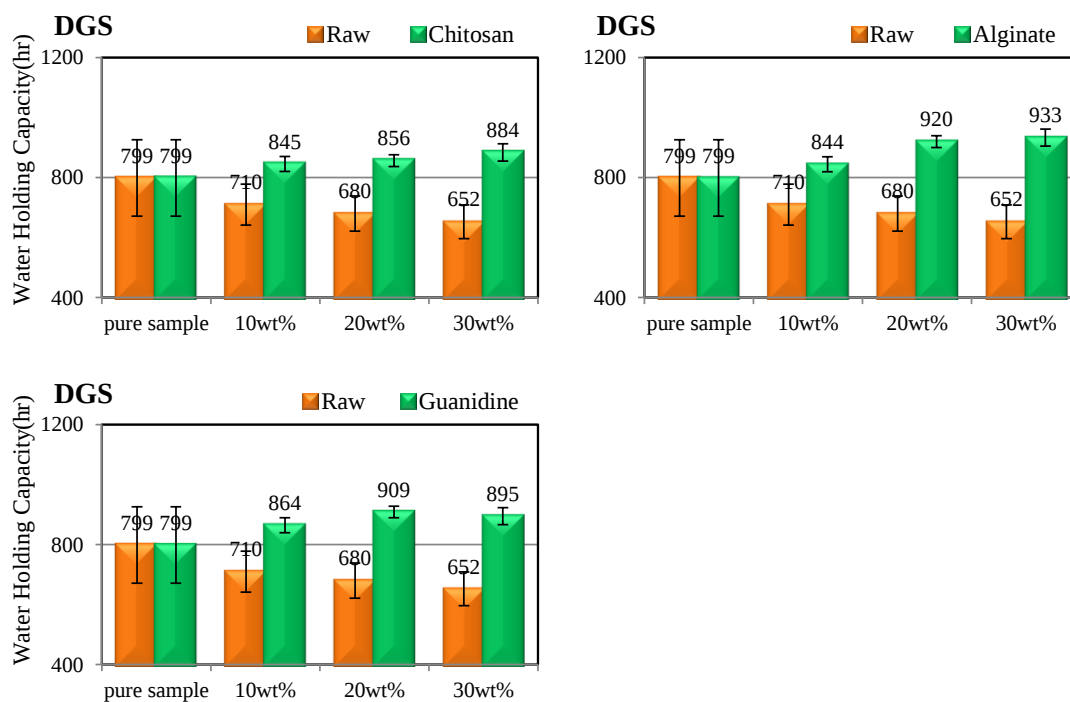


Figure 5-26 WRC of DGS mixed with raw FA or organic treated FA at 40 °C

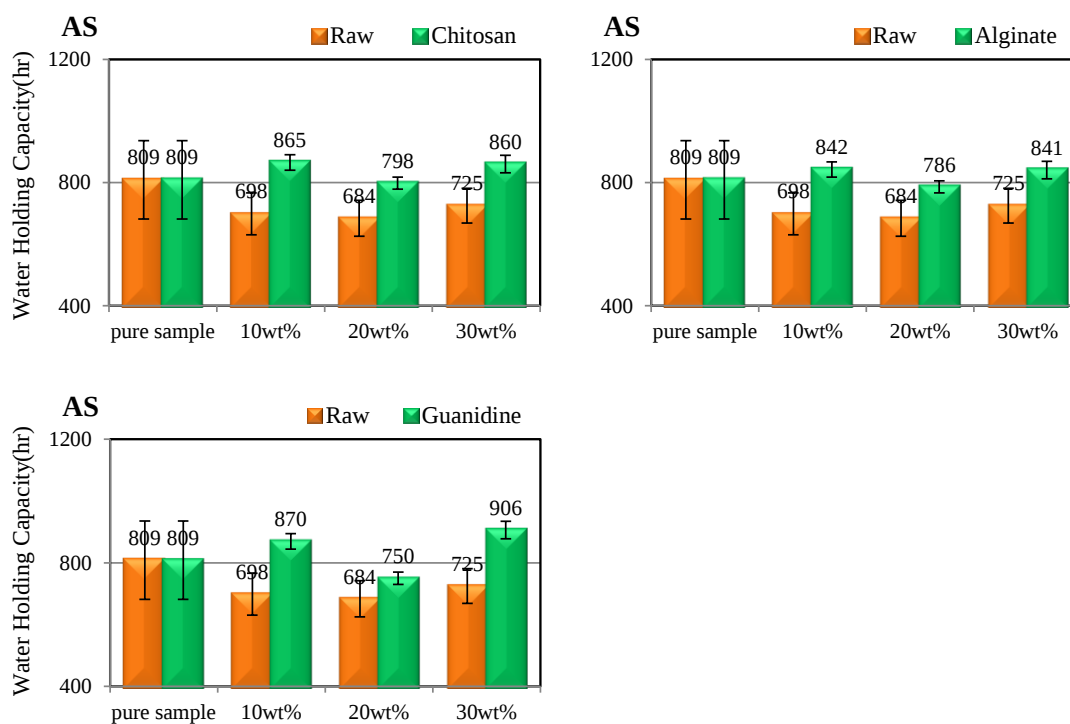


Figure 5-27 WRC of AS mixed with raw FA or organic treated FA at 40 °C

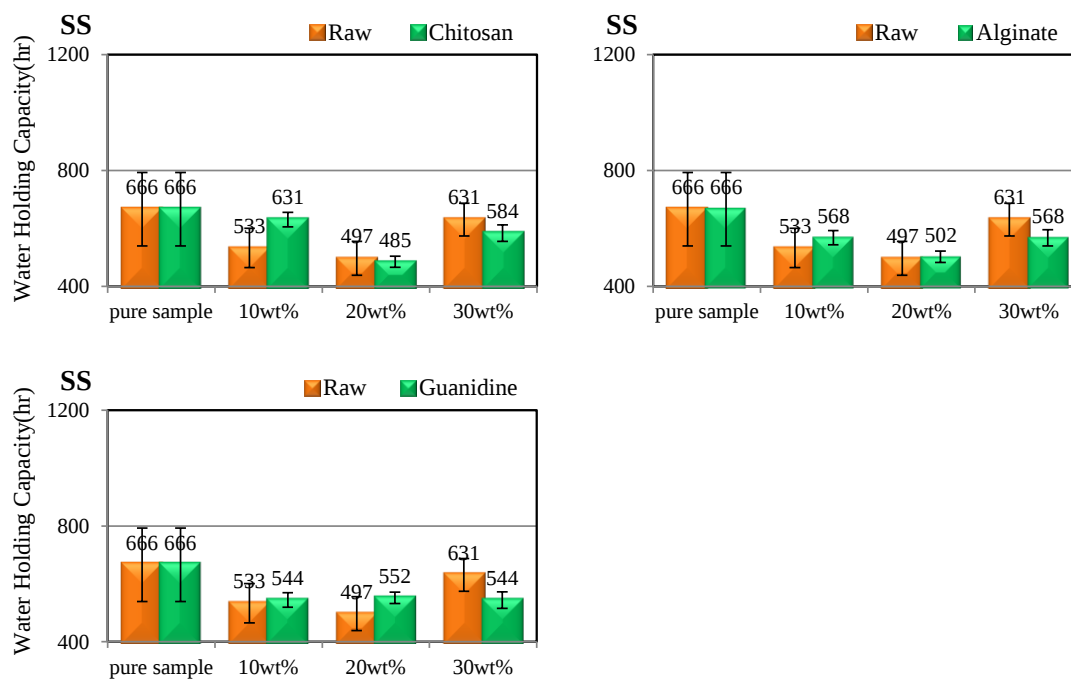


Figure 5-28 WRC of SS mixed with raw FA or organic treated FA at 40 °C

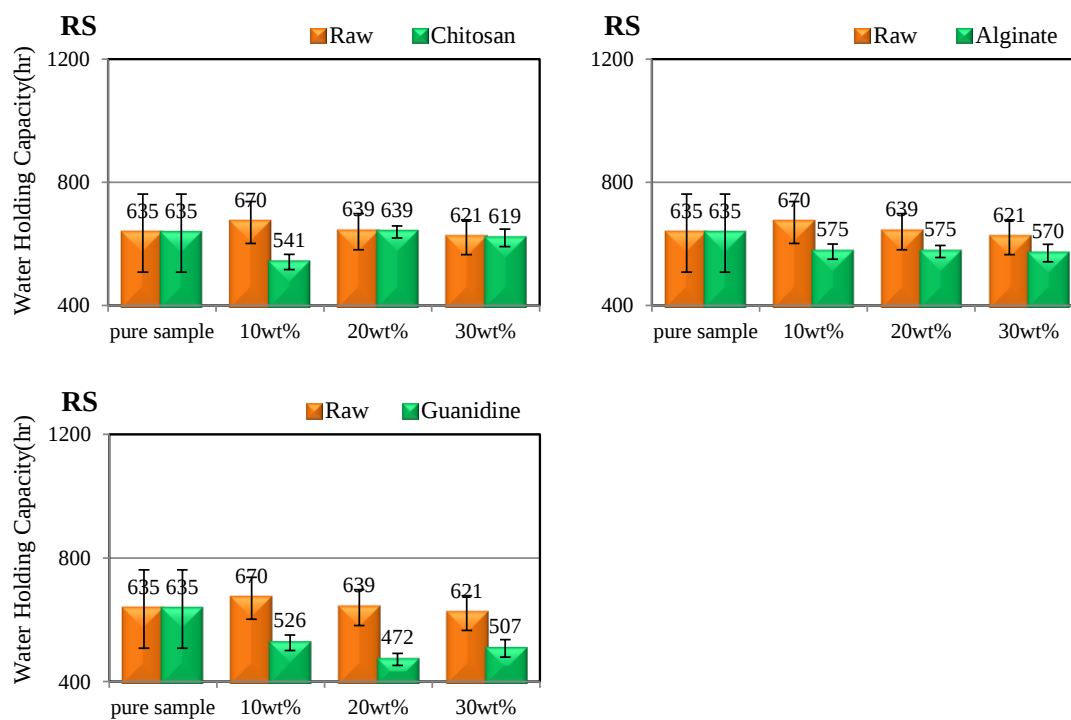


Figure 5-29 WRC of RS mixed with raw FA or organic-treated FA at 40 °C

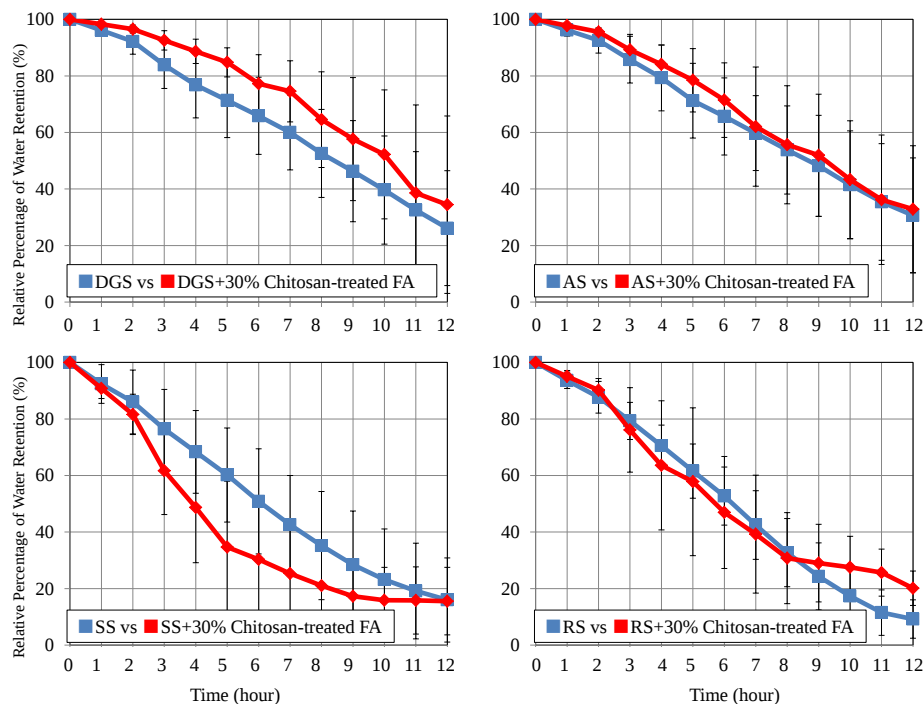


Figure 5-30 Comparison between water retention curves of soil/sand and soil/sand mixed with chitosan-treated FA at 30 wt% of mixing ratio and 40 °C

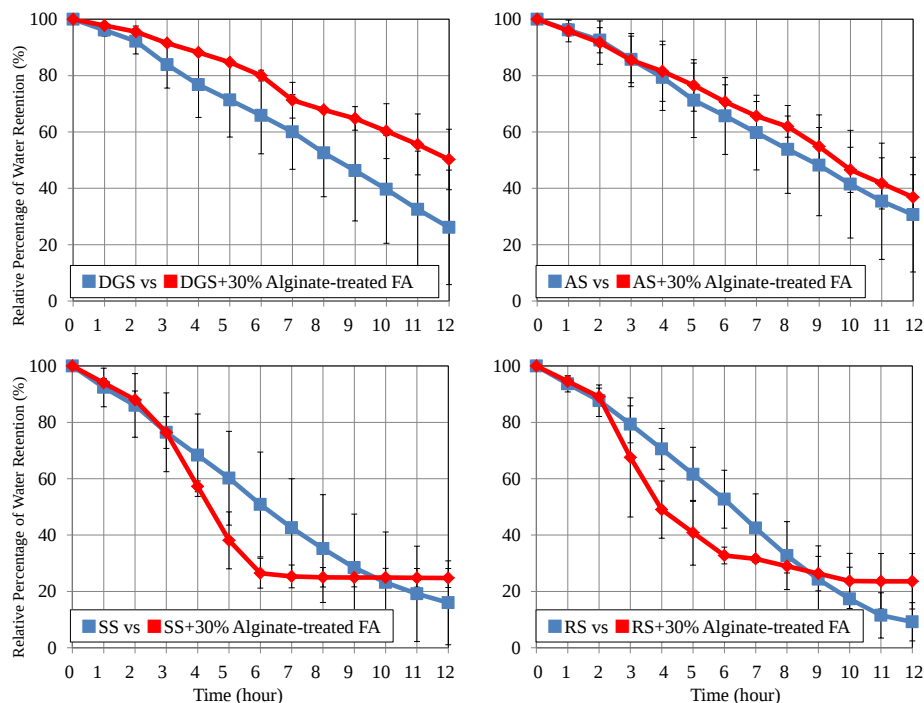


Figure 5-31 Comparison between water retention curves of soil/sand and soil/sand mixed with alginate-treated FA at 30 wt% of mixing ratio and 40 °C

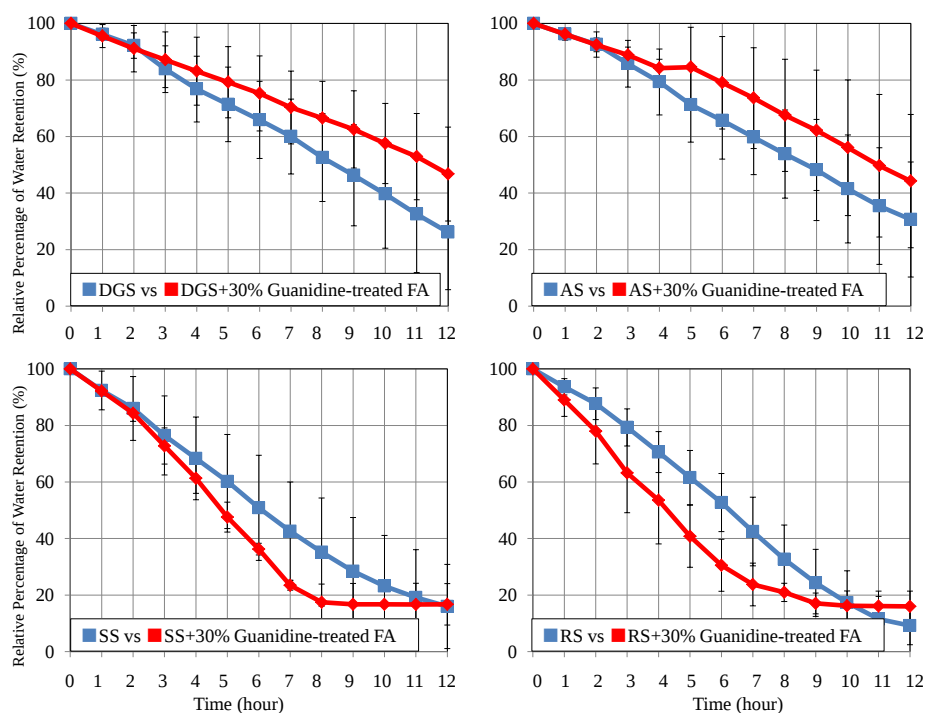


Figure 5-32 Comparison between water retention curves of soil/sand and soil/sand mixed with guanidine-treated FA at 30 wt% of mixing ratio and 40 °C

Table 5-3 Summary of WRC of soil/sand mixed with organic-treated FA at 40 °C

Flay ash		40 °C			
		DGS	AS	SS	RS
Raw FA		-11.1%**	-10.4%**	-5.3%**	—
Organic-treatment	Chitosan	—	—	-5.3%*	-2.5%**
	Alginate	+16.8%**	—	-24.6%**	-10.2%**
	Guanidine	—	—	-18.3%**	-25.7%**

All data was conducted by t-test, and “*” stand to “p value < 0.05”, “**” stand to “p value < 0.01” of t-test.

5.3.1.4 Comparison of WRC changed by mixing organic-treated FA at between room and high temperatures

Effects of amending organic-treated FA on WRC of soil/sand were compared between room temperature and 40 °C. The results are shown in Table 5-4. It should be noted that these ratios were calculated using WRC changes which were regarded as within experimental errors by t-test. Therefore, discussions in this section might include some uncertainties. Amending chitosan-treated FA at 40 °C influenced WRC of soils and SS stronger than that at room temperature. For WRC of RS, when temperature increased, the effect of amending chitosan-treated FA became weaker. On the other hand, effects of mixing alginate-treated FA became stronger on WRC of DGS, SS and RS at 40 °C. The effect became weaker when alginate-treated FA is mixed into AS. The effects of chitosan- and alginate-treated FA on WRC of sands between room temperature and 40 °C are opposite. Effects of mixing guanidine-treated FA on WRC of soils at room temperature are also opposite to those at 40 °C. In addition, the effects became weaker when temperature increased. For sands, the effects of guanidine-treated FA became stronger at higher temperature. This clearly suggests a temperature dependency of the effects of mixing organic-treated FA on WRC of soil/sand. In addition, dependency to a soil/sand type and organic-treatment type were also found.

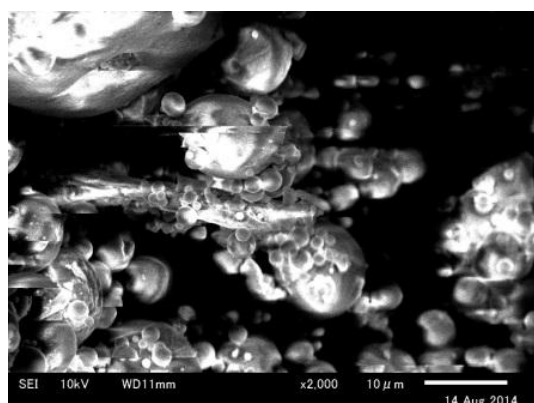
Table 5-4 Comparison between effects of soil/sand mixed with organic-treated FA at room temperature and 40 °C

Flay ash		40 °C/Room temperature			
		DGS	AS	SS	RS
Raw FA		-7.93	-10.40	-26.50	-0.71
Organic-treatment	Chitosan	2.12	1.82	-1.47	-0.51
	Alginate	2.90	0.64	-6.31	-1.59
	Guanidine	-0.86	-0.66	1.05	2.02

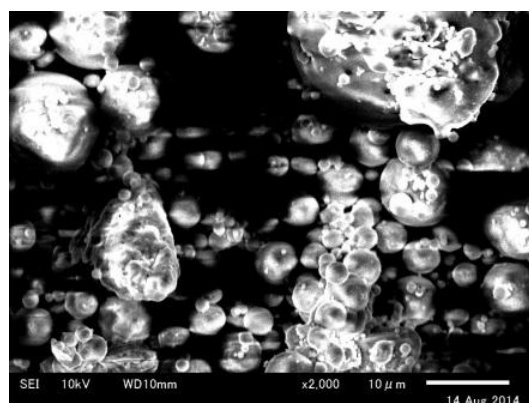
5.3.1.5 Surface morphology of organic-treated FA

According to SEM observation, organic-treatment aggregated FA particles by building up organic linkages (see Figure 5-33). Chitosan-treated FA has similar particle surface with alginate-treated FA. Smooth surface covering over FA particles were found. Larger aggregates of chitosan-/alginate-treated FA were found compared to

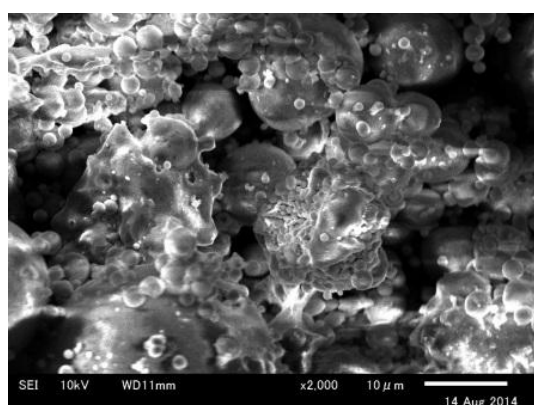
apatite-synthesized FA. Aggregates of such organic-treated FA are also larger than fine soil/sand particles (see Figure 5-34 and 5-35). Guanidine-treated FA was also aggregated with bigger size than chitosan-/alginate-treated FA (see Figure 5-36). Surface of guanidine-treated FA is rougher than chitosan-/alginate-treated FA. Regardless of organic-treatment type, organic-treated FA amendment decreased WRC of sands significantly. It is difficult to explain the effects of organic-treated FA amendment on WRC of sands only focusing on morphological changes of FA particle surface by organic-treatment. On the other hand, large size aggregates of organic-treated FA might change particle size distribution, in particular 1 to 100 μm ranges. It might explain the effect of organic-treated FA amendment although limited amount of available FA samples made size distribution measurement impossible.



