EXPERIMENTAL STUDY OF SULFOALUMINATE CONCRETE BASED MATERIALS

ETUDE EXPERIMENTALE D'UN BETON A BASE DE CLINKER SULFO-ALUMINEUX

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ABSTRACT - Sulfoaluminate clinker presents a very interesting alternative to Portland clinker regarding sustainable development. An experimental program is undertaken using a sulfoaluminate clinker mixed with micro-ionized gypsum. We carry out series of tests on different mixes: rheology tests, water porosity, expansion tests, compressive strength tests at various ages, measurement of the temperature evolution during the cement hardening, alkalinity measures of the cement paste. An experimental design method is used, varying the water content, the gypsum content through $\overline{S}/A$ ratio, allowing the optimal design of the concrete mixture proportioning. Then we compare an optimal solution using this binder with a classical formulation based on Portland cement. We also evaluate environmental impact of the optimal solution versus a Portland cement solution.

RESUME - Les clinkers sulfoalumineux présentent une alternative intéressante aux ciments Portland dans une optique de développement durable. Une étude expérimentale est menée sur des bétons à base de clinker sulfoalumineux et de gypse micro-ionisé. Plusieurs tests sont réalisés sur les différentes formulations : rhéologie, porosité à l'eau, mesure d'expansion, résistance à la compression à différents âges, exothermie et mesure de pH de la pâte de ciment. La méthode des plans d'expérience est utilisée en faisant varier deux facteurs : le rapport E/C et le rapport $\overline{S}/A$. L'exploitation des résultats de mesures permet alors de déterminer une formulation optimale vis-à-vis d'un cahier des charges. Nous comparons alors cette solution à une formulation plus classique à base de clinker Portland et nous évaluons l'impact environnemental des deux formulations.

1. Introduction

Concrete, usually made with Portland cement, is the most widely used building material on Earth. It represents about 1.7 x 10^9 ton/year (Gartner, 2004). However, to produce 1 ton of concrete induces carbon dioxide emission of about 0.08 ton. In France, 2.6% of carbon dioxide emissions are due to cement industry. At an international level, cement industry represents 5% of carbon dioxide emissions (Gartner, 2004).

We know that, nowadays, production of 1 ton of Portland clinker emits 815 kg of carbon dioxide and consumes, in North America, around 4.2GJ (Gartner, 2004). Energy consumption linked to the manufacturing process of clinkering varies a lot, because of the type of energy used (electric, hydraulic, …) and of the quality of kilns. In 1994, carbon dioxide emissions due to Portland cement manufacturing process used to come from raw materials (about 52%) and from fuels (about 48%) (Gartner, 2004). In order to reduce these emissions, improvements were brought by the optimization of the manufacturing process (precalciners, new kilns) and by the contribution of substitution fuels such as industrial wastes. These improvements relate more to the part of carbon dioxide emitted by the manufacturing process. Changing the raw materials used for the formation of clinker is another way of reducing carbon dioxide emissions. In that way, we are working on a sulfoaluminate clinker (Alaoui *et al*, 2006) which we are going to present in the following. This sulfoaluminate clinker, on which our work is based, is an experimental one. According to Gartner (Gartner, 2004) it is one of the most promising low-CO_2 alternatives to Portland cement.

After a presentation of the environmental advantages of this clinker, we present the experimental program made on mixes of gypsum and sulfoaluminate clinker. Then we compare an optimal solution using this binder with a classical formulation based on Portland cement. We also evaluate environmental impact of the optimal solution (mix of sulfoaluminate clinker and gypsum) versus a Portland cement solution. Actually, we compare carbon dioxide emissions in each case.

2. Sulfoaluminate clinker versus Portland clinker: the environmental point of view

2.1. Portland clinker

Portland clinker is made from a mix of 80% lime (from calcareous rocks) and 20% silica (from clay). This mix is put into a kiln at 1450°C, temperature which makes possible the clinkering (chemical transformation) of the Portland cement. From an environmental point of view this manufacturing process is not optimal. As a matter of fact, two factors need to be considered: energy consumption during the production and emission of carbon dioxide. A part of carbon dioxide emissions is due to raw materials: the clinkering, or chemical transformation, induces carbon dioxide emissions only because limestone is part of the raw materials and so it discarbonates. In addition, the high temperature (1450°C) at which the chemical transformation occurs, induces consumption of energy through fuels and so more carbon dioxide emissions. These two ways of production of carbon dioxide are linked but we have limited our work to the carbon dioxide emissions due to raw materials, which we detail hereafter.

