Cover page

Alpha Foundation for the Improvement of Mine Safety and Health

Final Technical Report

Project Title:	Prototype development of a hybrid geopolymer-biopolymer cementitious material for pumpable roof support
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1.0 Executive Summary

Effective roof support is critical to prevent ground falls and ground fall accidents. Among the different roof support techniques, pumpable roof supports have advantages over other roof support systems and have been increasingly used in underground mines. A major constituent of a pumpable roof support system is the cementitious material such as the Portland cement/fly ash (PC/FA) grout currently used in practice. However, the conventional PC/FA cementitious material (1) severally deteriorates when exposed to the air, and (2) cannot achieve the normally conflicting responses such as high peak strength and high residual strength required for effective roof support. To enhance the performance of pumpable roof supports, an unconventional cementitious material needs to be developed to minimize or alleviate those problems.

In the proof-of-concept project AFC518-24 completed in 2019, we have developed a new hybrid geopolymer/biopolymer (GP/BP) cementitious material for improving the performance of pumpable roof supports. For effective field applications, the hybrid GP/BP cementitious material was designed to be a mixture of two separate pumpable streams: stream 1 composed of FA, cement kiln dust (CKD), superplasticizer (SP) and water, and stream 2 containing sodium hydroxide (SH), sodium silicate (SS), BP and water. The FA is the aluminosilicate source for GP formation. The CKD is for adjusting and controlling the setting time of the hybrid cementitious material while the SP for improving the pumpability of stream 1. The SH is the alkali activator for GP formation and the SS is for adjusting the Si/Al ratio and providing additional Na+ cations for charge balancing. The BP (e.g., carrageenan – CAR) is for further enhancing the mechanical behavior of the GP. When the two streams stay alone, they remain as a slurry and a solution, respectively, and can be easily handled and transported. When they are mixed together, a GP/BP composite cementitious material is formed.

To demonstrate the application of the hybrid GP/BP cementitious material and validate its effectiveness in field scale, eight (8) full-size (0.61 m diameter and 1.52 m height) cribs were produced in collaboration with Minova and tested at the NIOSH Mine Roof Simulator (MRS) Laboratory under this follow-up project AFC518SP-94. These full-size cribs were produced at different conditions to evaluate the effect of water to solid (W/S) ratio, PC content and BP dosage. During the production of the full-size cribs, small size (0.15 m diameter and 0.30 m height) un-bagged specimens were also produced for evaluating the physical, chemical, and mechanical properties of the hybrid cementitious material. The results clearly demonstrated and validated the effectiveness of the hybrid GP/BP cementitious material in (1) eliminating the issue of deterioration when exposed to air, and (2) increasing the peak strength and residual strength of pumpable cribs compared with the conventional PC/FA cementitious material currently used in practice. On average, the peak UCS and the highest residual UCS after peak of the full-size cribs produced from the hybrid GP/BP cementitious material are 1.90 and 1.33 times of those of the Jennmar PC/FA based full-size cribs and 2.32 and 1.66 times of those of the Minova PC/FA based full-size cribs, respectively. It is noted that PC instead of CKD was used in the production of the full-size cribs because CKD was no longer widely available in the market. Because PC is less reactive than CKD, to ensure the self-supporting of the crib based on the quick setting of the cementitious material, a larger amount of PC should be used.

Like the conventional PC/FA based cribs, the hybrid GP/BP based cribs are very stiff with a significant load shedding event following the peak load. In this regard, it is recommended that the hybrid GP/BP based cribs can be further enhanced by increasing their (initial) ductility while maintaining the high peak and residual bearing capacities. Based on the observations during the full-size crib tests, a viable way to achieve this is by increasing the compressibility of the top portion of the cementitious material in the crib bag. The high compressibility of the top portion not only increases the displacement required to reach the peak bearing capacity but also ensure a “mushroom” failure pattern, leading to a larger crib-roof contact area and a more stable support.

2.0 Technology Description and Mission Statement

Pumpable roof supports are increasingly used in underground mines to prevent ground falls. In current practice, the mainly used pumpable support cementitious material is Portland cement/fly ash (PC/FA) based grout. However, the PC/FA based pumpable supports have limitations, including (1) when exposed to the air, the PC/FA based cementitious material severely deteriorates, potentially rendering the support much weaker and adversely affecting the overall safety, and (2) the residual strength is too small and the peak strength tends to be inconsistent, adversely affecting the performance of pumpable roof supports.

Therefore, the *overall goal* of the proof-of-concept project AFC518-24 completed in 2019 and this follow-up project AFC518SP-94 is to develop, demonstrate and validate an unconventional cementitious material to minimize or alleviate the problems of the conventional PC/FA based cementitious material, *aiming to enhance the performance of pumpable roof supports*.

In the proof-of-concept project AFC518-24, we have successfully developed a new hybrid geopolymer/biopolymer (GP/BP) cementitious material for improving the performance of pumpable roof supports. As a preliminary demonstration and validation, small size (0.15 m diameter and 0.30 m height) bagged specimens were produced and tested in the laboratory. The results clearly show that the bagged specimen produced from the hybrid GP/BP cementitious material has much higher peak and residual strength than the crib bagged pumpable roof supports currently used in practice (see Fig. 1).

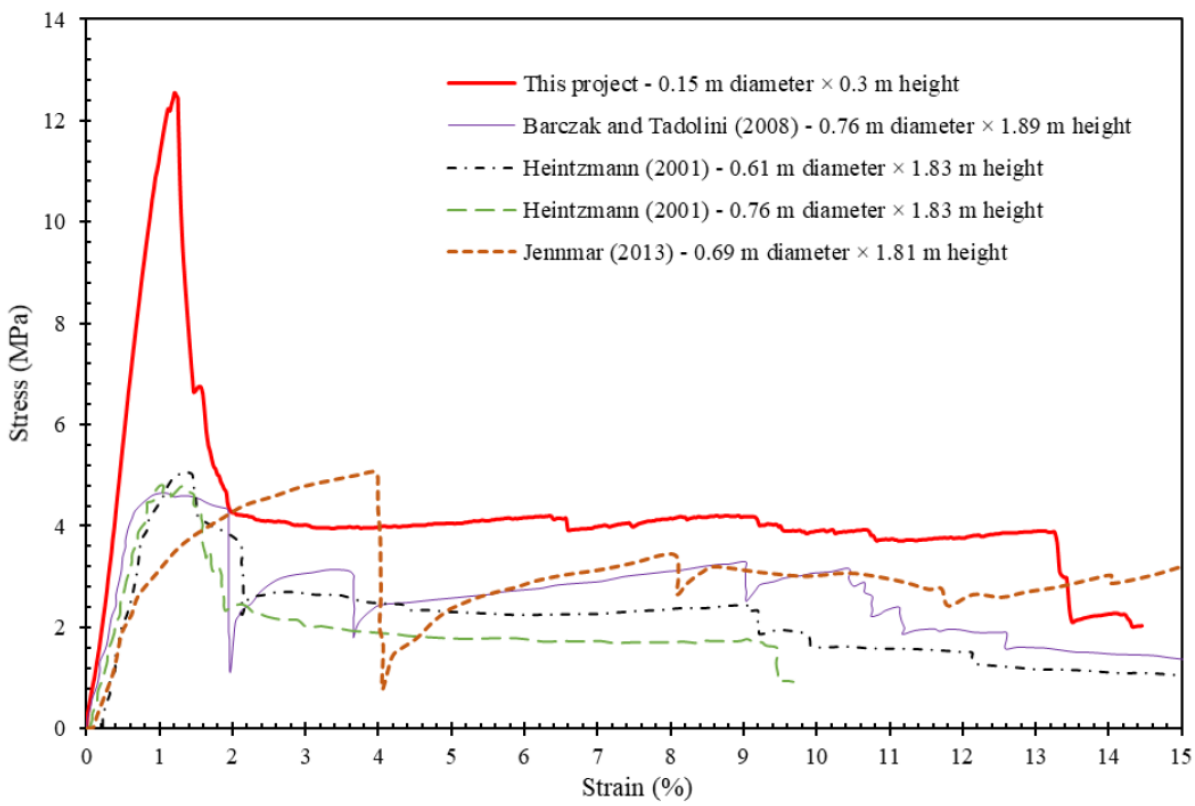


Fig. 1: Comparison of stress-strain curves of the small size 0.3 wt.% BP (carrageenan) specimen with polyester bag and plastic cable ties in the proof-of-concept project with those of full-size crib bag specimens used in practice

Before the hybrid GP/BP cementitious material based pumpable supports are applied in practice, their superior performance and effectiveness need to be demonstrated and validated in a field scale. In this regard, with this follow-up project AFC518SP-94, eight (8) full-size (0.61 m diameter and 1.52 m height) cribs were produced in collaboration with Minova and tested at the NIOSH Mine Roof Simulator (MRS) Laboratory. These full-size cribs were produced using the hybrid GP/BP cementitious material at different conditions in order to evaluate the effect of water to solid (W/S) ratio, PC content and BP dosage. During the production of the full-size cribs, small size (0.15 m diameter and 0.30 m height) un-bagged specimens were also produced for evaluating the physical, chemical, and mechanical properties of the hybrid cementitious material.

3.0 Technology Description and Design Strategy

A pumpable roof support contains the crib bag and the cured cementitious material pumped into it. For a pumpable roof support to provide effective and safe support to the roof, the key is to ensure that the support system, especially the cementitious material, to have high peak strength and high residual strength. However, the conventional Portland cement/fly ash (PC/FA) cementitious material currently used in practice cannot achieve the two normally conflicting properties because the cementitious product characteristics are primarily focused on strength not ductility. It is also noted that PC/FA cementitious material severally deteriorates when exposed to the air, potentially rendering the support much weaker and adversely affecting the overall safety. To significantly enhance the performance of pumpable roof supports, an unconventional cementitious grout material that can effectively minimize or alleviate the problems of the conventional PC/FA cementitious material needs to be developed.

In the proof-of-concept project AFC518-24, we have developed a new cementitious material based on a novel cement called geopolymer (GP). GP is a class of cementitious material that is formed by chemical dissolution and subsequent recondensation of aluminosilicates to form an amorphous three-dimensional framework structure (Duxson et al. 2007; Dimas et al. 2009; Majidi 2009; Davidovits 2020). GP has many advantages compared to the conventional PC, including rapid strength gain, high strength, low shrinkage, high thermal resistance, excellent acid resistance, and significantly reduced energy usage and greenhouse gas emissions (Davidovits 2020). Therefore, GP was selected as the starting material for developing the new cementitious material for pumpable roof supports.

Like the conventional PC, however, GP also tends to be brittle with low tensile strength, ductility, and fracture toughness. Therefore, we used biopolymer (BP) to increase the ductility of the cementitious material. The underlying mechanism for this improvement is that the BP dissolved in alkaline solution creates thin films around the unreacted particles and creates a bridge between cracks, providing high residual strength (Li and Zhang 2016).

For convenient field applications, the new hybrid GP/BP cementitious material was designed to be a mixture of two pumpable grout streams: stream 1 composed of FA, cement kiln dust (CKD), superplasticizer (SP) and water, and stream 2 containing sodium hydroxide (SH), sodium silicate (SS), BP and water. The FA is the aluminosilicate source for GP formation. The CKD is for adjusting and controlling the setting time of the hybrid cementitious material while the SP for improving the pumpability of stream 1. The CKD can be substituted by PC considering that CKD is no longer widely available in the market. The SH is the alkali activator for GP formation and the SS is for adjusting the Si/Al ratio and providing additional Na+ cations for charge balancing. The BP (e.g., carrageenan – CAR) is for further enhancing the mechanical behavior of the GP through formation of an interpenetrating cross-linked network binding and toughening the GP matrix (Li and Zhang 2016). When the two streams stay alone, they remain as a slurry and a solution, respectively, and can be easily handled and transported. When they are mixed together and poured into a crib bag (Fig. 2), a GP/BP composite cementitious material is formed. The new hybrid GP/BP cementitious material can be tailored and used in practice at different conditions to achieve the optimum performance by simply adjusting the relative amount of the different components.

With the successfully developed hybrid GP/BP cementitious material in the laboratory under the proof-of-concept project AFC518-24, full-size pumpable cribs were produced and tested to demonstrate and validate the effectiveness of the hybrid GP/BP cementitious material in a field scale under this follow-up project AFC518SP-94. Specifically, eight (8) full-size (0.61 m diameter and 1.52 m height) cribs were produced in collaboration with Minova and tested at the NIOSH Mine Roof Simulator (MRS) laboratory.

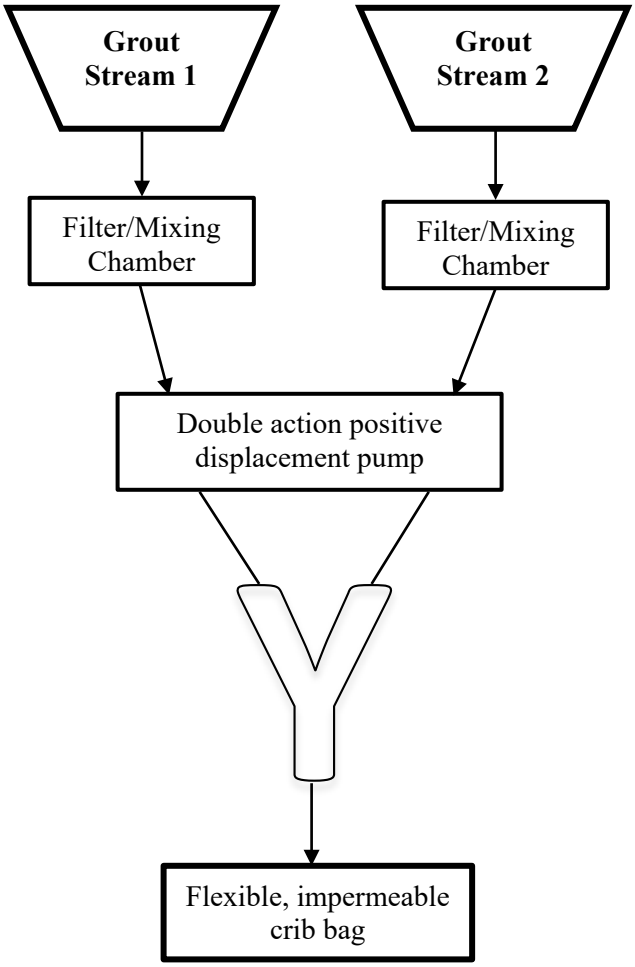


Fig. 2: Flow chart of two grout streams pumped to a crib bag to form pumpable roof support

4.0 Technology Evaluation

This section describes the production and test of full-size pumpable cribs for evaluating the performance of the hybrid GP/BP cementitious material at different conditions. Specifically, the source materials and supplements used in the crib production, the test configurations and conditions, and the detailed results and analyses/discussion are presented.

