



CO₂ sequestration and simultaneous zeolite production by carbonation of coal fly ash: Impact on the trapping of toxic elements

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1 **CO₂ sequestration with simultaneous zeolite production and toxic elements**

2 **trapping by carbonation of Coal Fly Ash**

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11 **ABSTRACT**

12 Coal-fired power plants are main contributors to atmospheric CO₂ emissions. They also produce
13 huge amounts of coal fly ash (CFA) waste, which is typically landfilled, posing significant
14 environmental risks due to its high content of potentially toxic elements (PTE). However, CFA
15 is an alkaline aluminosilicate-rich waste, which offers the possibility of CO₂ mineral capture and
16 the production of economically-relevant mineral by-products such as zeolites. Yet, the combined
17 carbonation and zeolite production from CFA resulting in PTE trapping has never been
18 explored. Here we show that under mild hydrothermal conditions (150 °C) and depending of
19 process parameters such as pH and background alkali metal ion in alkaline (bi)carbonate
20 solutions, a carbonation efficiency of up to 79%, with a net CO₂ mineral capture of 0.045 g/kg
21 CFA can be achieved, even when using a low Ca and Mg (3.72 wt% CaO, 1.74 wt% MgO)
22 Class F fly ash. Moreover, amorphous zeolitic precursors and different crystalline zeolites (yield

up to 60 wt%) are simultaneously obtained, and PTE in CFA are effectively trapped into the newly formed calcite, zeolitic precursors, and zeolite phases. These results have important implications for carbon capture and storage, as well as for the safe reutilization and disposal of CFA waste.

INTRODUCTION

Coal combustion is the second energy source most used worldwide, with a consumption of 1.4 billion tonnes in 2018, 4% higher than the previous year.¹ It accounts for more than 30% of the global yearly anthropogenic CO₂ emissions, being a key contributor to climate warming and the associated changes in the oceans and atmosphere equilibria.¹ Coal firing also produces huge amounts of coal combustion waste products (CCP), which include coal fly ash, CFA (~70 % of CCP),² bottom ash, boiler slag, and fluidized bed combustion wastes.^{3,4} Global CFA generation was over 700 million tons (Mt) per year in 2012^{3,4}, and this figure kept growing in recent years⁵. Management of the huge amounts of CFA waste produced globally is a significant problem, with important economic, health, and environmental implications.⁴ Worldwide, ~70% of CFA is disposed of in ash ponds or landfills, the rest being recycled for several applications.³ Only in the U.S., 34 Mt of CFA were generated in 2016,^{1,6} of which 20 Mt were used mainly as a construction material due to its pozzolanic properties (e.g., concrete products, blended cements, road base) or in mining applications; still, 14 Mt of CFA were discarded and subjected to ponding or landfilling.⁷ In addition to the huge area needed to store or dispose of CFA,⁸ this waste includes a significant amount of potentially toxic trace elements (PTE)⁹⁻¹¹ which may

limit its recycling capability and make CFA spilling or leaching a hazard resulting in contamination of soils, water bodies and groundwater.^{12–16}

Reutilization processes for CFA waste other than its use in construction include: (i) synthesis of zeolites^{17–19}, which are microporous crystalline aluminosilicates formed by corner-sharing tetrahedral groups conforming voids and channels that allow the adsorption of gases, metal ions and organic molecules.^{9,18,20–22} Due to their pore characteristics and high ion exchange capacity,²³ CFA-derived zeolites are employed for CO₂ (and other pollutant gases) capture, removal of toxic metals, water decontamination, and soil improvement.^{18,19,24–26} CFA-derived zeolite synthesis has focused on the use of NaOH (and KOH) for hydrothermal, alkali fusion, or microwave-assisted production.¹⁹ A few works explored the use of alkali carbonate activators for hydrothermal zeolite synthesis (120 °C), reporting a limited zeolite yield but, interestingly, resulting in calcium carbonate precipitation.²⁰ The latter suggests that the combined carbonation and zeolite synthesis using CFA is feasible. Although several works have shown that zeolites formed after CFA can be used to capture PTE^{18,19}, no study has evaluated the actual trapping of PTE present in the CFA used for zeolite synthesis; and (ii) to a lesser extent, CFA has been used for carbon capture and storage (CCS) via accelerated mineral carbonation.^{27–33} Despite the limited foreseen contribution of CFA to mineral carbon sequestration (~7.6 Mt/CO₂/y),³⁴ its use for carbon capture, utilization and storage (CCUS) must be considered as it could contribute to the reduction of the C footprint of coal-fired power plants,^{1,6,30} result in the production of economically-valuable by-products such as carbonates and zeolites, and in a reduction of the

63 potential leaching of PTE during CFA disposal.³⁰ Previous works have evaluated the
64 carbonation efficiency (CE) and net CO₂ capture of CFA from different sources and
65 compositions under a range of process conditions (e.g., direct and indirect carbonation, dry vs.
66 wet processes, pH, *T*, solid/solution ratios, aqueous solution composition, *p*CO₂).^{3,35} These
67 studies show that CE values are typically <<80%^{5,36}, and the net CO₂ capture can be as low as
68 ~8 kg per ton of CFA. With a few exceptions (CFA with CaO + MgO > 20 wt%^{2,11,33}), the
69 average CaO content in CFA is 7±3 wt%,³⁵ resulting in relatively low values of effective CO₂
70 mineral capture. The limited CE and relatively low net CO₂ capture capacity have been strong
71 handicaps for the widespread implementation of CCS strategies for CFA. In spite of some
72 efforts to improve CE values,^{5,37} progress in this direction has been limited, mostly because the
73 mechanisms of CFA carbonation are not fully understood. For instance it has been assumed that
74 only the easily leached crystalline phases containing calcium (e.g., CaO and Ca(OH)₂) were able
75 to feed the solution for CFA carbonation.^{30,33} However, a significant fraction (≥50%) of CaO
76 (and MgO, which can also contribute to CO₂ mineralization) in CFA is present in the not-so-
77 easily leachable amorphous aluminosilicate phase, which typically accounts for ≥70 wt% of
78 CFA.¹¹ It is thus necessary to better understand the carbonation mechanisms of CFA and to
79 explore means to effectively leach the Ca and Mg present in such amorphous phase in order to
80 achieve the highest possible CE. Moreover, no work has evaluated the potential of CFA
81 carbonation as a means to achieving an effective CCUS by the simultaneous production of
82 valuable zeolite by-products, while trapping PTE.

The aim of the present work is to experimentally disclose the key features of CFA carbonation under mild hydrothermal conditions using alkaline (bi)carbonate solutions, combined with the formation of zeolites and the effective capture of PTE present in CFA.

