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The benefit of delithiated beta spodumene to reduce the carbon footprint of cemented paste backfill

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Abstract

Delithiated beta spodumene (DBS) is the leach residue produced after lithium refining. It represents the largest material stream produced in the process; approximately seven to ten tonnes of DBS is generated per tonne of lithium hydroxide monohydrate produced. The material is characterised as pozzolanic and is featured in the recently published standard AS3582.4:2022 Supplementary cementitious material: Manufactured Pozzolans. This paper presents an experimental study on the strength behaviour of cemented paste backfill (CPB) containing DBS by investigating different CPB mix designs produced with nickel tailings, mine site-specific recycled process water, and various types of binders. The primary motivation of this collaborative research work was to find ways to reduce CPB's carbon footprint by using locally sourced material as a binder additive.

For this study, several laboratory tests were undertaken at the Nova nickel-copper mine to explore the use of DBS in paste fill design. DBS was used as a partial replacement material for ground granulated blast-furnace Slag (GGBFS) in 9:1 slag-lime binder and mixes with other cementitious binder types such as general purpose (GP), general blended (GB), high early strength (HE), and low heat (LH) cement. The results demonstrated that CPB samples with the DBS-GB, DBS-GP, DBS-HE and DBS-LH mixed binders showed promising results with DBS replacement ratios of up to 40 wt.%; however, CPB samples with the DBS- lime mixes failed to perform to an acceptable strength. Nevertheless, these performed well in achieving the compressive strength required for use at the Nova mine site. At 40 wt.% binder replacement with DBS, paste CO_2 emission will be reduced by around 28%. Future studies may consider the long-term performance and other mining applications of DBS.

Keywords: *cemented paste backfill (CPB), recycling, delithiated beta spodumene (DBS), cementitious material, lithium leach residue*

1 Introduction

Material production is a factor in more than 25% of global greenhouse gas (GHG) emissions (Pauliuk et al. 2021). The cement industry is one of the largest carbon dioxide (CO_2) producers. It contributes to 5% of worldwide emissions of this gas, primarily from burning fuels in cement kilns, with 40% specifically from the combustion of fossil fuels and 50% from the chemical process when calcium carbonate is thermally decomposed, producing lime and CO_2 (Lehne & Preston 2018; Lindstrom & McArdle 2009; Sakai & Kawai 2006; Zambrano et al. 2002). In the mining industry, cement or binder, as the more generic term, is used globally to make concrete (or Fibrecrete by adding fibres into the concrete mix), grouts, and in cemented fill materials such as cemented paste backfill (CPB), cemented hydraulic fill (CHF), and cemented rockfill (CRF).

CPB benefits in deep underground mining cannot be easily ignored (Belem & Benzaazoua 2004; Kesimal et al. 2005; Bentz 2008; Helinski et al. 2011). The commissioning of over 94 paste plants in China alone between 1996 and 2017 proves the need for this filling method (Wu et al. 2017). Paste fill technology allows mining companies to utilise fine tailings to fill in stopes caved out from underground mining operations, significantly reducing waste stream generation. To make paste, wet tailings as a live feed from the mill or dry tailings reclaimed from a tailings storage facility (TSF) are mixed with processing water (decant water) and a binder, normally at 3-10 wt.% of the total paste fill mix. The paste is then transported underground hydraulically using either gravity feed or a positive displacement pump to support the adjacent stopes under vertical and horizontal exposures (Belem & Benzaazoua 2004).

Kawai et al. (2005) reported the CO_2 emission of producing concrete. Based on this report, Table 1 summarises the CO_2 emission of General Portland cement (GP), ground granulated blast furnace slag (GGBFS or slag), limestone powder, fine aggregate, three m^3 concrete mixer (same size as the Nova paste plant mixer), and normal curing of CPB.

Table 1 CO_2 emission of materials and processes related to CPB (Kawai et al. 2005)

	Unit	CO_2 emission
GP	kg/t	766.6
GGBFS	kg/t	458.7
Lime stope powder	kg/t	16.1
Fine aggregate	kg/t	3.7
3 m^3 concrete mixer	kg/m^3	0.6
Normal curing	kg/m^3	0

However, the CO_2 emission of different binder types used in this study is calculated as 1,008 kg/t, 146 kg/t, 446 kg/t, and 1,100 kg/t for GP, Slag, Low Heat (LH) cement, and hydrated lime (transported from Kwinana, WA, Australia), respectively. Using these numbers as a baseline, the CO_2 emission of a CPB mix with 6% GP binder composition is estimated to be 150 kg/m^3. This estimation for the Nova mine site is 44 kg/m^3 due to a high GGBFS fraction in its paste mixture (9:1 GGBFS: lime ratio). Note that this estimation accounts for 7% cement transportation from Kwinana, WA, to the mine site, 8% tailings agitating and filtration, and 15% paste manufacturing. Cement production still comprises the most significant part at 70%, as shown in Figure 1.

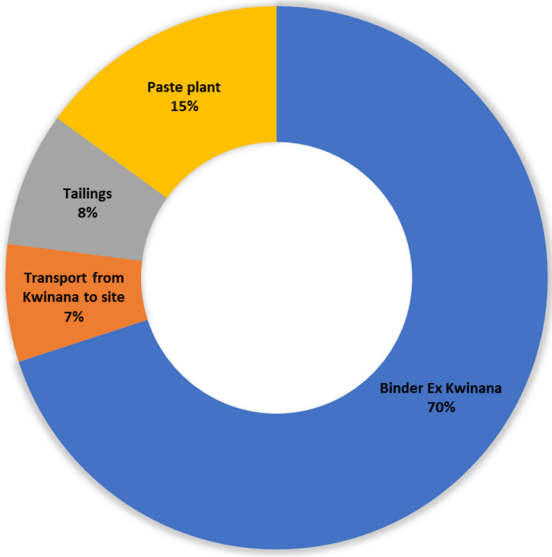


Figure 1 Nova mine CPB CO_2 emission

Moreover, the binder cost constitutes a significant part of the total backfill cost. It has dramatically increased over 2022, brought about by the global pandemic and its adverse impact on the supply chain. Chen et al. (2022) recently highlighted the need to investigate new materials and methods for CPB to address the rising cost of cement and, most importantly, reduce the carbon footprint of mining activities (Ding & Zhang 2020; Su et al. 2019). The latter is particularly a significant objective for IGO. The company is known as a leader for its sustainability initiatives, e.g., the first mine site to lower energy costs via its hybrid solar PV-diesel power plant (Creagh 2018). Also, IGO is included in the DJ Sustainability Index, an index representing the top 30% of Australian companies that demonstrate leading sustainability performance (ASX:IGO 2022).

