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CHEMICAL CHARACTERIZATION AND ECONOMIC EVALUATION OF THE COAL FLY ASH PRE-WASHING AND CARBONATION PROCESS

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ABSTRACT

In the present laboratory-scale study, the combination of washing and carbonation processes was examined to evaluate the feasibility to reduce the environmental impact of coal power plants. Three different washing solutions (tap, distilled and sea water) were used to pre-treat coal fly ash and the corresponding effect on direct gas-solid carbonation and final metal leaching was evaluated. Finally, a preliminary economic evaluation of the process was performed. In terms of captured CO_2*, the results have shown that significant amounts can be captured, although, as expected, the leaching of soluble salts in water such as Ca and Mg reduce the* CO_2 *uptake. In terms of heavy metal's leaching, the application of pre-washing and carbonation treatment significantly affected the metal immobilization on the final residue. The pre-washing with sea water allowed to reach a sensible improvement since only selenium, chlorides and sulphates resulted outside the range for disposing of the carbonated residue in landfill for non-hazardous waste.*

Keywords: *coal fly ash, pre-washing, gas-solid carbonation, leaching, process integration.*

INTRODUCTION

According to the news reported by the New York Times, 1,600 coal plants are planned or under construction in 62 countries, expanding the world´s coal power capacity by 43 % [1]. Without any doubt, coal has a high carbon intensity and many countries are encouraging the use of more sustainable feedstocks or they are announcing phase out policies. According to the European Coal Map, about 280 coal power plants are still operating in Europe and actions finalized to reduce their environmental impact are of great interest for the research community [2]. The International Energy Agency declared the dominance of coal in the global power generation, reporting a share of over 40 % in 2016 [3]. A more alarming data, reported in the same study, is the fact that 30 % of new coal power capacity additions in 2015 used low-efficiency subcritical technologies, highlighting even more the necessity to promote new retrofit options to reduce the environmental impact of coal power plants.

Coal power plants are characterised by three main impacts: on the air quality through the emissions generated by the combustion, on the soil through the ashes generated as combustion residue, and on the water through the ashes leaching. The composition of the fumes emitted depends on the coal composition and in general different pre-treatments are included to reduce the generation of NO_x and SO_x.NO_x are generated by reaction of the nitrogen contained in the coal and in the air with oxygen. Their formation can be limited by controlling the combustion conditions and by selective catalytic reduction [4]. Regarding the formation of SO_x, depending of the amount of sulfur in the coal, a Claus plant could be considered to recover elemental sulfur as valuable by-product [5]. Another solution is the simultaneous removal of NO_x and SO_x in the so-called SNO_x process [6]. The carbon dioxide generated by the combustion is one of the main concerns in the coal power plant economy and, released to the atmosphere, it heavily contributes to the global warming. Currently, at industrial level, the most accepted solution is the chemical absorption in amine-based solvents [7]. The solvent is regenerated in a stripping unit producing a stream of concentrated carbon dioxide usually stored into suitable geological formations (e.g. depleted gas/oil reservoir, unmineable coal seams and/or saline formations).

With respect to the management of the solid residues generated by the coal combustion, usually referred as coal fly ash (CFA) and bottom ash, alternative applications are required. In particular, CFA mainly consisting of silica (SiO_2), alumina (Al_2O_3), lime (CaO) and iron oxide (Fe_2O_3), with traces of unburned coal, is one of the most complex anthropogenic material, and its improper disposal has become an environmental concern due to the potential to contaminate groundwater reservoirs by leaching of heavy metals. Many works have been focused in redefining its use in order to limit the disposal in ash ponds. Possible solutions are its use as partial substitute of the binder in the concrete [8] or in agriculture as alternative to lime [9]. Moreover, mineral carbonation has recently raised interest, consistently with the possibility to capture CO_2 in a safe and permanent way. To this regard, CFA has great potential to be used as a raw material for mineral carbonation.

In the present work the impact due to the carbon dioxide emission and to the fly ash's leaching is considered in a process where the fly ashes are first washed and then used to adsorb part of the carbon dioxide emitted. Although the washing and carbonation processes could appear to be competitive with each other, this approach has the potential to reduce the leaching of some elements by the pre-washing step, whilst the carbonation allows the formation of a stable residue which can be safely disposed. Simultaneously the amount of carbon dioxide stored could be reduced.

Ash pre-washing was already considered by different authors, and many works are focused in the treatment of municipal solid waste (MSW). Fedje et al. [10] reported how washing MSW fly ash with EDTA can give a good removal of Cu and Pb, while NH_4NO_3 is effective for Cu recovery. Kashiwakura et al. [11] examined the specific case of boron removal by washing the coal fly ash with a diluted solution of HCl. The recovery of selenium was studied by Kashiwakura et al. [12] washing the coal fly ash with a solution of H_2SO_4. Cheng et al. [13] targeted chlorides as elements to be removed by water-washing to use the fly ash in cement kiln. A more comprehensive study was done by Chen et al. [14] where MSW fly ash was treated with a combination of water-washing electrodialytic separation and thermal treatment at 1000ºC to reduce the heavy metal leaching. Wang et al. [15] studied the effect of water and acid-washing of MSW fly ash on the bioavailability of heavy metals concluding that only washing pre-treatments can not reduce the actual risk to an acceptable level. Even if there is a clear interest in fly ash recycling or safe disposal, it is missed the economic evaluation of the process where the fly ash produced by a coal power plant are washed and carbonated before their safe landfill storage. In this study three different washing solutions using water as the solvent ("TW" - tap water, "DW" - distilled water and "SW" - sea water) were considered and the corresponding effect on the carbonation and on the final metal leaching was evaluated. The three scenarios were then compared performing an economic evaluation of the process. The carbonation process without the pre-washing step was considered as benchmark to evaluate the trade-off between washing and reduced carbonation capacity.

