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Chemical changes and the mechanisms in the sintering process of sea silt

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When sea silt that contains more soluble salt is used for the sintering of building materials, its adverse impact is a widespread concern. Lianyungang sea silt in Jiangsu Province is taken as an example. The changes of weight and heat, soluble salt and chlorine content in the sintering process are studied by laboratory experiments. The results show that the ion content of chlorine, sodium and sulfate is higher in the sea silt, the content of SO_4^{2-} reaches a peak of 18‰ at 500 ℃, less than 4‰ after 1000 ℃; the content of Na^+ decreases dramatically above 600 ℃, but remains 0.1 ‰ after 1000 ℃; the content of Cl^- decreases sharply above 600 ℃ and is almost zero at 900 ℃. The XRF (X-ray fluorescence diffraction) test of sintering sea silt at 1000 ℃ shows that chlorine has disappeared and does not exists in a crystalline and glassy ionic state; the possible mechanism of sintering sea silt is dechlorination such that sodium chloride melts to a volatile solution at 800 ℃, the sodium chloride gas reacts with the water vapor, carbon or carbon dioxide to yield hydrogen chloride. In this study, the quantitative change of the soluble salt in the sea silt is proved by the change of the sintering temperature. The content of the soluble salt is very low when the sintering temperature is above 1000 ℃, which can eliminate the concerns for the sintering materials of sea silt. The transfer and transformation process of sodium chloride was revealed, which suggests that the tail gas treatment should be strengthened in the production of sintering building materials.

Keywords: sea silt, sintering, chlorine, physical, chemical

INTRODUCTION

With the rapid development of the coastal development strategy, the sea sediment production brought about by harbor excavation and waterway dredging increase dramatically, which if abandoned, will seriously affect the appearance of the city and produce the secondary pollution problems of dust and wet mud. More and more sea dredged mud is dumped into the ocean and the selection of the sea dumping site is increasingly difficult, which is a serious impediment to the development of the port and waterway [1]. Sea silt will also bring seawater eutrophication and even result in blocked or even abandoned seawater farms. Another aspect is the ban to use sintered clay bricks and a shortage of alternative raw materials occurs. The way to utilize sea mud is for building materials also by using waste, not to reduce the occupation of cultivated land, thus protecting the environment and providing alternative products for the construction market, with good economic and social benefits [2]. Therefore, it is very important to study the development and utilization of sea silt as a resource.

The feasibility of sea silt sintering building materials has been confirmed [3, 4]. The feasibility of sintered brick was studied by Salim W, et al. [5] with dredged sea sludge extracted at Kuala Perlis. That local sea silt contains the appropriate brick materials SiO2 and Al2O3. The scumming degrees of two kinds of sea silt sintered perforated brick with iron tailings and fly ash were studied by Dongyan Han, et al. [6]. It was found that the iron tailings reduce the scumming degree of the sintered bricks and these are more suitable for the admixture. A study of the Xiamen sea silt sintered brick has been made by Zhou Min [7], which shows that the scumming degree is very slight, only in the corners and can even be neglected. The addition of fly ash can effectively reduce the temperature of the scumming. Andrea Mezencevova, et al. [8] have made a study of the strength of a sintered brick using 100% dredged silt and dredged silt adding 50% clay respectively. It was found that two kinds of sintered brick can be used for construction. The compressive strength of the pure sea mud brick is 8.3~11.7 MPa while the compressive strength of sea silt with 50% clay added to the sintered brick is up to 29.4 MPa. In addition to sintering building materials, a very effective water purification and adsorption material that uses the seabed sediments and can remove heavy metals was sintered at 400℃ by Dabwan Ahmed H A, et al. [9]. In the sintering process of sea mud, salinity is an important feature. Many researchers worry that sodium chloride has adverse effects including scumming [7, 10].

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Dehydration and desalination technology were used to reduce the salt content in the sea mud [11, 12]. There is also a study showing that the salt content during the sintering process will greatly decrease.

The physical and chemical changes of the sea silt during sintering are presented in this paper, including the change in weight, soluble salt and chloride content and the transfer and transformation mechanism of sodium chloride.