To address this challenge, a newly available material in Australia, delithiated beta spodumene (DBS), was tested as a binder material to partially replace the current binders used for the CPB mixes. DBS is a by-product of lithium refining. This material has pozzolanic properties (Karrech et al. 2019; Karrech et al. 2021) and has been tested in numerous laboratory trials as a supplementary cementitious material with a comparative performance at replacement ratios of 20-35 wt.% (Haigh et al. 2013; Munn et al. 2017; Munn et al. 2021). DBS is also featured in the recently published Australian standard AS3582.4:2022 *Manufactured Pozzolans*. In a more relevant scenario, He et al. (2020) demonstrated that DBS in CPB mixes dosed with sodium hydroxide reached 32 MPa on a 28-day strength. In contrast, this current study will utilise DBS as a run-of-plant product without an additional chemical activator.

2 Experimental study

2.1 Material preparation and characterisation

2.1.1 Tailings and water

Fresh tailings cake filtered from the Nova Nickel-Copper ore body in the Fraser Range of Western Australia was used for the test work. Table 2 presents the chemical analysis. Most of the tailings comprised silica at 39.70 wt.%, pyrite at 22.40 wt.%, and other iron minerals, accounting for approximately 84 wt.% in total.

Table 2 Chemical analysis of composite tailings sample

Element	Wt.%
Cu	0.05
Ni	0.45
Co	0.01
Fe	21.90
Mg	3.44
S	9.34

Figure 2 shows the particle size distribution of the tailings; the P_{80} is 145 µm. This particle size distribution is in the upper operational range for tailings and has a much larger coarse fraction than the average used in paste fills (Sivakugan et al. 2006). In addition, the material has a specific gravity (SG) of 3.4.

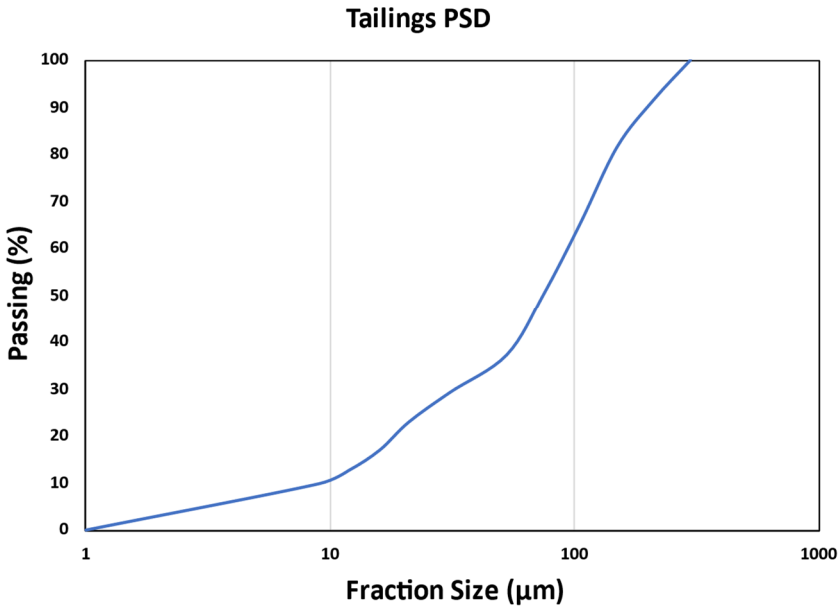


Figure 2 Nova mine tailings' particle size distribution

To adjust the solid content of specimens to a range of flowable mixes, this study used mine decant water, with properties as follows: 3.91 pH, 332 ppm of K, 24,000 ppm of Na, and TDS of 120.3 g/L. The processing decant water used for this test work represented normal water for the Nova mine site's paste fill plant.

2.1.2 Binders

Binder contributes up to 75% of the total operating costs of backfilling (Grice 1998). Recently, the potential for cost saving has attracted more attention, and several studies have been conducted to optimise binder use in CPB mixes (Bentz 2008; Chen et al. 2017; Deng et al. 2018; Safarizadeh & Taheri 2021). The most common binder in CPB recipes is ordinary GP and LH, used in different ratios to arrive at the minimum required strength. However, the CPB chemistry for Nova mine is based on a GGBFS and hydrated lime mix in a 9:1 ratio. As a result, Nova's average 28-day CPB strength is measured above 3.4 MPa for a 6% (w/w%) CPB mixed with a 9:1 ratio GGBFS:lime binder.

The binders used in this trial included GGBFS, hydrated lime, GP, LH, High Early (HE), and General Blend (GB) cement. GB and LH are cost-effective binders that comply with AS3972 and are manufactured from a mixture of Portland Cement clinker, limestone, and gypsum but also blended with GGBFS. GB comprises 35% Slag: 65% GP, while LH consists of 65% Slag: 35% GP. GGBFS is typically used in concrete or mining backfill applications that require a lower heat of hydration and where resistance to aggressive groundwater and adverse environmental conditions are present. Generally, the early age strength of CPB plays a critical operational role in mining activities. To cover this, our study also tested HE, a high early-strength GP characterised by finer PSD.

Table 3 summarises the composition of the binders used in this trial.

Table 3 Comparative components list of binders used in this study

Ingredient	CAS Number	Content - GB/LH	Content - GP/HE	Content - Lime	Content - GGBFS	Content - DBS
		Wt.%				
PORTLAND CEMENT	65997-15-1	30 - 85	<95	-	-	-
QUARTZ (CRYSTALLINE SILICA)	14808-60-7	<10	<1	0.5 -3	<1	<5
GYPSUM	13397-24-5	<8	2 - 8	-	2 - 5	<2
CALCIUM CARBONATE	471-34-1	<5	<8	-	-	-
GROUND BLAST FURNACE SLAG	65996-69-2	<70	-	-	>90	-
CALCIUM HYDROXIDE	1305-62-0	-	-	65- 75	-	-
MAGNESIUM HYDROXIDE	1309-42-8	-	-	3.5 - 5	-	-
ALUMINIUM OXIDE	1344-28-1	-	-	0 - 1.5	-	-
IRON (III) OXIDE	1309-37-1	-	-	0 - 1	-	-
LIMESTONE	1317-65-3	-	-	0 - 2	-	
DBS	1302-37-0	-	-	-	-	<80

2.1.3 Delithiated beta spodumene

The availability of DBS in Australia is expected to significantly increase in the next five to 10 years when three major lithium refineries will be operational and hit full production capacity. As a result, considerable volumes of approximately 1.1 million tonnes per annum will be produced in Western Australia (Casella & Olivares 2021). This volume is also expected to increase as the demand for lithium chemicals continues to rise and new refineries are built, or existing ones increase capacity.

Tianqi Lithium Kwinana in Western Australia commenced commercial production in December 2022. (ASX:IGO 2022). The company produces DBS as a run of plant material with moisture content of 20-26 wt.% and an SG of 2.5-2.7. Since the material is produced from an acidic leaching process, the pH of the material is between 2.8-4.0. The commercial name of the company's DBS is Tianqi aluminosilicate or TAS. As the name suggests, TAS' major mineral components are silica at 60-65 wt.% and alumina at 20-24 wt.%. The PSD of TAS ranges at 27-41 µm (P_{50}).

