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Remediation of saline–sodic soil with flue gas desulfurization gypsum in a reclaimed tidal flat of southeast China

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ABSTRACT

Salinization and sodicity are obstacles for vegetation reconstruction of coastal tidal flat soils. A study was conducted with flue gas desulfurization (FGD)-gypsum applied at rates of 0, 15, 30, 45 and 60 Mg/ha to remediate tidal flat soils of the Yangtze River estuary. Exchangeable sodium percentage (ESP), exchangeable sodium (Ex_{Na}), pH, soluble salt concentration, and composition of soluble salts were measured in 10 cm increments from the surface to 30 cm depth after 6 and 18 months. The results indicated that the effect of FGD-gypsum is greatest in the 0–10 cm mixing soil layer and 60 Mg/ha was the optimal rate that can reduce the ESP to below 6% and decrease soil pH to neutral (7.0). The improvement effect was reached after 6 months, and remained after 18 months. The composition of soluble salts was transformed from sodic salt ions mainly containing Na^+, HCO_3^- + CO_3^{2-} and Cl^- to neutral salt ions mainly containing Ca^{2+} and SO_4^{2-}. Non-halophyte plants were survived at 90%. The study demonstrates that the use of FGD-gypsum for remediating tidal flat soils is promising.

Introduction

Saline–sodic soils are an important land resource widely distributed on the earth. They occupy an area of 9.5×10^7 ha, accounting for almost 25% of total global area (Arunin, 1995). Unfavorable physical and chemical properties seriously impede plant growth and restrict their agricultural production (Malcolm and Sumner, 1998; Rengasamy, 2002). It is a challenge to improve saline–sodic soils for restoring vegetation, improving land ecosystems and developing agriculture. Many studies have focused on ameliorating saline–sodic soils by using techniques such as water conservancy measures, chemical measures, and physical measures (Barrett-Lennard, 2002; Yang and Wan, 2014). However, many of these methods need a long time to ameliorate soil. Furthermore, irrigation also requires abundant freshwater resources and easily washes away soil nutrients.

Mined gypsum is the most commonly used product to remediate sodic soils and for agricultural management of sodic soils in irrigated lands (Shainberg et al., 1989; Oster and Jayawardane, 1998). In recent years, flue gas desulfurization (FGD)-gypsum has become widely available and is also considered an effective ameliorant for saline–sodic soils because of its low cost and quick reaction compared with other reclamation practices (Yang and Wan, 2014). FGD-gypsum is a by-product produced during the process of removing sulfur from the flue gas of coal fired power plants (Laperche and Bigham, 2002). It has the same basic chemical composition as mined gypsum ($CaSO_4 \cdot 2H_2O$). Compared with mined gypsum, the purity of FGD-gypsum is higher

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and its composition is more stable, its particle size is smaller and more uniform and its dissolution rate is much higher (USEPA, 2008; Amezketa et al., 2005). Many studies have shown that FGD-gypsum has great potential for saline–sodic soil remediation while it does not cause recontamination (Chen et al., 2014; Chun et al., 2001; Li et al., 2014; Wang et al., 2008; Watts and Dick, 2014). The principle is that gypsum is able to provide Ca^{2+} to replace exchangeable Na^+ on the colloid's cation exchange sites (Frenkel et al., 1989), which leads to improvements in soil chemical, physical and biological properties.

Most of the studies reported to date have focused on FGD-gypsum improving the soil of arid and semiarid areas (Amezketa et al., 2005; Lee et al., 2007; Li et al., 2012; Yu et al., 2014a, 2014b). However, only a limited amount of work has been done to evaluate the effects of FGD-gypsum in tidal flat soils. Compared with saline–sodic soils in dryland areas, coastal saline–sodic soils are characterized by higher soil salinity, groundwater salinity, and water table levels and lower natural desalinization rates because their formation is strongly affected by sea water and soil transpiration (Rengasamy, 2006). A relevant study has shown that FGD-gypsum could significantly change aggregation and hydraulic conductivity of tidal flat soil in the Yangtze River estuary (Cheng et al., 2014). So we hypothesize that amelioration with FGD-gypsum is an effective technology for remediation of saline–sodic soils in tidal flats.

Therefore, a field-scale demonstration study was conducted on a tidal flat soil in the Yangtze River estuary, China to evaluate the effects of different FGD-gypsum application rates on salinization and sodicity in tidal flat soil at different depths by measuring the changes in exchangeable Na^+, exchangeable sodium percentage (ESP), pH and the concentrations and composition of soluble salts, and to determine the optimal rate that could reduce the ESP to below 6%, decrease soil pH to neutral and transform the composition of soluble salts from sodic salt ions to neutral salt ions.

1. Materials and methods

1.1. *Study site description*

A field study was conducted on a reclaimed tidal flat soil (silt loam), located in Chongming Island (31°37′06″ N 121°33′12″E), near Shanghai, southeast China, where it lies against the north shore of the Yangtze River Delta. The region has a typical subtropical monsoon climate, and the annual average evaporation capacity (1346 mm) is higher than the annual average precipitation (1078 mm). In this area, Na^+ and Cl^- were the major ions in groundwater with average concentrations of 10.8 and 19.4 g/L, respectively (Han, 2013). The soil was characterized as saline–sodic soil (Richards, 1954), and the main soluble salt was NaCl followed by bicarbonate. Selected chemical properties of soil (0–30 cm) from the experimental site are presented in Table 1.

