

The role of slags and other by-products within circular economy in the steel industry

- Upcycling methods for Electric Arc Furnace steelmaking slags: phosphorus removal from wastewater and fillers for polymers
- Giulia Bragaglia
- PhD project funded by ABS Acciai S.p.A., under the coordination of Danieli S.p.A.

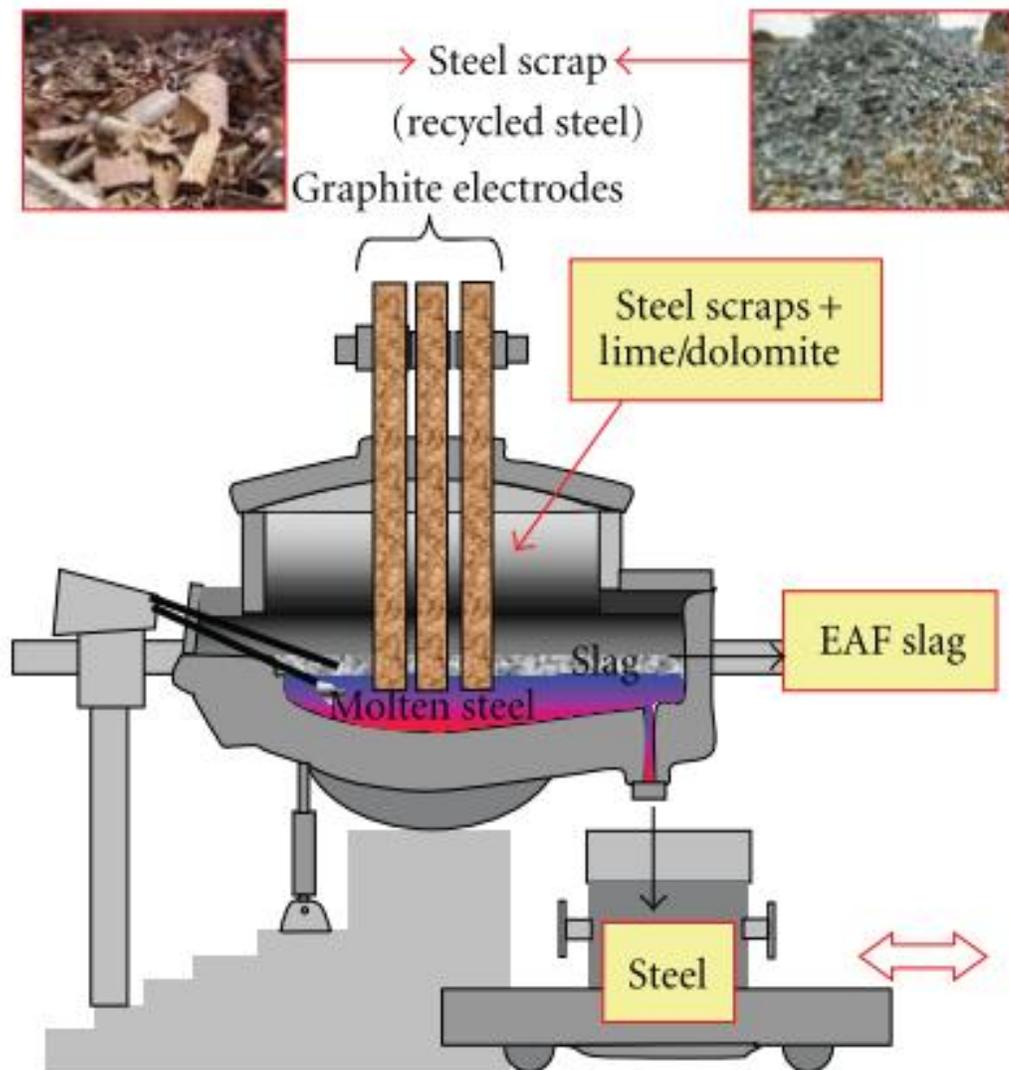


*ESTEP Focus
Group Circular
Economy &
FEHS-Institute*

*5.-6.
MARCH
2025*

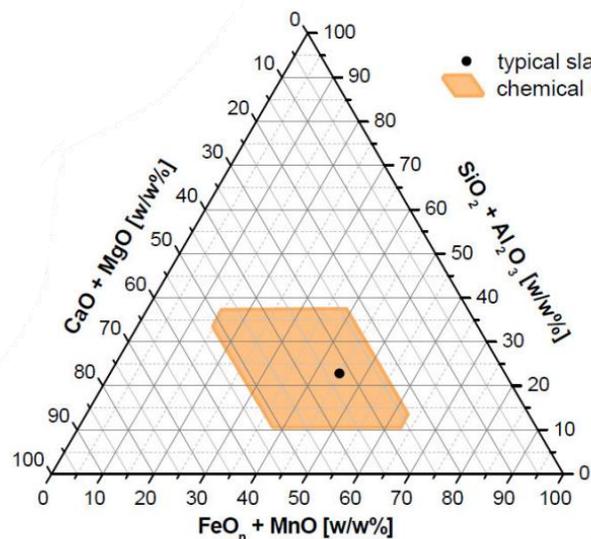


EAF-slag formation process



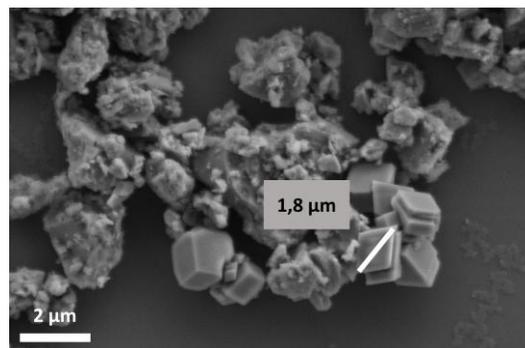
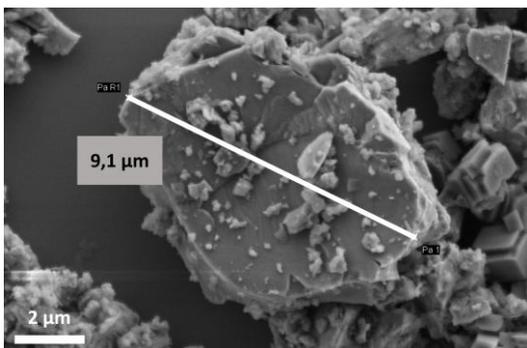
EAF-slag → Ecogravel®
UNI EN 12620-13043-13242