EXPERIMENTAL

Coal fly ash

The coal fly ash samples were collected from the bag filters of the combustion and desulfurization section of the coal-fired "Grazia Deledda" power plant. The plant is located in the Sardinia´s coastal area of the southwestern province of Carbonia-Iglesias (Italy) and it is designed to produce 590 MWe [16]. In 2016, according to the environmental declaration published by ENEL (the multinational that owns the plant), 281,875 tons of coal have been burned, 678,379 tons of carbon dioxide were emitted, and 56,246 tons of fly ash were disposed in landfill [17].

In order to obtain representative laboratory subsamples, a composite sample of 50 kg was collected over a

72 h period and re-sampled by the quarter method. The subsample of around 5 kg was shredded in a rod mill to a final particle size < 0.212 mm, oven-dried at 45 °C for 24 hours and transferred into hermetically sealed bottles until use, in order to prevent contact with atmospheric moisture and CO_2.

Analytical methods

CFA moisture content, volatile matter, ash and fixed carbon content were determined according to ASTM D 5142-02 method using the thermogravimetric LECO-MAC 400 Proxymate Analyzer; ultimate analysis was performed using LECO-CHN 1000. Specific gravity was determined by AccuPyc 1330 pycnometer. The pH value was measured by mixing dry material with distilled water at a liquid:solid ratio (L/S) of 10 and stirring the suspension for 24 h; the eluate was analysed using a pH-meter Crison GLP 22. Chemical composition was analysed by digesting 1 g of dry material with a concentrated mixture of 3 ml of HNO_3, 9 ml of $HClO_4$, 9 ml of HCl and 5 ml of HF. After digestion, the resulting liquid sample was filtered over a 0.45 µm membrane filter and diluted to 100 ml by distilled water. The major cation content and the metal concentrations were determined by means of Inductively Coupled Plasma spectrometry (ICP-OES Optima 7000 DV). The chemical-physical characteristics of the CFA are summarised in Table 1.

The mineralogical characterization was performed using a Rigaku Geigerflex X-ray diffractometer (XRD), with Cu Kα radiation Ni filter, at 30 KV of voltage and 30 mA of current intensity, wavelength of 0.15418 nm, at 0.052 (count time = 3 s) and at 25°C. The phase-mineral composition of raw CFA is shown in Fig. 1. According to Vassilev and Mendez [18], on the basis of their origin different kind of minerals have found into CFA:

- calcite ($CaCO_3$), gypsum ($CaSO_4 \cdot 2H_2O$) and quartz (SiO_2) linked to original coal minerals composition;
- anhydrite ($CaSO_4$) and ettringite ($3CaO \cdot Al_2 \cdot 3CaSO_4 \cdot 32H_2O$) formed during coal combustion process);
- brucite ($Mg(OH)_2$) and portlandite ($Ca(OH)_2$) formed by reaction of CFA with water treatment and/or atmospheric moisture.

The leaching tests were carried out according to the standard EN 12457-2 using a L/S of 10 for 24 hours. The chlorides and sulphates concentrations were measured using DIONEX ICS-90 Ion Chromatography System, after dissolution with water according to the Italian standard test procedure UNI 8520.

Pre-washing tests

SW, DW, and TW were used in pre-washing treatment of fly ash samples. The chemical composition of the water-washing solutions was analysed before and after the experiments in order to determine the metal and the major cation (Na, K, Ca, Mg) concentrations. The initial characterization is reported in Table 2.

The samples, after shaking for 24 hours at 175 rpm,

Table 1. Physical and chemical properties of the coal fly ash.

Chemical-physical Property	Value [% w/w]	Major Elements	Concentration [mg/kg ash]	Minor elements	Concentration [mg/kg ash]
Water content	5.45 ± 0.32	Al_2O_3	87,600 ± 1,264	Ba	251.3 ± 8
Volatile matter	17.95 ± 0.26	Fe_2O_3	64,500 ± 1,058	Cd	1.2 ± 0
Ash	75.4 ± 1.18	MgO	18,960 ± 845	Cr	42.9 ± 3
Fixed carbon	1.2	CaO	319,500 ± 8,547	Cu	25.5 ± 1
C	2.14 ± 0.03	K_2O	8,300 ± 245	Mo	3.2 ± 0
H	1.65 ± 0.02	Na_2O	9,330 ± 312	Ni	32.0 ± 2
N	0.07 ± 0	TiO_2	4,800 ± 98	Pb	68.4 ± 6
		SiO_2	272,900 ± 3,451	Sb	4.1 ± 0
		SO_3	21,100 ± 1,140	Se	8.2 ± 0
pH	12.3 ± 0.1			Zn	129.5 ± 4
Density [g/cm^3]	2.64 ± 0.14	Anion	[mg/kg ash]		
		Cl^-	8,694 ± 187		
		SO_4^{-2}	18,437 ± 986		

