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Geopolymers Based on Mechanically Activated Non-Ferrous Slags

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Abstract

Geopolymerisation behaviour of Imperial Smelting Furnace (ISF) Zn slag and granulated Cu−Ni slag, mechanically activated in air and in CO_2 atmosphere ($P = 10^5$ Pa) has been studied by XRD, SEM, FTIR, and isothermal conduction calorimetry. Mechanical activation of the slags has been carried out in a centrifugal-planetary mill AGO-2. Geopolymer samples have been prepared by mixing of the mechanically activated slag powders with NaOH solution or liquid glass and curing at (20±2) °C for up to 180 days. It has been observed that the ISF Zn slag and the granulated Cu−Ni slag are suitable for the synthesis of building materials through geopolymerisation. The effect of milling atmosphere on properties of geopolymers is found to be alkaline reagent specific. A suitable combination of the milling atmosphere and alkaline reagent is required to realize the beneficial effect on mechanical properties of the geopolymer.

Key words: Zn slag, Cu−Ni slag, geopolymerisation, mechanical activation, carbon dioxide, reactivity, compressive strength

INTRODUCTION

Traditionally slag produced by non-ferrous smelters has been considered as waste. Generation of nonferrous slags collectively all over the world amounts to several million tones; however, a very limited amount of these slags is used in Portland slag cement production and in hot mix asphalt pavements [1−3]. Disposal of the remaining huge quantities in open air requires large space; besides hazardous heavy metals contained in certain amounts in such slags can pose serious threat to the environment, which is one of the main reasons of its limited commercial application.

Geopolymerization is a prospective way of non-ferrous slag utilization. Geopolymers or alkali activated cements are binding systems based on alkali activation of aluminosilicates of natural or synthetic origin [2−11]. The common raw materials for geopolymer synthesis are metakaolin (thermally activated kaolin) and industrial wastes such as fly ash and ground granulated blast furnace slag. Sodium hydroxide solution or liquid glass is usually used as alkaline activator. Geopolymers are distinguished by the simplicity of the processing, generating 80 % less CO_2 than Portland cement [12] and by the high physicomechanical properties relative to the traditional materials used in construction and building applications. It should be stressed that geopolymers can also immobilize toxic materials including heavy metals [8, 13−16]. This virtually eliminates the apprehension of environmental hazard expected from the leaching of heavy metals from the non-ferrous slags.

Nonferrous slags differ in chemical composition from the blast furnace slag and exhibit lower reactivity in geopolymer synthesis. Reports say that mechanical activation (MA) of granulated magnesia-ferriferous Cu−Ni slag, particularly in CO_2 atmosphere, considerably enhances its reactivity and as result the mechanical properties of the synthesiszed geopoly-

mer has improved [17, 18]. The use of CO_2 is caused by the following reason. It is well known that MA medium is an important factor that affects the reactivity of the surface layers of powder particles [19−22]. A previous study has shown that prolonged grinding of Ca,Mg-containing silicates leads to absorption of large amounts (>10 mass %) of atmospheric CO_2 by these minerals [23]. The carbonization effect enhances in the case of MA in a purely CO_2 atmosphere [24]. It should be noted that a deep mechanically induced interaction of silicates with carbon dioxide was not accompanied, contrary to expectations, by formation of calcite, magnesite, and other carbonate materials. Under the influence of MA, CO_2 molecules penetrate into the bulk of a structurally disordered silicate matrix generating distorted carbonate groups. As a result, not only the structure, but also the chemical composition of outer layers of particles directly involved in hydration reactions are substantially modified.

In this paper, the characteristics of geopolymers based on Zn and Cu−Ni slags mechanically activated in air and in carbon dioxide atmosphere are discussed.

MATERIALS AND METHODS

Materials

Water quenched granulated (Imperial Smelting Furnace (ISF) Zn slag and Cu−Ni slag used in the study have been supplied by M/S Hindustan Zinc Ltd. (Chittorgarh, Rajasthan, India) and Pechenganickel Smelter Plant (Murmansk Region, Russia), respectively. Chemical composition of the Zn slag and Cu−Ni slag are given in Tables 1 and 2, respectively.

