The electric surface interaction in the soil-slag-biological solids system

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Abstract. The issue of wastes reclaiming in large cities is really a pressing problem today. First of all, the wastes which occupy wide areas of land need to be reclaimed. The metal production slag and waste water sediments are typical examples of such waste products. They create a wide area of ecological and social discomfort when collected and accumulated in large quantities after treatment. The purpose of this study is development of new soil materials which include waste products. The material properties can be influenced in a level of electric-surface interaction of the studied system components. The phase boundary presence and high degree of dispersion of the components require considering the sign of the charge of the particle surface and the particle size, influence of the charge on the nature of interaction between the surfaces and thus allows defining possible methods of modifying the surface properties in order to obtain materials needed. This includes modification of the surface of the aggregates and filling agents, activation of the functional groups, dispersed system stability, coagulation control, etc.

1. Introduction

Nowadays the soil composition materials are widely used with the various additives which allow increasing bearing capacity [1]. One of the additives is slag – stone-like or glass-like substance that is alloy of the non-stoichiometric mineral oxides with the main component SiO₂. It is currently accepted that the slag harden under alkaline component. But in the literature sources the cases of the slag usage without activation are described [2, 3, 4]. The binder for stabilization of expansive soils that consists of a mixture of fly ash and ground granulated blast furnace slag is evaluated in study [5]. The joint usage of these two materials to form a binder provides new opportunities to enhance pozzolanic activities that may reduce the swell potential and increase the compressive strength of clays. The mineralogical and morphological studies of soil specimen suggested the formation of hydrated particles and cementitious compounds as a result of the reaction between the clay and the binder.

Improvements of soft soils by mechanically mixing cementitious additives have been widely practised for construction of infrastructure. Mixing of additives improves strength and compressibility properties of soils through the development of soil structure. It was found in [6] that the yield stress of treated soil increases with the increase of curing and slag contents, when the slag to lime ratios were
0.67 and 1.0. The increase of yield stresses was associated with the increase of amorphous mineral quantity resulting from the formation of poorly crystalline cementitious reaction products. The presence of additional amount of pyrite was found to have a minimal effect on the maximum value of strength except for the 20 wt. % slag at curing 180 and 365 days, where a drop of maximum strength was observed. The drop could be due to the degradation of soil structure resulting from the formation of deleterious minerals (thaumasite-etrtingite) as identified through scanning electron microscopy.

The main objective of research [7] was to investigate the feasibility of stabilization of organic soils and sewage sludge to obtain low cost alternative embankment material by the addition of two different slag. Slag was used as a replacement for weak soil at ratios of 0%, 25%, 50%, 75% and 100%, where sewage sludge and organic soil were blended with slag separately. Laboratory tests results indicated that blending slag with organic soil or sewage sludge improved the engineering properties of organic or sewage sludge [7]. Therefore, it is concluded that slag can be potentially used as a stabilizer to improve the properties of organic soils and sewage sludge. However, there are not the literature sources where the interaction between soil, slag, and organic sludge was explained.

2. Study aim
This study aims the theoretical rationale of the soil structure formation in the compositions including both organic and inorganic component.

3. Theoretical stage
For this stage, the concepts about the electric surface potential of elementary substances described in [8] were used. These concepts are based on the fact that the electrode potential depends on the number of electrons on external orbitals of the atoms in elementary substances, namely, metals and nonmetals. The electrode potential value is a quantitative characteristic of the oxidation-reduction properties of the measured electrode against the oxidation-reduction properties of the hydrogen electrode. An elementary substance with the negative standard electrode potential has an excess number of electrons in the surface layer or the dipole layer (due to the tunneling of electrons) even before dipping the electrode into the solution, i.e. has the absolute surface potential. The atoms of alkali metals have one electron in the external orbit, which is attracted to one proton of the nucleus, and each out of seven electrons of the halogens is attracted by seven protons of the nucleus. Therefore, alkali metals donate electrons and get oxidized easier than other substances. But the halogens take electrons and restore themselves easier than other substances. The surface potential formed through the oxidation-reduction reaction was called in [8] the absolute electric surface potential so that to describe its place of appearance (on the surface of the substance), thus distinguishing it from the surface potential (the term accepted in electrochemistry) and its electrostatic nature (formed by charges). Actually, this electric surface potential is the absolute value, as opposed to a measured standard electrode potential.

