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Sulfate attack on cementitious materials containing limestone filler — A review

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ABSTRACT

This review summarizes the results of sulfate performance in laboratory and field tests where limestone is used as a constituent of cement (PLC) or as a sand replacement where it is particularly beneficial to the properties of self compacting concretes (SCC).

Laboratory studies on paste, mortar or concrete specimens exposed to Na_2SO_4 and $MgSO_4$ solutions in a wide range of concentrations at different temperatures as well as mixtures with different compositions, cement compositions and limestone proportions are considered in a conceptual analysis as for the resistance to external sulfate attack and, especially, thaumasite sulfate attack.

A detailed analysis of environmental aggressiveness (concentration, temperature and pH), mixture composition and cement composition used in each study are presented for PLC and SCC. Reported field studies are also shown, only a few cases have used limestone filler in their composition. A conceptual graphical analysis is then proposed to relate the degree of surface deterioration and mineralogical composition of attacked surface to the main variables of external sulfate attack: water/cementitious material ratio, limestone content and C_3A content of the cement. Observation of graphical analysis clearly shows that deterioration by ESA is mainly governed by effective w/c ratio and C_3A content of the cement. Surface damage is controlled when low effective w/c ratio and low C_3A are used. In $MgSO_4$ solution, low temperatures increase the degree of deterioration. Thaumasite is the last attack stage in the different sulfate environments.

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1. Introduction

1.1. General background

1.1.1. Limestone filler in cementitious material

For the past decades, the production of Portland cement with different replacement levels of limestone filler (PLC) has increased in

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Table 1
Details and results of most important experimental researches about sulfate performance where limestone is used as a constituent of cement

Author, [reference]	Specimens characteristics					Solution characteristics					Time, months	Cement composition				Surface characteristics								Main conclusions
	Material[a]	Size, mm	Water/ binder	Sand/ binder	Previous curing, days	$[SO_4^{2-}]$, g/l	$[Mg^{2+}]$, g/l	Temp, °C	Renew or pH	ACI 201 and EN 206[b]		C_3A	C_3S	LF replac., %	w/c[c]	Register[d]	Raiting[e]	Compounds[f]						
																		Technical	E	T	G	B	P	
Soroka and Setter [17,18]	M	25×25×159	0.70	2.75	28	33.8	–	20	nd	C3/ XA3	11	≅11	–	0	0.70	P	3	No data reported						LF improves SR of mortars to a limited time. But, it did not produce a sulfate resisting mortar.
														10	0.78		3							
														20	0.88		3							
														30	1.00		3							
														40	1.17		4							
Hooton [19]	M	25×25×294	0.49	2.75	2–3	33.8	–	23	nd	C3/ XA3	12	10.4	51	5	0.51	t	3	No data reported						LF has no influence on SR, except when diluting the C_3A-content
												9.0	55	5	0.51		3							
												8.0	45	3	0.50		2							
González and Irassar [20–23]	M	25×25×294	0.49	2.75	3–7	33.8	–	20	pH c	C3/ XA3	12	0.0	40	0	0.49	G	0	XRD	E		G		p	Penetration of attack, CH depletion and gypsum are deeper when increases LF content. Thaumasite was found on specimens containing 10 and 20% LF. But, it cannot be detected in both low C_3A cements with LF.
														10	0.54		2				G		p	
														20	0.61		3				G		p	
												1.0	74	0	0.49		0		E		G		p	
														10	0.54		0				G		p	
														20	0.61		1				G		p	
											24	6.0	51	0	0.49		2		E		G		n	
														10	0.54		3		E	T	G		n	
														20	0.61		4		E	T	G		n	
Irassar et al [24]	M	25×25×294	0.49	2.75	28	33.8	–	20	3 m	C3/ XA3	36	2.0	58	0	0.49	P	1	XRD			G		n	For 0 and 12% LF, expansion was lower than failure criteria. For 18% LF, it failed after 6 m.
														12	0.55		1		E		G		n	
														18	0.59		2		E		G		n	
Tezuka et al [25]	M	40×40×160	0.48	3.00	28	33.8	–	23	nd	C3/ XA3	6	6.0	58	0	0.49	t	0	SEM	–					Prisms show no mass loss and no surface damage. SEM analysis near the surface showed a homogeneous inter-growth of ettringite, CH and CSH in PLC.
														5	0.51		0		–					
														10	0.53		0		–					
														15	0.56		0		–					
														25	0.64		0		–					
														35	0.74		0		E				P	
Mulenga et al [26]	M	40×40×	0.60	3.00	14	29.8	–	20	1 m	C3/ XA3	4	3.2	56	0	0.60	t	0	XRD		T				Prisms at 20 °C expand more than prisms at 8 °C. No damage in SRPC.
		16010×										>10	–	15	0.71		3		E	T	g			
		40×160						8				>10	–	15	0.71		4		E	T	g			
Jutnes [27]	M	40×40×160	0.50	3.00	28	33.8	–	5	nd	C3/ XA3	10	≅10		20	0.63	P	2	SEM		T	G			Mass loss, expansion and strength retrogression.
Bellmann and Stark [28]	M	40×40×160	0.60	3.00	1+14	1.5	–	8	1 m	C1/ XA2	36	≅12	45	0	0.60	t	3	XRD	E	T			P	Thaumasite formation can be avoided when an appropriate pozzolan was used.
														15	0.71		2		E	T			P	
												9.8		12	0.68		2		E	T			P	
Lee et al [29]	M	50×50×50	0.45	2.00	1+6	33.8	–	20	1 m	C3/ XA3	12	9.7	43	0	0.45	P	1	XRD	E	T	G		P	High replacements of LF produce a more pronounced ESA. Expansion was high in mortar exposed to Na_2SO_4 solution, while loss of compressive strength and surface deterioration were more pronounced in $MgSO_4$ solution.
														10	0.50		2		E	T	g		P	
														20	0.56		3		E	T			p	
														30	0.64		4		E	T				
						33.5	8.5	20	1 m	C3/ XA3	12	9.7	43	0	0.45	P	1	XRD	E	T	G	B	P	
														10	0.50		2		E	T	G	B	p	
														20	0.56		3		E	T	G	B		
														30	0.64		4		E	T	G	B		
Matthews [30]	C	100×100×100	0.60		28	18.0	–	20	3 m	C3/ XA3	24	13.1	–	0	0.60	W	4	XRD	No comment reported					Sulfate performance of concrete was dependent on C_3A content of the cement. Addition of 5 and 25% LF produced no consistent effect; it sometimes improved, but others, it worsened. The performance
														5	0.63		4							
														25	0.80		4							
												10.3	–	0	0.60		4							
														5	0.63		4							
														25	0.80		1							
												8.5	–	0	0.60		1							
														5	0.63		1							

														25	0.80		1							of 25% LF was better in Na_2SO_4 and worse in $MgSO_4$. It was suggested that thaumasite formation is not independent from ettringite formation.
												5.3	–	0	0.60		0							
														5	0.63		0							
														25	0.80		0							
						18.0	4.6	20	3 m	C3/ XA3	24	13.1	–	0	0.60	W	4	XRD	Thaumasite was detected in samples damage. It was more frequent in cement with in high C_3A cement. Ettringite and gypsum were also found.					
														5	0.63		4							
														25	0.80		4							
												10.3	–	0	0.60		4							
														5	0.63		3							
														25	0.80		4							
												8.5	–	0	0.60		2							
														5	0.63		2							
														25	0.80		3							
												5.3	–	0	0.60		1		No thaumasite formation					
														5	0.63		1							
														25	0.80		1							
Crammond and Halliwell [31]	M	20×20×15	0.60	3.00	1 + 20	4.2	1.1	5	–	C2/ XA3	24	≅13	–	20	0.75	T	4	XRD	E		G			Faster rate of deterioration when increased C_3A content. For the same C_3A content, the attack depended on LF content, particularly at low temperature.
												≅10	–	20	0.75		4		E	T	G			
												≅9	–	20	0.75		–		E	T				
												≅5	–	25	0.80		–			T				
												≅ 0	–	35	0.92		0		E	T	G			
Barker and Hobbs [32]	M	40×40×160	0.50	3.0	28	4.2	–	5	1 m	C2/ XA3	12	0.0	61	0	0.50	T	0	XRD	–					SR of OPC and PLC was similar, although the mode of attack was different. OPC-mortar exhibited a larger expansion than PLC mortar. Instead, PLC mortar showed a more extended surface damage. Deterioration of PLC mortars was greater in $MgSO_4$ solution.
												10.0	70	0	0.50		1		–					
														15	0.59		2		–					
			0.75	4.5								0.0	61	0	0.75		1		–					
												10.0	70	0	0.75		3		E				p	
														15	0.88		4		E	T			n	
			0.50	3.0		4.2	1.1	5	1 m	C2/ XA3	12	0.0	61	0	0.50	T	0	XRD	–					
												10.0	70	0	0.50		2		–					
														15	0.59		2		–					
			0.75	4.5								0.0	61	0	0.75		1		–					
												10.0	70	0	0.75		4		–					
														15	0.88		4		E	T			n	
Hartshorn et al [33]	P	ϕ×10×10	0.50	–	28	26.6	3.6	5	3 m	C3/ XA3	14	8.5	49	0	0.50	T	2	XRD	E		G			Attack increased with increasing time and with increasing LF. Thaumasite formation was greater for high LF.
														5	0.53		2		E		G			
														15	0.59		3		E	T				
														35	0.77		4		E	T				
Hartshorn et al [34–38]	M	40×40×160	0.50	2.50	28	14.4	3.6	5	3 m	C3/ XA3	12	8.5	49	0	0.50	P	1	XRD	E					At 5 °C, prisms presented a more extended damage and it increases when LF increasing. Thaumasite was formed after 5, 7 and 9 months for 35, 15 and 5% LF samples, respectively. Thaumasite solid solution was also formed in the corroded parts of mortar without LF.
														5	0.53		1		E	T				
														15	0.59	t	2		E	T				
														35	0.77		3		E	T	G	b		
											60	8.5	49	0	0.50	t	1	XRD	E	T	G	b		
														5	0.53		3		E	T	G	b		
														15	0.59		4		E	T	G	b		
														35	0.77		4		E	T	G	b		
						14.4	3.6	20	3 m	C3/ XA3	12	8.5	49	0	0.50	t	0	XRD	–					
														5	0.53		0		–					
														15	0.59		1		–					
														35	0.77		1			T		B		
Tsivilis et al. [39]	M	40×40×53	0.50	2.50	1+6 w+ 21 air	14.4	3.6	5	3 m	C3/ XA3	11	6.7	66	0	0.50	P	1	XRD		T	G		n	PLC-mortars suffer from TSA at a low temperature, and its formation was accompanied by brucite and gypsum
														15	0.59		2			T	G		n	
														30	0.71		4			T	G		n	
						14.4	3.6	25	3 m	C3/ XA3				0	0.50	T	0	No data reported						
														15	0.59	P	0							
														30	0.71	P	0							

