Puzolana Natural Calcinada Q

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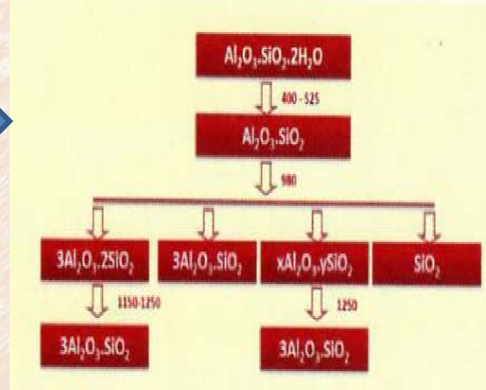
Puzolana Natural Calcinada (UNE EN197-1):Materiales de origen volcánico, arcillas, pizarras o rocas sedimentarias activadas térmicamente

Arcilla	Reacción de deshidroxilación	Rango de temperatura de activación
Caolinita	$Al_2(Si_2O_5)(OH)_4 \rightarrow Al_2Si_2O_7 + 2H_2O$	700 ºC [35] 630 ºC [36] 700-750 ºC [37-40] 650-850 ºC [41]
Illita	$(K, H_3O)(Al, Mg, Fe)_2(Si, Al)_4O_{10}[(OH)_2(H_2O)] \rightarrow 3{,}5H_2O + (K)(Al, Mg, Fe)_2(Si, Al)_4O_{10,5}$	700 ºC [42 y 43] 715 ºC [44] >800 ºC [45] 850 ºC [46]
Montmorillonita	$(Na, Ca)_{0,3}(Al, Mg)_2Si_4O_{10}(OH)_2.nH_2O \rightarrow (n+1)H_2O + (Na, Ca)_{0,3}(Al, Mg)_2Si_4O_{11}$	>800 ºC [19 y 45] 830 ºC [47] ≈850 ºC [48]
Esmectita	$(K, Ca)(Si_4Al)O_{10}(Al, Mg, Fe, Ti)(OH)_2 \rightarrow H_2O + (K, Ca)(Si_4Al)O_{11}(Al, Mg, Fe, Ti)$	900 ºC [49] 930 ºC [47]
Moscovita	$K\,Al_2(Si_3Al)O_{10}(OH)_2 \rightarrow H_2O + KAl_2(Si_3Al)O_{11}$	700 ºC [42] 850 ºC [50] 1.000 ºC [51]
Clorita	$(Fe, Mg, Al)_6(Si, Al)_4O_{10}(OH)_8 \rightarrow 4H_2O + (Fe, Mg, Al)_6(Si, Al)_4O_{14}$	700 ºC [52] 800 ºC [53]

M. A. Sanjuan y A. Zaragoza, C y H 2020



http://www.rafagalindoceramica.com/

UNE EN 197-1

Tabla 1 –Los 27 productos de la familia de los cementos comunes

Tipos principales	Designación y denominación de los 27 productos (tipos de cementos comunes)		Composición (proporción en masa [a])										
			Componentes principales										Componentes minoritarios adicionales
			Clínker	Escoria de horno alto	Humo de sílice	Puzolana natural	Puzolana natural calcinada	Ceniza volante silícea	Ceniza volante calcárea	Esquisto calcinado	Caliza	Caliza	
			K	S	D [b]	P	Q	V	W	T	L	LL	
CEM I	Cemento Portland	CEM I	95-100	–	–	–	–	–	–	–	–	–	0-5
CEM II	Cemento Portland con escoria	CEM II/A-S	80-94	6-20	–	–	–	–	–	–	–	–	0-5
		CEM II/B-S	65-79	21-35	–	–	–	–	–	–	–	–	0-5
	Cemento Portland con humo de sílice	CEM II/A-D	90-94	–	6-10	–	–	–	–	–	–	–	0-5
	Cemento Portland con puzolana	CEM II/A-P	80-94	–	–	6-20	–	–	–	–	–	–	0-5
		CEM II/B-P	65-79	–	–	21-35	–	–	–	–	–	–	0-5
		CEM II/A-Q	80-94	–	–	–	6-20	–	–	–	–	–	0-5
		CEM II/B-Q	65-79	–	–	–	21-35	–	–	–	–	–	0-5
	Cemento Portland con ceniza volante	CEM II/A-V	80-94	–	–	–	–	6-20	–	–	–	–	0-5
		CEM II/B-V	65-79	–	–	–	–	21-35	–	–	–	–	0-5
		CEM II/A-W	80-94	–	–	–	–	–	6-20	–	–	–	0-5
		CEM II/B-W	65-79	–	–	–	–	–	21-35	–	–	–	0-5
	Cemento Portland con esquisto calcinado	CEM II/A-T	80-94	–	–	–	–	–	–	6-20	–	–	0-5
		CEM II/B-T	65-79	–	–	–	–	–	–	21-35	–	–	0-5
	Cemento Portland con caliza	CEM II/A-L	80-94	–	–	–	–	–	–	–	6-20	–	0-5
		CEM II/B-L	65-79	–	–	–	–	–	–	–	21-35	–	0-5
		CEM II/A-LL	80-94	–	–	–	–	–	–	–	–	6-20	0-5
		CEM II/B-LL	65-79	–	–	–	–	–	–	–	–	21-35	0-5
	Cemento Portland compuesto [c]	CEM II/A-M	80-88	<------ 12-20 ------>									0-5
		CEM II/B-M	65-79	<------ 21-35 ------>									0-5
CEM III	Cemento de horno alto	CEM III/A	35-64	36-65	–	–	–	–	–	–	–	–	0-5
		CEM III/B	20-34	66-80	–	–	–	–	–	–	–	–	0-5
		CEM III/C	5-19	81-95	–	–	–	–	–	–	–	–	0-5
CEM IV	Cemento puzolánico [c]	CEM IV/A	65-89	–	<------ 11-35 ------>					–	–	–	0-5
		CEM IV/B	45-64	–	<------ 36-55 ------>					–	–	–	0-5
CEM V	Cemento compuesto [c]	CEM V/A	40-64	18-30	–	<------ 18-30 ------>			–	–	–	–	0-5
		CEM V/B	20-38	31-49	–	<------ 31-49 ------>			–	–	–	–	0-5

[a] Los valores de la tabla se refieren a la suma de los componentes principales y minoritarios adicionales.

[b] La proporción de humo de sílice está limitada al 10%.

[c] En los cementos Portland compuestos CEM II/A-M y CEM II/B-M, en los cementos puzolánicos CEM IV/A y CEM IV/B y en los cementos compuestos CEM V/A y CEM V/B, los componentes principales diferentes del clínker se deben declarar en la designación del cemento (véanse los ejemplos en el capítulo 8).

Grupo de Reciclado de Materiales

MINISTERIO DE CIENCIA E INNOVACIÓN

CSIC

Estos cementos tendrán las denominaciones y designaciones siguientes:

Denominación	Designación
Cemento portland 350 blanco	P—350—B
Cemento portland 450 blanco	P—450—B
Cemento portland 550 blanco	P—550—B
Cemento compuesto 200 blanco	P—200—B

RC-75

CUADRO Nº 1

CLASIFICACION DE LOS CEMENTOS

Tipos	Clases	Categorías	Designaciones
Portland		350 450 550	P-350 P-450 P-550
Portland con adiciones activas		350 450 550	PA-350 PA-450 PA-550
Siderúrgico	I	350 450	S-I-350 S-I-450
	II	350	S-II-350
	III	250 350	S-III-250 S-III-350
Puzolánico	I	250 350 450	PUZ-I-250 PUZ-I-350 PUZ-I-450
	II	250 350 450	PUZ-II-250 PUZ-II-350 PUZ-II-450
Compuesto		200	C-200
Aluminoso		550	A-550
Natural	Lento	30 80	NL-30 NL-80
	Rápido	20	NR-20

1.7.1.2. Puzolanas.

Se entiende por puzolana, el producto natural que es capaz de fijar cal a la temperatura ambiente, en presencia de agua, formando compuestos con propiedades hidráulicas.

