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A COMPARISON OF THE CHEMICAL AND ENGINEERING CHARACTERISTICS OF ANCIENT ROMAN HYDRAULIC CONCRETE WITH A MODERN REPRODUCTION OF VITRUVIAN HYDRAULIC CONCRETE*

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The authors have completed structural and compositional analysis of Roman hydraulic concrete using large cores taken from a variety of maritime structures. In 2005 an 8 m^3 block of hydraulic, pozzolanic concrete was built in the sea at Brindisi (Italy), applying the materials and procedures specified by the Roman architect Vitruvius. Cores were taken at 6 months and 12 months after construction and subjected to the same analyses as the first-century BC *cores from pilae associated with the Villa of the Domitii Ahenobarbi at Santa Liberata. Results show that a slight variation on the Vitruvian formula yields results closest to the Roman material, and that substantial curing requires 12 months.*

KEYWORDS: ROMAN HYDRAULIC CONCRETE, POZZOLANA, VITRUVIUS, HARBOUR CONSTRUCTION, *PILA*

BACKGROUND: THE ROMAN MARITIME CONCRETE STUDY (ROMACONS)

Nearly all long-distance trade in the Roman world was carried by sea, and during the period from *c*. 200 BC to AD 300 the Mediterranean Sea was thronged with merchant ships. Of the almost 1200 documented pre-modern shipwrecks in the Mediterranean, 761 (63%) belong to this period (Parker 1992, 8–15). Maritime trade on a large scale was the main factor allowing the rise and survival of the Roman Empire. Although not all ships and cargoes required extensive harbour installations to assist the process of loading and unloading cargo, such facilities were essential for most port cities, and for the enormous trade in bulk foodstuffs and construction materials that sustained the great cities around the Mediterranean. This period of active maritime trade and widespread harbour construction coincides almost exactly with the florescence of Roman construction with hydraulic concrete. This material, a Roman invention, made possible the construction of elaborate and durable harbour facilities, as well as bridge footings and coastline fish-raising tanks. Although not strictly necessary, hydraulic mortar was also used for many structures on land. The bibliography concerning Roman concrete is enormous. Some of the most important secondary sources are cited in Oleson *et al*. (2004b, 2006), but see in particular Blake (1947, 21–69, 308–52; 1959); Lugli (1957, 363–436); Lamprecht (1996); DeLaine (1997); Felici (1998); Gazda (2001); Lancaster (2005).

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Hydraulic concrete is so-called because it can set while immersed in water; a chemical reaction between the lime and a pozzolanic additive supplies the mortar with its own CO_2, allowing the mortar to set and cure out of contact with atmospheric CO_2. For the Romans the pozzolanic additive was a loose volcanic ash, first exploited near ancient Puteoli (modern Pozzuoli) on the Bay of Naples and thus called *pulvis puteolanus* ('powder from Puteoli'; Vitruvius, *On Architecture* 5.12.2; Seneca, *Speculations about Nature* 3.20.3; Pliny, *Natural History* 16.202). This material is rich in aluminosilicates and the particles have a particularly large surface area. Modern hydraulic mortars, such as Portland cement, for the most part use artificially produced pozzolanic additives, such as fly ash from furnaces. Around 25 BC the Roman architect Vitruvius described the materials needed for hydraulic concrete, their proportions, and some of the procedures to be used for building structures in the sea (Vitruvius, *On Architecture* 2.5.1, 2.6.1–5, 5.12.2; Dubois 1902; Schläger 1971; Oleson 1988; Felici 1993, 95–98; Brandon 1996; Oleson *et al*. 2004b, 199–203; 2006). His mortar is composed simply of 2 parts pozzolana, 1 part slaked lime, and sufficient seawater to create a stiff mix. Our samples have shown that the aggregate could be either tuff, or local limestone and sandstone, in the approximate proportions 35:65, aggregate to mortar. There are useful discussions of pozzolana and pozzolanic mortars and concretes in Blake (1947, 41–44, 313–315); Massazza (1988); Lugli (1957, 394–401); Turriziani (1964); Siddall (2000); Lancaster (2005, 51–67); Oleson *et al*. (2006).

Despite the recognized importance of hydraulic concrete to the development of Roman architecture and thus to the success of the Roman system (Lechtman and Hobbs 1987), no proper engineering analysis of samples of Roman hydraulic concrete was attempted until 2002, by the authors. Applying a completely new methodology, Brandon, Hohlfelder, and Oleson used a Cordiam Model M60-0 hydraulically powered coring device to take intact cores 0.09 m in diameter and up to 6.0 m long from Roman maritime structures, both above and below sea level. These cores, of which 29 have been taken at eight different sites in Italy (Portus, Anzio, Cosa, Santa Liberata, Baia), Israel (Caesarea), Egypt (Alexandria), and Greece (Chersonissos) between 2002 and 2007, have supplied large, intact samples that for the first time allow an accurate evaluation of the structural characteristics of Roman hydraulic concrete. Bottalico, Cucitore, and Gotti have subjected the samples to a complete range of chemical and mechanical tests at the research laboratories of the CTG Italcementi Group in Bergamo (Italy) (Oleson *et al*. 2004a,b, 2006). Through chemical analysis of the samples, we have documented a previously unsuspected international bulk trade in pozzolana from the Bay of Naples, recording use of this material at Caesarea in Israel and Chersonisos in Crete (Branton and Oleson 1992; Brandon *et al*. 2005). In October 2004, Brandon, Hohlfelder, and Oleson built a full-scale Roman style formwork in the harbour of Brindisi (Italy), and constructed an 8 m^3 block of hydraulic concrete with the precise materials and the formula specified by Vitruvius (Hohlfelder *et al*. 2005; Oleson *et al*. 2006). The Romans termed this type of structure, an important component of harbour design, a *pila* (Oleson *et al*. 2006, 29). This pioneering experiment revealed new information about the methods used by the Romans for building formwork and placing concrete in the sea. In order to obtain information concerning the rate at which Roman concrete cured, and the efficacy of the Vitruvian formula involving 2 parts pozzolana to 1 part lime, we cored the reconstructed *pila* after intervals of six, 12, and 24 months (19 March 2005, BRI.2005.01; 14 November 2005, BRI.2005.02; 22 November 2006, BRI.2006.01), employing the same equipment that we have used on the ancient concrete structures. As part of the experiment, we modified the Vitruvian formula to 2.7 parts pozzolana to 1 part lime for the upper part of the structure. We then subjected cores BRI.2005.01 and BRI.2005.02 to visual, chemical, and engineering analysis and compared the results with those produced by a 6 m long core taken from a *pila* associated with the Villa