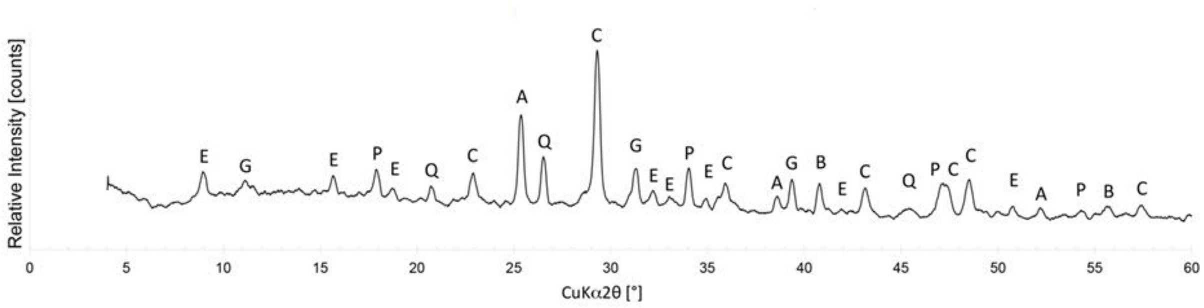

Fig. 1. Raw CFA XRD Pattern (A – Anhydrite, B – Brucite, C - Calcite, E – Ettringite, G – Gypsum, P – Portlandite, Q – Quartz).

according to a L/S of 10, were centrifuged at 4000 rpm for 20 minutes and then filtered with a 0.45 µm membrane filter. The solid residues were dried at 105°C for about 48 hours until each sample reached constancy of weight and subjected to carbonation tests.

Carbonation tests

Carbonation tests were performed applying progressively CO_2 pressure of 1.0, 2.5, 5.0, 7.5, 10.0,15.0 bar at 35°C temperature, by using the experimental apparatus described by Mazzella et al. [19], shown in Fig. 2.

The set-up is designed to perform CO_2 uptake tests within a thermostatically controlled setting: the equipment is basically formed by a double cells system of 500 cm^3 seated into a thermostatic bath. The cells are temperature and pressure monitored.

Applied carbonation tests procedure can be summarised by the following sequential steps:

- Sample preparation: 100 g of raw or pre-washed dried fly ash were quartered into two subsamples and 50 g were placed into the sample cell;
- Atmospheric gas purge: the experimental apparatus was brought under vacuum conditions to avoid any atmospheric gas interference;
- CO_2 injection: once 35°C temperature reached, CO_2 was insufflated to the reference cell until the starting pressure value is reached;
- CO_2 pressure equilibration and cells connection: after the time required to stabilize the reference cell pressure (about 5 minutes at 35°C), the valve between

Table 2. Pre-washing solutions characterization.

	Unit of measure	SW	DW	TW
pH	-	8.0	5.8	7.6
Na	g/L	10.7	n.d.	0.020
K		0.39	n.d.	0.002
Ca		0.41	n.d.	0.029
Mg		1.29	n.d.	0.013
Ba	mg/L	0.020	n.d.	0.153
Cd		< 0.002	n.d.	< 0.002
Cr		< 0.005	n.d.	< 0.005
Cu		0.012	n.d.	0.006
Mo		0.034	n.d.	0.009
Ni		0.023	n.d.	0.005
Pb		0.075	n.d.	< 0.02
Sb		< 0.005	n.d.	0.023
Se		< 0.001	n.d.	0.032
Zn		< 0.01	n.d.	< 0.01
Cl^-	mg/L	21,558	n.d.	37
SO_4^{2-}		2,822	n.d.	26

