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Vitrification of a waste water flocculate from a petroleum catalyst manufacturer

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Abstract

Chemical and mineral compositions of a waste water flocculate generated in a manufacturer producing fluidized-bed catalytic cracking catalysts were analyzed. The flocculate was then calcined at 1200–1350 °C. X-ray diffraction analysis results indicate that the flocculate can be directly vitrified at 1350 °C without the addition of any other ingredients. The density and chemical durability of the directly vitrified product are comparable with commercial soda-lime-silicate glasses. However, the viscosity of directly vitrified glass melt was very high. Thus, the refining and shaping of the glass melt were difficult. With the addition of minerals such as limestone, dolomite and fluorite, workable glasses could be formed. The influence of MgO on the structure and properties of the obtained glasses is discussed. Results show that the density and hardness of the glass increase with the increase of MgO, whereas the chemical durability, transition and crystallization temperatures decrease. The present study provides a general way to utilize waste water flocculates in glass production.

Keywords: D. Glass; Mineral addition; Vitrification; Waste water flocculate

1. Introduction

Large quantities of solid wastes are generated around the world from ore mining and industrial production [1]. One example is waste water flocculates from petroleum catalyst manufacturers. In the production of fluidized-bed catalytic cracking (FCC) catalysts, a lot of waste water is produced. The waste water is flocculated using organic and inorganic flocculating agents under a certain pH condition which is adjusted by caustic quick lime. After this treatment, the waste water can be recycled. However, water-containing flocculate is generated. After it is further treated with a pressure filter, water is squeezed out. The resultant wet waste flocculate is then disposed. Environmental problems arise from the disposal of the wet flocculate. First, the flocculate is acidic in water (pH = 5–6). Second, there exist leaching and/or dissolution of the organic and inorganic flocculating agents in surrounding water. Both aspects will inevitably cause groundwater and soil pollution [2]. In addition, the disposed flocculate occupies precious land. Therefore, we need to find a better solution to deal with the flocculate.

The utilization of solid wastes in industrial production could save not only natural resource but also production cost. In addition, it is a measure for environment protection [3,4]. The vitrification of solid wastes is attractive. On the one hand, unstable wastes could be transformed into chemically stable glasses. On the other hand, the resultant glasses are useable and could be recycled again and again after they finish their service [5]. The utilization of solid wastes as main raw materials in the preparation of glasses has been reported in the literature. For example, with the addition of some additives, coal fly ash, steel slag and municipal solid waste fly ash were used to prepare glasses and glass–ceramics [6–9]. There is no report so far dealing with the waste water flocculate from petroleum catalyst manufacturers.

In this study, chemical and mineral compositions of a waste water flocculate from a petroleum catalyst manufacturer were first analyzed. The flocculate was then directly vitrified and the products were studied. To improve the workability of glass

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melt, cheap mineral materials, such as, dolomite, limestone and fluorite were added in the batches made of flocculate [10]. The influence of the amount of MgO on the physical and chemical properties of the obtained glasses is discussed.

2. Materials and methods

A steam-dried waste water flocculate was taken from a FCC catalyst manufacturer and ground shortly to have a homogenous composition. The loss on ignition (LOI) of the flocculate was determined after the sample was heated in a furnace at 900 °C for 2 h. For the direct vitrification trials, the flocculate was heated in alumina crucibles in a furnace at 1250, 1300 and 1350°C for 2 h. Finally, it was cooled to room temperature in the furnace. The chemical compositions of the raw flocculate and the calcined products were analyzed using the X-ray fluorescence spectroscopy (XRF) technique on an S8 TIGER spectrometer (Bruker AXS, Germany). Mineral phases in the raw flocculate and the calcined products were examined on a D8 ADVANCE X-ray diffractometer (XRD) (Bruker, Germany) using Cu $K_\alpha$radiation.

