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Limestone aggregate concrete, usefulness and durability

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Abstract

Inland and on sea coasts, crushed limestone aggregate has been used in France and elsewhere for structural concrete when gravel aggregates were not available. Crushed limestone fillers have, since the oil crisis, been allowed as partial constituent of cement; they are now currently used as additions in concrete mixtures, as partial replacement of Portland cement. Limestone aggregate concretes have not been considered inferior to gravel aggregate concretes, particularly in durability. However, recently some cases of alkali–silica deleterious reactivity and one case of sulphate attack, have questioned their good performance status.

Keywords: Crushed limestone aggregate; Limestone fillers; Composite Portland cement; Limestone additions to concrete; Alkali–silica reaction; alkali–carbonate reaction; Dedolomitazion; Thaumasite form of sulphate attack

1. Introduction

Formerly, the solid constituents of concrete were only ordinary Portland cement and aggregates, now in most cases, other types of cement, active or nearly inert additions and chemical admixtures are currently used, even for medium strength concrete. In Western Europe, alluvial sources of aggregate are often nearly exhausted, and crushed quarried rocks, mainly as coarse aggregate, are transported from great distances to the construction sites. Hard limestone — Los Angeles abrasion loss less than 40% — can be quarried in many parts of France. This explains the development of its use: as a constituent in composite Portland cement, as an addition to the concrete mixture, as well as coarse or even fine aggregate. The present paper is divided into three parts: (1) limestone in composite Portland cements; (2) limestone as partial replacement of Portland cement; and (3) limestone aggregate concrete, its durability.

2. Portland limestone cement

This has been manufactured in France since 1976 as composite Portland; it was not unknown before, although crushed sand or crushed limestone were not allowed as partial replacement of Portland clinker. Candlot wrote in 1906:

'... It is very difficult to know if the increase in strength produced by adding a material other than Portland clinker is the result of a chemical reaction or merely physical. A greater increase of strength is obtained as a matter of fact with the addition of a very fine limestone powder than with the addition of trass or slag, evidently there is basically a physical effect brought about by adding a powder which gives a greater denseness to the mortar.

When blending other inert matters a similar effect is obtained; these additions were practised long ago, almost always fraudulently. Some years ago, however, a product was proposed, made up of a blend of sand and cement ground together to the greatest fineness, the only novelty in this process was the greater fineness of the blend, for such blends were practised long ago. The advantages which were claimed, were debatable, and it will always seem difficult to convince buyers to pay a relatively high price for sand that they would be able to add themselves to the cement when mixing. And also, these blends being made without stated regulations and at will by the manufacturer, would not offer guarantee as their regularity would be dubious. In some cases, however, such processes can be usefully applied and deserve to be developed; presently, such applications, I believe, are not to be attempted except on large civil work sites. In such cases, an important machinery is available to make the blend

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on site and, above all, to control it. Cement plants must limit themselves to deliver pure products if they intend to be trusted by buyers' [1].

The state-of-the-art, and above all, the state of the production control both of cement and of concrete on the site were such that Candlot was right in his severe rejection of such blends. Interestingly, he foresaw the modern practice of the site blending of Portland and various additions which prevailed in most developed countries and which, in France, is progressively replacing the blended cements of the 1980s. During the oil crisis (1974–1980), cement manufacturers who had a long experience of the blending of Portland clinker with blast-furnace slag, pozzolans and fly ash decreed that inert (or nearly) inert finely ground mineral materials be allowed also as secondary constituents in composite Portland cements, to replace 35% of Portland clinker as the other secondary constituent (which passed from 15 to 35% with NP P 18 301 — 1976). As remarked by Hawthorn: 'Limestone fillers have been previously used in concrete for many years in France and we found articles on this experience published before 1945. Producing filler cement with a significant amount of filler seems new, but masonry cements have been produced for many years.' and 'By the end of 1978, filler cements have been produced in a small number of plants with generally low filler content, between 10 and 15%. Then, up to now, gradually, number of factories producing filler cement increased, and the filler content also increased.' [2] Practically, except in very few cases it was not ground sand which was used, but ground limestone or crushed limestone introduced with the clinker in the grinding mill. In the CPJ 45 class (medium strength 35 MPa), the proportion of filler never reached the 35% allowed in 1976, it passed 25% in only a few cases. Presently, the mean content of CPJ CEM II filler content is 21% in strength class 32.5 (NF P 18 301 — 1994) on 27 products (Table 1) and 12% in class 42.5 (NF P 15 301 — 1994) on 11 products.

