Geopolymerization as Effective Measure for Reducing Risks during Coal Ashes Handling, Storage and Disposal

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In this paper a research on the synthesis of geopolymers based on coal ashes, with consequent reduction to a consolidated form, was reported with the aim of proposing a procedure to transform potentially dangerous wastes into safe and possibly useful secondary materials (e.g. bricks and boards). Ash from pulverized coal (PC) combustion plant was used in tests of geopolymerization, performed with different ash/alkali compositions. The produced samples were characterized with particular focus on stability in water and leaching behaviour in comparison with raw ashes. The results of the research prove that coal ash can be converted into geopolymers in a rather simple way. The leaching of elements is not dramatically affected by the basic attack, but some controversial findings need further investigation. In general, the geopolymerization increases the safety of ash handling and disposal, thank to higher particle size and lower exposed surface.

1. Introduction

Coal contains around 10 % by mass of ashes that are mainly released in the combustion chamber as fine powder in size range 0.5-100 μm and separated downstream by cyclones, filters and electrostatic precipitators. Hundred million tons of coal ashes are produced every year only in USA and Europe (Twardowska and Stefaniak, 2006), causing a large impact on the environment as consequence of transportation and landfill as well as unavoidable partial dispersion in the atmosphere during handling. Although coal ashes are normally considered as non-hazardous waste, pollution can derive from the presence of heavy metals and leachable elements (e.g. As, Cd, Cr, Hg, Pb, Cu, V) in coal ashes, when they are exposed to water and rain. Furthermore, accidents during transportation by train or trucks, as well the collapse of the ash temporary deposits may represent a serious source of hazards for the environment and human health. So far, the huge ash spill occurred at the power plant of the Tennessee Valley Authority in 2008 was emblematic (Ruhl et al., 2010), demonstrating that large stocks of coals ashes can be cause of catastrophic events, if effective measures are not taken for risk minimization.

Apart from landfill, fly ash can be used as additive for ordinary Portland cement, offering a contribution in environmental as well as in economic concern (Ondova et al., 2011). However, the legislation on cements composition and the characteristics of the ashes pose limits to the full utilization of all produced ashes. Another possibility is offered by the sorptive behaviour of coal fly ashes toward heavy metals in wastewaters upon beneficiation treatments (Balsamo et al., 2013).

The geopolymerization (GP) is a chemical-induced consolidation process leading to the formation of amorphous three-dimensional alumina-silicate materials. Although this option has very ancient origin (e.g. production of hydraulic puddles by Romans), geopolymers have been systematically studied since a couple of decades (Davidovits, 2008). The synthesis of geopolymers occurs at low temperature from room temperature to 80 °C by alkaline activation of alumina-silicates obtained from natural minerals, calcined clays, industrial wastes or mixtures of these materials. In this concern, fly ashes have been used for producing geopolymeric cements with mechanical strengths up to around 60 MPa (Palomo et al., 1999) and composite materials with excellent bonding between the geopolymer binder and filler (Temuujin et al.,

2010). Coal ash properties and combustion conditions are expected to affect the easiness of the GP process and the final characteristics of the products.

In this paper, the results on the synthesis of geopolymers based on coal fly-ash are reported. Ash from pulverized coal (PC) combustion was used in tests of geopolymerization, performed with different ash/alkali compositions. The results are presented and critically discussed in the paper, enabling to assess the benefits of the geopolymerization in reducing the risks for the environment and the health during ash handling and disposal.

2. Experimental

2.1 Materials

Pulverized coal (PC) combustion fly ash, obtained at high temperature (1,200-1,300°C) from Enel SpA (Italy) power plant was used as primary raw material for geopolymerization tests. PC ash was characterized in terms of granulometric distribution. The chemical composition was determined by EDS for major elements concentration (Al, C, Ca, Fe, Mg, Si, O) and ICP-OES for trace elements. Results are presented in Table 1 and Figure 1.

