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A method developed to quantify lime and gypsum consumed by mineral additions

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ABSTRACT

This paper presents an original method developed to quantify the reactivity of mineral additions based on the measurement of the lime (CaO) and gypsum ($CaSO_4$, $2H_2O$) consumed by mineral additions in a paste. Three mineral additions were tested: a Siliceous Filler (SF), a natural pozzolan (Poz) and a Wastepaper Sludge Ash (WSA). The results obtained on SF, considered as a reference, show the efficiency of this method. Its application to Poz and WSA permits the quantity of lime and gypsum consumed by these additions to be evaluated and, thus, the amount of each component to be optimized in Hydraulic Road Binders.

1. Introduction

Mineral additions have long been used in cement-based materials and their use is standardized today for cement [1] and concrete [2]. These additions are either natural or artificial and the majority of them are by-products of industry (e.g. Ground Granulated Blast Furnace Slag (GGBFS), silica fume or coal fly ash). These mineral additions are used to replace a part of the clinker in cements for several reasons. The first one is economics, as such materials are generally much less expensive than clinker. Then, research on these additions has shown that they can improve some characteristics of cement-based materials. For example, it is clearly established today that pozzolanic additions improve the durability of concrete and that silica fume strongly reduces the porosity of high performance concrete and thus strongly increases both strength and durability [3,4]. Lastly, in recent years, the ecological impact of binders has become increasingly important. The production of clinker consumes a lot of energy and generates significant emissions of CO_2 in comparison with that of mineral additions. Also, the replacement of clinker by mineral additions makes it possible to reduce the carbon emissions of cements and their energy consumption [5]. Thus, even more than before, the advantages of using mineral additions in cement-based materials are seen as significant. Much research has been initiated to test new materials (natural materials or industrial by-products) for their potential use as mineral additions in cement-based materials. This could be interesting if the amounts produced are sufficiently high, if these materials do not lead to pollution and, finally, if they do not deteriorate, or better if they improve, the properties of cement-based materials.

In terms of reactivity, European standard EN 206-1 distinguishes two types of inorganic addition [2]: nearly inert additions (type I) and pozzolanic or latent hydraulic additions (type II). It is very useful to evaluate the reactivity of the mineral additions in binders, in particular to optimize the proportion of each component introduced into these binders. A method used frequently to quantify the reactivity of the mineral additions in cement-based materials is to measure the activity index and the *k*-values (“strength activity index” in ASTM C311 [6]). The activity index “*i*” is the ratio of the strength of a mortar containing 25% of addition and 75% of cement to the strength of a reference mortar (100% of cement). The *k*-values, used in particular in the concept of equivalent binder, are calculated by the relation $k = 3i - 2$. However, this method can be applied only for binders rich in cement. Nowadays, the trend is to develop new binders containing as little cement as possible, especially for Hydraulic Road Binders (HRBs) that have characteristics different from those of conventional cements [7]. The compositions of these binders are based on the use of reactive mineral additions (hydraulic, latent hydraulic or pozzolanic) activated by lime, gypsum or other activators, the proportions of which must be determined.

This paper presents an original method developed to quantify the reactivity of mineral additions used as major components in

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HRB. Two types of activators were studied: lime (CaO), which is necessary for the occurrence of the pozzolanic reaction, and gypsum ($CaSO_4$, $2H_2O$), which is known to be an excellent activator for numerous materials such as Ground Granulated Blast Furnace Slag (GGBFS) or coal fly ash [4], Basic Oxygen Furnace slag [8] and Wastepaper Sludge Ash [9].

The method presented in this paper was applied to pastes containing the tested mineral addition, gypsum and lime. The method consists of measuring the amounts of gypsum and lime consumed by the mineral addition in the paste at different ages. Three mineral additions were tested using this method: a Siliceous Filler (SF), a natural pozzolan (Poz) and a Wastepaper Sludge Ash (WSA). Firstly, the main characteristics (physical, chemical and mineralogical) of the mineral additions used in the study will be presented. The second part of the paper will be devoted to the description of the method developed and the presentation of the results. Finally, the results obtained will be applied to the optimization of HRB compositions.