TABLE 1

Chemical composition of Zn slag

Radicals	Mass, %	Radicals	Mass, %
SiO_2	18.08	Mn_2O_3	1.33
Al_2O_3	8.17	ZnO	9.21
Fe_2O_3	34.28	PbO	1.22
CaO	17.91	S	1.41
MgO	1.93	GOI	5.68
Na_2O	0.68	Insoluble residue	6.28
K_2O	0.71		

TABLE 2

Chemical composition of Cu−Ni slag

Radicals	Mass %	Radicals	Mass %
SiO_2	36.87	ZnO	0.04
Al_2O_3	7.44	Co	0.10
FeO	31.08	Ni	0.24
Fe_2O_3	2.47	Cu	0.16
CaO	2.11	Cr	0.13
MgO	11.92	S	0.76
Na_2O	1.18		

Methods

MA has been carried out in an AGO-2 laboratory centrifugal-planetary mill [20] at a centrifugal factor of $40g$ in air and in CO_2 ($P = 10^5$ Pa). In order to have similar specific surface area of the slag powders (for ease of comparison), duration of MA of Zn and Cu−Ni slag has been 180 and 270 s, respectively. 8 mm steel balls have been used as milling media with a ball to powder ratio of 6. Prior to milling in CO_2 atmosphere, grinding vial with balls and sample has been purged with a slow jet of CO_2 for 2 min to displace the air. The moisture content of CO_2 was less than 0.05 % by volume. Uniform grinding is ensured by scrapping off the material sticking to the vial after stopping the mill and mixing it thoroughly after 1.5 min of milling. Milling is resumed after refilling the vial with CO_2 as detailed above.

Geopolymer samples are synthesized by mixing the mechanically activated slags with a sodium silicate solution (liquid glass) or 6 M sodium hydroxide solution. A molar oxide ratio SiO_2/Na_2O of the liquid glass has been equal to 1.5. A mass ratio of Na_2O (present in liquid glass or sodium hydroxide solution) to mechanically activated slag in the paste has been equal to 0.03. These optimal parameters of the synthesis are arrived at based on the results of preliminary studies. Little amount of water is added to the paste to achieve a suitable workability so as the water/slag mass ratio became 0.2 (taking into account water in alkaline activator). Fresh mortars cast into specimens of size $1.41 \cdot 1.41 \cdot 1.41$ cm^3 are allowed to cure at room temperature (($20{\pm}2$) °C) for 24 h before being

removed from the molds. These specimens are then cured under relative humidity of (95±5) % at ambient temperature of (20±2) °C up to 180 days. Such samples are tested for their compressive strength after curing for 1, 7, 28 and 180 days. Compressive strength data presented are average strength of three samples.

The carbon content of the slag samples was determined with an ELTRA's CS-2000 analyzer. Particle size distribution has been measured using laser diffraction based equipment (Mastersizer, Malvern, UK). The specific surface area has been measured using by BET method with a Flow-Sorb II 2300 instrument (Micromeritics, the USA). Powder X-ray diffraction (XRD) patterns are recorded on a XRD-6000 instrument (Shimadzu, Japan) using CuK_α radiation and a scanning speed of $2°(2\theta)/min$. Phases present in the samples are identified by comparing the XRD data with that of the JCPDS files of expected phases. FTIR spectra have been recorded on a Nicolet 6700 FTIR spectrometer using potassium bromide tablets. Scanning electron microscopic (SEM) images are obtained using a FEG scanning electron microscope.

The progress of geopolymerization has been monitored in terms of the rate of heat evolved using an eight channel isothermal conduction calorimeter (TAM AIR, Thermometric AB, Jarafalla, Sweden). The equipment has been calibrated with the standard power of 60 mW before the experiment using the procedure given in the equipment manual. The sensitivity of the equipment is 0.1 mW. Ground slag sample of mass 7 g is mixed with 6 M NaOH solution or liquid glass in specified container and then sealed. After placing the sealed sample containers in their designated slots, calorimeter is started. Heat evolved has been recorded as a function of time at the temperature of 27 °C.

