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Using Dealuminated Metakaolin in Concrete as Microsilica Substitute

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ABSTRACT

In the present paper, dealuminated metakaolin was studied as addition to concrete and as potential clinker substitute in cement. In particular because of its high fineness and pozzolanic activity, dealuminated metakaolin was investigated as microsilica replacement in concrete. A comparison with the behaviour obtained in a parallel use of metakaolin was also done. Different ways of introducing dealuminated metakaolin in concrete (dry, ground, slurry ones) were tried. The experimental plan included chemical and granulometrical characterization of the starting materials and physical-mechanical tests in mortar and concrete both in the fresh and hardened state.

INTRODUCTION

Dealuminated metakaolin (DK) is a by-product of aluminium sulphate industry and it derives from acid leaching of metakaolin (MK) (e.g. calcined kaolin, $Al_2O_3{\cdot}2SiO_2$).

As result of the dealumination process, the SiO_2/Al_2O_3 ratio and B.E.T. values are increased. The increasing of specific surface observed as consequence of acid attack was found due to the increasing of the pore volume without an appreciable increasing of the mean pore size distribution [Vollet, R.V. et al., 1994].

Some researchers [Mostafa N.Y. et al., 2001] studied mixes of DK and lime and they have founded, by isothermal calorimetric tests, that DK shows an appreciable pozzolanic activity. The pozzolanic activity of DK in blended cements was also demonstrated by the same method [Mostafa, N.Y et al., 2005]. They also reported that DK exhibits higher B.E.T values than silica fume (SF).

Other researchers [Macedo J.C.D. et al., 1994] has also shown that the porous structure of MK particles doesn't collapse owing to the acid attack.

Considering the limited but promising studies on this subject and, in the meanwhile, the increasing interest for the research of alternative sources of succedaneum materials for clinker, in the present work DK was studied as partial clinker substitute and as addition for concrete.
It is also worth noting that the substitution of clinker with high reactive pozzolanic material can lead to an appreciable improvement of the resulting performances and to an efficient reduction of CO_2 emissions.

EXPERIMENTAL

STARTING MATERIALS

The following starting materials have been used:

- CEM I 52.R, CEM II/A-LL 42.5R (EN 197-1), provided by Italcementi Group;
- Clinker to produce Portland cement (EN 197-1), provided by Italcementi Group;
- Two dealuminated metakaolin from different Egyptian sources (DK1, DK2); water content was 36,2% in DK1 and was 19,6% in DK2;
- Silica Fume (SF), provided by Elkem Microsilica;
- Two sources of calcined metakaolin by AGS Group as dry source (MK1) and 50% water slurry source (MK2).
- Superplasticizer admixture for concrete: AXIM DRIVER 2E.

In

Table I the chemical analysis of the pozzolanic starting materials are reported.

Table I. Oxide composition of pozzolanic materials.

%	DK1	DK2	SF	MK1	MK2
l.o.i	13,66	11,53	1,86	1,51	2,23
reactive SiO_2	54,26	51,44	87,88	54,84	43,28
Ins. res. in HCl - KOH	18,28	25,42	2,24	18,5	16,38
SiO_2	66,87	71,84	89,9	57,12	55,36
Al_2O_3	8,29	7,71	1,32	36,44	36,03
Fe_2O_3	0,26	0,58	1,78	1,25	2,44
CaO	0,39	0,12	2,98	0,67	0,68
SO_3	5,06	3,95	0,23	< 0,06	0,07
TiO_2	5,09	3,89	0,1	1,46	1,62
SiO_2/Al_2O_3	8,07	9,32	68,11	1,57	1,54

From

Table I it arise the high content of reactive SiO_2 shown by all the materials; reactive silica represents the fraction of silica able to react in basic environment and for this reason it doesn't include silica quartz; in particular it is highlighted the very high content of reactive SiO_2 in SF.

MK1 and MK2 have different origins from the ones subjected the dealumination process; nevertheless the averaged value of Al_2O_3 in DK (8.00%) is significantly lower than corresponding value of MK (36.23%). This lead to an appreciable increase of SiO_2/Al_2O_3 ratio (from 1,56 for average value of MK to 8,67 for average of DK).
In concrete mixes, sand stone gravel was used with maximum aggregate dimension of 20 mm.

Different conditioning procedures were also adopted for DK before using it as concrete addition: DK was adopted as raw source after drying in oven at 100°C for 12h ("dry"). The dry source was also used after further grinding ("ground"); the ground source was also used after further dispersion as water slurry ("ground-slurry"). Dry DK source was used for the production of laboratory cement.

