Review

A review of glass-ceramics production from silicate wastes

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Glass-ceramics are produced by crystallization of glass. It is also produced using waste materials, and particularly silicate based wastes such as: coal ash, slag, fly-ash and waste from incinerators. The production of glass-ceramics from these wastes using different methods is considered in this paper. The properties of the product are also considered; this review focused on silicate wastes into useful production of glass ceramics products. Previously, a review using general wastes applicable in glass-ceramics production has been reported. In addition to oxide composition in the waste materials, the effect of adding other oxides such as titanium oxide on the mechanical and physical properties of the product in relation to the desired property needed for various forms of applications. Avoiding incineration of the waste material for the reduction of environmental pollution, as a result of immobilization of the toxic waste in the matrix of the glass-ceramic are also considered in this review.

Key words: Effect, silicate-based waste, properties enhancement, glass-ceramics.

INTRODUCTION

Mineral waste can be defined as the residues, tailings or other non-valuable material produced after the extraction and processing of materials to form mineral products (Harrison et al., 2002). There is no universally recognized classification scheme that takes account of the economically important characteristics of the waste, especially its potential end use and the degree of processing needed. A simple scheme was proposed by Harrison et al. (2002) in Table 1 with four descriptive categories:

- Type 1 waste represents the mineral that could be used with minimal processing, largely as a construction material with classic large volume and low value industrial mineral. The market would be within a short radius of the mine, but large amounts of the waste would be removed.
- Type 2 wastes would only require a small amount of mineral processing product, for example removing iron-bearing impurities from a quartz-rich waste to produce silica sand. Large amounts of waste would be removed with a small amount of secondary waste produced. The market would be largely local with the possibilities of some national trade.

- Type 3 waste contains small amounts of valuable mineral that would require a significant level of potentially complex processing to cover. The disadvantage of this is that a large volume of mineral waste would remain and major capital investment would be needed for the processing plant. It is likely that the market for these high-value industrial mineral commodities would be international.
- Type 4 mineral waste contains very small quantities of a highly valuable target mineral (or more likely a metal content) with similar requirements and disadvantage to Type 3. The industrial revolution changed the world; it generates the great humanity process. But the industrialization is accompanied by the generation of wastes, which could be negative to the natural environment. Unfortunately, environmental issues were not remembered, as should be.

One general conclusion from Gungor and Gupta (1999) in their literature review is that environmental issues are gaining popularity among society, governments and industry due to negative environmental developments. The current state of manufacturing processes consume enormous tons of different forms of natural resources like

Table 1. Classification of mineral wastes.

Group	Description	Example	Potential end use
Type 1	Unprocessed wastes	Quarry scalpings quarry blocks colliery spoil	Fills low grade road stones, armourstone and brick clay
Type 2	Processed wastes reclaimed mineral	Silica sand waste limestone wastes building stone waste	Silica sand, kaolin, brick clay and mineral filter aglime aggregate
Type 3	Processed wastes- added- value products	Lead/zinc wastes pegmatite wastes	Fluorite, barite, feldspan, rare earths and mica heavy minerals
Type 4	Beneficiated wastes	Silica sand wastes certain mine waste	Gemstones, high value metals

Source: Mitchell and Harrison (2003).

raw-materials, energy, water, etc.

There are many reasons to increase the amount of waste being utilized or re-utilized. Firstly, disposal costs are minimized; secondly, less area is reserved for disposal, thus enabling other uses of the land and decreasing disposal permitting requirements; thirdly, there may be financial returns from the sale of the by-product or at least an offset of the processing and disposal costs; and fourthly, the by-products can replace some scarce or expensive natural resources (Ahmaruzzaman, 2010).

The economic potentials of waste management and its impact on environment have been evaluated (Hauwa, 2008).

CERAMIC PRODUCTS FROM WASTE

Waste such as ashes from coal, municipal solid waste, wood, etc., have good potential for use in ceramic products. Various ceramics systems have been shown to be suitable for producing products that are thermally and mechanically stable and exhibit good chemical durability. Palomo et al. (1999) activated fly ash for applications in building sites. The studies of Barbieri et al. (1999) and Leroy et al. (2001) are examples of the glass-ceramics obtained using fly ash. The results obtained by Zimmer and Bergmann (2007) indicate that fly ash, when mixed with traditional raw materials, has the necessary requirement to be used as a raw material for production of ceramic tiles (Table 2).

Blast-furnace slag was the first silicate waste to be thoroughly investigated as a raw material for glass-ceramics production in the late 1960s and early 1970s (Davies et al., 1970; Gross et al., 1970; Pavlushkin, 1970). It has now been established that a wide range of silicate-rich wastes, including coal ash (DeGuire and Risbud, 1984; Baccaccini et al., 1996), incinerator filter ash (Baccaccini et al., 1995; Romero et al., 1999) and red mud from zinc hydrometallurgy (Pehno et al., 1994)

can be reused in the production of glass-ceramic materials.

Fly ash is a by-product of coal, oil-fired, electric power stations and thermal power plant. An increasing amount of fly ash from power plants and urban solid waste incinerators has caused environmental problems with technological and economic damages all over the world.

Selecting raw materials and other wastes in the forms of bottom ash, slag and mining residue, new products have been developed, such as glass fibres and glass-ceramics for potential architectural and decorative applications which have chemical and mechanical properties comparable to, if not better than commercial ones (Karamanov et al., 2003; Bernardo et al., 2006).

It is also known that glasses containing from about 2 to 20 wt% T_iO_2 crystallize with the formulation of uniform fine grained microstructures (Beall and Duke, 1993; McMillan, 1976; Strnad, 1986). The optimum amount of T_iO_2 is dependent on the composition of the glass and increases with decreasing S_iO_2 content. However, the presence of more than 20 wt% T_iO_2 can lead to the precipitation of T_iO_2 crystals and a decrease in the nucleation and growth of the desired crystalline phases.