MATERIALS AND METHODS

Characterization of unreacted Coal Fly Ash and reaction products. CFA used in this study was provided by the Compostilla thermal power plant in León (Spain). The concentrations of major/minor and trace elements in unreacted CFA were determined on a Bruker AXS S4 Pioneer X-ray fluorescence (XRF) equipment. Identification and quantification of mineral phases in unreacted CFA and solid products collected after carbonation experiments (see below) was performed by powder X-ray diffraction (XRD), using a X'Pert PRO diffractometer (PANalytical) with the following instrumental parameters: Cu-K α radiation, Ni filter, 40 mA current, 45 kV tension, 3-70 °2 θ exploration range, 0.004 °2 θ step size, and 29.84 s per step. The HighScore Plus 2.2.4 software (PANalytical) was used to process the XRD patterns and to identify mineral phases by matching the experimental diffraction patterns to those included in the PDF-2 database.³⁸ Quantitative mineralogical analysis was performed by Rietveld analysis³⁹ using the Internal Reference Method⁴⁰ (5 wt% crystalline Si powder added as internal standard) and the crystal structures provided by the American Mineralogist Crystal Structure Database (Supplementary Material Table S1). Solids were also analysed by Fourier transform infrared spectroscopy (FTIR) with an attenuated total reflectance (ATR) sample holder (Jasco 6200 FTIR) in the frequency range 400–4000 cm⁻¹, with a spectral resolution of 2 cm⁻¹, step size of

0.48 cm⁻¹ and 126 accumulations. Thermogravimetric analyses, TGA (TGA-DSC3+, Mettler Toledo) were performed under flowing N₂ using a linear heating rate of 20 °C min⁻¹, from 30 to 950 °C. Reactant CFA and solid products were also analyzed by field emission scanning electron microscopy (FESEM, Auriga Carl Zeiss SMT) equipped with energy dispersive X-ray spectroscopy (EDS). Prior to analysis, solids were carbon coated. Further ultrastructural and compositional details of reactant and product phases were studied by means of transmission electron microscopy (TEM) on a FEI TITAN at 300 kV acceleration voltage, and equipped with a high angle annular dark field detector (HAADF) for Z-contrast imaging. Analytical electron microscopy (AEM) was performed by EDS microanalysis (under scanning-TEM operation mode) using the thin-foil method⁴¹ and *k*-factors determined using standard minerals of known composition. Once each carbonation run was completed, the concentration of selected ions in solution after filtration was determined by ICP-OES (Perkin Elmer, Optima 8300 or Varian 720ES). Finally, N₂ sorption isotherms of unreacted CFA and carbonation products were performed at 77 K on a TriStar 3000 equipment (Micromeritics), after sample degassing at 150 °C for 12 h under vacuum (0.07 torr) in a Flow Prep device (Micromeritics).

CFA carbonation experiments. To disclose the effect of pH and background electrolyte on carbon capture and zeolite synthesis efficiency, direct carbonation experiments in aqueous solution were performed under hydrothermal conditions (150 °C):³³ (i) without dissolved inorganic carbon (DIC) (control, A-experiments), and (ii) with dissolved sodium or potassium (bi)carbonate (N-, and K-experiments, respectively). Table 1 shows details of the different

experimental runs. A T of 150 °C was selected to favour the dissolution of mullite and quartz present in the unreacted material.⁴² 0.0043 mol mL⁻¹ Na₂CO₃, NaHCO₃, K₂CO₃ and KHCO₃ solutions were prepared using ultrapure MilliQ water (resistivity 18.2 MΩ·cm, Millipore) and >97%-grade solid reactants from Sigma-Aldrich. A relatively high reactant concentration was selected in order to ensure an excess of carbonate and to achieve a range of pH values from ~8 up to ~12. In a previous work we showed that a similar alkali (bi)carbonate reactant concentration was optimal for the carbonation of pseudowollastonite (CaSiO₃).⁴³ Note that such alkali metal (bi)carbonate solutions are a proxy for alkali metal hydroxide solutions in which CO₂ gas is dissolved, and the solutions can be regenerated via CO₂ injection,⁵ which could be the actual protocol for implementing *ex situ* carbonation involving CO₂ capture at emission point sources. 1 mL of the solutions was added to 500 mg of CFA in a PTFE vessel (polytetrafluoroethylene, 3 mL total volume). Afterwards, the PTFE vessel was inserted into a steel reactor designed for high T - P conditions. After sealing, the reactors were heated to 150 °C for 72 h (longer runs for up to 7 days showed no additional changes in the progress of the reaction). Then, the autoclaves were cooled down to room T and opened. The content of the vessels was immediately filtered (0.2 µm membrane filter, Millipore) and the solids were oven-dried for 24 h at 60°C. The pH of the solutions before and after the experiments was measured at room T using a glass electrode (Metrohm) calibrated with three standard solutions (pH= 4.01, 7.01 and 10.01 at 25 °C) with ±0.01 uncertainty. In order to ensure statistical representativity, all runs were performed in triplicate.

Calculation of Carbonation Efficiency (CE). We considered that all amorphous and

crystalline Ca- and Mg-containing phases (excluding already formed CaCO_3) in unreacted CFA

can contribute to the leaching of Ca and Mg in solution and therefore, to the effective

carbonation of CFA.^{35,44} Multiple equations have been proposed to calculate the CE for CO_2

sequestration.^{5,28,30,37,45,46} In this study, we calculated the CaO contained in the calcite present in

unreacted CFA using eq. 1:

$$iCaO = wt_{CaCO_3} \times \frac{M_{CaO}}{M_{CaCO_3}} = 0.56 \text{ wt \%} \quad (1)$$

where wt_{CaCO_3} is the wt% of CaCO_3 determined by the XRD analysis of the unreacted material

using the Rietveld method, M_{CaCO_3} is the molar mass of CaCO_3 (100 g mol^{-1}) and M_{CaO} is the

molar mass of CaO (56 g mol^{-1}). $iCaO$ is subtracted from the total CaO + MgO content of the

unreacted material, to determine the theoretical sequestration capacity of our CFA using the

Stenoir formula,^{28,45,46}

$$Th_{Cc} = (wt_{CaO} - iCaO) + wt_{MgO} = 4.87 \text{ wt \%} \quad (2)$$

where wt_{CaO} and wt_{MgO} are the content of CaO and MgO, respectively, in unreacted material

measured by XRF. Finally, we adapted the equation used by Dananjayan et al.²⁸ to calculate CE

(%) as follows:

$$CE = \frac{[(\Delta \text{wt \% } 590^\circ\text{C} - 800^\circ\text{C}) \times (M_{(Ca,Mg)CO_3} / M_{CO_2})] - 1}{Th_{Cc}} \times 100 \quad (3)$$

where $(\Delta \text{wt \% } 590^\circ\text{C} - 800^\circ\text{C})$ was calculated from TGA analyses, and $M_{(Ca,Mg)CO_3}$ is the molar

mass of calcite in the products, which can include a fraction of Mg replacing Ca (i.e., Mg-

calcite) (see Results below).

