J Mater Sci (2009) 44:4296–4302
DOI 10.1007/s10853-009-3637-y

Novel sintered glass-ceramics from vitrified oil well drill cuttings

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Received: 18 February 2009 / Accepted: 21 May 2009 / Published online: 13 June 2009

Abstract An amorphous glass was obtained by melting drill cuttings from oil and gas exploration and production operations in the North Sea that have been blended with sodium and calcium oxides to minimise the melting temperature. Mixtures containing dried drill cuttings:sodium oxide:calcium oxide in the weight ratio 8:1:1 held at 1300 °C for 5 h produce an amorphous solid that can be further treated at temperatures between 750 and 800 °C to give a largely crystalline glass-ceramic. The glass-ceramics have been characterised by physical, chemical and mechanical analyses and shown to have properties of machinability, strength, wear-abrasiveness, thermal resistance, resistance to crack propagation, and stability towards leaching that make the materials suitable for tiling applications, allowing diversion of the drill cutting wastes from final disposal in landfill.

Introduction

The grinding action of drill bits against the rocks in a well during drilling operations in the oil and gas exploration and production industry gives rise to drill cuttings, with each well generating about 1000 m^3 over the lifetime of the drilling operation [1]. Oil well drill cuttings are, therefore, the largest solid waste stream from the industry. Drill cuttings are heterogeneous and their composition varies with the type of rock in the well, the drilling process employed and the separation technology applied as well as the drilling mud applied. Drilling mud is added to aid the drilling process in various ways including: cleaning the bottom of the hole by carrying cuttings up to the surface, transmitting hydraulic power to the bit, and lubricating and cooling the drill bit. Drilling muds can be water-based, oil-based or pneumatic, and a variety of chemicals are added to give the mud the desired functional properties. These chemical additives include: viscosity control agents, density control agents, emulsifiers, biocides, lubricants, pH control agents, fluid-loss control agents and organic polymers [1, 2]. It is these additives that increase the hazardous potential of the mud and therefore the drill cuttings which are coated by the mud. In the European Waste Catalogue (EWC) as adopted in the European Commission Decision 2000/532/EC, these wastes are listed as absolute (01 05 05*) and mirror entries (01 05 06*).

Cuttings from oil wells in the Caspian Sea, for example, contain 60–80% of rock solids with 8% organic matter, 6% mineral salts, and components of the drilling mud [3], including clay, weighting agents, oil products, stabilisers, viscosity regulators and other materials. Drill cuttings are brought to the surface by the drilling mud in its flow cycle. This combined mixture of drill cuttings and drilling mud is normally separated by mechanical means, allowing the recovered drilling mud to be returned along a mud line to the drill cycle, while the residual rock cuttings are treated by thermal desorption before being landfilled. Thermal desorption involves heating the cuttings at temperatures below 600 °C in a special unit, and this process is usually carried out onshore to give a waste residue which is suitable for landfill. There is, however, a growing need to

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minimise the landfill of waste and to promote the zero end-of-life final disposal. Cuttings re-injection can be used as an alternative means of disposing of the drill cuttings by injecting them, as a slurry, down disused or dedicated wells into geological formations. This can be considered a beneficial reuse process if the cuttings are injected into formations around current wells to change underground pressures and improve crude oil recovery, but this process has had limited application. There is still a major requirement to find methods of diverting drill cuttings, produced from the thermal desorption processes, from landfill.

A number of processes have been considered as a means of recycling drill cuttings including using them as a kiln feed in the manufacture of Portland cement [4, 6], in the manufacture of bricks and concrete blocks [5, 6] and as substrate in wetlands restoration [7–10]. The presence of chloride and sulphide in most drill cuttings, however, is disadvantageous, in that chlorides will leach out from the final product and sulphides will adversely affect the cement setting process [6, 11]. We now report, for the first time, on the conversion of oil well drill cuttings to glass-ceramics by a vitrification/devitrification technique, which has previously been used in treating slags, ashes and other wastes from metallurgical processes [12]. Vitrification is a method of immobilising waste by melting it to produce a glass. Melting is achieved by high-temperature treatment of the waste material, either as-received or with the addition of fluxing agents such as alkalis and waste glass. Further controlled heating of the waste-derived glass causes crystallisation of the glass into its ceramic analogue, and this is known as devitrification. The product of the vitrification with devitrification process is a glass-ceramic. The composition of the base glass significantly determines its crystallisation characteristics, and glass composite systems which are difficult to crystallise would require the addition of nucleating agents to promote the formation and growth of crystals within the glass matrix. TiO_2 and P_2O_5 are commonly used nucleating agents.