- It can be used as **substitute for basaltic aggregates**

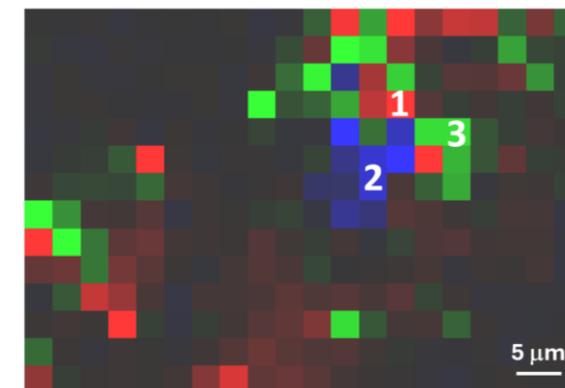
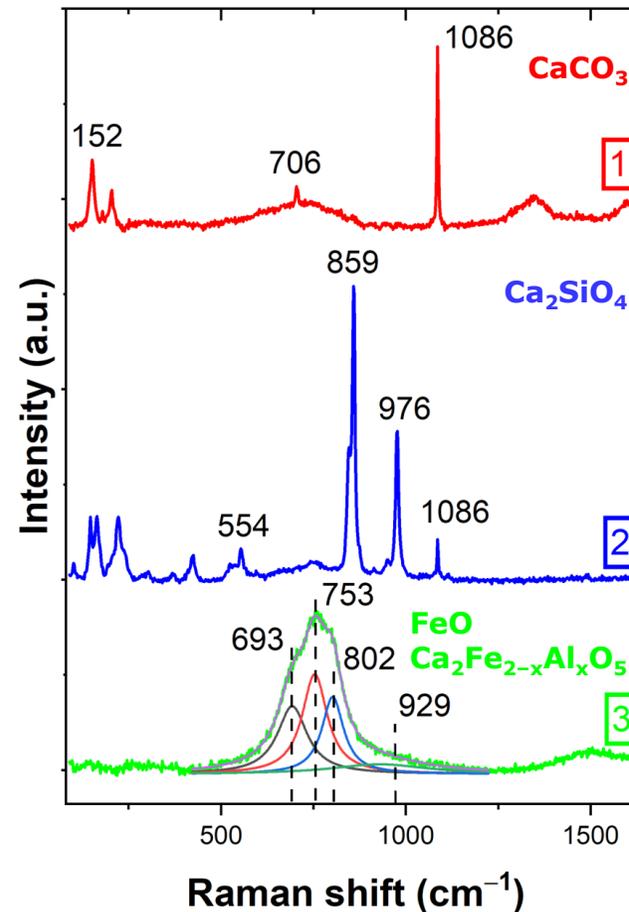


- **Density:** $\approx 3,5 \text{ g/cm}^3$
- **Water solubility:** $\approx 1 \text{ g/L}$
- No oxidizing properties
- Insoluble in organic solvents

SEM measurements



Raman mapping

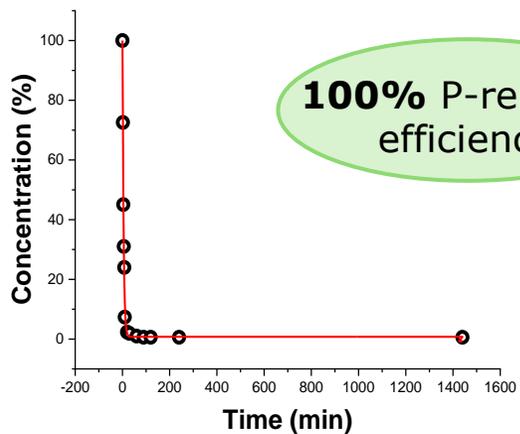


Phosphorus removal from wastewater

Ecogravel®



Phosphorus removal
through **slag-adsorption**



100% P-removal efficiency

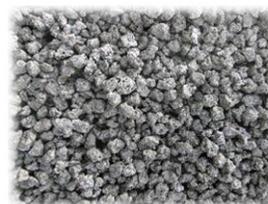
Precipitation of $\text{Ca}_5(\text{PO}_4)_3\text{OH}$

Leaching of phosphorus with organic acids

Reinforcing polymers with Ecogravel®



Ecogravel®



- Polypropylene (**PP**)
- Polypropylene-grafted (**PP-gr**)
- Polystyrene (**PS**)
- Polymethyl-methacrylate (**PMMA**)

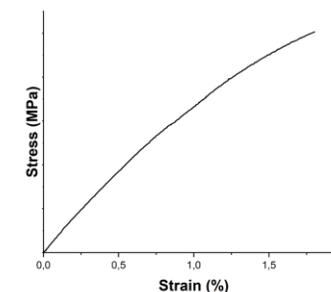
Pure PMMA



PMMA with
40 %wt. of Ecogravel®



Tensile test



...unveiling the microstructure

...why phosphorus?



It is both a **waste** and a **resource**



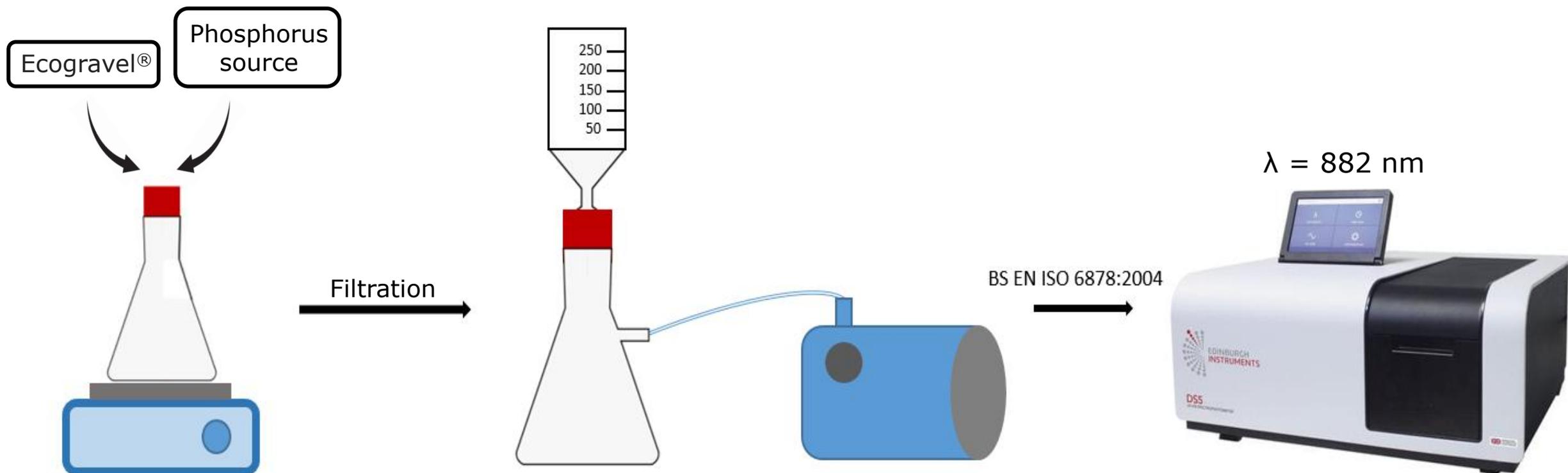
- **It is a pollutant**
- It causes *eutrophication*

- Annually, around **20 Mt are extracted from earth**, by mining phosphate rocks, a finite resource
- **Phosphorus is fundamental for life**, as an essential element
- **From 2020** it is **considered a critical raw material**