TEST MATERIALS AND METHODS

Materials

The test samples of the sea silt are taken from Oriental Garden of Lianyungang, Jiangsu Province, China. Its main minerals are halloysite, calcite, magnesium chlorite, quartz, albite and glauconite. As shown in Table 1, the characteristics of its main chemical composition are with a slightly low silicon content, high content of potassium, sodium and salt. The content of SiO2 is slightly low, while the content of Al2O3 is middle to high. Table 2 shows that it contains more K2O and Na2O that are fusible as well as CaO and MgO that can reduce the refractoriness of clay. It is similar to fusible acid clay in chemical composition. $CaCO_3$ will break down at 898℃.

Test methods

The method of X-ray diffraction XRD analysis studies the mineral composition together with X-ray fluorescence diffraction XRF used in chemical composition analysis; a German Netzsch simultaneous thermal analyzer (DSC/DTA-TG) STA 449 F3 is used in the thermo-gravimetric analysis; tests of the solubility of salt; the sintered soil samples at different temperatures (including 105, 200, 300, 400, 500, 600, 700, 800, 900, 1000, 1100 ℃) were respectively cooled to a room temperature. 10 g of milled powder were weighed and dissolved in 100 ml of deionized water, filtered by filter paper after 48 h and the water samples diluted 10 times at the end.

The cations (Na^+, K^+, Ca^{2+}, Mg^{2+}) were registered by a Wantong ion chromatograph, automatic sampler and cation chromatographic column at 30 ℃, with a flow rate of 0.9 ml/min and an eluent of pyridine dicarboxylic acid system while the anions (Cl^-, $SO4^{2-}$, NO^{3-}) were registered by a Wantong ion chromatograph, automatic sampler, conductance detector and eluent generator at 30 ℃, with a current of 50 mA, a flow rate of 1.0 ml/min and an eluent of 20 mMol dilute KOH solution.

THERMO GRAVIMETRIC ANALYSES

The thermo-gravimetric analyses curves of sea silt are shown in Figure 1. The quality decreases slowly before 400 ℃ is reached; it begins to decrease drastically between 400-665 ℃; the trend of change begins to decrease between 665-900 ℃; the quality changes rarely and remains almost unchanged after 900 ℃. Heat is generally generated in the direction of absorption. The heat absorption is very small prior to reaching 400 ℃, while the endothermic range increases gradually after 400 ℃. There is a significant change in heat fluctuation at 975 ℃.

Possible reasons for this phenomenon are the weakly adsorbed water and strongly bound water separated in turn by the increase in temperature and the heat absorption due to the gradual increase in dehydration. At 975 ℃ a strong endothermic reaction occurs, the reason is that $CaCO_3$ is possibly decomposed into CaO and CO_2 gas with heat absorption. A large amount of the heat absorption above 1000 ℃ is related to the heat absorption and phase transformation of the soil when melting.

Table 1. Chemical composition of sea silt

Name	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	SO_3
Composition content/%	57.10	17.30	11.30	3.10	2.17	4.01	3.10	0.71

Note: detection limit of SO_3 ≧30ppm.

Table 2. Physical properties of the main components of sea silt

Component	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	$CaCO_3$	Na_2SO_4	K_2SO_4
Melting point/℃	1650	2054	1565	2572	2800	770	1132	825	884	1069
Boiling point/℃	2230	2980	3414	2850	3600	1500	1275	*	1404	1689
Decomposition/℃								898		

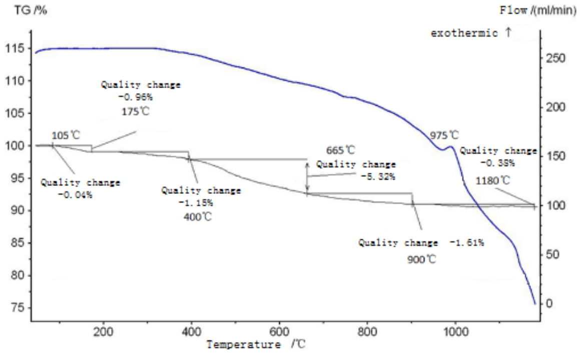


Fig. 1. Thermo-gravimetric analysis curve of sea silt.

CHANGES OF SOLUBLE SALT CONTENT

The changes of soluble salt content are shown in Figure 2.

(a) SO_4^{2-} ions are of a higher content and almost unchanged before 400 ℃ and increase gradually to a peak concentration of 18‰ between 400-500 ℃, the reason is still not clear but the decomposition of some substance containing sulfate is suspected; it decreases gradually after 500 ℃, indicating thermal decomposition or a chemical reaction for the molten state of sulfate; it is below 4‰ after 1000 ℃.

