CLEAN clinKER by calcium looping for low-CO_2 cement

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CO_2 mineralization in cement sector: Lab scale experiments on burnt oil shale and concrete demolition wastes

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Layout

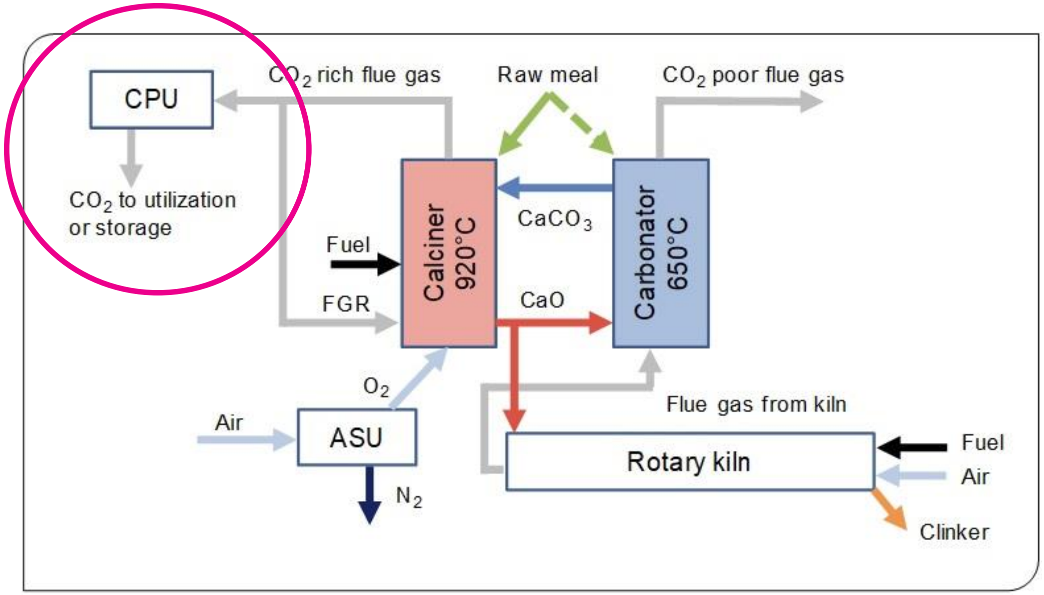
- Background
  - CLEANKER Project
  - Mineral Carbonation
  - Oil shale sector in Estonia
- Characterization of the materials
- Identifying the most promising materials for CO_2 capture
- Methodology of wet carbonisation
- Results
- Conclusion

Co-funded by the Horizon 2020 Framework Programme of the European Union

Background: CLEANKER project

Lab-scale carbonisation experiments on
- **burnt oil shale**
- **concrete demolition waste**

Recommendations for the design of the pilot in Vernasca



Martina Fantini, EU research project CLEANKER Technology, progress and project perspectives, 17th October 2018, Brussel - Belgium ECRA/CEMCAP/CLEANKER Workshop "Carbon Capture Technologies in the Cement Industry"

Objective	Key indexes	Target
CO_2 emissions	• CO_2 capture efficiency • CO_2 specific emissions	• Cement plant CO_2 capture efficiency >90% • Negative direct CO_2 emissions by biomass co-firing (Bio-CCS) • Reduction of total CO_2 specific emissions (kg_{CO2} per ton of cement) >85%*
Economics	• Cost of cement • Cost of CO_2 avoided	• Increase of cement cost < 25 €/$_{tcement}$ • Cost of CO_2 avoided <30 €/t_{CO2}

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Background: Mineral carbonation

- **Natural minerals**
- **Mg-silicates: olivine, serpentine**

+ **Long storage time and large capacity**

- **Large amount of mineral required** (mining, transport)
  1.6-3.7 t per 1 t CO_2

- **Increased costs!**

- **Slow natural reaction** (additives, extreme conditions)

- **Waste residues**

from power plants, steel and cement industry

- **Ca-silicates, CaO, $Ca(OH)_2$**

+ **Situated near the CO_2 emission source (No mining)**
+ **More reactive towards CO_2!**
- **Limited storage capacity**

Further points:

+ **Stabilization of wastes**
+ **Commercial by-products**

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Background: Oil shale sector in Estonia

Estonian oil shale industry in 2016 [1]:

- **Sales revenue: 742 mil. EUR**
- **Oil shale used: 15.2 Mt**
- **Energy content: 8 MJ/kg**
- **The lowest level on energy imports in EU - 8.9% dependent in 2014 [2]**

Problem:

Ash produced: 7.0 Mt

95% of the ash generated is not utilized

CO_2 generated: 11.5 Mt

[1] – Eesti Energia (2016). Annual Report 2016

[2] – Eesti Energia (2015). Estonian oil shale industry yearbook 2015

The aim of the study

- **To study wastes (burnt oil shale - BOS and concrete demolition wastes CDW) as sorbents in CO_2 wet mineralization process**
    - **To identify the most promising materials for CO_2 capture**
    - **To specify reaction kinetics and operating parameters for a scale up**
- **The mineralization pilot is planned to use CO_2 captured from the Ca-looping demo system in Vernasca Cement Plant.** *The re-carbonated wastes will be tested via concrete casting in order to demonstrate the quality of the commercial product in the following stages of the CLEANKER project.*

