Equilibrium calculations in aqueous carbonation of oil shale waste – sulfur compounds

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Layout

- Background, motivation
- Calculations methodology
- Results
  - ***Aqueous carbonation of CFBCA (circulating fluidized bed ash) systems***
  - ***Aqueous carbonation of SHCA (solid heat carrier ash systems***
- Conclusions

Background I

The main energy source in the Republic of Estonia is the local fossil fuel - **oil shale (OS)** - which is used for the power as well as **shale oil (SO)** production.

As a consequence:

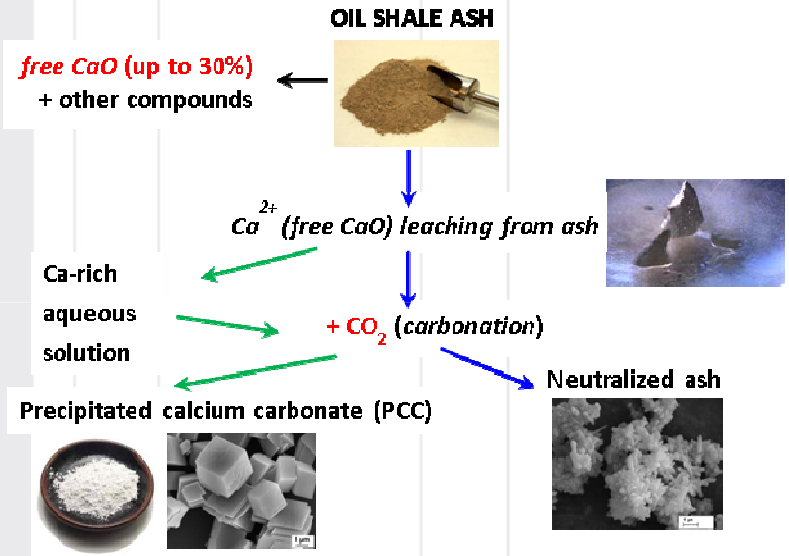
- large quantities of **OS mineral waste ~8.0 MT of OS waste per 2013**
- gaseous emissions of **CO_2, SO_x and NO_x** are produced.

Oil shale ash (OSA) is classified as a **"hazardous waste"** in Estonian registry of waste due to the highly alkaline leachates **(pH 12 - 13)** formed at hydrotransportation and open-air deposition of OSA.



foto: AS Narva Elektrijaamad

Background II

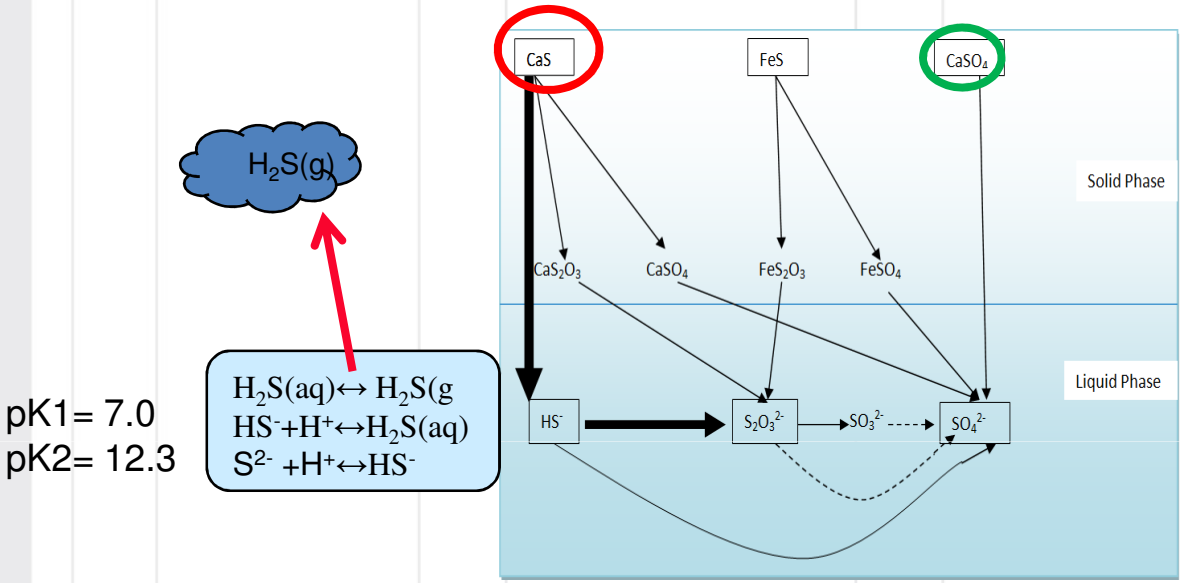


OS waste can be used as sorbents in the **CO_2 mineralization process**

Chemical stabilization of ashes can be achieved

Alkaline ash transportation water could be considered as a resource for **the production of PCC** ($CaCO_3$)

Background III - motivation

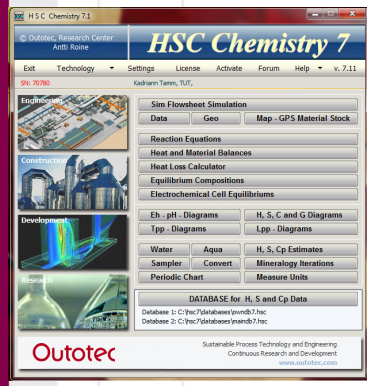


A transformation scheme of sulfur compounds in ash-disposal system

In order to minimize the environmental risks accompanied by utilizing OS wastes as a CO_2 trap and/or cheap Ca-source for PCC production the routes of sulfur compounds transformations have to be explored in different conditions

To better understand OS waste leaching/carbonation process, that we could reliably design technological schemes

