Journal of Thermal Analysis and Calorimetry, Vol. 67 (2002) 249–255

THERMAL AND SINTERING CHARACTERIZATION OF IGCC SLAG

A. Acosta[1]*, I. Iglesias*[1]*, M. Aineto*[1]*, M. Romero*[2] *and J. Ma. Rincón*[2]

[1]Laboratory of Applied Mineralogy, Universidad de Castilla, La Mancha, Ciudad Real, Spain
[2]The Glass Ceramics Lab., Inst. E. Torroja de Ciencias de la Construcción, CSIC, Madrid, Spain

Abstract

IGCC slag is a vitreous residual product from the new induction gasification combined cycle gasification thermal power plants. In order to characterize this waste as secondary new material for the production of new glasses and glass-ceramics as construction materials; this slag from the Puertollano, Ciudad Real, Spain power plants has been fully thermally investigated. After controlled heating this waste gives rise to hematite, anorthite, and cristobalite crystallized materials.

Keywords: IGCC, industrial waste, slag, thermal characterization

Introduction

Induction gasification combined cycle (IGCC) process is a fully different electrical power production process for getting energy from burning of a mixture coal and coke coming from petroleum refining. In this new process inorganic wastes are produced as fly ashes and slag residual material. IGCC technology is based in a coal gasification process, namely the conversion of coal into combustible gas that is then subjected to an exhaustive cleaning process [1]. The result is a synthetic gas virtually free of pollutants that can be burned with high efficiency in a combined – cycle electricity – generating unit. The gross energy efficiency of this power plant is 47.12% while the net efficiency reaches 42.5% [2].

A solid waste is obtained in the form of vitrified slag not soluble in water, and therefore, the use or storage presents no environmental problems. The sulphur is recovered in elementary form and is therefore suitable as a marketing product. This is not the case of slag that, until now, has not been recycled to other industrial processes to be eventually used as secondary raw material. This slag waste is produced in a quantity of 100 000 ton/year in the only one plant existing in Spain at this moment in working operation. This plant has been the second installed production in Europe [3, 4]. Nowadays, this waste is used as a filling mining material.

With respect to its composition this waste is unique as an inorganic residue and is not related to other slag obtained in conventional thermal power plants [5]. Due to the intrinsic nature of IGCC process this new type of power plant gives rise to a huge amount of slag with respect to the fly ash produced in the same plant. Up to now, it

1418–2874/2002/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

has never been proposed as a candidate for recycling as a secondary raw material in other industries. Nevertheless, since 1996 some European research projects have been carried out in the CECA Programme [6, 7]. On the other hand, recently similar inorganic industrial wastes have been investigated for the production of new glasses and glass-ceramics [8]. Recycling as glasses and glass-ceramics of industrial wastes is being considered recently as a possibility for inertization and production of new materials [9].

The aim of this paper is to show the thermal behaviour by all the usual thermal methods of a representative vitreous slag from the Puertollano IGCC thermal power plant.

Experimental

Materials

The general physico-chemical characterization of a IGCC slag from Puertollano company (ELCOGAS, S.A.) has been given in a previous paper [5]. Thus, the sample E-11 as most representative of this type of slag has been selected for a more extended thermal behaviour characterization. This slag is composed basically of SiO_2 (57.27%), Al_2O_3 (23.01%), CaO (8.39%) and Fe_2O_3 (5.67%) as major components and minor components below 2.5%: K_2O, Na_2O, MgO, TiO_2, as well as sulphur (expressed as SO_3=1.48%) and very small proportion of MnO and P_2O_5 (0.06%). The ternary components are ($9.46CaO\cdot 25.95Al_2O_3\cdot 64.59SiO_2$% composition). The main structure characteristic of this waste is its vitreous (amorphous XRD exploration) character, with density value of 2.59 g cm^{-3}.

Methods

The most useful methods for thermal characterization have been applied in order to know the high temperature as well as sintering capabilities of this vitreous slag: an equipment Adhamel-Llomargy DTA/TG has been used in air static atmosphere with a heating rate of 15°C min^{-1} to 1100°C, HSM (heating stage microscopy) (II A-P Leitz) at 10°C min^{-1} in an ambient atmosphere.

The TTT (time-temperature-transformation) curve has been determined by following static heat treatments of powdered sample (<50 microns) at previously selected time (0.5–4 h) and temperature (850–1050°C) ranges. These treatments have been carried out by introducing 0.5 g from ambient to previously stabilized temperature for each specimen into a small kanthal furnace camera and cooling directly to the ambient air after heating ('air quenching method'). The crystalline phases formed after TTT thermal treatments have been identified by XRD with λ=1.5405 (Philips PW-1710).

