# Changes to the Triaxial Composition of the Hydrated Phases (CaO/Al<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub>) in the Metakaolin/Lime System

Rosario García Giménez,<sup>‡,†</sup> Olga Rodríguez,<sup>§</sup> Raquel Vigil de la Villa,<sup>‡</sup> and Moisés Frías<sup>¶</sup>

<sup>‡</sup>Unidad Asociada CSIC-UAM, Departamento de Geología y Geoquímica, Facultad de Ciencias, Universidad Autónoma, C/Francisco Tomás y Valiente, 7, 28949 Madrid, Spain

<sup>§</sup>Department of Primary Metallurgy and Materials Recycling, National Center for Metallurgical Research, CENIM (CSIC), Avda. Gregorio del Amo, 8, 28040 Madrid, Spain

<sup>¶</sup>Instituto Eduardo Torroja (CSIC), C/Serrano Galvache, 4, 28033 Madrid, Spain

This study examines the composition of certain hydrates (calcium silicate, aluminum silicate, and related phases) produced by the pozzolanic reaction of waste-paper sludge that had previously been activated at different temperatures. It summarizes and compares the evolution of the oxide compounds, and records their stability intervals. Changes to their mineralogical composition were analyzed using X-Ray Diffraction, scanning electron microscopy, and energy dispersive X-ray spectroscopy. The hydration products from 1 to 360 days of curing time were CSH gels, hydrotalcite-type compounds (LDH), and stratlingite (C2ASH8). CSH gels were employed as substrates for growing other materials and their morphologies were modified from fibrous to hexagonal layers. The composition of the LDH-type compounds observed in the carbonate group varied with changes in curing time. Two LDH-type compound types were identified: (a) with and (b) without magnesium. Stratlingite was the only stable material after long-curing times.

# I. Introduction

T HE benefits of partially replacing Portland cement with alternative cementitious materials are widely acknowledged.<sup>1</sup> At present, new pozzolans are under investigation, particularly in the form of activated paper sludge.<sup>2-6</sup> A by-product of the paper industry, waste-paper sludge is valued because of its high content of organic matter (cellulose) and inorganic compounds, such as clays and calcium carbonate, used in the processes of de-inking, whitening, etc. High pozzolanic activity due to thermal activation under controlled calcination transforms the clayey materials, mainly kaolinite, into calcined products, mainly metakaolinite.<sup>7</sup>

The high pozzolanic activity of this activated waste compared with other industrial by-products traditionally used in cements (fly ash, silica fume) was first reported by Frías *et al.*<sup>8,9</sup>

The substances that comprise cement can be divided into two groups: crystalline and amorphous. In the present context, "crystalline" refers to substances with a sufficiently regular internal structure, in terms of atomic, ionic, and molecular arrangements, to enable characterization using conventional crystallographic methods.

When Portland cement is hydrated, its main component is calcium silicate hydrate (C–S–H), which results from anhy-

drous silicate phase hydration ( $C_3S$  and  $C_2S$ ).<sup>10</sup> The C–S–H nanoparticles are responsible for setting the cement paste due to the electrostatic forces that exist between them.<sup>11–13</sup>

Aluminate phases are the second most important ones in the hydration of Portland cement. It is well known that aluminum may substitute silicon in C–S–H.<sup>14</sup> Therefore, the C–S–H that occurs in a cement paste will not be pure C–S–H, but Al substituted-C–S–H referred to as C–A–S–H.<sup>15</sup>

The pozzolan/lime/water system is very simple and helps the interpretation of pozzolan blended cement behavior. Knowledge of the hydration products generated during the pozzolanic reaction, their morphological characteristics, chemistry, and structural composition will help determine whether the pozzolan may be used in cements.

Thus, the purpose of this article is threefold: first, to analyze the composition of the most important calcium (aluminum) silicate hydrates and their related phases, which should be a useful reference source for others interested in these phases; secondly, to analyze the evolution of the oxide compounds and finally, to record their stability intervals.

### **II.** Materials and Methods

# (1) Materials

The waste-paper sludge used in this work was provided by Holmen Paper S.L., Madrid, which uses 100% recycled paper as a raw material. Its chemical composition by FRX analysis is CaO (25%), SiO<sub>2</sub> (11%), Al<sub>2</sub>O<sub>3</sub> (7%), MgO, Fe<sub>2</sub>O<sub>3</sub>, SO<sub>3</sub>, TiO<sub>2</sub>, Na<sub>2</sub>O, K<sub>2</sub>O, P<sub>2</sub>O<sub>5</sub> (<1%), and PPC (mass after calcinations) 54%.