1.2. *FGD-gypsum*

FGD-gypsum was obtained from a coal-fired power plant in Shanghai with 74.7% $CaSO_4{\cdot}2H_2O$ and 25.3% moisture. Chemical components of FGD-gypsum were determined by the Center Testing International Corporation, Shanghai. Hg and As of FGD-gypsum were measured by atomic fluorescence spectrometry (AFS-830, Perkinelmer, USA) while other heavy metals were analyzed by inductively coupled plasma spectrum spectrometry (Optima8300, Perkinelmer, USA) after total acid digestion. The concentrations of major hazard pollution elements (As 5.1 mg/kg, Cr 0.47 mg/kg, Pb 14.7 mg/kg, Hg 0.20 mg/kg) were far below the secondary standard of environmental quality standard for soils (Administration, 1995) and control standards of pollutants in fly ash for agricultural use (Administration, 1987).

1.3. *Experimental design and soil sampling*

A field experiment was established in December 2011. The treatments included five FGD-gypsum rates: 0 (Control), 15, 30, 45 and 60 Mg/ha that were arranged in a randomized block design with four replicates. There were 20 plots in total, and each plot area was 10 × 10 m. FGD-gypsum was thoroughly mixed with the surface 10 cm depth of soil.

Six months and 18 months after FGD-gypsum application (Mid-July of 2012 and 2013), soil samples were collected from surface to 30 cm depth and sub-sampled at 10 cm intervals using an auger (5 cm inner diameter × 40 cm length) at each plot. Then soil samples were air-dried and crushed to pass through a 2-mm sieve. Soluble cations and anions were extracted at the rate of 1:5 (soil:water, W/W). Exchangeable cations were extracted with 1 mol/L NH_4OAc. The concentrations of soluble and exchangeable cations were measured using inductively coupled plasma atomic emission spectroscopy (IRIS Intrepid IIXSP, Thermofisher, USA). The concentrations of

Table 1 – Selected chemical properties of flue gas desulfurization gypsum (FGD)-gypsum and soil (0–30 cm) from experimental site at the initiation of experiment.

Sample	pH	ESP (%)	EC (ds/m)	Water-soluble anions (cmol/kg)			Water-soluble cations (cmol/kg)			
				SO_4^{2-}	$HCO_3^- + CO_3^{2-}$	Cl^-	Ca^{2+}	Mg^{2+}	Na^+	K^+
Soil	8.62	32.8	4.03	0.07	0.86	1.42	0.41	0.49	2.87	0.23
FGD-gypsum	7.25	0.17	ND	25.5	0.11	0.39	46.6	3.29	0.31	0.04

ESP: exchangeable sodium percentage;
EC: electrical conductivity (soil:water, 1:1, W/W);
FGD: flue gas desulfurization;
ND: the value was not determined.

soluble SO_4^{2-} and Cl^- were determined by ion chromatography (ICS-2500, Thermofisher, USA). The concentrations of soluble $HCO_3^- + CO_3^{2-}$ were determined by the titration method. Soluble salt concentration was calculated according to (LY/T1251-, 1999). All ions were expressed in cmol/kg. Soil pH was determined on a 1:5 ((soil:water, W/W)) mixture using a glass electrode. The ESP was calculated according to (LYT 1249-, 1999) by the following equation where the concentrations of exchangeable cations are expressed in cmol/kg:

$$ESP = Na^+/(Na^+ + K^+ + Ca^{2+} + Mg^{2+}) \times 100\% \qquad (1)$$

1.4. *Statistical analyses*

ANOVA followed by the least significant difference (LSD) test was used to determine differences of soluble salt composition (cations: Ca^{2+}, Mg^{2+}, K^+ and Na^+; anions: $HCO_3^- + CO_3^{2-}$, Cl^- and SO_4^{2-}), soluble salt concentration, pH, exchangeable sodium (Ex_{Na}) and ESP among different rates of FGD-gypsum treatments. ANOVAs were run using SPSS 17.0. Significance was declared at $p < 0.05$.

2. Results and discussions

2.1. *Soluble salt concentration*

The soluble salt concentrations in the upper layer (0–10 cm) significantly increased with increasing FGD-gypsum application rates (Fig. 1). Six months after FGD-gypsum application, it averaged 15.0 cmol/kg more than that in the control treatment. This is due to the dissolution of $CaSO_4 \cdot 2H_2O$ to produce soluble Ca^{2+} and SO_4^{2-} in the soil. In the 10–20 cm soil layer, only 60 Mg/ha FGD-gypsum significantly increased soluble salt concentration by 1.55 cmol/kg compared with the control. In the 20–30 cm soil layer, there was no significant difference in the soluble salt concentrations among all the treatments. After 18 months of FGD-gypsum application, the change trends of soluble salt concentrations in soil were similar to those at 6 months after application.

Our result showing FGD-gypsum increased soluble salt concentrations in soil is consistent with the reports by Chen et al. (2009) and Clark et al. (2007). At the same time, there are other studies showing soluble salt concentrations decreasing over time due to leaching which plays a key role in the soil reclamation process (Chen et al., 2009; Qadir et al., 1996; Wang et al., 2005, 2013; Fang et al., 2012). We predict the increase of soil salt concentrations in this study will be only temporary, and will decrease as natural rainfall and irrigation cause leaching to occur.

2.2. *Concentration and composition of water-soluble ions in soil*

The concentration and molar percentage of water-soluble Ca^{2+} for all treatments were compared after 6 months and 18 months (Table 2). After 6 months, the concentrations of Ca^{2+} significantly increased with FGD-gypsum application rate in the 0–10 cm soil layer by 2.63–15.9 cmol/kg compared with the control, and the molar percentages were increased by 5.76–18.2 times, correspondingly. The concentrations of Ca^{2+} in the 45 and 60 Mg/ha FGD-gypsum treatments significantly increased by 1.46 and 3.09 cmol/kg in the 10–20 cm soil layer, respectively, and significantly increased by 0.27 and 0.35 cmol/kg in the 20–30 cm soil layers, respectively. Only the molar percentage of Ca^{2+} in 60 Mg/ha FGD-gypsum treatment significantly increased in both 10–20 cm and 20–30 cm soil layers, which increased by 6.29 times and 1.26 times, respectively. Similar trends occurred after 18 months of FGD-gypsum application, except for the difference that the concentrations of Ca^{2+} in all FGD-gypsum treatments significantly increased in the 10–20 cm soil layer after 18 months, and the molar percentages in both 45 Mg/ha and 60 Mg/ha FGD-gypsum treatments increased in the 10–20 and 20–30 cm soil layers. The Ca^{2+} increase resulted from the dissolution of the FGD-gypsum.

