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Upcycling Fluid Catalytic Cracking (FCC) Ash for Digital Construction

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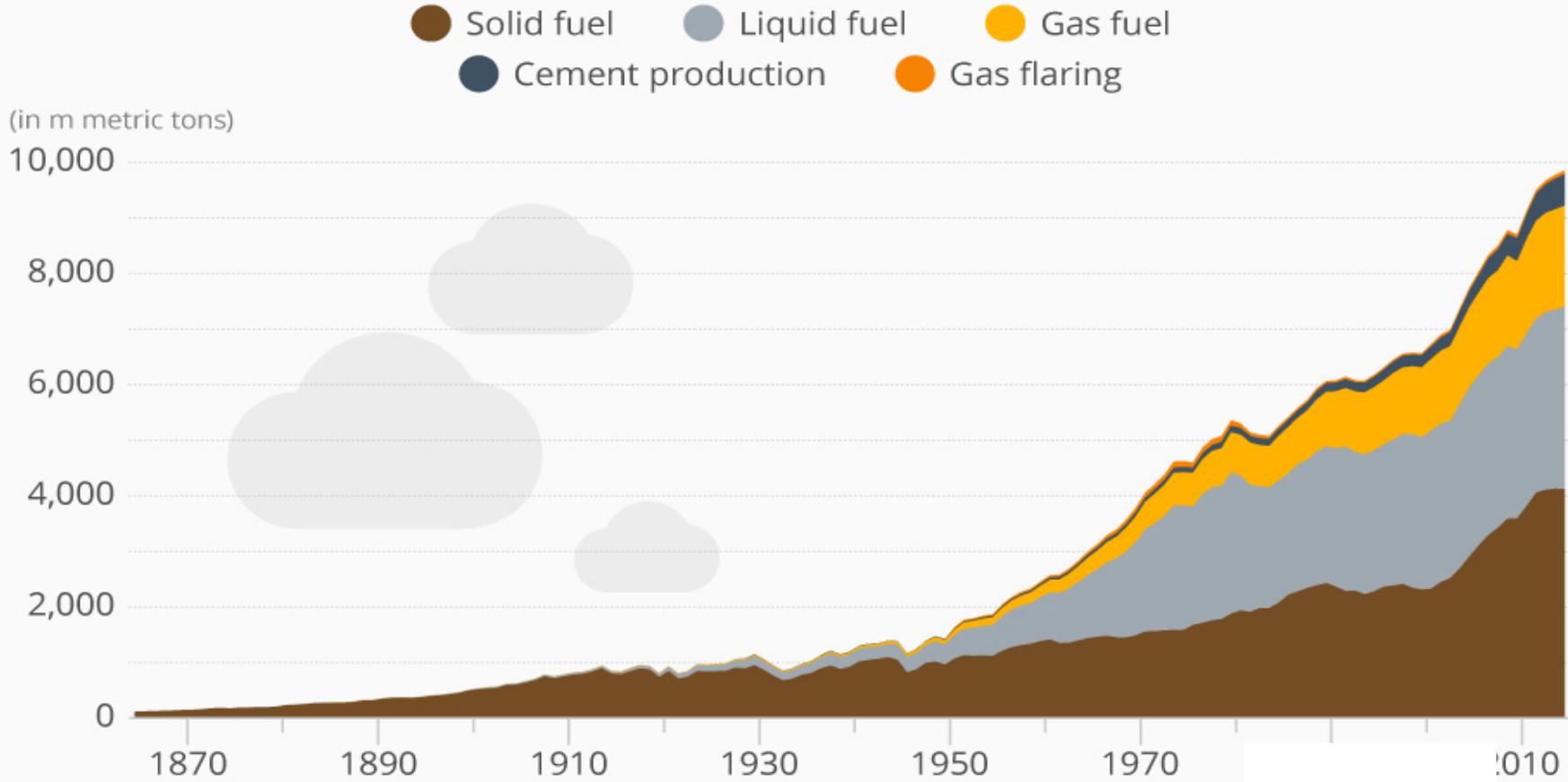
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Carbon Issue

The Carbon Age: 150 Years of CO₂ Emissions

Worldwide carbon emissions from fossil fuel consumption and cement production



@StatistaCharts Source: CDIAC



Construction Productivity vs. Rapid Urbanization

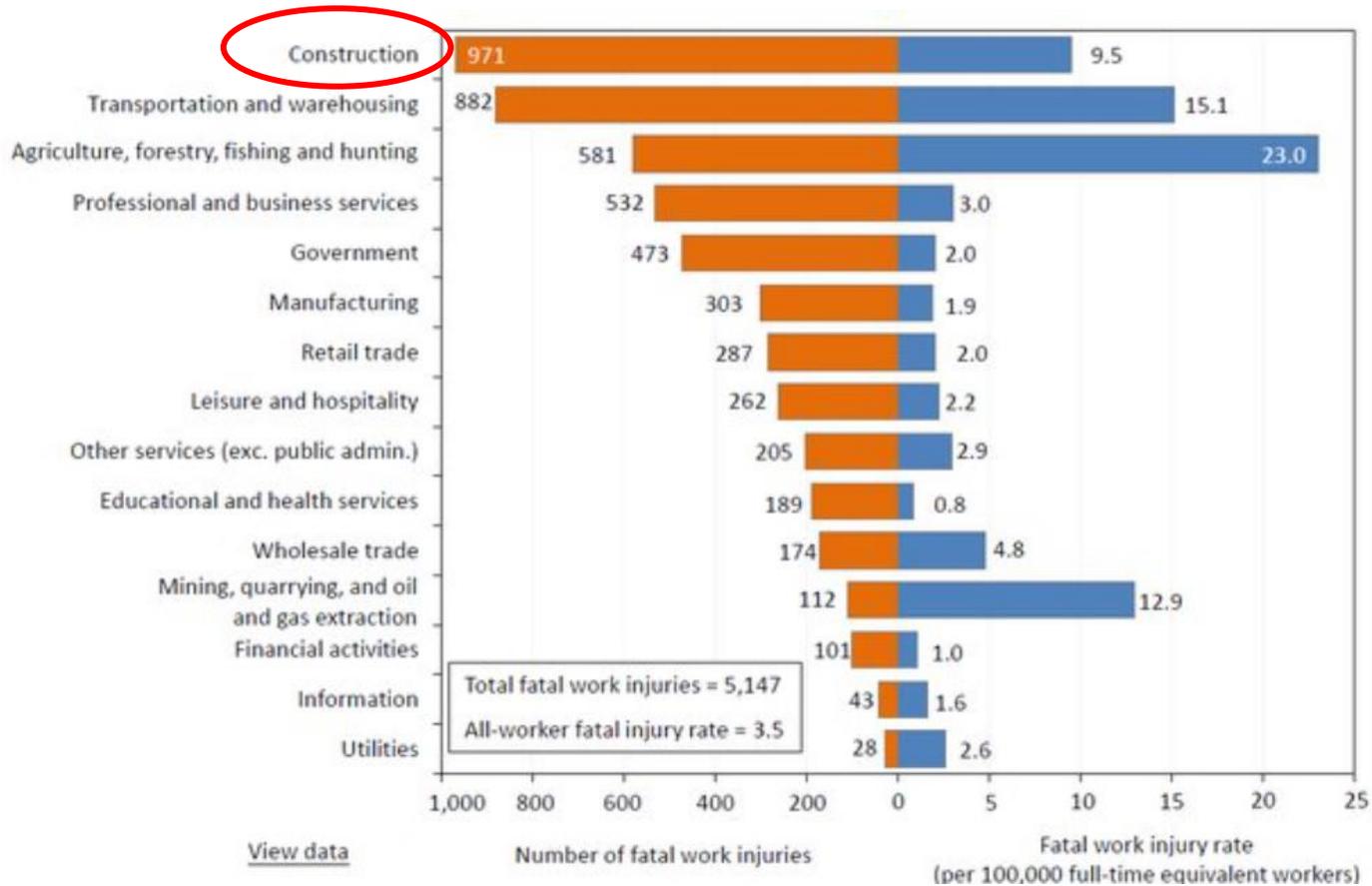


(The Economist, 2017)

