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Ceramic processing of municipal sewage sludge (MSS) and steelworks slags (SS)

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Abstract

Municipal sewage sludge from municipal wastewater treatment plants were thermally transformed into powders which were blended with two types of steelworks slags in different proportions. Mixtures of powders, performed by attrition milling, were pressed into specimens which were submitted to thermodilatometric tests in order to evaluate their shrinkage and then their softening temperatures on heating up to 1100 °C. Samples were then sintered in air using a muffle furnace and characterized by density, strength, hardness, fracture toughness measurements, X-Ray diffraction and SEM investigations.

The mechanical properties of the sintered specimens are satisfactory and this may be due to the formation of small grains that, in some cases, are embedded into a vitreous matrix.

Samples obtained by the various blends were aged in an acidic (HCl) water solution to evaluate the elution of the components and it was observed that, through the sintering procedure, it is possible to limit the release of many of the most hazardous metals contained in the starting powders.

Keywords: A. Mixing; A. Sintering; B. Microstructure-final; C. Mechanical properties; Slags

1. Introduction

Steelmaking slags (SS) contain all the principal compounds which may be used in the production of various consumer items. Mainly utilizations of SS imply production of cement, manufacture of different building materials, high temperature insulators and many others [1–4].

The main disadvantage of SS is the presence of a large amount of lime in their composition, but it is possible to hypothesize the use of these slags in conjunction with other products, like those obtained from calcined municipal sewage sludge (MMS), in order to obtain raw materials suitable for heavy clay products.

More precisely, SS are obtained from high-temperature steelworks production. This material is similar, in composition and in characteristics, to the blast furnace slag (BSF) which are commonly used for mixture cement production.

MMS is the product of the treatments of municipal wastewaters. Its content is mainly water (about 95%), but other substances are present too, such as insoluble and soluble organic matter, nutrients, microorganisms, pathogens, metals, soluble salts, minerals and others. Its composition varies as a function of the infrastructures of the respective residential area, weather conditions, season of the year, time of the day and so on. Actually, usual ways for sewage sludge disposal are mainly dumping in landfill and agricultural use, which have different environmental impact [5–8].

In many parts of the world landfill void spaces available for sludge deposits are however going to be exhausted and there are several logistic problems to locate new landfill

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Table 1
Composition (wt%) of the six mixtures prepared in the present work

Mixtures	Compositions		
	SS1	SS2	C
1	25	0	75
2	50	0	50
3	75	0	25
4	0	25	75
5	0	50	50
6	0	75	25

sites. One possible solution is the incineration of sludges after dewatering. In this way their volume is sensibly reduced and the resulting odorless product contains a mixture of several oxides. One eventual advantage of processing sludge in this way is that small incinerators can be located close to the site where the sludge is produced and consequently the costs of its eventual transport are sensibly reduced.

In the present research some slags coming from steelworks were added, in different ratios, to the sludges coming from a town of about hundred thousand persons. With this method, the large amount of lime present in the SS materials may produce a more balanced composition, with subsequent increase, after sintering, of mechanical properties and decrease of chemical reactivity.

2. Experimental

Two granulated slags having different steelworks origin, hereinafter named as samples SS1 and SS2, were used in conjunction with MSS, hereinafter called sample C.

MSS were dried at 170 °C for 24 h and then calcined at 850 °C for 2 h. The product was then ground in an agate mortar and the powders sieved through a 200-μm sieve. Granulated slags were used as received. A total of six mixtures were then prepared starting from the powders, in the proportions summarized in Table 1.

The test samples were prepared using powders blended by attrition milling for 3 h in water, using a plastic container and highly pure alumina spheres, at 300 cycles/min. The milling parameters were chosen on the basis of earlier papers [9]. The milled and dryed (80 °C) powders, after sieving through a 63-μm sieve, were pressed in a laboratory uniaxal press at 100 MPa into cylindrical [0.6 mm × 50 mm] or rectangular [4 mm × 5 mm × 50 mm] specimens.

