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Article

Conductive Geopolymers as Low-Cost Electrode Materials for Microbial Fuel Cells

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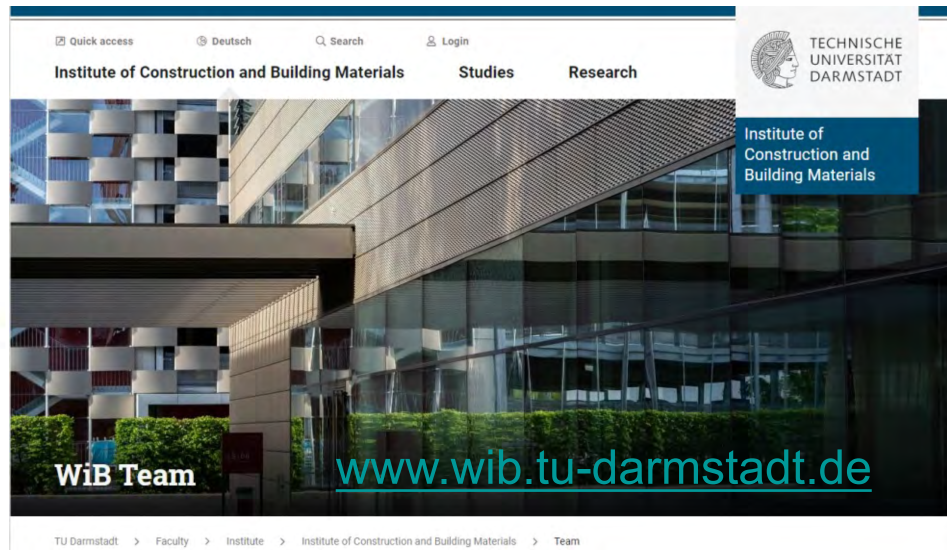

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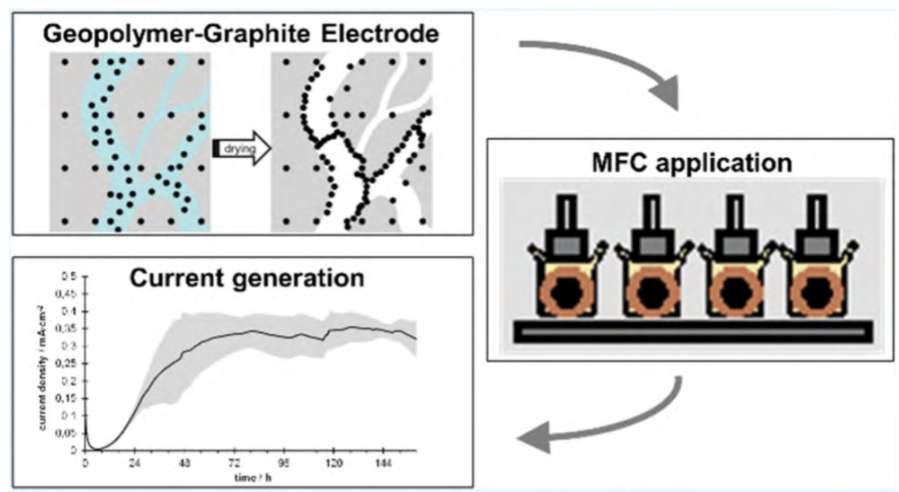
Sustainable Electrochemistry

Dr. Markus Stöckl

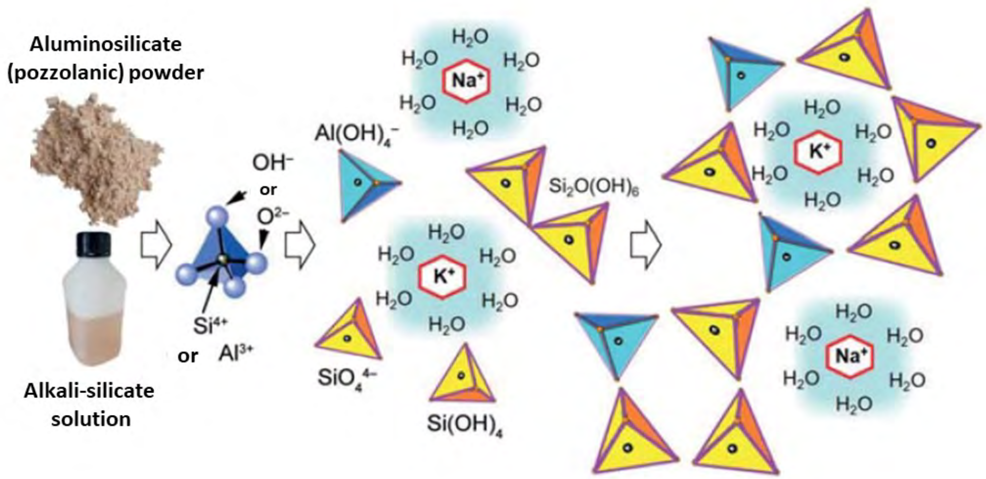
Outline

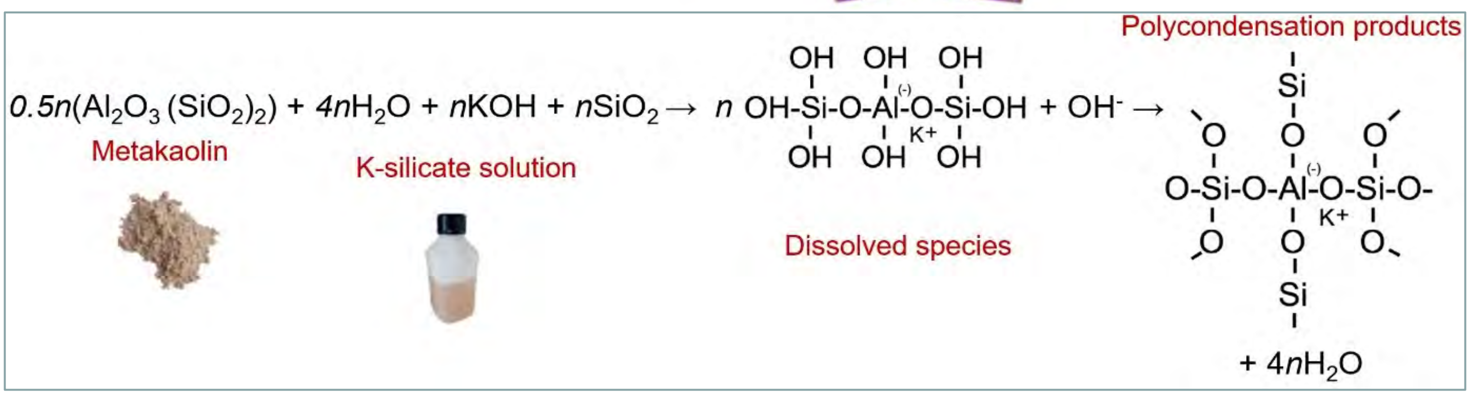
1. Intro
2. Raw Materials
3. Mix designs
4. Results
    a. Conductive geopolymer for MFC
    b. Leaching/acids durability
5. Conclusions



Geopolymers are nano-materials

Geopolymerisation → hydrolisis/condensation reaction



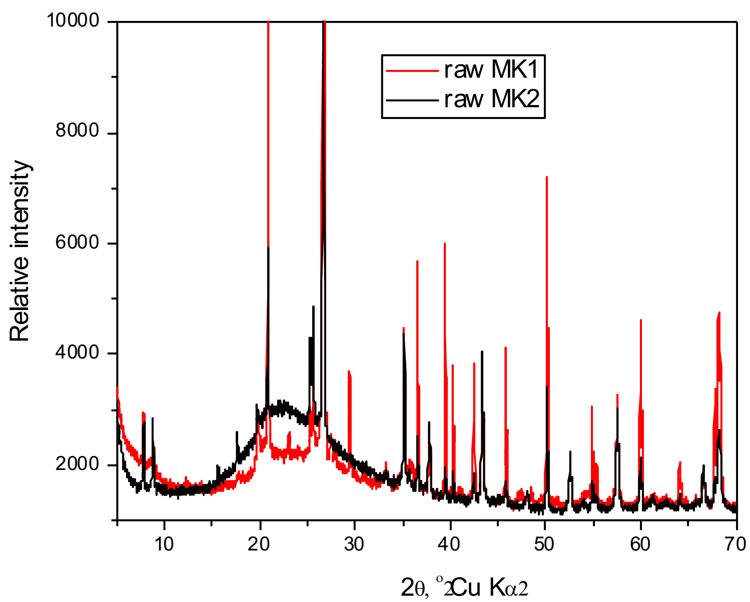


Vogt, Ukrainczyk et al. (2019) Reactivity and Microstructure of Metakaolin Based Geopolymers: Effect of Fly Ash and Liquid/Solid Contents, *Materials* 12(21) 3485. doi.org/10.3390/ma12213485

Raw materials: Metakaolin pecursors:
- Impure (Qz-rich) *vs.* Pure

MK1 ~ 52 % amorphous,
(40% quartz, 8 % Muscovite)

