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Engineering properties and microstructural features of the soda residue
碱渣的工程性质及其微结构特征*

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Abstract The soda residue has been utilized as the foundation soil. The specical chemical composition, formative process and micro-structure lead to the difference between the macro-properties of the soda residue and those of other natural soils. This paper analyzes the engineering properties and the microstructural features of the soda residue, and studies the interaction between the soda residue and the blended material—calcium-richened fly ash.
Key words soda residue, microstructure, micro-image, calcium-richened fly ash.
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文 摘 目前碱渣已被作为工程回填土用于大面积填垫工程,但是由于其化学成分、形成过程及其微结构的特殊性,其宏观性质与其它天然土相比有明显的不同。本文分析了碱渣的微观结构及其成因,并对碱渣与增钙灰之间的作用机理作了分析。
关键词 碱渣,微结构,微观图像,增钙灰。
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1 Introduction

Soda is a kind of important chemical material and takes a significant position in the national economy. The waste residue coming with the soda in the ammonia-soda process occupies large piece of land and spoils the local environment.

It's a effective method of disposing of the soda residue to treat it as the foundation soil. In practice, it is often blended with fly ash or calcium-richened fly ash to be used(so called soda residue soil). Up to now, the physical and the mechanical properties of the soda residue have been clear. The engineering practice substituting it for the general soil in the lowland has also been carried out in a large scale, and the research of making it as the highway foundation has been going on. Campared with other natural soils, the physical and the mechanical properties of the soda residue are special, for example, the water content, the liquid limit, the plastic limit and the void-ratio are very high but the strength is not very low as imaged. To make sure the reasonable utilization, it is necesary to study the micro-properties of the soda residue further.

Fly ash plays a important role in improving the physical and the mechanical properties of the soda residue. It's worth while to make clear the interaction between these two materials.

2 Engineering properties of the soda residue

The in situ vacuum consolidation test has been performed to the soda residue of Tianjin soda plant[2]. The physical properties before and after the consolidation are listed in Table 1. The results of the mechanical tests to the consolidated soda residue are listed in Table 2.

After the consolidation, the water content and the void-ratio are still very high but the mechanical properties have already been close to some clay soil. It can't be put into practice with such a high water content. In the practical engineering, the soda residue is often dried to or close to the optimum water content and blended with certain amount of fly ash. Fig. 1 and Fig. 2 are the compacion curve of the soda residue and the mixture of the soda residue and the calcium-richened fly ash (the ratio is 9:1) respectively. Both the optimum water contents are between 40%~60%.

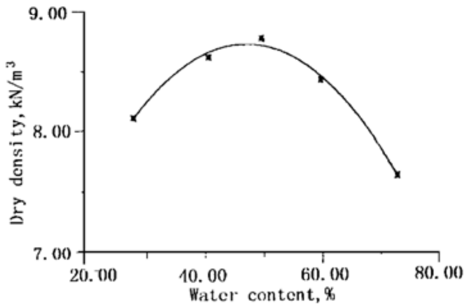

Fig. 1 Compaction curve of the soda residue

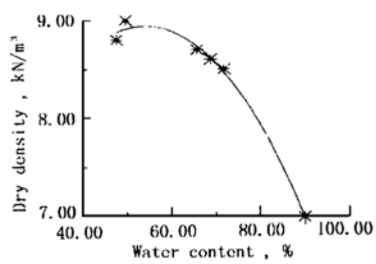

Fig. 2 Compaction curve of the soda residue soil

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Table 1 The physical properties of the soda residue before and after the consolidation

State	Water content w (%)	Density γ (kN/m^3)	Void-ratio e	Plastic index I_p	Coefficient of consolidation C_v (10^{-3}cm^3/s)	Grain size
before consolidation	213.2	12.0	6.606	47.7	11.4	silty soil
after consolidation	168.4	12.5	5.252	60.0	13.9	silty soil

Table 2 The mechanical properties of the soda residue

	Unconfined compressive strength q_u(MPa)	Quick shear		Consolidated quick shear		CU	
		φ(°)	c(kPa)	φ(°)	c(kPa)	φ(°)	c(kPa)
experimental value	13	8	8	1	1	1	1
extreme value	85～124	15～20	15～25	20	25	25	20
average value	103	18	21	—	—	—	—