n.d.: not detected

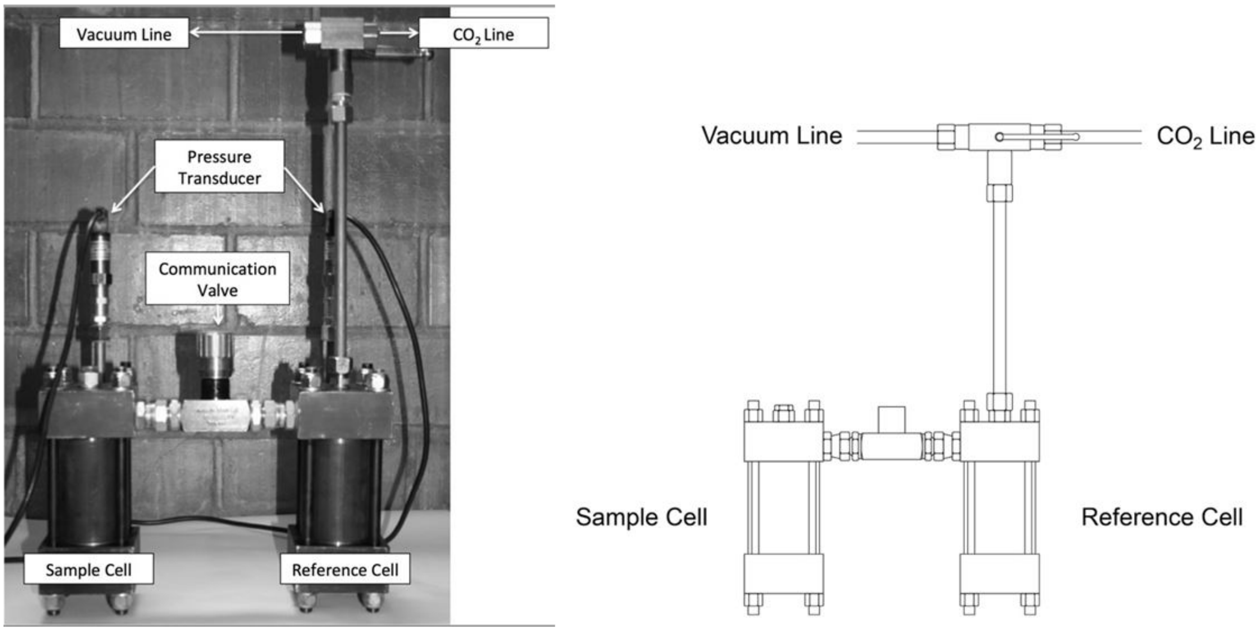

Fig. 2. Experimental set up used for the carbonation experiments.

the cells was opened allowing CO_2 pressure to equalize between the two cells;

- Experimental step execution: once CO_2 pressure reached the same value into both cells, the valve was closed and the pressure variation into both cells was registered;
- Current pressure step finalization: when the pressure change in the sample cell was less than 0.1 bar over a 30 minutes period, the step was stopped;
- Next pressure step execution: steps 3, 4 and 5 were repeated by increasing pressure into reference cell;
- CO_2 purge and sample removal: when the last pressure step was concluded, the apparatus was depressurized, disassembled and the sample removed.

All experiments were performed in triplicate and the results are presented as average values.

For each step, experimental data were collected considering time-depending decay of pressure into sample cell as the result of reaction between CO_2 and fly ash with the precipitation of Ca- and Mg- carbonates, as schematically reported in Fig. 3.

At equilibrium conditions, the CO_2 uptake capacity was calculated using Soave's modification of Redlich-Kwong equation of state [20] as described by Furcas et

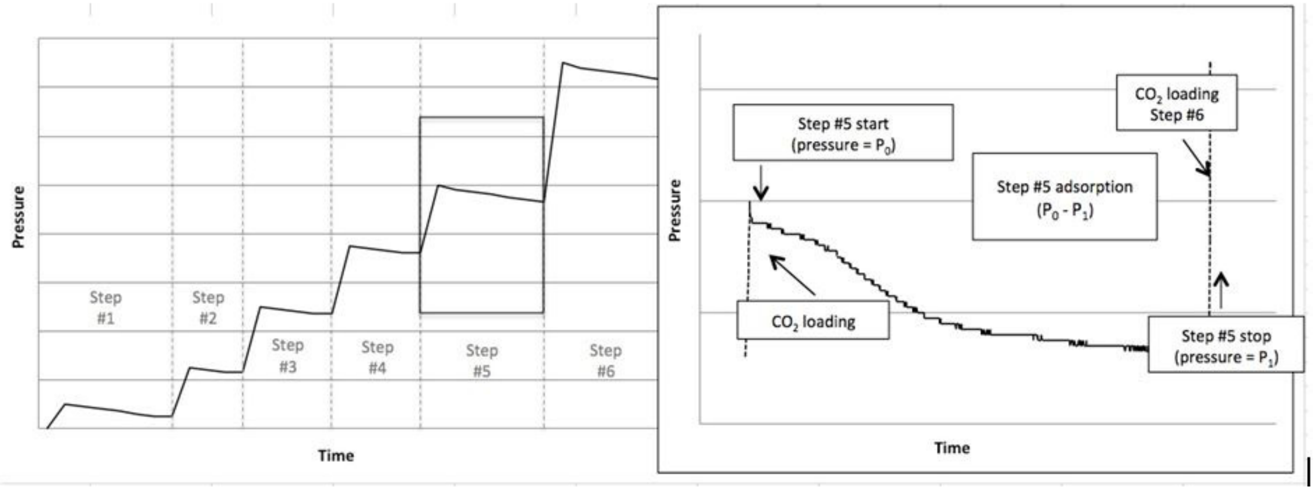

Fig. 3. Schematic representation of the experimental procedure and single step detail.

al. [21], and Mazzella et al. [19] and reported in Eq. (1):

$$P = (R \cdot T)/(V - b) - (a \cdot \alpha)/[V \cdot (V - b)] \quad (1)$$

in which P is the pressure, T is the temperature, R is the ideal gas constant, V is the molar volume (in this case it corresponds to the volume of 1 mole of CO_2), a and b are constants related to gas critical pressure and temperature and α is the acentric factor (which represents the influence of the non-sphericity of CO_2 molecules). The cumulated CO_2 uptake, expressed as g CO_2/kg dry ash, was obtained as the sum of the adsorbed moles for each step, multiplied for the CO_2 molar mass, divided by sample mass. The adsorbed moles of CO_2 for each step were evaluated as a difference between the number of moles initially transferred from the reference to the sample cell and the number of moles at the end of the step when the equilibrium conditions were reached, as described by Mazzella et al. [19].

RESULTS AND DISCUSSION

Pre-washing tests

The results of fly ash pre-washing tests are shown in Table 3. The concentrations are reported taking into account the initial content of each element determined on the washing solutions and calculating the net value.