Calculations methodology



Equilibrium Software HSC Chemistry

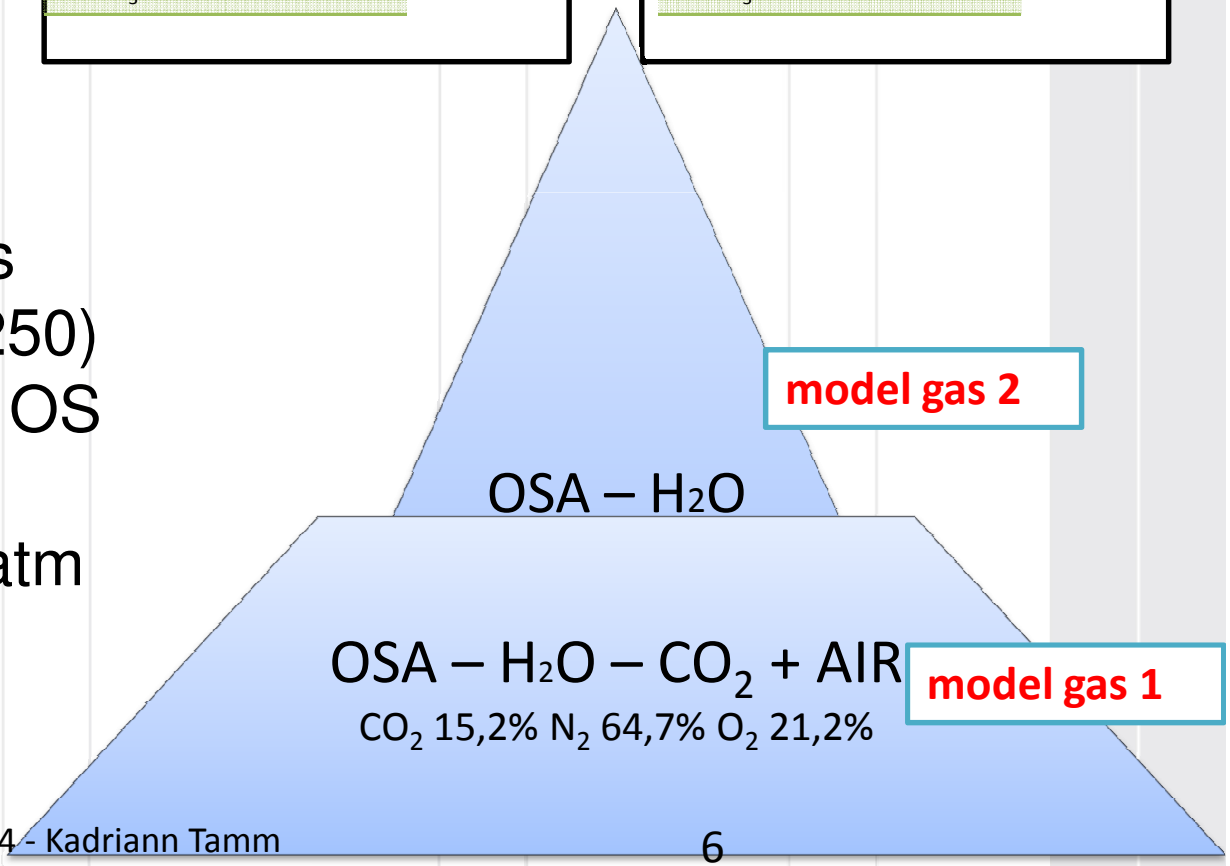
circulating fluidized bed ash (CFBCA)

Component	Wt%
CaO_{free}	10.44
CaSO4	5.47
CaS	0.64
MgO_{free}	3.94
$CaCO_3$	27.7

solid heat carrier ash (SHCA)