2. State of the art

Numerous methods already exist for evaluating the pozzolanic activity of mineral additions. These methods will be quickly described in this section in order to highlight the originality of the method presented in this paper. Most of the methods found in the literature are based on the measurement of the consumption of lime by pozzolanic materials. Firstly, the ‘‘Chapelle’’ test measures the fixation of the lime in a solution saturated with lime and containing the tested addition at 90 °C. This test has been criticized by Ambroise et al. because the high temperature strongly modifies the kinetics of the reaction and the nature of the hydrates formed [10]. The standard procedure EN 196-5 ‘‘Methods of testing cement – Part 5: Pozzolanicity test for pozzolanic cement’’ is based on the same principle [11]. The pozzolanicity of pozzolanic cements is assessed by comparing the concentration of calcium ions present in the aqueous solution in contact with the hydrated cement with the quantity of calcium ions necessary for saturating a solution of the same alkalinity. The cement is considered to satisfy the test if the concentration of calcium ions in the solution is lower than the saturation concentration. In 2007, Garcia et al. developed an accelerated test to evaluate the pozzolanic activity of paper sludge waste [12]. This test is an alternative to the Chapelle test with longer durations (1, 7, 28 or 90 days) and a more moderate temperature (40 °C).

It is also possible to evaluate the pozzolanic activity of materials by measuring the compressive strength of mixtures containing the tested addition and lime. That is the case, for example, in the ASTM C311, ‘‘Standard Test Methods for Sampling and Testing Fly Ash or Natural Pozzolans for Use in Portland-Cement Concrete’’ [6]. In this test, the 7-day and 28-day compressive strengths of mortar cubes with a 20% mass replacement of cement by pozzolan are compared to those of a control without pozzolan, at constant flow conditions. Bentz et al. have proposed an alternative method, in which the 20% pozzolan replacement for cement is performed on a volumetric basis and the volume fractions of water and sand are held constant [13]. Another example concerns the test specific to the pozzolans used in road foundations [14]. The reactivity of such pozzolans is evaluated from the compressive strength of a mixture containing pozzolan, lime (12%) and water (Proctor optimum) measured on cylinders 5 cm in diameter and 10 cm high, at 60 and 360 days. In another study, Argawal measured the pozzolanic activity of various siliceous materials [15]. The author worked on cement mortars by replacing a part (10%) of the cement by the addition to be tested. The originality of the method used by Argawal concerned the conservation of the samples in water at 65 °C to accelerate the occurrence of the pozzolanic reaction.

Finally, other mineralogical tools are often used to study the pozzolanic activity of materials, such as thermogravimetric analysis (TGA), which evaluates portlandite and calcite contents. But, the quantities of material tested with a conventional apparatus are often very low and thus the results are not representative of heterogeneous cement-based materials (some modern apparatus can test higher quantities of materials (between 2 and 3 g), thus reducing the severity of this problem).

This short review shows that methods to evaluate the reactivity of mineral additions exist but essentially concern pozzolanic activity. Many of these methods are carried out on solutions and often with excessive temperature to accelerate the reactions. This is very far from the real utilization of mineral additions in binders for concrete or road applications. In contrast, tests based on the evolution of compressive strength of mortar or compressed materials give results on the global efficiency of a mineral addition, but do not give information on its potential chemical reactivity. The method presented in this paper aims to provide such information and has the interest of being carried out on pastes and not on solutions.

3. Experiments

3.1. Materials

Siliceous filler was used as the reference in this study because it can be considered as chemically inert. The filler used was a commercial product with a fineness equal to 2000 cm^2/g and a SiO_2 content higher than 98.6%.

The pozzolan under study came from a French quarry where pozzolan is extracted, crushed, sifted and stocked as a 0/2 sand. The sample studied in this work was finely crushed in the laboratory.

The Wastepaper Sludge Ash (WSA) under study came from a paper mill equipped with an incinerator fed by biomass. This equipment uses the steam produced by the incineration of biomass to generate green electricity. After its passage in the turbine, the steam is reused in the paper making process, especially for the shrinkage of the paper. One half of the biomass incinerated is composed of waste coming from the paper mill (de-inking and waste water-treatment sludges in particular) and the other half comes from wood waste. The technology used in the boiler is a fluidized bed. As recommended by Directive 2000/76/EC, the sludge remains in the combustion zone for a few seconds (more than two) at 850 °C [16].

The gypsum and lime (CaO) were both pure commercial products of analytical quality.

3.2. Characterization procedures

3.2.1. Physical characterization

Specific surface area was measured by the Blaine test. This test was carried out according to European standard EN 196-6 [17]. The size distribution of the materials was analyzed by means of a laser particle size analyzer using a dry suspension with an air pressure of 0.5 bars. The density was determined by hydrostatic weighing of a powder sample in a non-reactive liquid (exxsol).

