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### Carbon Steel Slag as Cementitious Material for Self-Consolidating Concrete

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#### 1. Introduction

In Taiwan, self-consolidating concrete (SCC) exhibiting high-flow behaviour is a widely used concrete material to prevent conventional concrete problems such as honeycomb structures that occur as a result of poor practice. SCC is also used as the material of choice for heavily reinforced concrete structures located in seismic zones [Paczkowski Piotr,Kaszynska Maria, 2007.]. Pozzolanic materials are important ingredients for making SCC [Mihashi H, Yan X,1995.]. For many years, pozzolanic admixtures, such as blast furnace slag (BFS), pulverized coal ash (fly ash), silica fumes, and copper slag have been recycled to partially replace Portland cement in concrete mixtures. The main advantages of using pozzolanic materials are improvements in performance and significant reduction in the life-cycle costs of concrete structures; the latter, in particular, continues as a significant problem for engineers [Khalifa AJ, Ramzi T,2002. Li G, Zhao X.,2003. Zhang MH, Bilodeau A, Malhotra VM, Kim KS, Kim JC,1999.]. Materials such as steel slag, normally considered as waste, have promising applications as partial Portland cement replacements in concrete mixtures. Considerable research and development has been conducted to develop new concrete technologies such as SCC. Further, the construction of durable concrete has also been pursued. Initially, pozzolanic admixtures were solid waste and it was extremely costly to treat and dump them into a final storage area. Today, however, in the concrete industries in Taiwan and elsewhere, these admixtures are important materials for the production of low-cost durable concrete, and an example of environmental protection and resource conservation.

In Taiwan, carbon steel slag (CSS) is a by-product of the reduction during the production of refining carbon steel in an arc furnace, and is seldom recycled. On average, the production of one ton of carbon steel yields 10 kg of CSS waste, and hence, in Taiwan, more than 56,000 tons of CSS is produced each year. Due to the relatively small amounts of CSS relative to blast furnace slag (BFS), environmental protection agency (EPA) regulations had previously permitted the dumping of CSS. Today, the dumping of such waste is not permitted, and the proper disposal of CSS has become a huge problem. Since lime, coke and silicon iron are added to promote the reducing process during high-temperature-refinery scrap steel procedures, the CSS contains large amounts of CaO, SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>. This waste composition, however, is similar to BFS or Portland cement [Chiang CC, Chenn YY, Lin TY,

Hwang CL,2004.Yu-Chu Peng,2009.]. Hence, CSS can be considered for use as a pozzolanic admixture to partially replace Portland cement in a concrete mixture.

Rather than use CSS for backfill soil or as material to be retained in the plant, steel slag can be regarded as a low-quality clinker and can be used to partially substitute the clinker of composite Portland cement [Wu X, Zhu H, Hou X, Li H,1999.Sakuraya T,1999.]. In Japan and other industrialized countries, steel slag has already been applied for use in civil engineering applications such as road base construction and soil stabilization [Geiser J.,1999. Roy DM, Idorn GM., 1982.]. In Germany, anbout 17.1% of steel slag is used for highway construction, 5.4% is recycled, and 40.5% is used in agricultural fertilizer production [Luxán MP, Sotolongo R, Dorrego F, Herrero E.2000. Monshi A, Asgarani MK, 1999. Mihashi H, Yan X, Arikawa S.,1995. Hogan FJ, Meusel JW.,1981. ACI Committee 211.,1993.]. The mineralogical composition of steel slag is as follows: anhydrous calcium silicates and silicoaluminates; gehlenite, larnite and bredigite; magnetite and magnesioferrite and manganese oxides [Esfahani M. Reza, Kianoush M. Reza, 2005. Hwang Soo-Duck, 2008. Koehler Eric P., Fowler David W., 2008.]. Thus, some researchers have tested the effects of mixed iron slag (36%~45%), steel slag (6%~22%) and limestone (40%~64%) on the setting time of cement paste and the compressive strength at 3, 7 and 28 days [Schindler Anton K., Barnes Robert W., Roberts James B., 2007. Whitcomb Brent L., Kiousis Panos D., 2008.]. Nevertheless, other than documenting the chemical composition of CSS, there are few studies on the pozzolanic reactions after the addition of CSS.

