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Sustainable management of oil refining sludge by means of geopolymers production

Universidad de Jaén

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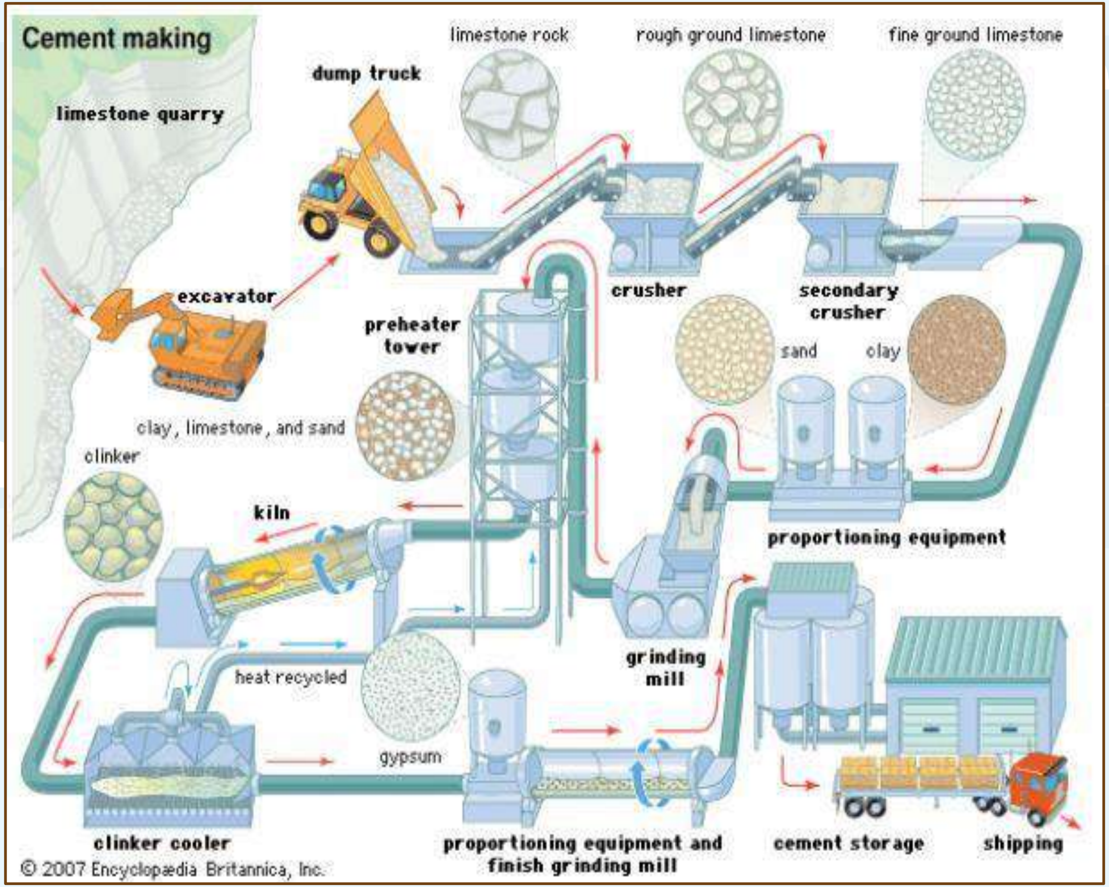
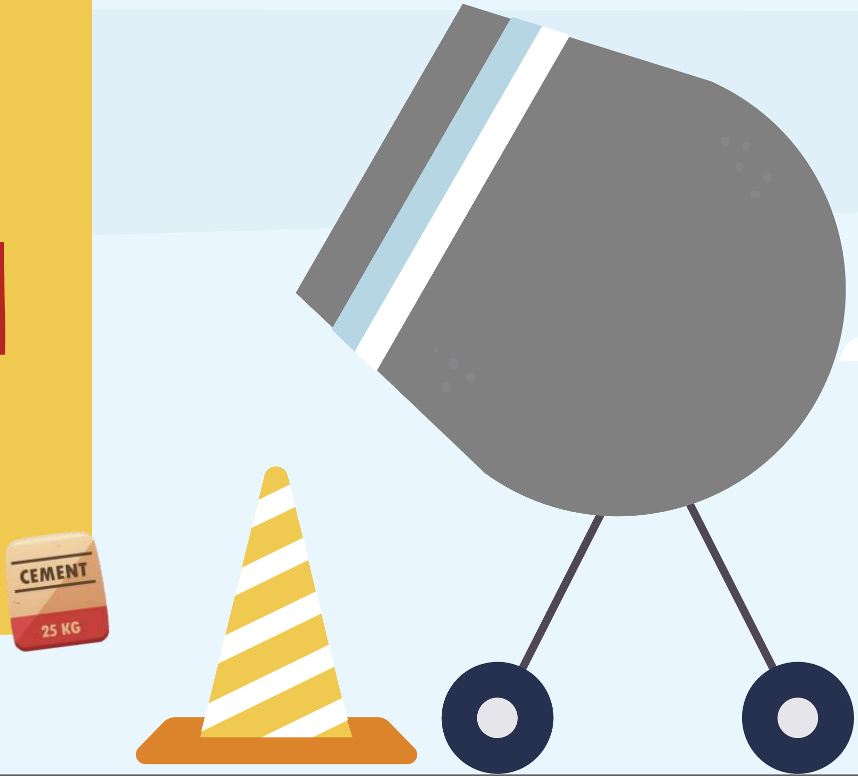


Portland Cement Production

Environmental problems

- Clinker production requires high temperatures (1450°C)
- 5-7% of global CO_2 emissions
- Extraction of raw materials

Alternative to Portland cement?



Sustainable management of oil refining sludge by means of geopolymers production

Industrial waste

↓

Environmental problems

- Huge amount of waste accumulates in landfills
- No chance of being reused

Oil refining sludge

Chamotte

Rice husk ash

Other use or application for industrial waste?

Sustainable management of oil refining sludge by means of geopolymers production

Alternative to Portland cement?

Another use or application for industrial waste?

→ **Geopolymers**

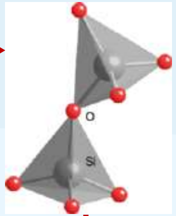
Resulting from

- Are Inorganic aluminosilicates
- 3D Amorphous Structure

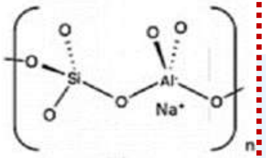
Reaction of Geopolymerization

Chemical reaction with low Tª

Form tetrahedral units (Td)



Sialat



$M_n\ (-(SiO_2)_z - AlO_2)_n * wH_2O$

Setting and hardening

Structure formed by polymer chains

It is necessary

1. **PRECURSOR**
   Material composed of Al and Si
2. **ACTIVATOR**
   Alkaline solution

Advantages

- Cementitious properties comparable to PC.
- Low emissions of CO_2
- Excellent properties:
  - Durability
  - Stability
  - Mechanical resistance

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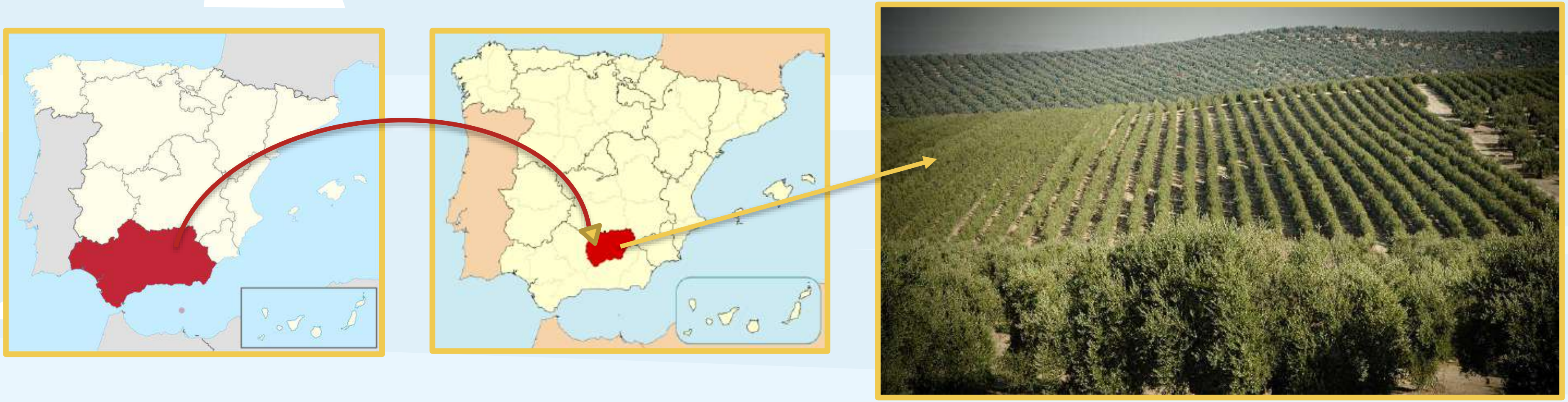
OBJETIVE

The main objective of this study is the development of **new geopolymeric** materials **using water treatment sludge from the oil refining industry** as a raw material, in order to valorise a new type of raw material that has not been used in the production of these materials.

Sustainable management of oil refining sludge by means of geopolymers production

1. Raw Material



Andalucía

There are 1.65 million hectares of olive groves

Season

4 million tonnes of olives are produced in an average olive season

Olive oil

Of this, around 3.7 million t/year are used for the production of olive oil

1. Raw Material

From olive oil production

Waste

Oil sludge

Raw material for the production of gepolymers

2. XRF of Raw Material

Oil sludge → Alumina-rich waste

Should be combined with silica-rich wastes

Chamotte

Rice husk ash

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	LOI
Oil Sludge (OS)	2.11	53.55	0.710	0.759	0.311	6.29	0.358	3.70
Chamotte (CH)	63.08	12.11	4.67	8.67	1.88	0.471	3.25	3.60
Rice husk ash (RHA)	73.60	-	0.286	0.780	0.720	0.144	1.63	20.83

Table 1. Chemical composition (XRF) of raw materials

2. XRF of Raw Material

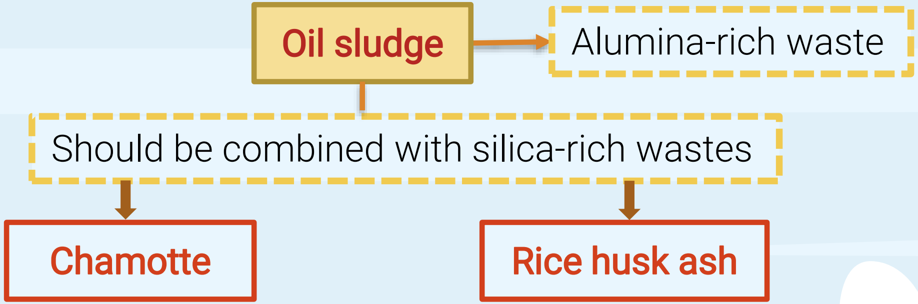


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Table 1. Chemical composition (XRF) of raw materials

3. Preparation of Raw Materials

1. Dry
2. Calcine (if necessary)
3. Crush
4. Grind
5. Sieve (0.100 mm)

The process takes weeks

Wastes used as raw materials

Oil sludge

Chamotte

Rice husk ash

4. Preliminary studies for the production of geopolymers

Precursors

- 100% Oil Sludge (OS)
- 80% Oil Sludge (OS) + 20% Rice husk ash (RHA)
- 80% Oil Sludge(OS) + 20% Chamotte (CH)

Activator : commercial solution

- Solution of 100% NaOH
- Solution of NaOH and Na_2SiO_3 at 50%.

+

NaOH

98 % purity

Na_2SiO_3

29.2 % SiO_2
8.9 % Na_2O
61.9 % H_2O

Compressive Strength

Precursors	7 days (MPa)	28 days (MPa)
100% Oil Sludge (OS)	2.3	6.6
80% Oil Sludge (OS) + 20% Rice husk ash (RHA)	8.8	9.6
80% Oil Sludge(OS) + 20% Chamotte	7.1	7.8

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Oxide content (%)	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	LOI
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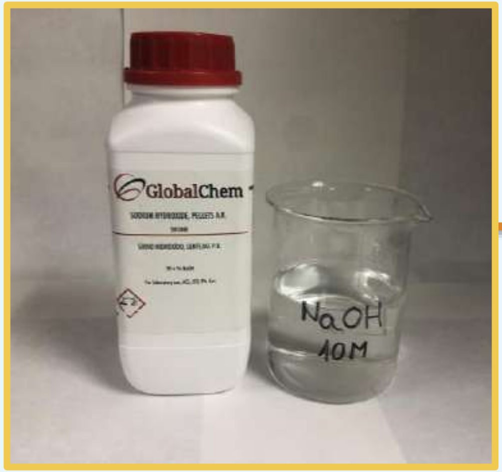
Problems with the commercial activator

Low mechanical strength

Specimens break in contact with water

5. Manufacture of geopolymers with alternative activator

Preparation of the alternative activator



1. A 10M NaOH solution is mixed with diatomites

2. 6 hours in the reactor with stirring at 80°C.

3. Vacuum filtration

4. Alternative activator

6. Mixtures

The first mixture was 100% of OS, (which could not be produced because the mixture was cracked) then the OS was substituted at different percentages by the precursor RHA or CH: 5%, 10%, 15%, and 20% (by weight).

