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Scientific paper

Mechanical Behavior of Cement Paste and Alterations of Hydrates under High-Pressure Triaxial Testing

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Abstract

High confining pressure works on concrete under various conditions such as concrete structures deep underground/sea, the lower floors of an extremely tall building and on the foundation concrete piles of an enormous structure such as dam. Understanding the performance of concrete and the deformation mechanism under high confining pressure is important for avoiding unexpected risks and for rationalization of design. A high-pressure triaxial test was conducted on cement paste to understand the mechanism of mechanical performance of concrete under a high confining pressure. The deviatoric stress-axial strain relationship of cement paste was independent of confining pressure during ductile deformation under confining pressures greater than 30 MPa. Ion-milled cross-sections of specimens were examined by scanning electron microscopy, and the obtained backscattered electron images were darker after the test. This darkening may indicate the alteration of hydrates at the molecular level caused by deformation involving crystal plasticity. Furthermore, the pore volume of the sample tested at 400 MPa was drastically reduced.

1. Introduction

Application of concrete is becoming more extensive because of new social demand and technology development. For example, high-level nuclear waste is disposed of underground at depths of more than 300 m, where concrete is expected to serve as both structural and water-sealing material (Owada *et al.* 2008). Another plan involves development of a city using concrete under the ocean at a depth of 3000 to 4000 m, which is expected to become technically feasible around 2030 (McCurry 2014). At this depth, water pressure is 30 to 40 MPa. These two examples share a common condition in which concrete is subjected to high confining pressure (P_c). In other examples, high pressure can act on the concrete in the lower floors of an extremely tall building and on the foundation piles of an enormous structure such as dam. When concrete is used with large quantities of expansive additive under strong confinement, e.g., by a steel pipe, large confining stress works on the concrete. A calculation based on the strain in the steel pipe indicated that the pressure was about 6 MPa (Nishigori 1977). Furthermore, impact loading can cause large triaxial stress. When an

object of 2.3 kg collides with concrete at 315 m/s, it can cause a mean stress of 150 MPa according to a simulation in which necessary parameters were validated by experiments (Gran and Frew 1997). As shown above, high P_c works on concrete in a wide variety of applications. Understanding the performance of concrete and the mechanism under such conditions is important for avoiding unexpected risks and for rationalization of design. Currently, an enormous amount of concrete is produced and disposed of all over the world. In Japan, over 90% of concrete waste is recycled, most of which is filled underground as base-course material. In the long run, buried concrete waste accumulates on the earth's surface and gradually becomes a component of the crust. Therefore, as well as natural rocks, it is important to understand how concrete behaves underground. In the future, the effects of weathering or leaching need to be studied by taking aging into account.

Many studies have investigated the performance of hardened concrete (HC) under high P_c (Gabet and Daudeville 2008; Malecot *et al.* 2010; Poinard *et al.* 2010). For example, the effects of cement paste volume, aggregate size (Vu *et al.* 2011) and shape (Poinard 2012), saturation degree (Vu *et al.* 2009), and loading rate (Zeng *et al.* 2013) have been investigated. These studies have revealed that the fracture style of HC changes depending on P_c (Sfer *et al.* 2002) (**Fig. 1**), where an increase in P_c reduces the effects of the cement paste volume (Poinard *et al.* 2012) while increasing the effects of the saturation ratio (Vu *et al.* 2009). Changes in the pores were also observed, and the relationship of confinement-induced microcracking and porosity reduction to the mechanical performance was discussed (Poinard *et al.* 2012). Although the changes in porosity and mechanical performance have been studied, the mineralogical changes in hydrates are not well known, possibly because they are

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Fig. 1 Fracture style of HC at different confining pressure σ_L . With permission of ASCE, from (Sfer *et al.* 2002).

difficult to evaluate. In concrete, the volume ratio of cement paste is about 30%, existing as interstitial filler between the aggregates of various sizes that occupy majority of the volume. Consequently, the observation of hydrates is difficult. In addition, we could not find any studies on the mechanical performance of cement paste under high pressure.

In the present study, a high-pressure triaxial test was conducted on hardened cement paste (HCP) to understand its mechanical performance under high P_c and the mechanism involved. To examine the altered hydrates, cross sections of the samples were prepared using an ion-milling method, and back-scattered electron images (BEIs) were captured. Porosimetry was used to evaluate any change in porosity. The obtained results were discussed through comparison with literature on HC and natural rocks with compositions or properties similar to

Table 1 Cement property.

Chemical composition (%)					Density	Fineness (Blaine)
Ig. Loss	MgO	SO ₃	Na ₂ O _{eq}	Cl ⁻	g/cm ³	m ² /kg
2.00	1.45	1.95	0.58	0.020	3.15	335

HCP, such as limestone, marble, and porous rocks.