1.5 million people are added to the global urban population **every week**



Construction Fatal Injury in U.S. and Singapore

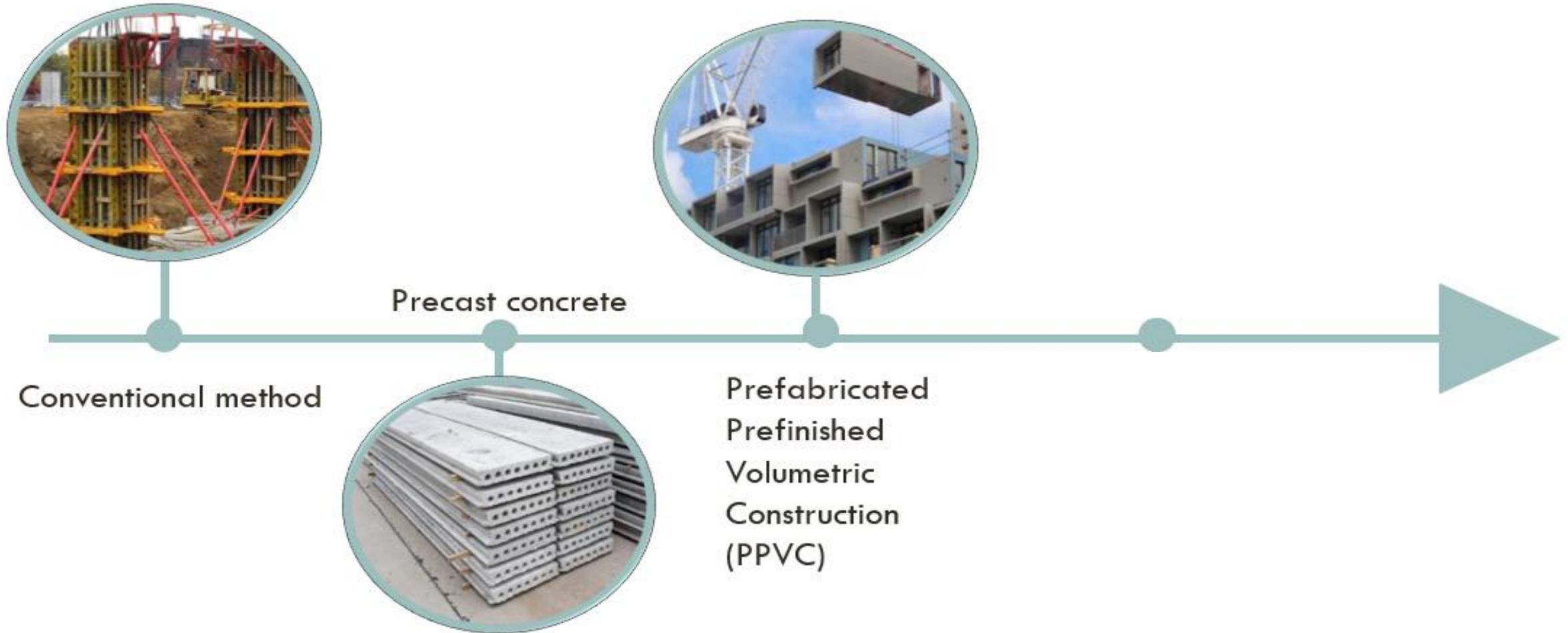


Industry	Number of Fatal and Major Injuries, 2022
Overall	660
Construction	171
Manufacturing	129
Transportation & Storage	70
Administrative & Support Services	57
Accommodation & Food Services	57
Wholesale & Retail Trade	41

(U.S. Bureau of Labor Statics, Current Population Survey, 2018)

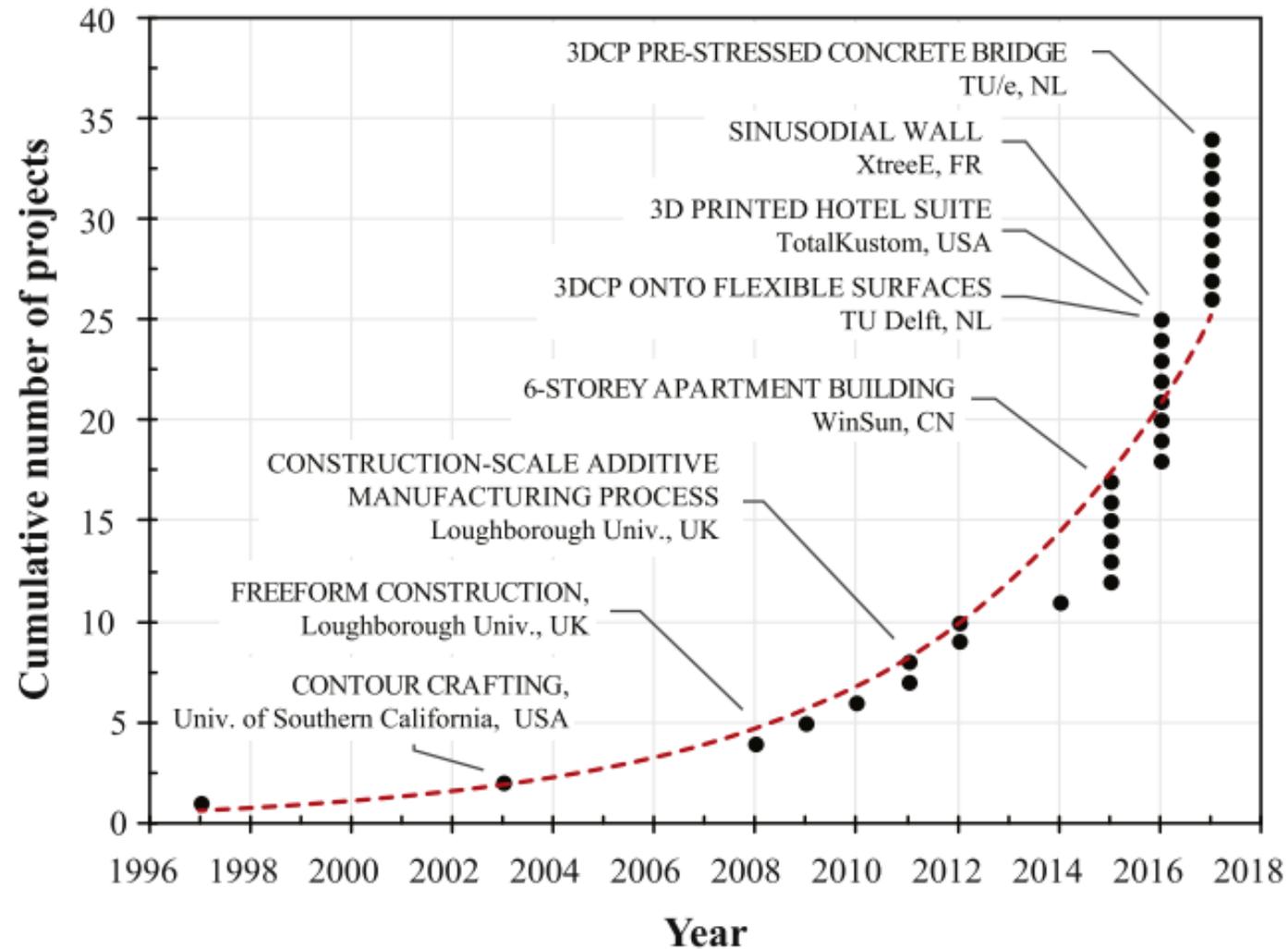
(Workplace Safety and Health Report 2022, Ministry of Manpower, Singapore 2022)