PC ash composition, as pointed out, is mainly defined by considerably high amounts of Fe, Ca and Mg. Si and Al were found to be relatively lower than what expected for a geopolymer precursor. Carbon and oxygen amount by themselves to almost 60 % of ash total weight.
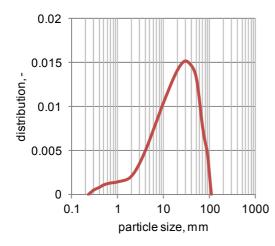
Table 1: Chemical composition of PC fly-ash (wt%)

Element	PC fly-ash	Element	PC fly-ash	Element	PC fly-ash
Al*	12.090	Cu	0.002	O*	32.460
As	0.001	Fe*	1.590	P	0.537
B	0.018	Hg	<0.001	Pb	0.002
Ba	0.105	K	0.072	Sb	<0.001
C*	25.360	Mg*	1.270	Se	<0.001
Ca*	4.110	Mn	0.020	Si*	15.660
Cd	<0.001	Mo	0.002	V	0.058
Cr	0.005	Na	0.077	Zn	0.003

*= Determined by EDS analysis

The granulometric analysis on PC ash (Figure 1) highlights a particle size range from 0.2 to 120 μm, with 50 % by mass of particles being over 34 μm. These large particles could result less reactive toward geopolymerization, but the reactivity might be more remarkably influenced by a relatively high specific surface area. The ash particles appear to be spherical in shape as shown in SEM image of Figure 2, confirming the melting of the material occurred during high temperature combustion.

The humidity of the ash was around 2.1 %, while total fixed carbon amount on dry ashes was 11.2 %. The real density is 2,336 kg/m^3, as determined by He pycnometer. Since the particles are porous, the apparent density is around 1,600 kg/m^3.
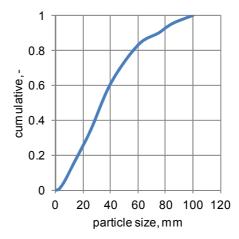

Figure 1: granulometric distribution of PC fly-ash

As the activating media, alkaline Na_2SiO_3 or NaOH aqueous solutions were alternatively used. Silicate activator was preferentially used, as its effectiveness in geopolymerization process is widely known. NaOH was tested as a cheaper alternative activator. Na_2SiO_3 solution was adjusted from a commercial solution (NaSil 38/40 R3.2, INGESSIL Industria Silicati) obtaining final ratios of SiO_2: Na_2O= 2 and H_2O: Na_2O= 23. NaOH solution (10 M) was prepared dissolving NaOH pellets (purity >99 %, Merck) in deionized water under magnetic stirring.
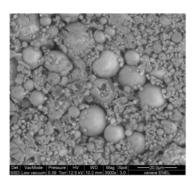

Figure 2: SEM image of a pressed sample of PC fly-ash

2.2 Preparation procedure

PC fly ash was activated using alternatively Na_2SiO_3 or NaOH solutions according to the formulations listed in Table 2 through mechanical mixing for 20 min at 100 rpm. PC-Sil1 formulation was obtained from stoichiometric molar Si/Al = 2. PC-Sil2 was tested as an ameliorative formulation aimed to decrease the silicate amount. PC-OH represents an already improved formulation respect the stoichiometric one with Na/Al=1. The obtained slurries were adjusted to a proper consistency adding extra water when required, then poured into plastic vessels, sealed and cured for 24 h at room temperature, unsealed and placed for further 48 h at 50 °C in a laboratory heater.
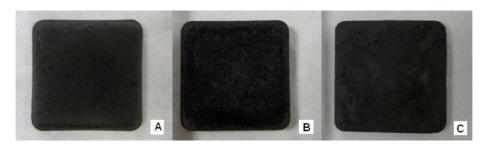

Figure 3: PC-ash based geopolymer tablets (30x30x8 mm); A) PC-Sil1, B) PC-Sil2, C) PC-OH

The consolidated tablets, obtained with the reported formulations, are shown in Figure 3. The dark appearance of the samples is to be attributed to the residual content of carbon in the ash that was not converted in the alkaline environment.

The geopolymer samples are coherent and easy-handling. The grinding of the samples in mortar resulted harder moving from PC-OH to PC-Sil1.

2.3 Chemical and physical tests

Water stability and mass loss after water immersion were determined on cured specimens by subjecting them to soaking/drying cycles in deionized water for 5 days.