#### 2. Research plan

#### 2.1 Material

The aggregate was quarried from I-Lan River, Northern Taiwan, and consisted of large amounts of elongate slate and fragile particles. The cement and superplasticizer (SP) used corresponded to ASTM C150 type I Portland cement and ASTM C494 type F high range water reducing agent (HWRA), respectively. A naphthalene lingo-sulfonate base was used for promoting the flow ability of SCC; the specific gravity was 1.18; ph, 6.93 and chloride ion content, less than 50 ppm. As a by-product of the carbon steel manufacturing process, while the carbon steel settles in the smelter (since its density is high), impurities remain on top. The carbon steel is then transported to a water basin maintained at a low temperature for solidification. The end product (CSS) is a hard solid material that is then sent to a crusher for further processing. The CSS is powdered to pass through sieve No. 4 (4.76 mm). Subsequently, it is re-ground for 3 h at a speed of 60 rpm to pass through sieve No. 200 (75 μm). In this study, type I Portland cement has been used. Class F fly ash and BF slag were obtained from Taiwan Power Company and China Steel Corporation, respectively. The SP was Glenium 51 obtained from Taiwan Durusle Company, Taiwan. In Table 1, the specific gravities of Portland cement and CSS are listed as 3.14 and 2.67, respectively; further, CSS powder and Portland cement (type I) have specific surface areas of 2504 cm<sup>2</sup>/g and 3622  $cm^2/g$ , respectively. Hence, CSS has the least fineness, which is characteristic of materials with low surface areas. As shown in Table 2, CSS is highly alkaline, with a pH of 11.50, an absorption capacity (SSD) of 7.60%, fineness modulus (FM) of 1.76 according to ASTM C136, and dry loose density of 1266 kg/m3 according to ASTM C29. Figure 1 shows the relationships of CSS with BFS and Portland cement; the percentage of the main composition (SiO<sub>2</sub> and CaO) of CSS lies between that of BFS and Portland cement.

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|                       | Item                                   | OPC   | CSS   |
|-----------------------|--|-------|-------|
|                       | Specific gravity                       | 3.14  | 2.67  |
|                       | Specific surface area $(cm^2/g)$       | 3622  | 2504  |
|                       | pН                                     | —     | 11.50 |
| Physical properties   | Absorption capacity (%)                | _     | 7.60  |
|                       | Fineness modulus (FM)                  | _     | 1.76  |
|                       | Dry loose density (kg/m <sup>3</sup> ) | _     | 1266  |
|                       | SiO <sub>2</sub>                       | 21.46 | 26.52 |
|                       | Al <sub>2</sub> O <sub>3</sub>         | 4.84  | 5.95  |
|                       | Fe <sub>2</sub> O <sub>3</sub>         | 3.12  | 3.78  |
|                       | CaO                                    | 62.34 | 46.45 |
| Chemical compositions | MgO                                    | 2.87  | 13.27 |
| (%)                   | SO <sub>3</sub>                        | 2.06  | 0.65  |
|                       | f-CaO                                  | 0.88  | 2.11  |
|                       | Na <sub>2</sub> O                      | 0.22  | 0.26  |
|                       | K <sub>2</sub> O                       | 0.70  | 0.11  |
|                       | CaO/SiO <sub>2</sub>                   | 2.91  | 1.75  |

Table 1. Physical properties and chemical composition of OPC and CSS.