RESULTS AND DISCUSSION

Characterization of the mechanically activated slags

Table 3 presents the BET and Blaine specific surface area of the Zn and Cu−Ni slags mechanically activated in air and in CO_2. The specific surface area for both slags is somewhat lower when MA was carried out in air. In the

TABLE 3

BET and Blaine surface area of Zn and Cu−Ni slags mechanically activated in planetary mill AGO-2 for 180 and 270 s, respectively

Samples	Atmosphere of MA	BET (m^2/g)	Blaine (m^2/kg)
Zn slag	Air	1.05	554
	CO_2	1.16	589
Cu−Ni slag	Air	1.26	515
	CO_2	1.87	565

case of Zn slag, the specific surface area values are very close for both milling atmospheres. The results for Cu−Ni slag is in contrast to a similar study on the same slag; a slightly lower (by 13 % BET and 4 % Blaine) surface area during milling in CO_2 atmosphere compared to that similar milling in air has been attributed it to increased plasticity and aggregation resulting from CO_2 sorption by outer layers of the slag grains [18]. It is conceivable that this discrepancy is due to the different MA conditions employed in this study, where milling has been carried out at 20 g and 5 mm balls were used as milling media [18].

In agreement with the specific surface area data, particle size analysis of the milled Zn slag powders in air have closely matched with that milled in CO_2 (Fig. 1). It is seen from Fig. 1 that milling of Zn slag results in distribution of the slag particles around certain maxima; nature of particle size distribution is beyond the scope of this paper.
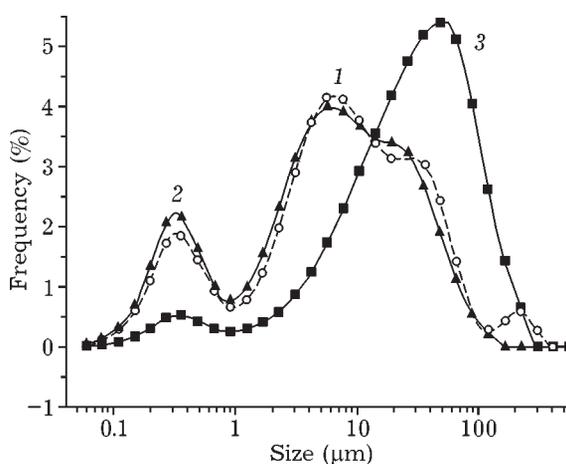

Fig. 1. Results of particle size analysis of Zn slag milled in AGO-2 mill for 3 min in air (*1*) and CO_2 atmosphere (*2*) along with that of the feed (*3*) to the AGO-2 mill.
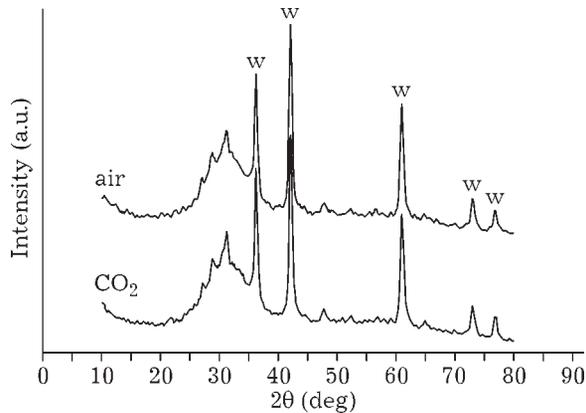
Fig. 2. XRD patterns of Zn slag samples mechanically activated in air and CO_2. w − wustite reflections.

XRD patterns of Zn and Cu−Ni slag samples mechanically activated in both atmospheres are shown in Figs. 2 and 3, respectively. The common feature is that milling atmosphere has not had any notable influence. It may be mentioned as well that the XRD patterns of the milled slag samples are broadly the same as those of the corresponding initial slags (not shown). In the case of Zn slag both samples are characterized by a broad and diffused background peak with a maximum of around $2\theta = 31°$ indicating the presence of amorphous phase (see Fig. 2). The peaks at higher angles correspond to that of wustite according to JCP-DS file No. 74-1886. XRD patterns of the Cu−Ni slag powders mechanically activated in air and in CO_2, displayed weak reflections of skeletal olivine crystals (JCPDS file No.71-794) against amor-
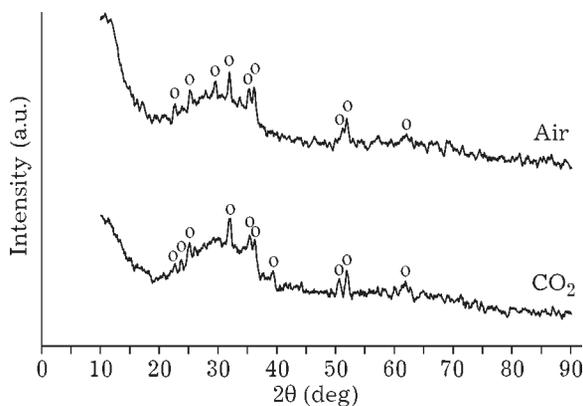

