PONENCIA 09

PAPER MILL SLUDGE AND GLASS CULLET AS MATERIALS FOR TILE PRODUCTION

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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.

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. At present, more than 1 billion ton/years sludge is produced in Europe by industries, minerals treatments and so on. 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 to obtain raw materials suitable for ceramic industry. By sintering of the sludge materials, 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) are classified as non dangerous products by CER (European Sludge Catalogue) and are commonly used in various manufacturing activities, as glass reforming or melting additives for ceramics, mainly for its low melting properties. It is important their colour when reused for ceramics production. 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.

The firing temperatures of the mixtures were determined by dilatometric tests, conducted up to the reaching of softening temperatures. The sintering were 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 means of Indentation Strength in Bending Method (ISB);

- Shrinkage measurements on cylindrical specimens;

- Water absorption evaluations after boiling of 3 hrs.

3. Results.

The start 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.

It can be observed that density ranges from a minimum of 2.58 to a maximum of 3.08 g/cm^3. Traditional ceramics usually display values lower than 2.70. 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 unsatisfactory only if compared to non traditional ceramics such as Si_3N_4 or PSZ, whereas they 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. The specimens' color changes by adding GC, as the samples made by PS alone or material 1 are pale brown, while all compositions having an amount of GC equal or greater than 20% (i.e. materials 2, 3, 4 and 5) appear white. The color of pale browned samples is due to their high sintering temperature promoting the diffusion of some species (i.e. Ti, Fe) from the bulk to the surface of the specimens. In this way the concentration of TiO2 and FeO on the free surface of the fired materials is higher than in the bulk. It follows that the surface is colored whereas the bulk remains white.

Material 1 (Fig. 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 around 1 µm.

Although the amount of glass cullet introduced in the PS is only 10 % wt higher than that of material 1, the microstructure of material 2 (Fig. 2) shows less vitreous phase.

In material 2 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 around 2 µm. The presence of elongated grains could justify the higher toughness of this material with respect to material 1, whereas the small dimension of the grains of the matrix could be responsible of its fair strength. Also in this case the presence of pores appears extremely limited and is responsible of the low water absorption.

As for material 1, also material 3 (Fig. 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 (Fig. 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 (Fig. 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 and platelets have higher shape ratio which ranges from 12 to 17 and their major dimension ranges between 15 and 23 µm. 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. In our laboratories, we cannot measure the grain size distribution of powders and, in order to minimize the great number of variables which can be changed during the ceramics processing of wastes, we have set the attrition milling time to 3 hrs, being aware that the grain size distribution and consequently the sintering of the compositions here examined could be changed by varying the attrition milling time. This statement does not mean that attrition milling is the best route to process waste, but, as a first approach and with the milling time set at 3 hrs, it may be useful in order to limit the high number of variables.

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] and could be a strong drawback for industrial production using recycled wastes, 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. In effect, it is commonly observed that, the higher the number of components, the lower is the melting temperature of a system, since the formation, at low temperatures, of multi component eutectics is highly probable. Furthermore, the presence of low melting components, such as Na_2O, even in low amounts (see table I: others), can develop the presence of scattered liquid zones in the bulk materials, not only under equilibrium, but also under dynamic conditions.

No significant amounts of Hg were detected in the starting PS and GC. This is can be easily explained for GC which derive from materials obtained by a high temperature process and, for PS, it is probably due to the relatively severe thermal treatment which was used for the calcinations of the starting PS. In fact, during the calcinations at 850°C, most of Hg-containing materials melt [14-15] and partial and/or total evaporation of products containing Hg cannot be avoided. It follows that during an eventual industrial process involving calcination of the starting materials it is necessary to consider also the abatement of these volatiles from the exhaust gases.

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. This fact is reasonable for white GC, but was unexpected for PS. 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) although the mechanical properties are good enough for the production of tiles, requires, on the other hand, a high sintering temperature and the resulting material is coloured.

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.

5. Conclusions.

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 if value-added product must be produced, 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.

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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.

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

Mixtures	Compositions %	
	PS	GC
1	90	10
2	80	20
3	70	30

4	60	40
5	50	50

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

Sample	Start of shrinkage [°C]	Softening point [°C]
1	860	1230
2	725	1185
3	895	1192
4	965	1157
5	855	1080

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

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

Figure 1. SEM imagine of sample n.1.


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2,05KX      25KV WD:5MM      S:00000 P:00001
20UM
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Figure 2. SEM imagine of sample n.2.

