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## Sintering of MSW fly ash for reuse as a concrete aggregate

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### Abstract

The sintering process of municipal solid waste (MSW) fly ash was investigated in order to manufacture sintered products for reuse as concrete aggregates.

Four types of fly ash resulting from different Italian MSW incineration plants were tested in this study. A modification of the chemical composition of MSW fly ash — through a preliminary four-stage washing treatment of this material with water — was attempted to improve the chemical and mechanical characteristics of sintered products.

The sintering treatment of untreated or washed fly ash was performed on cylindrical compact specimens (15 mm in diameter and 20 mm in height) at different compact pressures, sintering temperatures and times.

The sintering process of untreated MSW fly ashes proved to be ineffective for manufacturing sintered products for reuse as a construction material, because of the adverse chemical characteristics of these fly ashes in terms of sulfate, chloride, and vitrifying oxide contents.

A preliminary washing treatment of MSW fly ash with water greatly improved the chemical and mechanical characteristics of sintered products and, for all the types of fly ash tested, the sintered products satisfied the Italian requirements for normal weight aggregates for use in concretes having a specified strength not greater than 12 and 15 N/mm<sup>2</sup>, when measured on cylindrical and cubic specimens, respectively.

A compact pressure of 28 N/mm<sup>2</sup>, a sintering temperature of 1140°C, and a sintering time of 60 min were the best operating conditions for manufacturing sintered products of washed MSW fly ash. © 2001 Elsevier Science B.V. All rights reserved.

*Keywords:* MSW fly ash; Sintering; Washing pretreatment; Reuse

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## 1. Introduction

Fly ash resulting from municipal solid waste (MSW fly ash) incineration has to be regarded as a hazardous material, due mainly to its high heavy metals content. Therefore, MSW fly ash needs careful management and its disposal requires either high protection level landfills or treatment before landfilling, so as to reduce contaminants release into the environment.

At present, the most widely applied treatment for the inertization of MSW fly ash is the solidification/stabilization (S/S) process, generally using cement as a binder [1].

The main drawback of the S/S process is represented by the considerable increase in the volume of waste to be disposed of, due to the significant amount of cement utilized in the inertization process. However, a recent work [2] proved the feasibility of a washing pretreatment of MSW fly ash with water as a means of maximizing the incorporation of fly ash in cementitious matrices (ash content up to 75–90% by weight of total solid) without the risk of heavy metals leachability from solidified products.

Thermal processing of MSW fly ash represents a promising technique in view of both immobilizing the heavy metals and reducing the volume of residue to be managed [3]. Moreover, when properly conducted, thermal treatment can produce a suitable material for further utilization, so representing a cost-saving method of treating waste combustion residues.

Recently, thermal treatments such as melting or sintering were applied to MSW incineration residues for producing dense, amorphous material (vitrified products) [4] or coherently bonded particles (sintered products), respectively [5].

The vitrified products proved to be suitable for use as aggregates in Portland cement or asphaltic concretes for roadways, as well as for walking or garden tiles and high temperatures mineral wool insulation [4]. However, vitrification appears to be a too expensive process.

On the other hand, the possibility of using sintered products as concrete aggregates is largely depending on the operating conditions adopted for sintering. It is undoubted that the compaction degree of powders, the sintering temperature and time, as well as the chemical composition of fly ash can significantly affect the type and amount of porosity and, consequently, the specific gravity, mechanical strength and heavy metals leachability of sintered products, as well as their chemical stability in aqueous solutions.

In this regard, Wang et al. [5] found that, for one MSW fly ash collected from a mass burning incineration plant located at Taiwan, changes in the compact pressure (14–35 N/mm<sup>2</sup>), sintering temperature (1100–1140°C) and sintering time (10–60 min) caused a relevant variation of the apparent density, compressive strength, moisture absorption, and heavy metals leachability of sintered products.

At present, little is known about the effects of the chemical composition of MSW fly ash on the optimum sintering conditions and the properties of sintered products.

Therefore, the present study was undertaken to search thoroughly into this subject. Four types of MSW fly ash with different chemical composition were tested, and the sintering process of these materials was aimed at manufacturing sintered products for reuse as concrete aggregates.

A modification of the chemical composition of these fly ashes — through their preliminary washing treatment with water — was attempted to improve the chemical and mechanical characteristics of sintered products.

## 2. Materials and methods

The fly ashes used in this study came from MSW incineration plants located at four different Italian cities (Bologna, Forlì, Modena, and Reggio Emilia). These fly ashes were designated by notations indicating the respective place of origin (BO, FO, MO, and RE).

Each fly ash was preliminarily dried in an oven at 105°C and then analyzed for its particle size distribution and chemical composition.

The particle size distribution was evaluated by a laser diffraction technique. The chemical composition was determined by X-ray fluorescence, flame atomic absorption spectrometry, gravimetric and volumetric analyses.

An aliquot of each fly ash was also subjected to a washing treatment with distilled water in order to remove the water-soluble compounds.

Preliminary tests showed that a four-stage washing treatment (moderate stirring; liquid/solid weight ratio = 50; mixing time = 30 min for each stage of treatment) was effective in removing the water-soluble compounds almost completely. After the washing treatment, the cumulative percentage weight loss of each fly ash was evaluated and reported as loss on water-solubilization (LOS). Also, the LOS values of the various fly ashes were taken as a measure of their contents of water-soluble compounds.