Carbon dioxide emissions from raw materials are due to the "potential CO_2" contained within them through the limestone. Portland cement is composed of alite (C_3S), belite (C_2S), tetracalcium aluminoferrite (C_4AF) and tricalcium aluminate (C_3A). Alite and belite are the main components. While considering a Portland clinker composed of 20% of C_2S, 60% of C_3S, 10% of C_3A and 10% of C_4AF, we obtain that producing 1 ton of clinker emits 535 kg of carbon dioxide. Details are given in (Feraille *et al*, 2007).

2.2. Sulfoaluminate clinker

Sulfoaluminate clinker is made from a mix of limestone, bauxite and calcium sulphate. The clinkering of that mix occurs at a lower temperature than Portland clinker, around 1250°C – 1300°C. Its composition is: 60-70% of yeelimite or kleinite ($(CaO)_4(Al_2O_3)_3SO_3$ or $C_4A_3\overline{S}$), 10-20% of belite (C_2S), 0-14% of tetracalcium aluminoferrite (C_4AF), 0-7% of calcium aluminate ($(CaO)_{12}(Al_2O_3)_7Fe_2O_3$ or $C_{12}A_7$), [9].

The clinkering reactions of the various components of sulfoaluminate clinker are given in (Odler, 2000). The details and the mass of carbon dioxide emitted for every ton of clinker component fabricated are given in (Feraille et al, 2007).

The clinker we used consisted of the following majority hydraulic phases:

Table 1 : Mineralogical composition of sulfoaluminate clinker

$C_4A_3\overline{S}$	C_2S :	$C\overline{S}$	C_4AF :	residual:
53 %	18 %	12 %	15%	around 2%

Considering the previous percentage of the different components of the sulfoaluminate clinker on which we work, we obtain 305 kg of carbon dioxide emitted for 1 ton of clinker produced

(Feraille et al, 2007). So from the point of view of carbon dioxide emitted, sulfoaluminate clinker is interesting.

Clinkering temperature of sulfoaluminate clinker is lower than Portland clinker's one, it induces a clinkering cost less important. Sulfoaluminate clinker is also more friable than Portland clinker, so it induces a less important energetic cost due to crushing (Janotka I. and Krajci L., 1999).

2.3. Environmental assessment

The following table is given as a summary in order to compare sulfoaluminate clinker and Portland clinker:

Table 2 : Comparison of carbon dioxide emissions

	Portland clinker	Sulfoaluminate clinker
CO_2 emitted per ton of clinker produced	535 kg/t	305 kg/t
Specific heat consumption during clinkering (Popescu et al, 2002)	3.845 GJ/t	3.305 GJ/t *
Energetic cost of crushing (Janotka I. and Krajci L., 1999)	45 to 50 kWh	20 to 30 kWh

* This data has not been given exactly for our type of sulfoaluminate clinker. The clinker used by (Popescu et al, 2002) contained less $C_4A_3\overline{S}$ and more C_2S. So we can suppose that the specific heat consumption during clinkering associated to our clinker is less important. But because we don't have the specific heat consumption of the clinker we used, we are going to support our example on the data given by (Popescu et al, 2002).

3. Experimental program

3.1. Introduction

The $C_4A_3\overline{S}$ hydration has been extensively studied in the past (Beretka et al, 1996), (Odler, 2002), (Kasselouri et al, 1995), (Mehta, 1973), (Zhang, 2002), (Janotka et al, 2003), (Barnier, 1986), (Cottin, 1979). The hydration of $C_4A_3\overline{S}$ depends on whether calcium sulfate and calcium hydroxide are also present, and progresses at temperatures up to 75° C (Odler, 2002), (Hanic et al, 1989). A complete review is presented in (Alaoui et al., 2007).