Mix	OS (g)	RHA (g)	Relation L/S
100% OS	150	0	❌
5% OS	7.5	142.5	1.55
10% OS	15	135	1.55
15% OS	22.5	127.5	1.55
20% OS	30	120	1.55

Mix	OS (g)	CH (g)	Relation L/S
100% OS	150	0	❌
5% OS	7.5	142.5	1.45
10% OS	15	135	1.45
15% OS	22.5	127.5	1.45
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Table 2. Mix proportions for assessed simples.

7. Manufacture of geopolymers with alternative activator

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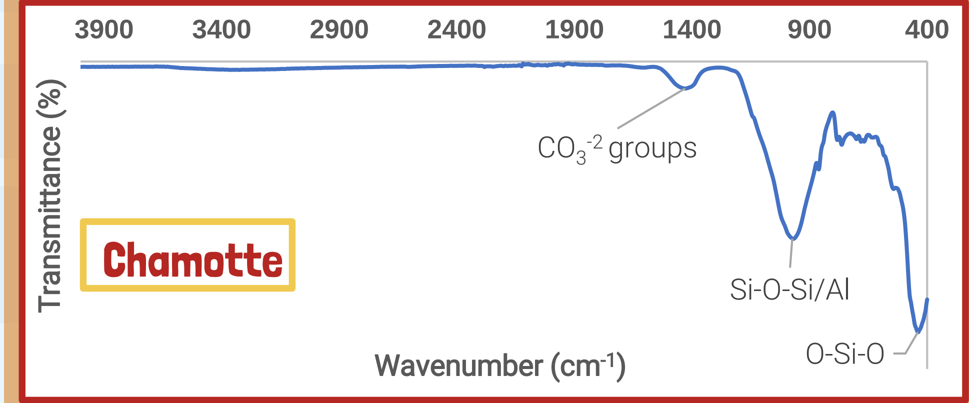
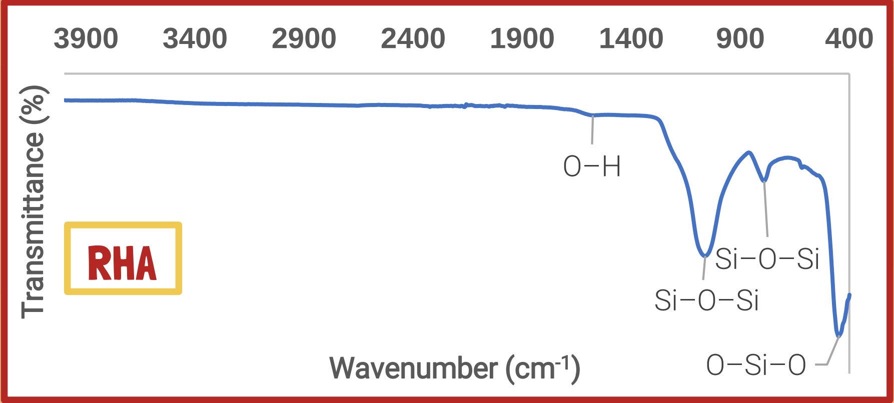
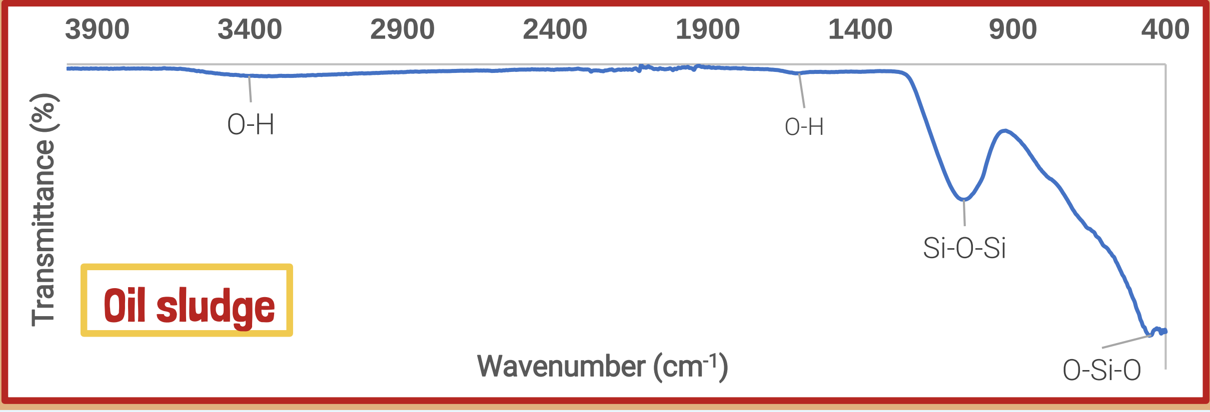
8. FTIR of Raw materials

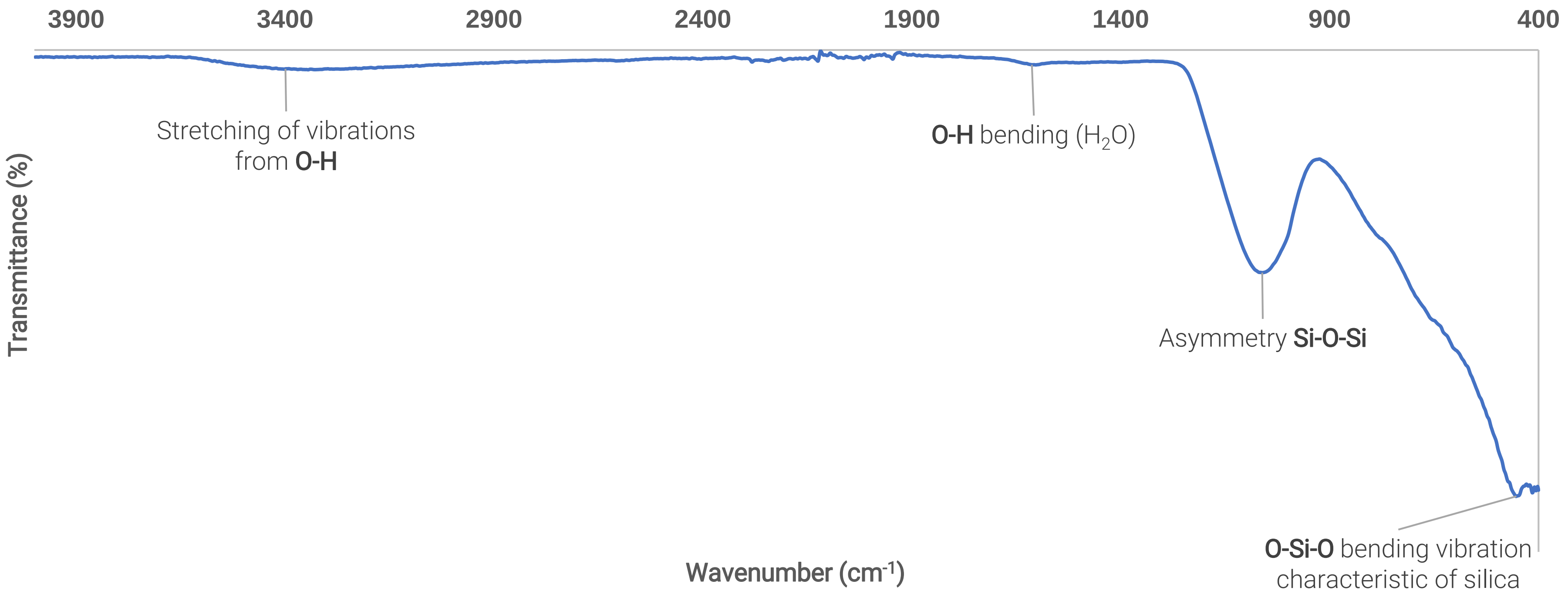






8. FTIR of Raw materials

FTIR of Oil sludge



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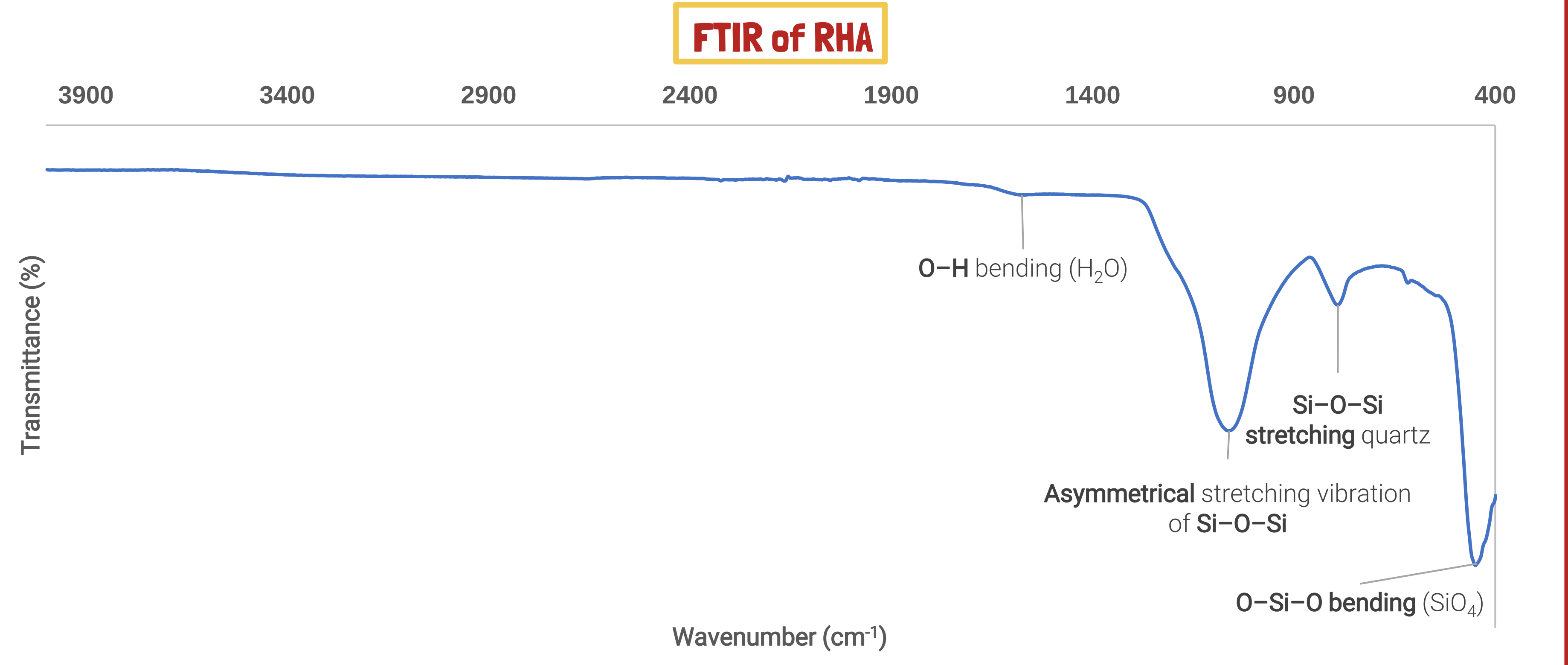
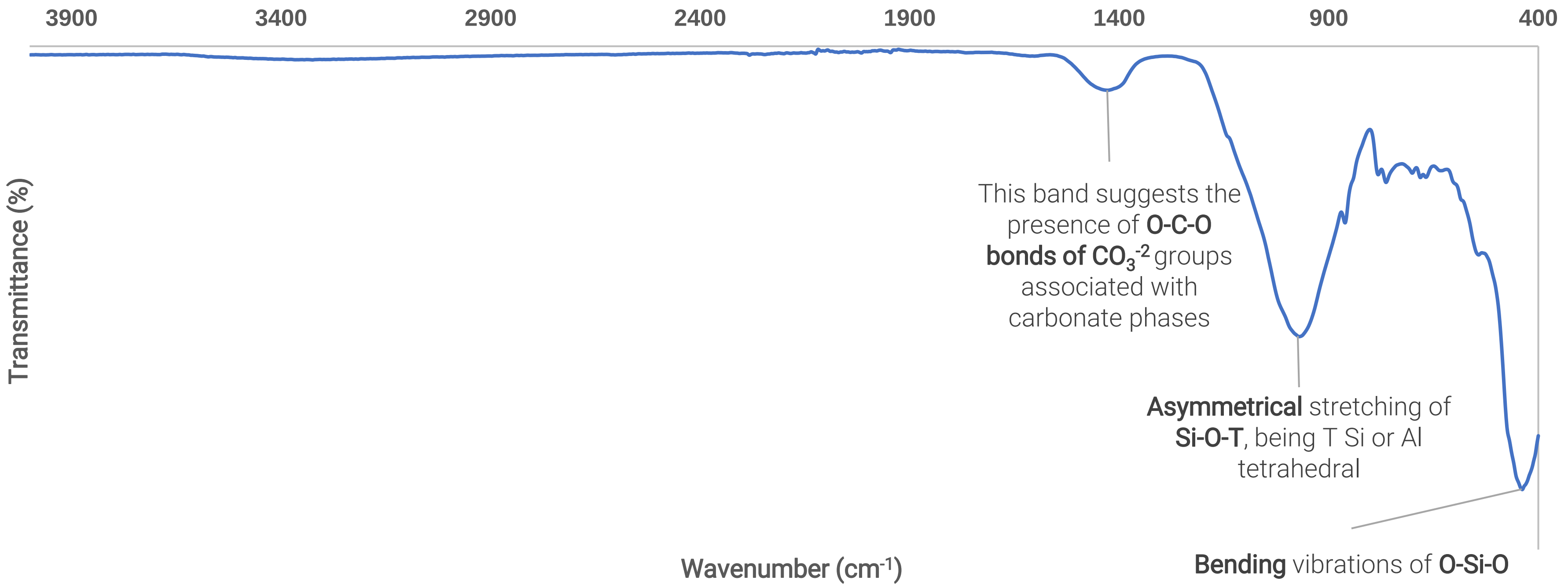
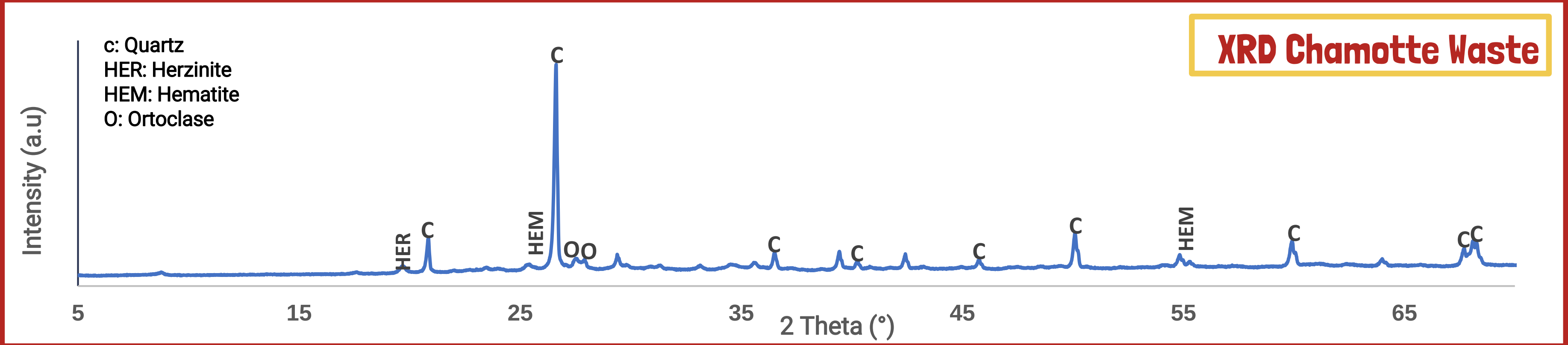