The properties of standard vitrified products are insufficient for architectural applications and structural building components, insulation or other specialized application. Yet, there is an effective way to improve these properties without major alterations to the process itself; the introduction of a controlled crystallization through a subsequent heat treatment, that is, by forming a glass-ceramic.

PRODUCTION OF GLASS-CERAMICS

Glass-ceramics articles may be produced by three routes:

1. The heat treatment of solid glass (traditional route).
2. The controlled cooling of a molten glass, known as the

Table 2. Chemical composition (wt%) of the investigated coal and incinerator ash.

Mineral	Coal fly ash content	Mineral	Incinerator fly ash content
Fe_2O_3	43.5	Na_2O	3.5
$S1O_2$	31.0	MgO	2.4
Al_2O_3	11.4	Al_2O_3	17.5
CaO	4.0	$S1O_2$	38.0
$T1O_2$	2.3	P_2O_5	1.6
ZnO	1.4	SO_3	0.2
MgO	1.3	Cl_2	-
Cr_2O_3	0.9	K_2O	1.8
Alkalis	2.2	CaO	21.1
Traces	N1,Cu, etc	T_iO_2	1.7
		Cr_2O_3	-
		MnO	0.4
		Fe_2O_3	8.0
		NiO	-
		ZnO	3.5

Source: Baccaccini and Rawlings (2002).

petrurgic method.
3. The sintering and crystallization of glass powders.

In the later case, the powders are densified at relatively low temperatures by exploiting a viscous flow sintering mechanism. After densification, the material is subjected to a crystallization heat-treatment to obtain the required glass-ceramic microstructure. Alternatively, both densification and crystallization may take place during a single sintering step.

Along with the economic advantage of using relatively low processing temperatures, the power technology route is suitable for the production of a range of advanced materials, including glass-ceramics with specified porosities and glass-ceramic matrix composites. Using the petrurgic method, the slow cooling from the molten state causes nucleation and growth of certain crystalline phases.

Therefore, the final microstructure, and hence, the properties depend mainly on the composition and the cooling rate (Baccoveini and Rawlings, 2002). Table 3 summarized the various properties of glass-ceramics obtained from silicate materials.

GLASS-CERAMIC BASED ON COAL ASH PRODUCTION

The very high iron oxide content of coal ash (Table 2) indicates the potentials for developing magnetic phases using appropriate processing. The ash received was calcined at 800°C for 2 h to remove any volatile compounds, including sulphur and carbon. The powder and petrurgic methods where implored, and gave products with different phase and microstructures. For the sintering experiments, calcined ash powder was mixed with various amounts (10 to 50 wt%) of borosilicate (pyrex) glass. The powder mixtures were uniaxial cold pressed to a cylindrical shape and sintered in air at temperatures in the range of 1,000 to 1,500°C for periods of 15 h (Baccaccini and Rawlings, 2002). The microstructure of a glass-ceramic containing equal proportion of borosilicate glass and coal ash, obtained by sintering for 5 h at 1,500°C revealed that the addition of borosilicate glass proved successful in promoting densification by viscous flow, resulting in highly dense product. The sintering process was optimized so that no 'barreling', swelling or other shape distortion effects occurred, and the samples retained their original cylindrical form. This is particularly important when fabricating components of complex shapes and good dimensional tolerances for technical applications.

The sintered materials exhibit a well-developed and reproducible glass-ceramic microstructure, comprising a silicate matrix with dispersed crystalline phases. The matrix was $B_2O_3.Fe_2O_3.CaO-S_iO_2-Al_2O_3$.glass with one of the crystalline phases enriched in metals, especially iron and titanium. This was identified as a ferrite-type phase. The most interesting feature of these samples is their magnetic behavior (Table 4). The magnetization curves are characteristics of soft ferromagnetic materials, with magnetization saturating at low fields (Baccaccini and Rawlings, 2002).

The review highlights the use of waste from silicate materials, because Nigeria is highly rich in these kinds of waste. So, its utilization and recycling will minimize environmental pollution and encourage establishment of glass-ceramic industry at both small and large scale

Table 3. Summary of properties of glass-ceramics obtained from a variety of silicate wastes.

Starting material	Main crystalline phase	Material properties					Hardness (GPa)
		Density (gcm^{-3})	Thermal expansion coefficient (X10^{6o}C^{-1})	Bending strength (Mpa)	Compression strength (MPa)	Young modules (GPa)	
Feldspar with limestone dust Na$_2$CO$_3$,Fe$_2$O$_3$,Cr$_2$O$_3$, phosphorus slurry Alumina, metallurgy slag and/or CaF$_2$	Diopside or diopside-heden-bergite solid solution	2.63 - 2.76	9.6 - 12.8	n/r	n/r	n/r	3.53 - 4.94 (Goronkhovsky et al., 2002)
100 wt% sewage sludge incinerated ash + 15 wt% CaO	Anorthite and wollastonite	n/r	6.7	n/r	164	n/r	n/r (Endo et al., 1997)
100 wt% sewage sludge incinerated ash + 50 wt% limestone	Anorthite diopside and forsterite	3.0	6.7	n/r	n/r	n/r	6 for Morh's hardness (Suzuki et al., 1997)
90 wt% sewage sludge incinerated ash + 10 wt% CaO	Diopside	2.87	8.3	92	n/r	n/r	6.23 (Park et al., 2003)
37.2 w% calcinated goethite + 23 wt% granite + 37 wt% glass cullet + 2.0 wt% T1O$_2$	Titanomagenetite franklinite (zinc ferrite) and diopside pyroxenes	3.104 (zero porosity and 75%crystallinity)	7.7	n/r	n/r	145	9.5 (Marabini et al., 1998)
60 wt% goethite + 10 wt% dolomite + 30 wt% glass cullet	Magnetite and franklinite	3.41*	9.0*	n/r	n/r	171*	6.85* (Romero et al., 1998)

n/r, Not reported; *properties of parent glass.

level.