Fig. 3. XRD patterns of Cu−Ni slag samples mechanically activated in air and in CO_2; o − olivine reflections.

TABLE 4

CO_2 content (mass %) of initial and mechanically activated Zn and Cu−Ni slags

Samples	Initial	MA in air	MA in CO_2
Zn slag	0.102	0.145	0.469
Cu−Ni slag	0.099	0.141	0.362

phous background of the glassy phase, and are in general similar in nature (see Fig. 3).

Table 4 presents the CO_2 content of initial and mechanically activated Zn and Cu−Ni slags. After MA in air the CO_2 content increases to a small extent due to the mechanosorption of atmospheric carbon dioxide by the slag samples. As expected, MA in CO_2 results in notably larger carbon dioxide content in comparison to that after MA in air. These data are consistent with FTIR spectra of the milled slags. In FTIR spectra of Zn and Cu−Ni slags milled in CO_2 (not shown), in accordance with the earlier obtained results for other silicates [23, 24], a double band in 1550−1400 cm^{-1} region corresponding to distorted carbonate group appears. In other respects, the FTIR spectra of the slags samples mechanically activated in CO_2 and in air are similar.

Geopolymerization process, involving dissolution of aluminosilicate phase, polymerization and reprecipitation of gel phase, and transformation of the gel phase into geopolymer of varying crystallinity and structure, is of long duration and the individual stages are often coupled and/or occur concurrently [25]. So, monitoring the entire process and individual identification of each stage of geopolymer formation is difficult. However, conduction calorimetry, which captures the heat evolved, is a powerful tool to monitor the process during the initial stages. The results of isothermal conduction calorimetry measurements of the geopolymerization of the milled Zn slag using NaOH solution and liquid glass are shown in Fig. 4, *a* and *b*, respectively. The initial sharp exothermic peak in all the cases indicates that reaction started as soon as the starting powders were mixed with alkali containing solution. This corresponds to wetting and partial dissolution of glassy content.

Interestingly, the geopolymerisation behavior of samples based on the Zn slag milled and air and in CO_2 prepared using liquid glass is similar over the all observed period (see Fig. 4, *b*).
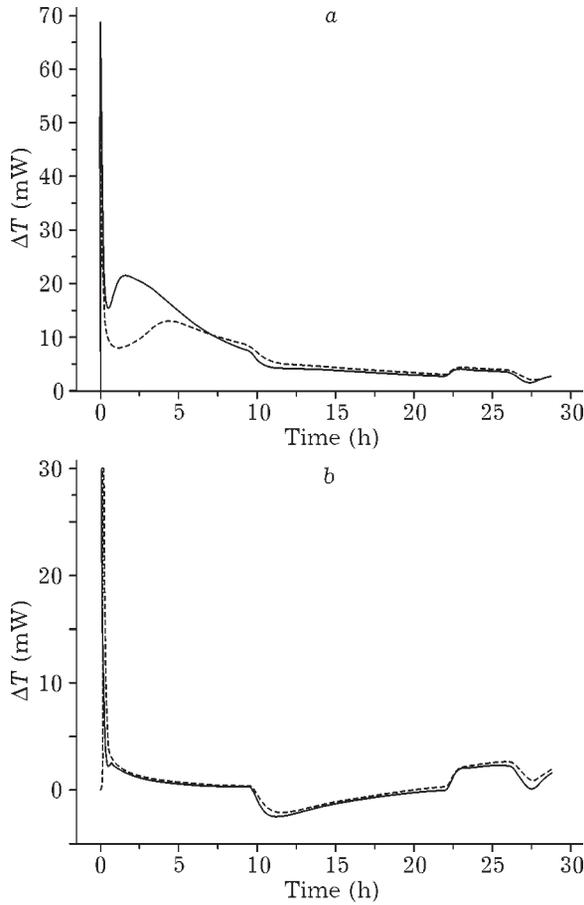
Fig. 4. Isothermal conduction calorimetry curves of the initial stages of geopolymerization of the Zn slag samples milled in air (dotted line) and in CO_2 (solid line): a − using NaOH, and b − using liquid glass as alkaline reagents.