(b) Overall the content of Ca^{2+} is low, probably because the soluble salt of calcium is very small in quantity especially the formation of micro soluble calcium sulfate in the presence of a large quantity of sulfate. The content of Ca^{2+} is basically unchanged before reaching 400 ℃, gradually increasing to its peak of only 0.56‰ at between 400-500 ℃ and gradually decreasing after 500 ℃. Ca^{2+} disappear after 1000 ℃, which indicates that Ca^{2+} have reacted with silicon and aluminum to give insoluble alumino-silicate.

(c) The content of K^+ is the lowest and the peak is only at 0.04‰ with a fluctuation in a minimum range before reaching 800 ℃. It decreases sharply after 800 ℃. As shown in Table 2, the melting point of K_2O is 770 ℃. After reaching that temperature, the oxide of potassium melts with the formation of an insoluble alumino-silicate vitreous body reacting with silicon and aluminum.

(d) The content of Na^+ doesn't change basically before 600 ℃, but decreases sharply above 600 ℃ and remains 0.1‰ unchanged after 1000 ℃, showing that sodium has reacted with silicon and aluminum to yield an insoluble alumino-silicate.

(e) The content of Mg^{2+} is rare and the highest percentage does not exceed 0.08‰. It fluctuates in the minimum range before 600 ℃, is reached and decreases gradually after 600 ℃, then the content becomes zero above 1000 ℃, indicating that magnesium has completely reacted with aluminum and silicon to synthesize alumino-silicate crystals.

(f) The content of Cl^- is relatively high. It fluctuates within a small range of 12-14‰ before 600 ℃ are reached and begins to drastically decrease over 600 ℃ and drops to almost zero after 900 ℃ are reached showing the transfer and transformation of chlorine during the high-temperature sintering process, which will be further analyzed as shown below.

THE CHANGES OF CHLORINE CONTENT AND ITS MECHANISM ANALYSIS

Changes of chlorine content

The chlorine content is higher before sintering, but the content of chlorine decreases significantly after sintering [3], ultimately falling to almost zero. In order to further study the whereabouts of Chlorine, XRF analysis is used to test the content for Chlorine in the sintered sea mud at 1000 ℃ and the test results are shown in Table 3. From the table, it is obvious that the content of chlorine is zero after the sintering process, which indicates that the chlorine is transferred during the sintering process.

Analysis on the change mechanism of the chlorine content

Basic properties and thermal properties of NaCl

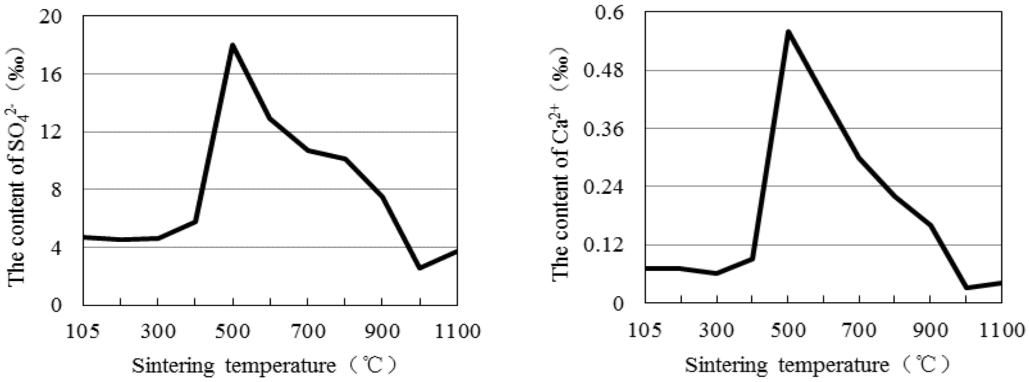
NaCl is soluble in water and with the increase of temperature, the solubility will increase but the change is not obvious. The solubility is 36.0 g at 20 ℃. The melting point is 801 ℃ and the boiling point is 1465 ℃.

The thermo-gravimetric analysis curve of sodium chloride is shown in Figure 3. At 54 min, the temperature is 800 ℃, the heat absorption peaks and the quality of sodium chloride begins to decrease. It decreases drastically to about 900 ℃, with the heat absorption peaking subsequently. This shows that sodium chloride melts with heat over 800 ℃ and begins to volatilize above 900 ℃, with a rapid reduction in quality.