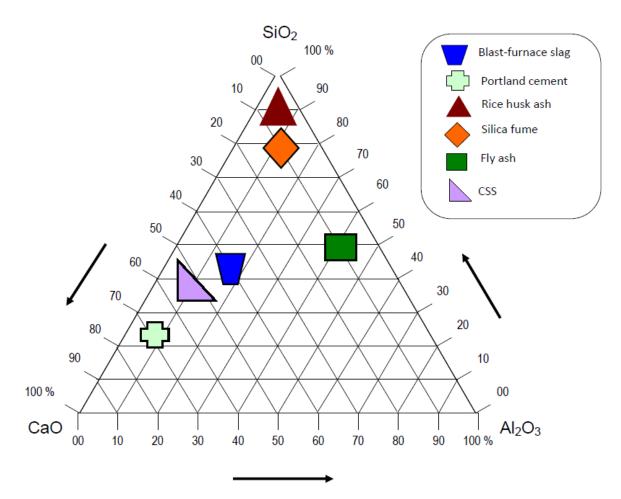


Fig. 1. Comparison of compositions of CSS, BFS and Portland cement.

#### 2.2 Mixture design

In order to obtain high-strength SCC with lower water content (160 kg/m<sup>3</sup>), in this study, w/cm ratios (water/(cement+CSS)) of 0.28, 0.32 and 0.40 were selected. Further, large amounts of SP were added to achieve better flow behaviour. CSS powder was used to replace the 5.0%, 7.5% and 10% weights of Portland cement. Mixtures with three different w/cm ratios were prepared for ordinary plain concrete (OPC) and carbon steel slag concrete (CSC), as shown in Table 2; designated as OPC28, OPC32 and OPC40 and CSC28, CSC32 and CSC40, respectively (Whitcomb Brent L., Kiousis Panos D.,2009, Kwan Albert K. H.,Ng, Ivan Y. T.,2008.)

|                         |               |                            | Mix Proportion (kg/m <sup>3</sup> ) |                       |                   |                     |       |     |               |
|-------------------------|---------------|----------------------------|-------------------------------------|-----------------------|-------------------|---------------------|-------|-----|---------------|
| Designation of concrete | w/c<br>ratioª | w/cm<br>ratio <sup>b</sup> | Cement                              | CSS/<br>cement<br>(%) | Fine<br>aggregate | Coarse<br>aggregate | Water | SPc | Water<br>+ SP |
| OPC28                   | 0.28          | 0.28                       | 572                                 |                       | 757               | 901                 | 145   | 15  | 160           |
| OPC32                   | 0.32          | 0.32                       | 500                                 |                       | 783               | 932                 | 148   | 12  | 160           |
| OPC40                   | 0.40          | 0.40                       | 400                                 |                       | 820               | 976                 | 152   | 8   | 160           |
| CSC28                   | 0.28          | 0.28                       | 545                                 | 5.0                   | 832               | 820                 | 146   | 14  | 160           |
| CSC32                   | 0.34          | 0.32                       | 465                                 | 7.7                   | 861               | 849                 | 149   | 11  | 160           |
| CSC40                   | 0.44          | 0.40                       | 364                                 | 10.0                  | 901               | 888                 | 153   | 7   | 160           |

<sup>a</sup> w/c ratio = water/cement

 $^{b}$  w/cm ratio = water/(cement + CSS)

<sup>c</sup> SP = Superplasticizer

Table 2. Mixture proportion of SCC.

#### 3. Results and discussions

#### 3.1 Workability of SCC

Figure 2 illustrates slump vs. different w/cm ratios for both OPC and CSC; the figure indicates that all slump values are greater than 230 mm, the specification for SCC with high flow. Concrete with a lower w/cm ratio than 0.28—implying significantly high binder content—may lead to higher slump and satisfactory flowability. For an identical dosage of SP mixtures, CSC has higher slump than OPC mixtures. Hence, it is clear that the use of CSS might improve the workability of SCC; and this is similar to the test results of the research papers referenced. Hence, the use of CSS in SCC can lead to high flow properties.

