

Sulphate and chloride durability of metakaolin-blended palm kernel shell concrete masonry units: separating the contributions of the pozzolan and the agro-waste aggregate

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Abstract

Palm kernel shell (PKS) is an established lightweight coarse aggregate and metakaolin (MK) an established supplementary cementitious material, yet the durability of masonry units containing both has been assessed only against a plain control. Such a comparison confounds pore refinement by the pozzolan with pore coarsening by the aggregate. Three solid concrete masonry units of 250 mm × 200 mm × 150 mm were produced: a control, a unit with 10% of the cement replaced by MK, and a unit with that replacement plus 25% PKS as coarse aggregate. All were immersed in 3% Na₂SO₄ and 3% NaCl for 56, 90, 150 and 180 days. Residual mass and compressive strength were measured at each age, with absorption, initial rate of absorption, seven wetting and drying cycles and electron microscopy. Water-accessible porosity, derived from absorption and oven-dry density, was 7.40%, 1.56% and 2.89%. Strength loss was first order in immersion period ($R^2 = 0.899$ to 0.946) and was not reproduced by a square-root-of-time law ($R^2 = 0.730$ to 0.832). MK reduced the rate constant by 19.9% in sulphate and 37.1% in chloride, while PKS returned 16.0% and 47.7% of that gain, leaving a net reduction of 7.1% in both media. The rate constant varied with accessible porosity only as the 0.14 to 0.28 power, so absorption is a weak proxy for durability. Strength loss exceeded mass loss by 8.1 to 11.6 times, indicating matrix softening. Cyclic damage after seven cycles was 35.8% for the control and 7.5% for the PKS-MK unit.

1. Introduction

Palm kernel shell is the woody endocarp discarded when the kernel is removed during palm-oil milling. Produced in quantity across South and South-East Asia and West Africa and disposed of largely as mill waste, it has a specific gravity near 1.2 and has therefore been studied extensively as a lightweight coarse aggregate [1, 2]. Compressive strengths adequate for structural work have been reported at moderate replacement levels [3], the material has been characterised as a concrete aggregate in its own right [4], and the bond and durability behaviour of oil palm shell concrete have both been examined [5, 6]. Application at the scale of a masonry unit is far less common, the closest precedent being the lightweight masonry block of Muntohar and Rahman [7], which characterised the unit but did not follow it into long-term chemical exposure.

The obstacle is transport rather than strength. Palm kernel shell is itself porous and its surface is waxy, so it raises the water demand of the mix, weakens the aggregate-paste interface and introduces a percolating network of aggregate-scale pores. In a unit intended for a plinth course, a coastal wall or a wall founded in sulphate-bearing ground, that network is the pathway along which aggressive ions arrive. The conventional remedy is a pozzolan. Metakaolin, the dehydroxylated product of kaolin calcined at 500 to 600°C, consumes calcium hydroxide and precipitates secondary calcium silicate hydrate, subdividing large capillary voids into smaller and less connected ones [8, 9, 10]. Its durability credentials are well established: improved sulphate resistance [11, 12], reduced absorption and sorptivity [13, 14], and reduced chloride diffusivity with chloride binding into the aluminate phases [15, 16, 17].

These two bodies of evidence are almost always combined in the same way. A ternary mix is cast, its durability is compared with a plain control, and the outcome is reported as a single net figure. The difficulty is that such a comparison confounds two opposing effects of similar magnitude, since the pozzolan refines the pore structure while the agro-waste aggregate coarsens it. A net figure cannot distinguish a pozzolan that contributed little from one that contributed a great deal and was almost entirely cancelled. The two readings carry opposite design consequences: in the first there is nothing to be gained by adjusting the pozzolan, whereas in the second its dosage, fineness and reactivity are the levers available to a designer seeking a higher agro-waste replacement level.

Separating the two effects requires a third series. If units containing the pozzolan alone are exposed alongside the plain control and the ternary unit under an identical schedule, the change from control to pozzolan-only measures the pozzolan contribution and the change from pozzolan-only to ternary measures the aggregate penalty. The present programme has that structure, with a plain control, a unit containing 10% metakaolin and a unit containing 10% metakaolin with 25% palm kernel shell immersed in 3% Na₂SO₄ and 3% NaCl for up to 180 days.

Three methodological points are addressed alongside the decomposition. First, durability results of this kind are customarily reported as residual percentages at the tested ages, which cannot be compared across studies with different schedules and carry no predictive content; fitting a kinetic law reduces each series to a single rate constant, and the choice of law indicates the rate-controlling step. Second, if pore refinement is the mechanism by which the pozzolan acts, the fitted rate constants and an independent measure of pore volume should be quantitatively linked, and that link can be tested rather than assumed. Third, the alternate wetting and drying test as commonly reported compares the saturated strength after cycling with the oven-dry strength after cycling, a moisture-state difference present in any concrete and not a measure of damage by cycling.

Unit-level physical properties of the control and PKS-MK blocks, and the optimisation that established the 10% metakaolin and 25% palm kernel shell proportions, were reported previously [18, 19]. They are restated here only as the baseline against which the exposure results are read, and every quantity derived from them is new. The complementary route of improving masonry performance through the mortar rather than the unit has been examined by the present authors for infill walls under cyclic load [20], and the masonry-assemblage behaviour of the units studied here is reported separately [21].

2. Materials and methods

2.1. Materials

Ordinary Portland cement of 53 grade conforming to IS 12269:2013 [22] was used as the binder. Commercial metakaolin served as the cement replacement, and manufactured sand and 12.5 mm crushed stone conforming to IS 383:2016 [23] as the fine and coarse aggregates. Palm kernel shell was obtained from a palm-oil mill, washed, air dried and used in the fraction below 12.5 mm with a shell

thickness of 0.5 to 3 mm. Properties relevant to transport and durability are given in Table 1. The 19.75% water absorption of the shell against 0.42% for the crushed stone it replaces is a fifty-fold difference, and is the origin of every transport effect reported below. Full characterisation of all five constituents is given in [21].

Table 1
Properties of the constituent materials.

Property	Cement	Metakaolin	M-sand	Crushed stone	PKS
Specific gravity	3.15	2.60	2.64	2.67	1.16
Water absorption (%)	-	-	-	0.42	19.75
Fineness modulus	-	-	3.08	6.82	1.97
Loose bulk density (kg/m ³)	-	400 to 500	1657	1307	388
Compacted bulk density (kg/m ³)	-	-	1775	1428	494
Median particle size, D_{50} (um)	-	1.5 to 2.0	-	-	-
Specific surface area (cm ² /g)	3200	-	-	-	-
Lime reactivity (mg Ca(OH) ₂ /g)	-	1050	-	-	-
SiO ₂ (%)	19.11	52 to 54	-	-	-
Al ₂ O ₃ (%)	6.43	44 to 46	-	-	-
CaO (%)	63.78	0.09	-	-	-
Loss on ignition (%)	1.34	1.50	-	-	-

2.2. Block production and the three series

Three block types were produced on the same semi-automatic hydraulic block-making machine to a nominal size of 250 mm × 200 mm × 150 mm from a 1:3:6 mix proportioned by volume, and were water cured for 28 days. The control (C) contained neither metakaolin nor palm kernel shell. The metakaolin series (MK) replaced 10% of the cement by mass with metakaolin. The ternary series (PKS-MK) combined that replacement with 25% substitution of the coarse aggregate by palm kernel shell. Both replacement levels are the optima established by the earlier optimisation programme, which examined 0 to 15% metakaolin and 0 to 30% palm kernel shell across water-binder ratios of 0.50 to 0.65 [19], and are taken as given here. Composition and 28-day properties are summarised in Table 2.

One asymmetry in the programme requires declaration. The control and PKS-MK series correspond to a water-binder ratio of 0.60, at which the control reached 11.53 N/mm², whereas the MK series corresponds to the 0.55 ratio at which that mix reached its own optimum of 14.43 N/mm². The control

strength at 0.55 was 11.62 N/mm², so the two candidate baselines differ by 0.8%. The rate constants reported in Section 3.2 are fitted to residual strength normalised by the 0-day strength of the same series and are therefore invariant to the baseline value.