4.1 Materials

The materials used in this investigation include class F fly ash (FA), ordinary Portland cement (PC), reagent grade 98% sodium hydroxide (SH) (NaOH), sodium silicate (SS) (Na_2SiO_3) solution, superplasticizer (SP), biopolymer (BP), and tap water. The FA is the aluminosilicate source for geopolymer (GP) formation and was purchased from Eco-Material Technologies in Cadiz, OH. The PC type I/II is a high calcium content material selected as an accelerator to adjust and control the setting time of the hybrid cementitious material and was obtained from Argos S.A. cement company through a local supplier. Table 1 shows the chemical composition of the FA and PC from XRF analysis. The FA contains mainly silica and alumina while the PC contains mainly calcite and silica. The NaOH is an alkali activator required for GP formation and was purchased from Chemical Store in Clifton, NJ. The sodium silicate solution (SiO_2 = 29%, Na_2O = 8%, and H_2O = 63%) is for adjusting the Si/Al ratio and providing additional Na^+ cations for charge balancing, and was purchased from Hawkins Inc in Roseville, MN. The SP is for adjusting and controlling the pumpability of the first stream and was purchased from Sika corporation, California. Kappa-carrageenan (CAR), a biopolymer, was used to further enhance the mechanical behavior of the geopolymer. The CAR is a natural high molecular weight polysaccharide produced from seaweed plant (Li and Zhang 2016) and was obtained from Ingredion Inc, Westchester, IL .

Table 1: Chemical composition of FA and PC

Chemical compound	SiO_2	Al_2O_3	CaO	Fe_2O_3	MgO	Na_2O	SO_3	K_2O	LOI	Others
FA (%)	49.92	27.64	2.45	12.48	0.76	0.79	1.29	2.38	2.90	1.11
PC (%)	19.4	4.8	62.2	3.0	2.8	0.69	3.1	NA	4.01	NA

4.2 Methods

The hybrid GP/BP cementitious material is designed to be a mixture of two separate pumpable grout streams: stream 1 composed of FA, PC, SP and water, and stream 2 containing SH, SS, CAR, and water. To prepare the first stream, the FA, PC, and water were first mixed in a ChemGrout 600 high pressure colloidal mixer (Fig. 3) and then the SP was added while mixing continued to obtain a homogeneous slurry. To prepare the second stream, the SS solution was first placed in a container and then SH pellets were dissolved in it and left at room temperature to cool down before used. When BP was used, the CAR was also added at the same time as the SH in order to be thoroughly mixed in the solution.

Fig. 3: ChemGrout 600 high pressure colloidal mixer used for mixing and pumping stream 1

After both streams were ready, they were pumped through two separate pipes and then mixed through a Y connection and poured into the crib bag (Fig. 4). The crib bags filled with the hybrid cementitious material (Fig. 5) were kept at the room temperature for 28 days and then transported to NIOSH Mine Roof Simulator (MRS) laboratory for testing. During the production of the full-size (0.61 m diameter and 1.52 m height) cribs, small size (0.15 m diameter and 0.30 m height) un-bagged specimens were also produced for evaluating the physical, chemical, and mechanical properties of the hybrid cementitious material (Fig. 6).

Fig. 4: Y-connection used to mix stream 1 and stream 2 right and pour the hybrid cementitious material in crib bag

Fig. 5: Crib bags filled with hybrid cementitious material

Fig. 6: Small size (0.15 m diameter and 0.30 m height) un-bagged specimens of hybrid cementitious material

In total, eight (8) full-size cribs were produced aiming to study the effect of main factors: water to solid (W/S) ratio (0.55, 0.60), PC content (20 wt.%, 30 wt.% of FA+PC), and CAR dosage (0 wt.%, 0.3 wt.% of FA+PC). The details of the 8 cribs are shown in Table 2. For all the cribs, SP at a dosage of 2 wt.% of FA+PC was used in stream 1, and a SH concentration of 5 M and a SS/SH ratio of 1 were selected for stream 2.

The uniaxial compression tests were conducted using the NIOSH MRS loading machine (Fig. 7) at a constant loading rate of 0.5 in/min to measure the peak uniaxial compressive strength (UCS) and the residual UCS of the cribs produced using the hybrid cementitious material at different conditions. Two cribs were tested at each condition.

Table 2: 8 full-size cribs produced using the hybrid cementitious materials at different conditions

Number of cribs	Composition of hybrid cementitious material					
	W/S	PC content (wt.% of FA+PC)	BP content (wt.% of FA+PC)	SP content (wt.% of FA+PC)	SH concentration	SS/SH
2	0.55	20	0	2	5 M	1
2	0.55	20	0.3	2	5 M	1
2	0.60	30	0	2	5 M	1
2	0.60	30	0.3	2	5 M	1

Fig. 7: NIOSH MRS loading machine used to test the full-size cribs

The small size un-bagged cylinder specimens were tested using a Humboldt compression machine at a loading rate of 0.25 MPa/sec to measure the UCS of the hybrid GP/BP cementitious material with no crib bag confinement.

SEM imaging was also performed in the SE conventional mode with a FEI INSPEC-S50/Thermo-Fisher Noran 6 microscope to investigate the microstructure of the hybrid cementitious material at different conditions. The fresh surface of failed specimens from the uniaxial compression tests, without polishing to keep the fractured surface "un-contaminated", were used for the SEM imaging. Along with the SEM, EDX was also conducted to evaluate the elemental composition of the hybrid cementitious material.

4.3 Results and discussion

4.3.1 Small size cylinder specimens

Fig. 8 shows the peak UCS of the small size cylinder specimens produced during the production of the full-size cribs. As can be seen, by increasing the biopolymer (CAR) content from 0 wt.% to 0.3 wt.% at W/S = 0.55 and 0.60, the peak UCS increased from 5.38 MPa to 6.11 MPa and from 8.36 MPa to 11.11 MPa, respectively. The peak UCS at W/S = 0.60 is higher than that at W/S = 0.55 mainly because a higher PC content (30 wt.% instead of 20 wt.%) was used at the higher W/S ratio.

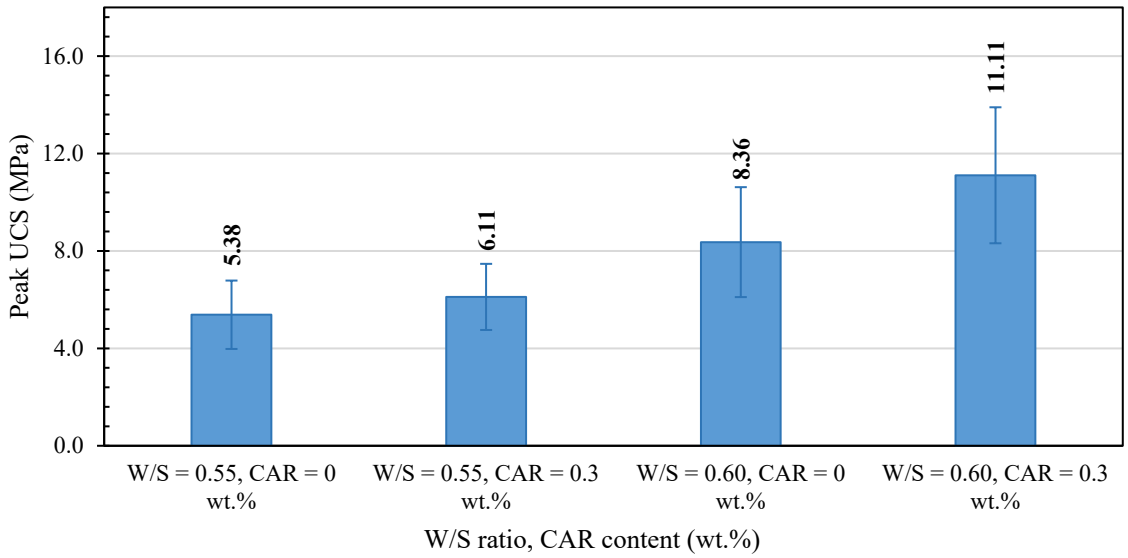


Fig. 8: Peak UCS of small size cylinder specimens produced from the hybrid GP/BP cementitious material during the production of full-size cribs

4.3.2 Full-size cribs

Fig. 9 shows the stress–strain curves of the full-size cribs produced from the hybrid GP/BP cementitious material with W/S = 0.55 and 20 wt.% PC, at 0 wt.% CAR (Fig. 9a) and 0.3 wt.% CAR (Fig. 9b), respectively. For comparison, the stress–strain curves of the full-size cribs from Jennmar and Minova with the conventional PC/FA cementitious material currently used in practice are also shown in the figure. As can be seen, the full-size cribs produced from the hybrid GP/BP cementitious material have much higher peak UCS and slightly higher or about the same residual UCS compared with the full-size cribs from Jennmar and Minova using the conventional PC/FA cementitious material.

Table 3 provides a summary of the peak UCS, the highest residual UCS after peak, the strain at the peak stress, and the number of shed events for the full-size cribs produced from the hybrid GP/BP cementitious material. As can be seen, the addition of 0.3 wt.% CAR improved the mechanical performance of the cribs. For example, by including 0.3 wt.% CAR, the peak UCS increased from 7.46 MPa to 8.64 MPa, although the highest residual UCS after peak slightly decreased from 5.00 MPa to 4.80 MPa. Also, by including 0.3 wt.% CAR, the strain at the peak stress increased from 3.31% to 3.96% and the number of shed events decreased from 4 to 3. This is probably because the shrinkage/micro-cracking was reduced during the drying process by creating thick and high tensile biopolymer dehydrates like films between the particles (Chang et al. 2016; Nakamatsu et al. 2017).

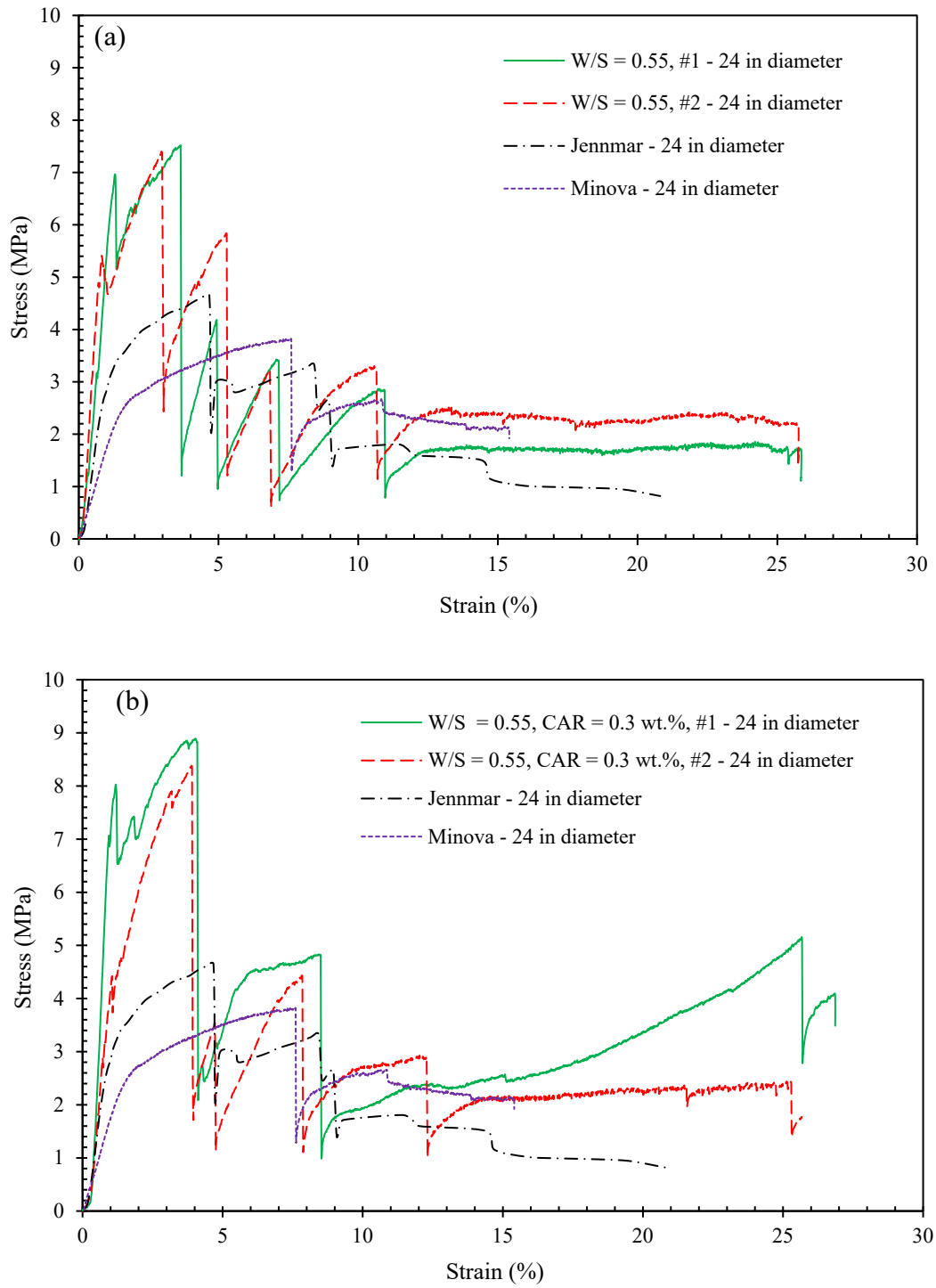


Fig. 9: Stress-strain curves obtained from uniaxial compression test of full-size cribs produced from the hybrid GP/BP cementitious material with W/S = 0.55 and 20 wt.% PC at (a) 0 wt.% CAR, and (b) 0.3 wt.% CAR