In order to investigate the thermal behavior of MSW fly ashes, a sample of each untreated or washed fly ash was subjected to simultaneous thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) by using a thermoanalyzer operating in static air at a heating rate of 10°C/min over a temperature range from 25 to 1300°C.

The sintering process of the fly ashes was investigated using cylindrical specimens (15 mm in diameter and 20 mm in height) produced by compacting a mixture of powder and distilled water with a moisture content of 8% by weight of solid. The powders used for the preparation of compact specimens were: untreated fly ash or preliminarily washed fly ash.

For each untreated or washed fly ash, five replicate compact specimens were prepared and then subjected to sintering treatment under established operating conditions.

The compact specimens of untreated fly ash were made at a compact pressure of 28 N/mm<sup>2</sup>, while the specimens of washed fly ash were formed at two different compact pressures (15 and 28 N/mm<sup>2</sup>).

All the compact specimens were dried in an oven at 105°C prior to sintering treatment.

In most cases, the sintering treatment was performed at a temperature of 1140°C for 60 min. Some specimens were also sintered at temperatures ranging from 1090 to 1140°C and sintering times ranging from 15 to 120 min.

After sintering, the percentage weight loss of the compact specimens was always evaluated and reported as loss on ignition of compact (LOI<sub>c</sub>) specimens.

All the sintered products were tested for unconfined compressive strength ( $R_c$ ) and chemical water-stability, taking in mind that high strength and high chemical water-stability are the most important prerequisites for a possible utilization of sintered MSW fly ashes as a construction material.

The chemical water-stability of sintered products was evaluated by contacting each sintered specimen with distilled water (liquid/solid weight ratio = 50) for 24 h at room temperature and measuring the percentage weight loss of this specimen after drying at 105°C. This weight loss, designated as WL<sub>s</sub>, was taken as a measure of the amount of water-soluble

compounds released from a sintered specimen under established operating conditions. Obviously, a high chemical water-stability was denoted by a very low  $WL_s$ -value.

The sintered products exhibiting satisfactory results in terms of both  $R_c$  and  $WL_s$  were also tested for particle density, dimensional change, and water absorption according to the experimental procedures reported in [6]. Heavy metals leachability was evaluated by the Italian standard acetic acid leaching test [7].

### 3. Results and discussion

#### 3.1. Sintered specimens of untreated fly ash

Table 1 gives the elemental analyses, LOS-values, and particle size distributions of untreated MSW fly ashes.

Table 1  
Elemental analyses, LOS-values, and particle size distributions (wt.%) of untreated MSW fly ashes

Element	BO	FO	MO	RE
Ca (%)	18.2	20.2	15.2	13.1
Si (%)	10.6	10.1	10.1	9.4
Al (%)	5.92	4.41	4.60	4.52
Na (%)	2.80	2.01	4.40	4.40
K (%)	3.61	5.40	6.21	7.30
Ni (%)	2.81	2.70	2.62	2.81
Fe (%)	1.01	1.05	1.22	1.62
Mg (%)	1.42	1.70	1.21	1.22
Zn (%)	0.64	0.37	1.80	2.05
Acid-soluble S <sup>a</sup> (%)	4.35	4.33	6.75	5.06
Water-soluble S <sup>b</sup> (%)	4.30	4.30	6.70	5.00
Cl (%)	5.60	7.20	8.70	11.7
Pb (%)	0.40	0.22	0.70	0.96
Cu (ppm)	900	600	1400	2100
Cd (ppm)	30	<0.25	240	160
Cr (ppm)	200	500	400	160
Hg (ppm)	<0.025	<0.025	<0.025	<0.025
As (ppm)	<0.053	200	<0.053	<0.053
LOS (%)	28.7	31.6	44.7	42.5
Particle size range ( $\mu\text{m}$ )				
100–150	10	5	3	2
75–100	12	5	8	7
50–75	13	18	13	12
36–50	17	17	13	16
25–36	11	16	13	14
15–25	16	18	17	22
5–15	16	13	17	18
<5	5	8	16	9

<sup>a</sup> Acid-soluble sulfates expressed as sulfur.

<sup>b</sup> Water-soluble sulfates expressed as sulfur.

It is well known that the particle size and the particle size distribution of powders are two very important factors in affecting the sintering process. In particular, surface diffusion and grain boundary diffusion are very sensitive to particle size [8].

As can be seen from Table 1, all the tested fly ashes were characterized by particle sizes less than  $150\ \mu\text{m}$  and did not significantly differ for the particle size distribution. Therefore, the different properties exhibited by the sintered products made with different types of fly ash under identical sintering conditions were to be ascribed only to the different chemical compositions of the fly ashes used.

All the tested fly ashes had very high contents of water-soluble compounds (LOS values of 28.7–44.7%) and low Si contents (9.4–10.6%) corresponding to  $\text{SiO}_2$  (amorphous network forming oxide) concentrations of 20.1–22.7%. Also, these fly ashes were characterized by low contents of aluminum (4.4–5.9%) that is a metal able to substitute Si into an amorphous network.