Figure 1 *Brindisi core 1 (BRI.2005.01): view. (Photo: C. Brandon).*

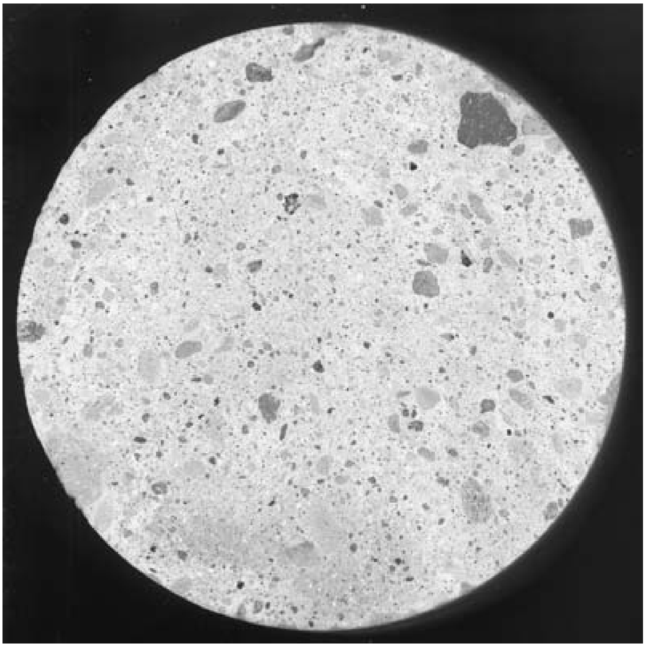

Figure 2 *Brindisi core 1 (BRI.2005.01): section. (Photo: Italcementi Group).*

of the Domitii Ahenobarbi at Santa Liberata (SLI.2004.01), dated most likely to the first century BC. The results of these analyses provide the first data on the curing rate of Roman concrete. Data concerning the 24-month core will be presented once analysis has been completed.

ANALYSIS OF BRINDISI CORES

Upon visual examination, the cores appear to be composed of large, brown tuff aggregate and well-compacted grey mortar (Fig. 1). The aggregate includes fragments with a vascular appearance and variable morphology and size. The mortar is composed of a fine, dark pozzolanic sand distributed in a light-grey matrix (Fig. 2). White nodules of apparently non-reacted lime are rarely observed. In order to characterize the mortar, two portions of each core were selected that showed a low frequency of large aggregates occupying the whole cross-section, and allowing sub-cores having a suitable length (L) to obtain specimens with an aspect ratio $L/D \geq 2$. Although such variation could affect the reliability of test results, nevertheless all the experimental data are congruent and allow us to accept the results. The sub-core samples correspond with depths of 35–85 cm (BRI.2005.01-top) and 105–145 cm (BRI.2005.01-bottom) for BRI.2005.01, and with depths of 20–75 cm (BRI.2005.02-top) and 95–152 cm (BRI.2005.02.bottom) for BRI.2005.02, measuring from the top end of the cores at the surface of the block. Some portions of the samples were prepared for testing to determine compressive strength and elastic modulus, while others were dried under vacuum at 50°C and prepared for chemical and microstructural analysis.

The dynamic Young's modulus of elasticity was measured by a non-destructive technique based on the detection of the fundamental resonance frequency of the specimen according to ASTM C215 (Fundamental transverse, longitudinal, and torsional resonant frequencies of concrete specimens) for the three independent vibrational modes (axial, flexural and torsional). The measurement is carried out by exciting the specimen with a low-intensity impulsive force and then analysing its vibrational response. The analysis of the signal is carried out by the Fourier transform in order to detect the resonance frequency. The typical response is a curve on which several peaks are evident; the first peak corresponds, in general, to the fundamental frequency of the specific vibrational mode under assessment. In some special cases the fundamental resonance is not the first peak (i.e., coupled vibrational modes); in those cases a well trained operator is able to detect the correct frequency. Furthermore the shape of the curve is correlated to the dumping of the signal. When the peaks are clearly detectable—that is they are relatively high and narrowly shaped—the dumping of the signal is in general low. In the case of the analysed specimens, clearly detectable peaks, indicating a low dumping of the signal, characterized the response signals. This property is an indication of good cohesion of the material and of excellent adhesion between paste and aggregate.

The compressive strength was determined according to ASTM C39 (Compressive strength of cylindrical concrete specimens). The only deviation to the procedure specified in the standard consisted in the interposition of two thin cork sheets between the base of the specimens and the load-applying plates of the testing machine. This expedient was adopted in order to distribute the load uniformly even in the presence of local geometrical irregularities in the lower faces of the samples. The presence of defects cannot be excluded, since the specimens were prepared by cutting without subsequent refacing, in order to avoid damage induced by that operation. The shape of the specimens after the rupture induced by the compressive strength test indicated that the load was in fact uniformly applied and that the cores were sufficiently homogeneous to provide good results. The values of Young's modulus and compressive strength of the Brindisi samples are listed in Table 1, while the correlation between them is shown in Figure 3.

As can be observed in Table 1, the mechanical performance of specimens from the same core is quite similar. The samples cored after 1 year show higher values of compressive strength and Young's modulus than the 6-month samples, indicating a progress of the hydration process. A clear correlation exists between Young's modulus and compressive strength, indicating that the sampling procedure and the testing of the specimens have been able to correctly identify the properties of the material.

Samples of mortar were ground to below 90 microns and the following chemical analyses carried out: loss on ignition; X-ray fluorescence; calcimetric determination of carbonate content; $Ca(OH)_2$ content by extraction with acetoacetic ester; insoluble residue at the acidic attack; soluble silica at the acidic attack. Results of chemical analyses are summarized in Table 2.

