Possible production of ceramic tiles from marine dredging spoils alone and mixed with other waste materials

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Abstract

Dredging spoils, due to their composition could be considered a new potential source for the production of monolithic ceramics. Nevertheless, abundance of coloured oxides in these materials preclude the possibility of obtaining white products, but not that of producing ceramics with a good mechanical behaviour. As goal of the present research we have produced and studied samples using not only dredging spoils alone, but also mixtures with other waste materials such as bottom ashes from an incinerator of municipal solid waste, incinerated seawage sludge from a municipal seawage treatment plant and steelworks slag. Blending of different components was done by attrition milling. Powders were pressed into specimens which were air sintered in a muffle furnace and their shrinkage on firing was determined. Water absorption, density, strength, hardness, fracture toughness, thermal expansion coefficient of the fired bodies were measured; XRD and SEM images were also examined. The fired samples were finally tested in acidic environment in order to evaluate their elution behaviour and consequently their environmental compatibility. It is observed that, although the shrinkage on firing is too high for the production of tiles, in all the compositions studied the sintering procedure leads to fine microstructures, good mechanical properties and to a limitation of the release of many of the most hazardous metals contained in the starting powders.
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1. Introduction

Dredging spoils (DS) are waste materials that derive from the escavation of lagoons, harbours, canals, rivers, marine areas and so on for navigation or environmental protection/remediation. These materials are characterized by a large variation in composition and by the presence of large amounts of water and organic matter [1–11]. In some cases they are classified as toxic waste, especially when they derive from contaminated areas, since they may contain heavy metal ions (Zn, Pb, Cu, Cd, As, Hg, Ni, etc.) and organic pollutants. The disposal into landfill is expensive and not always compatible with the regulations of many countries. It may be therefore convenient to investigate on the use of dredging spoils as a source for the production of materials where such drawbacks are minimized.

Municipal seawage sludge (MSS) is the product of the treatments of municipal wastewaters. It contains 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 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 since some hazardous compounds can be eluted into the hydrosphere [12–15]. Large scale disposal of sludge is a great problem for many municipal administrations and therefore there is the need for alternative solutions to this problem. One possibility is their incineration after dewatering. In this way their volume is sensibly reduced and the resulting odorless product contains a mixture of several oxides such as SiO_2, Al_2O_3, Fe_2O_3, MgO, CaO and many others. The ceramic

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processing of MSS alone or in addition with other waste materials were previously studied by some authors of the present research and reported elsewhere [16,17].

Another type of waste, which derives from incineration of municipal or industrial solid wastes is bottom ash (BA). It is classified as a simple waste and can be stored into a landfill at a quite low cost. Bottom ash is a highly heterogeneous burn-out mixture of slag, ferrous and non-ferrous metals, ceramics, glass, other non-combustibles and residual organic matter [18–20]. The extreme heterogeneity of bottom ash, combined with the potential leachability of heavy metals, mainly Cd, Cr, Cu and Pb, means that some other kind of processing is preferable as an alternative to disposal into landfill.

Steelmaking slags (SS) are obtained, in very large quantity, from high-temperature steelworks production. It is known that the production of 1 ton of steel implies the production of 100 kg of slag. Most utilizations of SS are involved in the production of cement, manufacture of different building materials and few others [21–24]. One of the main disadvantages of SS slag is the presence of a large amount of lime which causes a high softening temperature and a high sintering temperature for materials prepared using these powders without any other additive. Moreover, the presence of a large amount of calcia and silica could induce the formation of $2CaO \cdot SiO_2$ during high temperature thermal treatments. This component presents polymorphism and transforms, on cooling, into a phase having a larger specific volume [25]. This transformation therefore could cause extended fractures in the materials containing $2CaO \cdot SiO_2$ so that it is not easy to produce useful materials by simply recycling pure SS slags.

Dredging spoils, incinerated municipal seawage sludge, fly and bottom ashes from municipal solid waste incinerators and steelmaking slags, in addition to eventual toxic elements, also contain large amounts of silicium, aluminium, calcium, magnesium, and other elements which are not considered pollutant and can be transformed into the corresponding oxides by calcination under oxidative conditions. These oxides are as well commonly present in the raw materials used for the production of bricks, tiles or other ceramic materials. Inside the ceramic industry, mixtures of incinerated DS, MSS, BA or SS could represent an alternative raw material for the preparation of monolithic ceramic products by vitrification or sintering. The development of value-added reuse products would involve particular benefits both in terms of resource recovery and protection of the environment. Similarly to the vitrification process, high temperature sintering can convert particulate inorganic waste materials into more environmentally benign products that have no adverse effect on the environment and public health.