(continued on next page)

Table 1 (*continued*)

Author, [reference]	Specimens characteristics					Solution characteristics					Time, months	Cement composition				Surface characteristics								Main conclusions
	Material[a]	Size, mm	Water/ binder	Sand/ binder	Previous curing, days	$[SO_4^{2-}]$, g/l	$[Mg^{2+}]$, g/l	Temp, °C	Renew or pH	ACI 201 and EN 206[b]		C_3A	C_3S	LF replac., %	w/c[c]	Register[d]	Raiting[e]	Compounds[f]						
																		Technical	E	T	G	B	P	
Tsivilis et al [40–42]	P	30×40×50	0.40	–		14.4	3.6	5	nd	C3/ XA3	12	6.7	65	0	0.40	T	1	XRD/DTG/ SEM	–					Metakaolin (10%) or low Al_2O_3 BFS (50%) improves the SR of PLC with 15% LF [43,44]
														15	0.47		3			T	G	B		
														30	0.57		4		–					
Vuck et al [45]	P	ϕ 9×80	0.50	–	28	16.0	4.0	5	1 m	C3/ XA3	5	7.8	56	0	0.50	T	1	XRD/DTG	e	t	g	B	P	The use of low-content C_3A and C_3S limestone cement also showed good sulfate resistance.
														20	0.63		4		E	T	G	B	p	
												1.8	35	0	0.50		0		–					
														20	0.63		1		–					
Hill et al [46–48]	C	100×100×100	0.50	–	28	3.0	0.4	5	nc	C2/ XA2	24	≅4.0		0	0.50	P	2	XRD		T	G		B	PLC, OPC and SRPC showed signs of chemical attack at low temperature. CH is a reactant.
			0.45									10.0		5	0.47		4			T	G	B		
												10.0		20	0.56		4			T	G	B		
Borsoi et al [49]	M	40×40×160	0.40	3.00	28	3.0	0.8	5	nd	C2/ XA2	12	8.1	63	10	0.44	P	0	XRD	–					Damage was mitigated using an SRPC and completely eliminated when this cement was blended with fly ash
												0.0	65	10	0.44		0		–					
											60	8.1	63	10	0.44		3		E	T	n		n	
												0.0	65	10	0.44		1		E	T	n		n	
Collepardi et al [50]	P	40×40×160	0.40	-	7	67.6	–	5	nd	C3/ XA3	3+4	12.4	48	0	0.40	t	0	XRD	E		G		p	No significant difference on SR performance of PC and PLC exposed to wet-dry cycles.
														15	0.47		0		E				P	
														30	0.57		1		E	T			p	

[a] Material: C = concrete; M = mortar; P = Paste.

[b] Classification of environment according ACI 201 [68] or EN 206 [69].

[c] effective w/c: calculated as (Water/binder)/(1.00–LF replac/100).

[d] Register: P = photograph, G = graphic; T = table; t = text; W = wear rating.

[e] Rating: visual appearance according Table 3.

[f] Compounds: E = ettringite; T = thaumasite; G = gypsum; B = brucite; P = portlandite; n = no-detected.

European and Latin-American countries and it is expected that its world production will increase due to the technical, economic, and ecological benefits [1].

For common cements, European Standard EN 197-1 (2000) allows up to 5% limestone as a minor additional constituent, and it also identifies four types of PLC containing 6–20% limestone (types II/A-L and II/A-LL) and 21–35% limestone (types II/B-L and II/B-LL), respectively. A similar trend in cement standard was followed by Latin-American countries. In Argentina, PLC (IRAM 50000/07) can contain from 0 to 25% calcareous materials, while the Brazilian standard (NBR 11578/91) defines type CPII-F of Portland composite cement containing from 6 to 10% limestone filler. In Mexico, composite cements containing from 6 to 35% limestone filler are also standardized (NMX C-414-0/99). The ASTM C150-04 standard has recently permitted up to 5% of limestone filler ($CaCO_3>70\%$) by mass in their cement types, so that the chemical and physical requirements of this standard are met. On the other hand, the ASTM C1157-03 standard (Hydraulic cement) specifies cement based on performance requirements and there are not any restrictions on its composition or its constituents. Since 1983, the Canadian standard (today Cementitious Materials Compendium — CSA A3000-03) allows the inclusion of up to 5% limestone addition for Type 10 and 30 Portland cement. Besides, the Canadian Standards Association is planning to incorporate a large proportion of limestone filler.

In self-compacting concrete (SCC), a large amount of fine particles, including limestone filler, is used in order to avoid gravity segregation of larger particles in the fresh mix. In this case, a high volume of limestone filler (from 50 to 200 kg/m³) is used as additional fine material to cement to make an SCC with a reasonable cost base [2].

According to what is currently known, the incorporation of a large amount of limestone filler in cement, mortar or concrete could affect its durability, especially, chloride ingress, carbonation, sulfate resistance and fire resistance. As regards external sulfate attack, cementitious materials with limestone filler are more susceptible to thaumasite formation. The Thaumasite Expert Group recommendation [3] included the complete restrictions to use PLC (LF range from 6% to 35%) in groundwater containing more than 0.4 g/l of SO_4^{2-}.

1.1.2. Sulfate attack and thaumasite formation

External sulfate attack (ESA) to cementitious matrix is a complex process that involves the movement of sulfate ions through the pores by means of different mechanisms of transportation and the interaction of aggressive solution with some compounds of cement paste (AFm phases, hydrogarnet phases, unhydrated alumina phases and CH) to form expansive compounds (ettringite and gypsum) that produce cracking, strength loss and softening [4,5]. The most important factor to prevent external sulfate attack is to reduce the permeability of the concrete (low water/cement ratio, high cement content, well compacted and well cured) [5]. In terms of cement composition, C_3A is the main compound involving sulfate resistance, whereas C_4AF, an alumina bearing phase, and CH released from silicates hydration can also affect the sulfate resistance of low C_3A Portland cements [6].

In an acidic sulfate environment ($pH<7$), gypsum formation causes local expansion, spalling and strength retrogression [7]. The acid media contribute to the gradual removal of CH from the paste until complete depletion, which promotes decomposition of C–S–H that causes loss of adhesion and stiffness. As for $MgSO_4$ attack, Mg^{2+} and SO_4^{2-} react with CH to produce gypsum and brucite in the surface forming a double layer. The reduction of alkalinity due to $Mg(OH)_2$ insolubility results in more Ca^{2+} release from C–S–H, increasing the gypsum formation and, finally, the decomposition of C–S–H to non cementitious MSH [8].

In a wet environment, thaumasite is readily formed by ESA when calcium silicate-ions and carbonate ions or atmospheric CO_2 dissolved in water are present in the pore solution of cement paste. Therefore, thaumasite sulfate attack (TSA) may occur in mortar or concrete containing limestone (CO_3^{2-}), as filler or aggregate, exposed to sulfate solution (SO_4^{2-}) when the attack causes the disintegration of C–S–H in cement paste (SiO_3) in the presence of Ca^{2+} [9]. This deterioration can proceed faster in cold environments (below 15 °C), and it is particularly more deleterious when sulfates are associated with the Mg^{2+} and low pH as both contribute to the decomposition of C–S–H [9,10]. This attack causes a gradual softening of the surface of concrete as well as a gradual inwards progression. Finally, cement paste is transformed into a non-cohesive mass leading to the loss of particles [10,11].

According to Bensted [9,12], thaumasite could be formed by two different but closely related routes. These are the direct route from C–S–H formed during hydration of silicate phases (C_3S and C_2S), and the woodfordite route from ettringite produced during hydration of the alumina bearing phases (C_3A and C_4AF) in the presence of calcium sulfate. The reasons and processes in the first transformation of tetrahedral SiO_4^- into octahedral SiO_6^- of thaumasite still remain unknown. In the second route, it is believed that the evolution of ettringite into thaumasite takes place through the discontinuous solid solution where ettringite crystal incorporates Si^{4+} in its structure, substituting Al^{3+} ions in the presence of CO_3^{2-}. Hence, all main phases of hydrated cement paste can slowly convert to non-binder thaumasite. Crammond [10] proposed the formation of thaumasite through a solution mechanism. For this mechanism, sulfate ions ingress into pore solution and react with alumina, calcium, carbonate or bicarbonates and silica ions to form ettringite, gypsum or thaumasite depending on concentrations of ions, relative solubility of the competing species and the stability of precipitates. A recent study of Kohler et al. [13] indicates that thaumasite is not formed via the woodfordite route and the direct route is extremely slow or unlikely. They propose that thaumasite formation occurs through the heterogeneous nucleation of thaumasite on the surface of ettringite when the disintegration of C–S–H takes place in cement paste.

For low permeable concrete (low *w*/*c*, well curing, no cracking), ESA occurs very slowly due to null or limited ion transport from solution to paste. However, for permeable concrete in contact with CO_3^{2-}, the use of sulfate-resisting Portland cements (SRPC, low C_3A cement, Type V) does not necessarily prevent the formation of thaumasite, because it can be formed from C–S–H present in the hardened paste. In this case, it is suggested that the rate of attack increases when coupled with other mechanisms (acid attack, magnesium attack or extreme carbonation of paste) that produce the decomposition of C–S–H [14,15] due to the reduction of the alkaline environment needed for its preservation [16]. A secondary cause that could increase vulnerability of SRPC in the sulfate environment is the increase of C_3S/C_2S in cement composition [6].

1.1.3. Laboratory studies and field experiences

Reviewing literature about sulfate performance of cementitious material containing limestone filler, numerous studies related to sulfate deterioration of paste, mortar or concrete containing LF exposed to different environmental conditions were found. Conclusions of these studies suggest that limestone filler impairs its sulfate resistance and several authors emphasize that a more pronounced deterioration is associated with the formation of thaumasite due to the presence of LF.

Tables 1 and 2 summarize the most important research results from recent publications that involve laboratory studies on sulfate performance of PLC or sulfate resistance of conventional concrete or SCC with limestone powder, respectively. The more important characteristics of specimens (size, w/b; curing regimen), aggressive solutions (type, concentration, temperature and pH-control), cementing material (C_3A, C_3S, and LF), damage and formed compounds at surface are included.

