Key factors affecting the pozzolanic reaction of steel slag-dredged soil mixtures
-From inorganic and organic perspectives-
浚渫土-製鋼スラグ混合土のポゾラン反応の鍵となる影響因子
-特に無機・有機の観点から-

Industrial byproducts and waste soils are environmentally low-impact resources for the construction industry. Construction materials made with such resources are particularly attractive for regional use close to the material sources, because of the feasibility in the transport and application associated with cost savings. Dredged soils, excavated sediments of water ways, and steel slags, byproducts of iron making processes, have potential to form civil engineering constructions close to seashores, as their mixtures develop strength. The utilization of such mixtures is still limited due to their unpredictable variation of strength development when different dredged soils or steel slags are applied. No previous studies have comprehensively investigated the key factors which affects the strength development of the mixtures. This study elucidates the key factors for the first time by identifying the contributions of both inorganic and organic components in steel slags and dredged soils to the strength development of the mixtures.

Chapter 1 reviews the literature on the general management of dredged soils and steel slags, current knowledge of technologies on their validation as construction materials, as well as the pozzolanic reaction, chemical reaction that develops strength of the mixtures, to identify the factors affecting the reaction. The state-of-art research on the key components that may affect

the strength development of the mixtures were suggested as the Ca and Si sources that contribute to the pozzolanic reaction, which forms the secondary phase, calcium silicate hydrates (C-S-H). However, the specific phases in steel slags and dredged soils which supply Ca and Si were not fully elucidated. In addition, dredged soils may contain soil organic matters. Organic matters are known to delay the cement hydration which also forms C-S-H as one of the major secondary phases, and soil organic matters are known to suppress the strength development of cement improved soils. Therefore, soil organic matters may also play a role in the strength development of steel slag-dredged soil mixtures, though its effect was not well investigated. Once key factors that affect the strength development of the mixtures are elucidated, the prediction of the strength development of the mixtures would be facilitated, which may enhance the utilization of steel slags and dredged soils. This study aims to comprehensively clarify the key factors affecting the strength development of the mixtures.

Chapter 2 focuses on identifying the factors among inorganic components in dredged soils and steel slags affecting the strength development of the mixtures. Four dredged soils and two steel slags were employed to form eight combinations of the steel slag-dredged soil mixtures. The strength development of the mixtures cured for the time between 3 to 91 days was measured by unconfined compressive strength tests, where mixtures made with different dredged soils and steel slags showed variation in their developed strengths. The mineralogical phases composition of dredged soils and steel slags were analyzed with X-ray diffraction (XRD) measurements, and for dredged soils, the content of amorphous silica was additionally measured with selective dissolution experiments. Amorphous silica in dredged soils and portlandite, $Ca(OH)_2$, in steel slags were identified as the key factors as major Si and Ca sources for the pozzolanic reaction, respectively. The Ca source was identified from the consumption of portlandite as a function of curing time of the mixtures, and because the steel

slag with higher content of portlandite formed mixtures that developed more strengths. The quantification of amorphous silica revealed that the dredged soils with higher content of amorphous silica to develop more strengths. In addition, the contribution of portlandite and amorphous silica to the pozzolanic reaction was confirmed with geochemical reaction modelling.

Chapter 3 focuses on identifying the effect of organic components in dredged soils to the strength development of the mixtures. This study employed four more dredged soils in addition to that of chapter 2, and a steel slag, to form the mixtures. The mixtures were formed to investigate the strength development capacity of eight dredged soils after mixing with a steel slag, from 3 to 28 days of curing, with unconfined compressive strength tests. Dredged soils were characterized in terms of their mineralogical composition and amorphous silica content, with XRD measurements and selective dissolution experiments, respectively. Also, total organic carbon was quantified with total organic carbon (TOC) analyzer, and extractable organic matter, humic acid was collected from eight dredged soils, and the content of humic acid was quantified. Elemental analysis of eight extracted humic acids was then carried out. Some dredged soils were clarified to develop insignificant strength, regardless to high content of amorphous silica. Such dredged soils were clarified to have a common characteristic in their soil organic matters fraction. Characteristics of dredged soils such as high sulfur content in humic acid fraction exhibited the soft mixtures, which suggested the strength development inhibition by soil organic matters. However, quantification of total organic matter content such as total organic carbon and humic acid content did not indicate the effect of soil organic matters to the strength development of the mixtures. Chapter 2 and 3 newly show that the quantification of particulars in inorganic and organic components of raw materials indicate the strength development of the mixtures. Discovery of the indicators would facilitate the

