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# STUDY ON TOURNAI LIMESTONE IN ANTOING CIMESCAUT QUARRY PETROLOGICAL, CHEMICAL AND ALKALI REACTIVITY APPROACH

J.-Sylvine Guédon-Dubied
Laboratoire Central des Ponts et Chaussées (LCPC)
58 Boulevard Lefebvre, 75732 Paris, France

Gaël Cadoret
Cadoret Consulting, 18 Avenue de la Bourdonnais, 75007 Paris, France

Vincent Durieux
Cimescaut Matériaux, Rue du Coucou, 37 7640 Antoing, Belgique

François Martineau
Laboratoire Central des Ponts et Chaussées (LCPC)
58 Boulevard Lefebvre 75732 Paris, France

Pascal Fasseu
Laboratoire Régional des Ponts et Chaussées de Lille, Rue du Marais Séquedin,
59482 Haubourdin, France

Vincent Van Overbecke
Carrières d'Antoing, rue du Coucou 8, Antoing, Belgique

## ABSTRACT

This study was carried out to determine the potential alkali-reactivity of the various levels of the Tournai limestone exploited in the Cimescaut quarry, Antoing, Belgium. This initial step in the investigation aimed at clearly defining the mineralogical and chemical characteristics, as well as the potential alkali-reactivity as determined by the standard P 18-590 autoclaving test, of the five stratigraphical units identified in the quarry. The second step consisted of evaluating the performance of this limestone in concrete with various alkali contents and determine the alkaline level above which the formula became reactive. The third phase of the project consisted at evaluating the possibility of using crusher's fines obtained from the processing operations of the Tournai Limestone in the Cimescaut quarry either as a granular corrector, an addition for hydraulic concrete or as an alkali-reaction inhibitor.

Keywords : limestone, alkali-reaction, autoclave, image analysis, performance test.

## INTRODUCTION

This study was carried out to determine the potential alkali-reactivity of the various levels of Tournai limestone exploited in the Cimescaut quarry, Antoing, Belgium. For the past few years, this potential alkali-reactivity has been recognized and related to the mineralogical characteristics of the limestone. This determination was performed on the overall limestone deposit, but did not take into account the possible variations that could be observed between the various levels exploited in the quarry.

The initial step in the investigation aimed at clearly defining the mineralogical and chemical characteristics, as well as the potential alkali-reactivity using the standard P 18-590 autoclaving test, of the five levels identified in the quarry.

The second step consisted of using a performance test to analyze this limestone with increasing alkali contents in order to determine the alkali level above which the formula became reactive. This approach is more and more widely used now, when in the context of a worksite, it is not possible to use non-reactive aggregates for a construction classified as requiring a 'C' prevention level (due to remoteness of the NON-REACTIVE (NR) deposit, for example). According to the "Recommandations pour la Prévention des Desordres dus à l'alcali-réaction", "when the supply of NR aggregates is particularly difficult, potentially reactive aggregates can be used subject to making an in-depth study of the planned formula, on contractually defined experimental bases." The conditions of suitability of a concrete formulation are based on performance tests.

The third phase of the project consisted at evaluating the possibility of using crusher's fines obtained from the processing operations of the Tournai Limestone in the Cimescaut quarry either as a granular corrector, an addition for hydraulic concrete or as an alkali-reaction inhibitor.

## DESCRIPTION OF DEPOSIT

### Geological Context

From a sedimentological and paleontological point of view, the Tournai limestone can be divided into two contrasting sub-units, separated by a sedimentological discontinuity of "gras délit". The underlying unit basically consists of micritic limestones (the term "micrite" is a contraction of "microcrystalline calcite") impregnated with diagenetic silica. At their base, they are clayey, but towards the highest point there is an essentially limestone sedimentation. These limestones always contain variable but abundant quantities of fossil fragments (called bioclasts) resulting from the on-site decomposition of organisms such as crinoids, bryzoa, and brachiopods, to which are added gasteropods, bivalves, nautiloids and trilobites at various levels. The "gras délit" is a clay seam of about 20-cm thickness, depending on the location, that makes an excellent reference level throughout the quarry deposit. The upper unit basically consists of micrites which are often clayey, and which are also impregnated with diagenetic silica. There are a considerable amounts of fossil fragments, which usually indicates a relatively large depth of water. These limestones also contain pseudomorphs of gypsum and anhydrite. Several « carboniaux » levels are identified in the two sub-units described above. TOS are extremely hard, rich in black chert nodules, and correspond to regional stratigraphic markers that permit to classify the Tournai limestone as part of the Tournasian stage

