Study on the desalination process and improvement effect of FGD-gypsum improving coastal saline-soil

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Abstract. To provide theoretical basis for the improvement of Shanghai coastal saline-soil, a soil column leaching experiment was carried out to study the process and improvement effect of soil desalination after soil applying 0.5%, 1%, 2.5%, and 5% mass ratio of FGD-gypsum, aimed at the characteristics of Shanghai coastal saline-soil. The result showed that, compared with the control, applying FGD-gypsum could increase soil saturated hydraulic conductivity by 5.1-6.5 times, increase leaching sodium quality by 11.0%-22.2%, decrease soil pH 0.41-0.11 units, decrease exchangeable sodium percentage (ESP) by 25.1%-76.7%. When FGD-gypsum improved the coastal saline-soil, the change rules of soil's physical and chemical properties were that, soil saturated hydraulic conductivity increased before leveling off, leaching sodium quality gradually increased, soil pH declined before leveling off, ESP reduced with increasing ratios of FGD-gypsum; soil leaching sodium ion concentration decreased sharply and then tended to equilibrium over time, and soil leaching out sodium was active in the first 2 days of leaching. In the process of FGD-gypsum speeding up soil desalination, soil leaching calcium quality and leaching sodium quality had relationship with soil hydraulic conductivity and the ratio of FGD-gypsum, and the leaching out sodium of FGD-gypsum-soil system was more accelerated when calcium ion concentration in soil leachate was higher.

1. Introduction
The coastal saline-soil is an important reserve resource for the development of coastal regional economies. In China, there are around 66,700 km² coastal saline-soil, which is distributed in coastal areas, such as Shandong, Hebei, Liaoning, Zhejiang, Fujian, Guangdong [1]. The coastal areas are at the junction of the sea and the land, which has high groundwater level, tidal erosion, frequent supply of seawater and evaporation-concentration, thereby a large expanse of saline-soil is formed [2, 3]. The physical and chemical properties of coastal saline-soil are poor due to the high content of salt, low natural desalination rate, heavy salinization. It is important to improve coastal saline-soil for improving ecological environment, development and utilization of land resources and relaxing man-land contradiction in coastal areas.

In recent years, FGD-gypsum as a saline-soil amendment is popular for its low cost, large output and fast repair rate [4]. FGD-gypsum improving saline-soil is native to mineral gypsum improving saline-soil, whose principle is that calcium ions could promote the aggregation of clay particles and displace excess sodium on soil colloids [4, 5]. Compared with mineral gypsum, FGD-gypsum has better physical and chemical properties and economic effects, such as finer particles, higher solubility, higher purity, greater production, lower cost and so on. The United States has applied FGD-gypsum in...
agriculture. In 2008, the United States EPA issued a paper of Agricultural Uses for Flue Gas Desulfurization (FGD) Gypsum. In the United States, the agricultural utilization rate of FGD-gypsum increased from 2% to 5% in the total output of FGD gypsum from 2006 to 2013. In 2015, the USDA officially put the FGD-gypsum as a soil conditioner as the best national agricultural practice [5, 6].

Shanghai is on the tip of the Yangtze Delta, which has distinctive physicochemical properties, has around 960 km² coastal saline-soil which accounts for more than 15% of the city’s land area. Shanghai as a globalizing metropolis is developing at a very high speed, thereby it is important to improve coastal saline-soil for Shanghai’s ecological environment and development and utilization of land resources. Meanwhile, with the promotion of FGD technology, there are millions of tons of FGD-gypsum needed to be treated in Shanghai every year. Studies on FGD-gypsum improving saline-soil have many at home and abroad, but saline-soil in different areas has its unique physical and chemical properties and we can not blindly copy the results of previous studies, thereby it is needed to be treated separately according to concrete conditions of different types of soil for FGD-gypsum improving saline-soil. In this paper, FGD-gypsum improving Shanghai coastal saline-soil is explored through soil column leaching experiment. In soil column leaching experiment, soil saturated hydraulic conductivity, leaching concentration and quality of calcium and sodium during the soil column leaching process were measured and analyzed for exploring the desalination process. And soil pH, exchangeable sodium, ESP before and after FGD-gypsum improving soil were measured and analyzed for exploring the improvement effect.