3.2.2. Chemical characterization

Major oxides composition was estimated on the basis of the macroelemental analysis carried out on digested samples by Inductively Coupled Plasma – Atomic Emission Spectrometry (ICP-AES). The loss on ignition (calcination at 1000 °C) was also measured according to European standard EN 196-2 [18]. The sulphate (SO_3) content was measured by ionic chromatography after acidic dissolution.

3.2.3. Mineralogical characterization

The crystalline phases were identified using a Siemens D5000 powder X-ray Diffractometer equipped with a monochromator using a Ka (λ = 1.789 Å) cobalt anticathode. Specific measurements were carried out on WSA in order to quantify the contents of calcite ($CaCO_3$) and lime (CaO). The calcite ($CaCO_3$) content was determined from the CO_2 volume measured during acidic dissolution. The free lime was measured by an acidimetric method according to standard EN 459-2 [19], the principle of which is to dissolve free lime in a saccharose solution and to titrate it with a standard solution of 0.1 mol/l hydrochloric acid.

3.3. Presentation of the method developed to quantify lime and gypsum consumption

3.3.1. Sample preparation

The principle of the method was to prepare a paste with lime and gypsum in excess and to measure chemically the amounts of lime and gypsum that had not reacted. Also, by comparing to the initial quantities, it was possible to calculate the quantity of lime and gypsum consumed by the mineral addition. Materials were mixed using the following proportions by mass: 65% tested addition, 20% gypsum and 15% lime. Then water was added to obtain a plastic consistency. The amount of water added to the mixture was weighed after the lime had been slaked (indicated by the decrease in temperature of the mixtures after about half an hour). As shown in Table 1, the amount of water added to obtain the same consistency for each paste differed according to the materials tested. For WSA and pozzolan, the water demand was higher than for the siliceous filler.

The pastes were then stored in hermetically sealed pills. They were divided into at least five samples for each hydration time and weighed to check for a possible loss of mass during conservation. At several hydration times (7, 28, 90 and 365 days), the pills were broken and all the hardened paste was crushed in an agate mortar.

3.3.2. Tests

To prepare the samples for chemical testing, the samples of fresh paste were crushed as finely as possible in an agate mortar. Because some of them were still wet, it was not possible to check the fineness of the samples after the crushing. This parameter could have an influence on the results obtained and it could be interesting to improve this step of the method in further developments.

The amount of residual gypsum remaining in the paste was determined using water dissolution. Two grams of paste were immersed in 250 ml of deionized water for 15 min with strong stirring. The solution was then filtered using a 0.45 μm membrane filter. The leachate was weighed and acidified with 2% HCl. Sulphate content in the leachate was measured using ion chromatography.

The residual lime and the calcite content were measured using the same procedures as that used for the characterization of the raw materials. The residual lime was expressed in "CaO" content even though the lime was hydrated in the paste.

Table 1
Compositions of the pastes.

	SF	Poz	WSA
Material (%)	43.2	40.7	40.4
$CaSO_4$, $2(H_2O)$ (%)	13.3	12.5	12.4
CaO (%)	10.0	9.4	9.3
Water (%)	33.6	37.4	37.8

Table 2
Physical characteristics of materials.

	SF	Poz	WSA
Blaine fineness (cm^2/g)	2000	11,000	3300
D 10 (μm)	9	0.3	1.5
D 50 (μm)	64	2	27
D 90 (μm)	177	8	300
Density (g/cm^3)	2.65	3.06	2.87

Table 3
Chemical composition of materials.

(%)	SF	Poz	WSA
SiO_2	98.6	45.3	28.0
CaO	<0.05	9.9	45.5
Al_2O_3	<0.75	12.6	13.2
Fe_2O_3	<0.05	13.6	1.3
MgO	–	10.0	4.0
Na_2O	–	2.9	0.4
K_2O	<0.6	1.3	0.7
TiO_2	<0.04	2.2	0.7
P_2O_5	–	0.8	0.4
MnO	–	0.2	0.1
Ignition loss	–	1.3	5.7
Total	~99.0	100.0	99.8

Finally, two grams of paste were dried in an oven at 50 °C with acetone and crushed in an agate mortar to fineness <80 μm. This powder was used to study the qualitative mineralogical evolution of the paste using XRD.