In order to reduce the viscosity of the calcined products, the amount of CaO was increased. The main components ratios were then adjusted to SiO_2:Al_2O_3:CaO = 52.9:16.5:30.6 (by weight). Since the raw flocculate has relatively more Al_2O_3 than SiO_2 and CaO, extra sand and limestone were added in the batches. Besides, 4, 8, 12 or 16 wt% of MgO was introduced by dolomite and 1 wt% of fluorite was added in each batch as a reflux. Detailed batch compositions are listed in Table 1. All the mineral materials were taken from a float glass production factory. The batches were melted in alumina crucibles in an electric furnace at 1450 °C for 2 h. The glass melts were cast in a mold and annealed. According to the amounts of MgO, the samples were encoded as M4, M8, M12 and M16. M0 was assigned for the sample prepared without dolomite.

The density of the obtained glasses was measured by the Archimedes method. The hardness of the specimens was analyzed by the indentation method using an HV-10B (Huayin, China) Vickers Hardness Tester. A load of 1500 mg and a loading time of 15 s were applied. The hardness (HV, 10^7 Pa) was calculated based on the following formula [11]:

$$HV = 2P\ \sin(136^\circ/2)/D^2 = 0.1890P/D^2$$

where P (N) and D (in mm) are the load and the diameter of the indentation, respectively.

Table 1
Batch compositions of the glass samples.

	M0	M4	M8	M12	M16
Raw flocculate	62.5	60.5	58.7	57.0	55.3
Limestone	30.8	25.0	19.5	14.4	9.6
Sand	5.7	5.5	5.4	5.2	5.0
Dolomite	—	8.0	15.4	22.4	29.1
Fluorite	1.0	1.0	1.0	1.0	1.0

Transmission spectra curves of the obtained glasses were measured on a 722 visible light spectrophotometer. The samples were cut into slides, ground and finely polished. The chemical stability of the glasses was estimated by the weight-loss method. In the tests, glass particles sized 250–425 μm were boiled in distilled water for 1 h. Under the same conditions, chemical stability of commercial float and container glasses were also tested for comparison.

Fourier-transformed infrared spectra of the glasses were recorded on a VERTEX 70 spectrometer (Bruker, Germany). Differential thermal analysis (DTA) curves were recorded on an HCT-1 thermal analyzer (Henven, China). Powder sized 105–125 μm was used for the DTA analysis. The heating rate was 5 °C/min. Glass transition (T_g) and crystallization (T_p) temperatures were determined from the DTA curves.

3. Results and discussion

3.1. Direct vitrification of the flocculate

The composition of the raw flocculate is shown in Table 2. A large LOI figure (23.9%) is shown for the raw flocculate. This loss was mainly due to combustion of the organic flocculating agents used in the water treatment, the loss of adsorbed and crystalline water, and the decomposition of whewellite (see the XRD results). The rest of components in the raw waste are mainly SiO_2, Al_2O_3, CaO and Na_2O, which are the basic constituents of commercial silicate glasses. It should be noted that the content of SO_3 (4.83%) is relatively high, which means that the corrosion of crucibles used for glass melting may be increased (Bingham and Hand, 2008). In addition, La_2O_3 and CeO_2 were originated from the catalyst production and might be helpful for improving glass chemical durability and optical properties [12].

The compositions of the samples which were calcined at 1250, 1300 and 1350 °C are also summarized in Table 2. Since most of the volatile components have been removed after the calcination, the amounts of the main components in the calcined products increase significantly when compared with

Table 2
Chemical composition of the raw flocculate and the calcined products (wt%).

	Raw flocculate	Calcined products		
		1250 °C	1300 °C	1350 °C
SiO_2	39.04	54.41	55.15	55.72
Al_2O_3	14.70	20.20	20.45	21.25
CaO	5.60	7.82	7.94	7.84
Fe_2O_3	0.37	0.45	0.47	0.47
MgO	0.29	0.37	0.46	0.42
Na_2O	7.33	10.60	9.52	9.75
SO_3	4.91	2.59	1.90	0.52
La_2O_3	1.60	2.22	2.17	2.20
CeO_2	0.76	1.05	1.09	1.05
Cl	1.1	—	0.09	0.10
LOI	23.9			
Trace	0.39	0.24	0.61	0.45