Dimensional compliance was verified on twenty units per type against IS 2185 (Part 1):2005 [24], which permits deviations of 5 mm in length and 3 mm in width and height. Measured deviations were 3.60, 1.60 and 0.75 mm for the control and 3.75, 1.55 and 0.60 mm for the PKS-MK units, so the nominal volume of $7.50 \times 10^{-3} \text{ m}^3$ is used throughout for density and porosity calculations.

Table 2
Composition and 28-day properties of the three block series.

Series	MK (%)	PKS (%)	w/b	f_c (N/mm ²)	Oven-dry density (kg/m ³)	Water absorption (%)	ϕ (% vol)	IRA (kg/m ² /min)
C	0	0	0.60	11.53	2181	3.39 (0.27)	7.40	1.20
MK	10	0	0.55	14.43	2193	0.71 (0.09)	1.56	not measured
PKS-MK	10	25	0.60	5.30	1980	1.46 (0.29)	2.89	0.96

Water absorption is the mean of three units with the standard deviation in parentheses. Oven-dry density is computed from the mean oven-dry mass and the nominal volume; the corresponding saturated-mass values reported earlier are 2187 and 2011 kg/m³ for the control and PKS-MK series [19]. Density, absorption and the initial rate of absorption of those two series were reported in [19]; the metakaolin series and the derived porosity are new.

2.3. Physical and transport properties

Oven-dry density was obtained on three units per type dried at 105°C to constant mass. Water absorption followed IS 2185 (Part 1):2005 [24]: three oven-dried units per type were weighed, immersed for 24 h, surface dried and reweighed, and absorption was taken as the mass gain as a percentage of the dry mass. The initial rate of absorption was measured to ASTM C67-05 [25] by standing an oven-dry unit in water 3.18 mm deep for one minute and dividing the mass gain by the bed area.

2.4. Chemical exposure

Resistance to sulphate and chloride environments was assessed within the framework of ASTM C452 [26] and ACI 318 [27], following the approach of Wild et al. [12] and Toledo Filho et al. [28]. Units of all three types, water cured for 28 days, were fully immersed in separate tanks holding 3% Na₂SO₄ and 3% NaCl by mass. Specimens were withdrawn at 56, 90, 150 and 180 days, surface dried, weighed and tested in compression on the 250 mm × 200 mm bed face. Residual mass and residual compressive

strength are expressed as percentages of the 0-day value for the same series. The solutions were not replenished or pH-controlled during exposure.

2.5. Alternate wetting and drying

Three units each of the control and PKS-MK types were subjected to seven wetting and drying cycles to ASTM C67 [25], each cycle comprising 24 h immersion followed by 24 h at laboratory temperature and humidity. Mass was recorded after every half-cycle. At the end of the seventh cycle, compressive strength was measured in two states: on saturated units immediately after the wetting half-cycle, and on units taken to constant mass in the drying half-cycle. The unconditioned 28-day strength of the same block type is used as the reference for cyclic damage, for the reason set out in Section 3.7.

2.6. Microstructural examination

Fragments taken from the interior of 28-day cured control and PKS-MK units were examined by scanning electron microscopy at 20 kV in secondary-electron mode at nominal magnifications of 1000× and 3000×. The specimens were not chemically exposed, so the micrographs characterise the pore structure that governs ingress rather than the products of attack.

2.7. Analysis

Water-accessible porosity is computed from the 24 h absorption and the oven-dry density. With w the absorption as a mass fraction of the dry mass, ρ_d the oven-dry density and ρ_w the density of water,

$$\varphi = w \rho_d / \rho_w \quad (1)$$

This converts a gravimetric measurement into the volumetric quantity used by transport theory, and it is the quantity that may legitimately be set beside the pore volume seen in a micrograph. It is an accessible and not a total porosity, since pores not filled within 24 h and pores unconnected to the surface are excluded; φ is therefore a lower bound on total porosity and an upper bound on the pore volume relevant to liquid-phase ingress.

Two competing kinetic laws are fitted to residual compressive strength. The first is first order in exposure time, appropriate where the rate-controlling step is a reaction whose extent is proportional to the sound material remaining,

$$S(t) / S(0) = \exp(-k t) \quad (2)$$

and the second is the square-root-of-time law characteristic of a diffusion-controlled advancing front,

$$S(t) / S(0) = 1 - a t^{1/2} \quad (3)$$

Both were fitted by least squares over the five measured ages, with $S(0)$ the 0-day strength of the same series, and are compared by coefficient of determination. From the fitted k , the time to a stated residual-strength threshold follows; the 70% level is adopted as a comparative serviceability marker,

$$t_{70} = \ln(1 / 0.70) / k \quad (4)$$

The deterioration mode is characterised by the ratio of proportional strength loss to proportional mass loss at 180 days,

$$D = (100 - S_{180}) / (100 - m_{180}) \quad (5)$$

in which S_{180} and m_{180} are residual strength and residual mass in per cent. A value near unity indicates that strength is lost in proportion to the material removed, whereas a large value indicates that the remaining material has been softened.

The decomposition is stated multiplicatively. For any property X , the metakaolin contribution δ_{MK} and the palm kernel shell penalty δ_{PKS} are

$$\delta_{MK} = X_{MK} / X_C - 1; \delta_{PKS} = X_{PKS-MK} / X_{MK} - 1 \quad (6)$$

and they compose to the net change as

$$\delta_{net} = (1 + \delta_{MK})(1 + \delta_{PKS}) - 1 \quad (7)$$

3. Results and discussion

3.1. Unit properties and accessible porosity

Metakaolin raises compressive strength from 11.53 to 14.43 N/mm², a gain of 24% over the control at the same water-binder ratio, consistent with the pozzolanic behaviour reported for metakaolin concretes generally [8, 15]. Replacing a quarter of the coarse aggregate with palm kernel shell reduces strength to 5.30 N/mm², 63% below the metakaolin unit and 54% below the control (Fig. 1a). The ternary unit nevertheless exceeds the 5 N/mm² required of a load-bearing solid concrete block by IS 2185 (Part 1):2005 [24], and its oven-dry density of 1980 kg/m³ remains above the 1800 kg/m³ minimum of the same standard.

The transport properties move in the opposite direction. Water absorption falls from 3.39% in the control to 0.71% with metakaolin, a reduction of 79%, and rises to 1.46% when palm kernel shell is introduced, an increase of 106% over the metakaolin value (Fig. 1b). The net result, 57% below the control, is the figure a two-series comparison would report, and read alone it suggests a moderately improved unit. Read as a decomposition it says something different: metakaolin removed four-fifths of the accessible pore space and palm kernel shell returned about half of what had been removed. The pozzolan is not making a marginal contribution that happens to survive, but is performing the task twice over, once to earn the improvement and once to pay for the aggregate.

Accessible porosity from Eq. (1) is 7.40% by volume for the control, 1.56% for the metakaolin unit and 2.89% for the PKS-MK unit (Fig. 1c), with the same structure of a 79% reduction followed by an 86% increase for a net reduction of 61%. The initial rate of absorption, available for the control and PKS-MK units, falls from 1.20 to 0.96 kg/m²/min, both inside the 0.25 to 1.5 kg/m²/min range that ASTM C67-05 [25] treats as acceptable for laying without excessive suction. Treating the one-minute uptake as a single-point estimate of initial sorptivity gives nominal values of 0.155 and 0.124 mm/s^{1/2}. These are upper bounds, because the first minute of uptake includes the filling of surface irregularities, which is why ASTM C1585 [31] fits a multi-point curve over 6 h [29, 30]; the ranking and the 20% separation between the two blocks are the defensible content. Both absorption values lie far inside the 10% by mass permitted by IS 2185 (Part 1):2005 [24], so absorption is not a binding criterion for either block and the interest in it is mechanistic.