Evolving Construction Industry



(The Straitstimes, 2019)

Large-scale 3D Printing Construction Applications



3D Printed Prefabricated Bathroom Unit



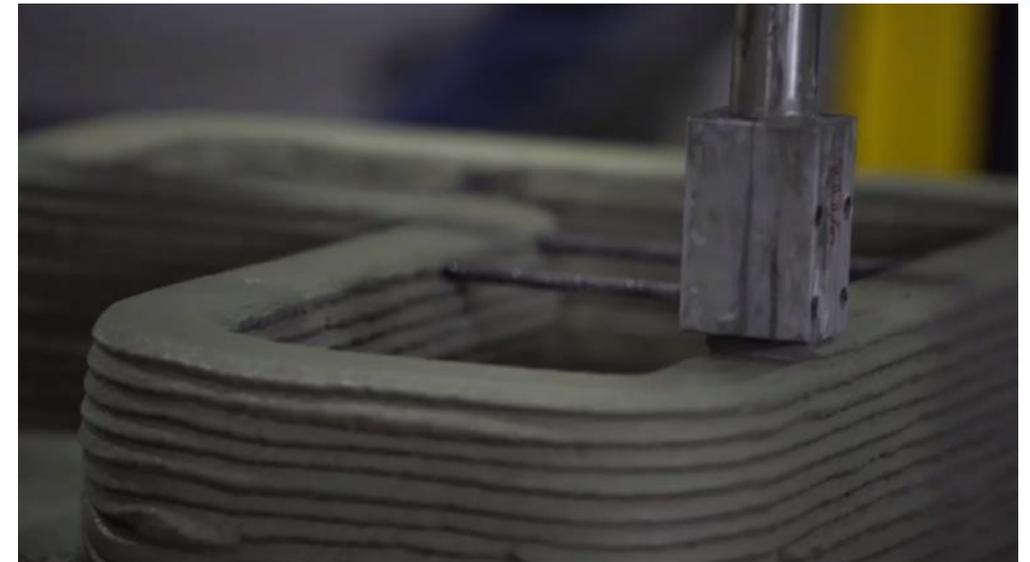
<https://www.youtube.com/watch?v=CzkgNz8oxjU>

3D Printed Prefabricated Bathroom Unit



Courtesy of CES_Innovfab Pte Ltd

3D Printed Concrete Structure at HDB Centre of Building Research



<https://www.straitstimes.com/singapore/housing/3d-printing-to-be-used-in-hdb-project-for-the-first-time-in-tengah-and-bidadari>

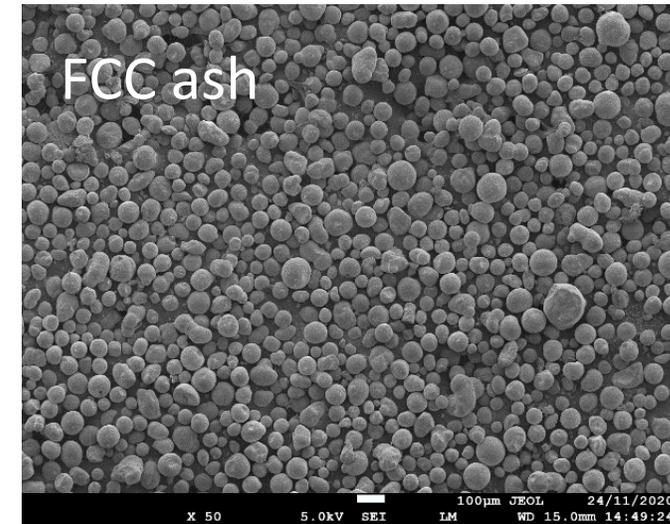
<https://fb.watch/kr3ddQIPOq/>

Fluid Catalytic Cracking Ash (FCC spent catalyst)

- FCC ash yield: around 3600 tons/year, current major waste treatment is landfill disposal
- Fine powder, rich in silica and alumina, with certain heavy metals
- It generally contains relatively large particles compared with cement and silica fume, but much larger specific surface area due to nano-porous structure
- Potentially a good cement substitute material



A crude oil refinery station off the coast of Singapore
(Reuters 2021)



50 times magnification

Particle Size and Specific Surface Area

Characterized items	Cement	FCC ash	Silica fume	Sand
D ₁₀ (μm)	6.317	49.169	0.124	14.065
D ₅₀ (μm)	23.422	81.859	0.227	113.683
D ₉₀ (μm)	51.573	125.796	0.523	394.028
Specific surface area (m ² /g)	4.548	112.597	11.677	1.006

Observation of FCC Ash Internal Structure

Bulk characteristics: SEM

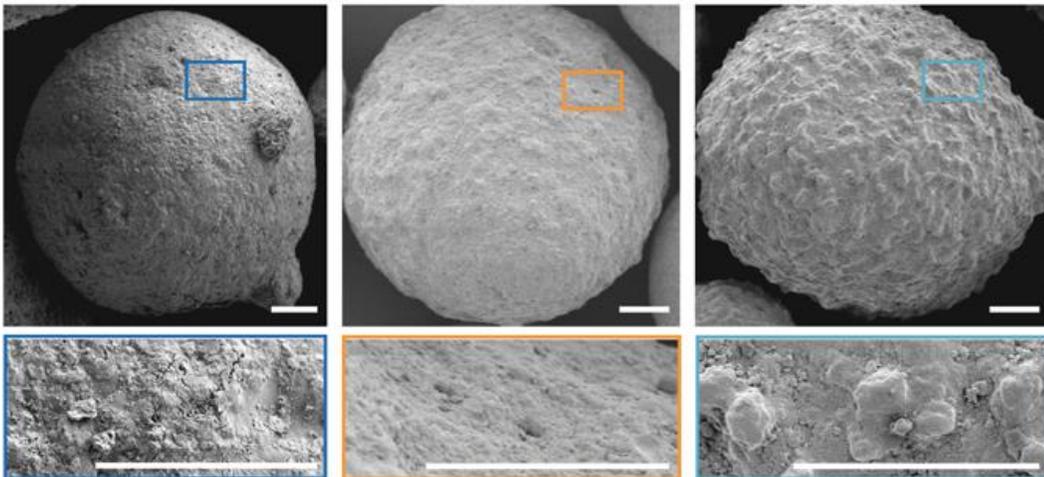
Internal structure observation: Ptychographic X-ray computed tomography

Pristine (FCC1) and commercially deactivated FCC catalysts (FCC2 and FCC3, increasing severity of catalyst deactivation).