Leaching experiments. Continuous flow-through experiments were performed to

evaluate the PTE leaching capacity of both the unreacted and reacted CFA. Leaching

experiments were performed at 25 °C using PTFE reactors ($V_{\text{tot}} = 30$ mL; lined with double

polycarbonate 0.2 μm filters to prevent solids loss) under constant magnetic stirring. 1 g of

solids was placed in each reactor and the experiments started by continuously flowing MilliQ

water at a rate of 2 mL min⁻¹. In order to evaluate the effect of pH on PTE leaching, experiments

were performed at a near-neutral pH 6 and at an alkaline pH 10 (adjusted using 1M NaOH), the

latter corresponding to the natural pH of the studied CFA (Table 1). Aliquots of the effluent

solution were collected at predefined time intervals (30 min, 60 min, 90 min, 3 h, 6 h, 9 h and 24

h) and their PTE content was determined by ICP-MS on a NexION 300D equipment.

Code	Solutions	Initial pH	Final pH	Zeolitic content (wt%)	Carbonate content (wt%)	Mg content (mol%)	CE (%)
A1	MilliQ H ₂ O	9.26	9.8	0	1	0	0
N1	3.4M Na ₂ CO ₃	11.63	10.77	60	4.9	1.19	79.26
N2	3.4M NaHCO ₃	8.26	9.79	0	3.2	7.74	34.29
K1	3.4M K ₂ CO ₃	12.02	11.35	33	3	1.36	44.96
K2	3.4M KHCO ₃	8.2	9.32	0	2.6	2.43	33.88

Table 1. Experiment codes, solution composition, initial and final pH, zeolitic content, carbonate content, Mg content in calcite and Carbonation Efficiency (CE) for each experimental run.

RESULTS AND DISCUSSION

Chemistry and mineralogy of unreacted CFA. XRF analysis (Table S2) shows that Si, Al and

Fe account for more than 80 wt% (expressed as oxides) of the CFA. Compositionally, this CFA

180 can be classified as Class F, the most common and abundant type of CFA worldwide⁴⁷. The
181 relatively low CaO plus MgO content (5.43 wt%), which approaches the average alkaline-earth
182 metal oxide content of CFA³⁵, poses a limit to the maximum net CO₂ capture capacity of this
183 CFA. Several PTE are present in significantly high concentrations (e.g., Ba=1345 ppm; V=849;
184 Cr=189; As=150 ppm), also on the same range of concentrations reported for other CFAs^{11,48}.
185 These results underline the potential toxicity of CFA leachates. XRD analysis (Figure 1a) shows
186 that this CFA is composed of a glass fraction (95±2 wt%), graphite (2.0±0.1 wt%), quartz
187 (1.2±0.1 wt%), mullite (1±0.1 wt%), calcite (1±0.1 wt%) and traces of hematite (<1 wt%). The
188 presence of calcite in the unreacted fly ash is likely due to partial hydration of free CaO to
189 Ca(OH)₂ and its subsequent carbonation to CaCO₃ during sample handling. Due to the low
190 calcite content in this CFA, very low intensity (not easily visible) carbonate bands were detected
191 in FTIR spectra (Figure 1b). FTIR analysis also shows high intensity bands at 1009 cm⁻¹ and
192 650-720 cm⁻¹, corresponding to the asymmetric and symmetric vibration of T-O (T = Si or Al),
193 respectively, and at 400-500 cm⁻¹, corresponding to T-O bending as well as combination modes
194 of the aluminosilicate glass.^{49,50} FESEM observations show that the CFA is made up of spheres
195 and cenospheres (and a few plerospheres) with size ≤ 20 μm (Supplementary Material, Fig. S1).
196 TEM-AEM analysis shows that this CFA is mainly composed of amorphous (see diffuse haloes
197 in SAED patterns) micrometer-sized aluminosilicate glass spheres and scarce C-rich aggregates
198 with embedded aluminosilicate spheres (Fig. S2). AEM point analyses (Table S3) yield the
199 following overall composition (wt%) for the spheres (N=6): 50.7±2.5 SiO₂, 32.7±1.8 Al₂O₃,

200 5.2 ± 1.1 Fe₂O₃, 3.1 ± 1.1 MgO, 2.6 ± 2.5 CaO, 3.8 ± 0.6 K₂O, 1.4 ± 0.2 Na₂O, and 0.6 ± 0.2 TiO₂,
201 values very similar to those of the bulk CFA determined by XRF analysis (Table S2). This is not
202 surprising considering that the glass phase accounts for nearly 95 wt% of CFA. Our AEM
203 results also show that the amorphous spheres include ~70 % and ~100 % of the total CaO and
204 MgO in the CFA, respectively. This underlines that to achieve the highest possible CE, the glass
205 phase has to be fully dissolved. EDS elemental maps show that the spheres include different
206 PTE, and quantitative AEM point analyses (Table S3) yield the following average contents for
207 selected PTE: V= 633 ppm, As= 416 ppm, Mn= 66 ppm; Cr= 16 ppm; Zn= 66 ppm, values
208 consistent with XRF results.

209 The chemical and mineralogical composition determined for our CFA is in very good
210 agreement with that reported by Moreno et al.¹¹ for CFA from the same source and, despite the
211 reported variability,³⁵ is very similar to that of other Class F CFAs.^{9,18–23,30,31} We are thus
212 confident that our CFA is representative for Class F CFAs from several coal-fired power plants.

213 **Carbonation/zeolitization reaction.** XRD patterns of reacted CFA are shown in Figure
214 1a. Rietveld quantification shows that in Na₂CO₃ (N1) runs, a zeolite yield of ~60 wt% is
215 obtained, which is substantial for hydrothermal CFA-derived zeolite synthesis (typical yields are
216 in the range 20-65%).⁵¹ Analcime (8 ± 2 wt%), Na-chabazite (17 ± 6 wt%), NaP1 zeolite (31 ± 9
217 wt%), and hydroxysodalite (4 ± 1 wt%) are identified, along with calcite (5 ± 1 wt%), hematite
218 (<1 wt%), quartz (<1 wt%), mullite (<1 wt%) and glass (33 ± 9 wt%). In K₂CO₃ (K1) runs, the
219 dissolution of the glass fraction and the subsequent precipitation of zeolites is more limited. Our

quantitative XRD results show the presence of K-zeolite (33 ± 9 wt%), calcite (3.4 ± 0.8 wt%), hematite (<1 wt%), quartz (<1 wt%), mullite (<1 wt%) and glass (61 ± 14 wt%). XRD analyses show no zeolites, nor any changes in terms of phase composition in N2, K2 and control (A1) runs, as compared with unreacted CFA.