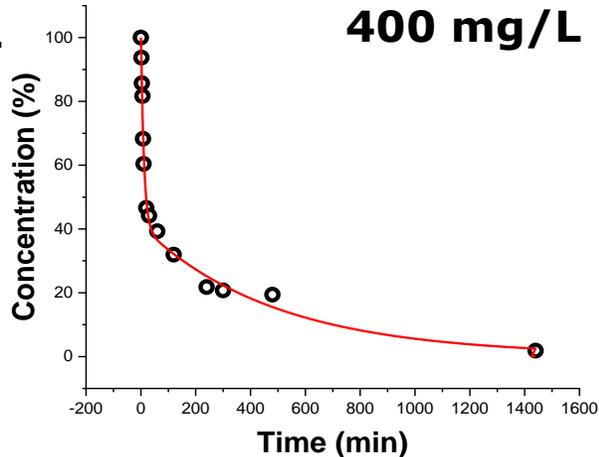
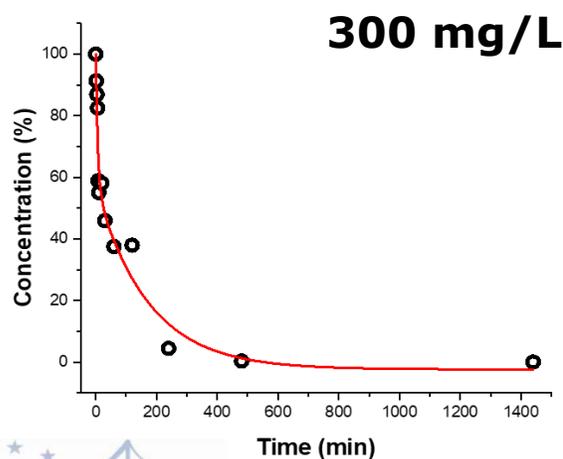
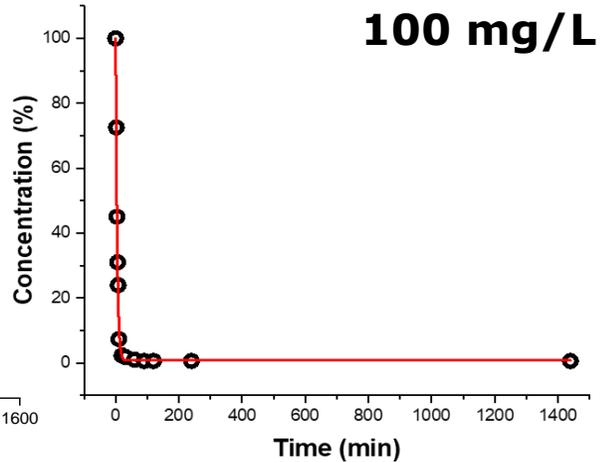
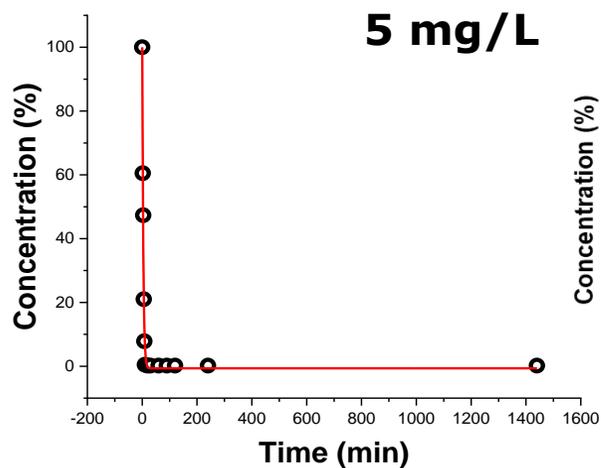
CRM



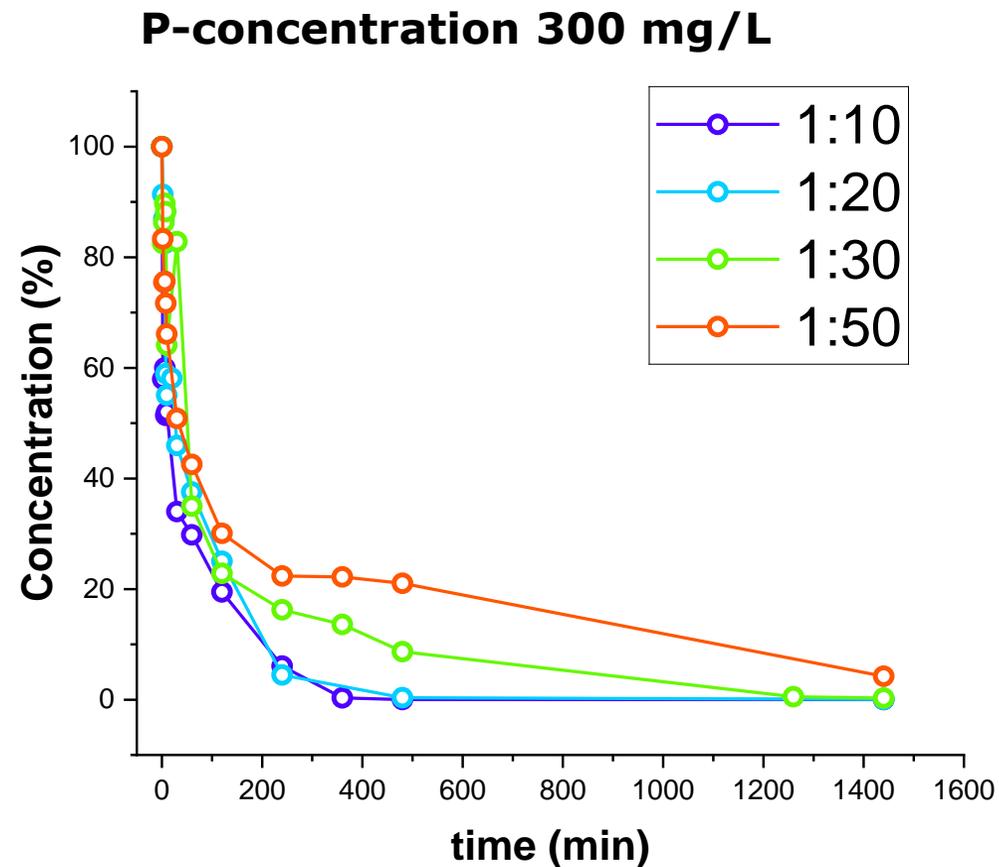


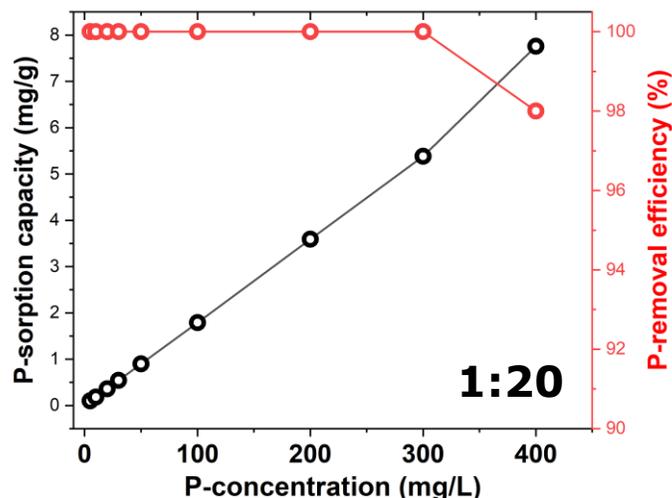
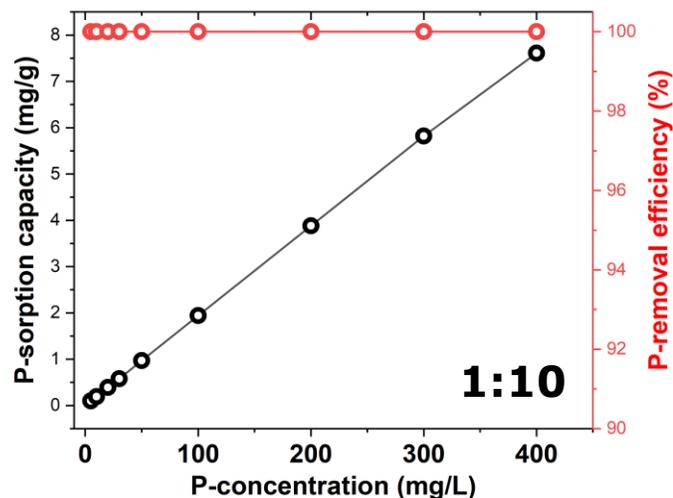
- **P – concentration** in the starting solutions (**mg/L**):
5, 10, 20, 30, 50, 100, 200, 300, 400
- **Solid/liquid w/v ratios:** **1:10, 1:20, 1:30, 1:50**