4. Results and discussion

4.1. Characteristics of materials

The physical characteristics of the three materials are presented in Table 2.

No physical treatment was applied to the siliceous filler or the WSA. These materials were used as they were received. Both were of average fineness, the characteristics of WSA being relatively close to those of conventional binders. Unlike the other two additions, pozzolan was crushed in the laboratory to extremely high fineness (specific surface was equal to 11,000 cm^2/g with an average diameter of 2 μm). The choice to crush the pozzolan so finely was a considered one. Although such crushing would not be realistic in industry, because it would be too expensive, the study of the reactivity on this sample permitted the "maximum" chemical reactivity of pozzolan to be measured independently of its particle size. This approach is relatively theoretical and, for real applications, it would be necessary to validate these results on less finely crushed samples.

The chemical compositions of the three materials are given in Table 3.

Table 3 confirms the purity of the siliceous filler (the silica content was higher than 98.6%). Concerning the pozzolan, the major elements were silicon, iron and aluminium (71.5%). Moreover, this pozzolan contained large quantities of calcium and magnesium. The composition of this pozzolan was relatively classical compared to those of other natural pozzolan [4]. Lastly, WSA was essentially composed of calcium, silicon and aluminium (87%). The amounts of the other major elements were small (less than 2%) except for MgO (4%). The chemical composition of our WSA was similar to those found in the literature although some slight differences existed (in particular, our WSA contained more calcium and less aluminium than other ashes) [9,20–22].

Table 4
Mineralogical composition of materials.

SF	Poz	WSA
Quartz (SiO_2)	Augite ($Ca(Mg,Fe,Al)(Si,Al)_2O_6$) Forsterite (Mg_2SiO_4) Magnetite (Fe_3O_4) Labradorite ($(Na,Ca)(Al,Si)_4O_8$) Amorphous phase	Gehlenite ($Ca_2Al_2SiO_7$) Calcite ($CaCO_3$) Lime (CaO) Quartz (SiO_2) Merwinite ($Ca_3Mg(SiO_4)_2$) Mayenite ($Ca_{12}Al_{14}O_{33}$) Dicalcium silicate (α'-Ca_2SiO_4)

The main minerals identified by XRD in the three materials studied are presented in Table 4.

As shown in Table 4, pozzolan contained conventional minerals of volcanic materials: augite, forsterite, calcic feldspars (labradorite) and iron oxides (magnetite). Moreover, the presence of a significant halo on the diffractogram confirmed the presence of an amorphous phase that is widespread in natural pozzolans.

The minerals contained in the WSA were: gehlenite ($Ca_2Al_2SiO_7$), calcite ($CaCO_3$), lime (CaO), quartz (SiO_2), merwinite ($Ca_3Mg(SiO_4)_2$), mayenite ($Ca_{12}Al_{14}O_{33}$) and α'-C2S (Ca_2SiO_4). This qualitative analysis was consistent with the chemical composition of WSA, which showed that WSA was essentially composed of CaO, SiO_2 and Al_2O_3. The minerals identified by XRD contained only these three oxides, except for the merwinite, which also contained MgO, justifying the relatively high content of this oxide in WSA. Moreover, specific measurements enabled the amounts of lime (5% by mass) and calcite (9%) contained in WSA to be quantified.

The mineralogical characteristics of pozzolan and WSA have strong consequences on their reactivity. The first one certainly has pozzolanic properties due to the presence and the nature of the amorphous phase that constitutes it. WSA contains minerals that are potentially reactive: lime (CaO), mayenite ($C_{12}Al_{14}O_{33}$) and α'-Ca_2SiO_4 which should certainly confer hydraulic properties on this ash. Moreover, there was no evidence of metakaolin or glassy materials in the WSA as there was no amorphous halo in the XRD pattern. Also, in contrast to other calcined paper sludges, which have pozzolanic properties due to the presence of metakaolin [12,21,23], there was no reason for the WSA under study to have pozzolanic properties.

4.2. Feasibility of the method: results on siliceous filler

The method was initially tested on a siliceous filler because it could be considered as an inert material which should not react with lime or gypsum (with the exception of the possible carbonation of lime during the conservation or preparation of the samples for the measurement of lime and gypsum contents).

