EFFECT OF AGEING PRE-TREATMENT ON PERFORMANCE OF PF OIL SHALE ASH FOR CO_2 SEQUESTRATION IN AQUEOUS SUSPENSIONS

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SUMMARY

Background

Ashes from oil shale combustion (pulverized firing *PF* and circulating fluidized bed combustion *CFBC* ashes) could generally be characterized as good sorbents for CO_2 sequestration in aqueous suspensions. Aqueous carbonation of less porous *PF* ash depends to a great extent on the liquid phase composition. During continuous flow carbonation treatment the suspension aqueous phase is saturated with soluble ash and flue gas components which significantly affect the utilization of lime.

The aim of the study

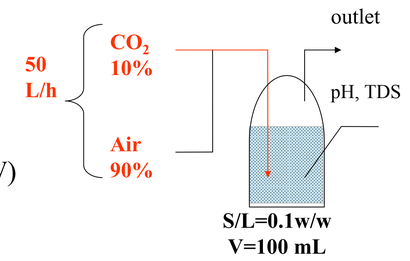
The study was focused on the ageing pre-treatment of *PF* cyclone ash (*PFCA*) to make the free lime trapped inside ash particles more accessible for reagents.

Conclusions

Experiments showed that ageing pre-treatment has increasing effect on the porosity of *PFCA* which in turn made the free lime trapped inside the ash particles more accessible for reagents. The utilization of lime was enhanced even in the aggravating carbonation conditions (suspension liquid phase was saturated with the components of ash and flue gas, mainly Ca^{2+}, OH^-, SO_4^{2-}, CO_3^{2-}, *or* HCO_3^-) from 16% to 37-68%.

EXPERIMENTAL DEVICE

Initial material:	**PFCA - pulverized firing cyclone ash** from Narva PP, Estonia
Conditions of ageing experiments:	**6 months** in open air conditions: **t~22°C, RH=40-60%.** Samples were taken after 1, 3 and 6 month.
Conditions of carbonation experiments:	**t~22-25°C; P~1 atm; τ~30min;** **Model gas: 10-15% CO_2** in air; **Suspension:** S/L=0.1w/w **Aqueous mediums:** Distilled water (**DW**) Recirculation water from Narva PP (**RW**) Carbonated RW (**CRW**)

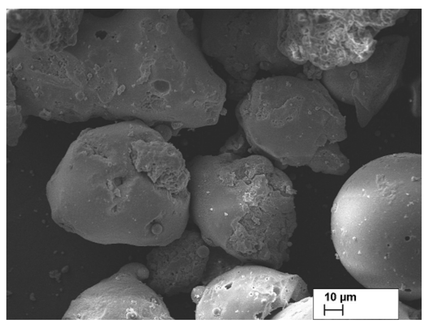


	pH	TDS g/L	Ca^{2+} g/L	SO_4^{2-} g/L	OH^- meq/L	HCO_3^- meq/L
RW	13,0	11,4	0,7	2,8	64,3	-
CRW	7,5	6,8	0,4	2,8	-	60,7

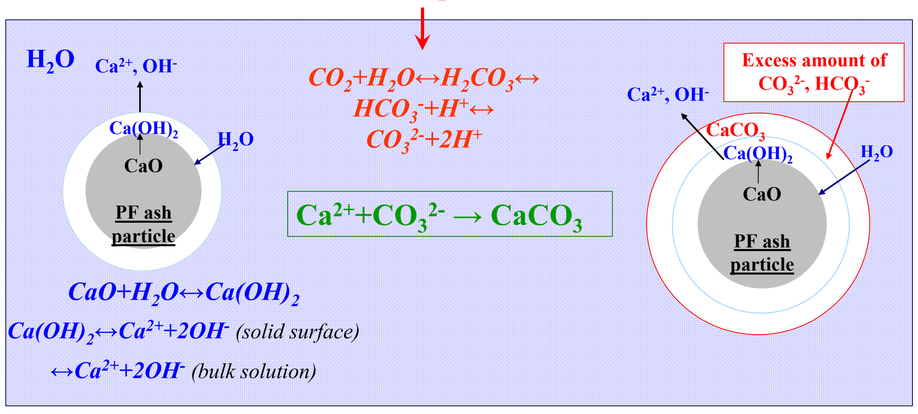
RESULTS and DISCUSSION

Rate determining mechanism

Initial PFCA



Chemical composition	%
CaO (total)	**49,71**
CaO (free)	23,00
$CaCO_3$	2,23
$CaSO_4$	5,34
MgO (total)	**6,49**
Physical characteristics	
SSA	**0,4 m^2/g**
d_{mean}	**47 µm**



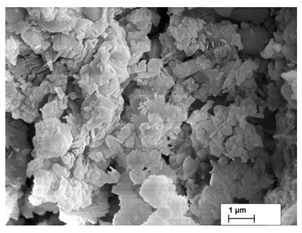
In the context of CO_2 sequestration and ash stabilization, the availability of lime for hydration and carbonation reactions is of key importance.