Contrary to this, the geopolymerisation processes occurring in the mixtures containing the slag milled and air and in CO_2 using sodium hydroxide solution differs substantially (see Fig. 4, a). It is evident that, the mixture containing the slag mechanically activated in CO_2 (see Fig. 4, a, solid curve) showed higher reactivity compared to mixtures containing slag mechanically activated in air (see Fig. 4, a, doted curve). In the former case, (after the initial peak) the reactions start earlier and the total heat evolved (determined by the cumulative area under the curve) is larger.

Characterization of the geopolymers

Compressive strength values of geopolymer samples prepared from mechanically activated Zn and Cu−Ni slag using NaOH solution and liquid glass are given in Table 5. It is obvious that the effect of milling atmosphere on geopolymer properties depends on the type of alkaline reagent employed. In agreement with the earlier results for Cu−Ni slag based geopolymers prepared using liquid glass, compressive strength is larger in case of CO_2 milled slag for all curing times [17, 18] . The same trend is observed in case of Zn slag based geopolymers synthesized using NaOH solution and is in line with the inferences from isothermal conduction calorimetry data (see Fig. 4, a). The higher reactivity of Cu−Ni slag milled in CO_2 in com-

TABLE 5

Compressive strength of geopolymer samples prepared from mechanically activated Zn and Cu−Ni slags using NaOH solution and liquid glass

Slags	MA atmosphere	Compressive strength (MPa) at days			
		1	7	28	180
Geopolymers prepared using NaOH solution					
Zn	Air	11.5	56.5	73.4	75.2
Zn	CO_2	22.9	58.9	87.5	88.7
Cu−Ni	Air	3.2	7.5	10.4	13.9
Cu−Ni	CO_2	2.6	4.5	7.9	10.9
Geopolymers prepared using liquid glass					
Zn	Air	41.6	78.8	87.0	93.8
Zn	CO_2	40.8	76.3	91.7	99.3
Cu-Ni	Air	43.4	64.8	83.9	85.9
Cu-Ni	CO_2	50.1	102.7	104.4	105.0

parison to that milled in air with respect to liquid glass as observed from isothermal conduction calorimetry measurements was reported previously [18]. Contrary to this, compressive strength of NaOH based geopolymers from mechanicallly activated Cu−Ni slag in CO_2 shows a small decrease in comparison to the geopolymer from air milled slag. In addition, the compressive strength of geopolymer prepared from Cu−Ni slag milled in both atmospheres with NaOH solution is one order of magnitude less than that of the geopolymer based on the same slag synthesized using liquid glass (see Table 5). For Zn slag based geopolymers prepared using liquid glass, influence of milling atmosphere on compressive strength is minor, particularly at the initial curing period (up to 7 days) and is in agreement with the isothermal conduction calorimetry results (see Fig. 4, b). However, at larger curing time (28 and 180 days) the positive effect of CO_2 (milling atmosphere) on the compressive strength of Zn slag + liquid glass geopolymers becomes evident. It may be mentioned that the setting time for geopolymer of this type was small; the setting started during the process of casting itself.