After drying, the paper sludge waste was calcined in an electric laboratory furnace at 700°C, 750°C, and 800°C for either 2 or 5 h of retention time. The resulting products were ground with a mortar and pestle and then sieved to a size of less than 45  $\mu$ m. The samples were grouped as follows: calcined paper sludge 1 (CPS1: 700°C/2 h), CPS2 (700°C/5 h), CPS3 (750°C/2 h), CPS4 (750°C/5 h), and CPS5 (800°C/2 h).

These materials were then mixed with a saturated lime solution  $(Ca(OH)_2)$  and cured in an electric oven at 40°C for 1, 7, 28, 90, 180, and 360 days of reaction. Further information concerning paper sludge pozzolanic activation may be found in previous references.<sup>16,17</sup>

# (2) Techniques

The mineralogical composition of the samples was determined using X-ray diffraction. The XRD patterns were analyzed using a SIEMENS D-5000 diffractometer (Munich, Germany), set at 3°–65° and at a scan speed of 2°/min, using a tungsten cathode and a copper plate anode (Cu $K_{\alpha}$ ). The current and voltage intensity applied to the generating X-ray

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tube were 30 mA and 40 kW, and the divergence and receipt splits,  $1^{\circ}$  and  $0.18^{\circ}$ , respectively.

The semi-quantitative mineralogical components were obtained using the reflectant powers method,<sup>18</sup> whereas the areas of talc, calcite, stratlingite, and LDH-type compounds were measured in the diffractogram. The quantitation of peak areas was determined by means of Gaussian adjustment and base-line subtraction. These calculations were done using a conventional math software program. The error in the semiquantitative analysis using XRD is 10%.

The textural study of the materials was performed using an Inspect FEI Company Electron Microscope (SEM; 5350 NE Dawson Creek Drive, Hillsboro, OR) with a tungsten filament source. The powder samples were fixed to a graphite plate on the metallic slide using a BIO-RED SC-502 super coater. The study was complemented using SEM/EDX chemical analyses with a lithium-drifted silicon detector and a DX41 analyzer. Data shown in the tables were the average value of ten measurements, performed in different fields.

Systematic observations were performed using this device (Inspect FEI Company; W source, DX4i analyzer, and Si/Li detector). The analyzer was previously calibrated with a multi-mineral sample: the USGS standard ADV – 1.<sup>19</sup> The semi-quantitative analyses by EDX were obtained as an average of 10 values taken in different grains for each power sample. The results are expressed in oxides (wt%), adjusted to 100%. From these data, the structural formulas are calculated considering 14 negative charges for stratlingite C<sub>2</sub>ASH<sub>8</sub> [Ca<sub>2</sub>Al<sub>2</sub>SiO<sub>2</sub>(OH)<sub>10</sub>·5H<sub>2</sub>O] and 14 negative charges for like-compounds LDH (possible structures type C<sub>4</sub>A $\overrightarrow{C}$  H<sub>12</sub> [Ca<sub>4</sub>Al<sub>2</sub>(CO<sub>3</sub>)(OH)<sub>12</sub>·12H<sub>2</sub>O], hydrotalcite type [Mg<sub>4</sub>A-l<sub>2</sub>(OH)<sub>14</sub>·3H<sub>2</sub>O], or kaolinite type [Si<sub>2</sub>Al<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub>]).

## III. Discussion

Figure 1 shows the XRD patterns corresponding to the CPS1 (calcined paper sludge at  $700^{\circ}C/2$  h) cured at 1, 7, 28, 90, 180, and 360 days of reaction, which provided examples of all the XRD patterns. These patterns are detailed in Table I,<sup>4</sup> which also shows chlorite and tobermorite among the trace contents.

Metakaolinite that results from the calcination of kaolinite paper sludge was only recognized using SEM/EDX, because it was an amorphous material. The different hydrated phases identified using XRD in this work were stratlingite (reflection peaks at 12.58, 4.18, and 2.49 Å) and LDH-type compounds. These materials were identified in two regions: between  $2\Theta = 11.01^{\circ}-12.32^{\circ}$  (8.03–7.17 Å) and  $2\Theta = 23.14^{\circ}-24.50^{\circ}$ (3.84–3.63 Å) corresponding to (003) and (006) reflections,



Fig. 1. XRD diffraction patterns for  $700^{\circ}C/2$  h at all reaction times.

respectively. The semi-quantitation of crystalline products by XRD is show in the Tables I and II. Stratlingite is the most abundant compound when both temperature and residence time in the oven increased, reaching a composition of 84% for CPS5 at 180 days (Table II). LDH-type compounds are stable and abundant at low temperatures (below 750°C with short residence time), and CPS2 at 7 days is the most favorable condition for obtaining these kinds of compounds (68%).