The concentration and molar percentage of water-soluble Na^+ decreased significantly in the upper layer (0–10 cm) with an increase in FGD-gypsum application rates except for the concentration of Na^+ in the 15 Mg/ha FGD-gypsum treatment after 6 months (Table 3). After 6 months, the concentration of Na^+ in 15 Mg/ha FGD-gypsum treatment was only slightly different from the control, and the concentrations of Na^+ in the other FGD-gypsum treatments significantly decreased 1.60–3.91 cmol/kg comparing to that in the control treatment. The molar percentages of Na^+ in all FGD-gypsum treatments significantly decreased by 26.9%–69.9%. In the 10–20 cm soil layer, the concentration of Na^+ in 30–60 Mg/ha FGD-gypsum treatments significantly decreased, and the decrease ranged from 0.75 to 1.37 cmol/kg. The molar percentage of Na^+

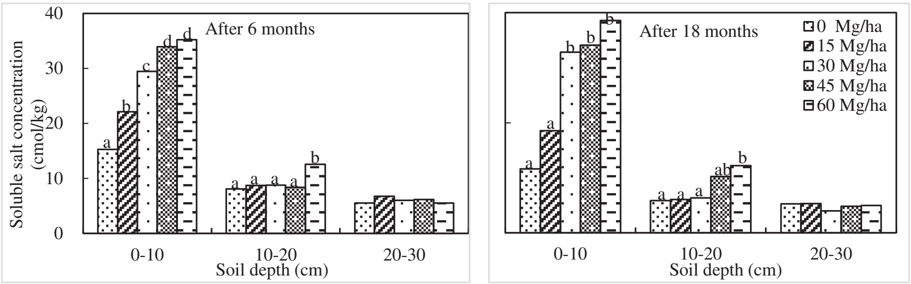

Fig. 1 – Soluble salt concentrations in different soil layers 6 and 18 months after application of FGD-gypsum. The same letters or no letters above the bars in the same soil layer indicate there was no significant difference among the different rates of FGD-gypsum treatments at $p < 0.05$ level.

Table 2 – Concentration and molar percentage of water-soluble Ca^{2+} in different soil layers 6 and 18 months after application of FGD-gypsum.

Gypsum rate (Mg/ha)	Concentration (cmol/kg)			Molar percentage (%)		
	0–10 cm	10–20 cm	20–30 cm	0–10 cm	10–20 cm	20–30 cm
After 6 months						
0	0.33a	0.30a	0.23a	4.08a	6.86a	7.87a
15	2.96b	0.86a	0.29a	27.6b	17.8a	12.6a
30	8.36c	0.71a	0.43b	54.3c	15.5a	8.58a
45	13.8d	1.76b	0.50b	69.6d	17.9a	11.6a
60	16.2d	3.39b	0.58b	78.2d	50.0b	17.8b
After 18 months						
0	0.18a	0.13a	0.10a	3.04a	4.80a	3.98a
15	3.30b	0.29b	0.21a	38.6b	9.54a	7.99a
30	12.1c	0.38b	0.12a	71.6c	14.0a	6.18a
45	13.7c	1.81c	0.41b	76.8c	40.3b	17.4b
60	17.0c	3.23c	0.37b	84.9c	55.4b	14.9b

Molar percentage represents the ratio of the concentration of water-soluble Ca^{2+} to the concentration of water-soluble cations × 100%. Water-soluble cations include Ca^{2+}, Mg^{2+}, K^+ and Na^+.
Means with the same letter in the same column within the same sampling time are not significantly different at $p < 0.05$.

significantly decreased by 58.4% only in 60 Mg/ha FGD-gypsum treatment. In the 20–30 cm soil layer, there was no significant difference in the concentrations of Na^+ among all treatments, while the molar percentage significantly decreased by 18.4% in 60 Mg/ha FGD-gypsum treatment. Similar trends also occurred after 18 months, but the concentration of Na^+ in 30–60 Mg/ha FGD-gypsum treatments significantly decreased by 26.1%–28.7% in the 20–30 cm soil layer. This is because the Ca^{2+} provided by FGD-gypsum can displace exchangeable Na^+ on soil colloids (Richards, 1954), which generated the water-soluble Na^+ that concurrently leached downward and accumulated at lower soil layers after natural rainfall events occurred (Wang et al., 2005). When excess Na^+ was removed, the concentration of water-soluble Na^+ was reduced, and the concentrations of total cations, especially due to Ca^{2+}, were greatly increased leading to the decrease of the molar percentage of Na^+ correspondingly.

The concentration and molar percentage of water-soluble Cl^- and $HCO_3^- + CO_3^{2-}$ decreased by different degrees with FGD-gypsum added to tidal flat soil (except for the concentration of water-soluble Cl^- in 15 Mg/ha FGD-gypsum treatment after 6 months) in the 0–10 cm soil layer (Table 4). For Cl^-, higher FGD-gypsum rates had more significant impacts; for $HCO_3^- + CO_3^{2-}$, there was no significant difference among the treatments with FGD-gypsum applied. After 6 months, when the application rate of FGD-gypsum was 60 Mg/ha, the concentration of Cl^- was lowest, which was 1.63 cmol/kg compared with 6.64 cmol/kg in the control, and the molar percentage of Cl^- was reduced from 91.6% to 11.2%. In the 10–20 cm soil layer, the differences of Cl^- concentration were significant among the FGD-gypsum treatments and the

Table 3 – Concentration and molar percentage of water-soluble Na^+ in different soil layers 6 and 18 months after application of FGD-gypsum.