Chitosan-treated FA

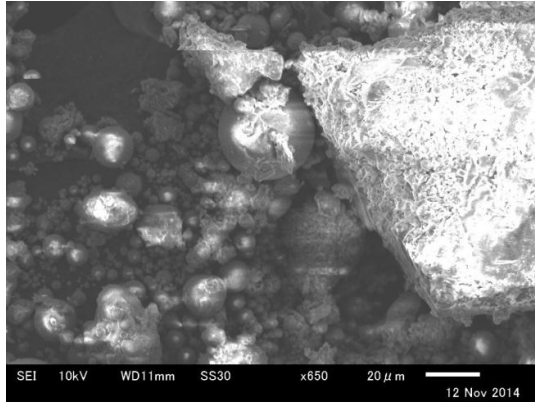


Alginate-treated FA

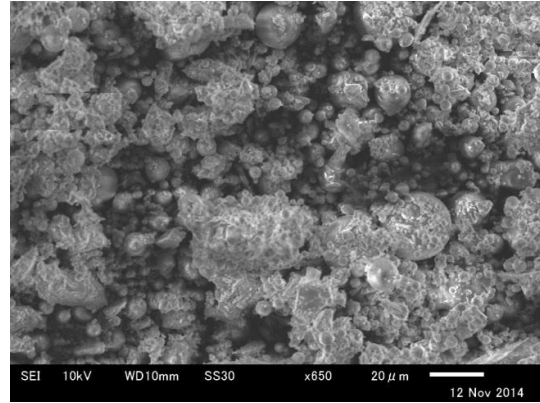


Guanidine-treated FA

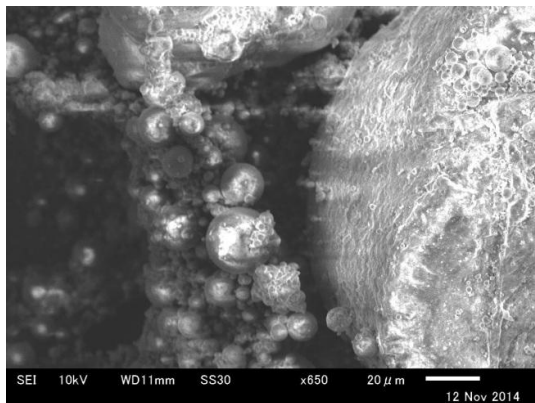
Figure 5-33 Surface morphology of organic treated FA



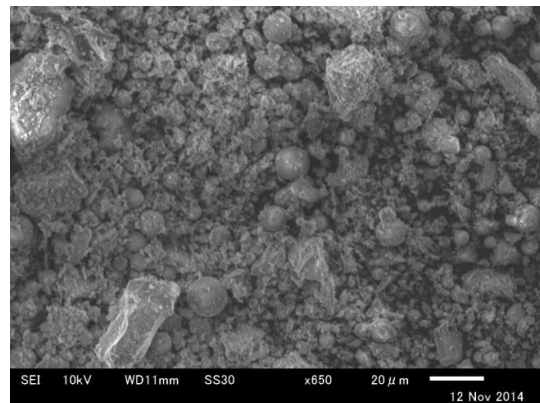
DGS + Chitosan-treated FA



AS + Chitosan-treated FA

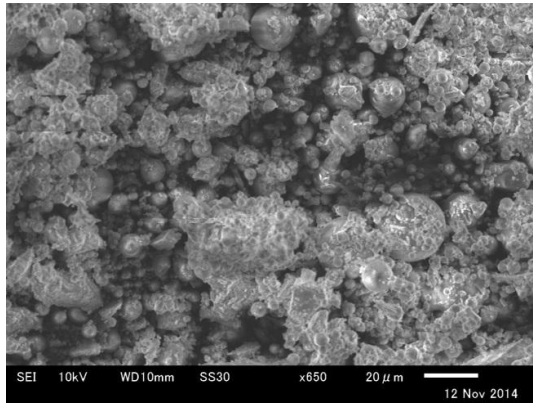


SS + Chitosan-treated FA

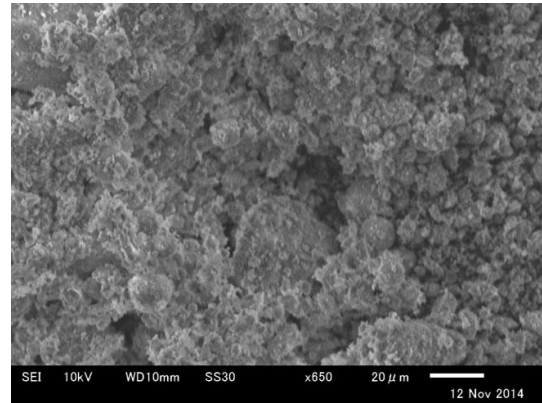


RS + Chitosan-treated FA

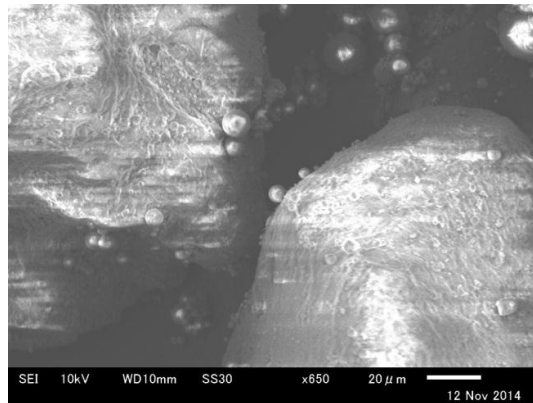
Figure 5-34 Surface morphology of soil/sand mixed with chitosan-treated FA



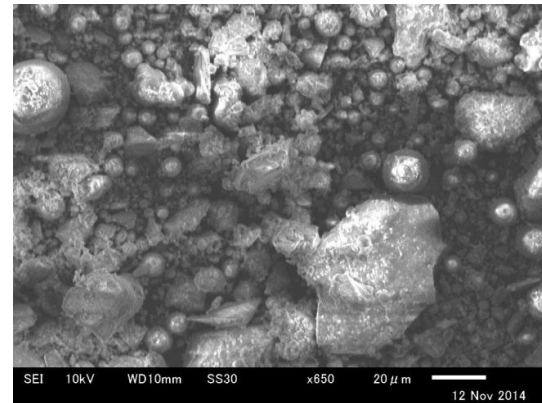
DGS + Alginate-treated FA



AS + Alginate-treated FA



SS + Alginate-treated FA



RS + Alginate-treated FA

Figure 5-35 Surface morphology of soil/sand mixed with alginate-treated FA

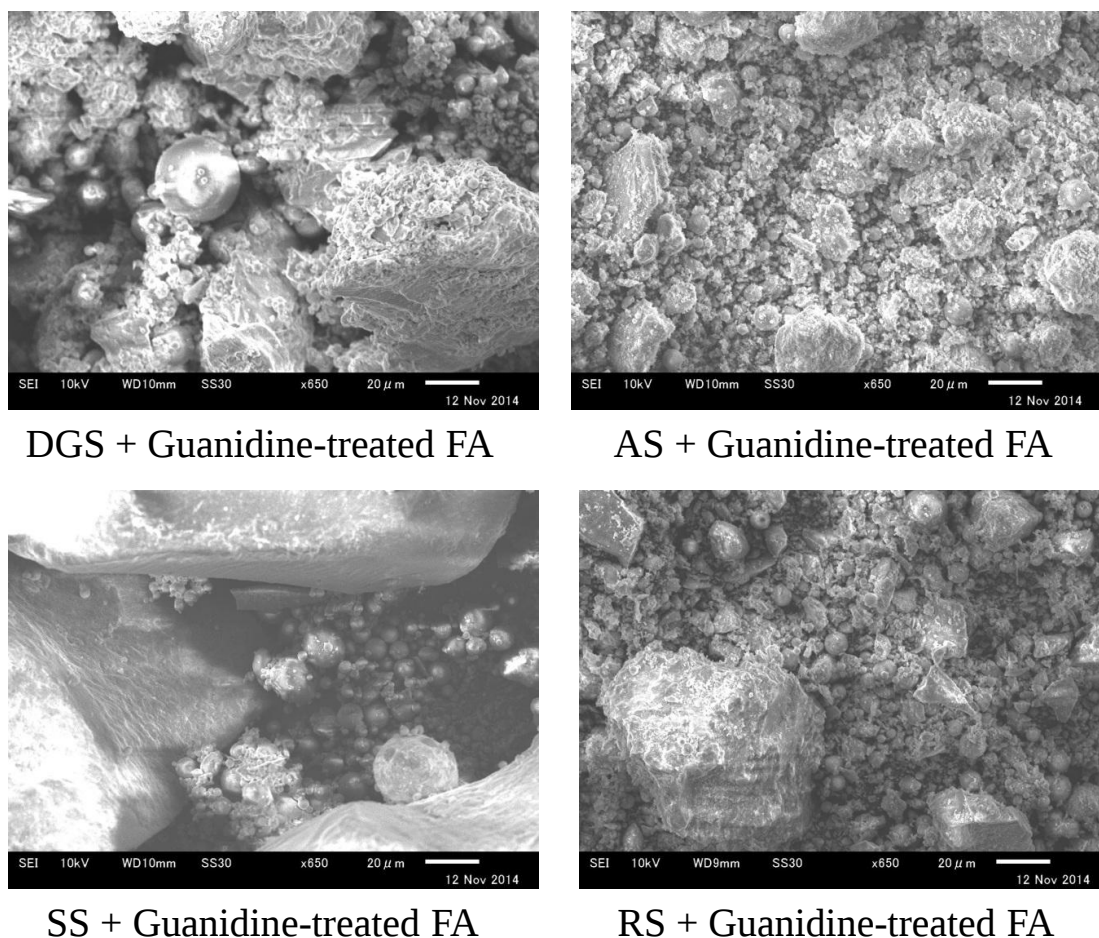


Figure 5-36 Surface morphology of soil/sand mixed with guanidine-treated FA

5.3.1.6 Capillary water content of soil/sand mixed with organic-treated FA

Capillary water content was measured only for alginate-treated FA and soil/sand mixed with alginate-treated FA because of limited amount of samples. The results were summarized in Table 5-5. Capillary water content of alginate-treated FA was higher than those of raw FA and DGS. It was higher than initial water content in WRC measurement (30 wt%). Therefore, WRC of alginate-treated FA at 40 °C means evaporation resistivity of only capillary water. When mixing alginate-treated FA into soil/sand, capillary water contents of DGS, SS and RS were increased. On the other hand, capillary water content of AS was decreased. The effects of alginate-treated FA amendment on capillary water contents of DGS, AS, and SS are the same with those of apatite-synthesized FA amendment. When the effects of alginate-treated FA and apatite-synthesized FA amendments on WRC of SS at 40 °C are compared, opposite results are found. Apatite-synthesized FA amendment increased WRC of

SS excluding treated FA with P/Ca ratio of 7.1. On the other hand, alginate-treated FA amendment decreased WRC of SS significantly although both treated FA increased capillary water content of SS. In the section 4.3.7, multi-regression analysis suggests negligible impact of capillary water content although the uncertainty should be concerned. This inconsistent effects of alginate-treated and apatite-synthesized FA amendment supports the suggestion of multi-regression analysis.

Table 5-5 Capillary water content of soil/sand and those mixed with organic-treated FA, organic-apatite treated FA and organic-added thermal treated FA

Capillary water content (wt%)	FA	DGS	AS	SS	RS
Pure sample	—	31.9(—)	63.1(—)	5.6(—)	26.0(—)
Raw FA	42.5	25.1(6.8↓)	56.8(6.3↓)	17.8(12.2↑)	27.8(1.8↑)
Alginate-treated FA	47.9	34.7(2.8↑)	56.4(6.7↓)	14.9(9.3↑)	27.8(1.8↑)
Alginate-apatite treated FA	46.2	32.9(1.0↑)	55.5(7.6↓)	13.8(8.2↑)	27.1(1.1↑)
Sucrose-added thermal treated FA	36.0	32.9(1.0↑)	—	—	—

5.3.1.7 Water repellency of soil/sand mixed with organic-treated FA

Because of limitation of tested samples, WDPT were measured only for DGS, AS and SS mixed with alginate-treated FA, respectively. The results are summarized in Table 5-6. WDPT of soils and SS were all increased obviously by mixing alginate-treated FA. It means that water repellency of soils and SS increased by alginate-treated FA amendment. Although apatite-synthesized FA amendment also increased WDPT of DGS and SS as well as alginate-treated FA amendment (see Table 4-1), its effect on WDPT of AS is different. Apatite-synthesized FA amendment decreased WDPT of AS. According to Table 5-3, WRC of DGS was increased significantly by mixing alginate-treated FA. On the other hand, WRC of SS was decreased beyond experimental errors by alginate-treated FA amendment. As the same with capillary water content, inconsistent effects of alginate-treated FA and apatite-synthesized FA amendment on WRC of SS are found although both FA amendment increased water repellency of SS. As shown by multi-regression analysis in the section 4.3.7, sign of water repellency term is negative. It means that more hydrophobic property of SS

system promotes water evaporation and correspondingly decreases WRC of SS. The effects of alginate-treated FA amendment on WRC of SS is consistent with the expectation but that of apatite-synthesized FA amendment is contrastly different. In the cases of soils, both alginate-treated FA and apatite-synthesized FA made DGS more hydrophobic but increased WRC of DGS. It is also contrast to the expectation. As described in the section 4.3.4, correlation between water repellency and WRC have dependency to soil/sand type and FA treatment. These complex effects of FA amendment on WRC of soils and sands imply that some other unconsidered factors/mechanisms give a non-negligible impact on the mechanism between water repellency and WRC. It would be discussed again in the section 5.3.2.7.

Table 5-6 Water repellency of soil/sand and those mixed with organic-treated FA, organic-apatite treated FA and organic-added thermal treated FA

WDPT (s)	FA	DGS	AS	SS	RS
Pure sample	—	1.26	6.05	0.21	4.09
Alginate-treated FA	2.56	+117.57%	+27.59%	+150.24%	—
Alginate-apatite treated FA	2.38	+89.40%	+31.03%	+230.81%	—
Sucrose-added thermal treated FA of set II	2.81	+303.43%	—	—	—

5.3.2 Organic-apatite treated FA

5.3.2.1 WRC of organic-apatite treated FA at room temperature and 40 °C

Water retention curves of organic-apatite treated FA are shown in Figure 5-37 and 5-38. WRC of soil/sand, raw FA and organic-apatite treated FA are shown in Figure 5-39. At room temperature, WRC of organic-apatite treated FA are around 1000 hr, slightly higher than those of soil/sand and raw FA. At 40 °C, WRC of organic-apatite treated FA decreased a lot compared to that at room temperature. They decreased lower than WRC of raw FA. Water retention curves of organic-apatite treated FA were type C. It means water evaporation rates were constant at whole drying time. At 40 °C, all water retention curves became type L and water content left after 12 hours drying at high temperature was lower than that at room temperature. According to the results of WRC of organic-apatite treated FA at high temperature, it is predicted that mixing organic-apatite treated FA would obviously decrease

WRC of soil/sand at 40 °C. The effects of organic-apatite treated FA amendment would be discussed in the following sections.

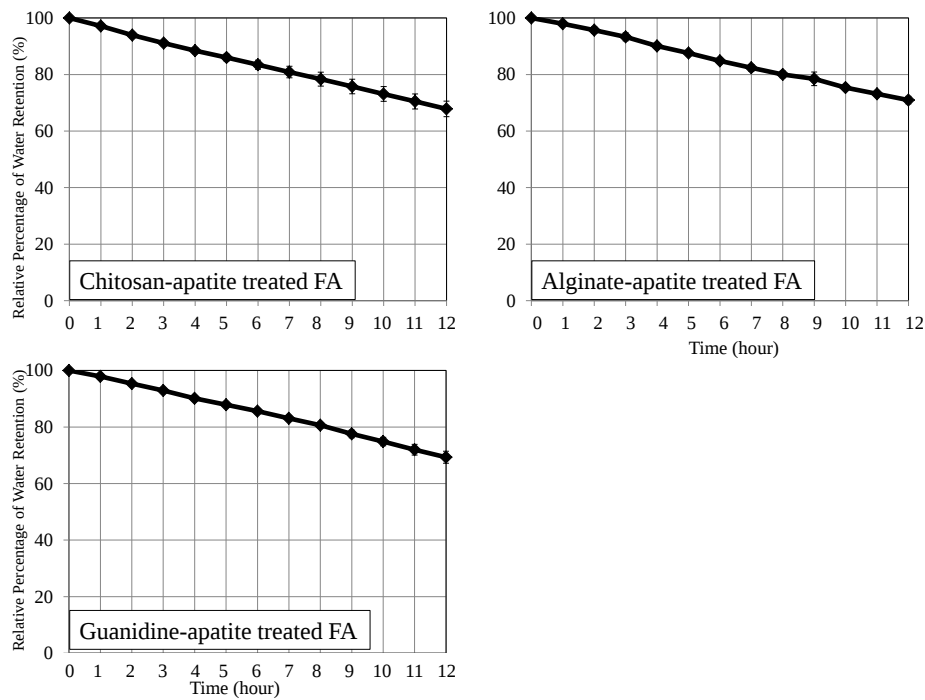


Figure 5-37 Water retention curves of organic-apatite treated FA at room temperature

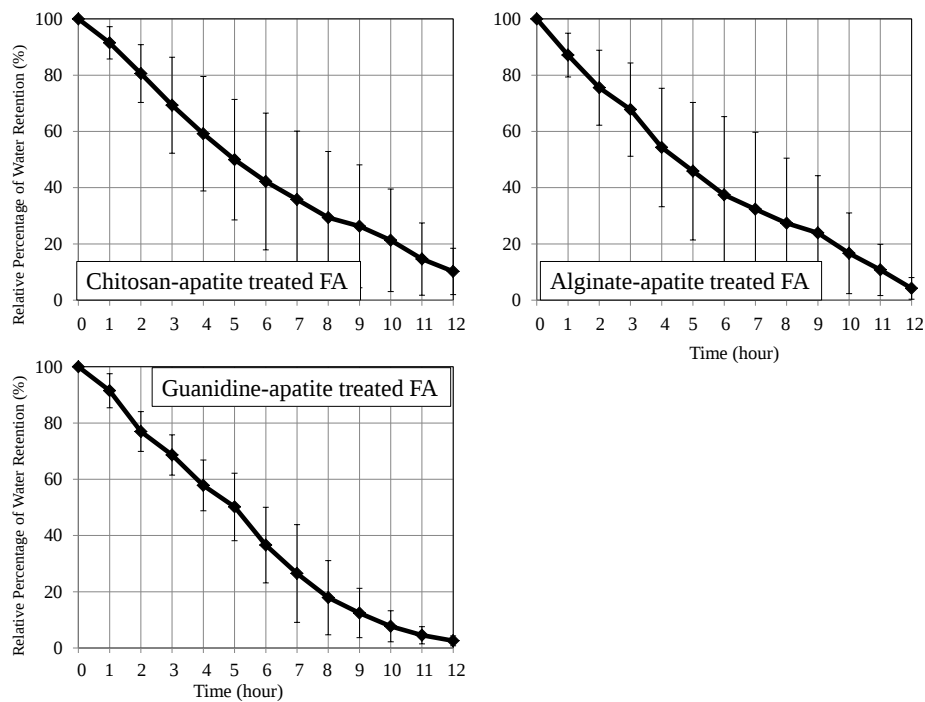


Figure 5-38 Water retention curves of organic-apatite treated FA at 40 °C

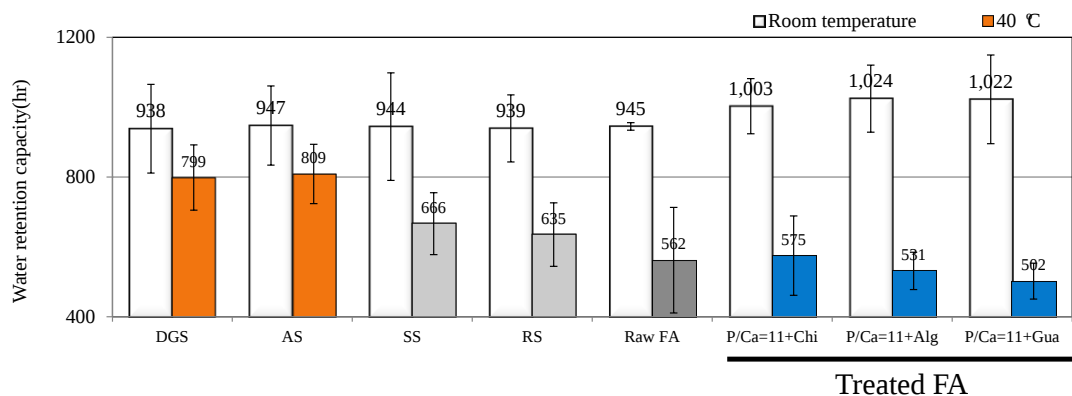


Figure 5-39 WRC of pure soil/sand, raw FA and organic-apatite treated FA

5.3.2.2 WRC of soil/sand mixed with organic-apatite treated FA at room temperature

Water retention curves of soil/sand mixed with organic-apatite treated FA at room temperature were shown in Figure 5-40 to 5-48. WRC of soil/sand with organic-apatite treated FA were shown in Figure 5-49 to 5-52 and summarized in Table 5-7.

Chitosan-apatite treated FA increased WRC of soil/sand slightly. WRC variations are 3.9 % for DGS, 3.3 % for AS, 10.3 % for SS and 10.4 % for RS, respectively. However, only effects on WRC of sands were regarded as significant by t-test. According to Figure 5-40 to 5-42, all water retention curves of FA-amended soil/sand were type C_w , which means water evaporation rate was constant in all drying process. Residual water contents of all soil/sand mixed with chitosan-apatite treated FA was higher than that in pure soil/sand at room temperature. These suggests that amendment of chitosan-apatite treated FA inhibited water evaporation at whole drying time and finally increased residual water content. Therefore, it increased WRC of soil/sand at room temperature.

Alginate-apatite treated FA also increased WRC of soil/sand. Increases of WRC are 8.1 % for DGS and 7.7 % for AS, 7.1 % for SS and 8.4 % for RS, respectively. According to t-test, however, only effects on WRC of soils were regarded as significant. Figure 5-43 to 5-45 show that water retention curves of all soils are categorized as type S, in which water evaporated slow at first 3 hours and then became fast until 8 hours, at last water evaporation rate became very slow when capillary water was nearly dried out. Figure 5-53 is the comparison of water retention curves between pure soil/sand and soil/sand mixed with

alginate-apatite treated FA at mixing ratio of 20 wt% and room temperature. Water retention curves of soils changed from type C to type S_u but those of sands had the same evaporation type (type C_u). Water content left after 12 hours drying were all higher than those of pure soil/sand. Water evaporation of soil/sand was inhibited by mixing alginate-apatite treated FA when compared to those of soil/sand at room temperature in the whole drying process. Therefore, alginate-treated FA increased WRC of soil/sand at room temperature although effects on WRC of sands were regarded as insignificant.

Guanidine-apatite treated FA was also effective on increasing WRC of soil/sand. Increases of WRC are 8.7 % for DGS and 8.6 % for AS, 13.0 % for SS and 14.1 % for RS respectively. They were all regarded as significant by t-test. As shown in Figure 5-46 to 5-48, water retention curves of soil/sand were all identified as type C, which means water evaporation rates were constant. In addition, water content left after 12 hours drying were higher than those of pure soil/sand. This suggests that water evaporation in soil/sand mixed with guanidine-treated FA was inhibited, and it led to significantly increase of WRC of soil/sand mixed with guanidine-treated FA.

According to Table 5-7, the results are summarized that mixing chitosan-apatite treated FA gave no effect on WRC of soils but gave positive effect on sands at room temperature. On the other hand, alginate-apatite treated FA amendment increased WRC of soils but gave no effect on WRC of sands. Mixing guanidine-apatite treated FA increased WRC of both soils and sands significantly.