3.2. Kinetics of strength loss under chemical exposure

Residual mass and residual compressive strength for all three series are given in Tables 3 and 4 and plotted in Fig. 2. Every series loses strength monotonically and none disintegrated within 180 days. Mass changes are small, between 2.4% and 4.2% at 180 days, while strength losses lie between 27% and 38%. Residual percentages in Tables 3 and 4 are recomputed from the measured masses and strengths; they differ from the values originally tabulated in two entries, where 98.80% and 95.42% were recorded against 98.50% and 96.40% on recomputation.

Table 3
Residual mass and compressive strength in 3% Na₂SO₄.

Series	Immersion (days)	Mass (kg)	Residual mass (%)	f_c (N/mm ²)	Residual strength (%)
C	0	16.39	100.00	11.53	100.00
	56	16.21	98.90	10.80	93.67
	90	16.11	98.29	9.20	79.79
	150	15.91	97.07	8.50	73.72
	180	15.80	96.40	7.40	64.18
MK	0	16.67	100.00	14.43	100.00
	56	16.58	99.46	13.80	95.63
	90	16.42	98.50	12.20	84.55
	150	16.31	97.84	11.20	77.62
	180	16.19	97.12	10.10	69.99
PKS-MK	0	15.06	100.00	5.30	100.00
	56	14.94	99.20	5.00	94.34
	90	14.85	98.61	4.30	81.13
	150	14.67	97.41	4.00	75.47
	180	14.43	95.82	3.50	66.04

Table 4
Residual mass and compressive strength in 3% NaCl.

Series	Immersion (days)	Mass (kg)	Residual mass (%)	f_c (N/mm ²)	Residual strength (%)
C	0	16.38	100.00	11.53	100.00
	56	16.29	99.45	11.00	95.40
	90	16.09	98.23	9.80	85.00
	150	15.98	97.56	7.80	67.65
	180	15.72	95.97	7.10	61.58
MK	0	16.69	100.00	14.43	100.00
	56	16.62	99.58	13.94	96.60
	90	16.47	98.68	13.00	90.09
	150	16.42	98.38	11.50	79.70
	180	16.29	97.60	10.60	73.46
PKS-MK	0	15.07	100.00	5.30	100.00
	56	14.99	99.47	5.10	96.23
	90	14.84	98.47	4.60	86.79
	150	14.76	97.94	3.70	69.81
	180	14.59	96.81	3.34	63.02

The two candidate laws are readily distinguished. The first-order form of Eq. (2) fits with coefficients of determination of 0.942 to 0.946 in sulphate and 0.899 to 0.926 in chloride, whereas the square-root-of-time form of Eq. (3) gives 0.805 to 0.832 and 0.730 to 0.753 on the same data (Table 5). The first-order law is the better description of all six series and the margin is substantial, the unexplained variance roughly tripling under the diffusion form. Over this exposure period the rate-controlling step is therefore not the advance of an ingress front into a large specimen but a reaction distributed through a small, fully immersed unit whose rate is proportional to the sound material remaining. This is physically reasonable for a 150 mm thick unit immersed on all faces, and it matters for extrapolation, since a first-order law predicts a slower late-age loss than a square-root law fitted to the same early data.

Fitted rate constants are 2.225, 1.782 and 2.068×10^{-3} per day in sulphate for the control, metakaolin and PKS-MK series, and 2.370, 1.491 and 2.201×10^{-3} per day in chloride (Fig. 3a). Chloride is the more aggressive medium for the control and the less aggressive for the metakaolin unit, a first indication that the pozzolan acts differently against the two ions. Expressed through Eq. (4) as a time to 70% residual

strength, the metakaolin unit gains 25% over the control in sulphate and 59% in chloride, while the PKS-MK unit gains 8% in both.

One inconsistency in the source records is declared here. The sulphate control series exists in two versions, with residual strengths of 93.67%, 79.79%, 73.72% and 64.18% in the record tabulated alongside the PKS-MK data and 93.67%, 77.19%, 65.92% and 50.30% in the record tabulated alongside the metakaolin data. The two agree at 56 days and diverge thereafter. The first has been adopted throughout, because it is the record tabulated with the series against which the comparison is drawn and because it is the conservative choice, giving the smaller apparent benefit for both blended units. The second is plotted in Fig. 2a and its consequence is quantified in Section 3.3. The chloride control series is identical in both records.

Table 5
Fitted kinetic parameters and derived durability measures.

Exposure	Series	k , Eq. (2) ($\times 10^{-3} \text{ d}^{-1}$)	R^2 , Eq. (2)	a , Eq. (3) ($\text{d}^{-1/2}$)	R^2 , Eq. (3)	k for mass ($\times 10^{-3} \text{ d}^{-1}$)	D , Eq. (5)	t_{70} (days)	Loss rate (N/mm^2 per 100 d)
3% Na_2SO_4	C	2.225	0.946	0.022	0.832	0.200	9.95	160	2.29
	MK	1.782	0.944	0.018	0.805	0.154	10.42	200	2.41
	PKS-MK	2.068	0.942	0.021	0.822	0.201	8.12	172	1.00
	C, second record	3.050	0.908	0.028	0.772	0.200	13.81	117	3.18
3% NaCl	C	2.370	0.913	0.023	0.753	0.197	9.54	150	2.46
	MK	1.491	0.926	0.015	0.752	0.125	11.08	239	2.13
	PKS-MK	2.201	0.899	0.021	0.730	0.160	11.61	162	1.09

3.3. Contributions of metakaolin and palm kernel shell

Applying Eqs. (6) and (7) to the rate constants (Table 6), metakaolin reduces the sulphate rate constant by 19.9% and palm kernel shell then increases it by 16.0%, leaving a net reduction of 7.1%. In chloride, metakaolin reduces it by 37.1% and palm kernel shell increases it by 47.7%, again leaving a net reduction of 7.1%. The near-identical net figures are a coincidence of these particular magnitudes and should not be over-read, but the structure behind them should not be under-read either. In chloride the pozzolan is nearly twice as effective as in sulphate and the aggregate penalty is three times larger, and the two happen to cancel to the same net value. A study reporting only the net figure would conclude that the two exposures behave alike, which they do not.

The asymmetry is consistent with the established mechanisms. Against sulphate, metakaolin acts mainly by consuming calcium hydroxide and so limiting the gypsum and ettringite available to form, with a secondary reduction in permeability [11, 12, 32]; that protection is chemical and depends only weakly on the transport path. Against chloride, protection comes from reduced diffusivity and from binding of chloride into the aluminate phases [16, 17], both of which act on the ingress path itself. A coarsened and better-connected pore system of the kind palm kernel shell introduces damages the second mechanism far more than the first, which is precisely the asymmetry the decomposition recovers.

The practical consequence is a design lever. Because the pozzolan contributes 20% to 37% and the aggregate costs 16% to 48%, the two are of the same order and the balance can be shifted. Raising the metakaolin dosage, increasing its fineness, or accepting a lower palm kernel shell replacement would each move the net figure, and the decomposition quantifies how far each would have to move. A net comparison offers no such guidance.

If the alternative sulphate control record of Section 3.2 is adopted instead, the metakaolin contribution in sulphate becomes a reduction of 41.6%, the palm kernel shell penalty is unchanged at 16.0%, and the net improvement becomes 32.2% rather than 7.1%. The conclusion that the pozzolan earns the durability and the aggregate consumes most of it is unaffected and indeed strengthened, but the quantitative net figure is not robust to this ambiguity, and the conservative value is the one carried into the abstract and the conclusions.

Table 6
Metakaolin and palm kernel shell contributions to each property.

Property	C	MK	PKS-MK	MK contribution (%)	PKS penalty (%)	Net change (%)
Compressive strength (N/mm ²)	11.53	14.43	5.30	+ 25.2	-63.3	-54.0
Oven-dry density (kg/m ³)	2181	2193	1980	+ 0.6	-9.7	-9.2
Water absorption (%)	3.39	0.71	1.46	-79.1	+ 105.6	-57.0
Accessible porosity (% vol)	7.40	1.56	2.89	-79.0	+ 85.7	-60.9
k , sulphate ($\times 10^{-3} \text{ d}^{-1}$)	2.225	1.782	2.068	-19.9	+ 16.0	-7.1
k , chloride ($\times 10^{-3} \text{ d}^{-1}$)	2.370	1.491	2.201	-37.1	+ 47.7	-7.1

A negative sign denotes a reduction in the property; for strength a reduction is adverse, while for absorption, porosity and the rate constants a reduction is beneficial. The metakaolin contribution to strength is + 24.2% if computed against the control at the matched water-binder ratio of 0.55.