It can be noted that chlorides, sulphates and major cations were mainly leached from the fly ash; among the minor elements, the leachate concentrations of Ba, Mo, and Se were significant, whilst for all other species were negligible.

Carbonation treatment

The results obtained from the direct gas-solid carbonation of coal fly ash and pre-washed fly ash are reported in Fig. 4; a total CO_2 amount of 169.8 g/kg dry raw coal fly ash was sequestrated at 35°C, whilst, at the same temperature, the captured CO_2 by pre-washed fly

Table 3. Washing wastewater characterization (% leaching was calculated with regard to the total element's mass in raw coal fly ash).

Element	Concentration [mg/L]			% leaching		
	SW CFA	DW CFA	TW CFA	SW CFA	DW CFA	TW CFA
Na	498 ± 4.6	632 ± 12.3	543 ± 8.2	53.4	67.7	58.2
K	324 ± 7.2	448 ± 11.4	450 ± 14.3	39.0	54.0	54.2
Ca	1548 ± 41.6	5149 ± 187.9	6412 ± 144.4	4.8	16.1	20.1
Mg	745.6 ± 24.4	1260 ± 53.1	1095 ± 36.9	39.3	66.5	57.8
Ba	1.45 ± 0.04	0.55 ± 0.02	0.45 ± 0.01	5.8	2.2	1.8
Cd	< 0.002	< 0.002	< 0.002	0	0	0
Cr	0.02 ± 0.00	0.05 ± 0.00	0.02 ± 0.00	0.5	1.2	0.5
Cu	0.01 ± 0.00	< 0.004	< 0.004	0.5	0	0.3
Mo	0.04 ± 0.08	0.13 ± 0.04	0.07 ± 0.03	12.9	41.6	21.5
Ni	< 0.005	< 0.005	< 0.005	0	0	0
Pb	0.04 ± 0.02	< 0.02	< 0.02	0.5	0	0
Sb	< 0.005	< 0.005	< 0.005	0	0	0
Se	0.12 ± 0.03	0.32 ± 0.02	0.21 ± 0.02	14.5	39.4	25.0
Zn	< 0.01	< 0.01	< 0.01	0	0	0
Cl^-	734 ± 27.1	536 ± 18.4	567 ± 34.2	84.4	61.7	65.2
SO_4^{2-}	427 ± 14.3	1046 ± 114.5	1149 ± 136.3	23.1	56.8	62.3

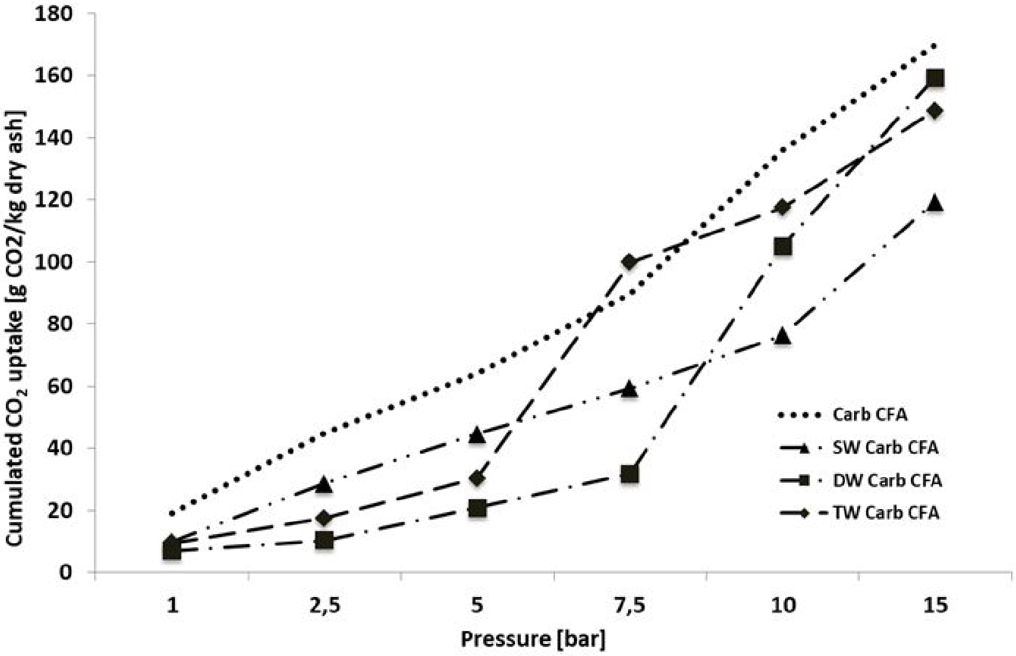

Fig. 4. Carbon dioxide uptake for raw and pre-washed fly ash.

ash, was 119.3, 148.7 and 159.2 g/kg using SW, TW and DW as washing solutions, respectively. As expected, the leaching of soluble salts in water such as Ca and Mg which can be carbonated in the presence of CO_2 has reduced the uptake of CO_2, but the results have shown that significant amounts of CO_2 can be captured, even after washing treatment of coal fly ash.