2. Experimental

2.1. Specimen preparation

In this study, we used HCP with a water-cement ratio (W/C) of 40%. The properties of the Ordinary Portland cement are presented in **Table 1**. The mixing procedure was based on JIS R 5201; the paste was first mixed for 60 sec at low speed (orbital rotation: 62 ± 5 rpm, planetary rotation: 140 ± 5 rpm). The mixer was stopped for 30 sec to 60 sec to scrape off cement paste on the side of the mixing bowl and the paddle. Then the paste was mixed for 90 sec at high speed (orbital rotation: 125 ± 5 rpm, planetary rotation: 285 ± 5 rpm). The mixed paste was cast in a steel prism mold of $10 \times 10 \times 40$ cm and sealed. It was demolded 24 h after casting and then kept under water for 28 days. The temperature of the room and water was 20°C. After curing, eight cylinders of $\phi 2 \times 4$ cm were cored from the prism HCP. Only the part deeper than 2 cm from the surface was used to avoid the effect of bleeding. Both ends of the cylinder were ground to achieve a parallelism of 0.005 and surface roughness of 0.25 μm . The prepared cylinders were immersed in acetone for 3 days to stop the hydration reaction and reduce capillary suction in the subsequent drying period. To eliminate the possible effects of pore pressure during the triaxial test, the cylinders were dried for two weeks at 40 °C and 10% relative humidity. The water content was 7.5% after drying, which was obtained from the weight loss during further drying at 105 °C for 24 h. Since HCP had been immersed in acetone, the 7.5% residual fluid was a mixture of water and acetone. Carbonation depth of a sample which had been kept in a sealed container (20 °C and 10% relative humidity) for one month after the drying at 40 °C was measured with 1% solution of phenolphthalein in ethyl alcohol. The sample was split horizontally with a chisel at the middle and the solution applied on the fracture surface indicated a carbonation depth of 0.3 mm (**Fig. 2**), meaning 97% of the cross-sectional area was not carbonated. The mixed paste was also placed in three plastic cylindrical molds ($\phi 50 \times 100$ mm) and sealed. They were demolded 24 h after casting and kept under water until the uniaxial compression test (based on JIS R 5201) at 28-day age.

2.2. High-pressure triaxial test

A high-pressure triaxial test was executed to study HCP under high P_c . The test apparatus is shown in **Fig. 3**. The steel spherical tank, located at the center of the loading frame, was filled with silicon oil (density: 0.935 g/cm³, kinetic viscosity at 25 °C: 10 mm²/s), the confining me-

Fig. 2 Carbonation depth of HCP measured one month after drying at 40 °C (One tick of the scale in the figure is 1 mm).

Fig. 3 Triaxial testing machine.

dium in the test (**Fig. 4**). The schematic view of the loading system is shown in **Fig. 5**. A specimen was assembled with tungsten carbide spacers and molybdenum sheets (55 μm in thickness), which was used to avoid cracking due to stress concentration at the sharp corner of the spacers. Laboratory atmosphere was led to the end face of the HCP sample through small center holes of the spacers and pistons to avoid pore pressure being generated during experiments. The entire assembly was placed on the tip of the piston (**Fig. 6**). The sample, spacers, and the tip of the bottom piston were enclosed with a heat-shrinkable FEP (Fluorinated ethylene propylene) tube which sealed the sample from the confining medium while securing the assembly to the bottom piston. The tube was heated up from the outside with a heat gun for shrinkage. To check the temperature of HCP specimen during heat treatment on the tube, a hole of 2 mm in diameter was prepared on a HCP sample and the temperature in the hole was measured using a needle probe thermometer. The distance from the sample surface to the hole was 2 mm. A heat-shrinkable FEP tube was placed over the HCP sample and heated until the tube touched the sample completely. The obtained maximum temperature reached was 46 °C, so we do not worry about the effect of this procedure. After fixing, the entire assembly was inserted into the tank shown in **Fig. 4**. A Teflon sheet of 0.5 mm thick was inserted into the contact point be-

Fig. 4 Closeup of steel tank. Top and bottom pistons were used to apply axial load to the specimen. Two horizontal pistons equipped for true-triaxial tests were not used and kept away from the specimen assembly.

tween the top face of the assembly and the tip of the top piston inside the tank to reduce lateral friction. Friction on the molybdenum sheets are higher, so lateral displacement that might occur as a result of the large asymmetric deformation of the HCP sample is taken by the sliding between the top piston and the top end piece, keeping the other parts (except inside the sample) centered to each other. P_c s of 30, 100, or 400 MPa were applied to the samples by pressurizing the oil with an intensifier. Only one specimen was tested under each P_c . Axial load (for differential stress) was then applied by moving the top and bottom pistons (**Fig. 4**) toward each other at a rate of 0.1 mm/min. The load was measured by the load cells on the pistons. If the tube was broken during the test, the oil would leak through the holes in the spacers. However, such leakage was not observed, and we concluded that the samples remained sealed throughout experiments. After the triaxial tests, the

Fig. 5 Schematic view of the loading system. Note the left and right pistons were not used for any active purpose in the present experiments. They never touched the sample assembly.

samples were removed and inspected by the naked eye while still in the tubes.

2.3. Scanning electron microscopy (SEM) observation inside the specimens

After each high-pressure triaxial test, the samples were removed from the steel tank. Following visual inspection, small ($2 \times 5 \times 10$ mm) pieces were taken out from the center of the samples. These pieces were washed with n-hexane to remove the silicon oil, embedded in resin and cut. Their cross-sections were milled with ion beam (Brodsch *et al.* 2013) to obtain flat surfaces at a molecular scale. We did not employ ordinary mechanical polishing to avoid deformation and scratch of the sample by abrasives. In ion milling, hardly any physical stress is induced (Brodsch *et al.* 2013). Platinum was spattered on the sample surface for conduction. The BEIs were then captured using an accelerating voltage of 10 kV. We also took a small piece from a virgin sample of the same age, embedded it (without washing) in resin, cut it and smoothed its cut surface using argon beam ion milling. To obtain quantitative information from the BEIs, a histogram with 256 grayscale levels was prepared.

2.4. Porosity analysis

Using the rest of the samples from the SEM observation, mercury intrusion porosimetry (MIP) was conducted to evaluate their porosity. Several cubes with edges measuring 3 mm (1.5 g) were taken from random locations of the sample and washed with n-hexane. The pieces were then immersed in acetone for 24 h, D-dried for 24 h, and analyzed. We followed the same procedure for the virgin sample but without washing.

