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# ALKALI ACTIVATION FOR GEOPOLYMERS PREPARATION

**Cristina LEONELLI<sup>1</sup>, Isabella LANCELLOTTI<sup>1</sup>, Chiara PONZONI<sup>1</sup>, Luisa BARBIERI<sup>1</sup>, Maria Chiara BIGNOZZI<sup>2</sup>**

<sup>1</sup> Department of Engineering “Enzo Ferrari”, University of Modena and Reggio Emilia, 41125 Modena, Italy

<sup>2</sup> Department of Civil, Chemical, Environmental, and Materials Engineering, University of Bologna, 40131 Bologna, Italy

*cristina.leonelli@unimore.it, isabella.lancellotti@unimore.it,  
chiara.ponzoni@unimore.it, luisa.lancellotti@unimore.it, maria.bignozzi@unibo.it*

## Abstract

*Ladle slag (LS) and urban incineration bottom ash (BA) are two wastes which are necessarily disposed of with few attention for re-use or recycling. Their chemical composition contains silica and alumina accompanied by lime and iron oxides. Mineralogically speaking a number of silicate and silicoaluminate phases are present combined with 20-30 vol% of amorphous matrix. The presence of an important amount of vitreous phase makes LS and BA particularly reactive in alkali media. The geopolymerisation process of 70 wt% of LS or of BA in a metakaolin matrix has been characterised in terms of morphology and crystalline phases evolution.*

## Introduction

Steel slag comes from the ladle (ladle slag, LS) where the refining process of steel produced by scrap melting in arc electric furnace or by the conversion of iron to steel in a basic oxygen furnace (BOF) occurs.<sup>1,2</sup> Slag is an unavoidable by-product of the steelmaking process and its numerous functions are very well known, for example, the slag formed in arc furnaces facilitates energy transfer and protects the walls of the furnaces from heat.<sup>3</sup> Ladle slag accounts for about 1/3 of the total amount of slag usually produced in electric arc furnaces and its European production can be estimated about 4 millions t/year.<sup>4</sup> Nowadays LS is generally treated as waste and dumped in landfills and very few attempts are present to evidence their commercial value when properly prepared and processed.<sup>3</sup> Beside aluminosilicate, ladle slag contains calcium–silicate, magnesium-silicate and calcium–aluminate compounds and minor amounts of heavy metals, mainly iron.

Other similar waste materials, very close to LS in terms of chemical composition and percentage of amorphous phases and soluble salts, are bottom ashes deriving from urban waste incineration. Incineration represents an energetic efficient alternative to

dump being using conducted till the total oxidation process of the combustible materials present in the waste. Thermal treatment aims at a volume reduction of the waste; at the destruction, capture, and concentration of hazardous substances; and evidently at the recovery of energy.<sup>5</sup> One of the most important disadvantages of the incineration technology is the production of significant amounts of solid residues: fly ashes (5% of initial weight of wastes) and bottom ashes (up to 30% of initial weight of wastes).<sup>6</sup>

Thus both ladle slags as well as urban waste incineration ash represent a challenging problem of waste management due to their amount of soluble salts and to the presence of high aluminium phases making its use in cement industry not particularly appreciated. On the other side their calcium content is too high for completely substituting metakaolin in structural geopolymer matrix.<sup>8</sup> Nevertheless, both wastes possess an important amount of vitreous fraction which make them very promptly attacked by alkali solution. Ladle slags have already been activated with sodium silicate but a complete investigation on the NaOH activation has never been carried out previously by other authors than those of this paper.<sup>7</sup> No literature, except from the authors,<sup>8</sup> is known to report an investigation about the use of high amount of bottom ashes in geopolymer formulations.

With these final considerations in mind, we report our recent work which represents a step forward in the understanding of the consolidation process of metakaolin based geopolymers added of 70 wt% of LS or of BA. Microstructure and mineralogical characterisation of the newly proposed formulations are also reported.