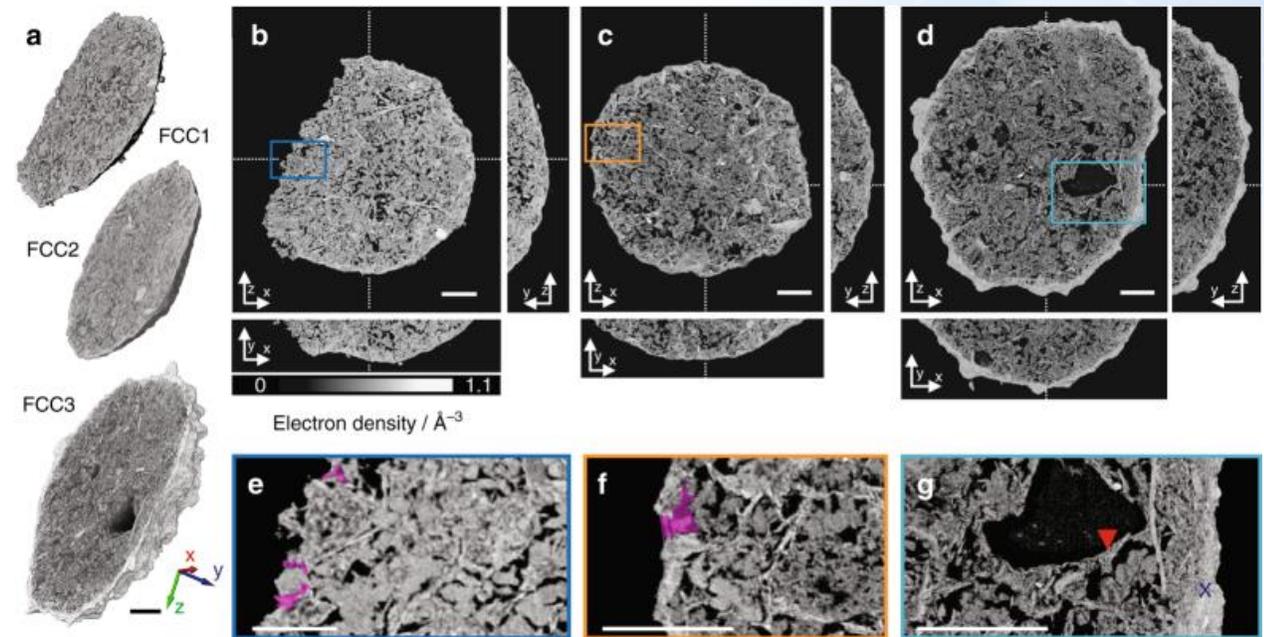
D_{50} : $76\mu\text{m}$
SSA: $264\text{m}^2/\text{g}$
FCC1

$74\mu\text{m}$
 $135\text{m}^2/\text{g}$
FCC2

$91\mu\text{m}$
 $118\text{m}^2/\text{g}$
FCC3

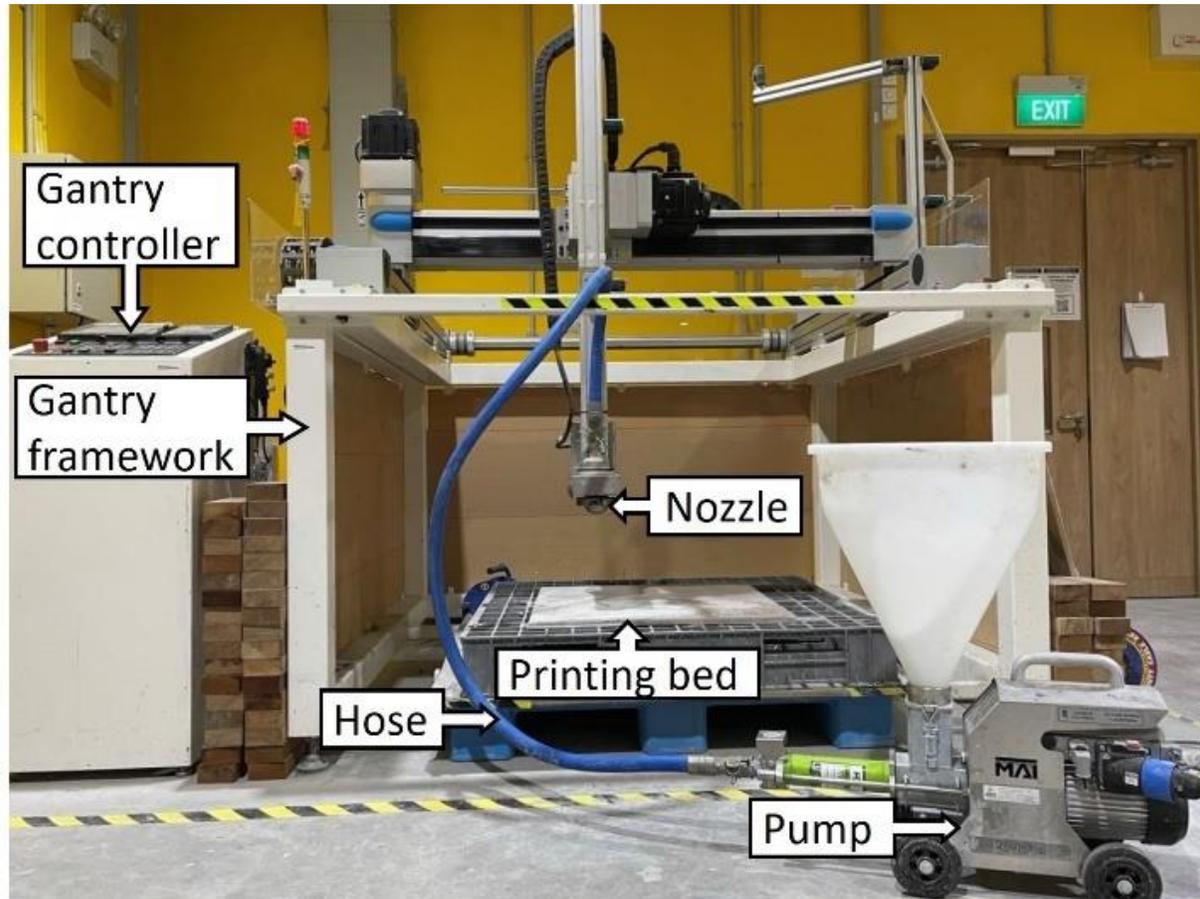


Electron micrographs of FCC catalysts. Shown are scanning electron micrographs of an FCC1, FCC2, and FCC3 particle. Scale bars are 10 μm (Ihli et al., 2017)