Early studies demonstrated that sintering of different waste materials allows for the immobilization of hazardous metals and destroys the organic pollutants [20–22,26–29], with the simultaneous advantage of achieving a significant reduction in the volume of waste which is around 80–90%.

Similarly to the vitrification process, high temperature sintering can convert particulate inorganic waste materials into more environmentally benign products that have no adverse effect on the environment and public health. A number of researchers have demonstrated reduced leaching from sintered products

compared to the original waste [16,17,19–21,26–33]. The use of waste incinerator BA to produce ceramics has been already reported [26–28]; SS [17,21–24] and MSS [16,17] can be processed just like BA, whereas the studies on the ceramurgic processing of DS or their mixtures with other waste materials are not so common. Few studies demonstrated that vitrification of DS is a suitable process for their reuse [29,30]. Nevertheless, it is our opinion that, when possible, the sintering process is to be preferred to vitrification since significant savings of implant and energetic costs can be obtained. Of course, fired materials shall have sufficiently good mechanical properties and their environmental compatibility have to be proved. Finally, it must be pointed out that the production of glass restricts the market of the final products, i.e. bottles or glasses for windows produced using waste materials do not seem marketable, whereas brick or tiles are probably better accepted by the population as low cost products.

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In the present research we produced ceramic monoliths using powders obtained from incinerated dredging spoils from the laguna of Marano Lagunare (Udine-Italy) escavated from a non-contaminated area in order to optimize navigation. In addition, we have also prepared mixtures between these powders and three other kinds of residues, respectively bottom ashes, steelmaking slag and incinerated municipal seawage sludge. Powders were blended, by attrition milling, and transformed into monolithic ceramics by sintering. Proportions of the different waste in the mixtures were established on the ground of their approximate quantity production in the italian Region of Friuli Venezia Giulia. Fired samples were characterized by shrinkage on firing, density, water absorption, microstructure, presence of different crystal phases, dilatometric thermal expansion coefficient, XRD imaging and some mechanical properties were measured as well. Sintered samples were also aged in an acidic (HCl) water solution to evaluate their leachability. The first objective of the present investigation is to demonstrate that, independently of the particular origin, extremely different typologies of waste can be mixed together and the resulting powders used in the ceramic industry; the second objective is to demonstrate that the ceramurgic process is useful to limit leachability of the produced materials and to assure their environmental compatibility.

2. Experimental

As received DS, MSS and BA were separately incinerated by calcination at 850 °C for 2 h. Incinerated DS and MSS were then ground in an agate mortar and the powder was sieved through a 200 μm sieve and stored under vacuum. After calcination of BA non-oxidized metallic particles were separated from the other products and subsequently stored in air. SS was used as received.

After this preliminary treatment, the four products were submitted to chemical analyses.

In the present work four different compositions were prepared and submitted to the ceramurgic processing: pure DS,

50 wt.% DS and 50% MSS (hereafter called DS + MSS), 50 wt.% DS and 50 wt.% BA (DS + BA), 10% DS and 90% SS (DS + SS). Mixtures were homogenized by attrition milling for 3 h, using a plastic container and highly pure alumina spheres, at 300 cycles/min in distilled water. Milling parameters were chosen on the basis of an earlier paper [25]. Attrition milling was used in order to reduce the long milling time relative to the traditional wet ball milling process. The milled powders, after sieving through a 200 μm sieve, were pressed by a laboratory uniaxial press at 100 MPa into cylindrical (0.6 mm × 50 mm) or rectangular (4 mm × 5 mm × 50 mm) specimens.

Cylindric specimens were used for sintering studies whereas rectangular specimens were used for investigating the mechanical behaviour. Softening temperatures were determined by testing green samples in an alumina dilatometer with heating and cooling rates of 10 °C/min and following the procedure already described in a previous paper [16].