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Characterization of the Materials

	d_{mean} [µm]	Std.Dev. [µm]	SSA [m²/g]
1. Burnt oil shale (Estonia)			
BOS1 (CFB ESPA from Eesti PP)	37.32	27.00	2.87
BOS2 (CFB total ash from Eesti PP)	44.02	38.47	3.12
BOS3 (CFB ESPA from Balti PP)	41.18	31.59	3.10
BOS4 (CFB total ash from Balti PP)	50.62	46.45	2.82
BOS5 (PF DeSOx)	14.85	11.73	1.77
BOS6 (total ash from Enefit 280)	280.8	420.64	2.55
BOS7 (CFB total ash from Auvere PP)	25.46	35.26	3.84
BOS8 (CFB ESPA from Auvere PP)	20.98	16.61	6.05
2. Concrete Demolition Wastes (Italy)			
CDW 1	0-8 mm sand		
CDW 2			
CDW 3			
CDW 4			

- Burnt oil shale delivered by AS Eesti Energia:
- from Auvere PP, Eesti PP, Balti PP, Enefit280
- Concrete demolition wastes CDW1 and CDW2 fromI.L.C. s.r.l (Rondissone, TO)
- Concrete demolition wastes CDW3 and CDW4 from Isoltrasporti (Isola Sant'Antonio, AL)

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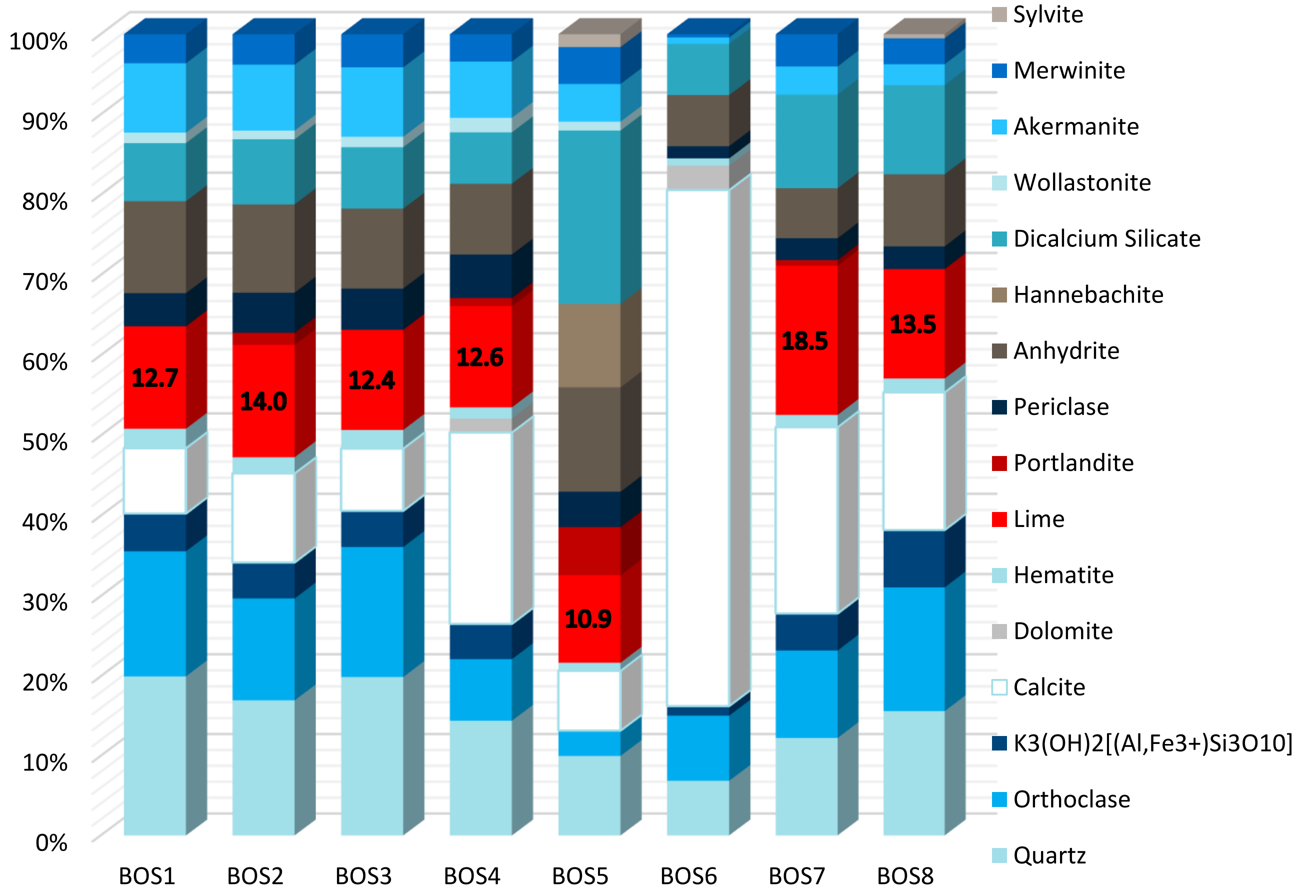
Identifying the most promising materials for CO_2 capture

