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Microstructure of ultra high performance concrete containing lithium slag

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ABSTRACT

Lithium slag (LS) is discharged as a byproduct in the process of the lithium carbonate, and it is very urgent to explore an efficient way to recycle LS in order to protect the environments and save resources. Many available supplementary cementitious materials for partial replacement of cement and/or silica fume (SF) can be used to prepare ultra high performance concrete (UHPC). The effect of LS to replace SF partially by weight used as a supplementary cementitious material (0%, 5%, 10% and 15% of binder) on the compressive strengths and microstructure evolution of UHPC has experimentally been studied by multi-techniques including mercury intrusion porosimetry, scanning electron microscope and nanoindentation technique. The results show that the use of LS degrades the microstructure of UHPC at early ages, and however, the use of LS with the appropriate content improves microstructure of UHPC at later ages. The hydration products of UHPC are mainly dominated by ultra-high density calcium-silicate-hydrate (UHD C-S-H) and interfacial transition zone (ITZ) in UHPC has similar compact microstructure with the matrix. The use of LS improves the hydration degree of UHPC and increases the elastic modulus of ITZ in UHPC. LS is a promising substitute for SF for preparation UHPC.

1. Introduction

Ultra high performance concrete (UHPC) is a new type of concrete with the 28-day compressive strength in excess of 150 MPa (in China, compressive strength over 100 MPa) and has already been used in construction projects all over the world, especially containing the landmark projects [1], due to its ultra high mechanical properties and excellent durability [2]. UHPC is characterized by high binder content (over 800 kg/m^3), very low water-binder ratio (w/b) and use of silica fume (SF), which results in a large amount of unhydrated cement causing waste of resources. It is well known that SF is an essential constituent for UHPC, which plays a significant role in improving the properties of UHPC. The prominent effects of SF in UHPC are filling effect, lubricating effect and pozzolanic effect [2–6]. However, the high cost, limited available quantity and uneven distribution of SF constrain greatly the application of UHPC in modern concrete construction, especially in the developing and backward countries and regions. Therefore, in order to enhance the application technology and expend the application range of UHPC, there is an urgent need for searching for other materials to substitute SF and/or cement.

Recently it has been well acknowledged that the use of widely available supplementary cementitious materials (SCMs), such as fly ash and slag for partial/complete replacement of cement and SF, can also been used to prepare UHPC, which reduces obviously the cost without sacrifice of strength, and has become the trends for the production of UHPC [2]. Li [7] reported that the ternary use of metakaolin, fly ash and cement in UHPC was of potential economic and environmental advantages. Calvo et al. [8] found that the substitution of SF by the corresponding amount of epoxy resin filled silica microcapsules and amine functionalized nanosilica increases the durability of the UHPC developed, guaranteeing a longer service life. Su et al. [9] reported that UHPC containing steel fibers and different kinds of nano materials including Nano-$CaCO_3$, Nano-SiO_2, Nano-TiO_2 and Nano-Al_2O_3 demonstrated the superior ductility and blast resistant capacity. Alsalman et al. [10] presented an experimental investigation of UHPC using locally available materials. Their results showed that the fly ash content had an important effect on the compressive strengths of UHPC, and a fly ash content of more than 20% decreased the compressive strengths at early ages, but increased the strengths at later ages. A fly ash content of 30% produced the highest 90-day compressive strength, while a content of 20% had minimal effect on the strengths at all ages. Soliman and Tagnit-Hamou [11] prepared a green ultra-high-performance glass concrete (UHPGC) with a compressive strength of up to 220 MPa. The UHPGC properties were improved when the cement and quartz powder were replaced with nonabsorptive glass-powder (GP) particles, providing technological, economical, and environmental advantages compared to traditional UHPC. Tafraoui et al. [12] reported that it was possible to replace SF by metakaolin which did not affect the durability

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of UHPC, which was used without any problem for the industry of powerful and durable UHPC [13]. Van et al. [14,15] found that rice husk ash (RHA) classified as “a highly active pozzolan” was suitable for use as a SCM to make UHPC, and the combination of 10% RHA and 10% SF proved to be optimum for achieving maximum synergic effect of UHPC. Huang et al. [16] investigated the effect of RHA on the strength and permeability of UHPC. Results from this investigation also suggested that the calcined RHA at 500 °C was a promising substitute for SF in UHPC production, and the RHA replacing SF ratio of 2/3 showed the best improving effect, increasing the compressive strength at 3, 28 and 120 days by 9.76%, 14.50%, 10.02%, respectively, compared to the traditional UHPC containing SF alone. Burroughs et al. [17] reported that the minor replacements of cement with limestone powder did not negatively affect properties of UHPC, the use of which as an inert filler in UHPC was proposed. Yazıcı et al. [18–20] prepared UHPC with Portland cement replaced with high content of granulated blast furnace slag and fly ash whose compressive strength was over 200 MPa after standard room curing, 234 MPa after steam curing and 250 MPa after autoclave curing. Peng et al. [21] found that the utilization of ultra-fine fly ash and steel slag powder in UHPC was feasible and the optimum steel slag powder/ultra-fine fly ash ratio was 1.5 for UHRC with the highest strength. Wang et al. [22] found that UHPC containing ground granulated blast furnace slag and limestone powder replacing cement achieved excellent workability with a maximum slump of 268 mm and compressive strengths of 175.8 MPa at 90 days and 182.9 MPa at 365 days. Therefore, the preparation of UHPC has already not been completely dependent on the costly and well-chosen materials, and a large number of widely available and low-cost SCMs replacing cement and/or SF all over the world can be used to prepare UHPC.