Regarding field studies, there are only few field cases where PLC or concretes with LF showed damage after three decades of its

Table 2
Details and results of most important experimental researches about sulfate performance where limestone is used as sand replacement

Author, [ref]	Specimens characteristics						Solution characteristics					Time, months	Cement composition			Surface characteristics								Main Conclusions
	Material[a]	Size, mm	Water/ cement	Cement content, kg/m³	LF content, kg/m³	Previous curing, days	$[SO_4^{2-}]$, g/l	$[Mg^{2+}]$, g/l	Temp, °C	Renew or pH	ACI 201 and EN 206[b]		C_3A	C_3S	LF replac., %	Raiting[c]	Register[d]	Compounds[e]						
																		Technical	E	T	G	B	P	
Sawicz et al [51,52]	C	50×50×150	0.50	350	26	28	33.8	0.0	20	–	C3/XA3	4	12.1		0		0	XRD	E					Expansion increases when *w/c* > 0.58. Limestone powder up to 14% decreases expansion.
			0.60		58												0		E					
			0.70		135												0		E					
Gao et al [53]	M	40×40×160	0.60	525	160	28	16.0	4.0	5	2	C3/XA3	12	12.0	34	0	P	4	XRD	E	T	G			Common cement and SRPC mortars showed signs of deterioration after 4 and 6 months, respectively. Resistance to TSA was improved by addition of silica fume (8%) or GGBFS (60%).
													4.0	46	0		3		E	T	g			
Persson [54]	SCC	ϕ 50×150	0.39	420	0	28	12.2	0.0	5	1	C3/XA3	30	1.7	57	0	t	0	No data reported						After 900 days, there are no evidences of deterioration.
					18												0							
					30												0							
					47												0							
Trägårdh and Kalinowski [55,56]	SCC	100×100×100	0.65	300	0	28	1.4	0.4	5	3 m	C1/XA2	22	4.6	–	10	W	2	SEM	*E*	*T*			*B*	SCC with 50 kg/m³ LF deteriorated faster than SCC without LF and concrete with 100 kg/m³ added. Thaumasite is detected with ettringite. SCC without LF showed no surface damage, while SCC with LF showed a minor spalling and wearing in the corner and edges. Reaction products consisted predominantly of gypsum with a small amount of thaumasite.
					50												3		*E*	*T*			*B*	
					100												2			*T*			*B*	
			0.65	300	0							22	7.8	63	0		4		*E*	*T*			*B*	
					50												4		*E*	*T*			*B*	
					100												3			*T*			*B*	
			0.40	415	0							48	1.8	56	0		0			*t*	*G*		*b*	
					90												1			*t*	*G*		*b*	
					180												1			*t*	*G*		*b*	
Friebert and Stark [57]	SCC	ϕ 50×150	0.5	350	0	7	33.8	0.0	8	nd	C3/XA3	4	>4	–	–		0	SEM		*t*				After 4 months, the relative tensile strength was >0.70 for both concretes. This is attributed to the high impermeability of its microstructure.
					200												0			*t*				

(3) *w/c* = effective water/cement ratio.

[a] Material: C = concrete; M = mortar; P = paste.

[b] Classification of environment according ACI 201 [68] or EN 206 [69].

[c] Rating: visual appearance according Table 3.

[d] Register: P = photograph, G = graphic; T = table; t = text; W = wear rating.

[e] Compounds: E = ettringite; T = thaumasite; G = gypsum; B = brucite; P = portlandite; n = not detected.

introduction in the market. According to Crammond's review (1960 to 2001) [58], any case reported involves the use of PLC cement, but some deteriorated concretes contain fine limestone aggregates. Among these cases, only one concrete was designed according to the rules of sulfate resistant concrete (SRPC, $w/c<0.50$, 400 kg/m^3 of cement), but the presence of honeycombs indicated deficient construction practices. At the First International Conference on Thaumasite in Cementitious Materials, thaumasite occurrence in the U.K. [10], in a sea environment [59], at moderate temperature [60]; and in deteriorated concretes [61] was reviewed. Among 30 cases of concrete deterioration associated with thaumasite formation reported in the UK, only two cases included concrete mixtures with SRPC and a w/c of 0.50–0.55 [62]. In this case, Hobbs and Taylor [63] have speculated that the aggressiveness of groundwater to concrete could have been greatly enhanced by the formation of sulfuric acid due to pyrites oxidation. Recently, the occurrence of thaumasite in a tunnel structure located in China has been reported [64, 65], but these concrete elements were not designed for external sulfate attack. Hooton and Thomas [66] reviewed the TSA in PLC and they revealed that there have been no cases reported after 25 years incorporation of 5% limestone filler in cement standard in Canada, despite its severe cold climate. Results of field experience reported by Crammond et al. [67] showed that cast-in situ concrete cubes (size = 250 × 250 × 200 mm^3, 320 kg/m^3 of cement; $w/cm = 0.53$–0.58) made with different aggregate types and PC with 9.9% C_3A were all attacked, while the influence of limestone aggregate is more noticeable in PC with 6.6% C_3A and SRPC concretes. Specimens of poor quality concrete made with PLC (15% LF, 290 kg/m^3 of cement; $w/cm = 0.72$–0.78) have the worst performance.

The most important laboratory and field investigations on thaumasite formation, experimental evidences were obtained on mixtures designed underestimating the rules for sulfate resistance material and analyzing LF from an active mineral admixture perspective. In the practice, there is no doubt that dense and impermeable concrete minimizes the external sulfate attack. This concrete requires the use of a relatively rich mix with a low w/c and a good workmanship (adequate compaction, uniformity, a hard finish, and good curing). A low C_3A cement also contributes to the stability of alumina phase compounds in sulfate environments. Thereafter, the main interest is to determine if TSA could be avoided using dense concrete with a low w/cm ratio, which restricts the access of sulfate ions and protects the stability of hydration products, instead of large proportions of limestone filler in its composition.

2. Scope of the paper

From literature examination, two questions arise in this subject. Firstly, does an LF addition reduce the sulfate performance of concrete, mortar or paste, when it is also properly formulated according to the aggressiveness of the environment?; and secondly, is thaumasite the main cause of deterioration or is it only the last stage of sulfate attack in permeable mixtures? In this paper, the use of a conceptual graphic is proposed to consider possible answers involving most of the reported data. This graphic takes into account the main factors of sulfate attack (type or mode of attack, ambient conditions, mixture design and characteristics of cementitious materials) in relation with an indicator of the deterioration degree and the compounds formed during the attack.

3. Main factors of external sulfate attack

The progress of ESA requires the presence of aggressive ions in solution, the transport of these ions into the cementitious matrix and the reaction with some hydrated cement products to produce expansion or degradation. This process starts on the surface and advances inwards into the specimens as the exposure time increases. From field and laboratory observations, Hobbs [62] inferred that the magnitude of TSA depends on the combination of several factors: wet conditions, low temperatures, exposure to sulfates associated with the magnesium cation, the prior formation of conventional sulfate attack products and the presence of at least between 10% and 35% of $CaCO_3$ by mass of the cement. These factors can be combined as follows:

- aggressiveness of sulfate environment (sulfate concentration, magnesium concentration, pH, temperature)
- composition of mixtures (w/c ratio, curing) that contribute to water transport
- characteristic cementitious materials (C_3A content, limestone filler content, C_3S/C_2S ratio).

3.1. Aggressiveness of the sulfate environment

According to the Durability Guide of ACI 201 Committee [68], the aggressiveness of sulfate environments is classified into four types based on the concentration of SO_4^{2-} (g/l) and it only suggests that groundwater containing $MgSO_4$ is more aggressive. In the European Concrete Standard EN 206 [69], exposure to chemical attack is classified into slightly, moderately or highly aggressive classes according to the SO_4^{2-}, Mg^{2+}, NH^{4+} concentration and pH. This classification is based on static water and temperatures between 5 and 25 °C. However, the temperature plays an important role in TSA; when the temperature drops below 15 °C, formation of thaumasite can arise and deterioration increases at a more rapidly rate in cold environments [9].

The effect of pH on the sulfate resistance test was studied by several authors [7,70,71] and it is considered an important factor in the aggressiveness of the media. Also, the control of pH can change the predominant phases of attack, especially gypsum formation by CH depletion. Sodium and magnesium sulfate solutions are neutral, but the evolution of pH in the solution-specimen system is quite different. In Na_2SO_4 solution, the pH increases rapidly (near to 12) when specimens are immersed in them due to CH dissolution, whereas $MgSO_4$ solution may be buffered at pH near 7 due to the insoluble nature of the $Mg(OH)_2$ produced [72]. In reviewed tests, this factor is controlled by renewing the solution every one-four months [24,26,28,29,30,32,33–38,45,51,53–56] or by daily or weekly pH-control [20,21,47]. Also, there is no information in some tests procedures [17–19,25,27,40,57]. Another condition to avoid this pH change in solution is to increase largely the volume of solution/volume of the specimen.

These test conditions results can be divided into sulfate solution with or without magnesium ions and temperature of storage lower or higher than 15 °C. Analyzing ions concentration according to the ACI 201 or EN 206, exposure test solution can be classified as follows (Tables 1 and 2):

- Na_2SO_4 solution at temperature > 15 °C: In all tests, sulfate content is higher than the limit for C3 Class of ACI 201 (> 10 g/l SO_4^{2-}) and XA3 Class of EN 206 (6 g/l SO_4^{2-}).
- $MgSO_4$ solution at temperature > 15 °C: Sulfate concentration allows to classify all solutions as C3 Class of ACI 201 and the concentration of SO_4^{2-} and Mg^{2+} (> 3 g/l) are above the limit of XA3 Class of EN 206.
- Na_2SO_4 solution at temperature < 15 °C: Most of tested solutions are C3 Class, except for Barker and Hobbs [32] (C2) and Bellmann and Stark [28] who used a weak solution in the upper limit of C1 Class (1.5 g/l SO_4^{2-}). According to EN 206 classification, all exposures are XA3 Class, with the exception of Bellmann and Stark [28] that is XA2.
- $MgSO_4$ solution at temperature < 15 °C: a wide range of concentrations are used for these conditions. Most solutions are C3 [29,33,34,39,40,45,53], two [32,46] are C2 and one is C1 class [55,56] of ACI 201; whereas most of test solutions are classified as XA3 Class of EN 206, two are in the upper threshold of XA2 Class (3 g/l SO_4^{2-}) [46,49] and Trägårdh et al. [55,56] used an exposure solution with Mg^{2+} and SO_4^{2-} concentration below the upper limits of XA2 class.

Most test solutions used provided a highly aggressive environment and, in this case, concrete codes required the design of a concrete mixture with a maximum *w*/*c*, compositional restriction in portland cement, a minimum specified compressive strength and an appropriated period of curing.

3.2. Composition of mixtures

Protection against ESA is achieved by using a concrete with low *w*/*c* and well cured that retards ingress and water movement [68]. Several authors [73–75] mention the importance of permeability and the ability of concrete to resist ingress and water movement to make a sulfate resistant concrete.

Water transport in cementitious materials depends on capillary porosity, its connectivity and the pore structure (tortuosity and constriction or disconnection); and these parameters are directly related to *w*/*c* ratio and the progress of cement hydration. According to the percolation concept developed by Garboczi and Bentz [76], transport of sulfate ions mainly occurs in the open capillary porosity and it was found that capillary porosity is disconnected when it is about 18%. For portland cement paste with a *w*/*c* of 0.40, 0.45 and 0.50, capillary porosity becomes disconnected when the hydration degree is approximately 0.72, 0.82 and 0.93, respectively. On the other hand, capillary disconnection is very difficult for *w*/*c* higher than 0.60, and impossible for *w*/*c* of 0.70. Considering a hydrated system where capillary porosity is less than the percolation threshold, main diffusion occurs through the C–S–H phase. In this case, SO_4^{2-} ions progress much more slowly than chloride ions into hardened cement paste. During sulfate attack, capillary porosity changes due to the consumption (CH) or growth (gypsum, ettringite) of the reaction products and the later microcracking also affects the transport of ions [77–79].