Gypsum rate (Mg/ha)	Concentration (cmol/kg)			Molar percentage (%)		
	0–10 cm	10–20 cm	20–30 cm	0–10 cm	10–20 cm	20–30 cm
After 6 months						
0	6.66d	3.80c	2.43	83.2d	86.1b	84.8b
15	6.04cd	3.16bc	2.98	56.3c	65.5b	75.8b
30	5.06bc	3.05ab	2.77	32.8b	66.5b	81.3b
45	4.47b	2.85ab	2.90	22.6ab	67.5b	78.4b
60	2.75a	2.43a	2.25	13.3a	35.8a	69.2a
After 18 months						
0	5.27d	2.43c	2.30c	91.0d	90.4d	91.8c
15	4.08c	2.48c	2.24bc	47.7c	82.7cd	86.2bc
30	3.45bc	1.95b	1.70ab	20.4b	72.3c	86.3bc
45	3.02b	2.09b	1.76ab	17.0b	46.4b	74.1ab
60	1.93a	1.75a	1.64a	9.66a	29.9a	66.2a

Molar percentage represents the ratio of the concentration of water-soluble Na^+ to the concentration of water-soluble cations × 100%. Water-soluble cations include Ca^{2+}, Mg^{2+}, K^+ and Na^+.
Means with no letter or the same letter in the same column within the same sampling time are not significantly different at $p < 0.05$.

Table 4 – Concentration and molar percentage of water-soluble $HCO_3^- + CO_3^{2-}$ and Cl^- in different soil layers 6 and 18 months after application of FGD-gypsum.

Gypsum rate (Mg/ha)	Concentration (cmol/kg)						Molar percentage (%)					
	0–10 cm		10–20 cm		20–30 cm		0–10 cm		10–20 cm		20–30 cm	
	HCO_3^- + CO_3^{2-}	Cl^-	HCO_3^- + CO_3^{2-}	Cl^-	HCO_3^- + CO_3^{2-}	Cl^-	HCO_3^- + CO_3^{2-}	Cl^-	HCO_3^- + CO_3^{2-}	Cl^-	HCO_3^- + CO_3^{2-}	Cl^-
After 6 months												
0	0.38b	6.64d	0.61b	2.83b	0.70b	1.87	5.19b	91.6d	16.7b	77.9c	26.6b	70.5
15	0.24a	5.92 cd	0.23a	1.97a	0.29a	2.13	2.11a	52.0c	6.01a	50.4b	10.5a	79.8
30	0.25a	5.25c	0.33a	1.67a	0.44a	1.90	1.78a	37.3b	7.91a	40.3b	17.0a	73.2
45	0.22a	3.76b	0.30a	1.95a	0.34a	1.94	1.55a	26.6b	7.26a	47.0b	13.7a	78.6
60	0.22a	1.63a	0.24a	1.43a	0.26a	1.50	1.53a	11.2a	4.17a	24.7a	11.7a	66.8
After 18 months												
0	0.93b	4.38d	0.72c	1.92c	0.84b	1.73b	16.0b	75.1c	24.4d	64.5d	30.4c	62.3c
15	0.39a	3.19c	0.46b	1.78bc	0.49a	1.80b	3.94a	31.8b	15.1c	58.5c	18.0ab	66.6c
30	0.30a	2.34bc	0.43ab	1.25ab	0.49a	1.12a	1.91a	14.7a	12.5bc	35.9b	24.5b	55.6b
45	0.29a	2.18b	0.30ab	1.32ab	0.40a	1.22a	1.80a	13.3a	4.89ab	21.5a	16.4a	50.3a
60	0.28a	1.16a	0.22a	1.20a	0.31a	1.21a	1.50a	8.90a	3.30a	17.8a	12.4a	48.7a

Means with no letter or the same letter in the same column within the same sampling time are not significantly different at $p < 0.05$.

control, but not significant in different FGD-gypsum treatments, while the molar percentage significantly decreased in 60 Mg/ha FGD-gypsum treatment than in the other FGD-gypsum treatments. In the 20–30 cm soil layer, the decrease of Cl^- concentrations in all FGD-gypsum treatments was not significant compared to the control. Similar trends occurred after 18 months. What should be specially pointed out was that Cl^- concentrations in 30–60 Mg/ha FGD-gypsum treatments significantly decreased compared to the control in the 20–30 cm soil layer. Liu et al. (2012) also reported a similar result in their study on a coastal soil.

The concentration of Cl^- in the control treatment was great because the underground water table level in the area was high, and Cl^- is the main anion in the groundwater. It moved up vertically by capillary action from subsoil layers resulting in the accumulation of Cl^- in the upper layer (Rengasamy, 2002). After application of FGD-gypsum, the dissolved Ca^{2+} of FGD-gypsum increased the soil infiltration and Cl^- was constantly moved downward with the soil reclamation and natural rainfall events. Thus, there was a decrease in the Cl^- concentration in soil treated with FGD-gypsum (Wang et al., 2013).

It is notable from Table 4 that there were no significant changes in the concentration and molar percentage of $HCO_3^- + CO_3^{2-}$ among the different FGD-gypsum treatments in the 0–10 cm, 10–20 cm, 20–30 cm soil layers after 6 months. However, the concentration and molar percentage of $HCO_3^- + CO_3^{2-}$ decreased in FGD-gypsum treatments compared with the control. Similar trends occurred after 18 months except for the difference that the concentration of $HCO_3^- + CO_3^{2-}$ in 60 Mg/ha FGD-gypsum treatment was significant lower than that in the other FGD-gypsum treatments in the 10–20 cm soil layers. This is mainly because the Ca^{2+} from the low rates of FGD-gypsum is

Table 5 – Concentration and molar percentage of water-soluble SO_4^{2-} in different soil layers 6 and 18 months after application of FGD-gypsum.