Table 5 presents the amounts of gypsum, "CaO" and $CaCO_3$ contained in 100 g of fresh paste and measured using the chemical procedures. The percentages of each phase were computed using the initial quantity introduced into fresh pastes. Moreover, in order to check the validity of the method, the quantity of equivalent lime, CaO_{eq}, was calculated. It represents the sum (taking the molar ratios into account) of measured CaO and $CaCO_3$. As was predictable, neither setting nor swelling was observed during the year of conservation of siliceous-filler-containing paste.

Table 5
Amounts of gypsum, calcite and "CaO" contained in 100 g of fresh paste with siliceous filler.

Age (days)		Mixture	7	28	90	365
$CaSO_4$, $2(H_2O)$	g	13.3	12.7	12.4	12.7	13.6
	%	–	**95**	**93**	**95**	**102**
$CaCO_3$	g	0	1.7	2.6	3.0	2.0
CaO	g	10.0	9.3	7.8	8.0	8.6
	%	–	**93**	**78**	**80**	**86**
CaO_{eq}	g	10.0	10.2	9.3	9.7	9.7
	%	–	**102**	**93**	**97**	**97**

Table 5 shows that the measured lime content is close to 100% if carbonated lime is taken into account (CaO_{eq}). In the opposite case, the precision decreases strongly, with an absolute error near 20%. Although the samples were preserved in hermetic pills, the lime contained in the pastes became carbonated. Two explanations can be proposed for this carbonation:

- CO_2 was trapped in the paste during its preparation and led to the carbonation of the paste during its conservation.
- The carbonation occurred after the extraction of the paste from the pills during the preparation of the samples for analysis. Special precautions were taken during the tests (analyses were carried out on the pastes as soon as possible after they were extracted from the pills) to avoid such carbonation, but these measures may not have been sufficient.

Concerning the measurement of gypsum content, the precision of the method was comparable to that for lime. In the worst case, the amount of gypsum remaining in the paste was equal to 93% of that introduced. The precision of the method seems to be relatively poor, but it can be considered as acceptable in relation to the objectives of the method. This is discussed more fully in Section 5.

4.3. Consumption of lime and gypsum for pozzolan and WSA

Tests carried out on the measurement of calcite content showed that the measurement was not precise, having an absolute error of 1%, which is very high compared to the calcite contents measured in the pastes [24]. Therefore, it was decided not to take the calcite content and the CaO_{eq} into account in the continuation of the study. Nevertheless, the results for calcite content will be presented to check that the phenomenon of carbonation remained limited in the pastes.

4.3.1. Pozzolan

The results for pozzolan-containing pastes are presented in Table 6. For these pastes, a slight swelling was observed at 7 days (appearance of small cracks on the pills) and then stabilized. The setting of the mixture started at 7 days and the hardening intensified gradually for a year (for the one-year-old sample, it was necessary to break the pill with a hammer to extract the paste).

The amounts of "CaO" and gypsum consumed by the pozzolan are presented in Fig. 1.

The curves of Fig. 1 show a rapid consumption of lime during the first 28 days (approximately 70% of the lime had been consumed at day 28). This consumption continued after 28 days, but at a slower rate. This behaviour is unusual for the pozzolanic reaction, which is known to occur rather late, generally between 28 and 90 days. It is possible that the very high fineness of the pozzolan used for this test (11,000 cm^2/g) had an influence on the kinetics of the reaction. This pozzolan, because of its significant fineness,

Table 6
Amounts of gypsum, calcite and "CaO" contained in 100 g of fresh paste with pozzolan.

Age (days)		Mixture	7	28	90	365
$CaSO_4$, $2(H_2O)$	g	12.5	11.6	12.3	12.3	11.1
CaO	g	9.4	6.0	2.8	1.9	1.5
$CaCO_3$	g	0	0.0	0.7	0.8	3.0

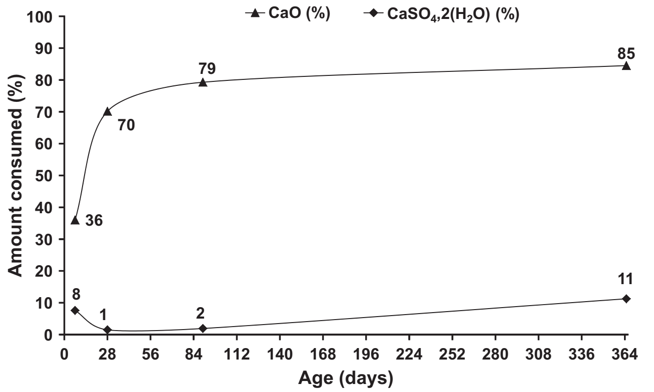

Fig. 1. Amounts of lime and gypsum consumed in pozzolan-containing paste.

would have reacted more quickly than what is usually observed. It is possible, too, that the presence of gypsum, even though its consumption was relatively weak, acted as an accelerator in this reaction.