Table 3: Summary of results obtained from the stress-strain curves of cribs produced from the hybrid GP/BP cementitious material with W/S = 0.55 and 20 wt.% PC at different CAR contents

Crib	Peak UCS (MPa)	Average peak UCS (MPa)	Highest residual UCS after peak	Average highest residual UCS after peak (MPa)	Strain at peak stress (%)	Average Strain at peak stress (%)	Number of shed events	Average number of shed events
W/S = 0.55, CAR 0 wt.%, #1	7.39	7.46	4.17	5.00	2.97	3.31	4	4
W/S = 0.55, CAR 0 wt.%, #2	7.52		5.83		3.65		4	
W/S = 0.55, CAR 0.3 wt.%, #1	8.89	8.64	5.16	4.80	4.04	3.96	2	3
W/S = 0.55, CAR 0.3 wt.%, #2	8.38		4.43		3.89		4	

Fig. 10 shows the stress–strain curves of the cribs produced from the hybrid GP/BP cementitious material with W/S = 0.60 and 30 wt.% PC, at 0 wt.% CAR (Fig. 10a) and 0.3 wt.% CAR (Fig. 10b), respectively. Again, for comparison, the stress–strain curves of the full-size cribs from Jennmar and Minova with the conventional PC/FA cementitious material currently used in practice are also shown in the figure. As can be seen, the full-size cribs produced from the hybrid GP/BP cementitious material have much higher peak UCS and slightly higher or about the same residual UCS compared with the full-size cribs from Jennmar and Minova using the conventional PC/FA cementitious material.

Table 4 provides a summary of the peak UCS, the highest residual UCS after peak, the strain at the peak stress, and the number of shed events. As can be seen, the peak UCS slightly decreased from 10.02 MPa at 0 wt.% CAR to 9.17 MPa at 0.3 wt.%. However, the highest residual UCS after peak increased from 3.33 MPa at 0 wt.% CAR to 4.56 MPa at 0.3 wt.% CAR. Also, the strain at the peak stress increased from 1.56% at 0 wt.% CAR to 2.53% at 0.3 wt.% CAR. This is probably due to the increase in fracture toughness of the hybrid cementitious material by the added biopolymer CAR (Li et al. 2013).

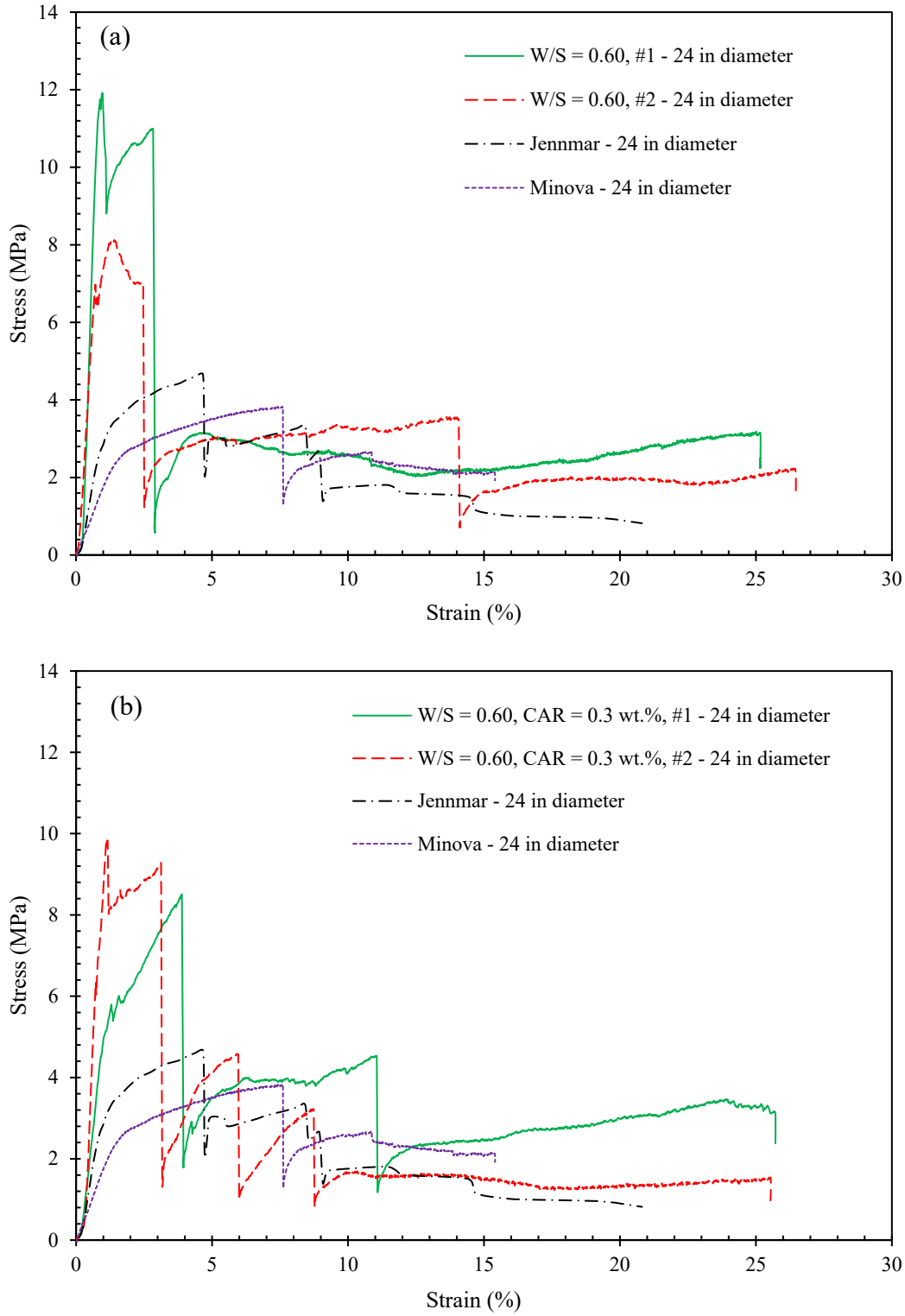


Fig. 10: Stress-strain curves obtained from uniaxial compression test of full-size cribs produced from the hybrid GP/BP cementitious material with W/S = 0.60 and 30 wt.% PC at (a) 0 wt.% CAR, and (b) 0.3 wt.% CAR

Table 4: Summary of results obtained from stress-strain curves of full-size cribs produced from the hybrid GP/BP cementitious material with W/S = 0.60 and 30 wt.% PC at different CAR contents

Crib	Peak UCS (MPa)	Average peak UCS (MPa)	Highest residual UCS after peak (MPa)	Average highest residual UCS after peak (MPa)	Strain at peak stress (%)	Average Strain at peak stress (%)	Number of shed events	Average number of shed events
W/S = 0.60, CAR 0 wt.%, #1	11.92	10.02	3.11	3.33	0.97	1.56	2	2
W/S = 0.60, CAR 0 wt.%, #2	8.12		3.55		1.34		2	
W/S = 0.60, CAR 0.3 wt.%, #1	8.51	9.17	4.53	4.56	3.89	2.53	2	3
W/S = 0.60, CAR 0.3 wt.%, #2	9.83		4.58		1.16		4	

Fig. 11 compares the peak UCS of the un-bagged small size cylinder specimens and the full-size cribs produced from the hybrid GP/BP cementitious material at different W/S ratios and CAR contents. Overall, the full-size cribs tend to have higher peak UCS than the small size un-bagged cylinder specimens simply because the crib bag with the steel wires provides confinement to the cementitious material.

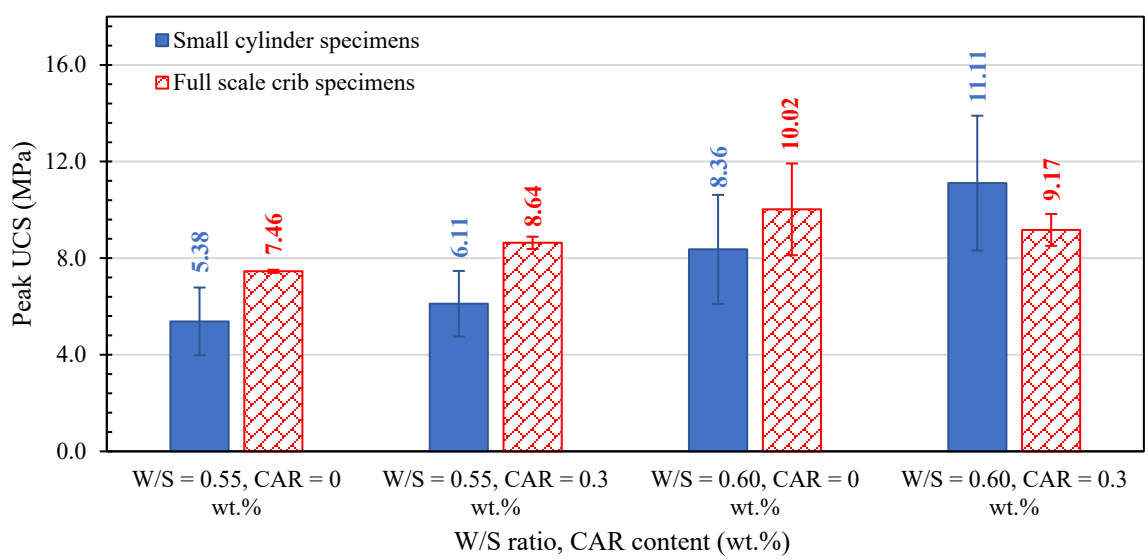


Fig. 11: Peak UCS of small size cylinder specimens and full size cribs produced from the hybrid GP/BP cementitious material at different W/S ratios and CAR contents

4.3.3 SEM imaging and EDX analysis

SEM imaging and EDX analysis were conducted to investigate the effect of W/S ratio and CAR dosage on the microstructure and elemental composition of the hybrid GP/BP cementitious material. Fig. 12 shows the SEM micrographs and EDX spectra of the hybrid GP/BP cementitious material at two different CAR contents and with the same W/S = 0.55 and 20 wt.% PC and cured at room temperature for 28 days. Due to the low dosage of CAR, the microstructure of both specimens (0 wt.% and 0.3 wt.% CAR) are similar. The sponge-like geopolymer gels and the calcium silicate hydrate (CSH) gels that act as the binder can be clearly seen. The formation of CSH gels is due to the presence of PC as a high calcium content material in the hybrid GP/BP cementitious material (Ahmari and Zhang 2013). Some cracks can also be observed which is due to the fast setting and curing at the presence of PC (Mehta and Siddique 2017). Some unreacted or partially reacted FA particles can also be clearly seen, which may be due to the low alkalinity (5 M NaOH) used in preparing the cementitious material. Also, due to the low dosage of CAR, the element compositions of the two hybrid cementitious materials (0 wt.% and 0.3 wt.% CAR) are similar.

Fig. 13 shows the SEM micrographs and EDX spectra of the hybrid GP/BP cementitious material at two different CAR contents and with the same W/S = 0.60 and 30 wt.% PC and cured at room temperature for 28 days. By comparing Figs. 12 and 13, it can be seen that there more cracks in the specimen in Fig. 13. This is simply because more PC (30 wt.% instead of 20 wt.%) was included and a quicker setting and curing occurred (Mehta and Siddique 2017).