Por extensión el término puzolana se aplica también a otros productos naturales o artificiales que tienen propiedades análogas, tales como la tierra de diatomeas, las arcillas activadas y las cenizas volantes.

MOTIVOS

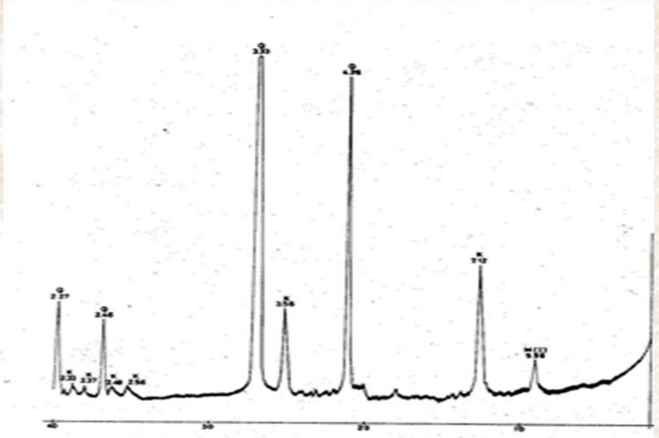
- ***POLÍTICAS MEDIOAMBIENTALES***
- ***COSTE ECONÓMICO Y ENERGÉTICO***
- ***PUZOLANAS ALTERNATIVAS***
- ***ESTABILIDAD DE LAS FASES HIDRATADAS***

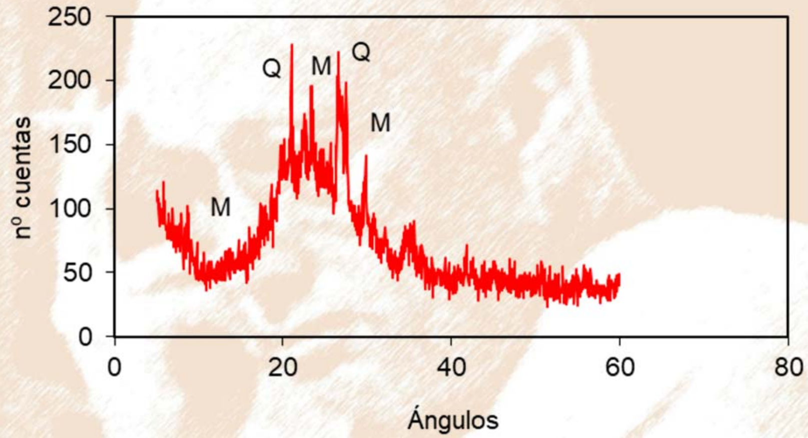
Presente y Futuro

- ***Falta de puzolanas tradicionales***
- ***España -1 cemento con arcilla calcinada***
- ***Elaboración de cementos LC3***
- ***UNE-EN 197-5:2021- CEM II***

CEM II	Cemento ternario Portland compuesto[d]	CEM II/ C-M	50-64	←---- 36-50 ----→