Burnt oil shale



Oil shale ashes delivered by AS Eesti Energia: from Auvere PP, Eesti PP, Balti PP, Enefit280, PF DeSOx

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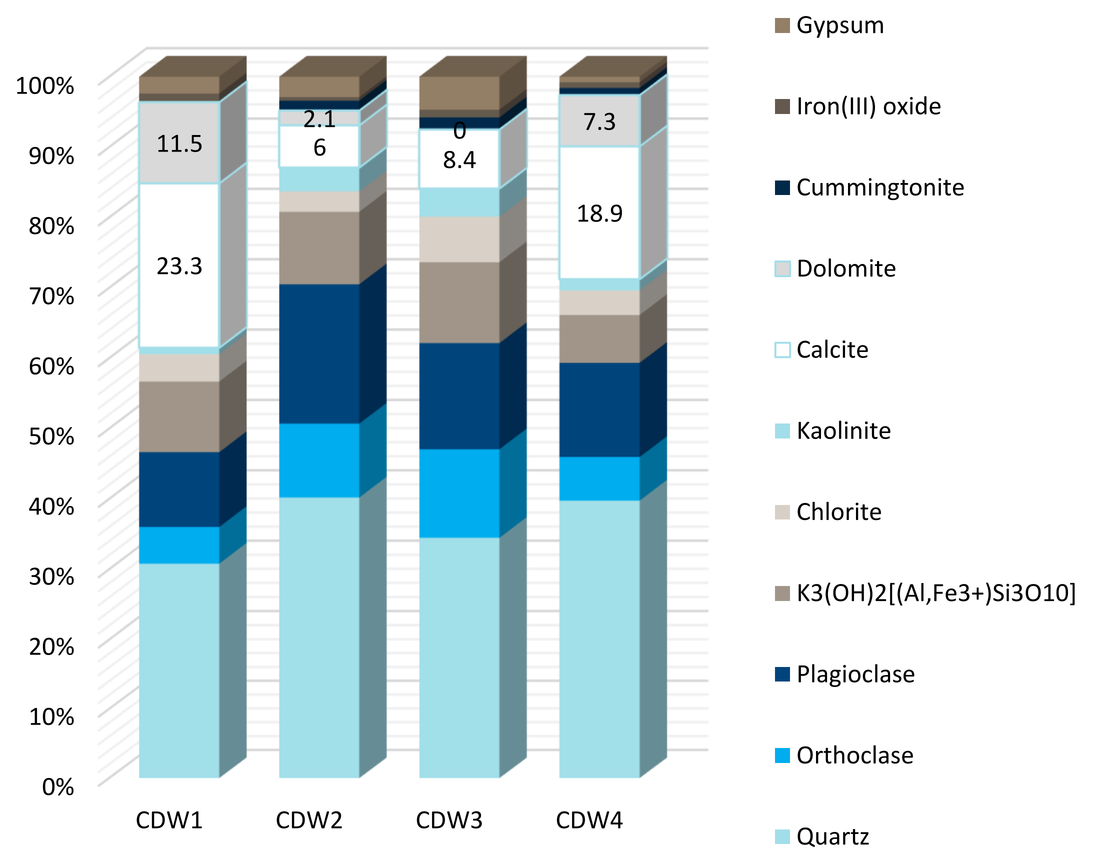
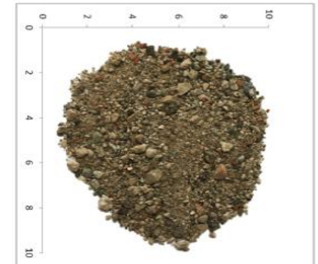
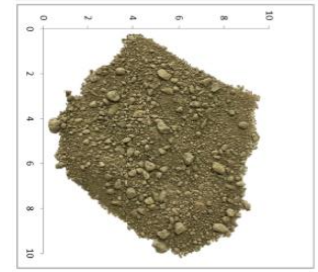
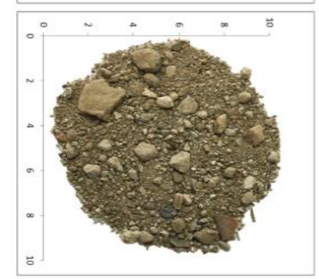
Identifying the most promising materials for CO_2 capture