Results and discussion

Figure 1 shows the DTA analysis of the vitreous investigated slag. T_g vitreous transformation temperature corresponds to the down slope of DTA curves detected at 346°C [10]. DTA trace gives also an exothermic peak produced at 637°C, due to the hematite formation [11].

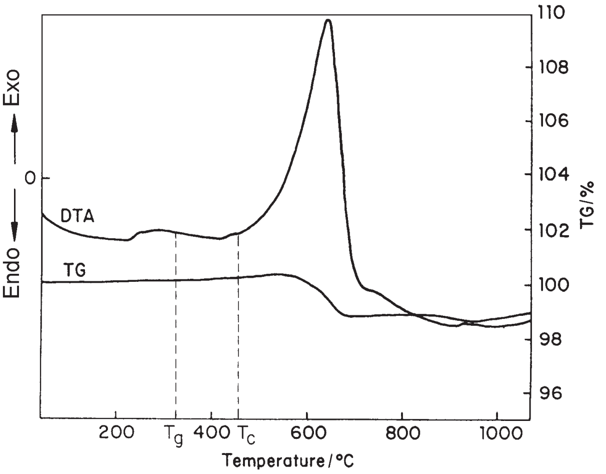

Fig. 1 DTA/TG of E-11 slag sample with 15°C min^{-1} heating rate

With respect to TG analysis several jumps of relative mass increases and losses are observed due to oxygen interchange with the iron oxide species. The higher loss is produced in the 550–700°C range with 1.25% percentage which can be due to the transformation of hematite phase observed by DTA at approximately 650°C.

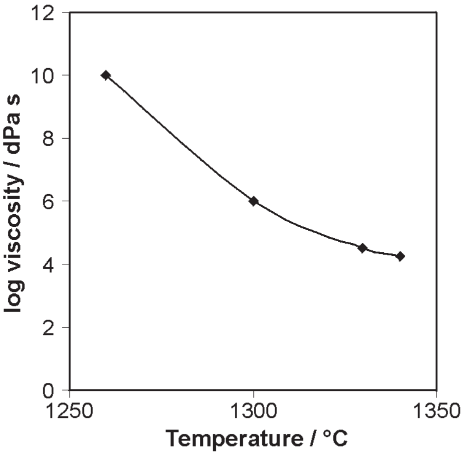

Fig. 2 Relative variation of viscosity with temperature determined by HSM

Figure 2 shows HSM giving the relative viscosity variation with temperature of the IGCC slag. The higher temperature (1340°C) corresponds to fluidity point of this slag. The relative variation of viscosity with temperature is typical of a 'short glass' behaviour with a variation of 10 to 4 dPas (logη) for a thermal range of 80°C. As is well known [10, 12] 'short glasses' depict high tendency to devitrification of crystalline phases from the original glass when they are thermally heated.

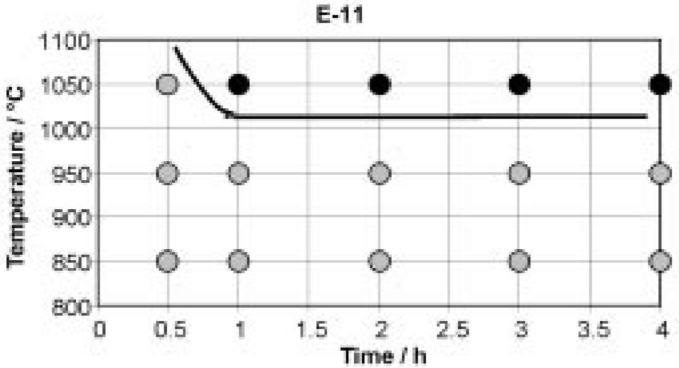

Fig. 3 TTT curve for the IGCC slag waste here investigated; ○ – partial crystallization, ● – crystallization

Figure 3 shows the TTT curve, where the range of crystallization for this glassy slag can be seen. The crystallization range is relatively high as compared to other $CaO–Al_2O_3–SiO_2$ glasses [13, 14] obtained from fly ashes of conventional carbon power plants. Partial crystallization is produced at high temperatures (950–1050°C) and longer times (4–1 h), respectively.

However, from lower thermal treatments (850–950°C) small crystallization has been detected, which is not growing with time and temperature. This initial crystallization must be due to surface crystallization produced by the iron diffusion.

From the average chemical composition located in the ternary: $CaO–Al_2O_3–SiO_2$ system, these vitreous slags can be located in the puzzolanic materials zone, with higher CaO and SiO_2 as compared to conventional fly ashes [14].