Cylindric specimens were also sintered for 1 h at different temperatures, in an electric muffle, in air atmosphere, choosing a thermal interval of 1000–1200 °C on the ground of thermodilatometric data, optimizing, in this way, the sintering temperature. Axial (h) and radial (Φ) shrinkage on firing was evaluated, on cylindric specimens, by the ratio between h_0–h_1 or Φ_0–Φ_1 and h_0 or Φ_0 (0 and 1 being the sample dimensions before and after sintering). The apparent density of sintered specimens was determined by the Archimedes method. In order to evaluate the water absorption, sintered samples were first weighted in air (W_1), then put into a becher were and boiled for 3 h. After boiling samples were cooled into water to room temperature and weighted again (W_2). Water absorption was evaluated by the ratio between W_2–W_1 and W_1.

Rupture strength (σ) was evaluated in four-points bend jig with a crosshead speed 0.2 mm/min using a Shimadzu AG10 equipment; Vickers hardness (H_v) was determined by a 100 N load with a Zwick indenter on polished (6 μm diamond paste) surfaces; fracture toughness (K_{IC}) was evaluated by means of Indentation Strength in Bending Method (ISB) breaking specimens indented with a load of 100 N. All mechanical data reported in the present research have been averaged over 10 measurements. Dilatometric thermal expansion coefficient in air was evaluated by a Netzsch alumina dilatometer at a heating rate of 10 °C/min up to a temperature of 500 °C. Three samples were analysed for each composition.

Microstructures were examined by an Assing Stereoscan scanning electron microscope (SEM).

Crystal phases of the fired materials were recognized by an XRG 3000 INEL X-ray diffractometer using the Co radiation whereas microstructures were examined by an Assing Stereoscan scanning electron microscope.

The elution release of the fired samples was determined after a 30 days ageing of an HCl solution (pH 4) at 60 °C.

Chemical analyses, carried out both on the starting powders and on the eluted solutions were done with a Spectro Mass 2000 induced coupled plasma (ICP) mass spectrometer.

3. Results and discussion

As displayed in Table 1, chemical analyses of the powders show a great dispersion of data, i.e. a great number of elements were detected in not negligible quantity in all samples. Si, Mg, Al, Ca and Fe are largely present in DS calcined powders. It can be observed that powders obtained from dredging spoils do not contain relevant quantities of heavy metals or other toxic elements. Si, Fe and Na are the most abundant elements in the MSS calcined powders; Al, Si, Mg, Ca, Fe and Na are predominant in BA product; Al, Ba, Ca, Fe, Mn and Si are largely present in SS powders. The amount of S and Cl appears quite low in all the calcined powders probably as a consequence of the severe thermal treatment which induces the evaporation–decomposition of most of S and Cl containing compounds present in the as received waste materials. It is worthwhile noting the very low amount of Hg in all powders (<50 ppm). This fact is probably due to the severe thermal treatments which were used for the calcination of the starting sludge (850 °C) or for the production of the slag during steel production which requires a melting temperature of about 1500 °C. In fact, at such temperatures, most of Hg-containing materials melt [35] and partial and/or total evaporation of products containing Hg cannot be avoided. It follows that the absence of Hg compounds in the products used in the present work is real in the case of SS, but can be the result of the calcinations treatment used to transform the wastes (i.e. DS, MSS and BA) into powders. Consequently, during an eventual industrial process involving calcination of sludge or of other waste it is necessary to take into account also the need of abatement of these volatiles from exhaust gases. The same problem arises when we consider other hazardous elements such as S, Cl, N and others.

The amount of heavy metals or other toxic elements is not very high in all tested materials although it must be observed the relatively high level of Cu and Zn in BA, Zn and Mn in MSS and Mn, Zr and Cr in the case of SS.

De-watering of DS and MSS does not represent a great problem for the production of ceramics since in all incinerators a great quantity of warm water is available, which must be drained into the environment. This warm water could be used to dry DS and MSS to a water content suitable for the following calcination. Calcination, on the other hand, is expensive since the original waste must be heated up to a high temperature and the corresponding cost could represent a great drawback for the production of tiles or other monolithic ceramics. The only point which is in favour of their ceramurgic processing is that both DS and MSS contain a sensible amount of organic matter which can burn during the heating and therefore contribute to supply part of energy which is necessary for this thermal treatment.