The application of waste from industries and landfills for the production of a new product will no doubt safeguard the environment and reduce depletion of raw-materials for the purpose of production. The chemical compositions of waste glass and fly ash do not vary from the compositions of the pure raw-materials as indicated in Table 6.

It follows that for efficient use of the world's resources, recycling and reuse of waste is necessary. Recycling is the selection, classification and reemployment of waste as a raw material to produce the same or very similar product to the parent material, for example, the use of waste glass known as cullet in glass production. Reuse is the processing of waste to produce a useful product that is not similar to the material whose manufacture, produced the waste.

The versatility of the glass ceramic production process is manifested by the many wastes that have been used as raw-materials or glass-ceramic which include coal fly ash (Cioffi et al., 1994; Baccaccini, 1996; Kumar, 2000; Erol et al., 2001), mud from zinc hydrometallurgy (Romero et al., 1998; Karamanov et al., 1998; Karamanov et al., 2000; Montanaro, 2001), slag form steel production (Rawlings, 1997; Topping, 1976; Ponton, 1986; Shaoqiu, 1992; Frantseynk, 1996; Khater, 2002; Fidancevska et al., 2003), ash and

Table 4. Mechanical properties of sintered glass-ceramics.

Property	Sintered glass-ceramic	As- quenched glass	Bulk glass-ceramic	Hot pressed borosilicate glass
Density (glcm^3)	2.74 ± 0.02	2.89 ± 0.02	2.89 ± 0.02	2.22
Hardness (GPa)	3.8 ± 0.2	5.5 ± 0.2	7.9 ± 0.3	5.1 ± 0.2
Young's modulus (GPa)	8.5 ± 4	93 ± 4	124 ± 5	63
Poisson's ratio	0.24	0.28	0.26	0.22
Thermal expression coefficient (X10^6/°C)	6.0 (20 – 700°C)	5.9 (20 – 600°C)	6.5 (20 – 700°C)	3.3 (20 – 600°C)
Indentation fracture toughness (MPa m½)	1.5 ± 0.1	0.6 ± 0.1	1.7 ± 0.1	0.7 ± 0.1
Modulus of rupture (MPa)	88 ± 9	90 ± 10	240 ± 20	60
Thermal shock resistance (water quench test DT(K)	-300	-150	-280	-250
Brittleness index (μm$^{-½}$)	2.5	9.5	4.6	7.2

Source: Baccaccini and Rawlings (2002).

Table 5. Chemical composition (XRF) of the ashes and glasses.

	Ash		SI			MAR		
Oxides	SI	MAR	G2	G3	G4	G2	G3	G4
S_1O_2	96.43	90.57	42.58	56.97	45.44	38.26	51.00	36.87
Al_2O_3	0.55	1.05	9.81	1.92	9.66	15.02	5.95	17.55
Fe_2O_3	1.47	2.46	0.37	0.48	0.37	0.92	1.26	0.98
Na_2O	<0.001	<0.001	6.24	< 0.001	9.55	5.75	<0.001	9.42
K_2O	0.72	3.03	0.45	6.34	0.49	1.29	7.61	1.33
CaO	0.10	0.56	38.12	32.5	32.99	36.94	31.70	32.15
MgO	0.17	0.62	0.70	0.54	0.75	0.91	0.79	0.95
T_1O_2	0.19	0.40	0.05	0.09	0.07	0.15	0.21	0.15
P_2O_5	0.18	0.55	0.23	0.25	0.16	0.37	0.41	0.28
L.O.I	0.10	0.73	0.61	0.22	0.36	0.30	0.26	0.39

Source: Teixeira (2011).

slag from waste incinerators (Baccaccini et al., 1994; Baccaccini et al., 1995; Ramevo et al., 1999; Baccaccini, 1997; Baccaccini et al., 1999; Rincon et al., 1999; Barbieri et al., 2002; Pollettini, 2004; WQang et al., 1998; Kim et al., 2003, Kim and Kim, 2004; Andreola et al., 2004; Stoch, 2004; Knoules and Brosnan, 1995), red mud from alumna production (Zhang and Yan, 2000), waste glass form lamp and other glass products (Sokolova et al., 1986) as well as electric-arc furnace dust and foundry sands (Gao and Drummond III; 1999).

In the production of appropriate parent glass for crystallization, the addition of the waste composition is often required. It must be pointed out however that, there is always a trade-off between the amount of waste recycled and the optimization of properties of the new

Oxide	Waste glass	Fly ash
SiO_2	73.36	40.47
Na_2O	13.01	-
CaO	6.43	25.04
MgO	3.02	6.52
Al_2O_3	2.49	21.48
K_2O	1.69	-
Fe_2O_3	-	6.49

Source: Soon-Do and Teon (2008).

products. In general, since the main objective is to re-utilize the waste material, the quantity of pure materials or non-waste addition introduced for improving performance must be kept as low as possible.

The present review focus on the use of silicate waste based glass-ceramic, unlike other reviews which are on general waste application in the production of glass based products. This paper reviewed silicate waste materials, such as slug form metallurgical processes, coals ash from power stations, residues from urban incinerator's and other silicate wastes (Bacccaccini et al., 2006).