Experimental procedure

Characterisation of oil well drill cuttings

Untreated drill cutting samples, from drilling operations in the North Sea, supplied by the company Shell (Aberdeen, Scotland), were characterised in terms of their physical, chemical and microstructural properties. The physical properties included density measurements using the Archimedes principle, particle size analysis by laser diffraction using a Coulter LS 100 particle analyser and determination of water content by heating the material at 105 °C to constant weight. Chemical analyses were obtained by determination of the elemental content by inductively coupled plasma—atomic emission spectrometry (ICP-AES) using a Varian Vista-Pro Axial equipment, and mass spectrometry (ICP-MS) with a Varian Model 810, following alkaline fusion with lithium metaborate and nitric acid extraction [13]. The microstructural analysis was carried out using X-ray diffraction (XRD) with a Philips P1830 diffractometer using Cu $K\alpha$ radiation to identify bulk and clay minerals, and thermal analysis was carried out by differential scanning calorimetery (DSC) using a Simultaneous Thermal Analyser STA 1500 (Rheometric Scientific). A leaching study was also carried out using a two-stage British Standard batch test methodology for leaching of granular waste materials [14].

Vitrification of oil well drill cuttings

Processing of glass-ceramics is carried out by controlled crystallisation of a base glass [15] and in order to obtain this glass, different mixtures of drill cuttings with fluxes (sodium oxide, calcium oxide and cullet) were melted in a Lenton elevator hearth furnace model EHF 17/5 at temperatures ranging from 1200 to 1400 °C. After holding in the furnace for times varying between 2 and 6 h at the set temperature, the melts were quenched in water and the frits crushed to a fine powder using a tungsten carbide Tema mill (Gy-Ro, Glen Cresten Ltd.). The produced powders were analysed by XRD and thermal analysis. Thermal analysis involved heating the samples at a rate of 10 °C min^{-1} from ambient temperature to 1100 °C in air using a Netzsch Simultaneous Thermal Analyser STA 449 C equipment.

Fabrication of sintered glass-ceramics from oil well drill cuttings-derived glass

Powdered samples of crushed drill cuttings-derived glass with a mean particle size distribution of 25 μm were compacted using a uniaxial hydraulic press at 50 MPa to form cylindrical specimens of 20 mm diameter and 5 mm height. These were heat-treated in a Lenton Eurotherm 2416CC furnace at a rate of 10 °C min^{-1} over the temperature range of 750–800 °C for different durations. This process led to sintering and crystallisation of the specimens. The sintered samples were allowed to cool inside the furnace. Bar-shaped specimens of dimensions $45 \times 5 \times 5$ mm^3 and $25 \times 6 \times 6$ mm^3 were also fabricated by cold uniaxial pressing and sintering at 800 °C for 2 h at a heating rate of 10 °C min^{-1}. These were used for determination of Young's modulus and thermal expansion coefficient respectively, as described below.

Characterisation of glass-ceramics

The crystalline phases precipitated in the sintered products were investigated using XRD and scanning electron microscopy (SEM) using a JEOL JSM-840A electron microscope for the microstructural analysis of the glass-ceramics produced, both on fractured samples and polished surfaces. Water absorption as a percentage of dry mass, apparent porosity and density of the glass-ceramics were also determined [16]. The hardness, H_V, and the indentation fracture toughness, K_{IC} (MPa$\sqrt{}$m), of the glass-ceramics were obtained using Zwick/Roell Indentec ZHV1-m Vickers Microhardness indentation equipment with indentation by a Vickers-diamond pyramid 136° indenter at a load of 300 g applied for 10 s [17, 18]. The Young's modulus of elasticity was also obtained by resonance method, which is most often used with flexure and torsion of slender bars and cylinders [18, 19], by measuring the vibration excitation of rectangular test bars. The coefficient of thermal expansion was obtained by dilatometric analysis in a Netzsch Dilatometer DIL 402 E, in which 25 ± 1 mm rectangular test bars of the glass-ceramic were heated at 10 °C min^{-1} from room temperature to 800 °C.