As reported in a previous paper [2], the highly water-soluble compounds of these fly ashes were halite ( $\text{NaCl}$ ) and sylvite ( $\text{KCl}$ ), accompanied by other salts of less solubility in water such as  $\gamma$ -anhydrite ( $\text{CaSO}_4$ ) and, in the case of FO fly ash, apththalite ( $(\text{Na,K})_3\text{Na}(\text{SO}_4)_2$ ).

The TGA–DSC thermograms of untreated fly ashes, shown in Fig. 1a–d, revealed that all the fly ashes melted over a wide temperature range, as evidenced by the large endothermic

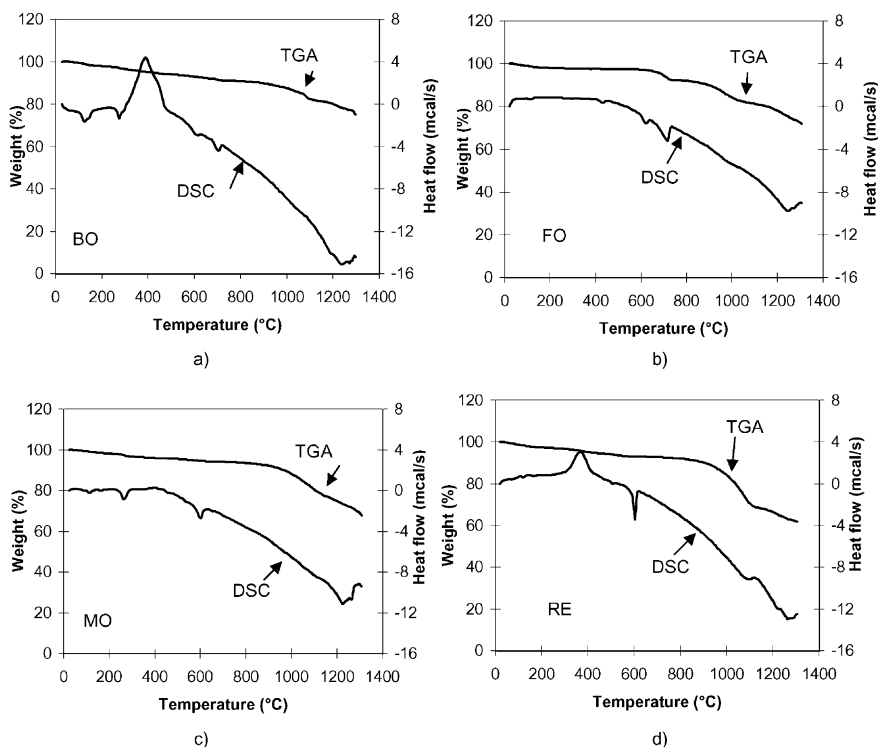


Fig. 1. (a–d) DSC–TGA thermograms of untreated MSW fly ashes.

peak located at a peak temperature of 1200–1250°C, depending on the type of fly ash tested (DSC patterns).

As evidenced by TGA patterns, the melting process was always accompanied by a significant percentage weight loss of fly ash (6.8–11.5%), that was mostly attributable to the decomposition of alkaline sulfates.

For all the fly ashes, some endothermic peaks associated with relatively low percentage weight losses (2.0–3.9%) were recorded at temperatures less than about 300°C. Furthermore, for BO, MO and RE fly ashes (Fig. 1a, c and d), an exothermic peak was recorded at 400°C and associated with carbon oxidation. For FO, MO and RE fly ashes (Fig. 1b–d), an endothermic peak was detected at 600°C and related to siderite ( $\text{FeCO}_3$ ) decomposition. For BO and FO fly ashes (Fig. 1a and b), an endothermic peak was also recorded at about 700°C and identified with calcite decomposition.

In every case, the overall percentage weight loss at 1140°C (19.0% for BO fly ash, 19.7% for FO fly ash, 22.3% for MO fly ash, and 31.7% for RE fly ash) was only in part (24–48%) attributable to the observed exothermic and endothermic transformations, thus, suggesting that a large volatilization of alkaline chlorides occurred at temperatures above about 800°C.

On the basis of the elemental analyses of untreated fly ashes (Table 1) and the percentage weight losses (Fig. 1a–d) determined within the range of temperature from 800 to 1140°C (9.8% for BO fly ash, 11.7% for FO fly ash, 15.8% for MO fly ash, and 24.1% for RE fly ash), it was estimated that, for all the fly ashes, volatilization of alkaline chlorides occurred almost completely within this temperature range.

Therefore, the sintering treatment of untreated MSW fly ash at 1140°C should be effective in producing sintered specimens with a very low content of chlorides. Conversely, the concentration of sulfates in sintered products should be greater than in unsintered fly ashes, as a result of an insignificant elimination of sulfates and a significant loss on ignition of fly ash during the sintering treatment at 1140°C.

According to the chemical requirements established by the Italian standard for normal weight aggregates for use in concrete [6], the water-soluble chloride content of these aggregates shall be not greater than 0.1% as Cl and the acid-soluble sulfate content shall be not greater than 0.2% as  $\text{SO}_3$ .