In special types of cement, very few limestone Portland are presently certified:

- for sea water resistance — label PM — on 12 products only 4, with limestone content from 7 to 8%
- for sulphate resistance — label Es — on 26 products from 16 plants, no constituent except perhaps in 3% of additions is allowed for this type of cement

(Table 2). It is hardly necessary to say that fillerized cements were not welcomed by the Contractors Federations who tested them on concrete for strength and durability and resented the fact that the saving claimed in energy to fabricate them, did not decrease prices.

Table 1
Composite Portland cements certified by AFNOR in June 1988 of which the only other constituent is limestone. Forty-one certified cements in metropolitan France, of which 4 are certified PM (i.e. sea water resisting)

Strength class MPa	Clinker content	Limestone content			Number of certified cements	
		Min.	Max	Mean	Total	PM label
32.5	94 to 65%	12	30	21%	27	0
42.5	94 to 65%	7	20	13%	11	3 (a)
52.5	94 to 65%	8	10	9%	3	1 (a)

(a) Limestone content (%) of PM certified above: L7, L8, L8 for the 32.5 MPa class and L8 for the 52.5 class.

Table 2
Sulphate-resisting cements (ES) certified by AFNOR in June 1988, 26 products in metropolitan France, complying with XP P 15 319, in column 2 constituents other than Portland clinker

Type	Constituents other than PC	Number of certified cements per strength class			Total number	Allowed constituents
		32.5	42.5	52.5		
CEM I	3%	–	1	7	8	As in P 15 301
CEM II	20 % max.	–	2	–	2	S, V, S/V, Z
CEM III	50% min.	7	3	1	11	Only S
CEM V	S 18/50 V 18/50	5	–	–	5	Only S and V

Content limits according to standard (S = slag, V = fly ash, Z = pozzolan). All are also labelled PM.

2.1. Limestone filler cements vindicated

At the 8th Congress on the Chemistry of Cement, in 1986, the results of the research on cement with additions by the CERILH in Paris were presented by Regourd [4], particularly limestone filler, differentiated from other fillers by its reactivity so that: 'half of the French composite Portland cements (62% of the French production of cements) are limestone filler cements.' Guyot, for the Lafarge Research Centre explained '...that in order to increase the economic value of the hydraulic potential of Portland clinker, for such 'valerization', it has to be more finely ground and blended with a filler, even an inert filler.' So, with a 55 MPa clinker blended with some 27% of filler of high fineness a 45 MPa cement was obtained. Durability tests established that for equivalent 28-day strength, the same resistance to various attacks was observed, on concrete as well as on mortar [5]. We may add that the cement content of concrete following the strength class of cement remained unchanged, but the price of this valorized product remained the same.

An elaborate chemical demonstration of the chemical reactivity of limestone through carboaluminates and an acceleration of the hydration of C_3A and C_3S rather than a mere 'filler effect' was presented: further tests on quartz filler/Portland cement blends showed that, with less dependence on the chemical composition of the clinker, the performances on mortar and concrete were of the same order [6], particularly the lowering of the penetration rate of chloride ions in concrete.

From a practical point of view the availability of limestone was greater — a cement plant is generally built at the foot of a limestone hill, and the grindability of even hard limestone is better.

2.2. Limestone cement, durability, carbonation

As long as the porosity, hydrate content and consequently strength, is the same, the behaviour at carbonation is the same for the same concrete strength. Ranc [6] found that after 4 years natural carbonation the depth was of the same order for limestone or siliceous filler cements of strength class 45 MPa (15 and 30% limestone filler, 10 and 25% siliceous filler).

2.3. Limestone cement, sea-water attack

From tests on ISO mortar prisms immersed in artificial sea-water, Ranc found after 4-year exposure that the presence of limestone does not affect the resistance of mortars which depend only on clinker chemistry, but Ramachandran on cement mortar discs containing precipitated or ground limestone at content of 0, 2.5 and 15% observed [7] that most mortars containing $CaCO_3$ have higher expansion than reference mortar, however, only ultra-fine ground limestone were tested by him. The lack of experience of these new cements in sea structures has led the writers of NF P 15 317 standard to limit to 10% limestone content of PM cements.