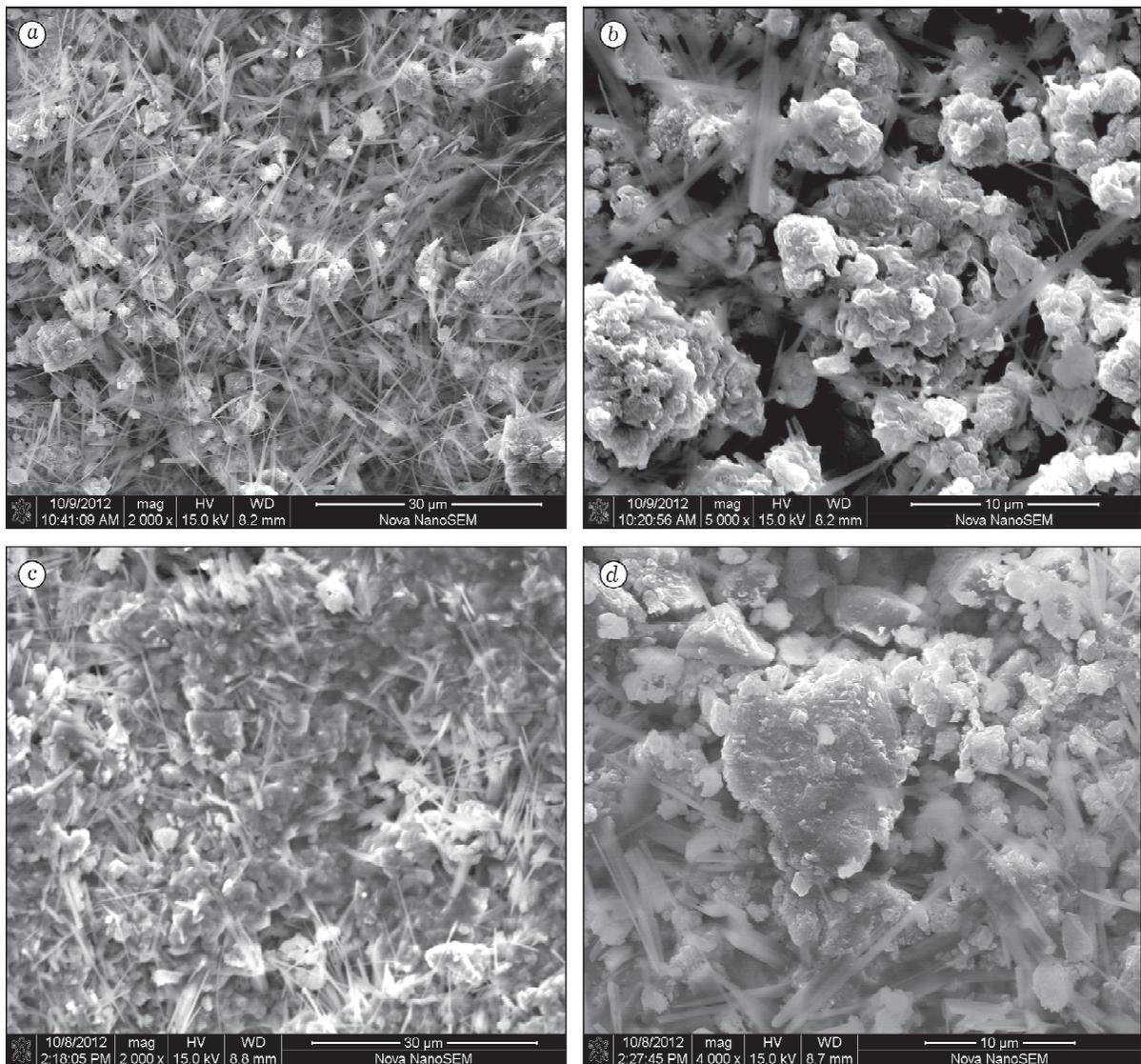Table 5 shows that liquid glass based geopolymers from Zn slag, has higher compres-

Fig. 5. SEM micrographs of Zn slag based geopolymers prepared using NaOH as alkaline reagent: a, b − from air milled, and c, d − from CO_2 milled slag after 180 days of curing.

sive strength in comparison to that based on sodium hydroxide solution, though the difference is not so pronounced as in case of Cu−Ni slag based geopolymers. The observed dissimilarities in geopolymerization behavior of Zn and Cu−Ni slags mechanically activated in air and in CO_2 are likely to be related to difference in the chemical composition of the slags as well as to appreciable sensitivity of geopolymerization reactions to the nature of alkaline reagent employed.

It is to be noted that the compressive strength values of Zn and Cu−Ni slag based geopolymers both milled in CO_2 and prepared using liquid glass after 180 days of curing are 99.3 and 105 MPa, respectively (see Table 5).