Milling, as well as all the thermal treatments, requires a great quantity of energy and the relative cost must be minimized. It is known that ball milling, the milling process used for traditional ceramics, requires long milling times (20–50 h) if powders must be obtained with a grain size distribution suitable for pressing and sintering. In is also known that attrition milling can lead to powders having the same properties as above in times which are around 1/10 shorter than ball milling. Other authors

Table 1
More abundant elements of the calcined powders determined by the elemental analysis (ppm)

Element	Material's source			
	Dredging spoils (DS)	Bottom ashes (BA)	Municipal seawage sludge (MSS)	Steelwork slag SS
Na	7520	14005	12400	<50
Mg	76900	37760	7500	1775
Sb	<50	355	450	<50
Ca	19050	22920	5200	8397
V	858	820	<50	<50
Cr	87	460	230	1147
Mn	365	770	1100	55287
Fe	13440	15875	89000	6645
Co	<50	<50	860	<50
Cu	<50	4885	680	<50
Zn	55	1953	4600	699
Al	36265	70825	6200	25732
Sr	123	212	<50	643
Sn	<50	260	220	<50
Pb	<50	660	260	<50
Si	115620	95000	81000	29735
As	150	153	<50	<50
Ba	70	602	360	2995
K	<50	<50	4270	423
Ni	<50	<50	150	<50
P	<50	<50	2820	<50
Ti	<50	<50	2100	570
Zr	<50	<50	<50	3052
S	1750	2300	2200	4300
Cl	490	950	350	140

Elements not reported were determined in quantity lower than 50 ppm.

[36] have demonstrated that 7 h of attrition milling are sufficient to transform coarse alumina powders into powders of particles <1 μm. Concerning waste materials, in a previous study [16], we have demonstrated that after 3 h of attrition milling, MSS can be transformed into powders suitable for pressing and sintering: prolonged millings do not greatly improve powders sinterability. In the present study, calcined DS look as fine powders containing few strong agglomerates, calcined MSS appear as a ceramic soft sponge, calcined BA and SS contain fine particles and strong agglomerates with a maximum dimension of 5 mm.

It is clear at this point of the discussion that the starting materials are extremely heterogeneous in grain size distribution. 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 ceramurgic processing of the waste, we have set the attrition milling time to 3 h, being aware that the grain size distribution and consequently the sinterability of the four 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 h, it may be useful in order to limit the high number of variables.

The thermodilatometric tests carried out on the green samples allowed for the determination of the starting temperatures of shrinkage and of the softening temperatures of the specimens. The optimal sintering temperature was thus detected for each composition (Table 2). For sake of brevity, in the present paper, we did not report any thermodilatometric diagram since we used

them only to optimize the sintering temperature. Axial and radial shrinkage were measured subsequently on the fired materials.

Table 2 shows that the sintering temperatures range from 1130 to 1180 °C and 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 firing ranges from 10% of DS + SS to 15.5% of DS + MSS. Such values are higher than those generally required for the production of ceramic tiles [37] and could be a strong drawback for industrial production using recycled wastes. Axial shrinkage is lower than the radial one due to the fact that powders where uniaxially pressed along that direction.

The colour of DS powders is pale brown, that of BA is pale grey, that of MSS is brick red and that of SS is dark grey. Concerning sintered samples, the colour of DS and DS + BA materials is yellowish, that of DS + MSS is brick red, due to the presence of a high amount of Fe in the starting MSS product. Finally, the colour of DS + SS strongly points to black, due to the presence of a high content of Fe and Mn ions in the SS powders.

Density (g/cm^3), bending rupture strength (MPa), Vickers hardness (GPa) and fracture toughness ($MPam^{1/2}$) values of the sintered materials are also listed in Table 2.