### Characteristics of the Tournai Limestone

Freshly broken Tournai limestone varies from grey to blue grey in color, which gave rise to the name « grey layers » and darker « blue layers ». Two different forms of silicious materials can be identified in the Tournai limestone. The first one is recognized at the macroscopic level and consist of the siliceous nodules (similar to cherts) found in the « carboniaux » levels. These have the texture and composition of chalcedony and/or opal and mainly consists of microcrystalline silica commonly considered as having a high potential for alkali-silica reactivity. The second form of silica, called « diagenetic silica » can only be observed at the microscopic level. In fact, after a slight acid attack of polished limestone sections (3 min in a HCl solution diluted to 1/200th), a fine silica "grid" is visible under the scanning electron microscope (SEM) (Fig. 1). This silica "grid" cannot be observed under a conventional petrological microscope, since the thickness of the grid is between 4 and 10 µm. These two types of siliceous materials, i.e. "carboniaux" and diagenetic silica, are present at different scales but are considered as the possible cause of the potential alkali-reactivity of the Tournai limestone.

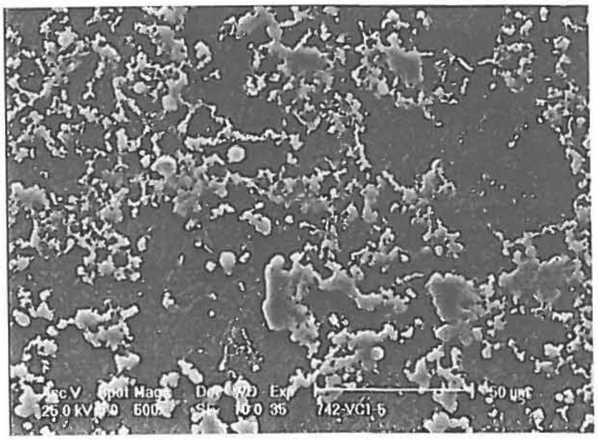


Fig.1: SEM micrograph of diagenetic silica (500 x magnification).

### Highlighting Potential Alkali-Reactivity

After having identified two possible causes for the potential alkali-reactivity of the Tournai limestone, it is necessary to quantify it. Even if "carboniaux" are siliceous materials that can be qualified as avoidable (this is valid at the scale of our sampling, but not on an operating scale), this does not apply to fine, diffuse silica grid. Analytical investigations were carried out to determine the relative contribution of the above siliceous materials to the potential reactivity of the Tournai limestone. To do this, conventional tests and analyses were carried out. These include a complete chemical analysis with determination of the insoluble residue content of the limestone and evaluation of its potential alkali-reactivity using the quick P18-590 autoclave test.

To discern more accurately the various forms of silica and to try to quantify them, a series of observations were made under the SEM on selected polished limestone sections after a slight acid attack.

**Chemical Analyses**

Chemical analysis were performed on insoluble residues obtained after complete digestion in $1/50^{th}$ HCl solution of limestone samples representing different levels in the Cimescaut quarry.

The results of chemical analysis given in Table 1 show that the insoluble residue content of the various limestone levels tested ranges from 8 to 35 %, leading to $SiO_2$ total contents ranging from 6 to 33 % (within the same layer P3).