In

Fig. 1 The particle size distribution obtained by laser diffractometer Sympatec of pozzolanic materials is reported. The lens had the following focal length: 50 mm for MK2 and SF; 100 mm for MK1; 500 mm for DK1; 1000 mm for DK2.
It is worth noting the that MK2 has shown a very high fineness, close to SF. Both DK1 and DK2 have shown a coarser particle size distribution.

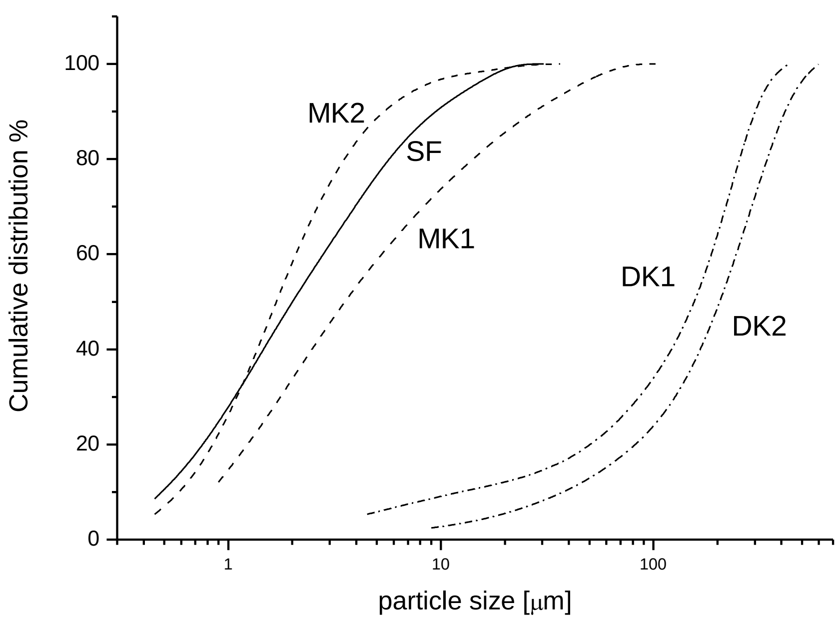

Fig. 1. Grain size distribution by laser granulometer.

B.E.T. analysis revealed a high fineness for DK (20 m^2/g for DK1 and 43 m^2/g for DK2). Nevertheless B.E.T. results seem to be not congruent with laser granulometry test results which indicate DK being coarse (Figure 1). This might be attributed to the surface texture of particles characterized by high roughness already observed by Vollet, R.V. et al. (1994). In particular a SEM investigation was performed on DK1 (Figure 2) and DK2 (Figure 3) sources and a layered morphology was evidenced that accounts for an increased exposed surface.

Positive reaction to pozzolanic tests at 15 days (EN 196-4) was given by both DK1 and DK2 (ground) when dry blended to 70% CEM I 42.5R.

Blue methilene test (UNI EN 933/9) results were 4,4 g/kg for DK1and 3,1 g/kg for DK2.

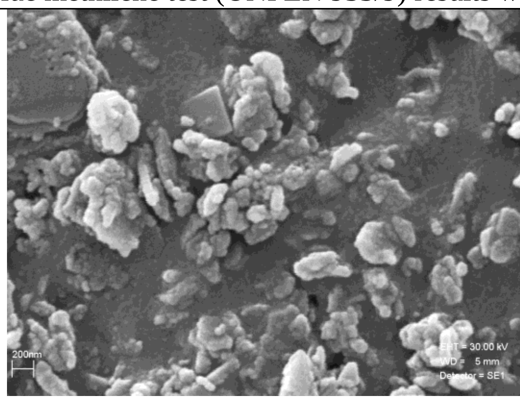

Fig. 2. DK1
Particle morphology (75000X)

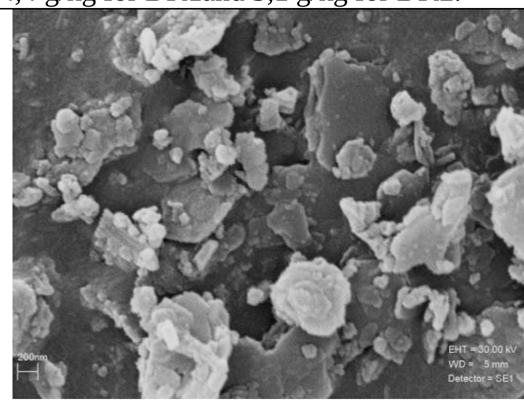

Fig. 3. DK2
Particle morphology (70000X)

DK AS CLINKER SUBSTITUTE IN CEMENT

In order to evaluate the potential use of DK as clinker substitute in cement, cements reported in Table II, were produced in laboratory.