Lithium slag (LS) is a byproduct, which is discharged in the process of the lithium carbonate using sulfuric acid method when the spodumene ore is calcined at high temperature of 1200 °C. According to the statistical analysis, about nine tons of LS are discharged when one ton lithium salt is produced in the production process of lithium carbonate. Today, about 8×10^5 tons of LS are discharged every year in China. LS as a promising SCM can also be used to prepare successfully different kinds of concretes and improve obviously the properties of concrete, especially the later properties, showing the similar physically filling and chemically pozzolanic effects with other SCMs such as ground granulated blast furnace slag and fly ash [23–25]. The aforementioned literature survey shows that, despite the considerable amount of work published in literature on UHPC prepared by all kinds of SCMs, and however, there is very little work on UHPC containing LS. LS is economical and abundant as a SCM, which is a promising substitute replacing SF in UHPC production.

It is well known that microstructure-property relationships are at the heart of modern materials science, and the evolution of microstructure can determine the properties of UHPC [4,15,26], which may demonstrate significant difference as compared to conventional concrete. In this paper, the compressive strength variations of UHPC containing LS were measured with time using an experimental method, taking into account of the effect of different ratio of replacing SF with LS. Meanwhile, the effects of LS on the microstructure evolution of specimens were investigated by mercury intrusion porosimetry (MIP), scanning electron microscope (SEM) and nanoindentation techniques.

2. Experimental

2.1. Materials

The cement used in the present study was Portland cement with strength grade of P·I52.5 in accordance with Chinese standard GB 175-2007. LS used was supplied by Sichuan lithium salt plant in China. Table 1 shows the chemical compositions of cement, SF and LS, used as the cementitious materials, which exhibits that the SiO_2 and CaO contents of LS fall between those of SF and those of cement, respectively, and the SO_3 and Al_2O_3 contents of LS are highest.

Table 1
Chemical compositions of cement, LS and SF (wt%).

Materials	SO_3	SiO_2	Fe_2O_3	Al_2O_3	CaO	MgO	K_2O	Na_2O	Loss on ignition
Cement	2.54	21.10	3.26	4.77	62.63	1.15	0.43	0.05	3.01
LS	7.15	53.22	1.48	17.11	10.11	0.41	0.53	0.33	8.25
SF	0.83	88.12	0.49	0.29	0.63	3.08	3.69	1.22	1.11

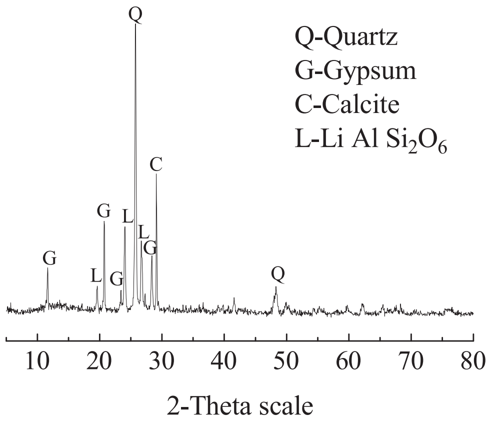

Fig. 1. XRD pattern of LS.

X-Ray diffraction (XRD) pattern of LS is given in Fig. 1. The mineral compositions of LS contain mainly quartz, gypsum, calcite and lithium aluminum silicate.

Fig. 2(a) shows the particle size distributions of the cement and LS determined by laser particle analysis using BT-9300 Laser Particle Analyzer, which exhibits that the size range of LS particles is wider than

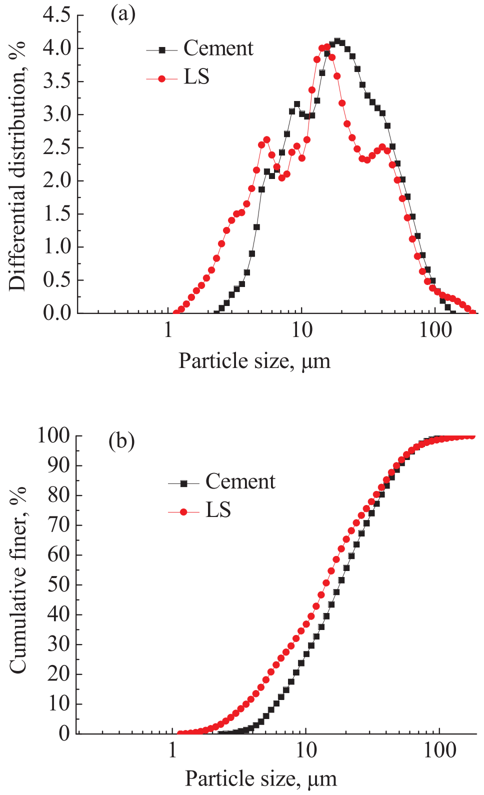

Fig. 2. (a) particle size distributions of cement and LS and (b) grading curves.