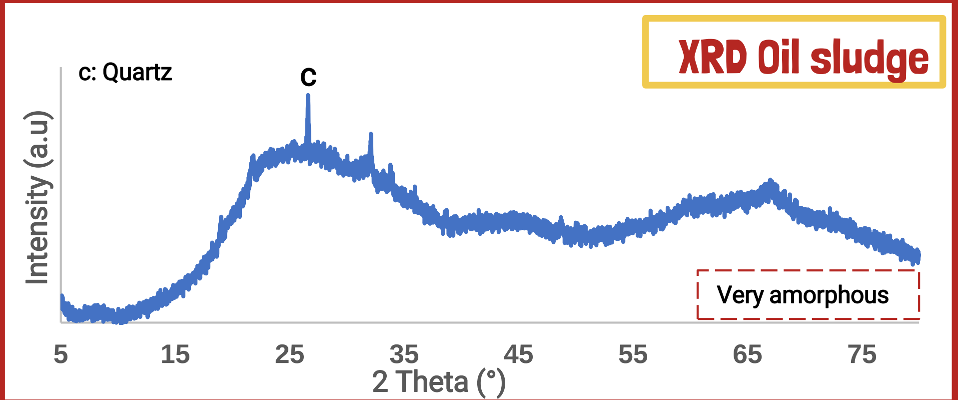
8. FTIR of Raw materials

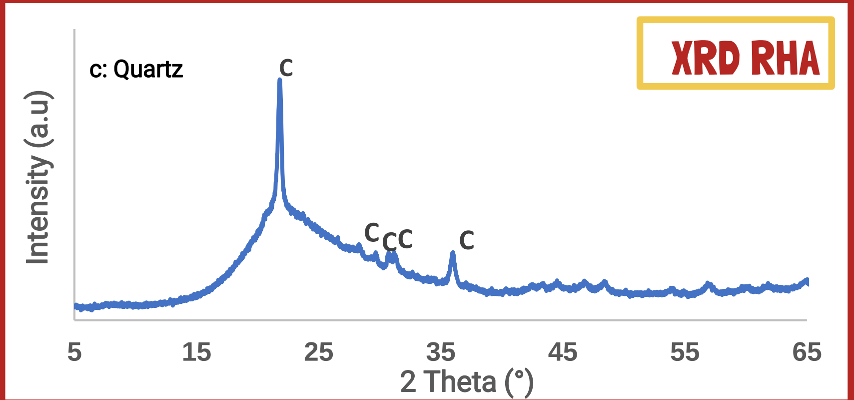
FTIR of Chamotte



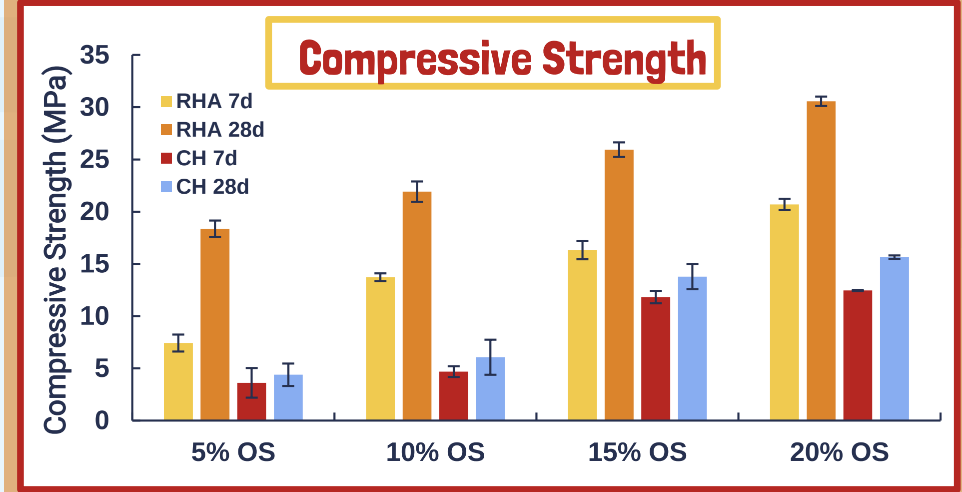
9. XDR Raw materials

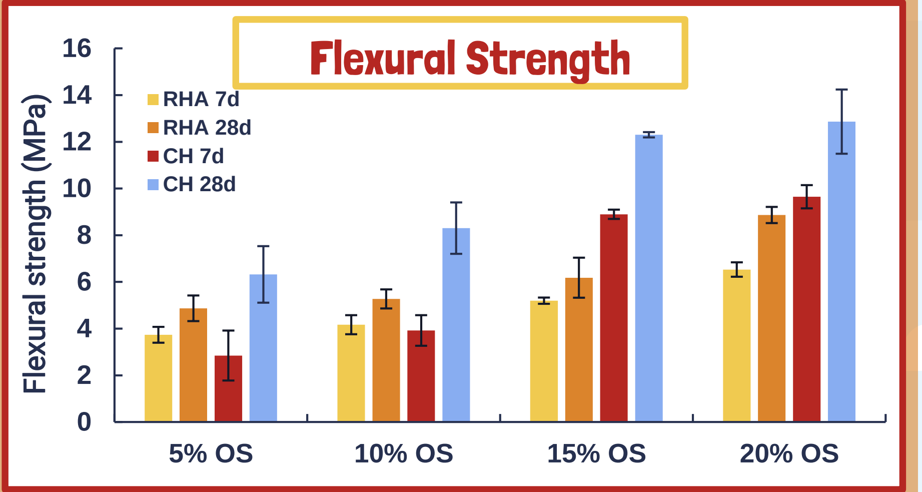






10. Mechanical and physical tests





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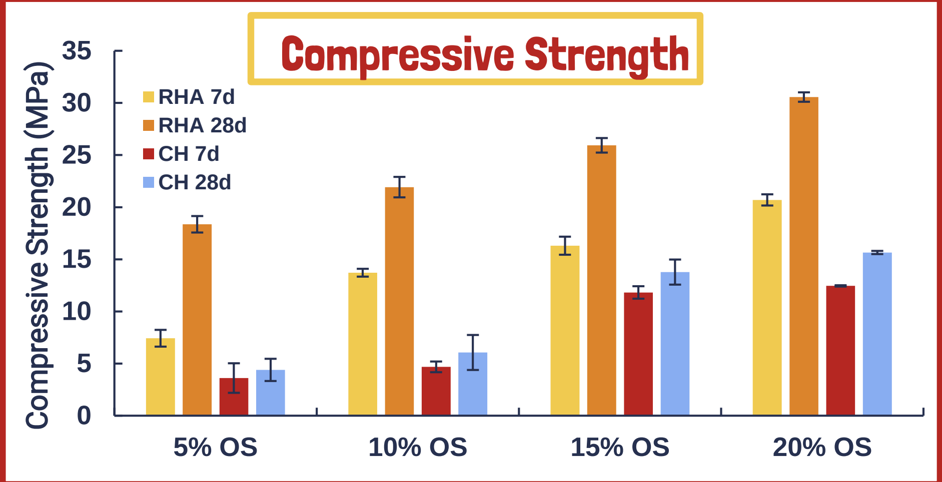

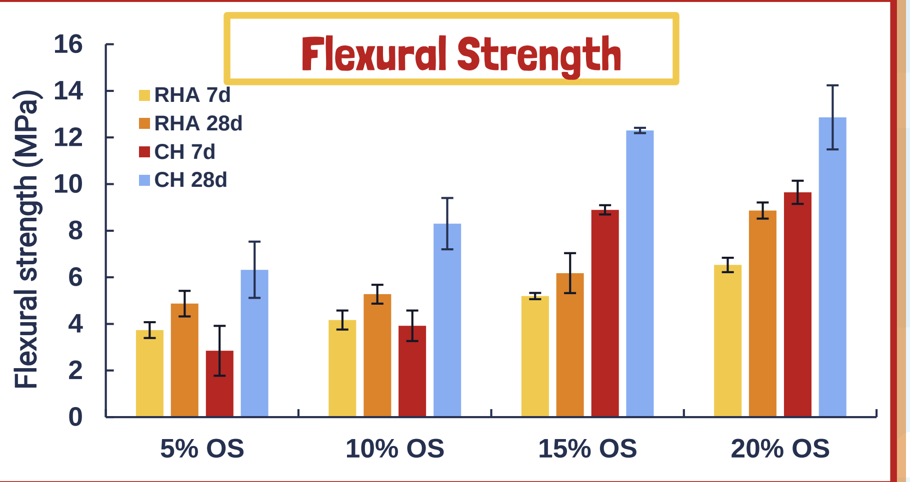

- Compressive strength increases with higher percentages of oil sludge (OS).
- Higher strengths are achieved with RHA residue.
- Maximum strengths are achieved at 28 days of curing with 20% oil sludge (OS), reaching 36.6 MPa with the RHA residue, while 15.7 MPa is achieved with the CH residue.

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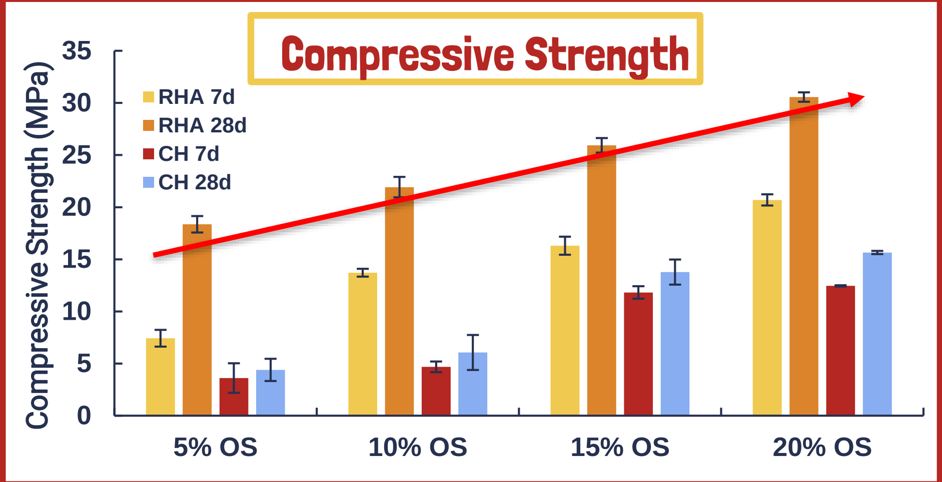