MK2 ~ 90 % amorphous



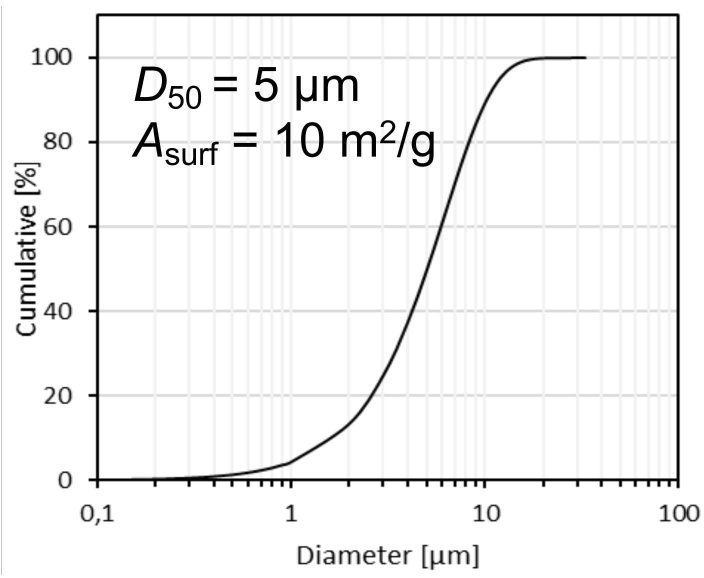
Na or K silicates

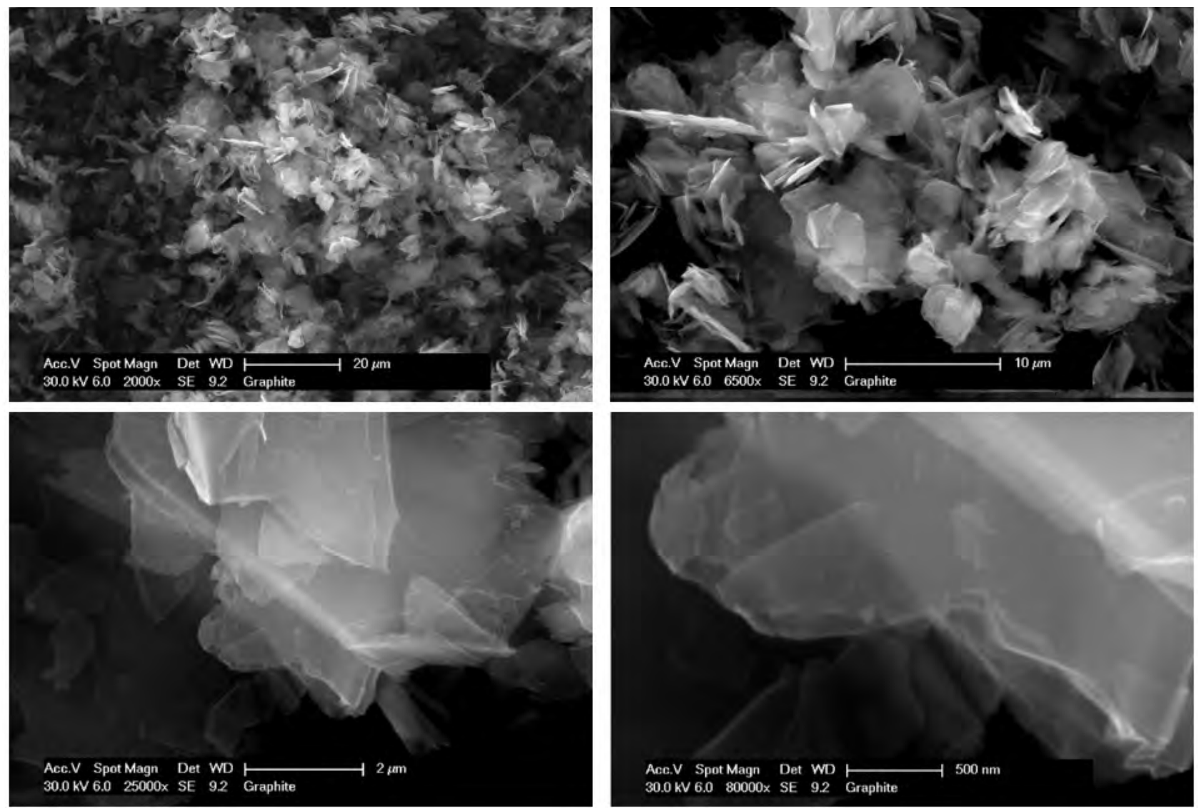
	Potassium silicate solution
Solid content [%]	45
Density [g/cm³]	1.51
Viscosity [mPas]	20
SiO_2/K_2O (molar) [-]	1.5

Raw materials: Graphite

Electrodes for MFC: high electrical conductivity, noncorrosiveness, high and accessible surface area, excellent biocompatibility, low costs, ease of fabrication, and scalability.

σ = 183 S/m



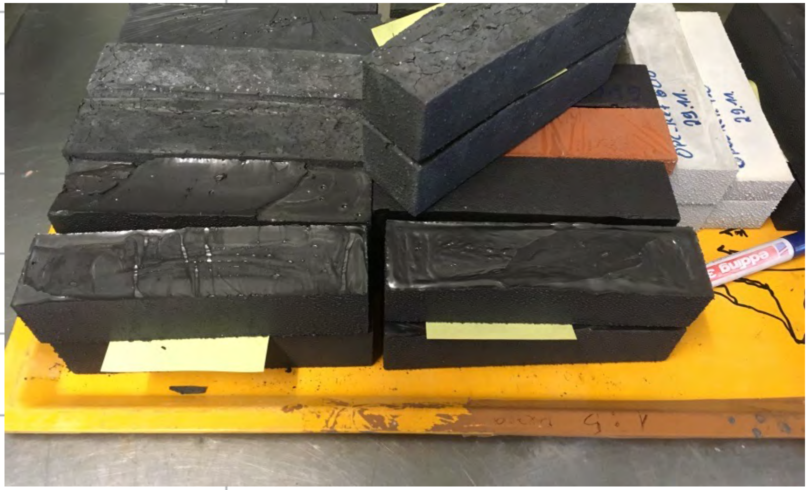


Mix designs: Geopolymer-graphite composite

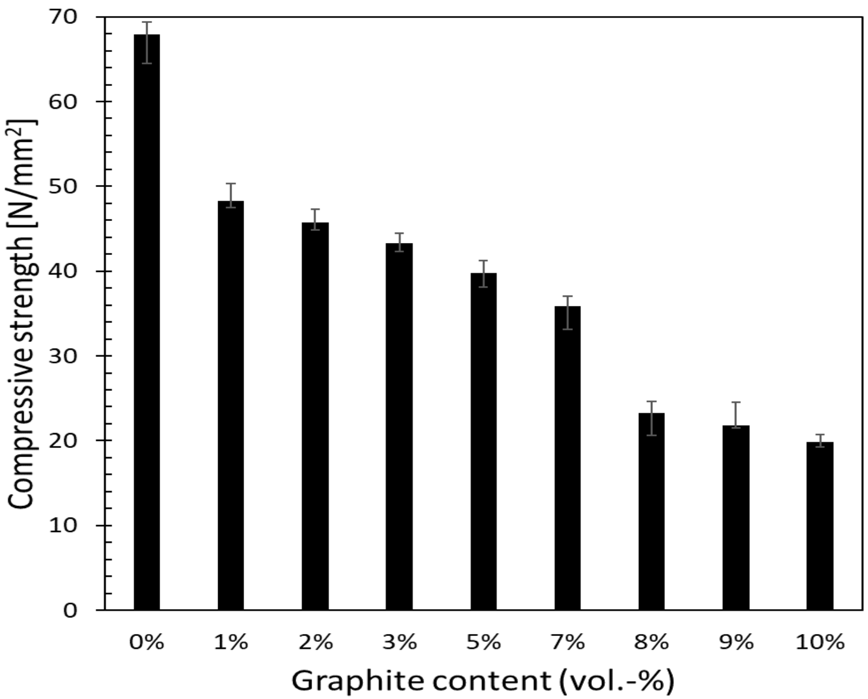
GP	wg/mtk in wt %	w/graphite in wt %	graphite in vol %	PCE/graphite
GP ref.	0.8		0	0.1
GP08 1W 1C	0.8	1	1	0.1
GP08 1W 2C	0.8	1	2	0.1
GP08 1W 3C	0.8	1	3	0.1
GP08 1W 5C	0.8	1	5	0.1
GP08 1W 7C	0.8	1	7	0.1
GP08 1W 8C	0.8	1	8	0.1
GP08 1W 9C	0.8	1	9	0.1
GP08 1W 10C	0.8	1	10	0.1
GP08 1.2W 10C	0.8	1.2	10	0.1
GP08 1.7W 10C	0.8	1.7	10	0.1
GP08 2W 10C	0.8	2	10	0.1

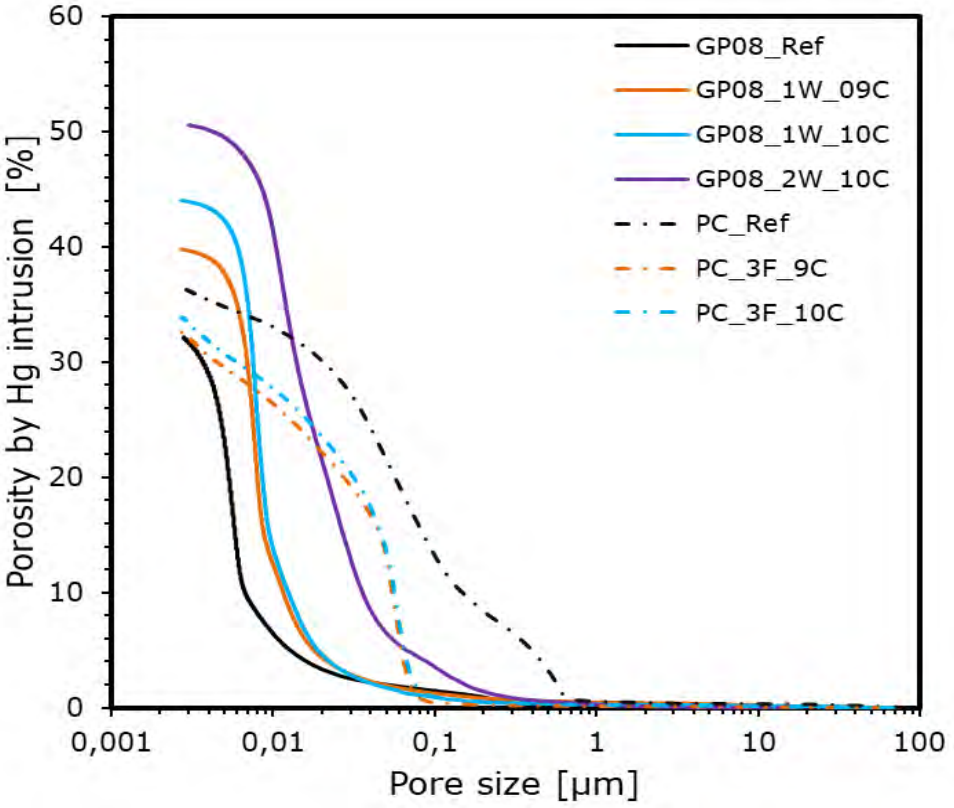
Mix designs: Portland Cement – Graphite

PCG	w/c in wt %	f/c in wt %	graphite (G) in vol %	PCE/graphite in wt %
PC ref.	0.6	0	0	0
PC06 1C	0.6	0	1	0
PC06 3C	0.6	0	3	0
PC06 4C	0.6	0	4	0
PC06 9C	0.6	0	9	0.1
PC06 3F 8C	0.6	0.3	8	0.1
PC06 3F 9C	0.6	0.3	9	0.1
PC06 3F 10C	0.6	0.3	10	0.1
PC75 8C	0.75	0	8	0.1
PC75 9C	0.75	0	9	0.1
OPC75 10C	0.75	0	10	0.1