SLAG FROM METALLURGICAL PROCESSES

The blast furnace slag consists, if CaO, SiO_2 and MgO decrease the amount as the main constituents, together with minor constituents, such as MnO, Fe_2O_3 and S. The first attempt to commercialize a glass-ceramic from slag was by the British Iron and Steel Research Association in the late 1960s (Davies et al., 1970).

This glass-ceramics was known as "slag ceram" and it was produced by the convectional, stage heat treatment method (Davies et al., 1970; Davies et al., 1970). Similar material, "slags tall", was developed in the former Soviet Union at about the same time (Bondarev and Pavlushkin, 1971; Borezhnoi, 1970). More recent works have investigated the effect of adding nucleating agents to the slag; in particular, glass-ceramics with acceptable properties were produced using a two-stage heat treatment and addition of titania (Ovecoglu, 1998).

Ovecoglu (1998) reported the effect of adding titanium oxide as a nucleating agent in glass ceramics production; this was due to the fact that this component oxide is usually present at a very low quality in metallurgical slag. It was noted that samples containing no additional titanium oxide show shallow exothermic peak which indicate that the surface crystallization was the predominant mechanism of glass-ceramic formation.

With the addition of extra titanium oxide, the peaks were much better defined suggesting that the bulk crystallization takes place at the main mechanism. The optimized crystallization temperature was found to be 1100°C and the main crystalline phase of the slag-based glass-ceramic with T_iO_2 as an additive was a melilite solid solution, containing gelilenite and kermanite ($Ca_2MgS_{i2}O_2$). The subsequent mechanical testing results showed the effect of the crystallization temperature and T_iO_2 content. The knoop hardness (1040 kg/mn^2) bending strength (340 Mpa) for the 5 wt% $T1O_2$ containing glass-ceramic produced by a 1100°C heat treatment were better than the values of sample with 3 wt% T_iO_2 crystallized at 1100°C and with 5 wt% T_iO_2 crystallized at 950°C (Ovecoglu, 1998). It was also observed that as the amount of nucleating agent increases, the wear rate of the glass-ceramic material appeared to be decreasing.

The study was based around a 20 wt% $L_{i2}O$ to 80 wt% SiO_2 glass mixed with slag up to a concentration of 3.5 wt%. It is well, documented that an addition of 30% $L_{i2}O$ to S_iO_2 reduces the liquidus temperature significantly from 1713 to 1030°C. Alaily (2003) was able to melt slag containing mixtures at 1350°C, which is 100°C or more lower than in previously discussed systems. Heat treatment involved 1 h hold at 500°C and then another 1 h hold at 850°C to complete crystallization.

Surprisingly, the hardness of the glass-ceramics was less than that of the parent glasses. This was attributed to micro-cracking associated with the crystals, although, from the text, it was not clear whether the micro-cracking was thought to occur at or when cooling form the crystallization temperature.

A typical composition of "silceram" parent glass (in wt%) is S_iO_2 48.3, T_iO_2 0.6, Al_2O_3 13.3, Cr_2O_3 0.8, Fe_2O_3 4.8, MnO_2 0.4, MgO 5.7, CaO 24.7, Na_2O, 1.2 and K_2O 1.1. The Cr_2O_3 and Fe_2O_3 content is of particular significance, as these oxides act as the nucleating agents. Either oxide alone is capable of initiating nucleation, but there is a synergistic effect if they are present. These oxides promote the formation of small crystal of spinel, which in turn act as nucleation sites for the main phase, a pyroxene.

The route of production of glass-ceramics is an important factor for nucleation during the course of crystallization. Although, it has been established that bulk nucleation may be achieved in parent glasses with a slag component, studies have also been carried out on fabrication of glass-ceramics by the powder route in which surface nucleation usually plays a more important role (Kim et al., 1988, Kim and Rawlings, 1989) with the denser samples being obtained at the higher end of this temperature range sintering at 1180°C produced the highest Young's modulus and best resistance to water absorption, similar to that specified for commercial floor tiles, whereas an 1160°C treatment resulted in a slightly better flexural strength.

In general, the mechanical properties become poorer when the content of slag increases, suggesting there is a trade-off between cost and strength when the more expensive feldspar is replaced by the slag (Baccaccini, 2001).

SLAG-BASED GLASS-CERAMIC MATRIX COMPOSITES

Particulate reinforcement was found to increase strength, but to have a negligible effect on toughness. The thermal shock and erosion resistance of different "silceram" matrix composites have been also investigated (Von Schweitzer et al., 1993; Rawlings, 1994; Saewong and Rawlings, 1998). The coefficient of thermal expansion of "silcerma" is too high (7.5×10^{-6} K^{-1}) for it to be considered as thermal shock resistant material. Nevertheless, during fabrication and service, materials may be subjected to rapid temperature change and hence, the thermal shock performance has to be considered. The standard method for determining thermal shock resistance is to hold samples to a known elevated temperature quench rapidly into water and then measure the residual strength. There are two kinds of coal ash generated from combustion of coal in thermal power stations: fly ash and bottom ash. Fly ash, which accounts for about 80% of the total ash generated, is trapped and recovered from gas flow. The remaining 20% is called bottom ash as it is collected at the bottom of the furnace. Mixtures of these wastes are sometimes stored and weathered in water ponds to give what is known as pond ash. Significant amount of fly-ash (for example, in the order of 15 million tons per annum in an industrialized country such as Germany (Baccaccini et al., 1996) are produced continuously as a by-product of coal combustion in power stations. However, only small percentage of the fly ash is utilized, mainly in the cement industry or in road construction (Carlson and Adriano, 1993; Jablonski and Tyron, 1988). Glass-ceramic production is an alternative for the reuse of coal fly ash, as documented by numerous reports in the literature. From the study of Benavidez et al. (2003) and others, it is clear that the principal difference between fly and bottom ashes is that the former has (1) a lower residual coal carbon content (2) a much higher proportion of spherical particles and (3) finer particles and a narrower particle size distribution. Although, there are exceptions as a general rule, coal fly ash contains more silica but less calcia than slag.