TABLE 1: Results of Chemical Analysis Performed on the Insoluble Residues of Limestone Samples from Various Levels of the Cimescaut quarry

| | | | Analysis of insoluble residue | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Ref | % carbonates | % insoluble residue | % $SiO_2$ | % $Al_2O_3$ | % $Fe_2O_3$ | % CaO | % MgO | % $Na_2O$ | % $K_2O$ | % $SiO_2$ total |
| CS1 | 77.31 | 22.69 | 84.09 | 8.88 | 2.62 | 0.37 | 1.01 | 0.14 | 1.81 | 19.08 |
| CI1 | 78.34 | 21.36 | 89.40 | 4.68 | 1.40 | 0.56 | 0.54 | 0.38 | 0.97 | 19.09 |
| CI2 | 81.88 | 18.12 | 92.58 | 4.58 | 0.05 | 0.47 | 0.50 | 0.27 | 0.93 | 16.77 |
| VC1 | 85.76 | 14.24 | 91.75 | 3.72 | 1.61 | 0.70 | 0.44 | 0.17 | 0.85 | 13.06 |
| VC2 | 83.84 | 16.16 | 86.45 | 5.97 | 2.35 | 0.65 | 0.70 | 0.15 | 1.20 | 13.77 |
| PR1 | 81.85 | 18.15 | 85.26 | 8.46 | 3.14 | 0.30 | 0.91 | 0.18 | 1.60 | 15.47 |
| P1 | 64.44 | 35.56 | 93.28 | 0.86 | 0.50 | 0.69 | 0.70 | 0.06 | 0.23 | 33.17 |
| P2 | 78.25 | 21.75 | 95.98 | 2.04 | 0.78 | 0.27 | 0.17 | 0.11 | 0.50 | 20.87 |
| P3 | 91.67 | 8.33 | 79.47 | 11.52 | 3.54 | 0.54 | 1.38 | 0.29 | 2.47 | 6.62 |

**P 18-590 Autoclaving Test**

The P 18-590 autoclaving test was carried out on a 0.16/5 mm sieve fraction, obtained through crushing of one piece of rock per level tested.

TABLE 2 : Results of the P 18 590 Autoclaving Test

| Ref. | CS1 | CI1 | CI2 | VC1 | VC2 | PR1 | P1 | P2 | P3 |
|---|---|---|---|---|---|---|---|---|---|
| Average% | 0.52 | 0.50 | 0.43 | 0.44 | 0.41 | 0.40 | 0.46 | 0.26 | 0.27 |

The expansion test results are given in Table 2. These results indicate that the potential alkali-reactivity of the limestone deposit exploited in the Cimescaut quarry is rather homogenous, and in all cases above the expansion limit of 0.15 % (from 0.26 to 0.52 %). This suggests that preferential exploitation of a level is not useful and that the entire deposit is potentially reactive (PR). In addition, if we refer to Table 1, it would seem that the reactivity cannot be correlated to the $SiO_2$ content, but maybe more to the form of siliceous material present within the limestone sample. This observation led us to a detailed microstructural study of the various levels.

### Analysis of Scanning Electron Microscope (SEM) Images

Use of an approach such as this was dictated by the fact that we had a complete sampling of a working face (representing sedimentation conditions of a single geological period), for which several types of information were available. It therefore proved of interest to check whether the analysis of the images made using a SEM could be directly linked to one or several of these parameters that we had available (chemical analysis or autoclaving test).

Samples of each limestone layer were polished, etched with diluted hydrochloric acid ($1/200^{th}$), and then examined under the SEM. An experimental framework was defined in order to be able to have a maximum amount of information on all the facies that showed a siliceous grid. The analysis was carried out on about ten images per sample so as to have the best statistical representativeness possible.

### Summary of Various Tests Performed

Table 3 summarises the various test results obtained for the different limestone samples investigated. The « free » $SiO_2$ content was obtained by substracting the $SiO_2$ that would be consumed in the formation of clay minerals using the following formula : $[Si_2\,O_{10}\,(OH)_2)\,Al_4]$.