## Materials and Methods

Ladle slag, BA and metakaolin's chemical characterisation is reported in Table 1.<sup>7,8,9</sup>

In Table 1 are reported also three ratios which are considered indicators of good quality structural building materials; in particular, for LS the low  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio and higher  $\text{CaO}/\text{SiO}_2$  with respect to the values required by cements make them unsuitable for cement preparation.<sup>2</sup> On the contrary the very high  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio for bottom ash, with respect to metakaolin natural ratio, requires an alumina-rich source addition to reach good structural geopolymer formulations.

The addition of metakaolin has been optimised in two separate studies for LS<sup>7</sup> and BA,<sup>8,10</sup> but the amount of 30 wt% was found a proper quantity for both wastes. Different amount of NaOH (8M, Carlo Erba, Italy) and sodium silicate ( $\text{SiO}_2/\text{Na}_2\text{O} = 3$ , Ingessil, Verona, Italy) solutions were added as reported in Table 2. The as-received wastes were dry mixed with the metakaolin and finally with the alkali solutions in

correct with solid to liquid ratio of 1.7, for LS and 2.5 for BA. The paste was moulded in small prisms.

**Table 1:** Chemical composition and other physical data of ladle slag and bottom ash added to metakaolin

(wt%)	Ladle slag	Bottom ash	Metakaolin
CaO/SiO <sub>2</sub>	3.32	0.35	-
SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	1.48	5.30	1.29
Na <sub>2</sub> O/Al <sub>2</sub> O <sub>3</sub>	-	0.61	-
SiO <sub>2</sub>	16.4	49.45	53,6
Al <sub>2</sub> O <sub>3</sub>	11.1	9.33	41,7
CaO	54.5	17.49	
MgO	4.0	2.88	
Na <sub>2</sub> O	traces	5.70	
K <sub>2</sub> O	0.04-0.2	1.41	2.5
Fe <sub>2</sub> O <sub>3</sub>	2.0-3.0	4.81	1.0
MnO	0.05-0.5	0.16	-
TiO <sub>2</sub>	0.04-0.2	0.81	0.5
Soluble fraction*	1.5	1.3	-
LOI**	9.81	4.77	-
Grain size	< 1 mm	<75µm	< 75 µm

\* determined as solubility in water (solid/liquid=1/4) for 2 hrs for 5 repeated treatments.

\*\* Loss of Ignition at 1100°C, for 2 hrs.

**Table 2:** Formulation of geopolymers referred to 100g of solid and final SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> and Na<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> molar ratio

	MK	LS	BA	NaOH 8M	Na silicate	H <sub>2</sub> O	SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	Na <sub>2</sub> O/ Al <sub>2</sub> O <sub>3</sub>
LS70- MK30	30g	70g	-	30g	30g	-	6.07	0.96
BA70- MK30	30g	-	70g	14 ml	20 ml	3ml	3.26	1.09

For bottom ash lower amount of alkali solutions was necessary due to the Na content of the ash, but water addition was necessary. For ladle slag geopolymer, instead, higher amount of activating solutions was necessary due to very low amount of alkali in the slag; the workability of the paste was satisfactory with no water introduction.

Mineralogical and microstructural characterisations were performed on both LS70-MK30 and BA70-MK30 samples (three specimens each formulation) after 24 hours in sealed mould plus 30 days unsealed and at room temperature (relative humidity was monitored and was found to be constant at about 60-70%).

Morphology studies were conducted on freshly fractured samples by ESEM (ESEM - Quanta200 - FEI) equipped with EDS in order to evidence phase distribution and degree of reactivity of LS and BA in the geopolymeric amorphous matrix. The mineralogy of the two geopolymers was investigated by means of X-ray diffractometry on powdered dried specimens with same curing time of 30 days.