It can be observed that density ranges from 2.79 g/cm^3 for sample DS + BA up to a maximum of 3.13 g/cm^3 for sample DS + SS. These values are higher than those usually measured on

Table 2
Softening temperature, sintering temperature, axial and radial shrinkage on firing, density, water absorption, rupture strength, Vickers hardness fracture toughness and dilatometric thermal expansion coefficient between 25 and 500 °C of the materials produced

Material	Softening temperature (°C)	Sintering temperature (°C)	Axial shrinkage on firing (%)	Radial shrinkage on firing (%)	Density (g/cm³)	Water absorption (%)	Rupture strength (MPa)	Vickers hardness (GPa)	Fracture toughness (MPam$^{1/2}$)	Dilatometric thermal expansion coefficient (×10^{-6} °C^{-1})
DS	1074	1180	6.7	10.9	2.87	4.1	57 ± 4	5.5 ± 0.1	3.6 ± 0.15	6.7
DS + MSS	1034	1150	12.2	15.5	2.94	1.1	79 ± 6	5.1 ± 0.25	1.8 ± 0.3	9.6
DS + BA	1040	1130	10.8	14.3	2.79	3.7	56 ± 3	6.1 ± 0.3	6.1 ± 0.32	7.1
DS + SS	1075	1180	5.9	10.0	3.13	3.6	10 ± 2	4.7 ± 0.3	0.8 ± 0.3	11.8

some traditional ceramics such as floor and wall tiles, tableware and sanitary ware [37].

Water absorption ranges from 1.1 of DS + MSS to 4.1 of DS alone. Such values are suitable for the production of earthenware [37]. In particular DS + MSS material appears very compact, having a low residual porosity.

The rupture strength data range from 10 MPa (sample DS + SS) to 79 MPa (sample DS + BA). Rupture strength values, except for DS + SS, are sufficiently high and satisfy the requests for ceramic wall and floor tiles which must have a rupture strength of 12 MPa and are somewhat higher than those reported for several materials produced using recycled waste [31–33,38–40].

Vickers hardness ranges from 4.7 GPa of sample DS + SS to 6.1 GPa of sample DS + BA and shows that DS, DS + BA and DS + MSS could have application, for example, as wall tiles, whereas the mixture DS + SS does not lead to materials suitable for civil applications [37].

Toughness data range form 0.8 MPam$^{1/2}$ measured on DS + SS to 3.6 MPam$^{1/2}$ measured on DS and are comparable with those of commercial tiles [37]. Dilatometric thermal expansion coefficients range from 6.7 of DS alone to 11.8×10^{-6} °C^{-1} of DS + SS. Data determined for DS, DS + MSS and DS + BA can be considered good for the production of tiles [37], also in perspective of an eventual glaze application. On the contrary the value of 11.8×10^{-6} °C^{-1} measured in DS + SS looks too high for the production of tiles even if no glaze application must be performed.

XRD analysis, done on the free surface of the sintered samples, showed the presence of several phases in each material. As an example Fig. 1 shows the XRD pattern of DS alone whereas in Table 3 we report only those phases that were indexed by a minimum of five representative peaks and in sufficiently good agreement with the PDF files. It can be observed the presence of diopside in samples DS, DS + MSS and DS + BA. In these samples the amount of DS in the starting mixtures reaches 50 wt.%. Considering that diopside is present, as the main phase, in pure DS material, we can state that this phase is brought into our samples by DS and is not hidden by the other components. On the contrary, samples prepared by using DS + SS mixture (90% SS and 10% DS), show the presence of other phases, but not diopside. This is due to the low amount of DS in the starting mixtures. It can be also observed that the phase identification program indicate that five of the observed peaks correspond to K_3FeO_2, a phase where iron is monovalent. The presence monovalent iron is unlikely, since the sintering process was carried out under oxidizing atmosphere. A possible explanation is that, due to the complexity of the mixture, the peaks attributed to K_3FeO_2 could be produced by other unidentified phases. Moreover the presence, in all our samples, of soluble salts such as sulphates, chlorides or others cannot be excluded even if XRD analysis did not reveal their presence. In fact, the calcination process was carried out at a temperature which is not sufficiently high to quantitatively evaporate-decompose all the non-metallic compounds which may be present in the as received wastes. Some of them might remain in the calcined powders and it cannot be excluded that they react with some metallic elements during the
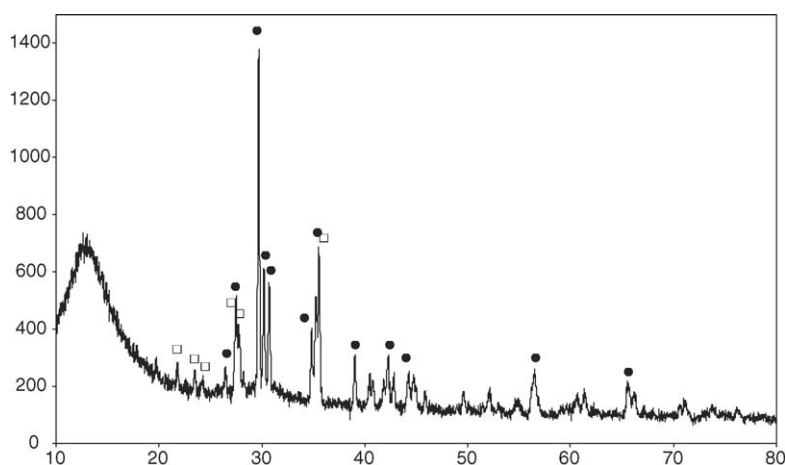
Fig. 1. XRD pattern of the free surface of a sintered sample of DS alone: peaks marked with the symbol (●) refer to hybonite whereas the symbol (□) is used to evidence anorthoclase.

