Development of insoluble gypsum using calcium sulfoaluminate cement

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ABSTRACT : Gypsum is a cheap binder but its utilization remains limited due to its bad water resistance. The solutions usually proposed to improve this water resistance consist in adding water repelling agents like organo-polysiloxanes to the mixing water. This paper shows that another solution is to mix calcium sulfoaluminate clinker and gypsum. When hydrating, such mixture becomes water-resistant and gypsum is converted into hydraulic binder. Therefore, it is possible to develop low cost housing materials, mainly based on gypsum. The experimental results show that the quantity of calcium sulfoaluminate clinker necessary to stabilize gypsum is in the range of 20 to 30% of the total amount of binder (phosphogypsum + calcium sulfoaluminate cement). In such case, resistance to wetting-drying cycles is very good. Building materials like concrete blocks, renders, and screeds were developed and behaved very well under natural weathering for more than 4 years.

1 INTRODUCTION

Phosphogypsum is a by-product from the production of phosphoric acid by the wet process. In this process, the raw phosphate is treated by sulphuric acid and, besides the main product which is phosphoric acid, gypsum and a small quantity of hydrofluoric acid are obtained. For each ton of anhydrous phosphorous oxide (P_2O_5) about 5 tons of phosphogypsum are obtained. The world production of phosphoric acid is about 22 Mt of P_2O_5 and thus the quantity of phosphogypsum corresponds to about 110 Mt [Kurdowski & Sorrentino 1997]. There are several areas of utilization for phosphogypsum. The two main fields are conversion of phosphogypsum to plaster and plaster products and replacement of natural gypsum in cement production. Unfortunately, because of high energy consumption needed to dry phosphogypsum and sometimes radioactivity problems, the utilization of phosphogypsum is limited: less than 4 Mt per year in building materials [Kurdowski & Sorrentino 1997]. As phosphogypsum is particularly abundant in developing countries (Morocco, Tunisia, Brazil, India, Egypt,…), it should be interesting to find new ways of valorization in order to develop low cost building materials.

This is the aim of the present study. In a first step, a new hydraulic binder containing phosphogypsum and calcium sulfoaluminate clinker was designed. It was mainly composed of phosphogypsum (70 to 80%) which is soluble in water. The addition of calcium sulfoaluminate clinker (20 to 30%) led to the production of a water-resistant binder. Therefore, it was possible, in a second step, to develop building materials based on this new binder and presenting very good weathering durability.

2 EXPERIMENTAL WORK

2.1 *Materials*

The phosphogypsum used in the present study contained 96.7% pure gypsum. The average diameter of the particle size distribution was 12 µm and the pH was slightly basic (pH = 8.8).

Two calcium sulfoaluminate clinkers (CK1 and CK2) were investigated. Their mineralogy assessed by X-ray diffraction and chemical analysis is shown in Table 1. The amount of yeelimite, also called “Klein’s compound”, was higher in CK2. This phase and mayenite are responsible of the development of early age strength. These clinkers were ground to get a Blaine specific area of 400 m^2/kg.

Table 1. Mineralogy of CK1 and CK2 (w_t %).

Phase	CK1	CK2
Belite – C_2S	17.2	15.6
Yeelimite – $C_4A_3\bar{S}$	60.9	66.4
Mayenite – $C_{12}A_7$		7.1
Perovskite – C_3FT_2	7.9	9.9
Ferrite – C_4AF	14.0	

2.2 *Improvement of the water resistance of phosphogypsum*

Gypsum based binders are generally cheap but their development is limited due to their bad resistance to water. The performance of gypsum based binders, and in particular their resistance to water, may be improved by combining calcium sulfate with limited amounts of some other constituents such as Portland clinker or cement, microsilica blended Portland cement [Bentur & al. 1994, Gutti & al. 1996, Kowler 1998, Odler & Yan 1994] and. fly ash [Singh & Garg 1995]. In the present study, calcium sulfoaluminate clinker was added to improve the water resistance of phosphogypsum, according to the following reaction:

$C_4A_3\bar{S} + 2C\bar{S}H_2 + 34H \Rightarrow C_6A\bar{S}_3H_{32} + 2AH_3$

where: $C = CaO$; $A = Al_2O_3$; $\bar{S} = SO_3$; $H = H_2O$.