Chemical resistance was investigated by treating 2 g of a crushed sintered sample for 1 h in 60 mL of acidic and alkaline solutions (0.01 M of hydrochloric acid and 0.01 M of sodium hydroxide) at 95 °C [20]. The percentage weight losses were obtained after washing and drying the sintered samples. Leaching studies were also carried out on the sintered samples using the two-stage batch test [14], with the leachate being analysed by ICP and ion-chromatography.

Results and discussion

Drill cuttings characterisation

The average dry residue of the as-received oil well drill cuttings, after drying them at 105 °C, was 83% and the particle density was 1.33 g cm^{-3}. Oven-dried samples which had been ground simply by crushing by hand, had a predominant particle size determined by laser diffraction, of about 29 µm, with 50% of the particles less than 19.5 µm. Wet-milled samples, however, had a particle size concentration of about 9.9 µm with 50% of the particles less than 8 µm.

The results of chemical analysis by ICP-AES following alkaline fusion of dried drill cuttings and extraction with nitric acid are given in Table 1. This oxide composition is typical for drill cuttings from operations in the central North Sea, as reported by Page et al. [21]. The heavy metal content is a critical factor in the potential reuse of this waste due to possible deleterious effects of leaching on future uses.

Table 1 Chemical composition of dried drill cuttings

Oxides	wt%	Heavy metals	(ppm)
SiO_2	47.60	As	11.8
Al_2O_3	13.54	Cd	0.3
BaO	11.39	Cr	116.0
Fe_2O_3	6.34	Cu	32.9
CaO	2.78	Ni	65.0
K_2O	2.33	Pb	11.2
MgO	2.31	Zn	125.0
Na_2O	1.17		
TiO_2	0.65		
MnO	0.17		
P_2O_5	0.10		
LOI	11.63		

LOI loss on ignition

The XRD pattern of a sample of drill cuttings, dried at 105 °C, is presented in Fig. 1. It shows that the waste is a silicate-based material with traces of albite, calcite, dolomite and barite, in agreement with previously reported results on North Sea cuttings piles, which identified quartz and barite as the two most abundant minerals in cuttings from the region [22]. Thermal analyses of drill cuttings previously dried at 105 °C showed dehydroxylation at around 500 °C as well as weight loss of approximately 12% by 900 °C. These weight losses are in agreement with the results of the chemical analysis. Further, the loss on ignition of the dried samples due to the thermal decomposition of anions on heating the sample at 1050 °C for 1 h until constant weight was found to be 16% [23]. This gave a combined weight loss of about 33% from the wet, as-received drill cuttings subjected to treatment at 1050 °C. XRD analyses of samples of drill cuttings which had been

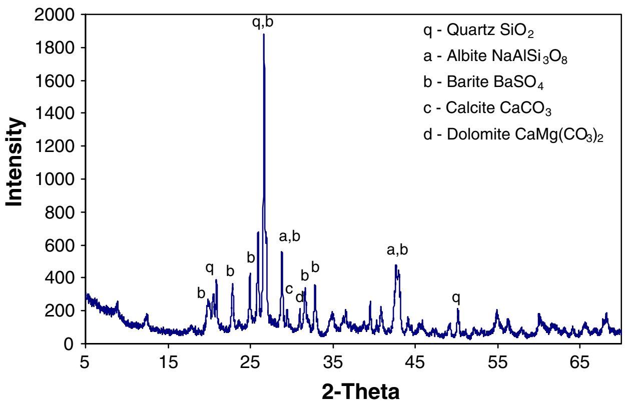


Fig. 1 XRD pattern of a sample of oil well drill cuttings dried at 105 °C

treated at a minimum of 1050 °C for 1 h showed a highly crystalline kaolinitic pattern.