#### 3.2 Setting time of SCC

Figure 3 shows the effects of CSS on the penetration resistance of concrete, indicating that as the w/cm ratio of OPC or CSC increases, the penetration resistance decreases and the setting time increases. Further, the setting time of CSC is longer than that of OPC irrespective of the w/cm ratio. This is due to the low PAI values of CSS. Thus, the setting time increases with the amount of CSS. This result is similar to the results in a previous study, which showed that the addition of BFS decreased the setting time of SCC [Mihashi H, Yan X, Arikawa S.,1995.].

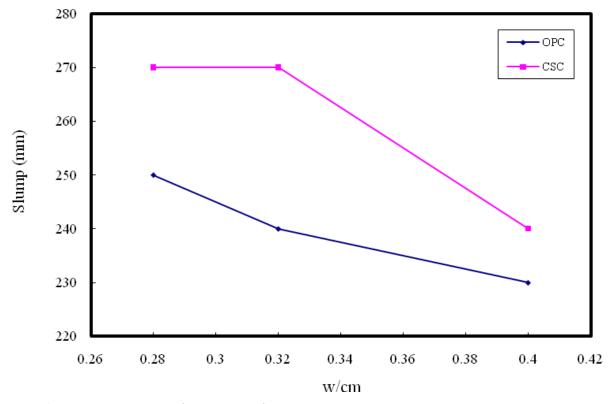


Fig. 2. Slump vs. various w/cm ratios of concrete.

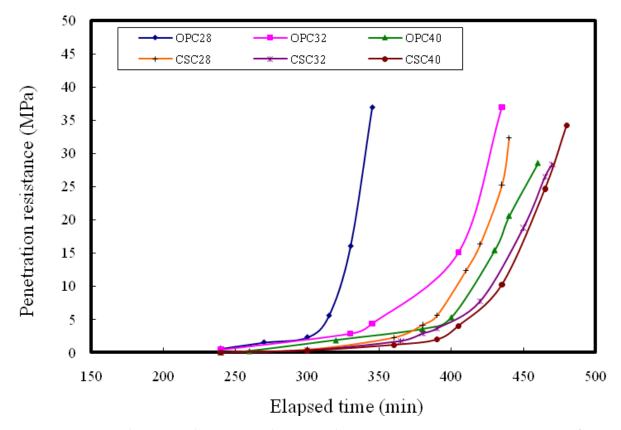


Fig. 3. Comparison between the OPC and CSC with respect to penetration resistance of concrete.

#### 3.3 Compressive strength of SCC

The compressive strength and percentage of concrete mixtures with different w/cm values at the specified age are shown in Table 3. The compressive strength of each mixture is greater than 41 MPa at 56 days. This satisfies the requirement that SCC must have high strength [Hogan FJ, Meusel JW., 1981.]. The compressive strength of OPC and CSC with a w/cm ratio of 0.28 is either equal to or higher than 83 MPa at 90 days; however, that of CSC28 at any age is lower than that of OPC28. In contrast, the percentage of compressive strength is higher than 90% at 28 days, and it is reduced to 76% at 90 days. This corresponds to a 15% reduction in the PAI at 28 days. The compressive strength of CSC with a w/cm ratio of 0.32 or 0.40 at any age, however, is higher than that of OPC, and the percentages of compressive strength are from 106% to 134% and from 108% to 121%, with respect to the w/cm ratio. This clearly indicates that the addition of CSS improves the strength development of cement paste as long as the water-to cement (w/c) ratio is greater than 0.32 or w/cm is higher than 0.28. This means that the reactions of strength development of cement with CSS will be enhanced with sufficient water contents. It is suggested, however, that the total water content of concrete, including the moisture in liquid admixture be maintained as low as possible to avoid large shrinkage and sedimentation. Figure 4 shows the influence of CSS content on compressive strength: higher CSS content mixtures will cause lower compressive strength.