those in the raw flocculate. In fact, the total weight losses of the samples calcined at 1250, 1300 and 1350 °C are 24.68, 25.7 and 27.63 wt%, respectively. These figures are larger than the LOI figure (23.9%) of the raw flocculate. The differences are mainly due to the evaporation of SO_3, which was produced by the decomposition of bassanite and hauyne (see the XRD results) at elevated calcination temperatures. In addition, there was certainly also loss of chemically bound water upon these calcinations. It should be mentioned here that the emission of SO_3 is strictly controlled in China. Desulphurization is necessary to reduce the pollution. The desulphurization then produces more gypsum which could be used as the flocculating agent. Therefore, if the flocculate is recycled in the future for the glass production, the potential environmental effect of the evaporation of SO_3 is controllable.

Depicted in Fig. 1 are the XRD patterns of the raw flocculate and the calcined products. The results show that zeolite Y, whewellite, bassanite, kaolinite are the major phases in the raw flocculate (Fig. 1a). Among them, zeolite Y and kaolinite were from catalysts. Whewellite and bassanite were generated in the waste water treatment process. After the flocculate was calcined at 1250–1300 °C, it turned opaque. XRD analysis indicates the formation of hauyne in the calcined products (Fig. 1b–c). Further increasing the calcination temperature to 1350 °C, the flocculate turned completely transparent. The XRD pattern of this product only shows a halo, characteristic of the amorphous state (Fig. 1d).

The DTA curve of the sample which was directly vitrified at 1350 °C is shown in Fig. 2. The glass has a transition temperature (T_g) of 750 °C, much higher than the commercial soda-lime-silicate glasses. This is attributed to the high content of Al_2O_3 in the sample [13]. Since a sharp crystallization peak at 925 °C is shown in the DTA curve, block glass sample was thermally treated at 925 °C for 1 h in order to check its crystallization tendency. However, not obvious crystallization was observed after the thermal treatment. This means that the bulk glass is resistant to crystallization. Since glass powder was used in the DTA measurement, the strong exothermic peak in the DTA curve implies that the glass sample has a tendency to surface crystallization [14].

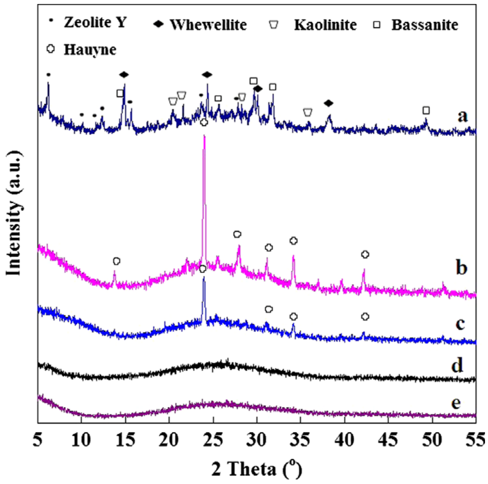

Fig. 1. X-ray diffractograms of the raw flocculate (a) and of the samples calcined at 1250 °C (b), 1300 °C (c) ,and 1350 °C (d).

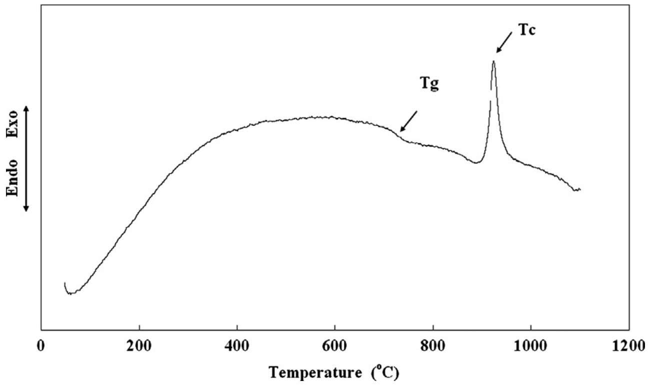

Fig. 2. DTA curve of the glass sample vitrified at 1350 °C.

