Elucidating the hydration properties of paste containing thin film transistor liquid crystal display waste glass

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ABSTRACT

This study discusses the thin film transistor liquid crystal display (TFT-LCD) waste glass-blended cement (WGBC) pastes. It presents their compressive strength, their products of hydration and solid silicates changes. The samples were subjected to Fourier transformation infrared spectroscopy, differential thermal and thermo-gravimetric analysis and ^{29}Si magnetic angle spinning/nuclear magnetic resonance. The experimental XRD results demonstrated the speciation of the TFT-LCD waste glass, and that the major component was SiO_2. At 40% substitution of TFT-LCD waste glass, at 28 days and 56 days, the compressive strength was 35% and 30% lower, respectively, than that of the Portland cement paste. The intensity of the $Ca(OH)_2$ band at $3710\,cm^{-1}$ in the 56-day hydrated products of the WGBC pastes that contain TFT-LCD waste glass exhibit comparatively weak peaks suggesting that much $Ca(OH)_2$ during hydration was consumed. Later, the C—S—H contents of the WGBC pastes increased, revealing that liberated $Ca(OH)_2$ was consumed in pozzolanic reactions.

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1. Introduction

The amount of waste glass that was dumped into landfills has accumulated to approximately 0.52 million tons in Taiwan whereas the amount of thin film transistor liquid crystal display (TFT-LCD) waste glass has reached 6000 tons [1]. The waste electrical and electronic equipment directive (WEEE directive) aims to minimize the effect of electrical and electronic goods on the environment, by increasing reuse and recycling and reducing the amount of WEEE going to landfill. Also, enterprises are compelled to use the collected waste in an ecologically friendly manner, either by ecological disposal or by reuse/refurbishment of the collected WEEE. The WEEE directive aims to prevent the generation and disposal of WEEE, largely via the introduction of reuse and recycling targets. It also aims to improve the environmental performance of all operators that are involved in the life cycle of electrical and electronic equipment.

TFT-LCD is a variant of liquid crystal display (LCD) in which thin film transistor technology is used to enhance image quality. Although an active matrix LCD, TFT-LCD is typically synonymous with LCD. Used in televisions, flat panel displays, and projectors, TFT-LCD is a cutting-edge display, which screens pictorial informa-

tion by adjusting the amount of light permitted. TFT is a circuit that is formed with semiconductor films on a thin glass substrate to control liquid crystals. This circuit is critical in controlling each pixel, the basic unit of a picture image. The color filter displays a color image by coating pixels (red, green, and blue) onto a glass substrate. The indium tin oxide (ITO) film on a glass substrate is ideal for flat panel displays that depend on thin films of the highest quality. It has excellent wear resistance, heat resistance, and transparency. Such components must satisfy the requirements of wear resistance, heat resistance, transparency, and lower resistivity.

The TFT-LCD panel is extensively adopted in daily electronic products, and increases in the demand for the TFT-LCD panel apparently have led to increases in the production of TFT-LCD waste glass. The TFT-LCD waste glass contains large amounts of glass. Conventional treatment of TFT-LCD waste glass does not suffice to meet the WEEE directive. Such waste as waste glass and scraps are effectively sorted for reuse. Waste glass can be reused as raw materials in ceramics [1], bricks [2], concrete [3,4], and pozzolanic materials [5]. TFT-LCD waste glass treatment must be developed to meet requirements of resource, reduction, stabilization, and safety. Accordingly, in Taiwan, treating TFT-LCD waste glass to recycle it and reuse it as a construction material has become increasingly favored. The goal of this study was to elucidate, using paste mixtures of TFT-LCD waste glass, the mechanism by which the strength and other hydration characteristics of waste glass-blended cement (WGBC) pastes are developed.