Results: physical properties





Results: el. conductivity

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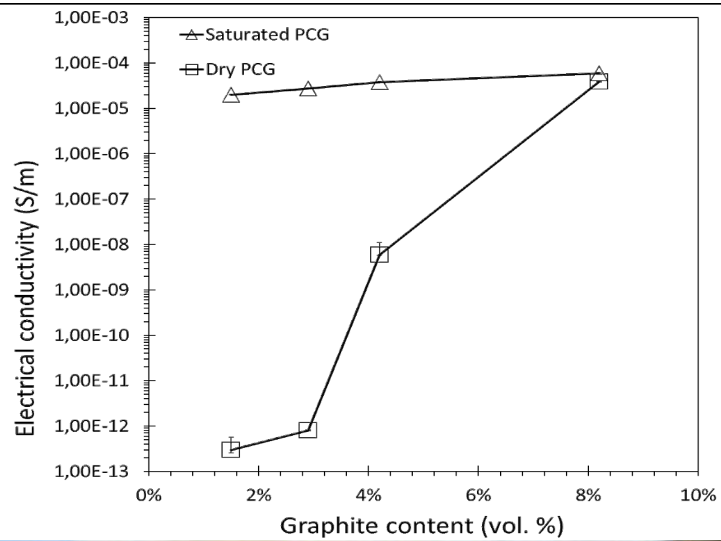
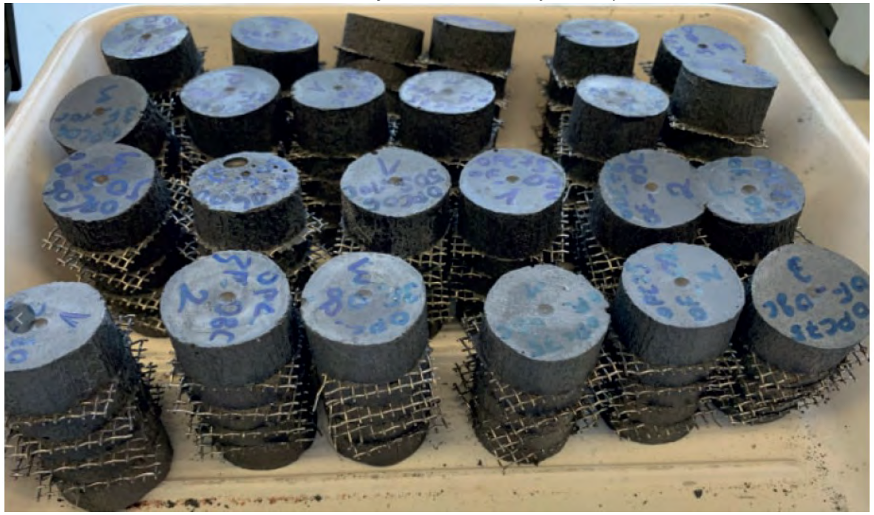
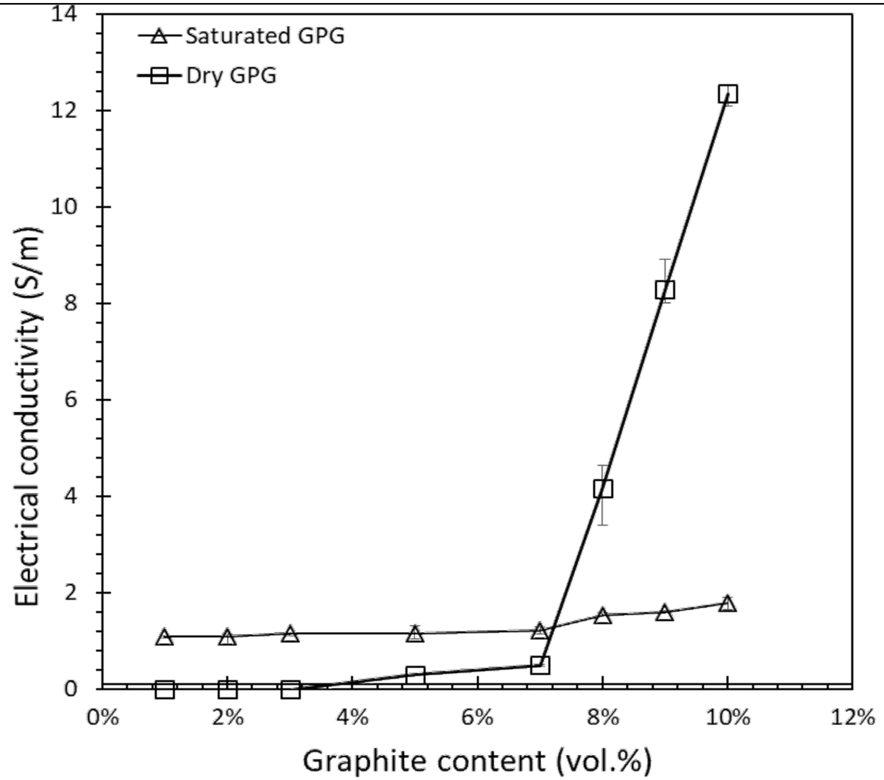
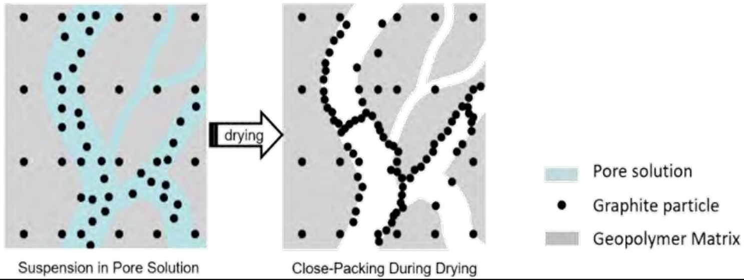


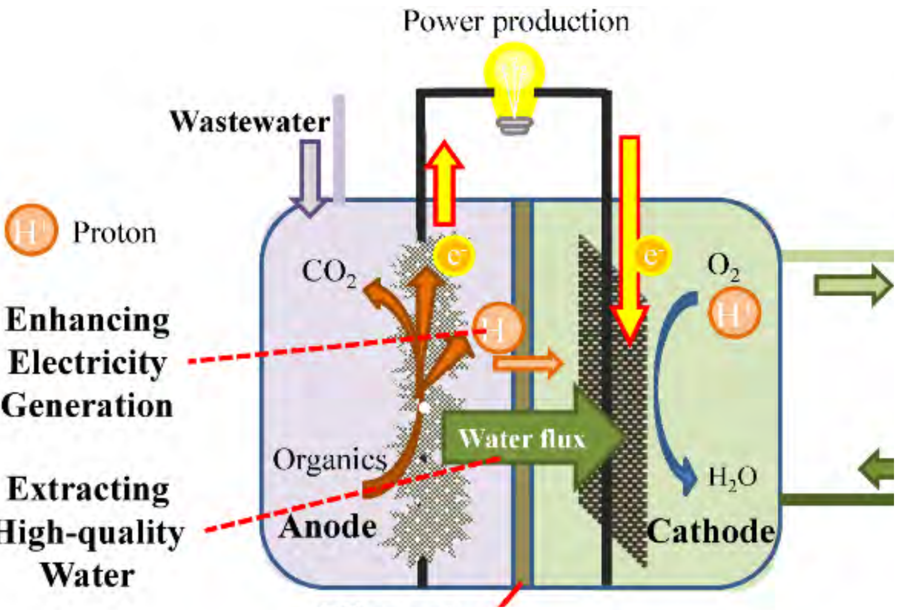






MFC electrochemistry

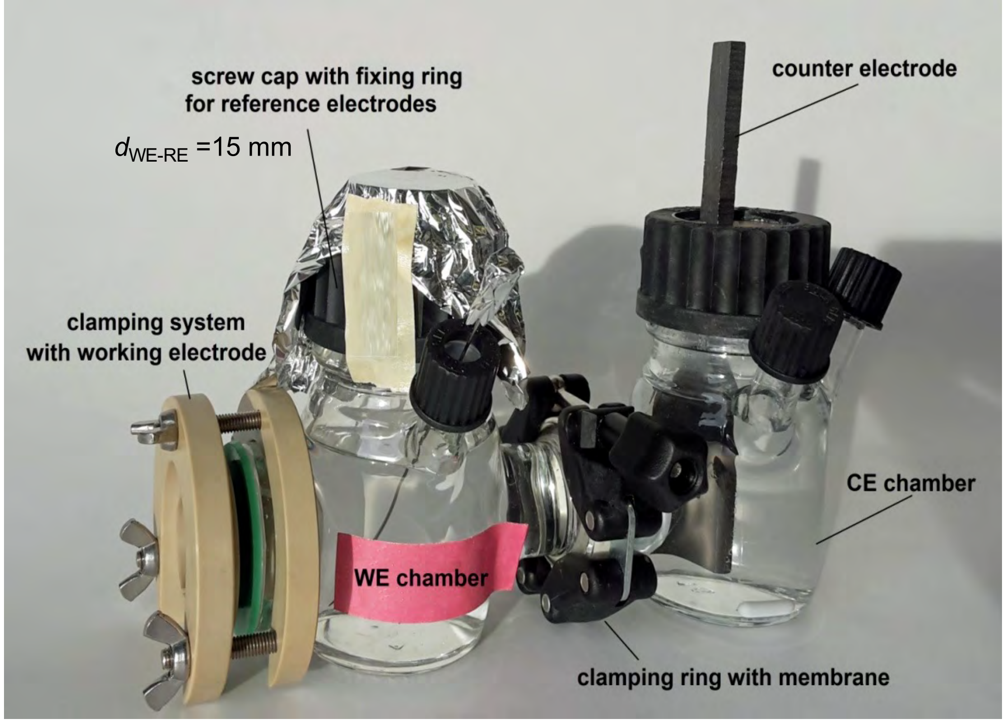
Lu et al. Water 2015 *(7)* 38-50



Cathode red. reaction: $O_2 \rightarrow H_2O$

If porous carbon (gas diffusion) cathode:

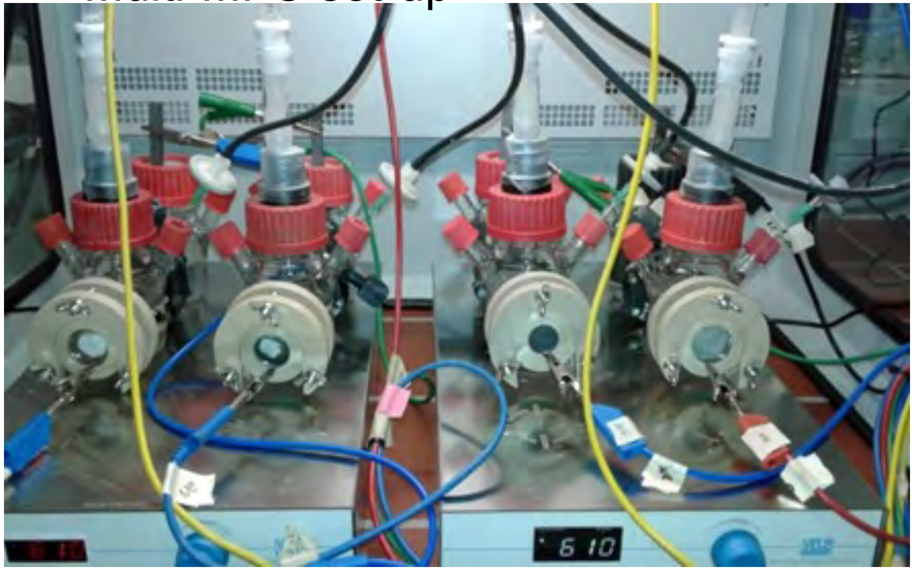
$O_2 \rightarrow H_2O_2$



Anode ox. reaction: organics → CO_2

Results: Electrochemical
- impedance spectroscopy & MFC current production

Multi-MFC set-up



Electrode Material	R_Ω (kΩ) M ± SD	i_{max} (μA cm^{-2}) M ± SD	$\overline{\sigma}_{160}$ (As cm^{-2}) M ± SD
PC Reference (3)	30 ± 17.3	-	-
PC75 0F 8C	2.5 ± 0.5	-	-
PC75 0F 9C	3 ± 1.0	-	-
PC75 0F 10C	3.2 ± 1.6	-	-
PC06 3F 8C (3)	5.1 ± 4.3	-	-
PC06 3F 9C (3)	2 ± 0.01	-	-
PC06 3F 10C (3)	3.9 ± 2.0	2.3 ± 2.3	1.2 ± 1.0
GP Reference (3)	2.7 ± 1.2	-	-
GP08 1W 8C (3)	0.8 ± 0.3	148.0 ± 107.1	67.4 ± 49.5
GP08 1W 10C (3)	1 ± 0.01	157.0 ± 42.3	72.0 ± 11.6
GP08 1.2W 10C (3)	0.4 ± 0.2	166.3 ± 52.3	78.2 ± 24.3
GP08 1.7W 10C (5)	0.1 ± 0.04	380.4 ± 129.5	155.9 ± 45.2
GP08 2W 10C (5)	0.1 ± 0.05	356.2 ± 178.2	140.7 ± 58.5
Graphite (5)	0.1 ± 0.05	401.3 ± 51.3	144.5 ± 19.9