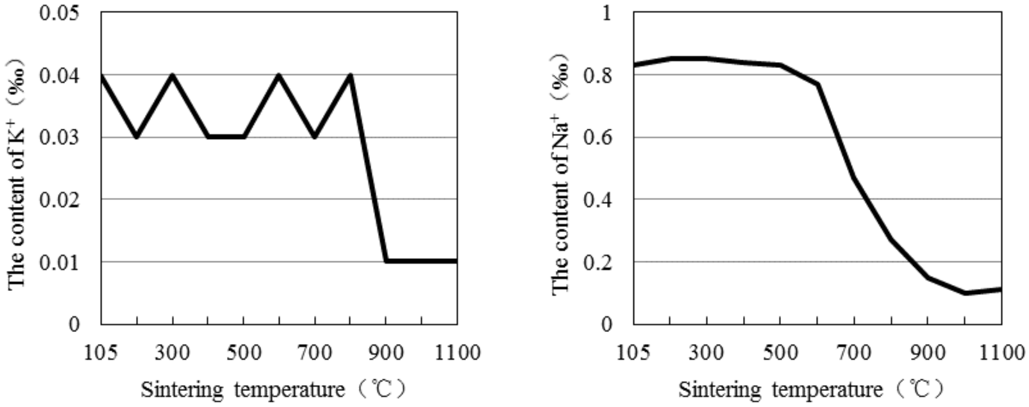
Table 3. Changes of chlorine content in sea silt

Names	The content of chlorine（%）	
	Before	After
Sample 1	2.37	0.000
Sample 2	2.78	0.000
Sample 3	2.19	0.000

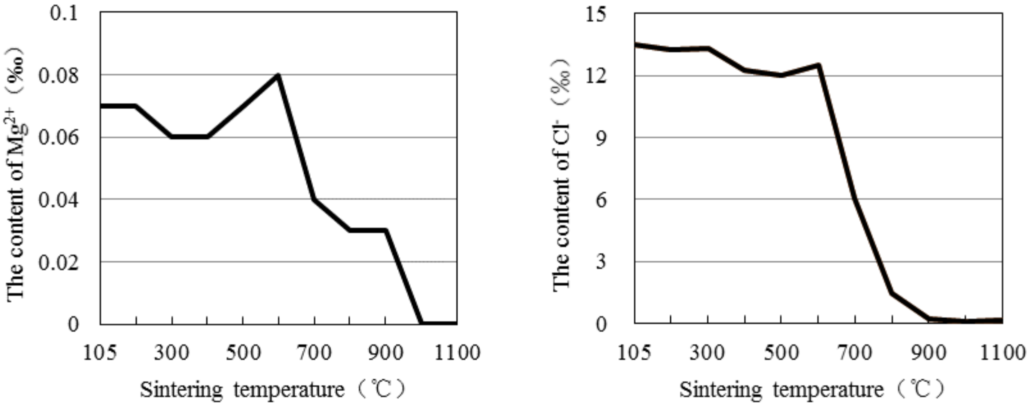
* Note: the sintering temperature is 1000℃.



(a) SO_4^{2-} (b) Ca^{2+}



(c)K^+ (d) Na^+



(e)Mg^{2+} (f) Cl^-

Fig. 2. Changes of soluble salt content with the change of sintering temperature.

Sodium chloride transfer

Under normal temperature and pressure, NaCl doesn’t react with water and its melting state also does not react with water at a high temperature. However, four substances of NaCl, the clay components ($Ai_2O_3 \cdot SiO_2 \cdot 2H_2O$), H_2O and C are indispensable materials to prepare hydrochloric acid and CO_2 or CO directly instead of C participating in the reaction. Therefore, when the temperature of a coal stove is higher than 800 ℃, sea silt in sintering will generate complex chemical changes and produce gaseous HCl, resulting in the heat absorption peak at 800 ℃ in Figure 3. The main reactions occurring in the sintering process are as follows [13]:

$$C + O_2 + 4NaCl \xrightarrow{\text{high temperature}} 2Na_2O + CCl_4$$

$$CCl_4 + 2H_2O \xrightarrow{\text{high temperature}} CO_2 + 4HCl$$

$$Na_2O + Al_2O_3 \cdot 2SiO_2 \xrightarrow{\text{high temperature、}} Na_2O \cdot Al_2O_3 \cdot 2SiO_2$$

This shows that the element chlorine participates in the reaction to produce HCl gas escaping from the product during the sea silt sintering process. The sintering product will not be of poor quality due to the presence of sodium chloride in the raw materials.