- Impact of solution composition
- Impact of specific surface area

Rate determining mechanism

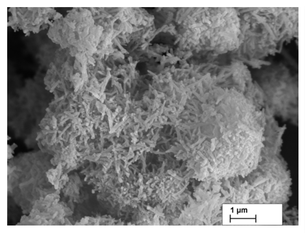
Process deceleration is caused by concurrence of two factors: low porosity of PF ash and high content of SO_4^{2-}, CO_3^{2-}, HCO_3^- -ions in suspension liquid phase

- Dissolution of $Ca(OH)_2$ is diffusion controlled;
- Reactions with CO_3^{2-}, HCO_3^- and SO_4^{2-} take place inside the pores and on the surface;
- Small-size pores of PF ash can plug easily;
- Layers of $CaCO_3$ and $CaSO_4$ hinder both lime slaking and further carbonation



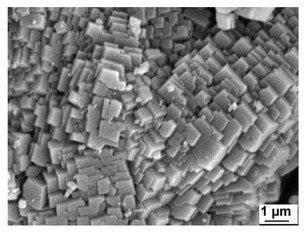
PFCA+DW	CO_3, %
Average (TC)	3,05
On the surface (XPS)	45,5

PFCA+DW: Hydration of lime causes ash particles to fracture and disintegrate (SSA=1,62 m^2/g)



PFCA+DW+FG	CO_3, %
Average (TC)	18,56
On the surface (XPS)	79,3

PFCA+DW+FG: Porous and permeable product layer (SSA=10,2 m^2/g)



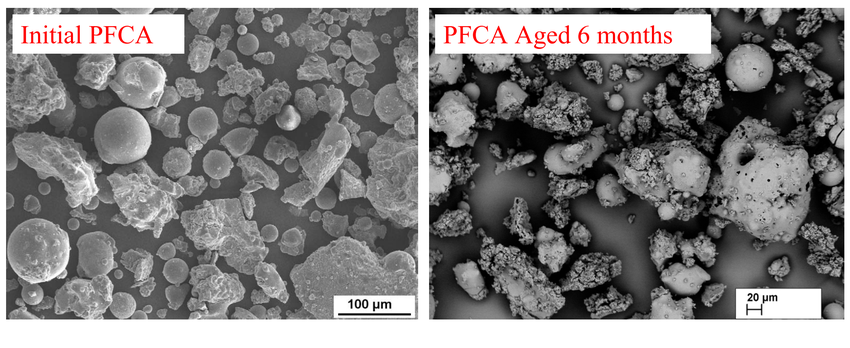
PFCA+CRW+FG	CO_3, %
Average (TC)	6,63
On the surface (XPS)	50,65

PFCA+CRW+FG: Crystalline and impermeable product layer (SSA=2,46 m^2/g)

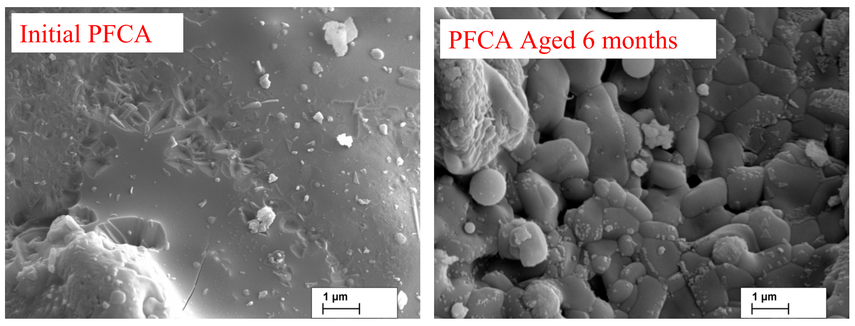
CO_3 concentrates on the surface layer of the ash particles

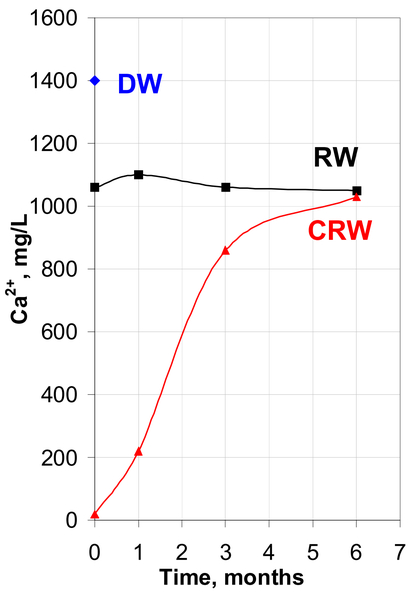
Effect of ageing pre-treatment on aqueous carbonation of PF oil shale ash

SEM:
During ageing pre-treatment hydration of PFCA by air humidity took place which caused ash particles to fracture and disintegrate.