These chemical requirements do not significantly differ from those recently prescribed by the European standard prENV12620 for normal weight aggregates [9]. According to this standard, the acid-soluble sulfate content shall not be greater than 0.2 or 0.8% as  $\text{SO}_3$ , depending on the type of aggregates. Also, the total sulfur content of the aggregates shall not exceed 1% as S. A water-soluble chloride content of 0.15% as Cl is specified as a guideline maximum Cl content of the aggregates for use in plain concrete.

On the basis of the above TGA–DSC thermograms and taking in mind the concentrations of chlorides and acid-soluble sulfates in untreated MSW fly ashes (Table 1), the sintering treatment of these fly ashes at 1140°C should be expected to be ineffective for manufacturing sintered products for reuse as concrete aggregates, because of an excessive sulfate content of these manufactured aggregates.

Furthermore, a large volatilization of alkaline chlorides during the sintering treatment will greatly contribute to the  $\text{LOI}_c$  specimens and will also cause a large increase of the porosity of these specimens. The increased porosity coupled with an insufficient formation of intergranular vitreous phase, due to the low contents of Si and Al in untreated fly ashes

Table 2

Compressive strength and chemical water-stability of sintered products of untreated MSW fly ash (1140°C; 60 min), and loss on ignition of compact specimens after sintering (compact pressure = 28 N/mm<sup>2</sup>)

Untreated fly ash	$R_c$ (N/mm <sup>2</sup> )	WL <sub>s</sub> (%)	LOI <sub>c</sub> (%)
BO	6.1	5.2	23.5
FO	6.3	5.3	20.1
MO	5.6	8.5	23.0
RE	4.2	6.7	33.1

(Table 1), could cause a low consolidation of the compact specimens and, consequently, an insufficient mechanical strength development.

A low chemical water-stability of such manufactured products and, consequently, a further reduction of their strength after water immersion should also be expected, taking in mind the high content of water-soluble sulfates and the low contents of Si and Al in untreated fly ashes.

All the above predictions were fully validated by the experimental results obtained when compact specimens of untreated MSW fly ash were formed at a pressure of 28 N/mm<sup>2</sup> and sintered at 1140°C for 60 min.

Table 2 gives the values of  $R_c$  and WL<sub>s</sub> for such sintered products, along with the values of LOI<sub>c</sub> for the respective compact specimens after sintering.

All the values of  $R_c$ , WL<sub>s</sub> and LOI<sub>c</sub> reported in this table and in the following tables were determined as the average of five measurements. The coefficient of variation for each parameter within a set of specimen was always less than 10%.

Regardless of the type of MSW fly ash tested, all the sintered specimens exhibited low  $R_c$  (4.2–6.3 N/mm<sup>2</sup>) and high WL<sub>s</sub>-values (5.2–6.7%). Also, the compact specimens after sintering had very high LOI<sub>c</sub>-values (20.1–33.1%) that were comparable to the respective percentage weight losses measured at 1140°C on powdered fly ash samples (Fig. 1a–d).

As can be deduced from the data in Tables 1 and 2, there was a consistent relationship between the compressive strength of sintered products, the LOI<sub>c</sub> specimens after sintering, and the total Al plus Si content of untreated fly ashes.

It should be considered that: (1) the poor properties of the sintered products made with untreated MSW fly ashes were essentially related to the adverse chemical characteristics of these fly ashes in terms of water-soluble compounds (chlorides and sulfates) and vitrifying oxides, and (2) a preliminary washing treatment of MSW fly ash with water could greatly reduce the content of water-soluble compounds and, at the same time, could increase the concentration of vitrifying oxides. Therefore, the sintering of preliminarily washed MSW fly ash could be a suitable way of manufacturing sintered products with proper chemical and mechanical characteristics for reuse as concrete aggregates.

### 3.2. Sintered specimens of washed fly ashes

Table 3 gives the elemental analyses of washed MSW fly ashes.

These analyses revealed that a four-stage washing treatment of untreated fly ash with distilled water was always effective in removing the water-soluble compounds almost

Table 3  
Elemental analyses of washed MSW fly ashes

Element	BO	FO	MO	RE
Ca (%)	19.6	22.4	16.4	14.6
Si (%)	14.6	14.8	18.2	16.3
Al (%)	8.10	6.44	8.26	7.80
Na (%)	0.04	0.02	0.04	0.03
K (%)	0.03	0.04	0.03	0.06
Ni (%)	3.90	3.90	4.65	4.82
Fe (%)	1.40	1.50	2.18	2.82
Mg (%)	1.93	2.40	2.09	2.12
Zn (%)	0.88	0.50	3.20	3.50
Acid-soluble S <sup>a</sup> (%)	0.07	0.06	0.07	0.07
Cl (%)	0.08	0.07	0.09	0.10
Pb (%)	0.56	0.30	1.20	1.60
Cu (ppm)	1260	1005	3580	3600
Cd (ppm)	40	–	600	260
Cr (ppm)	270	802	890	255

<sup>a</sup> Acid-soluble sulfates expressed as sulfur.

completely (98–99% removals). Thus, the washed fly ashes were always characterized by very low contents of Na, K, Cl, and acid-soluble S. A marked increment of the Si and Al concentrations was also attained, particularly for washed MO and RE fly ashes (percentage Si and Al increments of 73–80%). Conversely, no substantial change in the particle size distribution was observed after the washing treatment of fly ash.

Fig. 2a–d show the TGA–DSC thermograms of washed fly ashes.

