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ESTONIAN OIL SHALE ASH AS RAW MATERIAL FOR MANUFACTURING GLASS CERAMICS

Rein KUUSIK², Mauro MARANGONI¹, Enrico BERNARDO¹

¹Dipartimento di Ingegneria Industriale, Università degli Studi di Padova, Via Marzolo 9, Padova 35131, Italy

²Laboratory of Inorganic Materials, Tallinn University of Technology, 5 Ehitajate Str., Tallinn 19086, Estonia

rein.kuusik@ttu.ee, mauro.maragnoni@unipd.it, enrico.bernardo@unipd.it

Introduction

The Estonian kukersite oil shale (OS) is the largest industrially exploitable OS resource in the world.¹⁻³ About 60 % of the Estonia's fuel balance is covered by OS (annual mining output 14–18 Mt), and its share in heat and power production exceeds 80 %.^{3,4} The combustion of OS in electric power plants, based on circulating fluidized bed combustion (CFB) and pulverized firing (PF), is accompanied by the generation of vast amounts of waste ash (45–48 % of the OS dry mass).⁵ Only a small percentage of oil shale ash (OSA) is utilized, either in the building materials industry, in agriculture as a liming agent or in road construction. Most of the OSA is still deposited in ash sediment fields near the power plants (5–7 Mt annually).³

The present paper aims at evidencing the feasibility of a sintering approach for the production of strong and chemically stable glass-ceramics, based on glass frits. More precisely, the cost of overall glass-ceramic manufacturing can be significantly lowered if we consider that a glass is not formed (no refining is required upon glass melting) and surface crystallization, operating on fine glass powders, may lead to substantial crystallization by application of very short sintering treatments (fast heating – 40 °C/min – and limited holding stage)⁶. In addition, the impact of binders (of organic or inorganic nature), used to favour the shaping of fine powders, and recycled glass powders, considered in order to improve the chemical stability of the sintered bodies, has been discussed.

Materials and methods

The raw materials consisted of fly ash residues formed at combustion of Estonian oil shale at Estonian Power Plant (Estonia) at different combustion technologies. ESP1 is formed at pulverized firing of oil shale at temperatures 1200–1400 °C and ESP2 at circulating fluidized bed combustion of lumpy oil shale at temperatures 750–830 °C, which explains the differences in the chemical compositions of these ashes (Table 1). Both ashes are collected from an electrostatic precipitator, from the 3rd and 1st field,

respectively. More precisely are these ashes characterized in.⁷ The ashes were mixed with secondary components such as rhyolite, i.e. an inexpensive aluminosilicate volcanic rock, provided by Ce.Ri.Col. (Centro Ricerche Colorobbia, Vinci, Italy) and recovered soda lime cullet (SASIL SpA, Biella, Italy). Recovered soda lime glass corresponds to the fraction of recycled material which is hardly reused, after color selection and removal of metallic and polymeric residues, for the preparation of new glass articles, owing to the presence of ceramic contaminations. Addition of polyethylene glycol (PEG) and kaolin clay was used. The chemical composition of the raw materials, according to X-ray fluorescence analysis, is reported in Table 1, and in more details in the study of Marangoni *et al.*⁸.

Table 1: Chemical composition of the starting raw materials and formulation of the investigated glasses

	ESP 1	ESP 2	Rhyolite	Soda lime glass	Borosilicate glass	ASH 1 glass	ASH 2 glass
<i>Chemical composition</i>							
Oxide	Content (wt.%)						
SiO ₂	34.73	31.86	73.40	71.92	72	51.7	51.5
Al ₂ O ₃	9.42	9.06	15.20	1.22	7	10.7	10.7
B ₂ O ₃	-	-	-	-	12	-	-
Na ₂ O	0.19	0.25	1.70	14.35	6	2.2	2.6
K ₂ O	4.17	7.42	4.00	0.36	2	4.2	6.5
BaO	-	-	-	-	<0.1	-	-
MgO	5.89	3.43	0.30	3.95	-	4.9	3.1
CaO	27.66	27.77	0.50	7.49	1	21.7	21.3
Fe ₂ O ₃	4.36	3.76	1.50	0.35	-	3.7	3.2
MoO ₃	-	-	0.10	-	-	-	-
TiO ₂	0.47	0.54	0.10	0.06	-	0.3	0.4
MnO ₂	1.47	1.06	-	-	-	1.0	0.7
L.O.I.	11.64	14.85	4.80	0.30	-	-	-
<i>Formulation</i>							
Glass	Balance (wt.%)						
ASH 1 glass	67		23	10			
ASH 2 glass		65	23	12			