Increasing P-concentration

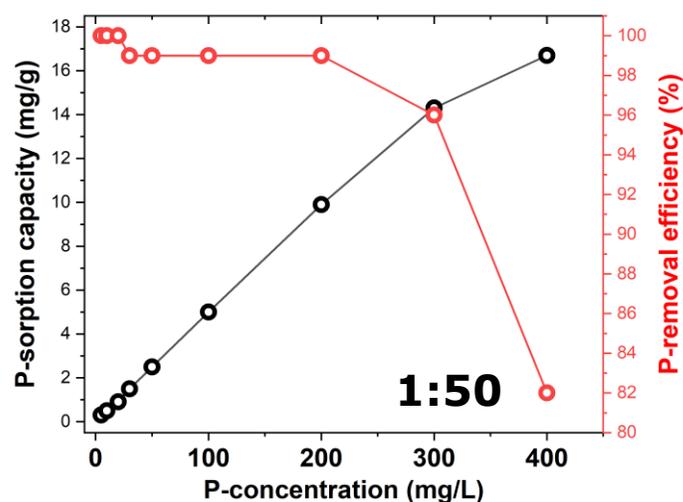
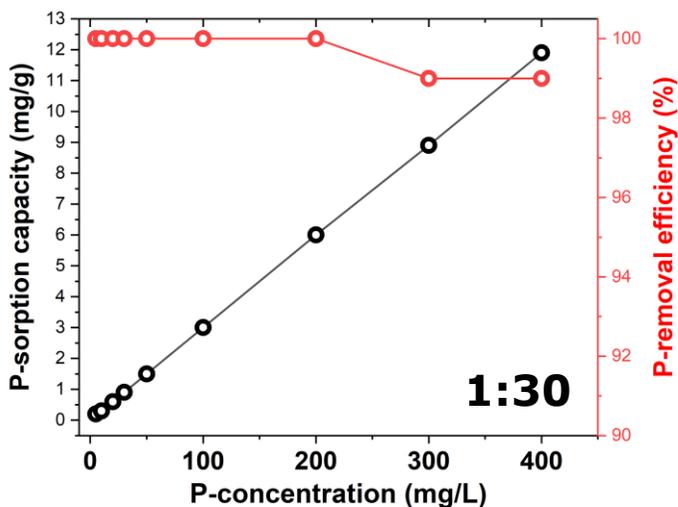


Decreasing solid/liquid ratio





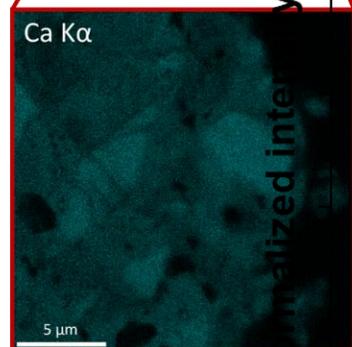
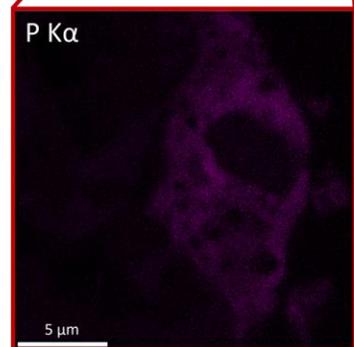
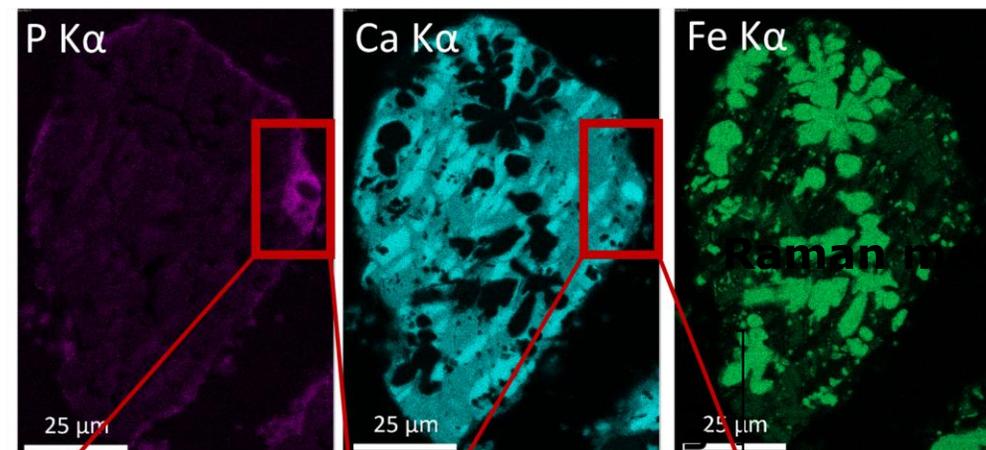
P-removal efficiency remained constant while increasing the P-concentration in the starting solution up to 400 mg/L from 1:10 up to 1:30



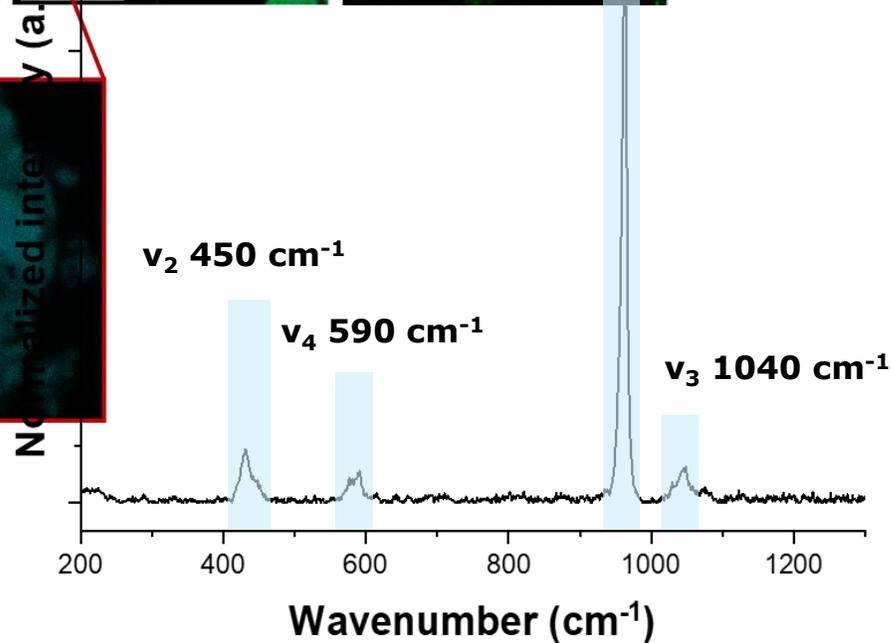
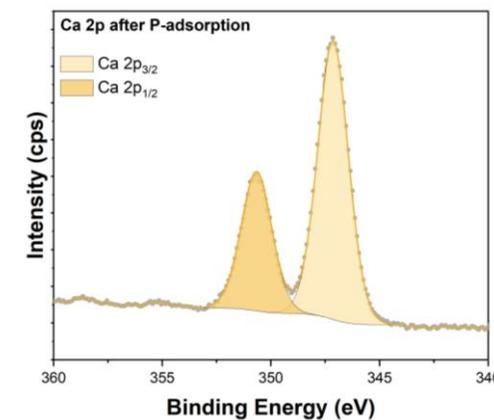
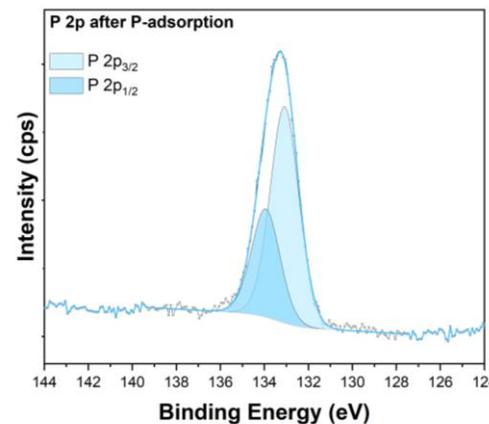
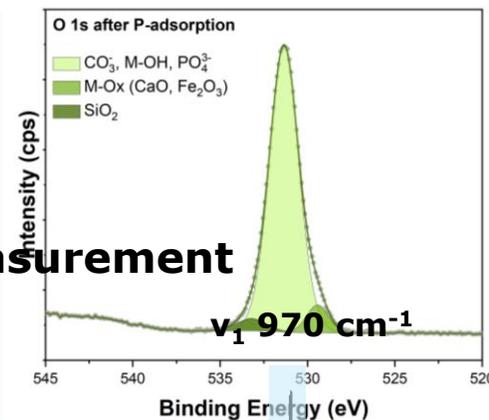
P-sorption capacity increased up to 11.9 P-mg/g-slag, triple value compared to those reported in literature