The DSC patterns of the washed fly ashes did not greatly differ from those of the corresponding untreated fly ashes (Fig. 1a–d), thus, indicating that the washing pretreatment of MSW fly ash with water essentially caused an elimination of water-soluble compounds, without generating new amorphous or crystalline phases detectable by DSC analysis. However, some differences between the DSC patterns of washed and untreated fly ashes were detected. First, the melting of washed fly ashes was always characterized by a not well-shaped endothermic peak, thus, suggesting that the final melting point was always shifted to temperatures above 1300°C. Second, for washed FO, MO and RE fly ashes, no endothermic peak was recorded at 600°C (Fig. 2b–d). Moreover, for all the washed fly ashes, a greater percentage of weight loss was recorded over the range of temperatures from 20 to 300°C (3.0–6.0% at 300°C) and this weight loss was related to an elimination of both chemically bonded and mechanically occluded water.

As can be calculated by the TGA patterns, the overall percentage of weight losses of washed fly ashes at 1140°C (15.9% for BO fly ash, 10.2% for FO fly ash, 8.1% for MO fly ash, and 8.9% for RE fly ash) were always much lower than those measured at the same temperature on the corresponding untreated fly ashes and this can be attributable to the very low contents of alkaline chlorides in washed fly ashes. Conversely, with respect to untreated fly ashes, washed fly ashes always exhibited higher percentage of weight losses at 800°C, because the washing pretreatment caused an enrichment of water-insoluble compounds undergoing thermal decomposition, such as carbon and calcite. This was particularly



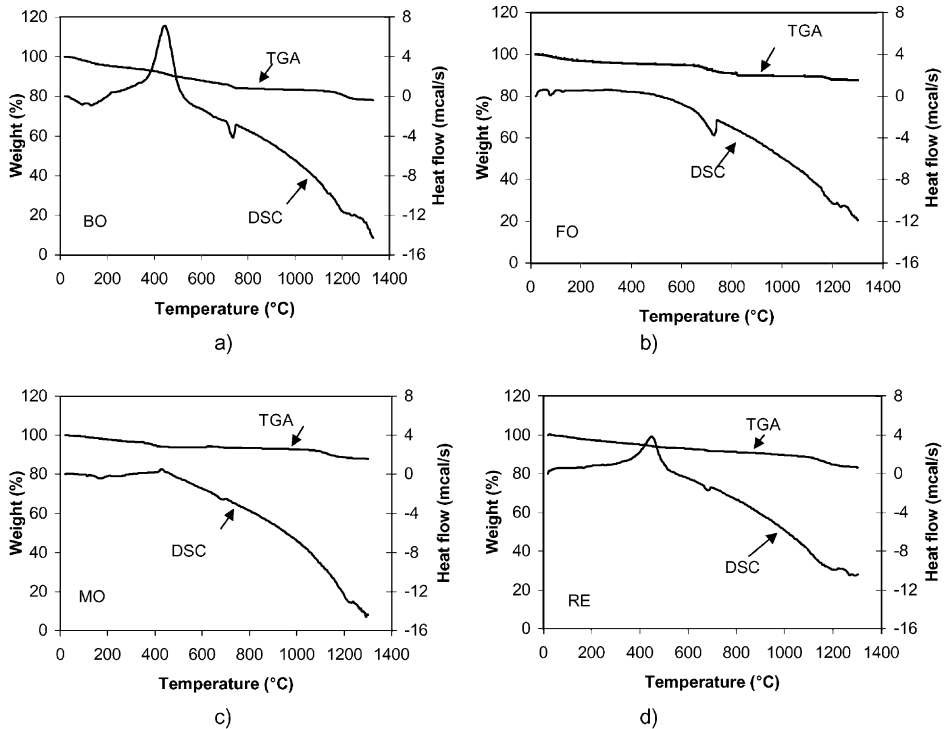


Fig. 2. (a–d) DSC–TGA thermograms of washed MSW fly ashes.

evident for washed BO fly ash which contained significant amounts of carbon and calcite (Fig. 2a).

Furthermore, due to the very low contents of alkaline sulfates in washed fly ashes, the melting process of these fly ashes was always accompanied by a lower percentage weight loss (0.7–2.0%). However, during the thermal treatment of washed fly ashes, volatilization of heavy metal compounds could be more pronounced, since these fly ashes resulted to be enriched in heavy metals after the washing treatment (Table 3).

Table 4 gives the values of  $R_c$  and  $WL_s$  for the sintered products obtained when compact specimens of washed fly ash were formed at two different compact pressures (15 and 28 N/mm<sup>2</sup>) and sintered at 1140°C for 60 min. In this table, the values of the percentage weight loss of compact specimens after sintering ( $LOI_c$ ) are also reported.