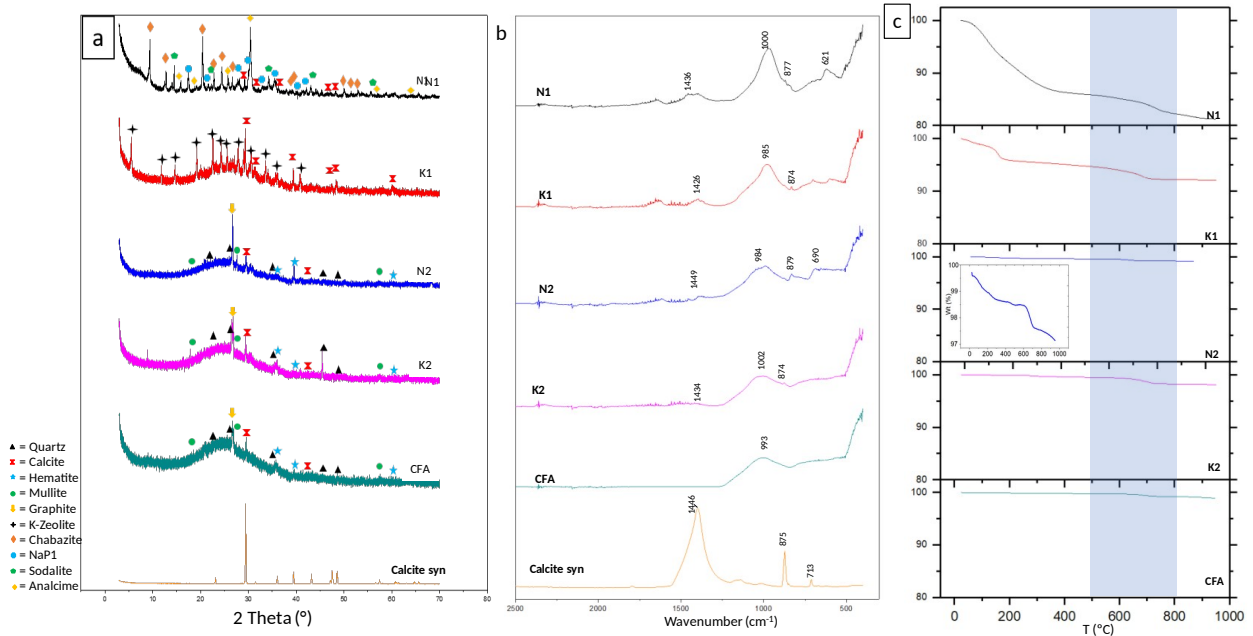


Figure 1. Unreacted CFA and products of its reaction in different carbonate solutions at 150°C; Na₂CO₃ (N1), K₂CO₃ (K1), NaHCO₃ (N2), KHCO₃ (K2). (a) XRD patterns showing the Bragg peaks of the different crystalline phases; legend in inset; (b) FTIR spectra; and (c) TGA traces (insets show TGA traces with enlarged Y-axis). The shaded blue area represents the starting and the final *T* of carbonate decomposition (550-800 °C).

FTIR spectra of samples K2, N2, K1 and N1 show well-defined bands at ~ 710 cm⁻¹, ~ 875 cm⁻¹ and/or ~ 1440 cm⁻¹ that confirm the new-formation of calcite (Fig. 1b). They also show the broad band at ~ 1000 cm⁻¹ (T-O asymmetric stretching) of aluminosilicate phases. Bands at ~ 650 - 870 cm⁻¹ corresponding to the T-O symmetric stretching, at ~ 442 - 503 cm⁻¹ corresponding to the T-O bending, and at 550 - 575 cm⁻¹ corresponding the double rings of

235 analcime,⁵² sodalite, NaP1 zeolite and Na-chabazite,⁵² as well as K-zeolite,⁵³ are observed in
236 runs N1 and K1 respectively. Solids collected after runs N2 and K2 (bicarbonate runs) show
237 similar T-O band as those described above. They also show the broad band at ~1000 cm⁻¹ (T-O
238 asymmetric stretching), and less intense (and poorly resolved) bands at ~650-870 cm⁻¹ (T-O
239 symmetric stretching) and the very intense, broad band at ~400-500 cm⁻¹ corresponding to the
240 T-O bending of aluminosilicate phases, consistent with the presence of unreacted CFA and
241 newly-formed zeolites (in the case of runs N1 and K1) (confirmed by TEM-SAED analysis, see
242 below).⁵⁴⁻⁵⁶ No changes are detected in the FTIR spectra of the control run (A1) as compared
243 with that of unreacted CFA. In combination with XRD, the FTIR results further demonstrate
244 that a hydrothermal treatment with pure water leads to no mineral or structural changes to CFA.

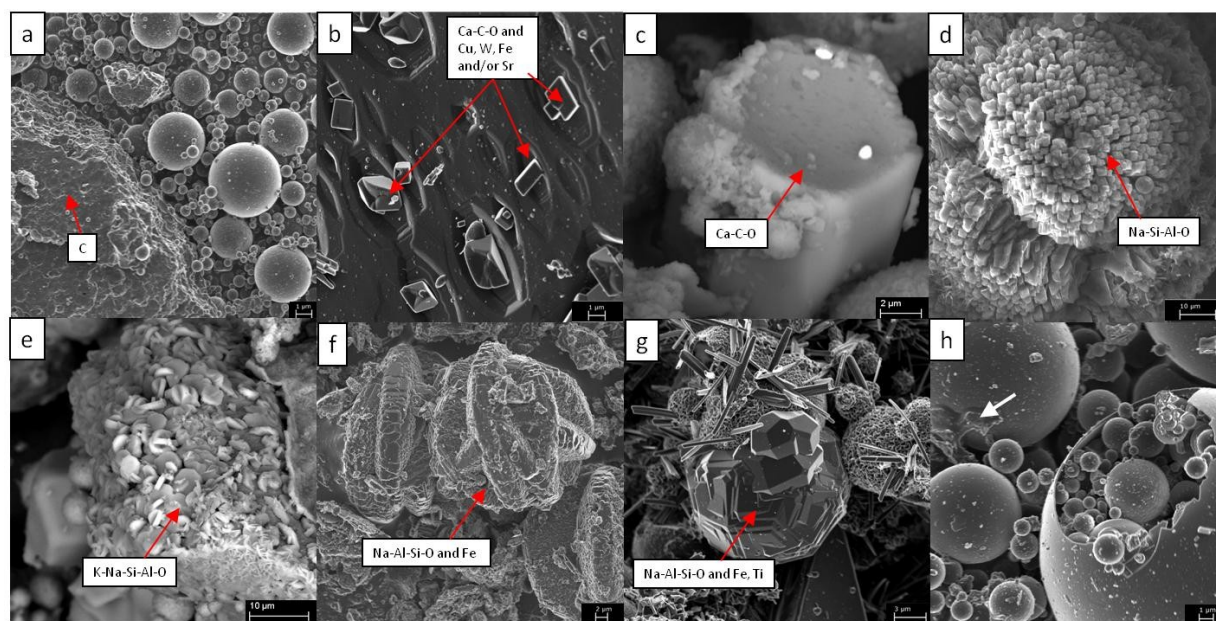
245 TG-DSC analyses (Fig. 1c) show that the starting material and all products display a
246 weight loss in the temperature range 550-800°C, related to the thermal decomposition of calcium
247 carbonate according to the reaction $\text{CaCO}_3 = \text{CaO} + \text{CO}_2$.⁵⁷ However, we observe that the
248 starting *T* for the thermal decomposition of carbonates differ among runs, suggesting that either
249 there are changes in calcite particle size (smaller size-fractions decomposing at lower *T* than
250 larger size-fractions) and/or that Mg partially replaces Ca in the calcite phase, forming a (low)
251 Mg-calcite, therefore lowering the starting decomposition temperature.^{58,59} Note that XRD
252 analyses show no (crystalline) magnesium carbonates. We performed unit-cell refinement using
253 Rietveld analysis to determine the Mg content in calcite using the method proposed by
254 Goldsmith and Graff (1958)⁶⁰ (results in Table 1). Calcite in unreacted CFA has no Mg. The