subsequent sintering process. It follows that sintered ceramics could contain soluble salts which may represent a serious drawback for the production of tiles.

SEM photographs, also made on free surfaces of the fired samples, are reported in Fig. 2a–e. It must be observed that the size of grains is not so large in all materials. Sample produced by sintering DS at 1180 °C (Fig. 2a) shows the presence of a vitreous phase which is evident in several zones where the microstructure is not perfectly visible since polycrystalline grains are covered by a layer of glass produced by the liquid phase present at high temperature during the sintering process. Some elongated grains (unknown crystal structure) are also visible and are probably responsible for the good toughness of this material. The residual porosity cannot be neglected having pores sized about 4 μm which contribute to the good toughness of this material.

Sample prepared by sintering material DS + MSS at 1150 °C (Fig. 2b) shows a great amount of glassy phase. The same material is mainly polycrystalline at the XRD analysis, therefore we suppose that the glass layer is sufficiently thick to hide the smallest grains under the SEM investigation, but not thick enough to hide their crystal structure under the XRD analysis, where the energy of the beam is higher than that of the SEM.

The specimen prepared by sintering material DS + BA at 1130 °C (Fig. 2c) have a low amount vitreous phase and equiax-

ial grains are better evidenced than in the other samples; the residual porosity is low with pores sized below 1 μm. Sample prepared firing DS + SS materials at 1180 °C (Fig. 2d) does not show the presence of glass, but rather two distinct polycrystalline phases: the main, dark, is magnesium iron silicate, the other, clear in the micrograph, is jacobsite. In this case too, grains are equiaxial and the residual porosity could be considered negligible. Despite the good microstructure, this material has very low mechanical properties due to the presence of large defects (Fig. 2e) produced by the sintering process. Such defects could be due to several synergic mechanisms. We suggest that one could be the transformation occurring in the SS powders alone [25]: homogenization with 10 wt.% of DS is not sufficient to completely suppress the formation of $2CaO \cdot SiO_2$ which remains, although in low amount, not detectable by XRD analysis, randomly dispersed into the material; a second mechanism could be due to the presence of soluble salts (sulphates, chlorides, chlorites and others) being responsible for efflorescence formation; other mechanisms could also concur in the formation of such large defects which have been detected in our specimens.

Nevertheless, the SEM analysis of the sintered materials shows a good correspondence between samples microstructure and mechanical properties of the materials produced in the present research.