2. Materials and Methods

2.1. Soil samples and FGD gypsum

Soil samples were taken from Chongming Island (E 121° 57′20″, N 30° 31′25″) in Shanghai, China, which is located in the Yangtze River. The region has a typical subtropical monsoon climate, the annual average temperature is 15.3°C, the hottest months are July and August (monthly average temperature 26.8-26.9°C), and the annual average evaporation capacity (1346 mm) is higher than the annual average precipitation (1078 mm) [6]. The soil samples were collected at plough layer, then air-dried, disaggregated, sieved (2 mm), and mixed well for soil column leaching experiment. The soil physicochemical properties were 2.64 g•cm⁻³ for soil density, 1.2 g•cm⁻³ for bulk density, 1.092 mS•cm⁻² for conductivity, 38% for moisture content, 1.29×10³ mg•kg⁻¹ for soil total salt, 9.07 for pH, 30.61% for ESP, which belonged to typical severe saline-soil, and the soil main soluble salt was sodic salt [6].

FGD-gypsum was chosen from a steelworks with 94% CaSO₄•2H₂O. The heavy metals contents in FGD-gypsum are shown in Table 1, which were determined by SGS Standard Technical Service Co. Ltd. Hg and As of FGD-gypsum were determined by atomic fluorescence spectrometry (AFS) while other heavy metals were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) after FGD-gypsum being pretreated according to US EPA Method 3052. When examining the heavy metals contents of FGD-gypsum, it was apparent that all heavy metals contents were far lower than the Class II of Environmental Quality Standard for Soils of China (GB15618-1995). Therefore, using FGD gypsum for improving coastal saline-soil has a low ecological risk.

| Sample          | Heavy metals contents (mg•kg⁻¹) |
|-----------------|---------------------------------|
|                 | As    | Cd | Cr  | Cu   | Ni   | Pb   | Zn   | Hg   |
| FGD-gypsum      | 2.2   | 0.37 | 5.5 | 8.7  | 13.2 | 19.8 | 11.3 | 0.36 |

Table 1. Heavy metals contents in FGD-gypsum.
Chinese environmental quality secondary standard for soils (GB15618–1995)

2.2. Soil column leaching experiment
Soil column leaching device is shown in Figure 1. Soil column leaching experiment was conducted with fine treatments, which were the natural soil, FGD-gypsum mixeded with natural soil under 0.5%, 1%, 2.5%, and 5% mass ratio of FGD-gypsum, each treatment was repeated thrice. After soil column filled, soil column was leached by deionized water, and deionized water leaching volume was designed to 1100 mL for simulating the annual average rainfall of Shanghai.

Figure 1. Soil column leaching experiment device.

2.3. Analysis and method
Selected soil characteristics were determined in accordance with the NY/T 1121-2006 Agricultural Standard of People’s Republic of China-Soil Testing. The calcium ion and sodium ion concentration in the leachate samples were determined by a flame furnace atomic absorption spectrophotometer. Soil pH was determined on a 1:5 (soil:water, W/W) mixture using a glass electrode. The exchangeable, sodium ions, cations, were extracted using 1 mol/L NH₄OAc, whose concentrations were determined using an flamephotometer. The ESP was calculated by the percentage of exchangeable sodium in soil exchangeable cations where soil exchangeable sodium ions and exchangeable cations were expressed in cmol•kg⁻¹. The soil saturated hydraulic conductivity was determined through the collected volume of leachate from soil column per hour [7].

2.4. Analysis and method
ORIGIN 9.0 and SPSS 17.0 were used to deal with the experimental data. Unless special instructions, the chart data are the average values of repeated treatment.