Results: MFC curent density

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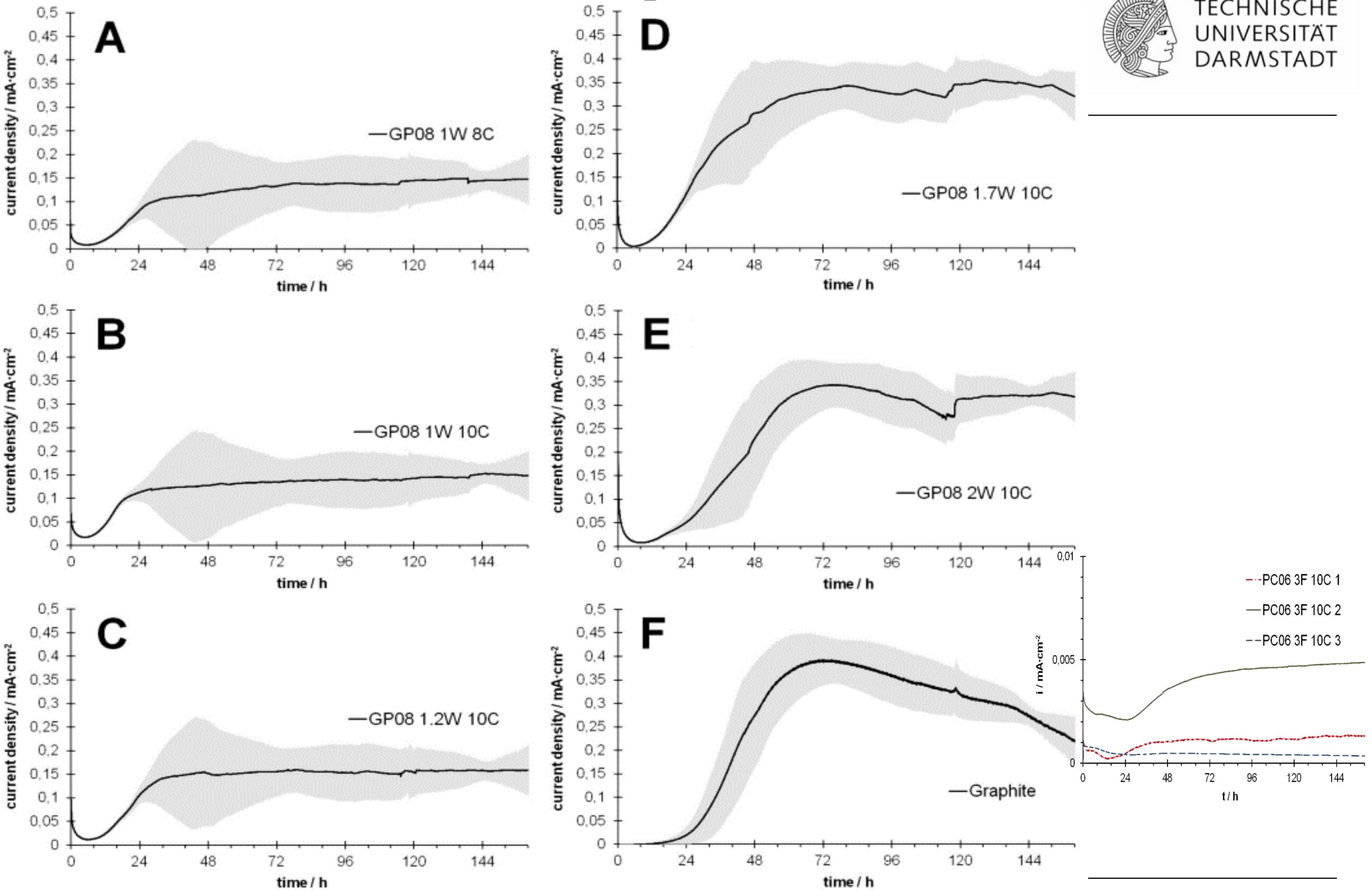
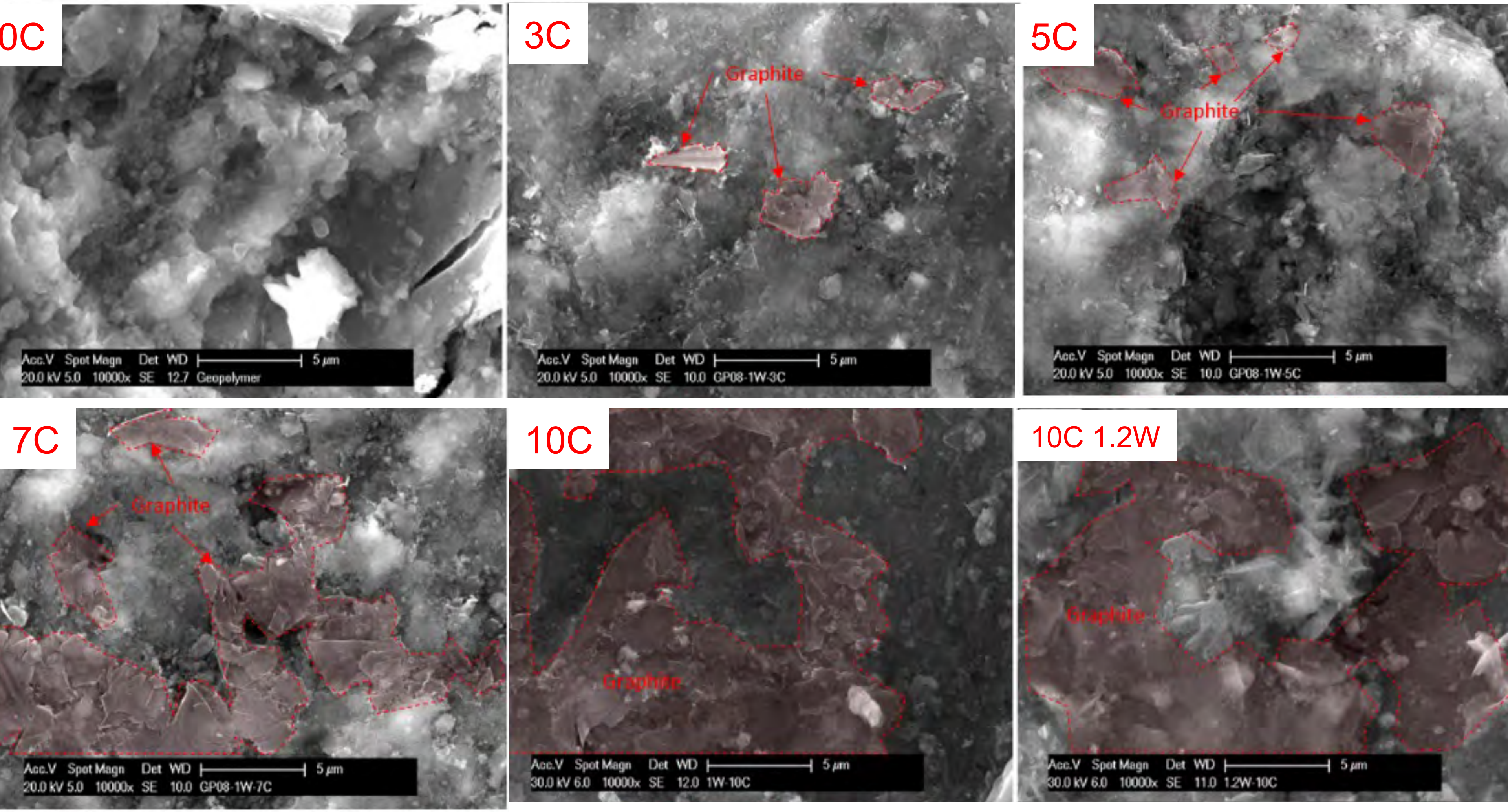
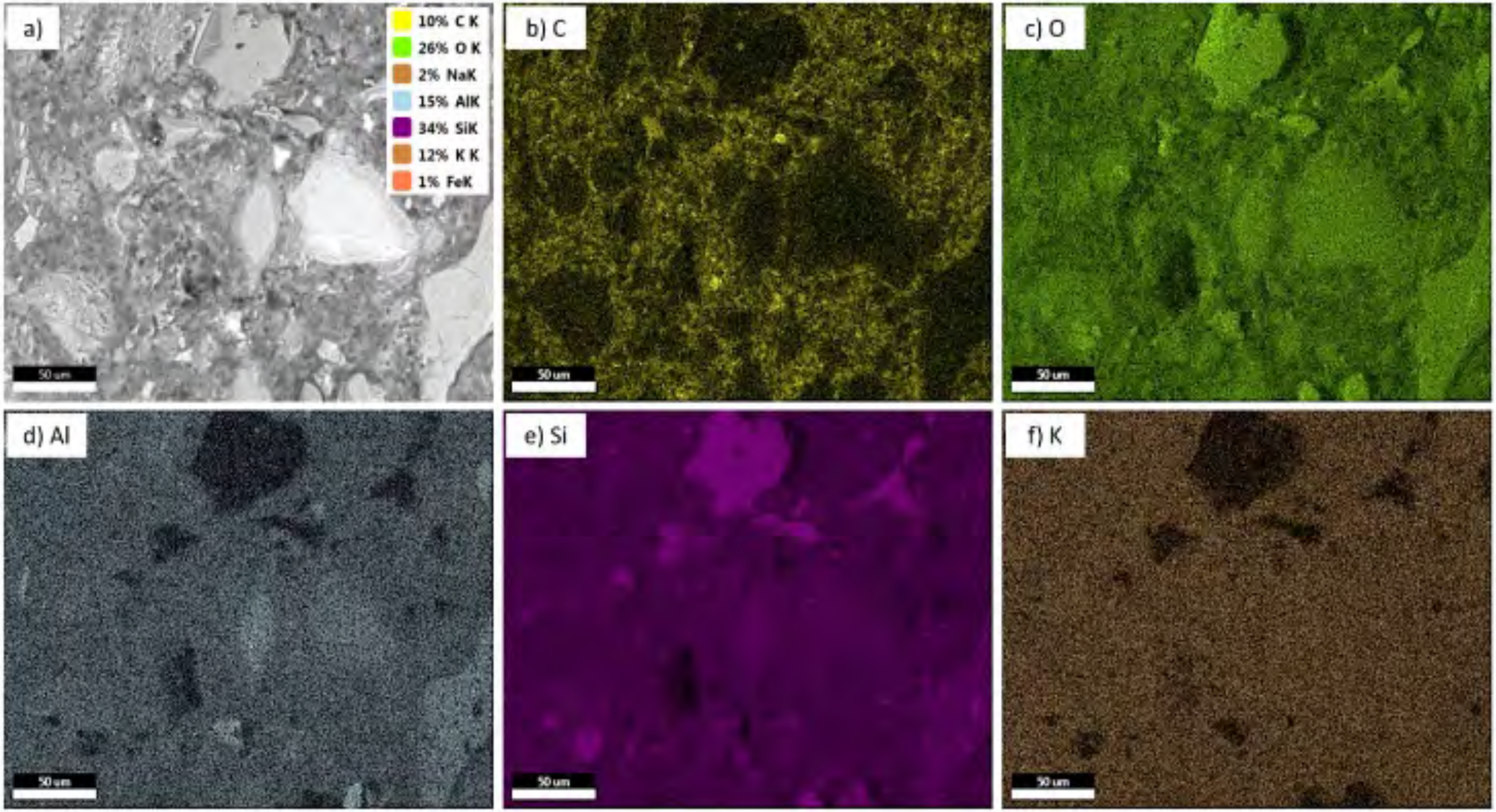