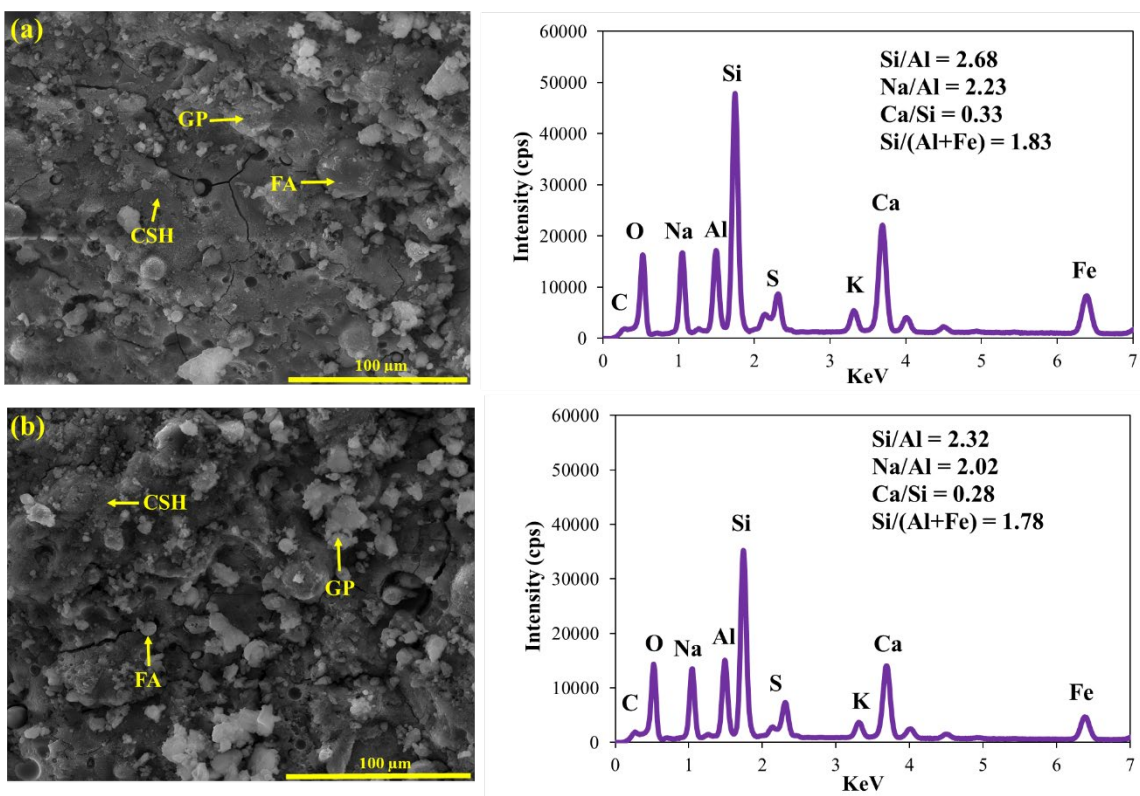


Fig. 12: SEM micrographs and EDX spectra of hybrid GP/BP cementitious material at W/S = 0.55, 20 wt.% PC, with (a) 0 wt.% CAR, and (b) 0.3 wt.% CAR

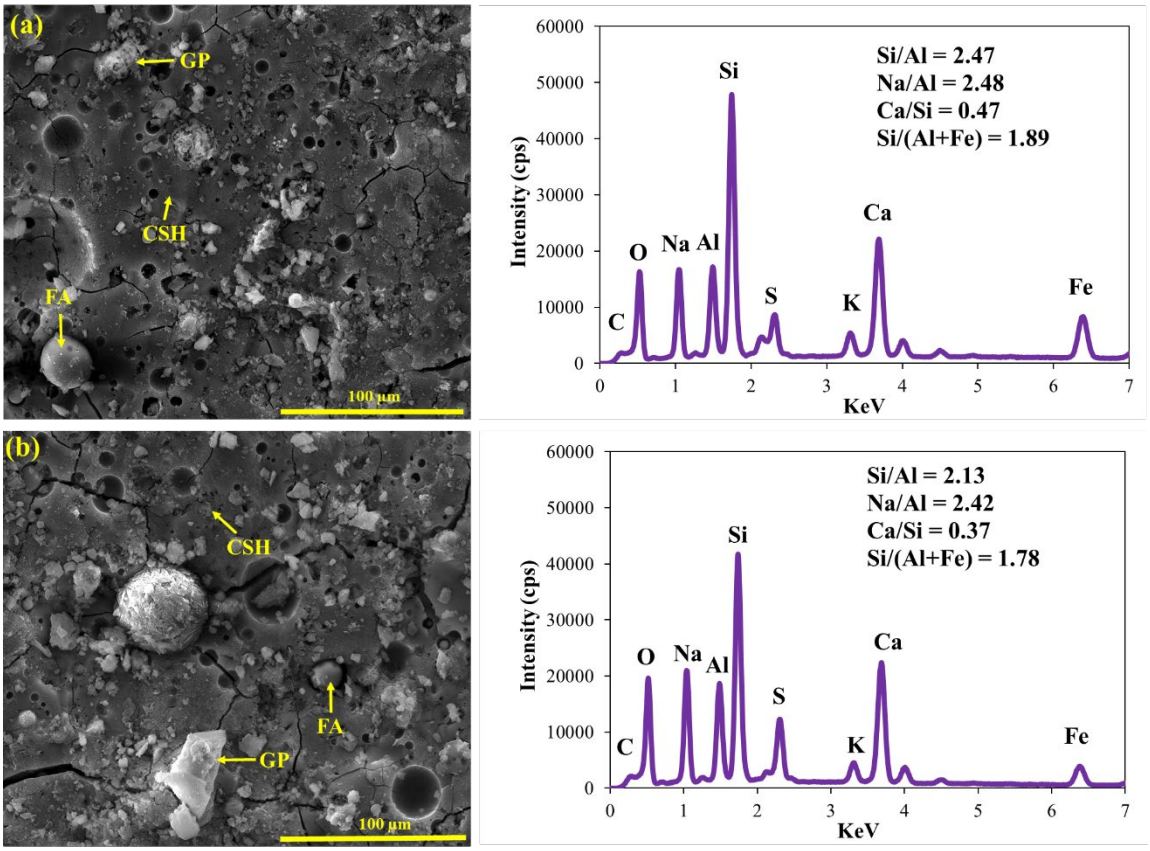


Fig. 13: SEM micrographs and EDX spectra of hybrid GP/BP cementitious material produced at W/S = 0.60, 20 wt.% PC, with (a) 0 wt.% CAR, and (b) 0.3 wt.% CAR

5.0 Technology Capability Assessment and Readiness Assessment

5.1. Summary of full-size crib test results

The full-size crib test results clearly demonstrated and validated the effectiveness of the hybrid GP/BP cementitious material in increasing both the peak strength and the residual strength of pumpable cribs compared to the PC/FA cementitious material currently used in practice. As shown in the summary Table 5, on average, the peak UCS and the highest residual UCS after peak of the full-size cribs produced from the hybrid GP/BP cementitious material are 1.90 and 1.33 times of those of the Jennmar full-size cribs and 2.32 and 1.66 times of those of the Minova full-size cribs, respectively.

Table 5: Comparison of peak UCS and highest residual UCS after peak of the full-size cribs produced from the hybrid GP/BP cementitious material at different conditions and those of the full-size cribs from Jennmar and Minova using conventional PC/FA cementitious material

Crib	Peak UCS (MPa) (divided by Jennmar value; divided by Minova value)	Highest residual UCS after peak (MPa) (divided by Jennmar value; divided by Minova value)
Hybrid cementitious material at W/S = 0.55, 0 wt.% CAR	7.46 (1.60; 1.96)	5.00 (1.50; 1.88)
Hybrid cementitious material at W/S = 0.55, 0.3 wt.% CAR	8.64 (1.86; 2.27)	4.80 (1.44; 1.80)
Hybrid cementitious material at W/S = 0.60, 0 wt.% CAR	10.02 (2.15; 2.63)	3.33 (1.00; 1.25)
Hybrid cementitious material at W/S = 0.60, 0.3 wt.% CAR	9.17 (1.97; 2.41)	4.56 (1.37; 1.71)
Jennmar – PC/FA based	4.65	3.33
Minova – PC/FA based	3.81	2.66

The full-size crib production and tests also proved that the hybrid GP/BP cementitious material can successfully avoid the air degradation problem of the conventional PC/FA cementitious material (see Fig. 14). This is because the SS is actively involved in the chemical reaction to form the GP gels, and thus no or very little SS is left for chemical reaction with the air.

During the production of the full-size cribs using the hybrid GP/BP cementitious material, it was noticed that the setting time was longer than expected. The main reason is that the hybrid GP/BP cementitious material was originally developed by using CKD as the high calcium content material in the laboratory, but PC was used as the high calcium content material in the production of the full-size cribs because CKD was no longer widely available in the market. The PC has lower calcium content and larger particle size and is thus less reactive than the CKD, leading to a longer setting time of the hybrid cementitious material. To address the long setting time problem, we did more laboratory experimental study aiming to decrease the setting time of the hybrid GP/BP cementitious material, as detailed in next subsection.

(a)

(b)

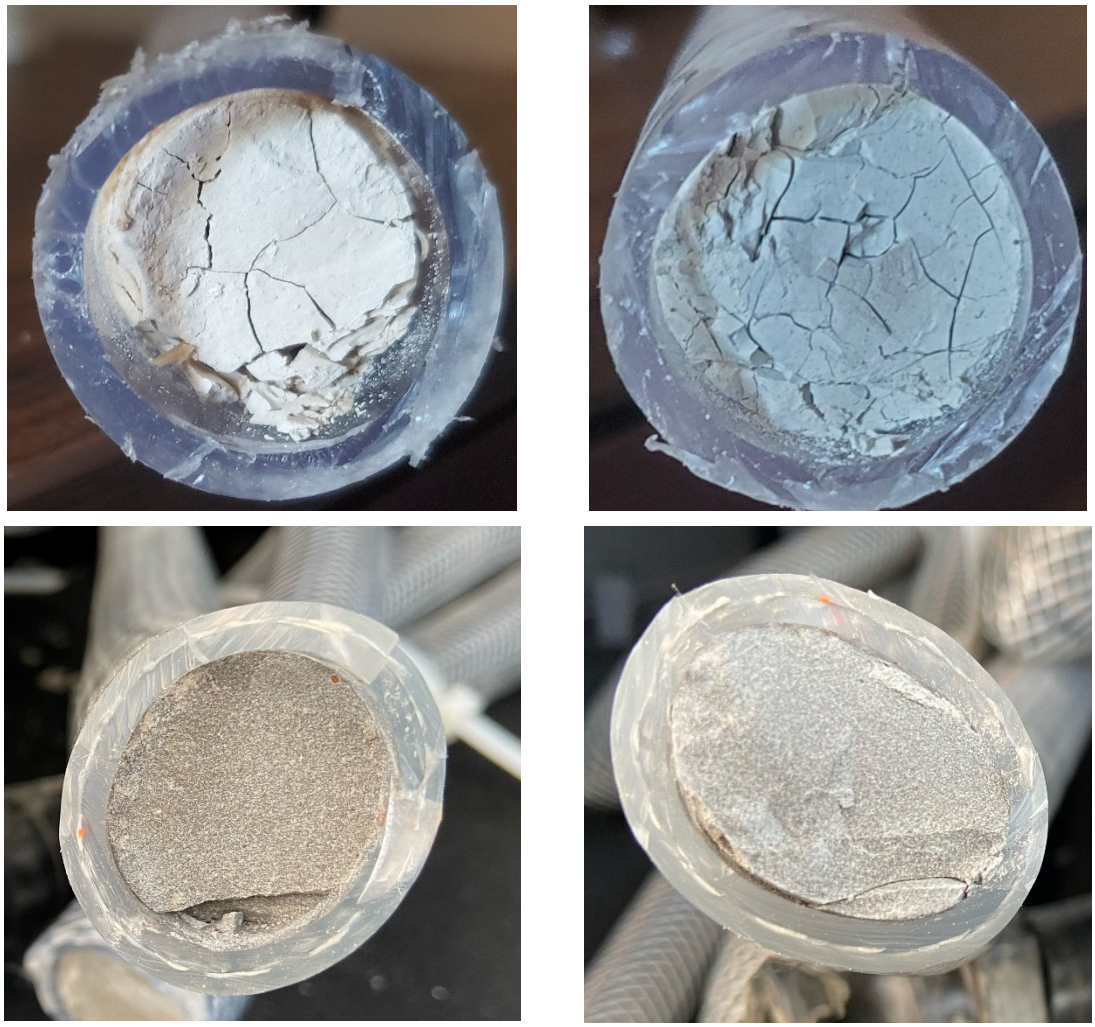


Fig. 14: Exposed cementitious material one day after cutting the pumping tubes connected to full-size pumpable cribs: (a) PC/FA based cementitious material – with many cracks formed; and (b) Hybrid GP/BP cementitious material – with no crack formed

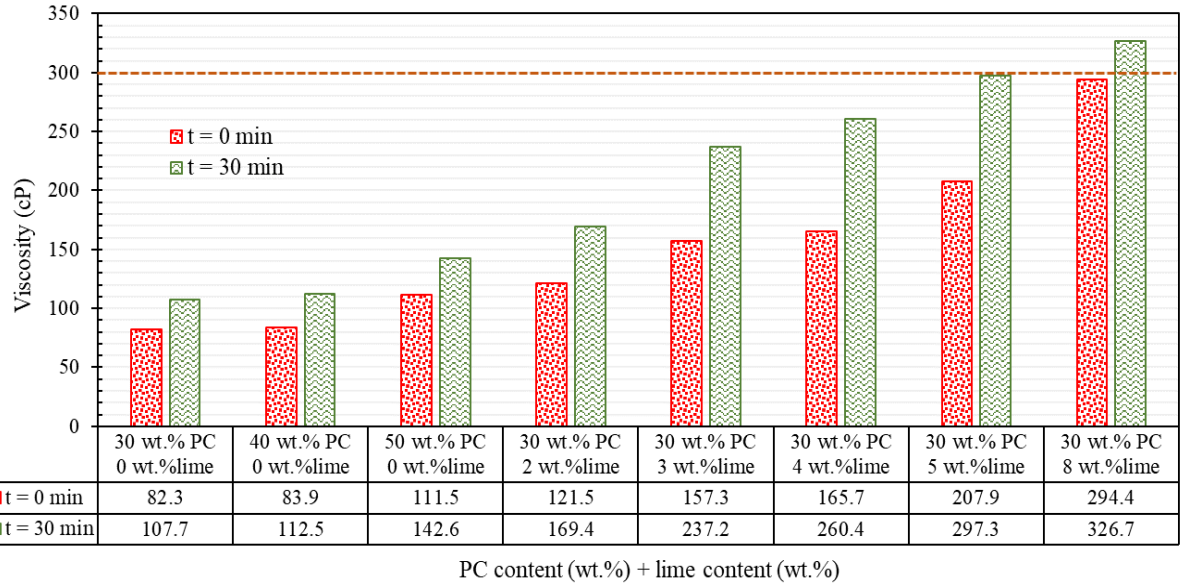
5.2. Adjusting the setting time of the hybrid GP/BP cementitious material

For field applications, it is important that the cementitious material has a short setting time. In other words, when stream 1 and stream 2 are mixed together and poured into a crib bag, the initial setting time of the cementitious material should be short enough to provide self-supporting to the crib.