Mixtures of yeelimite and gypsum yield ettringite ($C_6A\bar{S}_3H_{32}$) and gibbsite (AH_3) as products of hydration. These hydrates are insoluble in water. As calcium sulfoaluminate clinker is more expensive than phosphogypsum, the binder was mainly composed of phosphogypsum. Table 2 shows the different binders which were investigated. Six binders were prepared with CK1 and three with CK2. The clinker content varied from 5 to 30%.

Table 2. Composition of the binders (w_t %).

Binder	Phosphogypsum	CK1	CK2
1	95	5	-
2	90	10	10
3	85	15	-
4	80	20	20
5	75	25	-
6	70	30	30

2.3 *Preparation of mortars*

The objective of this study was to determine the minimum quantity of calcium sulfoaluminate clinker needed to obtain a material presenting good water resistance. Standard mortars were prepared with the binders described in Table 2, with sand-binder ratio of 1:3 and water-binder of 0.5.

The measurements carried out on fresh mortar were specific gravity and workability. Workability was assessed by means of the flow of a truncated cone (ϕ_{inf} = 100 mm, ϕ_{sup} = 70 mm, h = 50 mm) after 15 drops on a flow table.

Prismatic samples (40 x 40 x 160 mm) of mortar were cast. All mortars were demolded after 48 hours. One series of samples was kept at 20°C in sealed plastic bags until the age of (d-1) days, with d = 7, 28, and 90. The second series of specimens was stored in water at 20°C until the age of (d-1) days. Then, all the samples were stored at 20°C and 50% RH for 24 hours and subjected to mechanical testing.

To verify the durability of mortars, prismatic samples (40 x 40 x 160 mm) containing binders 4 and 6 (20% and 30% CK1 and CK2, respectively) were cast and demolded after 24 hours. They were stored at 20°C in sealed plastic bags for 7 or 28 days. At these ages, they were subjected to 25 wetting and drying cycles. Each cycle consisted in immersion in water for 18 hours followed by drying at 60°C for 6 hours. The flexural and compressive strengths were measured after these cycles.

The microstructure was investigated on plain pastes prepared with binders 4 and 6 by means of X-ray diffraction and DTA (Differential Thermal Analysis). Mini-cylinders (ϕ = 20 mm, h = 40 mm) of paste were prepared and cured in the same conditions as mortars.

2.4 *Development of building materials*

The binder leading to the best water resistance was used to design building materials: concrete blocks, renders, and screeds. The properties of these materials were compared to those of materials based on normal portland cement.

3 PROPERTIES OF MORTARS BASED ON PHOSPHOGYPSUM BINDERS

3.1 *Properties of fresh mortars*

The specific gravity and flow of fresh mortars are presented in Tables 3 and 4. The values obtained were equivalent, both for flow and specific gravity.

Table 3. Specific gravity of fresh mortars.

Binder	CK1	CK2
1	2.18	-
2	2.20	2.18
3	2.21	-
4	2.19	2.18
5	2.19	-
6	2.18	2.19

Table 4. Flow of fresh mortars (mm).

Binder	CK1	CK2
1	165	-
2	168	165
3	160	-
4	165	170
5	165	-
6	165	164

3.2 *Compressive strength*

The compressive strength of mortars prepared with clinker CK1 is shown in Figure 1. The strength of mortars prepared with binders 1, 2 and 3 was very low, regardless of the curing conditions. For these binders, the maximum strength was reached at 7 days of age and showed no further increase till 90 days. When binders 4 to 6 were used, the compressive strength development was continuous between 7 and 90 days. The level of strength was similar, regardless of the curing conditions. After 90 days, the maximum strength obtained was about 23 MPa.

The compressive strength of mortars prepared with clinker CK2 is presented in Figure 2.

