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Cold Isostatic Pressing of Cement Pastes to Produce Pore Reduced Cement (PRC)

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Abstract

In this paper we extend the method of cold isostatic pressing from the usual dry powders to water-saturated pastes. As an example, immature Portland cement paste, initially prepared under normal conditions of mixing and casting (high shear mixing of paste at water/cement ratio of 0·3), has been cold isostatically pressed to produce pore reduced cement (PRC). The combined pressing of paste and the removal of fluid is the basis of the PRC technique. The design of the tooling for isostatic pressing is very important and several sample tooling designs were tested to optimise the in-situ removal of fluid from the compressed paste. Pressed samples were characterised in terms of density, microstructure and mechanical performance after selected post-pressing curing times. Their properties were correlated with pre-curing time and rate of pressurisation. Comparisons are made with pastes prepared using a unidirectional pressing geometry permitting discussion of potential limitations of the pressing technique.

1 Introduction

1.1 Cold isostatic pressing (CIP)

Isostatic pressing[1] has traditionally been applied to dry powders, or powders containing lubricants. The production of saturated compacts by isostatic pressing is complicated because fluid requires to be expressed from the paste during pressing. It was therefore necessary to design tooling which: (i) could isolate the compact (and pore fluid) from the hydraulic oil of the press, (ii) would have low stiffness, and (iii) would contain a fluid-absorbing interface (a porous compact) between the container and the unpressed paste and which would not itself collapse and seal itself from further absorption of fluid. Thus, the combined stiffness of the containment material and the porous interface must be less than that of the paste. The design concept is illustrated in Fig. 1(a).

1.2 Pore reduced cements (PRC)

As an example of isostatic pressing of saturated pastes we focus on cement pastes. Previously pressing of cement pastes to high pressure has resulted in improved mechanical performance and has led to the development of Pore Reduced Cements. These are a family of high density products manufactured by the pressing of young (approximately 3 h old) cement pastes which are mixed at normal water/cement ratios (w/c). During pressing, much of the mix water that has not yet been consumed in hydration reactions is squeezed out of the paste to produce a compressed product with a very low residual w/c. Water remaining in the paste is available to react to a limited extent with the compacted cement grains allowing the strength of the paste to increase rapidly. The resulting microstructure is therefore of low porosity and is dominated by unreacted cement grains in a water-deficient matrix of hydration product. This is almost exclusively calcium silicate hydrate gel, C–S–H.

The mechanical and durability properties of PRC pastes previously reported[2–4] all relate to products pressed using a uniaxial, unidirectional pressing geometry [see Fig. 1(b)]. There has been some concern that the uneven distribution of stresses during pressing in this configuration will produce a non-uniformly compacted paste. The further argument that the remaining water acts as a lubricant, smoothing out inhomogeneities during pressing, seems equally appropriate. In either case,

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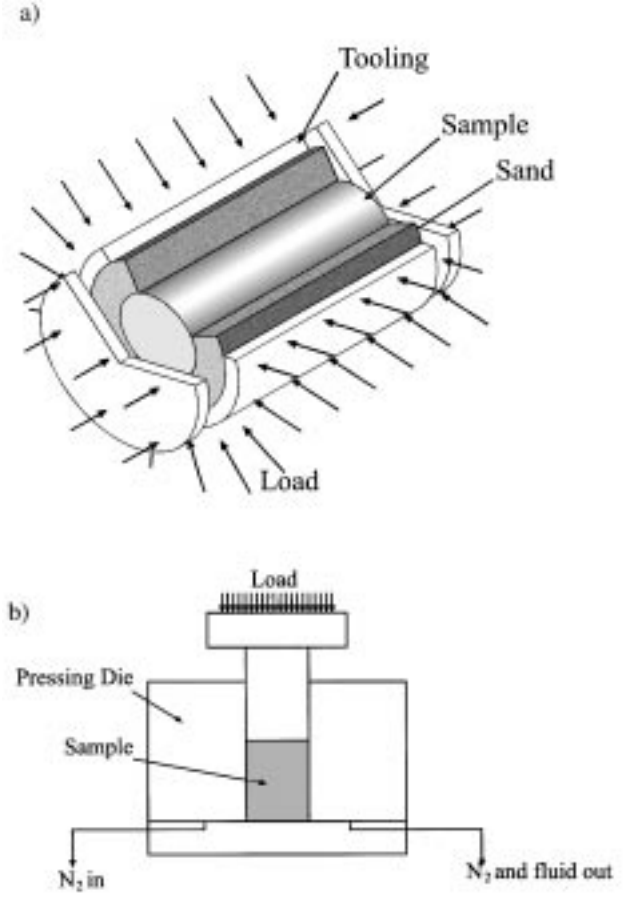