Moreover, it can be also observed that the kinetic of the process seems to be affected by the used washing solutions. As reported in Fig. 4, at low pressure values (< 5 bar), among the three pre-washing fluids, sea water exhibited the highest uptake even if it is lower than the raw CFA. More interesting is the pressure range 5 - 7.5 bar. In this range the uptake of CFA pre-washed with tap water sharply increased overcoming the capacity of the raw CFA. After 7.5 bar the uptake capacity of the CFA pre-washed with distilled water sharply increased showing the same behaviour of the CFA pre-washed with tap water. At a pressure of about 12.5 bar the uptake capacity of the CFA treated with tap water equaled the uptake of CFA treated with distilled water. Observing the partial CO_2 uptake in function of pressure, shown in Table 4, it can be noted that more than 67 wt % of the total CO_2 was captured in the fourth step (i.e. 7.5 bar) when TW was used as pre-washing solution; the same result was obtained in the fifth step (i.e. 10 bar) using SW and DW. It is worth to underline that the direct gas-solid carbonation of raw fly ash allowed to achieve only a total CO_2 uptake of about 50 wt % at 7.5 bar.

Leaching tests

The results of the leaching tests performed on the residues of gas-solid carbonation treatment are reported in Table 5 and showed the effects of carbonation on metal immobilization, presumably controlled by pH reduction and by pre-washing treatment. Considering

Table 4. Partial carbon dioxide uptake capacity as function of pressure, expressed as % of maximum captured.

	Pressure [bar]					
	1	2.5	5	7.5	10	15
Carb CFA	11.3	26.4	37.7	52.7	80.2	100
SW Carb CFA	8.3	24.0	37.4	49.7	64.0	100
DW Carb CFA	4.4	6.5	13.0	19.9	66.0	100
TW Carb CFA	6.3	11.7	20.4	67.2	79.0	100

Table 5. Leaching test results on untreated (Raw CFA), 35°C carbonated ash (Carb CFA) and 35°C carbonated ash pre-washed with SW (SW Carb CFA), DW (DW Carb CFA) and TW (TW Carb CFA); comparison with Italian landfill acceptance criteria [31].

Element	Concentration [mg/L]					Limit concentration landfills [mg/L]		
	Raw CFA	Carb CFA	SW Carb CFA	DW Carb CFA	TW Carb CFA	IW	n-HW	HW
Ba	1.03	0.59	0.38	0.41	0.33	2	10	30
Cd	0.00	0.00	0.00	0.00	0.00	0.004	0.1	0.5
Cr	0.06	0.04	0.00	0.00	0.00	0.05	1	7
Cu	0.03	0.00	0.01	0.00	0.00	0.2	5	10
Mo	2.19	2.28	0.88	2.80	2.54	0.05	1	3
Ni	0.20	0.00	0.02	0.02	0.02	0.04	1	4
Pb	0.22	0.02	0.04	0.05	0.04	0.05	1	5
Sb	0.43	0.12	0.06	0.20	0.18	0.006	0.07	0.5
Se	0.54	0.45	0.18	0.60	0.58	0.01	0.05	0.7
Zn	0.05	0.01	0.01	0.00	0.01	0.4	5	20
Cl^-	869.40	871.47	3,431.06	123.45	164.20	80	1,500	2,500
SO_4^{2-}	1,798.10	1,911.30	2,564.71	2,720.32	2,768.59	100	2,000	5,000

IW inert waste; n-HW non-hazardous waste; HW hazardous waste

the SW pre-washed and carbonated CFA, the leaching of heavy metals such as Ba, Mo, Se, and Sb (that for untreated material represent the most problematic elements) was significantly affected by the pre-washing and carbonation treatment, resulting in reduction of leaching concentrations (> 60 %). With regard to the other species, it is noted that the minimum solubility of Cd, Cu, Ni, Pb and Zn is attained in the pH range 7 - 10, values obtained after the carbonation process; in fact, the leachate concentrations fulfilled with regulatory limits for disposal of to landfills for inert waste. It can be noted that the carbonation process was not effective to immobilize heavy metals such as Mo, Se and Sb and their leaching exceeded the limits for disposal of to landfills for non-hazardous waste. Also leaching of chlorides and sulphates was unaffected by pre-washing and carbonation treatment.

XRD Analysis of SW prewashed and carbonated CFA

Having achieved the best results in terms of lower leaching using SW as pre-washing solution, an XRD analysis was carried out on SW pre-washed CFA before and after the carbonation treatment. The XRD characterization, shown in Fig. 5, underlined the presence of:

- original coal minerals (i.e. calcite ($CaCO_3$), gypsum ($CaSO_4 \cdot 2H_2O$) and quartz (SiO_2));
- new mineral phases formed during coal combustion process (i.e. anhydrite ($CaSO_4$) and ettringite ($3CaO \cdot Al_2 \cdot 3CaSO_4 \cdot 32H_2O$));
- new mineral phases formed by SW treatment and drying (i.e. halite (NaCl), brucite ($Mg(OH)_2$), portlandite ($Ca(OH)_2$));
- new mineral phases formed by carbonation test (i.e. calcite ($CaCO_3$) and magnesium calcium carbonate ($MgCa(CO_3)_2$));

The presence of a significant amount of calcite was presumably due to the natural carbonation occurred upon contact with atmospheric air in the ash disposal site as also found by Muriithi et al. (2013) [22]. The high amount of portlandite $Ca(OH)_2$ highlighted the occurred hydration process of the fresh material, essential for the further carbonation reaction. Indeed it has been observed that the reaction between the gas and the solid state material did not occur in absence of water and