Two TAS samples were supplied for this study, with properties summarised in Table 4. The samples have high moisture at around 24 wt.%. However, they did not behave as a very wet cake, as is evident in Figure 3a. This is because the moisture in TAS is interstitial, brought about by the zeolite-like property of the material.

Table 4 Summary of TAS sample chemical properties

Properties	Units	TAS1	TAS2
Moisture	wt.%	23.50	25.10
Al_2O_3		22.80	23.40
CaO		0.77	0.70
Fe_2O_3		0.95	0.78
K2O		0.56	0.40
MgO		0.22	0.22
Na_2O		0.59	0.30
P_2O_5		0.20	0.16
SiO_2		62.80	64.40
SO_3		4.05	3.43
LOI		7.97	8.63
Dx (80)	µm	59.80	85.70
pH		3.6	3.4

Both samples were dried in an oven at 100-110 °C for 48 h. This process brought the moisture of TAS to less than 0.01 wt.%. Wet TAS is lumpy, as seen in Figure 3a, but the lumps readily break when dried, as in Figure 3b. As a result, the powdery nature of dried TAS eliminated the need for crushing before mixing it into paste.

a) **b)**

Figure 3 a) wet TAS & b) dried TAS

2.2 Sample preparation

To prepare the tailings samples, 160 kg of tailings filter cake with 18 wt.% initial moisture was collected from the paste plant's belt filter and dried in the oven at 100-110 °C for 48 h. The dried tailings samples were then tipped and mixed to break down lumps formed on drying, as illustrated in Figure 4. Researchers observed discolouration due to oxidation; however, this effect can be disregarded as the same sample was used in all the mixes. Table 5 outlines the designed and measured tailings, binders, and water ratios. The binders were

blended with TAS; the team prepared several mixes without TAS as control specimens. The samples were then mixed for two minutes with a hand mixer, and the flowability of the samples was measured using a standard slump test cone to ensure the best practical mixes were prepared. Prior drying of tailings and TAS samples facilitated better control of desired solid content for a constant flowability of the mixes. The test aimed to keep the slump numbers around 190 mm as the optimum practical product to flow freely underground without any pumping requirement. Figure 4 visually summarises the sample preparation procedure.

Figure 4 Sample preparation method

3 Testing

3.1 Unconfined compression strength (UCS) test and test matrix

A VJ5011-RS Triplex 50 kN compression machine with strain rates of 0.01 to 50 mm per minute was used. After curing the samples in a humidifier to a specific curing time (1, 3, 7, 28, 56 and 365 days), samples were removed, demoulded, and the top sections of the samples were cut to bring the length to diameter ratio (L/D) of two - 2.5 (ASTM D 2166).

The samples were initially prepared with DBS mixes of 9:1 GGBFS: lime ratio as the standard binder mix at the Nova mine site. Unfortunately, most of the samples containing hydrated lime failed to achieve the required strength and the test plan was shifted to GP-based binders. Higher strength results were initially achieved with mixes containing GB, although, unfortunately, the GB binder product was removed from commercial sale by the supplier at the same time as this trial. Due to the lack of practical supply, further work on this binder was suspended. Hence, the remaining tests were conducted on GP, LH, and HE binders. Table 4 summarises the test matrix. All UCS tests were repeated twice and the average numbers reported.

Table 5 TAS trial test matrix

Sample ID	Target Solid content (%)	Target binder Content (%)	TAS %	Lime %	GB %	LH%	GGBFS %	GP %	HE %
TAS1	79	6%	22.5	0	0	77.5	0	0	0
TAS2	79	10%	50	0	0	50	0	0	0
TAS3	79	6%	22.5	0	77.5	0	0	0	0
TAS4	79	6%	45	10	0	0	45	0	0
TAS5	80.5	6%	19.6	2	0	0	78.4	0	0
TAS6	79	6%	29.4	2	0	0	68.6	0	0
TAS7	79	6%	39.2	2	0	0	58.8	0	0
TAS8	79	6%	49	2	0	0	49	0	0
TAS9	79	6%	18	10	0	0	72	0	0
TAS10	79	6%	36	10	0	0	54	0	0
TAS18	79	6%	27	10	0	0	63	0	0
TAS19	80.5	5%	50	50	0	0	0	0	0
TAS3C	79	5%	0	0	100	0	0	0	0
TAS3D	79	6%	22.5	0	0	77.5	0	0	0
TAS3E	79	6%	0	0	0	100	0	0	0
TBB2	80	6%	30	0	0	70	0	0	0
TBB6	80	6%	30	0	70	0	0	0	0
TBB7	80	6%	45	0	55	0	0	0	0
TBB8	80	6%	55	0	45	0	0	0	0
TBB9	80	6%	30	0	0	0	0	70	0
TBB18	80	6%	0	0	100	0	0	0	0
TBB30	79	6%	22.5	0	0	0	0	77.5	0
TBB31	79	6%	0	0	0	0	0	100	0
TBB32	79	6%	30	0	0	0	0	0	70
TBB33	79	6%	40	0	0	0	0	0	60
TBB34	79	6%	0	0	0	0	0	0	100
TBB35	79	6%	0	0	0	0	0	0	100
TBB36	79	6%	35	0	0	0	0	65	0
TBB37	79	6%	40	0	0	0	0	0	60

3.2 Chemical characterisation of paste fill mixes

Six samples from the TAS trial test matrix were chosen for X-ray diffraction analysis (XRD) analysis, as outlined in Table 5. The results showed four samples which passed Nova's UCS strength requirement (>500 KPa), one

which failed and one with low strength but still passed the strength requirement. An XRD test was done to ascertain the mineral phases comprising the paste fill mixes produced from different binder mixes.

A commercial lab Microanalysis, NATA accreditation no. 20283, did the XRD analysis. Samples were lightly ground to a PSD P_{90} 20 µm and ran through a Panalytical AERIS X-Ray diffractometer equipped with a cobalt X-Ray radiation source. The diffractograms were analysed using Bruker EVA 3.1 software and the ICDD PDF4 database.

4 Results and discussion

4.1 UCS test

The initial tests were conducted on the Nova mine site's current GGBFS:lime binder blend. Samples TAS5, TAS6, TAS7, TAS8, and TAS9 failed to gain any strength. Samples TAS4, TAS10, TAS18, TAS19, TBB8, and TBB18 only gained very low strength (<250 KPa). Although these results may be acceptable for many mine sites, this paper will not discuss them in detail since they do not meet the strength requirement for the Nova mine site. Furthermore, whether the minimal strengths gained were due to TAS or the remainder binder in the specimens is unclear. It appears that TAS relies on readily available calcium from lime to produce the strength-forming compounds, and a considerable number of paste samples were mixed and tested with different binder types and ratios to narrow down the test plan towards a promising mix.