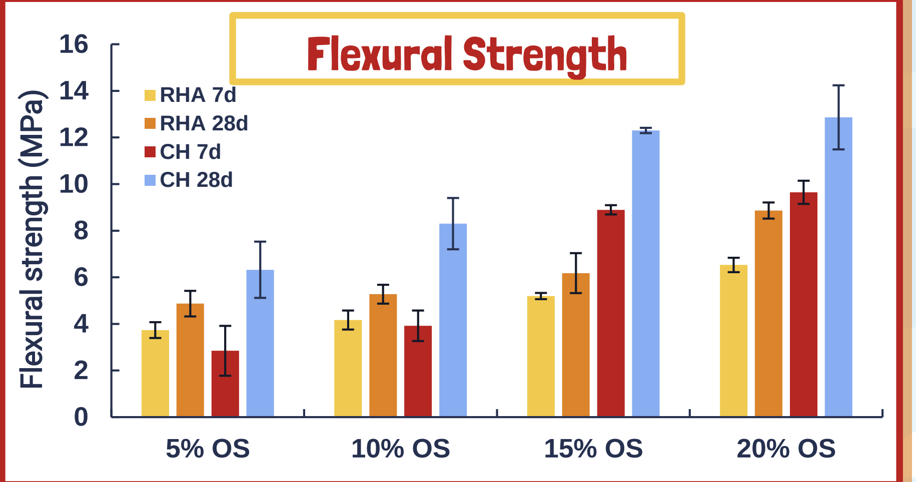

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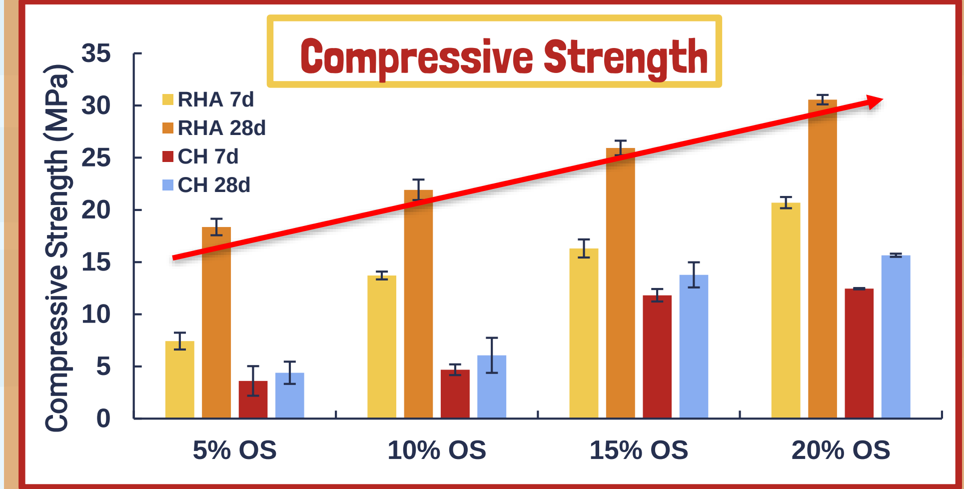

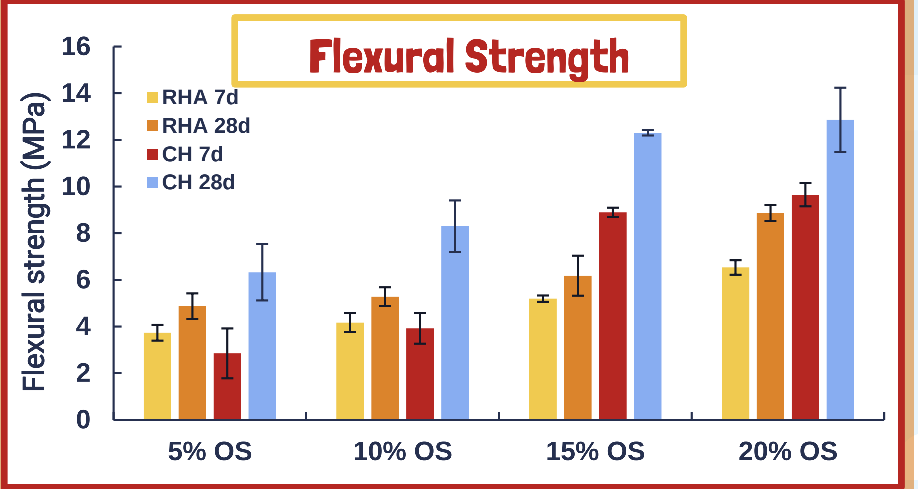

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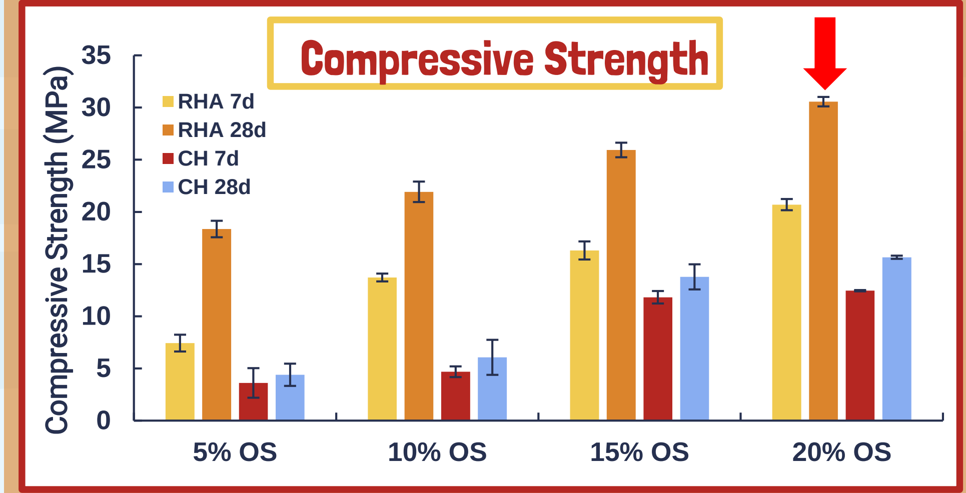

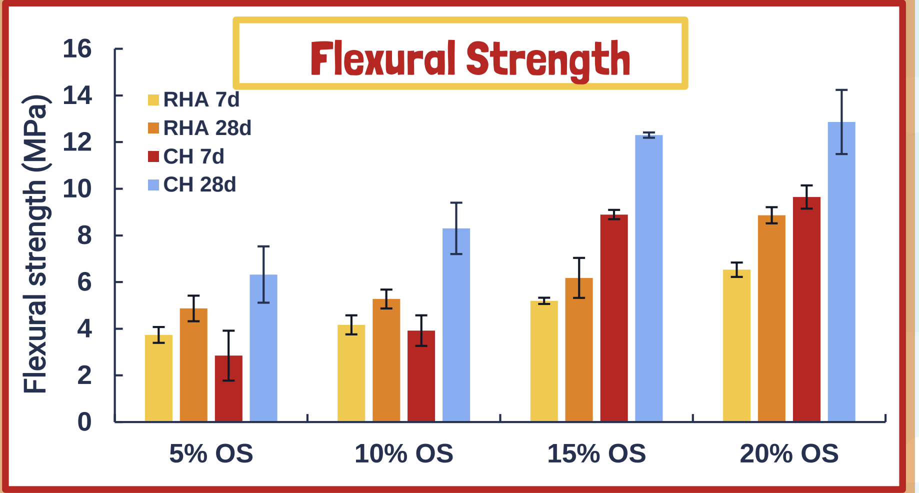

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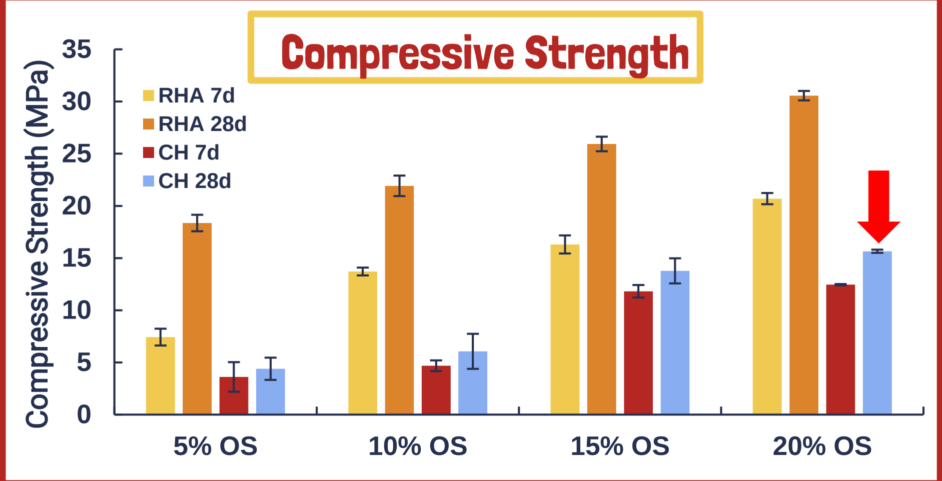

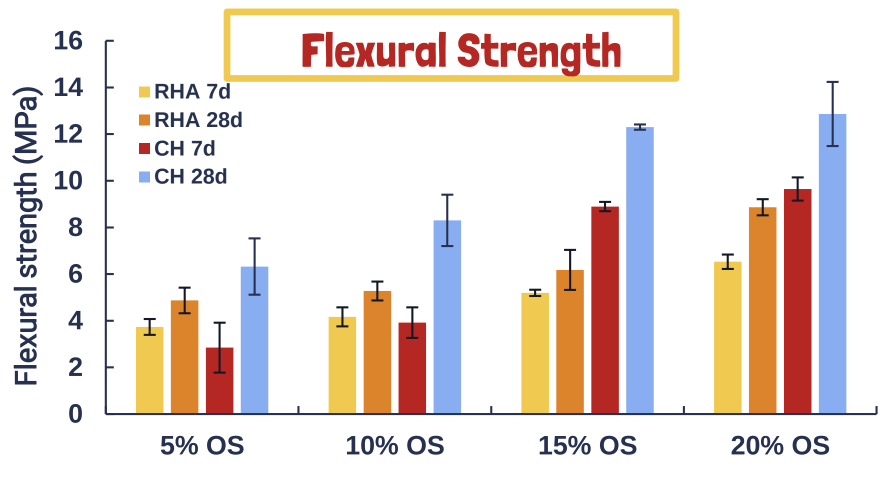

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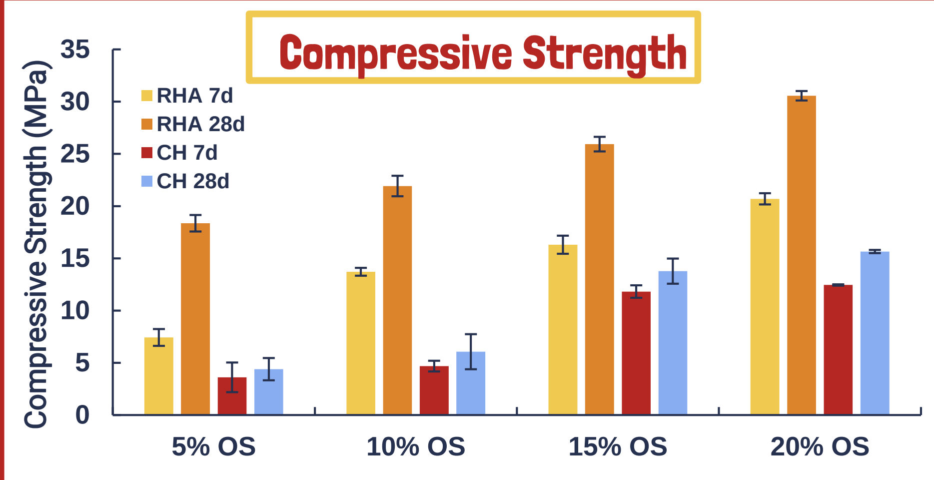

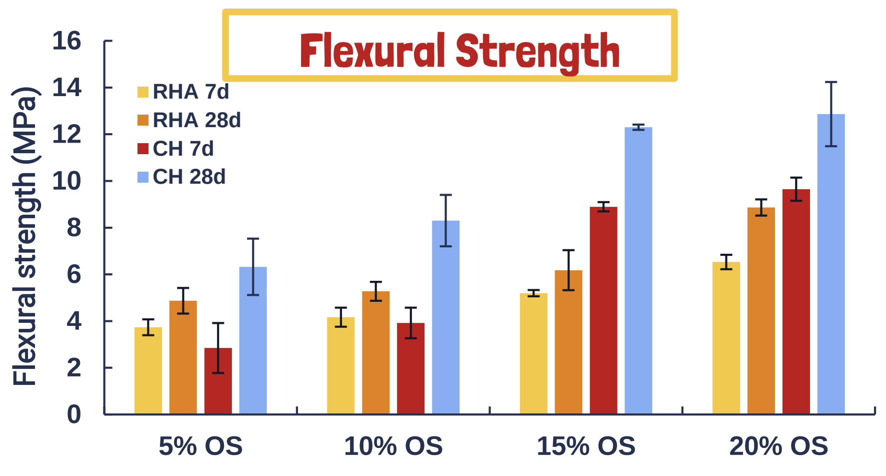

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- Flexural strength increases with higher percentages of oil sludge.
- Higher strengths are achieved with the CH residue.
- The maximums are achieved at 28 days of curing with 20% oil sludge, reaching 12.6 MPa with the CH residue, while 8.87 MPa is reached with the RHA residue.

