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Pozzolanic Activity of Recycled Red Ceramic Bricks

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ABSTRACT

The practice of using finely powdered red ceramic brick waste as a pozzolanic additive in cement, mortar and concrete is a viable alternative to traditional materials, with the technical, economic and environmental advantages of recycling construction waste that is often improperly discarded. This paper reports on a study of red brick waste, investigating its application as a pozzolanic additive. Structural and facing ceramic brick waste was used, and samples were ground into particles smaller than 45 μm, with a density of 2.82 and 2.81 g/cm³, respectively. The samples had a surface area of 4.26 and 8.46m²/g, respectively. An X-ray diffraction (XRD) analysis showed crystalline peaks identified as quartz and hematites, and partially identified as rutile and microcline, confirming the findings identified by X-ray fluorescence spectrometry. Pozzolanic activity tests on Portland cement classified the samples contained pozzolans.

INTRODUCTION

In recent decades, society has shown increasing interest in the use of new materials in place of traditional products, aimed at reducing the latter's environmental impact. The use of pozzolanic materials, which are generally industrial by-products, preserves natural resources that are used in the production of cement, mortar and concrete. Some of the advantages of using pozzolanic materials are: reduction of the alkali-aggregate reaction, resistance to attack by sulfates, reduction of heat of hydration in massive structures, etc.

The objective of this work was to process and characterize red ceramic wastes generated in the production of structural and facing bricks, aiming at their application as pozzolanic materials in mortars, cements and concretes. Two different types of samples were therefore used: structural and ceramic facing bricks.

POZZOLANIC MATERIALS

Pozzolanic materials are "silicon-like or silicon-aluminum materials that have little or no cementitious properties, but which, when finely powdered and in the presence of water, react with calcium hydroxide at room temperature to form compounds with cementitious properties" [ABNT NBR 12653]. These materials can be classified as: Class N: Natural and artificial pozzolans that meet standard requirements (e.g., diatomaceous earth and calcined clay); Class C: Fly ash produced by the combustion of coal in thermoelectric plants that meet standard requirements; Class E: Any pozzolanic material whose requirements differ from those of the aforementioned classes. Table 1 lists the chemical and physical properties required for pozzolans, according to the NBR 12653 standard [ABNT NBR 12653].

Table 1. Chemical and Physical Properties Required for Pozzolans

Properties	Class of Pozzolanic Material		
	N	C	E
$SiO_2 + Al_2O_3 + Fe_2O_3$ (min. %)	70	70	50
SO_3 (max. %)	4	5	5
Moisture Content (max. %)	3	3	3
Loss on Ignition (max. %)	10	6	6
Free Alkali as Na_2O	1.5	1.5	1.5
Retained Fraction ≠ 45µm (max. %)	34	34	34
Pozzolanic Activity Index with Cement at 28 Days (min. %)	75	75	75
Pozzolanic Activity with Lime at 7 Days (MPa)	6	6	6
Water Requirement (max %)	115	110	110

Unlike glass and volcanic tuff, clay reacts only when subjected to a thermal process. Exposure to temperatures ranging from 600 to 1000ºC changes the crystal structures of its silicates, turning clay into an amorphous compound that reacts with lime at room temperature. However, not all types of calcined clay present pozzolanic properties. Clays containing high proportions of very crystalline minerals, such as quartz and feldspar, do not produce reactive material [Mehta 1987]. The temperature must be controlled in order to avoid fusion of the material and to ensure the final product will react with $Ca(OH)_2$. According to Barata [1998], temperatures above 900ºC lead to the formation of stable crystalline compounds with a lower specific surface area and little pozzolanic activity.

Pozzolanic materials have the same oxides that are present in Portland cement (SiO_2, Al_2O_3 and Fe_2O_3), which react with $Ca(OH)_2$. The pozzolanic reaction is slower than reactions involving common Portland cement, delaying the release of heat and the increase in strength. Moreover, the reaction consumes the existing $Ca(OH)_2$ rather than releasing it. This interaction leads to the formation of products with cementitious properties of the same type as those formed in the hydration of C-S-H compounds, but with a different nature. These products have a lower CaO/SiO_2 ratio (lower alkalinity) and higher resistance to aggressive environments [Mehta and Monteiro 1994].