TABLE 3 : Summary of the Different Test Results

| | Insoluble residue, % | | Total analysis, % | | | P 18-590 | Image |
|---|---|---|---|---|---|---|---|
| Ref. | Insoluble (%) | $SiO_2$ | Total $SiO_2$ | $SiO_2$ (clays) | $SiO_2$ (« free ») | expansion, % | analysis, % |
| CS1 | 22.69 | 84.09 | 19.08 | 4.03 | 15.05 | 0.52 | 24 |
| CI1 | 21.36 | 89.40 | 19.09 | 2.00 | 17.09 | 0.50 | 35 |
| CI2 | 18.12 | 92.58 | 16.77 | 2.79 | 13.98 | 0.43 | 25 |
| VC1 | 14.24 | 91.75* | 13.06 | 2.79 | 10.27* | 0.44 | 22* |
| VC2 | 16.16 | 86.45 | 13.77 | 5.45 | 8.52 | 0.41 | 24 |
| PR1 | 18.15 | 85.26 | 15.47 | 9.25 | 6.22 | 0.40 | 16 |
| P1 | 35.56 | 93 28 | 33.17 | 0.31 | 32.90** | 0.46 | 45** |
| P2 | 21.75 | 95.98 | 20.87 | 2.67 | 18.21 | 0.26 | 28 |
| P3 | 8.33 | 79.47 | 6.62 | 1.00 | 5.62 | 0.27 | 10 |

By analysing the results presented in table 3, especially the column concerning the counts obtained through image analysis, an abnormally high figure of 45 % is noted for sample P1.

TABLE 4 : Elements of comparison between P1 and VC1 samples

| | | | | | | |
|---|---|---|---|---|---|---|
| %$SiO_2$(insoluble residue) | 93.28 | | P1 | 91.75 | | VC1 |
| % P18-590 | 0.46 | | | 0.44 | | |
| %"Free" $SiO_2$ | 32.90 | | | 10.27 | | |
| %Image analysis | 45 | | | 22 | | |
| | Number. particles | % particles | % area | Number particles | % particles | % area |
| $x < 25\ \mu m^2$ | 395 | 36 | 10 | 370 | 78 | 1 |
| $25 < y < 180\ \mu m^2$ ($75\ \mu m^2$ average) | 704 | 64 | 90 | 46 | 10 | 0.7 |
| $z > 180\ \mu m^2$ ($9\,000\ \mu m^2$ average) | 0 | 0 | 0 | 55 | 12 | 98.3 |

A comparison of the counts can be made between levels P1, and VC1 for example. These levels which shows similar silica content in insoluble residue (respectively 93.28% and 91.75%), and autoclave expansions (respectively 0.46% and 0.44%), but with great disparities for the so-called "free" silica (excluding clay) (respectively 32.9% and 10.27%) counts obtain through image analysis (respectively 45% and 22%). The table 4 shows the results of count by decomposing the number of particles, their sizes and the surface corresponding. If we consider that the fine silica grid, and therefore probably the most destructive one, because of its higher surface area has a maximum particle size determined following microscopic observations of about 180 $\mu m^2$, the VC1 sample has 100 % of its siliceous particles in this category, compared to less than 2% for sample P1. It therefore suggests that a minimum of 2% of this form of silica is enough to generate autoclave expansions > 0.15% limit. The coarser silica fraction also participates in the reaction, but probably to a lesser extent.

## TESTS ON CONCRETE

### Performance Tests

The first part of the study identified the potential alkali-reactivity of the Tournai limestone. We will now determine the maximum quantity of alkalies authorised in concrete formulas in order to use this aggregate in complete safety. The test selected to answer this question was the performance test, which is currently the only test available for testing the reactivity of the aggregate using an actual concrete formula. The conditions of this test are : concrete prisms (7x7x28 cm), temperature : 60°C, HR> 95%. The expansion limit is 0.02% at 3 months (« French recommended limit »). Several concrete batches were made using the Tournai limestone as coarse aggregate along with a non-reactive sand, but also formulas incorporating the complete Cimescaut limestone production, from the fine to coarse aggregate fractions.