During the production of full-size cribs , it was noticed that self-supporting is an issue for the crib due to the longer setting time of the hybrid GP/BP cementitious material than expected. The main reason is due to the substitution of CKD with PC.

To decrease the setting time of the hybrid GP/BP cementitious material, two different ways were designed and tested: 1) using a higher content of PC (40 and 50 wt.%), and 2) using the same 30 wt.% PC with an addition of 2, 3, 4, 5 and 8 wt.% lime. Viscosity tests were performed on stream 1 right after mixing and 30 minutes after mixing, respectively, to check the pumpability. The initial and final setting times of the two stream mixtures were measured to understand the self-supporting of the hybrid GP/BP cementitious material. Finally, uniaxial compression tests were performed to evaluate the compressive strength of the hybrid GP/BP cementitious material.

Fig. 15 shows the viscosity of stream 1 prepared with different contents of PC and lime, and at the same W/S = 0.60, 2 wt.% SP, and 0 wt.% CAR. As can be seen, increasing the PC or lime content resulted in a higher viscosity. In general, a cementitious material is pumpable if its viscosity is below 300 cP. Considering the viscosity limitation, it can be determined that using up to 50 wt.% PC or 30 wt.% PC with up to 4 wt.% lime will ensure the pumpability of stream 1 up to 30 min after mixing. Therefore, the next studies on the setting time and compressive strength of the hybrid GP/BP cementitious material are focused on these conditions.



	30 wt.% PC 0 wt.%lime	40 wt.% PC 0 wt.%lime	50 wt.% PC 0 wt.%lime	30 wt.% PC 2 wt.%lime	30 wt.% PC 3 wt.%lime	30 wt.% PC 4 wt.%lime	30 wt.% PC 5 wt.%lime	30 wt.% PC 8 wt.%lime
t = 0 min	82.3	83.9	111.5	121.5	157.3	165.7	207.9	294.4
t = 30 min	107.7	112.5	142.6	169.4	237.2	260.4	297.3	326.7

Fig. 15: Viscosity of stream 1 at 0 and 30 min after mixing at different contents of PC and lime

Fig. 16 shows the initial and final setting times of the hybrid GP/BP cementitious material prepared with different PC and lime contents, W/S = 0.60, 2 wt.% SP, 0 wt.% CAR, 5 M SH, SS/SH = 1, and at a room temperature. As can be seen, increasing the PC or lime content can significantly decrease the initial and final setting times.

Fig. 17 shows the 7-day peak UCS of the hybrid GP/BP cementitious material at different PC and lime contents. As can be seen, increasing the PC content resulted in a higher peak UCS. For example, the 7-day peak UCS increased from 6.39 MPa at 30 wt.% PC to 7.07 MPa and 7.85 MPa at 40 wt.% and 50 wt.% PC, respectively. At the same 30 wt.% PC content, increasing the lime content from 0 wt.% to 2 wt.% significantly decreased the 7-day peak UCS from 6.39 MPa to 3.79 MPa. However, by further increasing the lime content from 2 wt.% to 3 wt.% and 4 wt.%, the 7-day peak UCS increased from 3.79 MPa to 4.42 MPa and 6.18 MPa, respectively.

In summary, by considering the viscosity/pumpability, setting time and peak UCS, a 40 or 50 wt.% PC content can be selected for the production of full-size cribs.

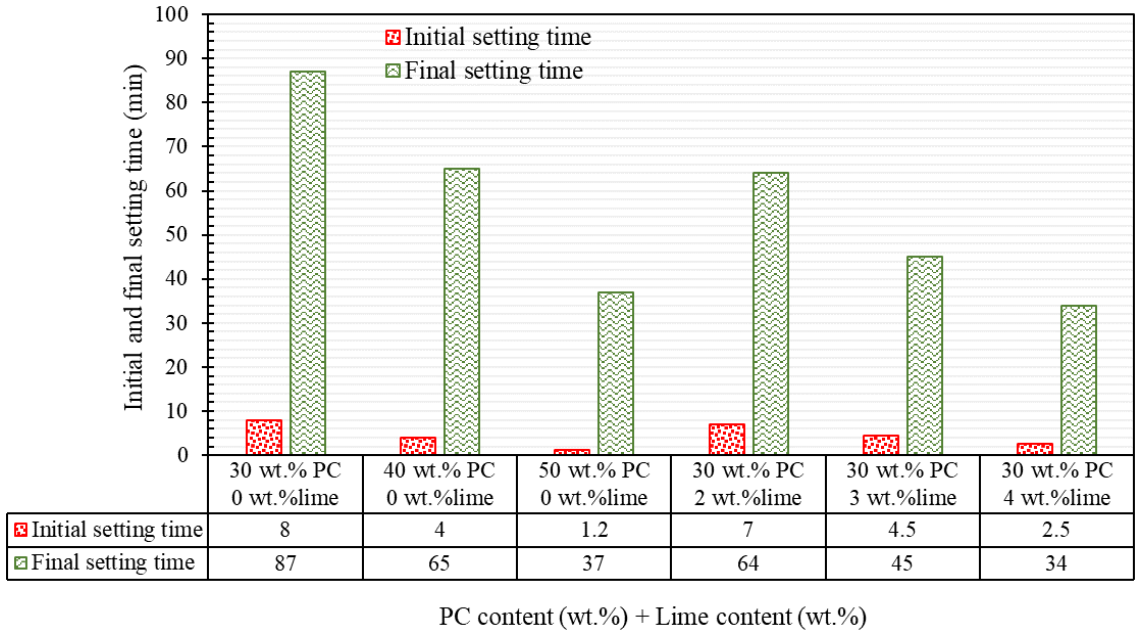


Fig. 16: Initial and final setting times of the hybrid GP/BP cementitious material at different PC and lime contents and at a room temperature

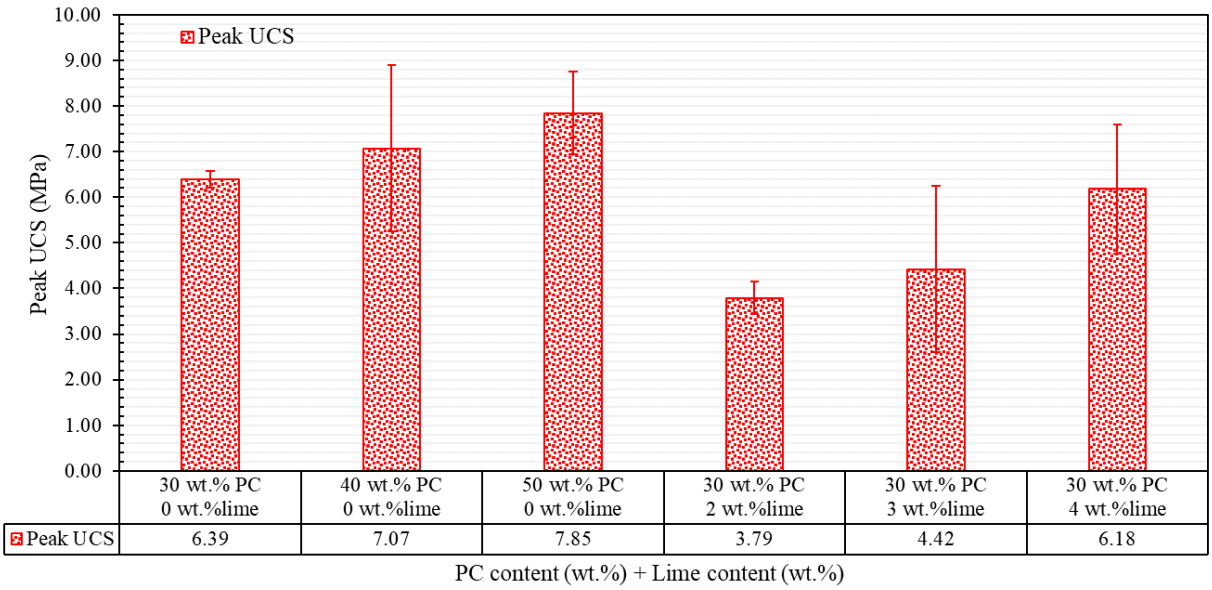


Fig. 17: 7-day peak UCS of the hybrid GP/BP cementitious material at different PC and lime contents

5.3. Field application plan

The systematic proof-of-concept laboratory investigations, the small-size demonstration/validation tests, and finally the full-size crib production/tests together clearly show the superior behavior of the new hybrid GP/BP cementitious material for enhancing the performance of pumpable roof supports. Compared with the conventional PC/FA cementitious material currently used in practice, the hybrid GP/BP cementitious material can (1) effectively eliminate the issue of deterioration when

exposed to the air, and (2) significantly increase the peak strength and the residual strength of pumpable cribs. To promote the application of the hybrid GP/BP cementitious material based pumpable supports in practice, we plan to continue the following activities:

- First, we will continue our successful collaboration with Minova to perform further techno-economic analyses in order to make the new hybrid GP/BP cementitious material completely ready for field applications.
- Second, we will continue our successful collaboration with mining companies. We expect that they provide suggestions, help and support related to the transfer of the new hybrid GP/BP cementitious material to applications in mining practice.
- Third, we will work closely with Tech Launch Arizona, the technology transfer department at the University of Arizona, to commercialize the new hybrid GP/BP cementitious material and transfer it to real applications in mining practice. The PI has already established a close collaboration with Tech Launch Arizona and has been collaborating with them to commercialize the mine tailings-based geopolymer cementitious material developed in his laboratory and to file patents for his other inventions.
- Finally, like the conventional PC/FA cementitious material based cribs, the hybrid GP/BP cementitious material based cribs still see a major load shedding event immediately following the peak loading. It would be desirable to increase the amount of displacement that occurs prior to the peak loading and load shedding event. In this regard, it is recommended that the hybrid GP/BP cementitious material based cribs are further enhanced by increasing their ductility while maintaining the high peak and residual bearing capacities. Based on the observations during the full-size crib tests, a viable way to achieve this is by increasing the compressibility of the top portion of the hybrid GP/BP cementitious material in the crib bag (see Fig. 18). The high compressibility of the top portion not only increases the displacement required to reach the peak bearing capacity but also ensure a "mushroom" failure pattern, leading to a larger crib-roof contact area, an increase of residual strength with strain and thus a more stable support. This can be clearly seen from Fig. 19 which shows the full-size crib produced from the hybrid GP/BP cementitious material at W/S = 0.55, 20 wt.% PC, and 0.3 wt.% CAR (#1) right before the testing was started and right after the testing was completed, and the obtained stress-strain curve. Because the crib bag on one side and close to the top was not fully filled with the cementitious material, the top portion had higher stress and larger strain than the portion below, causing the cementitious material at the top portion to fail and push the crib bag outward before the cementitious material below and leading to a "mushroom" failure pattern. This crib had the largest strain (4.04%) at the peak stress among the 8 cribs (see Tables 3 and 4) and had the residual stress increasing with strain up to a significantly large strain of 25.6%. All these are beneficial for enhancing the performance of the pumpable cribs.

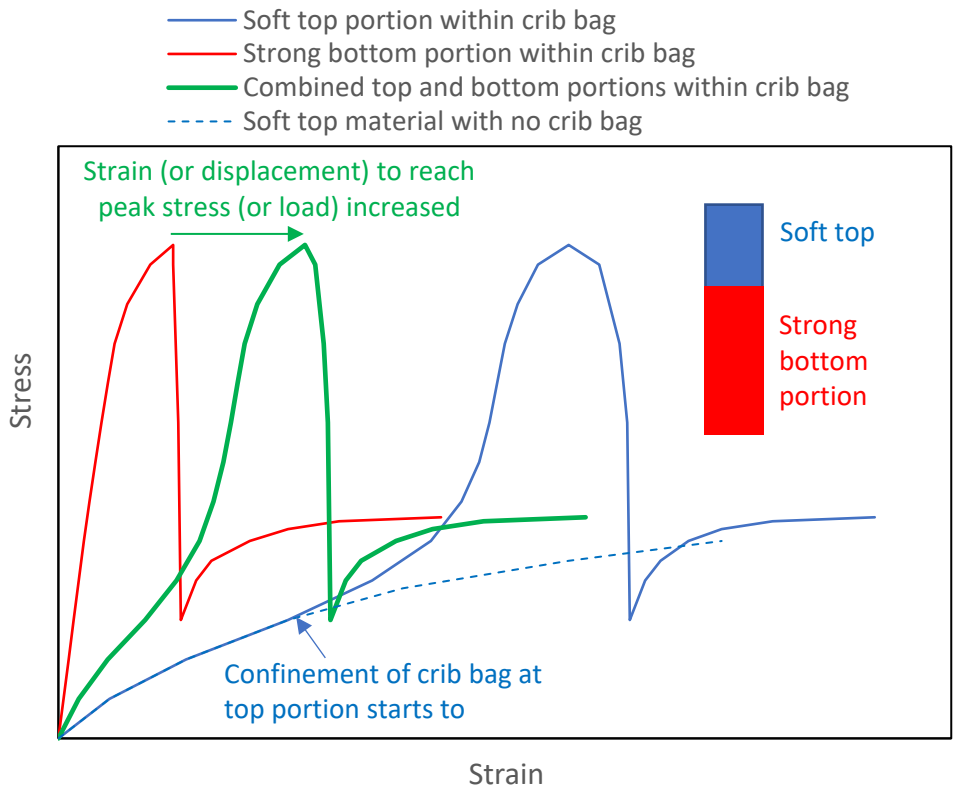


Fig. 18: Schematic showing the concept of using soft top portion to increase the strain (displacement) required to reach the peak stress (load) of hybrid GP/BP cementitious material based pumpable support