Our aim is to develop a tool for the formulation of these low-CO_2 concrete systems allowing the design of concrete mixtures according to any structural application and to assess the relevant long-term performance indicators. An experimental program is undertaken using a clinker provided by an industrial partner mixed with micro-ionized gypsum; the objective being to determine the optimum values of water to cement ratio (W/C) and added gypsum, for each application. Indicators used are compressive strengths at various ages and maximal expansion value of concrete, as the main hydrate produced is ettringite, which is known to be potentially expansive.

3.2. Materials

3.2.1. Cement and gypsum

The cement used is a mix of sulfoaluminate clinker and gypsum. The clinker used has the chemical composition which is presented in Table 3, where 'PF' is the loss in mass occurring at 1000°C.

Table 3: Chemical composition of sulfoaluminate clinker

component	PF	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	MnO	CaO	MgO	P_2O_5	SrO	SO_3	Na_2O	K_2O
% mass	0,75	7,35	31,51	1,65	1,58	0,04	41,15	0,76	0,14	0,19	13,80	0,19	0,51

From the chemical analysis, we determine the SO_3/Al_2O_3 ratio ($\overline{S}/A$ ratio) of the sulfoaluminate clinker (CSA). This leads to the value of 0.56. We then add gypsum to this clinker in order to obtain desired values of $\overline{S}/A$ (i.e. 1.1 and 1.64). These ratios are selected while being based on similar work on the mortar of (Sudoh et al, 1980). BLUE SULYKAL DH gypsum is used. The chemical composition is presented in the following.

Table 4: Chemical composition of gypsum

Chemical composition	P_2O_5	SO_3	CaO	K_2O	Na_2O	Fe_2O_3	Al_2O_3	SiO_2	F
%	0,06%	46,87%	32,25%	0,01%	0,15%	0,01%	0,02%	0,36%	0,01%

3.2.2. Aggregates

The siliceous aggregates Palvadeau are used to avoid undesired reactions. Three types of sand (0-0.315 mm; 0.315-1 mm; 1-4 mm) and two types of gravel (4-8; 8-12 mm) are used. The granular skeleton was optimized, using BétonLab Pro© software, in order to obtain the maximum aggregate packing density. The aggregate distribution (figure 1) is the same for all studied concretes.

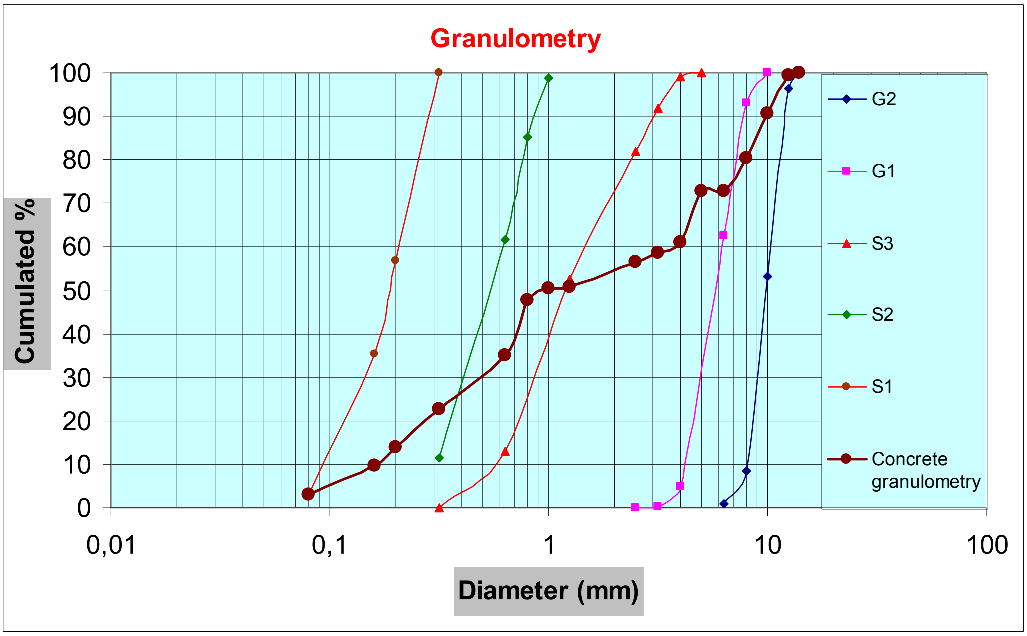


Figure 1: Aggregate grading of aggregates and concrete

3.2.3. Samples

In our experiments, tests are performed on cylindrical specimens to evaluate the expansion and compressive strengths of the concrete. The standard cylinder is 11 cm in diameter by 22 cm long. The samples are then kept in a conservation room at 20°C and more than 95 % of humidity.