2.4. Limestone cement, sulphate attack

From tests on 50/50/100 mm concrete prisms half immersed in sea-water and also in saturated $CaSO_4$ solutions, Guyot [8] concluded in 1983 that the replacement of low C_3A Portland cements by 15/20% of slag or fly ash does not affect their good behaviour. Since then limestone cement prisms have been added to the long-term durability programme of Lafarge Research Centre, but probably also with silico-calcareous Rhône aggregates. From tests on 2.5/2.5/28 cm prisms immersed in sulphate solutions or submitted to cycle of wetting/drying in sulphide solutions Berhandy [9] showed that the behaviour of 1/3 mortars with crushed limestone with 8% of clean filler was at least equivalent to mortars made with Seine sand or unfillerised limestone (Table 3 and Table 4).

3. Limestone filler as an 'addition'

ENV 203 has named 'additions', the mineral admixtures of American usage, and does not mention limestone filler as an active addition, although Pr EN 197 admits limestone among other constituents of

Table 3
Total immersion of 2.5/2.5/28 cm mortar prisms in sulphated water expansion in μm (mean of three prisms), at 20°C, 1/3 mortar, RHPC C_3A content 15%, RT Seine River sand, CT crushed limestone sand (washed) KC 8 crushed limestone sand of which 8% clean limestone filler [9]. The fillerised limestone mortar expands less than the river sand mortar

	Months									
	0	1	2	3	4	5	6	7	8	9
RT	–	207	–	283	300	312	320	320	385	640
CT	–	107	160	215	230	230	250	297	515	1031
KC8	–	72	155	180	180	187	187	203	281	453

Table 4
Immersion/drying (16 h at 20°C/8 h at 55°C), 5 cycles per week of the 2.5/2.5/28 cm of the mortar prisms of Table 4, expansion in μm (mean value of three prisms) [9]. Mortar prisms of river sand and washed limestone sand are destroyed, but not the fillerised limestone sand prisms

	Cycles						
	0	5	10	25	50	65	80
RT	–	0	0	214	357	1150	1620
CT	–	0	0	260	803	1320	1710
KC 8	–	0	0	90	303	563	840

composite Portland. Nevertheless, its use as an active addition is general in France, with Portland cement replacement from 15 to 25% and AFNOR standard [10] XP 18 305 — 1994 granted a cementious equivalence coefficient k of 0.25 for replacements less than 25% of CEM I 42.5, provided it complies with NF P 18 508 on limestone additions [11]. For medium strength concrete — from C20 to C30, while for job-mixed concrete CEM II are widely used (in the strength class 32.5 no more CEM I are produced in France), for ready-mixed concrete blends of CEM I and addition, mostly limestone, prevails, at the outset against a reluctant cement industry. The case of job-mixed against blended cements has been aptly stated in 1983 by Mather [12]: (1) a wider range of materials is available for blending [2] the quantity of blending materials can be varied at will. The main disadvantage is that it is necessary to test, store and control the addition, which is not the case for certified additions and for ready-mixed plants where the cost of extra silos is rapidly paid off. Moreover, in most parts of France, sources of apt limestone beds are present.

It is claimed by limestone filler producers that the addition of some 50–100 kg/m^3 increases the workability of concrete (its water demand is not different from that of cement of the same fineness) as the fineness content of the mix is increased and leads to better vertical surfaces of a lighter colour. The same — and even superior — advantages are claimed by quartz filler producers which are also allowed by XP18 305 standard and are defined by NF P 18 509 [13]. Recent tests have shown that for less than 25% replacement their k-value is also of the order of 0.25. For the most sold class the 25 MPa characteristic strength on cylinder specimens (C25), with equivalent cement content of 280 to 300 kg/m^3, the maximum filler addition content is therefore 90 kg/m^3.

3.1. Present trends

The new standard on aggregates for structural concrete (PR EN 12620) admits that the fines content (per cent passing the 0.065 mm sieve size) reach 16%. With a sand content of 800 kg/m^3 (quite usual for ready-mixed concrete production), 130 kg of fines are introduced in the mix: if these fines are clean limestone they present the same cementitious activity as the limestone fillers sold as 'additions'. Thus in crushed limestone aggregate concrete, why, except in compliance to the standard, use additions, particularly crushed stone additions, less active than fly ash or ground blast-furnace slag and why not reduce the cement content as if certified additions were used? The rheology of the mix is not affected, and the 28-day strength can be tested. This may explain why the standard in some regions is deliberately ignored.