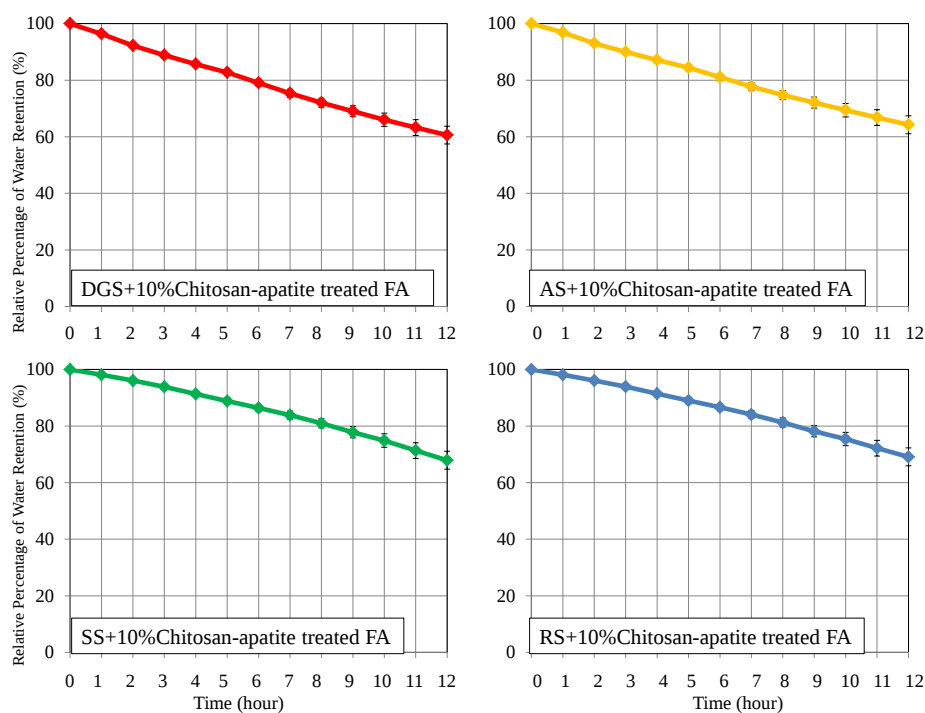


Figure 5-40 Water retention curves of DGS, AS, SS and RS mixed with chitosan-apatite treated FA at 10 wt% mixing ratio and room temperature

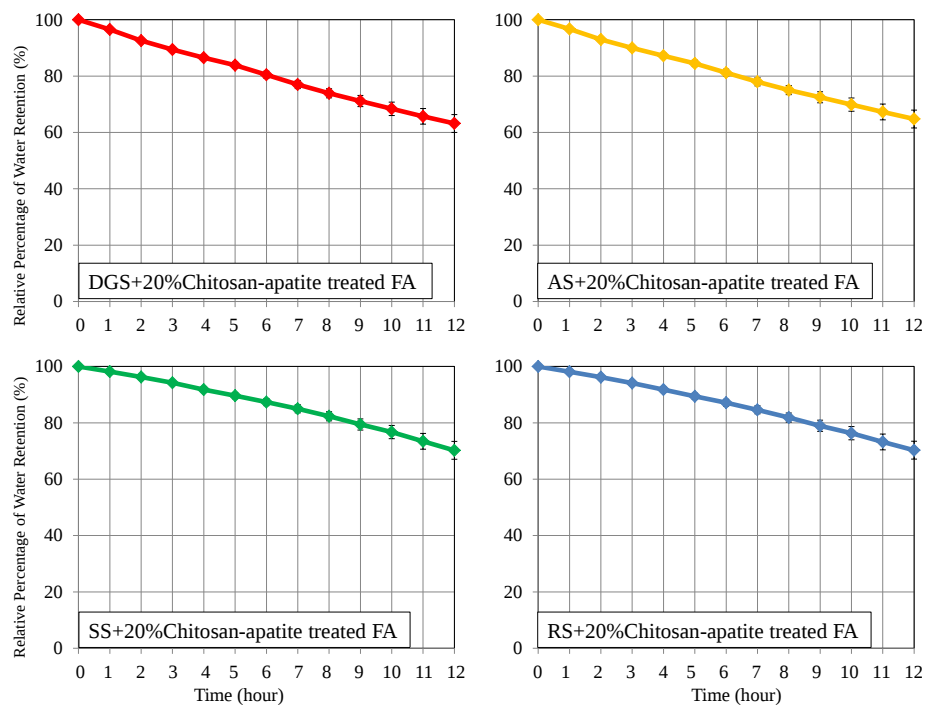


Figure 5-41 Water retention curves of DGS, AS, SS and RS mixed with chitosan-apatite treated FA at 20 wt% mixing ratio and room temperature

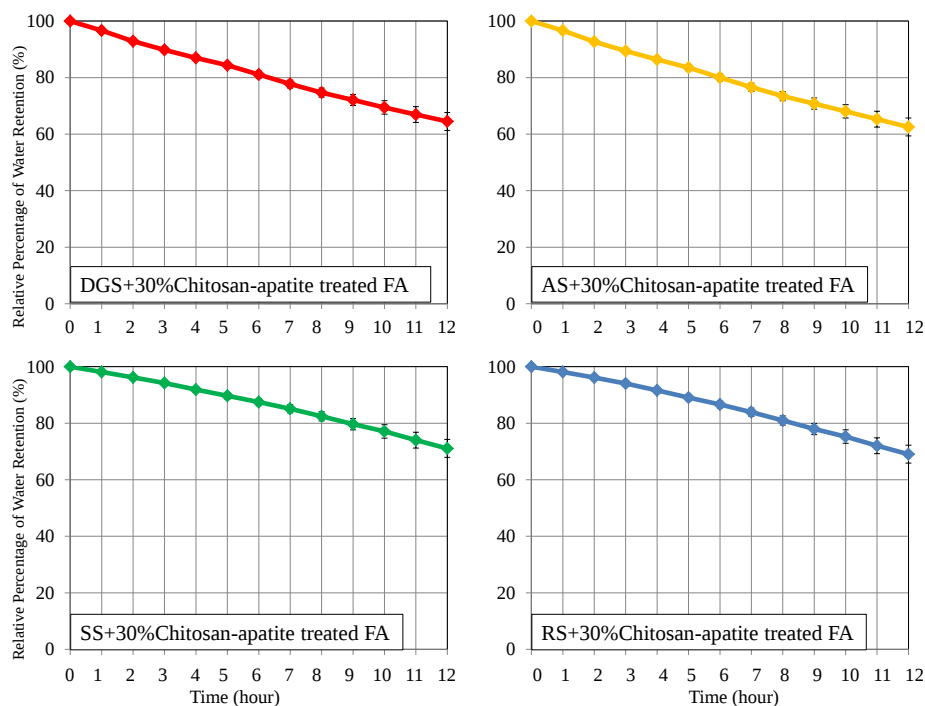


Figure 5-42 Water retention curves of DGS, AS, SS and RS mixed with chitosan-apatite treated FA at 30 wt% mixing ratio and room temperature

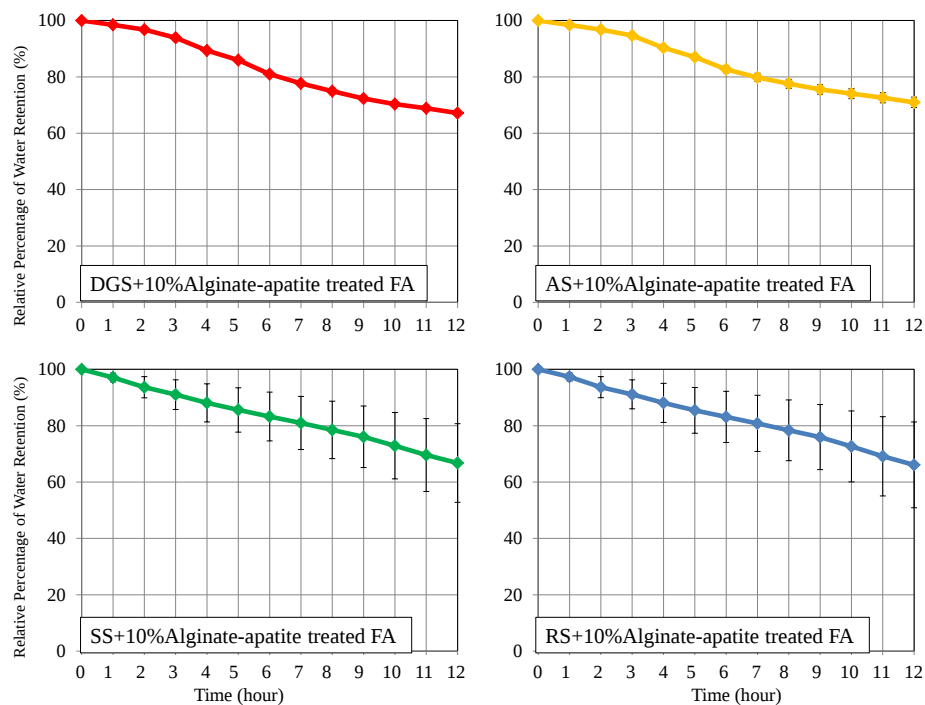


Figure 5-43 Water retention curves of DGS, AS, SS and RS mixed with alginate-apatite treated FA at 10 wt% mixing ratio and room temperature

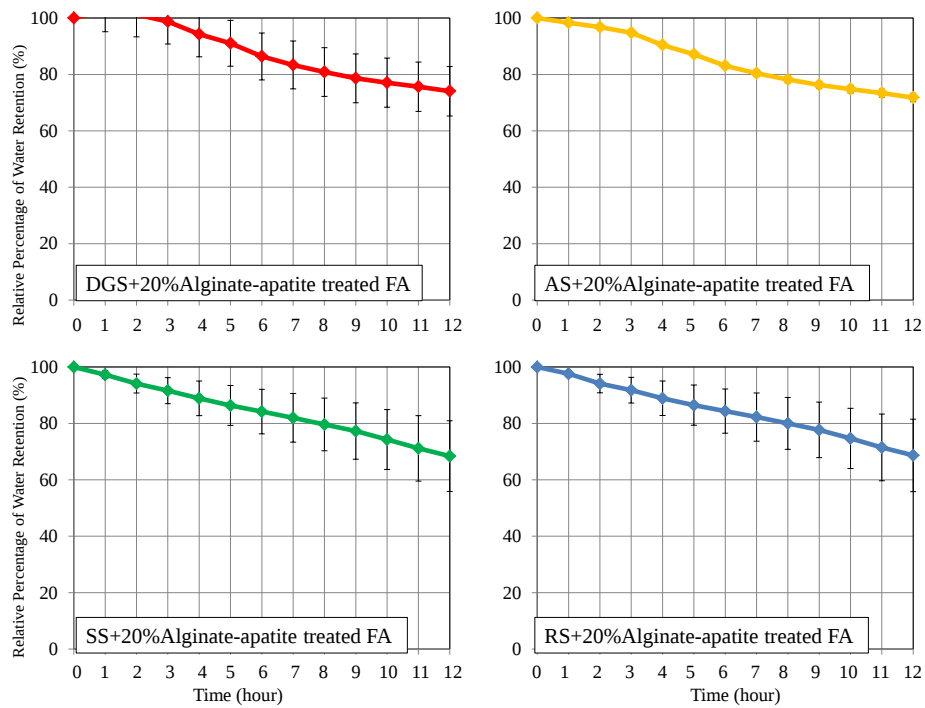


Figure 5-44 Water retention curves of DGS, AS, SS and RS mixed with alginate-apatite treated FA at 20 wt% mixing ratio and room temperature

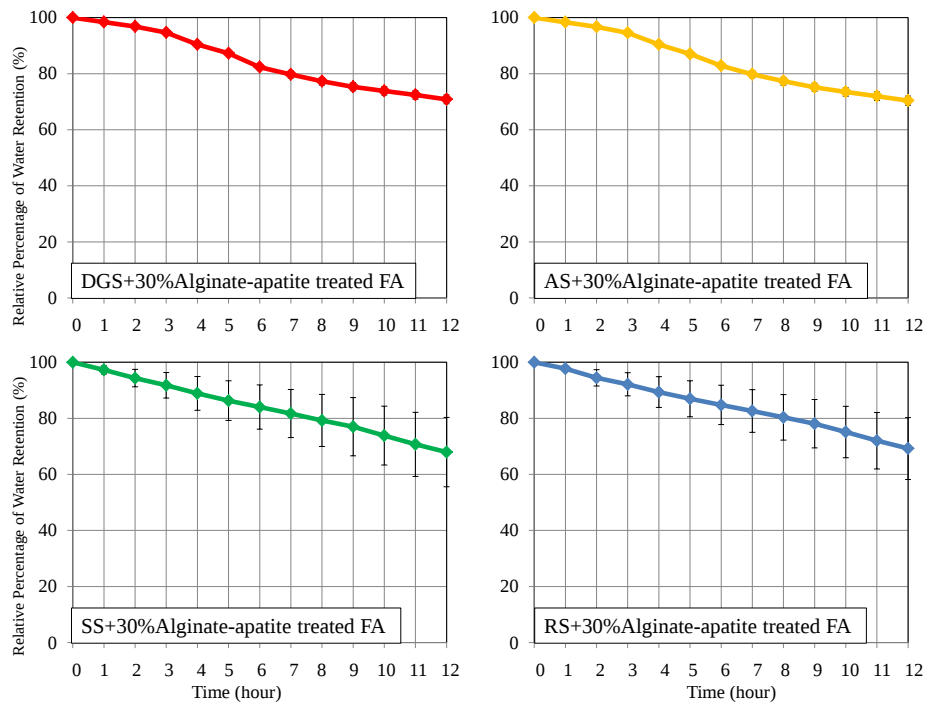


Figure 5-45 Water retention curves of DGS, AS, SS and RS mixed with alginate-apatite treated FA at 30 wt% mixing ratio and room temperature

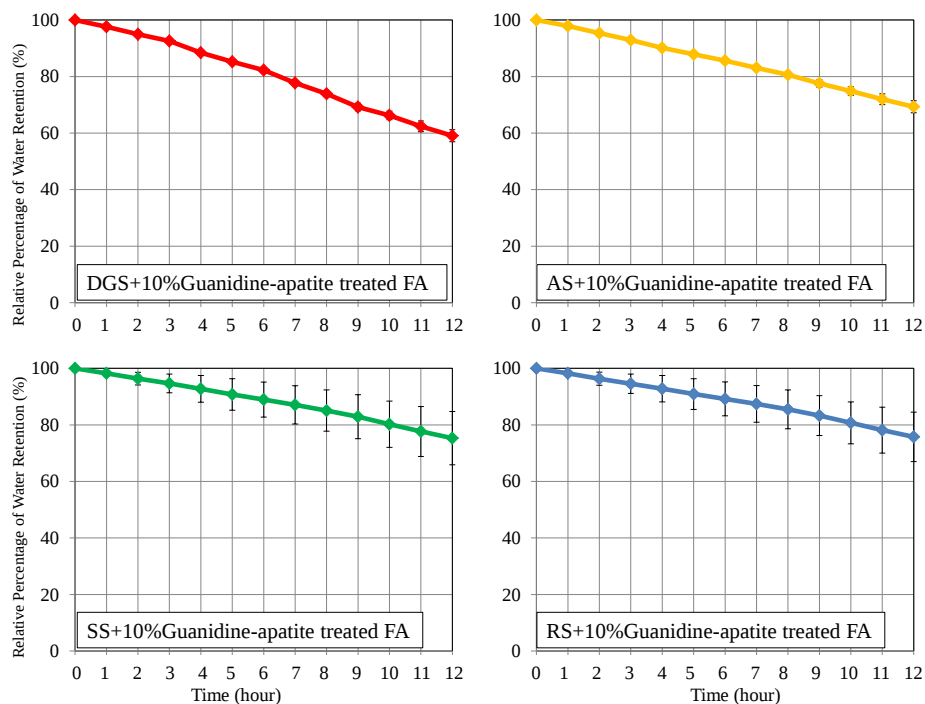


Figure 5-46 Water retention curves of DGS, AS, SS and RS mixed with guanidine-apatite treated FA at 10 wt% mixing ratio and room temperature

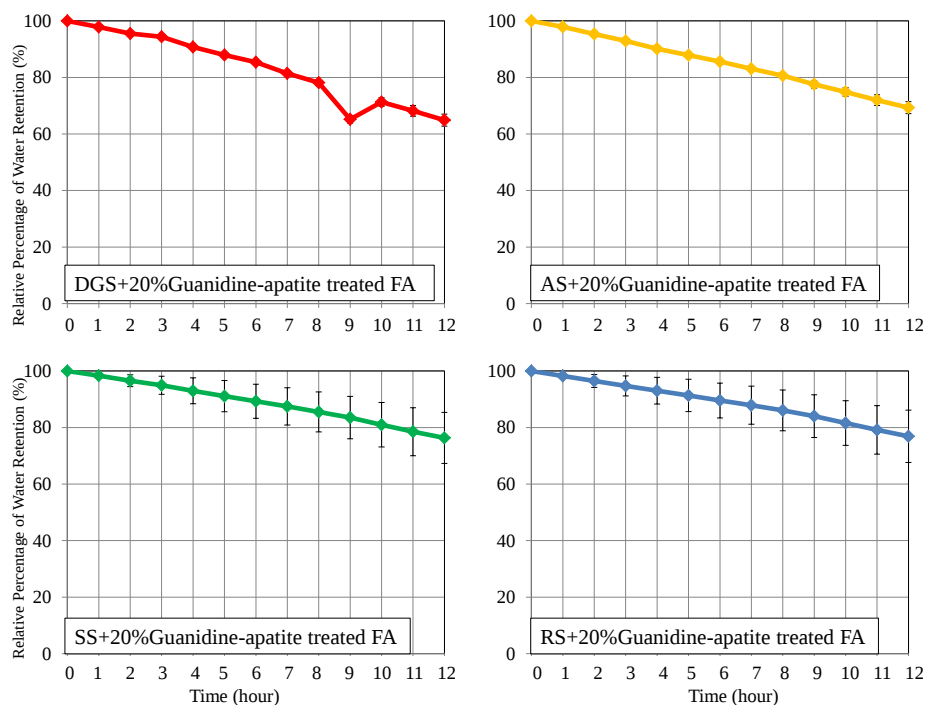


Figure 5-47 Water retention curves of DGS, AS, SS and RS mixed with guanidine-apatite treated FA at 20 wt% mixing ratio and room temperature

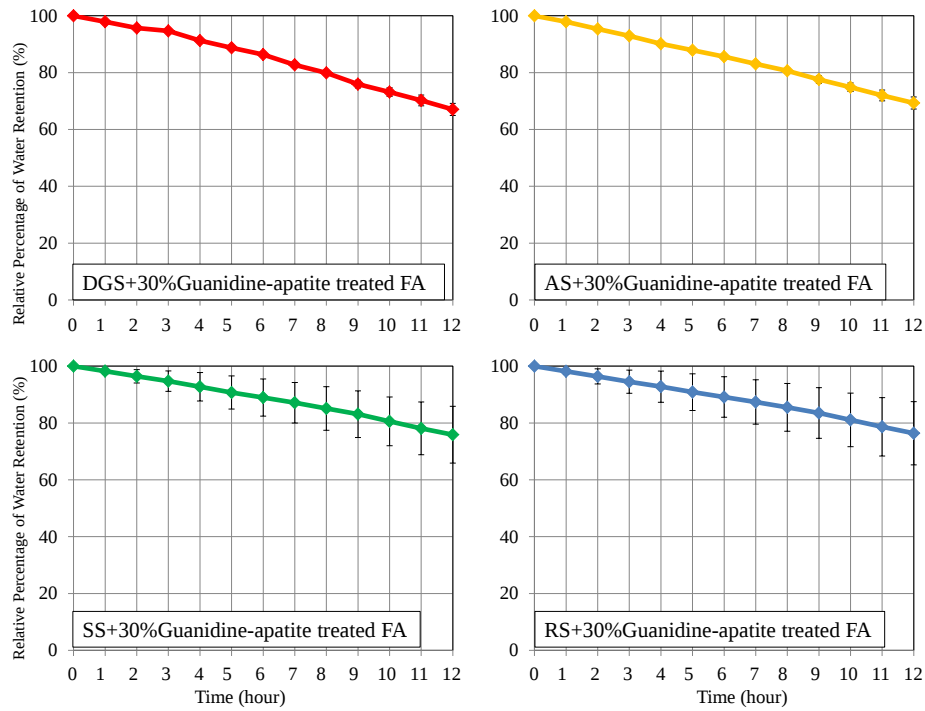


Figure 5-48 Water retention curves of DGS, AS, SS and RS mixed with guanidine-apatite treated FA at 30 wt% mixing ratio and room temperature

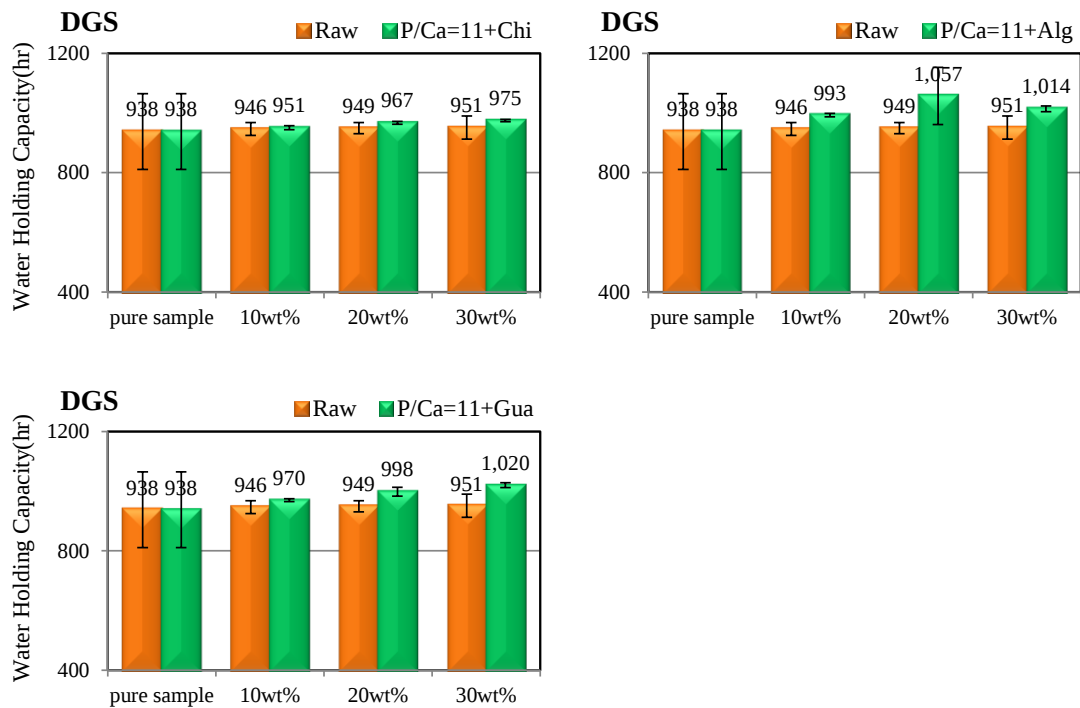


Figure 5-49 WRC of DGS mixed with raw FA or organic-apatite treated FA at room temperature

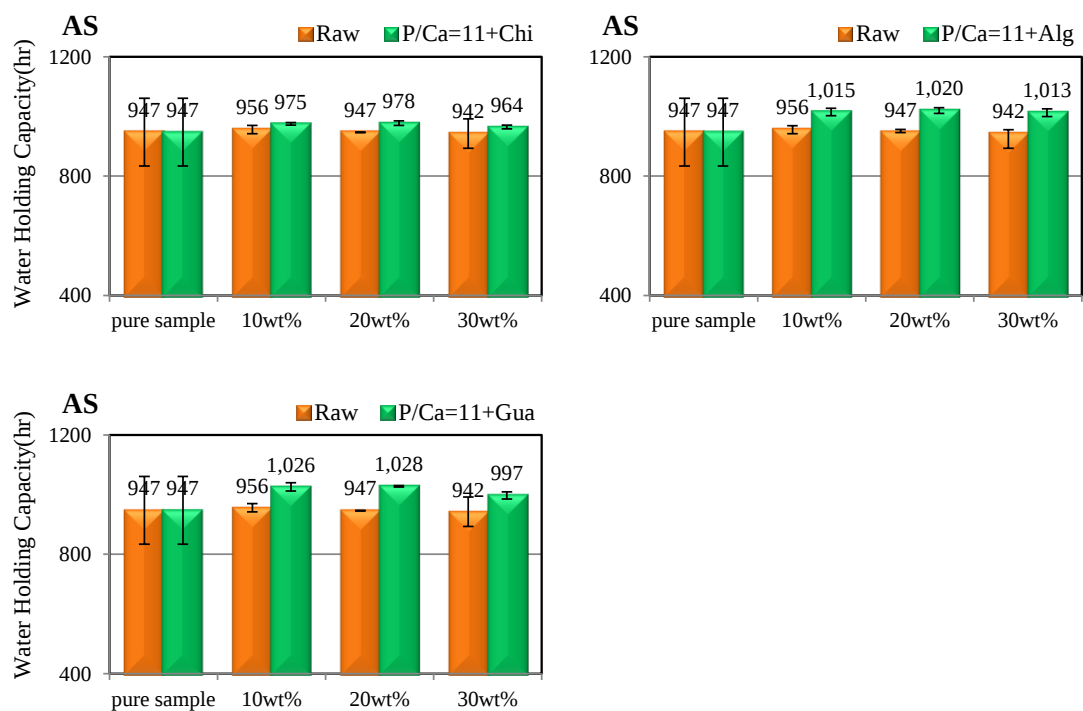


Figure 5-50 WRC of AS mixed with raw FA or organic-apatite treated FA at room temperature