3.4. Dependence of the degradation rate on accessible porosity

If pore refinement were the entire mechanism, the fitted rate constants should scale with accessible porosity. Figure 3b tests this. The three points are correctly ordered in both media, the series of lowest accessible porosity degrading most slowly, and a linear fit gives 0.065×10^{-3} per day per percentage point of porosity in sulphate ($r = 0.89$) and 0.122 in chloride ($r = 0.80$). With three points these correlations carry little weight in themselves.

The magnitudes are unambiguous and require no regression. Accessible porosity falls by a factor of 4.75 between the control and the metakaolin unit, while the rate constant falls by a factor of only 1.25 in sulphate and 1.59 in chloride. As a power law, k varies as $\phi^{0.14}$ in sulphate and $\phi^{0.28}$ in chloride. A five-fold reduction in the pore volume accessible to water buys a 20% to 37% reduction in the rate of strength loss. Pore volume is thus a weak predictor of durability in this material system, and the common practice of inferring durability from an absorption test, attractive because absorption is cheap to measure, is not supported by these data.

Two explanations are available. Total accessible volume may simply be the wrong descriptor, since ingress rate depends on the connectivity and characteristic size of the pores rather than on their volume, and metakaolin is known to shift the pore-size distribution more than the total porosity [9]. Alternatively, part of the protection is chemical rather than transport-related, through calcium hydroxide consumption against sulphate and chloride binding against chloride, and is therefore invisible to a porosity measure. The larger porosity exponent in chloride is consistent with chloride attack being the more transport-controlled of the two. Distinguishing the explanations requires mercury intrusion porosimetry or a multi-point sorptivity measurement, neither of which was available here.

3.5. Relation between mass loss and strength loss

From Eq. (5) at 180 days, the ratio of proportional strength loss to proportional mass loss is 9.95, 10.42 and 8.12 for the control, metakaolin and PKS-MK series in sulphate, and 9.54, 11.08 and 11.61 in chloride. All six values lie between 8 and 12, so strength is lost roughly ten times faster than mass throughout.

A unit losing strength by surface erosion would lose the two in proportion. A ratio near ten indicates instead that the material remaining has been weakened, by expansive product forming within the pore network in the sulphate case and by leaching of calcium hydroxide with local decalcification of the hydrate in the chloride case, the mechanism to which the reduced surface leaching of metakaolin-bearing mixes is usually attributed [14, 16]. There is a testing consequence. A durability assessment based on mass change alone, frequently all that is reported for masonry units because it is non-destructive, understates strength loss by an order of magnitude: at 180 days in sulphate the PKS-MK unit had lost 4.2% of its mass and 34.0% of its strength.

The ratio is not diagnostic of which block performs better, being nearly the same for all three. What differs is the absolute rate. In sulphate the control loses 2.29 N/mm^2 per 100 days of immersion against 1.00 N/mm^2 for the PKS-MK unit, and in chloride 2.46 against 1.09 N/mm^2 . The PKS-MK unit loses less than half as much strength in absolute terms, simply because it has less to lose, and this is the appropriate measure when the question is whether a wall retains its design capacity rather than which mix is intrinsically more resistant.

3.6. Residual load-bearing capacity

The 180-day residual strengths of the PKS-MK unit are 3.50 N/mm^2 after sulphate immersion and 3.34 N/mm^2 after chloride immersion, that is 70% and 67% of the 5 N/mm^2 minimum that IS 2185 (Part 1):2005 [24] requires of the load-bearing grade to which the units were manufactured. The control, at 7.40 and 7.10 N/mm^2 , retains 148% and 142% of that minimum.

The consequence for a wall follows from the masonry efficiency of the assemblage, measured at 53% to 66% for unplastered stack-bonded prisms of these units [21]. Applying that range to the residual unit strength gives a prism strength of 1.85 to 2.31 N/mm^2 after sulphate exposure and 1.77 to 2.20 N/mm^2 after chloride exposure, and a corresponding IS 1905:1987 [33] basic compressive stress of 0.46 to 0.58 and 0.44 to 0.55 N/mm^2 . Against the as-built values of 0.90 to 1.03 N/mm^2 for the same masonry [21], sustained immersion for 180 days would leave 52% to 56% of the permissible stress. A wall of this material in permanently saturated aggressive ground would therefore require design at approximately half the as-built permissible stress, or protection. Continuous immersion in 3% solution is a severe accelerated condition rather than a service condition for a wall above damp-proof course, so the calculation bounds the penalty rather than predicting it.

3.7. Alternate wetting and drying response

After seven cycles the control gave 4.80 N/mm^2 saturated and 7.40 N/mm^2 oven dry, and the PKS-MK unit 3.20 and 4.90 N/mm^2 (Fig. 4a). The customary metric is the difference between these two expressed as a percentage of the dry value, which yields 35.1% for the control and 34.7% for the PKS-MK unit: two nearly equal and apparently large reductions.

Those figures do not measure damage. Both strengths were obtained on the same specimens at the same age and differ only in moisture state, so the quantity is the familiar reduction in compressive strength of a saturated concrete relative to a dry one, caused by pore-water pressure and by the reduction in surface energy of the hydrate. The correct reading is that the two blocks have the same saturation sensitivity, the ratio of saturated to dry strength being 0.649 for the control and 0.653 for the PKS-MK unit. That the porous agro-waste aggregate does not increase saturation sensitivity is itself a useful result.

Damage by cycling is a different quantity and requires the unconditioned 28-day strength as reference. On that basis the control fell from 11.53 to 7.40 N/mm^2 oven dry, a loss of 35.8%, while the PKS-MK unit

fell from 5.30 to 4.90 N/mm², a loss of 7.5% (Fig. 4b). The conclusion reverses: measured as saturation the two blocks are indistinguishable, but measured as cyclic damage the PKS-MK unit is nearly five times more resistant. A plausible reading is that the control, with 7.40% accessible porosity in a stiff matrix, accumulates more microcracking from differential shrinkage and swelling than the PKS-MK unit, whose lower stiffness and compressible aggregate accommodate the same moisture-driven strain at lower stress.

This reading remains provisional on two counts. The seven-cycle mass gains of 2.23% for the control and 2.81% for the PKS-MK unit are not consistent with the 24 h absorption values of 3.39% and 1.46%: the control gains less than its absorption capacity, as expected from an air-dry starting condition, but the PKS-MK unit gains 1.9 times its measured absorption, which cannot occur if both tests begin from the same moisture state. Either the two tests used different initial conditions or one of the two absorption figures is in error. In addition, no unconditioned specimens were carried alongside the cycled ones, so the reference strength comes from a different batch.

3.8. Microstructure

The control matrix (Fig. 5a, b) presents an open texture in which large capillary voids are visible between angular hydration products and the boundaries between adjacent product clusters are distinct, indicating a connected void network. The PKS-MK matrix (Fig. 5c, d) is visibly finer and more continuous, the fields being filled by small, closely packed platy products with few resolvable voids at either magnification and a less sharp transition between clusters.

This is the texture expected of a metakaolin-bearing matrix. The pozzolanic reaction consumes calcium hydroxide and precipitates secondary calcium silicate hydrate which, although less dense than the primary gel, subdivides large capillary voids into smaller and disconnected ones [8, 9]. The filler contribution reinforces it, since metakaolin particles of 1.5 to 2.0 µm median size are roughly an order of magnitude finer than the cement they replace and occupy interstitial space that cement grains cannot reach [10]. The micrographs are consistent with the four-fold reduction in accessible porosity of Section 3.1. Two limits apply. The images are qualitative, since no image analysis was performed and no pore-size distribution was extracted, so they corroborate the direction of the porosity result without adding an independent quantity to it; and the specimens were unexposed, so the mechanistic statements of Section 3.3 rest on the kinetics and on the published literature rather than on these images.