Calcium silicate hydrate (C–S–H) gel is the principal amorphous hydration product in Portland cement hydration.<sup>20</sup> It presented particular problems, as it was insufficiently crystalline for the application of conventional crystallographic methods.

The available information<sup>21,22</sup> indicates that C–S–H gel has a layered structure containing calcium silicate sheets in solid solution with Ca(OH)<sub>2</sub> and H<sub>2</sub>O. Their semi-quantitation

 
 Table I.
 Variation in the Mineral Phases for All Samples and All Reaction Times

Mineral (%)	CPS1	CPS2	CPS3	CPS4	CPS5
1 day					
Talc	1	6	2	5	3
Zeolites	13	57	51	51	44
LDH-like	_	19	Traces	_	-
compound					
Stratlingite	_	_	_	_	31
$C_4AH_{13}$	Traces	-	-	6	Traces
Calcite	85	18	47	39	22
7 days					
Talc	2	2	5	3	2
Zeolites	_	-	Traces	_	-
LDH-like	24	68	7	53	_
compound					
Stratlingite	_	4	_	19	66
$C_4AH_{13}$	Traces	_	_	_	Traces
Calcite	74	25	88	25	32
28 days					
Talc	1	1	1	1	1
Zeolites	_	_	_	_	_
LDH-like	39	65	61	34	25
compound					
Stratlingite	3	13	7	48	55
$C_4AH_{13}$	Traces	Traces	_	_	Traces
Calcite	58	21	31	18	19
90 days					
Talc	2	3	2	1	1
Zeolites	_	_	_	_	_
LDH-like	24	28	24	32	19
compound					
Stratlingite	Traces	28	17	50	64
$C_4AH_{13}$	Traces	28	19	_	Traces
Calcite	74	23	39	17	15
180 days					
Talc	3	2	1	2	1
Zeolites	_	_	_	_	_
LDH-like	9	41	52	36	8
compound					
Stratlingite	3	13	6	36	84
$C_4AH_{13}$	Traces	11	_	_	Traces
Calcite	85	33	41	26	7
360 days					
Talc	2	3	2	3	1
Zeolites	_	_	_	_	_
LDH-like	Traces	46	23	27	_
compound					
Stratlingite	2	8	3	33	53
C4AH13	Traces	Traces	_	_	Traces
Calcite	96	43	72	37	47

Table II.Concentration of LDH-Type Compounds andStratlingite Determined Using XRD Under All Conditions

Concentration (%)	Stratlingite	LDH-like compounds	
1 day			
CPS1	_	_	
CPS2	_	19	
CPS3	_	Traces	
CPS4	_	_	
CPS5	31	_	
CPS1	_	24	
CPS2	4	68	
CPS3	_	7	
CPS4	19	53	
CPS5	66	_	
28 days			
CPS1	3	39	
CPS2	13	65	
CPS3	7	61	
CPS4	48	34	
CPS5	55	25	
90 days			
CPS1	Traces	24	
CPS2	23	28	
CPS3	17	24	
CPS4	50	32	
CPS5	64	19	
180 days			
CPSI	3	9	
CPS2	13	41	
CPS3	6	52	
CPS4	36	36	
CPS5	84	8	
360 days			
CPS1	2	Traces	
CPS2	8	46	
CPS3	3	23	
CPS4	33	27	
CPS5	53	_	

was not possible using XRD, because it was a noncrystalline compound; however, in this case, we have identified some peaks relating to CSH gel that suggest a higher degree of structural order.<sup>23</sup> These peaks, which corresponded to CSH gels type I and II,<sup>23</sup> are located at  $2\theta = 29.06^{\circ}$ ,  $31.94^{\circ}$ , and  $49.9^{\circ}$  (Fig. 1). The different hydrated phases had been analyzed using SEM/EDX at all curing times (1, 7, 28, 90, 180, and 360 days). The triangular diagrams (Fig. 3) were prepared to facilitate the interpretation of all the results linked to the stratlingite, LDH-type compounds plotting the Ca<sup>2+</sup>/Si<sup>4+</sup>, Ca<sup>2+</sup>/Al<sup>3+</sup>, and Si<sup>4+</sup>/Al<sup>3+</sup> ratios from the structural formula and CSH gel concentrations, by plotting the CaO/Al<sub>2</sub>O<sub>3</sub>, CaO/SiO<sub>2</sub>, and SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratios, as these are the main oxides with few exceptions in all of the analyses in which minor amounts of magnesia are identified (<2%).