Scanning electron micrographs of geopolymer samples from milled Zn slag synthesized using sodium hydroxide and liquid glass are presented in Figs. 5 and 6, respectively. These micrographs are from samples cured for 180 days. Indications of gel structure and hydration of slag sample is clearly visible in all geopolymer samples. However, a more porous structure is observed for the geopolymer based on air milled sample prepared using NaOH solution (see Fig. 5, a). Partially reacted grains
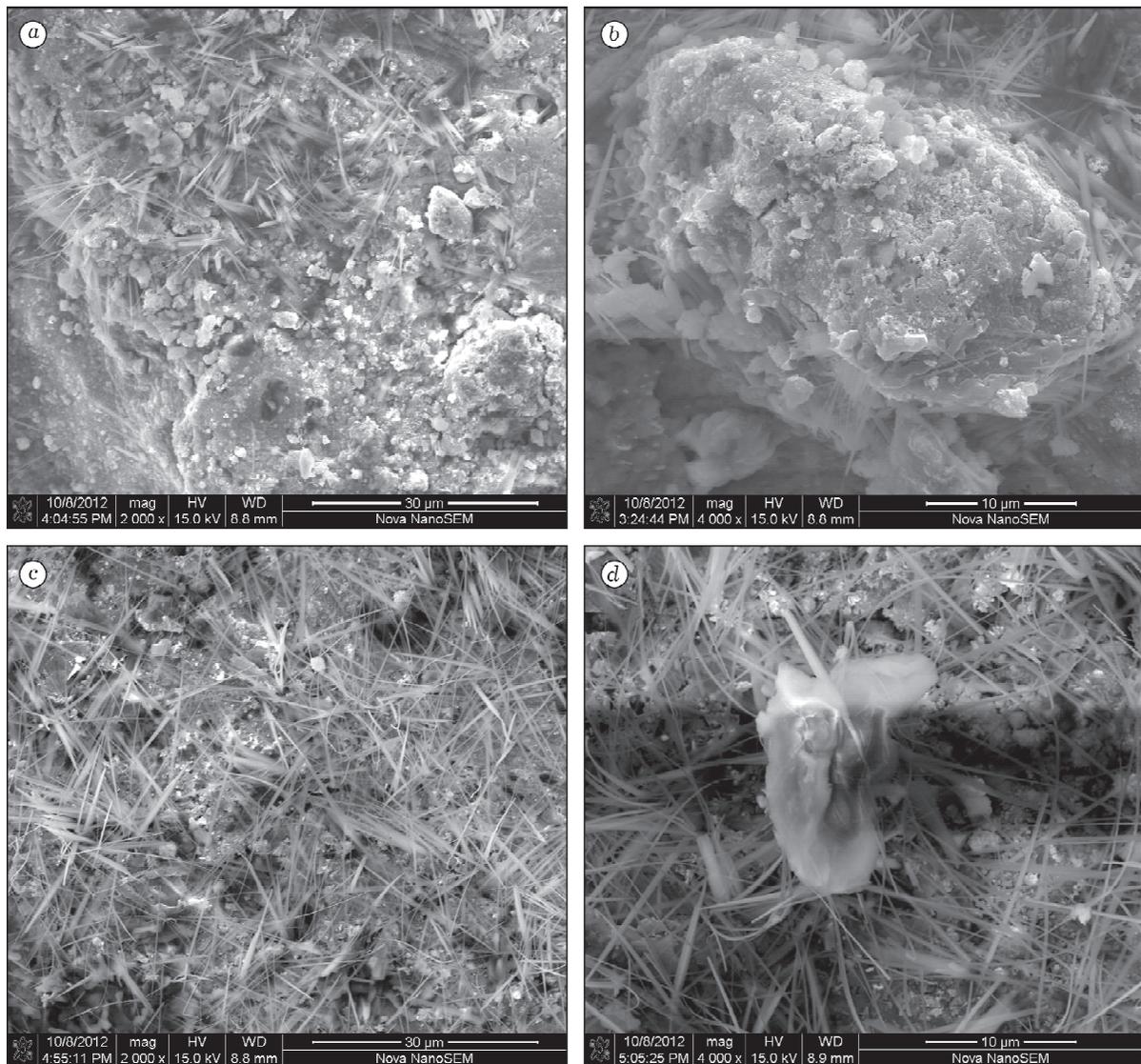

