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MECHANICAL ACTIVATION IN BLENDED CEMENT PROCESSING

Rakesh Kumar[1ξ], Sanjay Kumar[1], S.P. Mehrotra[1,2]
[1]National Metallurgical Laboratory, Jamshedpur – 831007, India
[2]Present address: Department of Materials Science and Engineering, Indian Institute of Technology, Kanpur – 208016, India

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Abstract

The foucs this paper is on the mechanically induced reactivity of granulated blast furnace slag and fly ash. Mechanical activation of blast furnace and fly ash is mill specific, that is, it depends on milling mechanism and mill dynamics. Slag after wet milling in an attrition mill hydrates completely in sharp contrast with ball milled slag of same fineness (~ 12 μm). The hydration product of attrition milled slag shows a number of unique characteristics, for example : increased crystallinity of the phases in the hydration product with an increase in the milling time, formation of cement phases that forms under hydrothermal conditions, etc. The vibratory milled fly ash showed higher lime reactivity vis-à-vis raw and attrition milled fly ash. The origin of mechanically induced reactivity, development of improved blended cements and their prospects are presented.

Introduction

Typically, 1-1.5 tonnes of limestone and 0.5 tonnes of coal are used per tonne of clinker produced Specific energy consumption in cement manufacturing amounts to 4000 MJ/tonne of cement with nearly 80% contributions arising from thermal energy (mostly for clinker formation) and rest from electrical energy (major contribution arising from grinding). Similarly, 0.8-1 tonne of CO_2/tonne of clinker is generated during clinker formation. Blended cement formulation differ from ordinary Portland cement in that a part of clinker is replaced by waste material, i.e.

Ordinary Portland Cement = Clinker (~95%) + Gypsum

Blended cement = [(1-x).Clinker+x.X] (~95%) +Gypsum

When X = Granulated blast furnace slag and fly ash, blended cements are typically referred to as Portland Slag Cement (PSC) and Portland Pozzolana Cement (PPC), respectively.

In India, typically, the fractional replacement x for PSC and PPC varies in the range 0.45-0.5 (granulated blast furnace slag) and 0.25-0.3 (fly ash), respectively [1,2] and energy saving and resource conservation potential of the blended cements produced can be easily understood. Similarly, the use of slag and fly ash results in a significant reduction in CO_2 and other gaseous emissions associated with clinker production. During 2007-08, out of the total cement (170 million tonne) produced, 25 per cent was OPC, 67 per cent was PPC and 8 per cent was PSC [3]. However, it is to be noted that inspite of the significant usage of fly ash and slag, the replacement is lower than the the limits prescribed by Bureau of Indian Standards (BIS), i.e. upto 70% for granulated blast furnace slag and 35% for fly ash. A benchmarking study of the cements showed a lowering of compressive strength, especially early strength, due to an increase in the replacement level [1]. The lowering of strength is believed to be associated with the reactivity of slag the and fly ash which shows latent hydraulic reactivity (can behave as cementious materials at its own) and pozzolanic reactivity (develop cementious properties after reaction with lime), respectively [1,2].

During 2002-06, National Metallurgical Laboratory, pursued the project 'Mechanochemical Activation in Improved Blended Cement Processing' under the New Millennium Indian Technology Leadership Initiatives (NMITLI) programme of Council of Scientic and Industrial Research. The objective of the programme was to develop as 'proof of concept' the processes to double the the utilisation of blast furnace slag and fly ash in blended cements, namely Portland Slag Cement (PSC) and Portland Pozzolana Cement (PPC). The research approach was based on the mechanical activation of blast furnace slag and fly ash to increase latent hydraulic reactivity and pozzolanic reactivity, respectively, and consequently higher utlisation in PSC and PPC [1,2,4-8]. In this paper, we present some interesting results that followed during the NMITLI programme and beyond. The foucs is on mechnically induced reactivity of blast furnace slag and fly ash and the blended cements prepared using these activated materials. Prospects and problems associated with the translation of 'proof of concepts' into commercial realities are also discussed in the paper.