The five XRD patterns presented in Fig. 2 show the mineralogical evolutions of the pozzolan-containing pastes. The gypsum peaks at 13° and 27° 2θ Co have been voluntarily cut because they are oriented peaks of the families of planes $00x$ whose intensity is strongly related to the preparation of the sample. These peaks cannot be used for even a semi-quantitative study and it is preferable to cut them in order to increase the intensities of the other peaks. Thus, to follow the gypsum consumption in the pastes, it is possible to use the peak with 34° 2θ Co, which remains high even after 1 year. From a purely qualitative point of view, the evolution of the gypsum peak is very slow up to 90 days but a significant decrease can be observed between 90 and 365 days. These results confirm those obtained previously by the chemical method. Moreover, this series of patterns clearly confirms the significant consumption of portlandite with the quasi-disappearance of all its peaks of diffraction (21°, 33.5°, 39.5°, 55.5°, 59.5° and 65° 2θ Co). Lastly, because of the number of minerals and the overlap of many peaks, it is difficult to clearly observe the evolutions of the mineralogical phases contained in the pozzolan (augite, forsterite, labradorite and magnetite).

Concerning the hydrated phases contained in the pastes, the presence of ettringite is observable at seven days but it is probable that this phase was formed earlier. The patterns show that this phase develops thereafter (strong increase in the intensity of the peaks at 11 and 18.5° 2θ Co). Moreover, the halo on the patterns highlights an increase in the amorphous phase with time, which could be attributed to the formation of Calcium Silicate Hydrate gel (CSH) produced by the pozzolanic reaction between the amorphous phase contained in pozzolan and the lime.

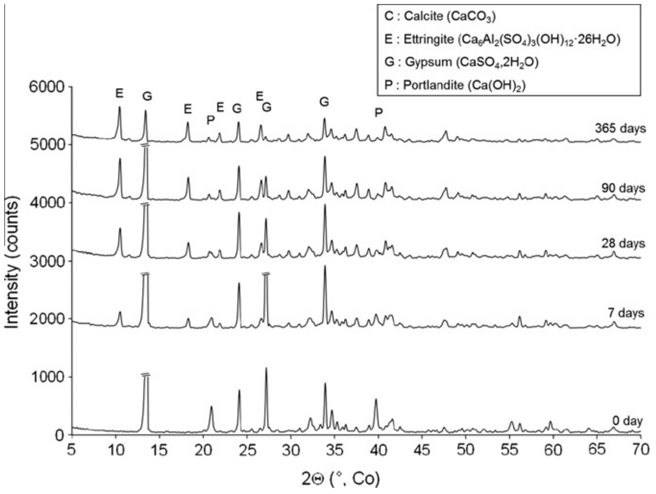

Fig. 2. XRD patterns of pozzolan-containing pastes.

4.3.2. WSA

The results for WSA-containing pastes are presented in Table 7. In this table, a column has been added because the WSA initially contained calcite and CaO; thus, the initial quantities of these two minerals contained in the pastes were calculated so as to be taken into account.

The setting and the hardening of WSA-containing pastes were quick, as could be expected from the mineralogical characterization of the WSA. At the end of 7 days, the mixture had hardened significantly. Moreover, a swelling of the pastes was observed, which seemed to occur in two steps:

- a first one during the first few days of hydration with a weak swelling at 7 days (appearance of small cracks on the pills),
- and a resumption of swelling at 28 days, which led to a significant cracking of the pills.

The amounts of "CaO" and gypsum consumed by WSA are presented in Fig. 3.

Firstly, Fig. 3 shows that WSA consumed little lime even after 1 year: it did not consume the quantity of lime that it contained (because, in this case, the proportion consumed would be higher than 18%). Moreover, as shown in Table 7, the increase in lime consumption could be partly explained by the carbonation of the pastes and did not correspond to a possible reaction between lime and minerals contained in the WSA. It is thus not necessary to add lime to activate the WSA.

Finally, Fig. 3 shows that WSA quickly consumed a significant amount of gypsum and this consumption of gypsum continued up to 365 days.