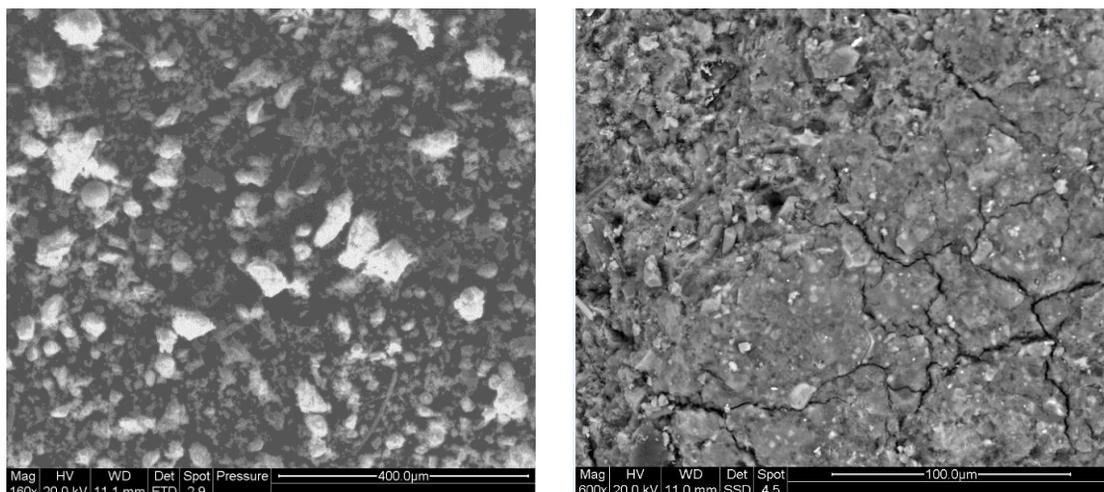
## Results

Ladle slag exhibits a complex structure where an amorphous matrix coexists with crystalline phases, such as calcium–silicates, calcium–aluminates, calcium–aluminium–silicates,<sup>11</sup> nevertheless they are able to be activated by alkaline solution when mixed with metakaolin in proper amounts.

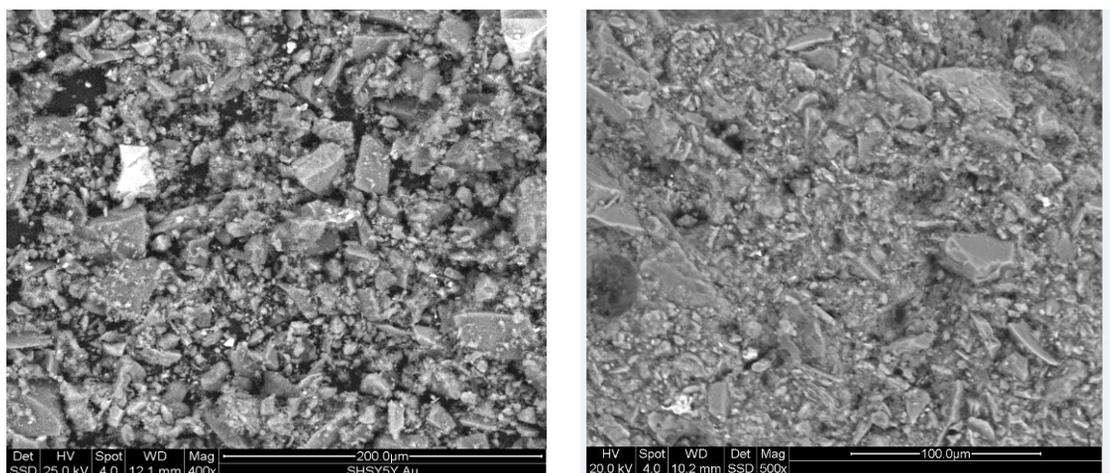
The as-received bottom ash presents a chemical composition (Table 1) with insufficient Al content with respect to silicon, therefore the ash has been mixed with metakaolin to ensure the proper Si/Al ratio for geopolymerisation.

### Comments on morphological studies

SEM images of as-received ladle slag (Figure 1) and bottom ash (Figure 2) present the starting raw materials used for the preparation of the specimens without any additional grinding. Particles size distribution is particularly wide in both samples



**Figure 1:** SEM images of untreated residue ladle slag (left), and geopolymer LS70-MK30 (right) cured for 30 days



**Figure 2:** SEM images of as-received bottom ash (left), and geopolymer BA70-MK30 (right) cured for 30 days

promising a good packing ability of the two aluminosilicate powders. Geopolymers with LS (Figure 1) and with BA (Figure 2) both at 70 wt% show their freshly fractured surface below.