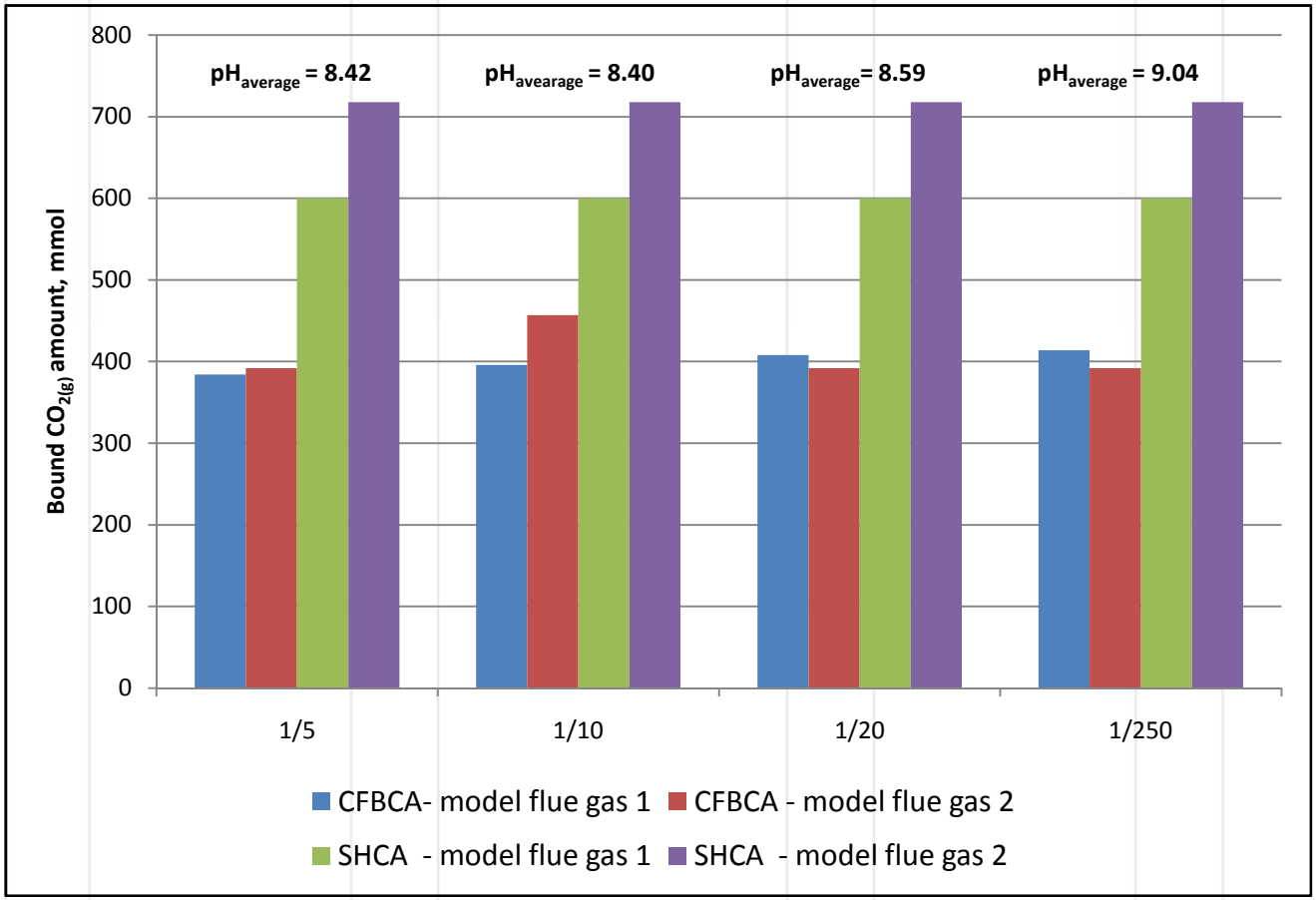
Component	Wt%
CaO_{free}	3.0
CaSO4	0.7
CaS	4.62
MgO_{free}	8.7
$CaCO_3$	29.4