3.9. Flexural strength measurement

Flexural strength was obtained in the source programme to IS 4860:1968 [34] by loading the unit across a 250 mm span and applying the modulus-of-rupture expression $f_r = 3PL / (2bd^2)$ with $b = 200$ mm and $d = 150$ mm, giving 8.06, 8.80 and 3.74 N/mm² for the control, metakaolin and PKS-MK units. These values are 70%, 61% and 71% of the respective compressive strengths, and recomputation confirms the arithmetic exactly, the expression reducing to $f_r = P / 12000$ for this geometry.

The arithmetic is not at fault. A modulus of rupture of 60% to 70% of compressive strength is not physically attainable in a cementitious material, for which the ratio is typically 10% to 20%; the IS 456:2000 [35] estimate $0.7f_c^{1/2}$ gives 2.38, 2.66 and 1.61 N/mm² for these blocks, between a half and a third of the reported figures. The cause is geometric. The span-to-depth ratio of the test is 1.67, whereas beam theory requires roughly 4 or more and the standard flexural test for concrete, ASTM C78 [36], uses 3. At a span-to-depth ratio of 1.67 the specimen behaves as a deep member in which load is carried substantially by direct compressive strut action to the supports, so failure occurs well above the load corresponding to the flexural tensile strength and the beam-theory expression converts that load into a fictitious stress. Taking $0.7f_c^{1/2}$ as the true modulus of rupture, beam theory would predict failure at 28.5, 31.9 and 19.3 kN against the 96.72, 105.6 and 44.88 kN measured, a factor of 2.3 to 3.4 and the expected order for arching action at this geometry.

No flexural strength is therefore reported for these units. The failure loads are reproducible and their ranking is meaningful, but they cannot be converted into a tensile strength by beam theory. Where a tensile property is required, splitting tension on cores or a flexural test on companion prisms of span-to-depth ratio at least 3 should be used. The point is recorded because the same computation appears in published work on agro-waste masonry units.

3.10. Limitations

Six limitations bound the conclusions. The exposure series report a single value at each age rather than a mean with scatter, so no confidence intervals can be attached to the rate constants and the coefficients of determination in Table 5 describe the fit of a curve to five single measurements; the internal consistency of the fits, all above 0.89 for the adopted law, is the only available evidence of precision. The two versions of the sulphate control series leave the net sulphate improvement uncertain between 7.1% and 32.2%, and the conservative figure is reported. No diffraction or spectroscopic examination was performed on exposed material, so the attack products are inferred rather than identified and the mechanistic discussion is correspondingly bounded. Sorptivity was measured at a single time point of one minute rather than fitted over 6 h to ASTM C1585 [31], so the reported values are nominal. The immersion solutions were not replenished or pH-controlled, so the effective severity may have declined with exposure time, which would bias the fitted rate constants downwards in proportion to the extent of solution depletion and affects all three series alike. Finally, the metakaolin series was produced at a water-binder ratio of 0.55 against 0.60 for the other two, as declared in Section 2.2; the rate constants are invariant to this, but the absolute strength comparison carries an uncertainty of about 1%.

Two of these are inexpensive to remedy and would materially strengthen the evidence: triplicate specimens at each age, and diffraction or spectroscopic identification of the products formed in the sulphate-exposed material.

4. Conclusions

Solid concrete masonry units of three compositions, comprising a plain control, a unit with 10% of the cement replaced by metakaolin, and a unit combining that replacement with 25% palm kernel shell as coarse aggregate, were immersed in 3% Na₂SO₄ and 3% NaCl for up to 180 days and characterised for absorption, accessible porosity, wetting and drying response and microstructure. The three-series design allows the durability change to be separated into a pozzolan contribution and an agro-waste aggregate penalty.

The three-series design separates the durability change into a pozzolan contribution and an agro-waste aggregate penalty. Water-accessible porosity, computed from absorption and oven-dry density, is 7.40% by volume for the control, 1.56% with metakaolin and 2.89% with metakaolin and palm kernel shell, so metakaolin removes 79% of the accessible pore volume while palm kernel shell returns 86% of what remains, for a net reduction of 61%. Loss of compressive strength under both exposures is first order in immersion period ($R^2 = 0.899$ to 0.946) and is not described by a square-root-of-time law ($R^2 = 0.730$ to 0.832), so the rate-controlling step over 180 days is a distributed reaction rather than the advance of a diffusion front.

Metakaolin reduces the first-order rate constant by 19.9% in sulphate and 37.1% in chloride, while palm kernel shell returns 16.0% and 47.7% of that gain, leaving a net improvement over the control of 7.1% in both media. The pozzolan therefore earns the durability of the ternary unit and the agro-waste aggregate consumes most of it, and because the two contributions are of the same order the balance between them is a design variable rather than a fixed property of the mix. The pozzolan is about twice as effective against chloride as against sulphate and the aggregate penalty is three times larger in chloride, which is consistent with chloride protection acting on the transport path and sulphate protection acting chemically, and which a two-series comparison cannot reveal. Pore volume alone does not account for the effect: the rate constant varies with accessible porosity as the 0.14 power in sulphate and the 0.28 power in chloride, so a 4.75-fold reduction in accessible pore volume yields only a 1.25 to 1.59-fold reduction in degradation rate, and absorption is therefore a weak proxy for durability in this material system.

Proportional strength loss exceeds proportional mass loss by a factor of 8.1 to 11.6 in every series, which identifies matrix softening rather than material removal as the deterioration mode and shows that a mass-change assessment understates strength loss by about an order of magnitude. After 180 days of continuous immersion the PKS-MK unit retains 3.50 N/mm² in sulphate and 3.34 N/mm² in chloride, that is 70% and 67% of the 5 N/mm² load-bearing minimum, while the control retains 142% to 148% of it. Applying the masonry efficiency measured on the same units, the residual strengths correspond to 52% to 56% of the as-built permissible compressive stress.

Two measurement conclusions follow from the same programme. The conventional alternate wetting and drying metric measures saturation rather than damage, the saturated-to-dry strength ratio being 0.649 for the control and 0.653 for the PKS-MK unit; referred instead to the unconditioned 28-day strength, cyclic damage after seven cycles is 35.8% for the control and 7.5% for the PKS-MK unit. The

modulus-of-rupture expression cannot be applied to a 250 × 200 × 150 mm unit tested over a 250 mm span, for which the span-to-depth ratio is 1.67, so the flexural strengths of 60% to 70% of compressive strength obtained in that way are an artefact of arching action and no flexural strength is reported here.

Taken together, the results support conditional use of metakaolin-blended palm kernel shell masonry units in load-bearing walling above damp-proof course and away from sustained chemical exposure, and they identify the metakaolin dosage rather than the palm kernel shell content as the variable through which durability is most efficiently obtained. Modification of the bed-joint mortar, examined by the present authors for infill masonry under cyclic load [20], offers a complementary route that the present programme does not address.

Declarations

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Author Contribution

N.J. and S.V.S.J. conceived and designed the study. N.J. procured and characterised the materials, cast and cured the masonry units, and carried out the sulphate and chloride immersion, mass loss, compressive strength, water absorption, initial rate of absorption, wetting–drying cycle and electron microscopy tests. N.J. and S.V.S.J. analysed the data, developed the kinetic and porosity models, and prepared all figures and tables. S.V.S.J. wrote the main manuscript text with input from N.J. G.H. provided supervision, resources and critical review of the experimental programme and results. S.V.S.J. and G.H. revised the manuscript. All authors reviewed and approved the final manuscript.

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Data availability

The data supporting the findings of this study are contained within the article.