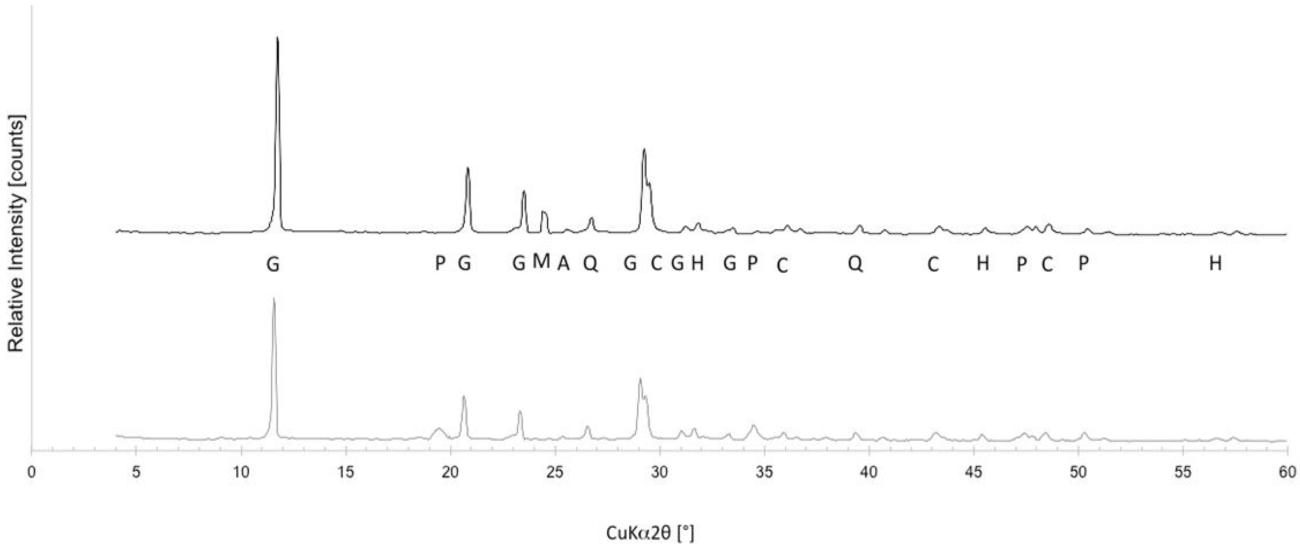

Fig. 5. Comparison between XRD Pattern of SW pre-washed CFA (light grey line) and SW pre-washed and carbonated CFA (black line) (A – Anhydrite, C - Calcite, E – Ettringite, G – Gypsum, H – Halite, M – Magnesium Calcium Carbonate, P – Portlandite, Q – Quartz).

water appears to be one of the most important factors in mineralization [23].

The comparison between XRD of SW pre-washed CFA and SW pre-washed and carbonated CFA evidences the disappearance of the portlandite peaks because of its carbonation and precipitation as calcite, the decomposition of ettringite in gypsum and the formation of magnesium calcium carbonate as result of reaction between brucite $Mg(OH)_2$ and carbon dioxide.

Economic evaluation

In order to quantify the advantages and drawbacks to include a pre-washing step in the carbonation process of CFA, a preliminary economic analysis was performed considering the cost related to the treatment of the wastewater produced during the pre-washing, the cost of carbon dioxide storage and the cost of the residue's final disposal. The unit costs related to the pre-washing liquids, the disposal and the wastewater treatment were obtained from Turton et al. [24] and are summarised in Table 6. The cost for the CO_2 storage was quantified in 9.5 \$/t CO_2 according to the values reported by Rubin et al. [25].

Different scenarios were considered in order to have a more comprehensive evaluation.

Scenario 1: base case represented by the untreated CFA; this scenario is used as reference to compare the other cases. In this case the CFA are disposed of in landfill for hazardous waste. The emission of CO_2 is not reduced and all the amount emitted needs to be stored. Based on the values reported in Table 5, due to the concentration of Mo, Sb and Se, the ashes must be

Table 6. Utility, disposal and treatment costs.

Utility / treatment	Cost
Processes cooling water (30/40/45ºC)	14.8 \$/1000 m^3
Distilled water	1 \$/1000 kg
Waste disposal – hazardous	1100 \$/t
Waste water treatment – Tertiary (filtration, activated sludge and chemical processing)	56 \$/1000 m^3

disposed of in landfill for hazardous waste.

Scenario 2: it is represented by the carbonated CFA without any further treatment. According to carbonation tests, the CFA have the potential to retain 169.8 g_{CO_2}/kg_{CFA} that corresponds to a global reduction of 1.4 % of the total amount sent for storage. However, the carbonation process was not able to reduce the concentration of Mo, Sb and Se to comply with the limits for disposal of in non-hazardous waste landfill. As for scenario 1, CFA must be disposed of in landfill for hazardous waste.

Scenario 3: it is represented by the CFA pre-washed with sea water and then carbonated. As expected the carbon dioxide uptake is reduced compared to the previous scenario. A value of 119.3 g_{CO_2}/kg_{CFA} was observed, reducing the amount sent for storage of 0.99 %. The pre-washing step would generate 562.460 m^3/y of wastewater that based on the chemical composition reported in Table 3 requires tertiary treatment for its appropriate management. Regarding the carbonated CFA even it is evident from the analysis reported in Table 5 that the pre-washing step was beneficial in reducing the concentration of most of the elements, Se, chlorides and sulphates are still in the range for disposal of waste to hazardous landfill.