Three strength levels of 500, 1400, and 1900 KPa were targeted as required for the Nova mine site due to the various stope sizes from 25 m height (H) to 75 m (H). The strength requirements also depended on the orientation and size of the face of the exposed paste. To ensure the trial was successful, the strength of samples was compared to the maximum requirement of 1900 KPa for the 30 mWx100 mH stopes. Results were compared with the main CPB mix with 4% binder content of 9:1 GGBFS:lime wt.% ratio. As can be seen in Figure 5, 10 test batches produced from TAS mixed with GP, LH, EH, or GB binders generated the required strength.

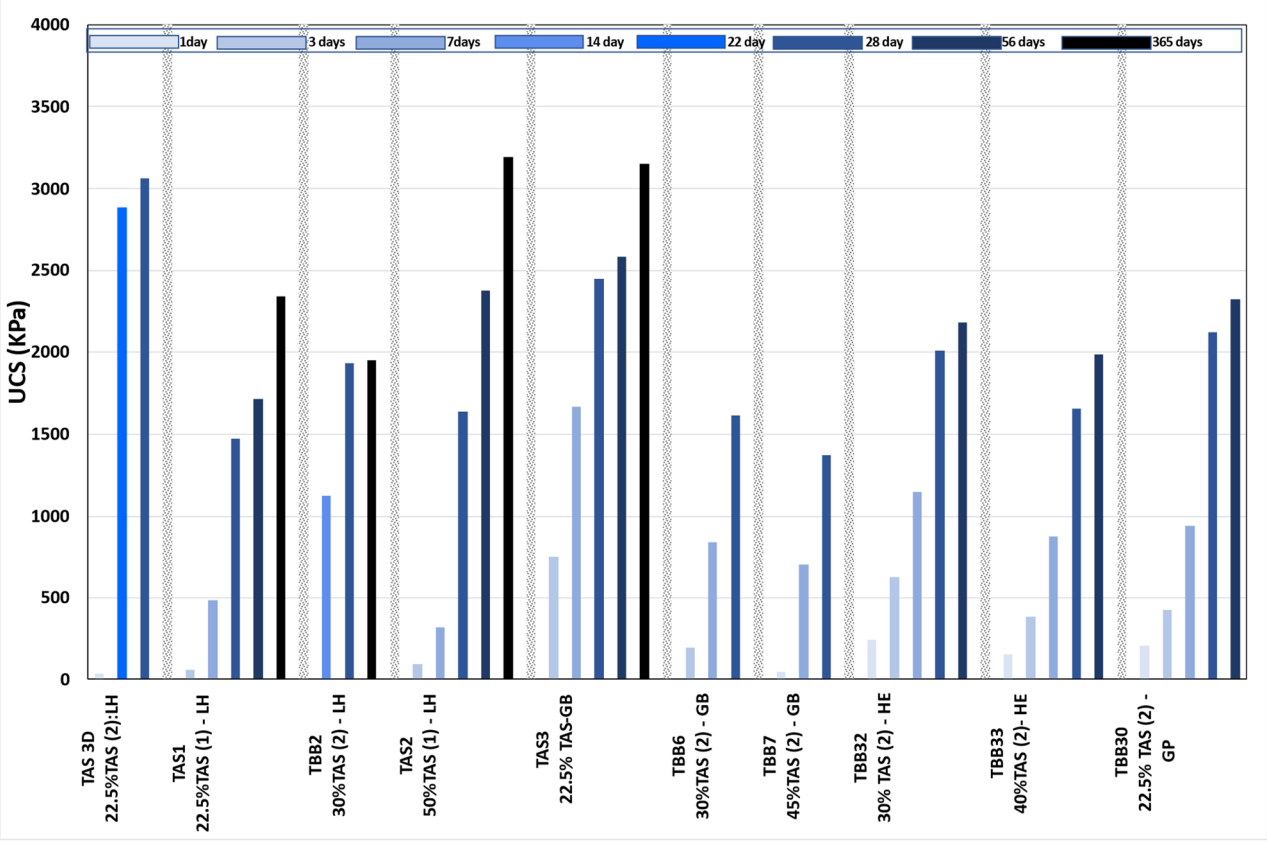


Figure 5 Paste UCS results for the accepted mix designs

Figure 5 shows that the TAS3D sample (22.5 TAS: 77.5 LH, wt.%) gained the highest 28-day strength. Meanwhile, TBB32 (30 TAS: 70 HE, wt.%) generated the highest early aged strength of 240 KPa in the first 24 hrs. The overall strength performance of the samples decreased by increasing the TAS portion, except for TAS2 (50 TAS: 50 LH, wt.%), as a higher binder ratio was used in the mix (10% w/w%). Also, the strength continued to increase, as shown in the 365-day strength in samples TAS1 (22.5 TAS: 77.5 LH, wt.%), TAS2 (22.5 TAS: 77.5 GB, wt.%), and TAS3 (50 TAS: 50 LH, wt.%).

Plastic behaviour after failure was observed for all low-strength samples (TAS4, TAS10, TAS18, TAS19, TBB8, and TBB18), in which large axial deformations happened without any clear failure surface. To contrast, the shear surface for the samples with GP-based binder was almost vertical (brittle), and as can be seen in Figure 6, the failure surfaces were captured between 70^{o} and 90^{o}.

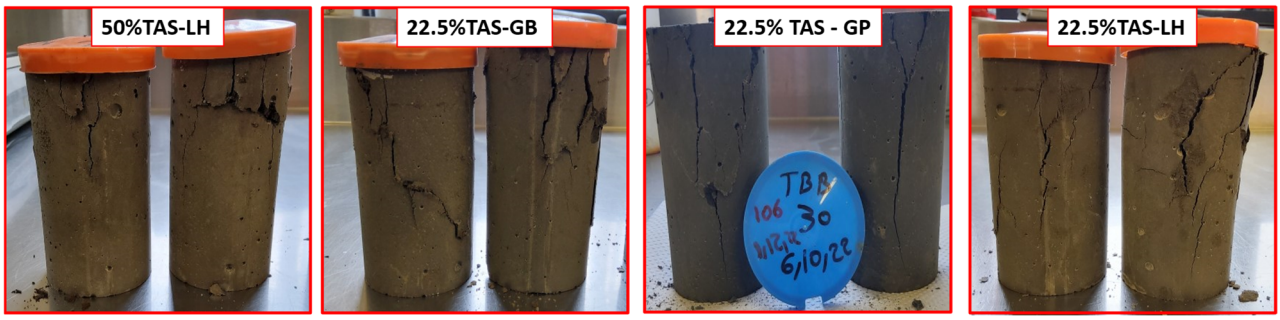
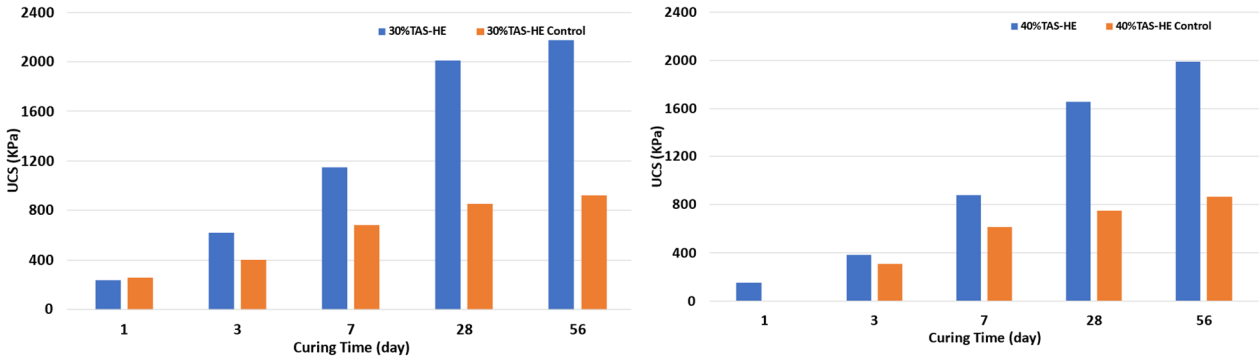