When forming compound substances, the values of absolute electric surface potentials of their atoms are summed up with consideration of the stoichiometric coefficients. If the atoms are characterized by different oxidation-reduction properties, the transfer of electrons from the reducing to the oxidizing agent with the appropriate saturation (neutralization) is occurred. Taken into account that the measure of oxidation-reduction properties is the standard electrode potentials, the algebraic summing of these potentials for elementary substances, composing the compound one, let us judge about the resulting oxidation-reduction reaction of the compound substance. Considering this statement, the electric surface potential of a compound substance can be defined as follows

$$
\psi^{0}_{\text{ESP,ABC}} = - \frac{a \cdot \psi^{0}_{\text{ESP,A}} + b \cdot \psi^{0}_{\text{ESP,B}} + c \cdot \psi^{0}_{\text{ESP,C}}}{a+b+c}
$$

where $a$, $b$, $c$ are the stoichiometric coefficients of substances $A$, $B$ and $C$ in the compound substance $ABC$; $\psi^{0}_{\text{ESP, A}}$, $\psi^{0}_{\text{ESP, B}}$, $\psi^{0}_{\text{ESP, C}}$ are the electric surface potentials of elementary substances, $\psi^{0}_{\text{ESP,ABC}}$ is the electric surface potential of the compound substance.
The equilibrium electric surface potentials $\psi^0_e$ of the substances on which a specific adsorption of the hydroxyl ions OH$^-$ or protons H$^+$ can occur, for example, oxides and hydroxides, for actual fluid dispersion mediums are defined according to the formula

$$\psi^0_e = \psi^0 + \frac{RT}{zF} \ln[H^+] = \psi^0 + 2.3 \frac{RT}{zF} \lg[H^+] = \psi^0 - 0.059 \rho H$$

(2)

where $T = 298.16$ K; $z$ is the valence of the hydrogen ion, 1; $[H^+]$ is the concentration of the hydrogen ion in liquid phase volume, mole/liter.

The absolute electric surface potentials, for example, of platinum, iron, silicon and oxygen are $\psi^0_{Pt} = 13.059 V$, $\psi^0_{Fe} = -1.77 V$, $\psi^0_{Si} = -1.23 V$ and $\psi^0_{O} = 1.44 V$ from [8].

The electric surface potential of quartz as a compound substance can be defined according to the formula (1)

$$\psi^0_{SiO_2} = -1.23 + 2 \cdot 1.44 = -0.55 V$$

The quartz surface when contacting with water is hydroxylated; the boundary layer of the water is characterized by a higher pH (about 9), therefore the equilibrium potential is formed on it which is the same as (2)

$$\psi^0_{SiO_2} = -0.55 V - 0.059 \cdot 9 = -1.081 V$$

In the air the metal surface is oxidized, so its electric surface properties are defined by electric surface potentials of the oxides. For example, for ferric oxide