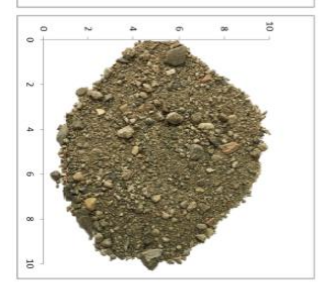
Concrete demolition waste







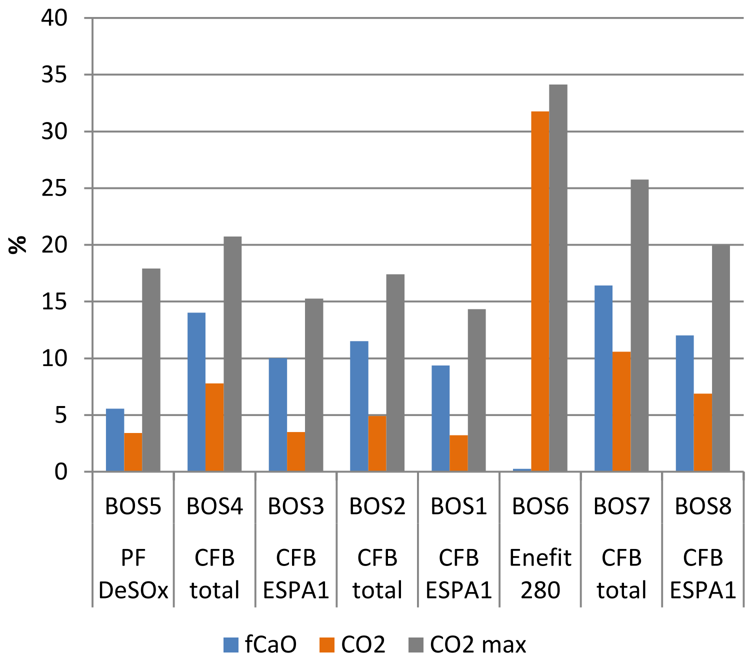


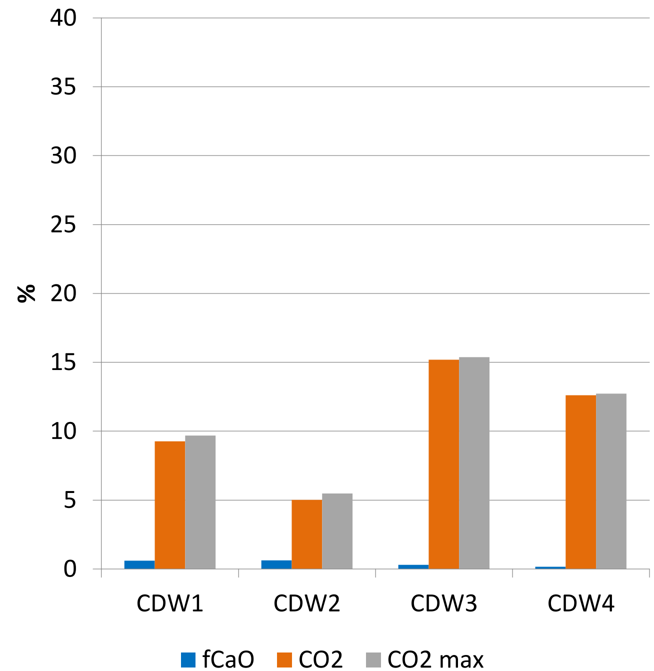


- In CDW1 and CDW2 quartz and silicates account for about 80% of the total mineral composition. CDW3 and CDW4 have a much higher amount of carbonates against a lower content of silicates.

Identifying the most promising materials for CO_2 capture:

Free lime and CO_2 content of initial materials and max possible CO_2 content





$$CO_{2max} = \frac{\frac{CaO^i * M(CO_2)}{M(CaO)} + \frac{2*Ca_2SiO_4^i * M(CO_2)}{M(Ca_2SiO_4)} + \frac{CaSiO_3^i * M(CO_2)}{M(CaSiO_3)}}{100 + \frac{CaO^i * M(CO_2)}{M(CaO)} + \frac{2*Ca_2SiO_4^i * M(CO_2)}{M(Ca_2SiO_4)} + \frac{CaSiO_3^i * M(CO_2)}{M(CaSiO_3)}} * 100\%$$

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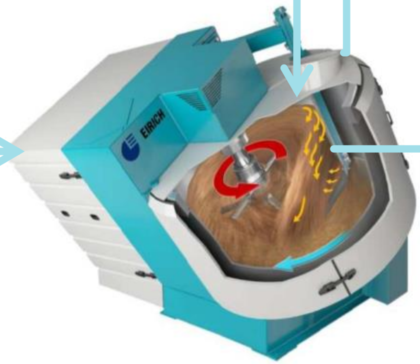
Methodology of wet carbonisation

Gas in:
- CO_2 rich flue gas



Gas out

Solid:
- Burnt oil shale
- CDW

Carbonated material:
- Solid

Water:
- Wet route: liquid to solid ratio = 0.2

Sample	Explanation	CO_2% in gas	V(gas), L/h	m(ash), g	Rotation speed, rpm
Burnt oil shale					
BOS1	Eesti PP ESPA1	20→70	30→200	200	300→3000
BOS2	Eesti PP total	20→70	30→200	200	300→3000
BOS3	Balti PP ESPA1	20→70	30→400	200→600	300→3000
BOS4	Balti PP total	20→70	30→200	200	300→3000
BOS5	DeSOx	20→70	30→200	200	300→3000
BOS6	Enefit280 total	20	100	200	3000
BOS7	Auvere PP ESPA1	20→70	30→400	200→600	300→3000
BOS8	Auvere PP total	20→70	30→200	200	300→3000
Concrete demolition wastes					
CDW2	I.L.C. s.r.l (Rondissone, TO)	20→70	30→200	200	300→3000