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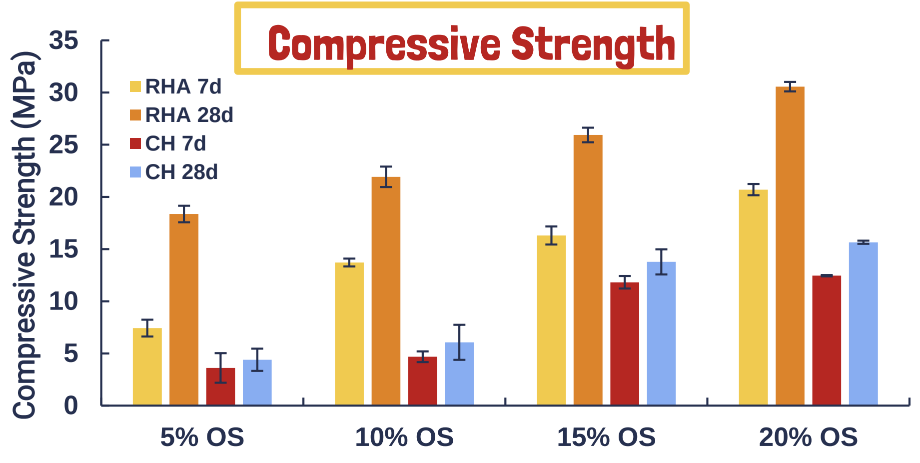

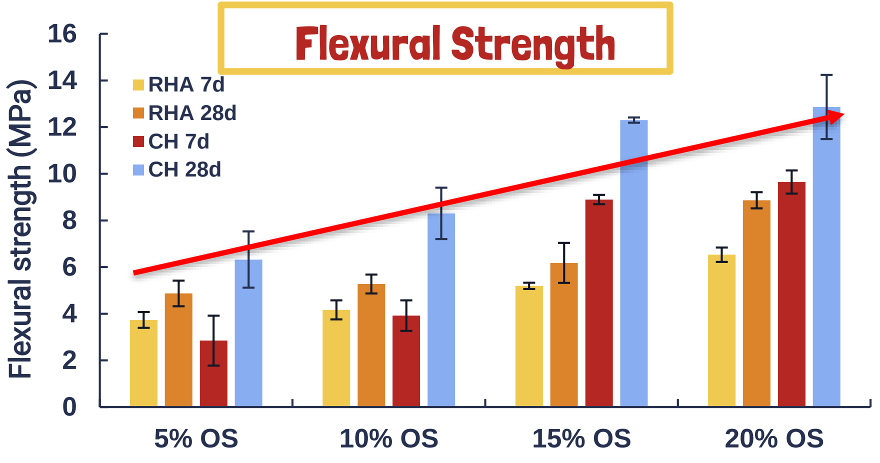

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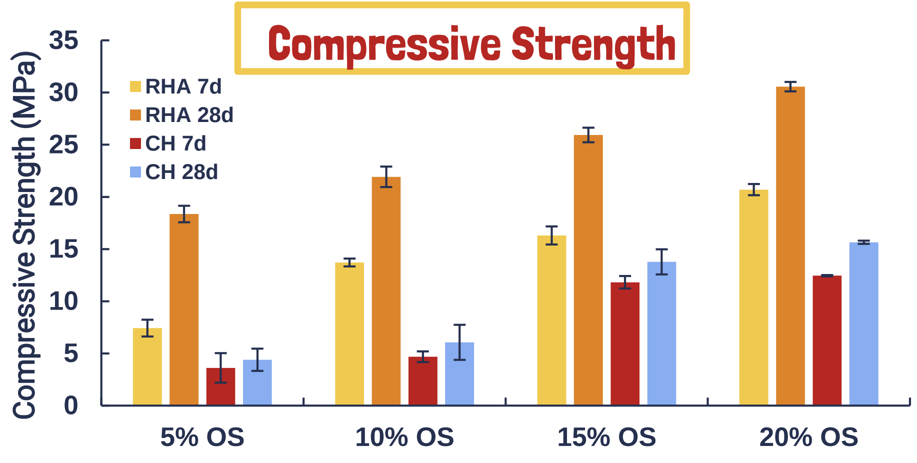

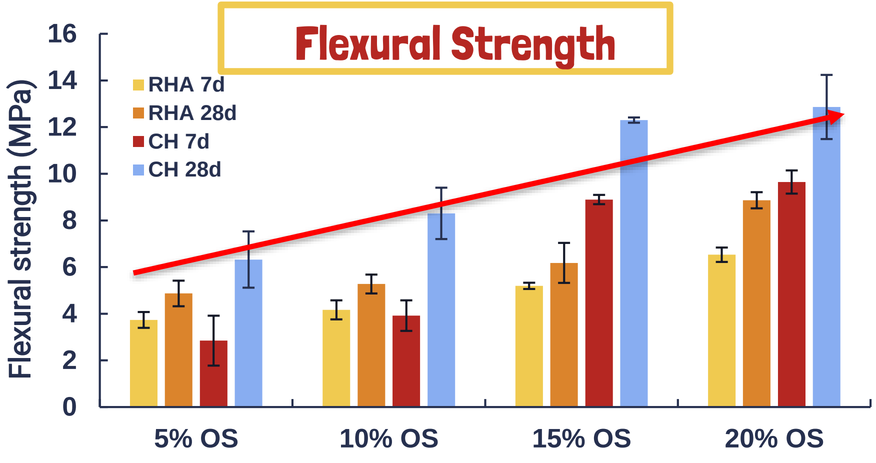

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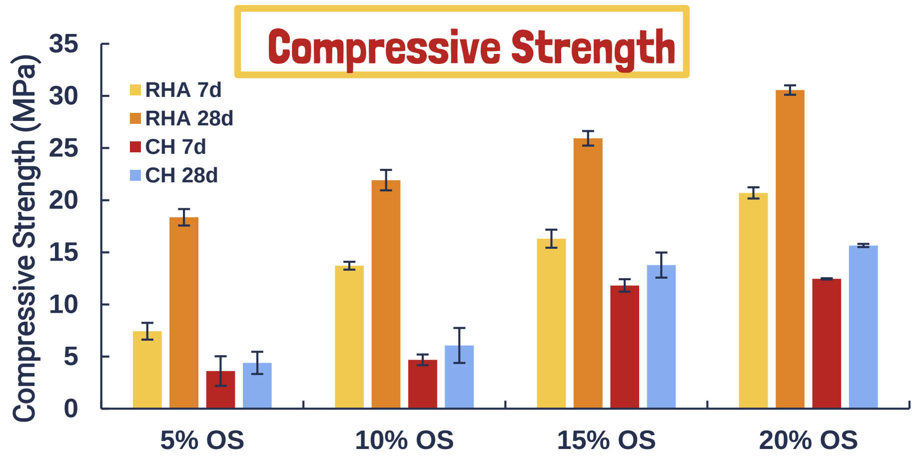

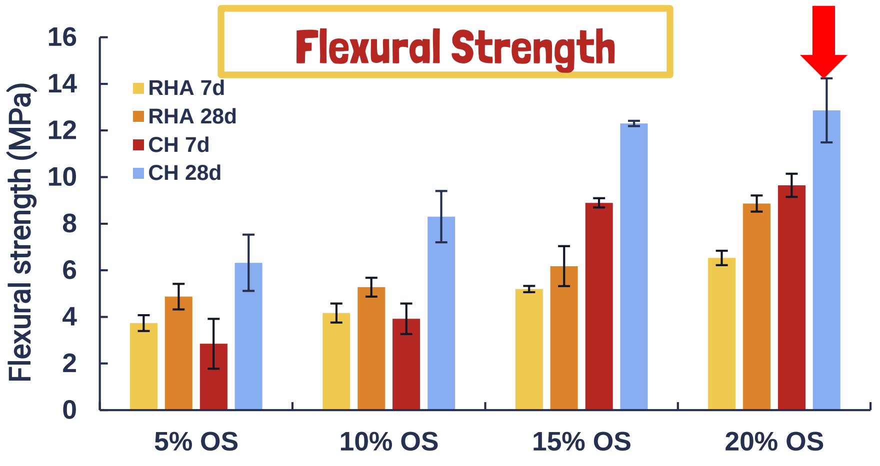

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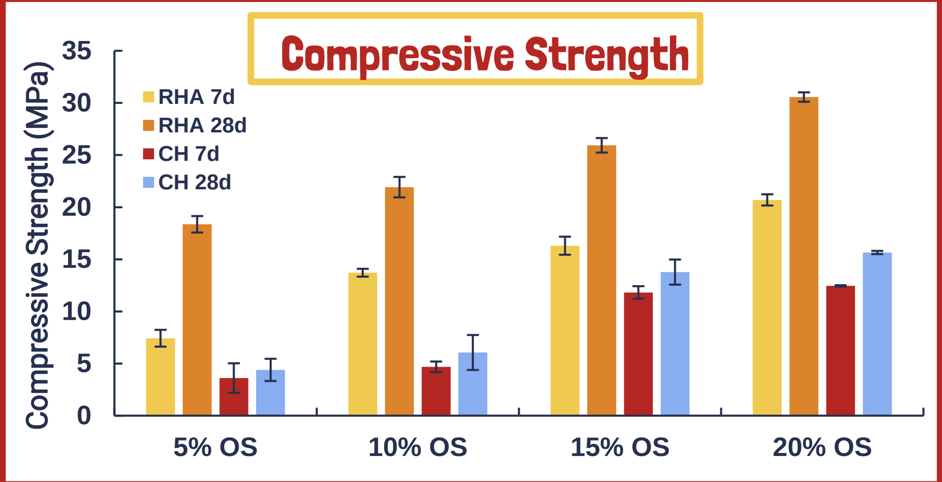

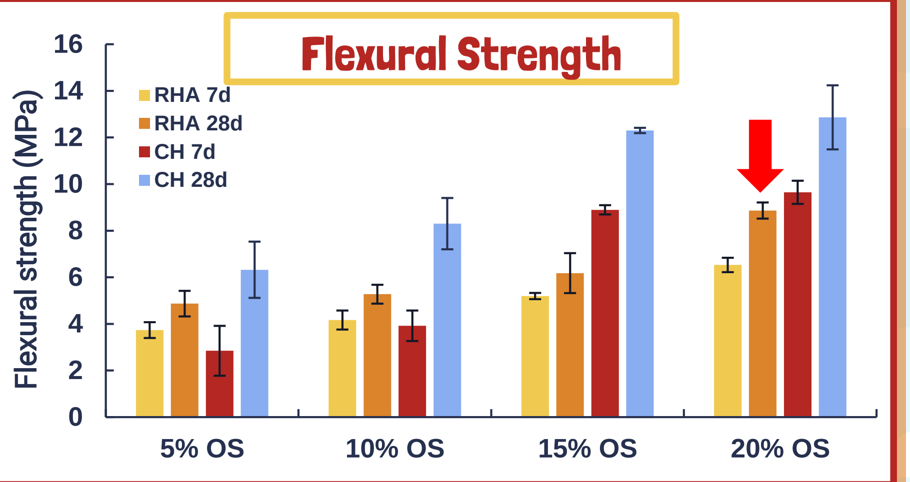

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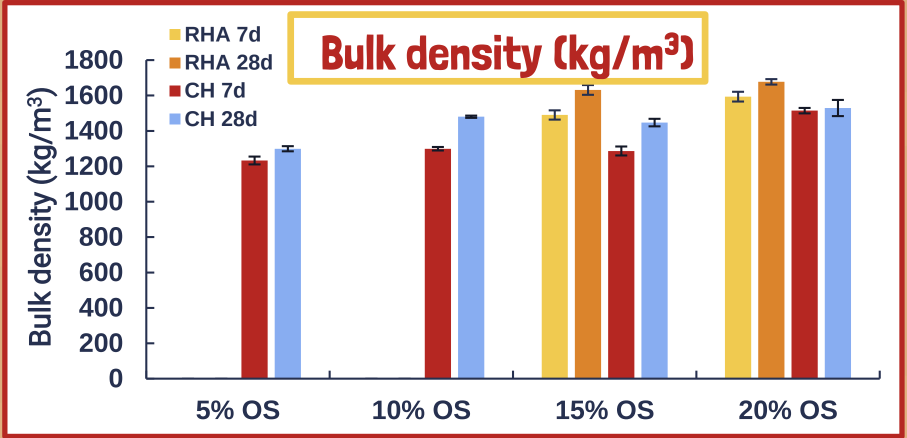
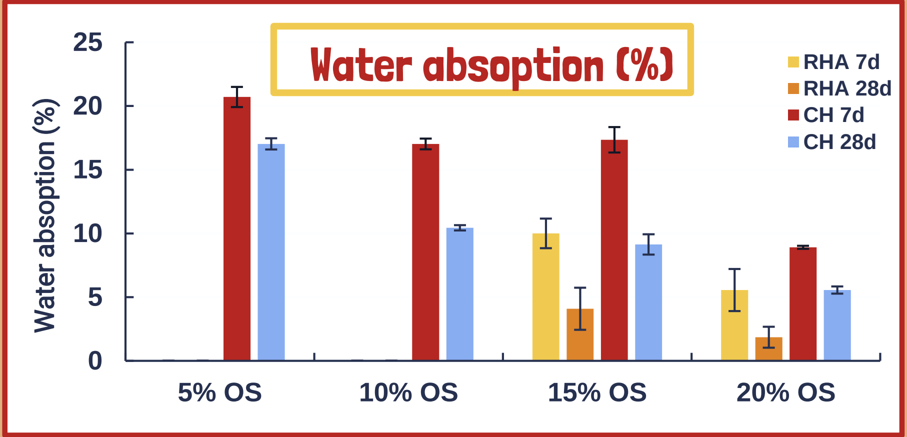

Bulk density (kg/m³)
RHA 7d
RHA 28d
CH 7d
CH 28d
Bulk density (kg/m³)
1800
1600
1400
1200
1000
800
600
400
200
0
5% OS
10% OS
15% OS
20% OS