3. Results and Discussion
3.1. Soil saturated hydraulic conductivity
When examining figure 2, it is apparent that FGD-gypsum accelerate soil saturated hydraulic conductivity, which increases before leveling off with increasing ratios of FGD-gypsum. Compared with the control, applying 0.5%, 1%, 2.5%, and 5% of FGD-gypsum could increase soil saturated hydraulic conductivity by 5.1, 6.5, 6.5, 6.2 times respectively, soil saturated hydraulic conductivity had no significant difference among 1%, 2.5%, and 5% of FGD-gypsum (p>0.05), and the maximum soil saturated hydraulic conductivity was reached to 15.2 mL•h⁻¹.
Study of Cheng et al. [7] has shown that FGD-gypsum could increase soil saturated hydraulic conductivity, whose change role is similar to that of the study. This is due to that, FGD-gypsum increases calcium ions in soil and positively charged calcium ions could reduce the dispersion of soil particles by promoting the aggregation of negatively charged clay particles, which improves the stability of soil structure and prevents soil crusting. Better soil particle aggregation and less crusting allow for greater soil hydraulic conductivity [4, 5].

3.2. Changes of calcium and sodium in desalination process
Sodium ion accumulation in soil solid phase or liquid phase is the main reason that causes the bad physical and chemical properties of saline-soil. Removal of sodium ions from soil is the key to the improvement of saline-soil. FGD-gypsum can improve saline-soil, whose main principle is that calcium ions act on saline-soil to remove sodium ions in the leaching process. Therefore, in this paper, only soil leaching calcium and sodium are involved in soil desalination process.

3.2.1. Calcium ion. When examining figure 3, it is apparent that, calcium ion concentration in soil leachate decreases sharply and then tends to dynamic equilibrium (or continues to fall) over time, and the decreasing slope of calcium ion concentration increases with increasing ratios of FGD-gypsum, calcium ion concentration tending to dynamic equilibrium or continuing to fall is emerged in the first 2 days of soil column leaching. Meanwhile, figure 3 also shows that leaching calcium quality increases with increasing ratios of FGD-gypsum, whose increasing extent gradually decreases with increasing ratios of FGD-gypsum. Compared with the control, applying 0.5%, 1%, 2.5%, and 5% of FGD-gypsum could increase leaching calcium quality by 17.4, 41.8, 48.8, 49.7 times respectively.

Study of Cheng et al. [7] is consistent with our study for the change rule of calcium ion concentration in soil leachate. Calcium ion concentration decreasing sharply is due to the decrease of FGD-gypsum with the leaching and reaction with soil and the inhibition function of more and more sulfate ion from FGD-gypsum for dissolution of FGD gypsum [8]. Then calcium ion concentration tending to dynamic equilibrium is due to calcium ion could get relatively adequate supplement from FGD-gypsum, or calcium ion concentration will fall. Leaching calcium ion is the kind of calcium ion that has not enough time to react with soil with the leaching.
Salt moving with water moving, within a certain range, the faster soil hydraulic conductivity, the more leaching calcium quality of soils is, thereby the leaching calcium quality is affected by soil hydraulic conductivity. In figure 3, the loss of calcium quality slightly increases when the soil saturated hydraulic conductivity tends to equilibrium, which indicates that the loss of calcium quality is also affected by the ratio of FGD-gypsum and soil hydraulic conductivity is dominant for accelerating the loss of calcium in this study.

3.2.2. Sodium ion. When examining figure 4, it is apparent that, leaching sodium ion concentration decreases sharply and then tends to equilibrium over time, and the decreasing slope of sodium ion concentration increases with increasing ratios of FGD-gypsum, sodium ion concentration tending to dynamic equilibrium is emerged in the first 2 days of soil column leaching. Meanwhile, figure 4 also shows that leaching sodium quality increases with increasing ratios of FGD-gypsum. Compared with the control, applying 0.5%, 1%, 2.5%, and 5% of FGD-gypsum could increase leaching sodium quality by 11.0%, 16.8%, 18.0%, 22.0% respectively.

Combined figure 3 and Figure 4, the change rule of sodium ion concentration decreasing sharply is similar to that of calcium ion concentration, which is in good agreement with studies of Cheng et al. and Cui et al. [7, 9] that the leaching sodium of FGD-gypsum-soil system is more accelerated when the calcium ion concentration in soil leachate is higher. In the stage of sodium ion concentration decreasing sharply, the soil leaching sodium includes water-extractable sodium and exchangeable sodium replaced by calcium ions from FGD-gypsum [9]. However, the soil leaching sodium only includes exchangeable sodium replaced by calcium ion in the stage of sodium ion concentration tending to equilibrium [7].