Table II. Laboratory cements

cement label	Clinker	DK1	DK2	SF	Gypsum	SSB	RRSB	
							xp	n
	%	%	%	%	%	cm^2/g	μm	-
M1	85,5	10	-	-	4,5	5020	19,3	0,73
M2	85,5	-	10	-	4,5	4900	15,9	0,81
M3	80,5	15	-	-	4,5	4900	23,5	0,70
M4	80,5	-	15	-	4,5	4830	17,2	0,80
M5	85,5	-	-	10	4,5	8390	12,8	0,68
M6	95,5	-	-	-	4,5	4521	14,7	0,79

Six laboratory cements were considered. Cement M1, M2, M3, M4 were obtained by laboratory by inter grinding clinker, DK dry and gypsum; M5 was produced by blending M6 (reference cement) with 10% SF. Fineness during grinding procedure was controlled in the range

≈4900±100 cm^2/g Blaine. Such procedure was adopted in order to limit the effect of SF to increase cement fineness.

In Table III test results according to EN 196 and UNI 7044 are reported. From Table III it can be observed that clinker substitution lead to an impairing of flow. It can be also noticed that such impairing was limited by using SF. In fact, despite the higher SSB and the lower average particle dimension (xp), SF evidenced a lower n parameter that highlights a certain spreading in the particle size distribution. Moreover the particle morphology of DK is far from being spherical; both these event comply with a better flow.

All cements 10% substituted (M1, M2, M5) reported in Table III comply with strength requirements of 52.5R class according to EN 197-1 as well as reference cement (M6). With exception of DK2, the clinker substitution reduced 2d strength. Activity index of cement 10% substituted is also reported in Table III. The one substitution whose activity index was always larger than one was DK2 at 10% (M2); SF activity index was larger than one only at 28 days. The higher 28 days strength value was obtained by DK2 at 15% (M4) wherein a reduction in setting times has also been shown. This could be explained taking into account for the very high B.E.T. value observed with DK2. The same effect was not evidenced with DK1 because of its reduced B.E.T. value. As consequence it can be concluded that both silica content (
Table I) and B.E.T. value should be considered to characterize the reactivity of DK.

Table III. Test results on laboratory cements from Table II (activity index are reported in brackets).

cement label	UNI 7044	EN 196				
	flow	i.set.	f.set.	2d	7d	28d
	mm	min	min	MPa	MPa	MPa
M1 (10% DK1)	75	160	211	31,7 (0,83)	45,3 (0,91)	55,1 (0,94)
M2 (10% DK2)	65	190	244	38,2 (1,00)	54,4 (1,09)	65,9 (1,13)
M3 (15% DK1)	55	180	253	24,5	40,6	51,5
M4 (15% DK2)	59	120	204	27,9	47,8	66,0
M5 (10% SF)	81	180	243	33,2 (0,87)	45,3 (0,91)	63,3 (1,08)
M6 (reference)	110	170	239	38,1	49,7	58,4

On the basis of their performances, the blended cements using DK considered in Table III could be considered as CEM II/A-Q 52.5 R assuming that DK could be regarded as a natural calcined pozzolana enriched in SiO_2.

Table IV. Concrete test results using laboratory cements. Activity index is reported in brackets with reference to M6.

cement label	cement	super.pl.	fresh density	flow	Rc2d	Rc7d	Rc28d	Rc2/Rc28
	kg/m³	%cement	kg/m³	mm	MPa	MPa	MPa	
M6 (reference)	370	1,41	2403	180	57,0	68,0	73,0	0,78
M1 (10% DK1)		1,69	2464	170	(0,88)	(1,03)	(1,05)	0,65
M2 (10% DK2)		1,69	2449	170	(0,94)	(1,16)	(1,22)	0,60
M5 (10% SF)		1,22	2400	190	(0,92)	(1,00)	(1,19)	0,60
M3 (15% DK1)	415	1,00	2421	200	37,5	59,0	66,7	0,56
M4 (15% DK2)		1,00	2390	200	41,5	69,0	80,5	0,52

The potential use of laboratory cements (Table II) was verified in ordinary concrete (Table IV). For these concrete mixes a constant w/c ratio (0,43) was used and the target value for consistency was S4. To perform this target the superplasticizer content was adjusted properly. Cement content was in the range of 370 – 415 kg/m^3. Test results obtained in concrete are also reported in Table IV: fresh density (EN 12350-6), slump flow (EN 12350-2) and cubic compressive strength (EN 12390-3) as mean value of three test specimens is reported as activity index (ratio to the compressive strength of reference).