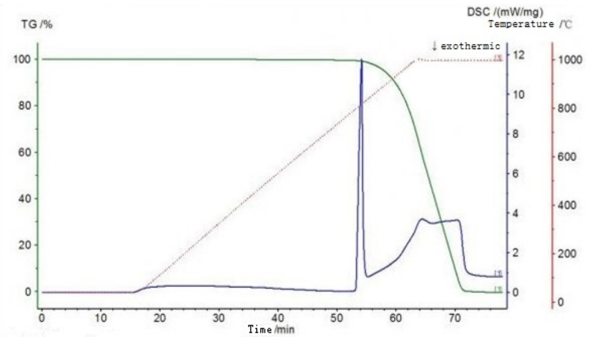


Fig. 3. Thermo-gravimetric analysis curve of sodium chloride

CONCLUSIONS

Through a series of laboratory experiments, the following conclusions can be listed:

(1) With the increase in temperature, the free water, weakly adsorbed water and strongly bound water separate in turn and the heat absorption of dehydration gradually increases. At 975 ℃, a strong endothermic reaction occurs the reason is possibly because $CaCO_3$ is decomposed into CaO and CO_2 gas with the absorption of heat. A large amount of heat absorption above 1000 ℃ is related to the heat absorption of phase transformation due to the soil melting.

(2) The content of SO_4^{2-} increases to a peak concentration of 18‰ at 500 ℃, the reason is still not clear but the decomposition of some substance containing sulfate is suspected; it decreases gradually after 500 ℃, indicating the thermal decomposition or chemical reaction of the molten state of sulfate; it is below 4‰ after 1000 ℃.

(3) Calcium, sodium, magnesium and potassium react respectively with silicon and aluminum compounds to synthesize an alumino-silicate vitreous body above 500 ℃, 600℃ and 800℃.

(4) Chlorine has disappeared and does not exists in a crystalline and glassy ionic state when the sintering temperature is above 1000 ℃ and the content of soluble salt is very low, which can eliminate the concerns of sintering materials from sea silt.

(5) Sodium chloride melts or becomes a volatile solution at 800 ℃, the gaseous chloride sodium reacts with the water vapor, carbon or carbon dioxide to yield hydrogen chloride as the gas escapes.

(6) HCl gas is generated with the transfer and transformation process of sodium chloride, which suggests that the tail gas treatment should be strengthened during the production of sintering building materials.

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ХИМИЧНИ ПРОМЕНИ И МЕХАНИЗМИ НА СИНТЕРУВАНЕТО НА МОРСКА ТИНЯ

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(Резюме)

Морските наноси, използвани за строителни материали имат вредно въздействие върху околната среда. Тинята от езерото Лянунганг в провинция Джиянгсу е взета като пример. Промените в теглото, топлината, съдържанието на соли и хлор, натрий и сулфати в процеса на синтеруването на тинята са изследвани експериментално. Резултатите показват, че съдържанието на йоните на хлора, натрий и сулфатите е по-високо в тинята, съдържанието на SO_4^{2-} достига максимум при 18‰ и 500 °C, по-малко от 4‰ над 1000 °C; съдържанието на Na^+ намалява драстично над 600°C, но остава 0.1 ‰ над 1000°C; съдържанието на Cl^- рязко намалява над 600 °C и е почти нула при 900 °C. Методът XRF (рентгенова флуресцентна дифракция) показва, че синтеруваната тиня губи напълно хлоридите при 1000°C и те не се намират нито в кристално, нито в йонно състояние. Възможният механизъм на дехлориране е стапянето на натриевия хлорид до летлива стопилка при 800 °C, като газообразният натриев хлорид реагира с водните пари, въглерода или въглеродния диоксид с получаването на хлороводород. В това изследване се доказват количествените промени при различни температури на синтеруване. Съдържанието на разтворима сол е ниско при температури на синтеруване над 1000 °C, което елиминира опасността за синтеруваните материали от тинята. Установени са пренос и трансформация на натриевия хлорид, което предлага отделяните газове от третирането трябва да се усили при производството на синтерувани строителни материали.