GLASS-CERAMIC MATERIAL FROM THE S_1O_2-AL_2O_3-CAO SYSTEM USING SUGAR-CANE BAGASSE ASH (SCBA)

In a recent study conducted by Teixeria et al. (2011) on the use of sugar-cane bagasse ash to produce glass-ceramics. Two sugar-cane bagasse ashes were collected which was used as a source of silica to obtain the glass frit. The ashes were mixed with carbonates of calcium and sodium or potassium in three different concentrations as G2 (49.1 ash, 45.9 calcium carbonate, 5.0 sodium carbonate), G3 (59.5 ash, 33.4 calcium carbonate, 7.1 potassium carbonate) and G4 (50.3 ash, 42.6 calcium carbonate, 7.1 sodium carbonate). The initial composition was chosen based on the desired temperature calculated for each on (Tf < 1450°C). The glasses were prepared in two steps:

1. The mixtures were kept for 2 h at 950°C in a muffle furnace for vaporation of volatile materials.
2. They were melted at 750°C/h using an oven for melting glass as 1500°C for 1 h.

The liquid was poured into a container with water at room temperature for production of frit. They were powdered and analyzed using the techniques of X-ray diffraction and fluorescence (XRD and XRF) to determine whether there was crystallization during cooling and determine the chemical composition of the glass.

The analysis was conducted by passing the powdered glass through a 170 mesh (< 88 µm) sieve using thermal analysis (differential thermal analysis (DTA)/differential scanning calorimetry (DSC)) equipment (TA Instruments Model SDT Q600) to determine the crystallization temperatures. A fraction of each sample was analyzed for 1 h using a laboratory furnace at temperatures just above crystallization temperatures. Some samples were also heated at temperatures around crystallization peaks and quenched. All treated samples were analyzed using XRD equipment (Shimadzu XRD-6000) to identify the formed phases and XRF equipment (Shimadzu EDX 700) to determine the samples chemical compositions. To study the kinetics, the crystallization of each glass sample was monitored using the thermal analysis equipment at heating rates of 10, 15, 20, 25 and 30°C/min by the Kissinger method (Teixeira et al., 2011).

As indicated in Table 5, the ash SI has a higher concentration of silica, because it was collected in the water channel that come from the gas washer and pass underneath the boilers carrying both ashes (fly and bottom). Therefore, this is a washed ash with higher silica and lesser salts concentrations. The main difference in the chemical compositions of glasses is due to differences in the ashes composition (ash MAR has more flux, iron oxide and nucleating agent, than the ash SI). The highest concentration of flux results in higher corrosion of alumina crucible, increasing the concentration of aluminum and sodium in the glass. Therefore, glass obtained with the ash MAR have higher concentrations of these two oxides. Ashes with sodium (G2 and G4) erode the crucibles more than those (G3) with potassium. The presence of alumina reduces the tendency to devitrification, increases the viscosity and melting temperature of the glass. It also induces the crystallization of silicates of the systems S_1O_2-Al_2O_3-CaO.

MELTING AND SUBSEQUENT HEAT TREATMENT

Glass-ceramics from coals fly ash were produced using

the melt quenching/hear treatment method as early as in the 1980s (DeGuire and Risbud, 1984). The fly ash was melted at 1500°C without any additives and then cast into graphite moulds. An unusual two stage nucleation treatment was used: 2 h at 650 or 700°C followed by 5 or 10 h at a temperature in the range 800 to 900°C, prior to a crystallization treatment at 1000 or 1150°C. It was claimed that the extent of crystallization was not significantly affected by the different nucleation treatments prior to the crystallization stage; hence, a single-stage nucleation heat treatment may be feasible. Cumpston et al. (1992) used $CaCO_3$ (20 wt%) and T_iO_2 additions to fly ash to achieve 40 vol% crystallinity with anorthite as the main crystalline phase. The addition of $CaCO_3$ lowered the melting temperature and the viscosity of the melt allowing a homogenous amorphous glass to be obtained with a melting temperature 100°C less than that used in the previous study (DeGure and Risbud, 1984). The small percentage of T_iO_2 added made little difference to the final degree of crystallinity and the main crystalline phase remained anorthite. However, the crystal morphology and distribution must have been affected as the hardness of the T_iO_2 containing glass-ceramic was higher than that of the glass-ceramic without additive. A decrease in crystallinity was observed with increasing crystallization temperature and this can be explained by the fact that the heat treatment temperature was above the maximum of the crystal growth rate curve. The glass-ceramic was heat treated for 48 h at 1000°C, which highlights the energy intensiveness of such processing method. Technical applications, such as high temperature crucibles or refractory materials were suggested for this glass-ceramics (Cumpston et al., 1992).

Based on the DTA analysis, nucleation temperature of 680°C and crystallization temperature of 924°C were employed for the cayirhan ash (Erol et al., 2000), whereas, the corresponding temperatures for the seyitomer ash were 728 and 980°C, respectively. The main crystalline phase in the glass-ceramics produced was diopside-alumina [$Ca(Mg.Al)$ $(S_i.Al)_2O_6$]. An interesting feature of the investigation was the correlation found between heat treatment and microstructure, hardness and wear resistance.

THERMAL ANALYSIS

Powder samples of different area (different particle size) were studied by DTA to determine the nature of crystallization mechanism.