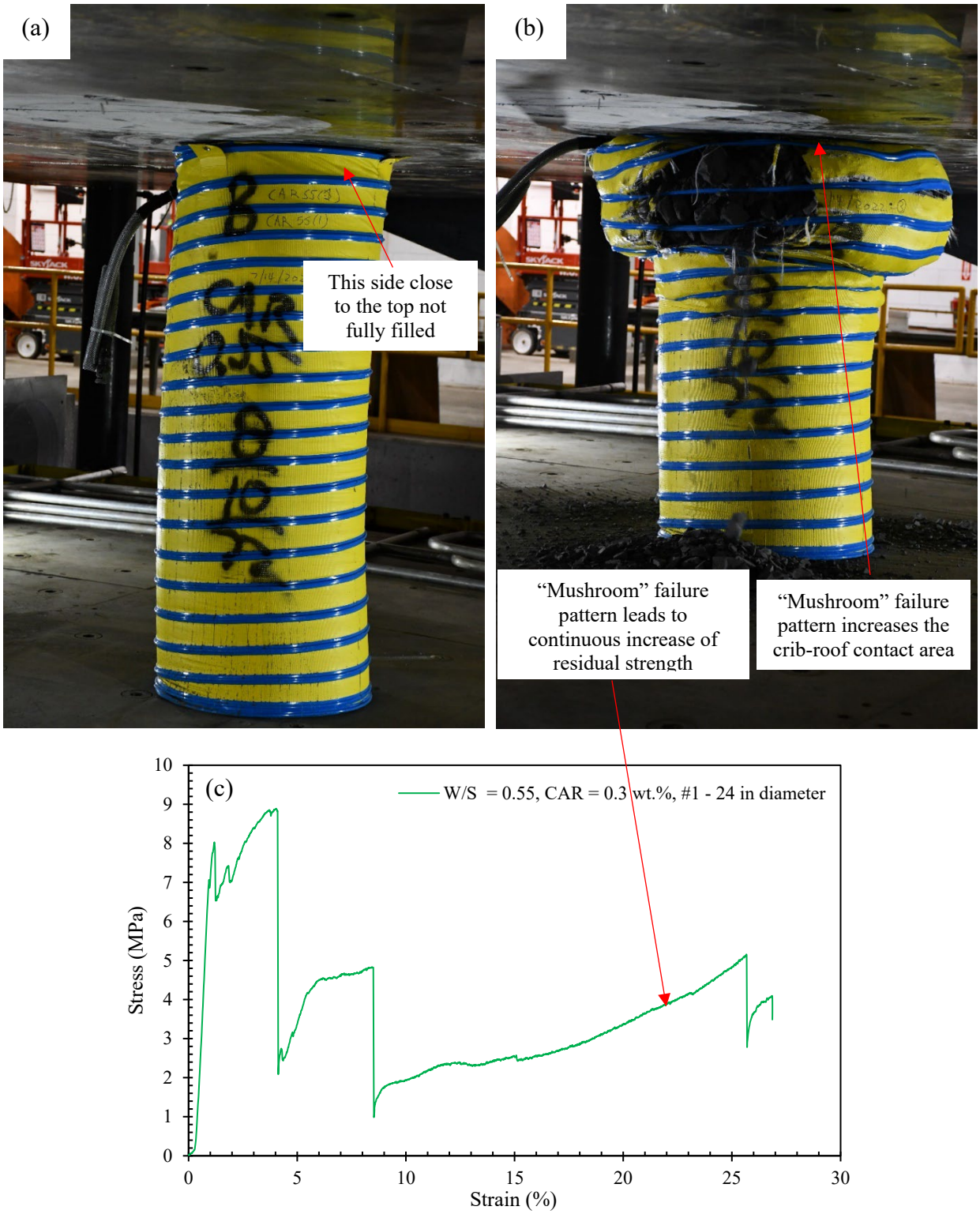


Fig. 19: Full-size crib produced from the hybrid GP/BP cementitious material at W/S = 0.55, 20 wt.% PC, and 0.3 wt.% CAR (#1): (a) right before testing was started, (b) right after testing was completed, and (c) obtained stress-strain curve

6.0 Publication Record and Dissemination Efforts

So far, three refereed journal papers and one refereed conference proceeding paper have been published:

- Nikvar-Hassani, A., and Zhang, L. (2022). "Development of a biopolymer modified geopolymer based cementitious material for enhancement of pumpable roof support." *Materials and Structures*, 55:116, https://doi.org/10.1617/s11527-022-01953-5.
- Nikvar-Hassani, A., and Zhang, L. (2022). "Synthesis of a CKD modified fly ash based geopolymer cementitious material for enhancing pumpable roof support." *Materials and Structures*, 55-64, https://doi.org/10.1617/s11527-022-01899-8.
- Nikvar-Hassani, A., Manjarrez, L., and Zhang, L. (2022). "Rheology, Setting Time and Compressive Strength of Class F Fly Ash-Based Geopolymer Binder Containing Ordinary Portland Cement." *Journal of Materials in Civil Engineering*, 34(1), https://doi.org/10.1061/(ASCE)MT.1943-5533.0004008.
- Nikvar-Hassani, A., and Zhang, L. (2020). "Development of a New Geopolymer Based Cementitious Material for Pumpable Roof Supports in Underground Mining." *Geo-Congress 2020*, February 25–28, 2020, Minneapolis, Minnesota, 10 pages.

A patent application has also been filed:

- Zhang, L., and Nikvar-Hassani, A. (2021). *Pumpable Hybrid Cementitious Material*, Application Number 63/285,757, Filling Date December 3, 2021.

Besides publishing papers and filling patent applications, we have also been actively working with Minova, mining companies and the technology transfer department at the University of Arizona to commercialize the new hybrid GP/BP cementitious material and transfer it to real applications in mining practice.

7.0 Appendices

This section presents the pictures of the produced cribs right before the test was started and right after the test was completed and the obtained stress-strain curves from uniaxial compression tests, including

- Figs. A1 – A2: cribs produced at W/S = 0.55, 20 wt.% PC, and 0 wt.% CAR
- Figs. A3 – A4: cribs produced at W/S = 0.55, 20 wt.% PC, and 0.3 wt.% CAR
- Figs. A5 – A6: cribs produced at W/S = 0.60, 30 wt.% PC, and 0 wt.% CAR
- Figs. A7 – A8: cribs produced at W/S = 0.60, 30 wt.% PC, and 0.3 wt.% CAR

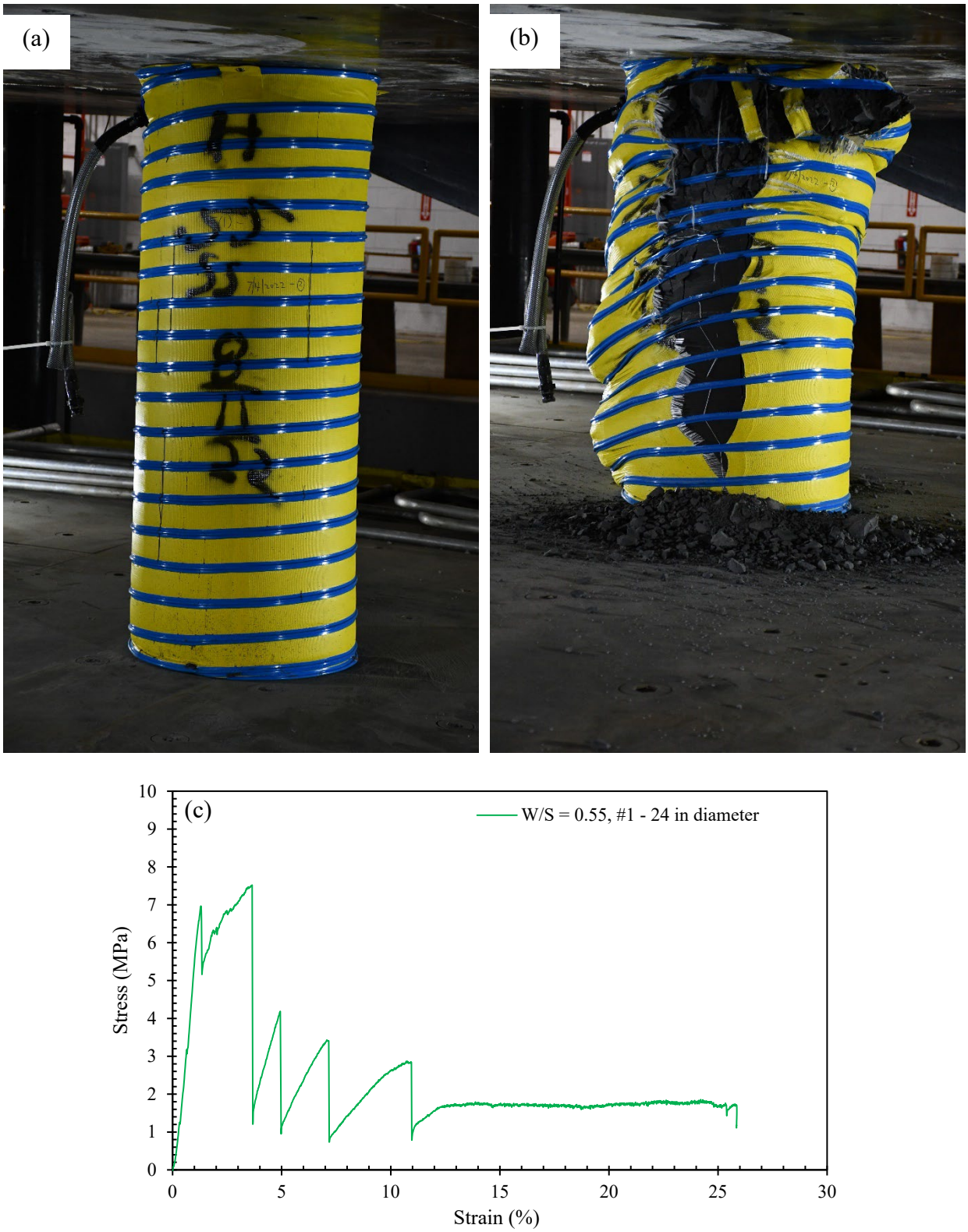


Figure A-1: Full-size crib produced from the hybrid GP/BP cementitious material at W/S = 0.55, 20 wt.% PC, and 0 wt.% CAR (#1): (a) right before testing was started, (b) right after testing was completed, and (c) obtained stress-strain curve

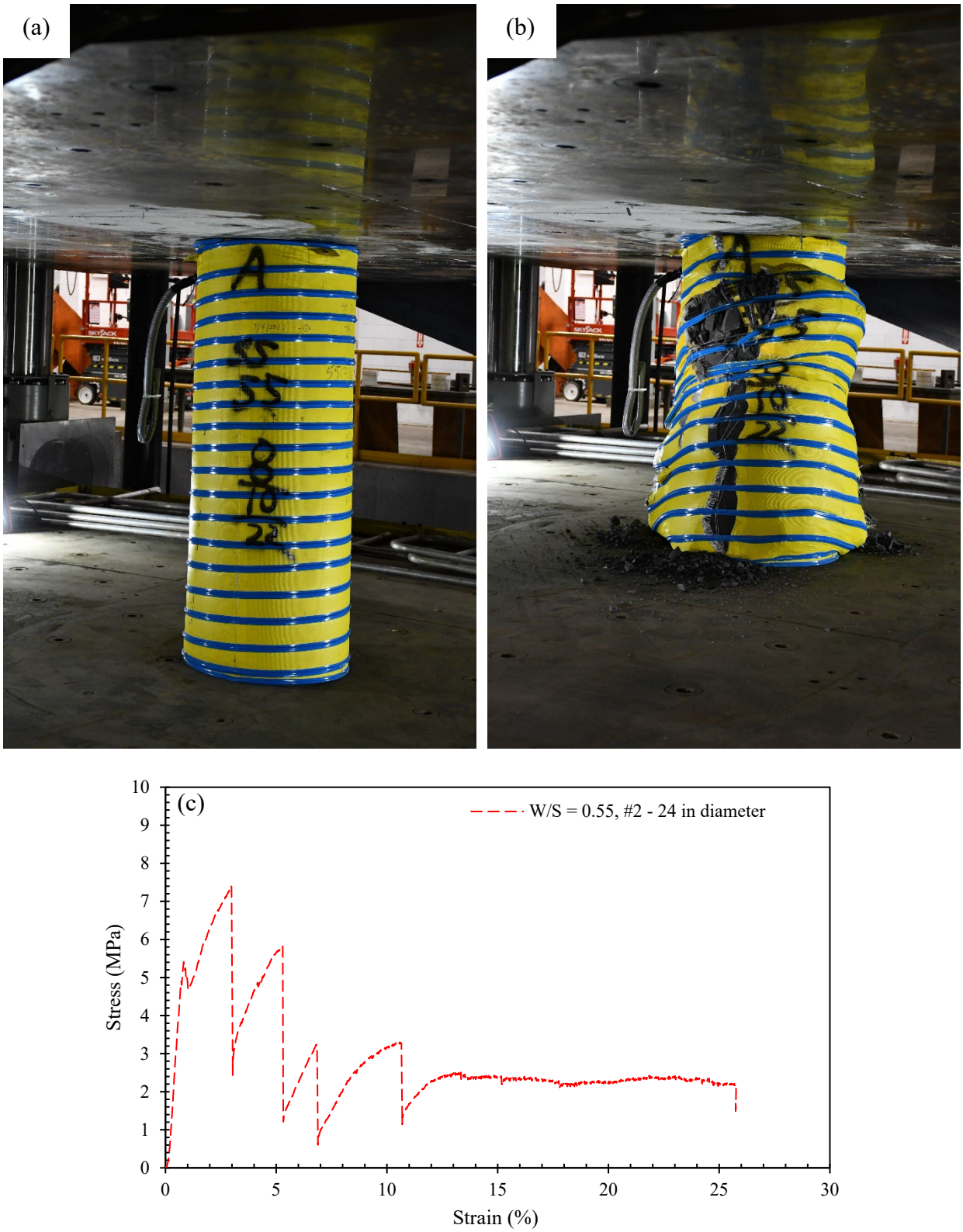


Figure A-2: Full-size crib produced from the hybrid GP/BP cementitious material at W/S = 0.55, 20 wt.% PC, and 0 wt.% CAR (#2): (a) right before testing was started, (b) right after testing was completed, and (c) obtained stress-strain curve