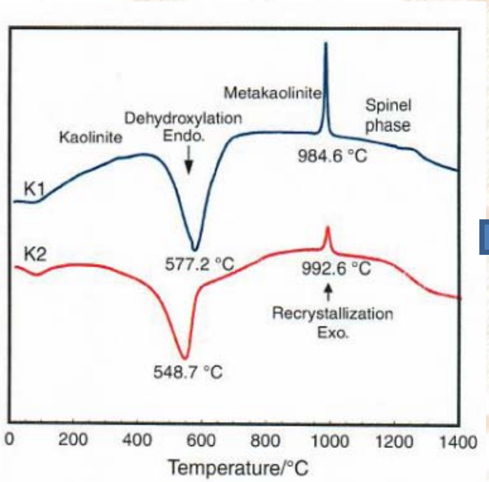
Activación térmica





CAOLINITA ------- METACAOLINITA

$2[Al_2 0_3.2Si0_2.2H_2 0]$ ------- $2[Al_2 0_3.2Si0_2] + 4H_2 0$

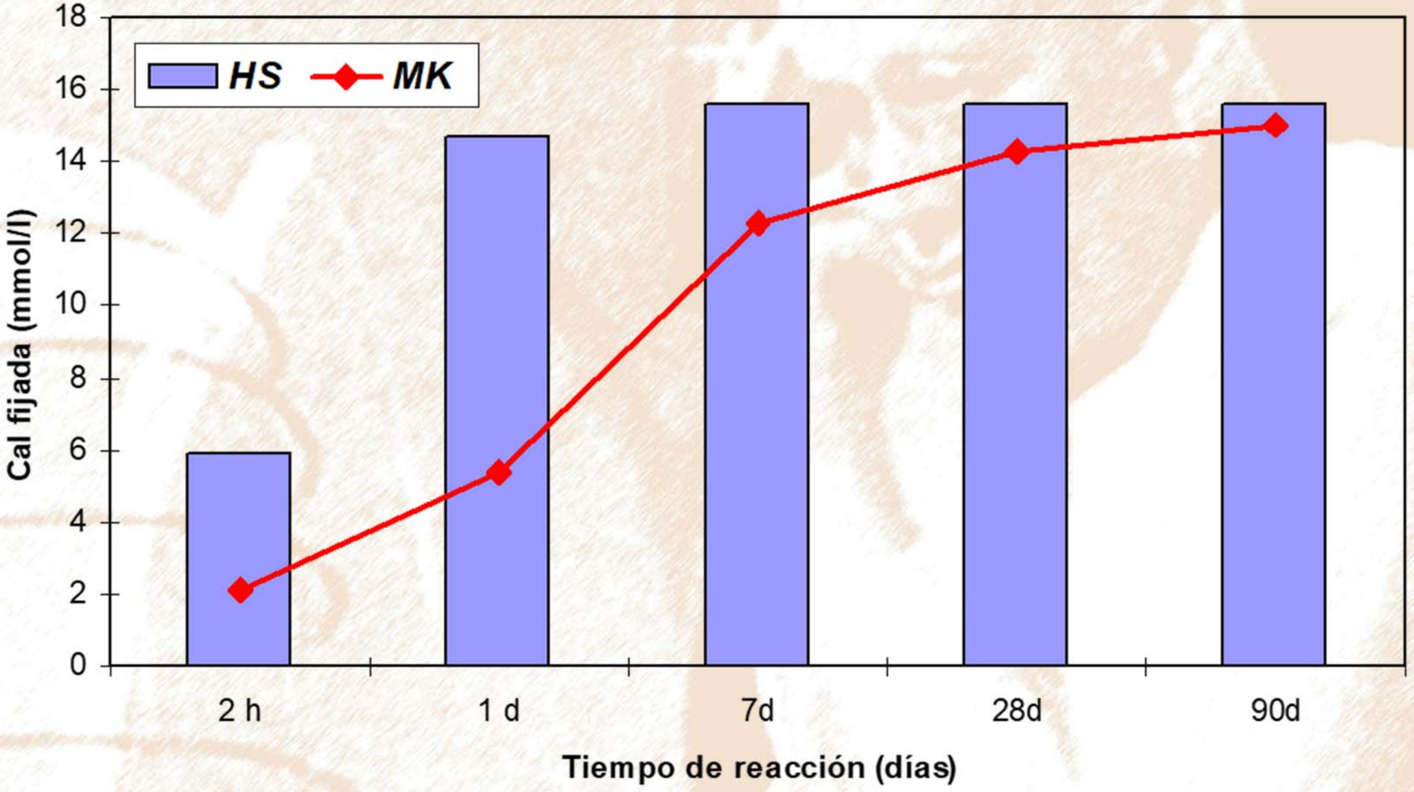


Tironi et al. 2014

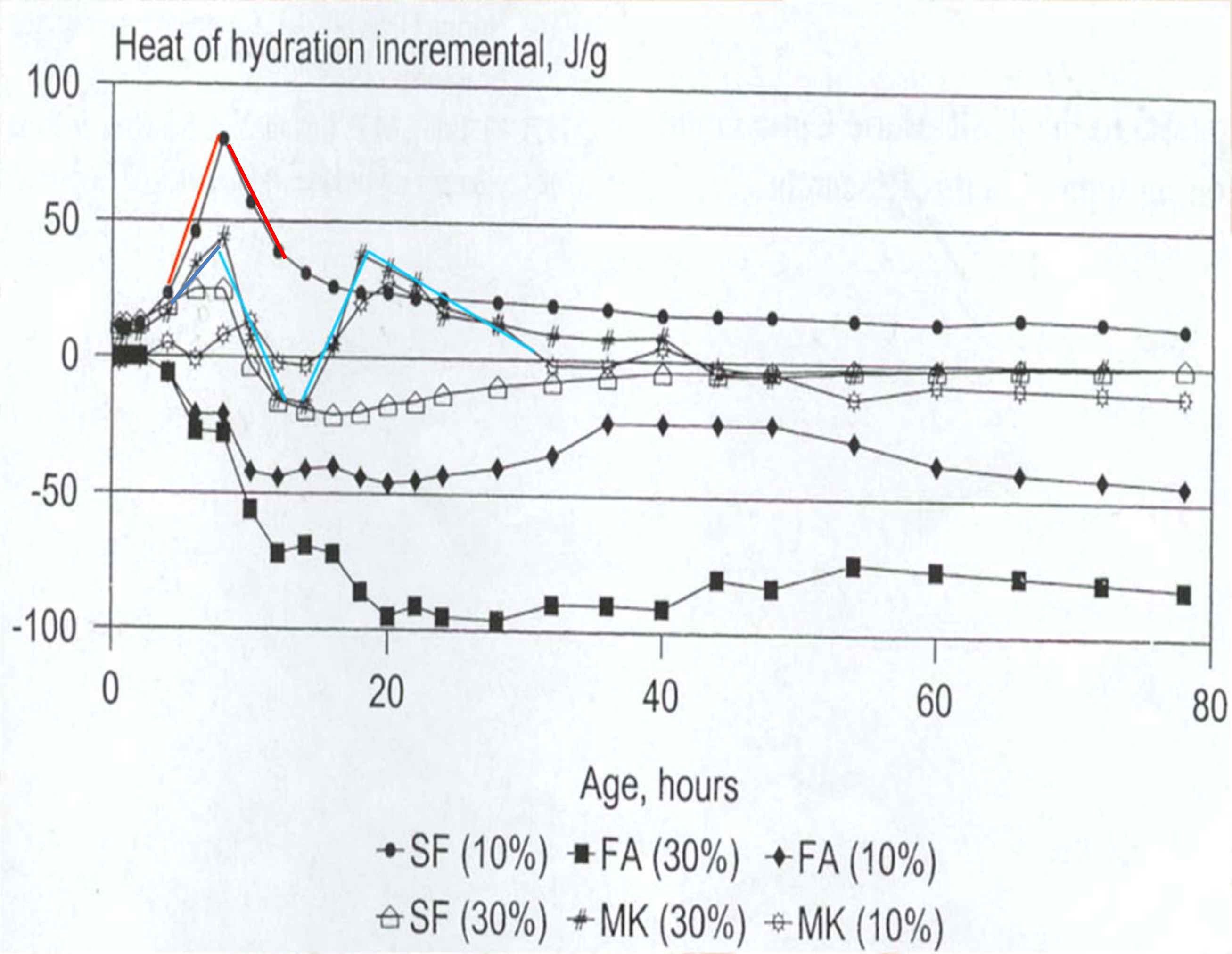
- 600-700 °C (T. óptima)
- Aglomeración partículas de MK
- Cristalización del MK

Pérdida de propiedades puzolánicas

Actividad puzolánica



Reacción exotérmica



Frías et al, CCR(2000)

Aspectos científicos

$$2AS_2 + 9CH + 12H \rightarrow C_2ASH_8 + C_4AH_{13} + 3C\text{-}S\text{-}H$$

$$\Downarrow$$

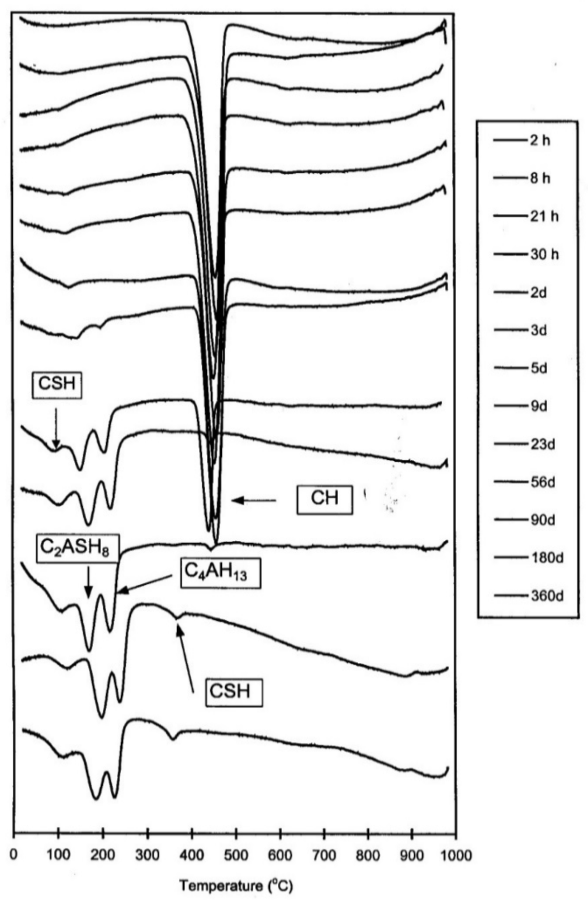
$$C_2ASH_8 + C_4AH_{13} \rightarrow 2C_3AS_{0.5}H_5 + 11H$$