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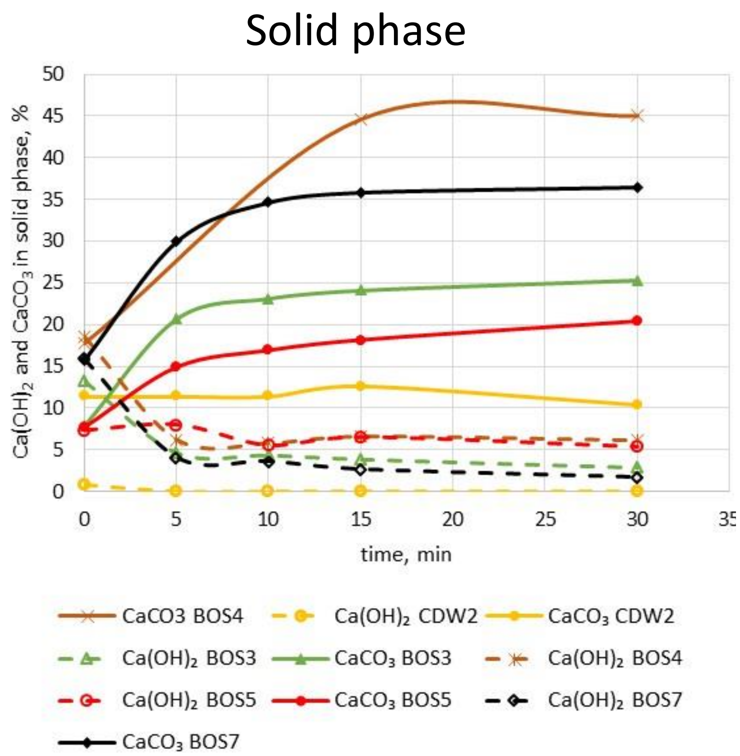
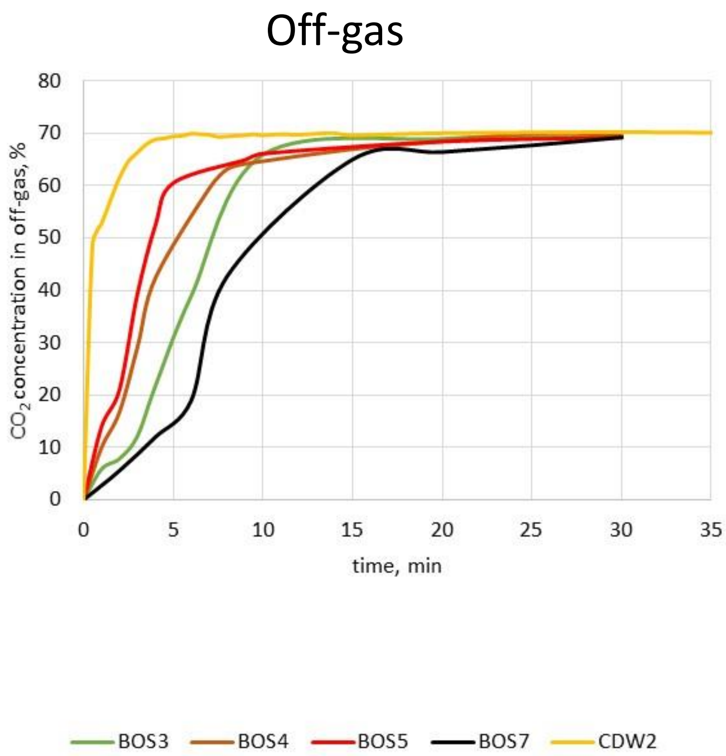
Results