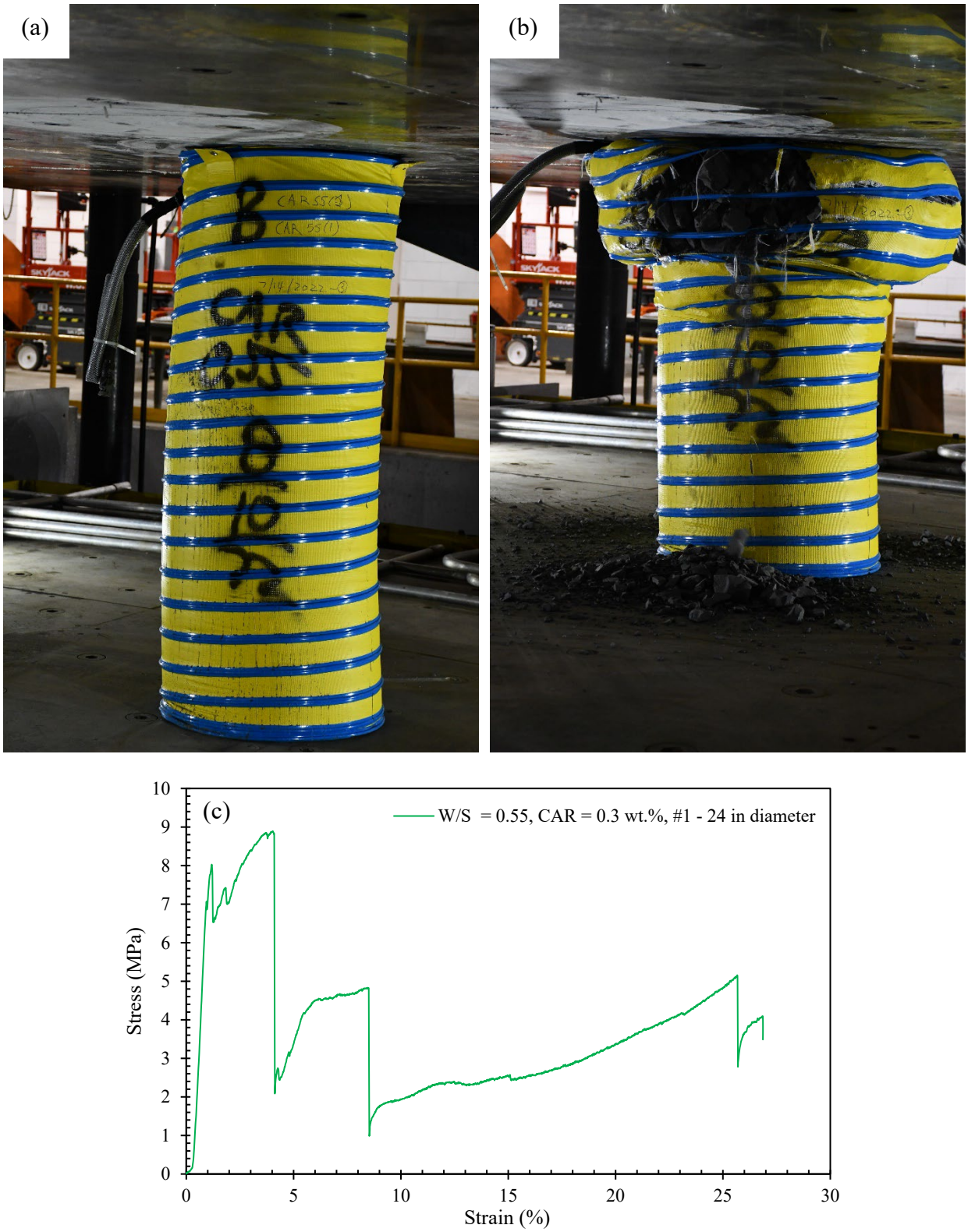


Figure A-3: Full-size crib produced from the hybrid GP/BP cementitious material at W/S = 0.55, 20 wt.% PC, and 0.3 wt.% CAR (#1): (a) right before testing was started, (b) right after testing was completed, and (c) obtained stress-strain curve

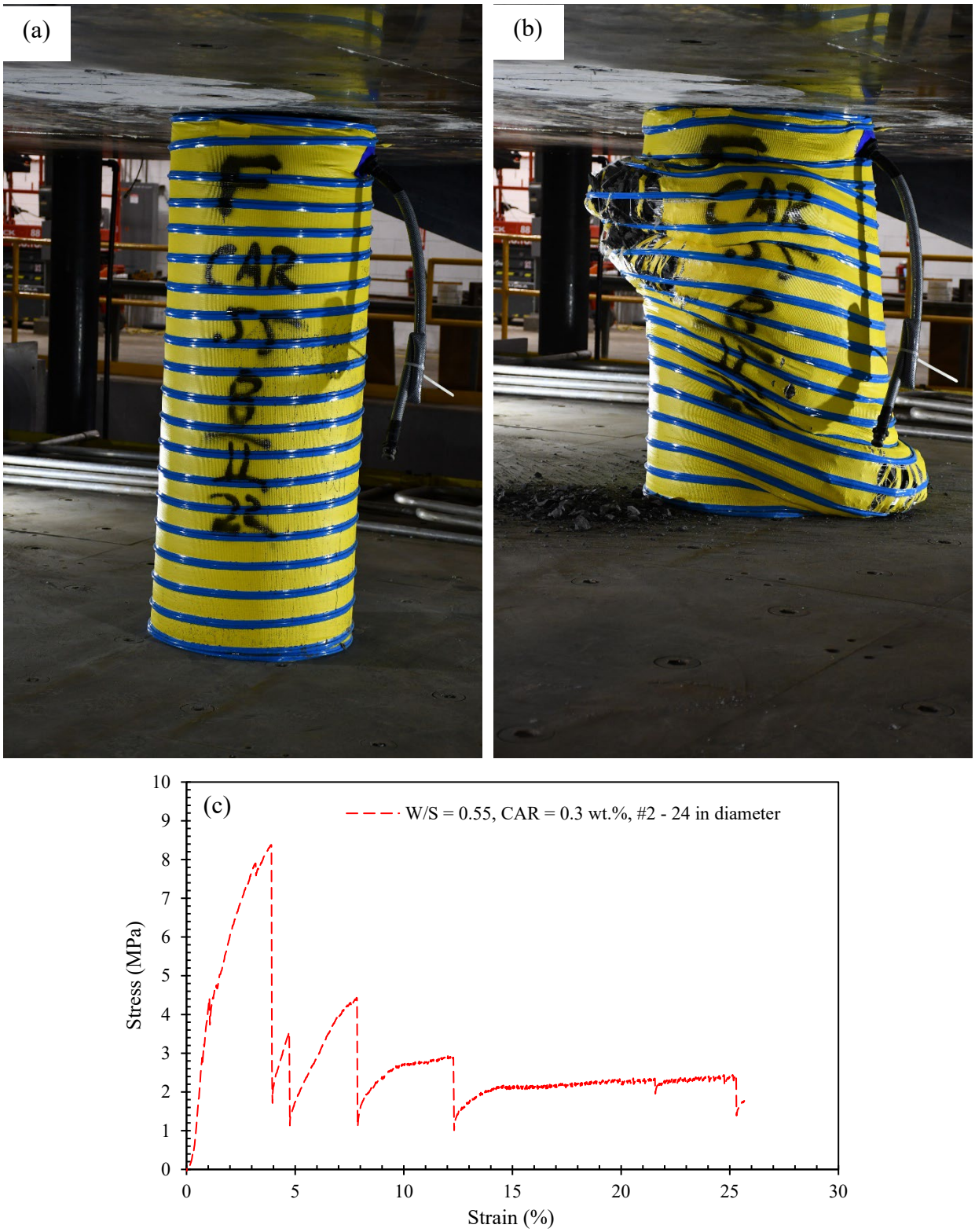


Figure A-4: Full-size crib produced from the hybrid GP/BP cementitious material at W/S = 0.55, 20 wt.% PC, and 0.3 wt.% CAR (#2): (a) right before testing was started, (b) right after testing was completed, and (c) obtained stress-strain curve

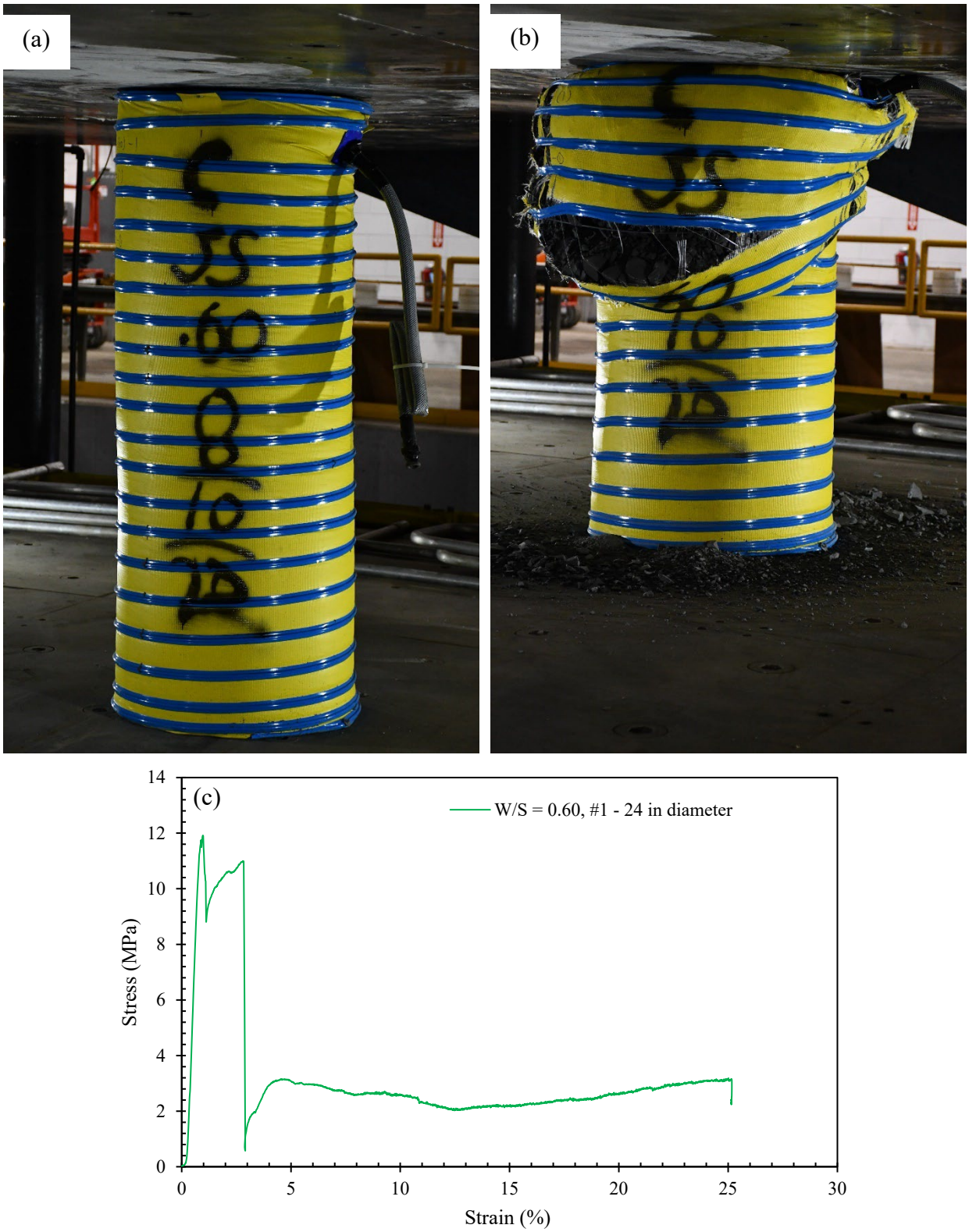


Figure A-5: Full-size crib produced from the hybrid GP/BP cementitious material at W/S = 0.60, 30 wt.% PC, and 0 wt.% CAR (#1): (a) right before testing was started, (b) right after testing was completed, and (c) obtained stress-strain curve