Melting behaviour of drill cuttings

The glass-forming potential of the drill cuttings sample was based on the weight percent composition of the main oxides in the sample. It was found that the silica content was within the glass-forming region of the SiO_2–Al_2O_3–BaO ternary system, occurring close to a eutectic point at 1296 °C as shown in Fig. 2. While pure silica has a liquidus temperature of just over 1700 °C, the estimated liquidus temperature of the drill cuttings sample was 1300 °C. In order to ensure proper refining of the melt at this temperature, the drill cuttings were mixed with different proportions of fluxes (Table 2). A very viscous homogenous melt was obtained from the mixture of drill cuttings:Na_2O:CaO in the ratio of 8:1:1 after a dwell time of 5 h at 1300 °C. XRD analysis of the cooled melt showed that it was completely amorphous (see Fig. 4a).

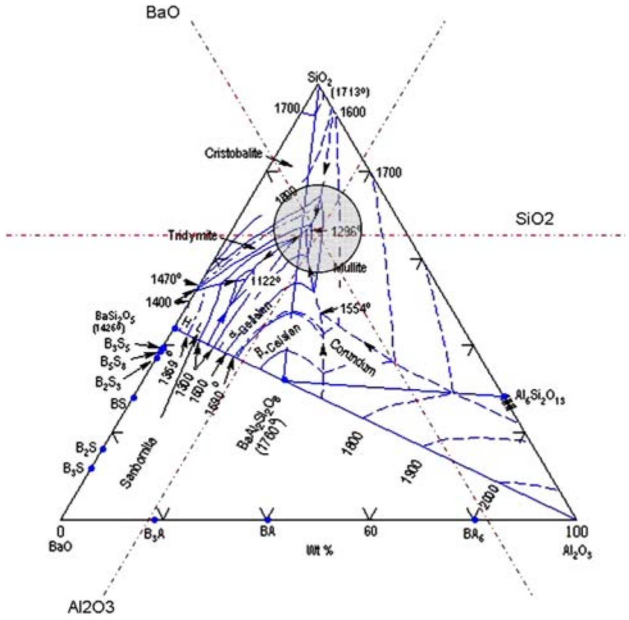


Fig. 2 BaO–Al_2O_3–SiO_2 ternary system [24] used to estimate the melting point of the drill cuttings system based on oxide weight percent composition

Sintered glass-ceramics: processing and characterisation

Although thermal analysis of the glass product obtained did not give conventional profiles, it was possible to identify and select heat treatment temperatures to investigate crystallisation from the exothermic peaks which were observed at around 750–800 °C in the DSC traces (Fig. 3). The exothermic peak is as a result of the crystallisation reaction, which is accompanied by heat release from the system. A smooth endothermic peak at around 650 °C was considered to be the transition temperature before the onset of crystallisation. Crushed samples of this glass composition, compacted at 50 MPa, were therefore sintered at temperatures within this range for different times, and dark brown, fully densified materials were obtained. XRD analysis of samples sintered at 800 °C showed a significant level of crystallisation (Fig. 4b) and based on this result, this sintering heat-treatment (800 °C, 2 h) was considered the most suitable to produce highly crystalline glass-ceramics. All further experiments were thus conducted on samples produced at this optimal sintering temperature. The high intensity diffraction peaks were consistent with the precipitation of three crystalline phases: hyalophane $(K,Ba,Al)Si_2O_8$, gehlenite $Ca_2(Mg,Al)(AlSiO_7)$ and nepheline $(Na,K,Al)SiO_4$. The crystallisation process during sintering is accompanied by shrinkage and densification with zero weight loss, and this was noticeable in the end-product. Crystallisation of the base glass was evident in the SEM images obtained from fracture surfaces. The SEM

Table 2 Different mixtures containing drill cuttings which were investigated for glass-forming potential

Composition (ratio)				Comments, melt status[a]
DC	Na_2O	CaO	Cullet	
1	–	–	–	Fair after 2 h hold at 1400 °C
8	2	–	–	Good glassy appearance after 6 h hold at 1300 °C
8	1	1	–	Good glassy appearance after 6 h hold at 1200 °C
8	1	1	–	Very good after 5 h hold at 1300 °C
1	–	–	1	Good glassy appearance after 6 h hold at 1200 °C
1	–	–	1	Very good after 5 h hold at 1300 °C
6	–	–	4	Good after 6 h hold at 1300 °C
7	–	–	3	Good after 6 h hold at 1300 °C
8	–	–	2	Good after 6 h hold at 1300 °C