Ladle slag presents irregular shaped grains (Figure 1) as well as more spherical particles indicating the high temperature environment in which they were generated. In the geopolymer produces with 30 wt% of metakaolin, LS undissolved particles around 10–30  $\mu\text{m}$  are difficult to distinguish from the gel matrix, very tightly connected to the particles surface. The EDS analysis carried out on LS mixes containing 50–70% of LS has highlighted the presence of C–A–S–H gels with different compositions (high and low Na content), together with Na-aluminosilicate (N–A–S–H) amorphous gel typical of metakaolinitic geopolymer.

Comparing the two morphologies of bottom ash formulations reported in Figure 2, it can be seen that after 30 days curing the geopolymeric matrix appear very dense, with a significant decrease of the particles' dimensions. From the chemical analysis of the not-reacted particles appears evident that they are bottom ash particles and not metakaolin particles. The chemical composition of the geopolymeric gel has been measured via EDS analyses: lower calcium content and higher Na, Si and Al content with respect to the chemical analysis of the starting composition of bottom ash (compare Table 1 with Table 3).

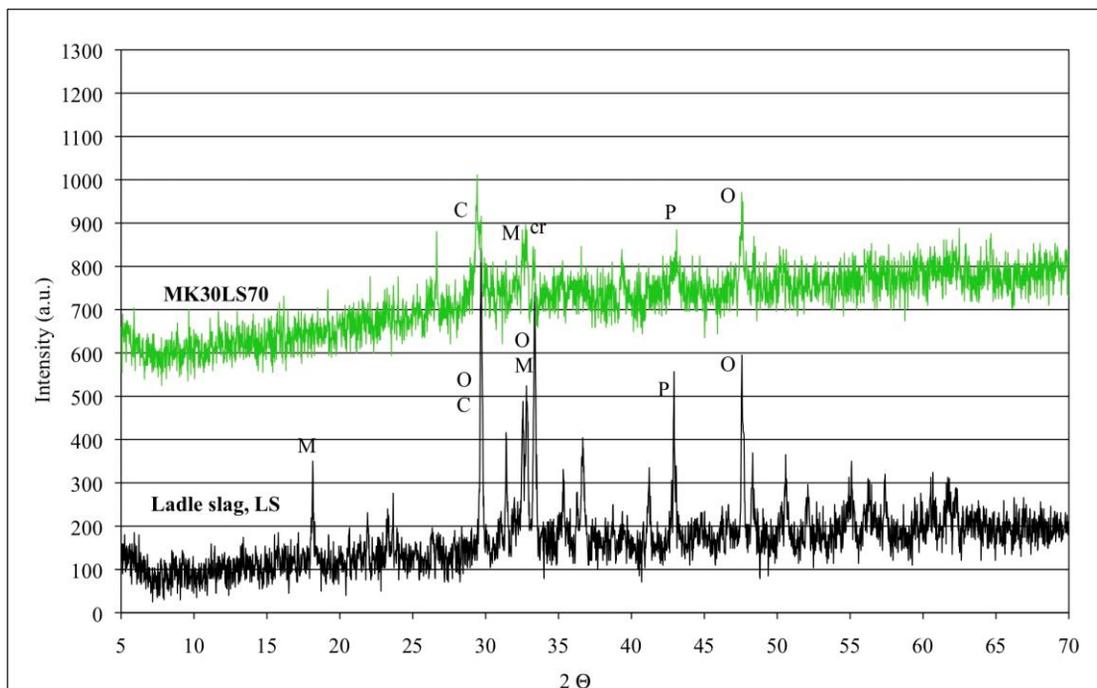
**Table 3:** Chemical composition of geopolymeric matrix as determined via EDS in samples reported in Figure 1

	Si	Al	Na	Ca	Si/Al	Na/Al
LS70-MK30	14.96	9.85	8.45	10.47	1.52	0.86
BA70- MK30	21.86	13.53	7.84	2.46	1.61	0.57