XRD patterns of WSA-containing pastes at various ages are presented in Fig. 4.

These patterns confirm the strong consumption of gypsum by WSA: the intensities of the gypsum peaks decrease strongly and the peaks almost disappear after 1 year. The gypsum reacted with WSA to form ettringite. Taking into account the evolution of the formation of ettringite, the expansions of the pastes observed after 28 days could be ascribable to the late formation of this expansive mineral. For the earlier expansions (before 7 days), complementary studies would be necessary to identify the reasons for these swellings (hydration of CaO, formation of ettringite or other?). Concerning the lime consumption, the patterns of Fig. 4 confirm the results of the chemical method: peaks of portlandite do not evolve between mixing and 1 year, which shows that the WSA does not consume (or consumes very little) lime.

Lastly, due to the number of minerals and to the overlap of many peaks, it is difficult to clearly observe the evolutions of the mineralogical phases contained in WSA. Nevertheless, the strong

Table 7
Amounts of gypsum, calcite and "CaO" contained in 100 g of fresh paste with pozzolan.

Age (days)		Mixture	Computed initial amount	7	28	90	365
$CaSO_4$, $2(H_2O)$	g	12.4	12.4	4.2	3.6	1.8	0.8
CaO	g	9.3	11.3	10.9	11.2	10.7	10.1
$CaCO_3$	g	0	3.6	3.9	3.5	5.3	6.1

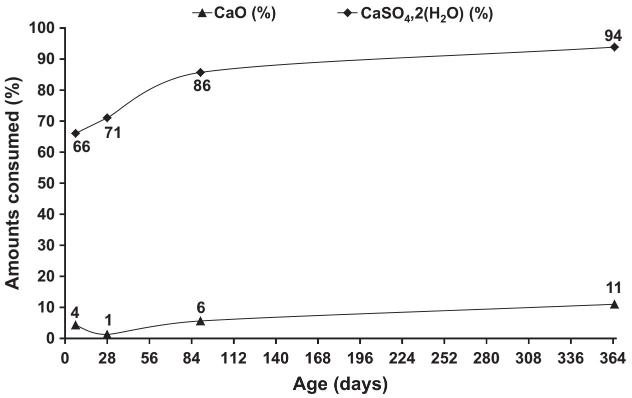

Fig. 3. Amounts of lime and gypsum consumed in WSA-containing.

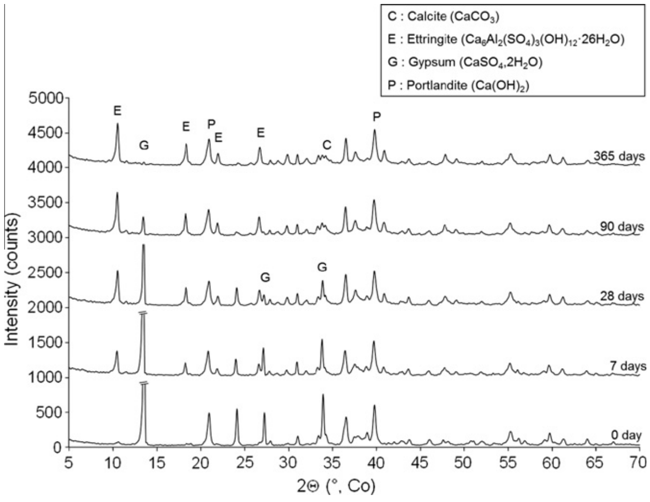

Fig. 4. XRD patterns of WSA-containing pastes.

decrease in the peak at 48° 2θ Co (overlapping of gehlenite, mayenite and α'-C_2S peaks) seems to confirm the consumption of both mayenite and α'-C_2S, which are two hydraulic minerals contained in WSA.

5. Application of the results: tool for the optimization of HRB compositions

One of the main objectives of this method was to help in the optimization of hydraulic binder compositions by taking account of the amounts of lime and gypsum that can react with the mineral addition used. Thus, starting from the results presented in Tables 6 and 7, it is easy to calculate the optimized proportions of each component for each time. For example, for pozzolan at 7 days: 65 g of pozzolan consumed 36% of the lime (36% of 15 g = 5.4 g) and 8% of the gypsum (8% of 20 g = 1.6 g). Thus, the proportion of pozzolan in the optimized mixture was: $65/(65 + 5.4 + 1.6) * 100 = 90.3\%$, that of CaO was 7.5% and that of gypsum was 2.2%. Table 8 presents the optimized compositions of binders containing pozzolan or WSA.