Table 1 *Values of Young's modulus and compressive strength*

Sample	*BRI.2005.01 top*	*BRI.2005.02 top*	*BRI.2005.01 bottom*	*BRI.2005.02 bottom*	*SLI.2004-A*	*SLI.2004-B*	*SLI.2004-C*
Length (mm)	204	191.5	205	188	190	200	200
Diameter (mm)	85	87.5	85	87	85	85	85
Density (kg/m^3)	1390	1369	1415	1398	1550	1523	1526
Young's modulus (MPa)	3730	4230	3880	5160	6940	6280	6040
Compressive strength (MPa)	3.9	4.5	3.5	5.6	8.5	8.1	7.5

Table 2 *Chemical composition of mortars*

Sample	*BRI.2005.01 top*	*BRI.2005.02 top*	*BRI.2005.01 bottom*	*BRI.2005.02 bottom*	*SLI.2004-A*
L.o.i. (wt %)	18.99	12.69	16.71	15.85	19.20
SiO_2 (wt %)	41.32	46.32	39.01	39.68	40.89
Al_2O_3 (wt %)	11.59	13.96	10.98	12.62	12.22
Fe_2O_3 (wt %)	2.55	2.68	2.35	2.49	3.28
CaO (wt %)	14.61	12.67	20.88	18.56	12.15
MgO (wt %)	0.91	0.93	0.74	0.88	2.38
SO_3 (wt %)	0.23	0.22	0.21	0.27	0.29
Na_2O (wt %)	2.77	2.88	2.62	2.69	3.11
K_2O (wt %)	5.62	6.27	5.32	5.54	4.72
TiO_2 (wt %)	0.28	0.27	0.26	0.24	0.34
Cl (wt %)	0.95	0.80	0.77	0.92	1.13
$CaCO_3$	15.81	3.50	5.07	4.25	8.78
Soluble SiO_2 (wt %)	6.97	8.59	9.57	10.19	7.93
$Ca(OH)_2$ (wt %)	0.41	3.92	7.74	7.84	0.17
Insoluble Residue (wt %)	56.11	56.59	48.52	45.75	48.7
Soluble SiO_2/Insoluble Residue	0.12	0.15	0.20	0.22	0.16

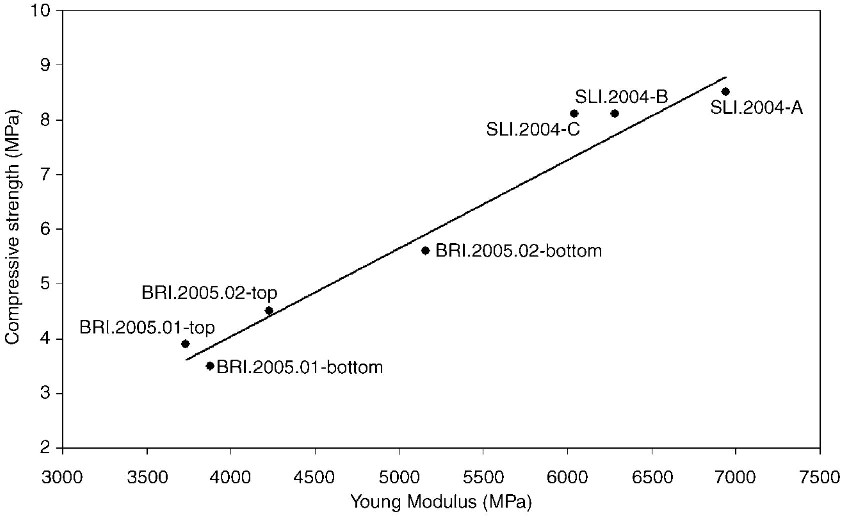

Figure 3 *Correlation between compressive strength and Young's modulus.*

Samples BRI.2005.01-bottom and BRI.2005.02-bottom show a higher amount of CaO and lower amount of SiO_2. This difference can be explained by the lower proportion of pozzolana to lime in the bottom part of the cores, since CaO is mainly introduced by the lime putty, while SiO_2 is mainly introduced by pozzolana. $CaCO_3$ content in sample BRI.2005.01-top is at least three times as high as the other samples. The high value obtained in sample BRI.2005.01-top probably depends on a lack of homogeneity and an anomalous carbonation of this sample. In the other samples, the amount of $CaCO_3$ is quite similar, indicating a low carbonation of the mortars.

Soluble SiO_2 at the acidic attack is proportional to the amount of pozzolana reacted to produce calcium silicate hydrates; the contribution of non-reacted pozzolana to the soluble SiO_2 can be considered negligible, while the insoluble residue at the acidic attack is proportional to the non-reacted pozzolana. The ratio of Soluble SiO_2 to Insoluble Residue can be considered an index of the progress of the chemical reaction. Soluble SiO_2/Insoluble Residue can be estimated at about 0.12 and 0.15 respectively at 6 months and 1 year for samples from the top of the *pila* and at about 0.20 and 0.22 respectively at 6 months and 1 year for samples from the bottom. These lower values in the top samples can be explained considering that the activity of pozzolana is strictly related to the alkalinity of the environment or, in other words, it is allowed by the calcium hydroxide dissolved in the interstitial solution. In the lower part of the *pila* the conditions are the most suitable for improved pozzolanic activity because of the larger availability of calcium hydroxide induced by the lower pozzolana/lime ratio. In fact, samples BRI.2005.01-bottom and BRI.2005.02-bottom contain a large amount of calcium hydroxide, which is present only in low amounts in samples BRI.2005.01-top and BRI.2005.02-top. Moreover the increase of the ratio between 6 months and 1 year indicates that the hydration process progressed.

Thermal analysis was carried out on the mortar samples, and results are summarized in Table 3. They confirm the $Ca(OH)_2$ and $CaCO_3$ contents detected by the chemical method. The loss of weight in the temperature range 200–440°C gives an estimation of the amount of water

Table 3 *Loss of weight by thermogravimetric analysis of mortars*

Temperature	*BRI.2005.01 top*	*BRI.2005.02 top*	*BRI.2005.01 bottom*	*BRI.2005.02 bottom*	*SLI.2004-A*
25–200°C					
Free water (wt %)	6.0	5.3	5.5	6.2	8.3
200–400°C					
Water from CSH (wt %)	2.5	3.1	3.4	3.8	2.6
400–500°C					
Water from $Ca(OH)_2$ (wt %)	—	0.7	1.5	1.3	—
$Ca(OH)_2$ (wt %)	—	2.8	6.2	5.5	—
500–800°C					
CO_2 from $CaCO_3$ (wt %)	6.1	1.8	3.4	2.2	3.9
$CaCO_3$ (wt %)	13.9	4.1	7.7	5.1	8.8

bound in the calcium silicate hydrates and indicates a larger amount of hydration products in the samples from the bottom part of the pila. In both cases the amount of calcium silicate hydrates increases between 6 and 12 months indicating a progress of the hydration process.