Figure 3. SEM imagine of sample n.3.
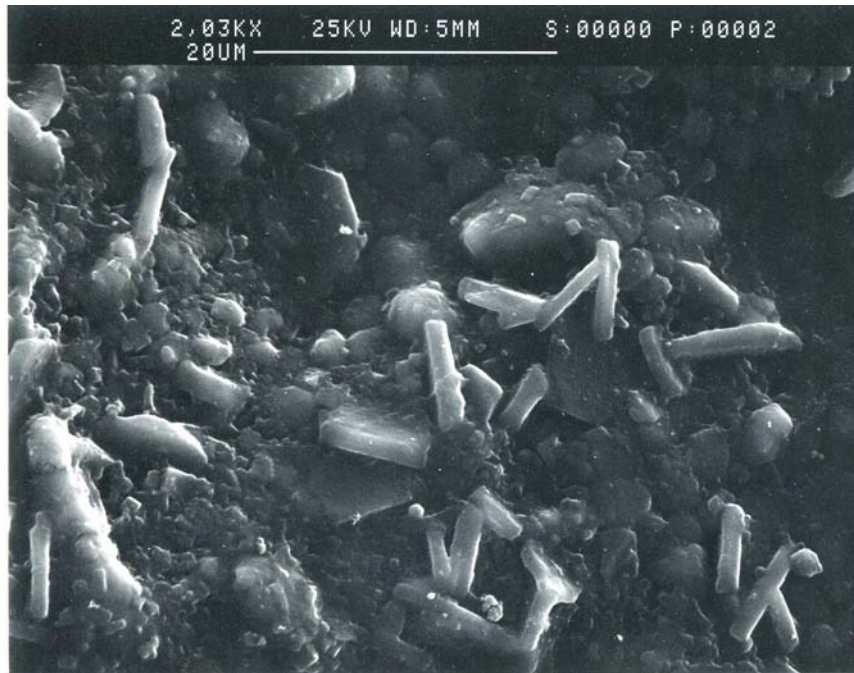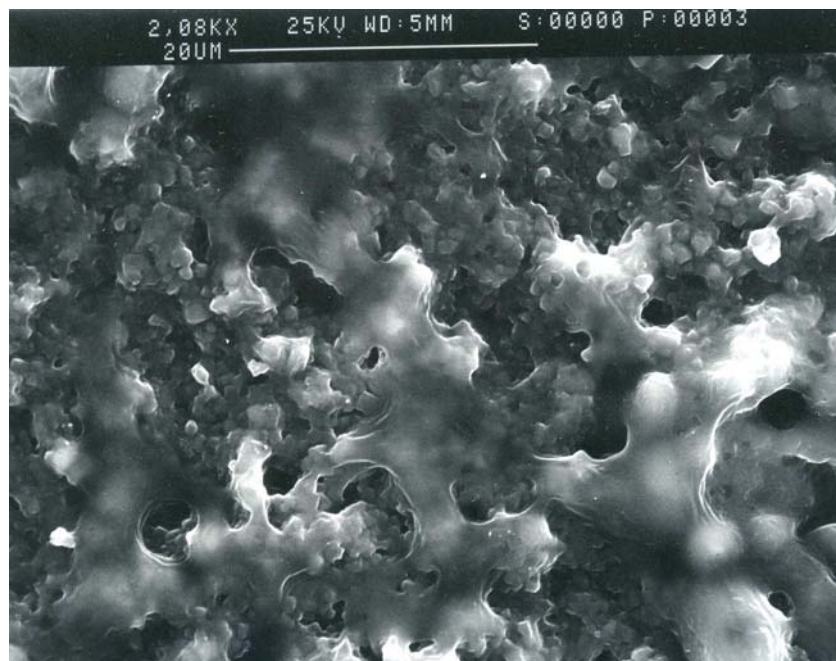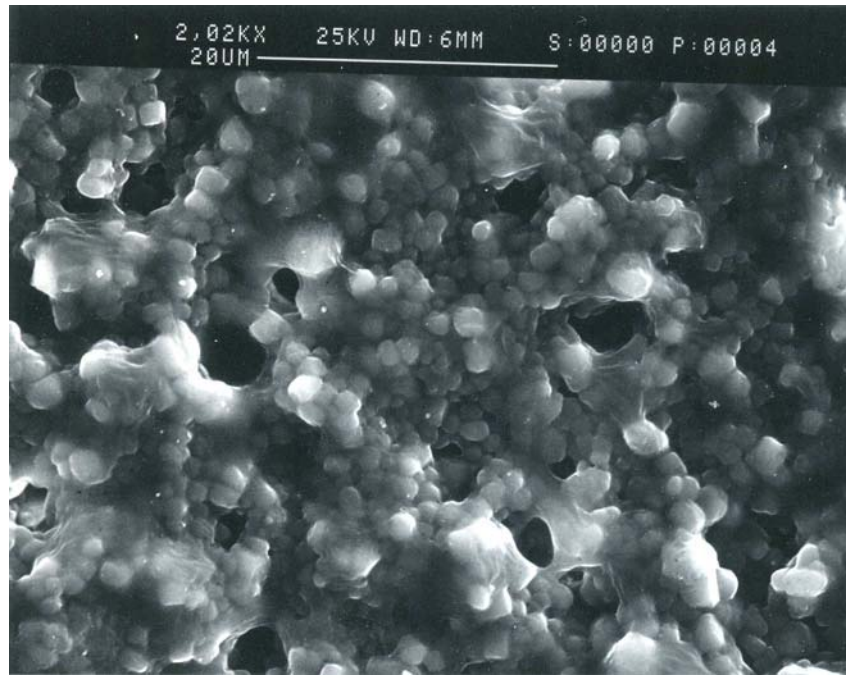

Figure 4. SEM imagine of sample n.4.

Figure 5. SEM imagine of sample n.5.