The first transition was an endothermic trough approaching 700°C, associated with the glass transition temperature. The next visible transition is two minor peaks (at around 700 and 810°C), followed by a major peak at about 840°C corresponding to the main crystalli-sation process. No further exothermic transitions were

visible at higher temperatures, suggesting that the glass can be converted into a glass-ceramic at a relatively low temperature. Finally, an endothermic reaction at -1070°C, which was originally presumed to be the melting of the glass, may have been in fact the dissolution of a particular crystalline phase since the resulting samples were similar (indeed the measured differences in peak temperatures were probably within experimental error). Considering the different morphology of the samples and hence, different sample-thermocouple contact indicating that the specific area of the sample was not significantly affecting any of the reactions. Consistent with the DTA results were the scanning electron microscopy observations which showed that surface crystallisation was not extensive and that the crystallisation process was dominated by internal (bulk) nucleation (Baccaccini, 2001).

PHYSICAL AND MECHANICAL PROPERTIES

A range of experiments, including 3-point bending test, Vickers' hardness indentation, dilatometry and compression strength test were conducted to determine physical and mechanical properties of the resulting glass-ceramic. The result for the glass and glass-ceramics heat-treated at 900 and 1100°C for 2 h are given in Table 2. Crystallization yielded a material with better mech-anical properties than the parent glass. The increase in heat-treatment temperature, which resulted in the precipitation of titanium-rich phases, also had a positive effect on the room-temperature mechanical properties of the glass-ceramic material, except for the hardness. As mentioned previously, XRD showed the reduction in the relative ratio between pyroxene and titanium-rich phase.

The slight improvement in the indentation fracture toughness of the glass-ceramic material may be caused by the presence of one of the titanium-rich crystals armalcolite, because of its high aspect ratio. A crack will therefore have to travel around these crystals in order to propagate further. Hence, the facture toughness improves as it takes higher energy for a crack to propagate. The behaviour of the glass-ceramic material (heat-treated at 1100°C) at elevated temperature was examined during the determination of fracture toughness by chevron-notched specimen technique. Tests were firstly carried out at room temperature and at 500°C. The fracture toughness slightly decreased with increasing temperature up to 500°C. There was an acceptable scatter of data from all measurement and the mean values give a trend of variation of K_{1C} (1.35 ± 0.12 Mp m½ at room temperature as compared to 1.13 ± 0.20 MPa m½ at 500°C). A standard student's t-test was carried out on the two data sets with the hypothesis that the data ranges overlap by chance. The result, however, showed that the difference in the fracture toughness values between room temperature at 500°C was significant

and thus, the hypothesis was rejected. The decrease in fracture toughness was surprising as it is unlikely that the elastic modules decrease significantly over that temperature range. An earlier study on a monolithic lithium aluminosilicate (LAS) glass-ceramic by Brennan and Prewo (1982) has shown that the elastic modulus has minimal reduction and the fracture toughness of the material remained constant from room temperature to 800°C.

The production of glass-ceramics materials has found their application in the field of abrasion-resistant materials, which are industrial floor coverings, wall facings, abrasion-resistant linings and high temperature insulators. Moreover, developing appropriate methods of new glass-ceramic materials from recycling fly ash has acquired particular importance (Cumpston et al., 1992; Cioff et al., 1994; Queralt et al., 1997).

However, much more effort is needed in resolving environmental waste recycling problems for the life and health of future generations. Many researches have been conducted on the utilization of fly-ash as a starting material for glass-ceramic production (Erol et al., 2001; Caoffi et al., 1993).

Glass-ceramics have been prepared using fly ash from a thermal power plant and waste glass (Park et al., 2007).

It is important to note that waste materials, such as fly ash and glass are recycled and that many recycling problems, such as chemical bonding by heat-treatment and economic loss caused by several thermal steps are solved by a mechanical processing method. In the present study, chemical durability and mechanical properties of glass-ceramics were investigated.

CONCLUSION

Waste management and recycling is an important aspect of environmental sanitation. It also reduces the exploit-ation of run-materials for the purpose of production. Glass - ceramics raw - material is obtained by digging landfills which leads to the distortion of the environment. The utilization of silicate-wastes for the purpose of this production is a welcome development that checks the environmental distortion. Economically, it is viable, but the process of productions that involves incinerations may lead to the production of toxic gases that pollute the environment. Proper control of this will enhance the environmental sanitation and reduce production cost in glass-ceramics industries.

REFERENCES

Ahmaruzzaman M (2010). A Review on the utilization of fly ash, progress in energy and combustion science, 36: 327-363.

Aldo R, Baccaccini RD, Rawlings Z, Chlup JP, Wu (2001). A Glass – Ceramic Derived from High T10$_2$-Containing Slag: Microstructural Development and Mechanical Behaviour.

Andreola F, Barbieri L, Corradi A, Lancellotti I (2004). New marketable products form inorganic residues. Am. Ceram. Sco. Bull., 3: 9401-9408.

Baccaccini AR, Bücker M, Bossert J (1996). Glass and glass ceramics from coal fly ash and waste glass, Title brick Int., 12: 515-518.

Baccaccini AR, Wu JP, Rawlings RD (2006). Glass – Ceramics: Their Production form Wastes. Rev. J. Mater. Sci., 41(3): 733-761.

Baccaccini AR, Köp FM, Ondracek G (1994). Neue techniken der abfallverwertung-zu den möglichkeiten einer verwertung von filterstuben aus abfallverbrennung durch wekstofftechische verfahren – zifur angewandte umweltforschung 7: 357-367.

Barbieri L, Corradi A, Lancellott L (2002). Thermal and chemical behaviour of different glasses containing steel fly ash and their transformation into glass – ceramics, J. Europ. Ceram. Sco., 22: 1759-1765.

Benavidez E, Grasselli C, Quarnata N (2003). Densification of ashes from a Thermal Powder Plant, Ceramics Int., 29: 61-68.

