

# Rheology of portland cement pastes with calcined clays additions

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## ABSTRACT

In this paper, the rheological behavior of pastes of Portland cement and different calcined clays additions were analyzed. For this purpose, two Portland cements with different mineralogical composition (low  $C_3A$  and high  $C_3S$  content and low  $C_3S$  and high  $C_3A$  content) combined with different replacement percentages of three minerals additions of aluminic nature (quartz as control, and two metakaolins) are used. Mineral admixtures have different crystallinity and morphology: the quartz is fully crystalline; metakaolins are vitreous with a small fraction crystalline. The vitreous phase gives to the calcined clays, pozzolanic properties. All determinations were performed on Haake Roto Visco at 25°C, just on the latency period of hydration. The results show that paste of Portland cement with low  $C_3A$  content and high  $C_3S$  content presents a great shear strength and the replacement by calcined clays addition affects the rheological behavior of pastes depending on the pozzolanic nature and the reactivity of addition.

**Keywords:** rheology, portland cement pastes, pozzolanic non pozzolanic additions.

## 1 INTRODUCTION

When portland cement is mixed with water, the hydration reactions begin. During the dormant period the rate of hydration reaction drastically decays and the paste has a plastic consistency allowing to place and to compact the mixture. This period extends until the reactions have an enough evolved to begin to set. This phenomenon can be clearly characterized in the heat released curve.

The rheological properties of cement pastes and the duration of dormant period are modified by the incorporation of mineral additions. The flow of portland cement pastes is a very important property during the mix, transport, placement and compaction operations of concrete. The shear stress for each rate of rotation may be determined using a rheometer test. [1, 2].

In previous paper [3], the rheometer test parameters (rotation rates and duration times of each cycle) were analyzed observing differences between the acceleration and deceleration responses. The behavior of the incorporation of crystalline mineral admixtures was also analyzed.

In this paper, the rheological behaviour of pastes made with two portland cements and three different mineral additions (one crystalline and two calcined clays) is analyzed.

## 2 MATERIALS AND METHODOLOGY

Two Portland cement were used: PC1 and PC2. The physical characteristics and its mineralogical composition of both portland PC are given in Table 1.

**Table 1:** Characteristic of materials

Parameters	Portland Cements		
	PC1	PC2	
$C_3S$ , %	51	79	
$C_2S$ , %	16	2	
$C_3A$ , %	14	0	
$C_4AF$ , %	5	10	
Alkalis eq., %	1.5	0.4	
Density	3.08	3.21	
SEB, m <sup>2</sup> /kg	319	301	
	Mineral additions		
	Q	MQ	M
SiO <sub>2</sub> (reactiv)	-	38.30	48.30
Al <sub>2</sub> O <sub>3</sub> (reactiv)	-	14.86	29.29
Alkalis eq., %	-	0.07	0.70
Density	2.70	2.55	2.52
SS Blaine, m <sup>2</sup> /kg	395	398	333
Absortion 1 day, %	0.41	2.24	2.48
Frattni test 2 day	negative	positive	positive
Frattni test 7 day	negative	positive	positive

The replacement percentages were 20 and 40% by weight of cement. Table 2 reports the water demand determined according to the EN 196-3 procedure, and the setting times using the procedure described in EN 196-3 for used pastes. The water demand of PC1 paste was greater than that of the corresponding to PC2 paste. It is due to the great water ability to form early aluminic compounds in PC1 that requires a large amount of water in their constitution. Therefore, the initial and final setting times of PC1 paste were shorter than that of PC2 paste. The water demand of pastes with Q addition is similar to the corresponding PC used. These results could be attributed to the low humidity absorption and the null pozzolanic activity

of Q. However, the setting time was in advance for pastes with PC1 while it was delayed for paste containing PC2. This behavior could be due to C<sub>3</sub>A stimulation (mainly for PC1) and the dilution of C<sub>3</sub>S (mainly for PC2).