Figure 4 shows XRD with identification and evolution of phases at 850 and 1050°C (Fig. 4b and c) and XRD pattern form the original slag (Fig. 4a). The first crystalline phase detected is hematite at 850°C for 30 min thermal treatment based on the diffraction lines corresponding to the interplanar distances d=2.70 and 2.52 Å. At 950°C for 30 min thermal treatment, the phases detected are hematite and incipient feldspar phase (anorthite: d=3.20 Å , I=100%). Similarly, at higher temperature (1050°C) and 30 min is crystallized anorthite based on the diffraction lines corresponding to the interplanar distances d=3.20, 3.70 and 2.90 Å) and cristobalite (other high temperature polymorph of SiO_2) and spinel which are compatible with hematite formation.

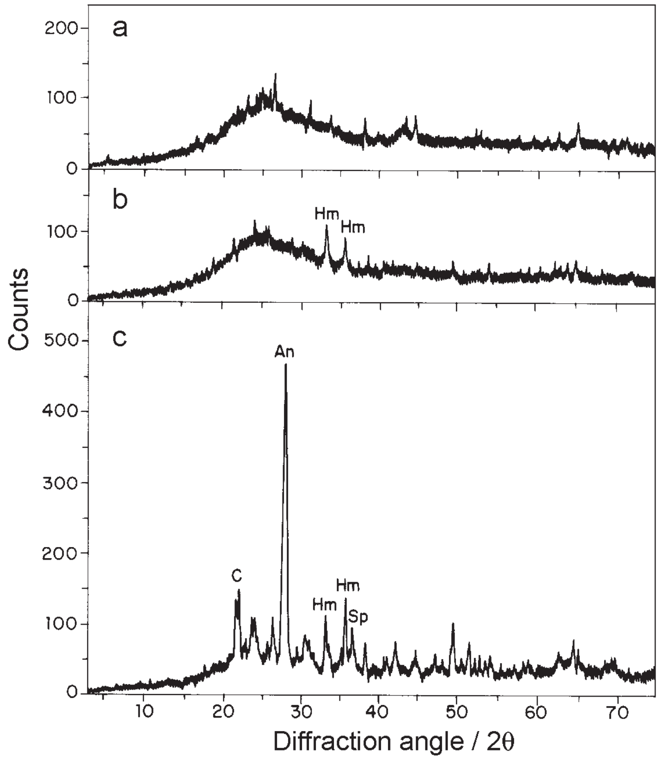

Fig. 4 XRD diagrams of IGCC slag (sample E-11) here investigated; a – original slag; b – 850°C 4 h; c – 1050°C 4 h; Hm: hematite; An: anorthite; C: cristobalite; Sp: spinel phase

By locating E-11 vitreous slag composition in the ternary diagram $CaO–Al_2O_3–SiO_2$ it can be seen in Fig. 5a that is located very close in the coexistence line of anorthite–silica and practically in 40% content of silica in the pseudobinary anorthite–silica (Fig. 5b), being close to the eutectic in this binary subsystem where the compatibility of anorthite with tridymite is possible in the cooling from liquid phase state [15, 16]. However, our results showed the crystallization of anorthite and cristobalite in the thermal treatment of this slag and not the formation of the silica phase tridymite. From the last results obtained by Longhi and Hays [16, 17] in the anorthite–silica subsystem with impurities added to SiO_2 it has been proved that glasses devitrified at 1100–1200°C for up to 12 h the silica polymorphism has been revised. There is a phase transition of cristobalite–tridymite in the presence of anorthite below 1244°C. As usual, in aluminosilicate systems the silica phase is a solid solution increasing the cristobalite stability field more than tridymite due to better accommodation of cristobalite into the aluminosilicate glassy structure [18]. Therefore, the presence of cristobalite in IGCC slag after thermal treatment is a consequence of the greater solid solution in cristobalite in the melting interval. On the other hand, E-11 composition is in the boundary of the mullite+liquid primary field of crystalli-