Direct aqueous (S/L=1/5 to 1/250) carbonation of OS wastes at 25℃ and 1atm

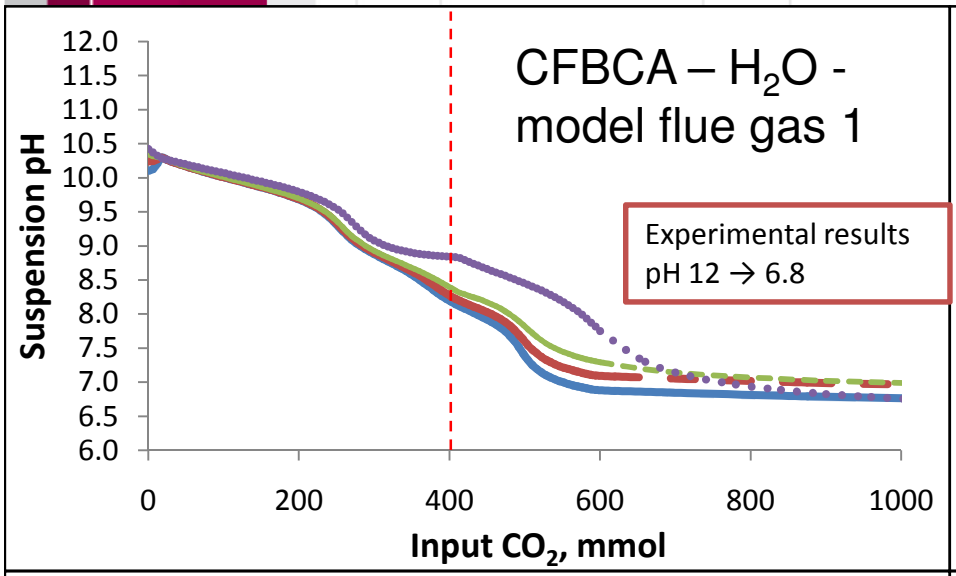


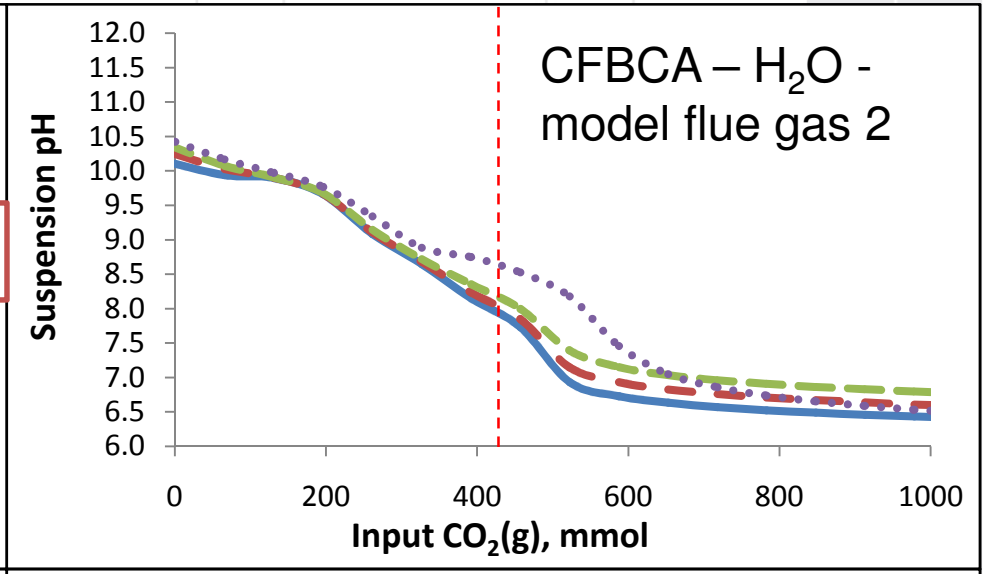
RESULTS

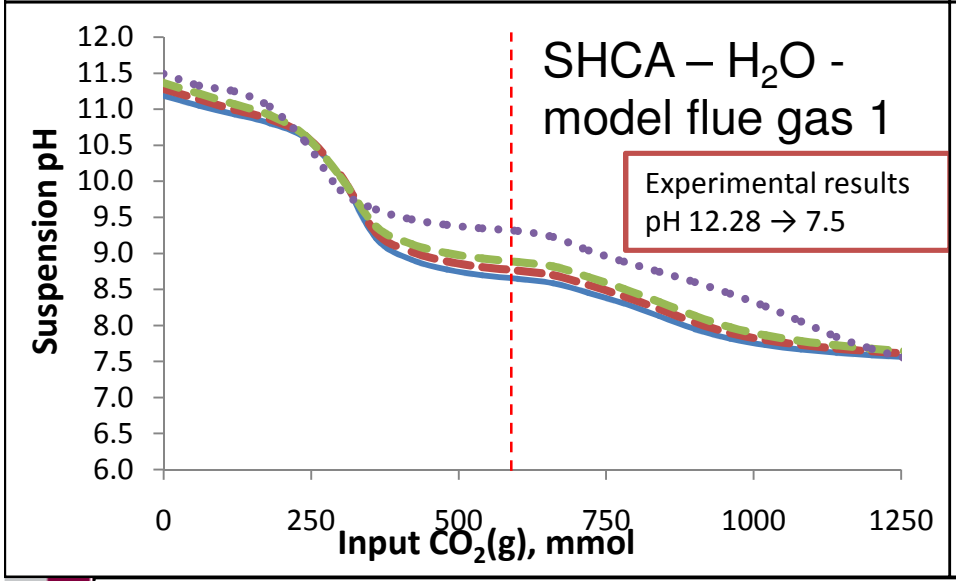
$CO_2(g)$ binding potential at aqueous carbonation of OS wastes