Wet carbonation of different samples

70% CO_2 in model gas, Vgas = 200 L/h, m(ash) =300 g, 300 rpm, L/S=0.2

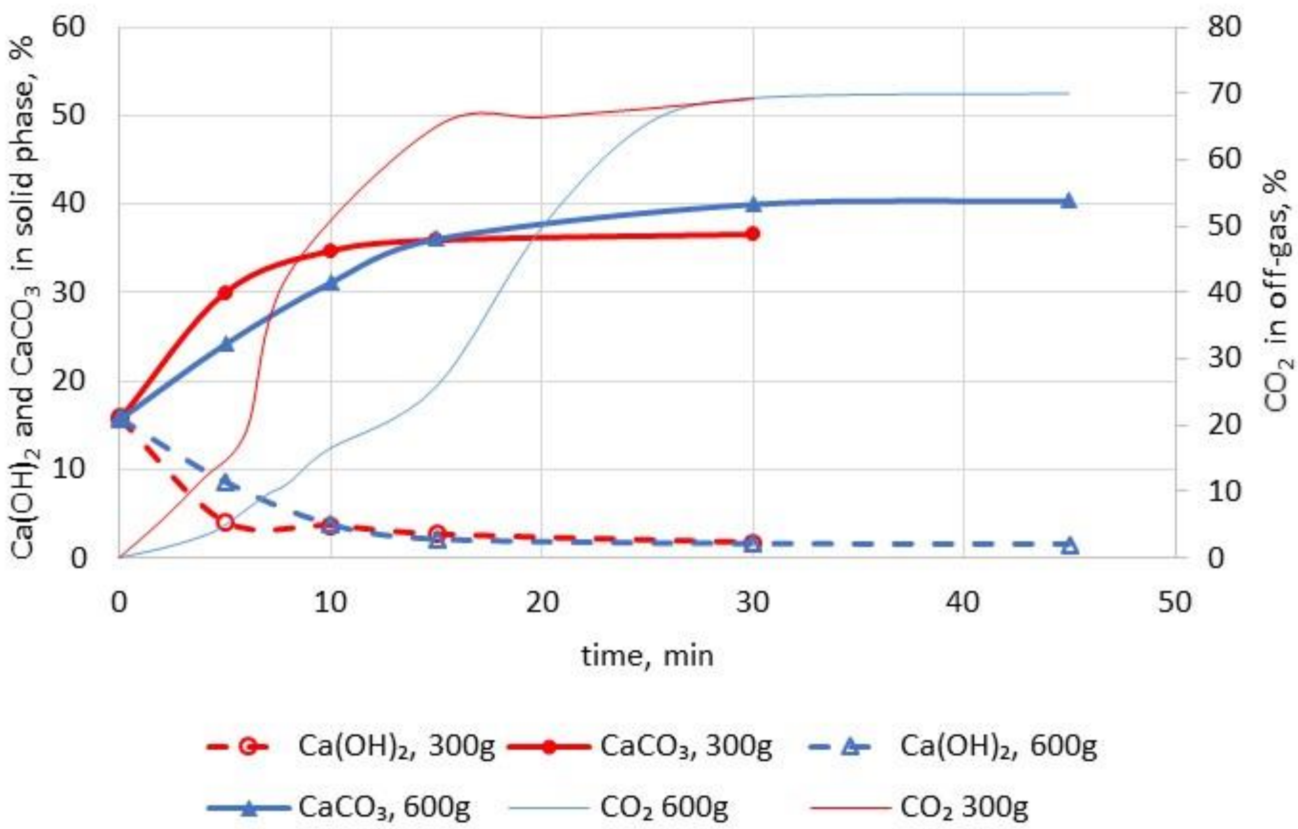




Results

The effect of sample mass in 1 L reactor

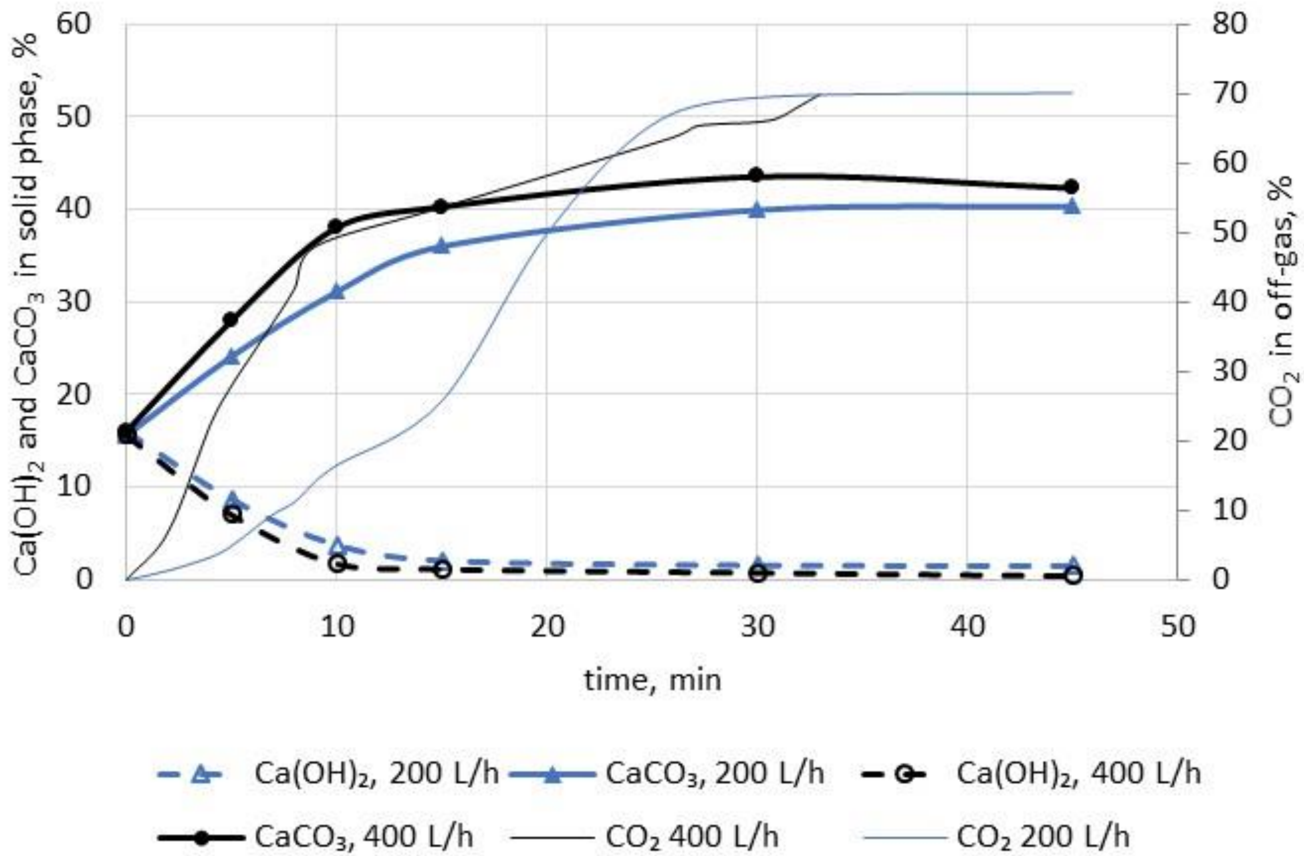
70% CO_2 in model gas, Vgas = 400 L/h, 300 rpm, L/S=0.2