A pozzolanic effect was evidenced by increasing the 28d strength (Table IV) of the reference concrete (produced using M6) with cements 10% substituted (M1, M2, M5). Nevertheless none cement has reached the same Rc2/Rc28 ratio as reference cement (0,78).

From Table IV it is shown that in case of 10% clinker substitution all the concrete have shown compressive strength higher than the reference concrete at 7 and 28 days 8activity index always larger than one). In all the case the superplasticizer content was limited to the range 1,0 to 1,7 % cement and slump to class S4.

It is worth noting that DK2 shows a high activity index at 28 days (increment in compressive strength of ~20%), that is also close to silica fume. Moreover the same Rc2/Rc28 ratio was obtained.

In order to introduce a higher DK content in cement without impairing rheology or strength, the cement content was increased from 370 to 415 kg/m^3. DK content up to 15% as cement constituent with limited superplasticizer content (1%) have produced 200 mm slump and Rc 28d of ~80MPa with $R_2/R_{28} \approx 0.52$.

DK AS TYPE II ADDITION FOR CONCRETE

Taking into account the pozzolanic activity of DK, it has been considered its potential use as type II addition for concrete according to EN 206-1. The efficiency of DK as addition has been verified in concrete mixes prepared with laboratory and industrial cements. Slurry form of addition was also adopted other than dry form. In any case addition were introduced as 10% content (on dry basis) with reference to the sum of cement and addition (c+a).

Concrete mixes using several additions were prepared according to the mix proportions reported in Table V. Objective of the experimental plan was to obtain medium-high strength class concrete in consistency class S4.

In all the cases superplasticizer was limited to the range 1,0 to 1,6 %; w/c to the range 0,40 to 0,43; slump to the range 170 to 220 mm and cement to the range 370 to 415 kg/m^3.
In Table V, density in the fresh state (EN 12350-6), slump flow (EN 12350-2) and cubic compressive strength (EN 12390-3) as mean value of three test specimens.

Using DK as addition for concrete using laboratory portland cement (reference to M6 in Table V) has lead to a reduced pozzolanic effect than using DK as cement replacement (see cement M1 and M2 in Table IV) likely due to a reduced efficiency in the dispersion of DK particles.

With reference to concrete produced using CEM II/A-LL 42.5R a similar pozzolanic effect was evidenced by both DK1 and DK2 at 7 and 28 days. The higher mechanical result at 28d was shown by both SF and MK2. Nevertheless a limited rheological improving shall be accounted for DK2.

With reference to concrete produced using CEM I 52.5R and dry additions, a cement content of 415 kg/m^3 was adopted and the lower w/c ratio compatible with the same superplasticizer content (1%). The lower value observed for DK2 than SF and DK1 is related to the higher w/c ratio adopted.

Despite the cement type and the specific addition form, mechanical results comply with results obtained in concrete using laboratory cements in terms of relative performances among SF, DK1 and DK2.

Table V. Concrete produced using additions.

<table>
<tr><td colspan="2">cement
(c)</td><td colspan="2">addition
(a)</td><td rowspan="3">w/
(c+a)</td><td>superpl.
admixt.</td><td>fresh
dens.</td><td>flow</td><td>2d</td><td>7d</td><td>28d</td><td rowspan="3">Activity Index
@28d</td></tr>
<tr><td rowspan="2">type</td><td>content</td><td rowspan="2">type</td><td>dry
content</td><td rowspan="2">%
(c+a)</td><td rowspan="2">kg/m^3</td><td rowspan="2">mm</td><td colspan="3" rowspan="2">MPa</td></tr>
<tr><td>kg/m^3</td><td>kg/m^3</td></tr>
<tr><td rowspan="3">M6</td><td>370</td><td>-</td><td>-</td><td rowspan="3">0,43</td><td>1,41</td><td>2403</td><td>180</td><td>57,0</td><td>68,0</td><td>73,0</td><td>-</td></tr>
<tr><td rowspan="2">333</td><td>DK1 ground-slurry</td><td rowspan="2">37</td><td>1,61</td><td>2361</td><td>170</td><td>45,0</td><td>61,0</td><td>73,5</td><td>1,01</td></tr>
<tr><td>DK2 ground-slurry</td><td>1,61</td><td>2392</td><td>180</td><td>43,5</td><td>63,5</td><td>75,5</td><td>1,03</td></tr>
<tr><td rowspan="6">CEM II
A-LL
42.5R</td><td>415</td><td>-</td><td>-</td><td rowspan="6">0,44</td><td>0,80</td><td>2368</td><td>190</td><td>38,5</td><td>52,5</td><td>63,5</td><td>-</td></tr>
<tr><td rowspan="5">373</td><td>DK1 ground</td><td rowspan="5">42</td><td>0,96</td><td>2336</td><td>190</td><td>37,5</td><td>54,5</td><td>66,5</td><td>1,05</td></tr>
<tr><td>DK2 ground</td><td>0,96</td><td>2359</td><td>220</td><td>32,5</td><td>53,5</td><td>65,5</td><td>1,03</td></tr>
<tr><td>SF</td><td>1,00</td><td>2345</td><td>200</td><td>35,5</td><td>50,5</td><td>70,0</td><td>1,10</td></tr>
<tr><td>MK1 dry</td><td>1,00</td><td>2368</td><td>185</td><td>35,0</td><td>52,5</td><td>67,5</td><td>1,06</td></tr>
<tr><td>MK2 slurry</td><td>1,00</td><td>2352</td><td>180</td><td>38,0</td><td>56,5</td><td>69,5</td><td>1,09</td></tr>
<tr><td>CEM I</td><td>415</td><td>-</td><td>-</td><td>0,40</td><td>1,00</td><td>2463</td><td>200</td><td>59,0</td><td>80,0</td><td>86,0</td><td>-</td></tr>
</table>