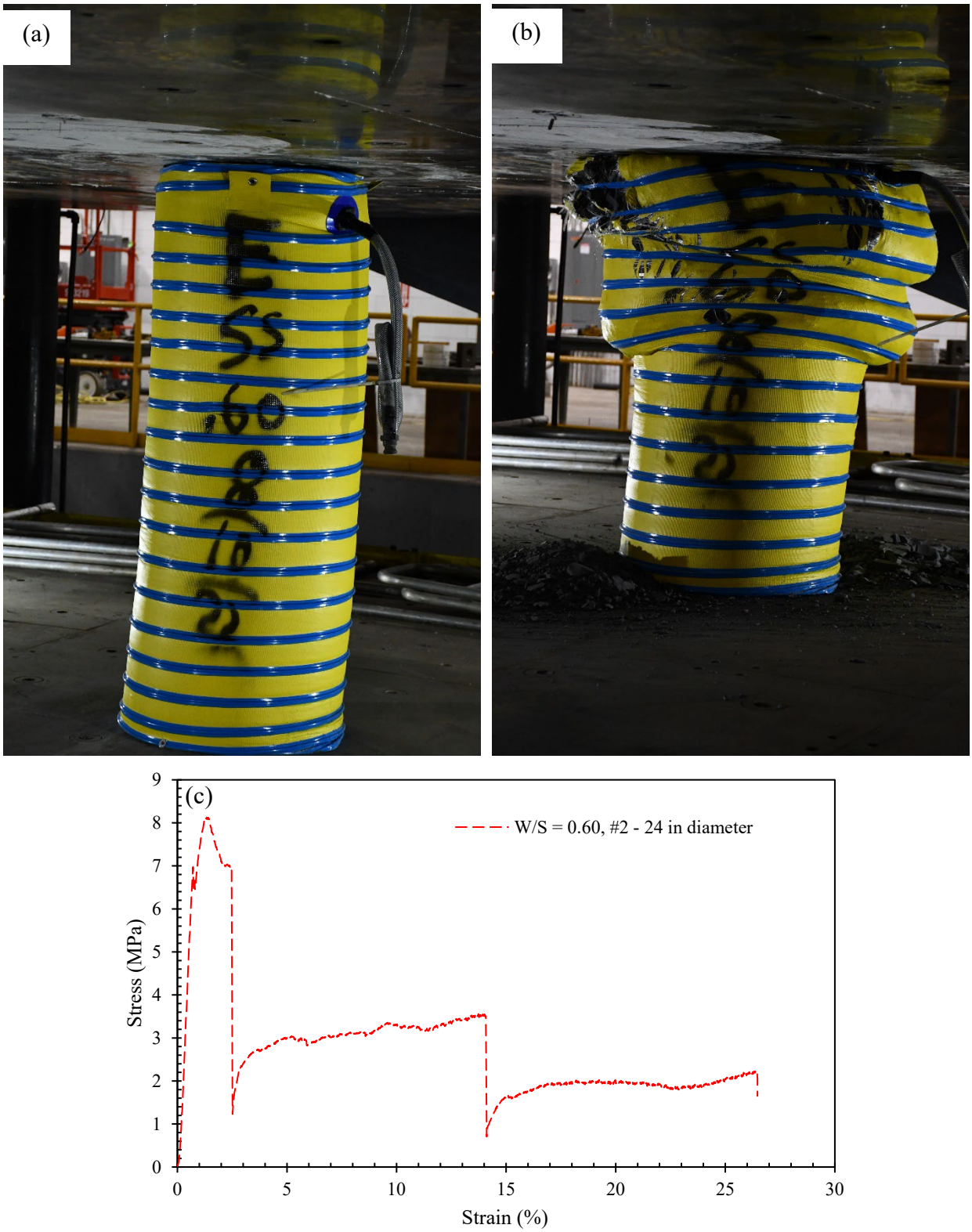
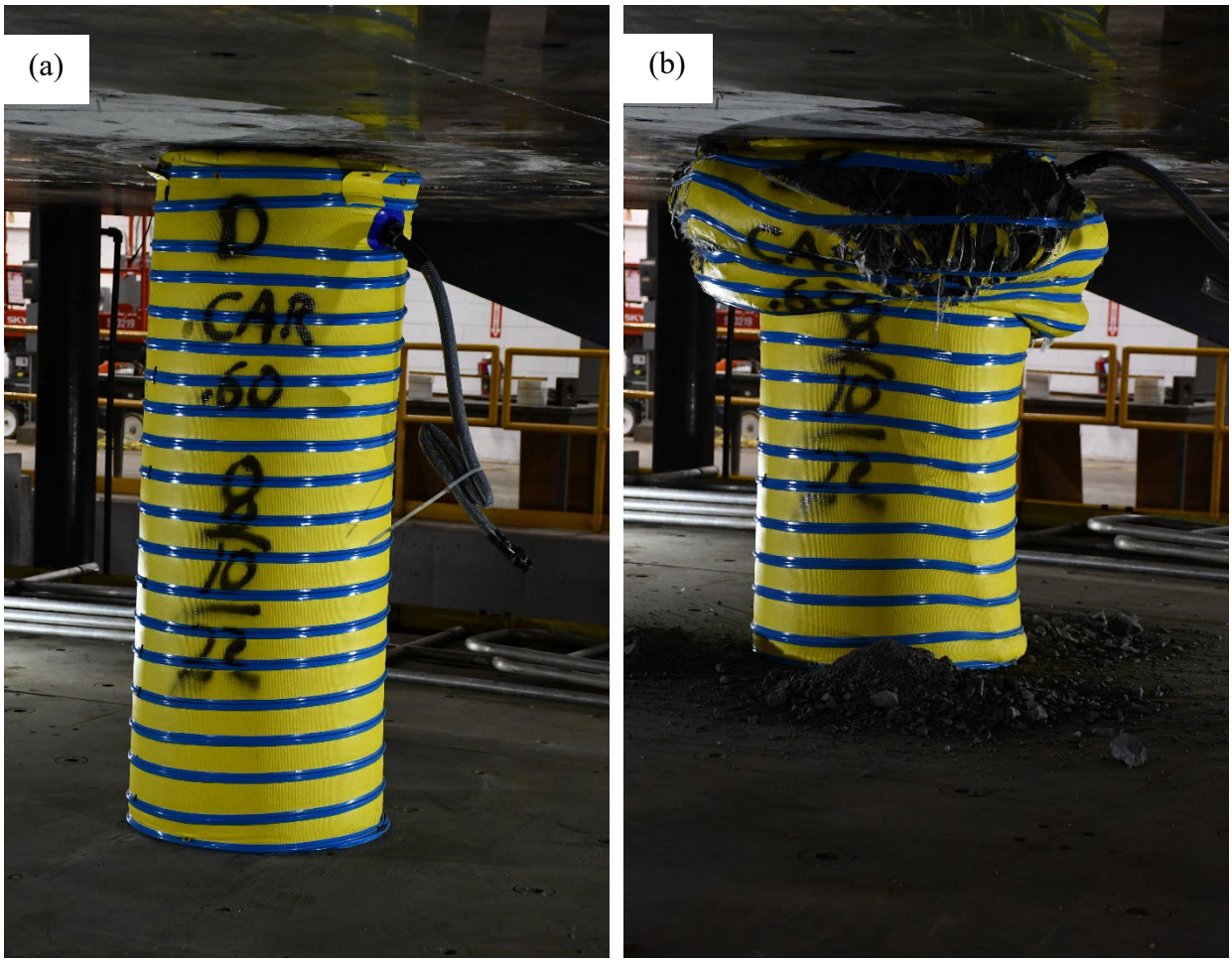


Figure A-6: Full-size crib produced from the hybrid GP/BP cementitious material at W/S = 0.60, 30 wt.% PC, and 0 wt.% CAR (#2): (a) right before testing was started, (b) right after testing was completed, and (c) obtained stress-strain curve



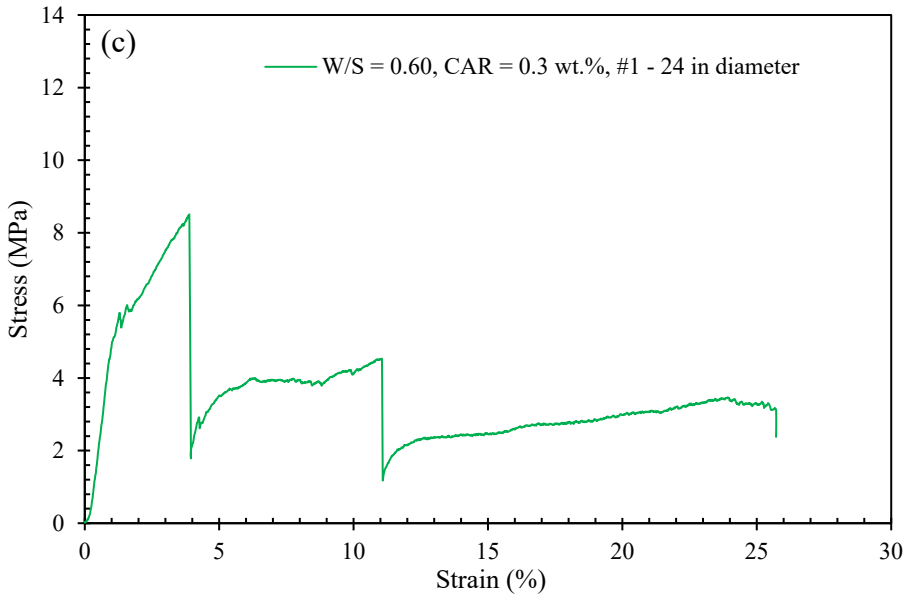


Figure A-7: Full-size crib produced from the hybrid GP/BP cementitious material at W/S = 0.60, 30 wt.% PC, and 0.3 wt.% CAR (#1): (a) right before testing was started, (b) right after testing was completed, and (c) obtained stress-strain curve

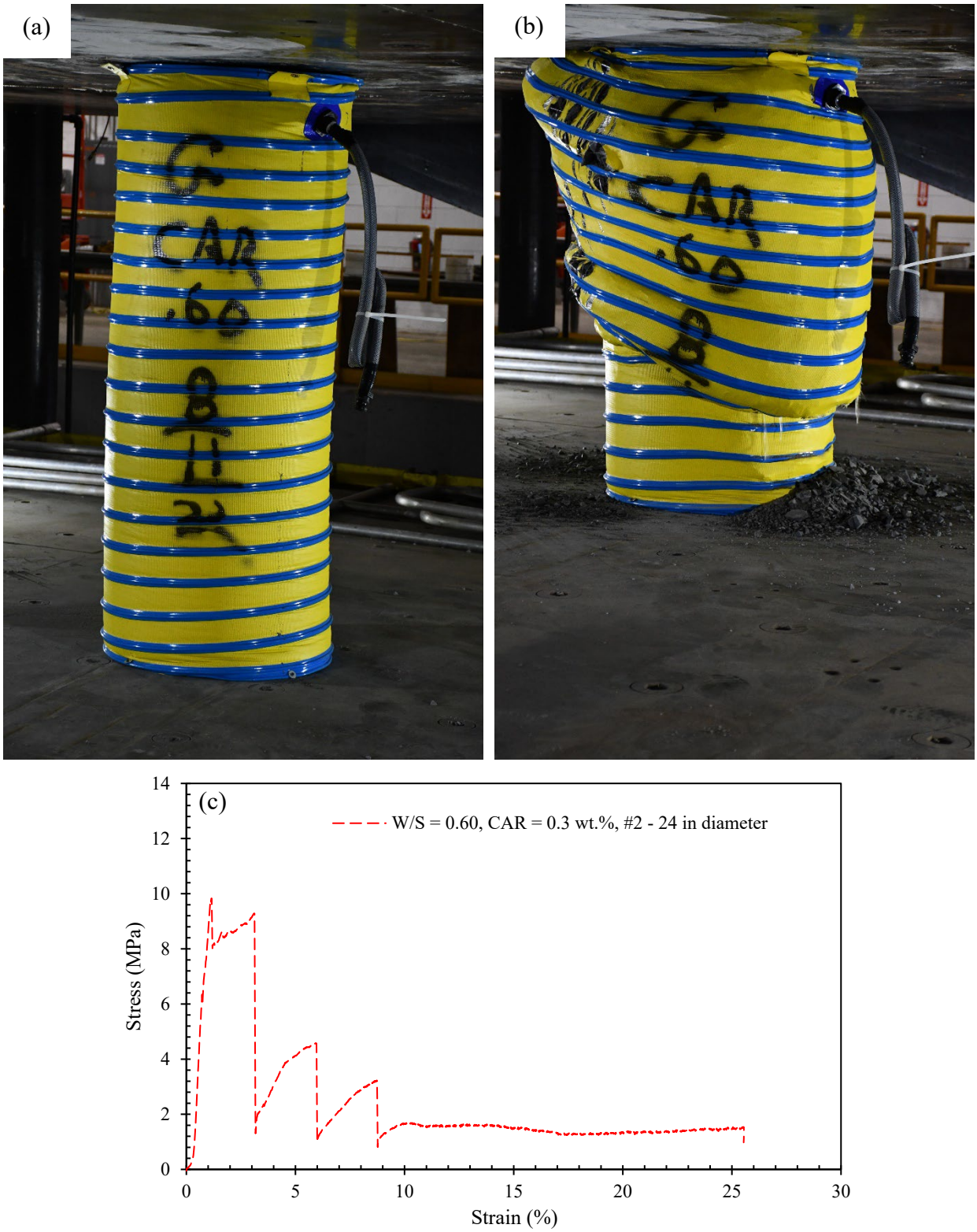


Figure A-8: Full-size crib produced from the hybrid GP/BP cementitious material at W/S = 0.60, 30 wt.% PC, and 0.3 wt.% CAR (#2): (a) right before testing was started, (b) right after testing was completed, and (c) obtained stress-strain curve

8.0 Acknowledgement/Disclaimer

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