Table 3
Main phases revealed by the XRD analysis in the sintered materials

| Material	Main phases		
	Mineral name	Chemical formula	JCPDS number
DS	Diopside	$CaMgSi_2O_6$	01-071-1494
	Anorthoclase	$AlK_{0.25}Na_{0.75}Si_3O_8$	01-075-1632
DS + MSS	Diopside	$CaMgSi_2O_6$	01-071-1494
	Potassium iron oxide	K_3FeO_2	01-081-1805
DS + BA	Diopside	$CaMgSi_2O_6$	01-071-1494
	Magnesium iron calcium aluminum silicate	$Al_{0.7}CaFe_{0.2}Mg_{0.6}Si_{1.5}O_6$	01-072-1379
	Calcium sodium aluminum silicate	$Al_{12}Ca_4Na_4Si_{12}O_{48}$	01-072-0083
DS + SS	Jacobsite	Fe_2MnO_4	01-088-1965
	Magnesium iron silicate	$Mg_{0.54}Fe_{0.46}SiO_3$	01-089-1595
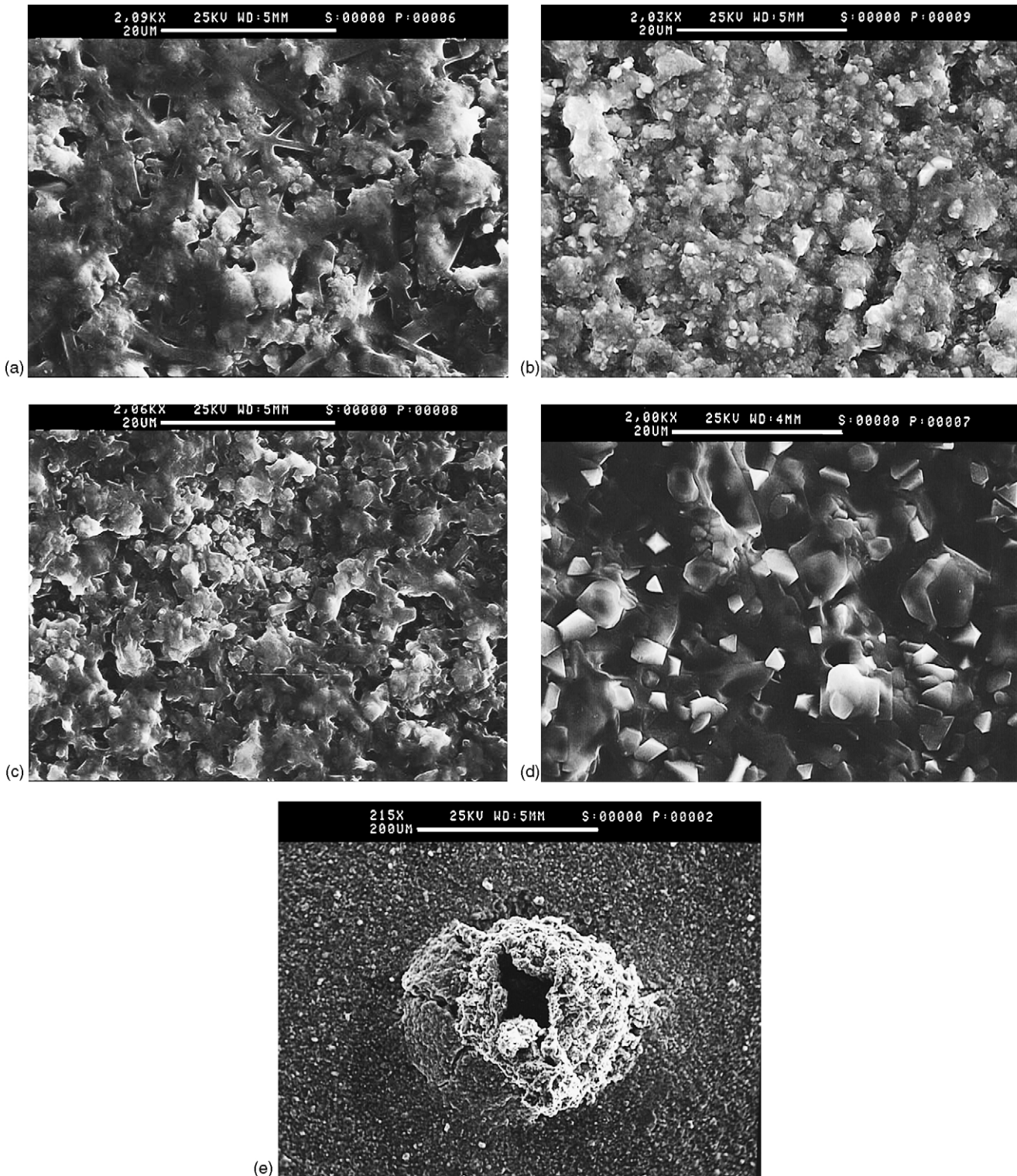
Fig. 2. SEM photographs of the free surface the fired samples produced in the present work: (a) prepared using DS powders alone and sintered 1 h at 1180 °C; (b) prepared using the mixture DS + MSS and sintered at 1150 °C; (c) prepared using the mixture DS + BA and sintered at 1130 °C; (d) prepared using the mixture DS + SS and sintered at 1180 °C; (e) macroscopic defect revealed on the surface of the sample DS + SS displayed at low magnification.