Reacción de Transformación

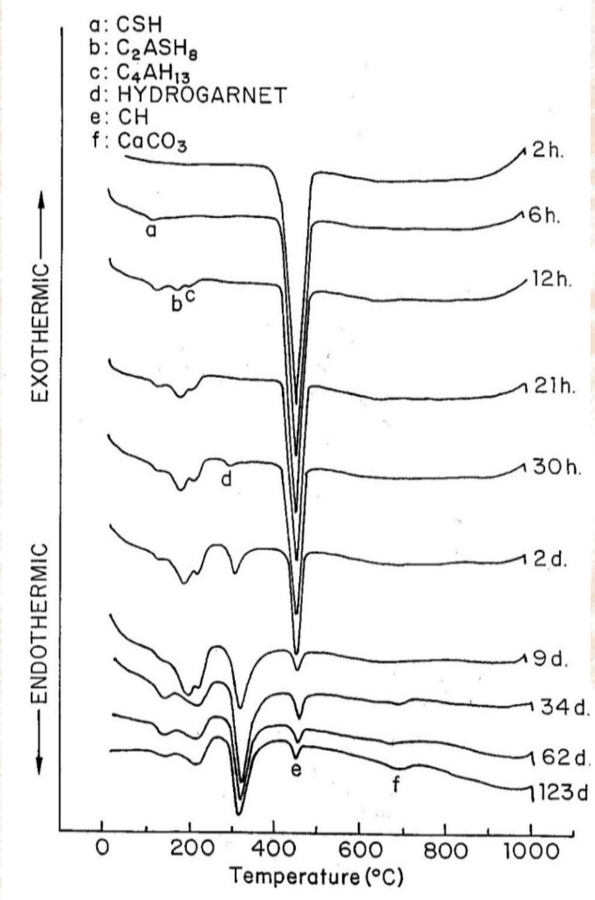
De Silva et al, ACR 1992

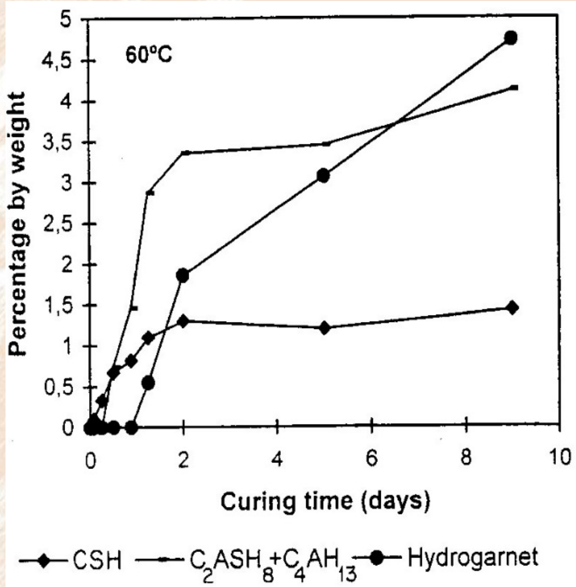
Reacción puzolánica MK/Cal

20º C



60º C

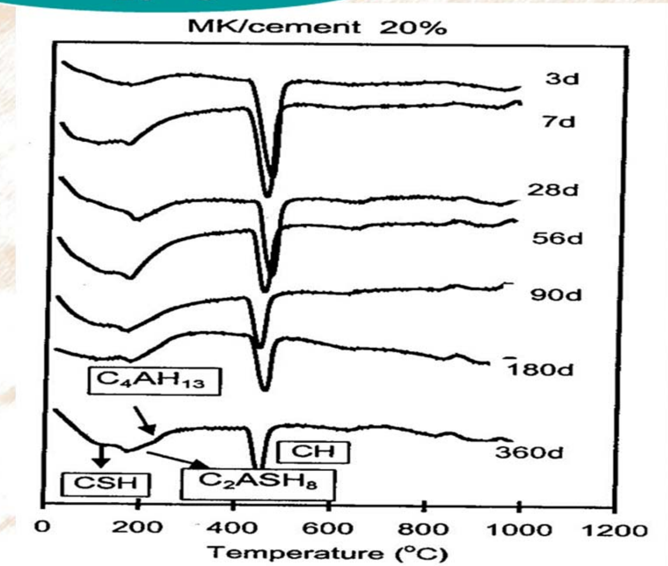


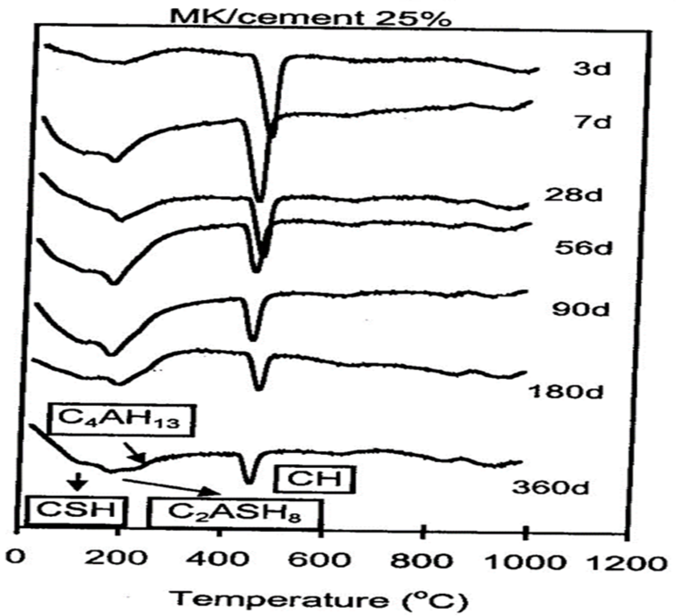


Frías et al 2000-05

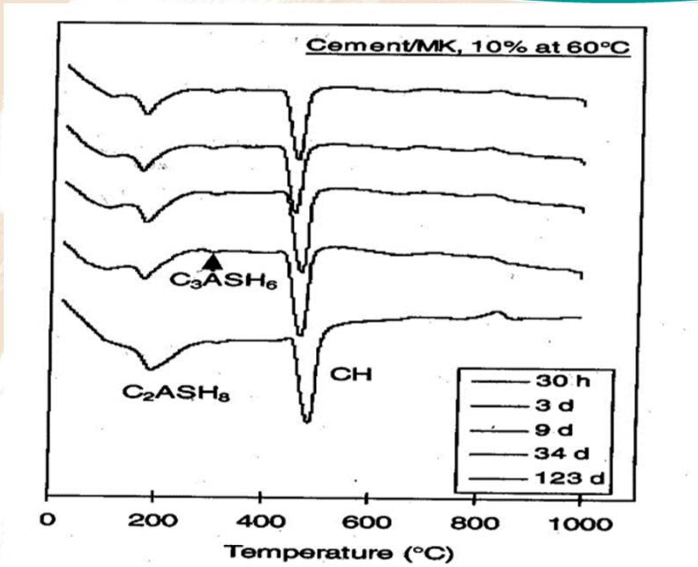
Reacción puzolánica MK/Cemento

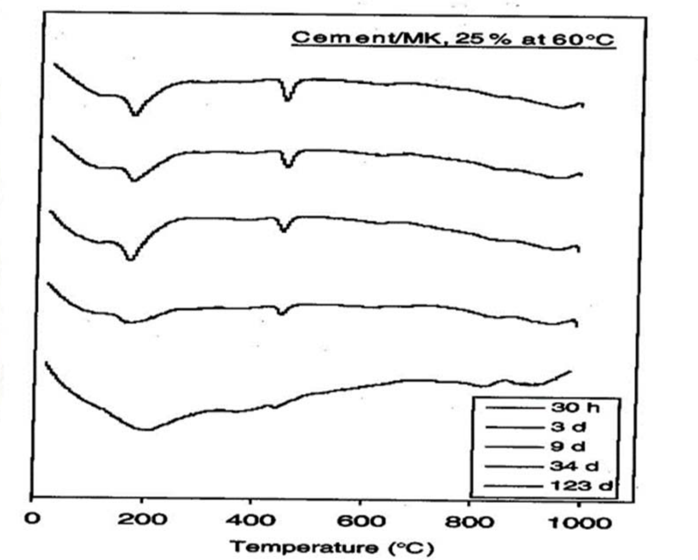
20º C





60º C

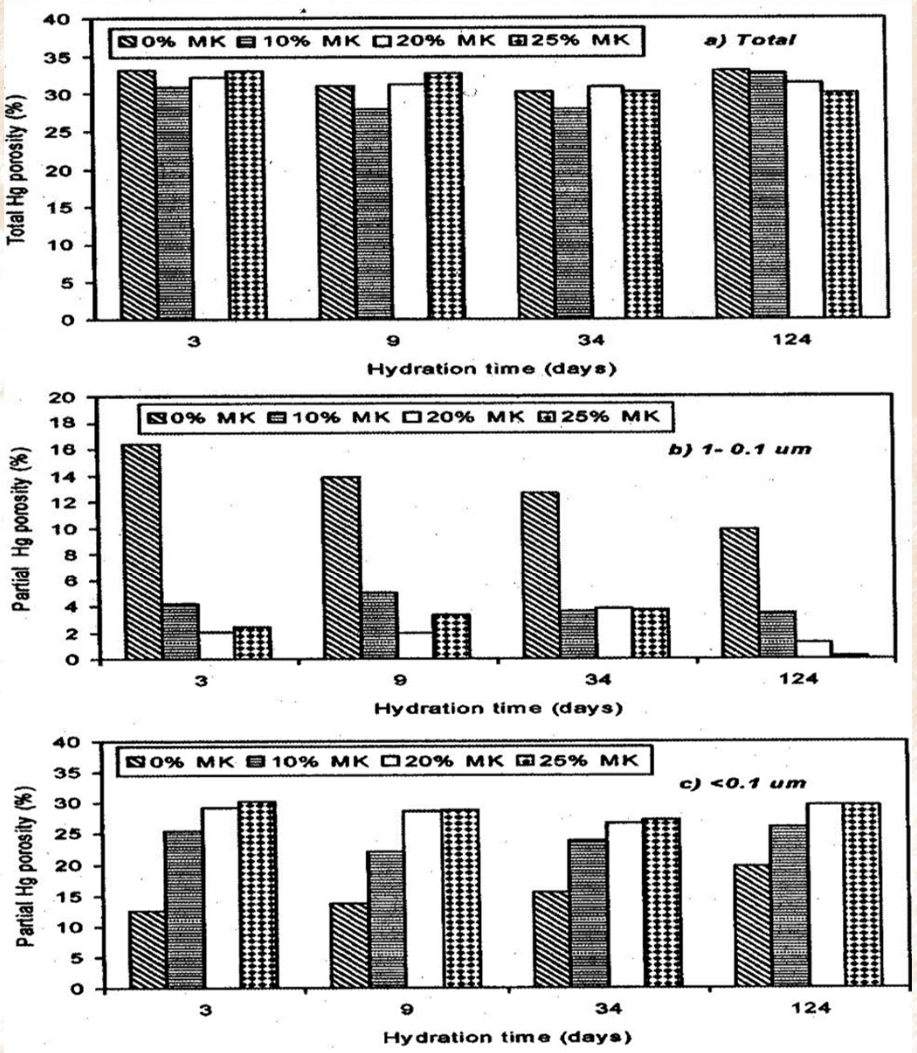




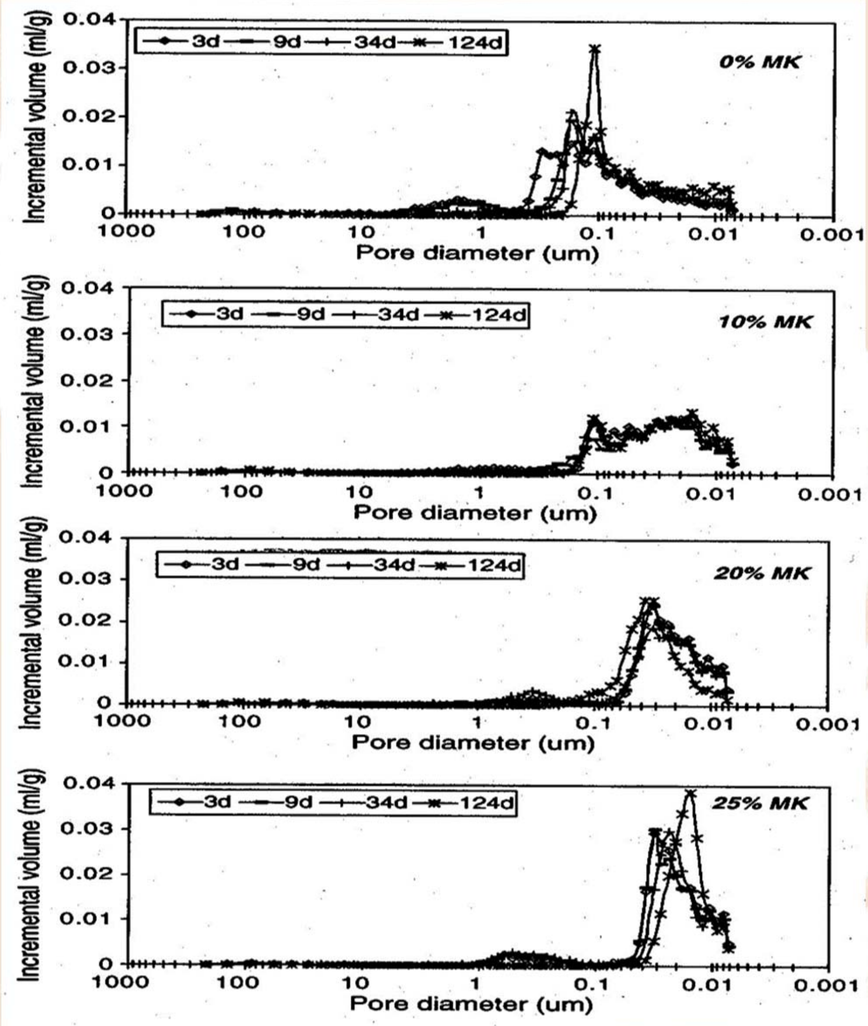
Frías et al 2000-05

Influencia del MK en las propiedades técnicas:

MICROPOROSIDAD a 60ºC



Frías et al CCR 2005



Frías et al, CCR / MC 2000

Influencia del MK en las propiedades técnicas:
RESISTENCIAS

Strength Development of Metakaolin Mortar and Paste

MIX	MK %	COMPRESSIVE STRENGTH (N/mm²) 3d	7d	14d	28d	90d	365d
A	0	27.8	36.0	40.0	44.3	51.4	53.4
B	5	29.3	37.8	44.9	47.4	56.6	57.7
C	10	30.2	46.6	56.7	61.8	65.9	66.3
D	15	26.1	46.0	56.4	58.4	56.8	60.4
PA	0	21.9	30.2	34.5	40.5	48.0	52.1
PB	5	21.2	32.5	39.6	42.9	45.6	50.5
PC	10	25.5	37.8	48.0	51.5	56.3	59.6
PD	15	22.0	41.8	47.5	54.5	58.5	61.6