First test – A first series of concrete mixtures was made with the Cimescaut potentially reactive coarse limestone aggregate (5/20 mm), a non-reactive sand (0/5 mm of limestone type), and concrete alkali contents ranging from 1.6 to 6.5 kg/$m^3$. Using a 0.02% expansion limit at 3 months, the following observations can be made from figure 2:

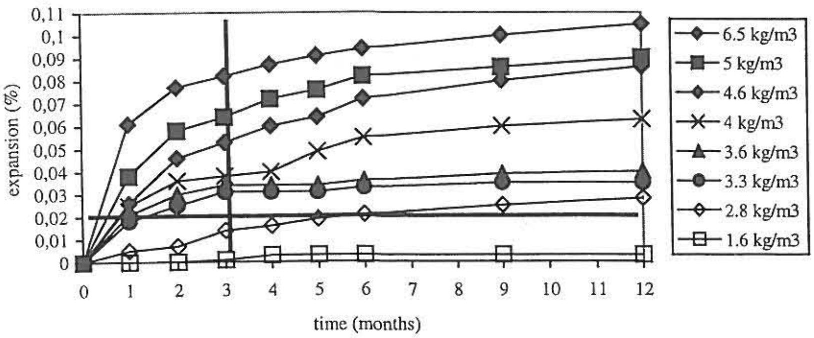


Fig.2 : Concrete Prism Expansion Test Results from Series 1

- The maximum authorised alkaline content for obtaining expansions less than the 0.02 % limit at 3 months should not exceed 2.8 kg/m$^3$.
- This alkaline content corresponds to a proportion of 400 kg/m$^3$ cement (proportion compatible with proportions usually used for civil engineering works) using a cement with a total alkali content of 0.77 % $Na_2O_{eq}$.
- For most contents, the curves are not asymptotic, even at 5 months. For the tests that were continued, the asymptote has still not levelled off even at one year.
- The use of a non-reactive sand was guided by the idea that if the finest part of the granular mixture is not reactive, the reactivity of the coarser fraction could be reduced; on the contrary, this is not so (Fig. 2).

Second test - A second series of concrete mixtures was made with the Cimescaut potentially reactive coarse and fine limestone aggregates and concrete alkali contents ranging from 2.8 to 3.5 kg/m$^3$. The following observations can be made from Fig. 3 :

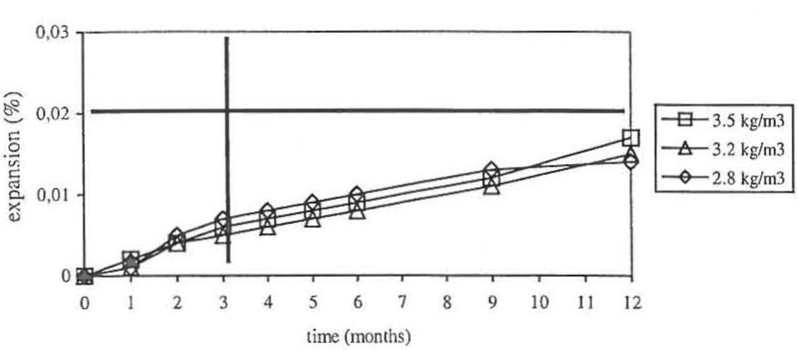


Fig.3 : Concrete Prism Expansion Test Results from Series 2

- Use of potentially reactive coarse and fine Cimescault limestone aggregates produces less expansion with comparable alkaline contents (2.8 % and 3.8 %)
- The 3.5 % $Na_2Oeq$ content is tolerable if the supply is entirely potentially reactive. This observation is new, and offers interesting perspectives for selling this limestone, since it offers a double advantage: the possibility of using a wider range of cements (with less constraints on alkali content), but above all of using the entire granulometric curve in the same supply (from 0 to 20 mm). The expansion after one year is under the limit (0.02%), we obtain a reduced expansion by using sand and gravel in the same mineralogy. When we see the rising of the curves, we must ask the question of the validity of the test's limit (3 months or 12 months or after...) ; we stop these tests at one year (that is very long with reference to the french recommendations) .