When LF is used in cementitious material, changes in capillary porosity occur due to several physical effects such as, dilution effect, filler effect, and heterogeneous nucleation [80–82]. The dilution effect is a consequence of the replacement of a part of cement by the same quantity of LF. The increase in the amount of LF involves a decrease in the amount of cement and, consequently, an increase in the effective *w*/*c* ratio, and this effect is omitted when LF is used as sand replacement. The filler effect implies a modification of the initial porosity of the mix, and it generally produces a decrease in the water required to maintain constant workability. Heterogeneous nucleation occurs because LF particles act as nucleation sites, increasing the early hydration of cement and, therefore, producing a more disoriented crystallization of CH. These physical effects depend on the proportion and fineness of LF used. In relation with these coupled effects on water transport, this is greatly affected by the increase of *w*/*c* when increasing the replacement of LF by cement, and it is only slightly compensated by the reduction of water to maintain the workability and the increase of the hydration degree in the fraction of cement particles. For example, to obtain the capillary porosity threshold in pastes made with PLC fully hydrated ($\alpha=1$) and a water/cementitious material ratio (*w*/cm) of 0.50, 0.45 and 0.40, the maximum percentage of LF addition will be 5, 15 and 25%, respectively. In other words, capillary disconnection of cement paste containing 5, 10, 20 and 35% LF will be obtained using a *w*/cm of approximately 0.50, 0.48, 0.43 and 0.34, respectively.

Likewise, it can be mentioned the European practical approach concerning the effect of supplementary cementing materials (SCM) on mechanical or durable properties using the SCM efficiency factor concept [83]. This concept introduces the following *w*/cm expression [$w/(c+k$ SCM)], where the weight of SCM is affected by the addition efficiency factor (k). For limestone filler, there is some experimental evidence that an increase in the replacement addition to cement with unchanged *w*/cm increases water penetration and LF presents a null or negative “efficiency factor” for chloride penetration [83–85], unlike other reactive fillers such as silica fume or fly ash.

Thereafter, assuming the null contribution of LF ($k=0$) to reduce ions penetration in well hydrated mortar/concrete exposed for a long time to sulfate solution, the effective *w*/*c* ratio will be considered to compare the sulfate performance of mixtures. For all test reviewed, the effective *w*/*c* ratio is presented in Table 1.

When LF is used as sand replacement in the SCC, *w*/*c* will be used to compare the water transport parameter. Zhu and Bartos [86] indicated that the SCC mixes had significantly lowered oxygen permeability and water sorptivity in comparison with the conventional concretes of the same strength grades ($w/c\cong0.60$ and 0.45 for C40 and C60 concrete, respectively). However, the chloride diffusivity appeared to be more dependent on the type of filler used. Recently, a comparative analysis of microstructure between SCC ($w/p=0.28$; $w/c=0.41$ and 0.48, LF=200 and 300 kg/m^3) and HPC concrete ($w/c=0.33$ and $w/c=0.48$) has shown that the pore structure, including the total pore volume, pore size distribution and critical pore diameter in the SCC, is very similar to that of HPC [87]. For this *w*/*c*, disconnection of capillary porosity can be produced at early ages of the concrete.

Finally, assuming that a large proportion of cement was hydrated during the curing of specimens made prior to sulfate attack, the main variable of mixture is the effective *w*/*c* ratio instead of the *w*/cm ratio, because it considers the *w*/cm and the proportion of LF in the mixture that determines water and ions transport.

3.3. Characteristic cementitious materials

At the same *w*/*c* ratio, sulfate resistance of cementing materials generally decreases with an increase in its C_3A content. This determines the amount of monosulfoaluminates (AFm-phase) or hydrogarnets in the hydrated portland cement paste prior to attack. This compound can potentially react with external SO_4^{2-} to form ettringite. Also, hydration of C_4AF results in AFt and AFm phases with similar structure to C_3A hydrates, where aluminum is exchanged for iron [88]. In a sulfate environment, this compound can react slowly, but the mechanism for sulfate attack is expected to be the same as for the C_3A phase [89]. Formation of Fe-substituted ettringite was reported [6,90]. After complete conversion of AFm phase to AFt phase, gypsum crystallization arises, resulting in the consumption of CH that finally leads to decalcification of C–S–H. At this stage, a low C_3S/C_2S ratio is important to prevent sulfate attack [6,91].

According to Hobbs [62], TSA requires the prior formation of conventional sulfate attack products (ettringite, gypsum and depletion of CH) and the presence of calcium carbonate. When carbonates are absent, ettringite is a stable phase in a sulfate environment with a pH greater than 10.7 [92]. Consequently, if most alumina present in cement prior to ESA is crystallized as ettringite, there is no attack. It is possible using a low C_3A portland cement because the C_3A/SO_3 ratio is appropriate to obtain stable ettringite in the hydrated paste. When LF is present in cementing material, alumina hydrated compounds are affected in two ways: the dilution effect that reduces the C_3A content in PLC; and the chemical interaction effect between $CaCO_3$ and C_3A phase (formation of some variant of the AFm phase and changes in the AFm/AFt relationship). The dilution effect can be evaluated using other inert materials, such as quartz [93–95]. But, it is more favorable when cement has a high C_3A content and LF replacement is less than 10%, producing a moderate increase of the *w*/*c* ratio. Hooton [19] concluded that LF addition (less than 5%) has no influence on expansion, except to dilute the C_3A-content, whereas in a recent paper [29], he and his coworkers pointed out that expansion of mortar specimens grows significantly when the replacement levels of limestone filler (0 to 30%) increase for the same C_3A content ($\cong$10%) using the same test method. Carbonate ions coming from limestone filler modify the C_3A hydration products according to the SO_3/C_3A and $CaCO_3/C_3A$ ratio. Monocarboaluminate are thermodynamically more stable than monosulfoaluminate and aluminates hydrates [96]. Hence, transformation of monosulfoaluminate into monocarboaluminate occurs at an early age [97] and the sulfate ions released from the AFm phase in this process contribute to additional ettringite formation [98,99]. Also, the amount of free portlandite must be affected by this change [99]. Ettringite formation increases the molar volume of paste solids and it probably causes a reduction of porosity and permeability in hardened cement pastes with low LF replacement [100].

A recent study on AFm phases hydration [100] showed that hydrated compounds are a function of SO_3/Al_2O_3 and CO_2/Al_2O_3 ratios. Given a typical low C_3A clinker ($Al_2O_3 \cong 3.0–3.5$), addition of a low proportion of LF (≅5%) produces AFt, monocarboaluminate and hemicarboaluminate as stable phases. On the other hand, a high proportion of LF (≅20%) will be needed to convert all monosulfoaluminate into moncarboaluminate when the clinker used has a large proportion of C_3A ($Al_2O_3 \cong 5.0–6.0$).

In the presence of external sulfate ions, monocarboaluminates, monosulfoaluminates, hemicarboaluminates and hydrogarnets are unstable phases and they will be transformed into ettringite leading to an extended deterioration for high C_3A content parent cement. Formation of ettringite in paste causes local expansion that produces micro cracking exposing a large surface area to aggressive solution. When carbonate ions are in cement paste, thaumasite is formed later in areas where damage like cracking or spalling has already occurred. Therefore, C_3A content is also a main variable on TSA and it will be related with the expansive damage that takes place before that thaumasite formation, independent of the exact formation mechanism. At later ages, thaumasite was also found on the sound surface of specimens made with SRPC cement indicating the very slowly reaction in no cracking paste.

Matthews [30] concluded that sulfate resistance of PLC (5 and 25% LF) presents a clear dependence on C_3A content of parent OPC and they may behave better or worse. Thaumasite detection and performance worsening of high C_3A cement containing 25% LF leads to include a limitation of PLC use in sulfate environments in the BS of cement and in the BRE recommendation. Nobst and Stark [101] confirmed that the tendency of cements to thaumasite formation is proportional to their C_3A and Al_2O_3 contents. Even small Al_2O_3 contents are capable of accelerating thaumasite formation, such as in SRPC. Some authors have used a test procedure that simulates the best chemical conditions for thaumasite formation. In this procedure, hydrated cement paste ($w/c = 0.5$, curing 28 days, drying at 105 °C) was finely ground and mixed in stoichiometric proportions with gypsum, calcium carbonate and 20% excess of water to form a paste, which was then stored at 6 °C at room temperature for 24 months. It was seen that the test used misjudged the physical properties of the paste that could hinder the penetration of sulfate solutions and the decomposition of ettringite at this drying temperature. Aguilera et al [102] compared the rate of thaumasite formation in permeable mortars ($w/cm = 0{,}70$, $s/b = 3$, curing = 90 days) made with low ($C_3A = 1.24\%$, $C_3S = 76.2\%$) and high ($C_3A = 13.3\%$, $C_3S = 55.1\%$) alumina content cement, both with and without over dosage of gypsum and addition of calcite. Prisms were subjected to accelerated and complete carbonation (absence of CH) and then exposed to cold water (5 °C). They concluded that thaumasite forms in mortar with C_3A low cement, but its formation rate is much slower than in mortars with high C_3A cement. In other works [103], some authors reported results of carbonated prism exposed to saturated $CaSO_4$ solution and $MgSO_4$ solution (11.2 g/l SO_4^{-2}) at ambient temperature (21 °C). In this laboratory study, carbonation of mortar provided sufficient carbonates for thaumasite formation in low and high C_3A content cements. In both experiences, unlike for ESA, it is suggested the influence of C_3A on thaumasite formation, while the presence of LF would be a secondary variable in the mixture.

The third component to thaumasite formation is the silica provided by decomposition of C–S–H. Instability of C–S–H is possible when complete depletion of CH occurs in a sulfate environment due to leaching, acid attack or magnesium attack that causes the provision of Ca^{2+} from C–S–H to solution. In the attacked specimens, it can be observed three zone of attack: the ettringite front inside with a low CH consumption in this expansive reaction, the gypsum and thaumasite zone with high CH depletion caused by attack reaction, and outer zone with absence of CH and decomposition of attack products due to low pH [22,55,79,91]. The severity and progress of this process also depends on the increase of permeability and microcracking caused by ESA itself.

In the conceptual graphics, C_3A content of clinker or parent portland cement is selected as the second main variable and LF content is reported below the bullet used assuming that the contribution of LF is to increase permeability. It can also be noticed that C_3A calculation according to Bogue's equation will cause discrepancy with XRD analysis results [104,105].