Fig. 1. Schematic representations of pressing geometries used in the preparation of PRC pastes: (a) isostatic pressing, and (b) uniaxial, unidirectional pressing.[2–4]

the mechanical property measurements, particularly the flexural strengths, suggest that there are significant areas of damage during manufacture resulting in critical flaw dimensions of several millimetres. This damage may arise during the pressing stage, as material is forced under loading, to flow into confined spaces, or it may arise during sample ejection from the pressing die. In the latter case, the sample is constrained laterally by the die but on ejection, the segments of the cylindrical specimens suddenly experience release as they protrude from the die. This would results in longitudinal tension. No evidence as yet been obtained from electron microscopy to support any mechanisms but the interpolation from mechanical measurements and the occurrence of regions with smooth textures on fracture surfaces provides sufficient proof of the existence of flaws.

2 Methodology

2.1 Preparation of cement pastes

Portland cement was mixed with water (w/c 0·3) in a domestic food blender for 10 min, with intermediate hand mixing, and then cast with vibration into a prospect mould to provide cylindrical specimens of dimensions 20 mm diameter, 40 mm high. Most samples were cured in air under a plastic sheet at room temperature (23°C) for approximately 3 h prior to demoulding and pressing in the CIP apparatus.

2.2 Tooling

2.2.1 Design fabrication and optimisation

Cylindrical containers were fabricated in three parts from polyurethane (3M Scotchcast™ resin 1471N*) and CIL Monothane A20†. The three parts consisted of a plain tube of dimensions 40 mm internal diameter, 5 mm wall thickness and length 100 mm, and two end caps. An alternative vessel was made from a length of laboratory rubber tubing (130 mm) of 25 mm internal diameter and 4 mm wall thickness. Rubber bungs were used as end caps.

A range of powdered materials were cast into a mould to provide tubular shapes of the appropriate dimensions (wall thickness, 10 mm). Where sand was used, it was mixed with a 2 wt% polyvinyl alcohol solution prior to casting. The tubular casting and one of the end piece shapes were carefully placed into the tooling. A cement cylinder was demoulded and placed into the available space in the CIP tooling. The second porous end piece was placed on the top before the tooling was closed with its own end caps. The assembly was then wrapped in a rubber balloon and placed in the CIP for pressurisation.

In a smaller number of cases, the lining material was machined into three segments, cut longitudinally through a machined sandstone tube. The segments were placed inside the tooling, separated by rubber tubing (2 and 4 mm diameter tubing were tested), prior to the cement cylinder being loaded (see Fig. 3).

The sample was compressed according to the procedure described below. On depressurisation, the sample was removed, labelled and its density was measured by a displacement method using n-hexane.[3] Given that all of the cement samples were prepared identically, the effectiveness of each of the porous lining materials can be approximately assessed from the densities of the pressed products. The higher the density, the more the sample has given up water to the lining. Lining performances are summarised in Fig. 2.

2.3 Pressing procedures

On placing the wrapped tooling in the hydraulic oil reservoir of the CIP apparatus (National Forge

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†Compounding Ingredients Ltd., Preston, Lancashire.

