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An evaluation of selected waste resources for utilization in ceramic materials applications

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Abstract

Many industrial processes generate large amounts of waste. Typical examples include the fertiliser industry (phosphogypsum), ferro-alloy and steel producers (slag), as well as the power generating industry (fly ash). Although some waste products are currently used to a limited extend (e.g. fly ash and cement in cement), there is a constant need to find more uses and new applications for these. This investigation describes work done to develop a novel ceramic body, which can potentially be used as a ceramic filter for purification of waste water and potable water.

Keywords: Slip casting; Porosity; Mechanical properties; Waste materials; Filters

1. Introduction

Typical examples of industrial waste include materials from the ferro-alloy and steel industries (slag or iron-rich waste) and the power generating industry (fly ash). These waste products are currently used in limited amounts. It is well known that coal is the main fuel of South Africa. In 1985, 124 million tons of coal were consumed by the local market.[1] Coal is used not only used to generate steam and electricity, but also to produce liquid fuels and chemicals. From an environmental viewpoint, such applications generate large quantities of ash, which mostly end up as large dumps near the points of use, and emissions of combustion products.[2]

This investigation was launched to find alternative applications for these materials. One such possible application is to manufacture water filters from them. The supply of clean drinking water is an urgent priority in South Africa, and a successful development of such a filter could contribute significantly to assist with the supply of clean drinking water to especially disadvantaged communities. Some of the most important criteria for such a filter will be, amongst others, sufficient porosity, mechanical strength to withstand handling and a reasonable head pressure of water, ease of cleanability, and ease of manufacturing. The materials used in this investigation will, therefore, be employed in various combinations to try and achieve as many of these objectives/desirable properties. In this specific paper only the physical properties of the filters will be addressed while the operational performance of the filters will follow in subsequent papers.

Several waste products have been identified for possible incorporation with clays in novel ceramic bodies intended for a water filter application. These include fly ash, ball clay, bentonite, phosphogypsum and iron-rich waste.

1.1. Fly ash

Fly ash is largely composed of glassy, spherical particles. The finest ashes are coarser than typical clays, with the average particle size of ash and clay somewhat above and below two microns, respectively. Shrinkage of clay bodies can be

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Table 1
Chemical composition of waste materials

Percentage	Lethabo fly ash	Iron-rich waste
SiO_2	52.59	2.71
TiO_2	1.68	11.96
Al_2O_3	34.59	3.70
Fe_2O_3	3.15	75.91
MnO	0.04	0.35
MgO	1.06	0.98
CaO	4.08	0.56
Na_2O	0.17	2.10
K_2O	0.60	<0.01
P_2O_5	0.28	<0.01
Cr_2O_3	0.04	0.27
NiO	0.02	0.02
V_2O_5	0.04	0.45
ZrO_2	0.08	<0.01
LOI	1.4	0.07
Total	99.82	99.09

lowered by fly ash additions.[3] Fly ash has a typical chemical composition as indicated in Table 1.

1.2. Ball clay

The ball clay used consists essentially of kaolinite with small amounts of mica and quartz and has a high organic content. Ball clays are used extensively in the whiteware ceramic industry as an ingredient in clay bodies composed largely of non-plastic materials, in order to impart the required plasticity and green and dry strengths.[4,5]

1.3. Bentonite

Bentonite refers to clay of volcanic origin, and it consists mainly of montmorillonite. Bentonite is used in bodies, glazes and enamels to improve plasticity and increase thixotropy.[6] The reactivity of bentonite arises from the crystal structure and small particle size.[6,7] The high working moisture of bentonite results in high drying shrinkage, thus the content should be restricted to no more than five percent.

1.4. Phosphogypsum

Phosphogypsum[8] is a by-product resulting from the phosphoric acid process for fertilizer production. It consists mainly of $CaSO_4{\cdot}2H_2O$ with further impurities such as P_2O_5, F^- and organic substances. Only 15% of the worldwide production of phosphogypsum is utilized while the remaining 85% causes an environmental problem and needs large disposal areas. Attempts have, therefore, been made to use phosphogypsum in applications such as road and rail works fills, stabilization of base course, and building products.[8]

The particle size of this gypsum is usually below 200 μm. Gypsum has low strength and poor adhesive properties, but is added to bodies to assist in setting.[9]

1.5. Iron-rich waste (Fe-rich waste)

The iron-rich waste used was a byproduct from a vanadium manufacturer (Vametco Mineral Co). Little information is recorded in literature on this material. Given the iron-rich composition, it can be used as a flux. A chemical analysis was performed on this material and is given in Table 1.