Boccaccini A, Rawlings R (2002). Glass – ceramics glass – ceramics from waste materials. Mater. World, 10(5): 16-18.

Boccaccini AR, Kern H, Rincon J, Ma Romero M, Petitmermet M, Wintermantel E (1999). Transforming municipal incinerator fly ash in glass and glass –ceramics, in: proc. r'99, recovery recycling, re-integration" conference. a barrage, x. edelmann (eds.), Published by EMPA, Switzerland, II: 152-157.

Boccaccini AR, Köpf M and Stumpfe W (1995). Glass – Ceramics from filter dust from waste incinerators, Ceramics Int., 21: 231-235.

Boccaccini AR, Petitmerment M, Wintermantel E (1997). Glass – ceramics from municipal incinerator fly ash. Am. Ceram. Soc. Bull., 76(11): 75-78.

Bondarev KT, Pavlushkin NM (1971). Slag – sitall – a material of the future in proc. 9th int. congress on glass, versailles, france, Sci. Tech. commun., 2: 1237-1250.

Borezhnoi AI (1970). "Glass – ceramics and photo-sitalls" trans. from russina, plenum press, New York and London.

Brennan JJ, Prewo KM (1982). "Silicon carbide fibre reinforced glass – ceramic matrix composites exhibiting high strength and toughness" J. Mater. Sci., 17(8): 2371-2383.

Carlson CL, Adriano DC (1993). Environmental impact of coal combustion residues J. Environ. Qual., 22: 227-247.

Cioffi R, Pernice P, Aronne A, Catauro M, Quattroni G (1994). Glass – Ceramic from fly ash with added L1O$_2$. J. Euro. Ceramic Soc., 13: 143–148.

Colombo P, Brusatin G, Bernardo E, Scarinci G (2003). Inertization and resuse of waste materials by vitrificaiton and fabrication of glass – based products. Current opinion in solid state and material science, 7: 225-239.

Cumpston B, Shadman F, Risbud S (1992). Utilization of Coal – Ash minerals for technological ceramics. J. Mater. Sci., 27: 1781–1784.

Dana K, Da SK, (2003). High Strength Ceramic Floor title Compositions Containing Indian Metallurgical Slags. J. Mater. Sci. letters, 22: 387-389.

Davies MW, Kerrison B, Gross WE, Robson WJ, Wichell DF (1970). Science of ceramics c. brosset and e. knopp (eds.). Swedish institute of silciate research, Gothenburg.

DeGuire EJ, Risbud SH (1984). Crystallization and properties of glasses prepared form illinois coal fly – ash. J. Mater. Sci., 19: 1760-1766.

El-Alaily NA (2003). Study of some properties of lithium silicate glass and glass ceramics containing blast furnace slag. Glass Technol., 44(1): 30-35.

Endo H, Nagayoshi, Suzuki K (1997). Production of glass ceramic from sewage sludge. Water Sci. Tech., 36: 235-241.

Erol M, Kucukbayrak S, Erosy-Mericboyu A, Ovecyglu ML (2001). Crystallization behaviour of glasses produced from fly ash. *J. Europ. Ceram. Sco.,* 21: 2835-2841.

Fidancevska E, Mongutova B, Milosevski D, Milosevski M, Bossert J (2003). Obtaining of dense and highly porous ceramic materials form metallurgical slag, Sci. Sintering, 35: 85-91.

Frantseyuk LI, Blintsova IV, Seredkin AE (1996). Synthesis of slag-glass ceramics. Glass Ceramics, 53: 356-361.

Gao Z, Drummond III CH (1999). Thermal Analysis of Nucleation and Growth of crystalline Phases in vitrified Industrial Wastes. J. Am. Ceram. Soc., 82: 561-565.

GorokhovskyA, Escalante-Garcia JI, Gorokhovsky V, Mescheryakov D (2002). Inorganic wastes in the manufacture of Glass and Glass-ceramic: Quartzfeldspar Waste of Ore-Refining, Metallurgica Slay, Limestone Dust and Phosphorus Slurry. J. Am. Ceram. Soc., 85: 285-287.

Gungor A, Cupta SM (1999). Issues in Environmentally Conscious Manufacturing and Product Recovery: A Survey. Comput. Ind. Eng., 36: 811-853.

Hauwa I (2008). The Need for Waste Management in the Glass Industries: A Rev. J. Scientific Res. Essay, 3(7): 276-279.

Jablonski GL, Tyron SS (1998). *Overview of Coal Combustion By – Product* Utilization. Proc. 5th Int. Pittsburgh Coal Conference, Pittsburgh, University. p. 15.

Karamanov A, Pelino M, Tagliceri G, Cantalani C (1998). Sintered Building Glass – Ceramics Based on Jarosite, in Proc. XVIII International Congress on Glass, San Francisco (USA), the American Ceramic society, Ohio, M. K. Choudhary, N. T. Huff and Ch. H Drummond III (Eds).

Karamanov A, Prisciella P, Cantalini C, Pelino M (2000). Influence of Fe^{3+}/Fe^{2+} Ratio on the Crystallization of Iron – Rich Glasses Made with Industrial Wastes, J. Am. Ceram. Soc., 83: 3153-3157.

Khater GA (2002). The Use of Saudi Slag for the Production of Glass – Ceramic Materials, Ceram. Inter., 28: 59-67.

Kim HS, Kim JM, Oshikawa T, Ikeda K (2003). Precaution and Properties of Glass – Ceramics from Incinerator Fly Ash, Mater. Sci. Forum, 439: 180-185.

Kim HS, Rawlings RD, Rogers PS (1988). In: Brit, Ceram, Proc. 42 Complex Microstructures, Durham, R. Stevens and D. Taylor. (989) 59-63.