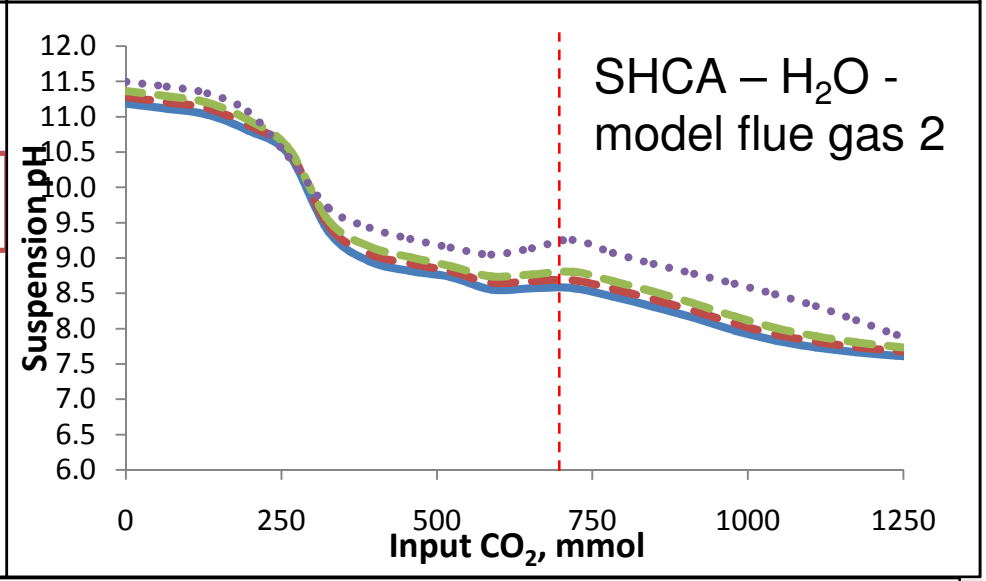


OSA suspensions pH changes



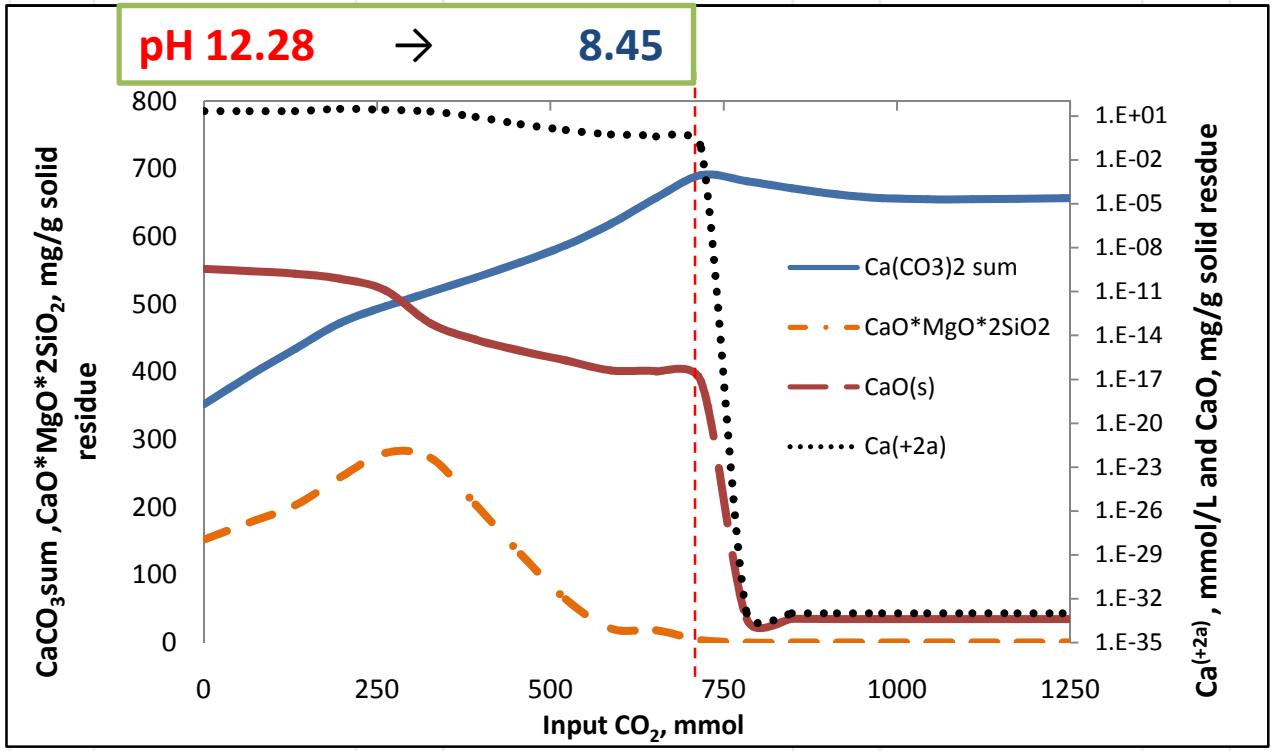






1/5 OSA/water — 1/10 OSA/water — 1/20 OSA/water ····· 1/250 OSA/water

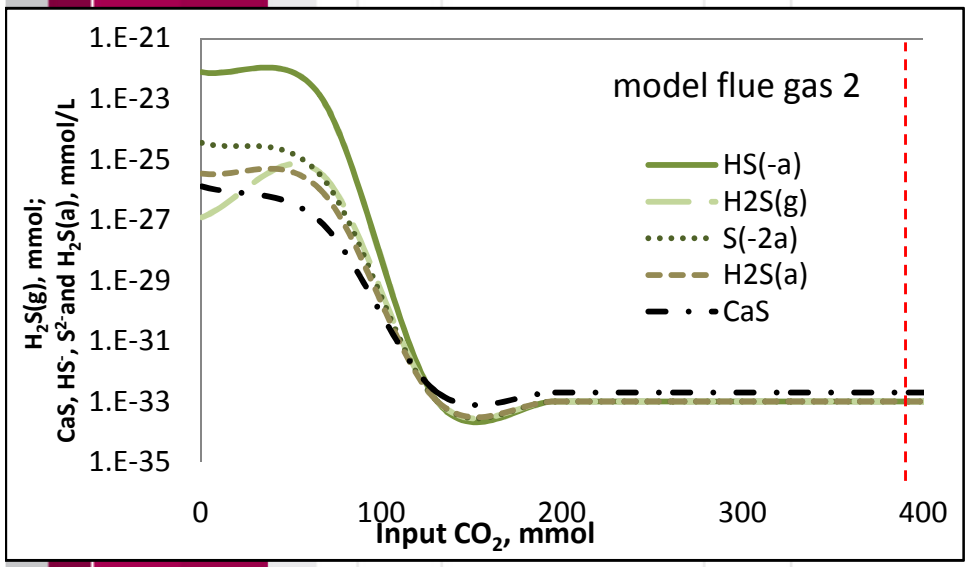
The behavior of Ca^{2+} -ion and solid phase in OSA - H_2O – flue gas systems