The microstructure of the mortar samples was observed under a scanning electron microscope (SEM), and the chemical composition of the mortar constituents estimated with the EDS (energy dispersive spectrometer) microanalysis system connected to the SEM. Observations were carried out on polished surfaces of the mortars, prepared with the following steps: (1) impregnation of mortars with epoxy resin; (2) grinding with SiC abrasive papers in order to obtain a good planarity of specimens; (3) final polishing with fine diamond powders spread on cloth to eliminate the defects produced in the previous step and to obtain a suitable resolution. The residues of non-reacted pozzolana are usually homogeneously distributed in a well compacted matrix mainly composed of calcium silicate hydrates (Figs 4–5). The main component of pozzolana is a vitreous vesicular part. The chemical composition of the glass, determined by point microanalysis (Table 4), shows a content of SiO_2 around 65% and a high content of K_2O (around 9%). These morphological and chemical characteristics are typical of pozzolanic materials from the Naples area. In fact, the pozzolana near Naples is richer in silica and alkalis and poorer in calcium than the Roman ones (Massazza 1976, 5–6; Massazza and Costa 1979, Table 1, nos. 1 (Bacoli), 2 (Salone, Rome), 9 (Segni); 1988, 472–478, Tables 10.3, 10.4; de'Gennaro *et al*. 1999, 314, Table 2). Moreover, the structure of the pozzolana from the Naples area is much more simple than those of the Latian group and its fundamental constituent is a pumiceous glass (Massazza 1988, 473).

The amount of non-reacted pozzolana inside the mortars is higher in samples from the top parts of the cores, confirming the results of the chemical analysis. Remarkable differences have been pointed out also in the composition of hydration products mainly consisting of calcium silicate hydrates (Figs 6–7). In fact, the Si/Ca molar ratio of hydration products in samples BRI.2005.01-top and BRI.2005.02-top is usually around 1.7 while the Si/Ca molar ratio in samples BRI.2005.01-bottom and BRI.2005.02-bottom is usually around 0.5. Pastes have also shown rather high amounts of chloride.

Porosity of samples was assessed by mercury intrusion (MIP), in a manner similar to that described in ASTM D4404 (Determination of pore volume and pore volume distribution of soil and rock by mercury intrusion porosimetry), on fragments of each mortar sample, and

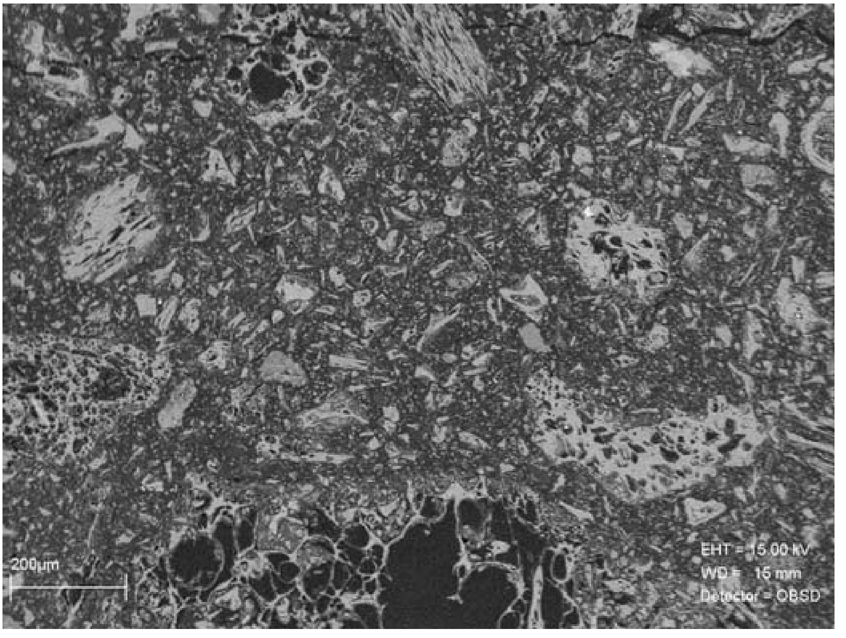

Figure 4 *SEM-BSE image of sample BRI.2005.01-top. (Photo: Italcementi Group).*

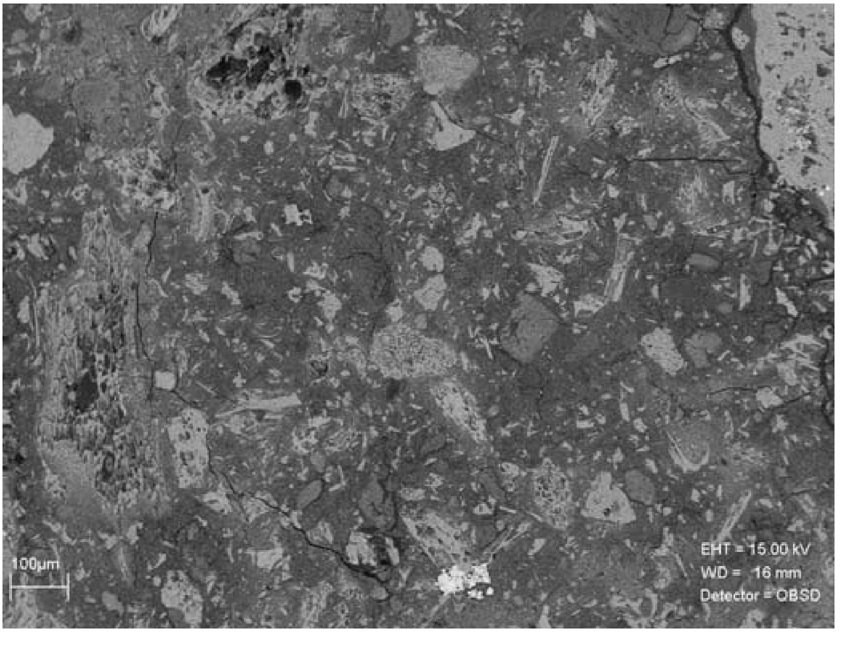

Figure 5 *SEM-BSE image of sample BRI.2005.01-bottom. (Photo: Italcementi Group).*