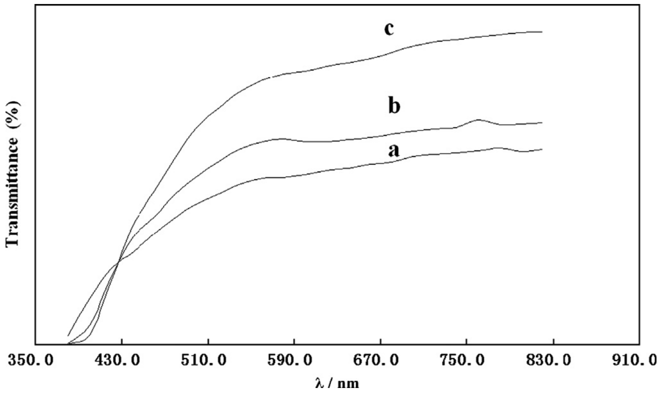

Fig. 3. Transmittance spectra of the directly vitrified sample (a), samples M0 (b) and Mg12 (c).

The density of the directly vitrified product is 2.542 g/cm^3. The weight loss of the glass sample after being boiled in a water bath for 1 h is 0.37%. Under the same conditions, the data for commercial float and container glasses are 0.24% and 0.34%, respectively. Both the density and weight loss values are comparable to those of common soda-lime-silicate glasses. The visible light transmittance spectrum of the directly verified glass is shown in Fig. 3a, which indicates that the sample selectively absorbs visible light with wavelength smaller than 550 nm. As a result, the glass sample is yellow. This color is mainly due to the existence of Fe^{3+} ions in the melt [15].

The above results suggest that the waste water flocculate can be directly vitrified at 1350 °C to form a chemically stable and crystallization-resistant glass without the addition of other components. However, even if the melting temperature was raised to 1400 °C, the viscosity of the glass melt was very high. The elimination of bubbles from the melt to form a pore-free glass and the shaping of glass was difficult. Therefore, the directly verified glass may only be used to prepare base glazes for ceramics [16].

3.2. Vitrification of the flocculate with mineral additions

The first attempt to reduce the viscosity of the glass melt with the addition of soda powder as reflux was not successful.

Thenardite and sodium calcium sulfate were formed on the top of the glass melt. This is due to the high content of SO_3 in the flocculate.

To effectively reduce the glass viscosity and facilitate the glass refining and forming, the contents of CaO and MgO in the glass composition were increased [12]. As expected, the high-temperature viscosity of the melts was greatly reduced and the melt could be easily poured out of the crucible for glass forming. Transparent glasses were obtained in the cases of M0, M4, M8, and M12. However, sample M16 was partially devitrified, suggesting a possible phase separation in this sample due to its high content of MgO. Therefore, sample M16 will not be further discussed.

Physical and chemical properties of glasses M0–M12 are compared in Fig. 4. It can be seen that the density, the Vickers microhardness (V_{HD}) and the weight-loss increase with the increase of MgO (Fig. 4a,b,c). The increasing weight loss (Fig. 4c) indicates that the chemical durability of the obtained glass decreases with MgO. The changes of the physical and chemical properties of the glasses reflect the variation of glass structure with the addition of MgO.

FTIR spectra of the samples are shown in Fig. 5. With the increase of MgO, the following changes can be observed in the spectra. The band at around 490 cm^{-1} corresponding to the bending vibration of Si–O–Si and O–Si–O bonds [17] gradually shifts to larger wave-numbers. The band at 974 cm^{-1} ascribed to the asymmetric stretching vibration of Si–O–Si bonds [18] in M0 shift to a larger wave-number in the case of M4, indicating an increase in the Q^3 and Q^4 species. However, from M4–M12, this band shifts to smaller wave-numbers again, which suggests the increase in the amount of Q^1 and Q^2 species [19]. Similarly, the band at around 695 cm^{-1} ascribed to the Si–O–Si symmetric stretching [17] first becomes more symmetric from M0 to M4 and M8, then the asymmetry of this band increases again for sample M12, suggesting the first increase and then the decrease of bridging oxygen atoms in the glass networks [17]. These changes in the spectra identify that the glass network are generally strengthened with the addition of MgO. However, with the increasing addition of MgO, the glass network tends to be weakened again. Calculations show that following the increase of MgO, the molar ratios of (Na_2O+K_2O+CaO)/(Al_2O_3+MgO) in glasses M0, M4, M8 and M12 are 3.08, 2.33, 1.87 and 1.57, respectively. Nevertheless, the ratios of (Na_2O+K_2O+CaO)/(MgO) decrease from 2.20 for M0 to 0.85, 0.53 and 0.38 from M4, M8 and M12. Therefore, MgO which was introduced by the flocculate rather then the added dolomite acts as a network former in sample M0. However, with the increase of MgO, partial Mg^{2+} ions may be located in the voids of the silicate glass network of other samples (especially of M12) [20].