The waste materials have been characterized with the aim to incorporate these in novel ceramic products. The present study describes the development of such a product for possible use as a ceramic water filter, to replace sand filters in the purification of waste and potable water.

2. Methods

Three ceramic bodies were formulated with the following compositions:

- 80% fly ash; 15% ball clay and 5% bentonite (FCB);
- 80% fly ash; 15% ball clay and 5% iron-rich waste (FCI);
- 80% fly ash; 5% gypsum and 10% iron-rich waste and 5% over-burden bentonite (FPIB).

The method used to manufacture the samples for the formulated bodies were casting. The samples were prepared with the optimum amount of deflocculant, and then cast in a plas-

Table 2
Physical properties of starting materials fired at different temperatures

Property	Temperature (°C)	Kaolin	Fly ash	Lime	Gypsum	Fe-rich waste	Feldspar
Shrinkage (%)	800	3.84	2.35			3.58	
Strength (MPa)	800	5.22	6.32			16.14	
Water absorption (%)	800	25.61	17.63			8.05	
Shrinkage (%)	850	3.74	2.38		3.54	4.03	3.88
Strength (MPa)	850	5.01	4.33		2.32	11.59	3.63
Water absorption (%)	850	25.21	17.53		63.34	7.85	15.76
Shrinkage (%)	900	3.94	2.23	5.59	5.21	4.30	2.18
Strength (MPa)	900	11.13	11.85	2.93	3.50	18.38	5.22
Water absorption (%)	900	0.64	16.63		57.43	8.20	16.03

Some raw materials such as the kaolin, lime and feldspar are not discussed in the text as they are not waste materials. These materials were evaluated as possible additives to the mixtures, which in the end did not prove necessary.

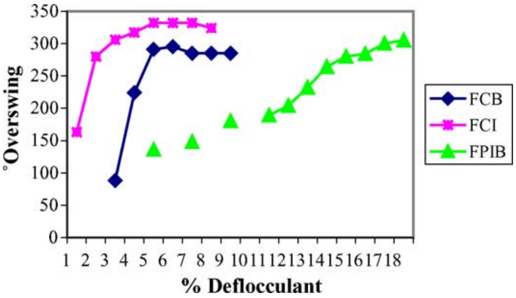

Fig. 1. Fluidity of ceramic clay bodies.

ter of Paris mould to extract most of the water from the slurry and to end with samples of a square nature.

The properties of the materials were determined according to the methods as explained in the Appendix.

3. Results and discussion

The chemical and physical properties of the respective starting materials are provided in Tables 1 and 2.

3.1. Flow properties of ceramic bodies

The fluidity and thixotropy of ceramic bodies as measured by torsion viscometer are graphically represented in Figs. 1 and 2. From these Figures, it can be seen that the amounts of sodium polyacrylate utilised to reach the turning point of the fluidity are high for all the mixes. This can be attributed to the high amounts of fine material in the mixtures. The FCB material shows better flow properties compared to the others, indicating that it can be deflocculated with less difficulty.

3.2. Ceramic properties of clay bodies

The results obtained on the fired samples are graphically presented in Figs. 3 and 4. Fig. 3 presents the firing shrinkage of the bodies investigated. All the materials show relatively low shrinkage at 1050 °C. The FPIB mixture shows the highest shrinkage, which can be attributed to the high clay content (bentonite) as well as the relatively high amount of iron-rich waste. The shrinkage and strength of the FPIB body were not available as the samples broke during firing. However, it was possible to determine the water absorption and bulk density on the broken pieces. The iron-rich waste contributed to a high shrinkage by acting as a flux as can be seen in Figs. 3 and 4. The shrinkage of FCB has a maximum at 950 °C and then decreases by increasing the temperature due to the high clay content in the mix and the kaolin change to meta-koalin at ±950 °C, which results in an increase in volume.