3.3. Concrete composition

The concrete was composed of siliceous aggregates and a mix cement of sulfoaluminate clinker – gypsum. The compositions of 9 concrete formulations are presented in Table 5, where the water to cement ratio (W/C) is 0.5, 0.6 and 0.7, and $\overline{S}/A$ ratio is respectively 0.56, 1.1 and 1.64, corresponding to added gypsum of 0%, 22% and 36%. All the concretes have the same binder content: 400 kg/m^3.

Table 5 : Composition of a 1m^3 of concrete

Formula	W/C	$\overline{S}/A$	CSA (kg)	Added gypsum (kg)	% added gypsum	Water (kg)
AG	0,5	0,56	400	0	0	200
BG	0,5	1,1	310	89	22	200
CG	0,5	1,64	254	145	36	200
AE	0,6	0,56	400	0	0	246
BE	0,6	1,1	310	89	22	246
CE	0,6	1,64	254	145	36	246
AF	0,7	0,56	400	0	0	286
BF	0,7	1,1	310	89	22	286
CF	0,7	1,64	254	145	36	286

3.4. Tests

3.4.1. Expansion test

This test allows measuring the expansion of the samples conserved immersed in water. Tests are performed at 'Service Physico-Chimie des Matériaux" at LCPC. The principle of this test consists in jointing studs on three generators of the specimen placed at 120°. On each generator, the initial distance between the two studs (*l_0*) is almost equal to 10 cm and is precisely measured. We then measure the evolution of this distance between the two studs (*l*) to determine the expansion: $\varepsilon = \dfrac{l - l_0}{l_0}$

3.4.2 Compressive strength tests

Compression tests on concrete samples are carried out at the LAMI at ENPC. The loading is ensured by a press QUANTRIS 3R whose maximum loading capacity is equal to 3000 kN. The test is controlled in force. In our case, the loading rate is set to a value 3 kN/s. Tests are performed at ages of 1 day, 3 days, 7 days, 28 days, 90 days and 120 days. Each time, three samples of each mix-composition are tested.

4. Results and discussion

4.1 Expansion results

Measures were conducted for more than five months and are still continued. For each concrete formula, three samples are equipped and we present results on figure 2. The mean value corresponds to nine measures (three samples with three pairs of studs). The error bar represents twice the standard deviation of the measures. As we see on figure 2, concrete formula with $\overline{S}/A$ = 0.56 are instable and lead to an expansive concrete. For other values of $\overline{S}/A$, the strain is quite moderate, mainly expansive, so for optimization purposes, we will use the maximal value. But the great surprise came from the "explosion" of all samples of formula CF after immersion into water, as shown on the image. This is the reason why no expansion result is available for this formula, and for the optimization we took a value of 5 mm/m.