3. Results

3.1. High-pressure triaxial test

The obtained deviatoric stress-nominal axial strain (SS) curves for tests under different P_c s are shown in Fig. 7. The deviatoric stress (σ_d) was calculated by dividing the difference between the measured load and the load due to oil pressure by the sample's cross-sectional area. The

Fig. 6 Sample assembly.

nominal axial strain (ϵ_a) was calculated by dividing the relative displacement of the top and bottom pistons by the sample length. This included elastic deformation of the pistons and spacers, which was not important in the present study where much greater inelastic deformation of the sample was concerned. Also, the piston and spacer deformation was much less than the elastic deformation of our sample with low Young's modulus. In Fig. 7, measured data up to the point just before the start of the unloading operation are shown. The broken line in the figure indicates the average uniaxial compressive strength (78.1 MPa). All the three curves show similar linear trends up to $\epsilon_a = 0.5\%$ and $\sigma_d = 100$ MPa, indicating a linear elastic stage. After that, σ_d increases with a reduced slope in all cases, an indication of ductile deformation. The yielding point was clear and almost the same ($\epsilon_a = 0.5\%$ and $\sigma_d = 100$ MPa) for $P_c = 30$ and 400 MPa. The yielding for $P_c = 100$ MPa was gradual, but starting at more or less the same strain. The strain-hardening slope is similar for the three tests. Duc-

Fig. 7 Deviatoric stress-nominal axial strain response for different confining pressures.

Fig. 8 Samples after triaxial test (Numbers below figures indicate confining pressures).

Fig. 9 Failure style of Wombeyan marble at different P_c . From left to right, $P_c = 0, 3.5, 28, 46$ and 100 MPa. Published with permission of Geological Society of America, from (Paterson 1958).

tile deformation lasted longest at the highest P_c of 400 MPa, up until $\varepsilon_a = 3.5\%$, where a small sudden stress drop occurred. Here, 'ductile deformation' doesn't contain the stress descending portion. For $P_c = 30$ and 100 MPa, similar sudden stress drops occurred at an earlier strain of $\varepsilon_a = 2$ to 2.5% . As the result of the longest-lasting ductile stage with strain-hardening, the test at $P_c = 400$ MPa showed the highest peak strength. On the other hand, the strain-hardening curves of the three tests do not show a systematic dependence on P_c . As we will discuss in §4.3, this may imply that the ductile strength was mainly limited by crystal plasticity, rather than frictional cataclastic flow (Paterson and Wong, 2005), at all the tested levels of P_c (30 to 400 MPa).

In Fig. 8, tubed samples after the test are shown. With 30 MPa of confinement, single macroscopic shear plane developed at an angle of about 30° off the most compressive principal stress axis. This faulting style is universally seen in triaxial compressive tests in brittle regime but with significant confinement to suppress the splitting mode of failure typical of zero or very low P_c

(Hatanaka *et al.* 1987; Sfer *et al.* 2002; Paterson 1958) (Fig. 9). Under a P_c of 100 MPa, the middle of the sample bulged locally. There were several axial cracks of 0.3 mm wide on the sample surface and axial and circumferential cracks at the bulge, but these were all thin hair-line cracks and shear displacement in them appeared nil. At $P_c = 400$ MPa, the sample was thinned laterally as if it had been squeezed by P_c . The diameter decreased by 10% and one horizontal macrocrack was observed. At the middle of the sample, there were creases in the tube horizontally and at an angle of 20° from the horizontal plane. On the other hand, lateral bulging occurred only at the top end of the sample.

3.2 SEM observation inside the specimens

The cross sections of the pieces taken from the virgin and tested samples were observed using SEM. The BEIs of the ion-milled surface are shown in Fig. 10. They are also shown in Fig. 11 as a histogram of gray-scale integers that range from 0 (black) to 255 (white). In Fig. 10, compared with the virgin sample, the area of voids

Fig. 10 Reflected electron images of samples after ion beam milling. (Numbers below figures indicate confining pressures)

Fig. 11 Histogram of gray value of images in Fig. 7.

(shown in black) is reduced as the P_c increases. However, in the sample tested with a P_c of 400 MPa, many microcracks are observed in multiple directions. These voids and microcracks have a gray value of around 0 and the magnified figure in **Fig. 10** demonstrates the reduction of their area. Note that pores smaller than $0.1 \mu\text{m}$ in diameter (§3.3), which was smaller than the resolution of **Fig. 10**, $1 \mu\text{m}$, contributes a lot to the total porosity shown in **Fig. 13**. In all SEM photos, fairly large white isolated clasts up to about $30 \mu\text{m}$ are buried in the gray

matrix. In the virgin sample, the entire gray matrix is uniform in tone. **Fig. 11** shows this graphically, there is a narrow peak with its center at the gray value of 160. At a closer look, there are few small darker gray phenocrysts, but the amount is so minor that it is not recognized in the histogram. After testing with P_c s of 30 and 100 MPa, the dark gray area increases so as to surround the light gray area. In **Fig. 11**, the change appears as an asymmetric widening of the distribution toward darker, lower gray values. In the case of $P_c = 400 \text{ MPa}$, many small spots of

further darker (~90) gray appear in the matrix. In **Fig. 11**, the peak of the distribution shifts to the left, and the frequency at a gray value of around 90 increases three-fold compared with the others. Additional observations were made while tilting the sample, but no change was observed by doing this.