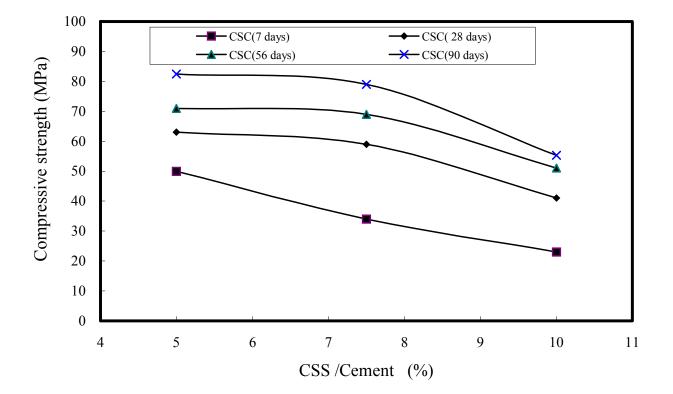


Fig. 4. Effect of CSS content at different ages on the compressive strength of SCC.

| Designation of concrete | w/c<br>ratio | w/cm<br>ratio | Compressive strength, MPa (% compressive strength <sup>a</sup> ) |            |            |            |            |
|-------------------------|--------------|---------------|--|------------|------------|------------|------------|
|                         |              |               | 3 days   | 7 days     | 28 days    | 56 days    | 90 days    |
| OPC28                   | 0.28         | 0.28          | 46.5 (100)   | 53.9 (100) | 69.6 (100) | 93.7 (100) | 95.6 (100) |
| CSC28                   | 0.29         | 0.28          | 42.9 (92)  | 50.0 (93)  | 63.2 (91)  | 71.0 (76)  | 82.5 (86)  |
| OPC32                   | 0.32         | 0.22          | 25.0 (100)   | 32.0 (100) | 49.6 (100) | 57.3 (100) | 59.1 (100) |
| CSC32                   | 0.34         | 0.32          | 26.5 (106)   | 34.1 (107) | 58.5 (118) | 69.4 (121) | 78.9 (134) |
| OPC40                   | 0.40         | 0.40          | 16.3 (100)   | 22.2 (100) | 37.1 (100) | 45.1 (100) | 45.8 (100) |
| CSC40                   | 0.44         | 0.40          | 17.6 (108)   | 24.1 (109) | 40.7 (110) | 50.6 (112) | 55.3 (121) |

Table 3. Compressive strength and percentage compressive strength of concrete.

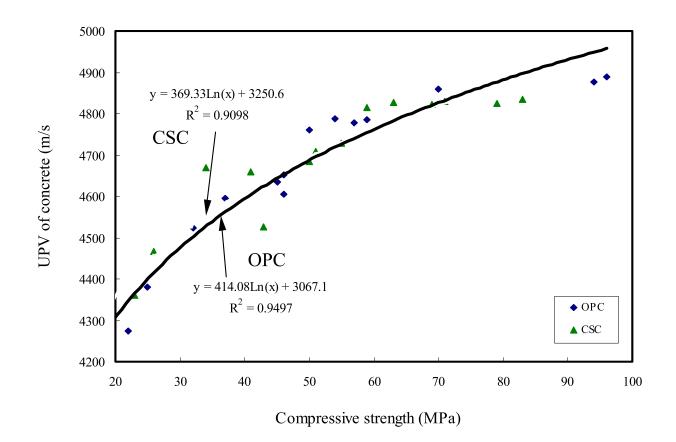
#### 3.4 Ultrasonic pulse velocity (UPV) of SCC

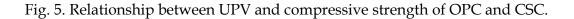
Theoretically, the ultrasonic pulse velocity (UPV) of a solid object is higher that of air, and a high-density solid will have high UPV. Therefore, the UPV is a good measure of the soundness of hardened concrete. It is generally acknowledged that the UPV increases with concrete density. In our study, the UPV of all mixtures was greater than 4200 m/s. Table 4 shows the UPV and the difference in UPV between CSC and OPC (as a percentage) at each w/cm ratio, from 3 to 90 days. The UPV of CSC28 at all ages is lower by 1% to 2% than that of OPC28; however, the UPV of CSC32 and CSC40 is higher by 3% than that of OPC32 and OPC40, respectively. This result is similar to trend in compressive strength – the addition of CSS enhances the pozzolanic reaction with high w/c or w/cm ratios, i.e., sufficient water. Figure 5 shows a good linear relationship between the compressive strength and UPV of concrete for both OPC and CSC. In other words, UPV is a good method for evaluating the performance and homogeneity of SCC.

