J Therm Anal Calorim (2012) 108:493–496
DOI 10.1007/s10973-011-1961-3

Study of properties of the glass batch melting filter dust

**Zuzana Jakubíková · Marek Liška ·
Alfonz Plško · Jana Pagáčová**

3rd Joint Czech-Hungarian-Polish-Slovak Thermoanalytical Conference Special Chapter

Abstract The filter dust from the container glass production was studied by the X-Ray powder diffraction, differential thermal analysis (DTA), X-Ray fluorescent spectroscopy, and Raman spectroscopy. The analysis of the elemental composition indicated that the major portion ($\approx$96 wt%) of filter dust is comprised of sulfates. Predominant abundance of sodium sulfate was confirmed by comparative DTA of investigated filter dust. The characteristic redox property (COD—Chemical Oxygen Demand) was determined. The raw materials used in manufacturing of container glass in Vetropack Nemšová with 0, 25, 50, 75 or 100 wt% of filter dust as a substitution of sulfate raw material were used for the preparation of samples of glass batch. Thermal properties of prepared samples were characterized by means of DTA. The substitution of sulfate raw material by filter dust does not significantly affect the thermal properties of the examined glass batches and consequently the course of the glass melting.

Keywords Filter dust · Container glass · Glass batch melting · Differential thermal analysis (DTA)

Z. Jakubíková (✉) · M. Liška
Vitrum Laugaricio—Joint Glass Center of the Institute of Inorganic Chemistry, Slovak Academy of Sciences, Alexander Dubček University of Trenčín, Faculty of Chemical and Food Technology, Slovak Technical University, and RONA, j.s.c, Študentská 2, 911 50 Trenčín, Slovak Republic
e-mail: zuzana.jakubikova@tnuni.sk

A. Plško
Alexander Dubček University of Trenčín, Študentská 2, 911 50 Trenčín, Slovak Republic

J. Pagáčová
Faculty of Industrial Technologies Alexander Dubček University of Trenčín, I. Krasku 492, SK–020 32 Púchov, Slovak Republic

Introduction

In the glass manufacturing, waste of various types and character is produced depending on the type of glass and technology used to its melting. The cullet and the filter dust are wastes that are recycled in the glass manufacturing. While problem of cullet recycling has been solved and this method is commonly used in container glass production, recycling of filter dust that is collected at the electrostatic or cloth separating filters has been gradually introduced under the growing environmental and economic pressure. However, the chemical composition of filter dust is problematic as it influences the process of glass melting and fining and also certain properties of the final product. From the chemical composition point of view, the major part of container glass filter dust comprises sulfates which are important in the glass fining. The excess of sulfate content could have undesirable effect in the form of sulfate melt phase separation on the surface of melted glass. Other case is manufacturing of high-lead crystal glass, where the filter dust contains an excessive amount of PbO [1, 2]. The filter dust compositional problem is analyzed in detail in a study by Smrcek [3]. His results are based on the published data of samples from various Czech glassworks.

Therefore, recycling of dust in the glass manufacturing has to take into account the source of dust (type of glass, raw materials, and melting method), which crucially influences its chemical and mineralogical composition, as well as the type of glass produced, in which the dust will be added (the case of using of strange filter dust produced in another glasswork is envisaged in this respect). The present study is devoted to initial examining of specific filter dust produced at the containers glass manufacturing in the glass factory Vetropack Holding AG in Nemšová.

Experimental part and results

The investigated dust samples were collected from electrostatic separating filters. Sustainable monitoring of elemental composition of filter dust realized in Vetropack Nemšová by means of X-ray fluorescence spectroscopy (Brucker, Explorer) provided average values summarized in Table 1. The results suggest that about 96 wt% of filter dust is formed by sulfates.

The Raman spectra were measured on a Renishaw Invia Raman spectrometer, using an Ar-laser excitation line of 514 nm. In the spectrum (Fig. 1), characteristic vibrations of SO_4 structural units lying in area between 456 and 462 cm^{-1} with a maximum at 454 cm^{-1}, the 622 and 1006 cm^{-1} were identified [4–6].

X-ray powder diffraction (Bruker D8 diffractometer, Cu–Kα, ICT Prague) also confirmed a content of Ca_2SiO_4, Na_2SO_4, and Pb_3SiO_5 except for the amorphous phase portion (Fig. 2).

Total content of organic and inorganic compounds oxidizable by potassium dichromate under acidic condition with catalytic amount of Ag^+ ions was expressed as a consumption of oxygen in mg necessary to oxidize 1 g of filter dust sample (COD test—Chemical oxygen demand test [7]. The obtained value was COD = 19.1 mg/g.