Figure 6 UCS tested samples failure surfaces for (a) 50%TAS-LH; (b) 22.5%TAS-GB; (c) 22.5%TAS-GP; & (d) 22.5%TAS-LH

To create a baseline for the effect of DBS on CPB strength, separate control tests were conducted for the potential mix designs. The control tests were prepared with the exact ratios ignoring the DBS portion. As can be easily seen in Figure 7, the strength of samples with DBS was higher than the control tests in almost all cases. Only the one-day strength for 30% TAS-HE mixes (Figure 7a), 22.5%TAS-LH mixes (Figure 7d) and the one and three-day strength of 22.5%TAS-GP mixes (Figure 7e) have control specimens at higher strength. When comparing these results to the results on the 28 and 56-day strengths, it can be reasoned that DBS significantly increased the strength.



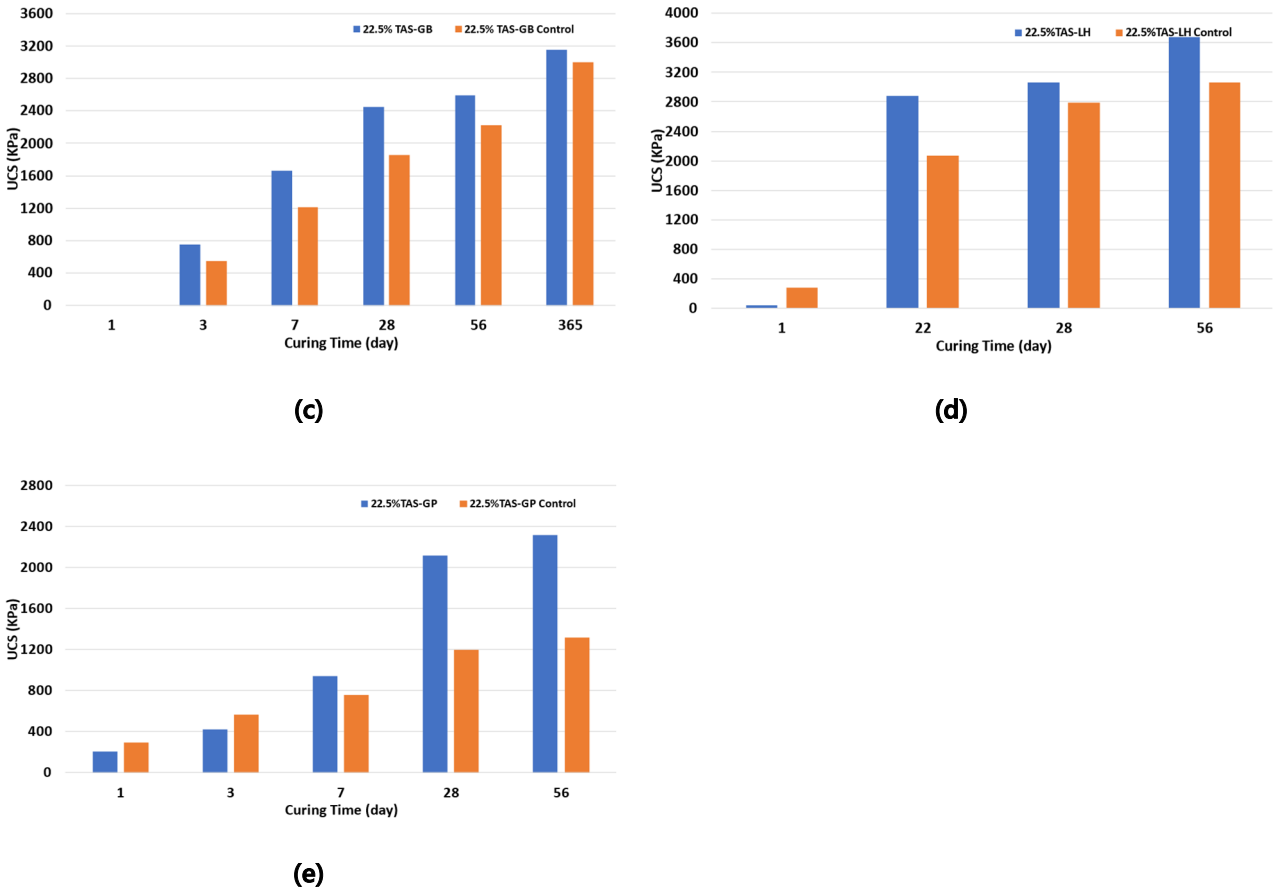


Figure 7 Comparison graphs of Control tests for (a) 30%TAS-HE; (b) 40%TAS-HE; (c) 22.5%TAS-GB; (d) 30%TAS-LH; & (e) 30%TAS-GP CPB mixes

While generating a comparatively lower strength at 2119 KPa and 2011 KPa, respectively (compared to LH and GB mixes), GP and HE-based mixes produced the widest gap strength vis-à-vis the control mix. Case in point, sample TBB 30 (22.5 TAS: 77.5 GP, wt.%) resulted in a 28d strength of 2119 KPa compared to the control mix at 1194 KPa. Similarly, sample TBB 32 (30 TAS:70 HE, wt.%) has a 28d UCS strength at 2011 KPa, while the UCS strength for the same curing time of the control mix was only 853 KPa. Adding TAS in the mixes resulted in the doubling of strength for the same curing time. The reactive aluminosilicate components in TAS likely bring this about, which is responsible for its pozzolanicity (Lim & Ghisi 2021). These reactive components work well with cement-based mixes, as was consistently shown in earlier studies with TAS (Munn et al. 2017; Munn et al. 2021). Further studies will investigate the textural effect of DBS on CPB mix strength.