After small pieces were taken from the specimens for the SEM observation, the FEP tubes were removed (**Fig. 12**). The sample tested under a P_c of 30 MPa split into two parts, and no small fragments were found. On the other hand, for $P_c = 100$ and 400 MPa, after the removal of the tubes, the specimens collapsed into fragments and powders. The fine powders were about 1 and 0.1 mm in diameter in the cases of 100 and 400 MPa, respectively.

3.3. Porosity measurement of the specimens

The cumulative pore volume measured by MIP is shown in **Fig. 13**. Compared with the virgin sample, the others had much less porosity after the triaxial test. Especially, the sample after testing at $P_c = 400$ MPa had very few pores, even the smallest ones. The cumulative pore volume at 3 nm pore diameter was about 18% before the test. However, it decreased to less than 1% after the test at $P_c = 400$ MPa.

4. Discussion

4.1 Macroscopic fracture pattern

Here, we focus on the macroscopic fracture style. As shown in **Fig. 8** and **Fig. 12**, fracture patterns differed depending on the P_c . At 30 MPa (**Fig. 8a**, **Fig. 12a**), single oblique macroscopic shear fracture surface was formed. This pattern is known to occur in brittle regime under moderate confinement. A similar pattern was reported in the case of Wombeyan marble at 3.5 MPa (Paterson 1958) and in the case of HC at 9 MPa (Sfer *et al.* 2002). When the P_c was increased to 100 MPa, our HCP sample deformed by bulging laterally without forming a distinct macroscopic fracture surface (**Fig. 8b**). The Wombeyan marble showed similar deformation when the P_c was increased above 30 MPa (Paterson 1958). In HC (Sfer *et al.* 2002), macroscopic fracture

occurred up to their highest P_c of 60 MPa, though the fracture geometry at 30 and 60 MPa was clearly not of shear-faulting type. So, it appears that the range of P_c exhibiting a macroscopic shear fracture surface or lateral bulging (distributed deformation) depends on the material and the testing condition. At $P_c = 400$ MPa, the sample became thinner as if it had been squeezed laterally, and horizontal-subhorizontal (20°) creases occurred on the tube (**Fig. 8c**). The squeezing and crease indicate shortening of the sample in the radial and axial directions, respectively. The horizontal crease may have been caused by a local compaction band, which is reported for HC (Malecot *et al.* 2010), porous sandstone (Wong and Baud 2012), and so on, all under very high P_c s. In **Fig. 13**, the porosity decreased drastically in the 400 MPa case compared with the 100 MPa case. In porous rock, a sudden volume decrease due to the collapse of pores at certain very high pressures was reported (Curran and Carroll 1979; Wong and Baud 2012). In HCP, sudden pore collapse might take place between $P_c = 100$ and 400 MPa and this collapse could be one of the reasons for the pulverization shown in **Fig. 12**.

As shown above, failure properties of HCP were basically similar to those of carbonate rocks but there are

Fig. 13 Pore size distribution.

Fig. 12 Samples after removal of tube. (Numbers below figures indicate confining pressures)

some differences. These differences are likely to be attributable to material properties such as chemical composition, porosity (Vajdova *et al.* 2004), or grain size, but possible effects from sample preparation and test method, such as aspect ratio and friction at the ends of the samples (Paterson 2005), cannot be ruled out at this point. In the future, with HCP, the effects of the aspect ratio and friction at the sample ends need to be examined. Nonetheless, we can say that the range of P_c from 30 to 400 MPa has turned out to be sufficient to create different fracture styles for HCP, namely, brittle faulting, distributed ductile fattening, and pore collapse/pulverization.

4.2 Brittleness and ductility in the deviatoric stress-nominal axial strain curve

As mentioned earlier, elastic limit of the tested HCP was about $\varepsilon_a = 0.5\%$, in the all tested P_c s of 30, 100, and 400 MPa (Fig. 7). Significant ductile deformation followed in every case, but the duration of ductile stage differed. At $P_c = 30$ and 100 MPa, peak stress was shortly followed by an abrupt stress drop of a few tens of MPa that occurred at $\varepsilon_a = 1.8$ to 2.5% , marking the end of ductile deformation, while a similar stress drop occurred significantly later at $\varepsilon_a = 3.5\%$ under $P_c = 400$ MPa, meaning greater ductility. The general increasing trend of ductility (in terms of SS curves) with P_c is well known for rocks (Heard 1960; Edmond and Paterson 1972; Vajdova *et al.* 2004; Paterson and Wong 2005) and HCs (Sfer *et al.* 2002), however, correspondence to the fracture pattern differs as we discuss in detail below.

We begin by comparison with the brittle-ductile transition of rocks, where certain systematic trends have been established after many years of research (Paterson and Wong, 2005). Especially, carbonate rocks are structurally close to HCP in that they are aggregates of soft minerals with relatively sorted grain size.

The distinct fracture surface, 30° off the maximum principal stress, seen as in our 30 MPa test (Fig. 8a, Fig. 12a), is a typical 'brittle' failure style of rocks (Paterson 1958). For hard silicate rocks at room temperature, such brittle faulting is not preceded by significant ductile deformation (Paterson and Wong 2005). In contrast, faulting in the present test at 30 MPa most likely occurred concurrently with an abrupt stress drop at $\varepsilon_a = 2.5\%$, so was preceded by ductile strain of about 2%. This, actually, is quite common for carbonate rocks, whose constituent minerals are much softer than tectosilicates. Examples include coarse-grained Wombeyan marble at $P_c = 3.5$ to 14 MPa (Paterson 1958). Heard (1960) found similar behaviors for fine-grained Solenhofen limestone at higher P_c of 40 to 75 MPa but only at raised temperatures of 150 to 400°C. At room temperature, brittle faulting of the limestone was not preceded by significant ductile deformation. Fine-grain carbonate rocks require a much higher P_c to exhibit ductility than coarse-grained carbonate rocks (Fredrich *et al.* 1990). Our HCP sample is definitely 'fine-grained,' but the results rather resembled to the coarse-grain marble,

showing significant ductility at P_c as low as 30 MPa. This is presumably attributable to inherent low plastic strength of the constituent minerals (hydrates), compared with calcite.

