THE CO_2-BINDING BY Ca-Mg-SILICATES IN DIRECT AQUEOUS CARBONATION OF OIL SHALE ASH AND STEEL SLAG

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SUMMARY

The aim of the study

This study was focused on direct aqueous carbonation of waste materials in which Ca and Mg are partially or generally bound as silicates. The experiments were carried out at mild conditions (atmospheric pressure and room temperature).

Conclusions

- Quantitative XRD analysis indicated that Ca_2SiO_4 and $Ca_3Mg(SiO_4)_2$ were the main CO_2 binding low water-solubility components of PFA as well as steel slags.
- The main carbonation product was calcite ($CaCO_3$), indicating that Mg-compounds were not in most cases reactive towards CO_2 at these mild conditions.
- The CO_2 uptake for PFA was **29 CO_2 g/100 g PFA** (56% bound by lime and 33% bound by Ca-silicates).
- The CO_2 uptakes for steel slags were **8.7g CO_2/100 g EAFS1**, **1.9 g CO_2/100 g EAFS2** and **4.6 g/100g LS**.
- CO_2-binding ability of different wastes depends significantly on the origin of the material as well as on the pretreatment conditions.
- Based on multifaceted studies about carbonation of oil shale ash, a new method for eliminating CO_2 from flue gases by Ca-containing waste material was proposed.

EXPERIMENTAL DEVICE

Materials used:

- pulverized firing oil shale ash (**PFA** from Narva Power Plants, Estonia)
- electric arc furnace slag (**EAFS**, types 1 and 2 from Uddeholm Tooling, Sweden)
- ladle slag (**LS** from Uddeholm Tooling, Sweden)

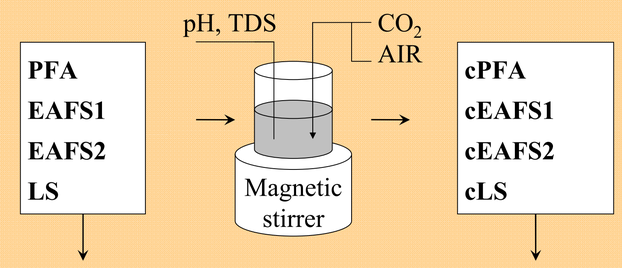
Experiment conditions: room temperature, atmospheric pressure, S/L=0.1

Pretreatment:

EAFS were ground in a ball mill (d<100µm)

PFA and LS were used as received basis

Carbonation treatment



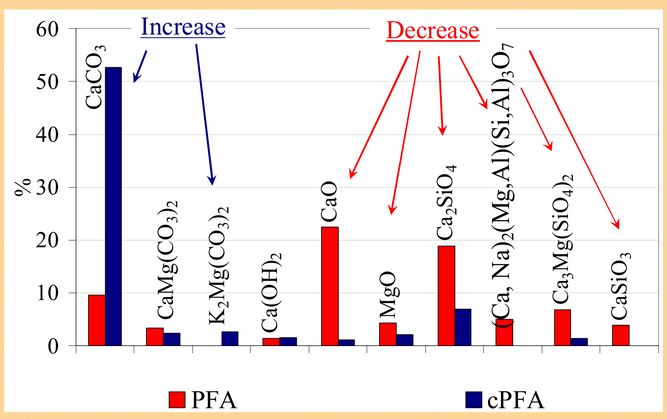
Characterization of solid samples: q-XRD; chemical analysis; SEM; BET

RESULTS and DISCUSSION

Direct aqueous carbonation of oil shale ash PFA

Characterization of the initial ash (PFA)

Chemical composition	%	
CaO^t		51.19
MgO^t		4.93
Phase composition	%	
Calcite $CaCO_3$	9.55	
Dolomite $CaMg(CO_3)_2$	3.34	12.9%
Portlandite $Ca(OH)_2$	1.42	
Lime CaO	22.4	23.8%
Periclase MgO	4.27	
α -Ca_2SiO_4	1.99	
β -Ca_2SiO_4	16.92	
Melilite$(Ca,Na)_2(Mg,Al)(Si,Al)_3O_7$	4.99	
Merwinite $Ca_3Mg(SiO_4)_2$	6.81	
Wollastonite $CaSiO_3$ 2M	3.88	34.6%
Anhydrite $CaSO_4$	4.48	
*Gypsum $CaSO_4$*$2H_2O$*	0.76	5.3%
Hematite Fe_2O_3	1.19	
Quartz SiO_2	7.38	
Orthoclase $KAlSi_3O_8$	3.51	
Σ	93	



Distribution of Ca-Mg-compounds in the initial (PFA) and treated materials (cPFA) according to qXRD.