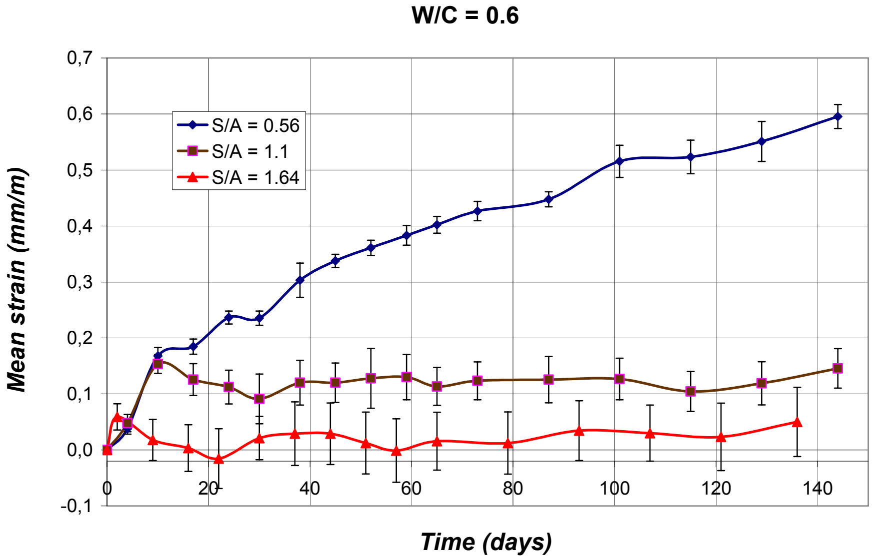


Figure 2: Expansion evolution for some of the concretes

4.2 Compressive strengths results

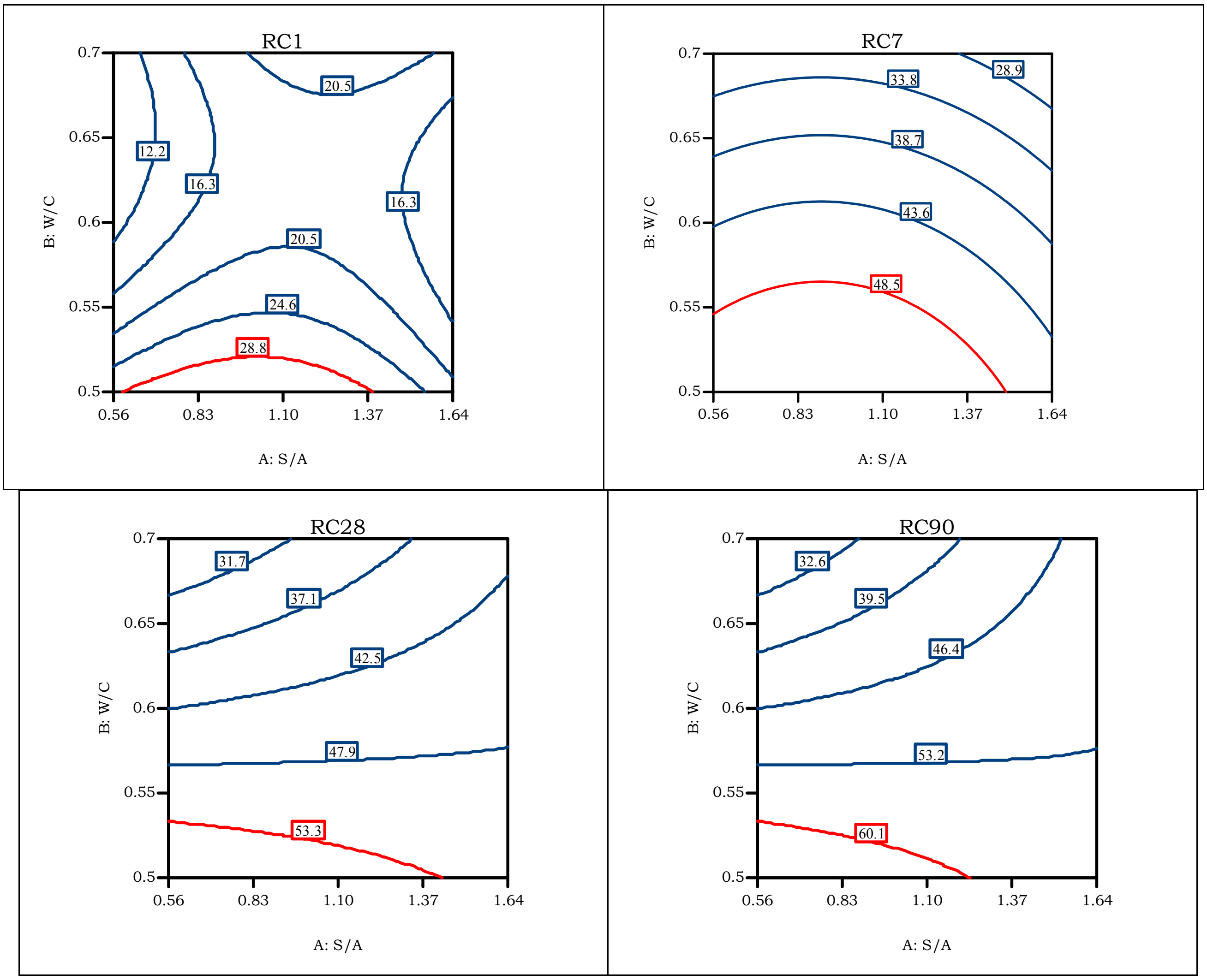


Figure 3: Compressive strength evolution results (in MPa)