4. Results of external sulfate attack

4.1. Surface deterioration degree

For ESA, the formation of compounds into the matrix induces a change in porosity, microcracking, expansion, tensile, flexural or compressive strength loss, spalling, mass loss and severe degradation on the surface. For the same aggressiveness of the environment and *w*/*c*, the evolution of deformation, mass loss or mechanical properties depend on constitution of specimens (paste, mortar, concrete), size of specimens, and type of sulfate used. For example, the expansion of specimens exposed to Na_2SO_4 solution is higher than that of mortar specimens exposed to $MgSO_4$ with a similar solution concentration of sulfate ions and specimens size. On the other hand, loss of compressive strength is high in mortars exposed to $MgSO_4$. For this reason, it is very complex to compare data obtained from different studies.

To assess the sulfate performance of the cementitious system, most investigations have included a description of the visual appearance of specimens. Several techniques such as visual rating, photographical records, and proportion of surface or edge of specimens affected have been used for this purpose. At the first stages of attack, pores are filled with deposition of sulfate attack products that cause no visible deterioration and white powdery coating is sometimes detected. Regardless of exposure solutions, the first sign of attack was the deterioration the specimen corners followed by extensive cracking along the edges and, finally, spalling and disintegration on the specimen surfaces. Table 3 summarizes the visual rating used to classify surface deterioration of different research papers analyzed. The degree of surface deterioration progress in time and results with more than four months of exposure are only included in the conceptual graph.

For this degradation indicator, Fig. 1 is the conceptual graphic including most data reported of cementitious materials exposed to different environments, with different proportions of mixture (effective *w*/*c*) and cementitious materials of different composition (C_3A, LF content). In this figure, the colour of the bullets intensifies when the specimen surface deterioration grows.

Analyzing this conceptual graphic, the following general considerations can be pointed out in relation to the degree of surface degradation:

- For all test environmental conditions (four quadrants), it grows when relevant factors such as the effective *w*/*c* and C_3A content increase.

Table 3
Visual rating used to classify surface deterioration

Rating	Description
0	No visible deterioration
1	Deterioration at corners and edges
2	Cracking along the edges
3	Extensive cracking and expansion
4	Spalling and disintegrations of surface

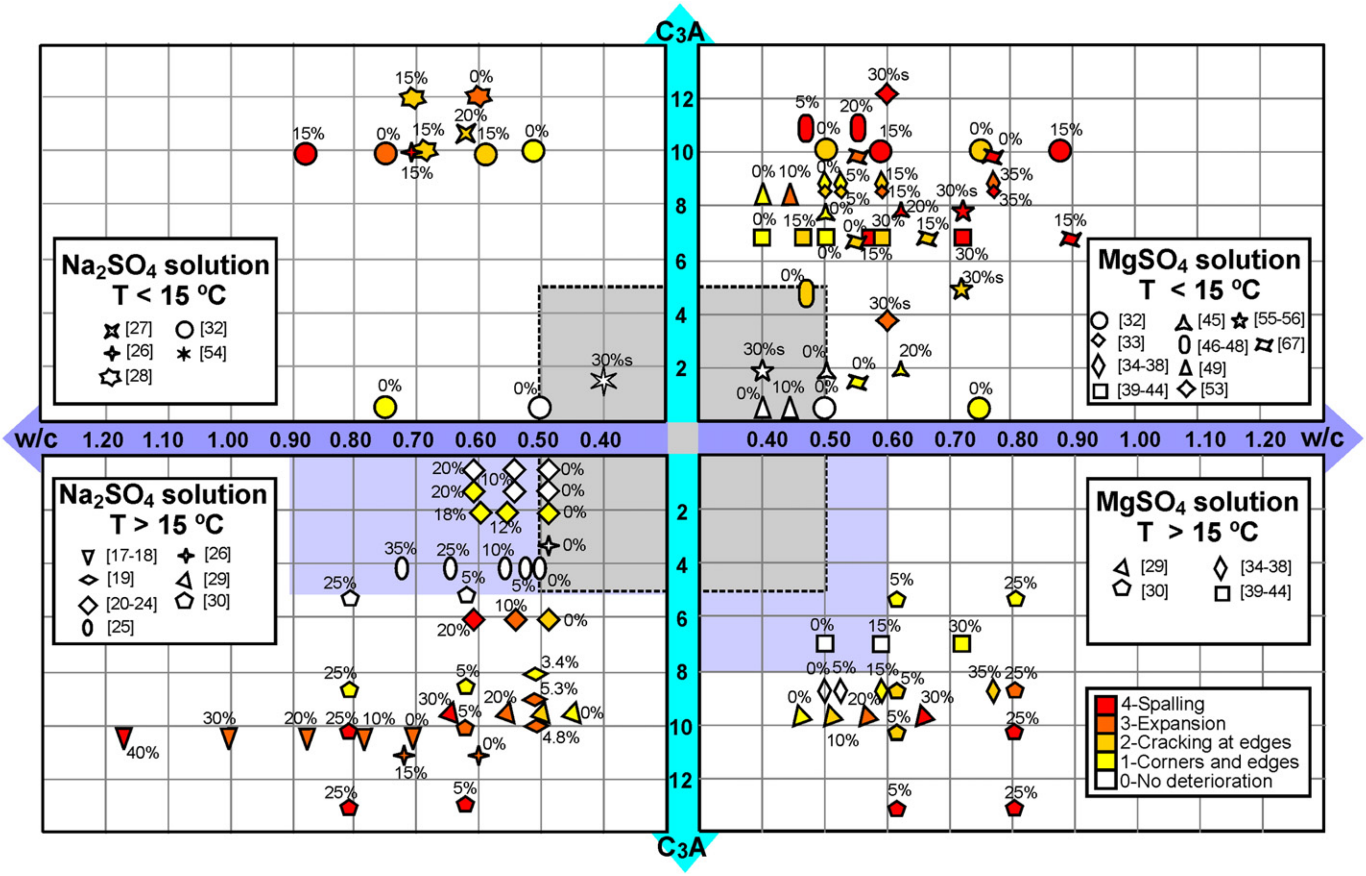

Fig. 1. Conceptual graphics indicating the surface deterioration degree as a function of effective *w*/*c* ratio and C_3A content in clinker or parent cement. Percentage of cement or sand replacement(s) by LF is indicated for each bullet.

- For the same experimental procedure, an increase of LF replacement produces a worsening behavior in parent cement, but most results reported are for parent cement with $C_3A > 5\%$.
- For short time exposure, no surface deterioration was reported for cementing mixtures (mortar, conventional concrete or SCC) design according to limits given by ACI 201 for C2 class of exposure ($w/c \leq 0.45$ and $C_3A < 5\%$) or by XA2 environment of EN 206 (i.e. DIN 1045-2: w/c ratio ≤ 0.50, $C_3A < 3\%$). It is observed in spite of test solution used are more aggressive and it will be require a mixture with $w/c < 0.40$, low C_3A cement plus a good reactive pozzolan. In Fig. 1, all experimental results including in the grey zone limited by $C_3A < 5\%$ and $w/c < 0.50$ showed no visible deterioration in the four quadrants.
- At a temperature <15 °C, surface deterioration is more extended for the same exposure time, especially in $MgSO_4$ solution.
- For $MgSO_4$ solution at temperatures higher than 15 °C, specimens with $w/c < 0.6$ and moderate sulfate resistant cement ($C_3A < 8\%$) [30,33,34,39] showed no deterioration in this environment (see light grey zone in Fig. 1). This could result from the evolution of a protective layer of brucite and carbonates, as occurs in seawater environments.
- For Na_2SO_4 solution at temperatures >15 °C, no significant surface deterioration was reported by low C_3A parent cements allowing a large proportions of LF, deterioration depended on pH of environment and the C_3S/C_2S ratio that lead to large gypsum formation and decomposition of C–S–H. In Fig. 1, the light grey zone ($C_3A < 5$) includes results without surface deterioration, except for high C_3S portland cement [6,20,21].
- In all cases where LF is used as sand replacement, the same considerations can be made. Only a great deterioration occurs in Gao et al experience [53].

4.2. Mineralogical composition of surface layer

The second question is to determine the formation of thaumasite on the surface layer of specimens exposed to sulfate attack using the same conceptual graphics. Most investigations have used the XRD techniques for this purpose. Thaumasite is very difficult to distinguish from ettringite and it is well established that both compounds form a solid solution, and have a miscibility gap associated with a change in the lattice parameters [106,107].

Depending on ESA progress, mineralogical analysis of surface layer can present a combination of thaumasite, gypsum, ettringite, CH, brucite and calcium carbonate (calcite and aragonite). Fig. 2 shows the conceptual graphic using the mineralogical analyses of surface for the last reported test age of each reference. In this figure, the compounds presented are classified into: ettringite, ettringite–gypsum, gypsum, thaumasite–ettringite–gypsum, and thaumasite. Brucite occurs in magnesium environments and the presence of CH is discussed later. In most studies, samples analyzed by XRD were taken from deteriorated specimens surface, but they revealed that the mineralogical composition of degraded cementing materials shows a significant change in less than 0.1–1 mm as the layer by layer analysis proves [22,108]. Also, it can be agreed that the mineralogical composition of the surface develops with the time of exposure and also results depend on the last analysis reported in each test program. Several studies [22,33,35,49] presented the composition prior to attack (surface or core of specimens) finding alumina phases (ettringite, monosulfoaluminate, monocarboaluminate or C_3AH_6 depending on the mineralogical composition of cement) and CH. Then, it is developed ettringite, gypsum with the consequent depletion of CH, decalcification of C–S–H and formation of thaumasite. For example, Irassar et al [22] reported for mortar exposed at Na_2SO_4 ($C_3A = 6.0\%$) monocarboluminate and CH