**Table 2:** Characteristic of pastes

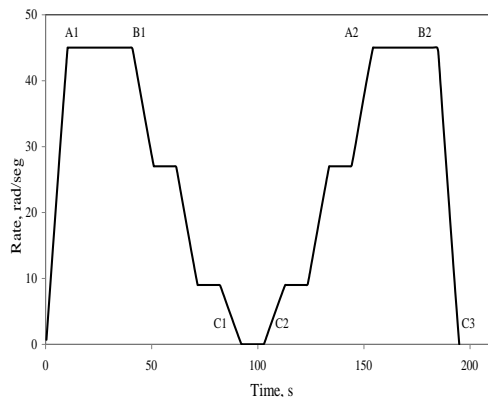
Samples	Water demand, w/cm	Initial set, hours:min	Final set, hours:min
PC1	0.310	3:20	5:10
20% Q	0.320	2:45	4:30
40% Q	0.320	3:15	4:45
20% MQ	0.360	2:55	4:40
40% MQ	0.435	3:10	5:10
20% M	0.365	3:05	4:55
40% M	0.450	2:40	5:05
PC2	0.280	4:30	6:15
20% Q	0.291	5:05	7:00
40% Q	0.300	5:00	8:00
20% MQ	0.350	4:15	8:05
40% MQ	0.420	6:20	8:20
20% M	0.350	6:10	7:25
40% M	0.450	5:10	6:20

For both PCs, the replacement by MQ and M additions causes an increase in the water demand and it increases when the replacement level increases. This could be due to the low density and the high humidity absorption (Table 1) of the calcined clay additions.

The setting time of pastes containing 20 and 40% of MQ and M has a similar tendency to the values reported by Q addition: it occurs in advance for PC1 and it is delayed for PC2.

All powders were dry blended prior to wet mixing. The paste was prepared with distilled water and the water to binder ratio (w/b) was 0.5 for all samples.

All pastes were stored at 25 °C until the time reported in Tables 3 and 4. This time correspond to the minimum in the heat released curve during the dormant period. Additionally, the crystalline compounds present in the pastes were determined by XRD analysis at this time.



**Figure 1:** Mixing sequence

The rheological test was carried using a Haake rotational viscometer, compound by a viscometer Rotovisco 1, a profiled rotor Z38 DIN 53018, a glass Z43 DIN 53018, equipped with a control temperature unit for coaxial cylinders and a circulation thermostat DC 30-B3 [4]. The mixing sequence of paste is showed in Figure 1. It consisted of a ramp up to 45 rad/s staying 30 s, following by a ramp down from 45-to-0 rad/s with two steps down of 10 s and a ramp up from 0-to-45/s with the same step. Then, the paste staying 30 s at 45rad/s and finally down to 0 in 10 s without step [5]. Shear stress was measured at singular points (A1, B1, C1, C2, A2, B2, and C3).

### 3 RESULTS AND DISCUSSION

Tables 3 and 4 summarize the shear stress of the singular points (A1, B1, C1, C2, A2, B2, and C3) for all studied pastes. Figures 2 and 3 show the XRD-pattern for plain and blend pastes containing PC1 and PC2 cement, respectively.

**Table 3:** Shear Stress at singular points

Time, min.	PC1	20% Q	40% Q
Shear stress, Pa	120	100	125
A <sub>1</sub>	91.91	78.50	122.7
B <sub>1</sub>	54.07	55.34	74.48
C <sub>1</sub>	11.48	12.81	15.09
C <sub>2</sub>	12.30	13.90	13.60
A <sub>2</sub>	47.20	36.97	48.06
B <sub>2</sub>	46.15	34.77	44.98
C <sub>3</sub>	11.35	12.76	13.75

Time, min.	20% MQ	40% MQ	20% M	40% M
Shear stress, Pa	100	165	95	90
A <sub>1</sub>	95.73	212.0	167.9	282.1
B <sub>1</sub>	57.81	88.87	82.67	120.7
C <sub>1</sub>	15.31	31.16	25.00	45.01
C <sub>2</sub>	18.43	36.39	31.39	53.32
A <sub>2</sub>	49.32	65.98	63.57	106.0
B <sub>2</sub>	47.79	64.37	61.98	97.85
C <sub>3</sub>	15.13	26.33	24.27	41.10

At the time of minimum in the dormant period, the PC1 paste has an initial shear stress of 91.91 Pa (A1 point), this value may be due to the ettringite formation (see Fig. 2) that occurs in this high C<sub>3</sub>A-content cement. After 30 s at 45 rad/s, the paste shows a thixotropic behavior causing a significant decrease of shear stress (B1 point). When the

rotor stop (C1 point), the paste shows a remaining shear stress, and 10 s later it recovers part of stress (C2 point) reaching to 12.3 Pa. At A2 point, the shear stress is reduced about 50% with respect to the value obtained at A1 point. On the other hand, the shear stress at B2 point is reduced about 15% compared to the value at B1-point after that paste remains 30 s at 45 rad/s. Finally, the value of shear stress at C3 point remains with similar value that obtained at C1 point. For PC1 paste, all results show a high thixotropic recovery.