The obtained results are treated using a computerized tool of experimental design (Design Expert). This allows us to model the measured responses with respect to the studied factors (W/C and $\overline{S}/A$) within the working domain and the relevance of modeling is analyzed through a variance test.

Results presented on figure 3 confirm the very good strength at early ages of these binders, which makes it possible to consider them in applications like prefabrication or quick demolding. Moreover, absolute strength values are quite high for all classical applications and so are long term resistances.

According to the evolution of resistances, it appears that the optimum could be reached for a value of water content lower than 0.5. However the workability of the mixture becomes problematic around this value and, to increase it, there is a need for the addition of superplasticizers.

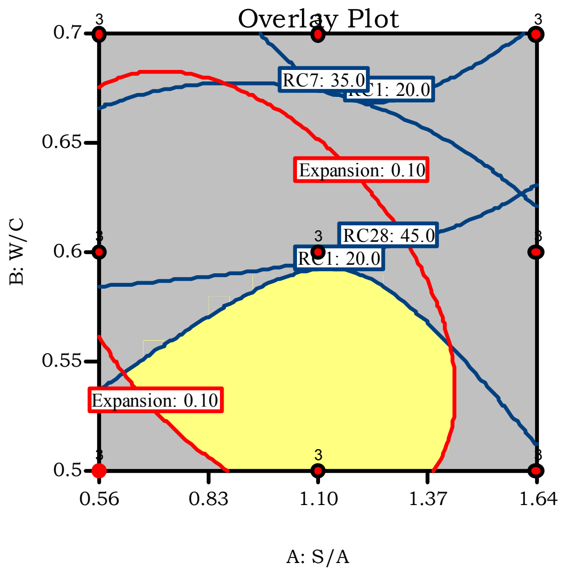
6. Conclusions

The objective of this study was to build a tool for the mix-proportioning of low-CO_2 concrete systems, based on sulfoaluminate clinker, allowing the design of concrete mixtures according to any structural application and the assessment of a long-term performance indicator, the maximal expansion value. A complete experimental program, varying values of the two main factors known to be influent (W/C and $\overline{S}/A$), has been conducted using experimental design.

Obtained results allowed us to model the chosen responses (compressive strengths at 1day, 3 days, 7 days, 28 days, 90 days and 120 days) and expansion of the mixes. With these results we can now perform an optimization for any structural application, which criteria are based on the measured responses.

For example, we show on next graph, the optimal domain (light zone) obtained using the following criteria, which correspond to applications, like prefabrication, where high early age strengths are required:

- Resistance at 1 day > 20 MPa
- Resistance at 7 days > 35 MPa
- Resistance at 28 days > 45 MPa
- Expansion < 0.1 mm/m



We can now choose, within this domain the optimal point with respect to environmental considerations. It corresponds to W/C = 0.53 and $\overline{S}/A = 1.44$. We then perform an environmental analysis about carbon dioxide emissions compared with a similar concrete made of Portland cement (CEM II), having the same resistance at 28 days, with the same binder amount per m^3 (i.e. 400 kg).

Table 6 : Environmental evaluation of the two concretes

	Portland concrete	Sulfoaluminate concrete
CO_2 emitted for clinker producing	171.2 kg/m^3	83 kg/m^3
Specific heat consumption during clinkering	1.232 GJ/ m^3	0.9 GJ/ m^3

We see that carbon emissions are divided by two, while Portland concrete does not make it possible to obtain the required early age strength. However the CSA mix deserves a thorough study on the rheology with low water content, and the assessment of reliable durability indicators.

7. References

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