Results: SEM

Percolation of graphite plates

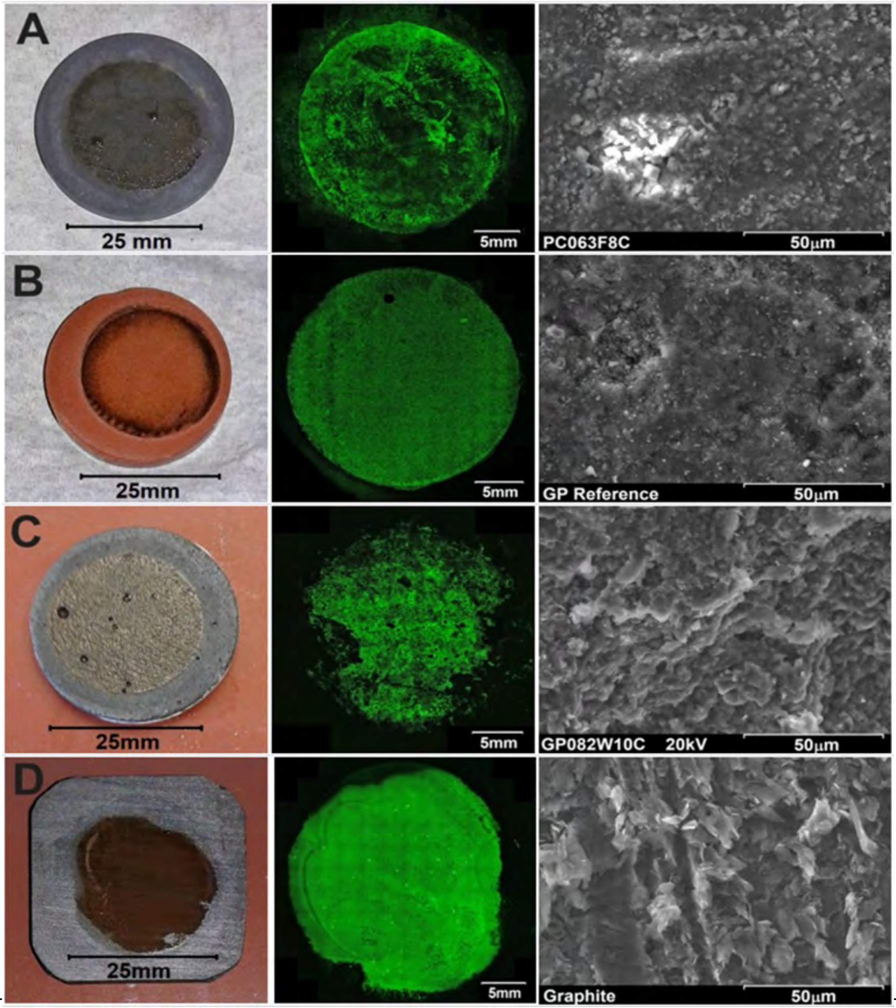


Results: e-SEM-EDS



Results: Biofilm affinity

CLSM



Conclusion Part1: GP-MFC

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- Good electrical conductivity (G) by percolation of Graphite (@7-8 vol.%)
    - ionic conductivity has minor contribution
    - Only for GP, but not PC (very poor anode performance)
    - Drying increased G (percolation, interface chemistry? effects)
- More graphite in GP increases G and MFC current density
    - Comparable to Graphite reference anode
- Porosity provides space for microorganisms
    - increases G (fixed 10 vol.% Graphite, but more percolated in solid part)
- Low cost electrode
    - to increase feasibility of MFC large-scale applications

Ongoing research: Nano-GP project

DFG Deutsche Forschungsgemeinschaft

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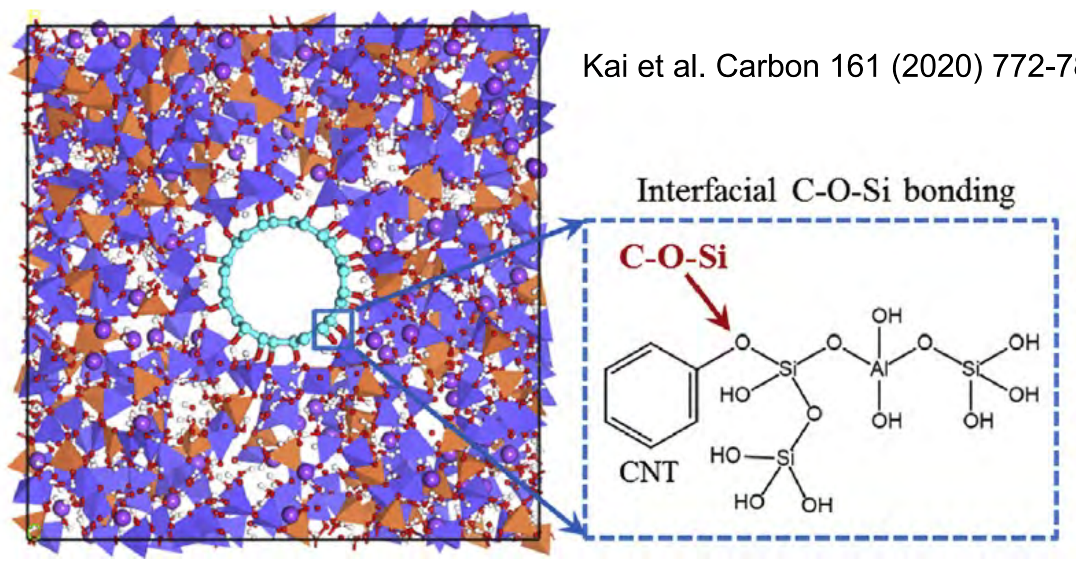
Exp. n-Materials Scientist

Computational chemistry
DFT-KMC

Multiscale modeling of advanced nano-reinforced geopolymer/CNTs materials

https://gepris.dfg.de/gepris/projekt/446266595

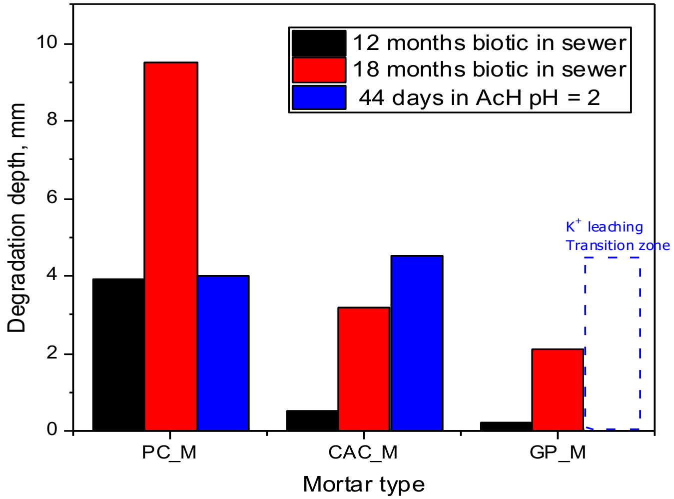


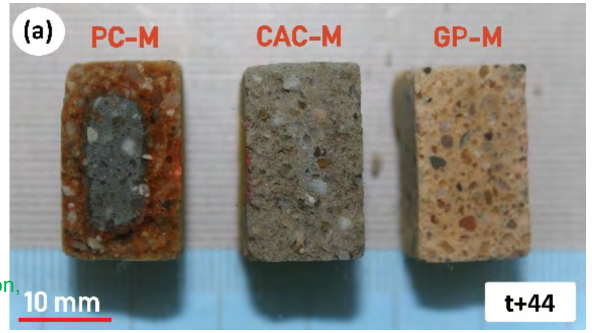
Kai et al. Carbon 161 (2020) 772-783

Past research:
GP durability: leaching in water and acids

Harsh (bio)acid enviroments:

- Sewers
- Wastewater treatment plants
- Food industry
- Agricultural industry
- Biogas
- CO_2 sequestration
- …





Ukrainczyk et al. (2019) Geopolymer, Calcium Aluminate, and Portland Cement-Based Mortars: Comparing Degradation Using Acetic Acid, ***Materials*** 12(19) 3115. doi.org/10.3390/ma12193115

Grengg, Ukrainczyk et al. (2020) Long-term in situ performance of GP, CAC and PC-based materials exposed to microbially induced acid, *Cement and Concrete Research* 131106034. doi.org/10.1016/j.cemconres.2020.106034

Drugă, Ukrainczyk* et al. (2018) Interaction between wastewater microorganisms and geopolymer or cementitious materials, *Int. Biodeter. & Biodegradation*, 134 58-67. doi.org/10.1016/j.ibiod.2018.08.005

Sedić, **Ukrainczyk*** et al. (2020) Carbonation of Portland-Zeolite and geopolymer well-cement composites under geologic CO_2 sequestration, Cement and Concrete Composites, 111 103615. https://doi.org/10.1016/j.cemconcomp.2020.103615

Comparison of acid attack:

- different binders and acid types

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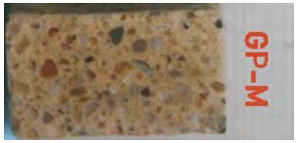

		Geopolymers (low C)	**Calcium aluminate cement (low S)**	**Portland cements (low A)**
Solubility	High	K^+/Na^+ from K(Na)-A-S-H gel	C_3AH_6; (CAH_{10}, $C_2A(S)H_8$)	CH; Ca from C-S-H
	Medium	Al from A-S-H gel	A-H gel; (AH_3)	(A-H gel)
	Low	S-H gel	(S-H)	S-H gel
Precipitation	**in H_2SO_4**	**Expansive salts inducing cracks:**		
		$KAl_3(SO_4)_2(OH)_6$; $KAl(SO_4)_2 \cdot 12H_2O$; $K_2Ca(SO_4)_2 \cdot H_2O$; $CaSO_4 \cdot xH_2O$	$CaSO_4 \cdot xH_2O$	$CaSO_4 \cdot xH_2O$
	in acetic acid (or HCl, HNO_3)	Practically no precipitation of highly soluble acid salts		

How to measure and model geopolymers leaching and acid attack?