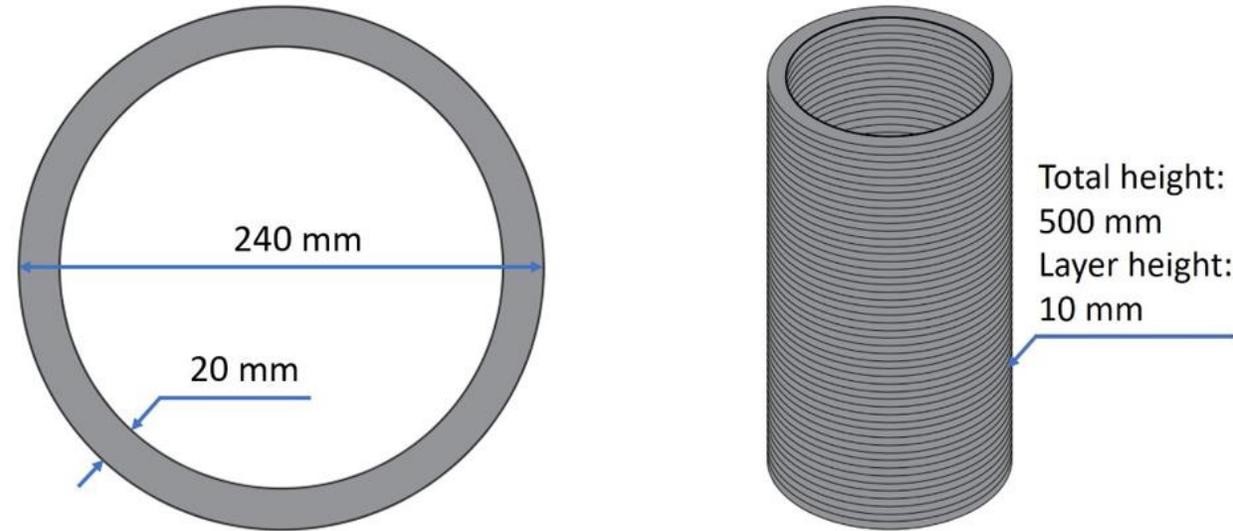


Ptychographic image reconstructions. **a** Volume reconstructions of FCC1, FCC2, and FCC3. Orthoslices through the retrieved electron density maps are shown in **b–d**, respectively. Shown in **e–g** are enlarged versions of selected areas. Scale bars are 5 μm. (Ihli et al., 2017)

Printing Setup and Requirement of Printable Material



3D concrete printing system in NTU SC3DP



- ✓ Suitable rheological properties for **good pumpability and buildability**
- ✓ Low **toxicity**

Rheological Requirements of 3D Concrete Printing

➤ Good pumpability

$$P = \left(\frac{8\tau_0}{3R} + \frac{8k}{\pi R^4} Q \right) L$$

Pumping
pressure

τ_0 **Dynamic yield stress**

Minimum shear stress to maintain flow

k **Plastic viscosity**

Shear stress increment with unit change of shear rate

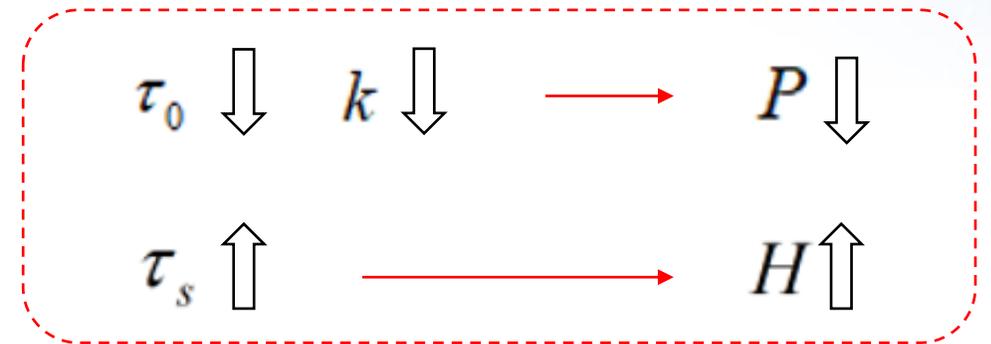
➤ Good buildability

$$H \propto \tau_s$$

Maximum
printing height

τ_s **Static yield stress**

Minimum shear stress to
initiate flow



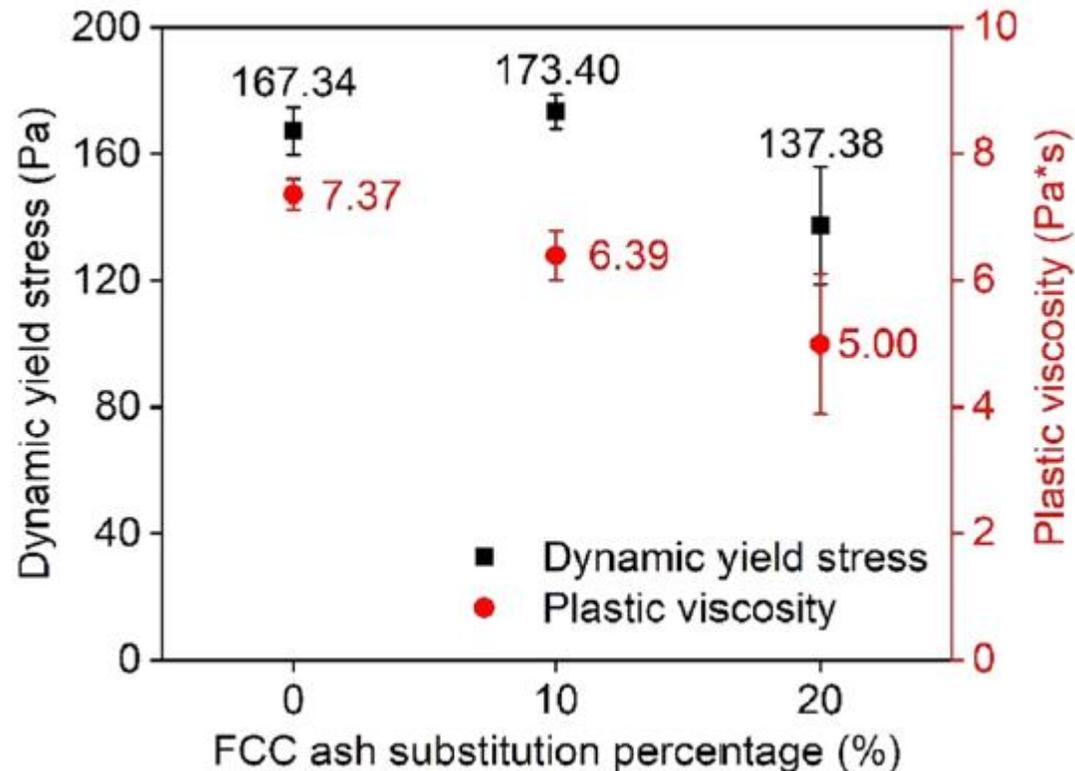
Mass Proportion of the Designed Mortars

Mixture	Cement	FCC ash	Silica fume	Silica sand/binder *	Water/binder *
Control	1	0	0.05	0.32	0.38
FCC10	0.9	0.1	0.05	0.32	0.38
FCC20	0.8	0.2	0.05	0.32	0.38
FCC30	0.7	0.3	0.05	0.32	0.38