From the UCS results above, the best CPB mixes, likely to be adopted at the Nova mine, used 22.5 wt.% TAS: 77.5 wt.% LH. This mixture yielded the highest 28-day UCS strength at 3066 KPa. For this replacement ratio, it is estimated that the CO_2 reduction will be 5 kg/m^3 for the Nova mine site and 35 kg/m^3 for a CPB mix containing 6% GP. Mixes using 30:70 TAS: HE (wt.%) will likely be adopted for high early strength application requirements. More tests are planned to confirm and optimise these mixes.

4.2 XRD Test

The semi-quantitative XRD analysis of sample TAS9 (18:72:10 TAS:GGBFS:lime wt.%) and sample TAS18 (27:63:10 TAS:GGBFS:lime wt.%) is shown in Table 6. These samples have a high content of halite, and no ettringite phases were detected, understandably, as these mixes were prepared without any cement-based material. For reference, Nova's existing binder of GGBFS and lime mixes has killalaite mineral, a hydrated

calcium silicate ($2Ca_3Si_2O_7.H_2O$) as its major strength-forming mineral (Lim & Mirela 2021). Killalaite was not detected for these samples, as seen in Figure 8.

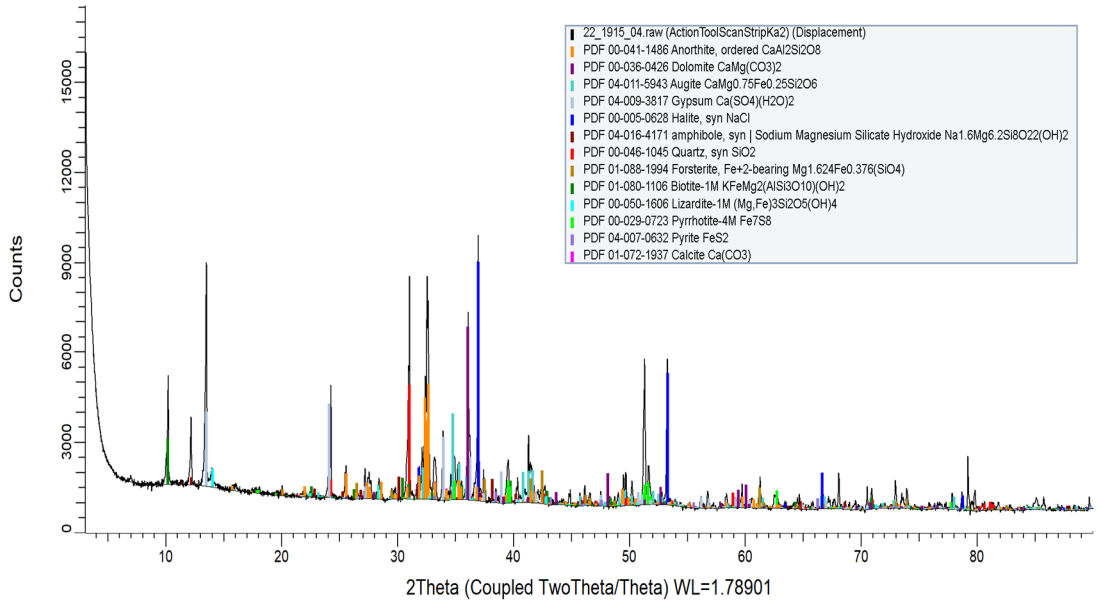


Figure 8 XRD diffractogram of sample TAS9, binder mix composed of 18 wt.% TAS, 72 wt.% GGBFS and 10 wt.% lime

Table 6 Comparative semi-quantitative XRD analysis of some CBP mixes tested

Crystalline mineral phase	Concentration (wt.%)					
	TAS2	TAS3	TAS3D	TAS9	TAS18	TBB32
Albite/anorthite low ($Na_{0.52}Ca_{0.48}Al_{1.48}Si_{2.52}O_8$)	38	-	46	-	-	26
Anorthite, Na-bearing, intermediate ($(Ca,Na)(Si,Al)_4O_8$)	-	-	-	-	19	-
Anorthite, ordered ($CaAl_2Si_2O_8$)	-	52	-	39	-	-
Forsterite, Fe+2-bearing ($Mg_{1.641}Fe_{0.359}(SiO_4)$)	15	5	5	5	7	14
Amphibole, syn | Sodium Magnesium Silicate Hydroxide ($Na_{1.6}Mg_{6.2}Si_8O_{22}(OH)_2$)	12	6	9	7	7	24
Biotite-1M ($KFeMg_2(AlSi_3O_{10})(OH)_2$)	7	2	5	4	9	3
Quartz, syn (SiO_2)	7	7	6	5	11	4
Gypsum ($CaSO_4{\cdot}2H_2O$)	6	2	-	8	4	6
Ettringite, syn ($Ca_6Al_2(SO_4)_3(OH)_{12}(H_2O)_{26}$)	6	3	4	-	-	2
Lizardite-1T ($Mg_{2.6}Fe_{0.4}Si_2O_5(OH)_4$)	3	1	-	3	-	2
Pyrrhotite-4M (Fe_7S_8)	3	-	1	1	7	1
Ankerite | Calcium Magnesium Iron Carbonate ($CaMg_{0.27}Fe_{0.73}(CO_3)_2$)	2	-	-	-	-	5

Pyrite, syn ($FeS_{1.92}$)	1	-	-	1	-	1
Augite ($CaMg_{0.75}Fe_{0.25}Si_2O_6$)	-	12	7	9	-	-
Antigorite ($Mg_3Si_2O_5(OH)_4$)	-	10	10		-	-
Dolomite | Calcium Magnesium Carbonate ($CaMg(CO_3)_2$)	-	-	6	12	8	-
Calcite ($CaCO_3$)	-	-	2	Trace		4
Halite, syn (NaCl)	-	-	-	8	27	8
Brownmillerite, Fe+3-bearing, syn (Ca_2FeAlO_5)	-	-	-	-	1	-

The previous section on UCS test results also showed that TAS in cement-based binders performed remarkably better than the control, consistently at various curing times. The highest strength produced (28 days for all comparisons) at 3066 KPa was a TAS-LH mix of 22.5: 77.5 (wt.%), labelled as sample TAS3D. The XRD diffractogram for sample TAS3D is shown below in Figure 9 and shows the major minerals albite (blue peak) and antigorite (light blue peak). These minerals are also the major components of Nova's mine tailings. No gypsum was detected on the sample, while the ettringite content was detected at 4% (Table 6). Sample TAS2 with 50:50 (wt.%) TAS: LH ratio had a strength of 2400 KPa, and its XRD analysis showed a higher ettringite content of 6 wt.% and gypsum of 6 wt.%.

GB-based mixes (TAS3) also generated high strength at 2453 KPa, with the ettringite content at 3% and gypsum at 2% (Table 6). Ettringite are calcium silicate hydrates characteristic of GP hydration reactions (Prince 2003).