Table 3 The physical and the mechanical properties of the soda residue soil

Optimum water content(%)	Plastic limit W_p(%)	Liquid limit W_L(%)	Quick shear		Unconfined compressive strength q_u(MPa)	Grain size
			φ(°)	c(kPa)		
53	62.3	80.2	45	35	250	silty soil

Table 4 Chemical composition of the soda residue(dried) (%)

Composition	$CaCO_3$	$CaSO_4$	$CaCl_2$	CaO	$NaCl$	Al_2O_3	Fe_2O_3	SiO_2	$Mg(OH)_2$	H_2O
Content	45.6	3.9	10.5	10.3	2.7	3.0	0.7	7.8	9.0	6.3

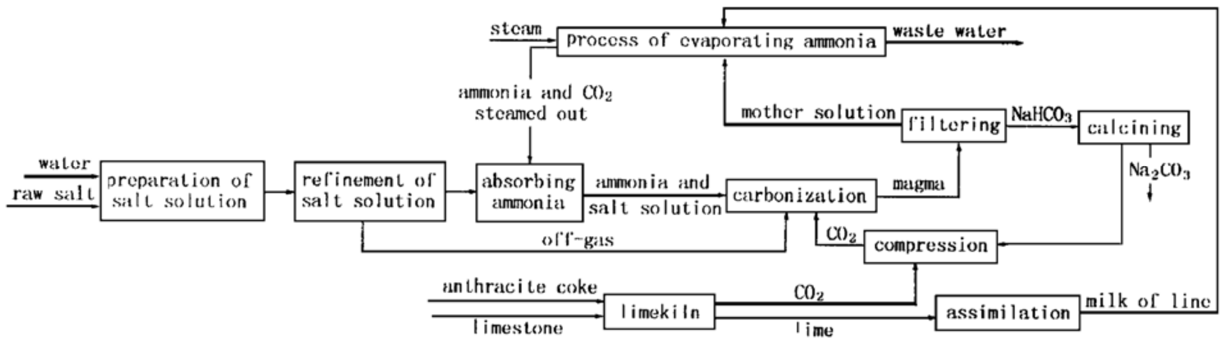

Fig.3 Process of producing of the soda residue

The calcium-richened fly ash lowers the plastic limit and the liquid limit and increases the strength of the soda residue. The physical and the mechanical properties of the mixture are listed in Table 3[1].

3 Microstructure of the soda residue

3.1 Storage of the soda residue

The technological process of producing soda is shown in Fig. 3. The soda residue is discharged in the process of evaporating ammonia. The main chemical reactions in the process are as follows[5].

Reactions in the process of preheating:

$$NH_4OH \xrightarrow{\triangle} NH_3\uparrow + H_2O$$

$$(NH_4)_2CO_3 \xrightarrow{\triangle} 2NH_3\uparrow + CO_2\uparrow + H_2O$$

$$NH_4HCO_3 \xrightarrow{\triangle} NH_3\uparrow + CO_2\uparrow + H_2O$$

Reactions in the process of evaporating lime cream:

$$Ca(OH)_2 + 2NH_4Cl \longrightarrow CaCl_2 + 2NH_3 + 2H_2O$$

$$Ca(OH)_2 + CO_2 \longrightarrow CaCO_3\downarrow + H_2O$$

The waste water is piped from the soda plant to the storage ground, then after a period of time of precipitation it is drained away to the ocean. Thus the waste residue piled up layer upon layer. If the height of the residue is over the designed value the waste water is transported to another place. From the last reaction equation above, it can be known that the main chemical composition of the soda residue is $CaCO_3$.

3.2 Chemical composition of the soda residue

Table 4 shows that the calcium carbonate is the main composition of the soda residue, and there are not too much but still certain amount of soluble salts such as calcium chloride, sodium chloride and calcium sulphate . Differential thermal analysis and x-ray phase analysis indicate that the aragonite is the main mineral composition of the soda residue and there is a little calcite.

3.3 Analysis of the microstructure of the soda residue

The microstructure of the soda residue is surveyed under the SEM. To keep the natural structure of the soda residue unchanged, it is air-dried under the natural condition. To view the single grain in detail, it is bombarded to dispersed state with ultrasonic in the acetone. The following three figures show the pictures taken by SEM. Corresponding energy spectrum analysis is also performed to identify the different chemical substances.