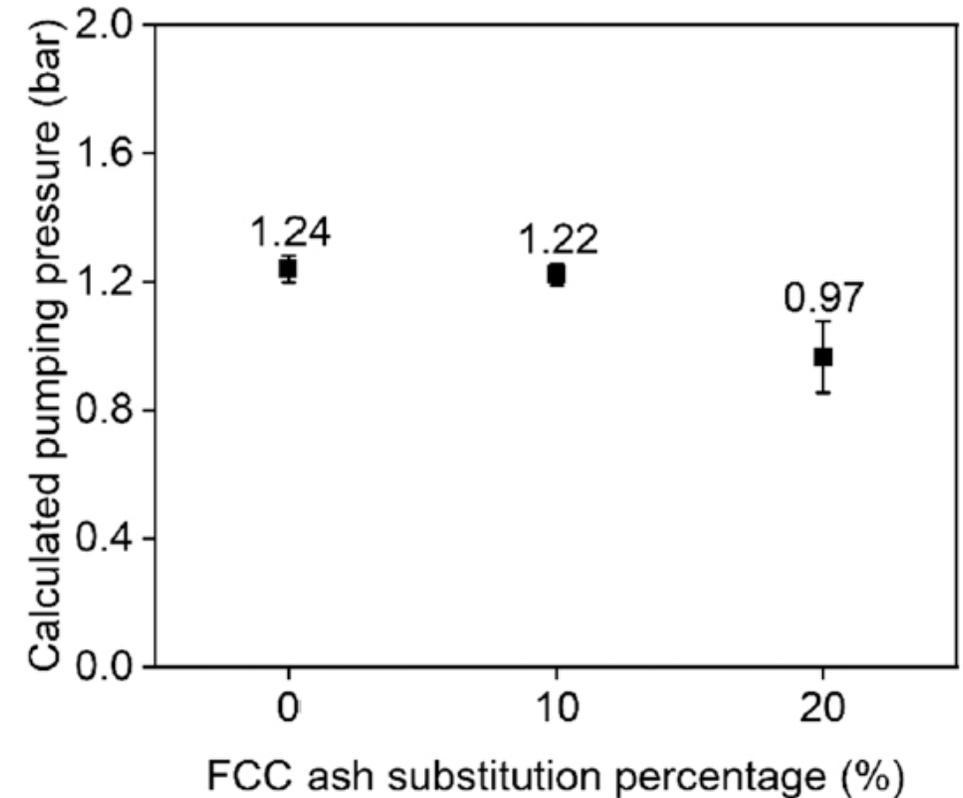
* **Annotation:** binder consists of cement, FCC ash, and silica fume.

Rheological Properties and Pumpability

- Dynamic yield stress & plastic viscosity generally show decreasing trend.
- As a result, calculated pumping pressure also decreased (which is favorable).



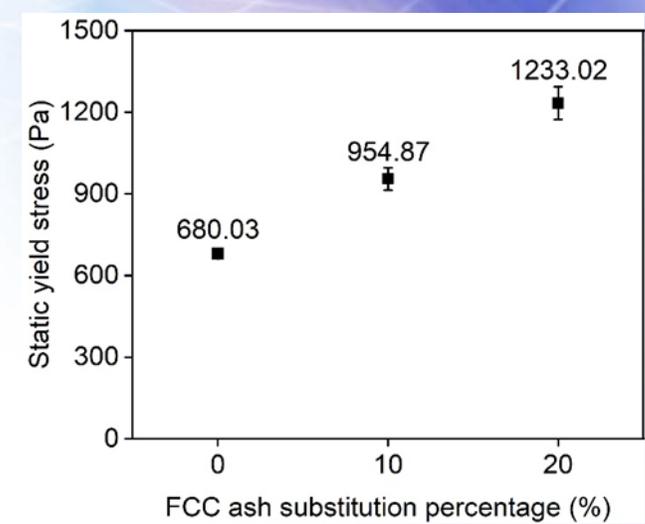
Dynamic yield stress and plastic viscosity of the designed mixtures



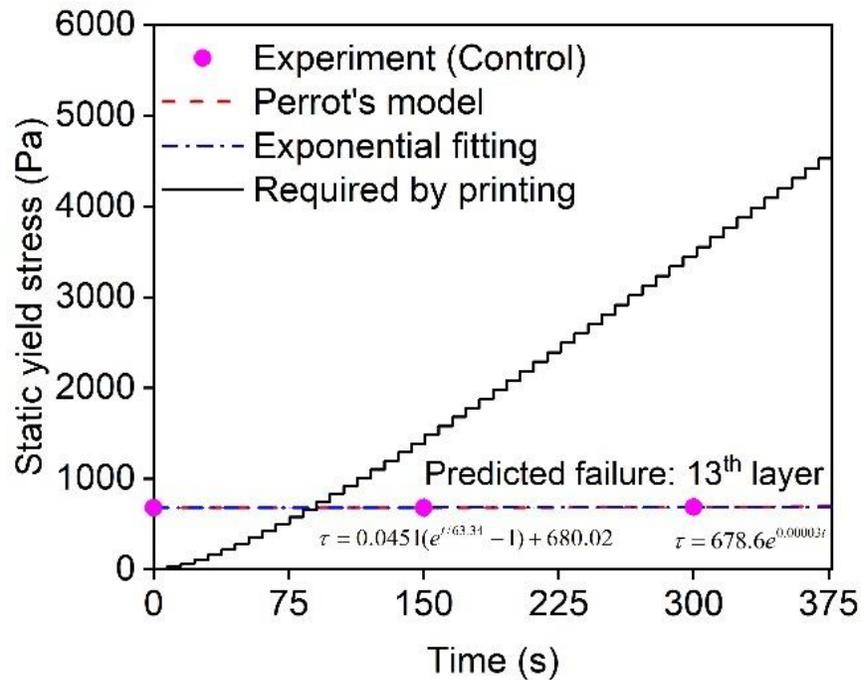
Calculated pumping pressure of the designed mixtures