Differential thermal analysis (DTA) measurements were performed on DERIVATOGRAPH MOM Budapest equipped with the PC A-D data collection, using the heating rate of 10 °C/min. and the sample mass of m_{sample} = 0.15 g. On the DTA record of investigated filter dust (Fig. 3) two significant endothermic peaks can be seen. The first one at the temperature about 330 °C could be ascribed to thermal decomposition of KNO_3 [8]. In the temperature range around 320 °C, endothermic effect associated with the decomposition of calcium carbonate T_d = 315 °C can be seen. Significant endothermic peak at the temperature range 830–900 °C corresponds to Na_2SO_4 melting. Fig. 4 show the DTA record of sulfate (technical raw material) containing sodium sulfate. Analogous course of DTA curves in Figs. 3, 4 confirm the dominant content of sulfates in the sample of filter dust.

Samples of glass batch with different content of filter dust were prepared. They consisted of raw materials used in manufacturing of container glass in Vetropack Holding AG in Nemšová with 0, 25, 50, 75, or 100 wt% of filter dust as a substitution of sulfate raw material. The prepared samples of glass batch were studied by means of DTA (DERIVATOGRAHP MOM Budapest), using the heating rate of 10 °C/min in the temperature range of 50–1000 °C. Thermal properties of prepared glass batch samples were studied in terms of products resulting from cross-reactions between different components of the batch with an added filter dust. On the DTA records (Fig. 5) of prepared samples, two significant endothermic peaks were observed. One effect is observed in temperature range of 390–420 °C and the second one about 870 °C. Analogous course of DTA curves of glass batch samples with different content of filter dust suggests that the filter dust as a substitute for sulfate does not affect the glass batch thermal behavior in the investigated temperature interval.

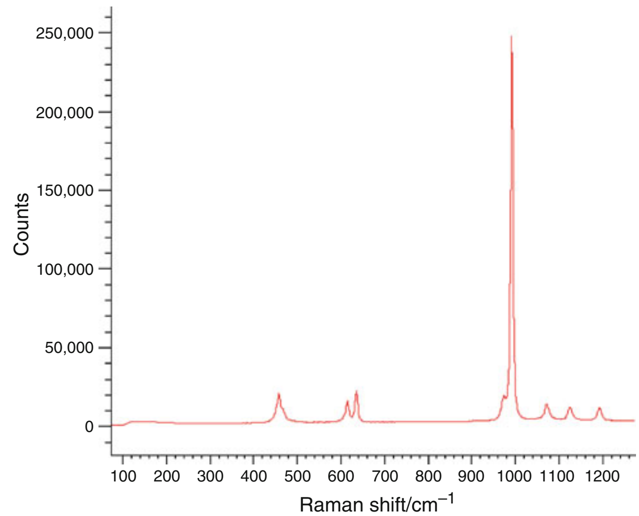

Fig. 1 Raman spectrum of the filter dust

Oxidation–reduction reactions play very important role in the glass technology. The wide temperature range covers all the basic processes of glass production: melting, homogenization, processing, and cooling. In the melting area, the redox affects mainly fining and color [9]. Effect of addition of recycled filter dust on the batch melting process was investigated in the optical observation furnace. Melting and clearing observed for "pure" batch (i.e., glass

Table 1 Average composition of the investigated dust from the Vetropack Nemšová, expressed as oxide

Oxide	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	Cr_2O_3	Sb_2O_3
wt%	0.718	0.080	0.0412	0.641	0.008	36.68	4.298	0.633	0.775
Oxide	SO_3	PbO	P_2O_5	MnO	CuO	ZnO	As_2O_3	Rb_2O	SnO
wt%	51.07	4.431	0.109	0.001	0.021	0.362	0.040	0.025	0.051