## STUDY OF CIMESCAUT FILLER

According to these two tests became the idea of pushing the logic even further, by using crusher's fine from the Cimescaut limestone quarry in order to obtain a more complete granulometric curve in the fines, (i.e using their granular corrector capacities and, possibly, any binding function, to determine an inhibiting reaction with regard to alkaline reaction).

In light of the objectives, it was necessary to answer the three following questions:
a- Are the properties of the filler homogeneous in all the quarry?
b- Does the filler have an activity under the terms of the NF P 18-508 standards of July 1995 for limestone additions?
c- Does the filler have a reducing or rather inhibiting effect for the alkaline reaction in the concrete formulations known to manifest this pathology? And if such is the case, does its incorporation into concretes not subject to alkaline reaction cause the appearance of this behaviour?

A classic study was undertaken in view of determining the physical-chemical characteristics of this filler. The results are summarised below.

**Homogeneity of Filler**

Production of this 742-F filler was chemically analysed over a period of 6 months. This filler showed 18.8 % of insoluble residue made up of 79 % $SiO_2$. From these results and their dispersion, we deduce that the contents could be extended to the entire production of the filler, with the following composition:

TABLE 5 : Average total chemical analysis of the 742 F filler.

| $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | $TiO_2$ | MnO | CaO | MgO | $SO_3$ | $K_2O$ | $Na_2O$ | $P_2O_5$ | P.F | total |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 16.15 | 1.71 | 0.76 | 0.11 | 0.01 | 43.12 | 1.29 | 0.73 | 0.58 | 0.05 | 0.15 | 35.16 | 100.2 |

$Na_2O_{eq.} = Na_2O\,\% + 0.658\ K_2O\,\% = 0.43\%$

TABLE 6 : Comparison with another additions conventionnally used in concrete.

| | Density ($g/cm^3$) | Blaine surface area ($cm^2/g$) | $\%SiO_2$ | $\%Na_2O_{eq.}$ |
|---|---|---|---|---|
| Silica fume | 2.25 | 18 600 | 91 | 1.46 |
| Fly ash | 2.55 | 4 100 | 55 | 1.94 |
| Slag | 2.92 | 3 500 | 35 | 0.72 |
| Filler 742F | 2.67 | 4 500 | 16.15 | 0.43 |

**742-F Size Grading**

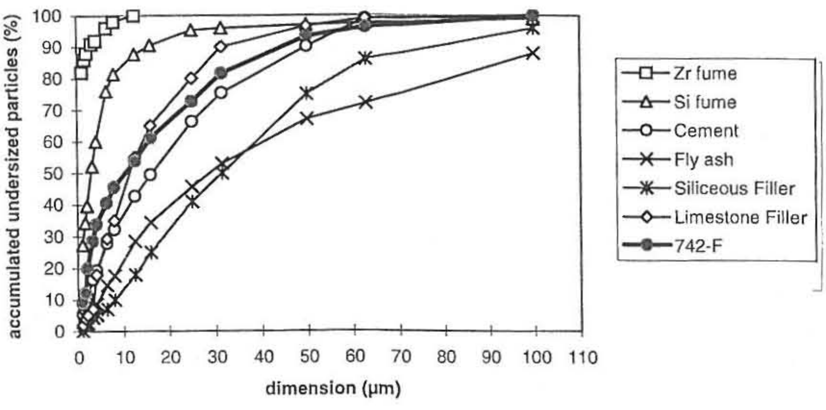


Fig.4 : Position of 742-F filler as compared to other conventional additions.

Apart from zircon and silica fume, for which the median grain sizes are respectively 0.1 and 2 µm, the Cimescaut filler has a median diameter of 10 µm, making it one of the finer elements as compared to CEM I 52.5 type cement, and quite favourably in relation to a limestone filler. Graduation of the 742-F filler puts it in a favourable position as compared to fly ash and the siliceous additions sold in the North of France (therefore regionally comparable to the Cimescaut filler). From a granulometric point of view, the median diameter of 10 µm is a determining element allowing amorphous siliceous components (and therefore reactive to alkalies, as are silica and zircon mists) to develop a reactivity during hydration of the concrete.