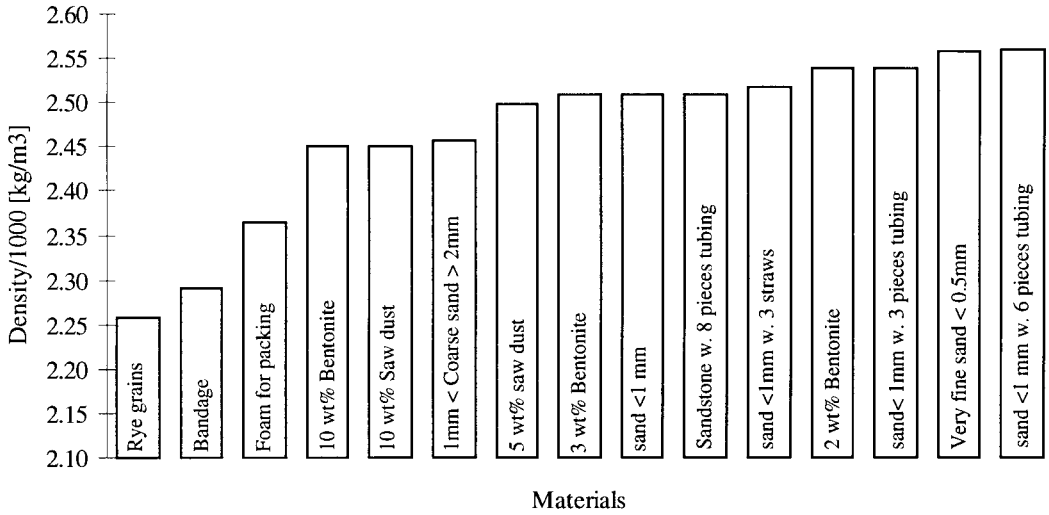

Fig. 2. Performances of various granular materials as absorbers of fluid expressed from PRC pastes during isostatic pressing. Best performances give higher paste densities. Where a 'wt%' entry is shown, the remaining material weight was made up with < 1 mm sand. Where straws or tubing are mentioned, the absorber was configured in three or four longitudinal segments separated by straws or tubing

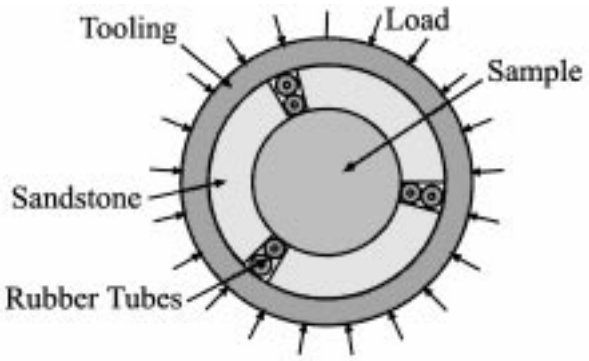

Fig. 3. Schematic representation of the tooling design with the porous interface and the cement sample in the middle

Europe SO 5-7263-0), the lid was fitted and secured. By appropriate manipulation of compressed air and hydraulic oil supply valves, the pressure was brought up in stages to a maximum of 25 000 psi ($\approx$170 MPa). A range of pressurisation rates and holding pressures were employed. The following procedure was adopted as optimum: 0–10 MPa hold for 2 minutes; 10–80 MPa hold for 1 min; 80–170 MPa hold for 5 s and depressurise over 3 min.

3 Sample characterisation

As before,[2,4] residual w/c was calculated based on sample weights before and after pressing, using the expression:

$$\mathrm{w/c}' = (W_2 - 0{\cdot}77W_1)/(0{\cdot}77W_1)$$

where W_1, and W_2 are the weights of the sample before and after pressing, respectively. It is assumed that there has been no water loss during curing, that the paste is homogeneous with respect to the distribution of water and cement, and that W_2 is not influenced by loss (or gain, i.e. from the porous interface) of solids on release after pressing. As in a previous study,[2] w/c data are correlated with densities and are presented in Fig. 4.