Detailed description of methods, tiles preparation procedures and measurements used is available in the study of Marangoni *et al.*⁸.

Results and Discussion

Sintering treatments of ASH1 glass at 950 °C, led to the separation of different phases, in form of a Ca-Fe rich pyroxene (omphacite, $\text{Fe}_{0.52}\text{Al}_{0.48}\text{Ca}_{0.47}\text{Na}_{0.53}\text{Si}_2\text{O}_6$, PDF#71-1403), a Ca-Na feldspar (sodium exchanged anorthite, $\text{Na}_{0.45}\text{Ca}_{0.55}\text{Al}_{1.55}\text{Si}_{2.45}\text{O}_8$, PDF#85-1415) and β -wollastonite (CaSiO_3 , PDF#72-2284). Omphacite traces are visible even at low temperature, for short holding times, whereas wollastonite and feldspar formed at higher temperature or for long sintering treatments (900 °C and 120 min holding time). ASH2 glass, led to a more complex phase assemblage, based on the previously identified crystal phases with further formation of akermanite ($(\text{Ca}_{1.53}\text{Na}_{0.51})(\text{Mg}_{0.39}\text{Al}_{0.41}\text{Fe}_{0.16})(\text{Si}_2\text{O}_7)$, PDF#72-2127), a K-rich feldspathoid (leucite, $\text{K}(\text{AlSi}_2\text{O}_6)$, PDF#851626). Akermanite phase was observed especially at low temperature and for short treatments; at higher temperature or for longer holding times akermanite practically disappeared, replaced by the other phases.

The manufacturing of larger sintered glass-ceramic samples was associated to some refinements, concerning the impact of binders. In fact, kaolin and PEG were introduced. The adhesion forces among kaolin and glass powders improved the green body strength. Moreover kaolin was subjected to dehydration into metakaolin at about 550 °C, in turn decomposing at about 925 °C into fine-grained mullite and silica. From the XRD analysis no mullite formation was observed; however anorthite peaks became more significant compared to those associated to wollastonite. PEG introduction, did not modify substantially the phase assemblage, compared to the one without binders, because of its organic nature (PEG burn out was performed at about 300 °C).

Table 2: Mechanical properties of optimized sintered glass-ceramics

Glass	Binder	E (GPa)	ρ (g/cm ³)	Total porosity (%)	Strength σ_4 (MPa)	Weibull		Strength σ_{eq} (MPa)	H_v (GPa)
						σ_0 (MPa)	m		
ASH1	PEG	92 ± 6	2.62 ± 0.04	7	87 ± 20	95	4.6	16.4	6.3 ± 0.3
	Kaolin	79 ± 2	2.52 ± 0.02	7	90 ± 19	98	3.9	14.8	6.8 ± 0.2
ASH2	PEG	67 ± 6	2.44 ± 0.08	6	94 ± 10	99	10.7	48.0	6.1 ± 0.4
	Kaolin	67 ± 8	2.49 ± 0.06	8	99 ± 17	107	6.2	29.5	5.9 ± 0.4
ASH2 + BSG	PEG	59 ± 4	2.27 ± 0.03	7	72 ± 11	77	6.7	25.0	6.0 ± 0.8

The values of bending strength, Young's modulus and Vickers microhardness reported in Table 2 compare favourably with other waste-based glass-ceramics.⁹ The bending strength, in particular, is quite high considering an amount of total porosity estimated not to be lower than 6 % (reasonable owing to the gas release from PEG or kaolin residues, upon firing), from image analysis of polished surfaces.