255 highest Mg content in newly-formed calcite is observed in N2 runs, followed by K2, K1 and N1
 256 runs. These results are in full agreement with TGA results and with the first derivate of the DSC
 257 analyses (Figure S3), showing a lower starting decomposition T for the Mg-calcites with the
 258 highest Mg content. We suggest that at a moderately alkaline pH (bicarbonate runs), the higher
 259 $[\text{Ca}^{2+}]/[\text{CO}_3^{2-}]$ ratio (closer to unity) as compared to higher pH runs (with higher $[\text{CO}_3^{2-}]$) could
 260 enable faster calcite growth favoring Mg incorporation.⁶¹ From the weight loss in the T range
 261 550-850 °C, CE values of 34%, 34%, 45% and 79% are obtained for K2, N2, K1 and N1 runs,
 262 respectively. TGA analyses show an additional weight loss at 105-200°C in N1, K1, N2 and K2
 263 runs. In the case of N1 and K1 runs, this is likely due to loss of zeolitic water. Conversely, in
 264 runs N2 and K2, which lack crystalline zeolites, the weight loss is likely due to the
 265 decomposition of residual NaHCO_3 and KHCO_3 according to the reaction $2\text{MHCO}_3 = \text{M}_2\text{CO}_3 +$
 266 $\text{CO}_2 + \text{H}_2\text{O}$, where M is a monovalent cation (K or Na). However, we cannot rule out the
 267 possibility that this weight loss is due to dehydration of an amorphous zeolitic precursor. In any
 268 case, it should be noted that Na_2CO_3 and K_2CO_3 (if present as a residual) would undergo melting
 269 at 850°C and 900°C, respectively, therefore not interfering with the calcium carbonate
 270 decomposition, nor releasing any CO_2 at lower T .⁶² In all runs, including the control and
 271 unreacted CFA, the limited initial weight loss at $T < 550$ °C is likely due to dehydration of
 272 amorphous silica.⁴³ Note that such a weight loss overlaps with the weight loss associated with
 273 zeolitic water in runs where zeolites (and zeolitic precursors) are formed.

274 FESEM images show the presence of calcite (as indicated by XRD analysis) in all

275 carbonation runs (Fig. 2). Calcite appears as micrometer sized rhombohedral crystals attached to
276 CFA spheres (Fig. 2b-c). Reacted CFA spheres have irregular surfaces coated by newly formed
277 precipitates (Fig. 2b-c). It was, however, not possible to clearly differentiate by EDS
278 microanalysis the composition of these precipitates from that of the unreacted spheres.
279 According to Murayama et al.²⁰ these coatings are most likely composed by new Si-Al phases
280 formed after partial dissolution of the spheres and re-precipitation at the sphere-solution
281 interface. Such newly-formed precipitates could act as a passivation layer on CFA particles,
282 acting in a similar way as the amorphous silica-rich surface layers formed during weathering of
283 primary silicate minerals.⁶³⁻⁶⁶ SEM-EDS analysis corroborates XRD analyses showing the
284 presence of NaP1 (Fig. 2d), Na-chabazite (herschelite) (Fig. 2e), hydroxysodalite/cancrinite, and
285 analcime (Fig. 2f) in N1 run, and K zeolite in K1 run (Fig. 2g).^{9,52} SEM-EDS analysis also show
286 that Sr, W and Ce are incorporated into the newly formed carbonates (Fig. S4a-b), V is trapped
287 in zeolite phases, and Cu is incorporated in both newly-formed phases (Fig. S4c-d). Conversely,
288 SEM-EDS analysis of carbonates formed in N2 and K2 experiments shows no trapping of PTE,
289 although we observe the presence of scattered shapeless coatings on some CFA spheres (Fig.
290 2h), likely corresponding to an amorphous zeolitic precursor,⁵⁵ as confirmed by TEM-SAED and
291 AEM analyses (see below). Due to the background signal from the underlying spheres we could
292 not clearly determine using EDS microanalysis whether or not PTE are trapped in these latter
293 precipitates. We argue that the extensive dissolution of the glass particles in N1 and K1 runs
294 favored the release and subsequent trapping of PTE into the newly formed carbonate and zeolite

295 phases. No trapping of PTE into the limited amount of newly formed crystalline phases (i.e.,
 296 carbonates) in runs N2 and K2 is detected by SEM-EDS, likely due to the limited dissolution
 297 and PTE release from the glass phase Yet it is likely that the newly-formed amorphous zeolitic
 298 precursors formed in the bicarbonate runs also trapped PTE (see TEM-AEM results below).



299 **Figure 2.** FESEM images of: (a) unreacted spheres of CFA and a graphite (C) particle; (b)
 300 calcite in N1; (c) calcite in K1; (d) NaP1 zeolite in N1; (e) K-zeolite in K1; (f) Na-chabazite
 301 (herschelite) in N1; (g) analcime in N1; and (h) large plerosphere (lower left) and solid spheres in
 302 run N2. The white arrow points to a shapeless deposit with features resembling an amorphous
 303 zeolitic precursor. The EDS elemental composition of the red-arrowed particles are shown in the
 304 insets.

306 TEM-AEM analysis of reacted CFA shows significant mineralogical and compositional
 307 changes in the case of run N1, i.e., the run with the highest carbonation and zeolitization level
 308 (Fig. 3). Aggregates of newly formed poorly crystalline zeolitic nanophase with diffuse Debye
 309 rings in the SAED pattern and with d_{hkl} values consistent with a Na-chabazite (precursor) phase
 310 are observed (Fig. 3a). In addition, well crystallized Na-chabazite crystals are identified by their

SAED pattern (Fig. 3b). HAADF images and corresponding EDS maps confirm the formation of Na-zeolites, which include different PTE (Fig. 3c-d).