1:30 solid/liquid ratio and **400 mg/L** of phosphorus

Cross-sectional EDX measurements



XPS analysis



→ **The peaks** are related to the presence of **hydroxyapatite** $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$

We employed the **DoE approach** to better rationalize the **leaching experiments**, in order to reach the target with a statistical approach

A **Full Factorial Design** was used, with **4 factors** and different levels

Factors	N° of levels	Levels
Acid	4	Oxalic acid Acetic acid Lactic acid Citric acid
Concentration (M)	2	0,5 0,001
time (h)	2	1 4
Solid : liquid ratio (g : mL)	2	1:10 1:50



- **Lactic acid 0.5 M**
- **1 hour** treatment
- **1:50** solid/liquid **ratio**

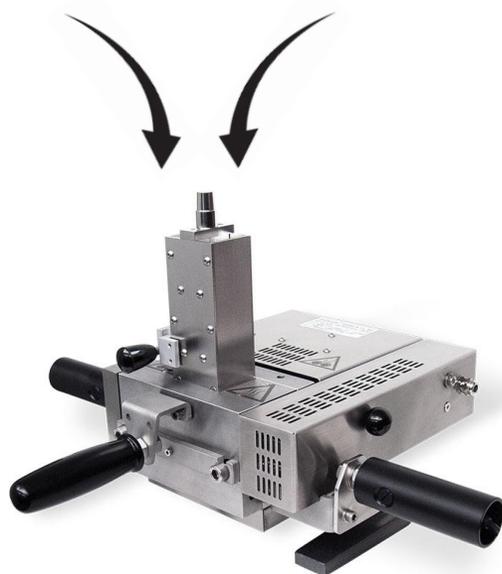


Ecogravel® as filler for polymeric matrices

- Polypropylene
- Polypropylene-grafted
- Polystyrene
- Polymethylmethacrylate

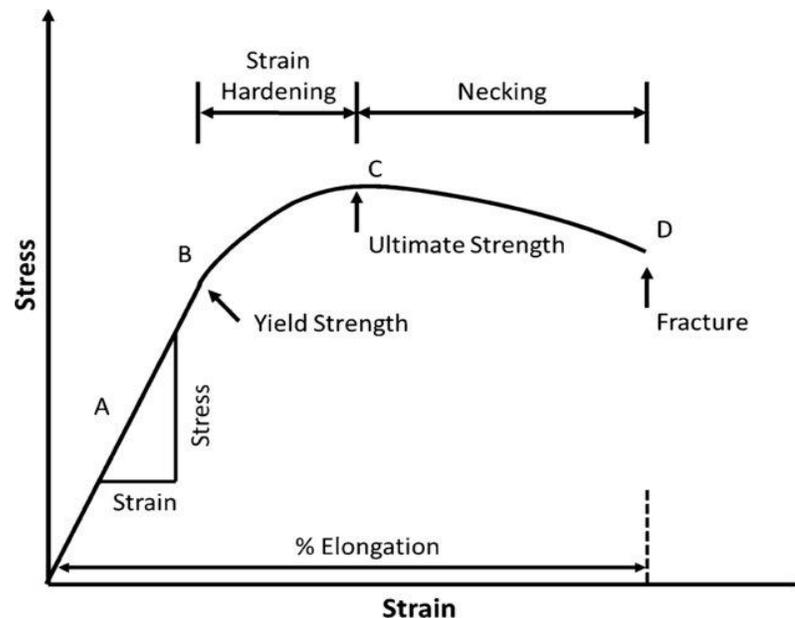
Ecogravel® added in different **weight percentages**:

- 5 %wt.
- 15 %wt.
- 30 %wt.
- 40 %wt.



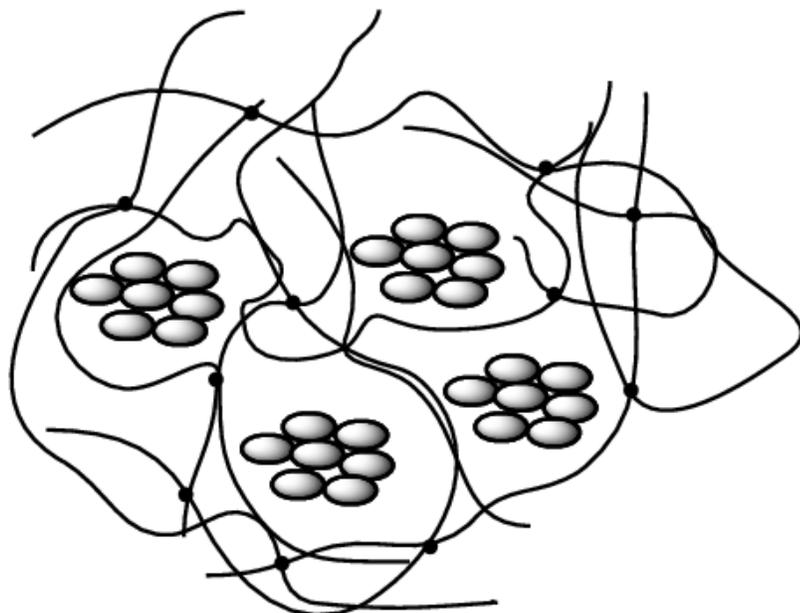
Plastograph

Tensile tests



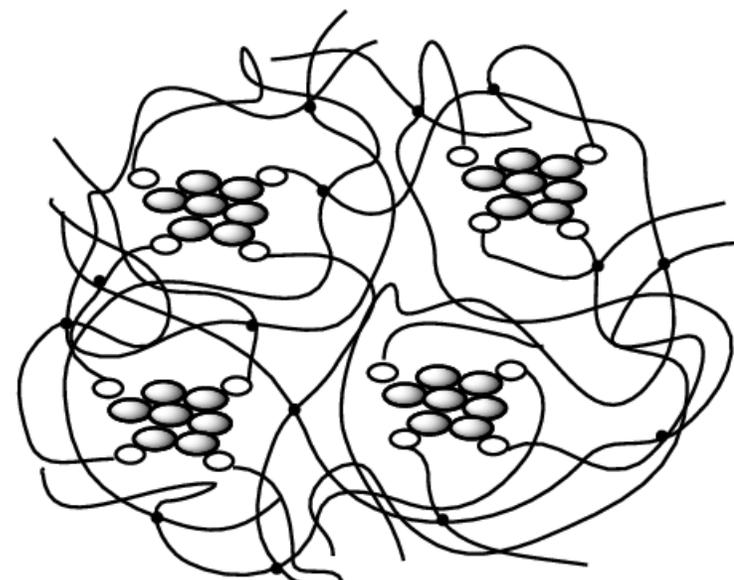
...how to further improve the interaction between the organic and the inorganic fraction?