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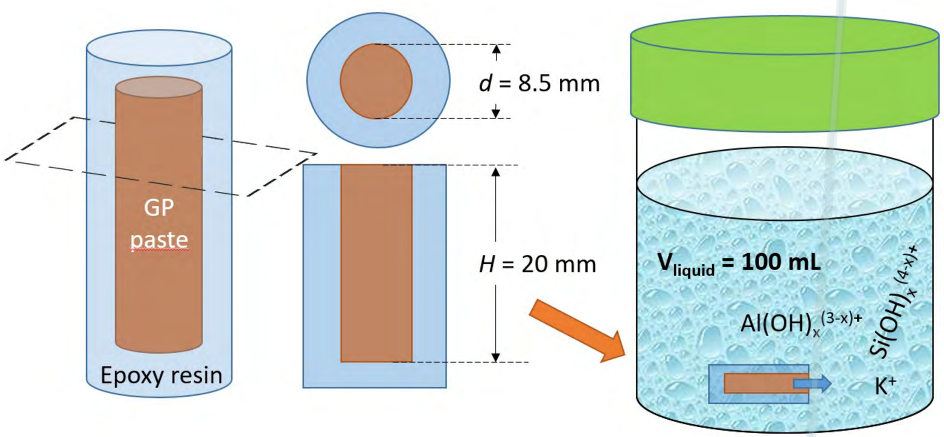
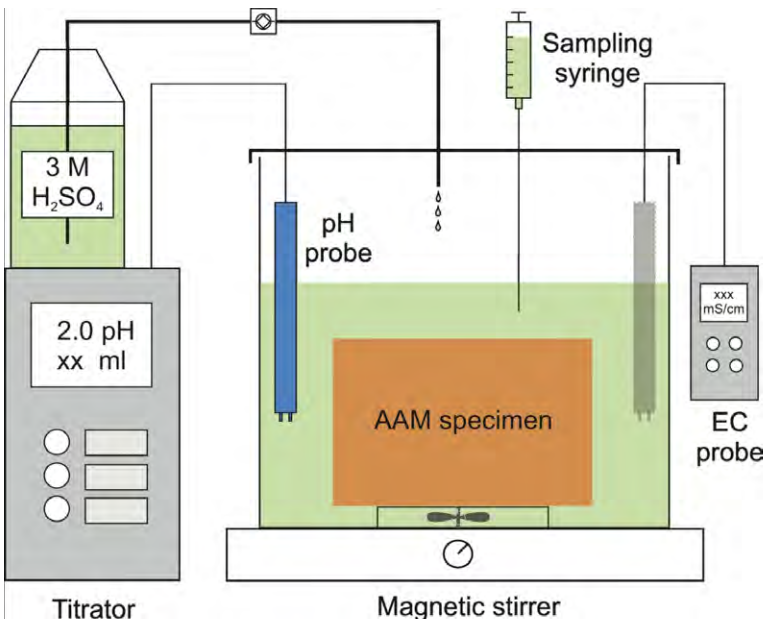
Leaching in **water**: CEN/TS 16637-2:2014, ASTM C1308-08, ..
Acid attack: ASTM C267-01, DIN 19573

…. Should be **adapted** for geopolymers**!**

Grengg, Gluth, Ukrainczyk et al. (2021) Deterioration mechanism of AAMs in **sulfuric acid**, *Cement and Concrete Research,* 142 106373. https://doi.org/10.1016/j.cemconres.2021.106373

V_{liquid}/S_{solid}=?!

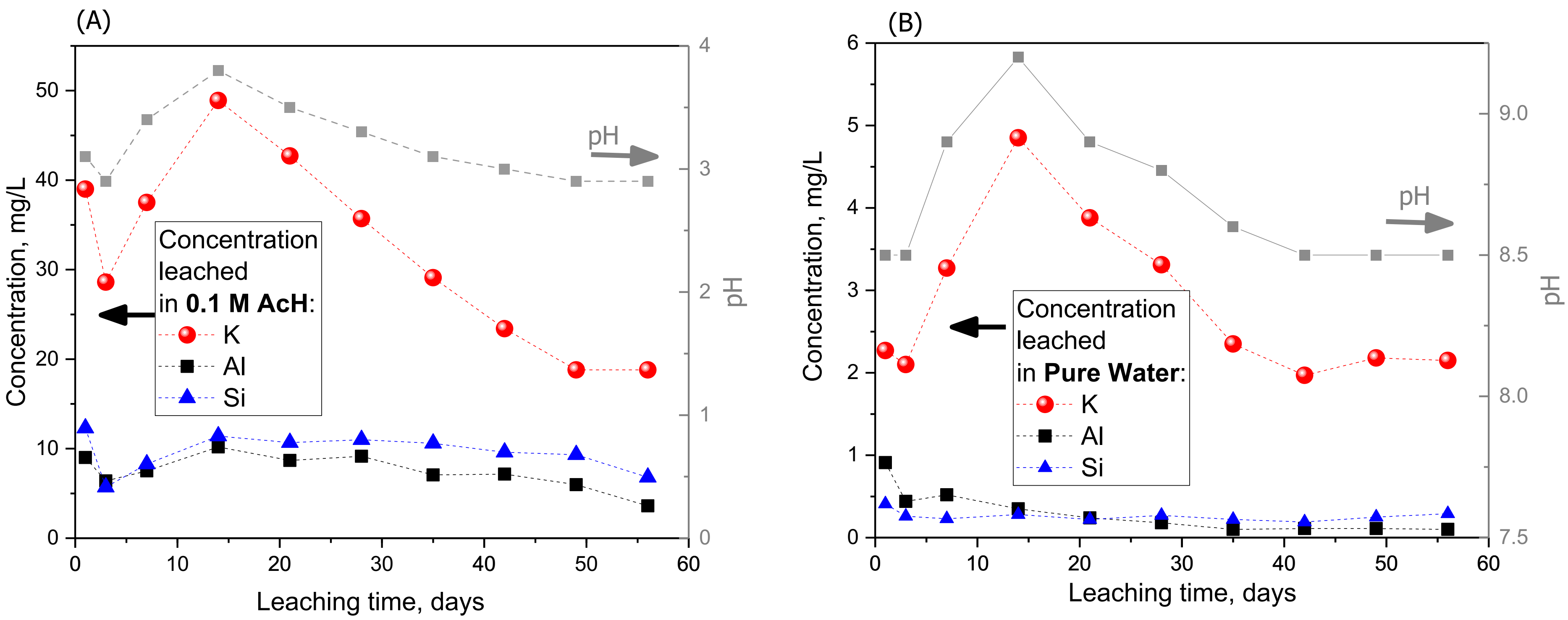




Ukrainczyk and Vogt (2021) Geopolymer leaching in **water and acetic acid**, *Rilem Technical Letters*, 50, 163-173. doi.org/10.21809/rilemtechlett.2020.124

Ukrainczyk (2021) Simple **Model** for Alkali Leaching from Geopolymers, *Materials* 14(6):1425. doi.org/10.3390/ma14061425

Acid *vs.* Water
(pure MK2)



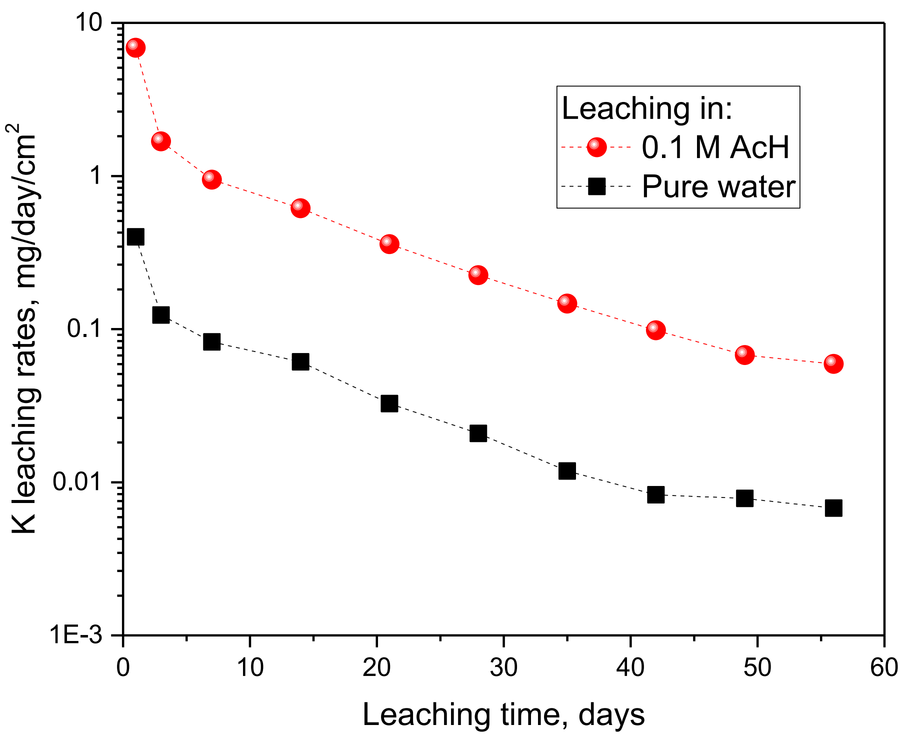
Ukrainczyk and Vogt (2021) Geopolymer leaching in water and acetic acid, *Rilem Technical Letters*, 50, 163-173. doi.org/10.21809/rilemtechlett.2020.124