Scenario 4: it is represented by the CFA pre-washed with distilled water and then carbonated. In this case the pre-washing step reduced the CO_2 uptake capacity to 159.2 g_{CO_2}/kg_{CFA} allowing a reduction of 1.3 % the amount sent for storage. As the previous scenario, the wastewater generated need tertiary treatment and the carbonated CFA needs to be disposed of in hazardous waste landfill due to the Mo, Sb, Se and sulphates concentration. Moreover, this scenario is penalized by the cost of the distilled water used for the pre-washing process and reported in Table 6.

Scenario 5: it is represented by the CFA pre-washed with tap water and then carbonated. For this case the uptake capacity was 148.7 g_{CO_2}/kg_{CFA} correspondent to a 1.2 % reduction of the carbon dioxide sent for storage. Considerations about the wastewater produced and carbonated CFA are analogous to the scenario 4. The cost correspondent to the tap water was evaluated according to the data reported in Table 6.

The contribution of storage, wastewater treatment, and disposal on the total cost for all 5 scenarios is shown in the histogram reported in Fig. 6.

From the comparison it is clear that all cases have an equal penalty due to the storage as hazardous material since it was not possible to reach the target concentration for all the elements. The reduction of carbon dioxide sent for disposal is limited since in the best case only the 1.4 % of the total CO_2 emitted can be sequestrated in the CFA. Moreover, scenario 4 is further penalized by the cost of distilled water used as washing liquid. Considering only the economy of the process appears that the pre-washing is not a feasible solution to reduce the environmental impact of the management of CFA. However, it should be noticed that the pre-washed CFA

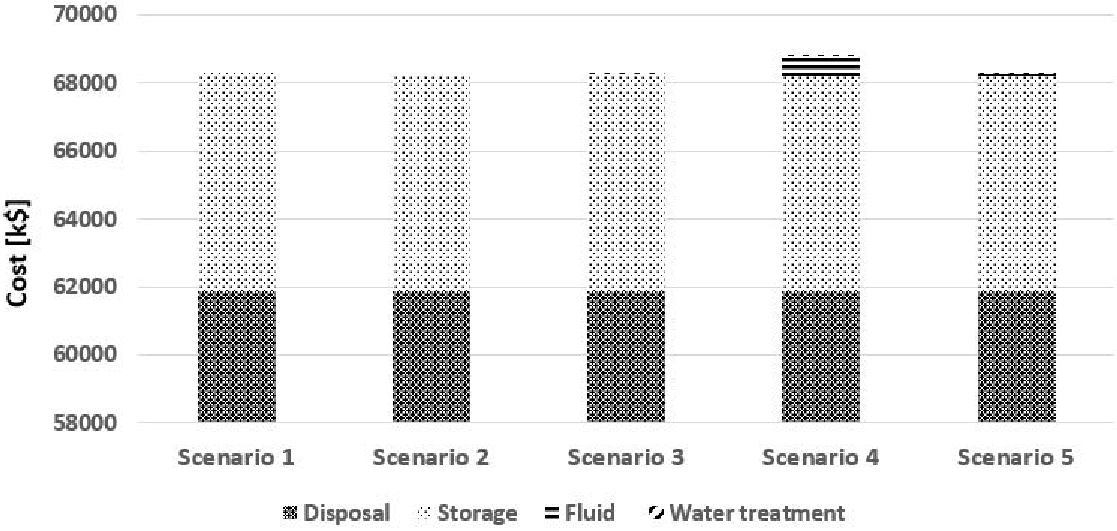

Fig. 6. Economic comparison between the scenarios considered.

with SW represented an interesting option to approach the limit imposed for disposing of the ashes in landfill for non-hazardous waste since only selenium, chlorides and sulphates were above the limit requested. High selenium concentrations in CFA were reported by different researches focused on the definition of the selenium oxidation state and its mobility with pH [26 - 28]. Mbagwu [29] studied the feasibility of using fly-ash amendments to produce selenium adequate crops showing a good potential on low-selenium soils.

Nevertheless, the transition between being an essential element for animals (> 0.05 ppm) and being toxic (5ppm) is quite narrow and the selenium management should be carefully considered [30].

As hypothetical condition, if the CFA pre-washed with SW could be disposed of in non-hazardous waste landfill, the disposal cost would drop from 1100 to 36 $/t reaching 87 % cost reduction compared to pure carbonation process of Scenario 1. Opportunities are still open in this topic and further researches are necessary to economically target the removal of specific elements.

CONCLUSIONS

The influence of CFA pre-washing on carbonation and ashes final disposal was studied from a qualitative and an economic point of view. Sea, tap and distilled water were considered as pre-washing solutions. The results highlighted how none of the liquids considered was able to reduce the impact of the carbonated ash. However, among all, the pre-washing with sea water reached a sensible improvement of the solid residue where only selenium, chlorides and sulphates resulted outside the range for a disposal in landfill for non-hazardous waste. From the economic point of view this solution is economically supported by the free availability of sea water. The economic analysis performed could be considered as a preliminary tool for process screening, whilst a more detailed analysis should consider also the capital costs.

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