Table 4 *X-Ray microanalysis of the vitreous structure of pozzolana samples*

Sample	*BRI.2005.01 (Top)*	*SLI.2004-A*
SiO_2 (wt %)	65.4	63.0
Al_2O_3 (wt %)	16.9	17.1
Fe_2O_3 (wt %)	3.2	4.4
CaO (wt %)	2.9	3.6
MgO (wt %)	0.5	0.7
Na_2O (wt %)	1.6	1.4
K_2O (wt %)	9.5	9.8

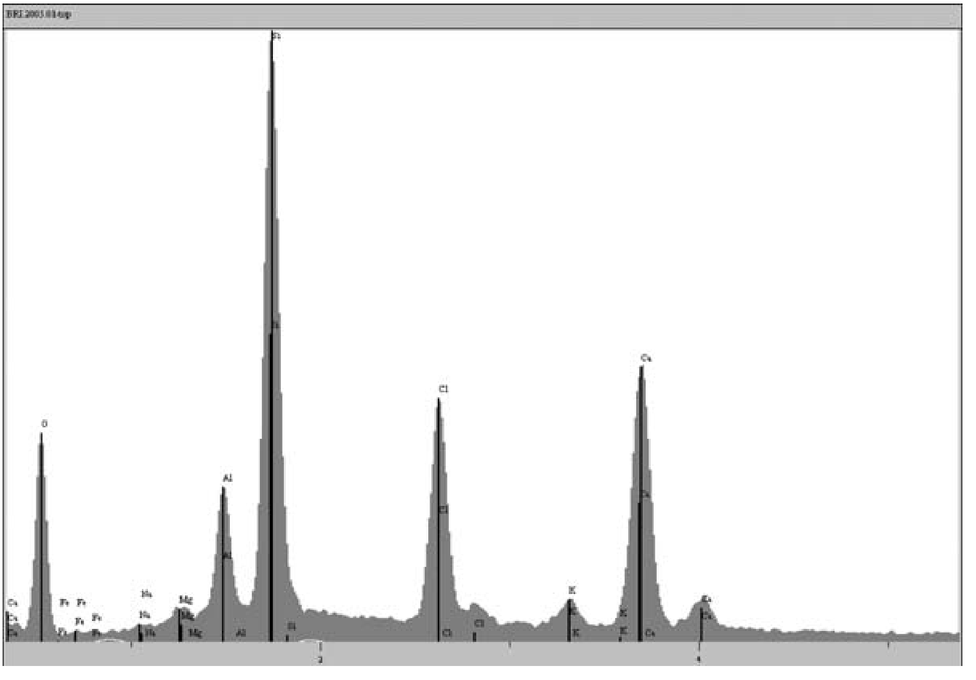

Figure 6 *X-Ray microanalysis of paste in sample BRI.2005.01-top. (Photo: Italcementi Group).*

averaging the results. With this technique it is possible to measure pore diameters in the range between 3.5 nm and 200 μm; the method assumes that the pores have cylindrical shape. Results are summarized in Table 5 while in Figures 8 and 9 cumulative and relative pore size distributions are shown. Pore sizes of all the samples are shown to fall within the characteristic field of hydration product porosity, usually considered below 100 nm.

Samples show rather high amounts of total porosity (about 60% by volume) and analogue mono-modal and broadened shape of pore size distribution. Total porosity decreases with curing both in the top and in the bottom of the cores. Moreover, sample BRI.2005.02-top shows a remarkable shift of pore sizes towards smaller values. Both these effects are related to the progress of the hydration process.

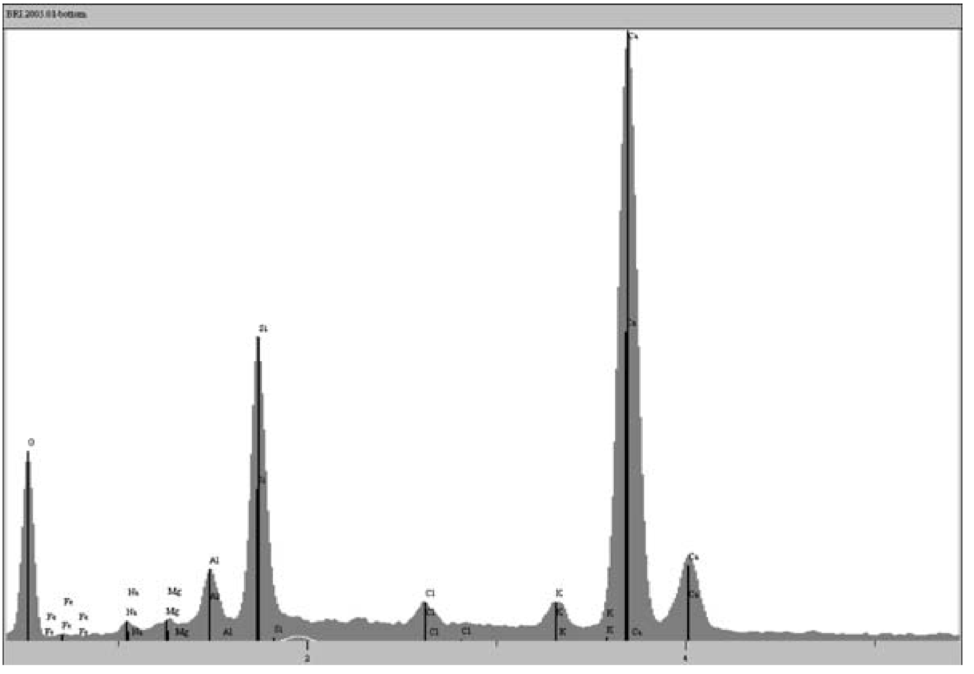

Figure 7 *X-Ray microanalysis of paste in sample BRI.2005.01-bottom. (Photo: Italcementi Group).*