31%

34%

S. Wild et al CCR 1997

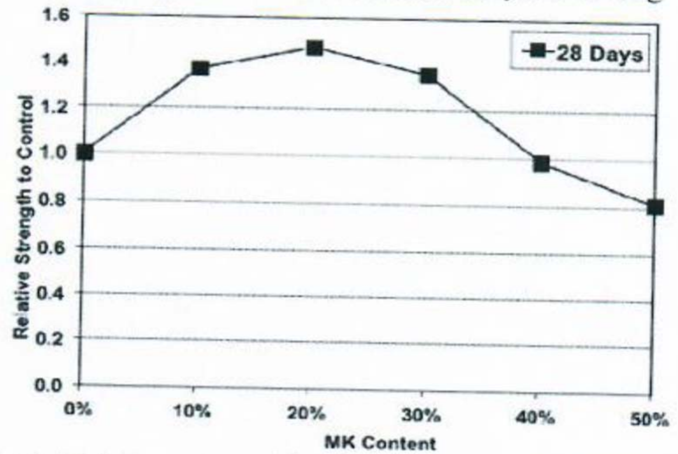
Compressive strength of control and blended cement pastes

Mix	Compressive strength (MPa) 3 days	7 days	28 days	90 days
Control	70.38	90.46	105.1	111.55
5% MK	75.96	91.53	105.55	118.4
10% MK	82.84	103.4	126.4	133.9
20% MK	72.10	96.4	118.3	123.8

20%

Poon et al CCR 2001

Fig. 2: Compressive strength of mortars containing varying amounts of MK at 28 days of curing



Khatib et al, 2012

Influencia del MK en las propiedades técnicas:
DURABILIDAD en Hormigones

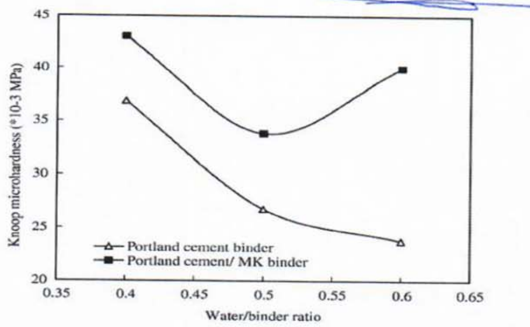


Fig. 8. Variation in micro-hardness of ITZ with water/binder ratio and binder composition (Asbridge et al., 2002).

were cured for periods from 3 to 365 days (Wild and Khatib, 1997). The Portlandite content at different ages was determined by thermogravimetric analysis and was related to changes in relative strength. $Ca(OH)_2$ in mortars was found to be less than that in pastes. In the metakaolin mortars and pastes removal of Portlandite by pozzolanic reaction reached a maximum of about 14 days, corresponding with a maximum in relative strength. Beyond 14 days severe retardation of the pozzolanic reaction was observed and relative strength rapidly declined.

5. Durability properties of concrete containing metakaolin

5.1. Alkali-silica reaction

Ramlochan et al. (2000) reported that incorporation of high-reactivity metakaolin (HRM) as a partial cement replacement between 10 and 15% may be sufficient to control deleterious expansion due to alkali-silica reaction in concrete, depending on the nature of the aggregate. Amount of HRM required to control the expansion to <0.04% at 2 years was found to be between 10 and 15% depending on the aggregate. The mechanism by which HRM may suppress expansion due to alkali-silica reaction appeared to be entrapment of alkalis by the supplementary hydrates and a consequent decrease in the pH of pore solutions.

5.2. Chloride-ion diffusion

PC–MK concrete showed significantly lower conductivity values than the PC concrete (Zhang and Malhotra, 1995). Thomas et al. (1997) and Hooton et al. (1997) determined the chloride penetration resistance of concrete of w/b ratios 0.3 and 0.4 containing 0, 8 and 12% replacement of PC with 'high-reactivity MK' (HRM). Data were presented in the form of 'apparent diffusion coefficients' calculated using Fick's second law of diffusion from chloride concentration–depth profiles after 28, 90 and 140 days exposure to 1.0 mol/l NaCl solution. Cabrera and Nwaubani (1998) reported that PC–MK and the PC–PFA pastes gave lower chloride diffusion coefficients than the PC paste, and the former gave particularly low values.

Table 12
Chloride diffusion rates for mortars with CEM I 42.5, metakaolin and kaolin (Courard et al., 2003)

Material	Breakthrough time (days)	Apparent diffusion coefficient (m^2/s)
CEM I 42.5	13	1.29×10^{-12}
5% metakaolin	45	4.71×10^{-12}
10% metakaolin	82	3.31×10^{-12}
15% metakaolin	203	1.23×10^{-12}
20% metakaolin	Not after 1 year	–
10% kaolin	4	1.81×10^{-12}

Gruber et al. (2001) determined the chloride diffusion up to 365 and 1095 days. The apparent diffusion coefficients decreased with increasing exposure time and decreasing w/b ratio, and showed marked decreases with increasing HRM content.

Asbridge et al. (2001) studied the effect of metakaolin and variations in aggregate volume content on the diffusion kinetics of chloride ions in hydrated Portland cement mortars. 10% metakaolin was used as partial replacement for Portland cement (Table 11). Chloride diffusion was monitored under steady- and non-steady state conditions, and capillary porosity data were obtained. Results showed that metakaolin reduced the rate of chloride diffusion through the hydrated cement matrix and also tended to enhance the resistance to chloride transport of the ITZ material within the mortars.

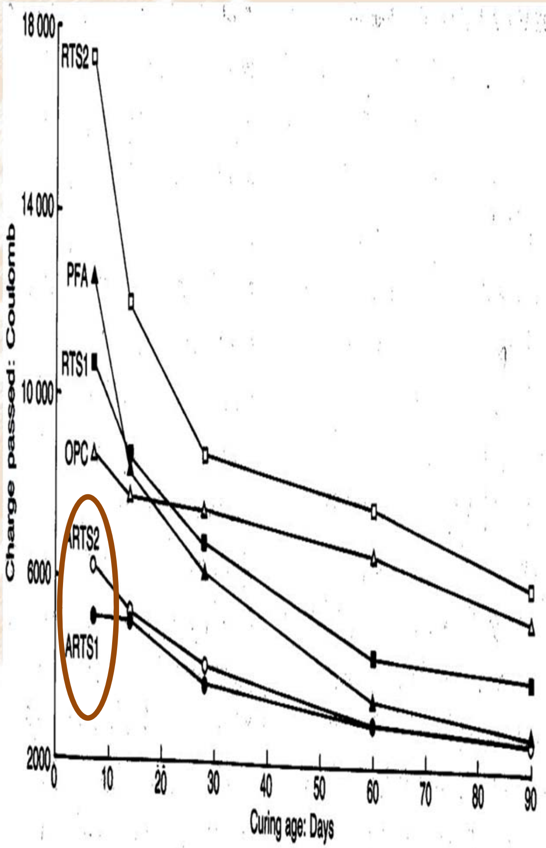
Bai et al. (2003b) reported that significant reductions in chloride penetration depths were observed when PC was partially replaced with MK in concrete, exposed to seawater. These reductions increased with both increasing total replacement level and increasing exposure time. This was attributed to the relative changes in intrinsic diffusivity and chloride binding capacity with age exhibited by the different binder compositions; Courard et al. (2003) measured the chloride diffusion rates of mortars containing 0, 10, 15, and 20% metakaolin as partial replacement of cement. Apparent diffusion coefficient of mortar (m^2/s) increased with the increase in metakaolin content from 5–15% (Table 12); however, no diffusion was observed in mortar with 20% MK even after 1 year. Kaolin had no effect and seemed on the contrary to accelerate the phenomenon of diffusion in comparison with the reference mixture.