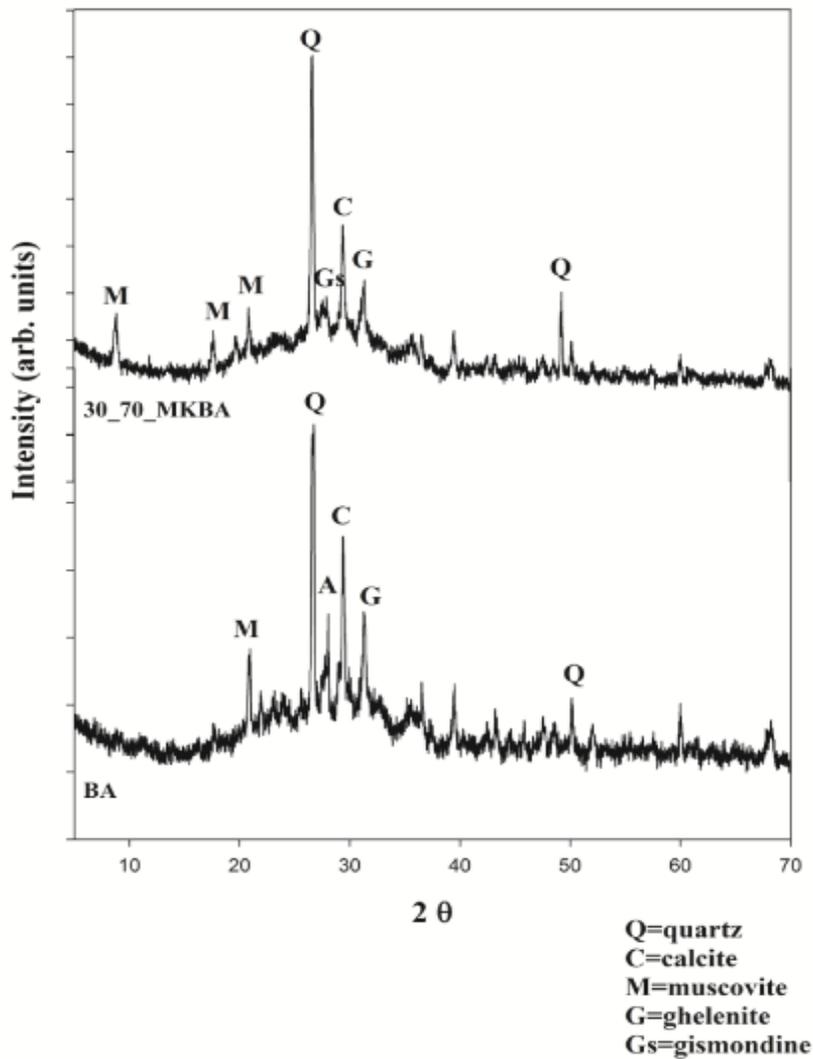
## Comments on mineralogical studies

X-ray diffraction patterns collected on ladle slag and its geopolymer are presented in Figure 3. Mineralogical analysis of LS shows many crystalline phases identified as follows:  $\gamma$ - $\text{C}_2\text{S}$  or  $\text{Ca}_2\text{SiO}_4$ , olivine (ICDD # 180–941),  $\text{Ca}_2(\text{Al}(\text{AlSi})\text{O}_7)$  gehlenite (ICDD #174–1607),  $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$  mayenite,syn (ICDD #170-2144) and iron-magnesium-calcium-silicate. Trace of: i) periclase  $\text{MgO}$  (ICDD #45–0946), from the ladle refractory lining; ii) oldhamite  $\text{CaS}$  (ICDD #38–1420), from the desulphuration process; and iii),  $\beta$ - $\text{C}_2\text{S}$   $\text{Ca}_2\text{SiO}_4$ ,  $\text{Ca}(\text{OH})_2$ , calcium and magnesium carbonates have also been determined.<sup>11</sup> A percentage of about 20% of amorphous phase can be deduced comparing the XRD pattern of LS with literature results as discussed in Ref.7.