Results

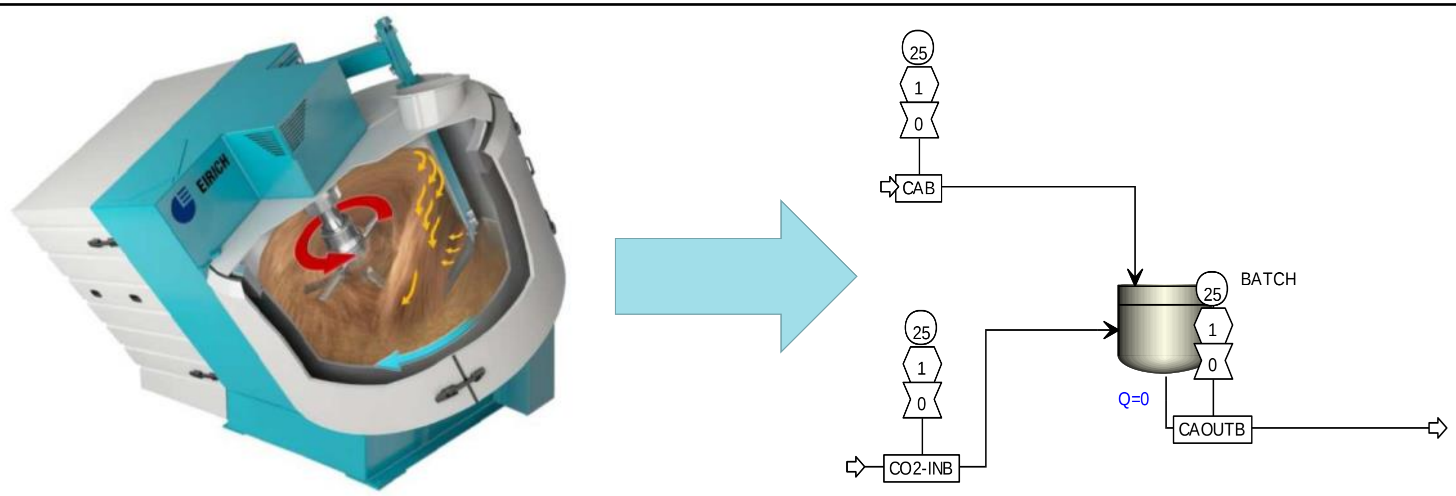
The effect of gas flow rate in 1 L reactor

70% CO_2 in model gas, m(ash) = 600 g, 300 rpm, L/S=0.2



Results: Kinetic reaction model

No	Stoichiometry	k
1	CO_2(MIXED) + H_2O(MIXED) → HCO^{3-}(MIXED) + H^+(MIXED)	2.4×10^{-2} s^{-1}
2	H^+(MIXED) + HCO_{3-}(MIXED) → CO_2(MIXED) + H_2O(MIXED)	5.7×10^{4} $L(mol\cdot s)^{-1}$
3	CO_2(MIXED) + OH-(MIXED) → HCO_3^-(MIXED)	8.4×10^{3} $L(mol\cdot s)^{-1}$
4	HCO_3^-(MIXED) → OH^-(MIXED) + CO_2(MIXED)	2×10^{-4} s^{-1}
5	OH^-(MIXED) + H^+(MIXED) → H_2O(MIXED)	1.4×10^{11} $L(mol\cdot s)^{-1}$
6	H_2O(MIXED) → OH^-(MIXED) + H^+(MIXED)	1.3×10^{-3} $mol(L\cdot s)^{-1}$
7	HCO_3^-(MIXED) + OH^-(MIXED)→CO_3^{2-}(MIXED) + H_2O(MIXED)	6×10^{9} $L(mol\cdot s)^{-1}$
8	CO_3^{2-}(MIXED) + H_2O(MIXED) → HCO_3^-(MIXED) + OH^-(MIXED)	1.2×10^{6} s^{-1}
9	Ca^{2+}(MIXED) + CO_3^{2-}(MIXED) → $CaCO_3$(CISOLID)	1.9×10^{6} $L(mol\cdot s)^{-1}$
10	$CaCO_3$(CISOLID) → Ca^{2+}(MIXED) + CO_3^{2-}(MIXED)	9.0×10^{-3} $mol(L\cdot s)^{-1}$
11	$CaCO_3$(CISOLID) + H^+(MIXED) → Ca^{2+}(MIXED) + HCO_3^-(MIXED)	0.1×10^{7} s^{-1}
12	Ca^{2+}(MIXED) + HCO_3^-(MIXED) → $CaCO_3$(CISOLID) + H^+(MIXED)	0.4×10^{3} $L(mol\cdot s)^{-1}$
13	$Ca(OH)_2$(CISOLID) → Ca^{2+}(MIXED) + 2 OH^-(MIXED)	$1.5\times10^{-3}s^{-1}$
14	Ca^{2+}(MIXED) + 2 OH^-(MIXED) → $Ca(OH)_2$(CISOLID)	508.0 $L(mol\cdot s)^{-1}$