3.2. Its use in high strength concrete (HPC)

In France, the name 'high performance concrete' is preferred as many properties of structural concrete are improved when higher compressive strengths are obtained. Above grade 60 MPa — C60 according to ENV206 — CEM I 52.5 cement has to be used and very often with silica fumes. Cement contents from 350 to 400 kg/m^3 and above have been used, thus the fines content of concrete is usually adequate, but in some instances, to reduce the heat development in the hardening concrete, limestone filler is specified to partially replace cement: this is the current EDF practice.

This has been the case for the HP mix of the containment building of the Civaux Nuclear Power Plant (containment without steel liner) near Poitiers (Table 5) with only 266 kg/m^3 of cement for 393 kg/m^3 passing the 0.08 mm mesh, and a mean 28-day strength of 67 MPa.

Blends of CEM I cement with several additions are not allowed by ENV 206 as by XP 15 301, but this is common practice for HP concrete, as in Civaux. This has not been allowed merely for control reasons as it is allowed for composite cements: the CEM-II class of NF P 15 301 admits any blends of the seven non-clinker constituents totalling 6–35% of these constituents, but the manufacturer should declare the proportion of each.

3.3. Blends of CEM I 52.5 and addition

Of the 56 CEM I cement produced and certified in France, only 9 remain in the 42.5 class. Consequently, blends of CEM 1 52.5 are frequent, but the standard is built on the assumption that a 42.5 cement is employed. For a C25 concrete mix, with a free water plus admixtures content of 170 l/m^3, the same 28-day strength is obtained with 280 kg/m^3 of CPJ 32.5, or 250 kg/m^3 of CEM I 42.5 and 60 kg/m^3 of limestone filler, or with 220 kg/m^3 of CEM I 52.5 and 70 kg/m^3 of

Table 5
An all limestone concrete: the high performance mix of the containment building of the Civaux Nuclear Power Plant

High strength concrete for a NPP containment building designed by the LCPC for Civaux NP plant (EDF)	
Composite Portland cement CPJ55 (89% Portland clinker/11% limestone filler)	266 kg/m^3
Limestone filler	87 kg/m^3
Silica fume	40.3 kg/m^3
Added water	161 kg/m^3
Rheobuild 1000	9.08 kg/m^3
Limestone crushed aggregates	
0/5 mm	786 kg/m^3
4/12.5	309 kg/m^3
12.5/25	791 kg/m^3
28 Day compressive strength on 16/32 cm cylinders	67 MPa
28 Day splitting strength	4.1 MPa
28 Day Young's modulus	36 000 MPa
Bending strength on 14/14/56 beams 28 days	5.5 MPa

Assuming a cementitious efficiency factor of 2.0 for the silica fume, and an ISO strength of 65 MPa for the composite cement, the efficiency factor of the limestone filler would be near 0.25.

limestone filler. The standard ignores this fact as it assumes that the safe W/C limit for durability is independent of the strength obtained for the concrete. The last quoted cementitious content is current in ready-mixed practice, at least in France where the production of high strength cements is perhaps the exception in Europe.

To prepare such changes a research programme decided by contractors as well as addition producers was carried out from 1995 to 1998 by the CEBTP in St Remy les Chevreuse laboratory. Six additions were tested for durability on: porosity, capillary rise, air permeability, carbonation, chloride penetration, on 2 types of mixes: C25 and C40. For the most frequently used additions, fillers and fly ash, slight differences were found, although compared with the reference series in CEM II (named CPJ in France), they do not comply with the present standard as shown in Table 5.