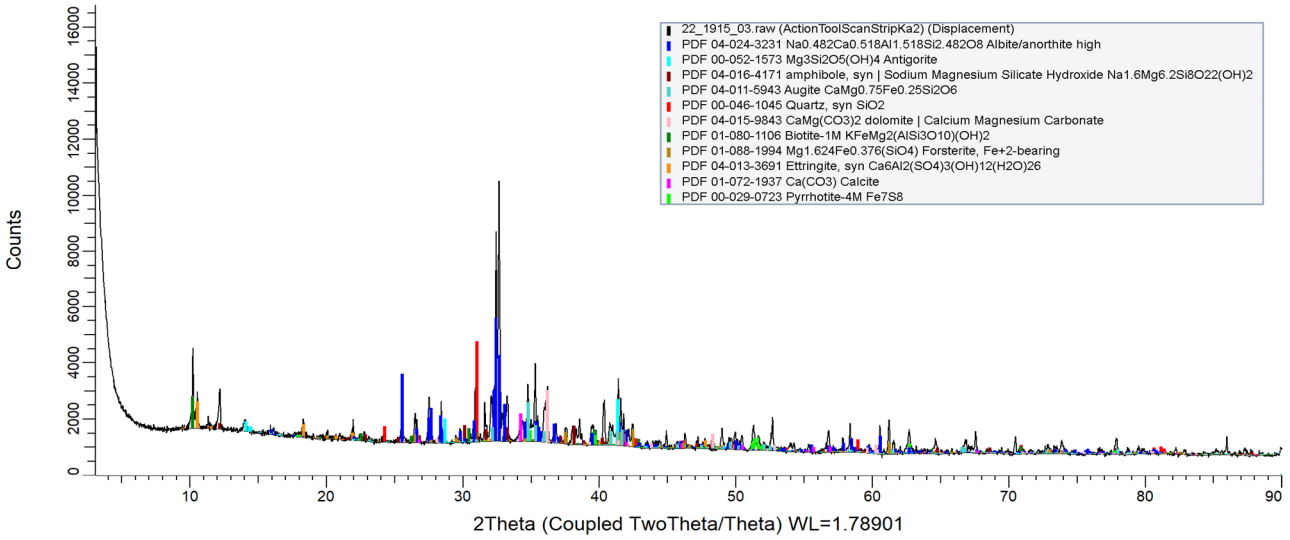


Figure 9 XRD diffractogram of TAS3D sample, binder mix made from 22.5% TAS and 77.5% LH (*Phase identification is listed in decreasing order)*

It is also interesting to note how the composition of the major mineral anorthite shifts in composition from Na-bearing to Ca-bearing, as well as changes in the crystallinity from low to ordered using different binder materials.

5 Conclusion

This study investigated the use of DBS material in CPB mixes combined with different typical binders. The results determined that DBS can be used in low-binder content applications such as CPB to fill underground mines. The primary outcomes are as follows:

CPB samples blended with TAS-hydrated lime-slag failed to meet minimum UCS requirements or only produced very low strengths of < 250 KPa; from XRD analysis, these mixes failed to show killalaite mineral phases which is the distinctive strength forming compounds for GGBFS: lime mixes;

CPB samples blended with TAS-GP-based products were acceptable based on the site UCS requirements of 500-1900 KPa; ettringite phases were detected in these mixes, which confirmed the use of GP-based ingredients;

The sample prepared with 22.5 wt.% of the second TAS sample and 77.5 wt.% LH gained the maximum strength in 28 days;

The highest early aged strength at 240 KPa was demonstrated by the sample with 30TAS – 70 HE (wt.%) binder mix;

Control tests were conducted to validate the effect of DBS on strength. The study found that DBS significantly increased the strength, as shown by the higher strength of TAS-containing samples compared to the control, particularly on the 28-day strength;

There was no significant reduction in paste strength compared to the samples prepared with the same binder ratio and different TAS samples. This finding will reduce further concerns about limiting the application of TAS in the low binder content applications;

The CO_2 reduction for the Nova paste system is estimated to be 5 kg/m^3. This result will lead to 8,564t less CO_2 emission for the mine life.

The promising outcomes of this study lead to the possibility of developing a new binder type replacing up to 40 wt.% of the current binders used in the CPB mixture. This replacement would significantly lead to decreasing the carbon footprint of CPB with considerable environmental benefits, e.g., by replacing a minimum of 30 wt.% of the current binders used in CPB with DBS, the CO_2 emission associated with the use of paste can be reduced up to about 42 kg/m^3.

For future studies, it has been suggested to test paste samples created with the tailings generated from gold processing and other minerals. Also, this material has the potential for different types of filling methods, such as cemented rock fill (CRF) and cemented hydraulic fill (CHF), to be investigated.

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References

ASX:IGO 2022, 'Commercial Production from Kwinana Refinery', press release, IGO Limited, South Perth, viewed 07 April 2023, https://www.igo.com.au/site/pdf/70af0281-0183-4f91-91e1-9525b16d239a/Commercial-Production-from-Kwinana-Refinery.pdf

Bentz, DP 2008, 'A review of early-age properties of cement-based materials', *Cement and Concrete Research*, vol. 38, no. 2, pp. 196–204, https://doi.org/10.1016/j.cemconres.2007.09.005

Belem, T & Benzaazoua, M 2004, 'An overview on the use of paste backfill technology as a ground support method in cut-and-fill mines', in E Villaescusa & Y Potvin (eds), *Ground Support 2004: Proceedings of the Fifth International Symposium on Ground Support*, Taylor & Francis, London, pp. 637–650.

Casella, J, & Olivares, M 2021, 'The Western Australia Lithium Industry- Enabling new and sustainable products beyond lithium chemicals', *Annual Western Australia Sustainable Infrastructure Symposium*, Australian Centre for Geomechanics, Perth, viewed 07 April 2023, https://www.iscouncil.org/wp-content/uploads/2021/11/WA-Conference-Program-V4.pdf

Chen, QS, Zhang, QL, Fourie, A, Chen, X & Qi, CC 2017, 'Experimental investigation on the strength characteristics of cement paste backfill in a similar stope model and its mechanism', *Construction and Building Materials*, vol. 154, pp. 34–43, https://doi.org/10.1016/j.conbuildmat.2017.07.142

Chen, Q, Zhu, L, Wang, Y, Chen, J & Qi, C 2022, 'The carbon uptake and mechanical property of cemented paste backfill carbonation curing for low concentration of CO2', *Science of The Total Environment,* vol. 852, article no. 158516, http://dx.doi.org/10.1016/j.scitotenv.2022.158516

Creagh, B 2018, 'Independence to introduce Australia-first energy solution at Nova', *Australian Mining*, viewed 07 April 2023, https://www.australianmining.com.au/news/independence-introduce-australia-first-energy-solution-nova/

Deng, XJ, Klein, B, Hallbom, DJ, de Wit, B & Zhang, JX 2018, 'Influence of particle size on the basic and time-dependent rheological behaviour of cemented paste backfill', *Journal of Materials Engineering and Performance*, vol. 27, pp. 3478–3487, https://doi.org/10.1007/s11665-018-3467-7

Ding, H & Zhang, S 2020, 'Quicklime and Calcium Sulfoaluminate Cement Used as Mineral Accelerators to Improve the Properties of Cemented Paste Backfill with a High Volume of Fly Ash', *Materials*, vol. 13, no. 18, article no. 4018, https://doi.org/10.3390/ma13184018

Grice, T 1998, 'Underground mining with backfill', In *Proceedings of the 2nd Annual Summit, Mine Tailings Disposal Systems*, Australasian Institute of Mining and Metallurgy, Brisbane, p. 14.