Chemistry and Nature of Blast Furnace Slag and Fly Ash

Ground granulated blast furnace slag (GGBFS) is a glassy granular material, essentially consisting of silicates and aluminosilicates of calcium and other oxides. It is formed when molten blast furnace slag produced as a by-product in the making of iron is rapidly cooled, usually by immersion in water, and then ground to improve its reactivity. The major oxides SiO_2, CaO, Al_2O_3, and MgO constitute bulk of the slag. Typical composition (in weight %) of a blast furnace slag from an Indian steel plant is as follows : SiO_2 - 33.1, Al_2O_3 - 21.6, Fe_2O_3 - 0.87, CaO - 33.0, MgO - 8.85. The glass content of the slag may vary between 85-95%. The main crystalline phase present is gehlenite (C_2AS) [conventional cement chemistry notations (C = CaO, A = Al_2O_3, S = SiO_2, and H = H_2O) have been used throughout the text]. The slag was characterised by a crystallisation temperature 915 ^oC. Median particle size (X_{50}) and density of the slag were 89.8 μm and 2.88 g/cm^3, respectively [5].

Fly ash, a silico-aluminate material from coal fired power plant, consists of SiO_2, Al_2O_3, Fe_2O_3 as the major constituents and varying amount of CaO, MgO, SO_3^{2-}. As per American Society

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[ξ] email : rakesh@nmlindia.org

for Testing Materials (ASTM C 618), fly ash containing more than 70% SiO_2, Al_2O_3 and Fe_2O_3 and less than about 5% CaO are classified as Class F fly ash and those containing higher CaO (> 5%) are referred to as Class C fly ash [2]. Wide variation in the composition of fly ash are observed, Typical composition of Indian fly ash (in weight %) is as follows : Al_2O_3: 13.0–35.0, SiO_2: 53.0–71.0, Fe_2O_3: 3.5–12.0, CaO: 0.6–6.0, MgO: 0.28–3.24, SO_3: 0.005–11. Majority of Indian fly ash belongs to Class F. The glassy (amorphous) siliceous spherical particulates are the active pozzolanic portion of fly ash. Typically, fly ash contains 30-50% glass, and quartz (SiO_2) and mullite ($Al_2Si_2O_8$) are the main crystalline phases present.

Figure 1 summarises the differences between blast furnace slag and fly ash in terms of chemistry, glass content and phases present, and morphology.

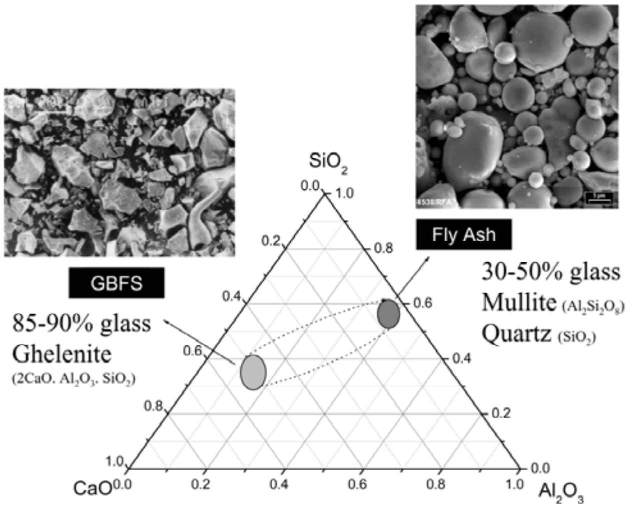

Figure 1. Differences between granulated blast furnace slag (GBFS) and Fly ash in terms of chemistry, morphology and nature of phases

The slag without an activator does react with water; however, the rate of hydration is very slow. Simplistic description of slag hydration in water is as follows :

GBFS + $H_2O \rightarrow$ C-S-H phases

On the other hand, pozzolanic reaction of fly ash can be represented as :

Fly ash + CH $\rightarrow$ C-S-H phases

CH for the pozzolanic reaction is supplied by the hydration reaction of cement phases (i.e. C_3S, C_2S). Class F fly ash shows primarily pozzolanic reactivity. Granulated blast furnace slag shows latent hydraulic activity and some pozzolanic reactivity is possible depending on the calcium content of the slag. The hydration of slag in water is inhibited due to the formation of an impervious hydration product layer on the surface of slag particles [9].

Mechanically Induced Recativity of Blast Furnace Slag

Role of Milling Device

Recent studies have shown that complete hydration of the slag is possible without a chemical activator if the slag is mechanically activated in an attrition mill [5]. The slag that was attrition milled for about 30 min or more was found to hydrate completely after 28 days (Fig. 2). This was an interesting observation since prolonged wet ball milling of slag for one month has been reported to result in only 15-20% slag hydration [10] and, even after 1-2 years, maximum reported hydration of slag in PSC is 45-75% [11].

