PAPER MILL SLUDGE AND GLASS CULLET AS MATERIALS FOR TILE PRODUCTION

Sergio Comuzzo, Erika Furlani, Dino Minichelli, Sergio Bruckner, Francesco Andreatta, Lorenzo Fedrizzi and Stefano Maschio

Università di Udine, Dipartimento di Scienze e Tecnologie Chimiche
Via del Cotonificio 108, 33100 Udine-Italy

ABSTRACT

Paper mill sludge was subjected to a previous thermal treatment and then blended by attrition milling in different proportions with glass cullet to obtain powders of different composition. These powders were pressed into specimens which were air sintered at temperatures as close as possible to the softening point by means of a muffle furnace. The fired samples were examined by XRD and SEM; water absorption, density, strength, hardness, fracture toughness were also determined. The mechanical properties of some sintered specimens are fairly good due to the formation of small grains that, in some cases, are embedded into a vitreous matrix. It was observed that, although the shrinkage on firing is too high for the production of tiles, in almost all the compositions the sintering procedure leads to fine microstructures and good mechanical properties. Owing to the low content of hazardous elements in the starting powders (<50 ppm), and considering that the sintering procedure is demonstrated to be effective in the inertization of most of heavy metals ions, no elution tests were done on the sintered materials.

1. INTRODUCTION

The impact of special sludge on environment is every day more severe. A way to transform these products into materials good for tile production is given by thermal treatment at high temperatures. In this way, it is possible to have an alternative to the exploit of new void spaces for waste disposal. The sludge transformation is given by a thermal process which gives raw materials suitable for ceramic industry. By sintering of the sludge, it is possible to obtain vitreous and/or semi-vitreous products that do not release hazardous materials contained in the starting materials[1-2]. Previous data show that leaching of sintered products is strongly lowered, if compared to original waste products[3-8]. Furthermore, a sintering process of sludge produces a significant reduction of the original waste volumes that can reach 80 – 90%. This process is suitable only if sintered materials show good mechanical properties.

Paper mill sludge (PS) is largely produced during paper making. This sludge is formed by small cellulose particles in conjunction with mineral fillers, and can be used for the production of heavy papers (cardboards and millboards). Another possible way to reuse PS, since the main constituent elements are Al, Mg and Si, that are oxides largely used in the ceramic industry, is their blending with natural raw materials extracted from the ores in the production of bricks or cements[9-11]. Glass cullet (GC) is classified as non dangerous product by CER (European Sludge Catalogue) and is commonly used in various manufacturing activities [glass reforming, melting additives for ceramics]. In the present investigation, we have used GC obtained from glass bottles, mainly containing SiO_2, CaO and Na_2O and few amounts of MgO, Fe_2O_3 and Al_2O_3. All the above mentioned oxides are commonly present in the natural raw materials used for the production of bricks, tiles or other ceramics. We suggest that mixtures of incinerated PS and GC could represent alternative raw materials for preparation of monolithic ceramic products, after sintering and/or vitrification.

In the present investigation, PS were obtained by a paper mill industry, previously heated at 800°C and then blended, in different proportions, with GC. The resulting mixtures were sintered at temperatures similar with those normally used in the ceramic industry. The final products were then characterized in order to evaluate the possibility to use them in ceramics production.

2. EXPERIMENTAL

The chemical analyses of the starting raw materials, done by a Spectro Mass 2000 ICP Spectrometer, are reported in the table I. PS was dried at 150°C for 24 h and then heated at 850°C for 2 h. The resulting material was ground in an agate mortar and blended with GC in the ratios reported in table II. Test samples were then homogenized in water by attrition milling for 3 h, using a plastic container and alumina spheres, at 300 cycles/min. The milling parameters were chosen on the basis of criteria described in earlier papers[1-2]. The milled powders were dried in an oven at 80°C, sieved through a 63 μm sieve and pressed in a laboratory press at 100 MPa to obtain rectangular [4x5x50 mm] specimens.