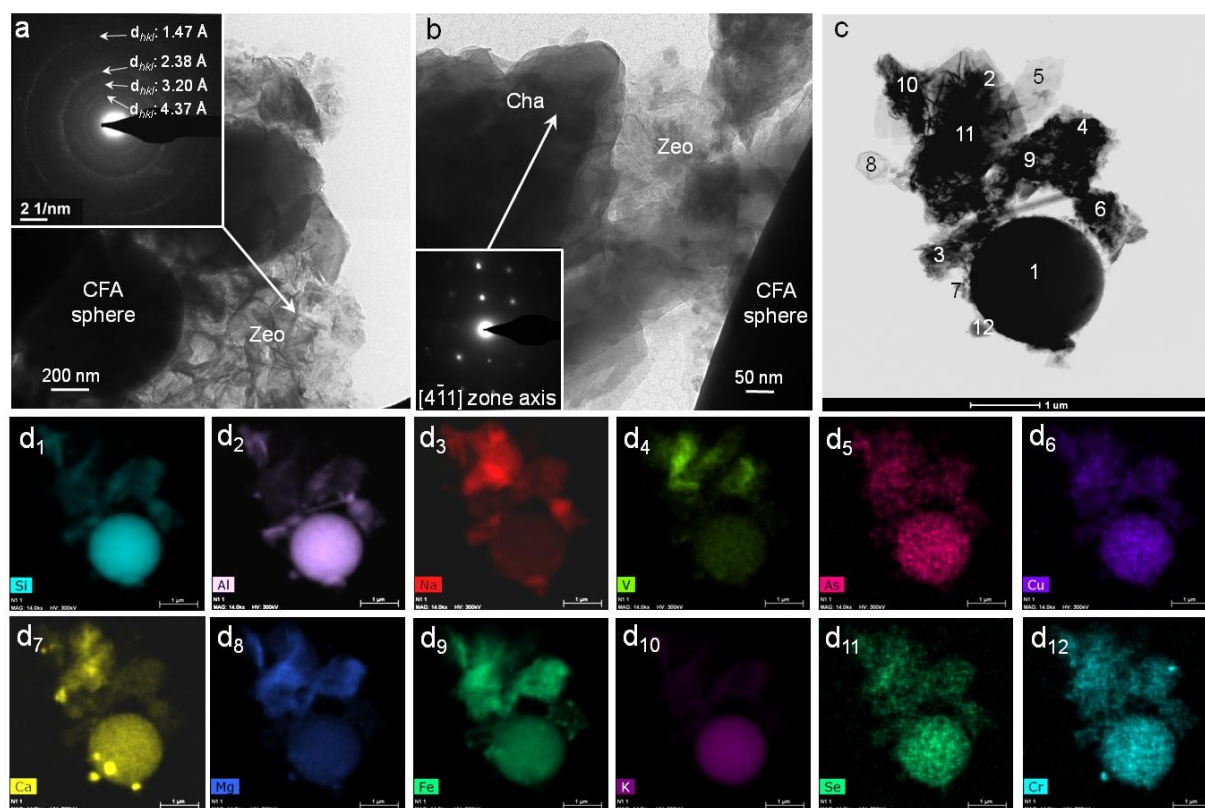


Figure 3. TEM-AEM analysis of reaction products of run N2. (a) Relict CFA sphere and newly formed zeolites (Zeo). The inset shows the SAED of the aggregate at the lower right. The diffuse Debye ring at the indicated d-spacing show the presence of a poorly crystalline precursor phase to Na-chabazite; (b) Large well-crystallized Na-chabazite (its [4-11] zone axis SAED pattern is shown in inset); (c) HAADF image of a sphere surrounded by newly-formed product phase. The numbers indicate AEM point analyses with composition reported in Table S4. (d1-d12) EDS elemental maps of the particles shown in (c).

Quantitative AEM point analyses (Fig. 3e and Table S4) demonstrate the presence of Na-chabazite with formula $\text{Na}_{3.4}\text{K}_{0.24}\text{Mg}_{0.28}\text{Fe}_{0.18}\text{Al}_6\text{Si}_{5.6}\text{O}_{24} \cdot 12\text{H}_2\text{O}$ (analysis 3 in Table S4), NaP1 with formula $\text{Na}_{6.32}\text{K}_{0.59}\text{Mg}_{2.69}\text{Fe}_{1.09}\text{Al}_{5.19}\text{Si}_{10}\text{O}_{32} \cdot 12\text{H}_2\text{O}$ (analysis 10 in Table S), and

325 hydroxysodalite with formula $\text{Na}_{5.53}\text{K}_{0.14}\text{Mg}_{0.09}\text{Fe}_{0.24}\text{Al}_{4.71}\text{Si}_6\text{O}_{24}(\text{OH})_2 \cdot 2\text{H}_2\text{O}$ (analysis 6 in Table
 326 S4) plus a Na-poor aluminosilicate phase with a Si/Al ratio of 0.7 (analysis 12 in Table S4),
 327 consistent with the presence of an amorphous (gel) zeolitic precursor.^{67,68} The zeolitic phases
 328 include significant amounts of PTE: up to 500 ppm Zn, 300 ppm V, and 800 ppm Cu in NaP1;
 329 up to 1000 ppm Cu, and 200 ppm As in hydroxysodalite, and up to 600 ppm Cu, 500 ppm Mn,
 330 500 ppm Zn, 3600 ppm Cr and 2400 ppm V in the amorphous zeolitic precursor (Table S4).
 331 Very similar results are observed in zeolitic products of run K1 (Fig. S5, Table S6), where K
 332 zeolite with a representative formula $\text{K}_{2.34}\text{Na}_{0.62}\text{Mg}_{0.68}\text{Ca}_{0.11}\text{Fe}_{0.22}\text{Al}_{3.33}\text{Si}_9\text{O}_{24} \cdot 7\text{H}_2\text{O}$ (analysis #5,
 333 Table S5) is identified. The newly formed K zeolite includes significant amounts of PTE: e.g.,
 334 up to 424 ppm V, up to 631 Cr and up to 406 Mn. In the case of the bicarbonate runs, TEM-
 335 SAED reveals the presence of aggregates made up of amorphous nanoparticles ~20-50 nm in
 336 size attached to the CFA spheres (Fig. S6). AEM analysis shows that in N2 runs they have a
 337 formula $\text{Na}_{3.56}\text{K}_{0.47}\text{Ca}_{0.74}\text{Al}_{5.97}\text{Si}_{10}\text{O}_{32} \cdot 12\text{H}_2\text{O}$ (analysis #3, Table S6), consistent with the
 338 formation of a (NaP1) zeolitic precursor. Similar nanosized amorphous zeolitic precursors have
 339 been observed previously.^{68,69} Interestingly, EDS mapping and AEM point analyses of CFA
 340 spheres in this same run show Na-enrichment (up to 2 wt% Na_2O ; analysis #2 in Table S6),
 341 which points to formation of zeolitic precursors blanketing the sphere. A relative high
 342 concentration of PTE such as Cu, V, and Mn is present in the reacted CFA spheres (Table S6).
 343 Altogether, these TEM-AEM results demonstrate that PTE originally present in CFA are
 344 preferentially incorporated into the newly-formed amorphous zeolitic precursor and zeolite

345 phases.