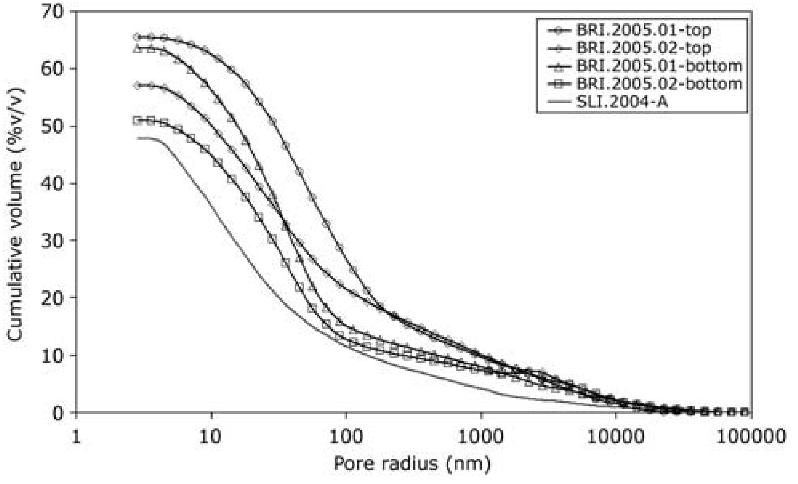

Figure 8 *Cumulative pore size distribution of mortars. (Photo: Italcementi Group).*

ANALYSIS OF THE ROMAN SANTA LIBERATA CORE (SLI.2004.01)

This is the longest core recovered so far by the ROMACONS program, 5.85 m in length. For the historical context of the *pila*, see Oleson *et al*. (2004b, 2006). Technical problems forced us to stop coring 0.15 m above the measured base of this enormous *pila*. To visual observation

Table 5 *Results of mercury intrusion porosimetry*

Sample	*BRI.2005.01 top*	*BRI.2005.02 top*	*BRI.2005.01 bottom*	*BRI.2005.02 bottom*	*SLI04-A*	*SLI04-B*	*SLI04-C*
Cumulative volume (cm^3/g)	0.62	0.63	0.66	0.66	0.39	0.38	0.39
Bulk density (g/cm^3)	1.06	0.91	0.97	0.77	1.23	1.18	1.21
Total porosity (vol %)	65.5	57.1	63.3	50.9	47.9	45.1	47.5

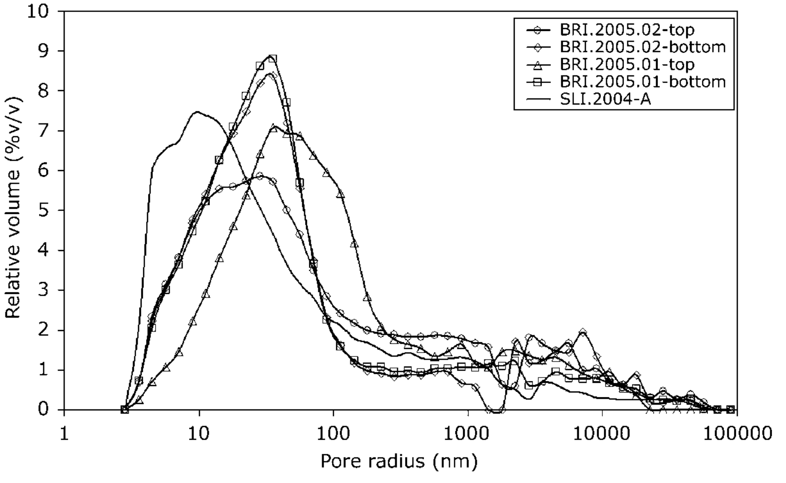

Figure 9 *Relative pore size distribution of mortars. (Photo: Italcementi Group).*

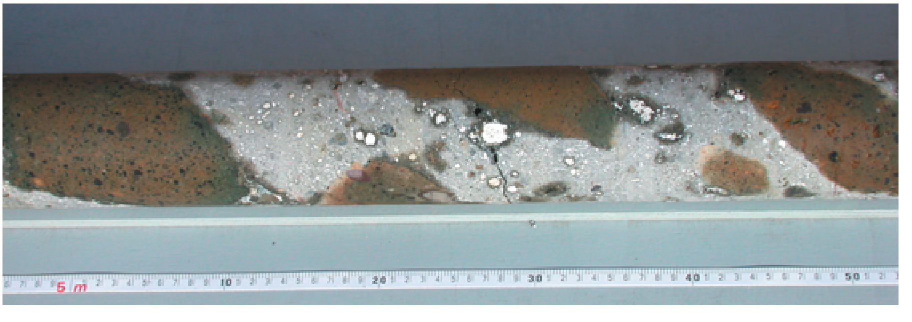

Figure 10 *Santa Liberata core (SLI.2004.01), side view detail, 4.96–5.53 m. (Photo: J. P. Oleson).*

the core is composed of large, brown tuff aggregate and well compacted grey mortar. The large aggregates show fragments with a vascular appearance and variable morphology and size (Fig. 10). The mortar is composed of a light-grey matrix in which are distributed dark pozzolanic particles, red fragments of crushed ceramics (*cocciopesto*), and white granules of apparently non-reacted lime (Fig. 11).

In order to characterize the mortar, portions of the core were selected showing a low frequency of large aggregate. These portions were taken at depths of 185–223 cm (SLI04-A),

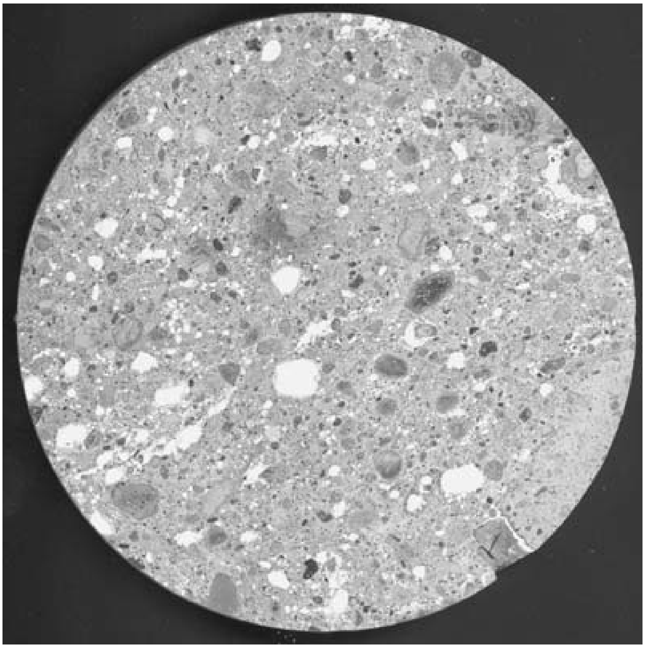

Figure 11 *Santa Liberata core (SLI.2004.01), section. (Photo: Italcementi Group).*

380–400 cm (SLI04-B) and 535–555 cm (SLI04-C) from the top end of the core, which started at the surface of the block. Portions of these samples were prepared for the determination of compressive strength and elastic modulus. Chemical and microscopic assessments were carried out on just one portion of mortar (SLI04-A).