All the sintered products exhibited satisfactory properties in terms of both  $R_c$  and  $WL_s$ . In particular, these specimens were always characterized by an insignificant  $WL_s$  (0.09–0.15%), thus, denoting a very high chemical water-stability. This high stability can be attributable to: (1) a very low content of water-soluble sulfates in the washed fly ashes (Table 3) and, consequently, in the sintered products (alkaline chlorides were mostly removed by the washing treatment and almost totally eliminated by the subsequent sintering treatment), (2) a reduced porosity of compact specimens after sintering, as a result of a lower loss on ignition

Table 4

Compressive strength and chemical water-stability of sintered products of washed MSW fly ash (1140°C; 60 min), and loss on ignition of compact specimens after sintering

Washed fly ash	Compact pressure (N/mm <sup>2</sup> )					
	15			28		
	<i>R<sub>c</sub></i> (N/mm <sup>2</sup> )	WL <sub>s</sub> (%)	LOI <sub>c</sub> (%)	<i>R<sub>c</sub></i> (N/mm <sup>2</sup> )	WL <sub>s</sub> (%)	LOI <sub>c</sub> (%)
BO	10.1	0.15	15.6	17.4	0.13	15.1
FO	12.7	0.13	10.2	20.5	0.10	10.0
MO	19.2	0.11	8.2	29.0	0.09	8.0
RE	15.8	0.12	9.2	24.7	0.10	9.0

of these specimens (Table 4), and (3) a greater formation of intergranular vitreous phase in virtue of a vitrifying oxides enrichment of washed fly ashes (Table 3).

For each type of fly ash, sintered products with higher *R<sub>c</sub>*- and lower WL<sub>s</sub>-values were always obtained when compact specimens were formed at a higher compact pressure (28 N/mm<sup>2</sup>), as a consequence of a reduced initial porosity of these specimens.

Compact pressure affected compressive strength to a much greater extent than chemical water-stability. Also, LOI<sub>c</sub> specimens after sintering was not virtually modified by changes in the compact pressure.

As can be deduced from the data in Tables 3 and 4, for compact specimens formed at a given pressure, there was a consistent relationship between the compressive strength of sintered products, the LOI<sub>c</sub> specimens after sintering, and the total Al plus Si content of washed fly ashes. Thus, for compact specimens formed at a pressure of 28 N/mm<sup>2</sup>, the highest *R<sub>c</sub>*-value (29 N/mm<sup>2</sup>) was measured on sintered products made with washed MO fly ash having both the lowest LOI<sub>c</sub>-value (8.0%) and the highest Al plus Si concentration (26.4%). Conversely, the lowest *R<sub>c</sub>*-value (17.4 N/mm<sup>2</sup>) was measured on sintered products made with washed BO fly ash having the highest LOI<sub>c</sub>-value (15.1%) and a lower total Al plus Si concentration (22.7%).

On the basis of the results in Table 4, washed BO and MO fly ashes were selected to investigate the effect of reducing sintering temperature on compressive strength and chemical water-stability of sintered products.

Compact specimens of these fly ashes were formed at a pressure of 28 N/mm<sup>2</sup> and sintered at different temperatures (1090–1140°C) for 60 min. The *R<sub>c</sub>*- and WL<sub>s</sub>-values, thus, obtained are shown plotted against sintering temperature in Fig. 3.

For both types of fly ash, a reduction in the sintering temperature below 1140°C always resulted in a decline of the properties of sintered products, especially in terms of *R<sub>c</sub>*, but this detrimental effect became particularly evident at sintering temperatures less than 1120°C. At 1090°C the compressive strengths of sintered products were by about 70–77% lower than those measured at 1140°C.

### 3.3. Kinetics of sintering

As evidenced by the results shown in Tables 2 and 4, and in Fig. 3, sintered products with the best properties in terms of both *R<sub>c</sub>* and WL<sub>s</sub> were obtained only if preliminarily washed

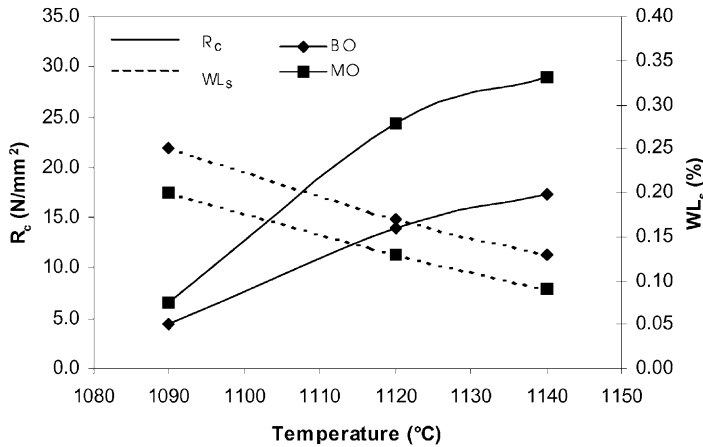


Fig. 3. Effect of sintering temperature on compressive strength and chemical water-stability of sintered products (compact pressure = 28 N/mm<sup>2</sup>; sintering time = 60 min).

MSW fly ashes were used and the sintering treatment was performed at a temperature of 1140°C.

Therefore, the consolidation rate of compact specimens during the sintering treatment was investigated at a sintering temperature of 1140°C, by using compact specimens made with washed BO or MO fly ash. These specimens were compacted at a pressure of 28 N/mm<sup>2</sup> and sintered at 1140°C for different times.

Within the range of sintering times investigated (15–120 min), all the compact specimens exhibited a linear shrinkage that increased with increasing sintering time. This indicated that densification of compact specimens progressively occurred during sintering. At a sintering time of 120 min, the linear shrinkage amounted to 6.8 and 8.7% for sintered specimens made with washed BO and MO fly ash, respectively.