52.5 R		SF			1,00	2431	200	54,5	77,0	93,5	1,09
	373	DK1 dry	42		1,00	2417	190	54,0	75,0	86,5	1,01
		DK2 dry		0,42	1,00	2431	200	48,0	73,0	82,5	NA

SUPPLEMENTARY TESTS

Supplementary tests were also performed to investigate further concrete properties: workability loss and resistance to aggressive environment. In such experiments concrete mix DK1 in dry form was used as addition to concrete using CEM II/A-LL 42.5R (see Table VI). Initial slump was within S5 class; a slump flow reduction up to 45 min was evidenced within S4 class. At 60 min a further flow reduction was observed (within S3 class). From the performed experiments, no substantial changes in the long term rheological behaviour can be ascribed to using DK as addition to concrete.

A limited series of experiments was also performed to assess the resistance to aggressive environments. In particular, such concrete was subjected to an accelerated carbonation test wherein a limited carbonation depth (≈2 mm) was measured conforming to UNI 9944 after exposure for 70 days at 25°C and 55% RH using 4% CO_2. Depth of penetration of water under pressure (EN 12390-8) was also measured and it was lower than 20 mm. Moreover a limited scaling (<1 mg/mm^2) was evidenced after test EN 1338. On the other hand with reference to resistance to internal freezing a limited resistance was registered likely due to the layered shape morphology of DK particles (see

Fig. 2 and
Fig. 3). In fact resistance to freezing and thawing cycles (UNI 7087) was limited to 100 cycles.

Table VI. Workability loss on concrete using CEM II/A-LL 42.5R.

cement		addition		superpl. admixt.	w/ (c+a)	slump flow [mm]				
type	content kg/m^3	type	content kg/m^3	%(c+a)		0min	15min	30min	45min	60min
CEM II/A–LL 42.5R	373	DK1 dry	42	0,8	0,44	240	220	220	200	150

CONCLUDING REMARKS

Two sources of dealuminated metakaolin (DK) were analyzed in the present study to investigate its potential application in cement and concrete industry. The two DK examined were characterized by a very high fineness and an appreciable pozzolanic activity due to the presence of high silica content. Both silica content and B.E.T. value were selected as main parameter to assess reactivity of DK.

As potential main constituent of cement, DK showed when inter ground with clinker, the possibility to reach compressive strength values in standard mortar tests (EN 196-1) very close to cement containing the same content of SF. With reference to portland cement the rheology is slightly impaired.

Using DK as addition for concrete was also verified with laboratory grinded and industrial cements. Also as addition for concrete, DK revealed a good pozzolanic activity in such a way to be classified as type II addition. Depending on the form in which DK is introduced into the mixer (ground and dry, ground-slurry or dry as arrived) its beneficial effect to the concrete strength could be milder than using it as cement constituent, even tough its pozzolanic effect is high enough to guarantee an activity index greater than one at 28 days.

Preliminary investigation on durability related properties and to resistance at aggressive environment was performed with a positive answer even though. A limited sensitivity to freezing and thawing shall be highlighted. Finally, on the basis of the results arising from the present investigation, DK seemed an interesting material to be considered also in terms of performance/cost ratio.

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