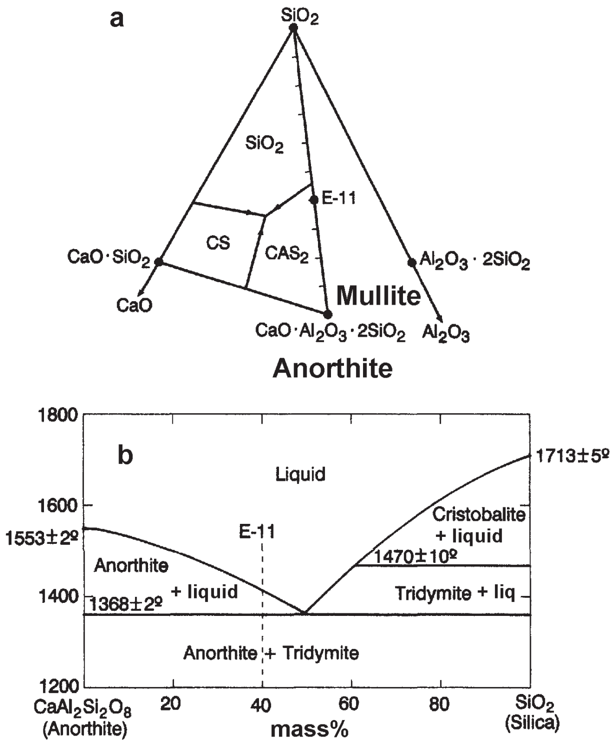

Fig. 5 a – Location of the vitreous slag E-11 in the ternary subsystem silica–anorthite–pseudowollastonite: CaO·SiO_2 (CS); CaO·Al_2O_3·2SiO_2 (CAS_2) and liquid (Liquid); b – Anorthite ($CaAl_2Si_2O_8$)–Silica (SiO_2) system (from [15], Fig. 634 in Phase Diagrams for Ceramists, Ed. by Amer. Ceram. Soc.)

zation being in principle open the possibility of precipitation of some mullite after thermal treatment of this slag. But no mullite has been clearly identified; nevertheless, not fully excluded the formation of some mullite crystals due to some X-ray diffraction lines of mullite compatibles with the quartz formation at higher temperatures of thermal treatment. Observations by electron microscopy are in progress in order to see if this mullite formation is possible from this slag.

Conclusions

From the thermal investigation behaviour of a representative IGCC residual slag it can be concluded that its vitreous character with high tendency to crystallization after controlled thermal treatment. There is a surface crystallization of hematite, while there are bulk crystallization of feldspar anorthite and spinel phases as well as cristobalite. The several pairs of temperature and time of thermal treatment can be useful for designing a wide range of new glass-ceramics produced by recycling of this industrial waste.

Many thanks are due to ELCOGAS, S.A. for financial of this research and giving approval for this publication. Also it is very acknowledged the help of the Prof. J. M. Criado from the Inst. Ciencia de los Materiales, CSIC, Sevilla for very kind help in the DTA determinations.

References

1 U. Sendín Puente, La gasificación del carbón integrada en ciclo combinado para la generación limpia de electricidad European Lecture Series on clean Coal Technologies – THERMIE Programme.
2 T. Takekmatsu, and M. Maude, IEA Coal Research, IEACR/37. March, 1991.
3 ELCOGAS. IGCC Puertollano Power Plant, Diffusion Brochure.
4 I. Méndez Vigo, (ELCOGAS); Puertollano Plant status and enviromental issues regarding the use of petroleum coke in Seminar on ‘The use of coal in mixture with wastes and residues’, Madrid, 1996.
5 A. Acosta, M. Aineto, I. Iglesias, M. Romero and J. Ma. Rincón, Materials Letters, 50 (2001) 246.
6 CECA Proyect ESC 7220-DE/072, ‘Valorization of IGCC power plant by-products as secodary raw materials in construction’ (VABYPRO).
7 CIEMAT-PROGRAMA I+D OCICARBON, Clean Coal Technologies Handbook Section 8: Ed. Comisión Europea, Directorio General de la Energía s.f.
8 J. Ma. Rincón and M. Romero, Materiales de Construcción, 242–243 (1996) 91.
9 J. Ma. Rincón, M. Romero and Ma. E. Zayas, Técnica Cerámica, 3–4 (1994) 220.
10 ‘El Vidrio’, J. M. Fernández Navarro, CSIC, Madrid. 1991.
11 R. M. Cornell and U. Schwertmann, ‘The Iron Oxides, Structure, Properties, Reactions, Occurrence and Uses’, Ed. VCH, Weinheim, Germany 1996.
12 J. M. Cáceres, J. E. García Hernández, Materiales de Construcción, 242–243 (1996) 61.
13 L. Barbieri, I. Lancellotti, T. Manfredi, I. Queralt, J. Ma Rincon and M. Romero, Fuel, 78 (1999) 271.
14 L. Barbieri, T. Manfredini, I. Queralt, M. Romero and J. Ma. Rincón, Glass Technology, 38 (1997) 165.
15 J. F. Shairer and N. L. Bowen, Bull. Soc. Geol. de Finlande, 20 (1947) 71.
16 Phase Diagrams for Ceramics, Eds L. Levin et al., DE. NBS and American Ceramic Society, 1974, pp. 302–304, Figs 6685 A–D.
17 J. Longhi and J. F. Hays, Am. J. Sci., 279 (1979) 876.
18 A. Simakin, T. Salova, M. Romero and J. Ma. Rincón, Materiales de Construcción 51 (2001) 263–264 and 5–19.