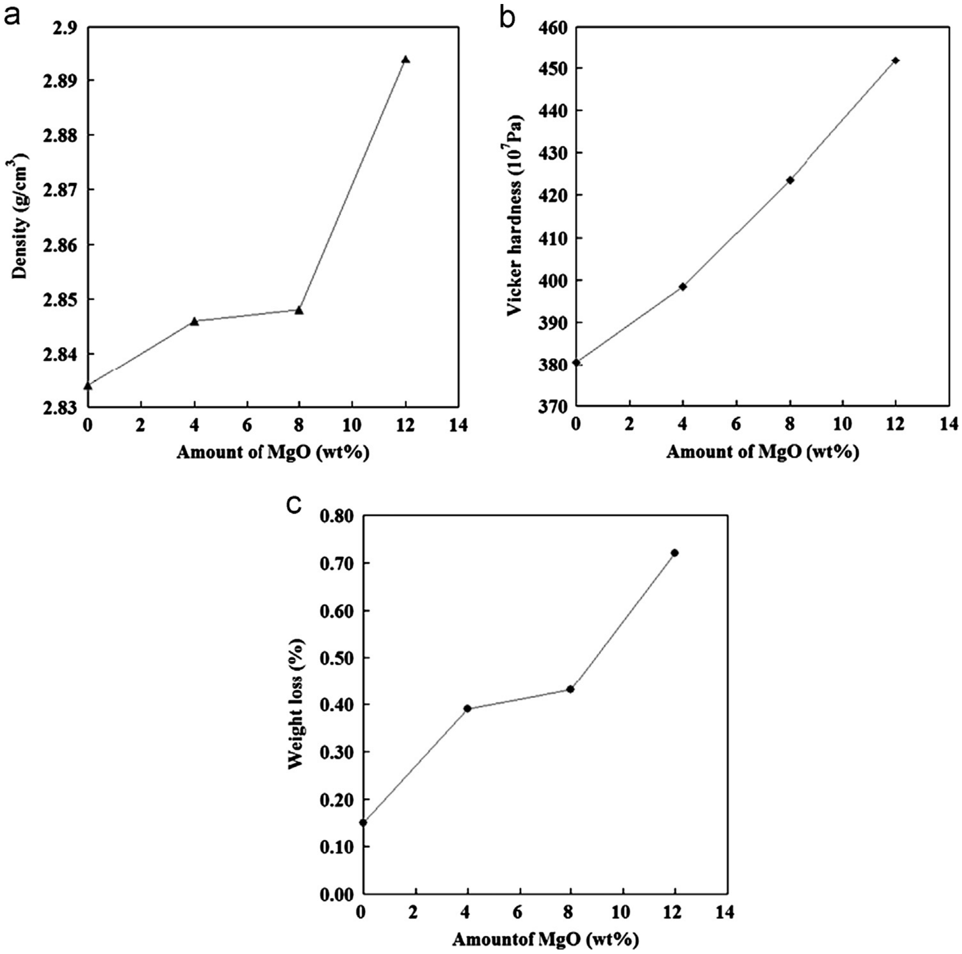

Fig. 4. The density (a), Vickers microhardness (b) and chemical durability (c) of the glasses with different MgO additions.