Table 1
Chemical composition and total heavy metals of TFT-LCD waste glass

Composition	TFT-LCD waste glass
SiO_2 (%)[a]	64
Na_2O (%)[a]	0.3
Al_2O_3 (%)[a]	ND
Fe_2O_3 (%)[a]	ND
CaO (%)[a]	ND
MgO (%)[a]	ND
SO_3 (%)[a]	ND
K_2O (%)[a]	ND
Cu (mg/kg)[b]	5.1
Zn (mg/kg)[b]	0.5
Pb (mg/kg)[b]	3.2
Cr (mg/kg)[b]	21.7

ND, CaO < 0.016%; Al_2O_3 < 0.016%; Fe_2O_3 < 0.014%; MgO < 0.014%; Na_2O < 0.012%.

[a] Analyzed by X-ray fluorescence.

[b] Analyzed by inductively coupled plasma atomic emission spectroscopy after $HF/HClO_4/HNO_3$ digestion.

2. Materials and methods

2.1. Materials

The TFT-LCD waste glass was obtained from a TFT-LCD manufacturing plant in Taiwan. It was first homogenized, and then oven dried at 105 °C for 24 h, before the chemical composition was characterized.

ASTM Type I Portland cement (OPC) from the Taiwan cement company was also used in this study. Its specific gravity was 3.15 and its physical–chemical properties met the requirements of ASTM C150. The major composition of the OPC is shown in Table 1.

2.2. Preparation of TFT-LCD waste glass

The TFT-LCD waste glass was then further pulverized in a ball mill until particles could pass through a #200 mesh sieve. The TFT-LCD waste glass had a Blaine fineness value of approximately 370 m²/kg, with a specific gravity of 2.79. The resultant pulverized TFT-LCD waste glass was desiccated before being tested. The pozzolanic activity of the TFT-LCD waste glass after being cured for 28 days was analyzed according to ASTM C311, and the results are also presented in Table 1.

2.3. Analysis methodology

The levels of TFT-LCD waste glass substitution in the blended cement were between 10% and 40% the weight of the cement. The water/binder (w/b) ratio of the WGBC paste was a constant of 0.4. Test cubes of 50 mm × 50 mm × 50 mm were prepared according to ASTM C109. The specimens were demoulded and cured in a container at 97% humidity at 25 °C, for periods ranging from 7 days to 56 days. After curing for 7 days, 14 days, 28 days, or 56 days, the samples were subsequently crushed and the hydration reactions were stopped with absolute alcohol. The crushed samples were filtrated in a vacuum, washed several times with acetone, and dried. Finally, the prepared samples were subjected to Fourier transformation infrared spectroscopy (FTIR), differential thermal and thermo-gravimetric analysis (DTA/TGA) and ^{29}Si magnetic angle spinning/nuclear magnetic resonance (^{29}Si MAS/NMR).

The major analyses performed on the WGBC pastes and the cube specimens included the following:

- *Unconfined compressive strength* (ASTM C39–72): At each testing age, four specimens were taken out of the moist room. The surfaces of the specimen were polished so that the load bearing surfaces were flat and parallel. Three specimens were used for the compressive strength tests while the fourth one was used for the microstructure examination. The average strength value from the three specimens is presented. The coefficient of variation of these results was less than 10%.

- *Toxicity characteristic leaching procedure* (TCLP): SW 846–1311 [6]. This extraction procedure requires the preliminary evaluation of the pH characteristics of the sample, to determine the proper extraction fluid necessary for the experiments. It was determined after testing that in this case the #B extraction fluid (pH 2.88 ± 0.05) should be used for the TCLP analysis. This fluid was prepared by adding 5.7 mL of acid to 500 mL of double distilled water, diluted to a volume of 1 L. A 25-g sample was placed in a 1-L Erlenmeyer flask after which 500 mL of extraction fluid was added. The samples were agitated for 18 h using an electric vibrator. The slurry was filtered with 6–8 μm pore size Millipore filter paper. The leachates were preserved in 2% HNO_3.

- *Chemical composition*: The X-ray fluorescence (XRF) analysis was performed using an automated RIX 2000 spectrometer. Specimens were prepared for XRF analysis by mixing 0.4 g of sample and 4 g of 100 Spectroflux at a dilution ratio of 1:10. The homogenized mixtures were placed in Pt–Au crucibles before being heated for 1 h at 1000 °C in an electrical furnace. The homogeneous melted sample was recast into glass beads 2 mm thick and 32 mm in diameter.

