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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_{α}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