Rheological Properties & Buildability

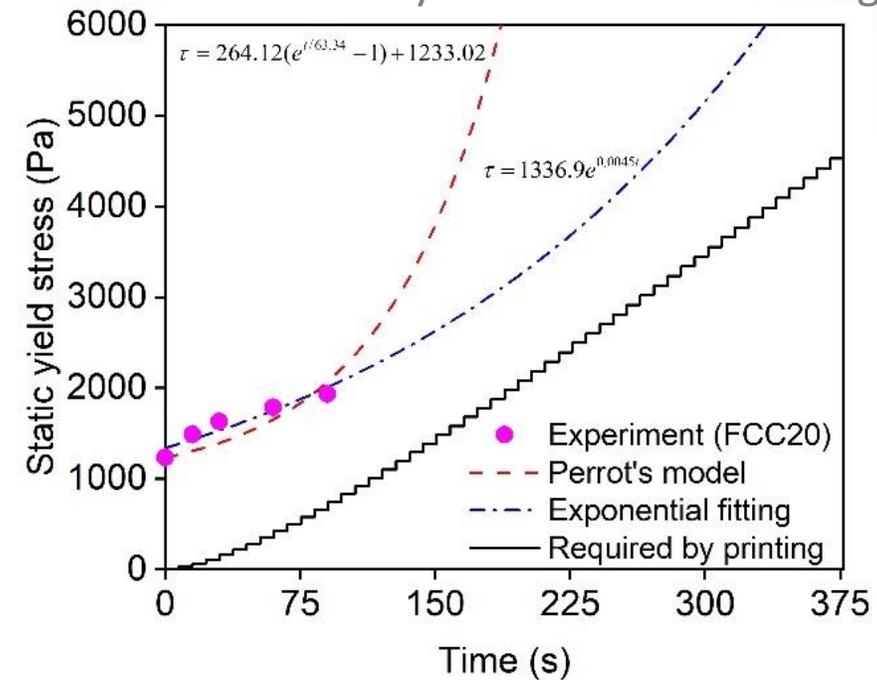
- With more FCC ash content, static yield stress is **increased significantly**.
- Partial replacement of cement by FCC ash **accelerates** static yield stress evolution.



Static yield stress of the designed mixtures



Static yield stress evolution of the control mixture

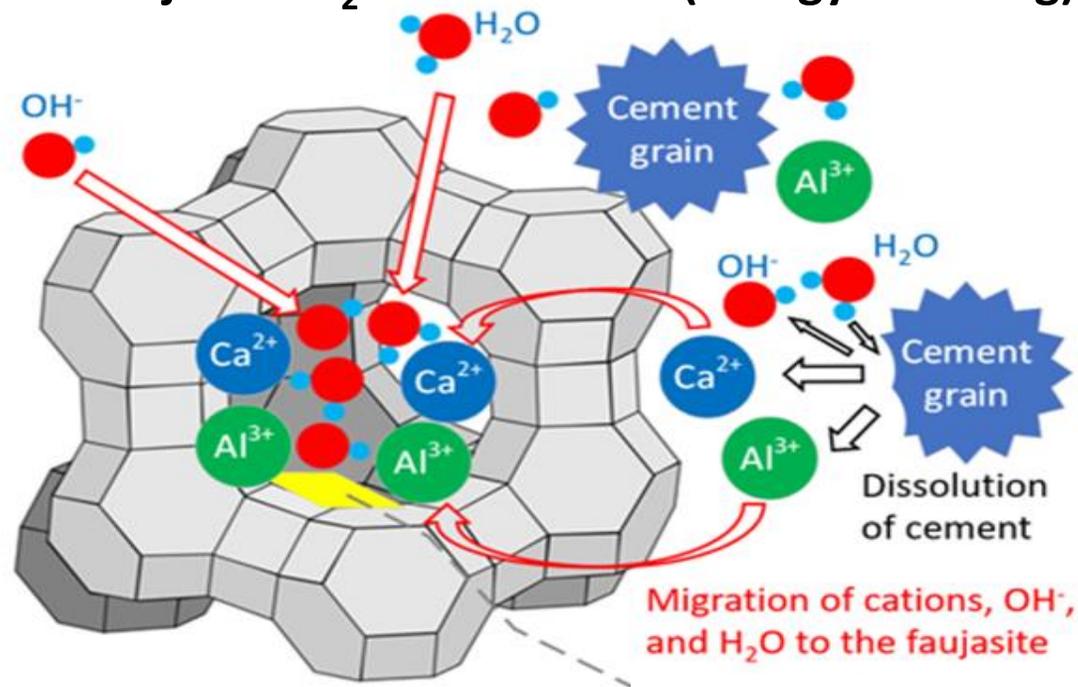


Static yield stress evolution of FCC20

Plausible Mechanism - Enhanced Rheological Property

Early Hydration rate ↑

- Cation absorption ↑
- Cement hydrolysis Accelerated ↑
- Faujasite+H₂O: Exothermic (energy releasing)

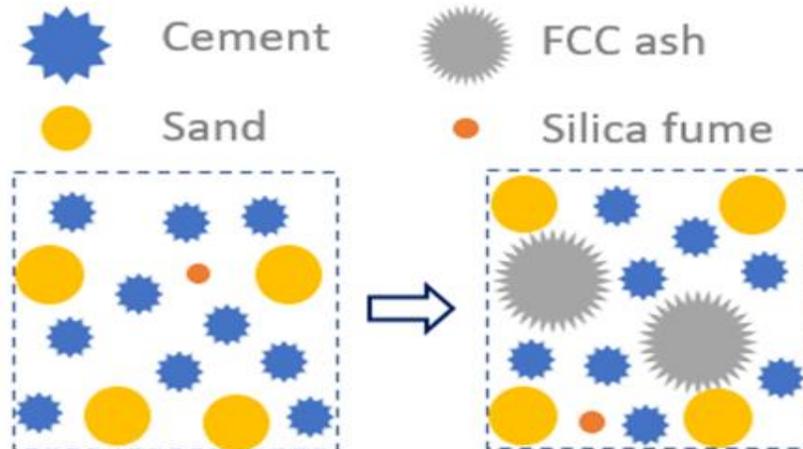


Faujasite in the FCC ash

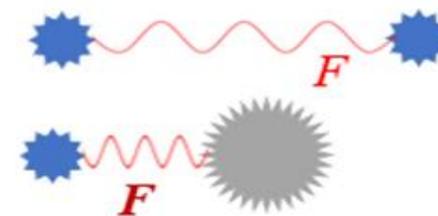
(Adapted from Tydlitát et al, 2014)

Particle separation distance ↓

- Volume of solids ↑
- Packing density ↑



Colloidal force ↑



Results based on YODEL Model

$$\tau_s = KF_c\Phi = \underbrace{\frac{1.8}{\pi^4} u_{k,k}}_{[L^{-2}]} \underbrace{\left(\frac{f_{\sigma,\Delta}^*}{R_{v,50}^2} \right)}_{[L^{-2}]} \underbrace{G_{\max}}_{[F]} \underbrace{a^* \frac{\varphi(\varphi - \varphi_{perc})^2}{\varphi_{\max}(\varphi_{\max} - \varphi)}}_{[F]}$$

- K Contribution from Particle Size Distribution
- F_c Contribution from Colloidal Force
- Φ Contribution from Packing Fractions