**Table 4:** Shear Stress at singular points

Time, min.	PC2	20% Q	40% Q
Shear stress, Pa	100	180	95
A <sub>1</sub>	162.5	138.7	119.4
B <sub>1</sub>	75.78	77.92	74.46
C <sub>1</sub>	13.44	12.99	11.19
C <sub>2</sub>	12.04	12.77	11.30
A <sub>2</sub>	46.15	48.77	47.37
B <sub>2</sub>	42.87	45.19	44.77
C <sub>3</sub>	12.83	10.58	11.36

Time, min.	20% MQ	40% MQ	20% M	40% M
Shear stress, Pa	180	130	140	105
A <sub>1</sub>	207.8	289.5	267.3	367.6
B <sub>1</sub>	112.5	146.6	134.1	227.2
C <sub>1</sub>	24.95	36.73	53.25	59.55
C <sub>2</sub>	26.82	38.65	54.92	62.93
A <sub>2</sub>	70.13	85.98	115.7	136.2
B <sub>2</sub>	65.93	82.16	106.1	124.1
C <sub>3</sub>	25.30	34.74	57.54	56.32

For PC2 paste at the minimum in the dormant period, the initial shear stress is 162.5 Pa at A1 point. It is observed that the shear stress is higher than that of CP1 due to the different mineralogical composition of cement. For PC2, the high content of C<sub>3</sub>S produces a different nature of reaction products at early stages of hydration (Fig. 3). After 30 seconds at 45 rad/s, the paste shows a thixotropic behavior with a significant decrease in the shear stress (B1 point) approximately a half as occurs in PC1 paste. When the rotor stop (C1 point), the paste has a residual stress (13.44 Pa) that decays up to 12.04 Pa after 10 seconds (C2 point). At the A2 point, the shear stress is reduced about 75% with respect to A1 point; while this stress reduction was about 45% between the B2-point and B1-point. Finally, the residual stress at C3 point was lower than that

determined at C1 point. For PC2 paste, all results show some difficulty for the thixotropic recovery.

When PC1 was replaced by Q addition, the shear stress was greater in the most of singular points and it also increases when the level replacement increases. This behavior could be partly attributed to the mineralogical composition of the cement and partly to the acidic nature of the addition. For PC1 with high C<sub>3</sub>A-content, the Q-addition stimulates the hydration of aluminic phases of cement due to its particle size and acidic nature, and it also increases the available water for reaction due to the dilution effect. Both effects contribute to the rapid recovery of links due to the renewed ettringite formation. From the PC1-results, it can be inferred that the incorporation of Q addition specifically stimulates the hydration of aluminic phases of cement.

When PC2 was replaced by 20 and 40% of Q addition, the shear stress was lower in the most of the singular points and it was reduced when the level replacement increases, unlike as occurred for PC1. This behavior reveals the low interaction between the Q-addition and PC with low C<sub>3</sub>A-content making very obvious the dilution effect. After 30 seconds at 45rad/s, the shear stress decreased about 40% (B1 point). When the rotor stop (C1 point), the pastes have a residual stress and 10 s later (C2 point) the shear stress decreases. Regarding Q addition-PC2 interaction, it has a low capacity to remake the links between particles, unlike as occurred for CP1 at the same points. At the A2 point, the shear stress is reduced about 60% with respect to A1 point; while this stress reduction was about 40% between the B2-point and B1-point. Finally, the residual stress at C3 point increases when increase the replacement level. Comparing the residual stress at C3 point with the value at C1 point, it was lower for 20% of Q and similar for 40% of Q.