Water absoption (%)
RHA 7d
RHA 28d
CH 7d
CH 28d
Water absoption (%)
25
20
15
10
5
0
5% OS
10% OS
15% OS
20% OS

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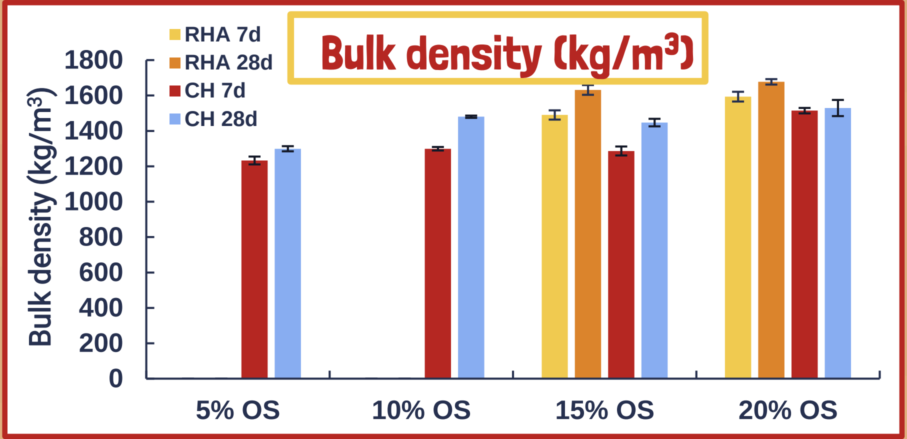
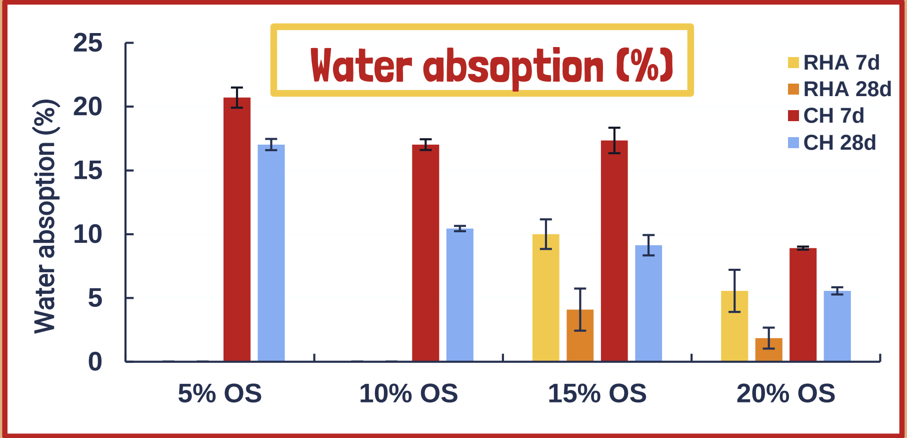
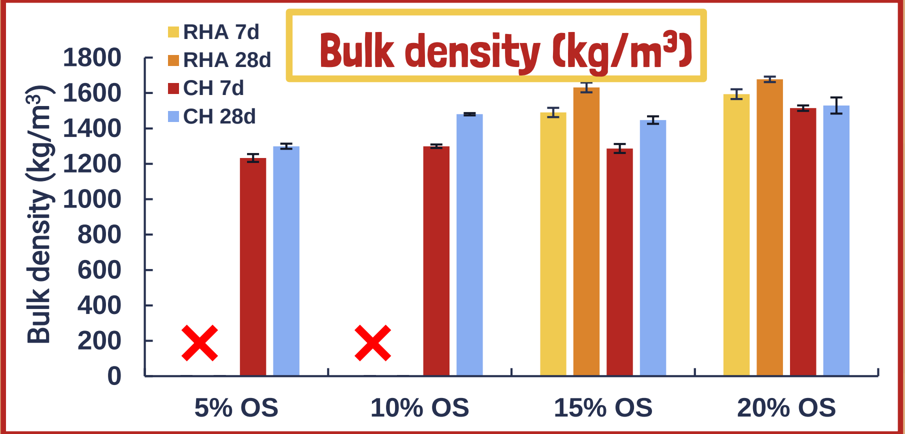
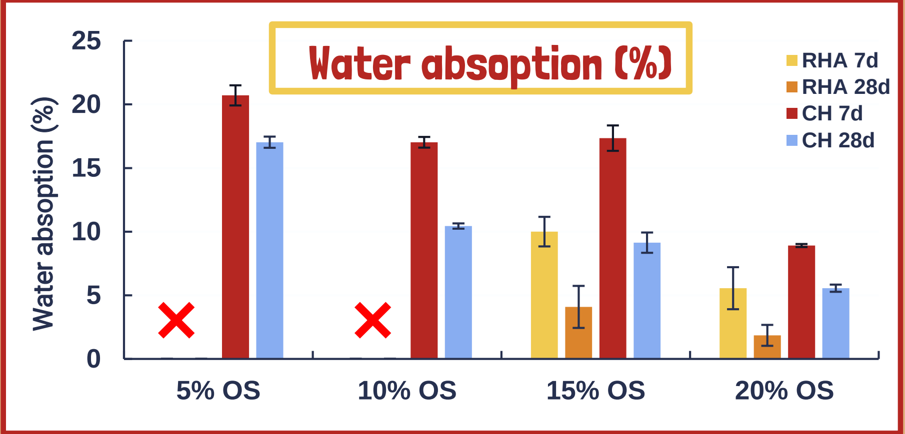




- The test specimens with **5% and 10% oil sludge** with the **RHA** residue were **broken in water**.
- Bulk density is similar, reaching maximums with 20% oil sludge.
- The lowest water absorption is reached at 28 days of curing with 20% oil sludge.
- The lowest absorption occurs with the RHA residue.
- Higher compressive strengths produce higher densities and lower water absorption.

Sustainable management of oil refining sludge by means of geopolymers production





- The test specimens with **5% and 10% oil sludge** with the **RHA** residue were **broken in water**.
- Bulk density is similar, reaching maximums with 20% oil sludge.
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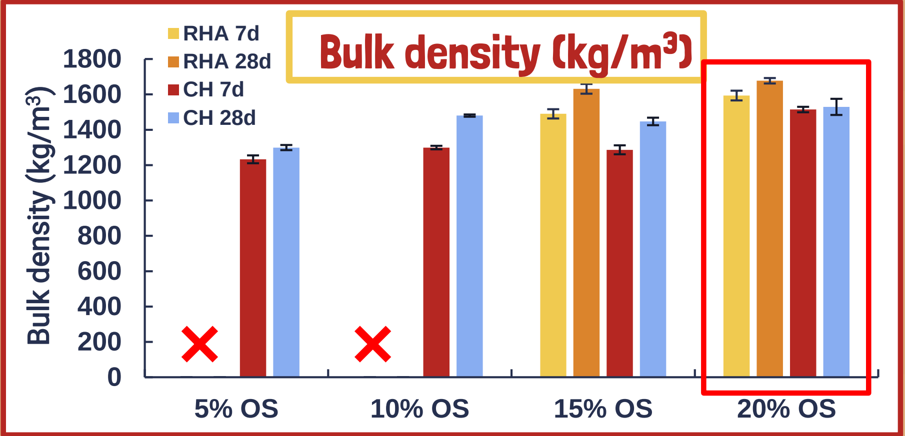

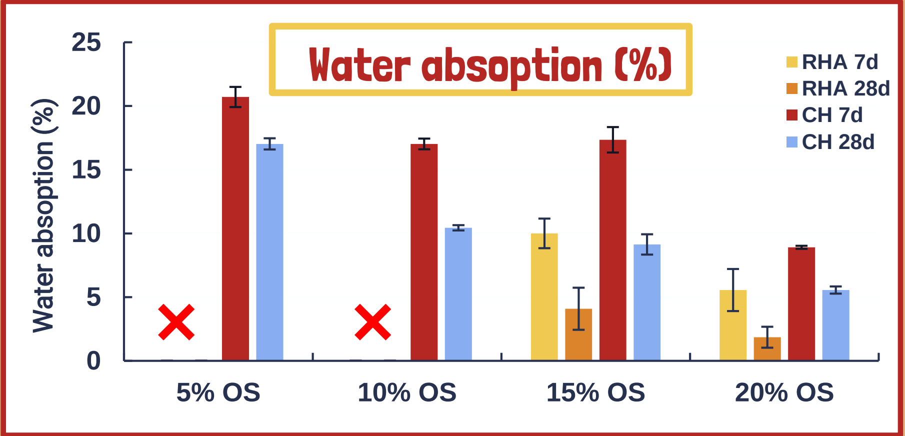

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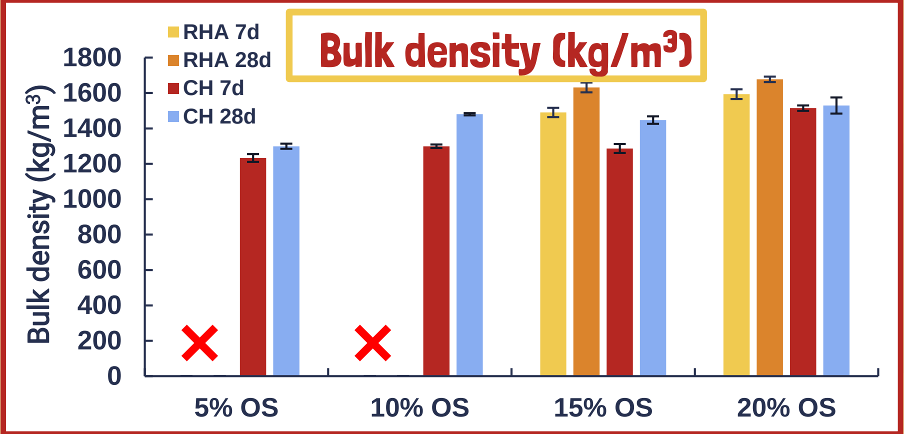

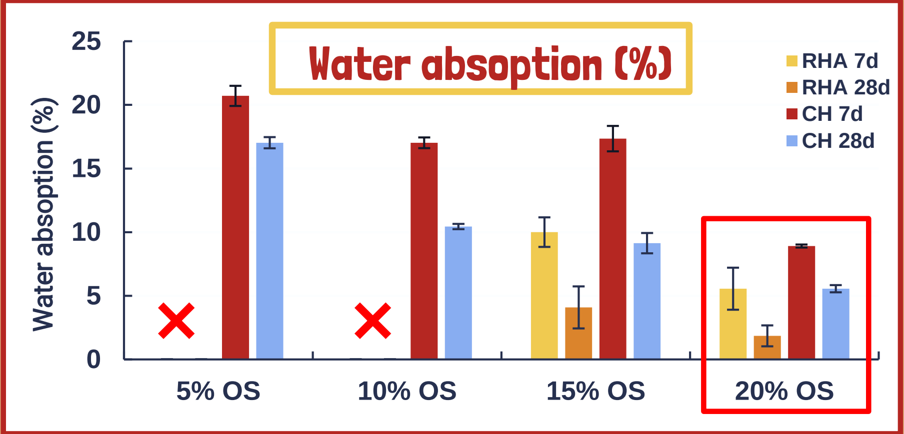

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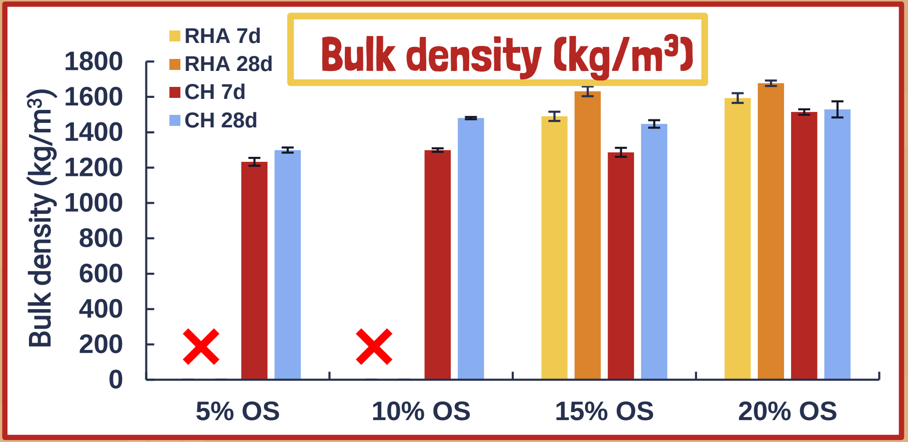