The strength developed by mortars cast with binder 2 remained very low, regardless of the curing conditions. When binders 4 and 6 were used, the strength development was continuous and the level of strength obtained was higher than using CK1. After 90 days, the maximum strength was obtained when samples were cured in water: 30 MPa. When mortars were kept in plastic bags, this strength was 23.5 MPa. At early age (7days), the use of CK2 led to higher strength than CK1. These results may be explained by the higher amount of yeelimite contained in CK2, leading to higher precipitation of ettringite. The strength obtained after 90 days of water curing (30 MPa) is particularly interesting, compared to that observed on standard mortars cast with usual calcium sulfoaluminate cement containing 20% of phosphogypsum: 70 MPa. In the present study, the amount of phosphogypsum is multiplied by 3.5 and the strength is only divided by 2.3.

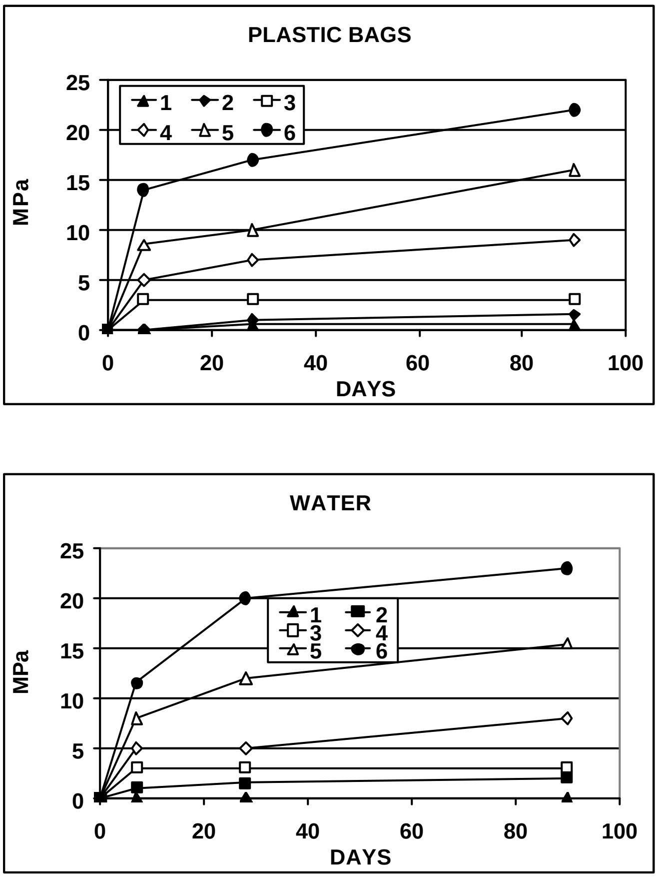

Figure 1. Compressive strength versus age for mortars prepared with CK1.

From these results, it can be concluded than mortars cast with binders 4 to 6 are water resistant: the strength continuously increases in water between 7 and 90 days. The minimum content of calcium sulfoaluminate clinker needed to get water resistance of phosphogypsum is 20%. This was verified by the wetting and drying cycles performed on mortars cast with binders 4 and 6. The results are shown in Table 5. Regardless of the age of mortars at the beginning of wetting and drying cycles (7 or 28 days), the compressive strength increased after 25 cycles: from 17 to 37%. Once more, the best results were reached with CK2.