[a] Melt status assessed by physical appearance

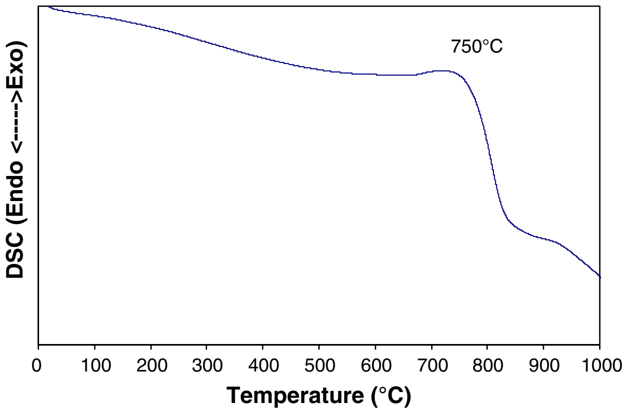


Fig. 3 DSC trace of drill cuttings-derived glass (drill cuttings:Na_2O:CaO mix 8:1:1)

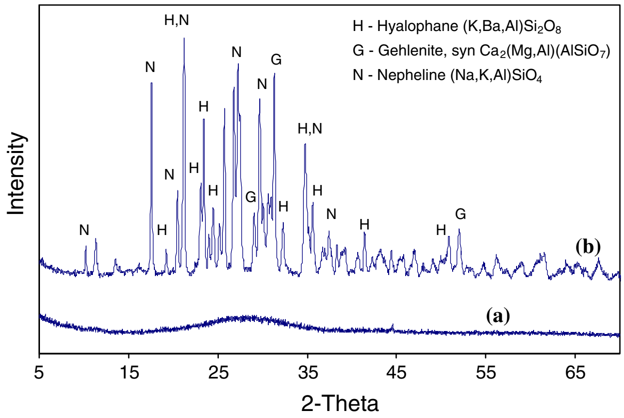
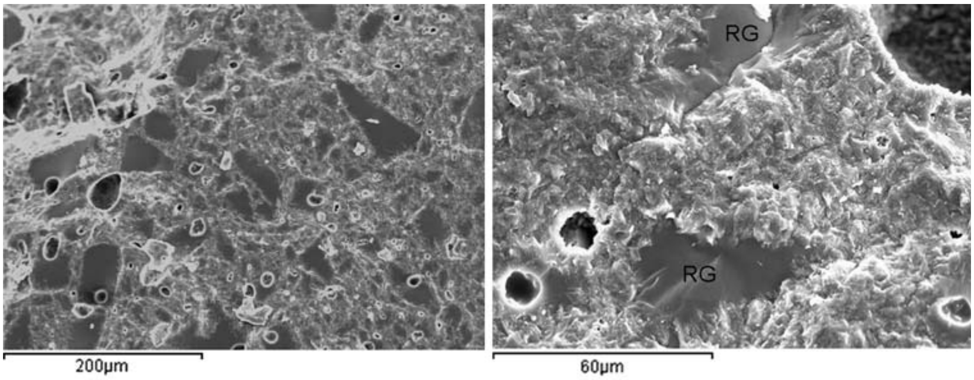


Fig. 4 XRD patterns of (a) base glass obtained from melting oil drill cuttings:Na_2O:CaO mix 8:1:1; (b) crystalline material obtained after sintering this base glass at 800 °C for 2 h