- *Pozzolanic activity index*: The test was performed according to ASTM Designation C 311.

- *Mineralogy*: The X-ray diffractometer (XRD) analyses were carried out by a Siemens D-5000 X-ray diffractometer with Cu Kα radiation and 2θ scanning, ranging between 5° and 70° (2θ). The XRD scans were run at 0.05°-steps, with a 1 s counting time.

- *Fourier transformation infrared spectroscopy*: FTIR was performed on the samples using a Bomem, DA8.3 spectrometer and the KBr pellet technique (1 mg powdered sample mixed with 150 mg KBr).

- *Differential thermal and thermo-gravimetric analysis*: DTA/TGA analyses of the samples were performed using a Seiko SSC Model 5000 Thermal analyzer. Dry N_2 gas was used, as the stripping gas and the heating rate was 0.5 °C. The samples were heated from 25 °C to 1000 °C.

- *Chemical shift of linear polysilicate anions in* C−S−H *by* ^{29}Si MAS/NMR: high-resolution ^{29}Si MAS/NMR spectra were recorded at 39.72 MHz on an MSL Bruker MAS/NMR-200 solid-state high-resolution spectrometer, using rapid (about 3 kHz) sample spinning at the magic angle to the external magnetic field. The ^{29}Si chemical shifts are given relative to the primary standard liquid tetramethylsilane (TMS) in the delta-scale (the negative signs correspond to up-field shifts). As a result of the degree of increasing condensation, there was an increase of diamagnetic shielding to the ^{29}Si nuclei, from the single tetrahedral structure of the monosilicates (Q^0) to the end groups (Q^1), to the chain middle groups (Q^2), to the layers and the branching sites (Q^3), and finally to the three-dimensional networks (Q^4), which led to well-separated, analytically useful chemical shift ranges for each type of SiO_4^{4-} unit.

3. Results and discussion

3.1. Characteristics of TFT-LCD waste glass

Chemical analysis (Table 1) revealed that the TFT-LCD waste glass sample was relatively poor in Na_2O and rich in SiO_2. The pH and density of TFT-LCD waste glass were 5.8 g/cm³ and 2.8 g/cm³, respectively. The chemical composition of the TFT-LCD waste glass was as follows: 64% SiO_2 and 0.3% Na_2O. As can be seen in Fig. 1, the fingerprint speciation of TFT-LCD waste glass (identified by the
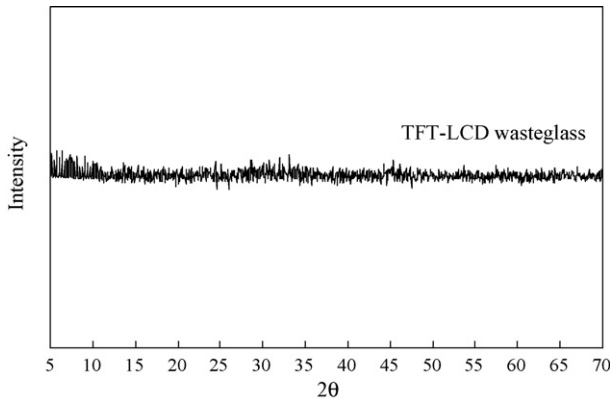
Fig. 1. XRD patterns of the TFT-LCD waste glass.

XRD techniques) indicated that the major component was SiO_2. The amorphous glassy matrix, contained large amounts of glass. Because TFT-LCD waste glass is amorphous material, which is indicated by the broad diffuse bands. It had a pozzolanic strength activity index of 89% at 28 days. From the aspect of strength, it can be regarded as a good pozzolanic material.

Table 1 indicates that the major heavy metals were Cr, Cu, and Pb, comprising 21.7 mg/kg, 5.1 mg/kg, and 3.2 mg/kg, respectively. To give some indication of the reusability of TFT-LCD waste glass, the heavy metal concentrations in the TCLP leachates have to be examined (Table 2). The leaching concentration of Zn in TFT-LCD waste glass was 0.09 mg/L. The leaching concentrations all met the current Taiwan EPA regulatory thresholds.