EXPERIMENTAL INVESTIGATION

Two types of materials were analyzed in this research: ceramic facing brick waste and structural brick waste. The waste samples came from a brickmaker located in Ribeirão das Neves, in the metropolitan region Belo Horizonte, Minas Gerais, Brazil. The samples were crushed in a jaw crusher and then milled in a ball mill with a capacity of approximately 25 liters, at a rotation speed of 52 rpm, using cast iron balls corresponding to about 30% of the mill's volume. The samples displayed different colors after milling. The facing brick sample was reddish, whereas the structural brick was grayish, as depicted in Figs. 1 and 2.

Fig. 1. Facing Brick

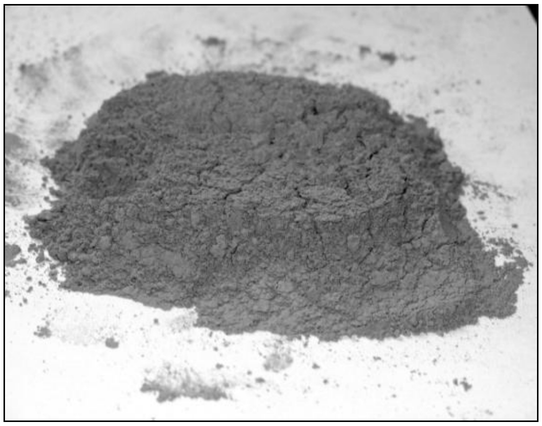

Fig. 2. Structural Brick

Specific gravity

Specific gravity was determined by means of a gas pycnometer (Quantachrome Stereopycnometer). The average density of the samples was very similar, i.e., 2.81 and 2.82 g/cm³ for the facing and structural bricks, respectively.

Specific surface area

The technique used was gas adsorption based on the BET (Brunauer, Emmett and Teller) method. The specific surface area of the facing brick sample was 8.4 6m²/g and that of the structural brick was 4.26 m²/g.

Identification of chemical elements

The elements were identified by X-ray fluorescence, using a Philips PW2400 Spectrometer. As expected, the samples showed similar results, since both originated from the same raw material. The elements most commonly found were silicon (Si), oxygen (O) and aluminum (Al), confirming the assumption that the samples showed some pozzolanic activity. Smaller amounts of iron (Fe) and magnesium (Mg) were also found. In addition to these elements, the samples contained traces of zinc (Zn), nickel (Ni), manganese (Mn), chrome (Cr), titanium (Ti), chlorine (Cl), calcium (Ca), cerium (Ce), phosphorous (P), potassium (K), sodium (Na), and sulfur (S).

Particle size

The particle size of the samples was analyzed using a Sympatec Helos 12LA particle size analyzer. Prior to this analysis, the particles were dispersed and deagglomerated by ultrasonication. The concentrations of dispersion medium used for the facing and structural brick waste samples were 22% and 20%, respectively. The results of this experiment, shown in Table

2, indicate that combustion and the original shape of each brick do not exert any significant the influence, based on the milling time and method applied.

Table 2. Particle Size (50 mm lens)

Facing Brick				Structural Brick			
Particle Size (µm)	APP (%)	Particle Size (µm)	APP (%)	Particle Size (µm)	APP (%)	Particle Size (µm)	APP (%)
0.45	1.99	5.25	64.13	0.45	1.47	5.25	54.61
0.55	3.4	6.25	68.9	0.55	2.58	6.25	59.1
0.65	5.05	7.5	73.3	0.65	3.93	7.5	63.47
0.75	6.9	9	77.42	0.75	5.44	9	67.8
0.9	9.9	10.5	80.91	0.9	7.93	10.5	71.53
1.1	14.12	12.5	84.85	1.1	11.46	12.5	75.75
1.3	18.4	15	88.65	1.3	15.07	15	79.92
1.55	23.61	18	91.81	1.55	19.47	18	83.54
1.85	29.39	21.5	94.04	1.85	24.38	21.5	86.29
2.15	34.52	25.5	95.55	2.15	28.74	25.5	88.46
2.5	39.72	30.5	96.91	2.5	33.17	30.5	90.97
3	45.95	36.5	98.47	3	38.51	36.5	94.26
3.75	53.45	43.5	99.88	3.75	45.03	43.5	97.82
4.5	59.41	51.5	100	4.5	50.31	51.5	100

*APP = Accumulated percent passing through the sieve.