Flexural strength measurements and indirect tensile strengths by diametrical compression testing (Brazilian splitting test) were made using a universal testing machine. All microscopy was carried out on polished sections. These were prepared by cutting slices from pressed cylinders using a diamond saw (South Bay Technology Inc., Model 650) and embedding them in epoxy resin. The sections were then polished in three stages using 600 grit paper, 6 μm diamond paste and 0·3 μm Al_2O_3

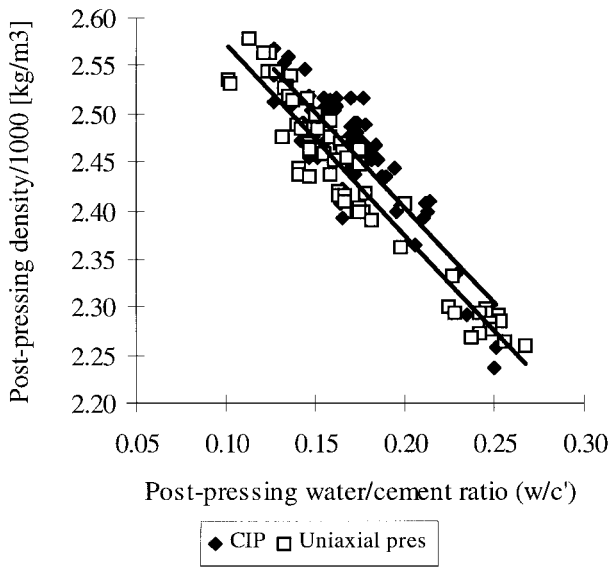

Fig. 4. Correlation between sample density and calculated w/c′. Superimposed data are from previous work using uniaxial, unidirectional pressing geometry.

paste prior to mounting on a stub and coating with carbon. The samples were loaded into the sample stage of an ISI-SS40 SEM.

4 Results and discussion

The material chosen for the tooling is very important to the quality of the pressed product. When the vessel was initially made from polyurethane, a stiff polymer, virtually all samples broke during pressing. Consistently better samples were obtained with the softer CIL Monothane A20 vessel and the rubber tubing, supporting the observation that the vessel should have a lower stiffness than the sample.[5]

An essential feature of the development of the isostatic pressing approach to PRC products lies in the design and fabrication of a fluid absorbing interface for the expressed pore water. The design of the interface requires that the material is porous and that it retains some porosity and water absorbing potential even after collapse under the applied pressure. Figure 2 shows the range of materials tested. The most effective interface was fabricated from < 1 mm sand, formed into a cylinder with PVA binder and then cut longitudinally into three segments. The segments were separated in the tooling by plastic tubes so that during pressurisation, the tubes collapsed preventing a surface consolidation or 'egg shell' effect (in which the centre of the sample would not be pressurised). Consistently this configuration gave products of highest density and so it was subsequently used routinely in the preparation of further samples for testing.

Figure 4 shows the very good agreement between the density–w/c data sets for isostatically pressed specimens and those produced using the uniaxial, unidirectional method.[2–4] This is however a property of the material rather than the method but it is encouraging that the same correlation between density and calculated w/c exists despite the different fabrication methods being used.

The strength data are presented in Fig. 5. Again, very good agreement between the indirect tensile strengths from both methods is observed and again, there is an exponential type relationship between the tensile strength and sample density as might be predicted from a Griffiths fracture model. As expected, the flexural strength follows the same general relationship.

In anticipation that the uniaxial, unidirectional pressing procedures were damaging samples, either by excessive shear or by sample ejection from the die, it was expected that the isostatic pressurisation approach would have improved strengths. The data show that the techniques have produced

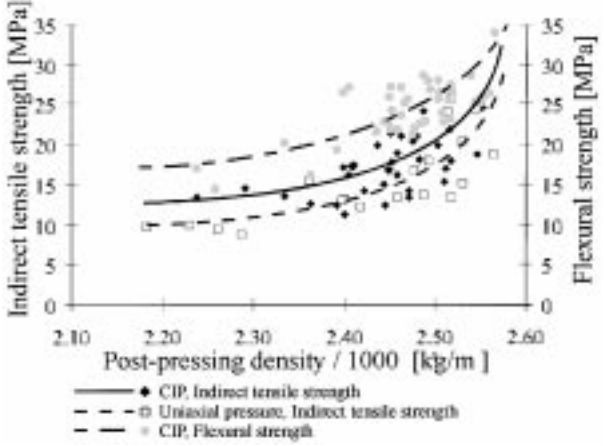

Fig. 5. Mechanical strength of PRC pastes produced by different pressing methods.