The SS curve of our HCP at $P_c = 100$ MPa showed an abrupt stress drop at $\varepsilon_a = 2\%$, similarly to the 30 MPa case (This is slightly earlier than the $P_c = 30$ MPa case, contrary to the expectation, but with limited number of experimental runs, this may well be a matter of experimental reproducibility.) However, a macroscopic fracture surface did not occur in the 100 MPa test (Fig. 8b), suggesting enhanced ductility compared with the 30 MPa test. Instead, the sample exhibited a localized bulging, which resembles a band of distributed plastic shear deformation, commonly seen in ductile deformation of carbonate rocks (Paterson 1958). They ideally occur at 45° off the maximum principal stress, i.e., on the plane of maximum shear stress because plastic strength of crystals does not depend on the normal stress to the crystallographic slip plane. Our bulged zone seems to be inclined at about 45° , indeed.

Abrupt stress drop in tests with a servo-controlled axial displacement means rapid shortening of the sample. In literature, we do not find the cases where abrupt stress drop occurred without forming some sort of macroscopic fracture surface. We speculate two possibilities to explain this contradiction. First possibility is the unstable acceleration of plastic deformation in the ductile shear band. Though plastic deformation is generally deemed to be a slow process, spatial localization implies the occurrence of strain weakening in the band as required for positive feedback in localization. Second possibility is hinted by the observation that the post-experimental sample was pulverized (Fig. 12). Though we do not know at what timing the pulverization occurred, this could be the cause of the abrupt stress drop at $\varepsilon_a = 2.5\%$. Pulverization was seen in HCP tested at 400 MPa as well, where, again, no macroscopic fracture surface occurred, while the SS curve had an abrupt stress drop at $\varepsilon_a = 3.5\%$. This stress drop event could be associated with the formation of subhorizontal compaction bands. Further experiments including AE monitoring might be useful to identify the reason for this perplexing phenomenon of stress drop without forming a macroscopic fracture surface.

Setting aside the reason for the strength drop event, it is important to note that the sample behavior significantly changed upon this event. In both 100 and 400 MPa tests, the strain-hardening trend was terminated upon the event. Hence, we tentatively surmise that the strain at which the abrupt stress drop occurred marks the end of ductile deformation of HCP.

The present HCP test at $P_c = 400$ MPa showed the greatest ductility as expected. However, the deformation style is far from the typical ductile deformation known from rocks. Lateral bulging, the icon of ductile deformation, is only seen at the contact with the end piece; for most part the sample diameter rather decreased! Fur-

thermore, the 3.5% of ε_a to the stress drop is unusually low for the P_c . Both marble and limestone take up more than 10% ductile ε_a at such a high P_c (Paterson 1958; Heard 1960). Thus, although the low plastic yield strength of cement hydrates allowed the onset of ductility at a fairly low P_c for the small grain size, macroscopic ductility of HCP is fairly limited even at the very high P_c of 400 MPa. In § 4.4, on the basis of microscopic sample observation, we propose that the resultant pulverization is a critical factor in the very high P_c regime. Note that ductile deformation tests with rocks are typically done with low-porosity specimens.

We now compare the present results with that of HC, mainly with the results reported by Sfer *et al.* (2002) at $P_c = 0$ to 60 MPa (**Fig. 1**, **Fig. 15**). In their tests, distinct brittle shear faulting occurred only at a very limited condition of $P_c = 9$ MPa. In this test, however, axial stress peaks at $\varepsilon_a = 0.5\%$ and then decreased gradually up to $\varepsilon_a = 10\%$ without causing an abrupt stress drop. Actually, abrupt stress drop was seen in his HC tests only at $0 \leq P_c \leq 4.5$ MPa, where axial splitting and/or distributed axial cracking of visible sizes played a major role, as universally seen in uniaxial compression tests of almost any rock. Therefore, while the SS curve at $P_c = 9$ MPa does not look brittle, it is not appropriate to take the disappearance of the abrupt stress drop at $P_c = 9$ MPa as the manifestation of brittle-ductile transition of the deformation mechanism of HC. As evidenced by the distinct shear fracture surface 30° off the maximum principal stress, Sfer *et al.*'s test at $P_c = 9$ MPa resulted in typical brittle faulting at ε_a as small as 0.5%; the gentle strain weakening after the peak would be rather ascribed to the frictional sliding on the rough fracture surface involving deep interlocking between large, hard gravels (Maekawa *et al.* 2003) and also deep plowing of the soft matrix made of cement and sand by the large gravels, that would cause gradual wear-induced weakening over a long slip distance. Such distinction has some practical implication. For example, HC under $P_c = 9$ MPa would lose its sealing capability at 0.5% strain while it still supports a fair amount of shear load up to several % strain.