Total amount of CO_2 bound by PFA
29 g CO_2/100 g PFA

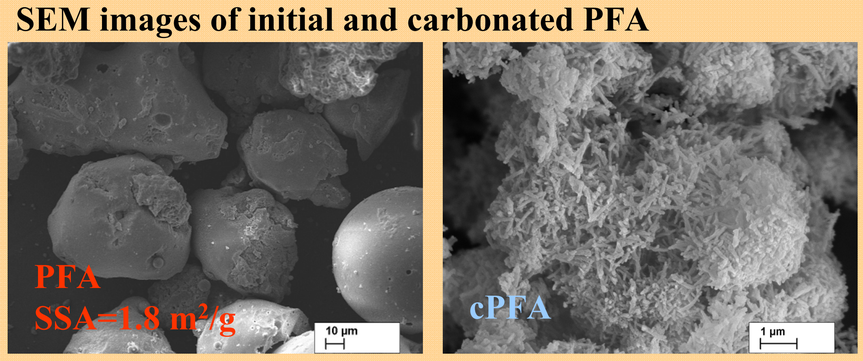
Theoretical CO_2 binding ability :
35 g CO_2/100g PFA

Free CaO
16.15 g CO_2/100 g PFA
CaO, $Ca(OH)_2$
~56% of the total CO_2 bound

Ca-silicates:
9.61 g CO_2/100g PFA
Predominantly *Ca_2SiO_4*
~33% of the total CO_2 bound

Other (Mg, K compounds):
3.1 g of CO_2/100g PFA
~11% of the total CO_2 bound

SEM images of initial and carbonated PFA



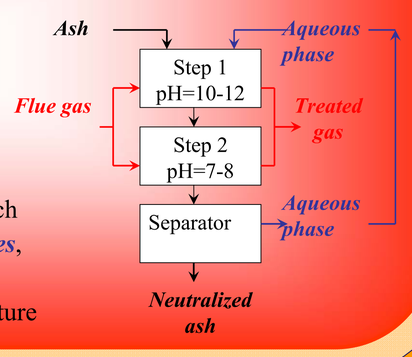
A new method for eliminating CO_2 from flue gases by Ca-containing waste material

The process includes contacting the aqueous suspensions of Ca-containing waste material with CO_2-containing flue gas in two steps:

First step: keeping the pH levels in the range of 10–12. The water-soluble components such as *free lime* are carbonated in the *first step*.

Second step: keeping the pH levels in the range of 7–8. The components of low water-solubility, in which *Ca is generally contained in the form of silicates*, are carbonated in the *second step*.

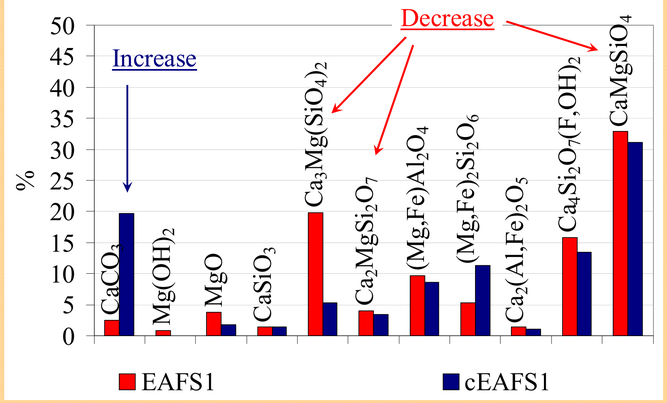
Conditions: atmospheric pressure, room temperature