Specimens were then sintered in an electric muffle in air atmosphere, in the thermal interval 1050–1150 °C, chosen on the basis of thermodilatometric data. The following tests were finally made on the fired samples:

- Thermo-dilatometric determinations up to softening temperature by an alumina dilatometer [heating rate 10 °C];
- Density determinations by the water displacement method;
- Bending strength determinations by a Shimadzu AG10 4-points bend jig [crosshead speed 0.2 mm/min]. Results are the average values of five tests for each composition;
- Vickers hardness (H_v) determinations using a 100-N load. Results are the average values of 10 measurements;
- Fracture toughness (K_{Ic}) determinations by means of Indentation Strength in Bending Method (ISB). Results are the average values of five tests for each composition;
- XRD diagrams by means of an XRG 3000 INEL attachment using Co radiation;
- SEM observation of microstructures by means of an Assing Stereoscan scanning electron microscope;
- Determination of elution releases after a 30 days ageing of an HCl solution (pH 4) at 60 °C;
- All the chemical analyses were done, both on the starting powders and on the eluted solutions, with a Spectro Mass 2000 ICP Spectrometer. Composition data of starting powders are summarized in Tables 2 and 3.

Table 2
Composition of SS powders (ppm)

Element	SS1 (mg kg^{-1})	SS2 (mg kg^{-1})
Al	**25732**	**43580**
Ba	290	651
Ca	**8397**	**20402**
Ce	50	<50
Cr	1146	**3134**
Cu	<50	87
Fe	**6645**	**80010**
K	422	185
Mg	1774	1628
Mn	**55287**	**40346**
Nb	<50	202
Si	**29735**	**72438**
Sr	643	185
Ti	569	1363
W	< 50	112
Zn	698	124
Zr	**3051**	**4911**
Sn	<50	1271

The amount of Pb, Be, Co, Se, Rb, Mo, Ag, Cd, Cs, La, Bi, Li, P, S, Nb, Sn, Sb are <50 ppm in the both powders. The more abundant elements are in bold characters.

3. Results

3.1. Thermal analysis data

The analysis of thermo-dilatometric diagrams allowed for the detection of the critical temperatures of the various specimens; for example the temperatures at which the sample starts to shrink or to soften. Furthermore, these data allowed for the optimisation of to the sintering cycle in the muffle furnace (see details reported in Table 4).

Table 3
Composition of powders obtained from MSS sludge calcined for 2 h at 850 °C (ppm)

Element	MSS (mg kg^{-1})
Al	**6200**
Ba	360
Ca	**5200**
Co	860
Cr	230
Cu	680
Fe	**89000**
K	**4270**
Mg	**7500**
Mn	1100
Na	**12400**
Ni	150
P	**2820**
Pb	260
Sb	450
Si	**81000**
Sn	220
Ti	**2100**
Zn	**4600**

The amount of Hg, Cd, As, V, Zr, Mo, Ce, Sr, Ag, W, Se, Rb are <50 ppm. The more abundant elements are reported in bold characters.

Table 4
Characteristic temperatures of the various samples obtained by the thermo-dilatometric analysis and used top sintering temperatures

Sample	Start of shrinkage (°C)	Softening point (°C)	Sintering temperature (°C)
1	895	1050	1100
2	970	1090	1150
3	950	1055	1125
4	885	1045	1100
5	935	1065	1125
6	950	1100	1150

3.2. Mechanical properties

Density data (g/cm^3) of sintered materials are listed in the Table 5, together with rupture bending strength (MPa), Vickers hardness (GPa) and fracture toughness (MPa m$^{1/2}$) values. It can be observed that density ranges from a minimum of 2.57 g/cm^3 (sample 5) to the maximum of 3.2 g/cm^3 (sample 3). These values are higher than those normally measured in the traditional ceramic industry. Rupture strength has a minimum of 58 MPa (sample 3) and a maximum of 71 MPa (samples 1 and 4). These values can be considered fairly satisfactory considering that MSS and SS are recycled raw materials. Hardness data range from 4.9 GPa (sample 3) to 6.5 GPa (sample 6). Fracture toughness data range from the lowest value of 1.7 MPa m$^{1/2}$ (sample 4) to the highest value of 4.5 MPa m$^{1/2}$ (sample 2).