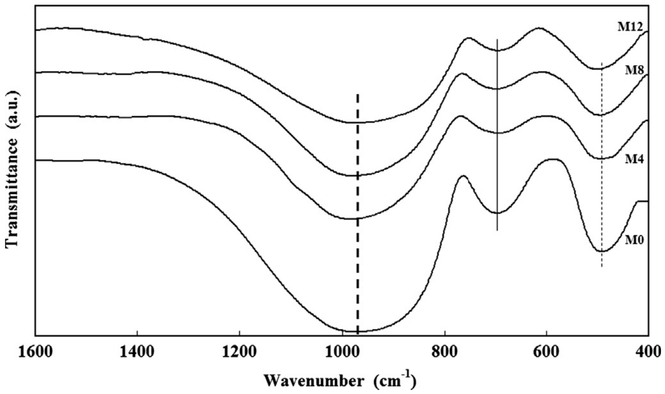

Fig. 5. FTIR spectra of the glass samples.

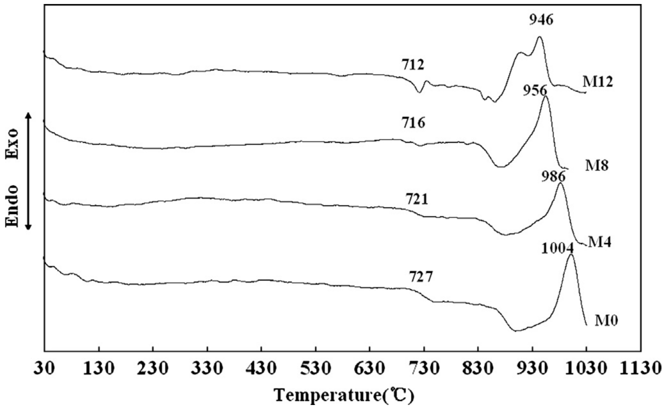

Fig. 6. DTA curves of glass samples.

A comparison of the visible-light transmittance spectra in Fig. 3 demonstrates that the addition of MgO does not result in any change of the color of the obtained glasses. However, the transmittance increases with the mineral additions, which is simply due to the decrease in the concentration of Fe^{3+}.

DTA curves of glass samples M0–M12 are depicted in Fig. 6. It shows that when the amount of MgO is increased, the glass transition temperatures (T_g) slightly decreases from 727 to 712 °C. In contrast, the crystallization temperature (T_c) significantly decreases from 1004 °C (sample M0) to 946 °C (sample M12). In addition, one can see that sample M12 depicts a second transition point and a doublet crystallization peak. This may imply that glass M12 has a tendency to phase separation on micro-scale [21]. It was mentioned before that glass M16 showed visible phase separation on macro-scale. The results suggest that MgO decreases the viscosity of the glass and facilitates the glass phase separation and crystallization.

4. Conclusion

The following conclusions can be drawn from this study:

(a) The studied waste water flocculate generated in a FCC catalyst manufacturer has Na_2O, CaO, Al_2O_3 and SiO_2 as main components. Zeolite Y, whewellite, bassanite and kaolinite are main phases in the flocculate.

(b) Upon calcining the waste water flocculate up to 1250 and 1300 °C, the original crystalline phases in the flocculate disappear and hauyne is formed. When the calcination temperature is 1350 °C, the flocculate can be fully vitrified without any other additions. The density and chemical durability of the directly vitrified glass are comparable to those of commercial float glass. However, the viscosity of the glass melt is very high.

(c) Glass melts with improved workability can be obtained after dolomite, limestone and fluorite are introduced into the batches containing the flocculate. The density, micro-hardness of the prepared glasses increase with MgO, however, the chemical durability, transition and crystallization temperatures decrease.

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References

[1] D.M. Franks, D.V. Boger, C.M. Cŏte, D.R. Mulligan, Sustainable development principles for the disposal of mining and mineral processing wastes, Resources Policy 36 (2011) 114–122.

[2] C. Fabiana, P. Mario, Waste management and problems of ground water pollution in karst environments in the context of a post-conflict scenario: the case of Mostar (Bosnia Herzegovina), Habitat International (2009) 63–72.

[3] R.U. Ayres, Metals recycling: economic and environmental implications, Resources Conservation and Recycling 21 (1997) 145–173.