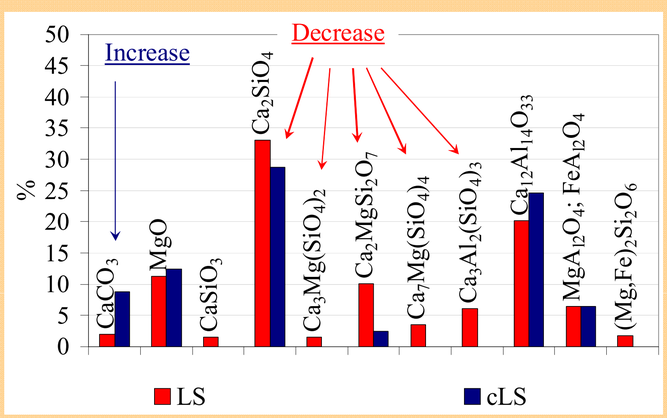


Direct aqueous carbonation of steel slag

Characterization of the initial slags

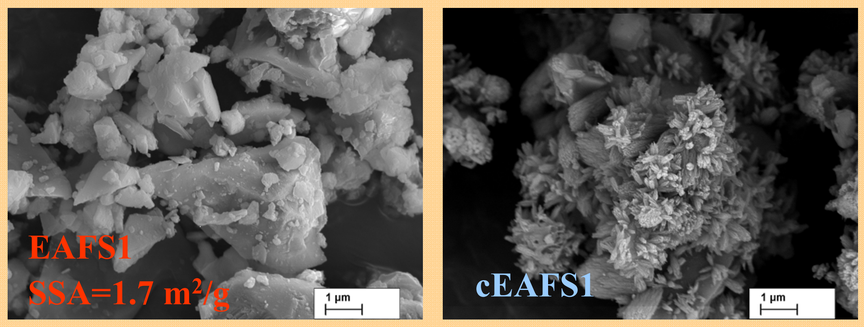
Chemical comp.	%	EAFS1	EAFS2	LS
CaO^t		36.12	26.91	42.22
MgO^t		18.95	18.95	14.99
Phase composition	%			
$CaCO_3$		2.5	2.3	1.9
MgO		3.8	tr	11.3
$Mg(OH)_2$		0.9	2.2	tr
α -Ca_2SiO_4				18.3
β -Ca_2SiO_4				14.8
$Ca_3Mg(SiO_4)_2$		19.8	1.4	1.5
$CaSiO_3$ 2M		1.4	2.3	1.5
$CaMgSiO_4$		32.9		
$Ca_4Si_2O_7(F,OH)_2$		15.8	14.8	
$Ca_2MgSi_2O_7$		4.0	3.3	10.1
$Ca_{12}Al_{14}O_{33}$				20.2
$Ca_7Mg(SiO_4)_4$				3.5
$Ca_3Al_2(SiO_4)_3$				6.1
$(Mg,Fe)_2Si_2O_6$		5.4	42.0	1.8
Mg_2SiO_4			10.6	
$MgAl_2O_4$		9.7	13.6	6.4
SiO_2		0.7	1.4	tr
$KAlSi_3O_8$		1.5	2.2	1.0
Σ		98.4	96.1	98.5



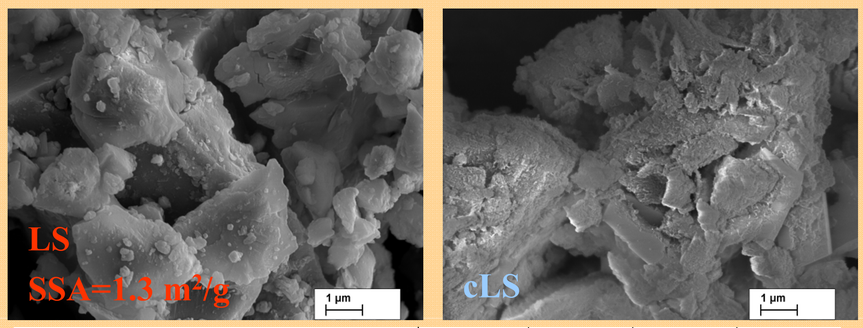


Distribution of Ca-Mg-compounds in the initial (EAFS1, LS) and treated materials (cEAFS1, cLS) according to qXRD.

SEM images of initial and carbonated EAFS1



SEM images of initial and carbonated LS



		EAFS1	EAFS2	LS	PFA
CO_2 bound	*g/100g*	8.7	1.9	4.6	29
Theoretical CO_2 binding ability	*g/100g*	48	41	48	35
Binding degree	*%*	18	5	10	83

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