| Designation of concrete | w/c<br>ratio | w/cm<br>ratio - | UPV of concrete, m/s (% UPV <sup>a</sup> ) |            |            |            |            |  |
|-------------------------|--------------|-----------------|--|------------|------------|------------|------------|--|
|                         |              |                 | 3 days                                     | 7 days     | 28 days    | 56 days    | 90 days    |  |
| OPC28                   | 0.28         | 0.29            | 4606 (100)                                 | 4787 (100) | 4859 (100) | 4876 (100) | 4890 (100) |  |
| CSC28                   | 0.29         | 0.28            | 4525 (98)                                  | 4683 (98)  | 4828 (99)  | 4830 (99)  | 4835 (99)  |  |
| OPC32                   | 0.32         | 0.22            | 4381 (100)                                 | 4523 (100) | 4760 (100) | 4777 (100) | 4785 (100) |  |
| CSC32                   | 0.34         | 0.32            | 4466 (102)                                 | 4669 (103) | 4814 (101) | 4821 (101) | 4825 (101) |  |
| OPC40                   | 0.40         | 0.40            | 4211 (100)                                 | 4274 (100) | 4595 (100) | 4635 (100) | 4651 (100) |  |
| CSC40                   | 0.44         | 0.40            | 4295 (102)                                 | 4361 (102) | 4659 (101) | 4709 (102) | 4728 (102) |  |

<sup>a</sup> Percentage UPV = (CSC/OPC) × 100 at fixed w/cm ratios

Table 4. UPV and percentage UPV of SCC.





#### 3.5 Microstructure observation

Scanning electron microscopy (SEM) observations are conducted with specimens at the ages of 3 and 28 days. The image characteristics of concrete at 3 days are shown in Figs. 6(a)-8(a). As shown in Fig. 6(a), at the early age of 3 days, considerable amounts of hexagonal-shaped calcium hydroxide (Ca(OH)<sub>2</sub>), spherical-shaped C-S-H gel in CSC28 (w/cm = 0.28) and certain amounts of fine pores (dark zone) exist. Figure 7(a) shows the presence of numerous rosette-shaped mono-sulfoaluminate (AFm) and small amounts of needle-shaped ettringite (AFt) in CSC32 (w/cm = 0.32). Figure 8(a) also shows that there are rosette-shaped AFm in CSC40 (w/cm = 0.40). Here, the w/cm ratio is greater than or equal to 0.32 as a result of increase in CSS amounts and the existence of high Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> contents. The primary hydration products are hexagonal-shaped Ca(OH)<sub>2</sub>, spherical-shaped C-S-H gel and a certain amount of rosette-shaped AFm. This observation confirms the conclusions made for both strength and UPV that the reaction of CSS with cement paste requires sufficient water to aid hydration. At a later age, as shown in Fig. 6(b), the microstructure of CSC28 is extremely dense. Figure 7(b) also shows the presence of numerous rosette-shaped AFm, but no needle-shaped Aft, while Fig. 8(b) shows large pores in CSC40 with a large amount of hexagonal-shaped Ca(OH)<sub>2</sub> in the reaction process. While this is advantageous for the hydration reaction of CSS, it also indicates that more pores are observed with higher w/cm ratios.