Table 5
Density (ρ), strength (σ), hardness (H_v) and fracture toughness (K_{Ic}) data measured in the sintered specimens

Sintered samples	ρ (g/cm^3)	σ (MPa)	H_v (GPa)	K_{Ic} (MPa m$^{1/2}$)
1	3.13	71	5.8	3.4
2	2.99	66	6.1	4.5
3	3.20	58	4.9	2.0
4	3.12	71	5.2	1.7
5	2.57	68	6.4	2.3
6	3.19	65	6.5	2.5

Table 6
Phases revealed in the sintered specimens, by XRD analysis, with their chemical formula and reference powders diffraction files (PDF)

Sintered samples	Crystal phases	Formula	PDF
1	Hematite	Fe_2O_3	00-024-0072
	Magnetite	Fe_3O_4	01-086-1348
	Essenite	$AlCaFeSiO_6$	00-040-0496
	Anorthite	$Al_2CaSi_2O_8$	01-085-1660
2	Essenite	$AlCaFeSiO_6$	00-040-496
	Pseudowollastonite	$Ca_3Si_3O_9$	01-074-0874
3	Andranite	$Ca_3Fe_2Si_3O_{12}$	00-010-0288
	Magnetite	Fe_3O_4	01-086-1354
	Gehlenite	$Al_2Ca_2SiO_7$	01-079-1726
4	Hematite	Fe_2O_3	01-085-0599
	Magnetite	Fe_3O_4	01-086-1361
	Essenite	$AlCaFeSiO_6$	01-084-1206
	Anorthite	$Al_2CaSi_2O_8$	00-002-0537
5	Magnetite	Fe_3O_4	01-086-1354
	Essenite	$AlCaFeSiO_6$	01-084-1206/ 00-025-0143
	Manganese iron oxide	$Mn_{1.03}Fe_{1.97}O_4$	01-074-2435
6	Magnetite	Fe_3O_4	01-086-1354
	Gehlenite	$Al_2Ca_2SiO_7$	01-079-1726
	Manganese iron oxide	$Mn_{1.07}Fe_{1.93}O_4$	01-073-1964

Table 7
Release, in parts per billion (ppb), of the main elements from the sintered specimens, after ageing for 30 days at 60 °C in a solution of HCl (pH 4)

Elements	1	2	3	4	5	6
Al	40	43	48	20	202	38
Ba	59	58	135	120	21	213
Ca	**10448**	**14367**	**20737**	**6889**	**7761**	**16343**
Cr	331	110	77	267	84	32
Fe	**1980**	**1981**	**1985**	**1934**	**1968**	**2001**
K	**5117**	**1452**	**1634**	**970**	**460**	**6664**
Mg	**1000**	**875**	**484**	**1654**	**1405**	**724**
Mn	**2063**	**1345**	**1040**	**1707**	**2231**	**2924**
Mo	251	94	41	165	25	92
P	657	687	772	188	196	1163
Rb	420	234	106	43	10	574
Si	**2504**	**2854**	**4875**	**1842**	**2202**	**3301**
Sr	182	193	159	171	62	273
Ti	231	299	331	101	112	371
W	70	71	52	44	58	159

The elements present in concentrations <50 ppb are not reported. In bold characters are evidenced the elements that have been eluted in significant quantities.