The weakening effect of residual porosity was likely well compensated by intensive crack deflection at glass/crystal interfaces, similarly to the case of dental glass-ceramics.¹⁰ The fracture surfaces visible in Figures 1a and 1b, for glass-ceramics from ASH2 glass, on one hand confirm the internal porosity, on the otherhand they feature a remarkable roughness. In particular applying Weibull's statistic approach on ASH2 PEG samples, the characteristic strength of 99 MPa is related to a remarkable Weibull's modulus (m), exceeding 10.

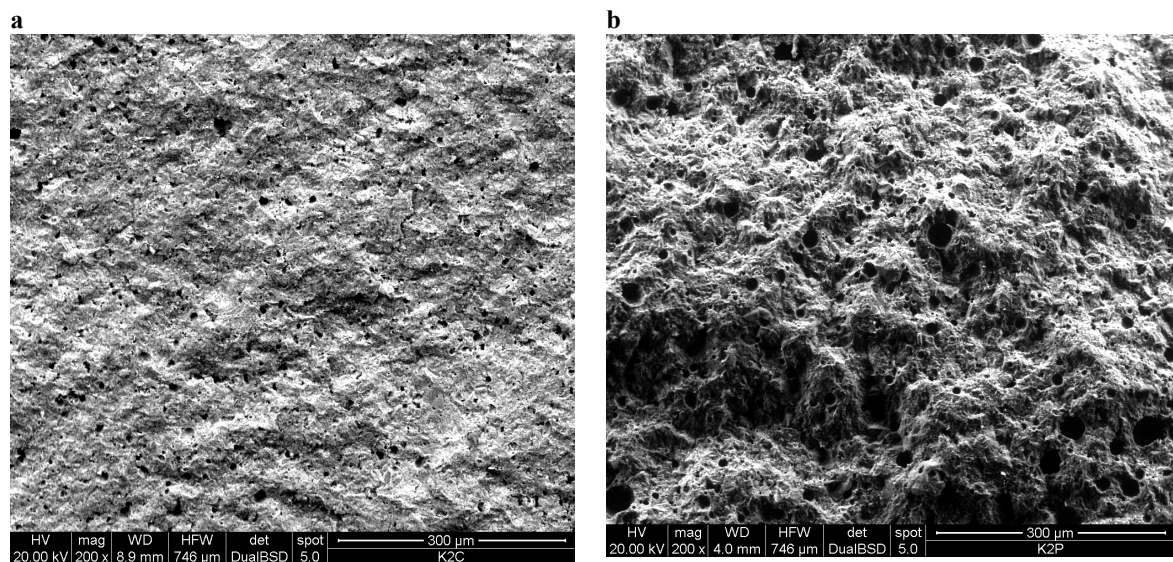
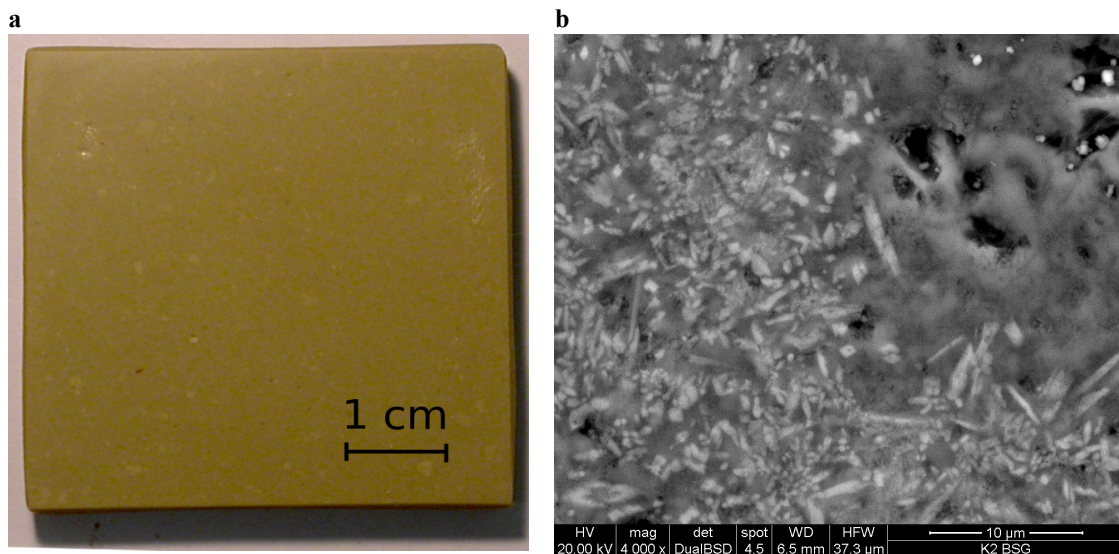