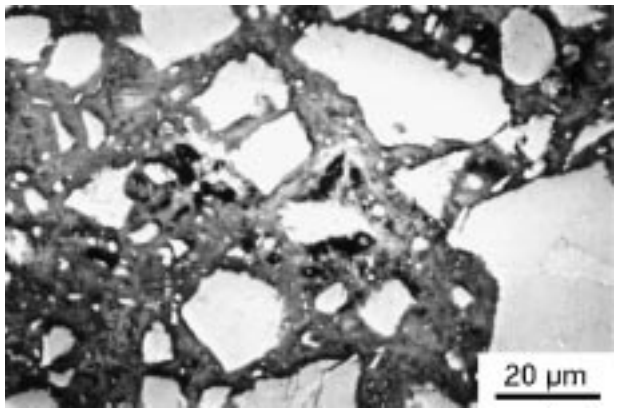

Fig. 6. Backscattered electron image of isostatically pressed cement paste showing regions of porosity within an otherwise densified matrix.

almost identical data sets and therefore, processing damage can not be the limiting factor in densification and strength enhancement. Instead, it is believed that these pressed materials develop macro-flaws during pressing, possibly by shearing, and these are not repairable by on-going hydration reactions. Consequently, neither technique is capable of improving the strengths of PRC pastes. Microscopy has again highlighted the dominance of unreacted cement and the densification of the matrix (see Fig. 6) but as in the products from the uniaxial pressing,[2–4] several zones of macroporosity are again observed. In general, the microstructures arising from both pressing techniques are comparable. No evidence of shear damage was observed, either macroscopically or microscopically, but they cannot be ruled out based on the results of mechanical strength testing.

5 Conclusions

It has been shown for the first time that hydrated materials can be partially de-watered during isostatic pressing by the suitable design of a sample

tooling. A porous interface between the sample and the container can be fabricated to effectively absorb the expressed fluid. In the case of hydrated cement pastes, as in this study, fine grained sand formed into a cylindrical shape using a mould and PVA binder is the most effective.

The physical and mechanical properties of isostatically pressed cement pastes are comparable to those pressed by uniaxial, unidirectional pressing geometry even though the isostatic pressing was limited to a pressure of 170 MPa compared with 200 MPa in the previous method. This suggests that strength limitations, observed in the previous studies,[2–4] are unlikely to be due to sample damage during ejection from the pressing dies.

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References

1. Morris, K. J., Cold isostatic pressing for forming ceramics. In *Encyclopaedia of Material Science and Engineering*, Vol. 1, ed. M. B. Bever. Pergamon Press, Oxford 1986, p. 707.
2. Macphee, D. E., PRC—pore reduced cement: high density cement pastes by pore fluid extraction.. *Advances in Cements Research*, 1990, **3**(12), 135–142.
3. Macphee, D. E., Lachowski, E. E., Taylor, A. H. and Brown, T. J., Microstructural development in pore reduced cement (PRQ). *Mat. Res. Soc. Symp. Proc.*, 1992, **245**, 303–308.
4. Geslin, N. M., Israel, D., Lachowski, E. E. and Macphee, D. E., Durability and microstructure of pore reduced cements (PRC). *Mat. Res. Soc. Symp. Proc.*, 1995, **370**, 237–244.
5. Merchant, I. J., thesis, Ph.D. 'The pressing of ceramic powders' University of Newcastle upon Tyne, 1993.