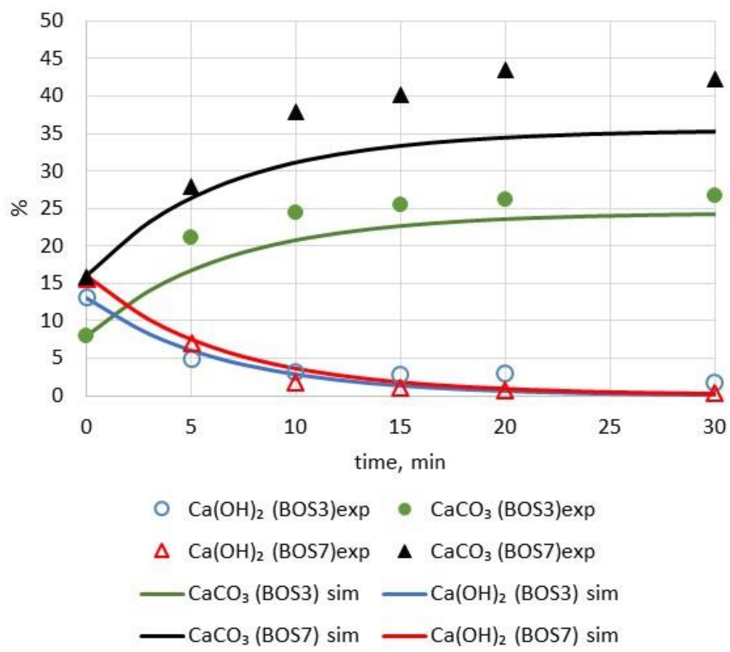


Results

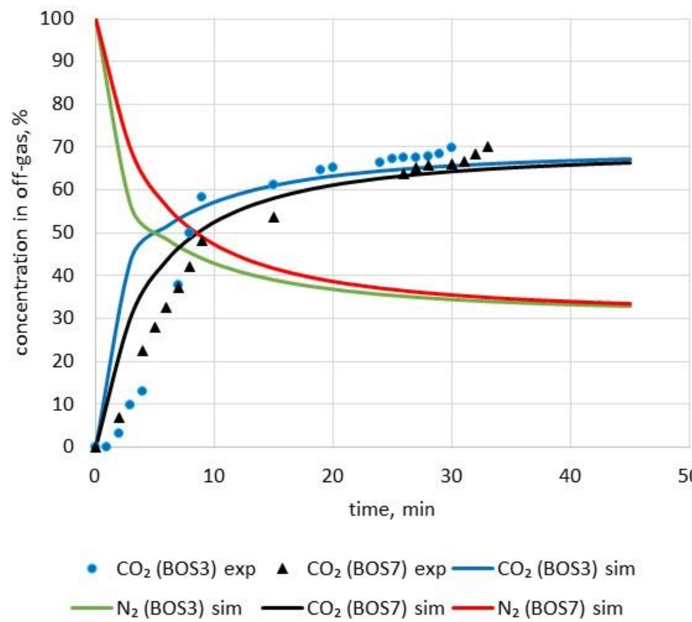
Simulation vs experiment

70% CO_2 in model gas, Vgas = 400 L/h, m(ash) = 600 g, 300 rpm, L/S=0.2

Solid phase



Off-gas



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Conclusions

- Different types of burnt oil shale and concrete demolition wastes were tested via wet route direct carbonation.
- Tests showed that the free lime content could be exhausted with 30 min in the conditions of low range water to solid ratio (0.2 w/w) and gas flow of 70% CO_2 in air.
- The CO_2 uptake was mainly attributed by the free lime content.
- Comparing different types of BOS samples indicated that free lime content was almost fully utilized in case of electrostatic precipitator ashes from CFB boilers, as the free lime in coarser total ashes and non-porous PF ashes was only partially utilized.
- Increasing sample mass and gas flow rate accelerated the wet carbonation process, as changing the mixing speed from 300 to 3000 rpm had negligible effect.
- A kinetic model was built to predict the composition of solid and gas phase at given operating conditions.
- Based on the results, selected types of burnt oil shale could be used as effective sorbents in the proposed CO_2-mineralization process, binding up to 0.18 kg CO_2 per kg of waste. Utilizing re-carbonated wastes in concrete application would support closing the CO_2 cycle of a cement plant by trapping the carbon dioxide into concrete.

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