Fig.4　The whole profile of the natural soda residue grain

Fig.5　Dispersed soda residue grains

Fig.6　The surface of a soda residue grain

These pictures indicate that the microstructure of the soda residue is special. Fig. 4 shows that the natural soda residue is a kind of loose porous substance that just like a honeycomb. From Fig. 5 and Fig.6 it is known that the diameter of the most of the grains is between 0.01 − 0.074 mm, and these grains are composed of many finer particles with a diameter of about 2 − 5μm. These finer particles are aragonite mainly and a few of them are other crystals such as magnesium hydroxide and calcium sulphate. The surface of the grain is very rough and there are still many voids in it. As the tiny particles adhere tightly, the strength of the grain is still very strong, whose withstanding the bombardment of the ultrasonic can be a clear proof. Just like other soil grains the soda residue grains can serve as skeleton when the soda residue is used as foundation soil. The specific microstructure of the soda residue determines the specific macro-properties of it.

First, the voids in the soda residue grains adhere the pore water strongly, so the water content of the soda residue is relatively high.

Second, voids in and between the soda residue grains make the soda residue a substance of high void-ratio. When the soda residue is compressed, the voids among the grains decrease but those inside the grains keep unchanged, which makes the sode residue a medium-compressible soil.

Third, loose structure, numerous voids and perfect permeability make the consolidation time of the soda residue very short when the vacuum consolidation method is adopted. But because of both the strong adsorption of the pore water by the soda residue grains and the stiffness of the grains, there is still a high water content of over 100% in the sada residue even after the consolidation.

By the microstructure and the effect of the vacuum consolidation it is known that the method of the vacuum consolidation is not available to the soda residue. So, it is prescribed in the norm that the soda residue is dried to or close to the optimum water content before use.

3.4　Analysis of the formative process of the microstructure of the soda residue

The production process of the soda residue can be expressed by the following circular model:

waste water → storage place → precipitation → drainage of the waste water → inpouring the new waste water.

There are always the following balances in the soda residue:

$$CO_2 + H_2O + CaCO_3 \rightleftharpoons Ca^{2+} + 2HCO_3^-$$
$$H_2CO_3 + OH^- \rightleftharpoons HCO_3^- + H_2O$$
$$CO_2 + OH^- \rightleftharpoons HCO_3^-$$
$$HCO_3^- + OH^- \rightleftharpoons CO_3^{2-} + H_2O$$

The balances move right or left with the change of the amount of CO_2, Ca^{2+} and PH value. Mg^{2+} and other ion make the balance system more complicated. In a long period of time after the precipitation, the existing environment of the soda residue grain changes periodically, which leads to the periodical movement of the above balances. So, the ultimate form of the soda residue grain experiences many times of crystallization, and the rough porous soda residue grain become reasonable.

Mg^{2+} has great effect on the mineral composition of the soda residue[6]. Earlier in 1910 Leitmieir had discovered the hindrance of the Mg^{2+} to the growth of the calcite. Relevant experiments performed by the later researchers of carbonate (e.g. Wray and Zeller, 1956; Wray and Daniels, 1957) also proved that when there is Mg^{2+} the crystal of $CaCO_3$ is aragointe otherwise calcite. To improve the mechanical properties, many experiments that transform the aragonite into calcite by inputting more carbon dioxide into the soda residue have been conducted. The result is not good. Apparently the existance of Mg^{2+} is a important cause that leads to the failure of the experiment.