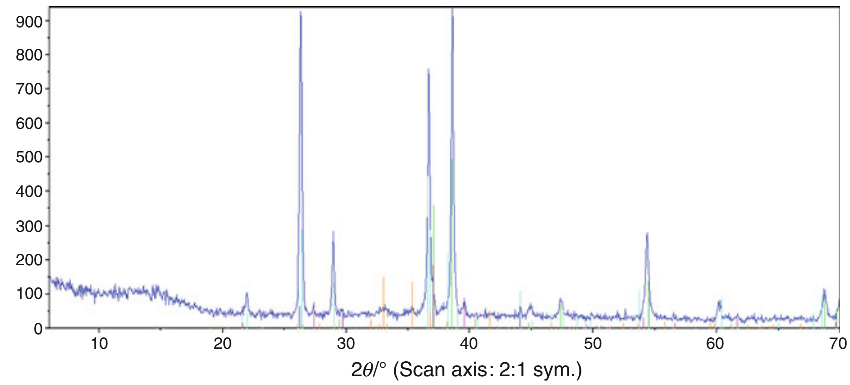

Fig. 2 X-ray powder diffraction of the filter dust

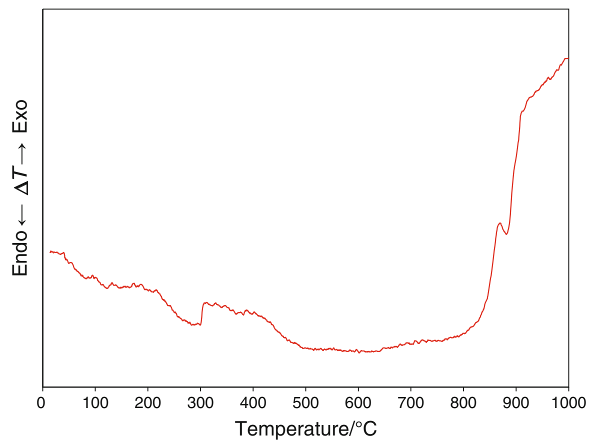

Fig. 3 DTA curves of the filter dust

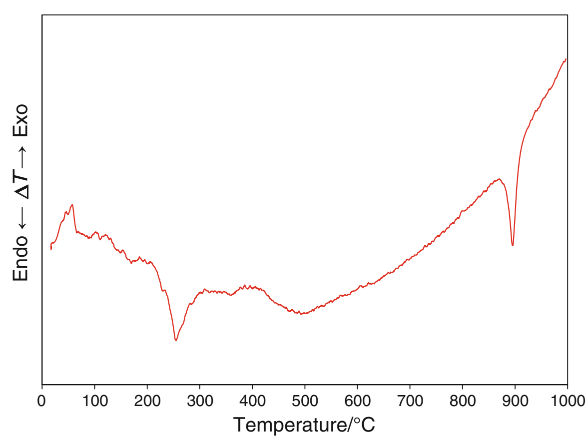

Fig. 4 DTA curves of sulfate

batch without addition of the filter dust) was considered as a reference state. The observational oven temperature regime replicating the process of glass melting batch was used for monitoring of fining process. During the experiment, there was observed no significant difference between the dust-free batch melting and the melting of prepared samples with different content of filter dust.

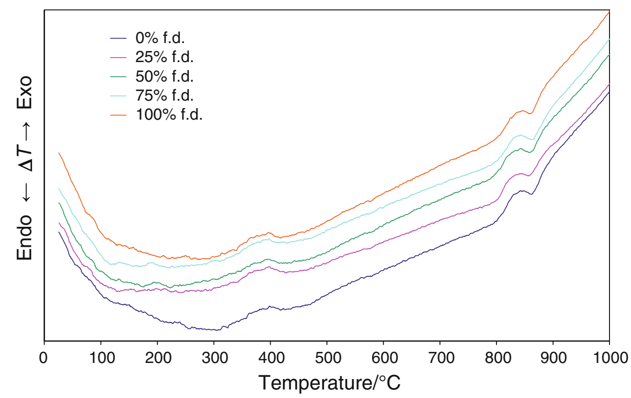

Fig. 5 DTA curves of glass batch and samples with different content of filter dust

Conclusions

The studied filter dust from the container glass production consists mainly of the sodium sulfate and potassium sulfate. It was found that partial or almost complete replacement of the sulfate raw material in the glass batch with the filter dust does not significantly affect the thermal properties of the prepared glass batches and consequently the course of the glass melting. These experimental results will be utilized within the filter dust recycling technology in the production of container glass.

Acknowledgements This study was supported by the Agency for Promotion Research and Development under the contract No. APVV LPP-1-0156-09 and by the Slovak Grant Agency for Science under the grant No. VEGA 1/0330/09.

References

1. Schaeffer HA. Recycling of cullet and filter dust in the German glass industry. Glass Sci Technol. 1996;69:101–6.
2. Hlaváč J. Basics of silicate technology. Praha: SNTL; 1988 (In Czech).
3. Smrček A. Deposits from industrial glass meeting tank furnaces. Sklář a Keramik. 2005;10:265–70 (In Czech).

4. Lenoir M, Grandjean A, Poissonnet S, Neuville DR. Quantization of sulphate solubility in borosilicate glasses using Raman spectroscopy. J Non-Cryst Solids. 2009;355:1468–73.
5. Krishnan TS, Narayanan PS. Raman spectrum of crystalline cadmium sulphate. Proc Math Sci. 1955;41:121–4.
6. Jakubíková Z, Liška M, Chromčíková M, Kraxner J, Pagáčová J. Study and analysis of properties of the glass batch melting. 32th international Czech and Slovak calorimetric seminar. Pardubice: University of Pardubice; 2010.
7. Křesťan V, et al. The analysis of glass material and raw material for its production. Praha: Práh; 2001 (In Czech).
8. Valigura D, et al. Chemical tables. Bratislava: STU; 2004 (In Slovak).
9. Smrček A, et al. Glass melting. Jablonec nad Nisou: ČSS; 2008 (In Czech).