SEM revealed that the initial crystalline growth presented nanometer-sized layers that grew on the sides, although their growth was conditioned by the lime concentration in the solution<sup>24</sup>: High concentrations of lime favored the axial growth of high CaO/SiO<sub>2</sub> in C–S–H<sup>25</sup> [Figs. 2(a) and (b)]. The first layers of particles appeared remarkably well organized, but, as the thickness of the layers increased, so did their roughness, and they tended to lose order. However, when aged in lime solutions, these disordered aggregated layers reorganized themselves to yield flat surfaces. In this study, the LDH-type compounds and the stratlingite nucleates on the C–S–H gel substrate [Fig. 2(f)]. These gels represent the first signs of crystallization and all the other reactive products with a hexagonal appearance grow over them, which can only be distinguished using SEM/EDX analysis. Variations of the oxides in the CSH gels, produced during the pozzolanic reaction of the sludges, are shown in Fig. 3. These are located in a zone where the  $SiO_2/Al_2O_3$  ratio, rather than CaO/SiO<sub>2</sub> (right side of diagram) predominates. C–S–H gels in CPS1 (700/2) were calcic at first, but as curing time increased, the predominant oxide was silica. This calcined sludge has a high content of the oxide CaO, drawn from the Ca(OH)<sub>2</sub> available in the system. As time elapsed, this concentration fell, but not at a constant rate; at 180 days, the CaO content was similar to that obtained on day 1.  $Al_2O_3$  and SiO<sub>2</sub> content remained almost the same throughout the process. MgO oxide appeared over longer reaction times.

C–S–H gels in CPS2 (700/5) at all ages showed a higher content of CaO oxide. Calcium oxide is incorporated at CSH gels in a way similar to CPS1 sludge. High silica content was also detected within the range of 7–180 days. The calcic nature was also confirmed in the CPS3 (750/2) at day 7 of the reaction, when the Al<sub>2</sub>O<sub>3</sub> content was low; however, over longer periods of time, the concentrations of CaO, Al<sub>2</sub>O<sub>3</sub>, and SiO<sub>2</sub> balanced themselves out, as shown in the triaxial diagram. The predominant oxides in sludges CPS4 (750/5) and CPS5 (800/2) consisted of silica with low alumina and MgO oxide.

Hydrotalcite-like compounds (HT) or double layered hydroxides (LDH) were identified after 7 days of pozzolanic reaction, although they were not present in all samples (Table II). This term is generally applied when carbonate ions occupy the interlayer spacing. When other interlayer anions such as nitrate or chloride are dominant, the materials are referred to as "Hydrotalcite-Type (HT) compounds".<sup>26,27</sup> Calcite content fell after the initial pozzolanic reaction at 28 days of reaction and then gradually increased until the end of pozzolanic reaction at 360 days. These observations are explained by the incorporation of the carbonate group in the hydrotalcite-type phases, in addition to a carbonation phenomenon of portlandite from atmospheric  $CO_2$ .<sup>28</sup>

Hydrotalcite-like compounds (DLH or LDH) are anionic clays. These are microporous minerals that have a lamellar structure and rhombohedric symmetry, comprised of positively charged hydroxide layers and interlayers of carbonate anions and water molecules. Growth occurred at the edges, resulting in the formation of hexagonal plate-shaped hydrotalcite (LDH-type compounds) crystals [Fig. 2(c)].

The changes in the structural formula from the DLH-like compounds in accordance with the temperature and the time in the furnace are shown in Fig. 3. The representation of the samples is located in the central position of diagram by the LDH-type compounds in which the three ratios are similar. These materials are identified in the treatment of 700/2 (CPS1) from 7 to 90 days of pozzolanic reaction. At first,  $Ca^{2+}$  content per structural formula was high; the concentration then fell, whereas the Al<sup>3+</sup> and Si<sup>4+</sup> concentrations increased. Mg<sup>2+</sup> content was low and appeared between 28 and 90 days.

With the increased time in the oven from 2 to 5 h, the DLH-like compounds were detected from 28 days until 360 days, with variable quantities of  $Ca^{2+}$  content that reached their maximum concentrations after 180 reaction days. The same situation was observed at a temperature change to 750°C for 2 h (CPS3).