References

1. Alengaram, U. J., Muhit, B. A. A., & Jumaat, M. Z. (2013). Utilization of oil palm kernel shell as lightweight aggregate in concrete: A review. *Construction and Building Materials*, 38, 161–172. <https://doi.org/10.1016/j.conbuildmat.2012.08.026>
2. Okafor, F. O. (1988). Palm kernel shell as a lightweight aggregate for concrete. *Cement and Concrete Research*, 18, 901–910. [https://doi.org/10.1016/0008-8846\(88\)90026-9](https://doi.org/10.1016/0008-8846(88)90026-9)
3. Shafigh, P., Jumaat, M. Z., & Mahmud, H. (2011). Oil palm shell as a lightweight aggregate for production high strength lightweight concrete. *Construction and Building Materials*, 25, 1848–1853. <https://doi.org/10.1016/j.conbuildmat.2010.11.075>
4. Mannan, M., & Ganapathy, C. (2004). Concrete from an agricultural waste-oil palm shell (OPS), Building and Environment 39 441–448. <https://doi.org/10.1016/j.buildenv.2003.10.007>
5. Teo, D., Mannan, M., Kurian, V., & Ganapathy, C. (2007). Lightweight concrete made from oil palm shell (OPS): Structural bond and durability properties. *Building and Environment*, 42, 2614–2621. <https://doi.org/10.1016/j.buildenv.2006.06.013>
6. Shafigh, P., Johnson Alengaram, U., Mahmud, H. B., & Jumaat, M. Z. (2013). Engineering properties of oil palm shell lightweight concrete containing fly ash. *Materials and Design*, 49, 613–621. <https://doi.org/10.1016/j.matdes.2013.02.004>
7. Muntohar, A. S., & Rahman, M. E. (2014). Lightweight masonry block from oil palm kernel shell. *Construction and Building Materials*, 54, 477–484. <https://doi.org/10.1016/j.conbuildmat.2013.12.087>
8. Siddique, R., & Klaus, J. (2009). Influence of metakaolin on the properties of mortar and concrete: A review. *Applied Clay Science*, 43, 392–400. <https://doi.org/10.1016/j.clay.2008.11.007>
9. Frias, M., & Cabrera, J. (2000). Pore size distribution and degree of hydration of metakaolin: cement pastes. *Cement and Concrete Research*, 30, 561–569. [https://doi.org/10.1016/s0008-8846\(00\)00203-9](https://doi.org/10.1016/s0008-8846(00)00203-9)
10. Weng, T. L., Lin, W. T., & Cheng, A. (2013). Effect of Metakaolin on Strength and Efflorescence Quantity of Cement-Based Composites. *The Scientific World Journal*, 2013. <https://doi.org/10.1155/2013/606524>
11. Khatib, J., & Wild, S. (1998). Sulphate Resistance of Metakaolin Mortar. *Cement and Concrete Research*, 28, 83–92. [https://doi.org/10.1016/s0008-8846\(97\)00210-x](https://doi.org/10.1016/s0008-8846(97)00210-x)
12. Wild, S., Khatib, J., & O'Farrell, M. (1997). Sulphate resistance of mortar, containing ground brick clay calcined at different temperatures. *Cement and Concrete Research*, 27, 697–709. [https://doi.org/10.1016/s0008-8846\(97\)00059-8](https://doi.org/10.1016/s0008-8846(97)00059-8)
13. Courard, L., Darimont, A., Schouterden, M., Ferauche, F., Willem, X., & Degeimbre, R. (2003). Durability of mortars modified with metakaolin. *Cement and Concrete Research*, 33, 1473–1479. [https://doi.org/10.1016/s0008-8846\(03\)00090-5](https://doi.org/10.1016/s0008-8846(03)00090-5)
14. Khatib, J. M., & Clay, R. M. (2004). Absorption characteristics of metakaolin concrete, Cement and Concrete Research 34 19–29. [https://doi.org/10.1016/s0008-8846\(03\)00188-1](https://doi.org/10.1016/s0008-8846(03)00188-1)

15. Ramezaniapour, A., & Bahrami Jovein, H. (2012). Influence of metakaolin as supplementary cementing material on strength and durability of concretes. *Construction and Building Materials*, 30, 470–479. <https://doi.org/10.1016/j.conbuildmat.2011.12.050>
16. Poon, C., Kou, S., & Lam, L. (2006). Compressive strength, chloride diffusivity and pore structure of high performance metakaolin and silica fume concrete. *Construction and Building Materials*, 20, 858–865. <https://doi.org/10.1016/j.conbuildmat.2005.07.001>
17. Chang, H., Wang, X., Wang, Y., Li, C., Guo, Z., Fan, S., Zhang, H., & Feng, P. (2023). Chloride binding behavior of cement paste influenced by metakaolin dosage and chloride concentration. *Cement and Concrete Composites*, 135, 104821. <https://doi.org/10.1016/j.cemconcomp.2022.104821>
18. John, N., Shanthi, R. M., Tensing, D., & Prospects of Metakaolin Admixed Palm Kernel Shell Solid Concrete Masonry Block. (2022). *A Review Civil Engineering and Architecture* 10 1354–1372. <https://doi.org/10.13189/cea.2022.100410>.
19. John, N., Tensing, D., Sam Jebadurai, V., & Srisanthi, S. (2023). V.G., Assessment of Metakaolin Blended Palm Kernel Shell Solid Concrete Blocks as a Sustainable Building Material, IOP Conference Series: Earth and Environmental Science 1237 012002. <https://doi.org/10.1088/1755-1315/1237/1/012002>
20. Jebadurai, S. V. S., Tensing, D., Pradhan, P. M., & Hemalatha, G. (2020). Enhancing performance of infill masonry with latex modified mortar subjected to cyclic load. *Structures*, 23, 551–557. <https://doi.org/10.1016/j.istruc.2019.11.001>
21. John, N., Vincent Sam Jebadurai, S., Hemalatha, G., & Tensing, D. (2026). Compressive and bond behaviour of load-bearing masonry built with metakaolin-blended palm kernel shell concrete blocks: prism slenderness, plaster contribution and code-based assessment, manuscript in preparation.
22. IS 12269: (2013). Ordinary Portland Cement, 53 Grade: Specification, Bureau of Indian Standards, New Delhi, 2013.
23. IS 383:2016. (2016). *Coarse and Fine Aggregate for Concrete*. Specification, Bureau of Indian Standards.
24. IS 2185 (. (2005). *Part 1):2005, Concrete Masonry Units, Part 1: Hollow and Solid Concrete Blocks*. Bureau of Indian Standards.
25. ASTM C67-05. (2005). *Standard Test Methods for Sampling and Testing Brick and Structural Clay Tile*. ASTM International.
26. ASTM C452 Standard Test Method for Potential Expansion of Portland-Cement Mortars Exposed to Sulfate, ASTM International, West Conshohocken, PA.
27. ACI 318 Building Code Requirements for Structural Concrete and Commentary, American Concrete Institute, Farmington Hills, MI.
28. Toledo Filho, R., Goncalves, J., Americano, B., & Fairbairn, E. (2007). Potential for use of crushed waste calcined-clay brick as a supplementary cementitious material in Brazil. *Cement and Concrete Research*, 37, 1357–1365. <https://doi.org/10.1016/j.cemconres.2007.06.005>

29. Hall, C. (1989). Water sorptivity of mortars and concretes: a review. *Magazine of Concrete Research*, 41, 51–61. <https://doi.org/10.1680/mac.1989.41.147.51>
30. Tasdemir, C. (2003). Combined effects of mineral admixtures and curing conditions on the sorptivity coefficient of concrete. *Cement and Concrete Research*, 33, 1637–1642. [https://doi.org/10.1016/s0008-8846\(03\)00112-1](https://doi.org/10.1016/s0008-8846(03)00112-1)
31. ASTM C1585 Standard Test Method for Measurement of Rate of Absorption of Water by Hydraulic-Cement Concretes, ASTM International, West Conshohocken, PA.
32. Marchand, J., Odler, I., & Skalny, J. P. (2001). *Sulfate Attack on Concrete*. Spon.
33. IS 1905:1987. (1987). *Code of Practice for Structural Use of Unreinforced Masonry*. Bureau of Indian Standards.
34. IS 4860: (1968). Specification for Acid Resistant Bricks, Bureau of Indian Standards, New Delhi, 1968.
35. IS 456 (2000). Plain and Reinforced Concrete: Code of Practice, Bureau of Indian Standards, New Delhi, 2000.
36. ASTM C78 Standard Test Method for Flexural Strength of Concrete Using Simple Beam with Third-Point Loading, ASTM International, West Conshohocken, PA.