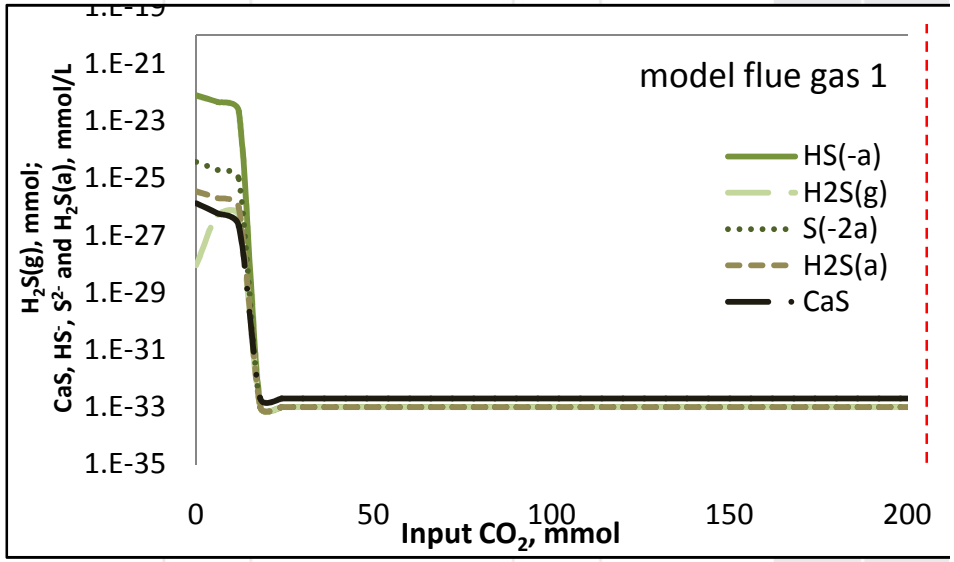


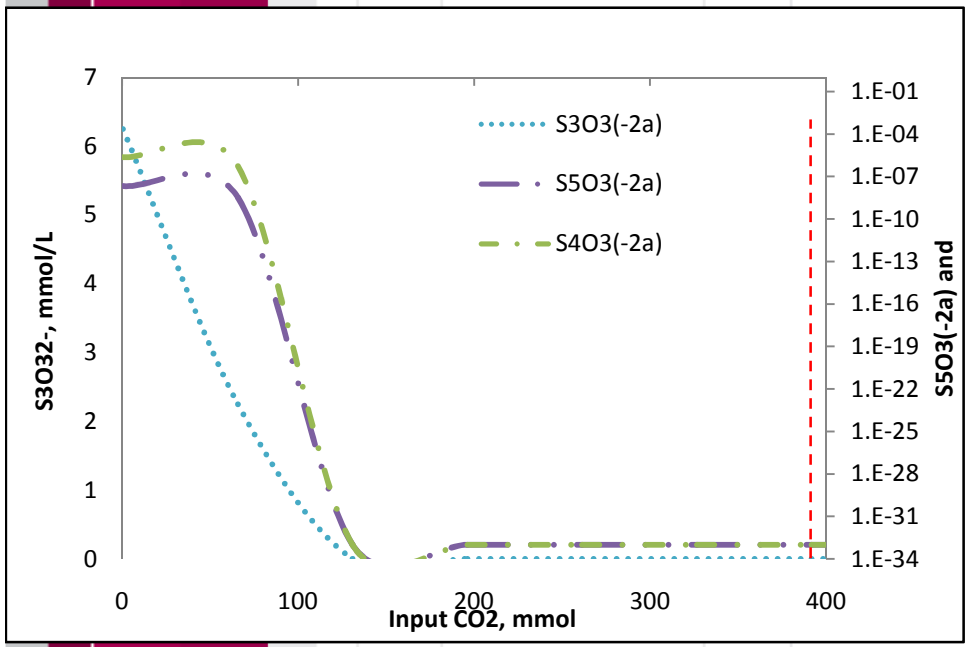
$$CaO + H_2O \leftrightarrow Ca(OH)_2 \leftrightarrow Ca^{2+} + \mathbf{OH^-}$$

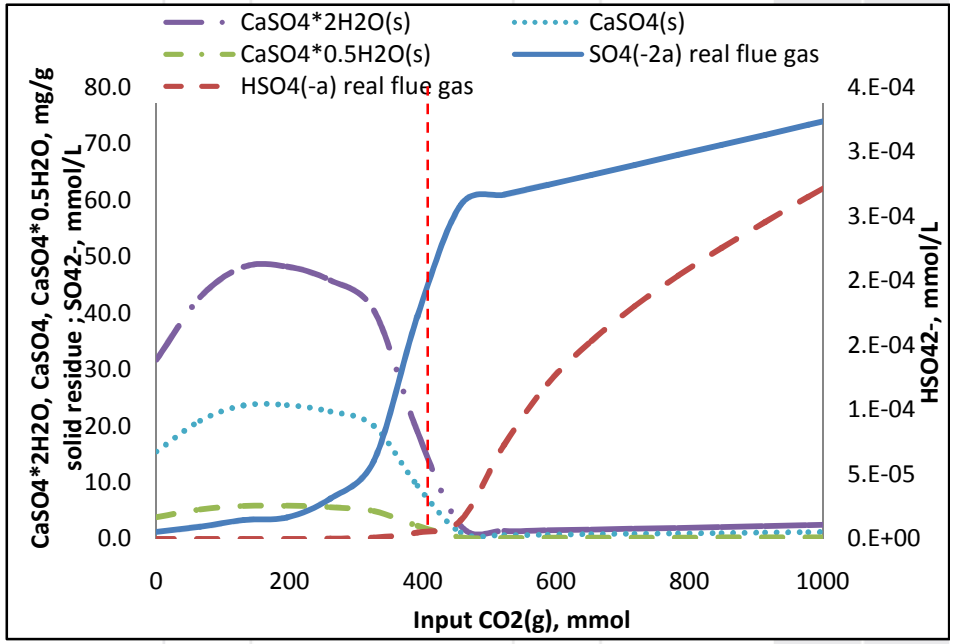
$$Ca^{2+} + CO_3^{2-} \leftrightarrow \mathbf{CaCO_3}$$