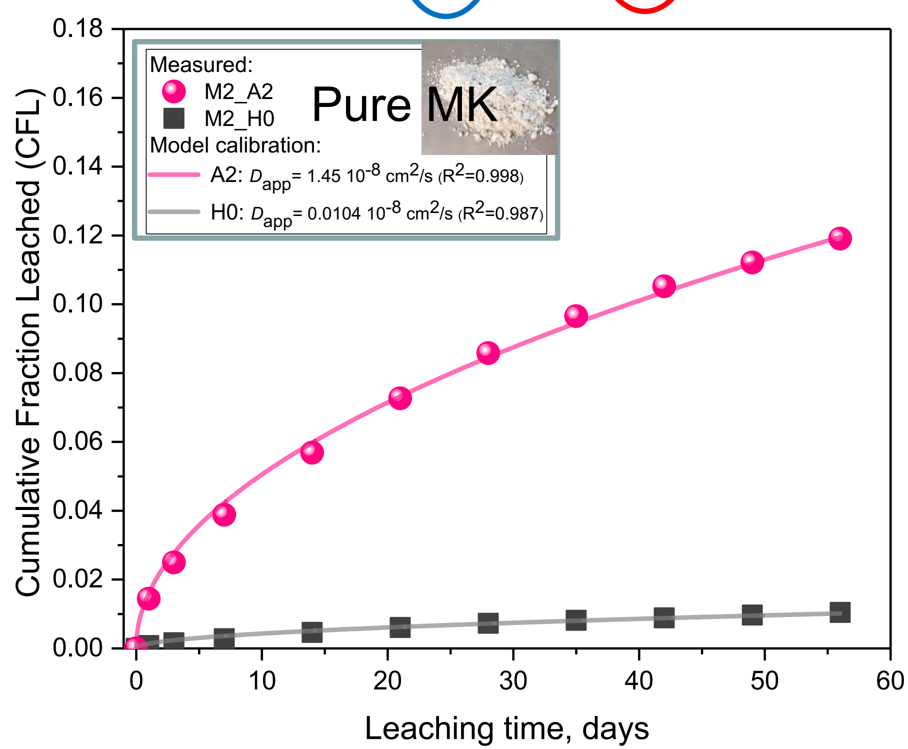
Leaching rates & Modeling (D_{app})

Perko, Ukrainczyk et al. (2020) *Influence of Micro-Pore Connectivity and Fractures on Calcium Leaching, Materials* 13(12) 2697. https://doi.org/10.3390/ma13122697

Physics Chemistry

$$D_{app} = D_{eff} / \left(1 + \frac{dC}{dc}\right)$$





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Ukrainczyk (2021) Simple Model for Alkali Leaching from Geopolymers, *Materials* 14(6):1425. doi.org/10.3390/ma14061425

Effects of: 1) ‚metakaolin purity‘ 2) acid concentration

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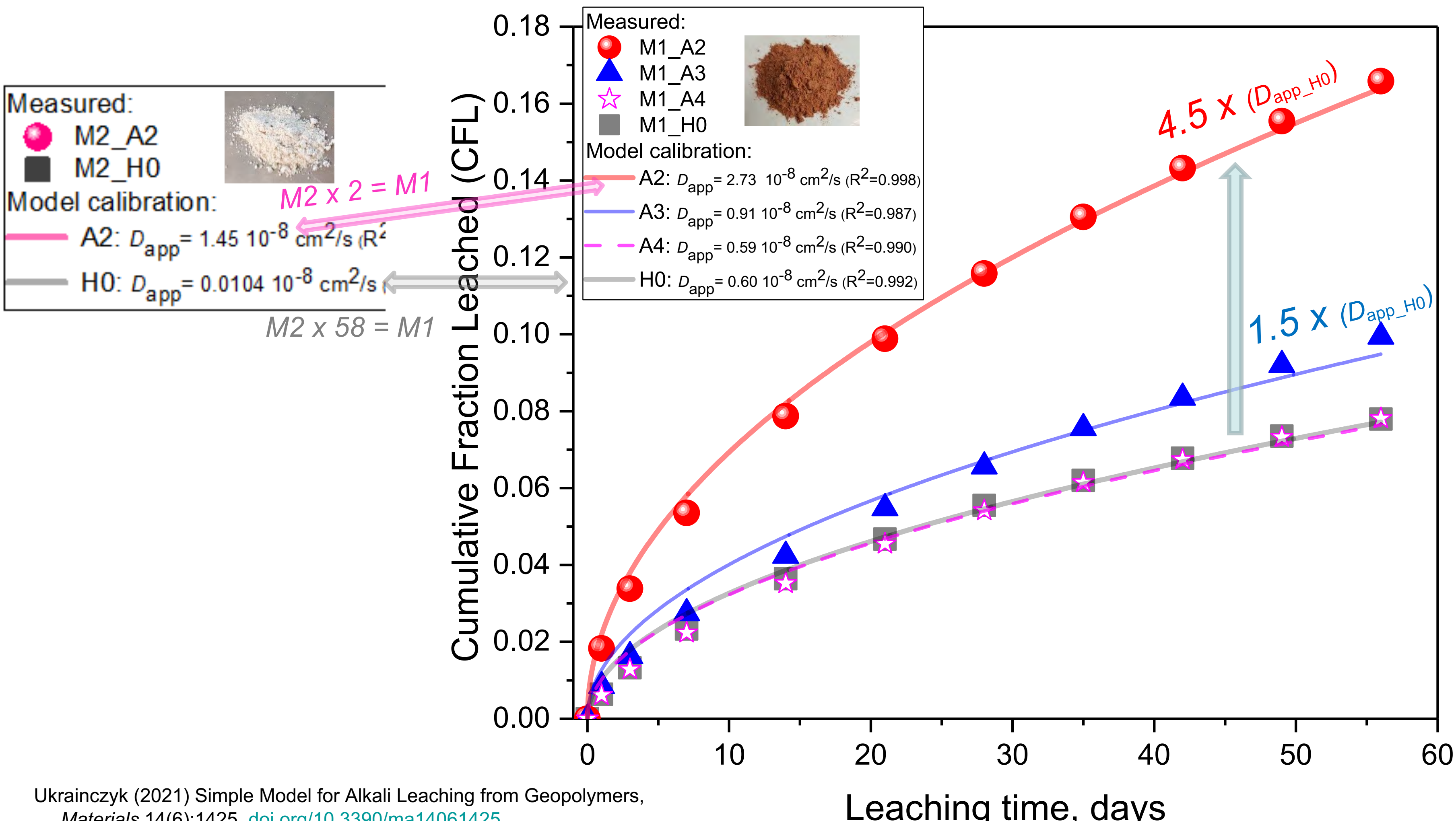
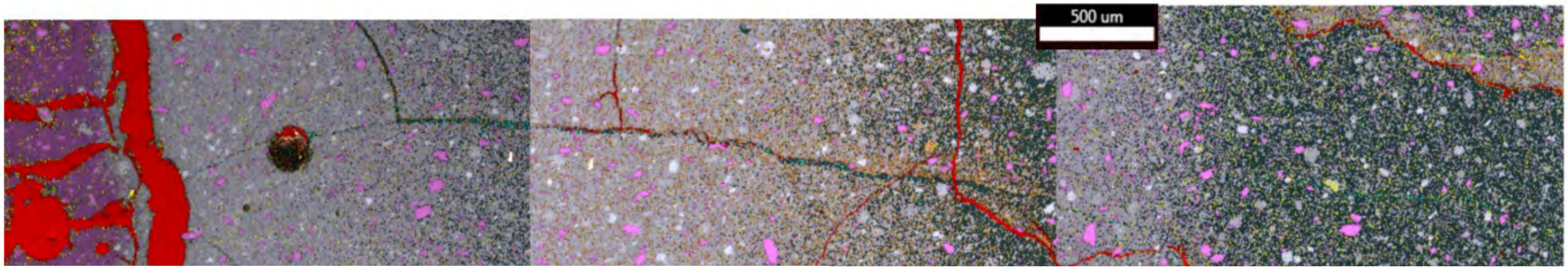
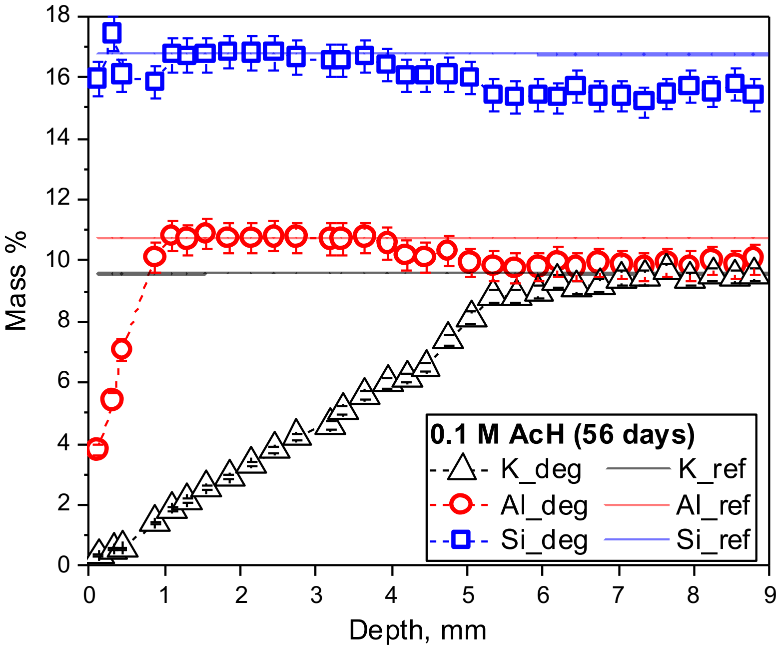


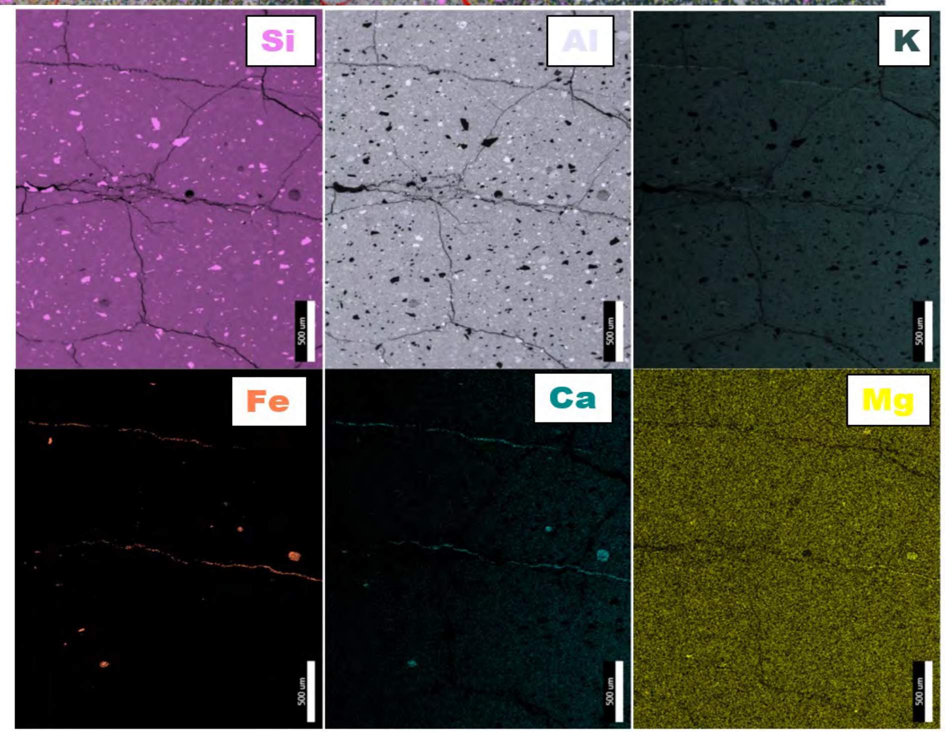
Ukrainczyk (2021) Simple Model for Alkali Leaching from Geopolymers, *Materials* 14(6):1425. doi.org/10.3390/ma14061425