The values of Young's modulus and compressive strength of the Santa Liberata samples are listed in Table 1, while the correlation between Young's modulus and compressive strength is shown in Figure 3. The data in Table 1 show that the mechanical performance of samples from Santa Liberata is generally higher than the performance detected for samples from the Brindisi *pila*, both in terms of Young's modulus and compressive strength.

It may be argued that the higher mechanical performance of specimens from Santa Liberata is a consequence of two effects: the first is longer ageing that improves mechanical performance (in the absence of degradation phenomena), and the second is the different, denser composition. It is not easy to determine which of these two effects is prominent. In any case, at least for the analysed specimens, a key role in the mechanical performance seems to be played, as usual, by the density of the material.

Results of the chemical analysis of mortar from sample SLI04-A are summarized in Table 2. The chemical composition of this sample is closer to that of samples BRI.2005.01-top and BRI.2005.02-top in terms of main oxides. This result indicates that the proportion of pozzolana and lime in SLI04-A is closer to that in the upper part of the Brindisi *pila* than in the lower one. The mortar from Santa Liberata is characterized by a higher amount of MgO, indicating that the lime used in Santa Liberata was less pure than that used in Brindisi. The ratio between soluble SiO_2 and insoluble residue, used as index of the reaction degree, is about 0.16 and is in line with

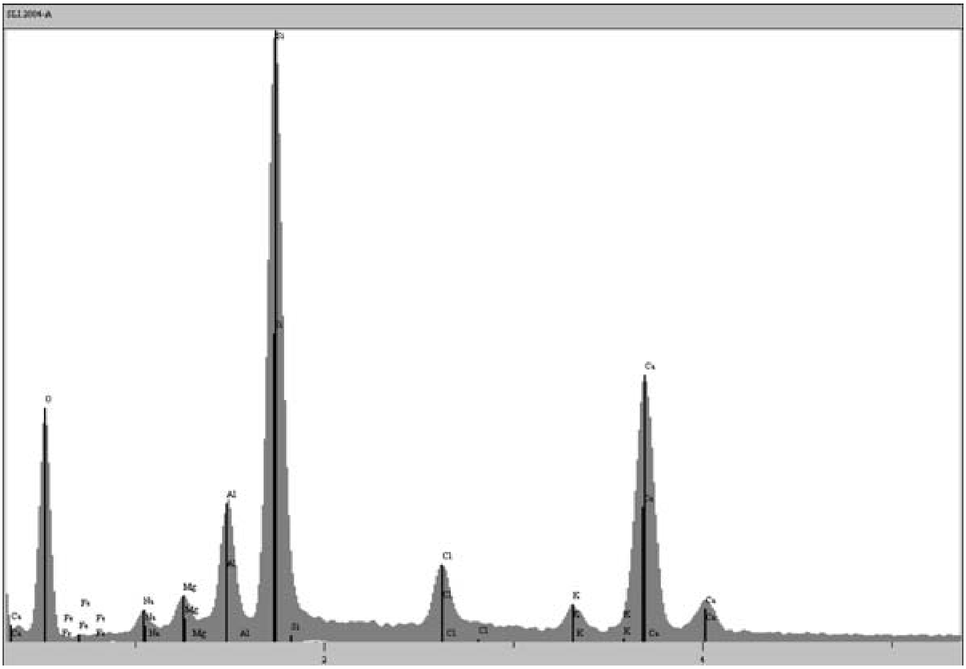

Figure 12 *X-Ray microanalysis of paste in sample SLI04-A. (Photo: Italcementi Group).*

the values obtained in the top part of Brindisi cores. The calcium hydroxide content is negligible, indicating that it has been completely consumed by pozzolanic reaction and by carbonation. Results of thermal analysis summarized in Table 3 confirm the $Ca(OH)_2$ and $CaCO_3$ contents detected by the chemical method. The loss of weight in the temperature range 200–400°C indicates an amount of hydration products in line with that of the upper parts of Brindisi *pila*.

The polished section of a mortar sample from portion SLI04-A was observed under the scanning electron microscope and the chemical composition of its constituents has been estimated with the connected EDS microanalysis system. The residues of non-reacted pozzolana are homogeneously distributed in a well compacted matrix mainly composed of calcium silicate hydrates. The microstructure (vitreous vesicular structure) and chemical composition of pozzolana (Table 4) are closely similar to those of pozzolana present in Brindisi mortars. On the basis of these results it can be suggested that the pozzolana used at Santa Liberata came from the Naples area. X-ray microanalysis of hydration products points out a large amount of Si (Fig. 12) that determines a Si/Ca molar ratio around 2.3. This value is higher than those detected in the Brindisi mortar and is closer to that detected in samples from the top part of the pila than to that of the bottom part.

Results of mercury intrusion porosimetry carried out on Santa Liberata samples are summarized in Table 5, and the average of cumulative and relative pore size distribution is shown in Figures 8 and 9. The samples indicate comparable amounts of total porosity and similar distributions of pore sizes. On average they show a total porosity lower than those detected for the Brindisi *pila*. The relative pore size distribution shows a mono-modal shape shifted towards smaller sizes.

CONCLUSIONS

Analysis of the modern and ancient mortar samples allows the following conclusions. The upper part of the Brindisi *pila* is characterized by a higher pozzolana/lime ratio, in line with that of Santa Liberata mortar. The lower part of the Brindisi *pila* shows a higher development of pozzolanic reaction that has allowed production of a large amount of calcium silicate hydrates. The lower and the upper parts of the Brindisi *pila* have shown similar performance at the same curing time. Curing has allowed a remarkable increase in performance, indicating that strength development is progressing. The composition of hydration products in the upper part of the *pila* indicates a higher Si/Ca molar ratio that is close to the ratio detected in the ancient Santa Liberata mortar. As expected, the pore sizes detected for the Brindisi samples are higher than the pore sizes detected for Santa Liberata. Ageing typically shifts pore size distribution in mortar toward lower dimensions. We have shown that the Vitruvian formula for pozzolanic concrete in fact produces a more or less appropriate result, although a slightly higher ratio of pozzolana to lime results in properties more in line with the ancient concrete samples tested so far. It may be that Vitruvius was following some ideal academic rule, rather than existing practice. Since lime is the most expensive component of mortar, a higher proportion of pozzolana would be more economical. Contractors in the first century AD may have skimped on the 'ideal' mix and found that the quality of the concrete in fact improved. Although these results are interesting and useful, we should keep in mind that they are based on the comparison of one modern mix with one first-century BC mix, and further research by the authors may lead to new or revised conclusions.