Chloride penetrability of the concrete with metakaolin (MK) at w/b ratios of 0.3 and 0.5 were reported by Poon et al. (2006) (Table 13). Both the MK concretes showed lower total ion penetration than the control. At w/b of 0.3, concrete with a 10% MK showed the best performance, while at w/b of 0.5, 20% replacement was the best.

5.3. Sulfate resistance

Khatib and Wild (1998) evaluated the effect of metakaolin on the sulfate resistance of mortar. Inclusion of metakaolin in two types of cements having high C_3A and intermediate C_3A content decreased the expansion of mortar systematically with the increase in MK (5–20%) content. Roy et al. (2001) reported that substitution of MK increased the chemical resistance of such mortars over those made with plain Portland cement.

Table 13
Chloride permeability of control and blended concretes (Poon et al., 2006)



Cabrera et al, MCR1993

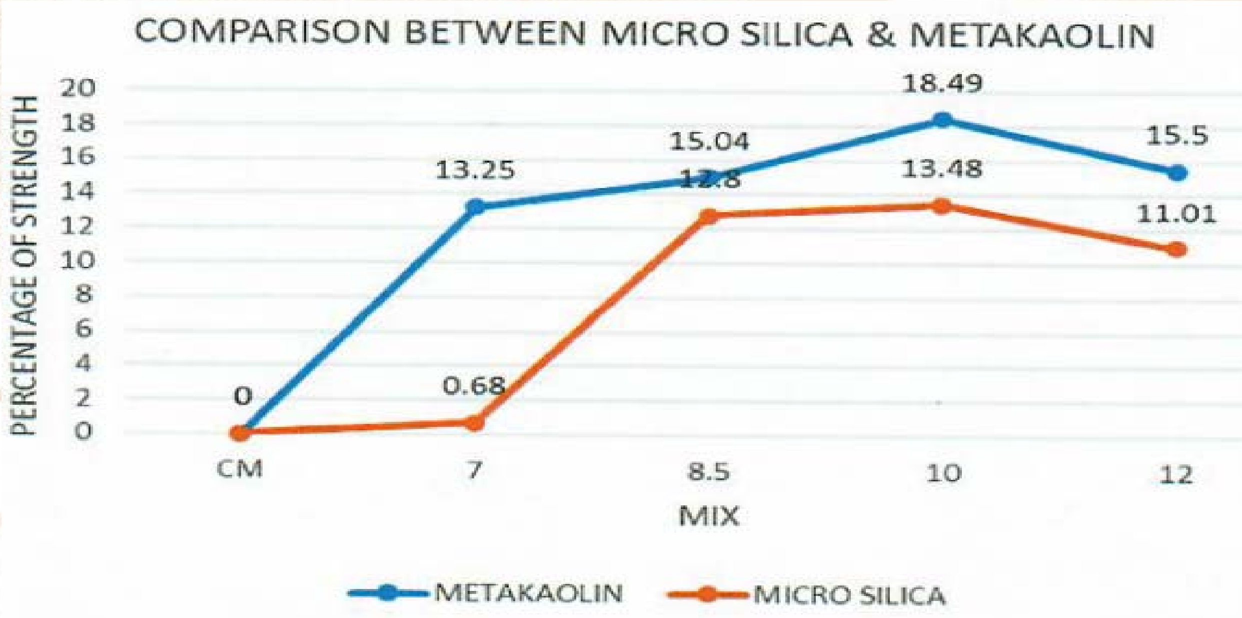
Influencia del MK en las propiedades técnicas:

DURABILIDAD :Hielo-Deshielo

Mortar	W/B	N	DF_i	DF_i/DF_o
$C_1 + MK_1$	0.58	40	0.79	1.90
$C_1 + AEA$	0.50	40	0.70	1.70
$C_1 + AEA$	0.54	40	0.42	1.00
$C_1 + MK_1$	0.625	23	0.11	0.30
C_1	0.54	3	0.01	0.04

Chabannet et al, CANMET, Barcelona 2000

Comparación Mecánica MK/Microsilice HORMIGONES



6. Conclusion

The compressive strength test results showed that the micro silica and metakaolin having higher compressive strength than the control mix. The graph indicates optimum percentage of replacement is 10% for micro silica.

Comparing the results of compressive strength test as a whole, metakaolin mix showed higher strength than micro silica and control mix.

The results of flexural strength indicate that the flexural strength of metakaolin formulation is greater than the control mix.

The flexural strength of metakaolin mix initially represents lower values, but with an increase in percentage, the strength increased by 36% than the strength of the control mix. Whereas initial flexural strength of micro silica mix is higher but it is reduced with increase in percentage content of micro silica.

Considering the cost benefit ratio, metakaolin supersedes micro silica in cost per cu.m. About 50% cost will be saved hence it can be the best economical alternative to micro silica.