Figures

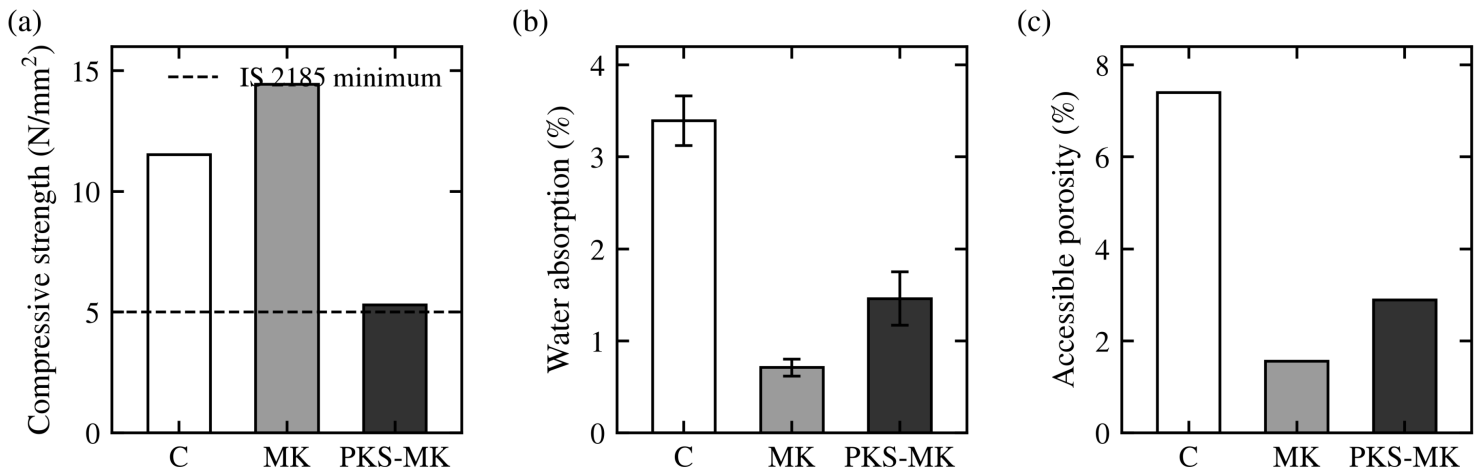


Figure 1

Compressive strength (a), water absorption (b) and accessible porosity (c) of the three block series.

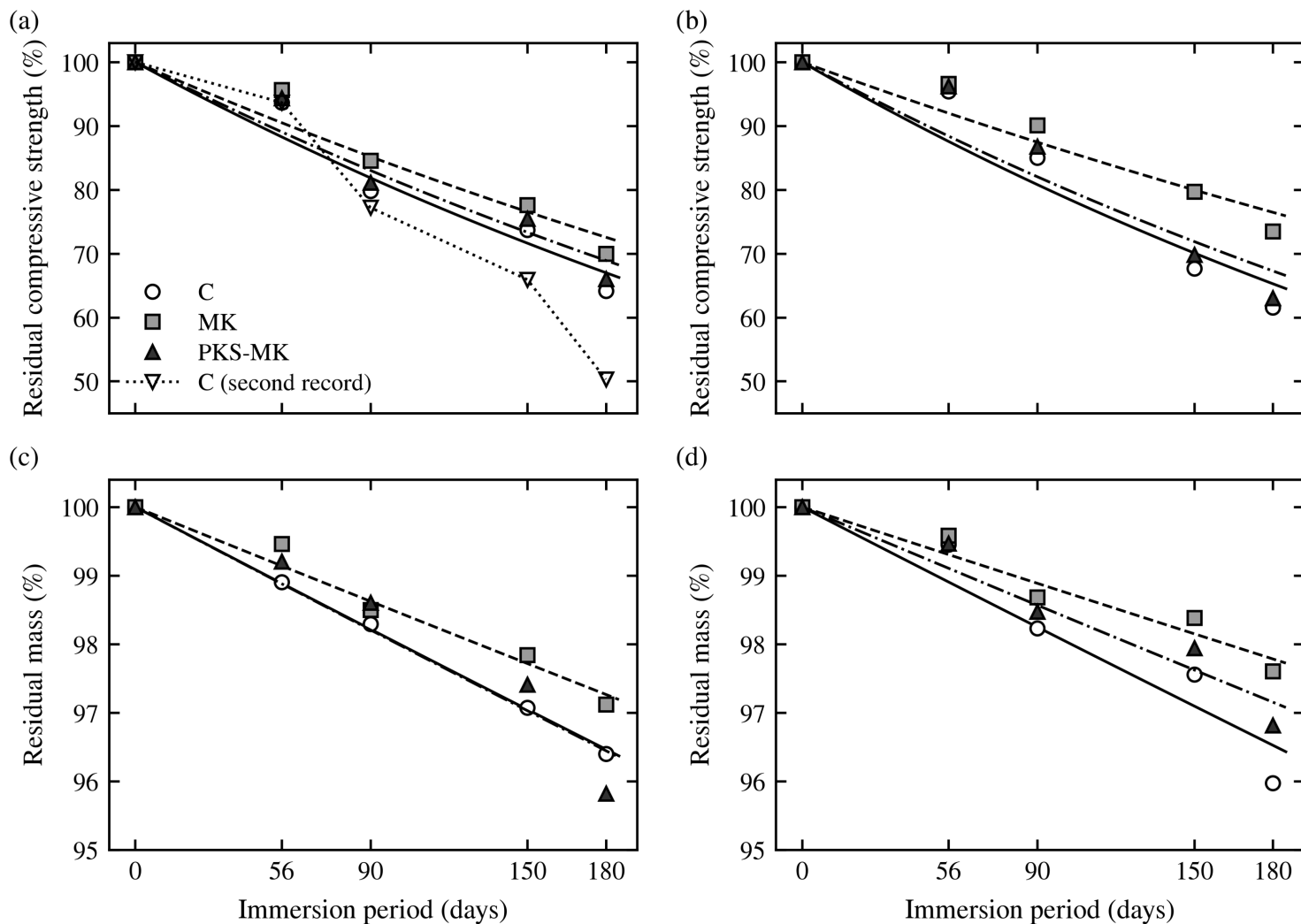


Figure 2

Residual compressive strength (a, b) and residual mass (c, d) in 3% Na_2SO_4 (a, c) and 3% NaCl (b,