Haigh, M, Dumitru, I, Munn, B & Papworth, F 2013, 'Development of new high performance supplementary cementitious material - a lithium production by-product', *Proceedings of the CIA Biennial Conference, Understanding Concrete*, Concrete Institute of Australia, North Sydney.

He, Y, Zhang, Q, Chen, Q, Bian, J, Qi, C, Kang, Q & Feng, Y 2020, 'Mechanical and environmental characteristics of cemented paste backfill containing lithium slag blended binder', *Construction and Building Materials*, vol. 271, article no. 121567, https://doi.org/10.1016/j.conbuildmat.2020.121567

Helinski, M, Fahey, M & Fourie, A 2011, 'Behaviour of cemented paste backfill in two mine stopes: Measurements and modeling', *Journal of Geotechnical and Geoenvironmental Engineering*, vol. 137, no. 2, pp. 171–182, https://doi.org/10.1061/(ASCE)GT.1943-5606.0000418

Karrech, A, Dong, M, Elchalakani, M, & Shahin, M 2019, 'Sustainable geopolymer using lithium concentrate residues', *Construction and Building Materials*, vol. 228, article no. 116740, https://doi.org/10.1016/j.conbuildmat.2019.116740

Karrech, A, Dong, M, Skut, J, Elchalakani, M & Shahin, M 2021, 'Delithiated beta spodumene as a geopolymer precursor', *Construction and Building Materials*, vol. 309, article no. 124974, https://doi.org/10.1016/j.conbuildmat.2021.124974

Kawai, K, Sugiyama, T, Kobayashi, K & Sano, S 2005, 'Inventory data and case studies for environmental performance evaluation of concrete structure construction', *Journal of Advance Concrete Technology,* vol. 3, no. 3, pp. 435-456, https://doi.org/10.3151/jact.3.435

Kesimal, A, Yilmaz, E, Ercikdi, B, Alp, I & Deveci, H 2005, 'Effect of properties of tailings and binder on the short-and long-term strength and stability of cemented paste backfill', *Materials Letters*, vol. 59, no. 28, pp. 3703–3709, https://doi.org/10.1016/j.matlet.2005.06.042

Lehne, J & Preston, F 2018, 'Making Concrete Change Innovation in Low-carbon Cement and Concrete Energy', report, Chatham House, London, viewed 07 April 2023, https://policycommons.net/artifacts/1423241/making-concrete-change/2037504/ CID: 20.500.12592/6hw862

Lim, H & Ghisi, M 2021, 'The Pozzolanic Activity of TAS', Tianqi Lithium Kwinana Internal Report, Australia, viewed 07 April 2023.

Lim, H & Mirela, G 2021, 'Update on Pastefill Studies (XRD Results)', Tianqi Lithium Kwinana Internal Report, Australia, viewed 07 April 2023.

Lindstrom, P & McArdle P 2009, 'Emissions of Greenhouse Gases in the United States 2008', *U.S. Energy Information Administration,* Office of Integrated Analysis and Forecasting, U.S. Department of Energy, Washington, DC.

Munn, B, Dumitru, I & Maree, D 2017, 'Assessment of the performance of new supplementary cementitious materials from lithium production residues', Proceedings of the CIA Biennial Conference, Advances in Concrete, Materials and Structures, Adelaide,

Munn, B, Ghisi, M & Skut, J 2021, 'Further development of new supplementary cementitious materials from processed lithium aluminosilicate materials', *Concrete 2021*, Sydney, viewed 07 April 2023, http://www.ciaconference.com.au/concrete2021/pdf/full-paper_236.pdf

Pauliuk, S, Heeren, N, Berrill, P, Fishman, T, Nistad, A, Tu, Q, Wolfram, P & Hertwich, EG 2021, 'Global scenarios of resource and emission savings from material efficiency in residential buildings and cars', *Nature Communications*, vol. 12, article no. 5097, https://doi.org/10.1038/s41467-021-25300-4

Prince, W 2003, 'Ettringite formation: a crucial step in cement superplasticizer compatibility', *Cement and Concrete Research*, vol. 33, no. 5, pp. 635-641, https://doi.org/10.1016/S0008-8846(02)01042-6

Safarizadeh, A & Taheri, A 2021, 'The effect of changing grinding cycle on the flow-ability of cemented paste backfill: effect of particle size distribution', in AB Fourie & D Reid (eds), *Paste 2021: 24th International Conference on Paste, Thickened and Filtered Tailings*, Australian Centre for Geomechanics, Perth, pp. 453-460, https://doi.org/10.36487/ACG_repo/2115_36

Sakai, K & Kawai, K 2006, 'Recommendation of environmental performance verification for concrete structures', *Guidelines for Concrete*, newsletter, *Japan Society of Civil Engineering (JSCE)*, viewed 07 April 2023, http://www.jsce.or.jp/committee/concrete/e/newsletter/newsletter08/Rec_Env.pdf

Sivakugan, N, Rankine, RM, Rankine KJ & Rankine KS 2006, 'Geotechnical considerations in mine backfilling in Australia', *Journal of Cleaner Production,* vol. 14, nos. 12-13, pp. 1168-1175, https://doi.org/10.1016/j.jclepro.2004.06.007

Standards Australia 2022, Supplementary cementitious materials, Part 4: Pozzolans — Manufactured (AS 3582.4:2022), Standards Australia, Sydney

Su, Z, Chen, QS, Zhang, QL & Zhang DM 2019, 'Recycling Lead-Zinc tailings for cemented paste backfill and stabilisation of excessive metal', *Minerals*, vol. 9, no. 11, article 710, https://doi.org/10.3390/min9110710

Wu, AX, Cheng, H, Yang, Y & Zhang, L 2017, 'Development and challenge of paste technology in China', in A Wu & R Jewell (eds), *Paste 2017: Proceedings of the 20th International Seminar on Paste and Thickened Tailings*, University of Science and Technology Beijing, Beijing, pp. 2-11, https://doi.org/10.36487/ACG_rep/1752_01_Wu

Zambrano, LH, Horta, RB, Bauer, H, Schmidheiny, T, Pesenti, G, Collomb, B, Walker, S, Ketsuwan, S, Kimura, M & Moraes, FE 2002, 'The cement sustainability initiative', *The World Business Council for Sustainable Development (WBCSD),* Conches-Geneva, ISBN 2-940240-24-8, viewed 07 April 2023, https://docs.wbcsd.org/2002/06/TheCementSustInitiative.pdf