Gypsum rate (Mg/ha)	Concentration (cmol/kg)			Molar percentage (%)		
	0–10 cm	10–20 cm	20–30 cm	0–10 cm	10–20 cm	20–30 cm
After 6 months						
0	0.23a	0.20a	0.08a	3.19a	5.48a	2.90a
15	5.23b	1.70ab	0.27ab	45.9b	43.6b	9.77a
30	8.56bc	2.15ab	0.25ab	60.9c	51.8b	9.77a
45	10.2cd	1.89ab	0.19ab	71.9c	45.7b	7.66a
60	12.7d	4.12b	0.48b	87.3d	71.1c	21.5b
After 18 months						
0	0.52a	0.33a	0.20a	8.93a	11.2a	7.25a
15	6.43b	0.80ab	0.42a	64.2b	26.4b	15.4b
30	13.3c	1.79ab	0.40a	83.4c	51.6c	19.9bc
45	13.9c	4.51bc	0.81b	84.9cd	73.6d	33.3c
60	16.7c	5.30c	0.97b	89.6d	78.9d	39.0c

Means with the same letter in the same column within the same sampling time are not significantly different at $p < 0.05$.

Table 6 – Concentration of exchangeable sodium (Ex_{Na}) (cmol/kg) in different soil layers 6 and 18 months after application of FGD-gypsum.

Gypsum rate ($Mg\ ha^{-1}$)	After 6 months			After 18 months		
	0–10 cm	10–20 cm	20–30 cm	0–10 cm	10–20 cm	20–30 cm
0	6.46c	3.41b	2.77b	7.02d	3.21c	2.90b
15	6.14bc	3.03b	3.07b	4.39c	2.65bc	2.50b
30	6.76bc	3.18b	2.91b	3.53b	2.04ab	1.95ab
45	3.59ab	2.70ab	2.88b	3.18b	1.95a	2.32ab
60	2.38a	2.31a	2.25a	1.72a	1.60a	1.71a

Means with the same letter in the same column are not significantly different at $p < 0.05$.

sufficient for reacting with $HCO_3^- + CO_3^{2-}$ (Sakai et al., 2010), leading to the decrease of concentrations of $HCO_3^- + CO_3^{2-}$.

The concentration and molar percentage of water-soluble SO_4^{2-} in the 0–10 cm soil layer significantly increased under all rates of FGD-gypsum treatments compared with the control (Table 5). After 6 months, the concentrations of water-soluble SO_4^{2-} under different rates of FGD-gypsum treatments were increased by 5.00–12.47 cmol/kg compared with the control, and the molality percentage was increased by 13.4–26.4 times, correspondingly. In the 10–20 cm and 20–30 cm soil layers, the concentration of SO_4^{2-} only in the 60 Mg/ha FGD-gypsum treatment significantly increased by 3.92 and 0.40 cmol/kg respectively, while the molar percentage of SO_4^{2-} was increased by 12.0 and 6.41 times, correspondingly. Similar trends occurred after 18 months. In addition, the concentration of SO_4^{2-} in not only 60 Mg/ha but also 45 Mg/ha FGD-gypsum treatment increased in the 10–20 cm and 20–30 cm soil layers after 18 months. The main component of FGD-gypsum is $CaSO_4{\cdot}2H_2O$, which dissolves in soil due to natural rainfall, so that the concentration of water-soluble SO_4^{2-} increased naturally.

2.3. Concentration and distribution of Ex_{Na} and ESP

The Ex_{Na} significantly decreased in the 45 and 60 Mg/ha FGD-gypsum treatments in the 0–10 cm soil layer (Table 6). After 6 months, the concentration of Ex_{Na} in the 60 Mg/ha FGD-gypsum treatment had the greatest decrease, decreased to 2.38 cmol/kg compared to 6.46 cmol/kg in the control. No significant difference was observed in the 10–20 cm and 20–30 cm soil layers except for the highest FGD-gypsum rate (60 Mg/ha). A similar trend occurred after 18 months. In addition, the concentration of Ex_{Na} in all the FGD-gypsum treatments significantly decreased by 2.63–5.30 cmol/kg in the 0–10 cm soil layer, and the concentration of Ex_{Na} in 30–60 Mg/ha FGD-gypsum treatments significantly decreased by 1.17–1.61 cmol/kg in the 10–20 cm soil layer. A similar result was observed by Wang et al. (2005) in a laboratory soil column leaching experiment.

The ESP decreased with FGD-gypsum application rate, significantly in the upper (0–10 cm) layer (Fig. 2). After 6 months, the ESP in the 60 Mg/ha FGD-gypsum treatment decreased down to 4.63%, while the ESP in the control treatment was up to 37.7%. The ESP in the 10–20 cm soil layer was decreased most by the 60 Mg/ha FGD-gypsum treatment, closely followed by the 45 Mg/ha FGD-gypsum treatment. No obvious effect was observed in the 20–30 cm soil layer. A similar trend happened after 18 months. The ESP in the FGD-gypsum treatments had an increasing trend with increasing soil depths, $ESP_{0-10} < ESP_{10-20} < ESP_{20-30}$ (Fig. 2). An opposite trend or no effect of treatment was observed for the control.