OXIDE	GC	PS
	Weight %	Weight %
Al_2O_3	6.02	44.13
SiO_2	65.47	30.10
CaO	13.86	16.75
Fe_2O_3	1.96	2.45
MgO	2.03	2.67
Na_2O	8.64	0.20
ZrO_2	0.01	1.97
Cr_2O_3	<50 ppm	0.99
TiO_2	0.08	0.39
SrO	0.02	0.21
MnO_2	<50 ppm	0.05
SnO_2	<50 ppm	0.04
$SO^{=}_3$	<50 ppm	0.87
Cl^-	<50	350 ppm
Others	1.92	0.04

Table I. Composition (wt%) of GC and PS after calcination at 850°C for 2h.
"Other oxides" represents Ba, Ce, Co, Cu, K, Nb, P, Pb, Sb, Zn determined in quantity lower than 50 ppm.

MIXTURES	COMPOSITIONS %	
	PS	GC
1	90	10
2	80	20
3	70	30
4	60	40
5	50	50

Table II. Composition (wt%) of the mixtures prepared in the present work.

The sintering of the specimens was then conducted in an electric muffle, and on the fired samples the following tests were then performed:

- Density determinations by water displacement method;
- Bending strength determinations;
- Vickers hardness (H_v) using a 100 N load;
- Fracture toughness (K_{IC}) determinations by ISB Method;
- Shrinkage measurements on cylindrical specimens;
- Water absorption evaluations after boiling of 3 hrs.

3. RESULTS

The beginning of shrinkage and softening temperatures were determined by observation of thermo-dilatometric diagrams and permitted to choose the sintering temperature for each composition, as summarized in table III. Samples made of pure PS require a high sintering temperature and therefore were not considered. The mechanical properties of the fired specimens are listed in table IV.

SAMPLE	START OF SHRINKAGE [°C]	SOFTENING POINT [°C]
1	860	1230
2	725	1185
3	895	1192
4	965	1157
5	855	1080

Table III. Characteristic temperatures of the various materials obtained by the thermo-dilatometric analysis.

MATERIAL	1	2	3	4	5
ρ[g/cm^3]	3.068	3.032	2.873	2.743	2.587
σ(MPa)	73±4	82±7	76±8	57±5	8±4
H_v (GPa)	4.3 ±0.2	5.5±0.3	4.9±0.1	5.1±0.2	3.6±0.1
K_{Ic} (MPa√m)	1.86±0.05	2.72±0.09	1.43±0.07	1.24±0.05	2.87±0.10
Shrinkage % [Φ]	22.6	20.1	18.7	17.5	14.4
Shrinkage % [h]	7.4	6.3	6.0	5.8	4.1
Water absorption [%]	2.4	1.8	3.4	5.5	6.1

Table IV. Density (ρ), strength (σ), hardness (H_v) and fracture toughness (K_{Ic}) values of the sintered specimens.

It can be observed that density ranges from a minimum of 2.58 to a maximum of 3.08 g/cm^3. The rupture strength appears quite good for samples 1-4, ranging from 57 MPa (sample 4) to 82 MPa (sample 1). On the contrary, sample 5 shows a very low value (8 MPa) and therefore materials having this composition could be not considered for industrial applications. The fracture toughness (K_{Ic}) data are satisfactory if compared with traditional materials.