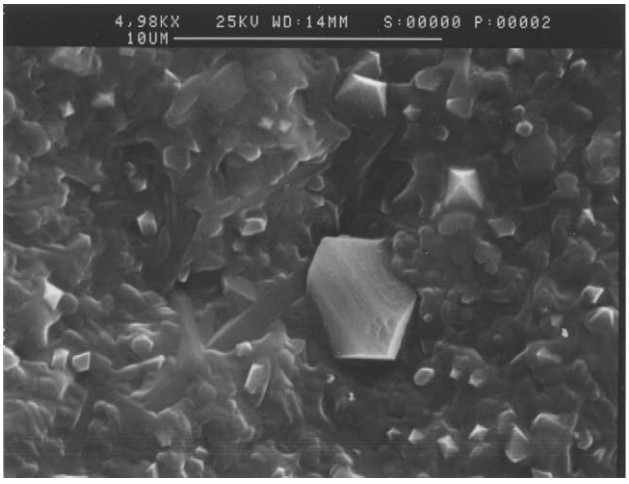

Fig. 1. SEM photograph of the free surface of sintered sample 1 (5000×). Mean size of grains: 1.9 μm.

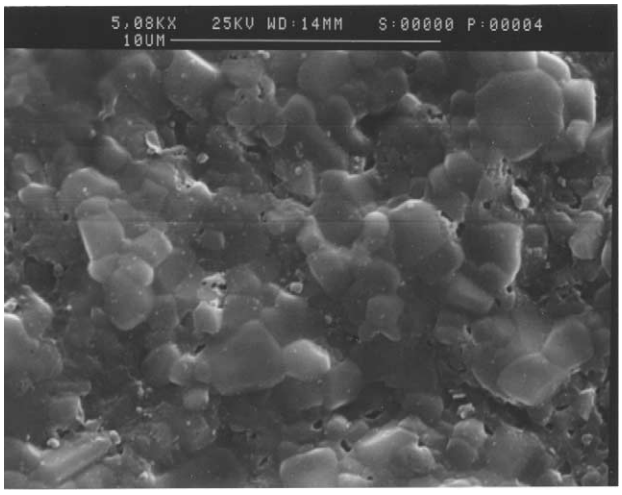

Fig. 3. SEM photograph of the free surface of sintered sample 4 (5000×). Mean size of grains: 2.5 μm.

3.3. Crystal and microtructural determinations

XRD analysis of the free surface of the sintered samples revealed the co-presence of several phases in each one. We have not observed a trend or, alternatively, the presence of a typical phase in a group of samples. Table 6 lists the most abundant phases that we have been able to identify.

SEM photographs, made on the same free surface of the sintered samples, are reported in the Figs. 1–4 and revealed the presence of micrometric grains, ranging from a minimum of 1.4 μm (sample 6) to a maximum of 3.1 μm (sample 2). It may be observed that samples 1 and 2 are characterized by the presence of a large amount of elongated grains which have a shape ratio between 10 and 15, whereas all the other are mainly constituted by equiaxial grains. It must also be observed that the measured average grain size of samples 1 and 2 includes also the elongated grains. The SEM microstructures of samples 3 and 5 are not reported since they do not differ significantly from those of samples 4 and 6, respectively and the grain sizes are similar too.

3.4. Elution data

The elution release was carried out at 60 °C for 30 days at pH 3–4. Data reported in the Table 7 must be red in terms of safety limits for the sintered materials and are therefore significant if compared with long-term attack of the materials by the environmental ageing.