The result shows that FGD-gypsum can play an important role in the reduction of Ex_{Na} in soil. This is because FGD-gypsum increased water-soluble Ca^{2+} in soil, replacing the Ex_{Na} in the soil colloids, which generated water-soluble Na^+ and caused aggregation of soil particles and resulted in improvement of soil permeability. The generated water-soluble Na^+ leached downward through the soil when rainfall occurred (Chun et al., 2001). The decreased concentration of Ex_{Na} resulted in decreased ESP in the topsoil layer (0–10 cm). The 60 Mg/ha FGD-gypsum reduced soil ESP to the greatest extent (less than 6.0%). The ESP value of non-sodic soil is less than 6% in the topsoil or 15% in the subsoil (Richards,

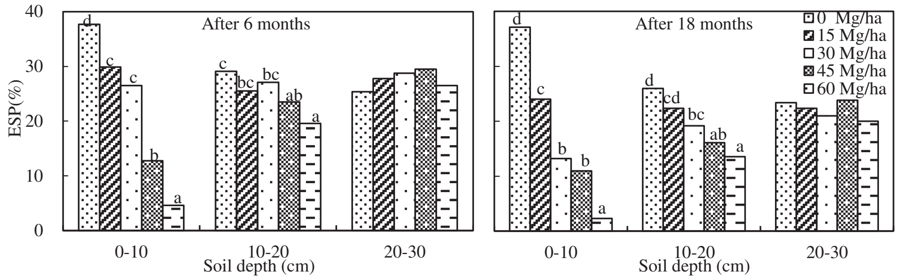

Fig. 2 – ESP in different soil layers 6 and 18 months after application of FGD-gypsum. The same letters or no letters above the bars in the same soil layer indicate there was no significant difference among the different rates of FGD-gypsum treatments at $p < 0.05$ level.

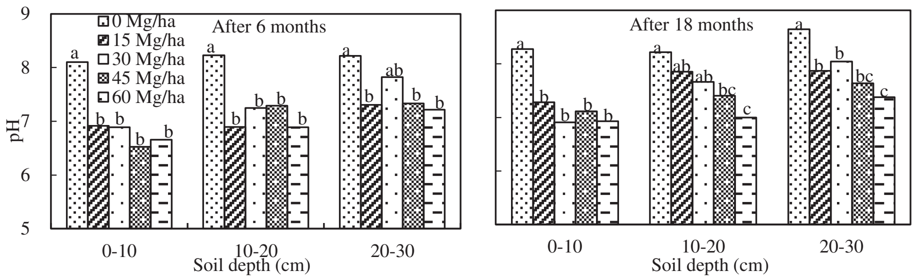

Fig. 3 – pH in different soil layers 6 and 18 months after application of FGD-gypsum. The same letters above the bars in the same soil layer indicate there was no significant difference among the different rates of FGD-gypsum treatments at $p < 0.05$ level.

1954). Meanwhile, the research of Li et al. (2014) showed that 60 Mg/ha was the most effective rate of FGD-gypsum to promote the growth of woody and shrubby plants and community succession of herbaceous plant, and not be depressed by the increase of soluble salt concentration in 60 Mg/ha FGD-gypsum treatment.

2.4. pH

FGD-gypsum significantly decreased the pH in all soil layers (Fig. 3). Six months after FGD-gypsum application, the pH was near to 7.0, decreased by 0.8–1.35 units compared to the control in each soil layer, but there was no significant difference among the various FGD-gypsum treatments. After 18 months, the change of soil pH showed a similar trend.

Studies of Chen et al. (2001) and Sakai et al. (2012) have shown that FGD-gypsum can slightly reduce the soil pH and sustain soil pH for an extended period in agricultural fields. The decrease in soil pH was greater in our studies than reported in the above cited studies. This is due to the pH being controlled by Ex_{Na} on soil colloids and water-soluble HCO_3^- + CO_3^{2-} (Mashhady and Rowell, 1978). FGD-gypsum made soil rich in Ca^{2+} and the Ca^{2+} reacted with HCO_3^- + CO_3^{2-} to produce $CaCO_3$ precipitation. In addition, Ca^{2+} can replace Ex_{Na} which is leached downward to deeper soil layers. These ions rapidly decreased by FGD-gypsum application and soil pH was thus reduced (Sakai et al., 2012).

3. Discussion

3.1. Effect on the plant growth

The year of 2015, 2 years after FGD-gypsum addition, diameter at breast height, plant height, and survival rate of bamboo willows, a non-halophyte, planted in the experimental site were measured to evaluate the effect of different rates of FGD-gypsum treatment on planted vegetation. Compared with the control, the survival rate of Bamboo-willow was improved with the ESP reduced 18 months after application of FGD-gypsum (Fig. 4b).

Plant height and diameter at breast height in the FGD-gypsum treatments with the rate less than 45 $Mg{\cdot}ha^{-1}$ weren't increased compared with the control, however, plant height and diameter at breast height were increased in 60 Mg/ha FGD-gypsum treatment (Fig. 4a). The improved growth was attributed to reduced soil ESP and water-soluble Na^+, Cl^- and CO_3^{2-} + HCO_3^-, elevated available soil Ca and S contents, as well as overall improvements in soil physical properties (Chen and Dick, 2011).

3.2. The environmental safety of FGD-gypsum

United States Environment Protection Agency (US EPA) and United States Department of Agriculture (USDA) in 2008 issued Agricultural Uses for FGD-gypsum, believing that the

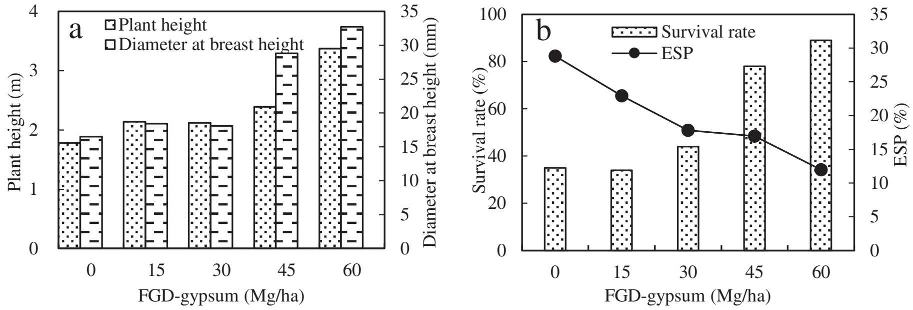

Fig. 4 – Height and diameter at breast height (a) and survival rate of Bamboo-willow (b) 18 months after application of FGD-gypsum.