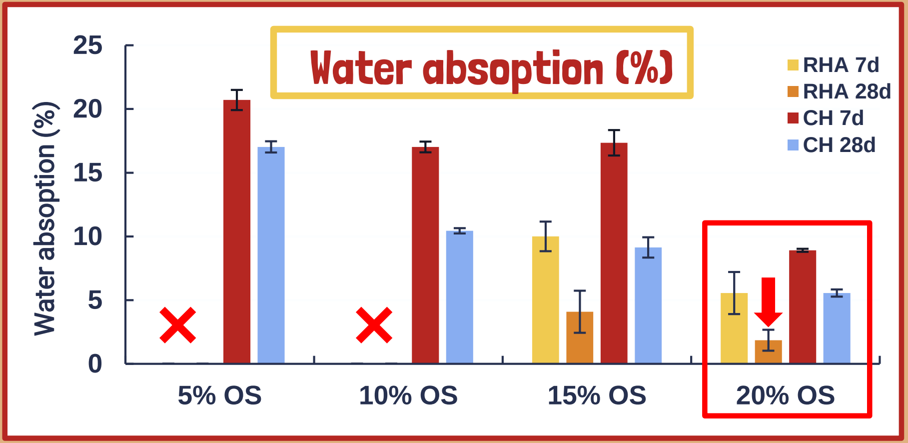

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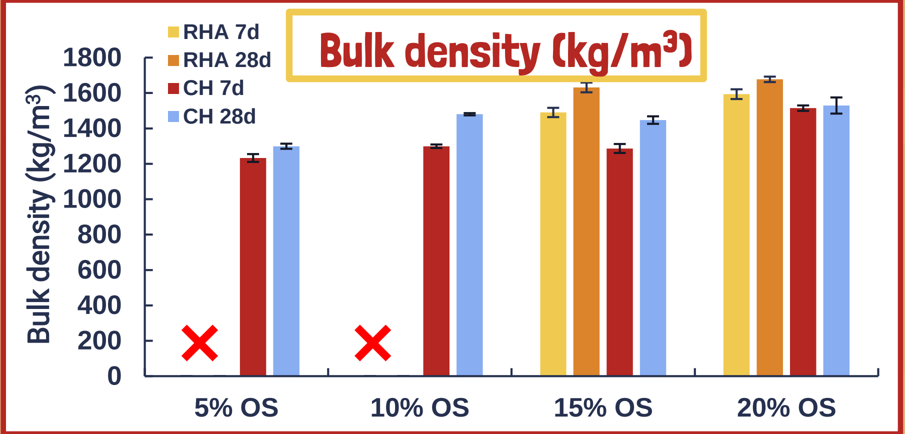

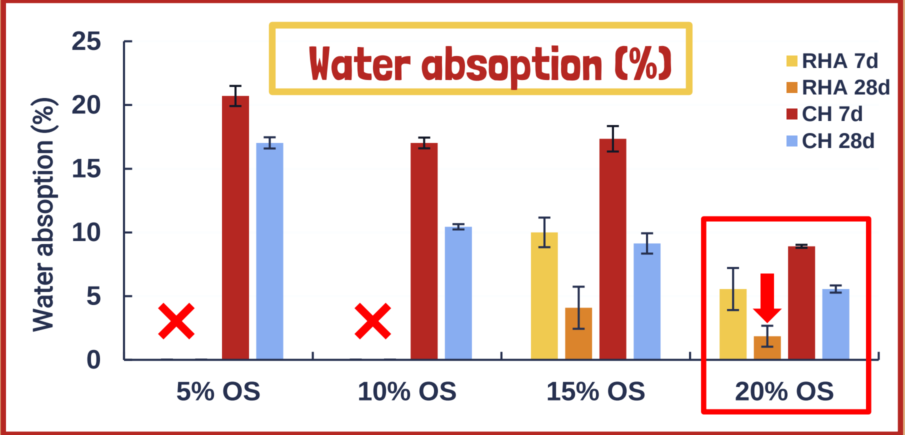

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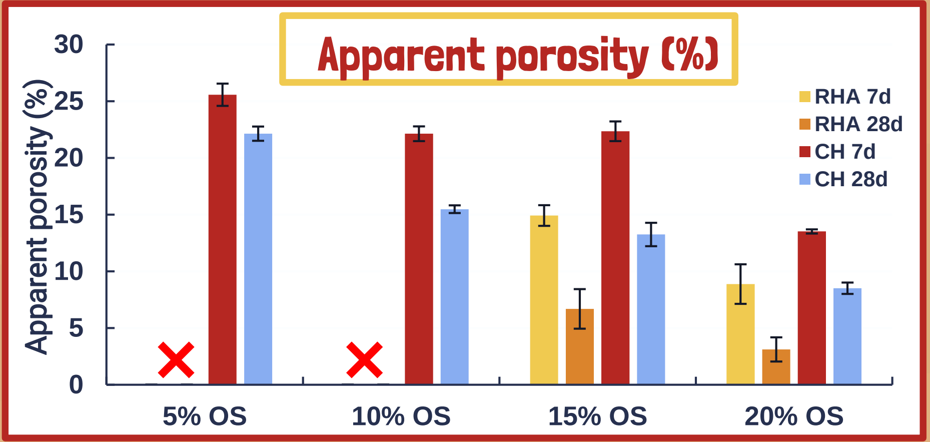
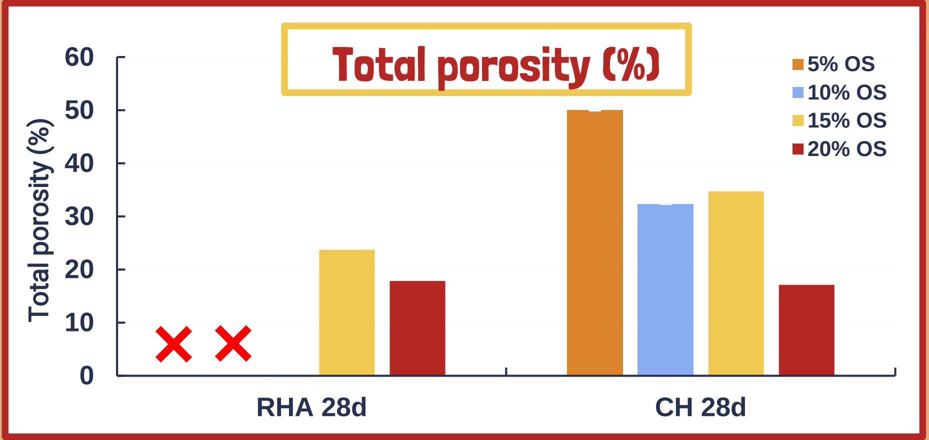
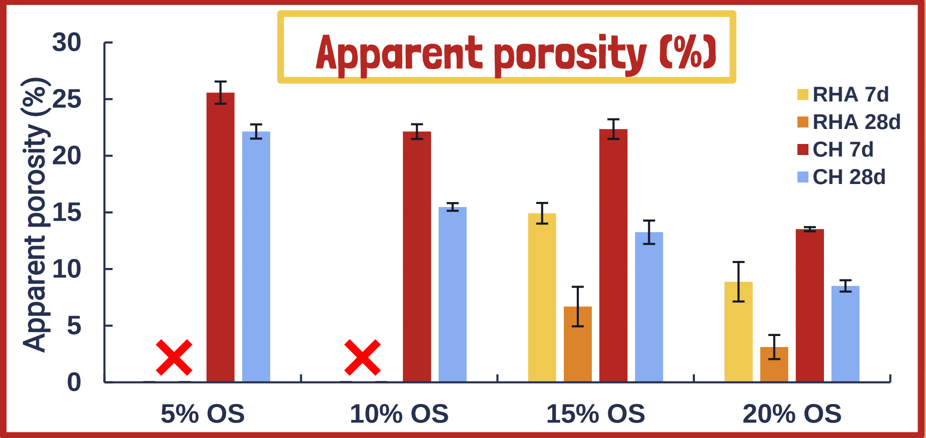
↑ Compressive strengths ↑ ρ ↓ Water absorption.

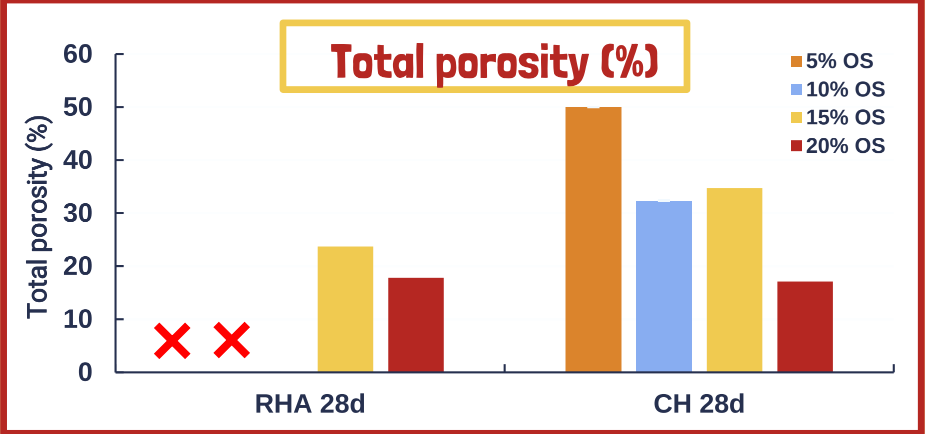

Apparent porosity (%)
Apparent porosity (%)
30
25
20
15
10
5
0
RHA 7d
RHA 28d
CH 7d
CH 28d
5% OS
10% OS
15% OS
20% OS


Total porosity (%)
Total porosity (%)
60
50
40
30
20
10
0
5% OS
10% OS
15% OS
20% OS
RHA 28d
CH 28d

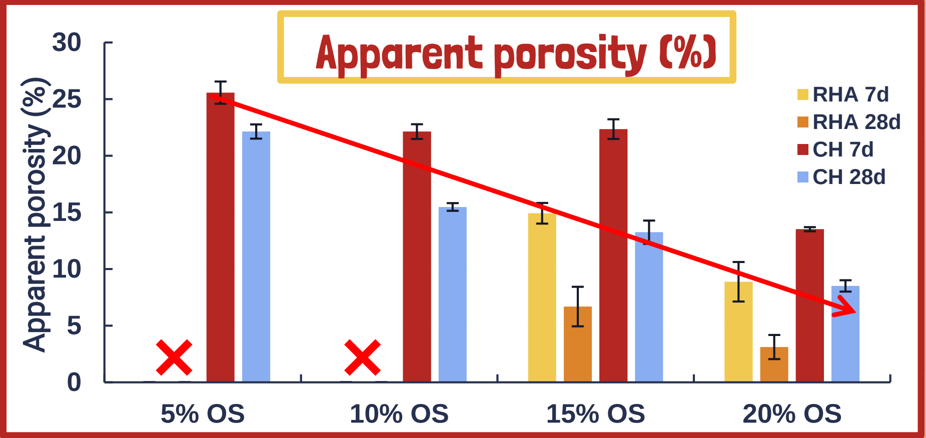
Sustainable management of oil refining sludge by means of geopolymers production



- The **apparent porosity** decreases with increasing percentage of oil sludge.
- This decrease is most noticeable after 28 days of curing.
- The RHA residue test specimens with oil sludge (percentages higher than 10%) show a lower apparent porosity.
- The test specimens with the lowest apparent porosity are those made with 20% oil sludge.



Sustainable management of oil refining sludge by means of geopolymers production



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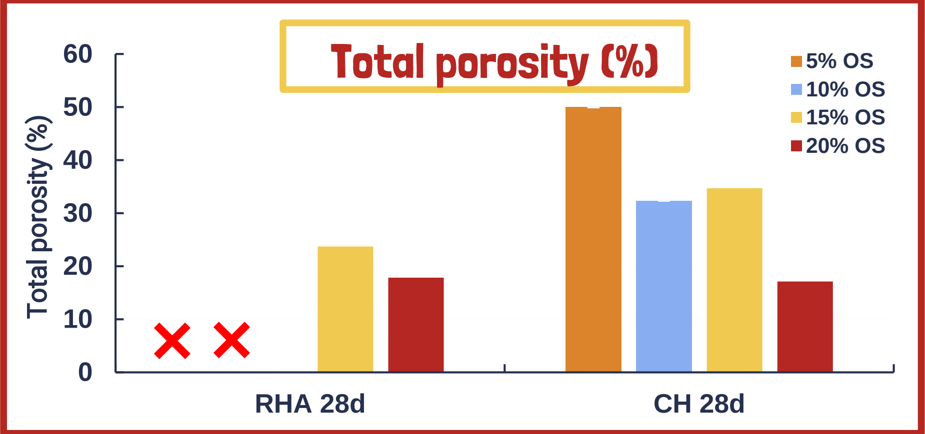

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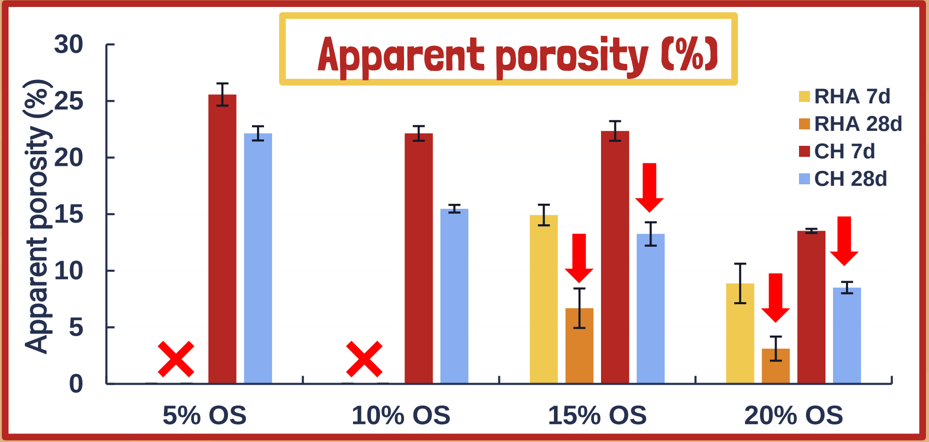