Mixtures	<i>K</i> (m ⁻²)	Φ	<i>F_c</i> (N)	<i>G_{max}</i> (N/m)	<i>a</i> [*] (μm)
Control	1.055×10 ¹⁴	2.248	2.866×10 ⁻¹²	5.241×10 ⁻⁷	5.469
FCC10	1.062×10 ¹⁴	2.436	3.692×10 ⁻¹²	5.303×10 ⁻⁶	0.696
FCC20	1.068×10 ¹⁴	2.642	4.368×10 ⁻¹²	1.630×10 ⁻⁵	0.268

Printing Performance

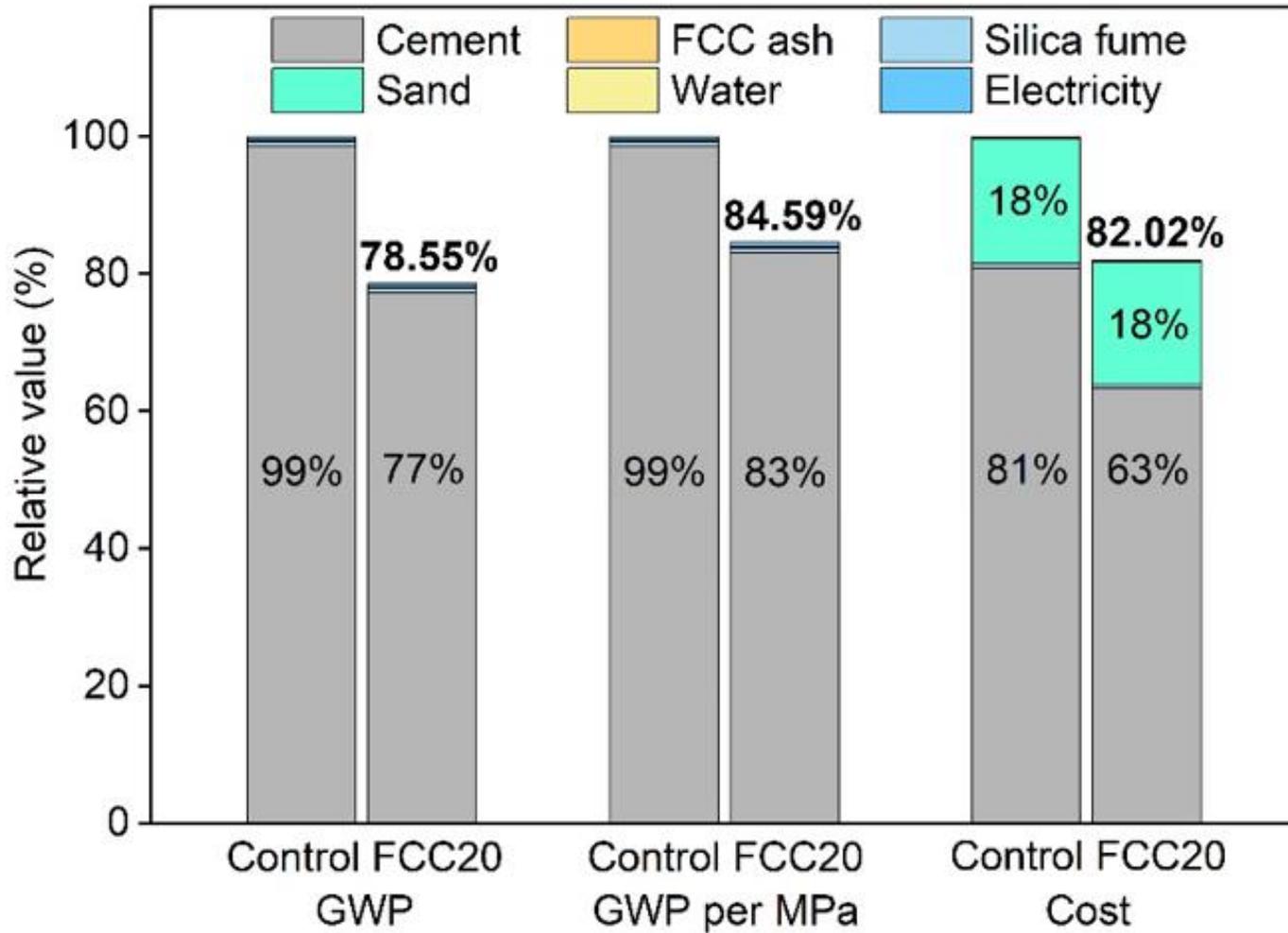
➤ Pumping rate:
450 rpm (1.2 L/min)

➤ Printing speed:
100 mm/s

➤ Printing time (50
layers):
Less than 6 mins
for diameter 240
mm and height of
500 mm hollow
core cylinder



Carbon Emission and Cost Comparison



FCC ash was counted as zero carbon emission and cost in this current scenario.

Even when the cost of FCC ash is counted as comparable to fly ash in the future large-scale application, the total cost is 83.28% of the control.

Leaching Performance of Cement/FCC ash Blends

- For both FCC ash and powder of printed FCC20 mixture, amounts of leached trace heavy metals are **much lower** than the acceptance criteria.
- Generally, FCC20 has **less** heavy metal leachates than FCC ash, especially for **As, Mn, Ni, and Zn** where reductions by dozens of times are observed.

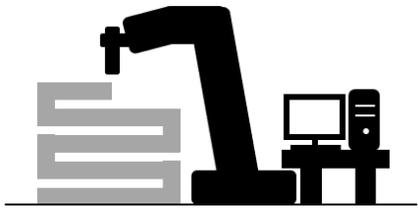
Item	As	Ba	Cd	Cr	Cu	Fe	Pb	Mn	Ni	Se	Zn
FCC	0.79	0.11	<0.02	0.05	0.06	0.08	<0.02	0.34	0.38	<0.02	0.18
FCC20	<0.02	0.76	<0.02	0.13	<0.02	0.02	<0.02	<0.02	<0.02	<0.02	<0.02
NEA criteria	5	100	1	5	100	100	5	50	5	1	100

(National Environment Agency, Singapore)

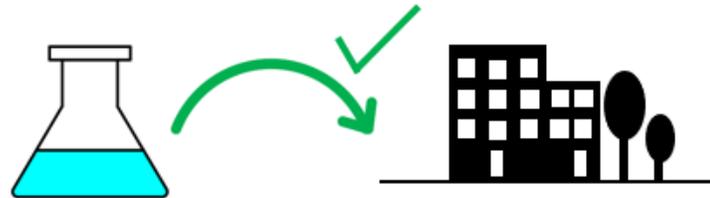
Conclusions and Impacts

- Partial replacement of cement by FCC ash contributes to the **early hydration**.
- Introduction of FCC ash regulates rheological properties. It significantly increases **static yield stress** and accelerates **static yield stress evolution**.
- As a result, buildability is significantly enhanced, leading to **superior printing performance**, **while** pumpability is maintained or improved.
- Carbon emission and total cost reduce by about **21%** and **18%** respectively.

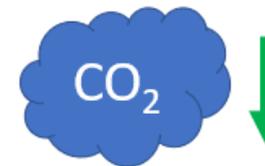
Smart construction



Leaching improvement



Carbon emission reduction



Alternative waste treatment



Benefits to Construction Industry & Petroleum and Oil Refinery Industry

Welcome to NTU, Singapore



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