Chemical compounds

The chemical compounds were identified by X-ray diffraction (XRD), using a Philips PW Series diffractometer operating at 40KV and a current of 20mA, with a step size of 0.060 and scanning angle of 3º to 80º. Figures 3 and 4 show the resulting XRD spectra, which reveal that both samples contained crystalline material in their composition, such as quartz and hematite and small amorphous halos. The XRD analysis also indicated the presence of partially identified peaks, probably rutile and microcline, in view of the elements found in the X-ray fluorescence tests (Ti, Al, K, Si). The presence of these two minerals hinders precise detection because one interferes with the measurement of the other.

Microscopic analysis

This analysis was carried out with a JEOL JSM-5410 microscope coupled to a NORAN EDS energy dispersive spectroscope. Figures 5 and 6 show images of facing and structural brick waste samples obtained by secondary electron imaging. Tables 3 and 4 present an overall chemical analysis (obtained by EDS) of areas of Figures 5 and 6. The facing brick sample (Figure 5) shows numerous fine particles with sizes of approximately 1 µm and irregular morphology, which can be ascribed both to their mineralogy and to the milling process to which they were subjected. Figure 6 depicts a number of particles of the structural brick sample with diameters above 1 µm. The specific surface area of the samples was confirmed in the microscopic analysis.

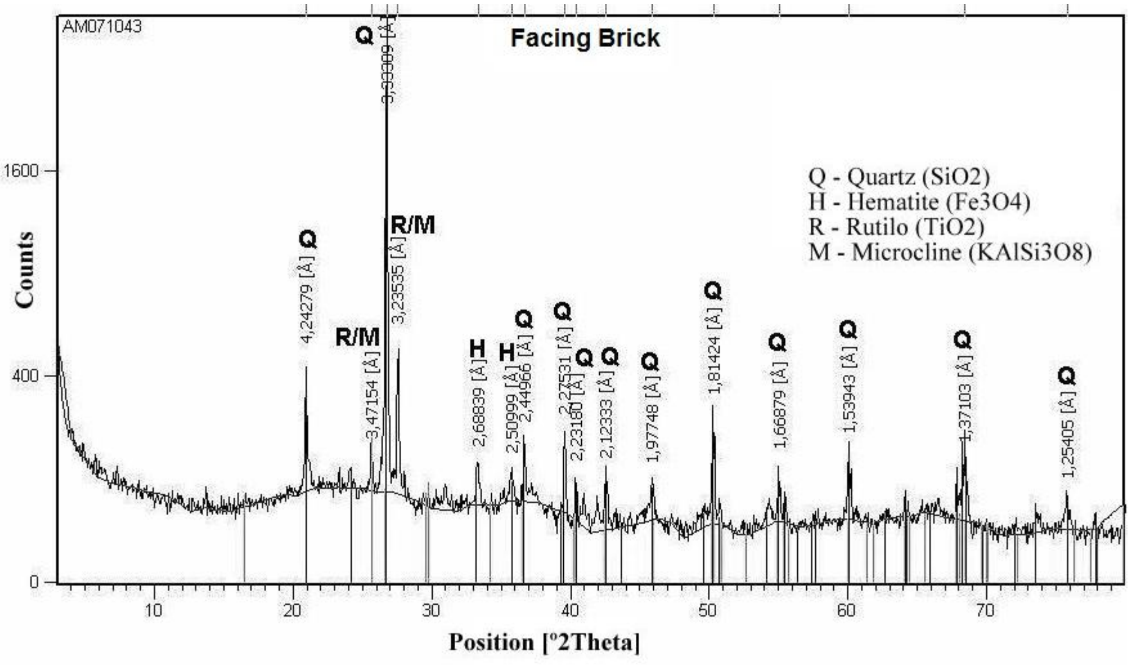

Fig. 3. Diffraction Spectra (Facing Brick)