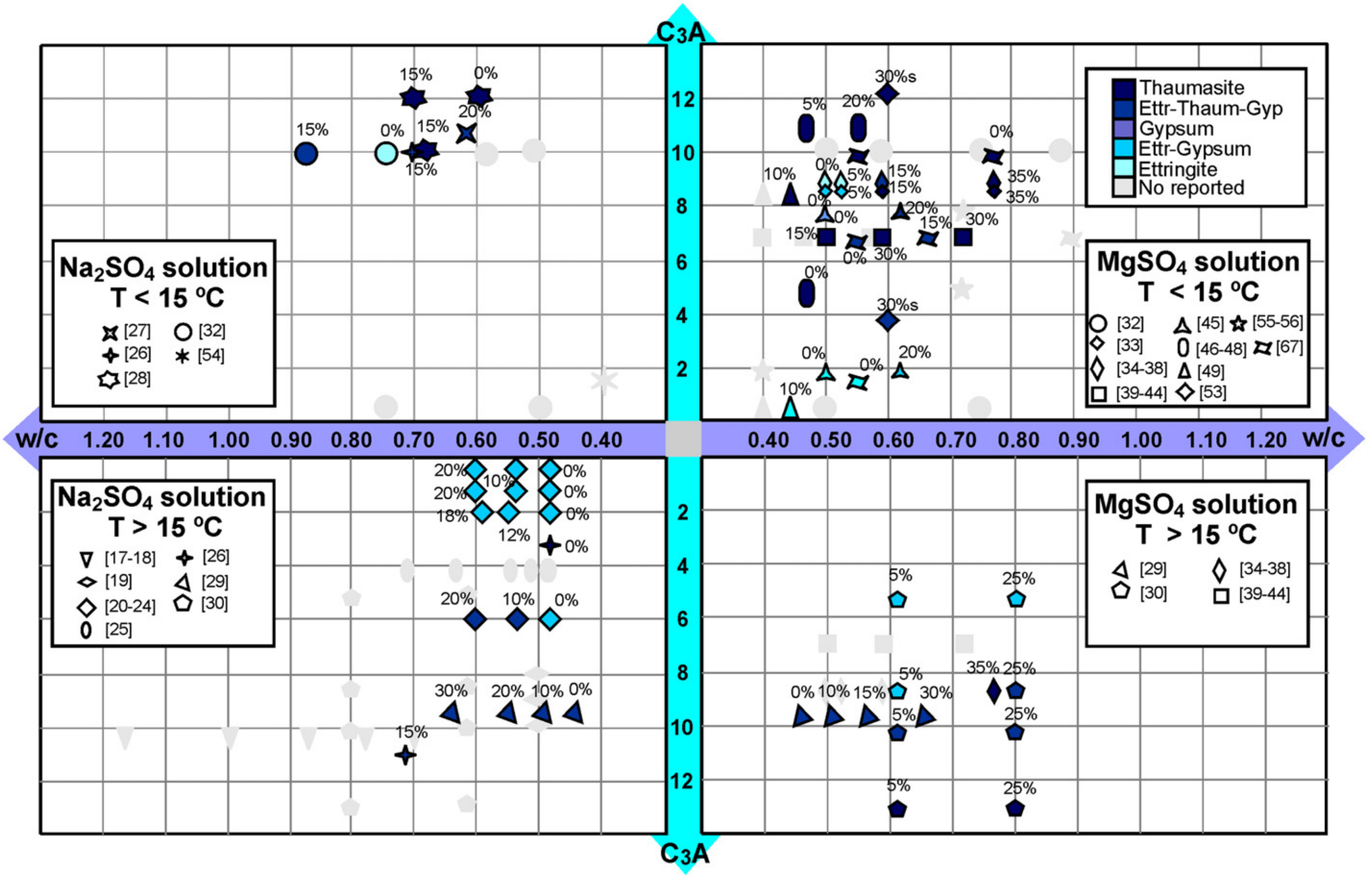

Fig. 2. Conceptual graphics indicating the mineralogical composition of surface as function of effective *w*/*c* ratio and C_3A content in clinker or parent cement. Cement or sand replacement (s) by LF is indicated for each bullet.

prior the attack, ettringite after 90 days, gypsum and ettringite after 12 months and thaumasite–ettringite and gypsum after two years. Hill et al. [47] reported no significant changes in mineralogical composition (thaumasite and calcite, CH is absent) on surface after 5 and 11 months. The formation of gypsum and brucite after 23 months [48] in $MgSO_4$ solution was then reported. In an acid sulfate environment (pH=4), these specimens surface is composed predominantly by gypsum [47].

Analyzing this conceptual graphics the following general considerations can be pointed out on the compounds formed on the surface:

- Thaumasite formation has been reported for specimens exposed to all environments (four quadrants). There are more reported results for $MgSO_4$ solution at low temperatures and it could be possible because its formation, while kinetically slowed by rising temperature, required a large time of exposition at temperatures > 15 °C [79] and the contribution of Mg^{2+} ions to decalcification of C–S–H.
- A high degradation degree (spalling and disintegrations of surface) matched with a large amount of thaumasite, accompanied by ettringite and/or gypsum. For all cases reported [22,26,29,32,33,35,39,40,53,48,67], specimens present a C_3A content > 6%, an effective *w*/*c* ratio > 0.6 due to a large proportion of LF (> 15%). These results agree with Matthews findings [30]. These XRD analyses also reveal that CH is completely depleted in the sample, providing a possible instability of C–S–H.
- Indeed, formation of thaumasite is also reported in specimens not accompanied by severe deterioration. Hartshorn et al [35] reported the formation of thaumasite in sound specimens with 35% LF prism exposed to $MgSO_4$ solution at 20 °C after 12 months, and Borsoi et al [49], in mortars with zero C_3A cement plus 10% LF after 43 months in mild $MgSO_4$ exposure. Also, thaumasite was found in cement without LF [23,29,35,39,68] showing a low deterioration degree exposed to Na_2SO_4 or $MgSO_4$ solution at cold or mild temperatures.
- For specimens made with low C_3A content, thaumasite was found with ettringite and/or gypsum. Commonly, this occurs at long test ages (43 months [49], 36 months [67], 24 months [48], 12 months [53]) in specimens exposed to $MgSO_4$. In all cases, the complete depletion of CH was found in the sample.
- For mixtures with effective *w*/*c*<0.6 showing an extensive deterioration (3 or 4), thaumasite was found in cementing materials made with parent cement containing more than 5.0% C_3A and LF (5% or more) on long time exposure (12, 24, 36 and 43 months) to Na_2SO_4 or $MgSO_4$ solution, at both cold and mild temperatures.
- For *w*/*c* ratio<0.6 and low content of C_3A, there are few reported data. Irassar et al [23] did not find thaumasite after two years in Na_2SO_4 solution at 20 °C. Borsoi et al [49] reported formation of thaumasite and ettringite and complete depletion of CH after 43 months in moderate aggressive $MgSO_4$ solution.
- There was no obvious dependence of thaumasite formation at limestone level in cement or concrete. Indeed, thaumasite was found in cement without LF [26,28,29,48] suggesting that the carbonates source was CO_2 dissolved in solution.

5. Conclusions

From this conceptual analysis of sulfate performance of cementing materials containing limestone filler, the following concluding remarks can be drawn:

- External sulfate attack of mixtures containing limestone filler is firstly governed by mixture resistance to sulfate ions penetration. When LF is used as cement replacement, effective *w*/*c* ratio is the main variable affecting ions transport. Therefore, a low proportion (<10%) of LF causes no significant changes in sulfate resistance of parent portland cement, while a large proportion (>15%) may worsen sulfate performance.

- PLC sulfate performance presents a clear dependence on C_3A content of the parent cement. Dilution of C_3A content or changes in hydrated products of alumina phases does not cause significant changes in long time sulfate performance.
- Thaumasite sulfate attack on PLC or SCC is mainly governed by the transport properties of mixture and the previous damage caused by expansive ettringite formation. Limestone filler only provides the calcium carbonate, a necessary ingredient to thaumasite formation.
- Extended surface deterioration with large quantities of thaumasite is reported for mixtures where sulfate-expansion damage had previously taken place. Then, evolution of surface attack corresponds to classical external sulfate damage. In the first place, ettringite and gypsum forms causing local expansion and micro-cracking that increases the surface area accessible to sulfate ions. During this time, severe dissolution of CH at the surface promotes the instability of ettringite and C–S–H leading to a favorable scenario to thaumasite formation in the presence of carbonate, sulfate and calcium ions in pore solution.
- Surface damage on specimens exposed to $MgSO_4$, increases at low temperatures. It could be also attributed to the development of thin or null protective layer of brucite–carbonate that accelerates the attack on the surface of specimens and the thaumasite formation.
- Regardless of limestone filler content, paste, mortar and concrete made with low-C_3A cements (<5%) and using a low effective *w*/*c* ratio (<0.50), which complies with the ACI 201 Recommendation for moderate sulfate environments, no early damage at low temperatures resulted. In this case, thaumasite is also found on the specimen surface on long time exposure, but it lacks relevance in the damage process.
- Further research efforts will tend to prove whether it is possible a lower sulfate resistance of PLC or SCC when using an appropriate *w*/*c* ratio and low C_3A cement.

References

[1] J.S. Damtoft, D. Herfort, E. Yde, Concrete binders, mineral additions and chemical admixtures: state of the art and challenges for the 21st century, in: R.K. Dhir, T.D. Dyer (Eds.), Modern Concrete Materials: Binders, Additions and Admixtures, Thomas Telford, London, 1999, pp. 1–16.

[2] A. Ghezal, K.H. Khayat, Optimizing self-consolidating concrete with limestone filler by using statistical factorial design methods, ACI Materials Journal 99 (3) (2002) 264–272.

[3] Department of the Environment, Transport and the regions, The thaumasite form of sulfate attack: risks, diagnosis, remedial works and guidance on new construction, DETR, London, 1999, Report of the Thaumasite Expert Group.

[4] E.F. Irassar, Sulphate attack and sulphate resistant cements, in: S.N. Ghosh (Ed.), Advances in Cement Technology: Chemistry, Manufacture and Testing, Thec Book Int., India, 2002, pp. 595–629.

[5] P.K. Mehta, Sulfate attack on concrete — a critical review, in: J. Skalny (Ed.), Material Science of Concrete, vol. III, American Ceramic Society, Westerville, USA, 1992, pp. 105–130.

[6] M.A. González, E.F. Irassar, Ettringite formation in low C_3A Portland cement exposed to sodium sulfate solution, Cement and Concrete Research 27 (7) (1997) 1061–1072.

[7] H.T. Cao, L. Bucea, A. Ray, S. Yozghatlian, The effect of cement composition and pH of environment on sulfate resistance of Portland cements and blended cements, Cement and Concrete Composites 19 (2) (1997) 161–171.

[8] D. Bonen, A microstructural study of the effect produced by magnesium sulfate on plain and silica fume-bearing Portland cement mortars, Cement and Concrete Research 23 (3) (1993) 541–553.

[9] J. Bensted, Thaumasite — background and nature in deterioration of cements, mortars and concretes, Cement and Concrete Composites 21 (2) (1999) 117–121.

[10] N.J. Crammond, The thaumasite form of sulfate attack in the UK, Cement and Concrete Composites 25 (8) (2003) 809–818.

[11] N.J. Crammond, M.A. Halliwell, The thaumasite form of sulfate attack in concretes containing a source of carbonate ions — a microstructural overview, in: V.M. Malhotra (Ed.), Second CANMET/ACI International Symposium on Advances in Concrete Technology, ACI SP 154, USA, 1995, pp. 357–380.

[12] J. Bensted, Thaumasite –– direct, woodfordite and other possible formation routes, Cement and Concrete Composites 25 (8) (2003) 873–877.

[13] S. Kohler, D. Heinz, L. Urbonas, Effect of ettringite on thaumasite formation, Cement and Concrete Research 36 (4) (2006) 697–706.

[14] P. Hagelia, R.G. Sibbick, N.J. Crammond, C.K. Larsen, Thaumasite and secondary calcite in some Norwegian concretes, Cement and Concrete Composites 25 (8) (2003) 1131–1140.

[15] M.E. Gaze, N.J. Crammond, The formation of thaumasite in a cement: lime:sand mortar exposed to cold magnesium and potassium sulfate solutions, Cement and Concrete Composites 22 (3) (2000) 209–222.