Environmental impact of hardened geopolymers was finally evaluated by leaching tests carried out in analogy with EN 12457-2 normative (EN, 2002). Samples of fine grinded powder (5 g) were treated in 50 mL of distilled water for 24 h. Then, the filtered solution was subjected to ICP analysis and attention was particularly focused on determining the concentration of the eluted heavy metals and other hazardous elements.

3. Results and discussion

Table 3: Water stability and mass loss of PC-ash based geopolymers

	WA, wt%	ΔW, wt%
PC-Sil1	1.3	-24
PC-Sil2	31.2	-11
PC-OH	9.6	-32

The WA values (percentage of water absorbed on mass basis) reported in Table 3 are indicative of the open interconnected porosity in the samples, whereas the weight loss values (ΔW) indicate the presence of unreacted alkaline activators that are dissolved in water. Between silicate activated materials, the lower value of WA and the higher value of weight loss found for PC-Sil1 both suggest the presence of an excess of silicate in the initial formulation. This is also supported by the visual aspect of the sample (Figure 3-A) that shows a glassy surface. In this respect PC-Sil2 represents an improved but not still optimized formulation.

Table 4: Leaching behaviour of heavy metals from PC fly-ash and geopolymers (µg/l)

	PC ash	PC-Sil1	PC-Sil2	PC-OH		PC-Ash	PC-Sil1	PC-Sil2	PC-OH
As	4.59	106.30	90.20	335.40	Mo	347.5	264.50	257.70	457.30
Ba	115.30	263.40	69.73	333.10	Ni	0.279	87.55	11.93	25.17
Cd	0.34	0.43	0.20	0.43	Pb	0.20	14.27	3.91	5.30
Cr	130.20	45.48	103.30	25.72	Sb	2.68	11.19	4.34	6.99
Cu	<0.20	20.30	2.07	3.16	Zn	<0.20	16.95	3.59	2.54
Hg	3.12	3.51	2.05	25.48					

Concerning hydroxide activated sample (PC-OH) the high weight loss might be attributed to two factors: i) an excess of unreacted hydroxides, similarly to silicate-based samples, 2) formation of debris by loss of the specimen coherence. So far, the consistency and resistance of the specimen appear worse than in silicate based ones.

Table 4 reports the comparison of the results from leaching tests performed with the raw ash and the geopolymer samples. In general, the leaching behaviour changes among the tested samples depending on the single element.

On the whole, PC-Sil2 represents the best solution to limit the leaching of the investigated elements, exhibiting beneficial effects for retention of Ba, Cd, Hg and Mo. In some cases (e.g. Cr), the excess of unconverted alkaline activator reacts with some elements during the material synthesis. In this way, they are mobilized and become more easily leachable from the final consolidated samples. This is in accordance with the previously discussed findings on material stability in water and weight loss (Table 3), which are linked with the activator excess. Cr represents an exception, showing a higher release from PC-Sil2, being the lowest from PC-OH. Further investigations are needed to elucidate the general trends for each element. Only for As and Ni there is a much higher presence in the eluate, indicating that these elements were preferentially extracted by action of the severe alkaline conditions during GP process.

4. Considerations about risk prevention and economics

The consolidation of the fly ash in granules, coarse agglomerates or large blocks is the prominent advantage arising from geopolymerization. Explosion events, even if improbable for coal ash unless contaminated by fuel, are prevented (Dastidar and Amyotte, 2002). Larger size has two beneficial effects in reducing the exposed surface of the solids, with 3rd power law on the diameter, as well as in increasing the terminal velocity of entrained particles in a stream.

It is likely that any accident occurring during fly ash handling or transport would have much lower impact on the environment, thanks to the confinement of the released materials in a short radius from the site. Upon accident, a vertical plume or cloud (Ansart et al., 2009) can be formed in the air by fugitive dust, in particular when explosion, structural collapse or impact take place. Thus, the airborne fraction of the ash is quickly and easily entrained by the wind and spread over a large area. Conversely, the dispersion caused

by water or air streams is largely lowered at increasing the size of the particles, the gravimetric setting velocity contrasting the dispersion over long distance.