According to Kingery [10], during intermediate-stage liquid-phase sintering, the time dependence of the shrinkage,  $\Delta L/L_0$ , may be expressed as follows:

$$\left(\frac{\Delta L}{L_0}\right)^n = kt$$

where  $L_0$  is the initial length of the specimen,  $\Delta L$  the linear dimensional change,  $k$  the rate constant,  $t$  the sintering time and  $n$  is an exponent that depends on the mechanism controlling densification. The value of  $n$  is 2 if interface reaction controls densification, while  $n$  is equal to 3 if densification is controlled by diffusion through the liquid-phase and grain shape accommodation.

Fig. 4 shows the shrinkage data for sintered specimens of washed BO or MO fly ash plotted against sintering time on a log–log basis.

Both sets of data fitted with a line having a slope of about 1/3, thus, indicating that, under the operating conditions adopted, sintering of washed MSW fly ash can be modeled by an intermediate-stage liquid-phase sintering system, and that densification of compact

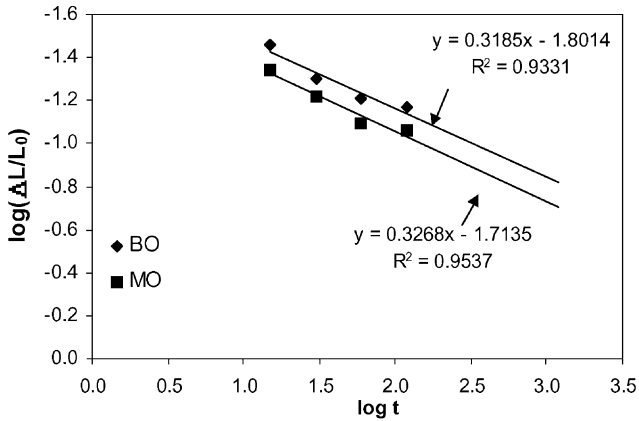


Fig. 4. Relationship between linear shrinkage of sintered products and sintering time.

specimens is controlled by diffusion through the liquid-phase and grain shape accommodation.

Fig. 5 shows the effect of varying sintering time on compressive strength and chemical water-stability of sintered products made with washed BO or MO fly ash (sintering temperature = 1140°C).

Both compressive strength and chemical water-stability always increased with increasing sintering time. However, sintering time affected  $R_c$  to a greater extent than  $WL_s$ , since the washed fly ashes were characterized by very low contents of water-soluble compounds (Table 3).

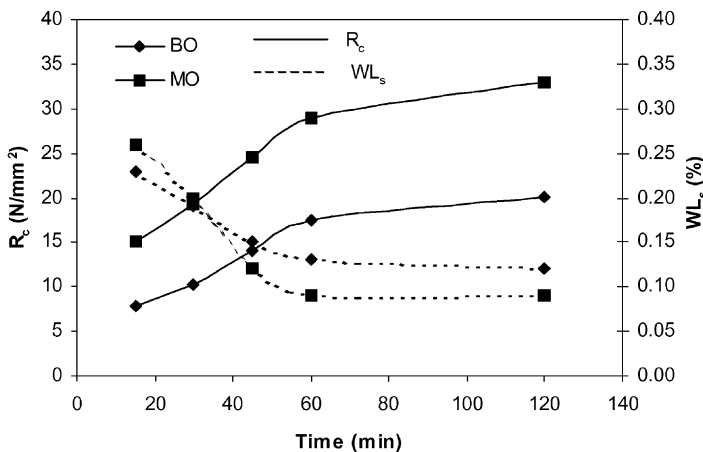


Fig. 5. Effect of sintering time on compressive strength and chemical water-stability of sintered products (compact pressure = 28 N/mm<sup>2</sup>; sintering temperature = 1140°C).

As the sintering time was increased over the range from 15 to 60 min, the compressive strength of sintered products was found to greatly increase as a result of the progressive consolidation of compact specimens.

If the sintering time was prolonged up to 120 min, a further increment of  $R_c$  was recorded but this gain of strength appeared to be too limited in relation to the excessive prolongation of the sintering treatment.

Therefore, the best operating conditions for sintering compact specimens of washed MSW fly ash resulted to be the following: compact pressure =  $28 \text{ N/mm}^2$ , sintering temperature =  $1140^\circ\text{C}$ ; sintering time = 60 min.

These operating conditions were very similar to those found by Wang et al. [5] in their study dealing with the sintering treatment of one MSW fly ash collected from a mass burning incineration plant located at Taiwan.

As reported by the above authors, this MSW fly ash was separated by a cyclone and had a loss on ignition of 5%. Unfortunately, no elemental analysis of this material was reported. However, on the basis of these informations, it is reasonable to suppose that the MSW fly ash tested by Wang et al. was virtually free of water-soluble compounds, especially alkaline chlorides and sulfates. In that case, the results of the present work are consistent with those reported by the above authors.

As evidenced by the LOS-values in Table 1, the washing pretreatment of MSW fly ash with water caused a significant loss of this material (28.7–44.7%). Also, this pretreatment produced a wastewater requiring appropriate treatment in order to remove heavy metals, especially Zn, Cd and Pb ions, as reported in a previous paper [2].