**Determination of Activity Coefficient**

The activity coefficient varies from 82% at 7 days to 75% for 28 and 90 days. The standard on limestone additions (the closest that can be applied to this filler) lays down a minimum value of 71% at 28 days, which, in the case of 742-F, is largely reached, including the comparison of mechanical strengths on mortars of the same workability.
The answers to the three questions we asked at the beginning of this section are therefore:
- Filler properties are homogeneous from a chemical, physical and granulométric point of view.
- The filler has an activity under the terms of the standards adopted.
New performance tests were run on concrete formulas in order to find out its effect with regard to alkaline reaction.

**Performance Tests Incorporating 742-F Filler**

The percentage of filler incorporation selected were 15 and 30 % : with 50 % of the weight substituted for cement and 50 % substituted for sand (making up the base of the granular curve). This distribution of the addition was designed to use, if necessary, the Pozzolanic effect", or the "filler effect ».

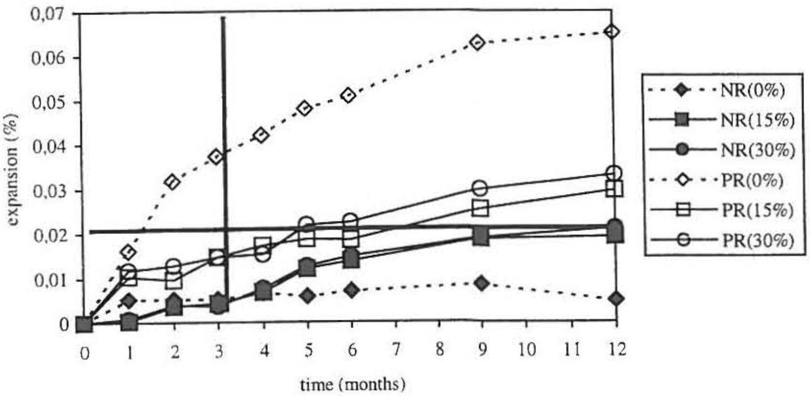


Fig. 5 : Tests incroporating Cimescaut potentially reactive aggregate and the 742-F « child » filler.

The idea is that if the filler elements are small enough with regard to the median size of the cement grains, they can fill in the empty spaces between these grains, and therefore contribute to an increase in workability. Or then again, with constant workability, could they be used to reduce the water content, always considerable when there is a potential risk of alkaline reaction?

The most unfavourable concrete formula was chosen (to have the most expansion) :
NR formulas : NR sand + NR gravel
PR formulas : NR sand + PR gravel
(the number within brackets refers to the percentage of filler replacement) (Fig.5).

The incorporation of the 742-F filler reduces constant expansion in the PR formulas; with the 15 and 30 % curves practically identical, choice of the quantity of fines to be incorporated will be planned as a function of parameters other than expansion.

## CONCLUSIONS

During the two years of study we accumulate full knowledge about the Tournai limestone deposit in the Cimescaut quarry.

- It is confirmed that the potential reactivity is rather homogeneous despite wide variations in the composition of the limestone, especially the $\%SiO_2$ and % insoluble residues.
- The elements identified as being responsible for this reactivity are both within the"carboniaux" levels (which was already known) as well as, and above all at microscopic scale, in a fine silica grid that is poorly crystallised.
- Performance tests on the concrete formula, carried out with increasing alkaline contents, gave the following results of interest. The maximum authorized alkaline content for a formula with Cimescaut PR gravel and NR sand is approximately 2.8 $kg/m^3$. This content can increase to approximately 3.5 $kg/m^3$ for a formula with Cimescaut PR (gravel + sand).
- The use of the filler extracted from this quarry production presents interesting characteristics (chemistry, activity and granulometry), and incorporated into the "all Cimescaut" formulas, it considerably reduces expansion.

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