346 Finally, Brunauer-Emmett-Teller (BET) analysis⁷⁰ shows that the unreacted CFA and
347 the control A1 have a surface area of $1.1 \pm 0.1 \text{ m}^2\text{g}^{-1}$, whereas N1, K1, N2 and K2 have a surface
348 area of $20.4 \pm 0.7 \text{ m}^2\text{g}^{-1}$, $4.3 \pm 0.1 \text{ m}^2\text{g}^{-1}$, $2.1 \pm 0.1 \text{ m}^2\text{g}^{-1}$, and $1.2 \pm 0.1 \text{ m}^2\text{g}^{-1}$, respectively. These
349 results show that the formation of zeolites in N1 and K1 runs significantly increases the surface
350 area, as expected for the presence of such microporous solids. They also show that the best
351 absorbent product is achieved using Na_2CO_3 as alkaline activator. Interestingly, in the case of
352 run N2, the surface area increases $\sim 100\%$ as compared with unreacted CFA. This is consistent
353 with the formation of the amorphous zeolitic precursor detected with TEM, which reportedly are
354 nanosized and have a relatively high surface area.⁵⁶ Following zeolite formation in run K1 and,
355 specially, in run N1, the isotherm of CFA changes from type II (typical of non-porous solids) to
356 a combination of type II and type IV with H4 hysteresis loop typical of micro/mesoporous solids
357 (Fig. S7).⁷⁰ The hysteresis loop is not that well defined in run N2, is nearly absent in run K1, and
358 is completely absent in the unreacted CFA and control run A1. The latter further confirms that a
359 zeolitic precursor is formed in the former runs, particularly in run N2.

360 **Factors affecting the progress of carbonation.** The higher carbonation reached in
361 carbonate solutions (K1, N1) as compared to bicarbonate solutions (K2, N2) can be explained
362 considering the much higher initial pH of the former solutions.⁷¹ CFA dissolution is significantly
363 pH-dependent, increasing the dissolution rate with increasing pH^{9,18–22,72–74}. This is similar to the
364 solubility trend of amorphous silica, which increases sharply for $\text{pH} > 9.0$.⁶² Since Ca (and Mg)

365 must be free in solution to be available for carbonation, an increase in pH should result in an
366 increase in the amount of (Mg)calcite formed.⁷⁵ Moreover, at pH>10.3, the dominant C species
367 in solution is CO_3^{2-} which is the species involved in the formation of carbonates, whereas at
368 pH<10.3, HCO_3^- is the main aqueous C species, this limiting the extent of carbonation.

369 The lower CE of K1 run as compared with N1 run cannot be associated with a pH effect,
370 because the initial (and final) pH of the former run was higher than the latter one (Table 1). The
371 Ca concentration in solution (and also Si and Al, see Fig. S8) was significantly higher in K_2CO_3
372 than in Na_2CO_3 experiments, although not much difference was observed in bicarbonate
373 experiments. This fact shows that the presence of Na^+ ions enhances the formation of crystalline
374 phases acting as “structure builders”, whereas K^+ ions hamper the precipitation of secondary
375 phases, in agreement with Monasterio-Guillot et al.⁶². Because Na^+ favours the precipitation of
376 secondary crystalline phases (carbonates and zeolites), a more thorough dissolution of the
377 amorphous Ca- and Mg-containing aluminosilicate spheres occurs, shifting the reaction towards
378 the product side and fully explaining the contrasting results of N1 and K1 runs.

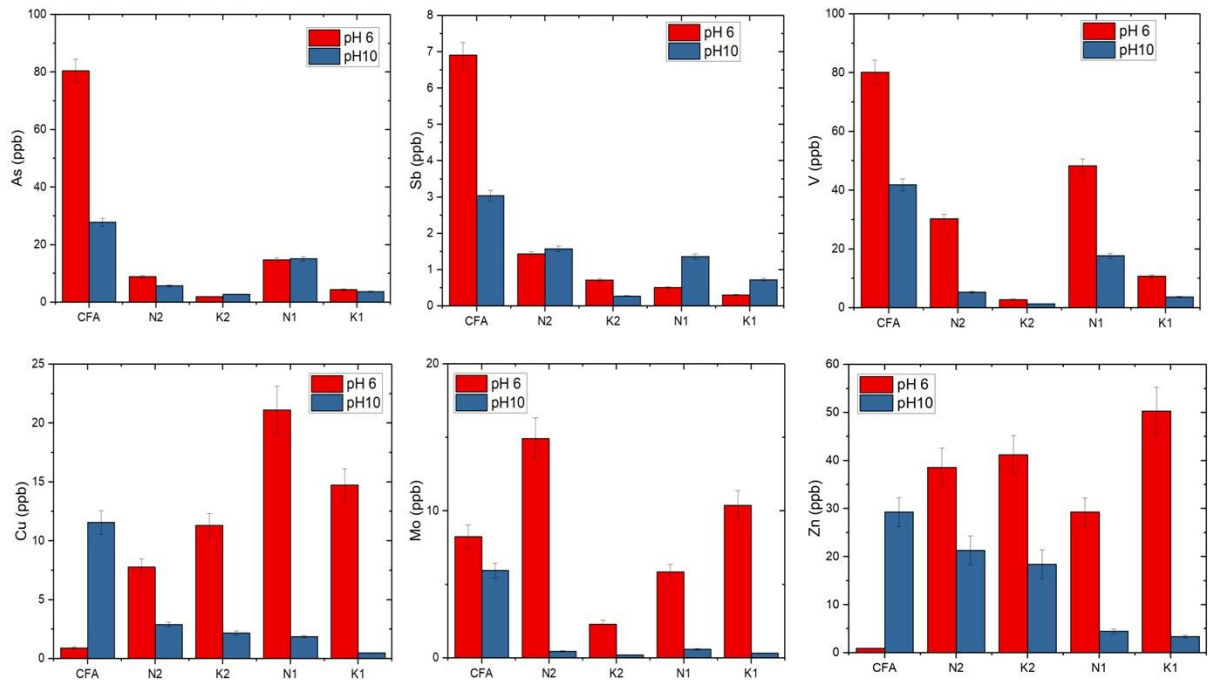
379 **Factors affecting zeolite formation.** Our results show that: (i) a wider variety of
380 zeolites are formed in the presence of Na^+ as compared to K^+ , under otherwise similar
381 experimental conditions, and (ii) higher zeolite yields are obtained with Na^+ as background ion,
382 in agreement with Zeng et al.⁴² Crystalline zeolites were not detected in bicarbonate solutions, or
383 in the controls with just water. Murayama et al.²⁰ showed that the presence of high OH^-
384 concentration in solution contributes to the release of Si and Al from CFA and, above 120°C,