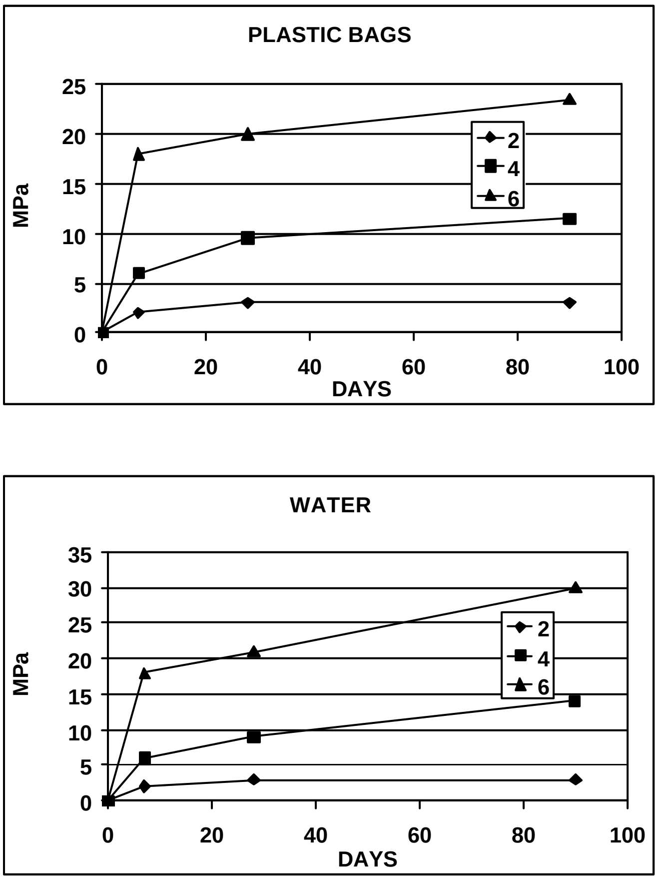

Figure 2. Compressive strength versus age for mortars prepared with CK2.

Table 5. Compressive strength after wetting and drying cycles.

CK	Binder	Age of mortar when starting cycles (Days)	Compressive strength (MPa)	
			0 cycle	25 cycles
CK1	4	7	5	5.9
		28	6.1	7.3
	6	7	13.7	17.7
		28	17.4	20.3
CK2	4	7	7.8	10.3
		28	9.6	11.8
	6	7	18.3	24.5
		28	21	28.8

3.3 *Microstructure*

Ettringite was the only hydrate observed by X-ray diffraction in each paste. Yeelimite was totally consumed after 7 days when pastes were cured in water, and after 28 days when pastes were kept in sealed bags. Unreacted gypsum remained in the pastes, but natural weathering tests showed that the long-term performance of materials was not affected. These results were confirmed by DTA, which also pointed out the presence of gibbsite (aluminium hydroxide).

4 DESIGN OF LOW COST BUILDING MATERIALS

Three types of materials based either on binder 4 (20% CK2 + 80% phosphogypsum) or binder 6 (30% CK2 + 70% phosphogypsum) were designed: concrete blocks, renders and screeds. Such materials based on normal portland cement are often used for low cost housing in North Africa (Tunisia, Morocco, Algeria), where phosphogypsum is abundant and can represent an interesting alternative.

4.1 *Concrete blocks*

Concrete blocks (150 x 200 x 400 mm) were industrially produced using either normal portland cement or binder 6. The composition and properties of these blocks are shown in Table 6. All blocks fulfilled the French standard specification: 7-day compressive strength higher than 4 MPa. A wall was constructed in April 2003 and subjected to natural weathering in Lyon. In summer 2003, it was submitted to temperatures as high as 40°C for about one month, then to storms, freezing and thawing cycles, and finally to strong rain (more than 120 mm within 2 days) in April 2005. Figure 3 shows that the durability of this wall is excellent. The joining mortar was prepared with binder 4.

Table 6. Composition and properties of concrete blocks.

Components (kg)	Control	Type 1	Type 2
Sand (0/5 mm)	400	400	400
Coarse aggregate (6/10 mm)	540	540	540
Cement CEM I 42.5	70	-	-
Binder 6	-	100	120
Water	91	91	91
Block weight (kg)	15.4	16.1	16.6
7-day strength (MPa)	5.4	6.4	7.1

Figure 3. Concrete blocks and screeds after 4 years of natural weathering.

4.2 *Renders*

The function of a render is to protect the wall against rainfalls and remain permeable to water vapour contained in air. In the present study, the requirements were those presented by commercial products based on normal portland cement:

- 28-day compressive strength: 10 MPa,
- time of workability: 60 minutes.

Three products were designed, based either on binder 4 or binder 6. Their composition and properties are shown in Table 7.

Normal portland cement (NPC) was introduced in the mixtures as accelerator [Ambroise & Péra 2003a, b, Péra & Ambroise 2004]. When hydrating, NPC yields calcium hydroxide which reacts with gypsum and yeelimite to precipitate ettringite and bring early-age strength:

$$C_4A_3\overline{S} + 8C\overline{S}H_2 + 6CH + 74H \Rightarrow 3C_6A\overline{S}_3H_{32}$$

Ettringite produced by this reaction is expansive and this property was exploited when designing render 3. The higher amount of NPC present in render 3 limited the drying shrinkage of this material.