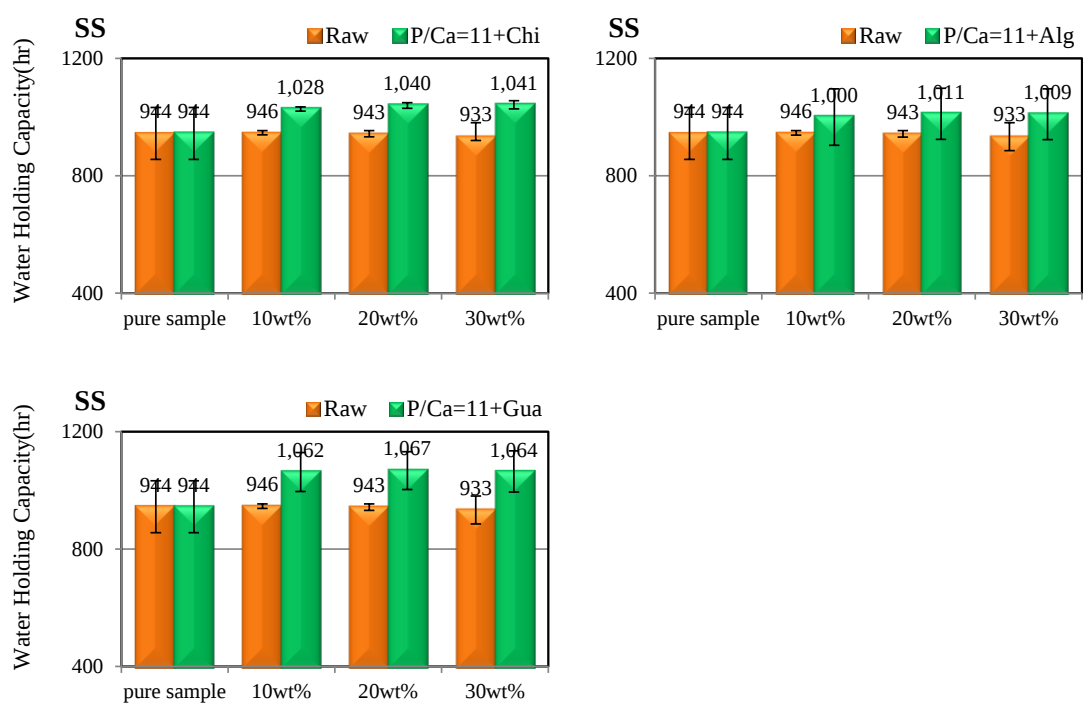


Figure 5-51 WRC of SS mixed with raw FA or organic-apatite treated FA at room temperature

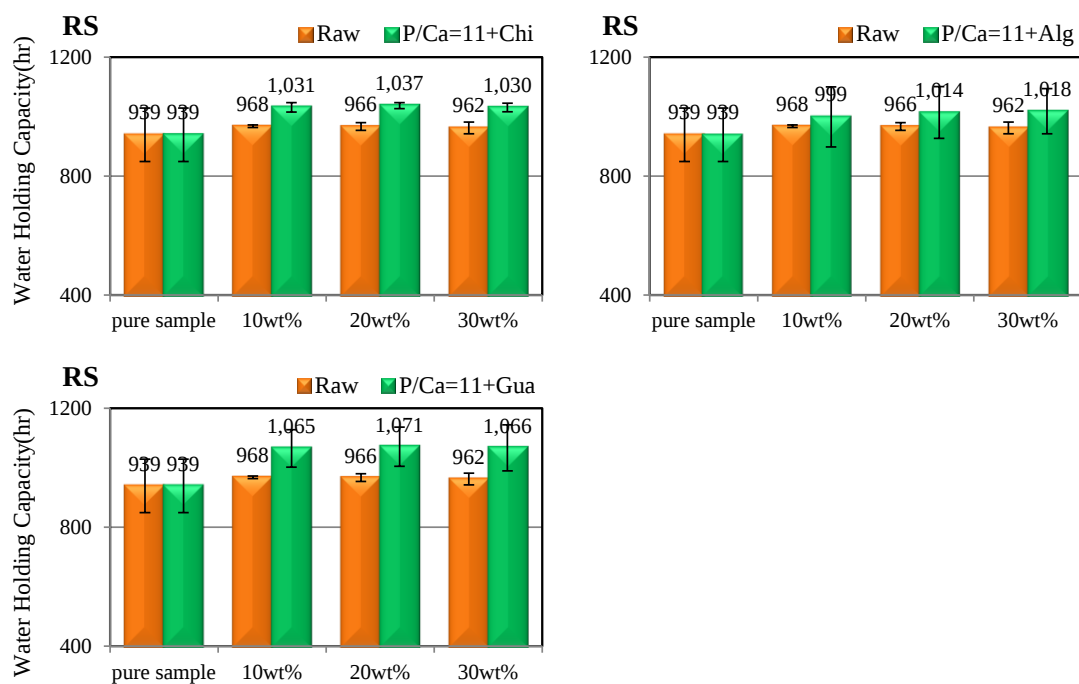


Figure 5-52 WRC of RS mixed with raw FA or organic-apatite treated FA at room temperature

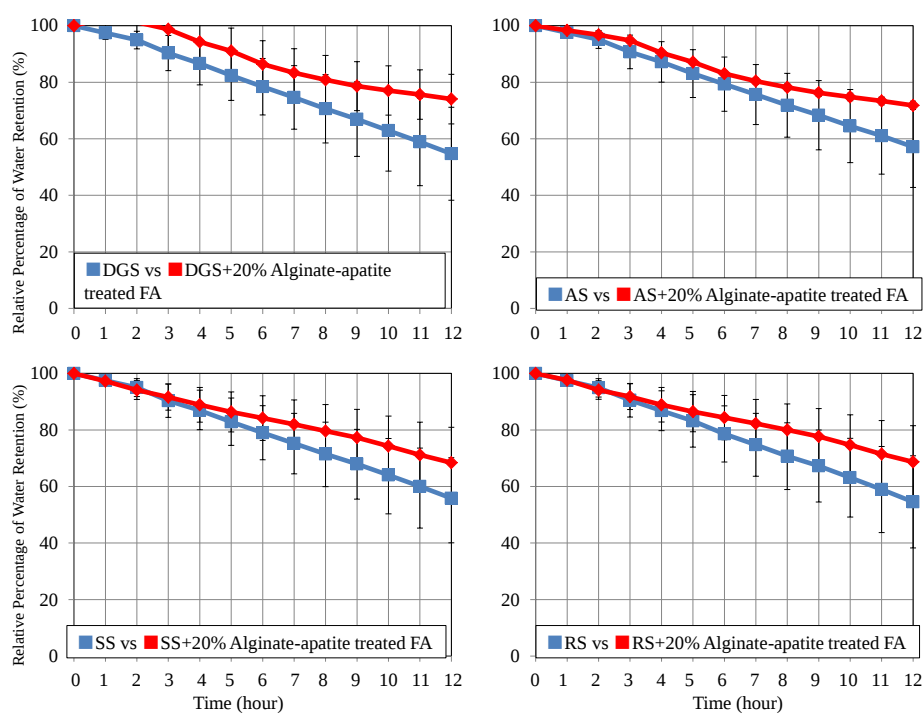


Figure 5-53 Comparison between water retention curves of soil/sand and soil/sand mixed with alginate-apatite treated FA at 20 wt% of mixing ratio and room temperature

Table 5-7 Summary of WRC of soil/sand mixed with organic-apatite treated FA at room temperature

Flay ash		Room temperature			
		DGS	AS	SS	RS
Raw FA		—	—	—	—
Organic-treatment	Chitosan-apatite	—	—	+10.3%**	+10.4%**
	Alginate-apatite	+8.1%**	+7.7%**	—	—
	Guanidine-apatite	+8.7%**	+8.6%**	+13.0%*	+14.1%*

All data was conducted by t-test, and “*” stand to “p value < 0.05”, “**” stand to “p value < 0.01” of t-test.

5.3.2.3 WRC of soil/sand mixed with organic-apatite treated FA at 40 °C

Water retention curves of soil/sand mixed with organic-apatite treated FA are shown in Figure 5-54 to 5-62. WRC of these samples are shown in Figure 5-63 to 5-66 and summarized in Table 5-8.

At 40 °C, chitosan-apatite treated FA decreased WRC of DGS by 6.1 % but regarded to be insignificant by t-test. Insignificant effect of chitosan-apatite treated FA amendment on WRC of DGS is the same with that of chitosan-treated FA amendment but different from that of apatite-synthesized FA (with the same P/Ca ratio). Apatite-synthesized FA amendment increased significantly WRC of DGS. WRC of AS was decreased significantly by 13.7 % when mixing chitosan-apatite treated FA. Different effects on WRC of AS are also found among apatite-synthesized FA, chitosan-treated FA and chitosan-apatite treated FA. Amendment of apatite-synthesized FA increased WRC of AS significantly but, chitosan-treated FA gave no significant effect. In the cases of sands, chitosan-apatite treated FA amendment increased WRC of SS and RS significantly by 22.4 % and 38.1 %, respectively. These effects on WRC of sands are opposite from those of chitosan-treated FA amendment but the same with that of apatite-synthesized FA on WRC of SS. As shown in Figure 5-54 to 5-56, water evaporation rates of all soil/sand mixed with chitosan-apatite treated FA were constant and categorized as type C. When comparing them to water retention curves of pure soil/sand at 40 °C in Figure 5-67, water retention of DGS mixed with chitosan-apatite treated FA was categorized as type C₀, and showed almost no difference from that of pure DGS. Water evaporation of AS mixed with chitosan-apatite treated FA was

promoted to be faster than that of pure AS in the whole drying process. Water retention curve of FA-mixed AS was categorized as type C_d as residual water after 12 hours drying was lower than that of pure AS at 40 °C. Therefore, WRC of AS was decreased by mixing chitosan-apatite treated FA. Water retention curves of FA-mixed sands were both categorized as type C_u . Water retention curves were both higher than those of pure sands. This means water evaporation of sands was inhibited in whole drying process. This led to significant positive effect on WRC of sands by chitosan-apatite treated FA amendment.

According to Figure 5-63 to 5-66, WRC of soils were decreased by mixing alginate-apatite treated FA significantly, which was 4.3 % decrease for DGS and 9.9 % decrease for AS, respectively. There are also different effects on WRC of soils among apatite-synthesized FA, alginate-treated FA and alginate-apatite treated FA. In contrast to alginate-apatite treated FA, both apatite-synthesized FA and alginate-treated FA increased WRC of DGS significantly. Although apatite-synthesized FA also increased WRC of AS, alginate-treated FA gave no significant effect. WRC of sands were increased by mixing alginate-apatite treated FA significantly, which was 26.1 % increase for SS and 34.6 % increase for RS, respectively. Although apatite-synthesized FA amendment also increased WRC of SS significantly, alginate-treated FA amendment decreased WRC of SS and RS significantly. Water evaporation rates of soil/sand mixed with alginate-apatite treated FA at 40 °C were all constant as shown in Figure 5-57 to 5-59. All water retention curves of soils mixed with alginate-apatite treated FA were categorized as type C_d and those of sands were categorized as C_u . Residual water content after 12 hours drying decreased by alginate-apatite treated FA amendment for soils and increased for sands. These suggest that water evaporation of soils was promoted and that of sands was inhibited. This led to significant decrease of WRC of soils and significant increase of WRC of sands when alginate-apatite treated FA was mixed at 40 °C.

Guanidine-apatite treated FA amendment decreased WRC of DGS and AS by 6.8 % and 8.0 %, respectively, and regarded as significant by t-test. On the other hand, mixing guanidine-apatite treated FA increased WRC of sands significantly, 28.2 % increase for SS and 38.1 % increase for RS, respectively. Therefore, the effects of guanidine-treated FA and guanidine-apatite treated FA amendments on WRC of soils and sands are almost the same

with those of other organic-treated FA and other organic-apatite treated FA. As shown in Figure 5-60 to 5-62, water retention curves of soil/sand mixed with guanidine-apatite treated FA are quite similar to those of soil/sand mixed with alginate-apatite treated FA. This means that all water retention curves of soils mixed with guanidine-apatite treated FA were categorized as type C_d and those of sands were categorized as C_u . Water evaporation of soils was promoted and that of sands was inhibited by guanidine-apatite treated FA amendment. Therefore, WRC of soils decreased and WRC of sands increased at 40 °C when guanidine-apatite treated FA was mixed.

As summarized in Table 5-8, organic-apatite treated FA decreased WRC of soils significantly at 40 °C except for WRC of DGS mixed with chitosan-apatite treated FA. On the other hand, mixing organic-apatite treated FA inhibited water evaporation strongly and thus increased WRC of sands dramatically and significantly.

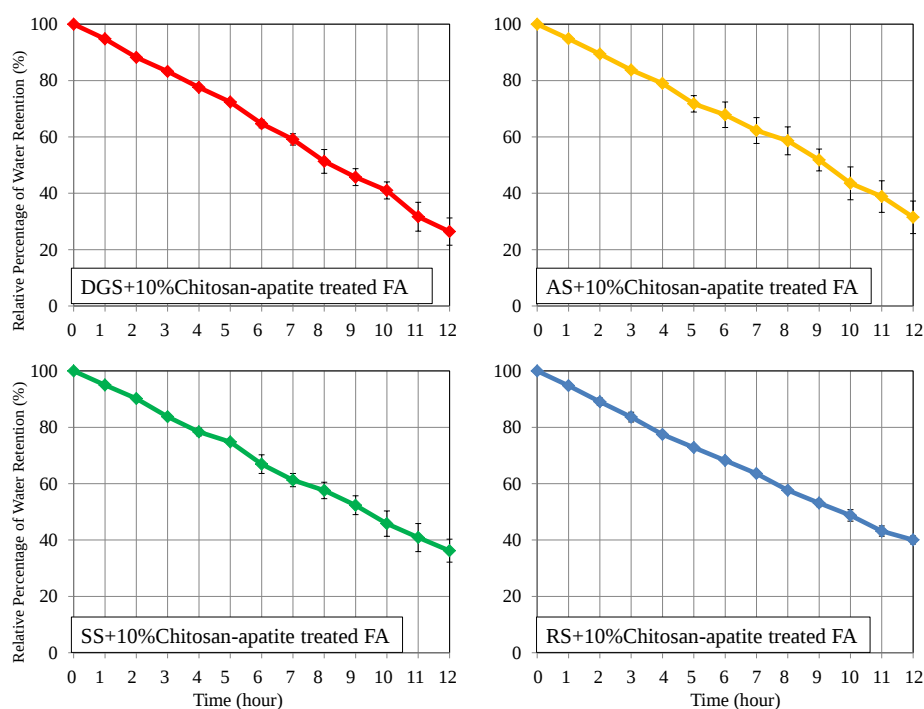


Figure 5-54 Water retention curves of DGS, AS, SS and RS mixed with chitosan-apatite treated FA at 10 wt% mixing ratio and 40 °C

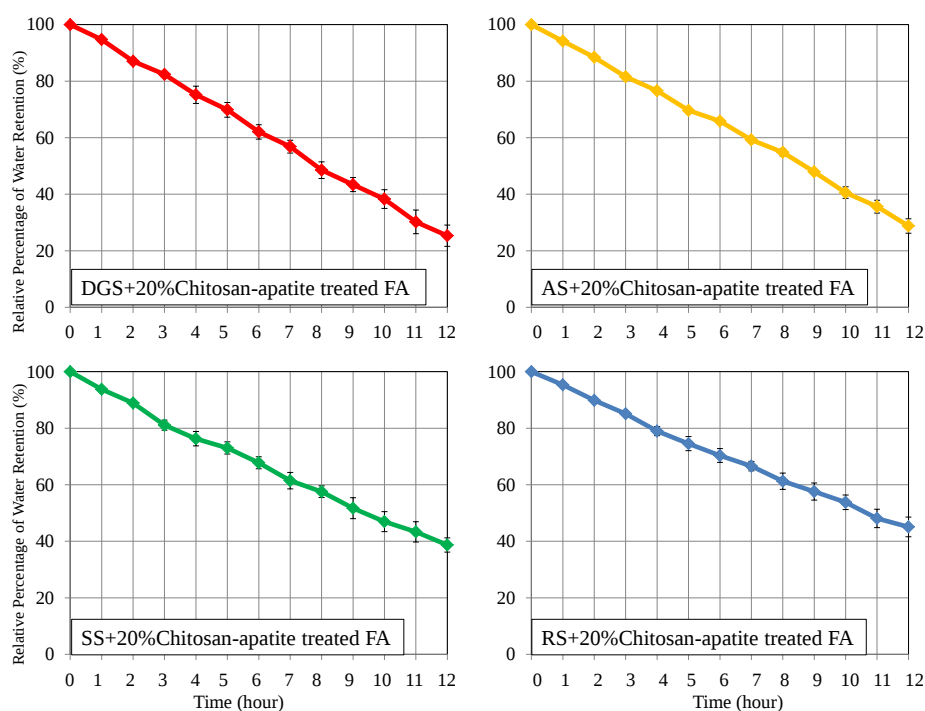


Figure 5-55 Water retention curves of DGS, AS, SS and RS mixed with chitosan-apatite treated FA at 20 wt% mixing ratio and 40 °C

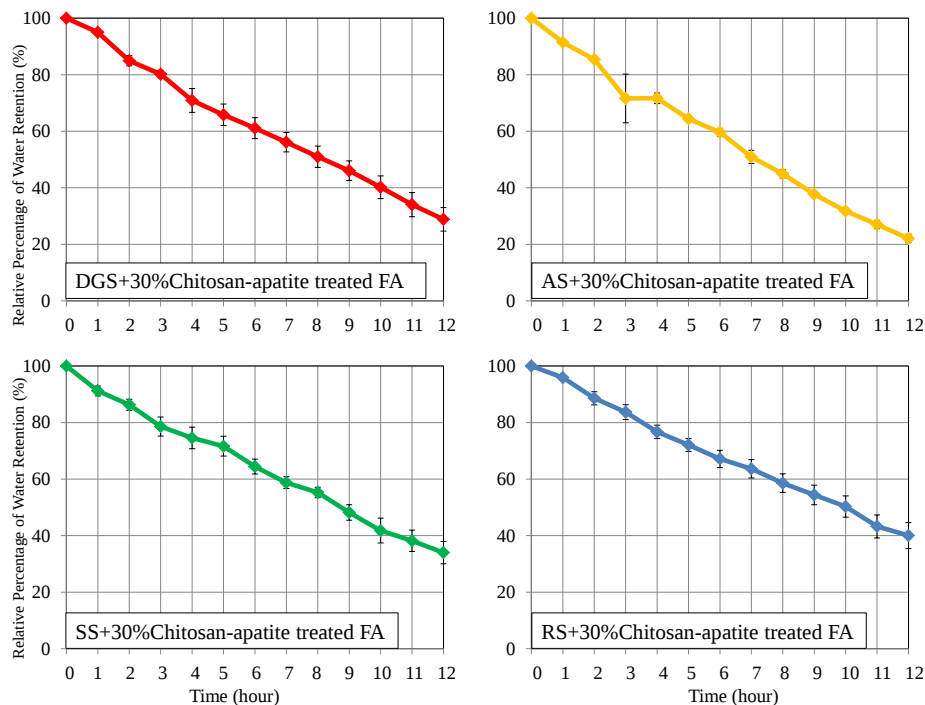


Figure 5-56 Water retention curves of DGS, AS, SS and RS mixed with chitosan-apatite treated FA at 30 wt% mixing ratio and 40 °C

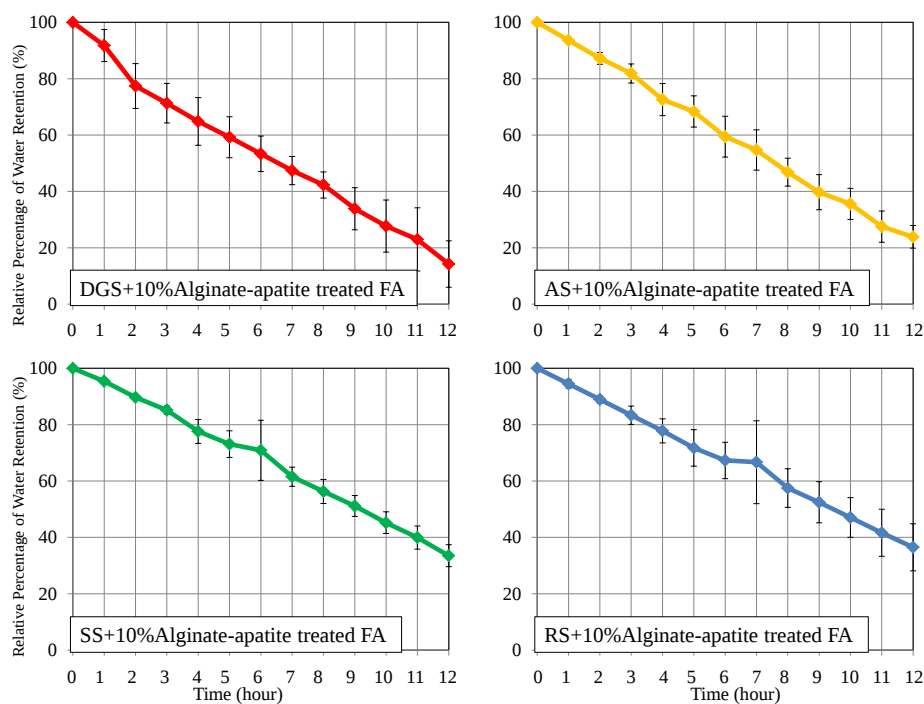


Figure 5-57 Water retention curves of DGS, AS, SS and RS mixed with alginate-apatite treated FA at 10 wt% mixing ratio and 40 °C

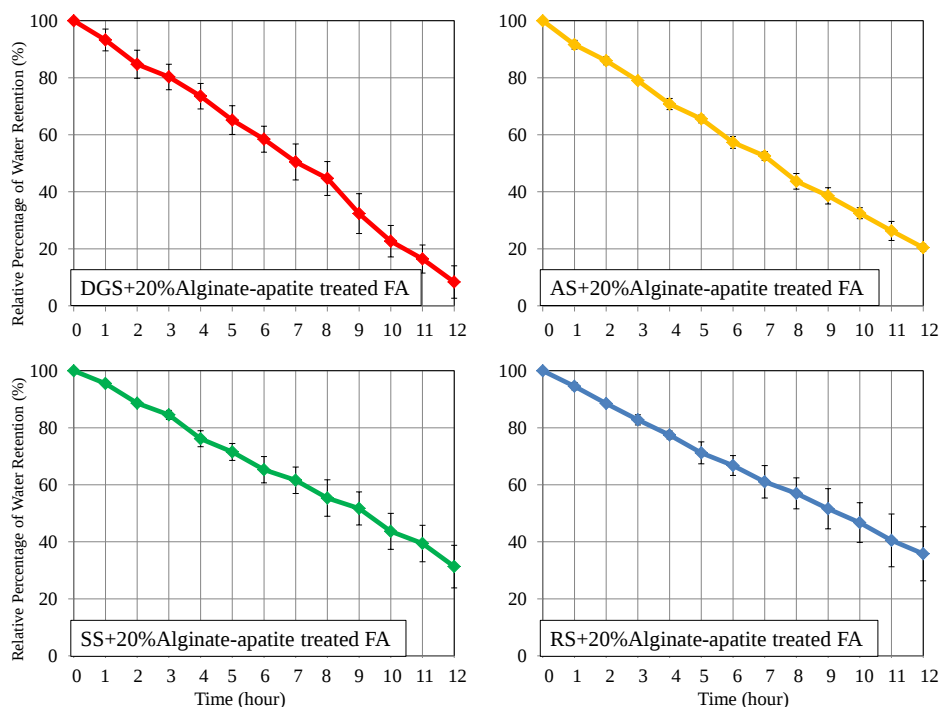


Figure 5-58 Water retention curves of DGS, AS, SS and RS mixed with alginate-apatite treated FA at 20 wt% mixing ratio and 40 °C