The variation was considerable at an activation temperature of 750°C over 5 h (CPS4). A new majority phase was identified at 7 days showing LDH-type compounds rich in  $Mg^{2+}$  content (LDH type II).<sup>6</sup> This magnesium proceeded from the total destruction of the crystalline lattice of the talc (Fig. 1), which disappeared at this temperature [Fig. 2(d)]. The maximum concentration of Ca<sup>2+</sup> ion was observed at 180 days.

Finally, the most aggressive treatment (CPS5) showed calcic LDH-like compounds (LDH type I)<sup>6</sup> within the range of 28/180 days with high Ca<sup>2+</sup> content (Fig. 3).



**Fig. 2.** (a) C–S–H fibrous gels. (b) C–S–H aggregate gels. (c) Laminar LDH-type compounds. (d) Fibrous LDH-type compounds. (e) Hexagonal plates of stratlingite. (f) Aggregates with C–S–H gels  $(\Box)$ , LDH-type compounds  $(\Delta)$ , and stratlingite  $(\circ)$ .



**Fig. 3.** Ratios of different oxides or ions for C–S–H gels, LDH-type compounds and stratlingite (included the stratlingite type).

The last compound under study—stratlingite—could only be detected at 28 days in CPS1, with a prevalence of  $Ca^{2+}$ content. In Fig. 3, stratlingite is located in an opposite area with  $Ca^{2+}/Si^{4+}$  ratios that are greater than the  $Si^{4+}/Al^{3+}$ the ratios. The increase in activation time from 2 to 5 h (CPS2), caused the stabilization of this phase from 28 to 360 days, with constant  $Al^{3+}$  concentration and  $Si^{4+}$  content increasing as the content of  $Ca^{2+}$  fell, producing practically the same quantity for the three ions.

When the activation temperature reached  $750^{\circ}$ C, 2 h (CPS3), stratlingite was detected from 28 days to 360 days. Under these conditions, the Si<sup>4+</sup> content remains practically constant, whereas the Al<sup>3+</sup> content grew over time, and the Ca<sup>2+</sup> content decreased over time at longer ages (360 days).

The waste-paper sludge that was calcined at 750°C for 5 h developed stratlingite after 7 days of reaction, remaining until the end of the study. At first, this phase is rich in Ca<sup>2+</sup> ions, whereas  $Al^{3+}$  and Si<sup>4+</sup> contents were 1.17 and 0.66, respectively. From this age onward, the Ca<sup>2+</sup> was reduced, the Si<sup>4+</sup> content remained constant, and the Al<sup>3+</sup> concentration stabilized at 1.95 (Fig. 3).

At the highest temperature,  $800^{\circ}C/2$  h (CPS5), stratlingite developed after only 1 day of reaction. It had a rich Ca<sup>2+</sup> ion composition and a low Si<sup>4+</sup> content, evolving over time "by means of" a decrease of Ca<sup>2+</sup> ions and increase in Si<sup>4+</sup>, with almost constant aluminum. All samples present the stratlingite with a hexagonal morphology [Fig. 2(e)].

In general terms, it could be said that stratlingite formation is favored by temperature and heating time; at first, stratlingite was rich in  $Ca^{2+}$  ions and poor in  $Si^{4+}$  content, with values of  $Al^{3+}$  close to 1.95. Later on, the ionic composition tended to compare between them (equilibrium situation, similar ionic concentrations). The evolution of this phase is conditioned by  $Ca^{2+}$  and  $Si^{4+}$  ions concentrations (that evolve in the opposite sense), whereas  $Al^{3+}$  ions concentration fluctuated within a small range.

The activated sludge that has been described in this article is very well adapted for use as a pozzolan, as has been demonstrated by the product's stability and stratlingite formation that followed calcination in the furnace.<sup>7</sup>

# **IV.** Conclusions

The activation of paper sludge at different temperatures and different times in the furnace resulted in products with important pozzolanic properties due to the presence of metakaolinite.

The hydration products from 1 up to 360 days of hydration were C-S-H gels, LDH-type compounds, and stratlingite

C-S-H gels are the compounds used as substrate for growing other materials. Their morphologies changed from fibrous to hexagonal plates.

LDH-type compounds were formed between layers in the carbonate group, and their composition changed with curing time. Two types of LDH-type compound structures were recognized: with and without magnesium.

Stratlingite was shown to be the stable material over longcuring times.

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