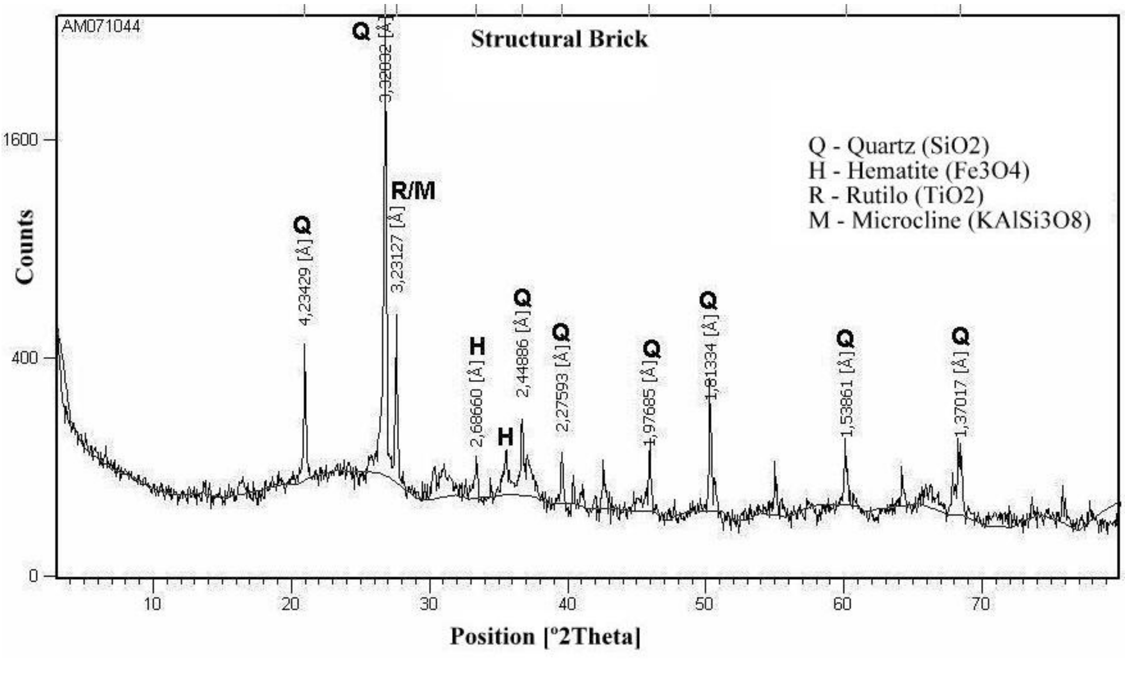

Fig. 4. Diffraction Spectra (Structural Brick)

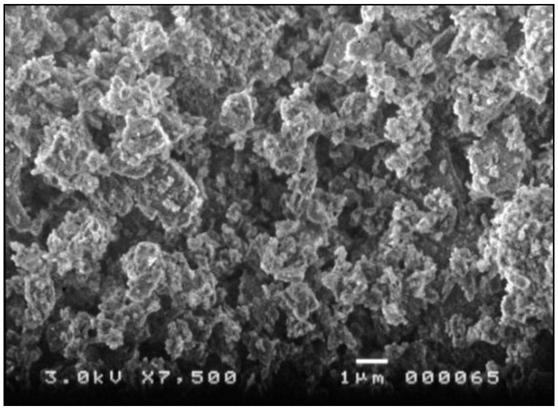

Fig. 5. Facing Brick (7500 X)

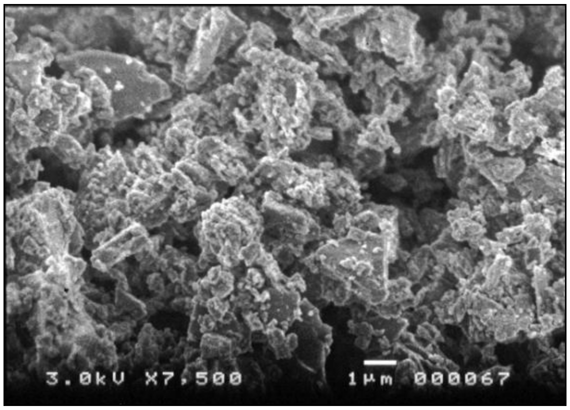

Fig. 6. Structural Brick (7500 X)

Table 3. Overall Chemical Analysis (Facing Brick)

Oxides	%	Oxides	%	Oxides	%
SiO_2	51.4	K_2O	2.73	CaO	0.57
Al_2O_3	26.94	ZnO	2.21	MgO	0.55
Fe_2O_3	13.98	TiO_2	1.28	Na_2O	0.34