Analyses of the eluted solutions, after strong acid attack, show that the elution of hazardous substances is low. Some elements, such as Ca, Mg, Si and K are actually present, and even in large amount, in the eluted solutions, but they can be considered non-hazardous elements. Other elements, such as Mn and Fe, are present in moderate amount, whereas more

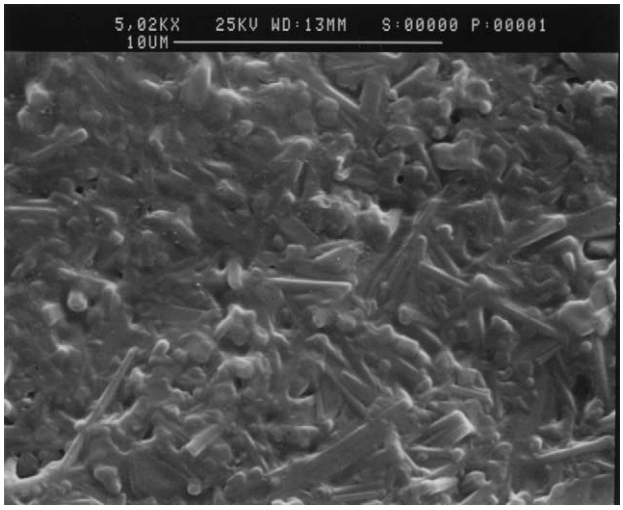

Fig. 2. SEM photograph of the free surface of sintered sample 2 (5000×). Mean size of grains: 3.1 μm.

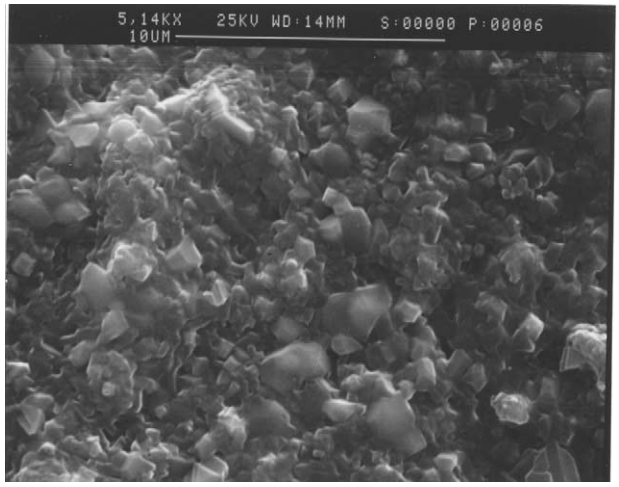

Fig. 4. SEM photograph of the free surface of sintered sample 6 (5000×). Mean size of grains: 1.4 μm.

toxic elements, such as Hg, Cd, Zn, Ni and others have not been detected or detected in a very low quantity. It can be also observed that Ca is present in large amount in all the eluted solutions, whereas the quantity of other elements if a function of the material composition. The quantity of iron in the eluted solutions seems to be independent of the material composition since such values are all around the same value of 2000 ppb.

4. Discussion

The chemical analyses show a great dispersion of data. A common feature is however that elements Si, Al, Fe, Mn and Ca are largely present in the SS samples; in addition a large amount of Ba is present in SS1 sample. Furthermore Si, Fe and Na are the most abundant elements detected in MSS sample. It is worthwhile pointing out the very low amount of Hg detected. This may be due to the relatively severe thermal treatment which was used for the calcinations of the starting sludges. In fact, during the calcinations at 850 °C, most of Hg-containing materials melt [10] and partial and/or total evaporation of products containing Hg cannot be avoided. It follows that during an eventual industrial process involving calcinations of MSS it will be necessary to consider also the abatement of these volatiles from exhaust gases.

The ceramic processing of pure MSS is reported in a previous paper (9) and not repeated here. It is important to mention however that the colour of the powders and that of the sintered samples produced with pure MSS is brick red. In addition, the two granulated SS are both dark grey. As a consequence all the samples prepared in the present research are dark after the sintering process. In addition the presence of a great amount of iron in all starting products can lead to the formation of further FeO during the high temperature sintering stage. Under the particular conditions adopted by us, this phase does not re-oxidize on cooling, but react with Fe_2O_3 to form black coloured magnetite. Samples 1, 3, 4, 5 and 6 contain magnetite as reported in Table 6 and, consequently, their colour ranges from dark grey to black presumably in dependence of the magnetite content. Sample 2 was dark brown. The colour of the materials prepared in this work might preclude the use of MSS and SS as raw materials in the whiteware industry and limits their use in the applications where the colour of the finished material is not important.