Fig. 6. SEM micrographs of Zn slag based geopolymers prepared using liquid glass as alkaline reagent: a, b − from air milled, and c, d − from CO_2 milled slag after 180 days of curing.

with large amount of fibrous structure are uniformly distributed throughout the structure. In the three remaining samples (see Figs. 5, *c* and 6, *a*, *c*), a more compact structure with formation of dense gel is observed. Figures 5, *b*, *d* and 6, *b*, *d* give a magnified view of the corresponding samples. This further clarifies that even though the air milled sample synthesized using NaOH solution is hydrated, gel formation or the reaction product is significantly lower and the structure is less dense (see Fig. 5, *b*) than those of the other samples (see Figs. 5, *d* and 6, *b*, *d*). These observations correlate, in general, with compressive strength values of the respective geopolymers: the geopolymer based on air milled Zn slag prepared using sodium hydroxide solution, which displays a more porous structure, is characterized by the lowest compressive strength among these 4 samples (see Table 5). We reported earlier that milling of Cu−Ni slag in CO_2 according to TEM measurements resulted in more dense and hard structure of the geopolymer synthesized using liquid glass in comparison to that of corresponding air milled slag based geopolymer [18].

By comparing all the results, it can be inferred that silica to alumina ratio in both types of slag has played a very important role in geopolymer formation and consequently properties development. In case of ISF slag, the SiO_2/Al_2O_3 ratio was 2.2 which is desirable ratio for the formation of three dimensional rigid network [8]. The higher strength in NaOH activator based ISF Slag geopolymer is due to the co-precipitation of C−S−H gel (C = CaO, S = SiO_2, H = H_2O) as the CaO in ISF slag is present in significant quantity (17.91 mass %). Good strength development due to co-existance of A−S−H (A = Al_2O_3) and C−S−H gel has been reported in literatures [26]. In Cu−Ni slag, SiO_2/Al_2O_3 was 4.95 which gives less rigid network during geopolymerisation [8]. The SiO_2 was more in this slag, but a portion of it was in the form of olivine which has low reactivity in geopolymers. Thus in the case of NaOH based activator, the strength development was low. However in the case of water glass, part of the amorphous silica came from activator resulting into higher compressive strength. Improvement in compressive strength of geopolymer derived from slag mechanically activated

in CO_2 atmosphere may be correlated with increase in surface area and reactivity, which resulted into formation of more reaction product and compact microstructure.

CONCLUSIONS

1. Granulated ISF Zn and Cu−Ni slags are suitable for the synthesis of building materials through geopolymerisation.

2. Particulate characteristics of Zn slag remain mostly unaffected by the milling atmosphere, while milling of Cu−Ni slag in CO_2 atmosphere resulted in slightly larger specific surface area in comparison to that generated by milling in air.

3. XRD has indicated that milling atmosphere has no effect on the bulk structural characteristics of both slags.

4. Milling of both slags in CO_2 atmosphere is accompanied by chemisorption of carbon dioxide by the outer layers of the slags particles in the form distorted carbonate groups. This may influence the reactivity of the slag.

5. The effect of milling atmosphere on geopolymer properties is found to be alkaline reagent specific. For Zn slag based geopolymers prepared using NaOH solution and Cu−Ni slag based geopolymers prepared using liquid glass compressive strength is larger in case of the CO_2 milled slags for all curing times in comparison to that of corresponding geopolymers based on air milled slags.

6. Milling of Cu−Ni slag in CO_2 results in a small decrease in compressive strength in comparison to the air milled slag based geopolymer when sodium hydroxide solution is used as alkaline reagent.

7. In case of Zn slag based geopolymers prepared using liquid glass positive effect of CO_2 as milling atmosphere on the compressive strength of the geopolymer becomes evident after prolonged curing.

8. The trend in compressive strengths is in agreement with the inferences from conduction calorimetry data and SEM observations.

9. Dissimilarities in geopolymerization behavior of Zn and Cu−Ni slags mechanically activated in air and in CO_2 is attributed to the difference in the chemical composition of the slags and to the nature of alkaline reagent employed.

10. A suitable combination of the milling atmosphere and alkaline reagent is required to achieve good mechanical properties.

Acknowledgements

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