allows the formation of an aluminosilicate gel, which is the precursor of zeolites. In our work, zeolites form due to a combination of the hydrothermal conditions ($T > 120^\circ\text{C}$) and the alkaline pH (> 10)^{9,18–22,25,72–74}. The release of Al and Si during dissolution of the CFA occurs in different stages, initially beginning with the dissolution of the glass, which is the most reactive phase, followed by quartz and mullite.¹⁹ Commonly, high concentrations of NaOH or KOH (typically 1 to 5 M) under hydrothermal conditions ($> 120^\circ\text{C}$) have been used to promote the dissolution of the glass fraction and the subsequent precipitation of zeolite-type phases.^{8,18,20–22,42,72,76} Interestingly, the high zeolite yield observed in the presence of Na^+ ions in run N1, which also yields the maximum amount of calcium carbonate, suggests that a synergistic action is at work during the precipitation of these phases. Apparently, higher levels of dissolution of the amorphous aluminosilicates in CFA are favored by the joint formation of both carbonates and zeolites, enabling a higher conversion of CFA into crystalline product phases. Remarkably, the high zeolite yield observed here is achieved at relatively mild T conditions with sodium carbonate solutions with lower $[\text{OH}]^-$ concentrations than typically used for zeolite synthesis via NaOH alkaline activation. Moreover, our route does not require alkali-fusion of CFA at high T ($> 500^\circ\text{C}$), or the use of energy intensive microwave synthesis²⁵, which is advantageous from an economic and environmental point of view.

Toxic elements leaching. Unreacted CFA shows a general higher release of PTE to the solution at both near-neutral and alkaline pHs as compared to reacted samples (Fig. 4). This effect is most marked in runs N1 and K1, although solids from run N2 and K2 also show a

405 significant reduction in PTE release. The release of As is pH-dependent for unreacted CFA,
406 being higher at pH 6 than at pH 10. It has been reported that alkaline CFAs, like the one used
407 here, show higher As release rates at high pH than at low pH, whereas the opposite is true for
408 acidic CFA.⁷⁷ Release of As from unreacted CFA is eight times higher than in reacted CFA.
409 Such a huge difference is ascribed to its adsorption/entrapment into newly formed zeolites (or
410 zeolite precursors in bicarbonate runs). The behaviour of V and Sb (Figure S4c and f) is very
411 similar to that of As⁷⁸, yet some subtle differences are observed. For instance, unreacted CFA
412 present a higher Sb release at near neutral pH than at alkaline pH, whereas reacted samples show
413 the opposite behaviour. This is likely due to the incorporation of this element in non-silicate
414 phases (iron oxides) which prevent its release at acid-neutral pH, but is solubilized at alkaline
415 pH.⁷⁷ Regarding heavy metal ions such as Cu, Mo and Zn (as well as Sr, Mn and Ni) we observe
416 that their release rate is strongly pH-dependent (Fig. 4). At alkaline pH a systematic reduction in
417 release rate occurs in reacted CFA as compared to unreacted CFA. This is consistent with the
418 trapping of these metals both in carbonate and zeolitic phases as shown by our TEM-AEM and
419 SEM-EDS. In the case of Cu, this is likely due to its incorporation into zeolites as nanophase
420 $\text{Cu}(\text{OH})_2$ or CuO , as demonstrated by Terzano et al.⁷⁹ In contrast, at pH 6 all these elements
421 tend to be released at a higher rate in reacted than in unreacted CFA samples. A likely
422 explanation for this behaviour is the release of such metals from their calcite host after the
423 proton-promoted dissolution of the latter phase. Altogether, our results show that the
424 precipitation of secondary phases plays a key role in the immobilization of PTE. Our leaching

425 results show that at alkaline conditions (i.e., the natural pH of this alkaline CFA), the PTE
 426 release of reacted samples including zeolitic precursors, zeolites and calcite, is significantly
 427 reduced as compared with raw CFA (i.e. As leaching in unreacted material (80 ppb) while in K2
 428 run (1.9 ppb) in pH 6; V leaching in unreacted material 80 ppb, while in N2 run 30 ppb).
 429 However, at mildly acidic conditions, release of some specific PTE trapped in newly formed
 430 carbonates might be an issue. Nonetheless, because after carbonation/zeolitization the pH of the
 431 CFA remains alkaline, such an acid-promoted PTE release will be unlikely if, for instance, the
 432 reacted CFA is disposed of in a pond or landfilled. Although CFA has been shown to be able to
 433 adsorb different acid gasses, including CO₂, and different PTE and organic pollutant, such an
 434 adsorption is known to be very poor.⁸⁰ Transformation of CFA into carbonates and zeolites can
 435 overcome such limitations as it is shown here.



436
 437 **Figure 4.** Results of leaching tests performed at pH 6 and pH 10. The total amount of selected

elements (As, Sb, V, Cu, Mo, and Zn) leached from the unreacted CFA as well as of product from runs N2, K2, Ni and K1 is presented. The total amount was calculated by integrating the amount of element released at the predetermined sampling time intervals indicated in Materials and Methods.

Implications. We demonstrate that 1 ton of CFA can contribute to the sequestration of 45 kg of CO₂, a value that is much higher than those reported for other CFA, even with higher CaO (and MgO) contents.^{28,81–83} Still, this capacity is relatively small if compared with other alkaline waste materials such as steel slag, cement kiln dust, municipal solid waste incinerator (MSWI) ash or air pollution control (APC) residues where values of net CO₂ mineral sequestration up to 290 kg of CO₂/ton of alkaline waste have been reported.³⁵ However, considering the amount of CFA produced annually worldwide, and the amount already landfilled, CFA carbonation can effectively contribute to the reduction of the C footprint of the coal-firing sector.

We also show that the background alkaline metal ion plays a key role in the carbonation and zeolitization efficiency. The “structure builder” role of Na⁺, led to 60 wt% conversion of CFA into zeolites, also reaching the highest CE of all runs (79.26 %). To our knowledge, these values are among the highest ones obtained for zeolite conversion and carbonation efficiency using CFA.^{18,19,52,73} In contrast, with K⁺ as background electrolyte, only a 30% zeolitic yield and about half the CE of the N1 run were achieved. These results demonstrate that the use of a sodium alkaline solution for CO₂ mineral capture and zeolite production is the best choice.

Finally, what is more important is that CFA carbonation/zeolitization makes less

460 hazardous these wastes for their disposal of in ponds or landfills, while simultaneously
461 increasing their value as a result of the formation of reaction byproducts (carbonates and
462 zeolites) with a potential commercial use in several applications, with promising capacities to
463 immobilize PTE from wastewaters, or for flue gas treatment and separation of different
464 greenhouse gases (e.g., CO₂, NH₄). Ultimately, our study opens a new pathway on the combined
465 carbonation and zeolitisation of CFA under hydrothermal conditions to add an extra value to
466 these wastes to form reusable materials and, also, to avoid the hazardous consequences due to
467 the leaching of potentially toxic elements.

468
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