For the C25 mix, P 18 305 requires $C \geqslant 280\,kg/m^3$, $W/(C+kA) \leqslant 0.60$, these requirements were met only by the composite cement mix CPJ of the 32.5 MPa class and the basic class for the ENV206 designers; for

Table 6
Composition and compressive strength of some of the 14 blends tested in the CEBTP programme 'Additions' on Seine River aggregate 0/20 mm, slump at *t* 160/180 mm for the C25 grade and 140/160 mm for the C40 concrete grade

Concrete constituents	Concrete grade C25			Concrete grade C40		
	CPJ	CPA/L	CPA/V	CPJ	CPA/L	CPA/V
Cement content: C (kg/m^3)	273	237	205	346	286	250
Cement grade: MPa	32.5	42.5	42.5	42.5	52.5	52.5
From cement plant	BF	BF	BF	BS	BS	RV
Actual ISO strength: MPa	43.1	42.3	42.3	56.1	67.9	9.3
Additions: A (kg/m^3)	–	54	78	–	60	80
Free water (+admixtures) (l/m^3)	165	168	177	158	159	161
Entrapped air (l/m^3)	17.5	15.5	12.5	17.5	13.5	12.5
A/(C+A)	0	0.19	0.18	0	0.17	0.24
k (XP 18 305 values)	1	0.25	0.40	1	0.25	0.40
C+KA	273	259	236	346	301	282
W/(C+kA)	0.60	0.65	0.75	0.46	0.53	0.57
Relative humidity %, 20°C: cured after demoulding	95/65	95/65	95/65	95/65	95/65	95/65
28-day Cylinder strength: MPa	30/25	30.5/25	29/24	48/38.5	47.5/39	48/40
90-day cylinder strength: MPa	32/26	34/41	36/26	52/38	50/39	58/47
180-day cylinder strength: MPa	35/24	37/42	40/26	56/41	50/39	67/45

L = limestone addition; V = fly ash addition.

Table 7
Some durability test results on the C25 and C40 selected series permeability

	Intrinsic permeability		Chloride penetration		Acc. carbonation depth on 59 mm OD cores	
	($m^2 \times 10^{-17}$)		(Coulombs)		(mm)	(cores)
Curing regime of /R.H.% the cored panels, 20°C	> 95	65	> 95	65	> 95	65
CPJ concrete B25 grade	3.3	5.1	4350	5600	13	14
CPA/limestone B25 grade	3.5	7.1	4750	7050	13	20
CPA/fly ash B25 grade	0.3	16	1700	4650	15	19
CPJ concrete B40 grade	1.3	2.6	3500	3500	0	0
CPA/limestone B40 grade	3.5	4.8	4250	3650	1	1
CPA/fly ash B40 grade	0.3	0.3	2050	3050	13	13

On the first 50 mm of 150 mm OD cores (skin concrete) through oxygen permeability results, *chloride penetration* AASTHO T 277 method on saturated discs cut from the first 50 mm of 80 mm OD cores, *accelerated carbonation* at 20°C 50% h atmosphere with a CO_2 content of 65% ±5 vol. 21 days duration. All cores extracted on test panels after 28-day hardening.

the C40 mix the limitations concern only sea-water or chemical attack which were not considered in the programme [14].

4. Limestone aggregate concrete

In several regions, such as around Marseille, Nice, Albi, hard limestone has been quarried for aggregate, mostly dolomitic limestone, for a long time. However, the alluvial deposits of the great river basins have been over-exploited and the opening of new sand/gravel pits is severely restricted. Thus, even in the Seine Valley, coarse aggregate from the Boulonnais or the Avesnois are sometimes used but with river sand. In the vicinity of the quarries an all limestone concrete is practised: such as for the Channel Tunnel Segments (French side), where only half of the crushed sand was replaced with a natural quartz sand to increase the finishability of the segment unformed surface [15].

4.1. Characteristics of all limestone concrete

With limestone of high or medium hardness (Los Angeles abrasion loss <40%) and of low water absorption (<2%), high strength concrete can be made with low coefficient of thermal expansion: all runways of the Paris airports were concreted with Boulonnais limestone (Los Angeles between 25 and 30). The relatively high tensile strength of these concretes has been explained by Farran [16] by the existence of an 'auréole de transition' connecting aggregate particles and cement paste. For low and medium strength concretes their drawback is the higher water demand of the mix, common to all origins of crushed rocks, which necessitates a higher cement content than with river gravel concrete of the same designed strength. For a C25 mix, 10–15% more cement will be needed with an all limestone against an all gravel concrete.