Salt moving with water moving, within a certain range, the faster soil hydraulic conductivity, the more leaching sodium quality of soils is, so the leaching sodium quality is affected by soil hydraulic conductivity. In figure 4, leaching sodium quality continues to increase when the soil saturated hydraulic conductivity tends to equilibrium, which indicates that the leaching sodium quality is also
affected by the ratio of FGD-gypsum. Therefore, the leaching sodium quality of soil is affected by soil hydraulic conductivity and the ratio of FGD-gypsum [10].

3.3. Soil pH
When examining figure 5, it is apparent that, FGD-gypsum reduces obviously soil pH which decreases and then tends to equilibrium with increasing ratios of FGD-gypsum. Compared with the control, applying 0.5%, 1%, 2.5%, and 5% of FGD-gypsum could decrease soil pH by 0.41, 0.51, 1.11, 1.06 units respectively. Applying 0.5%, 1% of FGD-gypsum cannot decrease soil pH to below 8.0 which is suitable for plant growth. But 2.5%, 5% of FGD-gypsum could decrease soil pH to about 7.6, and soil pH has no significant difference between 2.5% and 5% of FGD-gypsum (p>0.05).

Figure 5. Soil pH under different ratios of FGD-gypsum application. FGD-gypsum could decrease soil pH, but the decreasing extent of soil pH is not increased with increasing ratios of FGD-gypsum, which is consist with study of Sakai et al. [10]. Saline-soil's high pH is controlled by exchangeable sodium and water-soluble CO$_3^{2-}$+HCO$_3^{-}$. FGD-gypsum decreasing soil pH is due to that calcium ion from FGD-gypsum reacts with CO$_3^{2-}$+HCO$_3^{-}$ to generate CaCO$_3$ deposition and replaces exchangeable sodium which is leached out [10].

3.4. Soil alkalinity
When examining figure 6, it is apparent that, the cation exchange capacity (CEC) of all treatments have no significant difference (p < 0.05), which means FGD-gypsum will not reduce the water retain and fertilizer of soil. Meanwhile, figure 6 also shows that, FGD-gypsum could reduce soil ESP and exchangeable sodium, the change rule of ESP is similar to that of exchangeable sodium, which reduces with increasing ratios of FGD-gypsum. Compared with the control, applying 0.5%, 1%, 2.5%, and 5% of FGD-gypsum could reduce soil ESP by 25.1%, 64.7%, 67.2%, 76.7% respectively. When the ratio of FGD-gypsum was more than 1%, soil ESP would not continue to decrease sharply, and soil exchangeable sodium decreased by up to 76.8%.

Figure 6. Soil CEC, exchangeable sodium, ESP under different ratios of FGD-gypsum application. Our result showing FGD-gypsum would not reduce the water retain and fertilizer of soil is consistent with the study of Mao et al. [6]. Meanwhile, study of Mao et al. [6] also has shown that FGD-gypsum could reduce soil ESP and exchangeable sodium and the change rule of ESP is similar to that of exchangeable sodium. The key to the improvement of saline-soil is the reduction of soil ESP. FGD-gypsum reducing soil ESP is due to that, calcium ion's flocculation ability for soil clay particles is superior to that of sodium ion [4], calcium ions from FGD-gypsum could replace exchangeable sodium on soil colloids, then soil ESP is reduced.
4. Conclusions
FGD-gypsum could improve the physical and chemical properties of Shanghai coastal saline-soil in soil column leaching experiment. When FGD-gypsum improved the coastal saline-soil, the change rules of soil's physical and chemical properties were that, soil saturated hydraulic conductivity increased before leveling off, leaching sodium quality gradually increased, soil pH declined before leveling off, ESP reduced with increasing ratios of FGD-gypsum, soil leaching sodium ion concentration decreased sharply and then tended to equilibrium over time, and soil leaching out sodium was active in the first 2 days of leaching. In the process of FGD-gypsum speeding up soil desalination, soil leaching calcium quality and leaching sodium quality had relationship with soil hydraulic conductivity and the ratio of FGD-gypsum, and the leaching out sodium of FGD-gypsum-soil system was more accelerated when calcium ion concentration in soil leachate was higher.

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