3.2. Strength development of the WGBC pastes

The compressive strengths of the WGBC pastes at different ages (up to 56 days) are shown in Fig. 2. It can be seen that amount of TFT-LCD waste glass blended into the pastes affected the strength. The compressive strength of WGBC paste containing 0%, 10%, 20%, and 40% TFT-LCD waste glass at the age of 56 days, are 60 MPa,

Table 2
Leaching concentrations of the TFT-LCD waste glass

	Cd^a (mg/L)	Cr^b (mg/L)	Pb^c(mg/L)	Cu (mg/L)	Zn (mg/L)
Waste glass	ND	ND	ND	0.25	0.16
Regulatory limits	1	5	5	15	–

[a] Cd < 0.016 mg/L.
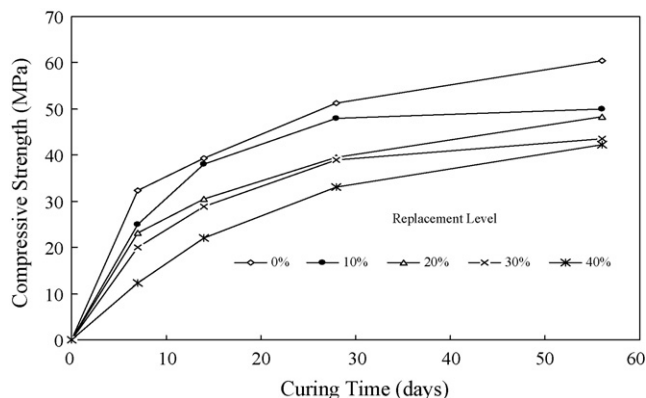[b] Cr < 0.016 mg/L.
[c] Pb < 0.014 mg/L.

Fig. 2. Compressive strength of the WGBC pastes.
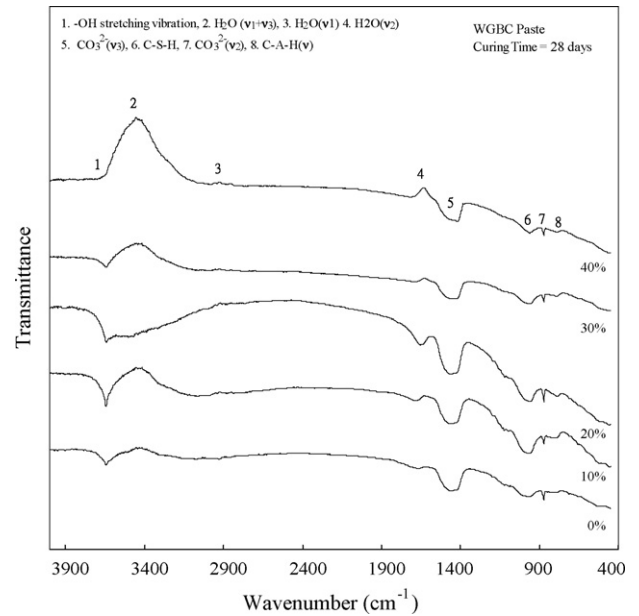

Fig. 3. FTIR patterns of the WGBC pastes at 28 days.

52 MPa, 48 MPa, 44 MPa, and 42 MPa, respectively. At age of 56 days, the strength of the WGBC pastes containing 10% and 20% TFT-LCD waste glass, the contribution to the compressive strength is 87% and 80%, respectively. There was an increase in strength at later stage. It is possibly that the amorphous structure of the ground waste glass which was, as fine as cement, and gradually reacted with the hydration products [7–9]. However, the strength development of the WGBC pastes decreased obviously as the amounts of TFT-LCD waste glass increased. When the substitution level was 40% the compressive strength declined from 35% at 28 days to 30% at 56 days, compared to that developed by the plain cement paste. The results indicated that increasing the amount of TFT-LCD waste glass reduced, the strength at all stages.