The behavior of sulfur in CFBCA -H_2O systems





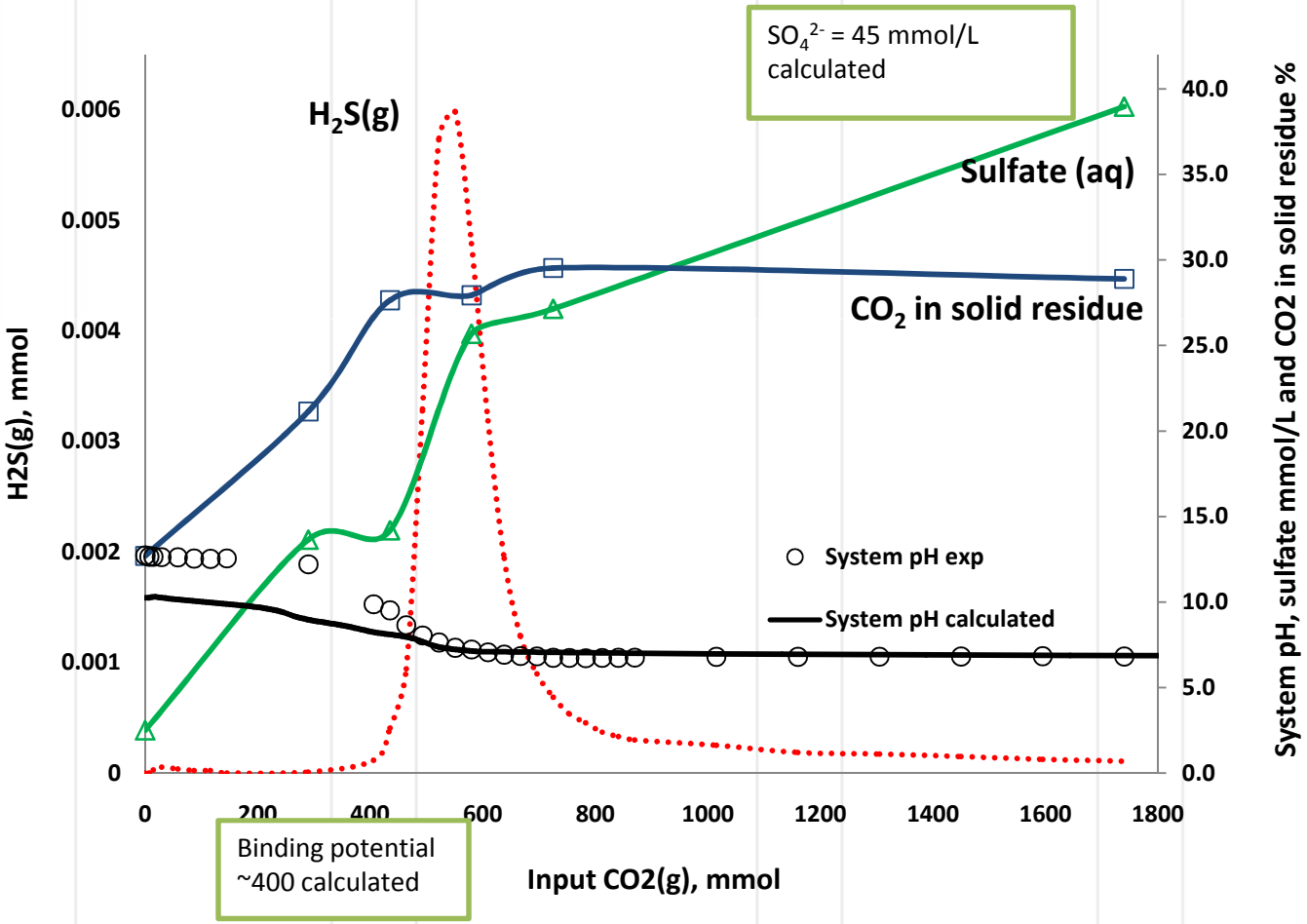




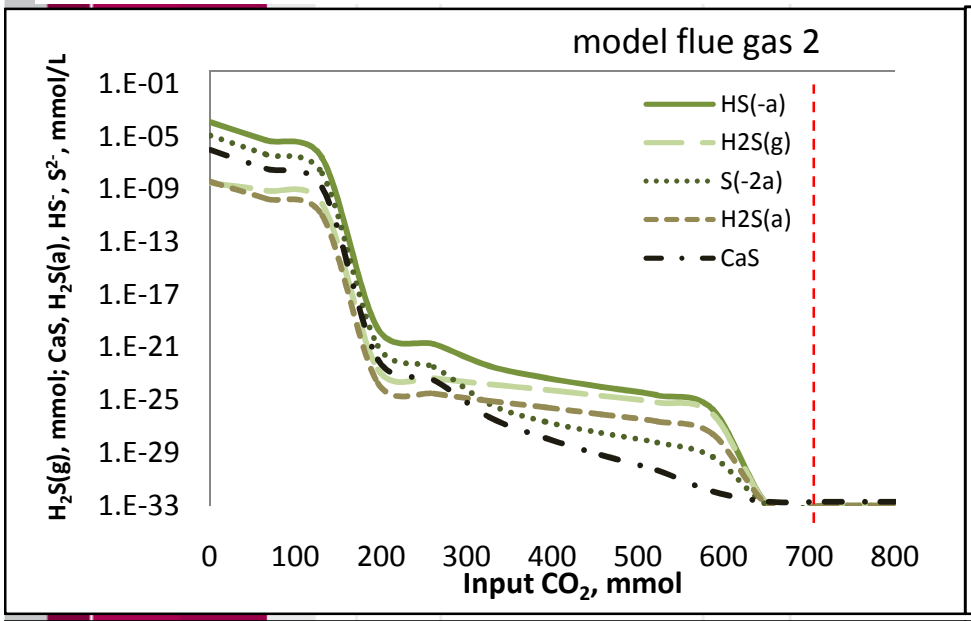
Experimental results OSA – H_2O –model flue gas systems; S/L = 1/10