Figure 1: SEM image of glass-ceramics from: ASH2 with Kaolin; b) ASH2 with PEG

Table 3: Results from TCLP testing of selected sintered glass-ceramics

Element	Limits for stability(ppm)	Limits for inertia (ppm)	Leachate from ASH2 [+PEG] (ppm)	Leachate from ASH2-borosilicate [+PEG]
As	0.2	0.05	0.0212	0.0115
Ba	10	2	0.0761	0.019
Cd	0.1	0.004	0.003	0.0014
Cr	1	0.05	0.0234	0.0072
Cu	5	0.2	0.5049	0.0154
Hg	0.02	0.001	< 0.0004	< 0.0004
Mo	1	0.05	< 0.0033	< 0.0033
Pb	1	0.05	0.1023	0.0047
Sb	0.07	0.006	< 0.0099	< 0.0099
Se	0.05	0.01	< 0.0122	< 0.0122
Zn	5	0.4	0.2114	0.2322

**Figure 2:** Details of sintered ceramics from the ASH2 glass with borosilicate glass: a) visual appearance; b) high magnification SEM image (backscattered electrons)

Mechanical strength is not the only key issue for a waste-derived material to be effectively employed in building applications. In fact, any waste-derived material should be chemical stable, i.e. provide a permanent immobilisation of pollutants.

Table 3 reports the results from leaching test: the best material (ASH2 with PEG binder) features limited release of ions, but cannot be considered as inert, according to current Italian standards.¹¹

An interesting strategy for stabilisation, according to recent studies¹², is not associated to the reformulation of waste-derived glasses, but to the sintering with a secondary glass. Considering the high percentage of fly ash employed (65-67 wt.%), the amount of heavy metals present in the parent glass is not negligible - under leaching conditions the heavy metals may be released both from the crystallites and the amorphous phase.

The increased chemical stabilisation achieved by adding an inert secondary glass to the waste derived glass may be due to the further dilution and embedding of both the crystallites and the heavy metals present in a chemically inert glass-ceramic. In other words, it is possible to improve the chemical stability not only before vitrification, but even after it by adding a more stable glass to a waste derived glass-ceramic. In the present case, ASH2 glass was mixed with recycled pharmaceutical glass (composition shown in Table 1, in the proportion 7:3, and processed with PEG binder, leading to the glass-ceramic sample shown in Figure 2a. Although related to a lower content of ASH2 glass, the mechanical properties of the new sample (after sintering at 1000 °C for 30 min), remain substantial, as testified by Table 2. Despite a lower degree of crystallisation, evident from the comparison with the glass-ceramic from ASH2 glass alone, the strength could be reasonably enhanced by the fine distribution of crystals, as illustrated by Figure 2b.

Conclusions

- Selected kinds of Estonian oil shale ash may be employed as the main raw material (being used in an amount exceeding 60 %) in the formulation of waste-derived glasses, to be converted into glass-ceramics;
- Sinter-crystallization, found to be active for the investigated compositions, allowed the obtainment of glass-ceramics by very fast and cost effective firing treatments (temperatures < 1000 °C, holding time of 30 min, fast heating);
- Optimized formulations, in terms of composition and selection of binders, led to strong glass-ceramics, with a high reliability (Weibull's modulus > 10);
- The chemical stability of the sintered glass-ceramics may be improved by mixing waste-derived glass with recycled borosilicate glass.

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