Table 4. Overall Chemical Analysis (Structural Brick)

Oxides	%	Oxides	%	Oxides	%
SiO_2	55.1	K_2O	2.61	Na_2O	0.47
Al_2O_3	23.09	TiO_2	1.17	MgO	0.25
Fe_2O_3	16.67	CaO	0.64		

The results were consistent with the data obtained by the X-ray fluorescence test, indicating a predominance of silicon, aluminum and iron oxides, with smaller amounts of magnesium, potassium, titanium, sodium, calcium and zinc. Taken together, SiO_2, Al_2O_3 and Fe_2O_3 comprise 92.32% of the facing brick waste and 94.86% of the structural brick. These figures exceed the minimum amount required by the ABNT standard [ABNT NBR 12653], which is 70%.

Pozzolanic activity with Portland cement – chemical method

The material employed to evaluate the pozzolanic activity of the wastes was Portland cement CPV-ARI, which, according to the ABNT standard – High Initial Strength Portland Cement [ABNT NBR 5733], should contain up to 5% of carbonate additive. The characteristics of this Portland cement are listed in Table 5. The compressive strength of the cement was obtained according to the [ABNT NBR 7215]. The ABNT standard recommends measuring the pozzolanic activity index in pozzolanic Portland cement by means of a chemical method to determine the amount of calcium hydroxide consumed by the sample [ABNT NBR 5753]. Pozzolanicity is determined by comparing the amount of $Ca(OH)_2$ in the liquid phase in contact with hydrated cement and the amount of $Ca(OH)_2$ which could saturate a medium such as alkali.

The samples contained 65% of Portland cement CPV-ARI and 35% of waste (in volume). These percentages were chosen based on the value recommended by the NBR 5752 standard [ABNT NBR 5752], allowing for a comparison of the results of the two methods. Figure 7 presents the test results.

Table 5. Characteristics of CPV-ARI Portland Cement

Thickness	Retained - Sieve 75 µm (%)	0.2
	Retained - Sieve 45 µm (%)	3
	Specific area (cm²/g)	4671
Setting time (h)		02:07
Compressive Strength (MPa)	1 day	26
	3 days	41
	7 days	46
	28 days	54.2