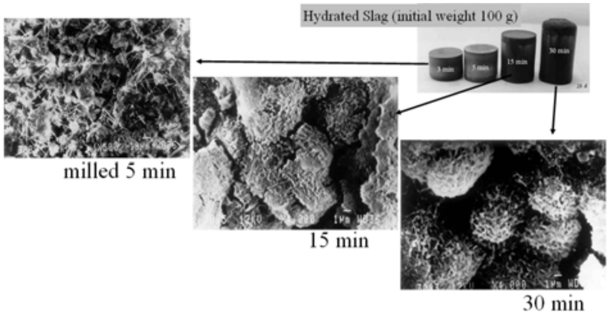

Figure 2. SEM micrograph of hydrated blast furnace slag after attrition milling for 5, 15 and 30 min [Hydration time 28 days, Temperature 27 ^{o}C]

The mechanical activation effect is clearly demonstrated during conduction calorimetric studies on ball milled and attrition milled slag of nearly same size (d_{50} ~ 12 μm) (Fig. 3). Unlike ball milled slag, attrition milled slag begins to hydrate after 48 h [5,10]. Thus, it is possible to prepare reactive blast furnace slag using attrition milling [12].

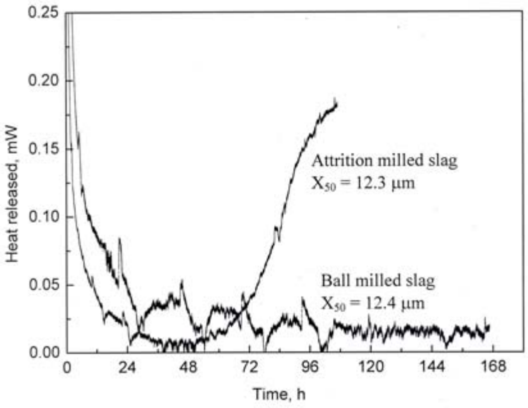

Figure 3. Calorimetric response at 27 ^{o}C showing comparison between ball milled and attrition milled slag

Ball mill and attrition mill differ in terms of mill energy which is directly proportional to the product of 'stress intensity (SI)' (measure of impact intensity) and 'stress number (SN)' (contact between media and material). Typically, attrition mills are characterised by two to three order of magnitude higher energy as compared to ball mills [13,14]. This means that milling energy plays a critical role in the activation process. X-ray powder diffraction and transmission electron microscopy did not reveal any change in the nature of slag after mechanical activation. Characterisation of the effect of mechanical activation on amorphous material such as granulated slag remains a challenging problem. The problem is made further complex when activation is carried out in the presence of water. Mechanical activation during wet milling in an attrition mill results in a change in surface charge as indicated by Zeta potential measurements. The change in Zeta potential suggests, additionally, possibility of surface activation [5,8]. It is likely that the impervious film formed during hydration of slag in pure water become unstable with time due to the altered nature of surface for attrion milled slag and consequently, continued hydration of the slag.

Nature of Hydration Product

The hydration product of the mechanically activated slag shows number of unique features. It is reported that slag after wet ball milling and simultaneous hydration, even after 28 days, shows only a small amount of amorphous product [10]. In sharp contrast to published literature on the nature of hydrated slag [9-11,15,16], the product formed after 28 days hydration of attrition milled slag has crystalline character and its crystallinity increases with milling time (Fig. 4). In addition, the presence of a di-calcium-silicate-hydrate phase (α-C_2SH) that normally forms under hydrothermal condition and a Ca-deficient and Si-Al- rich phase (average Ca/Si mole ratio < 0.1 and Si/Al ~ 3) is indicated, especially in the hydration product of slag that was activated for longer time [5].