**Ecogavel®
+
polymer matrix**



Physical interactions

**Functionalization of Ecogavel®
+
Monomer
+
Free radical polymerization**



Chemical interactions

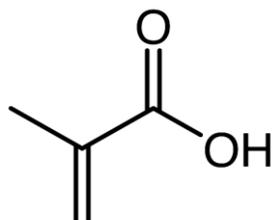
Functionalization and polymerization step

Ecogavel® was **functionalized with methacrylic acid**, since it is well-known the high affinity between carboxylic groups and metal oxides

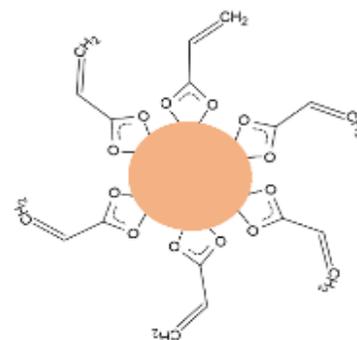
The functionalization was performed by following a **protocol already utilized in our work-group**



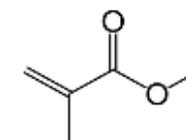
+



Methacrylic acid



Ecogavel® particle
functionalized with
methacrylic acid



MMA + BPO
85 °C, 1 hour



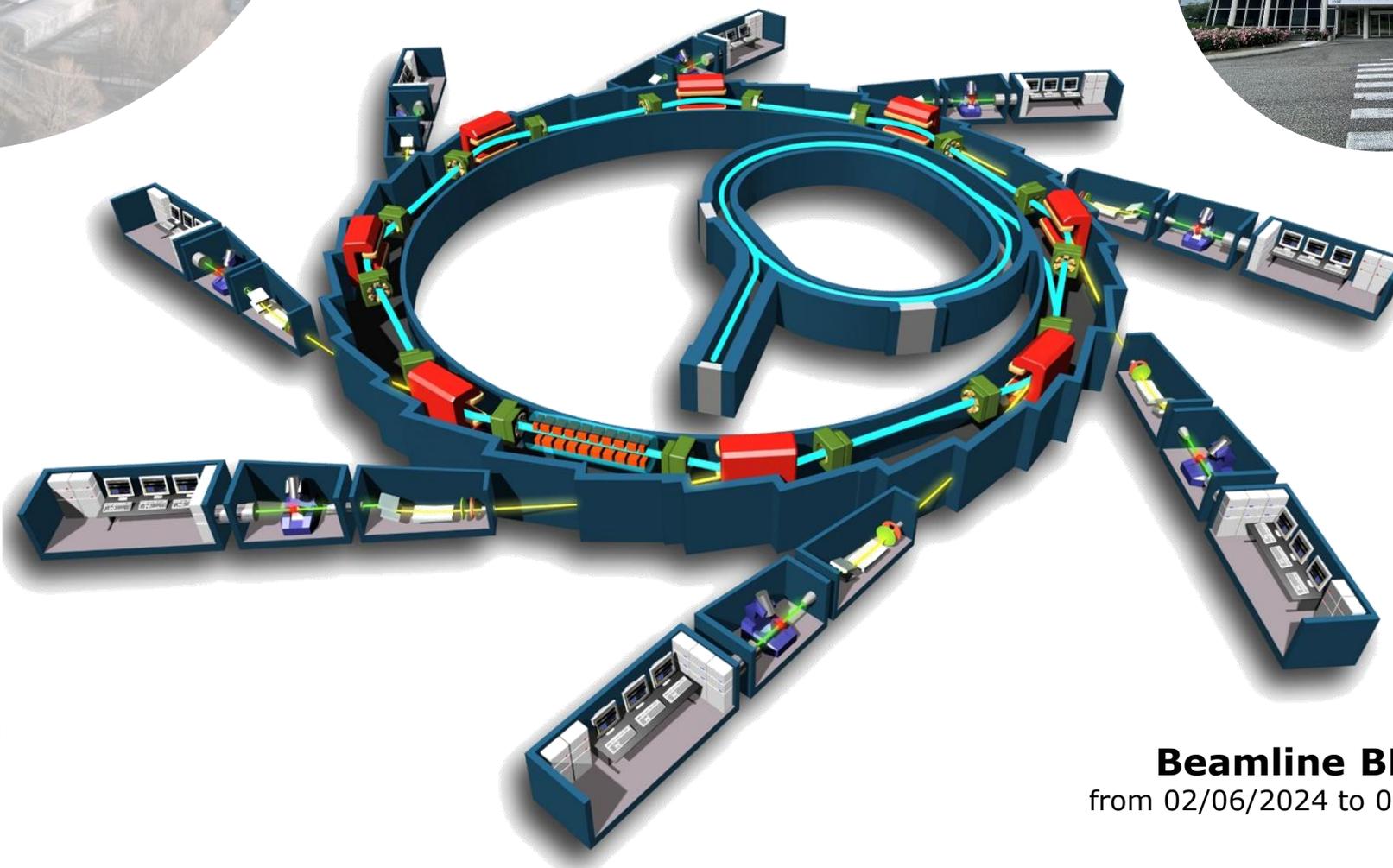
ATR analysis

TGA analysis



UNIVERSITÀ
DEGLI STUDI
DI PADOVA

Synchrotron ESRF in Grenoble



Beamtime STAFF



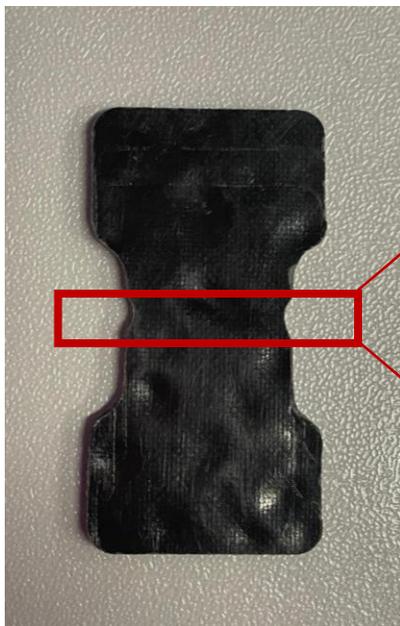
Beamline BM05

from 02/06/2024 to 06/06/2024

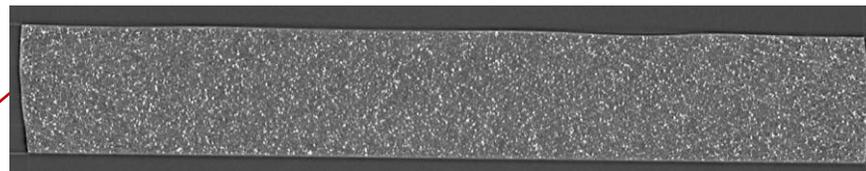


X-ray tomography imaging

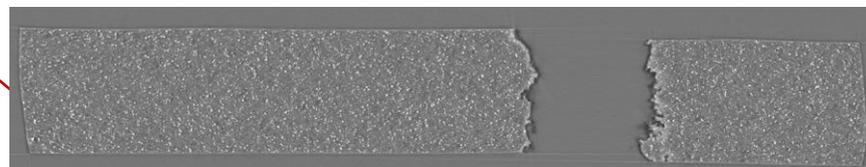
**PMMA with 40
%wt. of Ecogravel®**



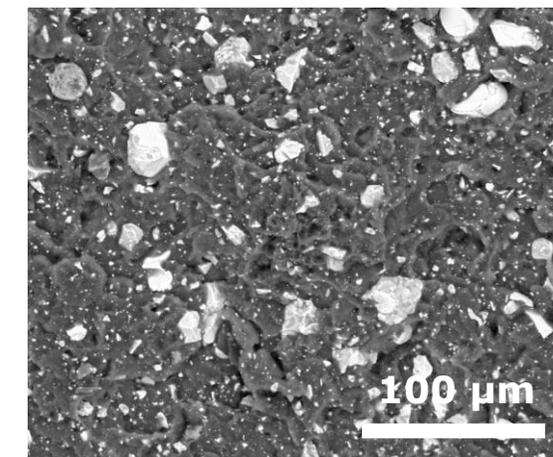
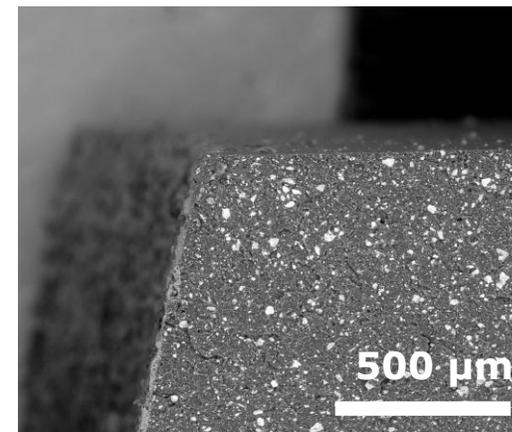
Before the crack