3.3. FTIR patterns of the WGBC pastes

The FTIR patterns of the 28-day and 56-day hydration products of mixtures in the 400–4000 cm^{-1} range are shown in Figs. 3 and 4, respectively. Different band assignments are given in Table 3 [10,11]. The FTIR patterns of OPC paste and WGBC pastes were similar in bands. The vibration of valence band at 3700 cm^{-1} is —OH, of the OH group of portlandite ($Ca(OH)_2$). The peaks around 3510 cm^{-1}, 2930 cm^{-1}, and 1650 cm^{-1} are due to water. The bands at 1390 cm^{-1} and 975 cm^{-1} are attributed to presence of CO_3^{2-}. The band at 975 cm^{-1} region is due to Si—O stretching vibration of C—S—H and that at 824 cm^{-1} is due to amorphous aluminosilicates. The FTIR patterns of the hydration products of all the mixtures are almost the same. The intensity of the $Ca(OH)_2$ band at 3710 cm^{-1} in the 56-day hydration products is comparatively

Table 3
FTIR band assignment of hydrated products

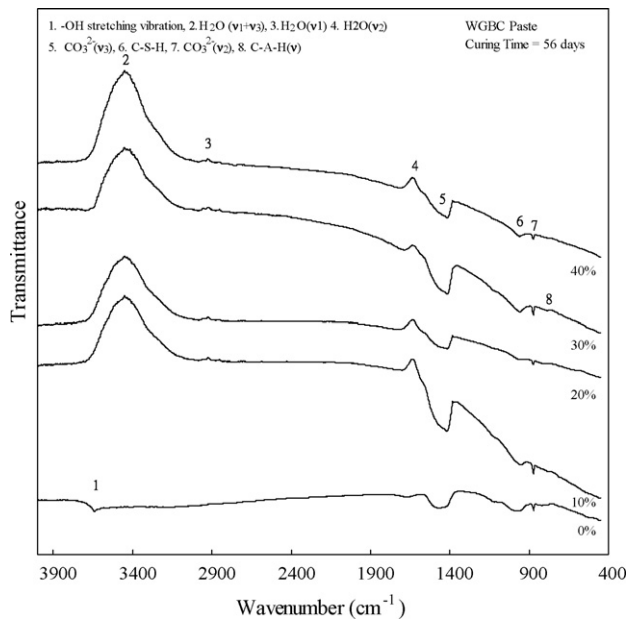| Characteristic vibrations	Wavenumber (cm^{-1})
—OH stretching vibration	3700
$\nu_1 + \nu_3$, H_2O	3510
ν_1, H_2O	2930
ν_2, H_2O	1650
ν_3, CO_3^{2-}	1390
SiO_4^{4-}, C—S—H	975
ν_2, CO_3^{2-}	880
ν, C—A—H	824

Fig. 4. FTIR patterns of the WGBC pastes at 56 days.

weak. It exhibited consumption of higher amount of Ca(OH)$_2$ during hydration.

3.4. Thermal analysis of WGBC pastes

The TG/DTA of the hydrated OPC and WGBC pastes cured at room temperature for various periods are presented in Figs. 5 and 6. The endotherms observed in the DTA curves, in the temperature regions from 100 °C to 180 °C, accompanied by breaks in the TG curves, are due to C–S–H [12,13]. The endotherms in the DTA curves, in the temperature ranges from 425–550 °C to 600–750 °C, accompanied with weight loss as exhibited by corresponding TG curves, are due to dehydroxylation of Ca(OH)$_2$ and decomposition of CaCO$_3$, respectively.

The Ca(OH)$_2$ contents in the cement pastes with respect to time are shown in Fig. 7.

The trend for a change in the amount of TFT-LCD waste glass in the pastes of different replacement levels is the opposite of the change in the Ca(OH)$_2$ content.