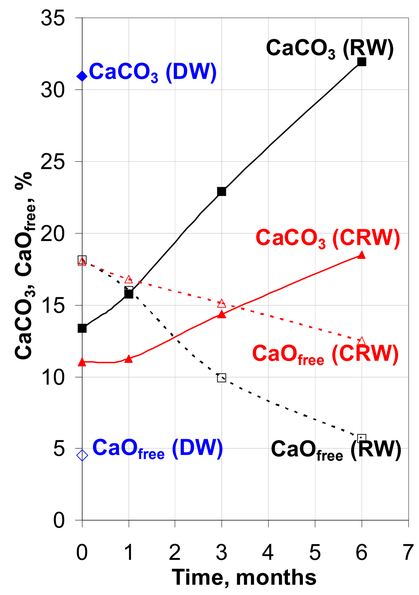


SEM:
The smooth surface of PFCA particles was gradually changed during pre-treatment period.

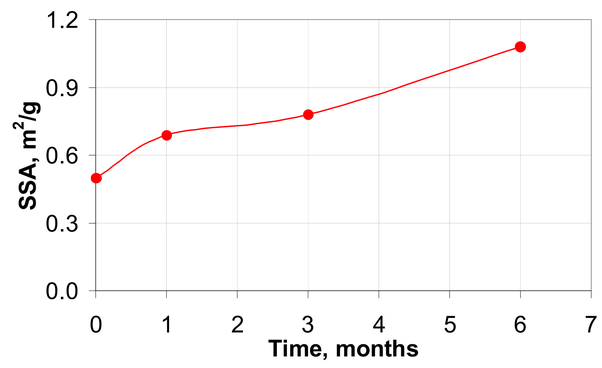




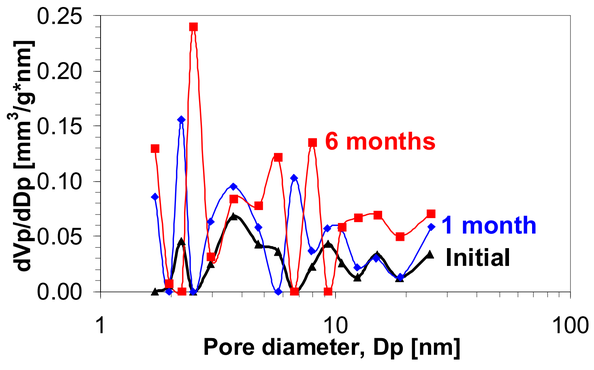
Ca^{2+}: 20 mg/L → 1030 mg/L
Ageing pre-treatment enhanced the dissolution of free lime from PFCA particles even in aggravating process conditions (CRW).



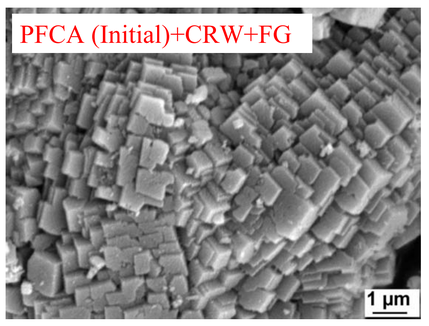
$CaCO_3$: 11-13%→19-32%
6-months of ageing pre-treatment enhanced the utilization of lime in the aggravating carbonation conditions from 16% to 37-68%



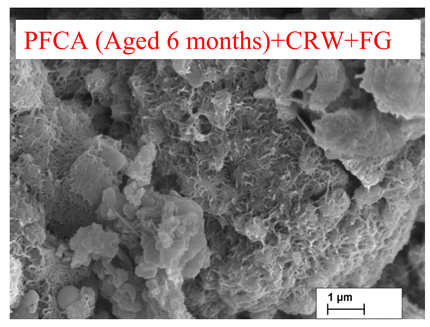
BET: SSA of nearly non-porous PFA increased from 0,5 to 1,08 m^2/g during 6 month.



BJH: The pore volume of 5 -12 µm size pores increased.



SEM: Crystalline and impermeable product layer (SSA=2,46 m^2/g)



SEM: More porous and permeable product layer (SSA=3,69 m^2/g)

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