Kalpana et al. Materials Today 2020

DURABILIDAD : Estudio comparativo MK/Ilita
HORMIGONES-25% BLENDED CEMENTS

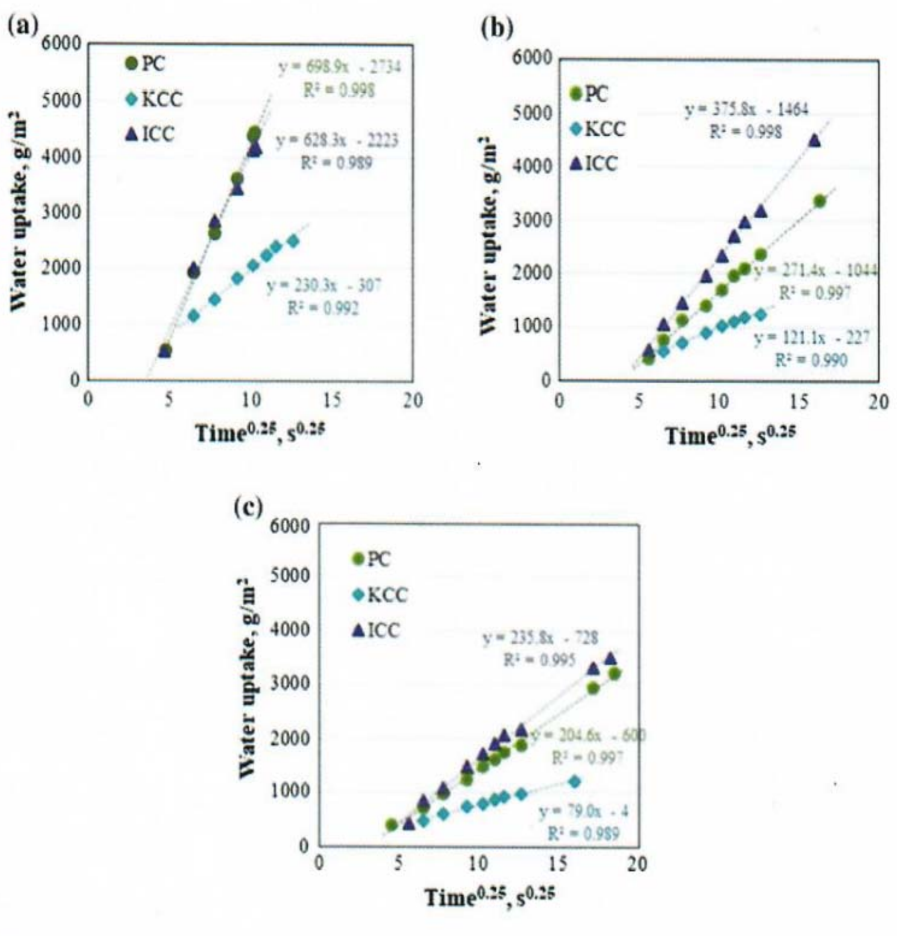
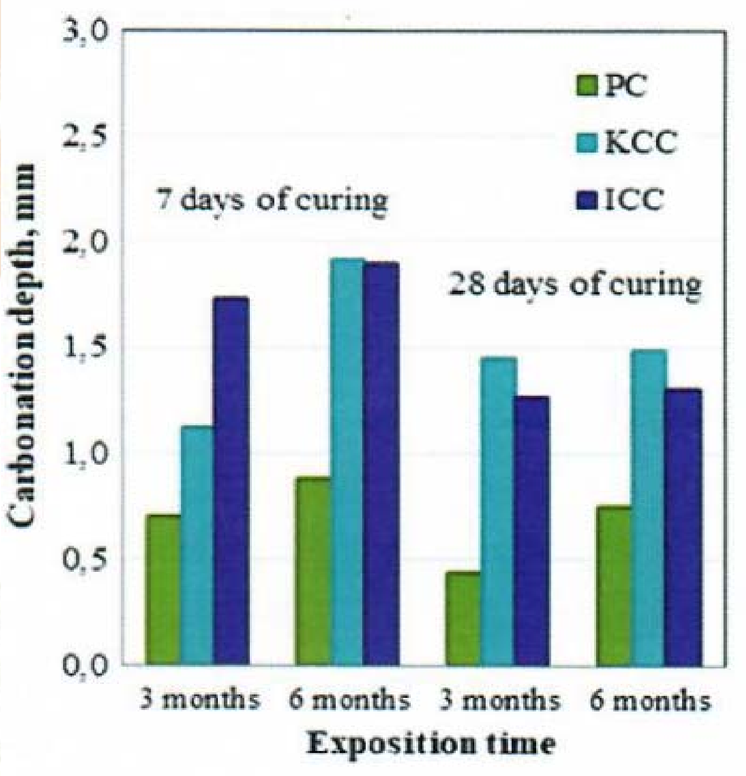


Fig. 1 Sorptivity test at **a** 2 days, **b** 7 days and **c** 28 days of curing



RC-28d

25%MK---15%↑

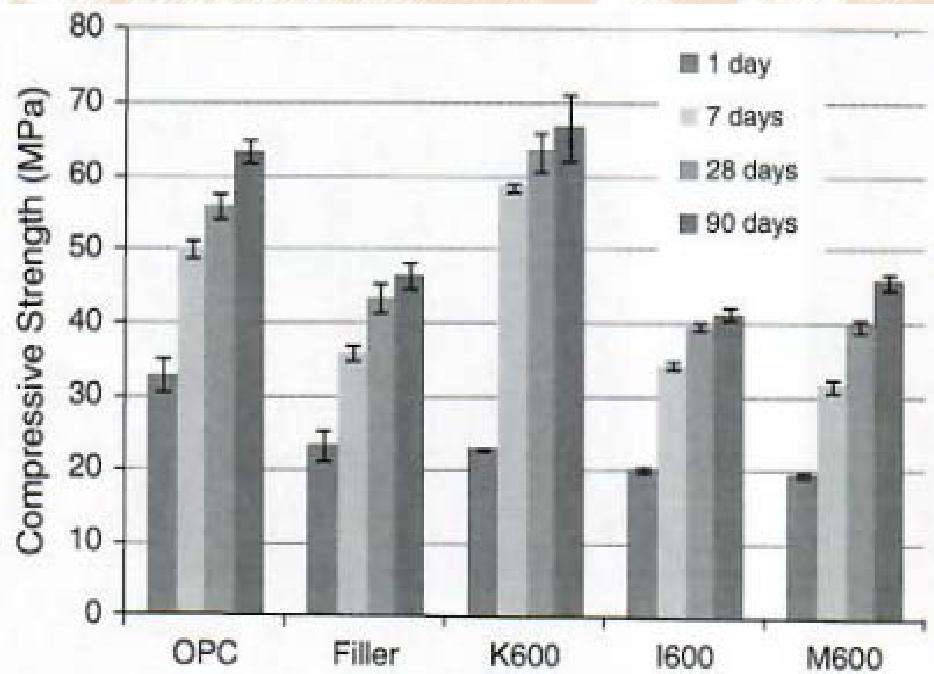
25% Ilita ---- 9% ↓

Córboba et al. 2020- RILEM BOOKS

Estudio comparativo K/Ilita/Montmorillonita

Table 3
Effect of calcinations on different physical properties of the clay minerals.

Method	BET		PSD	He-Picnometer	NMR	XRD
Parameter	Specific Surface [m^2/gr]		Median Diameter d50 [mm]	Bulk Density [gr/cm^3]	Al Coordination	Crystallinity
Kaolinite ref.	26.1512		4.88	2.67	$Al^{[VI]}$	High
Kaolinite 600 °C	24.6978	=	6.97	2.55	$Al^{[IV]}$, $Al^{[V]}$, and $Al^{[VI]}$	Low
Kaolinite 800 °C	24.1283		8.28	2.65	$Al^{[VI]}$, $Al^{[V]}$, and $Al^{[IV]}$	Low
Illite ref.	21.3277		3.79	2.80	$Al^{[VI]}$ and $Al^{[IV]}$	High
Illite 600 °C	18.4316	↓ 37,6%	4.48	2.69	$Al^{[VI]}$ and $Al^{[IV]}$	High
Illite 800 °C	13.3214		4.9	2.71	$Al^{[IV]}$	High
Montm. Ref.	31.0287		2.98	2.42	$Al^{[VI]}$ and $Al^{[IV]}$	High
Montm. 600 °C	21.386	↓ 68,7%	14.1	2.70	$Al^{[VI]}$ and $Al^{[IV]}$	Medium
Montm. 800 °C	9.7221		20.56	2.58	$Al^{[IV]}$	Medium



Morteros---30%

CONCLUSIONES

ADICIONES Q: Puzolana natural calcinada

VIABILIDAD CIENTÍFICA, TÉCNICA y DURABLE de matrices de cemento adicionadas con MK

- ✓ ODS
- ✓ E. Circular
- ✓ Neutralidad Climática 2050
- ✓ Planes Estratégicos
- ✓ Pacto Verde 2030
- ✓ H.R. 5Cs

RESIDUOS INDUSTRIALES BASE CAOLINITA

- ➢ Estériles de carbón (800-3.500 mtn/año)
- ➢ Lodos papeleros (1.500.000 tn/año)
- ➢ Residuos de Tratamiento de agua potable (1 m^3/s of volume genera 8.300kg/d de lodos)

RESIDUOS CERÁMICOS

- ✓ I. Cerámica (5-7% prod.)
- ✓ RCDs cerámica (50-55% total)

Frías et al,2003-2022

Sánchez de Rojas et al. y Medina et al. 2006-2023

MUCHAS GRACIAS POR SU ATENCIÓN

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Proyectos Nacionales: CEMAPEL,CESAR,CEMATEC,CUCEM-3D
CIDECAR (PID2021-122390OB-C21), etc
Proyectos C. de Madrid: Valrec