The Ca(OH)$_2$ content of all the pastes was high at the early ages. The high Ca(OH)$_2$ content in the 28-day hydration products was due to the liberation of Ca^{2+} ions from the clinker phases during hydra-

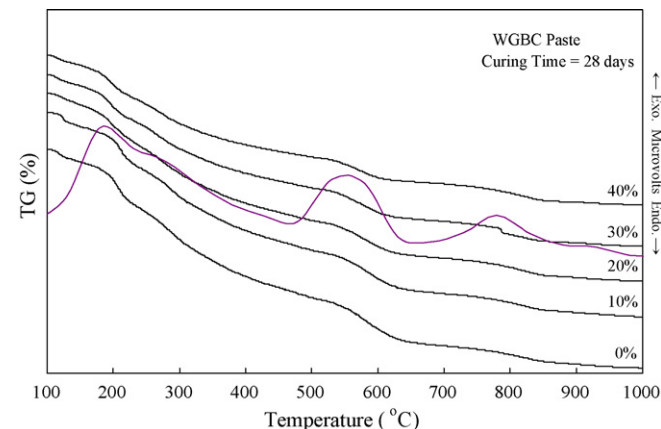tion. The Ca(OH)$_2$ contents in the WGBC pastes after hydration were lower than in the OPC pastes. The amount of TFT-LCD waste glass in the 28-day hydration products of WGBC pastes containing 10% TFT-LCD waste glass was 6.2%, but at 56 days, the Ca(OH)$_2$ (6.9%) of the WGBC pastes containing 10% TFT-LCD waste glass were similar to that of the OPC paste (7.1%). The Ca(OH)$_2$ contents of the WGBC pastes containing up to 40% TFT-LCD waste glass were always lower than that of the OPC paste. The amount of Ca(OH)$_2$ in the WGBC pastes decreased with increased curing time. The lower Ca(OH)$_2$ contents in the WGBC pastes were possibly due to consumption through pozzolanic reactions.

Further information is conveyed by the C–S–H content. The C–S–H hydration products increased when the hydration time was prolonged to 56 days (Fig. 8). The C–S–H content after the 28-day was higher in the OPC pastes than the WGBC pastes. The C–S–H hydration products in the WGBC pastes increased with increasing hydration time. At 56 days, the hydration products in the WGBC pastes containing TFT-LCD waste glass contained a higher amount of C–S–H than did the control sample, indicating the presence of a high amount of hydrated products in these compositions. After this period, the formation rate of C–S–H increased, finally reaching a level slightly higher than in the OPC pastes. At later ages, the C–S–H contents in the WGBC pastes also increased indicating consumption of liberated Ca(OH)$_2$ due to pozzolanic reactions. This indicates that of higher pozzolanic activity in the WGBC pastes at later ages.
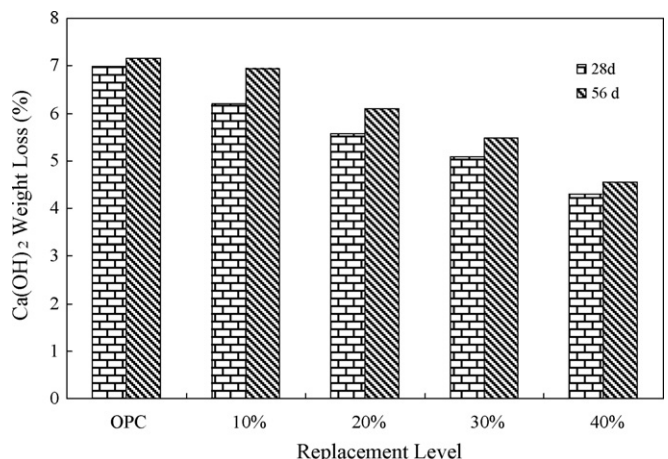

Fig. 5. TG and DTA of the hydrated WGBC pastes at 28 days.
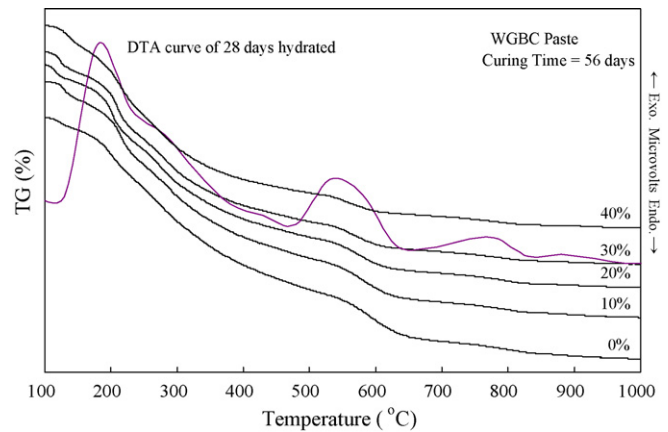
Fig. 6. TG and DTA of the hydrated WGBC pastes at 56 days.