In order to determine the extent of activation and the phase composition of the main reaction products of the geopolymerisation, Figure 3 reports the powdered LS70-MK30 XRD pattern. This pattern is characterised by an amorphous structure (broad diffraction hump from 25 to 37° 2 $\theta$ ) with peaks corresponding to calcite, mayenite, cristobalite, and periclase while olivine and gehlenite have been largely dissolved in the alkaline solution. From the dissolution of these two phases it can be assumed that the amorphous phase is rich in Na, Si, Al, and Ca (as indicated by EDS analyses) without compromising the stability of a typical metakaolinitic geopolymer. Recent studies carried out on synthetic sodium aluminosilicate hydrate gel<sup>12</sup> show the existence of a C–A–S–H gel more stable than N–A–S–H at high pH.



**Figure 3:** XRD patterns of as-received ladle slag (a) and geopolymer LS70- MK30 after 30 days of curing (O: olivine; P: periclase; M: mayenite; C: calcite; Q: quartz; cr: cristobalite)



**Figure 4:** XRD patterns of bottom ash and geopolymer BA70- MK30 after 30 days of curing

Figure 4 reports the XRD pattern of the as-received bottom ash and its derived geopolymer. The wide amorphous bump of BA sample indicate its vitreous nature accompanied by with few per cent of crystals: the main phase is  $\alpha$ -quartz ( $\alpha$ -SiO<sub>2</sub>, JCPDF file 33-1161) followed by calcite (CaCO<sub>3</sub>, JCPDF file 5-586), and aluminosilicates such as albitite (NaAlSi<sub>3</sub>O<sub>8</sub>, JCPDF file 10-393) and ghelenite (Ca<sub>2</sub>Al(Al,Si)O<sub>7</sub>, JCPDF file 35-755), reflecting the chemical analysis of an ash rich in calcium and sodium.

From X-ray analysis it is possible to evaluate if the geopolymerisation phenomenon is generating new crystalline phases or depredates those already present in the pristine raw materials.

The crystalline phases present in bottom ash (quartz, calcite, ghemelite, anorthite) are also present in geopolymers but with decreased intensity, because ash grains are reacting with alkali activator. Increasing curing time from 15 to 30 days a slight increase of the broad band corresponding to the geopolymeric gel occurs together with a decrease of the quartz peak, because silica enter in the geopolymeric gel for longer curing time.

Composition BA70-MK30 shows a new phase formed, corresponding to calcium aluminium silicate hydrate, i.e. gismondine  $\text{CaAl}_2\text{Si}_2\text{O}_8 \cdot 4\text{H}_2\text{O}$  (JCPDF file 20-452), due to the reactivity of calcium present in the ash, as found by Guo et al.<sup>13</sup>

## Conclusions

Geopolymers with high percentages (70 wt%) of ladle slag and bottom ash derived from the incineration of urban wastes have been presented. Their morphology is very close to that of metakaolinic pastes, i.e. structural 3D geopolymers. There is a complex evolution of the vitreous as well crystalline portion of the wastes.

It can also be noticed that the composition of ladle slag (Table 4) used for this work, differs from blast furnaces slag and from other ladle slag reported in literature.<sup>2,14</sup> The high Al content do not allow the reuse of LS in cement formulation (see Table 4 for ordinary Portland cement composition) as the content of soluble salts, while the amorphous portion allow a good alkali activation typical of geopolymer technology. Both LS and incineration wastes ash do not contain iron oxides avoiding deleterious condition during geopolymer aging.

According to the literature,<sup>12</sup> the presence of calcium coming from LS and BA can promote an ion exchange process with sodium, replacing it in the N–A–S–H gel and consequently forming C–A–S–H. The structure of the C–A–S–H gels has not been investigated in this paper, however it has been reported that the 3D structure typical of N–A–S–H is usually preserved at these pH values.<sup>12</sup>

**Table 4:** Comparison of Chemical composition of different types of slag (wt%)

	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO
Portland Cement <sup>2</sup>	20.70	3.70	3.00	62.90	4.20
Blast Furnace slag <sup>2</sup>	35.30	9.90	0.60	34.70	14.60
Ladle slag <sup>2</sup>	26.80	5.20	1.60	57.00	3.20
Ladle slag <sup>14</sup>	7.10	24.60	0.50	62.40	2.10
LS this work	16.4	11.10	8.70	54.50	4.00

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