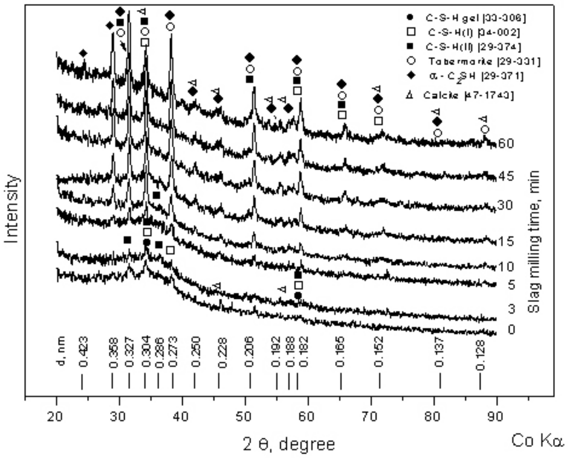

Figure 4. X-ray powder diffraction patterns showing increasing crystallinity of hydrated slag with milling time

Mechanically Induced Recativity of Fly Ash

Lime reactivity of raw fly ash (RFA) was compared with vibratory milled fly ash (VMFA) and attrition milled fly ash (AMFA). The mechanically activated fly ash samples show higher reactivity as compared to raw fly ash (Fig. 5). Possible origin of mechanically induced reactivity of fly ash is discussed elsewhere in this volume [17] and may be the result of polyamorphism and other structural changes during milling.

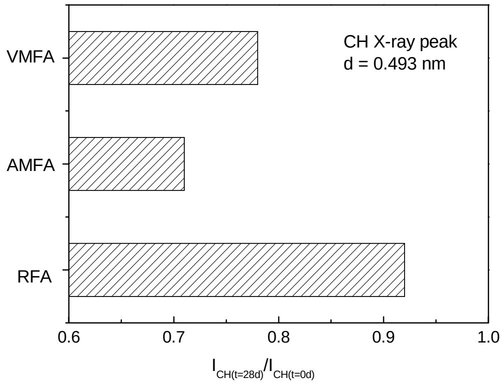

Figure 5. Lime reactivity of raw fly ash (RFA), attrition milled fly ash (AMFA) and vibratory milled fly ash (VMFA)

Studies of the morphological features of fly ash before and after lime reaction were quite revealing (Fig. 6). Small size cenosphere present in raw fly ash are preserved during attrition and vibratory milling (Fig. 6(a)-(c)). Presence of small cenospehere in the milled fly ash is significant for good workability during the use of mechanically activated fly ash in PPC. The higher reactivity of mechanically activated fly ash results in a compact structure as compared to raw fly ash (Fig. 6(d)-(e)). Formation of compact structure is important from the point of view of development of higher strength and lower diffusivity [2,6].

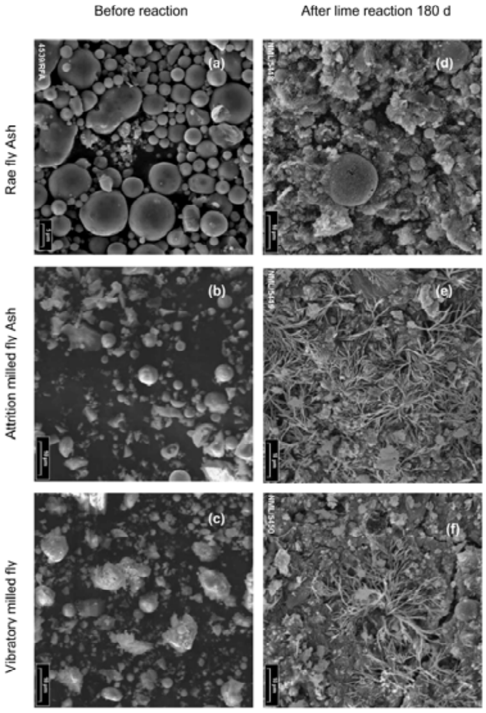

Figure 6. SEM micrographs showing morphological features of raw fly ash, attrition milled fly ash and vibratory milled fly ash before and after lime reaction (180 days)

Mechanical Activation and Utilisation of Blast Furnace Slag and Fly Ash in Blended Cements

Cement formulations containing mechanically activated BF slag in the range of 50-95% and fly ash 25-75% were evaluated in terms of compressive strength and other physical properties, such as setting time, consistency and autoclave expansion. Commercial cements from benchmarked cement plants containing ~ 35% BF slag and 25% fly ash were used as reference. It was found that upto 80% clinker can be replaced by attrition milled slag. However, replacement with vibratory milled slag of similar fineness (12-15 µm) was less effective. PSC containing attrition milled slag showed an increase in strength with increasing slag content upto 70%. Both attrition mill and vibratory mill gave good result in the case of fly ash (X_{50} ~ 5 µm) and 50-60% clinker could be replaced by mechanically activated fly ash [1,2,4,6-8].