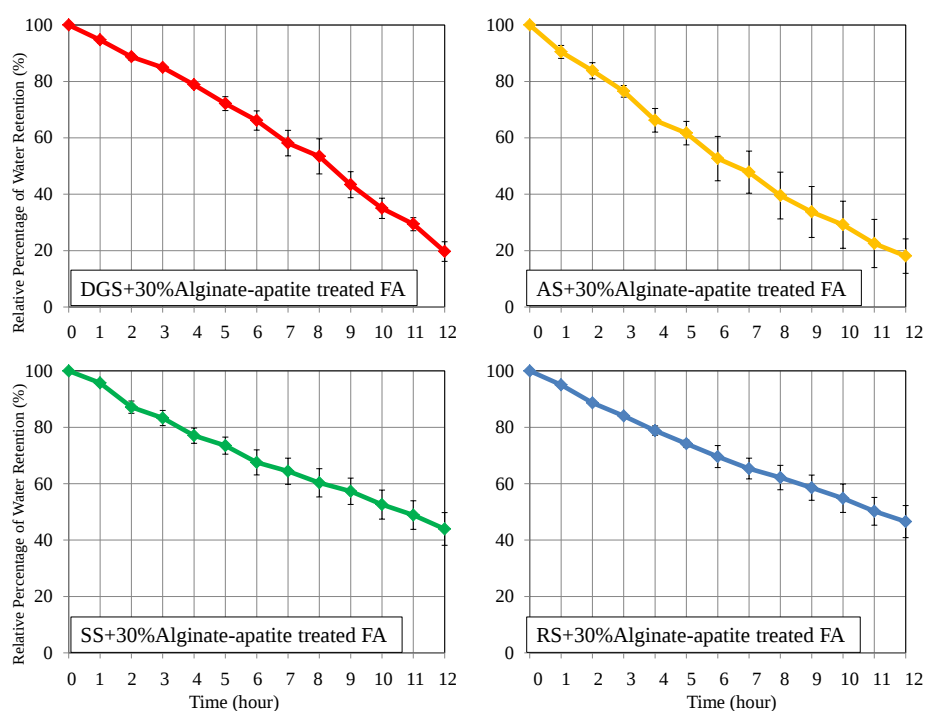


Figure 5-59 Water retention curves of DGS, AS, SS and RS mixed with alginate-apatite treated FA at 30 wt% mixing ratio and 40 °C

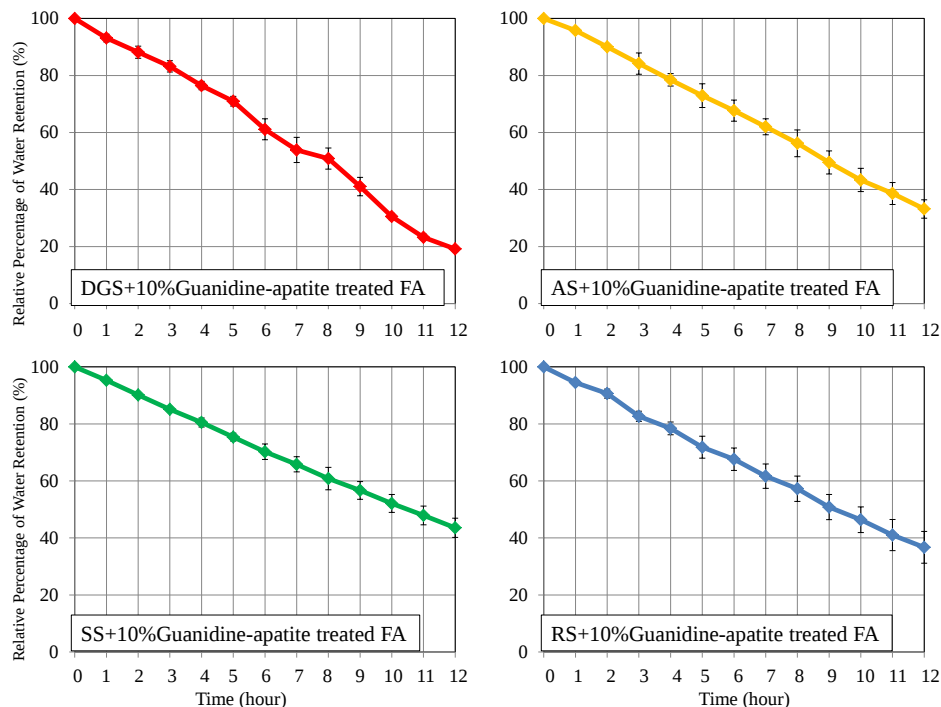


Figure 5-60 Water retention curves of DGS, AS, SS and RS mixed with guanidine-apatite treated FA at 10 wt% mixing ratio and 40 °C

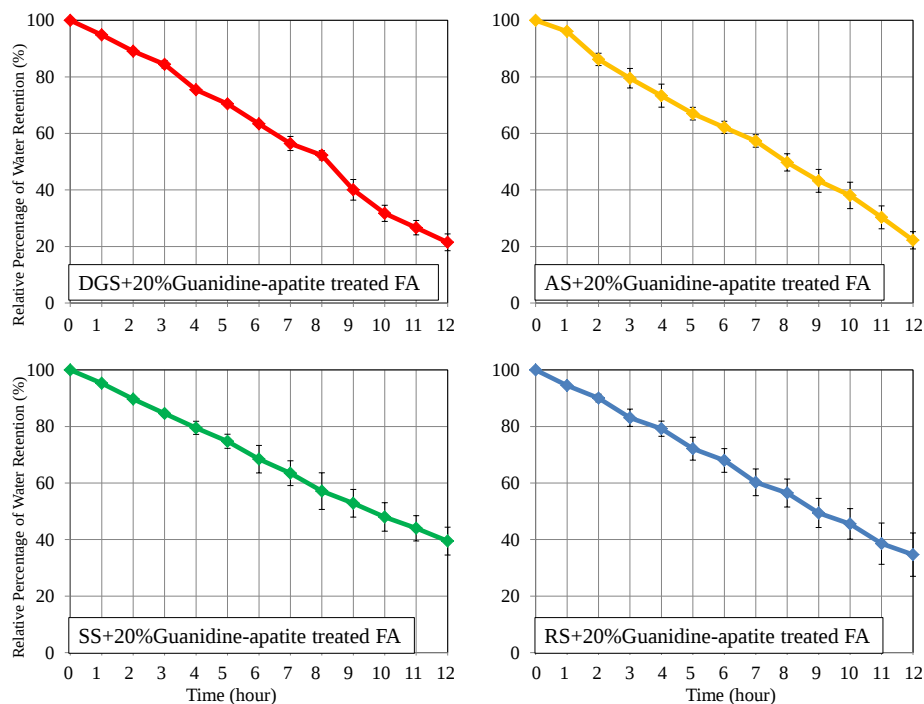


Figure 5-61 Water retention curves of DGS, AS, SS and RS mixed with guanidine-apatite treated FA at 20 wt% mixing ratio and 40 °C

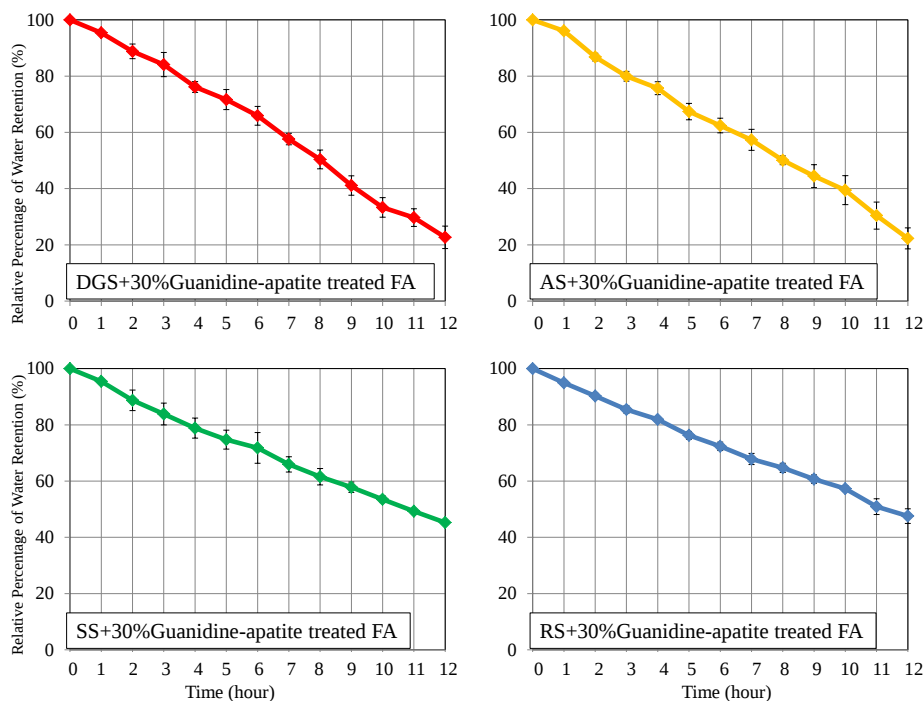


Figure 5-62 Water retention curves of DGS, AS, SS and RS mixed with guanidine-apatite treated FA at 30 wt% mixing ratio and 40 °C

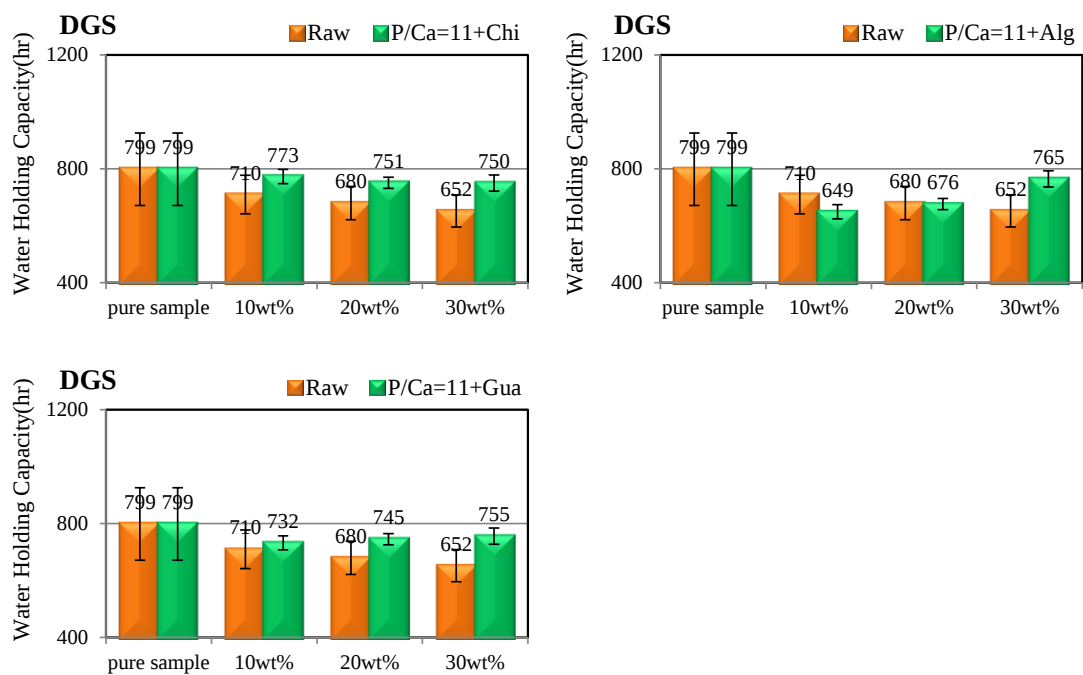


Figure 5-63 WRC of DGS mixed with raw FA or organic-apatite treated FA at 40 °C

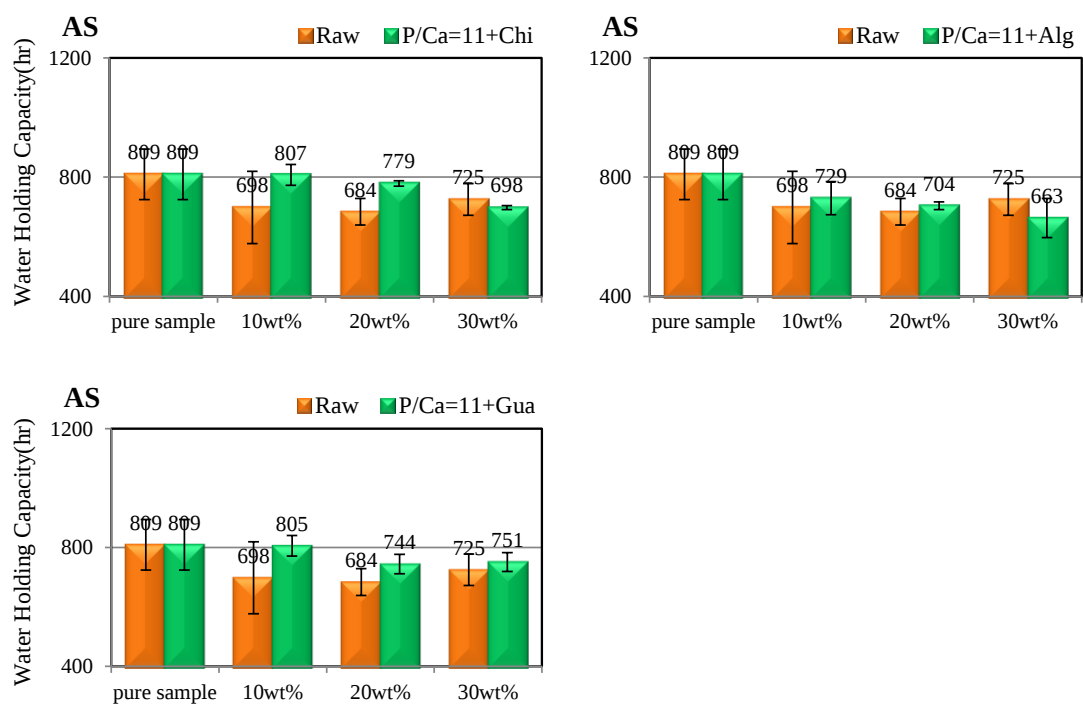


Figure 5-64 WRC of AS mixed with raw FA or organic-apatite treated FA at 40 °C

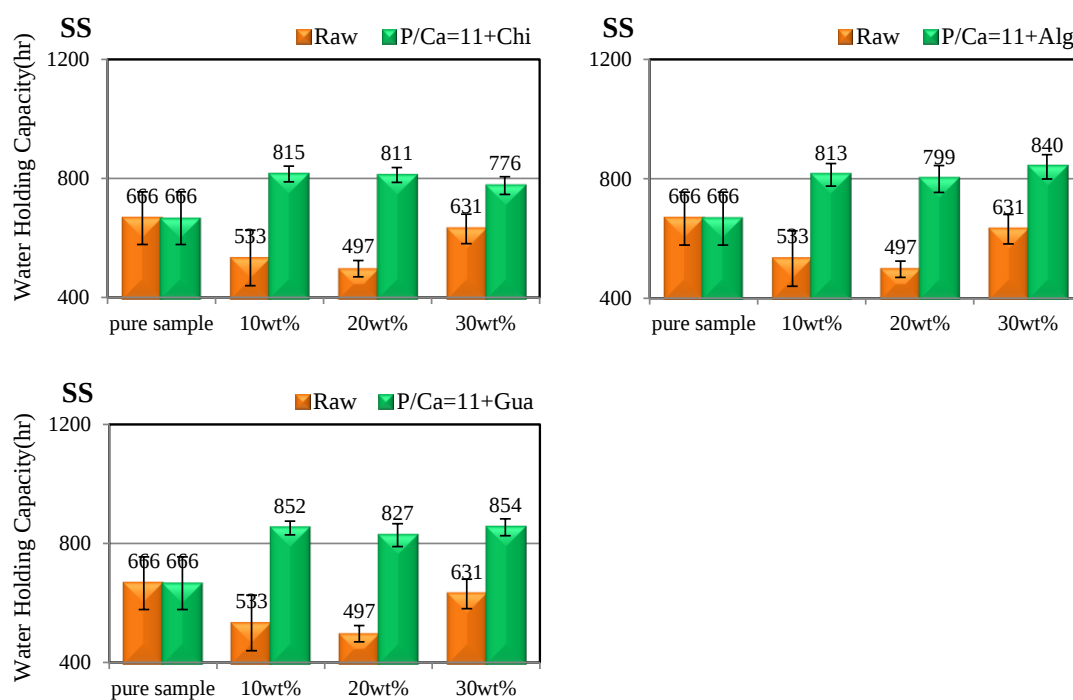


Figure 5-65 WRC of SS mixed with raw FA or organic-apatite treated FA at 40 °C

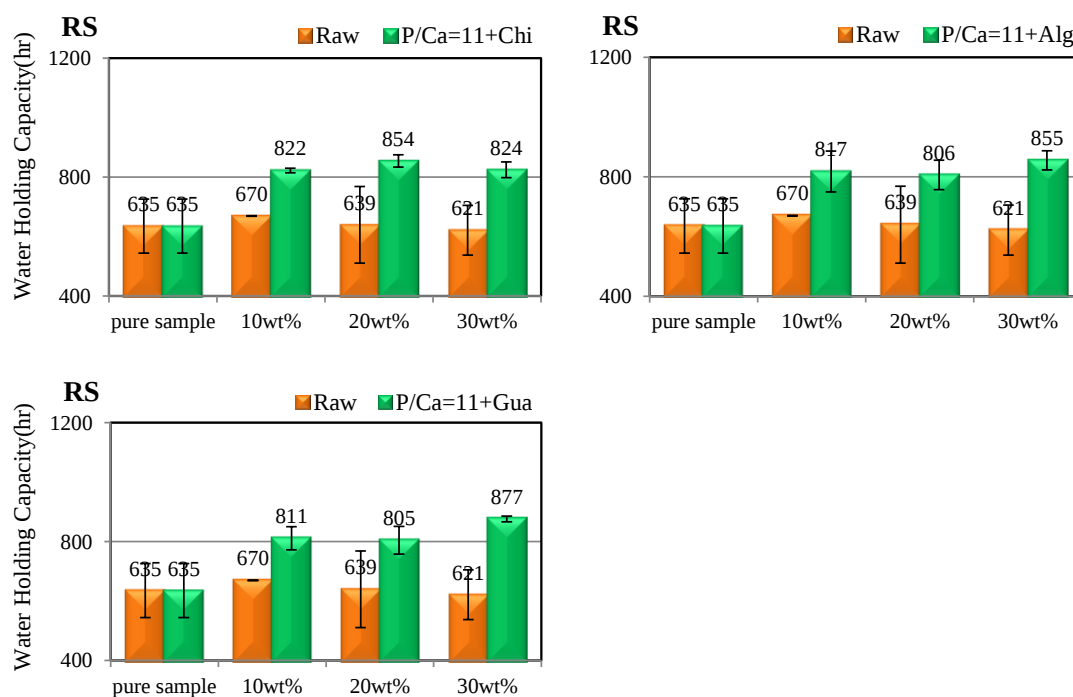


Figure 5-66 WRC of RS mixed with raw FA or organic-apatite treated FA at 40 °C

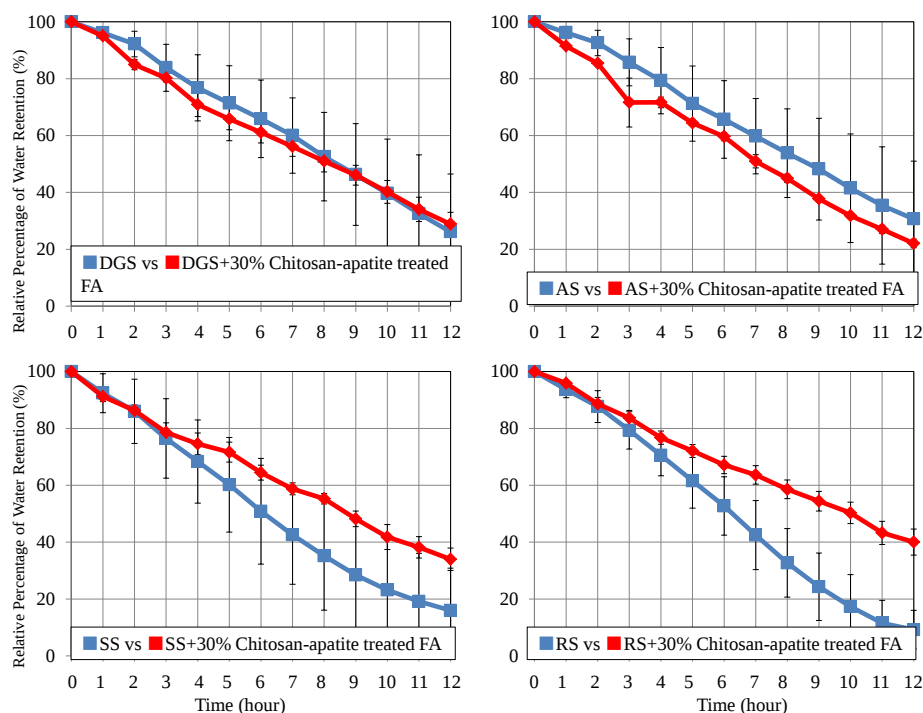


Figure 5-67 Comparison between water retention curves of soil/sand and soil/sand mixed with chitosan-apatite treated FA at 30 wt% of mixing ratio and 40 °C

Table 5-8 Summary of WRC of soil/sand mixed with organic-apatite treated FA at 40 °C

Flay ash		40 °C			
		DGS	AS	SS	RS
Raw FA		-11.1%**	-10.4%**	-5.3%**	—
Organic-treatment	Chitosan	—	-13.7%**	+22.4%**	+38.1%**
	Alginate	-4.3%*	-9.9%**	+26.1%**	+34.6%**
	Guanidine	-6.8%*	-8.0%*	+28.2%**	+38.1%**

All data was conducted by t-test, and “*” stand to “p value < 0.05”, “**” stand to “p value < 0.01” of t-test.

5.3.2.4 Comparison of WRC changed by mixing organic-apatite treated FA at between room and high temperatures

Effects of mixing organic-apatite treated FA on WRC of soil/sand between room temperature and 40 °C are compared in Table 5-9. It should be noted that these ratios were calculated using WRC changes which were regarded as within experimental errors by t-test. Therefore, discussions in this section might include some uncertainties. It is suggested that when temperature increased, effect of mixing chitosan-apatite treated FA on WRC of soil/sand became stronger than that at room temperature. However, those effects on WRC of soils at 40

℃ were opposite to those at room temperature. For soil/sand mixed with alginate-apatite treated FA, effects of mixing FA on WRC of almost all soils and sands were promoted when temperature was increased, except for that of DGS. It is the same with the effects of mixing chitosan-apatite treated FA. The effects of alginate-apatite treated FA on WRC of soils were opposite between room temperature and 40 ℃. Mixing guanidine-apatite treated FA increased WRC of sands at 40 ℃ more than at room temperature. This means that the effects became stronger when temperature is increased. For WRC of soils, the effects of mixing guanidine-apatite treated FA at 40 ℃ was opposite to those at room temperature. These effects were weakened at high temperature. All results suggest that WRC of soil/sand mixed with organic-apatite treated FA have significant soil/sand type dependency and temperature dependency.