[4] C. Ferreira, A. Ribeiro, L. Ottosen, Possible applications for municipal solid waste fly ash, Journal of Hazardous Materials 96 (2003) 201–216.

[5] P. Colombo, G. Brusatin, E. Bernardo, G. Scarinci, Inertization and reuse of waste materials by vitrification and fabrication of glass-based products, Current Opinion in Solid State and Materials Science 7 (2003) 225–239.

[6] J.K. Yang, D.D. Zhang, J. Hou, B.P. He, B. Xiao, Preparation of glass–ceramics from red mud in the aluminium industries, Ceramics International 34 (2008) 125–130.

[7] M. Erol, S. Küçükbayrak, A. Ersoy-Meriçboyu, Production of glass–ceramics obtained from industrial wastes by means of controlled nucleation and crystallization, Chemical Engineering Journal 132 (2007) 335–343.

[8] F. He, Y. Fang, J. Xie, J. Xie, Fabrication and characterization of glass–ceramics materials developed from steel slag waste, Materials and Design 42 (2012) 198–203 in Chinese.

[9] E. Bernardo, R. Castellan, S. Hreglich, Sintered glass–ceramics from mixtures of wastes, Ceramics International 33 (2007) 27–33.

[10] J. Ma, C.Z. Chen, D.G. Wang, X. Shao, C.Z. Wang, H.M. Zhang, Effect of MgO addition on the crystallization and in vitro bioactivity of glass ceramics in the CaO–MgO–SiO_2–P_2O_5 system, Ceramics International 38 (2012) 6677–6684.

[11] L. Wu, Q. Zhou, Y.H. Deng, M.X. Zhu, Automatically analyzing the impress image of Vickers hardness test using wavelet, China Mechanics and Engineering 15 (2004) 498–500 in Chinese.

[12] H. Scholze, in: M.J. Lakin (Ed.), Glass, Nature, Structure and properties, Spring-Verlag Inc., New York, 1990.

[13] Y. Xiao, M. Oorsprong, Y. Yang, J.H.L. Voncken, Vitrification of bottom ash from a municipal solid waste incinerator, Waste Management 28 (2008) 1020–1026.

[14] M. Rezvani, B.E. Yekta, V.K. Marghussian, Utilization of DTA in determination of crystallization mechanism in SiO_2–Al_2O_3–CaO–MgO (R_2O) glasses in presence of various nuclei, Journal of European Ceramic Society 25 (2005) 1525–1530.

[15] J.H. Hwang, C.Y. Kim, T.Y. Lim, S.S. Kim, Stabilization of color conversion process of various colors in glass production, Journal of Non-Crystalline Solids 354 (2008) 1431–1434.

[16] F.J. Torres, J. Alarcón, Pyroxene-based glass–ceramics as glazes for floor tiles, Journal of the European Ceramic Society 25 (2005) 349–355.

[17] A.M. Efimov, Section 1. Optical properties of oxide glasses: quantitative IR spectroscopy: applications to studying glass structure and properties, Journal of Non-Crystalline Solids 203 (1996) 1–11.

[18] L.P. Yu, H.N. Xiao, Y. Cheng, Influence of magnesia on the structure and properties of MgO–Al_2O_3–SiO_2–F^- glass–ceramics, Ceramics International 34 (2008) 63–68.

[19] J. Nordstrtröm, E. Nilsson, P. Jarvol, M. Nayeri, A. Palmqvist, J. Bergenholtz, A. Matic, Concentration- and pH-dependence of highly alkaline sodium silicate solutions, Journal of Colloid and Interface Science 356 (2011) 37–45.

[20] V.V. Gorbachev, An x-ray spectral study of the state of magnesium ions in sodium magnesium and sodium calcium magnesium silicate calcium magnesium silicate glasses, Soviet Journal of Glass Physics and Chemistry 9 (1983) 447–452.

[21] C.T. Moynihan, P.B. Macedo, I.D. Aggarwal, U.E. Schnaus, Direct observation of the double glass transition in a phase-separated glass, Journal of Non-Crystalline Solids 6 (1971) 322–328.