SEM-EDS (2D mapping → conc. profile)

1) Acetic acid (0.1 M, 56 days)







Demonstration results in sewers

Microstructural and Biofilm analysis

[a] Grengg, Ukrainczyk et al. (2020) Long-term in situ performance of GP, CAC and PC-based materials exposed to microbially induced acid corrosion, ***Cement and Concrete Research*** 131106034. doi.org/10.1016/j.cemconres.2020.106034

[b] Drugă, Ukrainczyk* et al. (2018) Interaction between wastewater microorganisms and geopolymer or cementitious materials, ***Int. Biodeter. & Biodegradation***, 134 58-67. doi.org/10.1016/j.ibiod.2018.08.005

Field conditions↓		**Geopolymers (low C)**	**Calcium aluminate cement (low S)**	**Portland cement (low A)**
Sewer [a] (biogenic H_2SO_4)	**1 year→**	**0.2 mm**	**0.5 mm**	**3.9 mm**
	1.5 year→	**2.1 mm**	**3.2 mm**	**9.5 mm**
Activated sludge tank [b] (35 days, biogenic HNO_3)		**0**	**45 µm**	**95 µm**

GPC

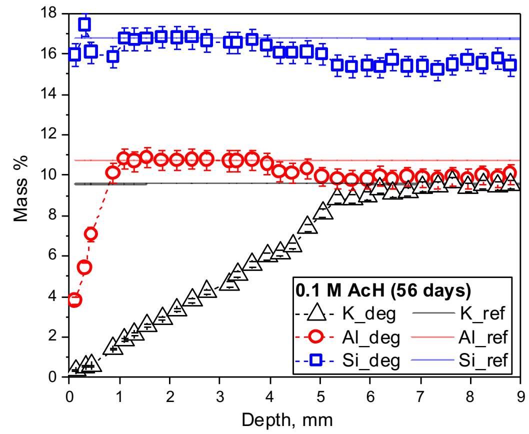
CAC

OPC

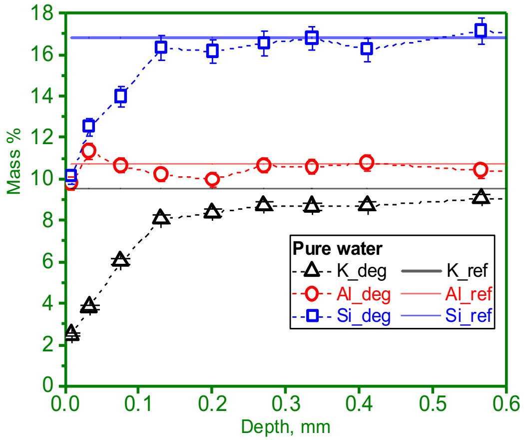
UHPC

Summary 2: leaching/acid resistance

- SEM-EDS & EPMA mappings are powerful tool for GP degradation
- **0.1 M <u>AcH</u>** (56d) resulted in sharp dissolution of Al:
    - degradation zone of 1 mm depth
  - K^+ profile: gradual dissolution
    - → a transition zone (0 - 5.5 mm depth)



- **in <u>water</u>**:
    - negligible dissolution of Al,
    - but significant dissolution of Si (and K) reaching
        - a degradation depth of 0.16 mm

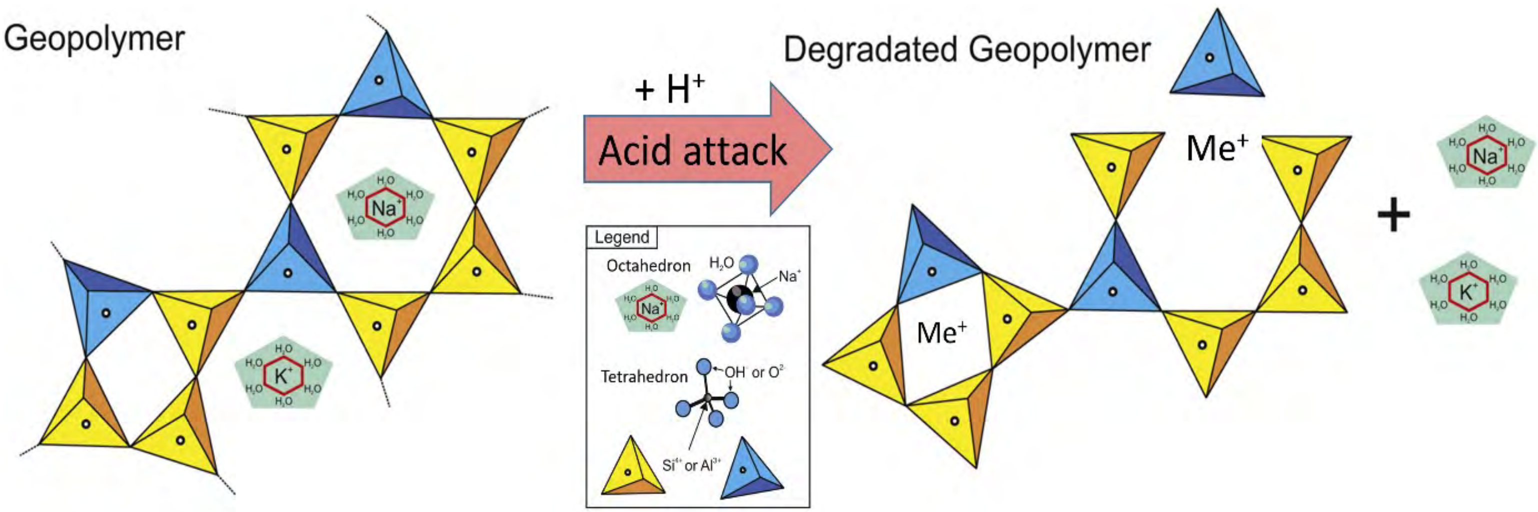


Ukrainczyk and Vogt (2021) Geopolymer leaching in water and acetic acid, *Rilem Technical Letters*, 50, 163-173. doi.org/10.21809/rilemtechlett.2020.124

Summary 2

Multi-stage mechanism for GP acid attack:

- **Cation exchange** reaction between the cation X^+ and the (Na^+ or K^+);
- Partial **de-alumination** dissolution of the aluminosilicate framework;
- Precipitation of acid anion **salts** (acetic highly soluble; sulfate - expansive);
- Dissolution and re-crystallization of the **Si-rich** aluminosilicate framework.



Ukrainczyk and Vogt (2021) Geopolymer leaching in water and acetic acid, *Rilem Technical Letters*, 50, 163-173. doi.org/10.21809/rilemtechlett.2020.124

Grengg, Gluth, Ukrainczyk et al. (2021) Deterioration mechanism of AAMs in **sulfuric acid**, *Cement and Concrete Research,* 142 106373. doi.org/10.1016/j.cemconres.2021.106373

Summary 2

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- **Lower** leaching rates in **pure**-metakaolin compared to quartz-rich one
  - due to different mix designs and (mechanical, porosity and chemical) properties.
  - D_{app} governed by **the chemistry** (cation exchange and dissolution)
    - and **not by D_{eff}** (porosity and pore morphology).

Ukrainczyk (2021) Simple Model for Alkali Leaching from Geopolymers, *Materials* 14(6):1425. doi.org/10.3390/ma14061425

- **New methodology**:
  - Standard for leaching in pure water
    - adapted for (acetic) acid attack of geopolymers
  - The diffusion model can accurately represent the (*CFL*) measurements

- **Future** (ongoing) research: - more advanced (numerical) models
  - to separate D_{eff} from **chemical part**

$$P\frac{\partial c}{\partial t} = -D_{eff}\frac{\partial^2 c}{\partial x^2} - (1-P)\,\rho_s\frac{\partial C}{\partial t}$$

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Article

Conductive Geopolymers as Low-Cost Electrode Materials for Microbial Fuel Cells

Shifan Zhang, Jürgen Schuster, Hanna Frühauf-Wyllie, Serkan Arat, Sandeep Yadav, Jörg J. Schneider, Markus Stöckl,* Neven Ukrainczyk,* and Eddie Koenders

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- Industrial Biotechnology

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Acknowledgement 2: Acid resistance

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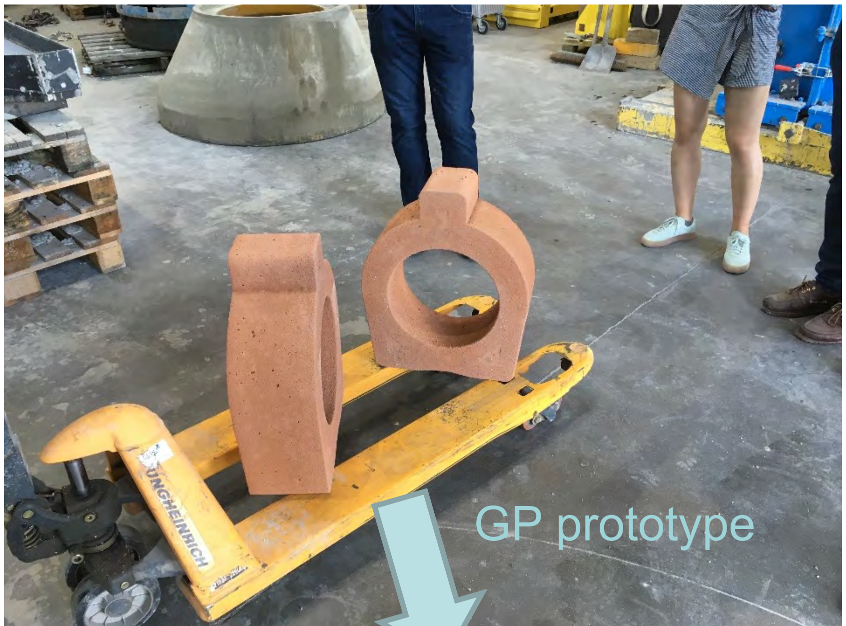

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