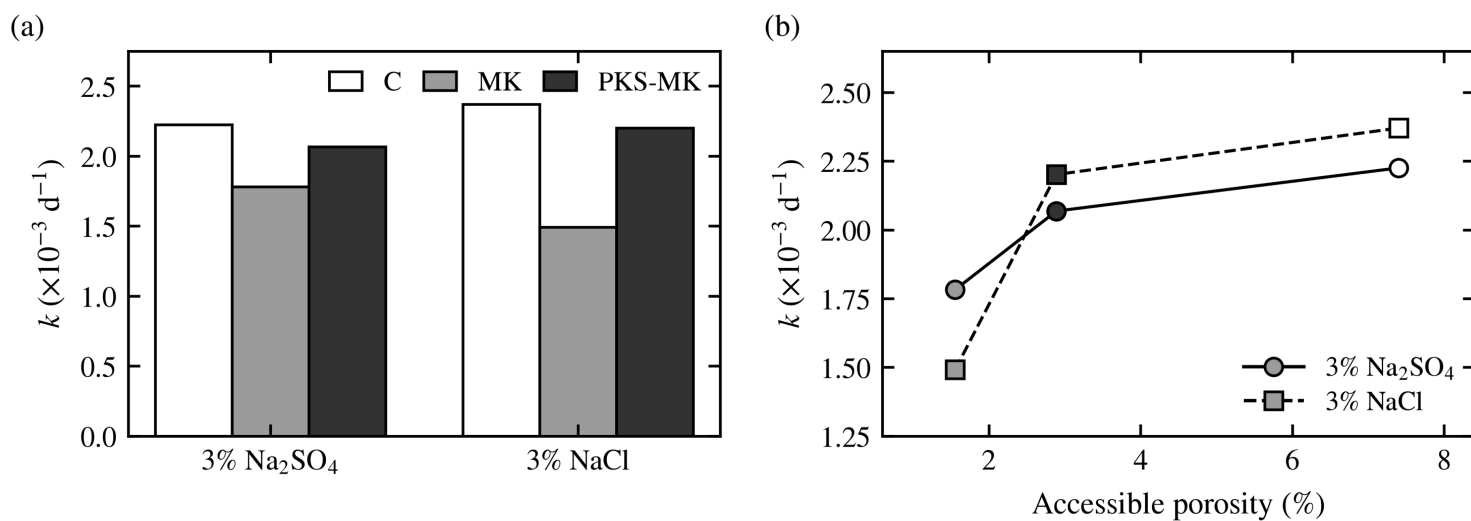


Figure 3

First-order rate constants (a) and their dependence on accessible porosity (b).

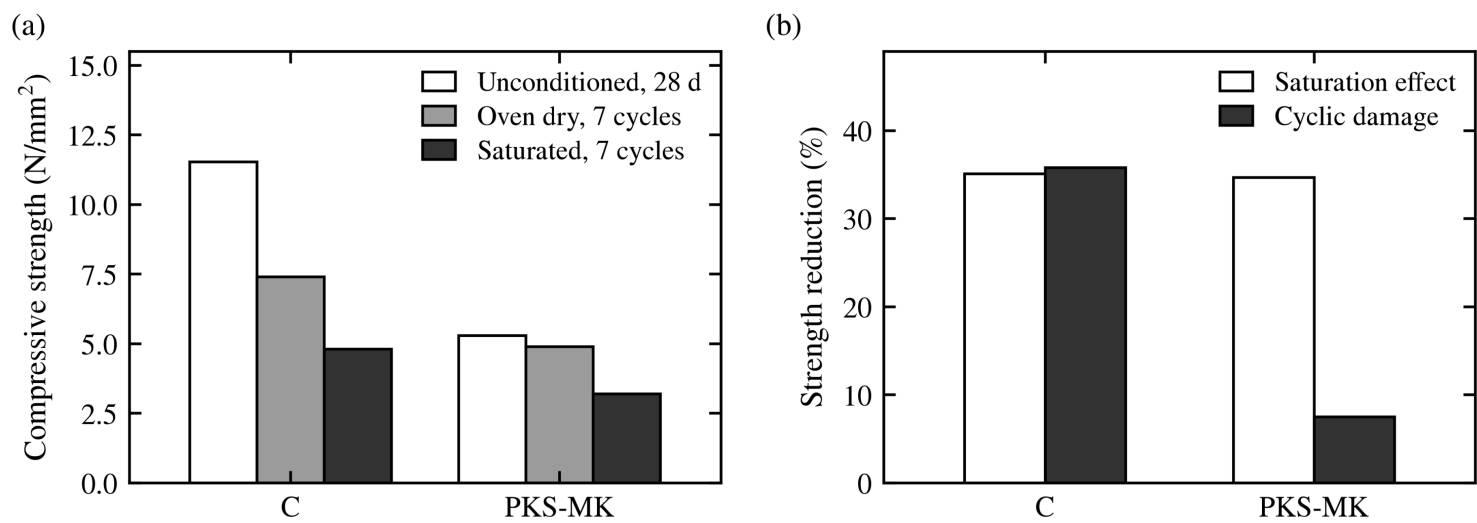


Figure 4

Compressive strength (a) and strength-reduction metrics (b) after seven wetting and drying cycles.

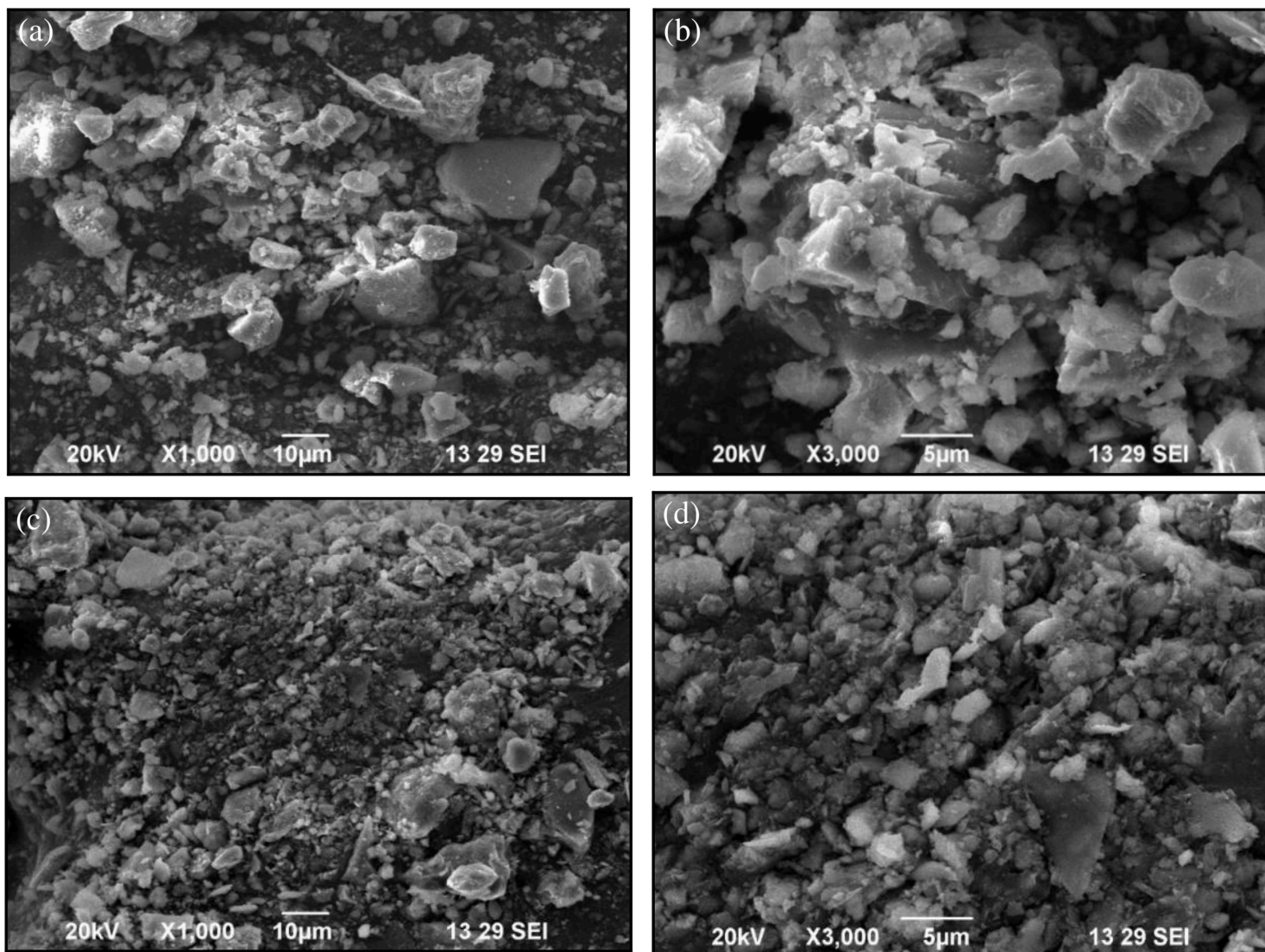


Figure 5

Micrographs of the control (a, b) and PKS-MK (c, d) matrices at 1000× and 3000×.