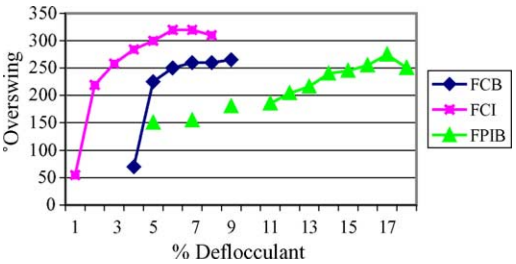

Fig. 2. Thixotropy of ceramic clay bodies.

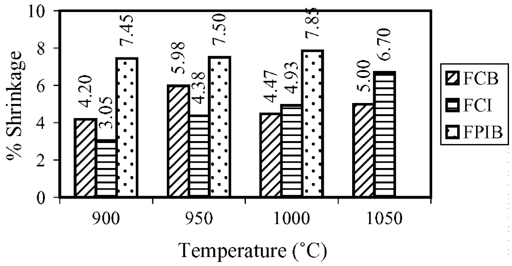

Fig. 3. Shrinkage of ceramic bodies fired at various temperatures.

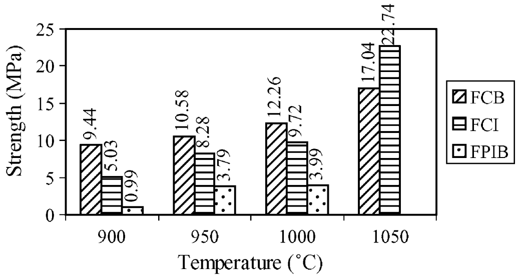

Fig. 4. Strength of ceramic bodies fired at various temperatures.

The modulus of rupture of the materials is presented in Fig. 4. In all cases the strength of the cast samples improved dramatically. The strength of FPIB is low and this can be attributed to the relatively large amount gypsum in the mixture. The high amount of Ca in gypsum is known to increase the vitrification temperature of the body into which it is incorporated.[6] However, all samples have sufficient strength for handling. At 1050 °C the Fe-rich waste begins to act as a flux and improved the strength of the mixtures due to ceramic bonding taking place.

Fig. 5 presents the water absorption of the materials. Water absorption is an indication of the porosity of the mixture or body. This parameter was the primary determinant to as-

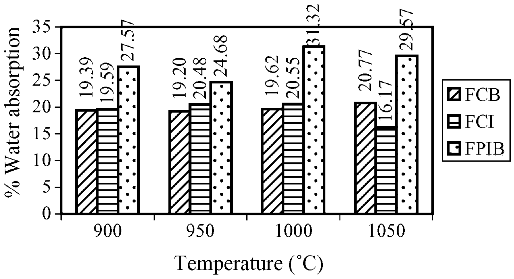

Fig. 5. Water absorption of ceramic bodies fired at various temperatures.

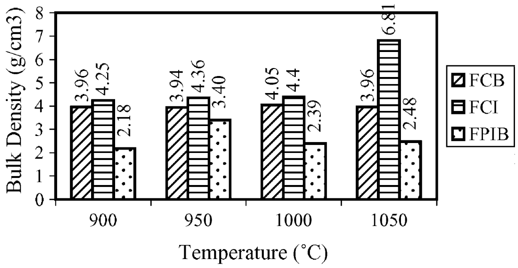

Fig. 6. Bulk density of ceramic bodies fired at various temperatures.

sess the potential of the manufactured bodies for possible use as filter material. The rationale not to measure pore size distribution in the initial phase of the investigation, was to first identify the most promising body from this suite of simple evaluations. The water absorption is low for FCB and FCI bodies, which is to be expected from the high shrinkages (see Fig. 3). Conversely, FPIB shows a high water absorption, as can be expected from the low shrinkage. A low shrinkage indicates that little vitrification took place, while high water absorption indicates that pores are not yet isolated through vitrification.

The bulk densities (Fig. 6) of all the bodies are high in the extruded state, with FPIB showing lower values than the other two mixes. This can be linked to the amount of bonding achieved in the fired material. The cast samples showed lower bulk densities than the extruded ones. The method of shaping also plays a role, since the FPIB was hand extruded. The FPIB mixture would be preferred due to its low bulk density. Low bulk density indicates less use of material, which implies lower costs. Furthermore, the low bulk density is indicative of a high porosity, which is favourable for a material intended as filtering medium.