On the other hand, a preliminary vitrifying oxides enrichment of untreated MSW fly ash — through addition of appropriate amounts of amorphous silica — followed by a sintering treatment of these mixtures, did not appear to be a suitable way of manufacturing sintered products for reuse as concrete aggregates, especially because of the very high content of sulfates in untreated MSW fly ashes (Table 1) and the severe limit established for this species in concrete aggregates [6].

#### 3.4. Sintered products for use as concrete aggregates

Table 5 gives the values of particle density and water absorption for sintered products made with washed BO or MO fly ash (compact pressure =  $28 \text{ N/mm}^2$ ; sintering temperature =  $1140^\circ\text{C}$ ; sintering time = 60 min). This table also gives the results of the standard acetic acid leaching tests on sintered specimens, along with the limit concentrations of the heavy metals established by the Italian law for solid waste disposal [11,12].

The data in Table 5 together with the results in Table 4 and Fig. 3 revealed that, with respect to the specimens made with washed BO fly ash, the sintered products of washed MO fly ash had a higher particle density and a lower water absorption (Table 5), and were also characterized by a greater linear shrinkage (Fig. 3), a higher compressive strength and a lower loss on ignition after sintering (Table 4).

These different properties of the two types of specimens may be explained taking in mind that: (1) water absorption is a rough measure of the open porosity of solids, (2) total porosity (closed and open pores) adversely affects both compressive strength and particle density, and (3)  $\text{LOI}_c$  specimens increases total porosity and reduces the densification effect.

Table 5

Physical and leaching properties of sintered products made with washed MSW fly ash

Heavy metals leachability		Heavy metal ion concentration in the leachate	
Metals	Limit-value <sup>a</sup>	BO fly ash	MO fly ash
Cd ( $\mu\text{g/l}$ )	20	2	10
Cr ( $\mu\text{g/l}$ )	2000, 200 Cr(VI)	65	140
Cu ( $\mu\text{g/l}$ )	100	50	80
Ni ( $\mu\text{g/l}$ )	–	85	120
Pb ( $\mu\text{g/l}$ )	200	95	160
Zn ( $\mu\text{g/l}$ )	–	175	320
Particle density ( $\text{g/cm}^3$ )		2.17	2.50
Water absorption (%)		16.4	8.8

<sup>a</sup> Limit concentrations for Ni and Zn are not established by Italian regulation [11,12].

In every case, the particle density ( $\rho$ ) of the sintered products ( $2.17\text{--}2.50\text{ g/cm}^3$ ) was within the range of  $\rho$ -values ( $2.0 < \rho < 3.0\text{ g/cm}^3$ ) established by both the Italian and the European standards for normal weight aggregates for use in concrete [6,9].

On the basis of the compressive strengths developed by the sintered products (Table 4) and according to the mechanical requirements established by the Italian standard for normal weight aggregates [6], the use of these manufactured aggregates shall be limited to concretes having a specified strength not greater than 12 and 15  $\text{N/mm}^2$ , when measured on cylindrical and cubic specimens, respectively. For such concretes, there is no established limit for the water absorption of the aggregates.

Further investigation on the mechanical properties of these manufactured aggregates is, however, needed to delimit in a better way their field of application, also by taking into account the mechanical requirements established by the European standard prEN12620 for normal weight aggregates [9].

As far as the contents of chlorides and sulfates of sintered products were concerned, the data in Table 3 revealed that the content of chlorides in washed fly ashes was 0.07–0.10% as Cl and the content of acid-soluble sulfates was 0.15–0.175% as  $\text{SO}_3$ . Moreover, alkaline chlorides were found to almost completely volatilize during the sintering treatment at  $1140^\circ\text{C}$ . Therefore, the contents of water-soluble chlorides and acid-soluble sulfates of sintered products were always lower than the respective limits established by both the Italian and the European standards for normal weight aggregates [6,9].

Although the washing pretreatment of fly ash with water always caused a heavy metals enrichment of washed fly ash (Table 3), the results of the standard acetic acid leaching tests on sintered specimens (Table 5) revealed that the concentrations of the various heavy metals in the leachate were always much lower than the respective limits established by the Italian law for solid waste disposal [11,12].

#### 4. Conclusions

The sintering treatment of Italian untreated MSW fly ashes is an ineffective process for manufacturing sintered products for reuse as concrete aggregates, because of the adverse

chemical characteristics of these fly ashes in terms of chloride, sulfate, and vitrifying oxide contents.

A modification of the chemical composition of MSW fly ash — through a preliminary four-stage washing treatment of this material with water — represents an effective way of improving the chemical and mechanical characteristics of sintered products.

For all the types of MSW fly ash tested, this washing pretreatment represents a basic step for manufacturing sintered products satisfying the Italian requirements for normal weight aggregates for use in concretes having a specified strength not greater than 12 and 15 N/mm<sup>2</sup>, when measured on cylindrical and cubic specimens, respectively.

A compact pressure of 28 N/mm<sup>2</sup>, a sintering temperature of 1140°C, and a sintering time of 60 min are the best operating conditions for manufacturing sintered products of washed MSW fly ash.

Under these operating conditions, sintering of washed fly ash can be modeled by an intermediate-stage liquid-phase sintering system, and densification of compact specimens is controlled by diffusion through the liquid-phase and grain shape accommodation.

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