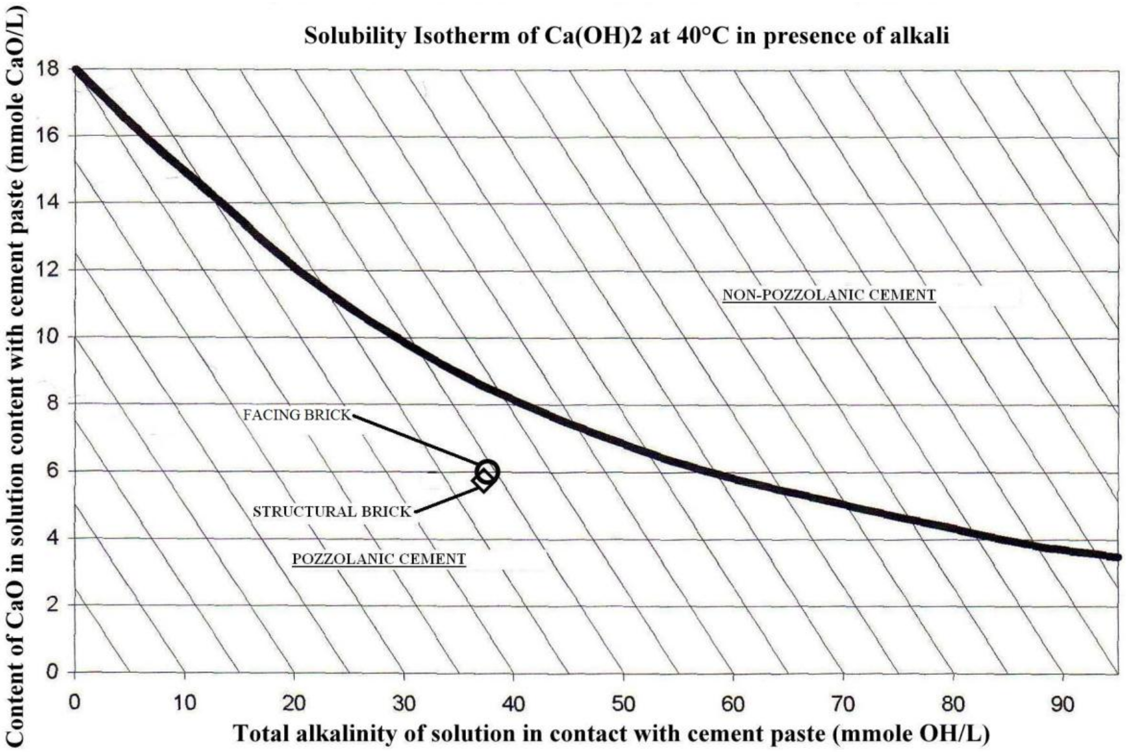

Fig. 7. Pozzolanic Activity

Pozzolanic activity index (PAI) with Portland cement – mortar method

The method used for the determination of the pozzolanic activity index with Portland cement was the NBR 5752 standard [ABNT NBR5752]. The method compares the strength of two types of mortar with standardized dosing and consistency. The amount of water required for each mortar is determined by the consistency index (which must be 225 ± 5 mm). The compressive strength of the mortars was determined according to the NBR 7215 standard [ABNT NBR 7215]. The results are presented in Table 6. The pozzolanic activity index (PAI) of the two waste samples was higher than that recommended by the NBR 12653 standard [ABNT NBR 12653], i.e., 75%, while the water requirement was lower than 110%. Both samples were considered pozzolanic materials, confirming the results of the chemical tests.

Table 6. Mortar Consistency Index

Sample	Water/(Cement + Waste) Ratio	Consistency Index (mm)	Water Requirement (%)	Compressive Strength (MPa)	PAI (%)
Reference	0.52	230	100	49.7	100
Facing Brick	0.54	230	100.2	39.1	78.7
Structural Brick	0.54	230	100.3	39.5	79.5

*PAI = pozzolanic activity index

CONCLUSIONS

The results of the granulometric characterization of the samples met the requirements for pozzolanic material, with a percentage of retained material of 45 µm < 34%. The specific surface area of the facing brick sample was approximately 100% larger than that of the structural brick sample (8.46 m²/g versus 4.26 m²/g). The chemical analysis by EDS revealed a predominance of SiO_2, Al_2O_3 and Fe_2O_3. The sum of these fractions was 94.86% for the facing brick and 92.32% for the structural brick samples, thus surpassing the chemical requirements for their classification as pozzolanic materials. The pozzolanic activity index with Portland cement for facing and structural brick samples was 78.7% and 79.5%, respectively. These values exceed the minimum of 75% specified by the standard. The chemical tests also confirmed the pozzolanic activity of both samples.

REFERENCES

ABNT NBR 5733. “High Early Strength Portland Cement - Specification.” *ABNT,* Rio de Janeiro, RJ, 5 pages. (in Portuguese).

ABNT NBR 5752. “Pozzolans - Determination of Pozzolanic Activity with Portland Cement – Method of Test.” *ABNT,* Rio de Janeiro, RJ, 3 pages. (in Portuguese).

ABNT NBR 5753. “Portland Pozzolanic Cement – Pozzolanicity Test – Method of Test.” *ABNT*, Rio de Janeiro, RJ, 5 pages. (in Portuguese).

ABNT NBR 7215. “Portland Cement – Determination of Compressive Strength.” *ABNT,* Rio de Janeiro, RJ, 8 pages. (in Portuguese).

ABNT NBR 12653. “Pozzolans - Specification.” *ABNT*, Rio de Janeiro, RJ, 3 pages. (in Portuguese).

Barata, M. S. (1998). “High Performance Concrete in Pará State: Economical and Technical Viability Study on Production of High Performance Concrete with the Available

Material in Belém Using Additions of Silica Fume and Metakaolin." Master' Dissertation, Federal University of Minas Gerais. Porto Alegre, RS, 167p. (in Portuguese).

Mehta, P. K. (1987). "Chapter 1: Natural Pozzolans". *Supplementary Cementing Materials for Concrete*. V.M. Malhotra, ed.; Minister of Supply and Services Canada, ISBN 0-660-12550-I, v.1, 428 p.

Mehta, P. K., and Monteiro, P. J. M. (2006). "Concrete - Microstructure, Properties, and Materials," 3rd Ed., McGraw-Hill.