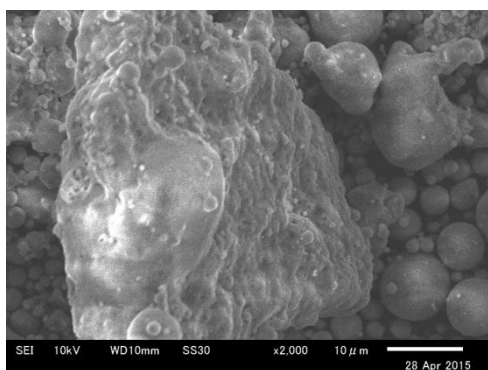
Table 5-9 Comparison between effects of soil/sand mixed with organic-apatite treated FA at room temperature and 40 ℃

Flay ash		40 ℃/Room temperature			
		DGS	AS	SS	RS
Raw FA		-7.93	-10.40	-26.50	-0.71
Organic-treatment	Chitosan	-1.56	-4.15	2.17	3.66
	Alginate	-0.53	-1.29	3.68	4.12
	Guanidine	-0.78	-0.93	2.17	2.70

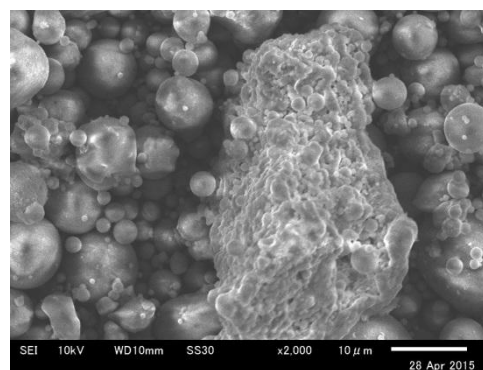
5.3.2.5 Surface morphology and specific surface area of organic-apatite treated FA

Figure 5-68 shows surface morphology of organic-apatite treated FA. Compared to surface morphology of organic-treated FA (see Figure 5-33), organic-apatite treated FA have bigger sized aggregation. Bigger aggregates normally have lower specific surface area. Specific surface area measurement shows that chitosan-apatite treated FA has 2.11 m²/g of specific surface area. Alginate-apatite treated FA and guanidine-apatite treated FA have 2.53 m²/g and 3.81 m²/g, respectively. All specific surface areas were lower than those of soils and RS. Surface areas of soils and RS are 15.64 m²/g for DGS, 136.9 m²/g for AS, and 4.70 m²/g for RS, respectively. However, surface areas of organic-apatite treated FA are higher than surface area of SS, which is 1.71 m²/g. As mentioned in section 4.3.7, specific surface area is

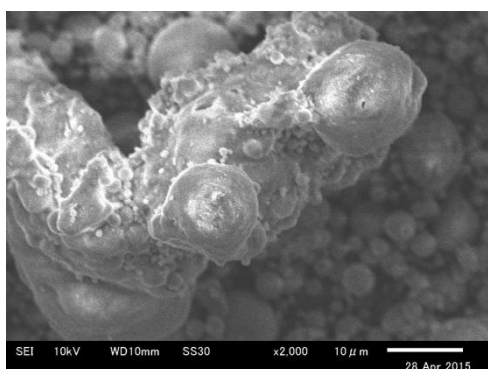
supposed to be an important factor that might increase WRC when surface area is high. If organic-apatite treated FA has larger proportions of big aggregates, it might decrease average surface area of FA/soil mixture and FA/RS mixture samples when organic-apatite treated FA is amended. It might decrease WRC of soils and RS. On the other hand, amendment of organic-apatite treated FA might increase average surface area of FA/SS mixture and thus increase WRC correspondingly. Expected effects of specific surface area on WRC of soils and SS agree with experimental results. In fact, organic-apatite treated FA, whose specific surface areas are larger than that of SS and lower than those of soils, increased WRC of SS and decreased WRC of soils. However, it still fails to explain contrast effect on WRC of RS.



Chitosan-apatite treated FA



Alginate-apatite treated FA



Guanidine-apatite treated FA

Figure 5-68 Surface morphology of organic-apatite treated FA

5.3.2.6 Capillary water content of soil/sand mixed with organic-apatite treated FA

Capillary water contents of soil/sand mixed with only alginate-apatite treated FA are shown in Table 5-5 because of the limitation of available samples. Similar with alginate-treated FA in section 5.2.1.6, capillary water content of alginate-apatite treated FA is higher than those of raw FA and DGS. They are higher than the initial water content (30 wt%) in WRC measurement. This means that only capillary water evaporated from alginate-apatite treated FA during WRC measurement. If capillary water influences WRC strongly, WRC of alginate-treated FA and alginate-apatite treated FA at 40 °C should be similar. However, WRC of alginate-treated FA is 917 hr, which is much higher than that of alginate-apatite treated FA (531 hr).

When mixing alginate-apatite treated FA into soil/sand, capillary water contents of DGS, SS and RS were increased and that of AS was decreased. This is, again, similar to those of soil/sand mixed with alginate-treated FA. When capillary water contents of soil/sand mixed with apatite-synthesized FA are compared, effects of alginate-apatite treated FA amendment on capillary water content of DGS, AS and SS are the same. When comparing WRC of soil/sand mixed with apatite-synthesized FA and alginate-apatite treated FA, their effects on WRC of SS by mixing apatite-synthesized FA and alginate-apatite treated FA were also the same. However, their effects on WRC of soils were opposite. WRC of DGS and AS was increased or not influenced by mixing apatite-synthesized FA. On the other hand, they were all decreased significantly by mixing alginate-apatite treated FA. These suggest that capillary water content is not sufficient to explain WRC of soil/sand mixed with alginate-apatite treated FA independently. This conclusion agrees with the results mentioned in section 4.3.7 that capillary water content might has no obvious effect on WRC of soil/sand.

5.3.2.7 Water repellency of organic-apatite treated FA on soil/sand

Water repellency were measured only for DGS, AS and SS mixed with alginate-apatite treated FA owing to the limitation of available samples. The results are summarized in Table 5-6. Mixing alginate-apatite treated FA increased water repellency of DGS, AS and SS. When comparing these to water repellency of soil/sand mixed with alginate-treated FA and apatite-synthesized FA (see Table 4-1), their effects on water

repellency of DGS and SS were the same. On the other hand, the effects on water repellency of AS by mixing apatite-synthesized FA were opposite to those of alginate-/alginate-apatite treated FA. At 40 °C, WRC of DGS was decreased by alginate-apatite treated FA, but increased by alginate-treated FA and apatite-synthesized FA. WRC of SS was increased by alginate-apatite treated FA and apatite-synthesized FA but decreased by alginate-treated FA. Alginate-apatite treated FA, alginate-treated FA and apatite-synthesized FA gave the similar effects on water repellency of DGS and SS, but their effects on WRC were inconsistent. As described in the section 5.3.1.7, this suggests that there might be unconsidered, physical, and/or hydraulic factors that influence the mechanism between water repellency and WRC. In fact, this factor depends on FA treatment method and soil/sand type. Because DGS and RS have similar size distribution but receive contrast effects by FA amendment, interactions between organic compounds contained in soil/sand and those of treated FA might be non-negligible.

5.4 Organic-added thermal treated FA

5.4.1 WRC of organic-added thermal treated FA at 40 °C

Three conditions of thermal treatments were tested for organic-added thermal treatment of FA. In the first experimental set (set I), FA and organic reagent mixing ratio is 7 : 4 as weight base. The mixture was heated at 300 °C for 3 hours. In the second experimental set (set II), FA and organic reagent mixing ratio was 10 : 1. The mixture was heated at 300 °C for 1 hour. In the third experimental set (set III), FA, organic reagent, and sodium bicarbonate mixing ratio was 10 : 1 : 1. The mixture was heated at 300 °C for 1 hour. It should be noted that all WRC measurement were conducted at 40 °C only one time because of limitation of available samples. Therefore, all discussions in this section need to consider some uncertainty. Comparison of water retention curves of raw FA and all organic-added thermal treated FA are shown in Figure 5-69 to 5-71. In Figure 5-72, WRC of pure DGS and raw FA, organic-added thermal treated FA with cellulose, sucrose and starch are shown.

In experimental set I, WRC of cellulose-/starch-added thermal treated FA is 708 and 770 hr, respectively and higher than that of raw FA. WRC of sucrose-added thermal treated FA was 553 hr and similar to WRC of raw FA (see Figure 5-72). According to Figure 5-69,

water retention curves of cellulose- and starch-added thermal treated FA were categorized as type C. This means that water evaporation rate of cellulose- and starch-added thermal treated FA were constant. Water retention curve of sucrose-added thermal treated FA was categorized as type L_d . When compared to water retention curve of raw FA at 40 °C, residual water content after 12 hours drying was lower than that of raw FA. Water evaporation of cellulose-added thermal treated FA was smaller than that of raw FA in the first 10 hours but residual water was finally less than that of raw FA until the end of drying process. Smaller water evaporation until 10 hours explains higher WRC of cellulose-added thermal treated FA in set I than that of raw FA. Water evaporation of sucrose-added thermal treated FA in set I was also smaller than that of raw FA at first 8 hours but residual water was finally dried out after 8 hours. After smaller water evaporation until 8 hours and larger evaporation after 3 hours were balanced, sucrose-added thermal treated FA had similar WRC with raw FA. Water evaporation of starch-added thermal treated FA was smaller than that of raw FA in the whole drying process. However, residual water content after 12 hours drying was similar with that of raw FA. These results explain higher WRC of starch-added thermal treated FA than raw FA at 40 °C.

In experimental set II, organic contents used in thermal treatment of FA were decreased. WRC of all organic-added thermal treated FA were also decreased compared to those in set I. WRC of cellulose-added thermal treated FA was 541 hr. WRC of sucrose-added thermal treated FA and starch-added thermal treated FA were 487 hr and 573 hr, respectively (see Figure 5-72). As shown in Figure 5-70, water retention curves of all thermal treated FA were categorized as L_d . In the first 8 hours of drying process, water evaporation of cellulose- and starch-added thermal treated FA were smaller than that of raw FA. However, water evaporation continued and residual water was dried out after 8 hours. Owing to the balance between smaller water evaporation at early drying stage and continuous evaporation to dry-out, cellulose-/sucrose-added thermal treated FA had similar WRC with raw FA. When WRC of organic-added thermal treated FA between set I and set II are compared, increase of organic reagent in FA treatment also increased WRC of treated FA. It is the same with WRC of raw and organic-treated FA. Organic-treated FA have higher WRC than raw FA. On the other hand, organic reagent addition in apatite treatment showed an opposite result.

Organic-apatite treated FA had smaller WRC than apatite-synthesized FA.

In experimental set III, WRC of organic-added thermal treated FA were increased slightly with increase of sodium bicarbonate. They are similar with each other. WRC of cellulose-added thermal treated FA was 637 hr. WRC of sucrose-added thermal treated FA and starch-added thermal treated FA were 610 hr and 626 hr, respectively (see Figure 5-72). Comparison between water retention curves of raw FA and organic-added thermal treated FA are shown in Figure 5-71. All water retention curves of organic-added thermal treated FA were categorized as S_u and residual water contents after 12 hours drying were higher than that of raw FA. In the first 8 to 9 hours, water evaporation of all organic-added thermal treated FA were smaller than that of raw FA but continuous evaporation made residual water dried out. Therefore, residual water contents of organic-added thermal treated FA were all lower than that of raw FA. As balanced between smaller water evaporation at early drying stage and continuous drying at late stage, WRC of organic-added thermal treated FA in set III were similar to raw FA at 40 °C. When WRC of organic-added thermal treated FA between set II and set III, foaming agent addition increased WRC of treated FA. Macro-porous structure of FA aggregates generated by foaming agent might contribute to the increase of WRC. It would be discussed in the section 5.4.2.4.

They are summarized that WRC of treated FA increased with increase of organic compounds in FA treatment. However, an opposite effect was found in apatite treatment. Foaming agent increased WRC possibly owing to macro-porous structure.

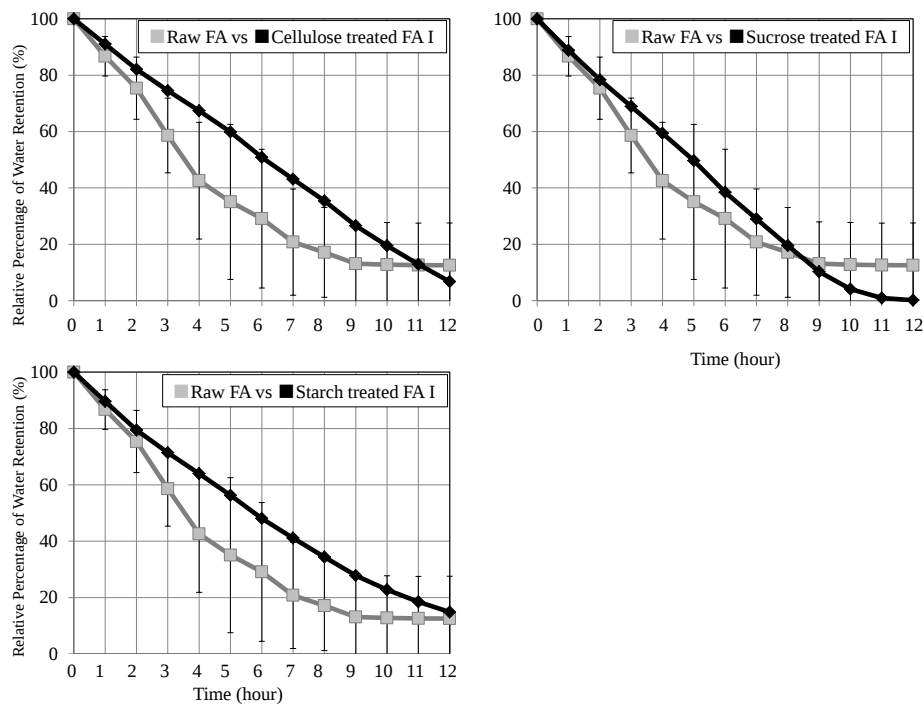


Figure 5-69 Comparison between water retention curves of raw FA and organic-added thermal treated FA of set I at 40 °C

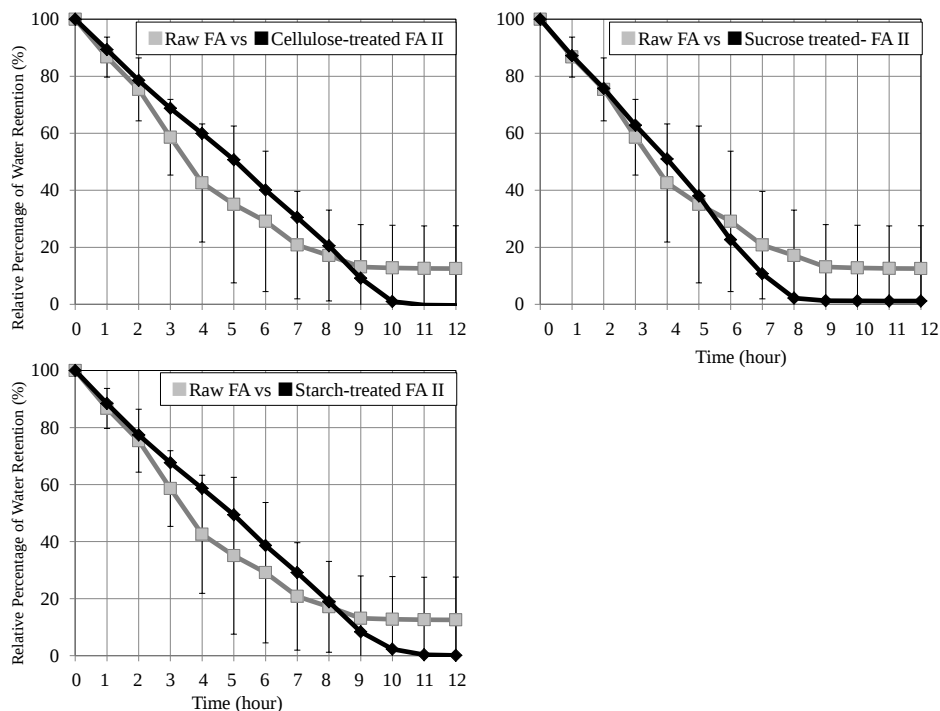


Figure 5-70 Comparison between water retention curves of raw FA and organic-added thermal treated FA of set II at 40 °C

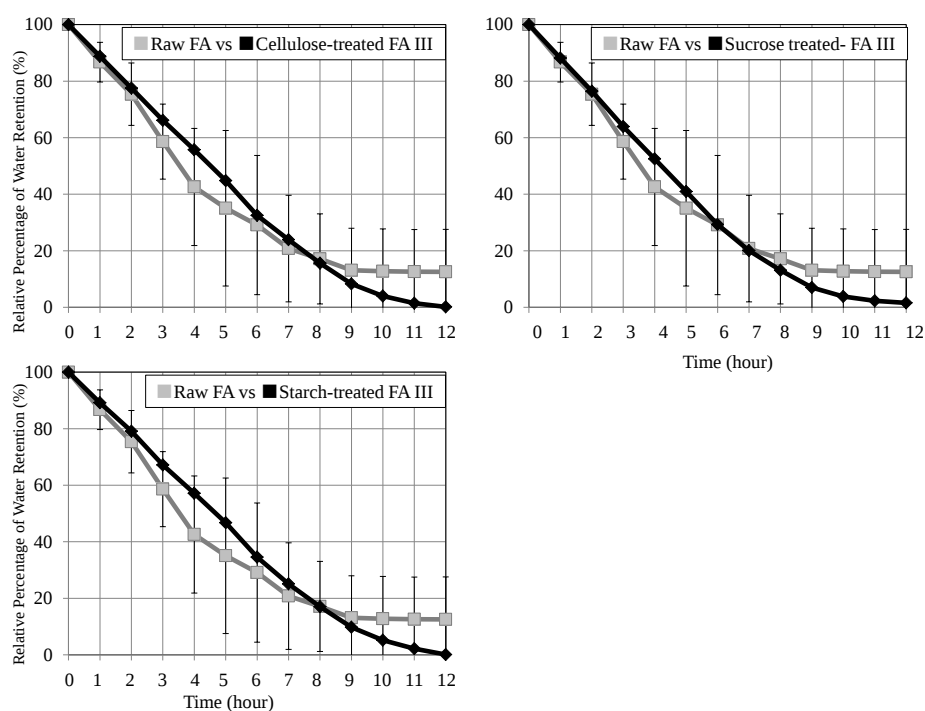


Figure 5-71 Comparison between water retention curves of raw FA and organic-added thermal treated FA of set III at 40 °C

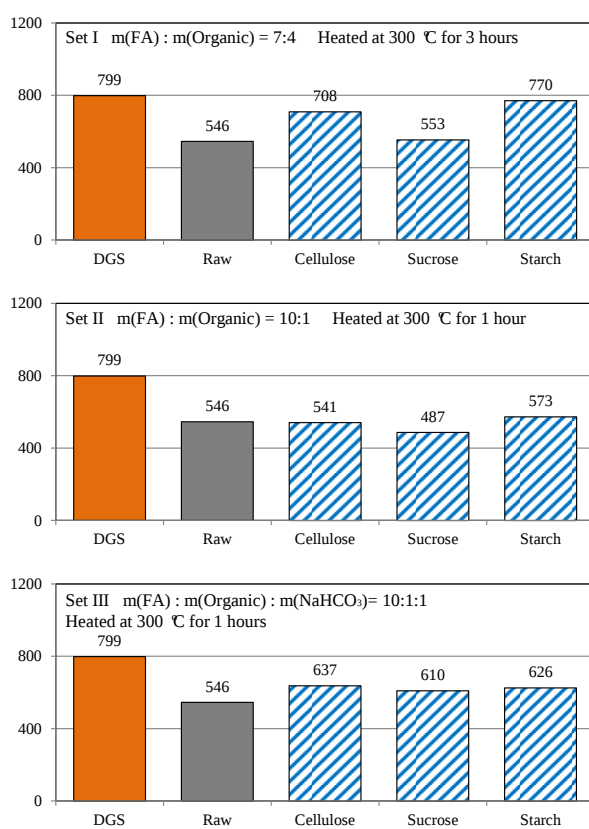


Figure 5-72 WRC of DGS, raw FA and organic-added thermal treated FA

5.4.2 WRC of DGS mixed with organic-added thermal treated FA at 40 °C

5.4.2.1 Organic-added thermal treated FA amendment (experimental set I)

Water retention curves of DGS mixed with organic-added thermal treated FA of experimental set I at 40 °C were shown in Figure 5-74 to 5-76 and their WRC were shown in Figure 5-73. When mixing cellulose-added thermal treated FA, WRC of DGS was decreased by 38.5 %. Sucrose-added thermal treated FA and starch-added thermal treated FA decreased WRC of DGS by 49.3 % and 36.4 %, respectively. According to Figure 5-74 to 5-76, water retention curves of DGS mixed with organic-added thermal treated FA were categorized as L_d except for water retention curve of DGS mixed with starch-added thermal treated FA (categorized as C_d). Water evaporation of all FA-mixed DGS were promoted and residual water contents after 12 hours drying were lower than that of pure DGS at 40 °C (see Figure 3-2). These resulted in lower WRC of DGS mixed with organic-added thermal treated FA of set I than those of pure DGS.