$$\psi^0_{Fe_2O_3} = -1.77 \cdot 2 + 1.44 \cdot 3 = -0.156 V$$

4. Calculative stage

The biological solids in biological waste disposal plants include three components: biological (microorganisms, protozoa, algae, fungi); organic (nucleic and amino acids, proteins, polysaccharides, humic acids, etc); inorganic (hydroxides, phosphates, carbonates, silicates, etc). The proteins contain the functional groups -COOH, -NH$_2$, -OH interacting with the hydroxyl groups located on the surface of soil particles and form spatial structures. Normally, the soil particles are hold by electric interaction forces which form layers of negatively charged ions on the surface of the particles. These layers determine the degree of wetting of the particles. After the replacement of the anions OH$^-$ with the molecules of the stabilizing agent on the surface of the soil particles, the stabilizing soil layer acquires higher density and additional stability. The humic-like substances are characterized by high affinity with solid surface. Interaction of humic acids with silicates and aluminum silicates is possible due to connection between the carboxyls of humic substances and the OH-groups of the adsorbent, or by forming mineral bonds. Addition of biological solids to the soil decreases the capillary ascent and capillary pressure force of the water due to higher density, lower diameter of soil pores and surface active agents which weaken the surface tension forces. These substances form waterproofing micelles with soil particiles, which associate with each other due to surface interaction and formation of ionic bonds.

The surface of ground slag is also characterized by electric potential. Its value greatly depends on the chemical compound of slag. It allows us to conclude that electric properties of the surface are the basis for stability of the soil-slag-biological solids system. Let us analyze the interaction forces between soil particles, slag and biological solids as far as the electric surface properties are concerned. Table I presents the electric surface potentials $\Delta\psi^0_{ESP}$ of substances which compose soil, slag and biological solid. The table also gives the calculated electric surface potential of some materials calculated by formula (1), where the percentage of oxides in soil or slag is taken instead of the stoichiometric coefficients.
Table 1. The values of electric surface potentials.

| Material      | Content of oxides in the material, % | $\Delta \psi_{ESP}$, V |
|---------------|--------------------------------------|------------------------|
|               | MgO  | Al$_2$O$_3$ | SiO$_2$ | SO$_3$ | CaO | Mn$_2$O$_3$ | Fe$_2$O$_3$ | TiO$_2$ |
| Slag          | 11.89 | 15.56       | 28.77   | 0.4    | 42.1 | 0.44        | 0.5         | 0.34    | 0.45 |
| Soil          | 6.56  | 18.29       | 55.16   | 2.9    | 4.25 | 3.22        | 6.37        | 3.25    | $-0.16$ |
| Biological solid | 1.6-11 | 7-27        | 7-35    | 1.5-7  | 8-17 | 0-6         | 7-20        | 0-6     | $-0.23$ |

With slag, from which lime was hydrated, proteins and, accordingly, activated sludge acquired properties of anionic surfactants and ability to be adsorbed on the positively charged surfaces of the lime and the soil carbonate components. It allowed applying activated sludge as an ionogenic surface-active material in order to create the optimal structure for soil materials. Better stability, water resistance, stress-strain behavior and soil swelling were provided due to application of materials with oppositely charged electro-surface potentials and creation of electro-heterogeneous contacts (between oppositely charged surfaces of soil particles, slag and activated sludge). The contact strength was provided by ion-ionic and ion-dipole interactions between potential-determining ions of particles of soil, slag, activated sludge and molecules of adsorptive layers of water between them. Such contacts guaranteed a further increase in strength and water resistance, better stress-strain behavior and soil swelling. In ordinary state soil particles were kept in aggregates, and aggregates were kept by capillary and molecular forces. After addition of slag and the inorganic component from activated sludge by hydrating it, a certain amount of calcium hydroxide was formed; it generated a certain amount of electro-heterogeneous contacts with aggregates of soil particles and activated sludge particles. Addition of anionic surfactants also stimulated peptization, i.e. disintegration of soil aggregates and creation of contacts between certain particles.

5. Conclusion

Greater stability and water resistance, a decrease in deformability and the swelling of clay soils can be provided through the usage of substances with electric surface potentials of the opposite charge, and formation of electro-heterogeneous (between oppositely charged surfaces of particles of soil, slag and biological solids) contacts. The stability of contacts is maintained by ion-ionic and ion-dipole interactions between charge determining ionic particles of soil, slag, biological solids and molecules of water adsorption layers between them. These contacts provide the maximum stability and waterproof behavior, decreased deformability and soil swelling.

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