[16] B. Lagerblad, Leaching performance of concrete based on studies of samples from old concrete constructions, Swedish Cement and Concrete Research Institute, Sweden, 2001 Technical Report TR-01-27, 80 pp.

[17] I. Soroka, N. Setter, Effect of calcareous fillers on sulfate resistance of Portland Cement, American Ceramic Society Bulletin, 55 (6) (1976) 594–595.

[18] I. Soroka, N. Setter, Effect of mineral fillers on sulfate resistance of Portland cement mortars, in: P.J. Sereda, G.G. Litvan (Eds.), Durability of building materials and components, ASTM, USA, 1980, pp. 326–335, ASTM STP 691.

[19] R.D. Hooton, Effects of carbonate additions on heat of hydration and sulfate resistance of Portland cements, in: P. Klieger, R.D. Hooton (Eds.), Carbonate Additions to Cement, ASTM, USA, 1990, pp. 73–81, ASTM STP 1064EB.

[20] M.A. Gonzalez, E.F. Irassar, Effect of limestone filler on the sulfate resistance of low C_3A Portland cement, Cement Concrete Research 28 (11) (1998) 1655–1667.

[21] E.F. Irassar, M.A. González, V.F. Rahhal, Sulphate resistance of type V cements with limestone filler and natural pozzolana, Cement and Concrete Composites 22 (5) (2000) 361–368.

[22] E.F. Irassar, V.L. Bonavetti, M.A. González, Microstructural study of sulfate attack on ordinary and limestone Portland cements at ambient temperature, Cement and Concrete Research 33 (1) (2003) 31–41.

[23] E.F. Irassar, V.L. Bonavetti, M.A. Trezza, M.A. Gonzalez, Thaumasite formation in limestone filler cements exposed to sodium sulphate solution at 20 °C, Cement and Concrete Composites 27 (1) (2005) 77–84.

[24] E.F. Irassar, V.L. Bonavetti, M.A. Trezza, G. Menendez, Sulfate attack on sulfate-resistant Portland cement containing limestone filler, IBRACON Materials Journal (Brazil) 1 (1) (2005) 17–32.

[25] Y. Tezuka, D. Gomes, J. Martins, J.G. Djanikian, Durability aspect of cement with high limestone filler content, Proc 9th International Congress on the Chemistry of Cement, New Delhi, India, 1992, pp. 53–59.

[26] D.M. Mulenga, J. Stark, P. Nobst, Thaumasite formation in concrete and mortars containing fly ash, Cement and Concrete Composites 25 (8) (2003) 907–912.

[27] H. Justnes, Thaumasite formed by sulfate attack on mortar with limestone filler, Cement and Concrete Composites 25 (8) (2003) 955–959.

[28] F. Bellmann, J. Stark, Prevention of thaumasite formation in concrete exposed to sulphate attack, Cement and Concrete Research 37 (8) (2007) 1215–1222.

[29] S.T. Lee, R.D. Hooton, H.S. Jung, D.H. Park, C.S. Choi, Effect of limestone filler on the deterioration of mortars and pastes exposed to sulfate solutions at ambient temperature, Cement and Concrete Research 38 (1) (2008) 68–76.

[30] J.D. Matthews, Performance of limestone filler cement concrete, in: R.K. Dhir, M.R. Jones (Eds.), Euro-Cements: Impact of ENV 197 on Concrete Construction, E&FN Spon, London, UK, 1994, pp. 113–147.

[31] N.J. Crammond, M.A. Halliwell, Assessment of the conditions required for the thaumasite form of sulfate attack, in: K.L. Scrivener, J.F. Yound (Eds.), Mechanisms of chemical degradation of cement-based systems, E&FN Spon, London, U.K., 1997, pp. 193–200.

[32] A.P. Barker, D.W. Hobbs, Performance of Portland limestone cements in mortar prisms immersed in sulfate solutions at 5 °C, Cement Concrete Composites 21 (2) (1999) 129–137.

[33] S.A. Hartshorn, J.H. Sharp, R.N. Swamy, Thaumasite formation in Portland-limestone cement pastes, Cement and Concrete Research 29 (8) (1999) 1331–1340.

[34] S.A. Hartshorn, R.N. Swamy, J.H. Sharp, Engineering properties and structural implications of Portland limestone cement mortar exposed to magnesium sulphate attack, Advanced Cement Research 13 (1) (2001) 31–46.

[35] S.A. Hartshorn, J.H. Sharp, R.N. Swamy, The thaumasite form of sulfate attack in Portland-limestone cement mortars stored in magnesium sulfate solution, Cement Concrete Composites 24 (3–4) (2002) 351–359.

[36] S.M. Torres, J.H. Sharp, R.N. Swamy, C.J. Lynsdale, S.A. Huntley, Long term durability of Portland-limestone cement mortars exposed to magnesium sulfate attack, Cement and Concrete Composites 25 (8) (2003) 947–954.

[37] S.M. Torres, C.A. Kirk, C.J. Lynsdale, R.N. Swamy, J.H. Sharp, Thaumasite–ettringite solid solutions in degraded mortars, Cement and Concrete Research 34 (8) (2004) 1297–1305.

[38] S.M. Torres, C.J. Lynsdale, R.N. Swamy, J.H. Sharp, Microstructure of 5-year-old mortars containing limestone filler damaged by thaumasite, Cement and Concrete Research 36 (2) (2006) 384–394.

[39] G. Kakali, S. Tsivilis, A. Skaropoulou, J.H. Sharp, R.N. Swamy, Parameters affecting thaumasite formation in limestone cement mortar, Cement and Concrete Composites 25 (8) (2003) 977–981.

[40] S. Tsivilis, K. Sotiriadis, A. Skaropoulou, Thaumasite form of sulfate attack (TSA) in limestone cement pastes, Journal of the European Ceramic Society 27 (2–3) (2007) 1711–1714.

[41] A. Skaropoulou, G. Kakali, S. Tsivilis, A study on thaumasite form of sulfate attack (TSA) using XRD, TG and SEM, Journal of Thermal Analysis and Calorimetry 84 (1) (2006) 135–139.

[42] A. Skaropoulou, K. Sotiriadis, G. Kakali, S. Tsivilis, A long term study on thaumasite form of sulfate attack (TSA) in limestone cement pastes, in: J.J. Beaundion, J.M. Makar, L. Raki (Eds.), Proc 12 International Congress on the Chemistry of Cement, Montreal, Canada, 2007, paper T4-06.2, 11 pp.

[43] S. Tsivilis, A. Kakali, A. Skaropoulou, J.H. Sharp, R.N. Swamy, Use of mineral admixtures to prevent thaumasite formation in limestone cement mortar, Cement Concrete Composites 25 (8) (2003) 969–976.

[44] S. Tsivilis, A. Skaropoulou, G. Kakali, J.H. Sharp, R.N. Swamy, The effect of mineral admixtures on long term durability of limestone cement mortars exposed to sulfate attack, in: J.J. Beaundion, J.M. Makar, L. Raki (Eds.), Proc 12 International Congress on the Chemistry of Cement, Montreal, Canada, 2007, p. 12, paper T4-06.1.

[45] T. Vuk, R. Gabrovsek, V. Kaucic, The influence of mineral admixtures on sulfate resistance of limestone cement pastes aged in cold $MgSO_4$ solution, Cement and Concrete Research 32 (6) (2002) 943–948.

[46] J. Hill, E.A. Byars, J.H. Sharp, C.J. Lynsdale, J.C. Cripps, Q. Zhou, An experimental study of combined acid and sulfate attack of concrete, Cement and Concrete Composites 25 (8) (2003) 997–1003.

[47] Q. Zhou, J. Hill, E.A. Byars, J.C. Cripps, C.J. Lynsdale, J.H. Sharp, The role of pH in thaumasite sulfate attack, Cement and Concrete Research 36 (1) (2006) 160–170.

[48] Q. Zhou, E.A. Byars, C.J. Lynsdale, J.C. Cripps, J. Hill, J.H. Sharp, Relative resistance of Portland and pozzolanic cements to the thaumasite form of sulfate attack, in: J.J. Beaundion, J.M. Makar, L. Raki (Eds.), Proc 12 International Congress on the Chemistry of Cement, Montreal, Canada, 2007, paper M4-03.4, 12 pp.

[49] A. Borsoi, S. Collepardi, L. Coppola, R. Troli, M. Collepardi, Sulfate attack on blended Portland cement, in: V.M. Malhotra (Ed.), Fifth CANMET/ACI International Conference on Durability of Concrete, American Concrete Institute, Farmington Hill, USA, 2000, pp. 417–432, ACI SP 192.

[50] M. Collepardi, S. Monosi, O. Favoni, J.J.O. Olagot, Resistance to sulfate attack of mixtures with limestone Portland blended cements, in: V.M. Malhotra (Ed.), Sixth CANMET/ACI International Conference on Durability of Concrete, American Concrete Institute, Farmington Hill, USA, 2003, pp. 941–950, ACI SP 212.

[51] Z. Sawicz, S.S. Heng, Durability of concrete with addition of limestone powder, Magazine of Concrete Research 48 (175) (1996) 131–137.

[52] W.G. Piasta, Z. Sawicz, G. Koprowski, Z. Osiak, Influence of limestone powder on microstructure and mechanical properties of concrete under sulphate attack, Proc 10 International Congress on the Chemistry of Cement, Sweden, 1997, paper 4iv018, 8 pp.

[53] J. Gao, B.G. Ma, H.J. Ba, Influence of cement types and mineral admixtures on the resistance of mortar to thaumasite form of sulfate attack, in: J.J. Beaundion, J.M. Makar, L. Raki (Eds.), Proc 12 International Congress on the Chemistry of Cement, Montreal, Canada, 2007, paper T4.06.4, 12 pp.

[54] B. Persson, Sulphate resistance of self-compacting concrete, Cement and Concrete Research 33 (12) (2003) 1933–1938.

[55] J. Trägårdh, M. Kalinowski, Investigation of the conditions for a thaumasite form of sulfate attack in SCC with limestone filler, in: O. Wallevik, I. Nielsson (Eds.), International RILEM Symposium on Self-Compacting Concrete, 2003, RILEM Publications 033.

[56] M. Kalinowski, J. Trägårdh, Thaumasite and gypsum formation in SCC with sulfate resistant cement exposed to a moderate sulfate concentration Second North American Conference on the Design and Use of Self- Consolidating Concrete and Fourth International RILEM Symposium on Self-Compacting Concrete, Chicago, USA, 2005, pp. 319–325.

[57] M. Friebert, J. Stark, Investigations to the durability of self compacting concrete, Beton 54 (2004) 184–186.

[58] N.J. Crammond, The occurrence of thaumasite in modern construction — a review, Cement and Concrete Composites 24 (3–4) (2002) 393–402.