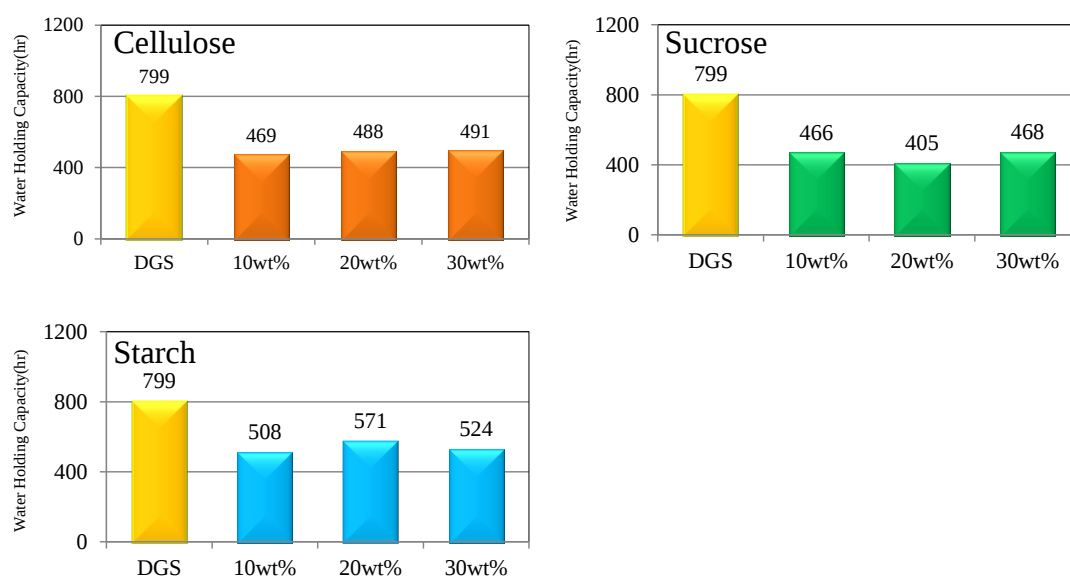


Figure 5-73 WRC of DGS mixed with raw FA or organic-added thermal treated FA of set I at 40 °C

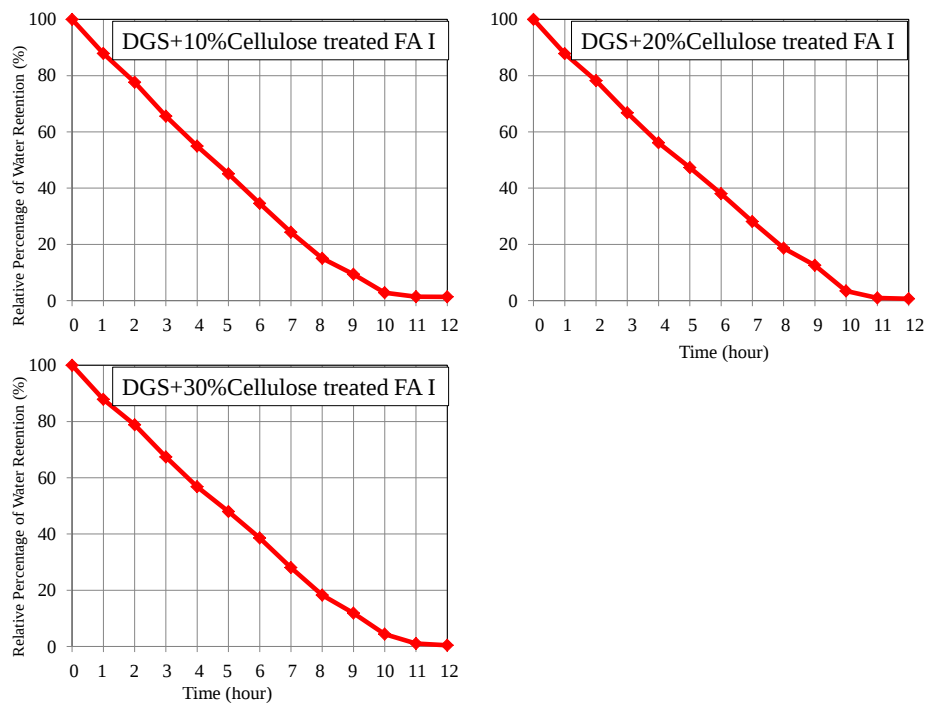


Figure 5-74 Water retention curves of DGS mixed with cellulose-added thermal treated FA of set I and 40 °C

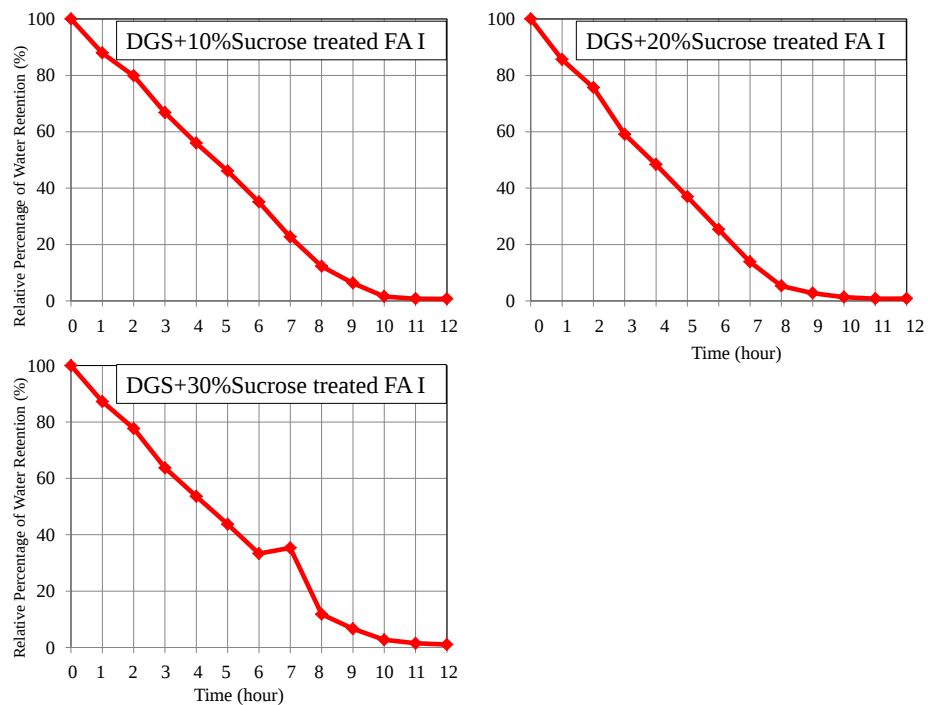


Figure 5-75 Water retention curves of DGS mixed with sucrose-added thermal treated FA of set I and 40 °C

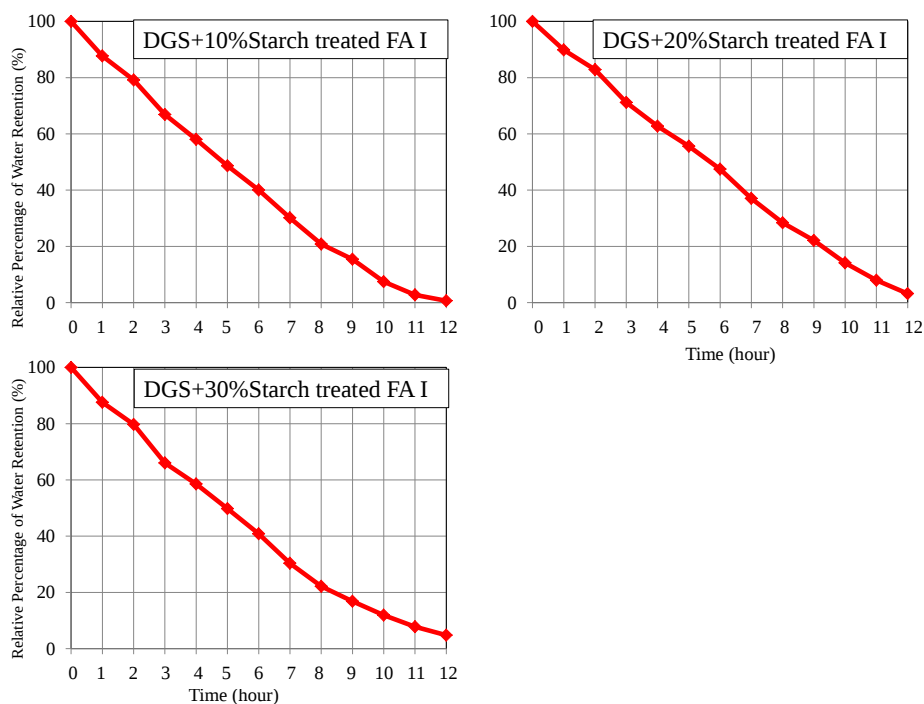


Figure 5-76 Water retention curves of DGS mixed with starch-added thermal treated FA of set I and 40 °C

5.4.2.2 Organic-added thermal treated FA amendment (experimental set II)

Comparison of water retention curves of DGS mixed with organic-added thermal treated FA of experimental set II to those of experimental set I at 40 °C were shown in Figure 5-78 to 5-80. Their WRC were shown in Figure 5-77. Although organic content was decreased in set II compared to set I and WRC was also decreased correspondingly, WRC of DGS mixed with organic-thermal treated FA were comparable between set I and set II except for some cases (see Figure 5-73). According to Figure 5-78 to 5-80, water retention curves of organic-added thermal treated FA of set II were similar to those of set I when there is no clear difference of WRC between set I and set II. In some cases like DGS mixed with sucrose-added thermal treated FA of set II, water retention curves of DGS mixed with organic-added thermal treated FA of set II was lower than those of set I in whole drying process. This means that water evaporation was promoted in DGS with “set II” FA compared to that in DGS with “set I” FA. Less organic compounds in FA thermal treatment decreased WRC of DGS when thermally treated FA was amended. However, these organic effect was found in only limited cases.

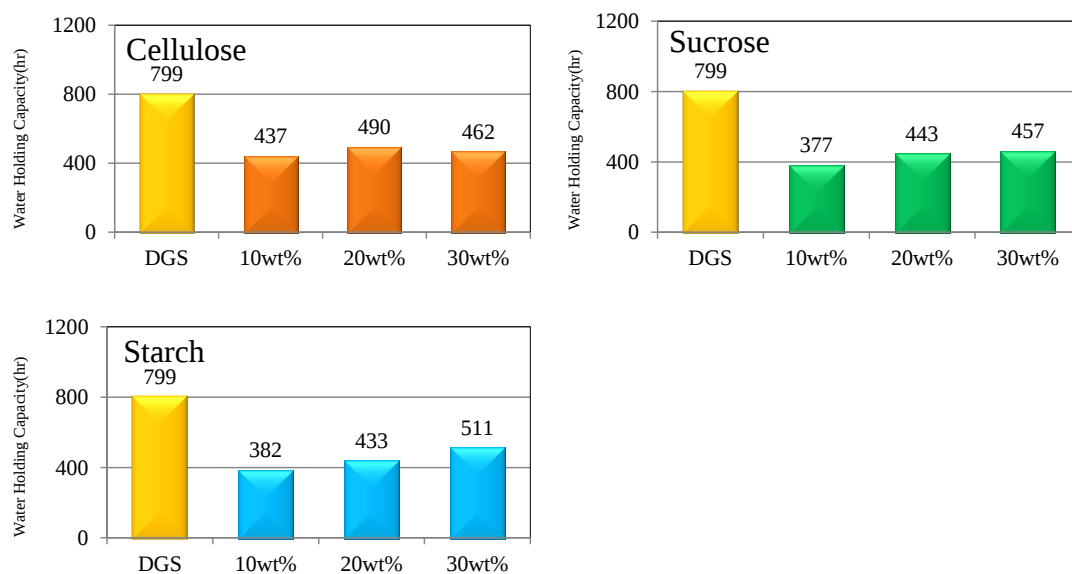


Figure 5-77 WRC of DGS mixed with raw FA or organic-added thermal treated FA of set II at 40 °C

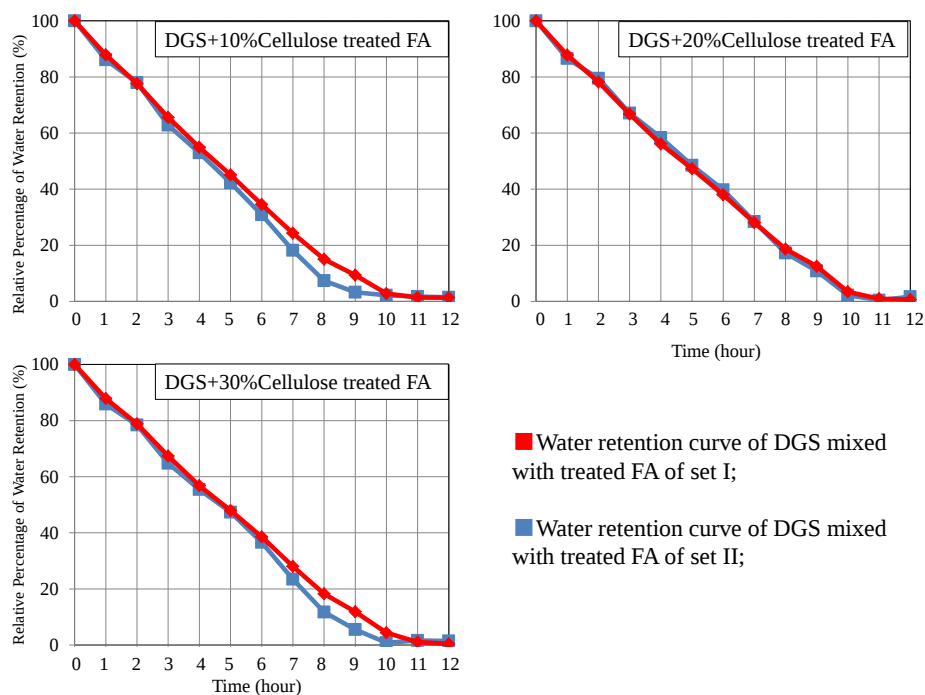


Figure 5-78 Comparison between water retention curves of DGS mixed with chitosan-added thermal treated FA of set I and that of set II at 40 °C

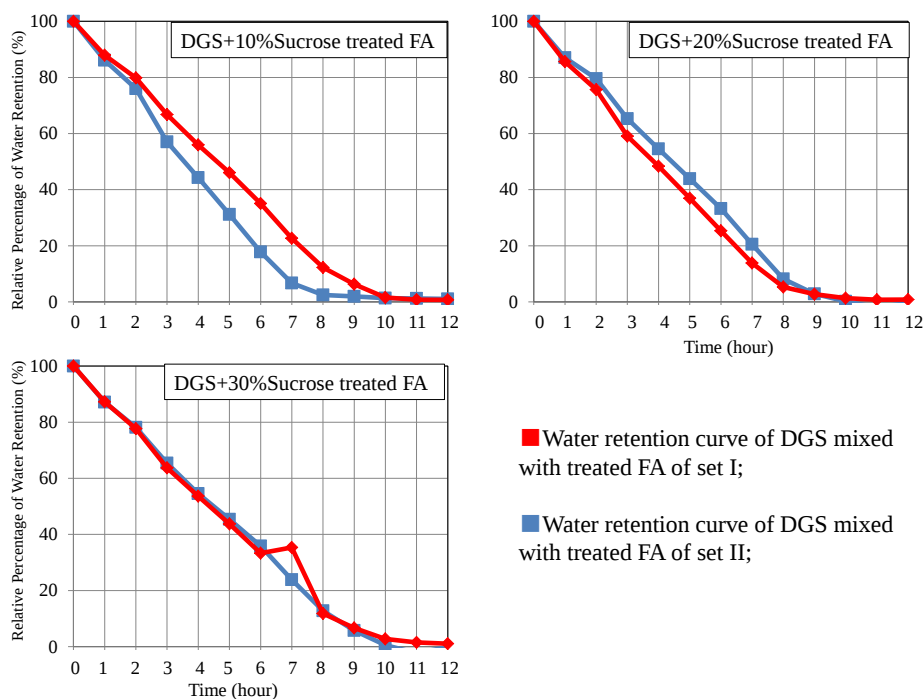


Figure 5-79 Comparison between water retention curves of DGS mixed with sucrose-added thermal treated FA of set I and that of set II at 40 °C

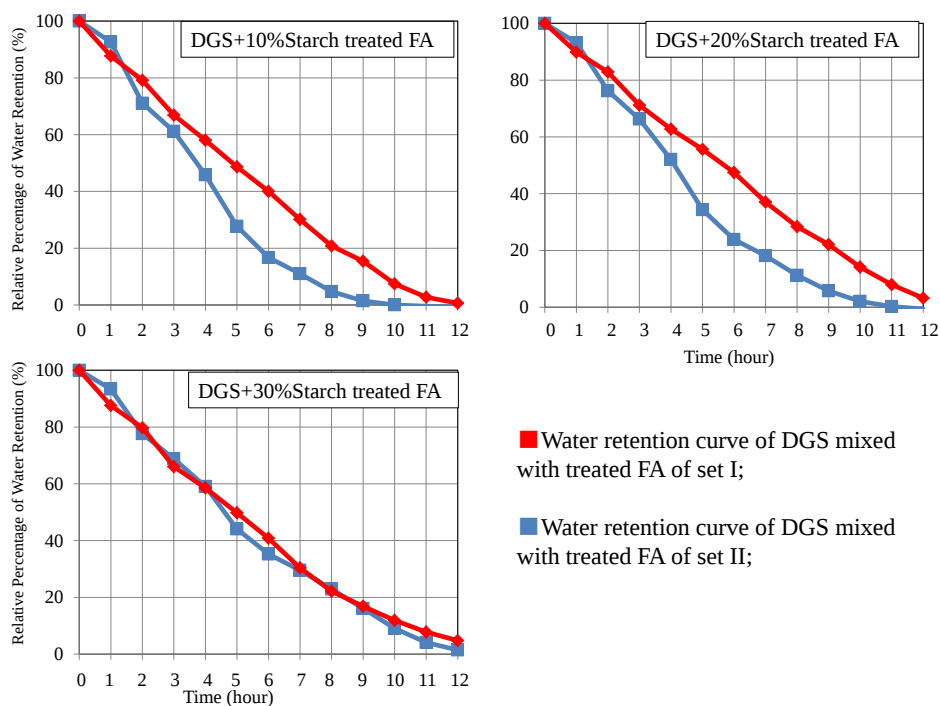


Figure 5-80 Comparison between water retention curves of DGS mixed with starch-added thermal treated FA of set I and that of set II at 40 °C

5.4.2.3 Organic-added thermal treated FA amendment (experimental set III)

Comparisons between water retention curves of DGS mixed with organic-added thermal treated FA of set II and set III are shown in Figure 5-82 to 5-84. WRC of these samples are shown in Figure 5-81. WRC are similar between set II and set III. According to Figure 5-82 to 5-84, water retention curves of DGS mixed with cellulose-added thermal treated FA of set II and set III are also similar with each other. In some cases like DGS mixed with sucrose-added thermal treated FA, water retention curves of DGS mixed with organic-added thermal treated FA of set II was lower than those of set III at the middle drying time. Foaming agent used in set III increased WRC of DGS with sucrose-added thermal treated FA compared to that of set II. On the other hand, lower WRC by foaming agent used in set III was also found. WRC of cellulose-added thermal treated FA of set III at 20 wt% mixing ratio decreased lower than that of set II. When modified FA is added to DGS, it is concluded that the effect of foaming agent used in FA thermal treatment on WRC of DGS are very limited. Macro-porous structure, generated by foaming agent, would give limited impact on WRC of FA-DGS mixture system.

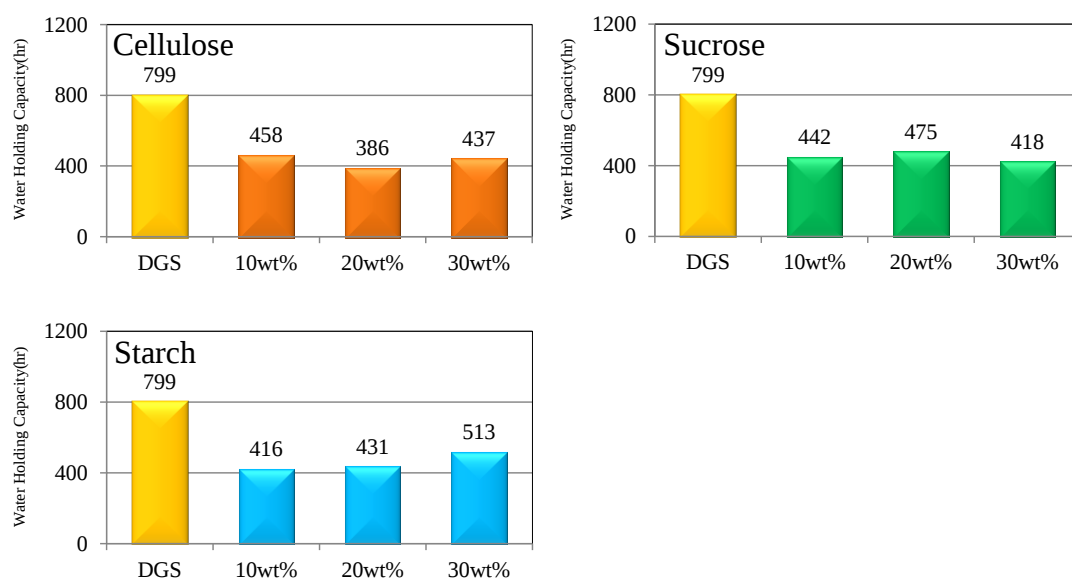


Figure 5-81 WRC of DGS mixed with raw FA or organic-added thermal treated FA of set III at 40 °C

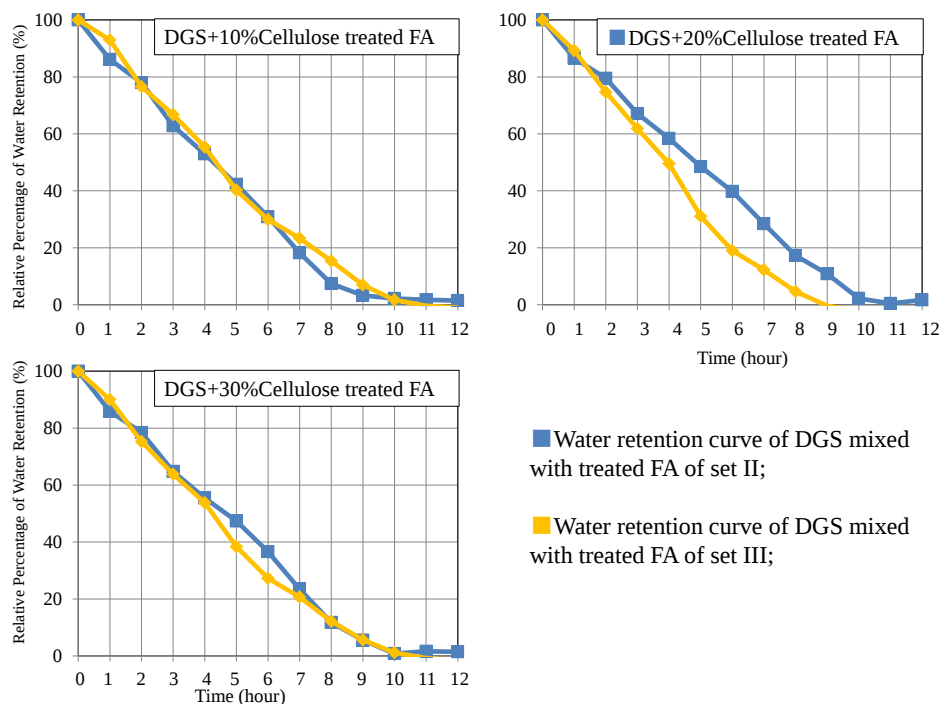


Figure 5-82 Comparison between water retention curves of DGS mixed with cellulose-added thermal treated FA of set II and that of set III at 40 °C

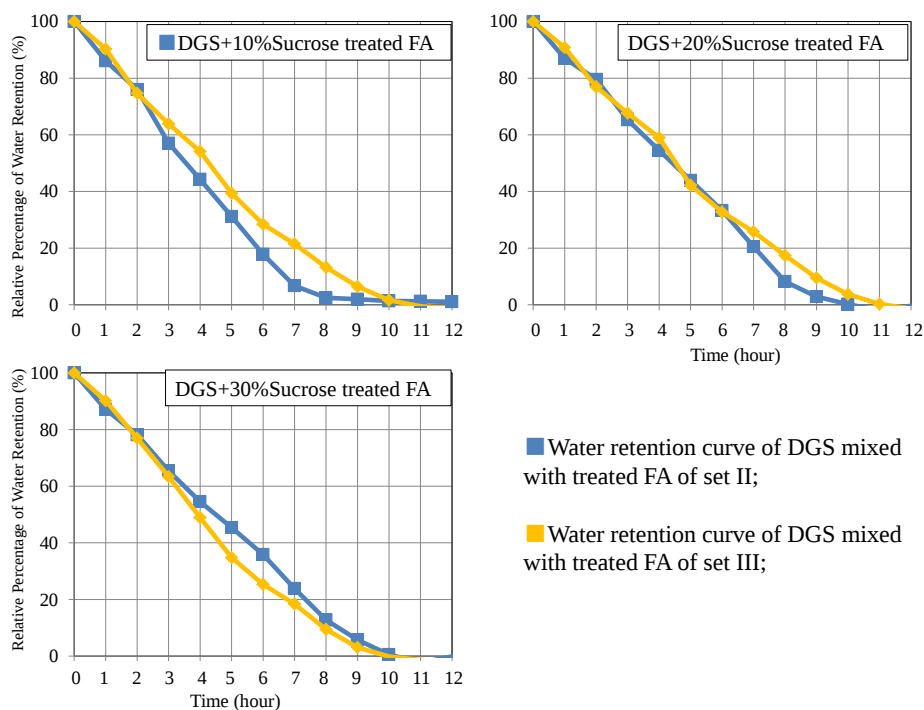


Figure 5-83 Comparison between water retention curves of DGS mixed with sucrose-added thermal treated FA of set II and that of set III at 40 °C

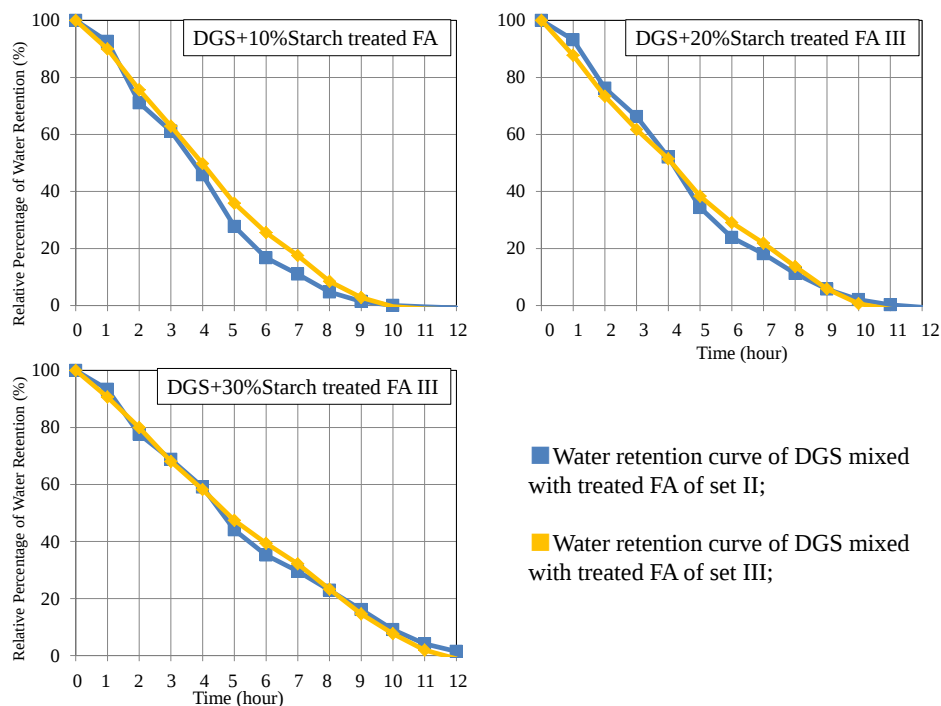


Figure 5-84 Comparison between water retention curves of DGS mixed with starch-added thermal treated FA of set II and that of set III at 40 °C

5.4.2.4 Surface morphology of organic-added thermal treated FA

Macro photos of starch-added thermal treated FA of three experimental sets were shown in Figure 5-85 and surface morphology of organic-added thermal treated FA, observed by SEM, were shown in Figure 5-86.