Prospects and Barriers

Table 1 and 2 show typical estimates of energy saving and resource conservation potential as a result of enhanced utilisation of slag and fly ash due to mechanical activation.

Table 1. Energy saving potential with enhanced utilisation of slag and fly ash (typical energy data taken from reference [18,19])

Unit operation/ process	Energy (kWh/t cement)	PSC 50% slag	PSC (80% MA slag)		PPC 25% FA	PPC 50% MA +Raw Fly Ash
			I[#]	II		
Raw material grinding	15	7.5	3	3	11	7.5
Raw material blending & homogenisation	10	5	2	2	8	5
Coal grinding	3	1.5	0.6	0.6	2.5	1.5
Clinker section						
Thermal (MJ/t)	3200	1600	640	640	2400	1600
Electrical	40	20	8	8	30	20
Cement grinding						
OPC	33	-	7	7.	-	17
PPC	35	-	-		35	-
PSC	40	40	-		-	-
Slag WM+ AM	30	-	24	24	-	-
Slag filtration & drying	6+WH	-	5	-	-	-
Vibratory milling of fly ash	-	-	-	-	-	35-90[*]

[#] I and II alternate strategies : I-in plant usage; involves wet milling & attrition milling (WM+AM) and filtration and drying steps; II-onsite usage which involves no solid-liquid separation and drying

[*] Typical estimate based on literature; energy saving possible even if the energy is as high as 360kWh/t Fly Ash !

Table 2. Resource conservation potential with enhanced utilisation of slag and fly ash (estimates based on data in [18,19])

Resource	Conservation	
	Fly Ash increase from 25% to 50%	BF slag increase from 50% to 80%
Lime stone (t/t cement)	0.25	0.3
Clay Sand etc (t/t Cement)	0.125	0.15
Coal (t/t Cement)	0.03	0.036
Refractory (g/t Cement)	90-100	90-100
Air (Nm^3/t Cement)	750	900

The values in Table 1 and 2 are indicative since continuous improvements in energy figures are taking place [20]. However, it is quite evident that immense energy savings and resource conservation potential exits for improved blended cements involving use of mechanically activated blast furnace slag and fly ash. In addition, a reduction in CO_2 (200-300 kg per tonne of cement produced) and other emissions can be anticipated. In spite of these advantages, there are number of barriers which need to be overcome for commercial exploitation of the processes developed as ‘proof of concepts’ at laboratory scale (Table 3).

Table 3. Mechanical activation based processes, mill(s) used, and barriers

Process/Product	Mill	Barriers
Portland Slag Cement (PSC)	Attrition mill	Wear related issues, e.g. life of agitator Portable mill for on-site usage in ready mix concrete industry Large size mills for cement plants
Portland Pozzolana Cement (PPC)	Attrition mill, Vibratory mill	100-200 fold increase in vibratory mill capacity Evaluation of the bank of vibratory mills

Various process innovations (Table 3) rely on attrition mill and vibratory mill. Attrition mills are now widely used for grinding solids down to the sub-sieve size range, finer than 20 micron or so, for instance. The number of installations of these mills in commercial mineral processing plants is increasing steadily during the last decade and currently there are over few hundred installations world over from different manufacturers. There has been a steady increase in the capacity of attrition mills, in particular the mills of horizontal type. The typical maximum size of a horizontal type mill in early 1990's was about 500 litre.

Subsequently 'NETZSCH' and 'Mount Isa Mines (MIM) Process Technologies' developed and commissioned the 3000 litre mill (1994) and more recently during March 2004, 'Xstrata Technology' announced the world's largest ultra fine grinding mill - the 2.6 MW M10000 IsaMill (10000 litre volume) that can treat 50 tonne material per hour [7]. While these are welcome developments, a further increase in mill capacity may be necessary to meet the requirement of cement plants treating few million tonnes of material every year. Typical vibratory mill capacity is in 2-5 t/h range. This means that the scale up issue is more serious in the case of vibratory mill. It may be noted that the capacity of existing mills may still be suitable for on-site usage in ready-mix concrete industry. However, the mill portability issue needs to be addressed.

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