At highest P_c s of 30 and 60 MPa, Sfer *et al.*'s HC showed continuous strain hardening up to $\varepsilon_a = 10\%$, where the differential stress abruptly dropped by 90% or more. Their post-experimental sample showed a few thoroughgoing, curved and kinked macroscopic fracture surfaces including a major part subparallel to the maximum principal stress, rather than the typical shear fracture surface by brittle faulting, which runs 30 degree off the most compressive principal stress axis. However, the broken pieces bound by those few macrofractures retained good mechanical integrity. This fracture style contrasts with our HCP tests at 100 and 400 MPa (**Fig. 12**), where the sample lost integrity everywhere by pervasive pulverization without forming any macroscopic fracture surfaces. It is interesting that, despite these differences, the SS curves from our HCP tests and their HC tests commonly exhibited similar ductile looks accom-

panied by considerable strain hardening. Although the timing of macroscopic fracture in Sfer *et al.*'s experiments is not known, the authors inferred that the macroscopic cracking (if not thoroughgoing) occurred early on and the subsequent apparently very ductile SS curves reflect the slip-hardening friction between interlocking pieces. If so, HC's ductile behavior at 30 and 60 MPa is also apparent, as we suggested for their HC result at 9 MPa.

4.3 Confining pressure dependence during ductile deformation

We here focus on the absolute levels of SS curves of HCPs (cylindrical shape of $\phi 20 \times 40$ mm and dried at 40°C for two weeks) obtained at different P_c s. One remarkable feature of our HCP tests is that SS curves at different P_c s overlap each other during both initial elastic portion ($0 < \varepsilon_a = 0.5\%$) and following ductile portion ($0.5\% < \varepsilon_a < \text{stress drop event}$). In typical brittle-ductile transition experiments of carbonate rocks, two systematic P_c dependences are usually observed. Firstly, differential strength during ductile deformation is positively dependent on P_c . Secondly, as a result of this, change from elastic to ductile deformation curves, indicated by the steep-to-gentle change of SS-curves slope, occurs at a greater strain and differential stress for higher P_c . These results from rocks suggest that their ductile deformation mechanism is not the pure crystal plasticity whose strength should be independent of P_c . Indeed, at extremely high P_c s, e.g., about 600 MPa in **Fig. 14** of Edmond and Paterson (1972), and/or high temperatures, 400°C for Solenhofen limestone of Heard (1960), both dependences are lost for rocks as well. Thus, it is generally accepted that brittle-ductile transition in rocks has a broad intermediate regime where both crystal plasticity and frictional-cataclastic processes play a role in ductile deformation. In light of this understanding, the presently observed P_c -independent SS curves for HCP suggest that ductile deformation was almost purely governed by the low plastic strength of cement hydrates. Although the fracture pattern that involves intensive pulverization at 100 and 400 MPa indicates that cataclastic processes could accommodate much strain, the strength during ductile deformation seems to have been strongly limited by crystal plasticity.

Such easy transition to fully plastic behavior is not seen in HC (**Fig. 15**). For example, Malecot *et al.* (2010) found clear increase of ductile strength up to $P_c = 400$ MPa. This is probably because much of the shear strength of HC is supported by the strong gravel framework, whose plastic flow would require extreme conditions.

In addition, we note that there is a tendency known that ductile SS curves of high-porosity carbonate rocks tend to lose P_c dependence above certain levels of P_c . For example, Solenhofen limestone (Paterson 2005), Tavel limestone, and Indiana limestone (Vajdova *et al.* 2004) have porosities of 3%, 10% and 15.6%, respectively.

Fig. 14 Stress-strain curves in ductile deformation of Carrara marble at different P_c (kb). With permission of Elsevier, from (Edmond and Paterson 1972).

They showed less dependence when the P_c exceeded 200, 100, and 20 MPa, respectively. Our HCP sample had high, 18% initial porosity, and exhibit pulverization at higher P_c s of 100 and 400 MPa, similarly to porous rocks subjected to high P_c s (Wong and Baud 2012). So, phenomenology resonates definitely. However, it is not established why of this phenomenon, given that cataclastic flow expected of pulverized sample is an inherently pressure-sensitive frictional process. One speculation may be that free grain rotation enabled by the pulverization help each grain align to the crystallographic orientation compatible with macroscopic deformation, providing the environment for crystal plasticity to contribute efficiently to the macroscopic deformation. Note that calcite, the constituent minerals of limestones and marbles, is a relatively soft mineral well known for the easy appearance of anisotropic crystal plasticity such as twinning at room temperature (Turner *et al.* 1954). Limestone and marble are known to show ductile deformation under low P_c s (Vajdova *et al.* 2004; Paterson and Wong 2005). In marble, before the macroscopic fracturing took place, local yielding was confirmed to occur in the crystal particles (Paterson and Wong 2005; Sakaguchi *et al.* 2011).

4.4. Pervasive microfractures due to high confining pressure

In general, as the P_c increases, the elastic limit, both in stress and strain, increases. However, they can decrease in porous rock (Baud *et al.* 2000; Vajdova *et al.* 2004; Paterson and Wong 2005), likely due to distributed microfracturing induced by hydrostatic loading. As shown in Fig. 12, when the samples tested under P_c of 100 and 400 MPa were taken out of the tubes, they collapsed into small pieces. In general, when the crystal plasticity takes

Fig. 15 Stress-strain curves of HC at different confining pressure σ_L . With permission of ASCE, from (Sfer *et al.* 2002).

place evenly, the sample does not show macroscopic fracturing. The coexistence of pulverization and full plasticity could be explained by assuming that the crystal plasticity of each grain occurred in different directions due to the random variation of crystallographic orientations or that the pressure required for crystal plasticity was very different among grains. This is, we propose, why the sample could behave full-plastically, as a whole, while pervasively microcracked due to local incompatibility between neighboring grains. However, it is reported for HC (Poinard *et al.* 2012) and rocks (Paterson 2005) that microfracturing can be introduced not only by applying P_c and load but also by unloading. Therefore, in future, to properly understand the deformation mechanism, further examination is required to identify when pervasive fracturing was introduced to the samples.