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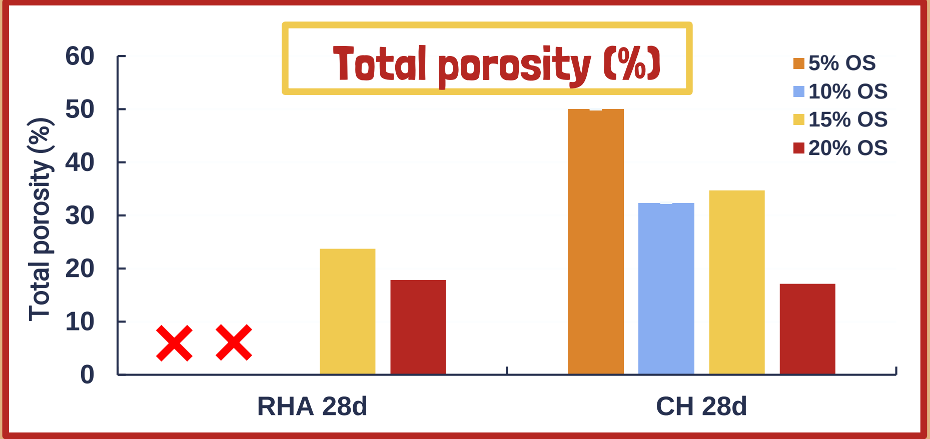

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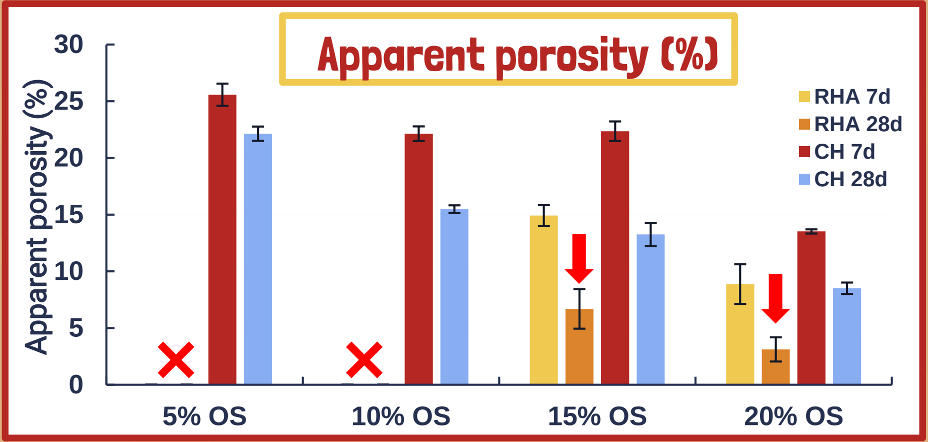

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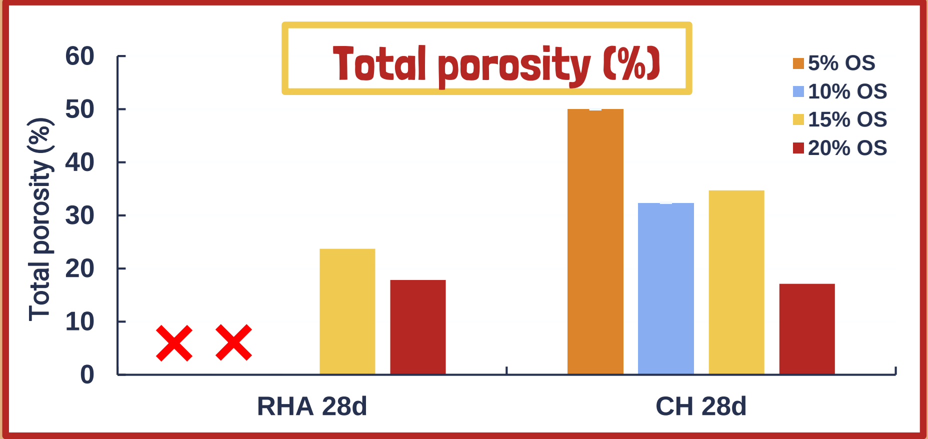

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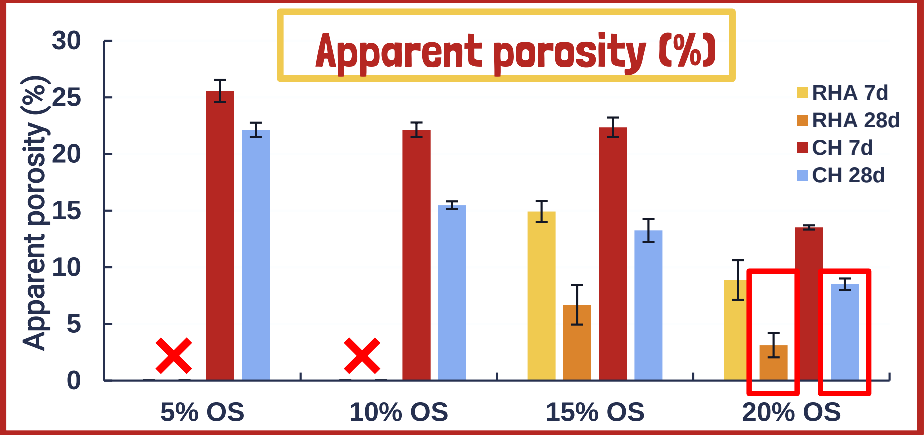

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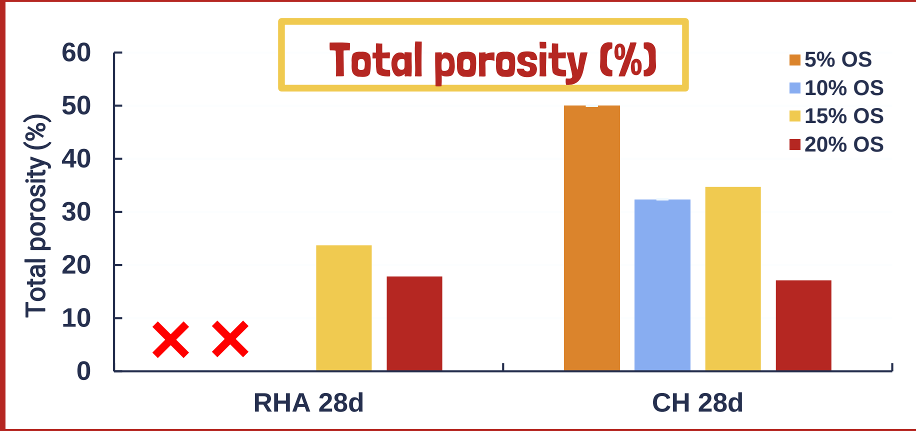

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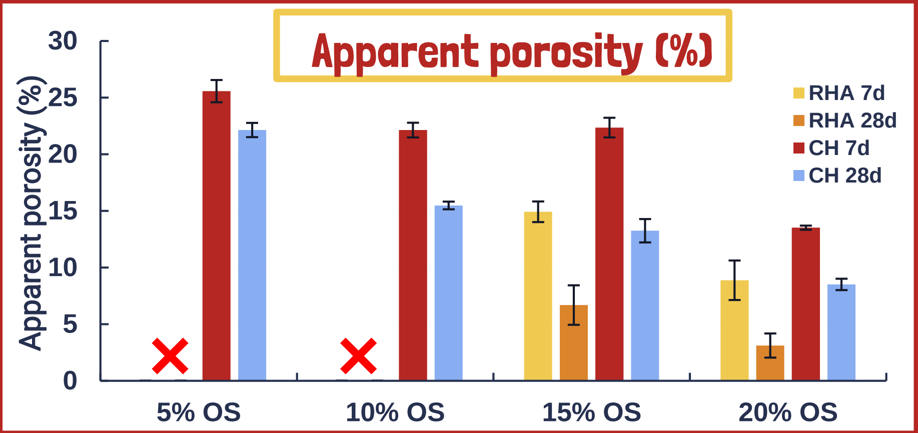

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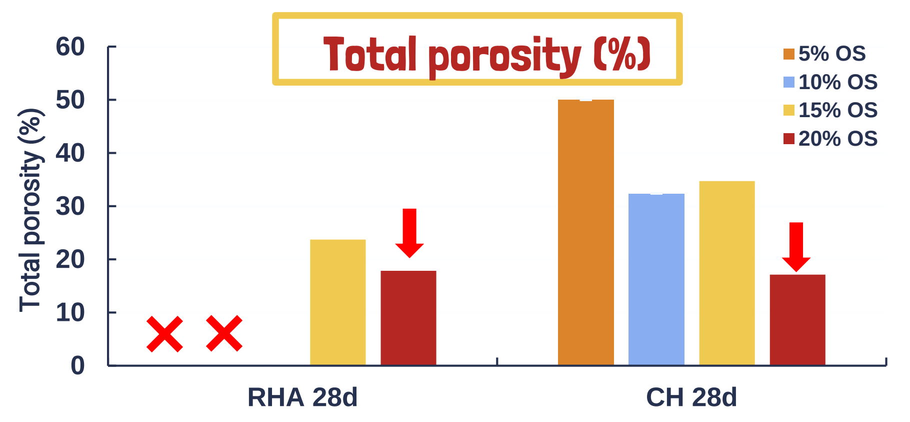
- **Total porosity** was only carried out after 28 days of curing.
- Porosities are lower with 20% oil sludge and similar with both wastes, RHA and CH.



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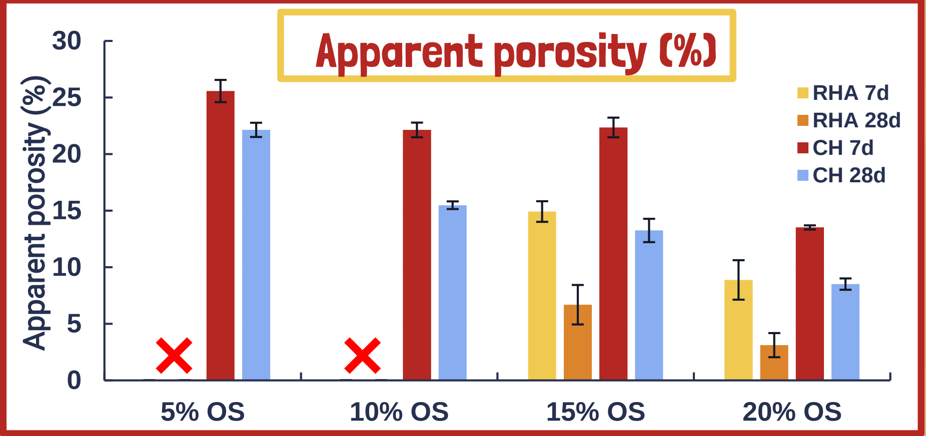

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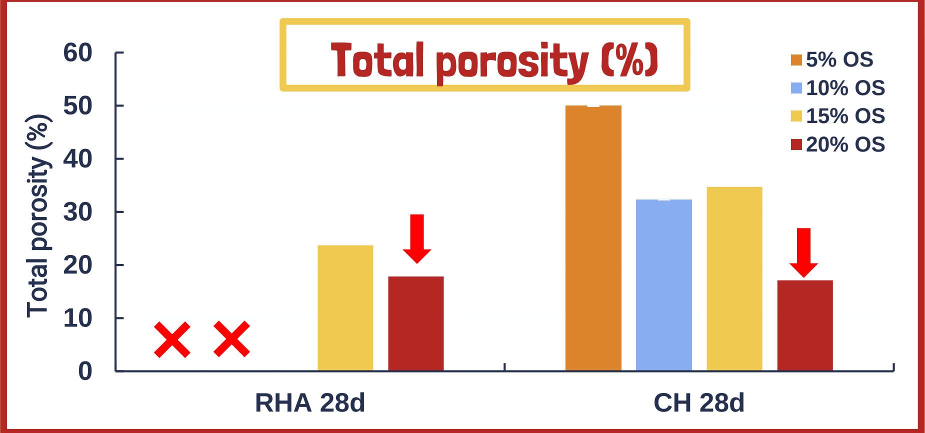

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Conclusions

These studies have shown that **the recovery of oil sludge is possible through the manufacture of new geopolymeric** materials, as their chemical characterisation indicates that they have a high alumina content, for this, it is necessary to mix them with other materials that have a high silica content. In this way, it is possible to recover these by-products, giving them a new use, bringing us closer to the **circular economy**.

Replacing oil sludge (OS) with RHA or CH improves the mechanical and physical properties of 100% OS. Promising physical and mechanical characteristics have been obtained.

The **alkaline activator** used **does not contain silicate** (the cause of most gepolymer contamination and its economic cost).

On the one hand, it has been proven that better mechanical and physical properties are obtained with the **RHA residue**, as long as the **presence of OS is in a percentage higher than 10%,** reaching compressive strengths of 36.6 MPa. On the other hand, although lower strengths are obtained with the **CH residue**, it can be combined with **low percentages of oil sludge** without the test specimens breaking in water.

This is a good environmental solution, as it is possible to develop an economical and sustainable material thanks to the use of industrial by-products.

Thank you!

E-mail: agdiaz@ujaen.es

ACKNOWLEDGMENTS

This work has been funded by the project Activalo2: Valorisation of Urban and Industrial Wastewater Treatment Sludge in the Manufacture of New Sustainable Alkaline Activated Materials for a Circular Economy (UJA-1380933) Proyectos de I+D+i en el marco del Programa Operativo FEDER Andalucía 2014-2020.