4. Conclusion

The aim of this project was to identify a potential promising filtering medium from waste materials, which can withstand physical handling and a head pressure without rupture or breakage, have sufficient water absorption (which was used as an indication of porosity) and can be manufactured easily and cheaply. Three material mixtures were investigated and the following conclusions reached:

(i) The FPIB mixture shows favourable water absorption and shrinkage for employment as a filter, but low strength. Strength may be increased by the incorporation of more Fe-rich waste, or a reduction of gypsum content, which seem to have a remarkable effect on strength. This mixture should be investigated further to see if better strength than that of the current body can be obtained without losing the desirable properties of low bulk density and high water absorption.
(ii) The FCB and FCI materials show lower water absorption and better strength, but appreciable shrinkage. These properties are more suited for use in high-pressure systems, where the filters need to have good integrity.
(iii) Organic materials that burn out on firing may be used to increase porosity of all the mixtures. It is recommended that all three mixes should be mixed with an organic material such as polystyrene and then evaluated, to determine the water filter properties. The influence of such an approach on the physical properties of mixtures should be undertaken. These aspects are currently under investigation and will be reported on in subsequent communications.
(iv) Casting seems to be the best method of manufacturing for the FPIB mixture, while extrusion will be more suitable for the FCB and FCI material mixes.

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Appendix A. Physical properties

Bulk density: The Doulton densometer was used to determine the bulk densities. A standardised test method previously developed in-house was used.[4]

The density was calculated using the following formula:

$$\text{Bulk density (BD)} = \frac{m_1}{m_2}\text{BD}_{\text{Hg}}\,(\text{g}\cdot\text{cm}^{-3})$$

where m_1 is the mass of sample in air (g); m_2, mass of sample in mercury (g); BD_{Hg}, density of mercury at the relevant temperature ($\text{g}\cdot\text{cm}^{-3}$).

Shrinkage: The shrinkage of samples was determined after drying at 110 °C (green shrinkage) and after firing at 900–1050 °C with 50 °C increments (fired shrinkage). The total shrinkage, which is the shrinkage from the wet state to the fired state, was also determined. The shrinkage was determined by making 100 mm marks on the samples and measuring the distance between the marks after drying and firing.

Strength: A Lloyds 200 three-point flexion bend test apparatus was used to determine the strength of samples at room temperature. A standardised test method developed previously in-house was used.[4] The distance between the knife edges was 100 mm. The samples were approximately 130 mm long. The samples were prepared by casting, and were approximately 25 mm × 25 mm, while extruded samples were 12 mm in diameter.

The modulus of rupture (MoR) was calculated for samples of rectangular cross-section as

$$\text{MoR} = \frac{3P\ell}{2bd^2}(\text{MPa})$$

and for samples of round cross-section as

$$\text{MoR} = \frac{8P\ell}{\pi\phi^3}(\text{MPa})$$

where P is the force (N); ℓ, distance between knife edges (mm); b, breadth (mm); d, depth (mm); ϕ, diameter (mm); $\pi = 3.14$; MoR, modulus of rupture (MPa).

Water absorption: Fired samples were boiled in water for 3 h prior to determination of water absorption. A standardised test method as developed previously in-house was used.[4] Water absorption was calculated as

$$\text{Water absorption (WA)} = \frac{m_2 - m_1}{m_1} \times 100\,(\%)$$

where m_1 is the dry mass (g); m_2, soaked mass (g).

Appendix B. Chemical analysis

Chemical analysis of fly ash and iron-rich waste was performed by XRF using a Bruker MPS 400 instrument with samples prepared as cast beads.

Appendix C. Flow properties

Deflocculation of the ceramic body is necessary to achieve a mixture with a very high fluidity and the lowest possible water content. To determine the correct amount of deflocculant, the fluidity and thixotropy were measured by a torsion viscometer. The slip was placed under the torsion weight and the fluidity was determined by measuring the degree of overswing after the fly wheel was rotated through 360°. The thixotropy of the material was determined after leaving the sample for 3 min in the torsion viscometer.

Appendix D. Sample preparation

The physical properties of the different waste materials were determined as the mean values of 10 samples. The materials were prepared with 20% addition of ball clay to facilitate forming of the samples. The samples were extruded with a hand extruder.

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