Elution release data, reported in Table 4, must be read in terms of safety limits for the sintered materials and are significant if compared with long term attack of the materials by the environment ageing. The pH value, settled between 3 and 4, approximates natural conditions that only in some particular and occasional events can be obtained in nature, but, in laboratory experiments, associated with the temperature of 60 °C for a sufficiently long time (30 days), should accelerate the elution of some components from the fired materials.

Table 4
More abundant elements eluted (μg/kg = parts per billion) from the sintered samples after aging for 30 days at 60 °C in H$_2$O/HCl solutions at pH 4 determined by the elemental analysis

Material	Mg	Al	P	K	Ca	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	Sr	Si	Ba
DS	**56074**	**11526**	307	742	4273	271	284	20	98	**5229**	221	74	184	64	**6456**	42
DS + MSS	**308126**	**23910**	**58226**	3088	**44555**	437	518	10	462	2294	87	899	579	491	**14901**	304
DS + BA	**289143**	**9385**	466	**6098**	**55596**	580	381	79	1002	856	244	2320	**3644**	318	**14319**	431
DS + SS	**14909**	1340	150	2317	**74949**	720	920	202	314	900	167	18	79	237	**13122**	447

In bold characters are evidenced those present in significant amount. Elements not reported in the table were determined in quantity lower than 25 ppb.

These data show that the elution of hazardous elements is low. Some elements, such as Mg, Ca, Si are present in large amounts in all the eluted solutions, but they are not considered hazardous elements. Al, which is not a heavy metal, is present in non-negligible amount in DS, DS + MSS and DS + BA, whereas a great amount of P was detected only in the DS + MSS eluted solution due to the relatively high quantity of P in the MSS starting material. Potassium was detected in moderate quantity in DS + MSS, DS + BA and DS + SS whereas Fe is significant in DS and DS + MSS. Copper and zinc cannot be neglected in DS + BA eluted solution. More toxic elements (Hg, Cd, Ni and others) were not detected or only detected in a very low quantity.

The leaching test adopted 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 [41] 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 is a further confirm that the sintering process of powders obtained from waste materials can be used for the production of monolithic ceramic, since it ensures the environmental compatibility of the sintered materials. In the present investigation we did not use any codified release test because the goal of the present research is the production of monolithic ceramics. The use of a codified test suitable for wastes would imply that the sintering process is only useful to transform the starting wastes into other types of waste, maybe more benign toward environment. It would be more interesting to follow a release test codified for monolithic ceramics, but we do not know any severe, codified test for ceramic bodies with low residual porosity. We therefore developed the release test reported in the present paper in order to supply a new approach to evaluate the release of some hazardous elements for the fired ceramic bodies we have produced.

4. Conclusions

The present investigation showed that the ceramic materials produced using powders obtained from calcined dredging spoils alone (DS), or in mixture with municipal sewage sludge (MSS), bottom ash (BA) or steelwork slag (SS) are able to immobilize most of the hazardous elements contained in the starting materials. The mechanical properties of the materials obtained by sintering DS alone, or mixtures DS + MSS and DS + BA are good, due to the formation of monolithic materials having fine grains embedded into a vitreous phase and a low residual porosity; those of the composition MS + SS are low since fired materials containing large defects.

DS and DS + BA materials have also a light colour and could be used to prepare value added products. The dark colour of MMS and SS containing sintered products could be clarified using a mixture of these recycled materials with other natural clays normally used as starting materials for ceramic productions.

Data obtained in the present research do not allow to suggest the use of SS, neither in moderate amount, in the ceramic industry since the materials produced in the present work have high shrinkage on firing, high thermal expansion coefficient and contain large defects. On the other hand, the same cannot be excluded for the powders obtained from incinerated DS, MSS and BA since the relative fired materials have fair mechanical properties and the release of hazardous elements is low. The shrinkage on firing is high for all the materials produced in the present work and further formulations are necessary before undergoing an eventual industrial production.

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