Fig. 7. The Ca(OH)$_2$ content of the hydrated WGBC pastes.
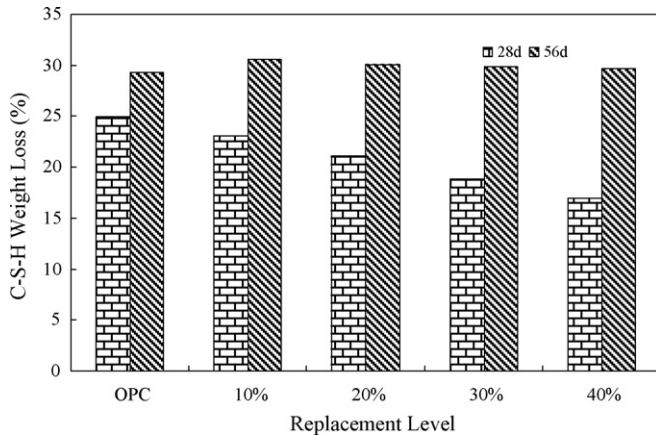
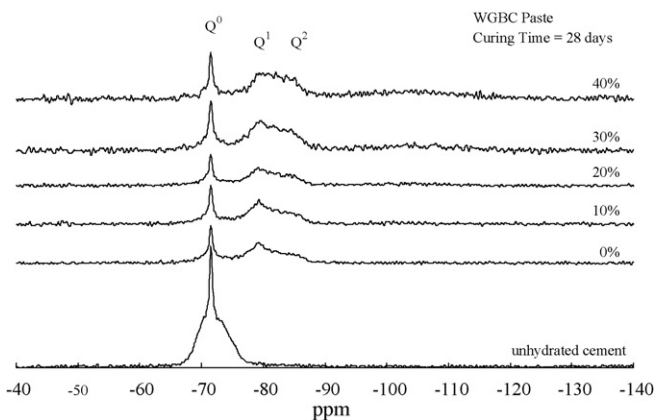**Fig. 8.** The of C—S—H content of the hydrated WGBC pastes.

Fig. 9. ^{29}Si NMR spectrum of the WGBC pastes at 28 days.
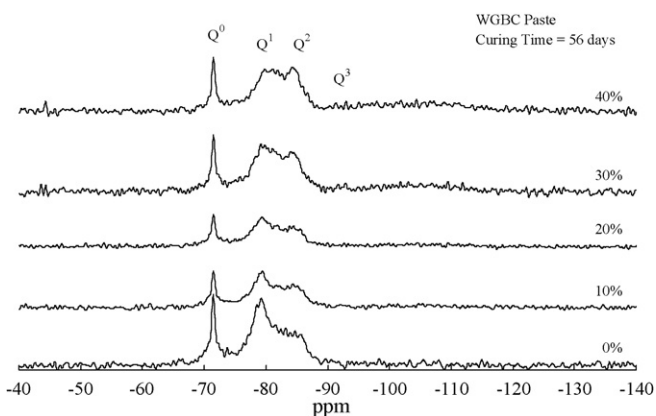

Fig. 10. ^{29}Si NMR spectrum of the WGBC pastes at 56 days.