4.2. Durability of limestone concrete

4.2.1. Acid water attack in water retaining structures

The deterioration of concrete then results from a reaction between the acids carried with the calcium hydroxide of the hydrated Portland cement, limestone aggregates are also attacked when no longer protected by the cement paste. For water of moderate aggressivity, AFNOR P 15 010 recommended in 1985 to specify [17] for low C_3S and C_3A Portland cements, and for severe aggressivity blast-furnace slag cement with at least 60% of slag with a maximum W/C of 0.50. Limestone aggregates were not blamed, but for such structures, generally public works structures such as water storage or treatment, the water absorption coefficient was limited to 2% against 5% for general construction, so that porous limestone — LA > 30%, water absorption > 3% — was banned.

4.2.2. Sea-water attack

In Europe most exposure stations were designed to test cements against moderate sulphate attack of sea-water, in mortar prism or even in concrete, siliceous aggregates available in the vicinity were employed, with the exception of the Marseille exposure sites where 7/7/28 prisms were half immersed in the salty Mediterranean outer port. The concrete structure of this port was almost exclusively built in limestone concrete, including the road tunnel under the outlet of the old harbour. To date, all are without particular damage for example, the sea defence blocks cast with the available coarse aggregate and beach sand: the Jorf-Lasfar tetrapodes in Morocco (dolomitic limestone) or the accropodes of the new Calais breakwater (Boulonnais limestone).

4.2.3. Sulphate attack

Experience and testing, for instance, tests on mortar prepared with dense or porous calciferous aggregate by Piasta [18] are not adverse to the use of limestone aggregate, in this case provided a dense concrete (W/C <0.50) and adequate cements are employed, as stated by Mather: 'It is useful to apply concrete with dense limestone as coarse and fine aggregate to structures subject to sulphate attack.' [19] A large choice of such cements is available in France: 26 products have been certified ES, i.e. sulphate-resisting by AFNOR (Table 2), including 11 blast-furnace cements (with more than 60% of slag), and four slag-fly ash cements (mean proportions 25/25/50).

For foundations in sulphate-bearing soils, particularly for cast-in-place piles or walls in the 1970s, the approved mixes were Q350 with 350 kg/m^3 of CLK — this is now known as CEM III/C (slag content > 81%) and a W/C of about 0.50 (the ratio was generally not specified but was recommended since 1985 by P 15010: 0.55 for moderate aggressivity, 0.50 for severe), strength 25/30 MPa, the strength class of CLK was and remains 32.5 MPa, and Q400 for severe aggressivity and W/C = 0.50, strength 35/40 MPa according to the level of grinding of the slag (only one plant ground the constituents separately). The present requirements of XP 15 305 are demanding (Table 8).

Consequently, for severe environments, so as not to increase the cement content above 400 kg/m^3, a CEM I 52.5 was used, as in this class there is only one slag cement on 8 labelled ES, which conflicts with all French experience. This explains why for the new undergound railway in Paris, the owner obtained CEM III 52.5 from the cement industry.

5. Thaumasite form of sulphate attack

This has been diagnosed by Regourd [20] in the disintegrated mortar of a masonary breakwater in front of Cherbourg, and by Berra [21] in the concrete lining of a diversion tunnel in the Italian Alps, where an OPC was used with crushed aggregate, most probably the excavated gneissic quartzite. In the Paris era, Lachaud [22] stated that some damage attributed to ettringite may be caused by thaumasite, the conditions of its emergence being a sulphatic and humid environment, low temperature (near 4°C) and in the concrete an alumina content from 0.4 to 1%. These conditions exist in many mortars or concrete. This is particularly the case as reported by Nolhier [23] when gypsum rendering or mortar are applied on concrete in a wet environment, and above all when blending of cement and gypsum is attempted by inexperienced people. More recently Crammond [24] diagnosed expansive thaumasite in the substructures of several bridges above the M5 motorway in Gloucestershire.

Table 8
Mix details

Aggressivity grade		W/(C+kA)	A/(A+C)	C+kA kg/m^3	Cement	$f_{c,28}$ MPa
Low	5a	0.55	(a)	330	PM	32
Moderate	5b	0.50	(a)	350	ES	35
Severe	5c	0.45	–	385	ES	40

[a]Addition maximum content: fly ash or slag 0.15, silica fume 0.03 of the cementitious blend.