4.5. Alteration of hydrates

Finally, we will discuss the change in hydrates due to the high-pressure triaxial test. As shown in Figs. 10 and 11, the BEIs became darker after testing at any P_c . The gray value in Fig. 11 can vary depending on the SEM observation condition, which is not completely-consistent from sample to sample. However, even if the curves are shifted relatively to correct the difference coming from the observation condition using the large white spots in Fig. 10 as a common reference, which is seen at gray values of around 200 and 220, the samples after testing are still darker than the one before testing. BEI brightness changes according to the atomic number, surface roughness, and molecular structure of the material (Lloyd 1987; Shimizu *et al.* 2006). In the field of metallurgy, BEIs are used to observe dislocations (Gutierrez-Urrutia *et al.* 2009). In our case, the atomic number could not change, and the prepared surfaces were smooth at a molecular scale. Reduction in porosity cannot be the reason of darker BEIs under higher confining pressure because denser material becomes brighter in

BEI, which is opposite to our results. Thus, the change in BEI brightness is likely due to a structural change at a molecular scale. As discussed in § 4.3, given that P_c -insensitive ductility is the manifestation of crystal plasticity due to intragranular slip or twinning, HCP likely suffered molecular-scale changes in its hydrates. The yielding strength of 100 MPa, commonly seen in tests at $P_c = 30$ to 400 MPa, indicates the low level of differential stress for such processes to operate. Additional experiments will be conducted in the future for validation purposes because, at this point, we cannot rule out the possibility that the alteration of hydrates occurred already by hydrostatic loading.

5. Conclusion

Triaxial tests of HCP, with 18% initial porosity, were conducted under P_c s of 30, 100, and 400 MPa. The results covered three representative failure styles previously known in triaxial tests of porous carbonate rocks composed of relatively soft minerals: the oblique brittle faulting, the distributed ductile deformation, and the pore collapse and resultant pulverization.

Typical oblique brittle faulting occurred only at $P_c = 30$ MPa, but the macroscopic failure by faulting was preceded by a significant ductile phase. At $P_c = 100$ MPa, bulging occurred as the sample exhibited a modestly strain-hardening ductile SS curve. Role of crystal plasticity was suggested by BEIs of the post-experimental samples where much of the matrix hydrates seems to have suffered molecular-scale alterations during tests. No macroscopic fracture surface was formed even after a small sudden stress drop occurred at 2.5% strain. Abrupt stress drop without a macroscopic fracture surface is probably not reported in previous literature, and we are not sure of the cause. Post-experimental samples of the present tests at $P_c = 100$ and 400 MPa were pulverized throughout, similar to the pore collapse phenomenon of porous rocks under very high P_c s. Consistently, sample porosity became lower after the tests; especially the sample tested at $P_c = 400$ MPa had a porosity of only 1%. Formation of compaction bands is suggested by visual inspection of the sample after this test.

Interestingly, SS curves at different P_c s overlapped each other, though the experiment (and ductile phase) lasted to a greater strain at a higher P_c . This implies that the strength during the ductile phase (from yield point at 0.5% strain to the small abrupt stress drop) was governed by the pressure-insensitive plastic strength of the hydrates, notwithstanding that the sample was totally pulverized in the tests at $P_c = 100$ and 400 MPa. This result contrasts with rocks and HC, where the ductile (-looking) SS curves have a positive dependence on P_c , suggesting that their ductile strength is partially controlled by frictional cataclasis. We propose that the low inherent plastic strength of cement hydrates is the reason for the difference, as supported by intensive alteration captured by BEIs. We argue that the occurrence of pulverization can

coexist with the easy flow of the hydrates, if we presume the crystallographic anisotropy of plastic strength and/or their inhomogeneity.

Overall, from the present experiments that cover a wide range of P_c , though clearly insufficient to propose anything quantitative, we surmise that HCP behavior under confinement seems to well compare to rocks, especially carbonate rocks, whereas some differences exist that are probably attributable to the extreme weakness of the HCP's hydrates compared with rock-forming minerals.

On the other hand, by comparing the fracture style and the SS curves of HC from literature, we note that behavior of HC under confining pressures are not straightforwardly compared with HCP and rocks. What makes HC intractable is that the appearance of SS curves does not correspond well to the fracture pattern in the regular way expected from rock experiments under high P_c . Notably, very rough irregular fracture surfaces, that almost look like a splitting failure in unconfined tests of rocks, occur even under a fairly high P_c . This is presumably a result of the large size of gravel stones compared to the specimen size, bound together by weak cement paste, which may be deemed as a flowable material under some confinement as we saw in the present experiments. Although such is the very structure that gives the HC the exceptional usefulness as structural material, in order to evaluate, understand, and predict HC's properties under high pressure, starting with less formidable HCP may be an approach worth considering. Systematic studies on HCP including the effects of porosity, cement type, etc. may be prerequisite to begin the comprehensive studies of HC under confinement.