When PC1 was replaced by the MQ and M additions, the shear stress was high in all the singular points and it also increases when the replacement level increases. This behavior can be attributed to the large volume occupied by the solid particles in the paste due to the low density of MQ and M and to the high pozzolanic activity of both metakaolins at early ages (Table 1). As occurred by Q addition, metakaolin stimulates the portland cement hydration. But, it also contributes with the proper pozzolanic reaction to the formation of additional C-S-H and ettringite (see in Table 1 the SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> reactive), increasing the shear stress when increases the percentage of replacement. This can be demonstrated by the XRD analysis (Figure 2) that shows the presence of ettringite, the absence of portlandite and a marked decrease in the C<sub>3</sub>S peaks inferring the formation of C-S-H. From the rheological test, a notable recovery of shear strength occurs when the rotor is stopped (C1 and C2) reaching to a shear stress two times greater than that obtained for CP1 paste.

When CP2 is replaced by M or MQ additions, the shear stress is also higher in all the singular points and it increases when the percentage of replacement increasing, as occurred for CP1. This increase is more important when the rotor is stopped (C1, C2 and C3), even exceeding the values at the same point obtained for paste with CP1, despite its high  $C_3A$  content. These observations highlight the high reactivity of metakaolin and its eminently aluminic character that causes a great stimulation on the CP2 hydration. Also, the aluminic character of metakaolin allows the recovery of the CP2-pastes when the rotor is stopped (between C1 and C2 point, Table 4). This behavior is opposite to those described for the CP2 paste.

The high shear stress produced by the incorporation of metakaolin could be due to the same reasons described for CP1-blended cement. But, in this case the formation of ettringite is from the  $C_4AF$  of CP2 and the reactive alumina of metakaolin. In XRD patterns (Figure 3), the absence of portlandite could be attributed to the consumption by the early pozzolanic reaction and the decrease of the  $C_3S$ -peak intensity to the formation of C-S-H that contributes to increase in shear stress.

## 4 CONCLUSIONS

From the results of rheological tests the following conclusions can be drawn:

For pastes made with portland cements, the initial shear stress was higher for PC2 (high  $C_3S$ -content), but both cement pastes show a similar reduction ( $\sim 50\%$ ) after 30 s at 45 rad/s. Then, the residual shear stress shows a high capacity to remake the links between particles for the PC1 (high  $C_3A$  content) cement due to renewed ettringite formation.

The Q addition (crystalline, not pozzolanic, regular water demand) produces an increased of shear stress on high  $C_3A$  content cement; while on cement with high  $C_3S$  content produces a decreased of shear stress.

The MQ and M calcined clays (with high pozzolanic activity and aluminic character) stimulate the hydration of the silicate phases and aluminate phases cements. This stimulation is too marked on the silicate phases as occurred in CP2. Furthermore, the high alumina reactive content in metakaolinite causes that the low  $C_3A$ -content blended cements invert its rheological behaviour during the rest time and they behave like a high  $C_3A$ -content portland cement.

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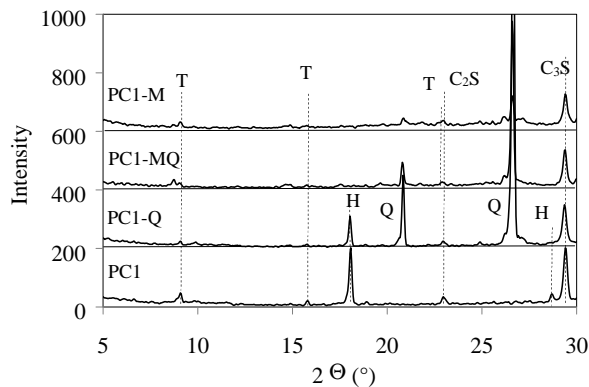


Figure 2: XRD-ray PC1 samples

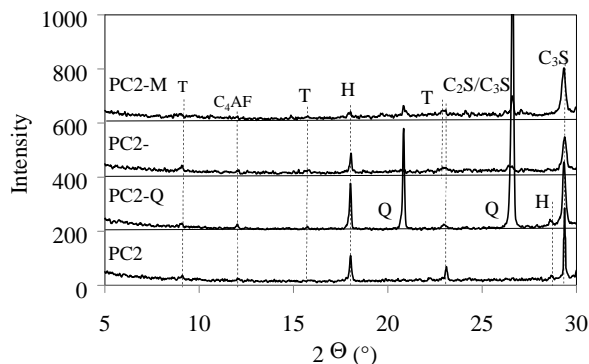


Figure 3: XRD-ray PC2 samples