The top sintering temperature of all the samples was kept at levels that are typical of traditional ceramic powders, ranging from 1100 to 1150 °C. In the present study, this is due to the large amounts of low-melting components such as Fe and Na which are present in the starting powders. The phase diagrams $FeO–Fe_2O_3–SiO_2$ [11] $CaO–Fe_2O_3–SiO_2$ [12] can be useful tools in order to foresee the experimental softening temperatures of the samples with reference to data obtained under equilibrium conditions. In these phase diagrams several eutectic compositions are present, their temperatures being around 1150–1200 °C. We may therefore assume that the maximum melting temperatures observed in our samples cannot exceed 1200 °C. Moreover, it is commonly observed that the higher the number of components, the lower the melting temperature of a material, as a consequence of possible formation of multicomponent eutectics at low temperature. Furthermore, the presence of low melting components such as Na_2O and K_2O, even in low amounts, can develop the presence of low melting zones randomly scattered in the bulk causing the presence of a liquid phase not only under equilibrium, but also under dynamic conditions.

The presence of small amounts of liquid phase was therefore assumed in all the sintered samples, in conjunction with a low shrinkage during the thermodilatometric tests and a low porosity of the fired samples. The low porosity was revealed both by density tests, where the water absorption was absent, and also by the SEM examination of the sintered samples, that showed full dense materials.

The fired products displayed moderate mechanical properties (bending strength, toughness, hardness), with the trend of a MOR decrease by increase of SS percentages in the mixture (Table 5). It can e observed that all samples have fine microstructures, but in samples 1, 5 and 6 their value is below 2 μm. It follows that the strength of these samples should be expected fairly high. However the strength values are, in all samples, lower than expected. We suppose therefore the presence of a vitreous phase at the grain boundaries which keeps the strength data around the value of 70 MPa. Differences may be due to the presence of randomly distributed defects in the bulk of the samples.

Hardness data are in agreement with reference values measured in ceramic materials prepared with recycling products [13]. In our case, their values can be considered low since the grains are small as results from SEM analysis, and this leads to suggest the presence of liquid at the grain boundaries during the sintering process.

Toughness tests revealed that sample 2 displays a good performance if compared not only to that of traditional ceramics or ceramics produced with recycling materials [13], but also if compared to that of some advanced ceramic materials such as alumina [14,15]. This unexpected result can be due to the presence of randomly dispersed elongated structures that develop in the material microstructure during the sintering process though an ‘‘in situ’’ reaction [16–18]. Such elongated structures, that we have not been however able to identify, may enhance the fracture toughness of the materials even in the presence of a glassy phase [16–20].

The leaching test used in the present investigation is not regulated by official standards, but it submits materials to a condition more severe than that proposed by Obermann and Cremer [21] in their pH-stat-test which is recommended as a worst-case elution test in the Federal State of North-Rhein-Westfalia. In any case the very small amount of heavy metals or other substances revealed by the elementary analysis confirms, that the sintering process of the powders obtained

from SS1, SS2 and MSS can be used for the production of monolithic ceramic, ensuring the environmental compatibility of the sintered materials.

5. Conclusions

The present investigation showed the following:

- The ceramic materials produced by sintering powders obtained after calcinations of municipal sewage sludge (MSS) and steelwork slags (SS) can immobilize many of the most hazardous metals contained in the starting powders.
- The mechanical strength of the sintered specimens is fairly good compared with traditional ceramics and this might be due to the small amount of vitreous phase at the grain boundaries.
- The powders obtained from incinerated MSS + SS can be used in the ceramic industry as raw material for the production of monolithic ceramic bodies where the colour of the finished product is not important.

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