3.5. ^{29}Si NMR spectrum for the WGBC pastes

Figs. 9 and 10 show the ^{29}Si NMR spectrum of the WGBC pastes. It can be seen that the range of ^{29}Si chemical shifts of Q^n units

in solid silicates included monosilicates (Q^0, −68 to −76), disilicates and chain end group (Q^l, −76 to −82), chain middle groups (Q^2, −82 to −88), chain branching sites (Q^3, −88 to −92), and a three-dimensional framework (Q^4, −92 to −129). As the curing time increased, the relative intensity of the Q^0 peak decreased. This is linked to an acceleration of the hydration kinetics with curing time, so that the anhydrous species were transformed into calcium silicate hydrate (C—S—H). The Q^2/Q^l ratio also increased with curing time. In addition, there were some apparent sites present in the WGBC pastes at a later age. These results indicated that increasing the curing time caused an increase in the polymerization of the C—S—H structure.

4. Conclusions

The following conclusions are based on research on the hydration characteristics of paste that contains thin film transistor liquid crystal display waste glass. The results can be summarized as follows. The fingerprint speciation of the TFT-LCD waste glass, obtained by the XRD techniques, demonstrated that the major component was SiO_2. The decline in compressive strength associated with 40% substitution levels of TFT-LCD waste glass, at 28 days and 56 days, was 35% and 30%, respectively, from that associated with plain cement paste. The intensity of the $Ca(OH)_2$ band at 3710 cm^{-1} in the 56-day hydrated products of the WGBC pastes that contain TFT-LCD waste glass yield comparatively weak peaks. They consumed more $Ca(OH)_2$ during hydration. Later, the C—S—H contents of the WGBC pastes increased, revealing the consumption of liberated $Ca(OH)_2$ in pozzolanic reactions. The Q^2/Q^l ratio increases with curing time. The results indicated that it is feasible to use TFT-LCD waste glass to replace up to 10% of the ordinary Portland cement.

References

[1] K.L. Lin, Use of thin film transistor liquid crystal display (TFT-LCD) waste glass in the production of ceramic tiles, J. Hazard. Mater. 148 (2007) 91–97.
[2] K.L. Lin, The effect of heating temperature of thin film transistor-liquid crystal display (TFT-LCD) electric-optical waste glass substitute partial clay as eco-brick, J. Cleaner Product 15 (2007) 1755–1759.
[3] Y. Shao, T. Lefort, S. Moras, D. Rodriguez, Studies on concrete containing ground waste glass, Cement Concrete Res. 40 (1) (2000) 91–100.
[4] A. Shayan, A. Xu, Value-added utilisation of waste glass in concrete, Cement Concrete Res. 34 (2004) 81–89.
[5] C. Shi, Y. Wu, C. Riefler, H. Wang, Characteristics and pozzolanic reactivity of glass powders, Cement Concrete Res. 35 (2005) 987–993.
[6] ASTM Standards, American Society for Testing and Materials, Philadelphia, USA, 1999.
[7] Y. Shao, T. Lefort, S. Moras, D. Rodriguez, Studies on concrete containing ground waste glass, Cement Concrete Res. 30 (2000) 91–100.
[8] W. Jin, C. Meyer, S. Baxter, Glascrete—concrete with glass aggregate, ACI Mater. J. 97 (2000) 208–213.
[9] C. Polley, S.M. Cramer, R.V. Cruz, Potential for using waste glass in Portland cement concrete, J. Mater. Civil Eng. 10 (1998) 210–219.
[10] G.M.M. Bell, J. Bensted, F.P. Glasser, E.E. Lachowski, D.R. Robarts, S.A. Rodger, Instrumental investigations of hydration of class J oilwell cement, Adv. Cem. Res. 5 (18) (1993) 71–79.
[11] R.K. Vempati, A. Rao, T.R. Hess, D.L. Cocke, Fractionation and characterization of Texas lignite class 'F' fly ash by XRD, TGA, FTIR and SFM, Cement Concrete Res. 24 (6) (1994) 1153–1164.
[12] P.S. De-Silva, F.P. Glasser, Phase relation in the system CaO–Al$_2$O$_3$–SiO$_2$–H$_2$O relevant to metakaolin–Ca(OH)$_2$ hydration, Cement Concrete Res. 23 (1993) 627–639.
[13] M.A. Serry, A.S. Taha, S.A.S. El-Jemaly, H. El-Didamony, Metakaolin-lime hydration products, Therm. Chim. Acta 79 (1984) 103–110.