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REFERENCES

Blake, M. E., 1947, *Ancient Roman construction in Italy from the prehistoric period to Augustus*, Carnegie Institution, Washington D.C.

Blake, M. E., 1959, *Roman construction in Italy from Tiberius through the Flavians*, Carnegie Institution, Washington D.C.
Brandon, C., 1996, Cements, concrete, and settling barges at Sebastos: comparisons with other Roman harbor examples and the descriptions of Vitruvius, in *Caesarea maritima: a retrospective after two millennia* (eds. A. Raban and K. G. Holum), 25–40, Brill, Leiden.
Brandon, C., Hohlfelder, R. L., Oleson, J. P., and Stern, C., 2005, The Roman maritime concrete study (ROMACONS). The Roman harbour of Chersonisos in Crete and its Italian connection, *Mediterranée*, **1**, 25–9.
Branton, G., and Oleson, J. P., 1992, The technology of King Herod's harbour, in *Caesarea papers. Straton's tower, Herod's harbour, and Roman and Byzantine Caesarea, Journal of Roman Archaeology Suppl. 5* (ed. R. L. Vann), 49–67, JRA, Ann Arbor.
de'Gennaro, M., Incoronato, A., Mastrolorenzo, G., Adabbo, M., and Spina, G., 1999, Depositional mechanisms and alteration processes in different types of pyroclastic deposits from Campi Flegrei volcanic field (Southern Italy), *Journal of Volcanology and Geothermal Research*, **91**, 303–20.
DeLaine, J., 1997, *The baths of Caracalla; a study in the design, construction, and economics of large-scale building projects in imperial Rome*, *Journal of Roman Archaeology, Suppl.* 25, JRA, Portsmouth, RI.
Dubois, C., 1902, Observations sur un passage de Vitruve, *Mélanges de l'École française de Rome*, **22**, 439–67.
Felici, E., 1993, Osservazioni sul porto Neroniano di Anzio e sulla tecnica romana delle costruzioni portuali in calcestruzzo, *Archeologia Subacquea*, **1**, 71–104.
Felici, E., 1998, La ricerca sui porti romani in cementizio: metodi e obiettivi, in *Come opera l'archeologo sott'acque. Storie dalle acque. VIII Ciclo di lezioni sulla ricerca applicata in archeologia* (ed. G. Volpe), 275–340, Edizioni all'Insegna di Giglio, Florence.
Gazda, E. K., 2001, Cosa's contribution to the study of Roman hydraulic concrete: an historiographic commentary, in *Classical Studies in Honor of Cleo Rickman Fitch* (ed. N. W. Goldman), 145–77, P. Lang, New York.
Hohlfelder, R. L., Brandon, C., and Oleson, J. P., 2005, Building a Roman *pila* in the sea—experimental archaeology at Brindisi, Italy, September 2004, *International Journal of Nautical Archaeology*, **34**, 123–7.
Lamprecht, H.-O., 1996, *Opus caementitium. Bautechnik der Römer*, 5th edn, Verlag Bau+Technik, Düsseldorf.
Lancaster, L., 2005, *Concrete vaulted construction in Imperial Rome: innovations in context*, Cambridge University Press, Cambridge.
Lechtman, H. N., and Hobbs, L.W., 1987, Roman concrete and the Roman architectural revolution, in *Ceramics and civilization*, Vol. 3 (ed. W. D. Kingery), 81–128, American Ceramic Society, Westerville, OH.
Lugli, G., 1957, *La tecnica edilizia romana, con particolare riguardo a Roma e Lazio*, 2 vols., G. Bardi, Rome.
Massazza, F., 1976, Chemistry of pozzolanic additions and mixed cements, *Il Cemento*, **73**, 3–38.
Massazza, F., 1988, Pozzolana and pozzolanic cements, in *Lea's chemistry of cement and concrete*, 4th edn (ed. P. C. Hewlett), 470–635, Elsevier, New York.
Massazza, F., and Costa, F., 1979, Aspects of the pozzolanic activity and properties of pozzolanic cements, *Il Cemento* **76**, 1–18.
Oleson, J. P., 1988, The technology of Roman Harbours, *International Journal of Nautical* Archaeology, **17**, 147–58.
Oleson, J.P., Brandon, C., and Hohlfelder, R.L., 2004a, The Roman maritime concrete study (ROMACONS): fieldwork at Portus, Anzio, Santa Liberata, Cosa, 2002–2003, in *Mediterraneum. Tutela e valorizzazione dei beni culturali ed ambientali Vol. 4, tutela del patrimonio culturale sommerso—protection of underwater cultural heritages* (ed. F. Maniscalco), 185–94, Massa, Naples.
Oleson, J. P., Bottalico, L., Brandon, C., Cucitore, R., Gotti, E., and Hohlfelder, R.L., 2006, Reproducing a Roman maritime structure with Vitruvian pozzolanic concrete, *Journal of Roman Archaeology*, **19**, 29–52.
Oleson, J. P., Brandon, C., Cramer, S., Cucitore, R., Gotti, E., and Hohlfelder, R.L., 2004b, The ROMACONS project: a contribution to the historical and engineering analysis of hydraulic concrete in Roman maritime structures, *International Journal of Nautical Archaeology*, **33**, 199–229.
Parker, A. J., 1992, *Ancient shipwrecks of the Mediterranean and the Roman provinces*, British Archaeological Reports, Intl. Series, Suppl. 580, BAR, Oxford.
Schläger, H., 1971, Die texte Vitruvs im lichte der untersuchungen am hafen von side, *Bonner Jahrbücher*, **171**, 150–61.
Siddall, R., 2000, The use of volcaniclastic material in Roman hydraulic concretes: a brief review, in *The archaeology of geological catastrophes* (eds. W. J. McGuire, D. R. Griffiths, P. L. Hancock, and I. S. Stewart), 339–44, Geological Society, London.
Turriziani, R., 1964, Aspects of the chemistry of pozzolanas, in *The chemistry of cements*, vol. 2 (ed. H. F. W. Taylor), 69–86, Academic Press, London.