[59] M.D.A. Thomas, C.A. Rogers, R.F. Bleszynski, Occurrences of thaumasite in laboratory and field concrete, Cement and Concrete Composites 25 (8) (2003) 1045–1050.

[60] S. Diamond, Thaumasite in Orange County, Southern California: an inquiry into the effect of low temperature, Cement and Concrete Composites 25 (8) (2003) 1161–1164.

[61] D.C. Stark, Occurrence of thaumasite in deteriorated concrete, Cement and Concrete Composites 25 (8) (2003) 1119–1121.

[62] D.W. Hobbs, Thaumasite sulfate attack in field and laboratory concretes: implications for specifications, Cement and Concrete Composites 25 (8) (2003) 1195–1202.

[63] D.W. Hobbs, M.G. Taylor, Nature of the thaumasite sulfate attack mechanism in field concrete, Cement and Concrete Research 30 (4) (2000) 529–533.

[64] H. Mingyu, L. Fumei, T. Mingshu, The thaumasite form of sulfate attack in concrete of Yongan Dam, Cement and Concrete Research 36 (10) (2006) 2006–2008.

[65] B. Ma, X. Gao, E.A. Byars, Q. Zhou, Thaumasite formation in a tunnel of Bapanxia Dam in Western China, Cement and Concrete Research 36 (4) (2006) 716–722.

[66] R.D. Hooton, M.D.A. Thomas, The use of limestone in portland cements: Effects on thaumasite form of sulfate attack, PCA, Skokie, Illinois, USA, 2002 PCA R&D Serial No 2558.

[67] N.J. Crammond, G.W. Collett, T.I. Longworth, Thaumasite field trial at Shipston on Stour: three-year preliminary assessment of buried concretes, Cement and Concrete Composites 25 (8) (2003) 1035–1043.

[68] ACI 201 committee, Guide to Durable Concrete 201.2R-01, American Concrete Institute, USA, 2000 41 pp.

[69] EN 206-1, Concrete - Part 1: Specification, Performance, Production and Conformity, Brussels, Belgium, 2000 64 pp.

[70] P.W. Brown, An evaluation of the sulfate resistance of cements in a controlled environment, Cement and Concrete Research 11 (5–6) (1981) 719–727.

[71] P.K. Mehta, O.E. Gjorv, A new test for sulfate resistance of cements, Journal of Testing and Evaluation 2 (6) (1974) 510–514.

[72] C.D. Lawrence, The influence of binder type on sulfate resistance, Cement Concrete Research 22 (6) (1992) 1047–1058.

[73] G.J. Verbeck, "Field and laboratory studies of the sulphate resistance of concrete," performance of concrete-resistance of concrete to sulphate and other environmental conditions, Thorvaldson Symposium, University of Toronto Press, Toronto, 1968, pp. 113–124, Also reprinted as PCA Research Department Bulletin 227, Portland Cement Association, Skokie, Ill., 1969.

[74] R.P. Khatri, V. Sirivivatnanon, J.L. Yang, Role of permeability in sulphate attack, Cement and Concrete Research 27 (8) (1997) 1179–1189.

[75] N. Hearn, J.F. Young, *w*/*c* ratio, porosity and sulfate attack — a review, in: J. Marchand, J. Skalny (Eds.), Materials Science of Concrete: Sulfate Attack Mechanisms, The American Ceramic Society, Westerville, USA, 1999, pp. 189–205.

[76] E.J. Garboczi, D.P. Bentz, Diffusivity-porosity relation for cement paste, in: J. Marchand, J. Skalny (Eds.), Materials Science of Concrete: Sulfate Attack Mechanisms, The American Ceramic Society, Westerville, USA, 1999, p. 259-164.

[77] P. Gospodinov, R. Kazandjiev, M. Mironova, The effect of sulfate ion diffusion on the structure of cement stone, Cement and Concrete Composites 18 (6) (1996) 401–407.

[78] R. Tixier, B. Mobasher, Modeling of damage in cement-based materials subjected to external sulfate attack. I: Formulation, Journal of Materials in Civil Engineering 15 (4) (2003) 305–313.

[79] F.P. Glasser, J. Marchand, E. Samson, Durability of concrete — Degradation phenomena involving detrimental chemical reactions, Cement and Concrete Research 38 (2) (2008) 226–246. Also In: J.J. Beaundion, J.M. Makar and L. Raki (Eds), Proc 12 International Congress on the Chemistry of Cement, Montreal, Canada, 2007, paper THPL-1, 48p.

[80] V. Bonavetti, H. Donza, V. Rahhal, E.F. Irassar, High strength concrete with limestone filler cements, in: V.M. Malhotra, et al., (Eds.), High-Performance Concrete, and Performance and Quality of Concrete Structures, ACI Special Publication, vol. 186, Farmington Hill, MI, USA, 1999, pp. 567–580.

[81] V.L. Bonavetti, H.A. Donza, G. Menéndez, O.A. Cabrera, E.F. Irassar, Limestone filler cement in low *w*/*c* concrete A rational Use of Energy, Cement and Concrete Research 33 (6) (2003) 865–871.

[82] M. Cyr, P. Lawrence, E. Ringot, Efficiency of mineral admixtures in mortars: quantification of the physical and chemical effects of fine admixtures in relation with compressive strength, Cement and Concrete Research 36 (2) (2006) 264–277.

[83] G. Fagerlund, Imaginable effects of limestone filler on chloride transport, Lund Institute of Technology, Division of Building Materials, Lund University, Lund, Sweden, 2005 Report TVBM-7187, 49 pp.

[84] M.A. González, V.F. Rahhal, V.L. Bonavetti, H. Donza, E.F. Irassar, Effect of curing on early chloride diffusion of filler cement concrete, in: R.N. Swamy (Ed.), Proc. International Conference on Infrastructure Regeneration and Rehabilitation, Improving the Quality Life Through Better Construction: A Vision for the Next Millennium, Sheffield Academic Press, UK, 1999, pp. 137–148.

[85] B. Persson, Assessment of the chloride migration coefficient, internal frost resistance, salt frost scaling and sulphate resistance of self-compacting concrete - with some interrelated properties, Lund Institute of Technology, Division of Building Materials, Lund University, Lund, Sweden, 2001 Report TVBM-3100.

[86] W. Zhu, P.J.M. Bartos, Permeation properties of self-compacting concrete, Cement and Concrete Research 33 (6) (2003) 921–926.

[87] G. Ye, X. Liu, G. De Schutter, A.M. Poppe, L. Taerwe, Influence of limestone powder used as filler in SCC on hydration and microstructure of cement pastes, Cement and Concrete Composites 29 (1) (2007) 94–102.

[88] I. Jawed, S. Goto, R. Kondo, Hydration of tetracalcium aluminoferrites in presence of lime and sulfates, Cement and Concrete Research 6 (4) (1976) 441–454.

[89] L.O. Höglund, Some notes on ettringite formation in cementitious materials — influence of hydration and thermodynamic constraints for durability, Cement and Concrete Research 22 (2–3) (1992) 217–228.

[90] R.S. Gollop, H.F.W. Taylor, Microstructural and microanalytical studies of sulfate attack: III. Sulfate-resisting portland cement. Reactions with sodium and magnesium sulfate solutions, Cement and Concrete Research 25 (7) (1995) 1581–1590.

[91] M. Santhanam, M.D. Cohen, J. Olek, Mechanism of sulfate attack: a fresh look. Part 2: Proposed mechanisms, Cement and Concrete Research 33 (3) (2003) 341–346.

[92] A. Gabrisova, J. Havlica, S. Sahu, Stability of calcium sulphoaluminate hydrates in water solutions with various pH values, Cement and Concrete Research 21 (6) (1991) 1023–1027.

[93] P.K. Mehta, Effect of fly ash composition on sulfate resistance of cement, ACI Journal Proc 83 (6) (1986) 994–1000.

[94] E.F. Irassar, J. Sota, O. Batic, Evaluation of sulfate resistance of blended Portland cements, Proc. Int. Conference Measurements and Testing in Civil Engineering - RILEM -GAMAC, I,. Lyon, France, 1988, pp. 301–310.

[95] P. Lawrence, M. Cyr, E. Ringot, Mineral admixtures in mortars. Effect of inert materials on short-term hydration, Cement and Concrete Research 33 (12) (2003) 1939–1947.

[96] C. Vernet, G. Noworyta, Mechanism of limestone fillers reactions in the system (C_3A–C–S–H_2–CH–CC–H), Proc 9th International Congress on the Chemistry of Cement, New Delhi, India, 1992, pp. 430–436.

[97] V.L. Bonavetti, V.F. Rahhal, E.F. Irassar, Studies on the carboaluminate formation in limestone filler blended cement, Cement and Concrete Research 31 (6) (2001) 853–859.

[98] E.F. Irassar, A discussion of the paper "durability of the hydrated limestone-silica fume Portland cement mortars under sulphate attack" by J. Zelic, R. Krstulovic, E. Tkalcec and P.Karlo, Cement and Concrete Research 30 (5) (2000) 831–832.

[99] T. Matschei, B. Lothenbach, F.P. Glasser, The AFm phase in Portland cement, Cement and Concrete Research 37 (2) (2007) 118–130.

[100] T. Matschei, B. Lothenbach, F.P. Glasser, The role of calcium carbonate in cement hydration, Cement and Concrete Research 37 (4) (2007) 551–558.

[101] P. Nobst, J. Stark, Investigations on the influence of cement type on thaumasite formation, Cement and Concrete Composites 25 (8) (2003) 899–906.

[102] J. Aguilera, S. Martinez-Ramirez, I. Pajares-Colomo, M.T. Blanco-Varela Formation of thaumasite in carbonated mortars, Cement and Concrete Composites 25 (8) (2003) 991–996.

[103] M.T. Blanco-Varela, J. Aguilera, S. Martínez-Ramírez, Effect of cement C_3A content, temperature and storage medium on thaumasite formation in carbonated mortar, Cement and Concrete Research 36 (4) (2006) 707–715.
[104] P.J. Tikalsky, D. Roy, B. Scheetz, T. Krize, Redefining cement characteristics for sulfate-resistant Portland cement, Cement and Concrete Research 32 (8) (2002) 1239–1246.
[105] N. Shanahan, A. Zayed, Cement composition and sulfate attack. Part I, Cement and Concrete Research 37 (4) (2007) 618–623.
[106] S.M. Torres, C.A. Kirk, C.J. Lynsdale, R.N. Swamy, J.H. Sharp, Thaumasite–ettringite solid solutions in degraded mortars, Cement and Concrete Research 34 (8) (2004) 1297–1305.
[107] S.J. Barnett, M.A. Halliwell, N.J. Crammond, C.D. Adam, A.R.W. Jackson, Study of thaumasite and ettringite phases formed in sulfate/blast furnace slag slurries using XRD full pattern fitting, Cement and Concrete Composites 24 (3–4) (2002) 339–346.
[108] J.G. Wang, Sulfate attack on hardened cement pastes, Cement and Concrete Research 24 (4) (1994) 735–742.