evaluation processes of the applicability of the mixtures to constructions. The further analysis on the steel slag-dredged soil mixtures is disadvantageous to trace the interaction of soil organic matters with the pozzolanic reaction, since soil organic matters and C-S-H are both amorphous that are not straight forward to detect or observe in the mixtures which also compose of other inert phases to the pozzolanic reaction. Therefore, chapter 4 focuses on simulating the interaction of soil organic matters with the pozzolanic reaction synthetically, to elucidate whether soil organic matters do or do not inhibit the pozzolanic reaction.

Chapter 4 experimentally proofs the inhibition of the pozzolanic reaction by soil organic matters, by designing an experiment of the pozzolanic reaction in coexistence of escalating amount of a model organic matter. Lignosulfonate, which contains sulfur in its structure, which is synthesized from natural wood was employed in the pozzolanic reaction, due to its structural similarity with soil organic matters. In addition, soil organic matters and lignosulfonate contain sulfur in the structure, and they are macromolecules of various organic constituents. Portlandite reagent and amorphous silica reagent was used to simulate the pozzolanic reaction in steel slag-dredged soil mixtures. The synthesis products of the pozzolanic reaction were separated into solid and solution phases, which mineralogical composition and the polymerized state of silica was measured for the solid phases with XRD measurements and single-pulse ^{29}Si magic-angle spinning nuclear magnetic resonance (^{29}Si MAS NMR). pH, dissolved organic carbon, and Ca and Si concentrations of the solution was also measured with a pH meter, TOC analyzer, and inductively coupled plasma-atomic emission spectroscopy (ICP-AES), respectively. The inhibition of the pozzolanic reaction with a threshold in the dosage of the lignosulfonate was observed through the analysis of the mineralogical phases composition. From analysis on the polymerized state of the pozzolanic reaction products and the solution compositions, the formation of unidentified secondary

phase which may not be C-S-H was suggested, that may be inhibiting the pozzolanic reaction. It indicated a dosage of some soil organic matters to inhibit the strength development of soft mixtures, as speculated in chapter 3.

Chapter 5 experimentally compares the effectiveness of soil organic matter reagents to the inhibition of the pozzolanic reaction. The pozzolanic reaction was again synthetically simulated, but with four organic reagents, Aldrich humic acid, Wako humic acid, and lignin, in addition to lignosulfonate. This chapter compares the effectiveness of organic reagents to the inhibition of the pozzolanic reaction with the characteristics of organic reagents. As chapter 4, the synthesis products were separated to solid and solution samples after the synthesis. The mineralogical composition was measured for solid phases with XRD measurements. pH, dissolved organic carbon, and Ca and Si concentrations of the solution was also measured with a pH meter, TOC analyzer, and ICP-AES, respectively. The organic reagent characterization was carried out to quantify the carbon species, sulfur redox states, and the content of acidic functional groups (carboxylic and phenolic functional groups) with solid-state 13C cross-polarization/magic-angle spinning nuclear magnetic resonance (^{13}C CP-MAS NMR), sulfur K-edge X-ray adsorption near edge structure (XANES), and acid titration experiments. Aldrich humic acid, lignin, and lignosulfonate caused the inhibition of the pozzolanic reaction at different dosages, within the experimental conditions. Together with the characterization of four organic reagents, this study suggests that the dosage of reduced sulfur and/or phenolic groups may trigger the inhibition of the pozzolanic reaction. It is because, between the thresholds of the inhibition of the pozzolanic reaction, not the dosage of total organic reagents but the dosage of reduced sulfur and phenolic groups were at similar values. However, the content of different carbon species did not indicate the thresholds. Chapter 4 and 5 newly show that the organic reagents with similar composition to

soil organic matters to inhibit the pozzolanic reaction. The key organic component to the inhibition of the pozzolanic reaction by soil organic matters in real steel slag-dredged soil mixtures was investigated in chapter 6, through further characterization of humic acids of dredged soils.