4　Interaction between the calcium-richened fly ash and the soda residue

4.1　Hydration of the calcium-richened fly ash

Table 5　Chemical composition of the calcium-richened fly ash(%)

Composition	SiO_2	Al_2O_3	CaO	Fe_2O_3	Mg	Substance burned off
Content	35	33	15	6	2	20

The calcium-richened fly ash possesses pozzolanicity. It can harden after being blended with water and cured for a period of time. In the hardening process, the calcium oxide reacts with water to produce calcium hydroxide, then the calcium hydroxide reacts with silicon dioxide or aluminum oxide to produce hydrated silicate or hydrated aluminate. These hydrates absorb water in the calcium-richened fly ash and adhere with other substance closely, which results in hardening. When the calcium-richened fly ash is blended with the soda residue, besides the hardening action of itself, the calcium sulphate in the soda residue continue to react with the produced hydrates. Thus it enhances the hardening effect. Because the amount of the calcium-richened fly ash is much less than that of the soda residue in the mixture, the hardening effect of the calcium-richened fly ash alone is more intense instead. Relevant chemical reactions are as follows[4]:

$$mCa(OH)_2 + SiO_2 + (n-1)H_2O = mCaO \cdot SiO_2 \cdot nH_2O$$

$$mCa(OH)_2 + Al_2O_3 + (n-1)H_2O = mCaO \cdot Al_2O_3 \cdot nH_2O$$

$$mCaO \cdot Al_2O_3 \cdot nH_2O + CaSO_4 \cdot 2H_2O = mCaO \cdot Al_2O_3 \cdot CaSO_4 \cdot (n+2)H_2O$$

4.2　Recrystallization in improving the mechanical properties of the soda residue

Results of the aging experiment on the mixture of 90% soda residue and 10% calcium-richened fly ash are listed in Table 6, which is obtained under the compacted condition with the optimum water content.

Table 6　Results of the aging experiment on the soda residue soil

Cured time	0 days	7 days	28 days	90 days
Unconfined compressive strength q_u(MPa)	0.35	0.38	0.43	0.46

The above data show that after 28 days the hardening process has almost completed and the strength is improved by 23%. It can be attributed to the pozzolanicity of the calcium-richened fly ash. The unconfined compressive strength of compacted pure soda residue with the optimum water content is 0.23MPa. Compared with the 0.35 in the above table, it is known that the strength of the mixture without any curing is 51% higher than that of the soda residue under the same condition. There must be a more significant factor that effect the strength of the mixed material.

Calcium oxide in the calcium-richened fly ash reacts with the water to produce calcium hydroxide. This reaction goes on rapidly and can finish in a short time. Increase of Ca^{2+} and OH^- in the soda residue promotes the following reactions:

$$Ca^{2+} + CO_3^{2-} = CaCO_3 \downarrow$$

$$Mg^{2+} + 2OH^- = Mg(OH)_2 \downarrow$$

$$Ca^{2+} + SO_4^{2-} = CaSO_4 \downarrow$$

The recrystallization caused by the reactions above plays roles in two respects. First, the calcium oxide in the calcium-richened fly ash absorbs some amount of pore water, which lowers the water content of the soda residue. Second, the chemical reactions above lower the amount of the soluble salt, and the reaction-products serve as adhesive among soda residue grains. Fig. 7 shows that the needle-like crystals of the calcium sulphate and the calcium carbonate have increased apparently in the soda residue.

Fig. 7　Needle-like crystals in the soda residue soil

5　conclusion

SEM images of the soda residue manifest that the soda residue is featured by porous grains composed of more tiny particles. These features strongly effect the macro-properties. The calcium-richened fly ash improves the mechanical properties of the soda residue. The recrystallization plays more important role than the pozzolanicity of the calcium-richened fly ash. In addition, this paper analyzes the formative process of the soda residue and points out that the storage environment has great effect on the microstructure of the soda residue.

References

1　Yan Shuwang, Qi Shouchi. Experimental study on the engineering behavior of the soda residue soil. J of Oil Engineering Construction, 1997(4).(in chinese)

2　Tianjin University. Report on the Application of the Soda Residue in Geotechnical Engineering. Tianjin: Tianjin University, 1996.(in Chinese)

3　Liu Yulun. Chemistry of Basic Element. Beijing: Higher Education Press, 1992. (in Chinese)

4　Li Sa. Mechanism Study and Design Calculation on the Consolidation of the Soft Soil with Pile [MS dissertation]. Tianjin: Tianjin University, 1997. (in Chinese)

5　Chen Wuping. Soda and Caustic Soda. Beijing: Chemical Industry Press, 1998.(in Chinese)

6　Robin G G, Bathorst Carbonate Sediments and Their Diagenesis. Amsterdam, London, New York: Elsevier Publishing Company, 1971.