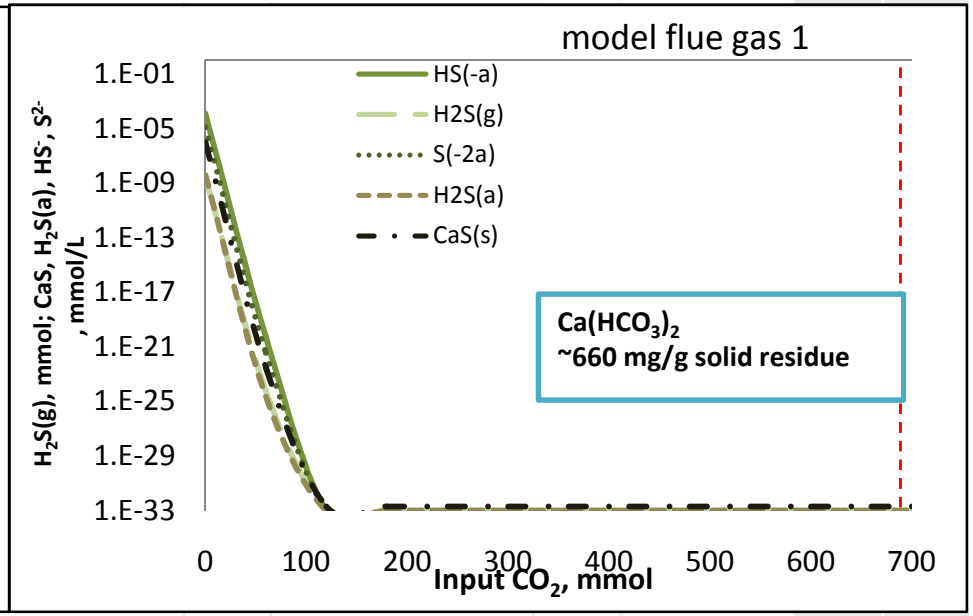


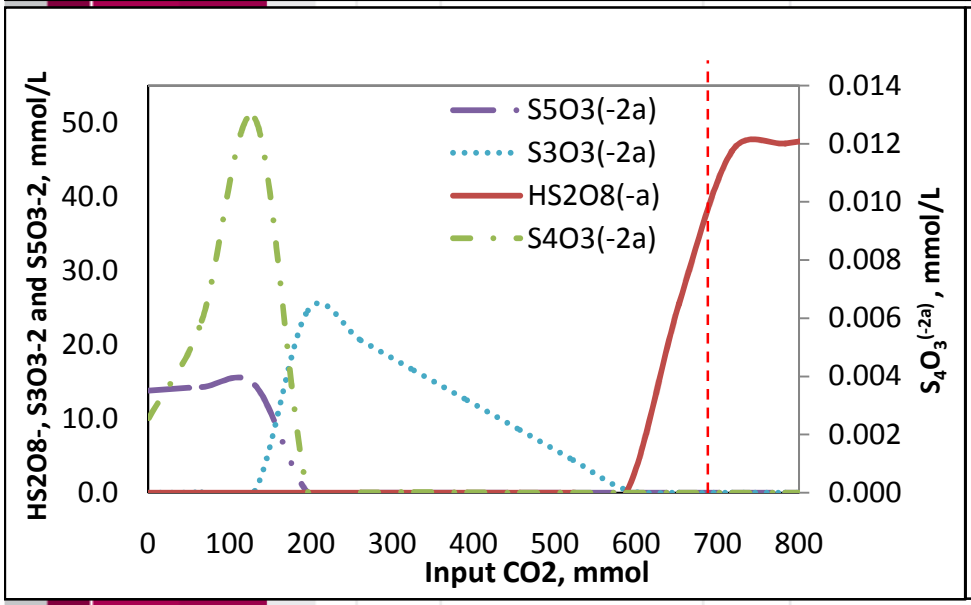
Batch reactor

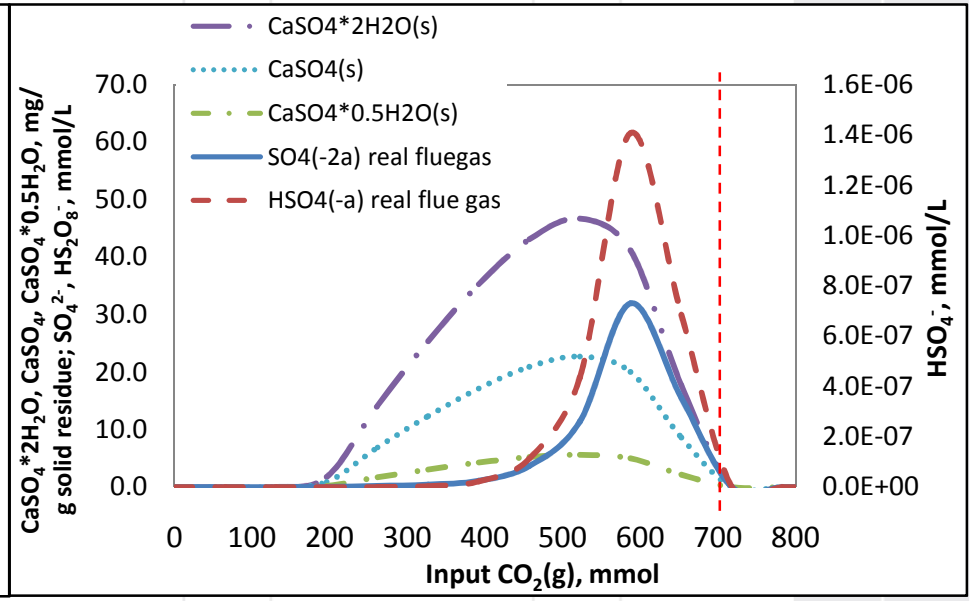


The behavior of sulfur in SHCA–H_2O systems









Conclusions

- Considering the amounts of deposited waste from OS sector, the mineral carbonation of acidic gases is a promising solution in reducing greenhouse gas emissions and utilizing OS waste, while monitoring the pH and oxidation potential of aqueous carbonation to minimise sulfur pollution.
- The study shows that oil shale waste are able to bind 264 – 308 kg of CO_2 per ton of mineral waste under certain conditions
- SO_4^{2-} —ions dominated (comparing with other sulfur species) in all OS waste – H_2O – acidic gases systems
- The behaviour of sulfates were dependent on the system pH, while thiosulfates depended on the equilibriums of sulfide forms
- If system pH < 9 sulfides were depleted
- The HSC calculation results of model systems were in reasonable accordance with the experimental results
- SHCA is not suitable for carbonation due to the high content of sulfide and because of the formation of bicarbonates

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Thank you for your kind attention.

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