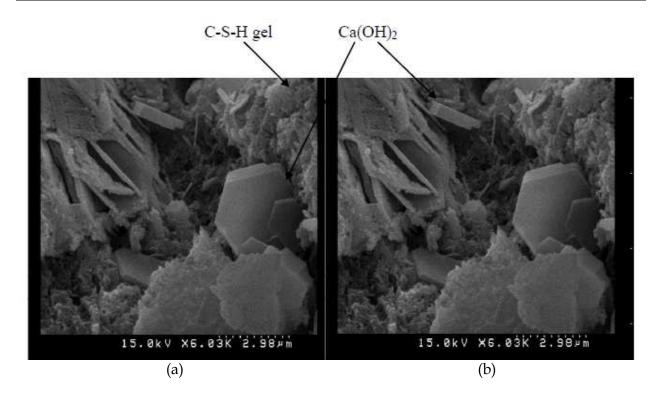


Fig. 6. SEM micrograph of CSC28: (a) at 3 days; (b) at 28 days.

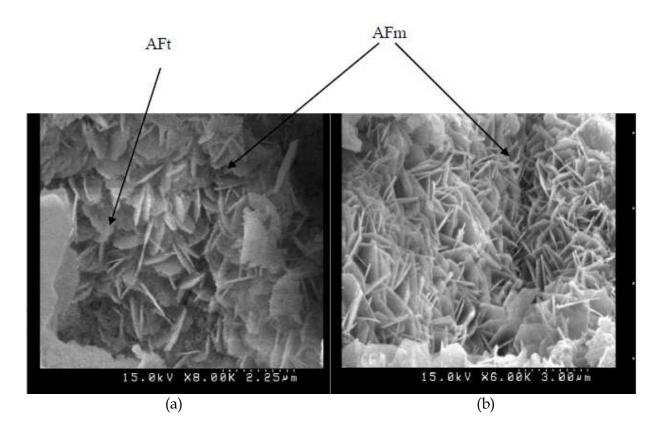


Fig. 7. SEM micrograph of CSC32: (a) at 3 days; (b) at 28 days.

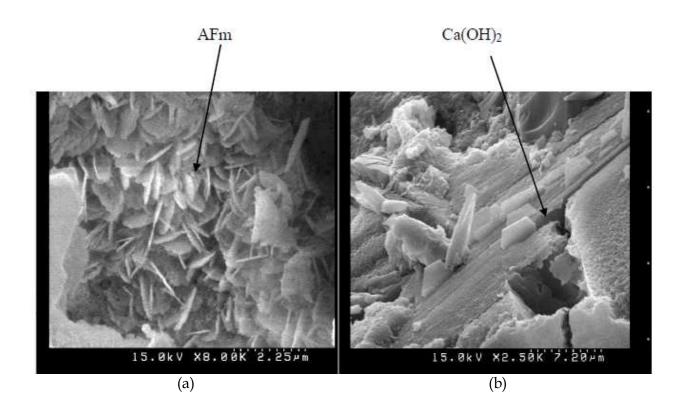


Fig. 8. SEM micrograph of CSC32: (a) at 3 days; (b) at 28 days.

#### 4. Conclusions

In this study, we have conducted investigations on the recycling of carbon steel slag CSS to produce SCC. Our conclusions are as follows:

- The major chemical compositions of CSS are CaO, Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub>, a composition similar to that of Portland cement and BFS. The PAI of CSS is 85% at 28 days. Hence, CSS can be expected to have good cementitious properties and effects.
- CSS can be designed as easily as SCC. In comparison with OPC, increasing the CSS content will increase the setting time.
- Concrete using CSS has a higher compressive strength than that using OPC. If w/cm ratios of 0.32 or 0.40 are used, the percentage of compressive strength increases by more than 21% at 90 days.
- As the amount of CSS in concrete increases, the compressive strength decreases. The strength is similar to other concrete, however, when CSS of 5.0–7.5% is used, except at 7 days.
- The SEM images show that the hydration rate of CSS is lower than that of OPC. Further, large amounts of Ca(OH)<sub>2</sub> and AFm are present in CSS as a cementitious material.

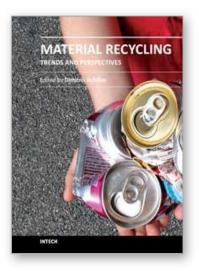
In this manner, we have shown that CSS can potentially be used as a cementitious material in self-consolidating concrete.

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