All the requirements were fulfilled and each render was applied on the wall constructed with the concrete blocks previously designed. After two years of natural weathering, they behave very well, as shown in Figure 4. Render 2 was the easiest to apply and presented very good uniformity.

Table 7. Composition and properties of renders.

Components (kg/m^3)	Render 1 (B4)	Render 2 (B6)	Render 3 (B6)
Sand 0/5 mm	1350	1350	1350
Phosphogypsum	340	297	280
Clinker CK2	85	128	120
NPC Normal portland cement)	25	25	50
Boric acid	0.8	0.8	1.6
Water	240	240	240
Time of workability (minutes)	60	65	60
Compressive strength (MPa)			
24 hours	11.4	20.3	20.9
28 days	23.5	30.1	30.1
Flexural strength (MPa)			
24 hours	2.5	3.1	3.1
28 days	4.0	3.9	3.8
Drying shrinkage at 28 days (µm/m)	690	710	70

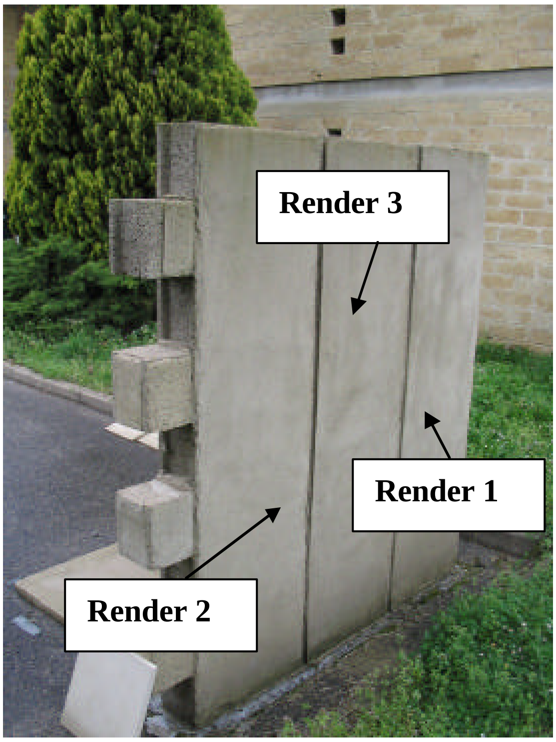

Figure 4. Renders after 4 years of natural weathering.

4.3 *Screeds*

Two types of screeds based on binder 6 were designed: one was traditionally cast and the other was self-leveling. Their composition and properties are presented in Tables 8 and 9.

Table 8. Composition of screeds.

Components (kg/m^3)	Traditional	Self-Leveling
Sand 0/5 mm	1350	1250
Binder 6	425	420
NPC (Normal portland cement)	5	10
Limestone powder	-	50
Boric acid	0.8	-
Water	240	260
Viscosity modifying agent	-	2
Anti foaming agent	-	0.35
Shrinkage reducing agent	-	5
Superplasticizer	-	6

Table 9. Properties of screeds.

Properties	Traditional	Self-leveling
Time of workability (minutes)	50	120
Initial set (minutes)	65	360
Compressive strength (MPa)		
24 hours	15.2	8.3
7 days	20.4	12.8
28 days	28.5	28.2
Drying shrinkage at 50 days (µm/m)	850	400

The early-age strength of the self-leveling screed is lower than that of the traditional one. At 28 days, the performances are equivalent. The drying shrinkage of the self-leveling screed is half that of the traditional one.

5 CONCLUSIONS

This study shows that phosphogypsum constitutes an interesting resource for the development of low cost housing materials. From the results obtained, it is possible to draw the following conclusions:

1. Regardless of the source of calcium sulfoaluminate clinker, it is possible to get a water resistant binder by mixing 70-80% phosphogypsum to 30-20% calcium sulfoaluminate clinker 2. The best performances are obtained by the binder containing 70% phosphogypsum. All yeelimite is consumed and the products of hydration are ettringite and gibbsite.
3. The use of this binder is recommended to design low cost building materials in developing countries possessing large amounts of phosphogypsum: concrete blocks, renders or screeds.
4. The performances (strength and durability) of these materials are excellent.

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