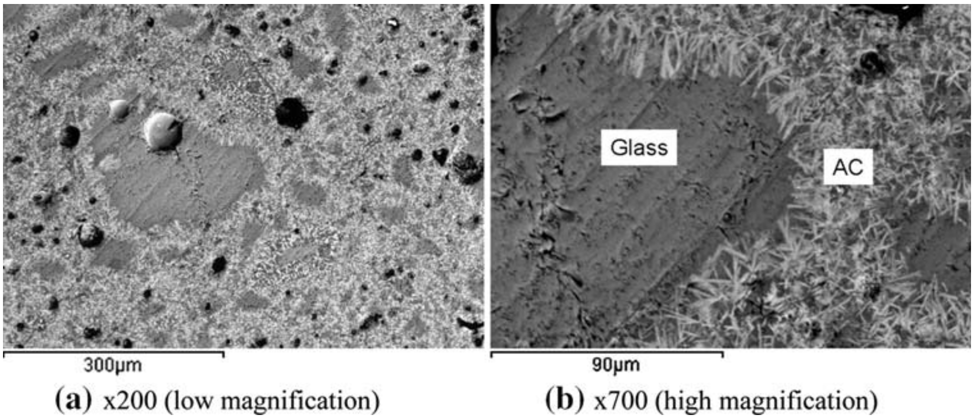
images in Fig. 5a and b show the microstructure of the sintered material indicating the presence of crystals surrounded by residual glass. A glass-ceramic contains typically 50–95% by volume of crystalline material with the remainder being residual glass [12]. Analysis of the polished surfaces of the glass ceramic produced by electron microscopy further revealed acicular crystal morphology, and evidence of heterogeneous crystallisation (Fig. 6a and b). Crystallisation appears to start at the contact planes of two glass grains sintered together, and to progress into each of the grains individually. Polishing of this material results in an aesthetic brown marble-like pattern, suggestive of possible applications in tiling.

The physical, thermal and chemical properties of the produced glass-ceramics were determined and are compared with some equivalent properties of a commercial glass-ceramic product and of glass-ceramics obtained from varieties of silicate wastes, as shown in Table 3. The density of the glass-ceramic obtained in this study was similar to that of a commercial glass-ceramic (Macor®), and of glass-ceramics obtained from other varieties of silicate waste, as reported elsewhere [12, 20, 25]. The zero porosity of the glass-ceramic obtained from vitrified drill cuttings provides a physical property advantage over conventional sintered ceramic products, which, due to residual porosity, are much more permeable in the environment. The property of “close to zero porosity” in the present glass-ceramics from drill cuttings also has a direct positive impact on their mechanical properties and structural integrity. It is well-known that more porous materials have lower hardness, fracture toughness and fracture strength. The present glass-ceramics have a hardness of 6.4 GPa, which is good in comparison to natural products such as marble [25] and granite [26]. The coefficient of thermal expansion is also comparable to that of marble and granite, and of other glass-ceramics obtained from silicate wastes [12]. Moreover, the brittleness index (*B*) of the drill cuttings glass-ceramics, which is the ratio of hardness to fracture toughness [27], has a value of 7 $\mu m^{-½}$. This value is similar to that of other technical glass-ceramics and indicates that machining the material to form complex-shape components may present difficulties [27]. However, the brittleness index value, which is also related to the wear

Fig. 5 Fracture surface SEM images of a sintered glass-ceramic (sintering temperature: 800 °C, sintering time: 2 h) derived from vitrified drill cuttings, **a** at low magnification **b** at higher magnification, showing crystals surrounded by residual glass—RG



(a) x200 (low magnification) **(b)** x1000 (high magnification)



(a) x200 (low magnification) (b) x700 (high magnification)

Fig. 6 Polished surface SEM images of sintered glass-ceramics (sintering temperature: 800 °C, sintering time: 2 h) derived from vitrified drills cuttings, **a** at low magnification, showing marble-like pattern **b** at higher magnification, showing acicular crystalline precipitation—AC—at grain boundaries

Table 3 Physical, thermal and chemical properties of sintered glass-ceramics (sintering temperature: 800 °C, sintering time: 2 h) derived from drill cuttings (DC) compared to a commercially available material and two examples of silicate waste-derived glass-ceramics

Property	DC glass-ceramic	Commercial glass-ceramic[a]	Leroy et al. [20]	Davim and Fernandes [25]
Density (g cm^{-3})	2.75	2.52	2.73	2.8
Porosity (%)	0.3	0	–	–
Hardness, H (GPa)	6.4 (300 g load)	–	–	7.37 (300 g load)
Young's modulus, E (GPa)	92	67	–	–
Fracture toughness, K_{IC} (MPa$\sqrt{}$m)	0.90	1.53	–	–
Coefficient of thermal expansion (10^{-6} mm °C^{-1})	9.6 (30–500 °C)	9.3 (25–300 °C)	10.1 (20–400 °C)	–
Chemical resistance (% wt loss)				
0.01 M HCl, 95 °C, 1 h	0.3	–	0.58	–
0.01 M NaOH, 95 °C, 1 h	0	–	0.56	–

[a] Macor® (Corning Incorporated)

and abrasion resistance [28], indicates a sound wear resistance of the material, e.g., for applications as floor tiles in heavy duty floors.