An estimation of the setting distance L can be obtained upon integration of the differential equations of particle motion in an air stream or more simply by calculating the setting time of the particle as the ratio between the terminal velocity U_t and the plume height H. U_t can be calculated following Haider and Levenspiel (1989) by Eqs. 1-3 as function of the spherical particle diameter d_p. Equation 4 provides the simple formula for computing the setting distance.

$$d^* = d_p \left[g\rho_g \frac{\rho_s - \rho_g}{\mu^2} \right]^{1/3} \tag{1}$$

$$u^* = \left[\frac{18}{d^{*2}} + \frac{0.5909}{\sqrt{d^*}} \right]^{-1} \tag{2}$$

$$U_t = u^* \left[\frac{\rho_g^2}{g\mu(\rho_s - \rho_g)} \right]^{-1/3} \tag{3}$$

$$L = H\, U_w / U_t \tag{4}$$

g, ρ, μ and U_w are the gravity acceleration, density, viscosity, and wind velocity, respectively.

The results reported in Figure 4 show that the setting distance sharply decreases with particle size, as consequence of the strong dependence of the terminal velocity. It is worth noting that fine particles (< 30 μm) are dispersed over distances of some kilometres.
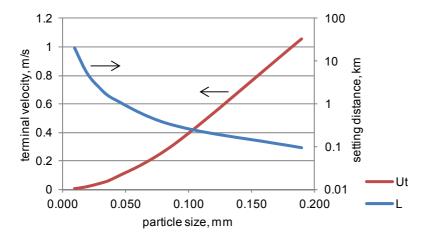

Figure 4: terminal velocity and setting distance of PC-ash particles (U_w=10 m/s, H=10 m, ρ_s=1600 kg/m3)

The fraction of breathable particles having size < 10μm (Koeppen and Stanton, 2009) and accounting for 10 % by mass in PC-ash (Figure 1), is totally suppressed upon geopolymerization, with evident benefits for the health of the operators at production and disposal sites. Again, possible accidental releases of airborne and breathable particles in the atmosphere are thoroughly prevented.

As shown in the previous section, the GP process may affect the leaching behaviour of some elements present in the ashes,. Nevertheless, it is worth noting that the results of ICP analysis were obtained from leaching of fine particles upon grinding in distilled water, in order to have a valid comparison with the original ash. Thus, the release of elements from consolidated constructs and the consequent risks of water contamination would significantly decrease because of the lower exposed surface to the leaching agent, as mentioned before.

The cost of the GP process is mainly due to the expensive alkali activators to be used, whereas cheap equipment would be required for their preparation (e.g. mixer, tanks, moulds, etc.) operated at ambient conditions. Also, the heat required for curing geopolymeric pastes can be easily available as waste heat from other processes, air at moderate temperature being suitable for the purpose.

By assuming the use of 400 kg of technical grade NaOH per ton of fly ashes at a price of 200 $/t, it results a rather high cost for ash treatment, namely around 80 $/t. The alternative use of Na or K silicate results more expensive. However, alkaline wastewaters can be available from industrial processes, such as those from paper, cellulose, leather, textile industries, laundries and dye works and others. Their application to this purpose could improve the economics of the GP process, reducing the ash treatment cost. Finally, the consolidated ashes can have a commercial value as filling materials or finishing components in the building sector, allowing to make profit from ash disposal.

5. Conclusions

The geopolymerization is effective in making the coal ash less dangerous with respect to accidental release of particulate in the environment or leaching of elements in the water. Both benefits are consequence of the reduced exposed surface and the increased size of the consolidated ashes, with consequent suppression of airborne particles.

Although the leaching results here reported are obtained under severe conditions, namely the reduction of the consolidated samples in fine powders, the alkaline treatment of the ash only slightly modify the leaching behaviour of the geopolymers with respect to untreated ashes, in some cases with beneficial effects. More investigations addressed at optimizing the mixture formulations for both leaching and mechanical improvements are needed.

A geopolymerization process immediately after the ash separation steps, though expensive because of the price of alkaline activators, could significantly increase the safety in ash handling, transport and disposal. The economic affordability can be improved by using waste heat/streams during the GP process as well as by producing secondary materials with added value.

The GP option could become attractive if the legislation on coal residues became more restrictive, as even more frequently claimed by environmentalists in the world.

6. Acknowledgement

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