The following step, which consists of determining the proportion of each component to obtain the most effective binder starting from these results, necessarily contains approximations. For example, pozzolan consumes a significant amount of lime but a small amount of gypsum. In order to take the purity of the industrial products used (and, in particular, of a slight carbonation of lime) into account, it would be relevant to use the highest values of lime consumption (15%). The case of the gypsum is more difficult. The method shows that its consumption is not zero and it is possible that the presence of gypsum would activate the lime consumption by pozzolan thus improving the reactivity of the pozzolan. Thus, from an industrial point of view, it is necessary to introduce gypsum in small but pertinent proportions. Lastly, it could be necessary to take into consideration the standards that limit the sulphate content in binders, e.g. to 4% in Hydraulic Road Binders [7]. Thus, regarding these parameters as a whole, a mixture optimized for pozzolan as studied in this article could be 80% pozzolan +15% lime +5% gypsum.

Table 8
Optimized compositions of binders containing pozzolan or WSA.

Time (d)	7	28	90	360
Pozzolan (%)	90	86	84	81
$CaSO_4$, $2(H_2O)$ (%)	2	0	1	3
CaO (%)	8	14	15	16
WSA (%)	83	82	79	78
$CaSO_4$, $2(H_2O)$ (%)	17	18	21	22
CaO (%)	0			

The case of WSA is much simpler because there is no lime to add to the mixture (the WSA studied did not consume all the lime it contained) and the reactions are much faster than in the case of pozzolan. Thus, whatever the time considered, the proportion of gypsum to be added is close to 20%. In this case, the optimized mixture (80% WSA +20% gypsum) would not respect the standard because its sulphate content would be too high.

These two applications show the interest of the method: it makes it possible to help the users of additions to evaluate the quantities of each component that should be introduced into their mixture. This is much simpler, faster and more effective than an optimization based on an experimental study of several mixtures with measurements of performance on materials incorporating these binders. Of course, it will be necessary to test the performance of the binders optimized by this method on mortars or specimens of stabilized soil according to the destination of the binder, but the number of tests to be performed will be strongly reduced. During these tests, special attention will have to be paid to the study of the potential expansions of the materials as the gypsum is added to voluntarily form ettringite in the mixtures. If it is controlled, this formation makes it possible to increase the mechanical performance of the mixtures, in particular by filling the porosity. However, the expansive property of the ettringite presents a considerable risk of swelling and deterioration of the material if it is formed in amounts that are excessive compared to the volume of porosity to be filled.

6. Conclusions

In this paper, the reactivity of three materials with various behaviours has been studied:

- A siliceous filler used as the reference because it can be considered as inert regarding its reactivity to lime and gypsum.
- A natural pozzolan that essentially reacts with lime but whose reactivity can be improved by the addition of a small amount of gypsum.
- A Wastepaper Sludge Ash that is hydraulic and that consumes a significant amount of gypsum because of its calcium aluminate content. For this ash, the results have shown that the addition of lime serves no purpose.

The results obtained on siliceous filler validate the method developed, which consists of measuring the amounts of lime and gypsum that have not reacted in pastes containing these reagents in excess. By comparing with the initial quantities, it is also possible to calculate the quantity of lime and gypsum consumed by the mineral additions. The absolute precision of the method is relatively low (5%) but it can be considered as acceptable considering that this method is intended to be used as a tool to evaluate the quantity of each component that needs to be introduced into Hydraulic Road Binders.

This study led to the formulation of two binders: 80% natural pozzolan +15% lime +5% gypsum and 80% WSA +20% gypsum. These mixtures are optimized from the chemical point of view but that does not necessarily mean that they will be the most efficient HRB. It is, for example, possible that some interactions with the soil (in case of soil stabilization) could modify the behaviour of these binders or that expansions could appear because of the significant formation of ettringite in the mixtures (in particular for the WSA-gypsum binder). To complete this study, it will be necessary to test the performances of these binders on mortars or on specimens of stabilized soil. During these tests, special attention will have to be paid to the study of the potential expansions of the materials, especially during their immersion.

Finally, complementary studies could be carried out to refine the precision of this method and it would be interesting to test it on other materials, such as clayey soils, metakaolin or coal fly ashes, for example.

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