The drill cuttings-derived glass-ceramics are also robust materials with good chemical resistance. The chemical durability was analysed by weight loss in acidic and alkali solutions, and found to be around 0.3% in both solutions. These values are comparable to those of glass-ceramics produced from coal ashes by Leroy et al. [20] which were considered to be within the first hydrolytic class of the ISO 719 standard. Weight losses are usually attributable to the dissolution of the glassy matrix [20] and an increase in crystallinity of the glass-ceramic produced corresponds to decrease in susceptibility to chemical attack. This is because the formation of crystalline phases during heat treatment results in more bonding in the glass-ceramic network than in the parent glass [29] and, therefore, less mobile cations to participate in the ion exchange which is initiated during chemical attack.

A significant aspect of recovering value from a waste material is concerned with the hazardous potential of the waste. Leaching studies carried out on the glass-ceramics produced in this study have been compared to those obtained for the as-received drill cuttings and the results are shown in Table 4. The potential for heavy metals and anions to leach out from the as-received oil well drill cuttings is sufficiently high enough for the waste to be considered hazardous, especially with regard to any future uses, and this further emphasises the importance of vitrifying the waste. It can be seen that the leachability, particularly for heavy metals, has been significantly reduced compared with the starting oil well drill cutting residues, suggesting that the glass-ceramics are safe materials which would not result in environmental problems when used in tiling applications.

Table 4 Results from leaching studies (mg kg^{-1})

Parameter	As	Cd	Cr	Cu	Ni	Pb	Zn	Cl^-	F^-	SO_4^{2-}
As-received drill cuttings	1.0	0	0.1	0.8	0.5	0	0.1	5,158	140	2,135
Glass-ceramic	0	0	0	0	0	0	0	16	2	21

Conclusions

Oil well drill cutting wastes are a major solid waste from the oil and gas exploration and production industry. In order to divert this waste from final disposal, for example to landfill, it is necessary to convert it into a material with sound mechanical properties and structural integrity that has both a specific commercial use and entrains any potential hazardous components, to prevent them from being leached out in their future applications. Most drill cutting residues are subject to thermal desorption processes to remove and/or recover any entrained oil, leaving a mineral residue. The vitrification and sintering/crystallisation process reported here represents a versatile technique that is capable of converting the residual cuttings to a glass-ceramic, while at the same time producing a safe material from which heavy metals and other impurities cannot be leached. Additional contaminants include salts and hydrocarbon coating on the cuttings due to the drilling mud used and the formations being drilled. Vitrification ensures that the salt impurities are encapsulated within the glass matrix as shown by the leaching test, while possible gas emissions can be controlled for example using furnaces fitted with gas scrubbing technology. These emissions, however, need to be investigated further. It is also suggested that the chemical durability be investigated further, with SEM and EDX for chemical composition, to provide more information on the effect of chemical attack on the drill cuttings-derived glass-ceramics.

The favourable properties of the produced glass-ceramic that determine its potential uses include relatively high hardness, fracture strength, fracture toughness and stability towards leaching. The glass-ceramics from drill cuttings have almost zero porosity resulting in attractive mechanical properties for possible applications as building materials, e.g., tiling. Other technological properties of relevance such as wear, abrasion and thermal shock resistance should be investigated to widen the application potential of these novel materials.

Acknowledgements The authors wish to thank Petroleum Technology Development Fund of Nigeria (for a grant to OEA), Shell UK E&P Aberdeen (for provision of drill cutting samples) and Professor John Donaldson and Dr. Amutha Devaraj for helpful advice.

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