After the crack

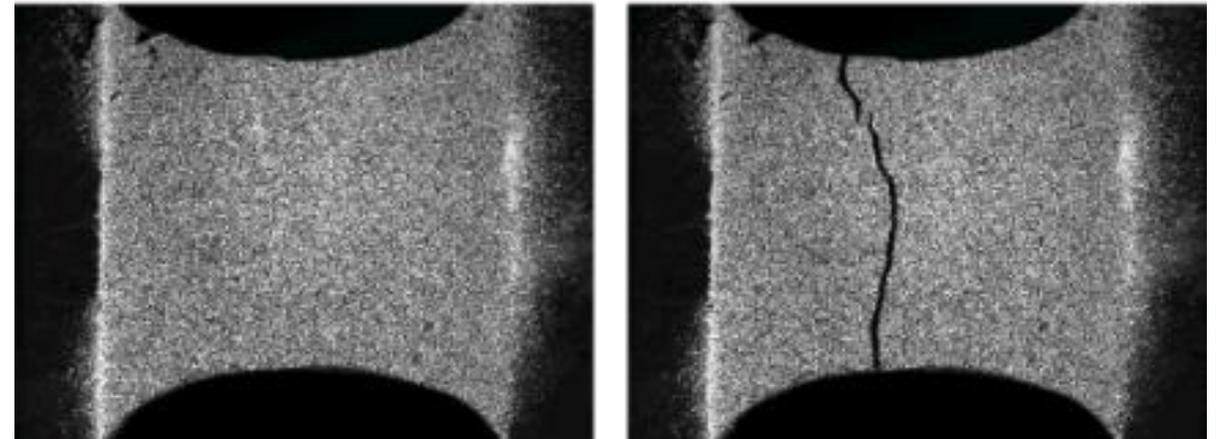
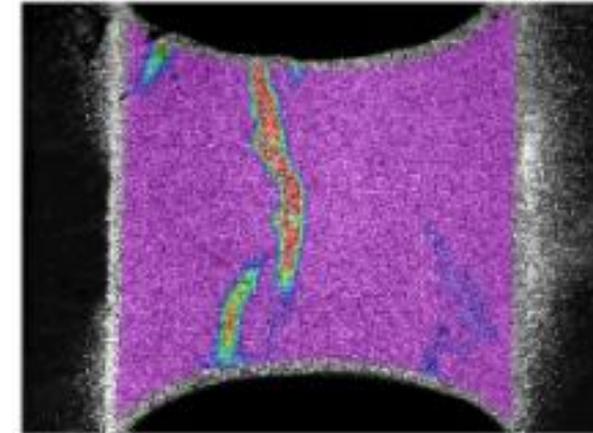
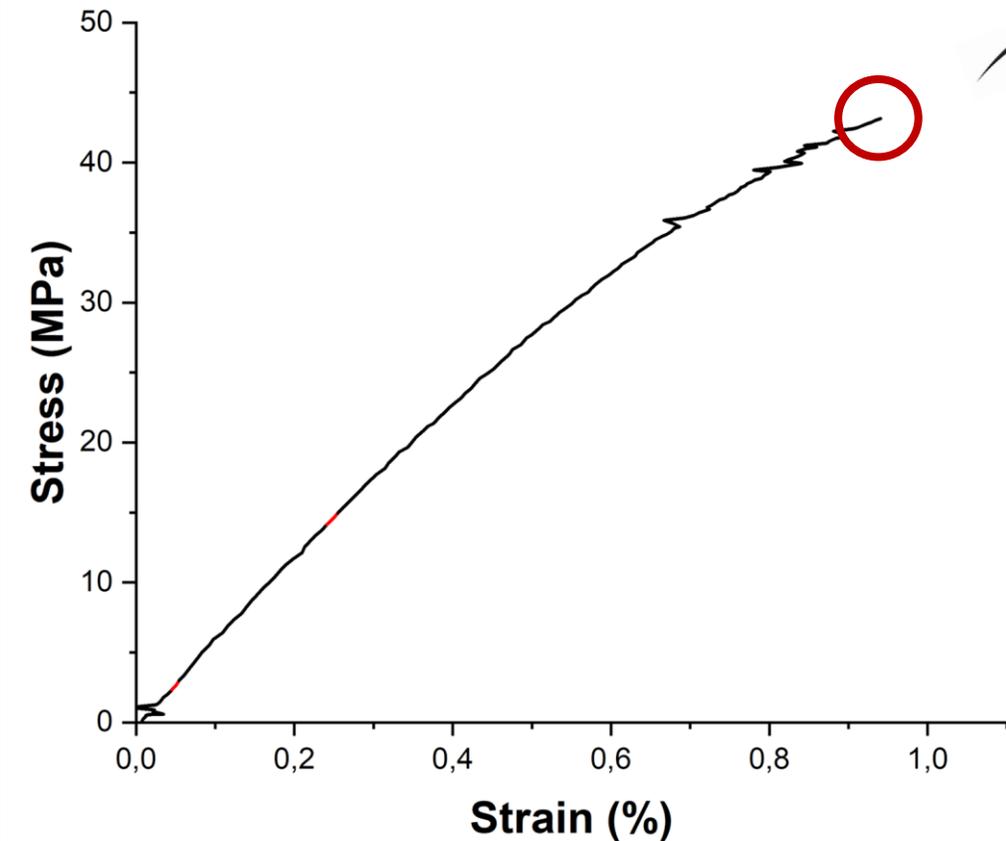