Chapter 6 characterizes the bulk soil organic matters extracted from eight dredged soils used in chapter 3, to identify particulars that may affect the pozzolanic reaction in the mixtures. The content of carbon species, the sulfur redox state, and the fragment qualification was carried out for eight humic acids, with 13C CP-MAS NMR, sulfur K-edge XANES, and TMAH pyrolysis gas chromatography/mass spectrometry (TMAH-py-GC/MS). The quantification of acidic functional groups was not carried out due to the limitation of humic acid samples. The sulfur indicator of soft mixtures, stated on chapter 3, was found to result from the difference in the content of reduced sulfur. Same as chapter 5, the quantification of carbon species was not an indicator of dredged soils that contain soil organic matters that inhibit the pozzolanic reaction. Discoveries in chapter 5 and 6 suggest reduced sulfur as a key component that plays a role in the inhibition of the pozzolanic reaction in steel slag-dredged soil mixtures. A key organic constituent to trigger the inhibition of the pozzolanic reaction maybe the reduced form of sulfur, though other components of soil organic matters may also play a role in the inhibition, which may exist in abundance in the organic matters treated in this study. Hence, the comparison of macroscopic analysis on carbon speciation between the samples which did and did not occur the inhibition of the pozzolanic reaction, was carried out in chapter 7.

Chapter 7 focuses on clarifying the interaction of soil organic matters with the pozzolanic reaction under microscopic scales. The synthetic C-S-H in coexistence of lignosulfonate, the pozzolanic reaction products formed in coexistence of lignosulfonate without C-S-H

formation, and the steel slag-dredged soil mixtures which did and did not show significant strength development was used as representative samples of the systems which soil organic matters did and did not play a role in the pozzolanic reaction. The grains of four samples were analyzed with Scanning Transmission X-ray Microscopy (STXM), to analyze the distribution oof carbon speciation. Additional to reduced sulfur and phenolic groups, the X-ray spectroscopic study on the distribution of carbon speciation in the mixtures and the synthesis products of the pozzolanic reaction suggested aromatic carbon to affect the pozzolanic reaction, as it selectively coexisted with the samples which the pozzolanic reaction was inhibited.

  Chapter 8 concludes the key factors that affect the strength development of the teel slag-dredged soil mixtures in the context of waste validation and shows research impact. Outstanding insights are derived from half-splitting analysis of key components in raw materials that promote and inhibit geochemical reactions in control of strength development of such construction materials. The key factors affecting the strength development of the mixtures was determined as the components which affect the pozzolanic reaction to form C-S-H. Ca source was determined as portlandite. Si source was determined as amorphous silica such as volcanic glasses and diatom frustules. The supply of Si and Ca are essential to forward the pozzolanic reaction, as they would determine the amount of C-S-H that are possible to form. Soil organic matters in dredged soils was clarified to inhibit the pozzolanic reaction in the mixtures. The existence of specific organic constituents was suggested to trigger the inhibition of the pozzolanic reaction. When the content of such constituents exceeds a threshold, the pozzolanic reaction was inhibited. The specific constituents were suggested as the reduced form of sulfur, phenolic functional groups, and aromatic carbon. Therefore, the tailor-made improvement of the strength development of the mixtures could become possible,

through analysis of the starting materials, by either adding portlandite and amorphous silica, or decreasing the abundancy of soil organic matters to become below the threshold or eliminating the effect of soil organic matters to the pozzolanic reaction. These findings in this study are unambiguously useful to enhance utilization of industrial byproducts and waste soils in the construction industry.