The presence of a small amount of liquid phase was detected in all the sintered samples by SEM investigation performed on the free surface of fired samples. Material 1 shows a great amount of vitreous phase which acts as binder for the grains and partially hides the microstructure. The shape of the grains, appears globular and equiaxial. Pores are in limited number and their dimensions are ≈ 1 μm. The microstructure of material 2 shows less vitreous phase: in this sample are visible several plate-like structures emerging from the matrix, showing dimensions ranging from 4 up to 8 μm. The equiaxial grains of the matrix have dimensions ≈ 2 μm. As for material 1, also material 3 contains a great amount of vitreous phase which partially covers the grains. It can also be observed that the grain size is smaller (around 1-2 μm) than in material 2, nevertheless in this case pores have larger dimension (around 3-4 μm). This fact could explain the higher water absorption of material 3 with respect to materials 1 and 2. Material 4 shows less vitreous phase than material 3 and grains look equiaxial. Also in this sample are visible several pores having dimension ranging from 3 to 5 μm and are responsible for the high water absorption and moderate strength and toughness. Material 5 has a microstructure similar to that of material 2. Nevertheless, in this case the matrix appears formed by grains with larger dimension than in material 2. The vitreous phase, although present and clearly visible, seems not to act as a binder for the matrix grains which have rectangular shape. Such microstructure is responsible for the poor mechanical properties with the exception of toughness and for the high water absorption. Such unexpected results, in a material where the amount of glass cullet is higher than that of all the other produced in the present investigation, could be due to the not optimal sintering process which is performed at a relatively low temperature. The top sintering temperature is probably not sufficient to melt many of the components of the starting mixture. On the other hand, the large dimension of the grains, both in the matrix and of the platelets could be the result of a thermal treatment which is sufficient to induce a great grain growth, but not enough to develop a liquid phase in quantity sufficient to bind the grains into a homogeneous and coherent material.

4. DISCUSSION

In a previous study on waste materials[12], we have shown that attrition milling can lead to powders having optimal properties in short times [3 hours], as compared with traditional ball milling. Table II shows that the chosen sintering temperatures, ranging from 1130°C to 1180°C fall in the temperature range usually adopted for the sintering of earthenware tiles (porcelain tiles are fired at temperatures ranging from 1200 and 1250°C). It is noteworthy that the presence of a small amount of liquid phase was detected in most of the sintered samples, in conjunction with a high shrinkage on firing. In fact, radial shrinkage on fired specimens varies from 14.4% of sample 5 up to 22.6% of material 1. Such values are higher than those generally admitted for the production of ceramic tiles[13] but may be corrected mixing the powders with a higher amount of inert materials. On the contrary, the water absorption yields values suitable for earthenware production[13], ranging from 1.8% of material 2 to 6.1% of material 5.

The chemical analyses show a great dispersion of data, but elements such as Si, Al and Ca are largely present both in the PS and in the GC powders. Iron oxide is remarkably present in both powders, and, in conjunction with Na_2O, promotes the melting, at relatively low temperature, of the materials prepared in the present work. No significant amounts of Hg were detected in the starting PS and GC. This is can be easily explained as a consequence of the relatively thermal treatment used for calcinations, since at 850°C most of Hg-containing materials melt[14-15] and partial and/or total evaporation of products containing Hg cannot be avoided.

Heavy metals or elements forming coloured oxides are present in low concentration in both the starting waste whereas other hazardous elements are present in negligible amount. A direct consequence of this favourable result is that all the materials prepared in our tests have light colours. If the mechanical properties of the fired materials are higher than those required for the preparation of tiles or sanitary ware, they could be used not only for heavy clay, but also for value-added products[16]. In Fact, the fired products have good mechanical properties (bending strength, toughness, hardness), except for PS alone and the composition n.5. Composition 1 (10% wt GC) is coloured and requires a high sintering temperature, together with good mechanical properties. Owing to the low content of hazardous elements in the starting powders (< 50 ppm), and considering that the sintering procedure is demonstrated to be effective on the inertization of most of heavy metals ions[1-6], no elution tests were performed on the sintered materials.

As conclusion, the present investigation permitted to obtain the following statements:

- waste materials as PS and GC appear feasible for industrial reuse;
- mixtures containing 20, 30 and 40% wt GC within PS showed sintering temperatures according to the ones used for several traditional ceramics, exhibiting good mechanical properties and clear colours;
- PS alone and mixtures containing 10 and 50% wt GC are, on the contrary, not suitable as raw materials for the ceramic industry owing to the high sintering temperature required and to the poor mechanical properties;
- The simple procedure followed in this investigation showed that PS and GC can be recycled into ceramics preserving environment from harmful products.