SEM analyses

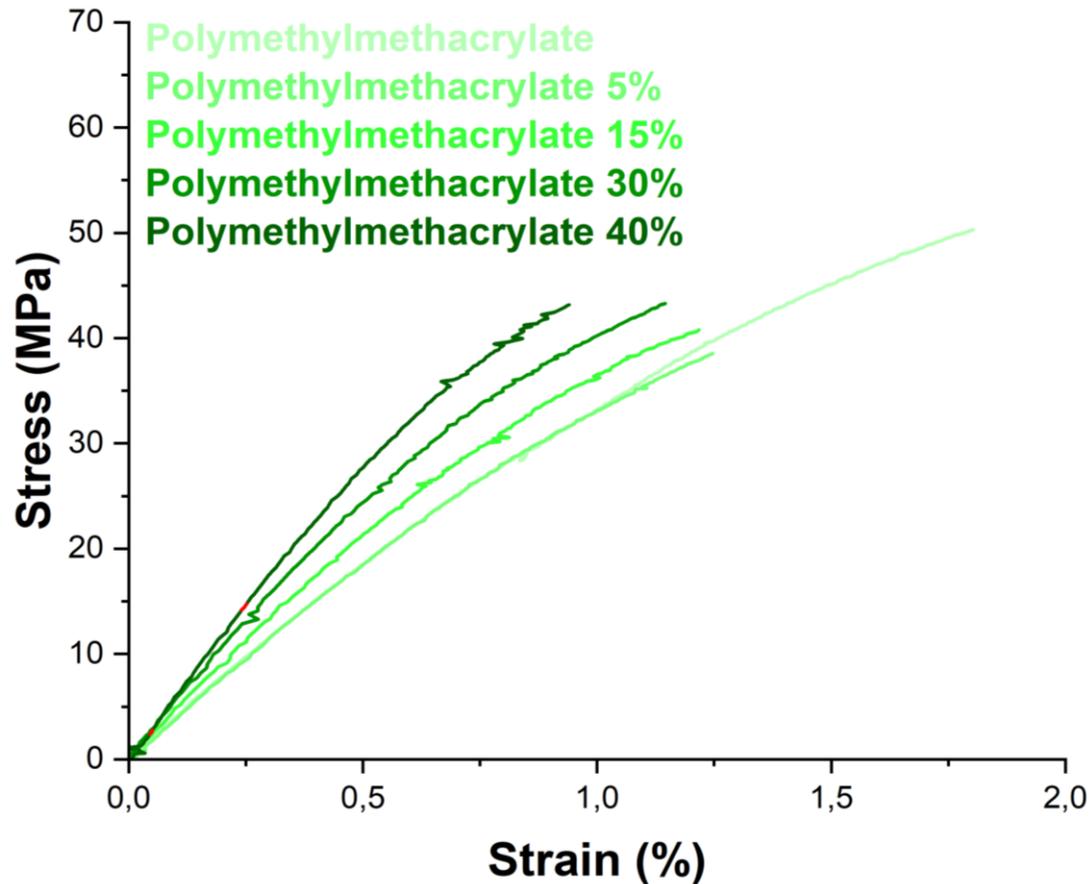


- **Homogeneous distribution** of the slag **into the PMMA** matrix
- **No defects visible on the crack**

PMMA with 40 %wt. of Ecogravel®



Digital Image Correlation was employed to observe the **crack formation** and **propagation** in the dog-bone samples



Ecogravel® content (% wt.) on PMMA	Young's elastic modulus (MPa)	Load at break (N)	Elongation at break (%)
0	3893,2 ± 0,5	1310 ± 20	1,3 ± 0,3
5	3883,4 ± 1,2	1000 ± 15	2,2 ± 0,8
15	4387,1 ± 0,8	1061 ± 18	2,45 ± 0,4
30	5163,3 ± 0,3	1127 ± 22	2,1 ± 0,5
40	5904,7 ± 1,5	1120 ± 21	1,8 ± 0,3

- **Increasing the Ecogravel® concentration** in the PMMA leads to a **more brittle material**, with an **increase in the Young's modulus**
- The **load at break is similar** to all the samples, **as the elongation at break**

Conclusions

PHOSPHORUS REMOVAL:

- **Ecogravel®** demonstrates the highest **P-removal efficiency** at 1:30 solid/liquid ratio at 400 P-mg/L
- **Phosphorus is adsorbed** onto the surface of Ecogravel®, **forming hydroxyapatite**

FILLERS FOR POLYMERS:

- **Ecogravel®** was successfully **incorporated** into different **polymeric matrices** (commercial and synthetic)
- By **increasing the slag** into the polymer a **change in the mechanical properties** was observed, from Young's modulus to load at break

Future perspectives

POLLUTANTS REMOVAL:

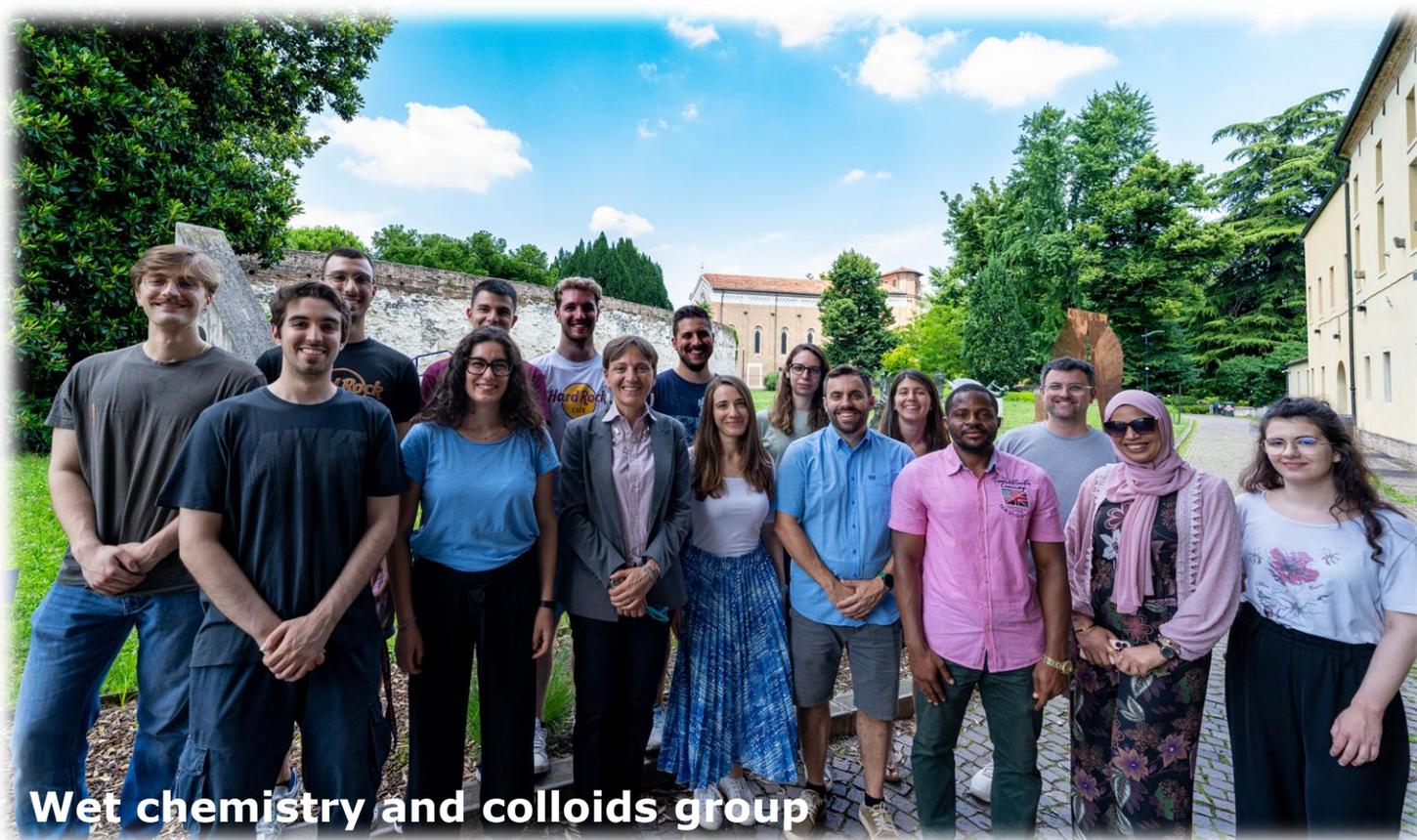
- **Recovery of phosphorus** through leaching processes
- **Test the removal of other pollutants** (e.g., nitrates, sulfates, p-nitrophenol)

FILLERS FOR POLYMERS:

- **Complete the mechanical tests** (i.e., flexural and compression tests)
- **End-of-waste procedure** on the best polymers
- **Extrusion** of different polymers **at Belluno Plast S.p.A.**



...what's next?



Wet chemistry and colloids group



Acknowledgements:

Dr. Annalisa Sandon, Dr. Mirko Prato for the measurements and prof. Patriarca and Boaretti for the experimental support



Thank you for your kind attention!