As shown in Figure 5-85, surface of starch-added thermal treated FA of set II shows macro-porous structures more than that of set I. This might be caused by more efficient decomposition of organic compound owing to less organic content in set II. Surface of starch-added thermal treated FA of set III has more macro-porous structures than that of set II. This should be caused by utilization of foaming agent. Because of high temperature, organic and foaming agents were decomposed into gases (Lerdkanchanaporn, 1999; Lerdkanchanaporn & Dollimore, 2000; Hirata and Nishimoto, 1991) and evaporation of water during thermal treatment formed countless porous structures. Although all treated FA were crushed after treatment for WRC measurement, semi-macro-porous structures around 500 μm or less remained in treated FA. This might influence WRC of FA-mixed DGS. When WRC of

DGS mixed with starch-added thermal treated FA was concerned, however, WRC of DGS mixed with treated FA of set II and III were similar with each other except for 10 wt% mixing ratio. This means that macro-porous structures gave a limited effect on WRC of DGS when starch-added thermal treated FA was amended.

According to pictures of SEM observation (see Figure 5-86), treatments are effective in changing surface morphology at micro-scale of raw FA. In cellulose-added thermal treatment of experimental set I, comparatively big and slender cellulose fibers were found. On the other hand, no obvious aggregation between FA particles and cellulose fibers was observed. Cellulose fibers are bigger than raw FA particles and seem to have lower surface area. This probably decreased specific surface area of treated FA compared to that of raw FA. Surface morphologies of FA after sucrose-added and starch-added thermal treatments of set I are similar. Big particle aggregation was found and they are sucrose/starch-bound FA particles. Organic compounds were covering over FA particles. This seems to make specific surface area of sucrose-/starch-added thermal treated FA lower than that of raw FA and also might increase water repellency of treated FA.

Decreasing the addition of organic content in experimental set II was supposed to decrease particle aggregation. Utilization of foaming agent in experimental set III was expected to generate micro-porosity in aggregation of organic compound and FA particles. This is supported by Figure 5-72, where WRC of organic-added thermal treated FA of set I were higher than those of set II. At the same time, WRC of organic-added thermal treated FA of set II were lower than those of set III. However, no obvious differences were found in micro-meter scale observation when surface morphology among treatments of set I, II and III were compared. SEM observations of apatite-synthesized FA, organic-treated FA and organic-apatite treated FA also found no obvious difference of surface morphology excluding big size aggregation generated by organic-treatment and organic-apatite treatment. It is reminded that amendment effects of these treated FA on WRC of DGS are very different. Organic-apatite treated FA (excluding chitosan-apatite) and organic-added thermal treated FA decreased WRC but organic-treated FA gave no significant effects on WRC of DGS or increased it significantly. Although potentially non-negligible impact of FA aggregates with 1 to 100 μm size on WRC was proposed in the section 5.3.1.5, different effects of various

treated FA amendment on WRC suggests that micro-scale hydraulic properties around FA and FA aggregates is more important than physical effect of FA aggregates. As suggested in the section 5.3.2.7, interactions between organic compounds contained in soil/sand and those of treated FA might be related to micro-scale hydraulic properties around FA and FA aggregates. It might promote or inhibit evaporation of capillary water in FA-soil/sand mixture system.



Starch-added thermal treated FA of set I



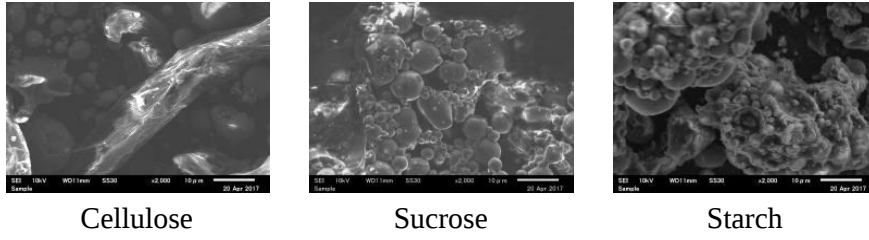
Starch-added thermal treated FA of set II



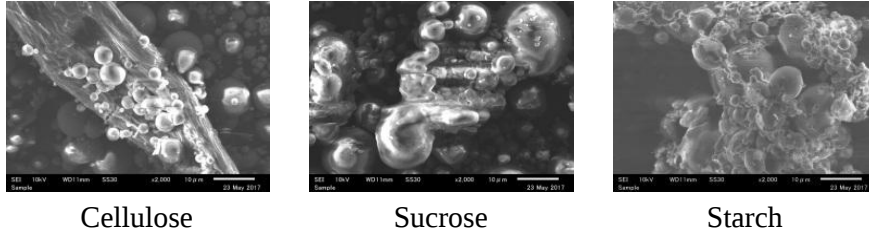
Starch-added thermal treated FA of set III

Figure 5-85 Macro photos of

Organic-added thermal treated FA of set I



Organic-added thermal treated FA of set II



Organic-added thermal treated FA of set III

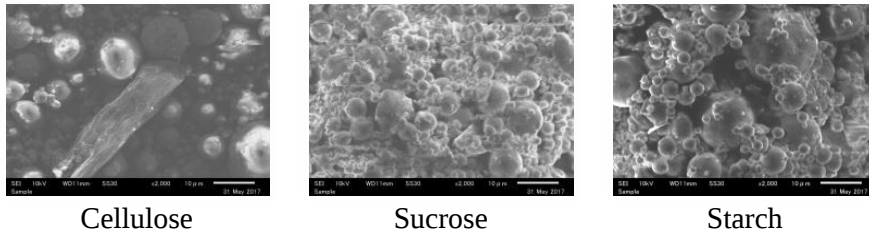


Figure 5-86 Surface morphology of organic-added thermal treated FA

5.4.2.5 Capillary water content of organic-added thermal treated FA

In this section, capillary water content was presented only for sucrose-added thermal treated FA and DGS mixed with sucrose-added thermal treated FA of experimental set II because of limitation of available samples. The results are shown in Table 5-5. Capillary water content of sucrose-added thermal treated FA of set II is 36.0 wt%, lower than those of raw/alginate-treated/alginate-apatite treated FA. Capillary water content of DGS was increased by 1.0 wt% compared to that of pure DGS when sucrose-added thermal treated FA of set II was mixed. Capillary water contents of both sucrose-added thermal treated FA of set II and DGS with the thermally treated FA are still higher than initial water content in WRC measurement. Capillary water content is supposed to weakly influence WRC in Chapter 4. The measurement results of amending sucrose-added thermal treated FA of set II to DGS also support it.

5.4.2.6 Water repellency of organic-added thermal treated FA

Water repellency was measured only for DGS mixed with sucrose-added thermal treated FA of set II because of limitation of available samples. WDPT of DGS mixed with sucrose-added thermal treated FA of set II is shown in Table 5-6. Compared to WDPT of DGS (1.26 s), WDPT of FA-mixed DGS was increased by 303.43 %. This means that water repellency of DGS was obviously increased by mixing sucrose-added thermal treated FA of set II. If the correlation between water repellency and WRC mentioned in section 4.3.7 is reliable, WRC of DGS mixed with sucrose-added thermal treated FA of set II should be decreased obviously. As shown in Figure 5-77, WRC of DGS was decreased obviously by 42.8 % to 52.8 % by mixing sucrose-added thermal treated FA of set II at mixing ratio from 10 wt% to 30 wt% at 40 °C. This supports the hypothesis that water repellency might negatively influences WRC, but it might still include non-negligible uncertainty because of limited experimental data.

5.5 Conclusion of Chapter 5

In this chapter, effects of amending organic-treated FA, organic-apatite treated FA on WRC of soil/sand, and organic-added thermal treated FA on WRC of DGS were presented. Surface morphology, capillary water content, water repellency of FA samples and FA-mixed soil/sand were measured and their influence on WRC were discussed.

When raw FA are treated by chitosan/alginate and guanidine treatment, guanidine-treated FA has lower WRC at room temperature than those of soil/sand, raw FA and other organic-treated FA. At 40 °C, WRC of organic-treated FA are higher than those of soil/sand. When organic-treated FA was amended to soil/sand, chitosan/alginate-treated FA amendment gave no effect on WRC of soil/sand at room temperature. Guanidine-treated FA amendment gave significantly negative effect only on WRC of SS. At 40 °C, the effects were different from those at room temperature. WRC of DGS was significantly increased by mixing alginate-treated FA. On the other hand, WRC of SS and RS were significantly decreased by all organic-treated FA. Effects of mixing organic-treated FA on WRC had obvious soil/sand type dependency and temperature dependency.

Organic-apatite treated FA have slightly higher WRC than soil/sand and raw FA at

room temperature. At 40 °C, WRC of organic-apatite treated FA decreased lower than that of raw FA. When chitosan-apatite treated FA was amended to soil/sand, it gave no effect on WRC of DGS and AS but significantly increased WRC of SS and RS at room temperature. Alginate-apatite treated FA amendment increased WRC of soils significantly but gave no effect on WRC of sands. Guanidine-apatite treated FA increased WRC both of soils and sands significantly. When temperature was increased to 40 °C, WRC of soils were decreased by mixing all kinds of organic-apatite treated FA (except for insignificant effect of mixing chitosan-treated FA on WRC of DGS). On the other hand, WRC of sands were increased by mixing all kinds of organic-apatite treated FA.

WRC of organic-added thermal treated FA increased when organic contents used in thermal treatment was increased and foaming agent was used. When treated FA was mixed into DGS, WRC of DGS was decreased obviously. On the other hand, water repellency of DGS increased greatly. It agrees with the expected mechanism between water repellency and WRC.

The effects of treated FA amendment on WRC are different depending on soil/sand types and FA treatment method/condition. Although multi-regression analysis suggests large impact of surface area on WRC, it also suggests non-negligible impacts of water repellency and other uncertain factors. When alginate-apatite treated FA, alginate-treated FA and apatite-synthesized FA are focused on, they gave the similar effects on water repellency of DGS and SS but their effects on WRC were inconsistent. This suggests physical and/or hydraulic factors that influence the mechanism between water repellency and WRC. This factor depends on FA treatment method and soil/sand type. Because DGS and RS have similar size distribution but receive contrast effects by FA amendment, physical factor related to pore size distribution might be excluded. On the other hand, interactions between organic compounds contained in soil/sand and those of treated FA is proposed.

References

- Bauer A., Black A.L. (1992) Organic-Carbon Effects on Available Water Capacity of 3 Soil Textural Groups, *Soil Sci. Soc. Am. J.*, 56(1), 248-254
- Hirata T., Nishimoto T. (1991) DSC, DTA and TG of cellulose untreated and treated with flame-retardants, *Elsevier Science Publishers B.V., Amsterdam, Thermochimica Acta*, 193(1991)99-106
- Hudson B.D. (1994) Soil Organic-Matter and Available Water Capacity, *J. Soil Water Conserv.*, 49(2), 189-194
- Lerdkanchanaporn S. (1999) A thermal analysis study of ibuprofen and starch mixtures using simultaneous TG-DTA, *Elsevier Science Publishers B.V., Amsterdam, Thermochimica Acta*, 340-341(1999)131-138
- Lerdkanchanaporn S., Dollimore D. (1999) The evaporation of Ibuprofen from Ibuprofen-starch mixtures using simultaneous TG-DTA, *Elsevier Science Publishers B.V., Amsterdam, Thermochimica Acta*, 357-358(2000)71-78

Chapter 6

Conclusions and recommendations

The purpose of this research is reutilizing FA for soil amelioration, in particular water retention agents in order to recycle raw FA high efficiently and mitigate desertification at the same time. Water holding capacity (WHC) is a conventional method to measure the amount of water held in soil system. WHC is measured based on mass loss of gravitational water and groundwater-related capillary water by gravity or transpiration under low air pressure conditions. Under real conditions of arid/semi-arid areas, however, major pathways of water loss in soil system is evapotranspiration by plants/grasses and physical evaporation to the atmosphere under ambient pressure and hydraulically unsaturated conditions. In this sense, this study proposed an alternative method to measure water evaporation resistivity of soil system, called as water retention capacity (WRC). WRC was measured based on mainly capillary water loss by evaporation at different temperature. Soil/sand samples were simply dried at target temperature and soil moisture was monitored for 12 hours at 1 hour interval. WRC was defined as the area of water retention curve. Therefore, WRC would be larger when moisture in soil/sand sample is retained more with longer time. In order to simulate real situations of arid or semi-arid areas after rainfall, initial water content in WRC measurement was set at 30 wt%. The temperature was set at room temperature and 40 °C. In this thesis, the effects of raw and treated FA amendment on WRC of soils (DGS and AS) and sands (SS and RS) were reported. In addition, some factors which might control WRC were discussed.

In Chapter 2, experimental materials and methods were described in details.

In Chapter 3, the effects of amending raw FA or apatite-synthesized FA on WRC of soil/sand are discussed. At 40 °C, the effects of amending apatite-synthesized FA on WRC of soil/sand are very complicated. They depend on not only P/Ca ratio of apatite synthesis treatments but also soil/sand type. FA mixing ratio is less important than P/Ca ratio and soil/sand type. This study found very complex mechanisms of WRC in soil/sand mixed with raw/treated FA, in which physical and hydraulic properties would be interactive and give complexity depending on soil/sand type, FA treatment condition, and FA mixing ratio.

In chapter 4, some physical and hydraulic factors that might control variation of WRC of soil/sand mixed with raw/apatite-synthesized FA were analyzed. They are surface morphology, specific surface area, size distribution, water repellency, capillary water content, and water potential (pF). SEM observations showed limited aggregations of FA particles and no clear difference of surface modification after apatite-synthesis treatment. Surface morphology observed in micro-meter scale is not sufficient to explain the effects of FA amendment on WRC of soil/sand. Because pore size distribution in soil/sand system is difficult to measure but related to particle size distribution of soil/sand and amended FA, particle size distribution of FA after apatite-synthesis treatment was focused on. This study found only negligible differences at any P/Ca ratios. Although apatite-synthesis treatment increased specific surface area of FA, it is concluded that specific surface area does not directly control WRC of soil/sand mixed with raw/apatite-synthesized FA. Both raw and apatite-synthesized FA amendments increase water repellency of soil/sand (DGS, SS, and RS) or decreased it (AS). On the other hand, complicated and inconsistent relations were found between water repellency and WRC, in particular for FA-amended soil/sand. It is concluded

that water repellency does not control WRC independently. Capillary water measurement shows that WRC measured in this study mainly reflected evaporation resistivity of capillary water. Only WRC of SS with/without FA amendment include not only capillary water but also gravitational water. Capillary water content is also suggested to be insufficient to explain WRC and its variation by FA amendment. Only for SS, pF measured in this study was within the range of water contents monitored during WRC measurement. The pF is also insufficient to explain WRC of SS with/without FA amendment. In order to consider the effects of water repellency, surface area and capillary water content on variation of WRC together, multi-regression analysis was tested using all WRC data. The regression curve was regarded as significantly reliable and it suggests that specific surface area is the most influential factor to WRC and specific surface area is less important. The effect of capillary water on WRC is negligible. It also suggests that other unconsidered factors can influence WRC as strongly as water repellency. However, regression results need further verification because no reliable regression curves were found when selected data of significant WRC variations were used for analysis.

In chapter 5, the effects of amending organic-treated FA, organic-apatite treated FA on WRC of soil/sand, and organic-added thermal treated FA on WRC of DGS were presented. Surface morphology, capillary water content, water repellency of FA samples and FA-mixed soil/sand were measured and their influence on WRC were discussed. When raw FA are modified by chitosan, alginate and guanidine treatment, WRC of organic-treated FA are higher than those of soil/sand at 40 °C. When organic-treated FA was amended to soil/sand, WRC of DGS was significantly increased by mixing alginate-treated FA at 40 °C. On the

other hand, WRC of SS and RS were significantly decreased by all organic-treated FA. Organic-apatite treated FA have lower WRC than that of raw FA at 40 °C. When organic-apatite treated FA was amended to soil/sand, WRC of soils at 40 °C were decreased significantly except for DGS with chitosan-treated FA. On the other hand, WRC of sands were increased by mixing all kinds of organic-apatite treated FA. Cellulose-/starch-added thermal treatment increased WRC of FA higher than that of raw FA. The effects on WRC increased with increase of organic contents used in thermal treatment and utilization of foaming agent. When thermally-treated FA was mixed into DGS, WRC of DGS was decreased obviously. On the other hand, water repellency of DGS increased greatly. It agrees with the expected mechanism between water repellency and WRC. It is summarized that the effects of treated FA amendment on WRC are different depending on soil/sand types and FA treatment method/condition. Although multi-regression analysis suggests large impact of surface area on WRC, it also suggests non-negligible impacts of water repellency and other uncertain factors. When alginate-apatite treated FA, alginate-treated FA and apatite-synthesized FA are focused on, they gave the similar effects on water repellency of DGS and SS but their effects on WRC were inconsistent. This suggests physical and/or hydraulic factors that influence the mechanism between water repellency and WRC. This factor depends on FA treatment method and soil/sand type. Because DGS and RS have similar size distribution but receive contrast effects by FA amendment, physical factor related to pore size distribution might be excluded. On the other hand, interactions between organic compounds contained in soil/sand and those of treated FA is proposed.

Because all results in this study are based on FA from a Japanese coal fired power

plant, and specified soil/sand. When focusing on FA recycling of China, textures/chemical compounds of coal FA, soil/sand are different and WRC shall be different. Processes of measuring and analysis, study of multi-regression analysis are useful for further study on finding critical parameters of different kinds of soil/sand mixed with different kinds of FA. Before land scale utilization, more mechanism should be studied in the future.

For example, porous structure observation of FA and soil/sand particles in sub-micro meter scale is highly recommended. It might be related to unknown factors that influence water evaporation resistivity of soil system. In addition, measurement of pore size distribution in soil/sand system is also recommended although this study expected small impact on WRC owing to very small changes of FA particle size distribution after FA treatment. Although this study focused on water repellency of soil/sand system using WDPT and found less importance than specific surface area for WRC, micro-scale water repellency of FA/sand/soil particle surface should be concerned. It might regulate evaporation of capillary water evaporation from particle surfaces. Interactions between organic compounds contained in soil/sand and those of treated FA seem to be related to micro-scale water repellency. To explain complex and sometimes inconsistent effects of FA amendment on WRC of soil/sand, microscopic viewpoint is necessary to find some unconsidered factors which give non-negligible impacts on the mechanisms between physical/hydraulic properties and WRC. They make the mechanisms look like complex and pseudo-inconsistent. At last, WRC measurement at different temperature is necessary. WRC at different temperature is likely better to evaluate water retention in the real soil system in semi-arid areas.

Acknowledgements

There is an end of a journey, here when I looking backward I should like to finish all the people that have in one way or another contributed to the making of this work.

Firstly, I want to show my sincere appreciate to Prof. Fumitake Takahashi and Prof. Kunio Yoshikawa for their help and guidance and for giving me the opportunity to work at one of the acclaimed *Tokyo Institute of Technology* among brilliant scientists. My research journey started from explanation session from kind Prof. Takahashi to the Japanese language school which I was studying in. When I decided to enter *Academy for Global Leadership (AGL)*, Prof. Takahashi kindly agreed immediately and supported my time consuming work in AGL. Thanks for Prof. Takahashi, I went to dozens of countries that I never visited nor concerned before. I appreciate to have an excellent experience of researching on anti-desertification for social contribution with dream and accompanied by Prof. Takahashi.

Then I want to show my sincere thankful to Prof. Kouji Tokimatsu, for his kind suggestion and guidance on my life and research. Academy for Global Leadership is thanked for the financial support. At the same time, on behalf of AGL, I met the most brilliant students all over *Tokyo Institute of Technology* and *Hitotsubashi University*. I want to thank Mrs. Ohno and Mrs. Takahashi, for their kind and unconditional help to my life and work. I would like to thank all my dear friends in a warm family at the whole lab: Mr. Kunta, Mr. Kitamura, Mr. Nakamura, Mr. Dai, Dr. Ding, Ms. Song, Ms. Jiang, Ms. Tian, Mr. Baskoro, Mr. Jo, Mr. Andile, Ms. Rosa, Ms. Astryd, Mr. Nutz, Mr. Sann, Ms. Mook, Ms. Ann, Ms. Annisa, Ms. Adisti, Mr. Alex, and so many more dear friends whose name are not mentioned because of the limitation of article. Many more thanks for scientific discussions and, more importantly, for so many non-scientific fun hours like BBQ, and countless happy parties. Special thanks go to whom for taking care of me in times of need. I am indebted to so many people for making my days and nights that much fun and the past years the experience of a life time, that I have probably forgotten to mention some of you, but I wholeheartedly thank each and every one of you none the less.

Finally, I want sincerely thank my family members for their unconditional supports and showing their solicitude for my life. I am so sorry for being far away from them and cannot taking care of them when they need me. Because of their support, I can now having this work and have the chance to running after my dream.