REFERENCES

[1] H. A. van der Sloot, D. Hoede, D. J. F. Cresswell and J. R. Barton, "Leaching behaviour of synthetic aggregates", Waste Manag., 21(2001)221-228

[2] A. G. Bernstein, E. Bonsembiante, G. Brusatin, G. Calzolari, P. Colombo, R. Dall'Igna, S. Hreglich and G. Scarinci, "Inertization of hazardous dredging spoils", Waste Manag.

[3] Selinger A., Schmidt V., "Investigation of sintering processes in bottom ash to promote the reuse in civil construction, Parts 1 & 2", Woolley G.R., Goumans J.J.J.M., Wainwright P.J., (Ed.) Waste Materials in Construction: Putting Theory into Practice, (1997), pp. 41-58 Elsevier, Amsterdam.

[4] M. Ozaki, H. Watanabe and B. Wiebusch, " Characteristics of heavy metal release from incinerated ash, melted slag and their re-products", Wat. Sci. Tech., 36(11)267-74(1997).

[5] B. Wiebusch, M. Ozaki, H. Watanabe and C. F. Seyfried, "Assessment of leaching tests on construction material made of incinerator ash (sewage sludge): Investigations in Japan and Germany", Wat. Sci. Tech., 38(7)195-205(1998).

[6] Romero M., Rincón J.Ma, Rawlings R.D., Boccaccini A.R., "Use of vitrified urban incinerator waste as raw material for production of sintered glass-ceramics", Materials Research Bulletin, Volume: 36, (2001), pp. 383-395.

[7] Cassan, A.; Goi, D; Tubaro, F.; Bruckner, S.; Bachiorrini, A.; Maschio, S., "Sintering behaviour of thermally treated municipal sewage sludge (MSS)", Ind. Ceram., 24(3)173-79(2004).

[8] Favoni, C.; Minichelli, D.; Tubaro, F.; Bruckner, S.; Bachiorrini, A.; Maschio S., "Ceramic processing of municipal sewage sludge and steelwork slags", Ceram. Int., 31 (2005), 697-702.

[9] Pera, J. and Amrouz, A, "Development of Highly Reactive Metakaolin from Paper Sludge", Adv. Cem. Bas. Mat., 7(2) 49-56(1998).

[10] Ernstbrunner, L., "Rejects from paper manufacture utilized in the cement works", Papier, 51(6):284-286(1997).

[11] Verhoeve, S.C.H.; Verden, N.L.; Jansen, E.J.A.; Huissen, N.L., "Verfahren für die Bereintung vom Papierschlammasche and deren Andwendung bei der Herstellung von Kalkstandstein", German Patent, 1989, No. DE 3838379 A1 (en alemán).

[12] A. Cassan, D. Goi, F. Tubaro, S. Bruckner, A. Bachiorrini, S. Maschio, "Sintering behaviour of thermally treated municipal sewage sludge (MSS)", Ind. Ceram., 24(3)173-79(2004).

[13] T. Manfredini and G. C. Pellacani, Engineering Materials Handbook, Vol 4, Ceramics and Glasses-ASTM, 1992, pp 925-929

[14] Handbook of Chemistry and Physics, 65ª edición, R. C. Weast, J. Astle and W. H. Beyer Ed., CRC Press (1985).

[15] M. Anderson and R. G. Skerrat, "Variability study of incinerated sewage sludge ash in relation to future use in ceramic brick manufacture", Br. Ceram. Trans. 102(3), 109-113 (2003).

[16] T. Manfredini and G. C. Pellacani, Engineering Materials Handbook, Vol 4, Ceramics and Glasses-ASTM, 1992, pp 925-929.