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References

- Baud, P., Schubnel, A. and Wong, T. F., (2000). "Dilatancy, compaction, and failure mode in Solnhofen limestone." *Journal of Geophysical Research: Solid Earth*, 105, 19289-19303.
- Brodusch, N., Boisvert, S. and Gauvin, R., (2013). "Flat ion milling: A powerful tool for preparation of cross-sections of lead-silver alloys." *Microscopy*, 62(3), 411-418.
- Curran, J. and Carroll, M., (1979). "Shear stress enhancement of void compaction." *Journal of Geophysical Research: Solid Earth*, 84, 1105-1112.
- Edmond, J. and Paterson, M., (1972) "Volume changes during the deformation of rocks at high pressures." *International Journal of Rock Mechanics and Mining Sciences & Geomechanics Abstracts*, 9(2), 161-182.
- Fredrich, J. T., Evans, B. and Wong, T. F., (1990) "Effect of grain size on brittle and semibrittle strength: Implications for micromechanical modelling of failure

- in compression." *Journal of Geophysical Research: Solid Earth*, 95, 10907-10920.
- Gabet, T. Malécot, Y. and Daudeville, L., (2008). "Triaxial behaviour of concrete under high stresses: Influence of the loading path on compaction and limit states." *Cement and Concrete Research*, 38(3), 403-412.
- Gran, J. and Frew, D., (1997). "In-target radial stress measurements from penetration experiments into concrete by ogive-nose steel projectiles." *International Journal of Impact Engineering*, 19(8), 715-726.
- Gutierrez-Urrutia, I., Zaefferer, S. and Raabe, D., (2009). "Electron channeling contrast imaging of twins and dislocations in twinning-induced plasticity steels under controlled diffraction conditions in a scanning electron microscope." *Scripta Materialia*, 61(7), 737-740.
- Hatanaka, S., Kosaka, Y. and Tanigawa, Y., (1987). "Plastic deformational behavior of axially loaded concrete under low lateral pressure." *Journal of Structural and Construction Engineering* (Trans. of AIJ), 377, 27-40. (in Japanese)
- Heard, H., (1960). "Transition from brittle fracture to ductile flow in Solenhofen limestone as a function of temperature, confining pressure, and interstitial fluid pressure." *Geological Society of America Memoirs*, 79, 193-226.
- Lloyd, G. E., (1987). "Atomic number and crystallographic contrast images with the SEM: A review of backscattered electron techniques." *Mineralogical Magazine*, 51(359), 3-19.
- Maekawa, K., Pimanmas, A. and Okamura, H., (2003). "Nonlinear mechanics of reinforced concrete." Taylor and Francis.
- Malecot, Y. Daudeville, L., Dupray, F., Poinard, C. and Buzaud, E., (2010). "Strength and damage of concrete under high triaxial loading." *European Journal of Environmental and Civil Engineering*, 14(6-7), 777-803.
- McCurry, J., (2014). "Ocean Spiral: Japanese firm plans underwater city powered by seabed." *The Guardian*, 2 May, 17.
- Nishigori, T., (1977). "Basic study on the use of expansive-cement concrete in steel-lined penstock." *Proceedings of the Japan Society of Civil Engineers*, 262, 129-142. (in Japanese)
- Owada, H., Nakanishi, H., Asano, H., Ogawa, H., Mori, D., Hiraishi, T. and Shibuya, K., (2008). "Development of waste packages for the long-term confinement of C-14 in TRU waste disposal: 1. Study on the long-term durability of the concrete package made from high strength and ultra low permeability concrete." *Journal of Nuclear Fuel Cycle and Environment*, 15(1), 3-11.
- Paterson, M., (1958) "Experimental deformation and faulting in Wombeyan marble." *Geological Society of America Bulletin*, 69(4), 465-476.
- Paterson, M. and Wong, T., (2005) "Experimental rock deformation-The brittle field." Springer.
- Poinard, C., Malecot, Y. and Daudeville, L., (2010). "Damage of concrete in a very high stress state: Experimental investigation." *Materials and Structures*, 43(1-2), 15-29.
- Poinard, C., Piotrowska, E., Malecot, Y., Daudeville, L. and Landis, E. N., (2012). "Compression triaxial behavior of concrete: The role of the mesostructure by analysis of X-ray tomographic images." *European Journal of Environmental and Civil Engineering*, 16(1), 115-136.
- Sakaguchi, A., Sakaguchi, H., Nishiura, D., Nakatani, M. and Yoshida, S., (2011). "Elastic stress indication in elastically rebounded rock." *Geophysical research letters*, 38, L09316.
- Sfer, D., Carol, I., Gettu, R. and Etse, G., (2002). "Study of the behavior of concrete under triaxial compression." *Journal of Engineering Mechanics*, 128(2), 156-163.
- Shimizu, K., Tachibana, S., Mitani, T. and Habazaki, H., (2006). "A new approach for cross-sectional examination of interfaces by FE-SEM/ESB." *Journal of The Surface Finishing Society of Japan*, 57(9), 622-629. (in Japanese)
- Turner, F. J., Griggs, D. T. and Heard, H., (1954). "Experimental deformation of calcite crystals." *Geological Society of America Bulletin*, 65(9), 883-934.
- Vajdova, V., Baud, P. and Wong, T. F., (2004). "Compaction, dilatancy, and failure in porous carbonate rocks." *Journal of Geophysical Research: Solid Earth*, 109, B05204.
- Vu, X. H., Daudeville, L. and Malecot, Y., (2011). "Effect of coarse aggregate size and cement paste volume on concrete behavior under high triaxial compression loading." *Construction and Building Materials*, 25(10), 3941-3949.
- Vu, X. H., Malecot, Y., Daudeville, L. and Buzau, E., (2009). "Experimental analysis of concrete behavior under high confinement: Effect of the saturation ratio." *International Journal of Solids and Structures*, 46(5), 1105-1120.
- Wong, T. and Baud, P., (2012). "The brittle-ductile transition in porous rock: A review." *Journal of Structural Geology*, 44, 25-53.
- Zeng, S., Ren, X. and Li, J., (2013). "Triaxial behavior of concrete subjected to dynamic compression." *Journal of Structural Engineering*, 139(9), 1582-1592.