Table 7 – Heavy metal contents in FGD-gypsum produced from Chinese 31 Power Plants.

	As (mg/kg)	Hg (mg/kg)	Pb (mg/kg)	Cr (mg/kg)	Cd (mg/kg)	References
Concentration range	0.10–17.0	0.01–3.99	0.01–63.4	0.47–69.2	0.01–2.10	Li et al., 2014; Du et al. (2010); Li et al. (2015)
Means	1.77	0.64	19.3	13.9	0.12	
Soil quality standard[a]	≤20	≤1.0	≤350	≤250	≤0.6	

[a] Environmental Quality Standard for Soils of China (GB15618-1995) Class II (pH ▯ 7.5).

use of FGD-gypsum in agriculture is safe in appropriate soil and hydrogeologic conditions. In 2014, US EPA in its February 2014 final report Coal Combustion Residual Beneficial Use Evaluation confirmed that the metals present in washed FGD-gypsum are below US EPA's levels of concern. Heavy metal contents in FGD-gypsum of Chinese 31 coal-fired power plants are presented in Table 7. The mean levels of As, Hg, Pb, Cr, and Cd in FGD-gypsum were lower than the Class II of Environmental Quality Standard for Soils of China. Based on the analyses of the FGD-gypsum and sodic soil, the ecological risk of using FGD-gypsum as a soil amendment is expected to be low. It is necessary to calculate appropriate applied rates of FGD-gypsum for Hg contents in FGD-gypsum from some coal-fired power plants were higher.

4. Conclusions

For the coastal tidal flat soil in the Yangtze River estuary, after FGD-gypsum application the pH decreased and the chemical properties were improved. FGD-gypsum reduced ESP and water-soluble Na^+, Cl^- and $CO_3^{2-} + HCO_3^-$ in the upper soil layer and reduced by different amounts or not reduced in the underlying soil layers. Moreover, the improvements brought about by FGD-gypsum applications remained stable after 18 months. The high FGD-gypsum rate of 60 Mg/ha gave the best results, which can obtain the most rapid reclamation effects, the ESP decreased to less than 6.0% and pH was near to neutral only after 6 months; survival rate of Bamboo-willow reached to almost 90%. Using FGD-gypsum for reclamation of saline–sodic soil in tidal flat has a low ecological risk. This research achieved the expected purpose of improving saline–sodic soil in a tidal flat area using FGD-gypsum, and FGD-gypsum is considered a promising ameliorant for such soils in other areas where saline–sodic soils are found.

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REFERENCES

Administration, T.S.E.P., 1987. GB 8173-87 control standards of pollutants in fly ash for agricultural use China.

Administration, T.S.E.P., 1995. GB 15618-1995 environmental quality standard for soils China.

Amezketa, E., Aragüés, R., Gazol, R., 2005. Efficiency of sulfuric acid, mined gypsum, and two gypsum by-products in soil crusting prevention and sodic soil reclamation. Agron. J. 97, 983–989.

Arunin, S., 1995. Management of coastal salt-affected soils in Thailand. Proceedings of the international workshop on integrated. Soil management for sustainable use of salt affected soils, Manila, The Philippines, pp. 199–211.

Barrett-Lennard, E.G., 2002. Restoration of saline land through revegetation. Agric. Water Mgt. 53, 213–226.

Chen, L., Dick, W.A., Nelson, S., 2001. Flue gas desulfurization by-products additions to acid soil: Alfalfa productivity and environmental quality. Environ. Pollut. 114, 161–168.

Chen, L., Ramsier, C., Bigham, J., Slater, B., Kost, D., Lee, Y.B., Dick, W.A., 2009. Oxidation of FGD-$CaSO_3$ and effect on soil chemical properties when applied to the soil surface. Fuel 88, 1167–1172.

Chen, L., Kost, D., Tian, Y., Guo, X., Watts, D., Norton, D., Wolkowski, R.P., Dick, W.A., 2014. Effects of gypsum on trace metals in soils and earthworms. J. Environ. Qual. 43, 263–272.

Chen, L., Dick, W.A., 2011. Gypsum as an Agricultural Amendment: General Use Guidelines. 8. The Ohio State University, Columbus, OH.

Cheng, J.R., Chen, X.H., Liu, Z.H., Li, X.P., Fu, R.B., Chen, Q.Y., 2014. The experimental study on the process and effect to the FGD-gypsum as an improvement in coastal saline-alkali soil. China Environ. Sci. 34 (6), 1505–1513.

Chun, S., Nishiyama, M., Matsumoto, S., 2001. Sodic soils reclaimed with by-product from flue gas desulfurization: corn production and soil quality. Environ. Pollut. 114, 453–459.

Clark, G.J., Dodgshun, N., Sale, P.W.G., Tang, C., 2007. Changes in chemical and biological properties of a sodic clay subsoil with addition of organic amendments. Soil Biol. Biochem. 39, 2806–2817.

Du, X.G., Ma, Y., Wu, Y.Q., Guo, M.S., Ma, X., 2010. Study on determination method of hazardous elements in fuel coal and other solid by-products in thermal power plants, their migration rules during combustion, and their influence upon environment. Thermal Power Generation 11, 16–22.