Sulphate-resistant Portland cement was used for the foundations of concrete as the substructure was built on clays susceptible to liberating sulphates, in order to prevent ettringite expansion (3CaO, Al_2O_3, $3CaSO_4$, 31 H_2O). However, the buried columns were attacked and expansive thaumasite ($CaSiO_3$, $CaCO_3$, $CaSO_4$, $15H_2O$) was identified. As limestone aggregate were employed for these concretes, it was thought that the carbonate ions were supplied by the aggregates, particularly from their fines. It must be observed that in other cases, the formation of ettringite or thaumasite has been ascribed to an 'endogenous sulphate activity', Divet [25] diagnosed this as the cause of the cracking of the cross-beams of Ondes Bridge on the Garonne River, as the environment was sulphate free the process was compared with that occurring in railway sleepers and front panels subjected to heat treatment and analysed by Ludwig [26].

In the Cedres Dam concrete (Canada), Regourd [27] found ettringite and thaumasite accompanying alkali–silica reaction gels, on the border of dolomitic limestone aggregates. The research programme initiated by the BRE concerns only the attack from external sulphate ions, its findings are presented by Crammond, from which three points are of general interest: (1) coarse aggregates as well as dust can be deleterious; (2) dolomitic limestone can be more detrimental than ordinary limestone; (3) with 70–90% slag content in the cement, concrete in cold sulphate solutions were not attacked. This explains, perhaps, why in France, where slag cement was almost exclusively used for underground concrete, when the groundwater was sulphate bearing, cases of deleterious sulphate attack were seldom encountered.

5.1. Alkali–aggregate reactions

Most limestone rocks contain some magnesium oxides and also some silica. This is particularly the case for the carboniferous limestone of North and East of Lille (Tournaisis and Avesnois) which can also contain pyrites according to Deloye [28] ranging from micrometres to several millimetres: such crushed hard limestone may in concrete exposed to a wet environment be harmful through the formation of alkali-gel accompanied by ettringite. A number of bridge abutments, piers and also affected decks have been cited by Godart [29] in the 9th ICAAR in London.

Most limestone in the South-East is dolomitic, and a partial de-dolomitization has been observed by Deloye in a bridge above Nice, but as it was not accompanied by expansion damages, it was concluded that for such dolomitic limestones, which are currently used in these regions: 'pure de-dolomitization is an unavoidable phenomenon, but that it is not deleterious *per se*.' However, it makes the affected concrete more sensitive to other attacks.

The reaction is very slow, resulting in a very low expansion, and the brucite ($Mg(OH_2)$) produced can be partially dissolved in water with a corresponding increase in concrete porosity. When there is a sufficient amount of clay in the rock, the so-called 'alkali–carbonate reaction' may be initiated. This deleterious phenomenon affects some beds of dolomitic limestone in Canada (the classical Kingston quarry in Ontario), it has until now not been reported in France.

6. Conclusions

1. In most parts of France, hard limestone has been quarried from time immemorial. Crushed limestone aggregates were and are in use, particularly for high strength concrete. Their main criterion of acceptance is the Los Angeles abrasion test: less than 25% loss for road slabs, less than 40% for general construction concrete (less than 50% for ASTM C33). Coquillat [30] has shown with concrete of 30% LA loss the same performances were obtained as with the best gravel concrete. In some regions, medium hardness limestone (LA loss from 40 to 60%) predominates, to promote their use in concrete, a national project was completed in 1995: MATERLOC-Calcaires. The increasing scarcity of alluvial aggregates will generalize their employment for ordinary concrete.
2. Since 1987 when ASR damages on motorway bridges were discovered near Paris and near Lille, limestone aggregates have been submitted to thorough examination and testing. This has been the case for the Boulonnais limestone, which was submitted to an elaborate system of evaluation to allow it to be employed for the concrete segments of the Channel Tunnel (French side). The Ministry of Transport issued in 1992 a guidance manual for the evaluation of quarries producing concrete aggregates [31].
3. As a partial replacement of Portland cement, limestone fillers (including dolomitic limestones) have been allowed since 1994 by the ready-mixed concrete standard. However, due to lack of experience, limestone additions are limited to 5% of the cement content when sea-water attack of the concrete is encountered and not allowed in concrete submitted to chemical attack.
4. The most common form of chemical attack, sulphate attack was up to now almost exclusively met with the use of blast-furnace slag cement of high slag content. The trend to produce higher strength cement has led, however, to a greater use of sulphate-resisting Portland cements irrespective of the carbonate content of aggregates.

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