Kim HS, Rawlings RD, Rogers PS (1989). Sintering and crystallization Phenomena in- Silceram Glass, J. Mater. Sci., 24: 1025-1037.

Kim JM, K.im HS (2004). Glass – Ceramics Produced form a Municipal Waste Incinerator Fly Ash with High Cl Content, J. Eupop. Ceram. Soc., 24: 2373.

Knowles SD, Brosmnan DA (1995). Composition and Properties of Glass Ceramics Produced form Incinerator Residuals, J. Canad. Ceramics Soc., 64: 231-234.

Kumar S, Singh KK, Ramachandrarao (2000). Synthesis of Cordierite from fly Ash and its Refractory Properties, J. Mater. Sci. Lett., 19: 1263-1265.

Marabini AM, Plescia P, Maccari D, Burragato F, Pelino (1998). New Materials from industrial and minning wastes: glass-ceramics and glass and rock-wool fibre, Int. J. Mineral Proc., 53: 121-134.

Montanaro L, Bianchini N, Rincon (2001). Sintering Behaviour of Pressed Red Mud Wastes from Zinc Hydrometallurgy. Ceram. Int., 27: 29- 37.

Ovecoglu ML (1998). Microstructural Characterization and Physical Properties of a Slag – Based Glass Ceramic Crystallized at 950 and 1000°C. J. Euro. Ceram. Soc., 18: 161-168.

Park YJ, Moon SO, Heo J (2003). Crystalline Phase control of glass ceramics obtained from sewage shidge fly-ash. Ceram. int., 29: 223-227.

Polettini A, Pomi R, Trinci L, Muntoni A, Lo Mastro SO (2004). Engineering and Environmental Properties of Thermally Treated Mixtures Containing MSWI Fly Ash and Low – Cost Additives, Chemosphere, 56: 901-910.

Ponton CB, Rawlings RW, Rogers PS (1986). Mechanical Properties of "Silceram" Glass-Ceramics. Proc. Brit. Ceram. Soc., 37: 229-234.

Rawling RD (1977). Production and Properties of Silceram Glass Ceramics, in Glass – Ceramic Materials. Fundamentals and Applications. Eds. T. Manfredini, G. C. Pellacani and J.M. Rincon. Mucchi Editore, Modena, Italy, pp. 115-133.

Rawling RD (1994). Glass – Ceramic Matrix Composites, Composites, 25: 372-379.

Rincon J, Ma Romero M, Baccaccini AR (1999). Microstructural Characteristic of a Glass and a Glass-Ceramic Obtained form Municipal Incinerator Fly Ash. J. Mat. Sci., 34: 4413-4423.

Romero M, Rawlings RD, Rincon JMa (1999). Development of a New Glass Ceramic by Means of controlled Vitrification and Crystallization of Inorganic Wastes from Urban Incineration. J. Europ. Ceram. Soc., 19: 2049-2058.

Romero M, Rincon JMa, Musik S, Kozhukharov V, Móśśsbauer (1998). Effect and X – ray Distribution Function Analysis in Complex Na_2O-CaO-ZnO-PbO-Fe_2O_3-Al_2O_3-$S1O_2$ Glasses and Glass – Ceramics, Mater. Res. Bull., 34: 1107-1115.

Saewong P, Rawalings RD, (1998). Proceedings Materials Solutions 197 – Wear of Engineering Materials, Indiana Polis, USA, J.A. Hawk (Ed.), ASM International, Ohio, USA. p. 133.

Shaoqiu T, Zhonjung L, Guorong Ch (1992). Studies of the Crystallization of antimony-Containing slag Glass – Ceramic. J. Am. Ceram. Soc., 75: 440-446.

Sokolava MM, Perunova VS,Sepanov VV and Kozlvo NV (1986). A Glass Ceramic Material Based on the Waste from Lamp Production. Glass Ceramic, 43: 133-135.

Soon–Do, Yeon–Hum Y (2008). Chemical Durability of Glass – Ceramics Obtained from Waste glass and Fly Ash. J. Ceram. Processing Res., 9(2): 135-139.

Stoch L (2004). Homogeneity and Crystallization of Vitrified Municipal waste Incinerator Ashes, Glass Technol., 45: 71-73.

Suzuki S, Tanaka M, Kaneko T (1997). Glass-ceramic from sewage shidge ash. J. mater. Sci., 32: 1775-1779.

Teixeira SR, Romero M, Rincón JMa, Magalhães RS, Souza AE,
Santos GTA 1, Silva RA (2011). 1Glass-Ceramic Material from the SiO2-Al2O3-CaO System Using Sugar-Cane Bagasse Ash(SCBA) IOP Conf. Series: Mat. Sci. Eng., 18: 112020

Topping JA (1976). The fabrication of Glass-ceramic Materials Based on Blast furnace Slag. A Rev. J. Can. Ceram. Soc., 45: 63-67.

Vonschweitzer CB, Rawlings RD (1993). Third euro-Ceramics Vol. 2 P. Daram and J.F. Fernamdez (Eds.) Faenza Editrice Iberica, Madrib.. 1139.

Wang KS, Chiang KY, Perng JK, Sun CJ (1998). The Characteristics Study on Secreting of Municipal Solid Waste Incinerator Ashes. J. Hazardous Mat., 59: 201-210.

Zhang P, Yan J (2000). Mossbauer and Infrared Spectroscope Investigation on Glass – Ceramics Using Red Mud, Z., Metallk. 91: 764-768.

Zimmer A, Bergmann CP (2007). Fly ash of Mineral Coal as Ceramic Tiles Raw – Materials Waste Management (Elmsford), 27: 59-68.