Fang, C., Su, D., Duan, Y., Chen, X., 2012. Effects of coupling of FGD gypsum and irrigation on chemical properties of harbor front saline soil. J. Soil Water Conserv. 26, 59–63.

Frenkel, H., Gerstl, Z., Alperovitch, N., 1989. Exchange-induced dissolution of gypsum and the reclamation of sodic soils. J. Soil Sci. 40, 599–611.

Han, Z., 2013. Analysis of seawater intrusion characteristics and tendency in the Chongming Island. First Institute of Oceanography of National Bureau of Oceanography, Shangdong, China, pp. 25–39.

Laperche, V., Bigham, J.M., 2002. Quantitative, chemical, and mineralogical characterization of flue gas desulfurization by-products. J. Environ. Qual. 31, 979–988.

Lee, Y.B., Bigham, J.M., Kim, P.J., 2007. Evaluate changes in soil chemical properties following FGD-gypsum application. Korean J. Environ. Agr. 26, 294–299.

Li, M., Jiang, L., Sun, Z., Wang, J., Rui, Y., Zhong, L., Wang, Y., Kardol, P., 2012. Effects of flue gas desulfurization gypsum by-products on microbial biomass and community structure in alkaline–saline soils. J. Soils Sediments 12, 1040–1053.

Li, X.P., Liu, X.C., Mao, Y.M., Chen, X.H., 2014. Effects of flue gas desulfurization (FGD) gypsum on desalination of reclaimed tidal flat soil. J. Environ. Eng. Technol. 4, 502–507.

Li, L.J., Zhang, Q., Liu, P., Bai, G.J., Wu, W.L., 2015. Survey and analysis of heavy metals in FGD gypsum from coal-fired power plants. J. Soil Water Conserv. 29 (2), 209–214.

Liu, Z., Chen, X., Li, X., Wang, X., Lu, J., Li, Q., Shi, X., 2012. Effect of different amendments combined with gypsum application on ion composition in coastal saline soil. J. Nanjing Agric. Univ. 35, 83–88.

LY/T1251, 1999. Analysis methods of water soluble salts of forest soil.

LYT 1249, 1999. Calculation of soil alkalinity.

Malcolm, E., Sumner, R., 1998. Sodic soils-distribution, properties, management, and environmental consequences. Oxford University Press, New York.

Mashhady, A.S., Rowell, D.L., 1978. Soil alkalinity. I. Equilibria and alkalinity development. J. Soil Sci. 29, 65–75.

Oster, J.D., Jayawardane, N.S., 1998. Agricultural Management of Sodic Soils. Oxford University Press, Now York, USA, pp. 125–147.

Qadir, M., Qureshi, R.H., Ahmad, N., 1996. Reclamation of a saline–sodic soil by gypsum and *Leptochloa fusca*. Geoderma 74, 207–217.

Rengasamy, P., 2002. Transient salinity and subsoil constraints to dryland farming in Australian sodic soils: an overview. Aust. J. Exp. Agric. 42, 351–361.

Rengasamy, P., 2006. World salinization with emphasis on Australia. J. Exp. Bot. 57, 1017–1023.

Richards, L., 1954. Diagnosis and improvement of saline and alkali soils. Washington: United States Salinity Laboratory. USDA Agric. Handb. 60, 160.

Sakai, Y., Aihara, T., Yamamoto, T., Sadakata, M., 2010. Evaluation of soil properties and additional application of desulfurization gypsum in an area of no amelioration after an initial application in sodic soil of China. Kagaku. Kogaku. Ronbun. 36, 275–280.

Sakai, Y., Matsumoto, S., Sadakata, M., 2012. Alkali soil reclamation with flue gas desulfurization gypsum in China and assessment of metal content in corn grains. Soil Sediment Contam. 13, 65–80.

Shainberg, I., Sumner, M.E., Miller, W.P., Farina, M.P.W., Pavan, M.A., Fey, M.V., 1989. Use of gypsum in soils: A review. Springer, US, pp. 1–111.

US EPA, 2008. Agricultural uses for flue gas desufurization (FGD) gypsum (EPA530-F-08-009).

US EPA, 2014. Coal combustion residual beneficial use evaluation: Fly ash concrete and FGD gypsum wallboard (EPA530-R-14-001).

Wang, J., Yang, P., Shumei, R., Guangming, X., 2005. Variation of chemical indices of alkaline soil ameliorated with desulphurization byproducts. Acta Pedol. Sin. 42, 98–105.

Wang, S.J., Chen, C.H., Xu, X.C., Li, Y.J., 2008. Amelioration of alkali soil using flue gas desulfurization byproducts: productivity and environmental quality. Environ. Pollut. 151, 200–204.

Wang, J., Bai, Z., Yang, P., 2013. Effect of byproducts of flue gas desulfurization on the soluble salts composition and chemical properties of sodic soils. PLoS One 8, 1–14.

Watts, D.B., Dick, W.A., 2014. Sustainable uses of FGD gypsum in agricultural systems: Introduction. J. Environ. Qual. 43, 246–252.

Yang, Z., Wan, B., 2014. Progress in techniques of improvement and utilization of saline-alkali land in China and its future trend. J. Soil Water Conserv. 2, 1–11.

Yu, H.L., Yang, P., Lin, H., Ren, S., He, X., 2014a. Effects of sodic soil reclamation using flue gas desulphurization gypsum on soil pore characteristics, bulk density, and saturated hydraulic conductivity. Soil Sci. Soc. Am. J. 78, 1201–1213.

Yu, H.L., Gu, W., Huang, J.Y., Lin, H.S., 2014b. Impact of addition of FGDB as a soil amendment on physical and chemical properties of an alkali soil and crop yield of maize in northern China coastal plain. J. Chem. 1-11, 540604.