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Solid sorbents for CO₂ capture applications

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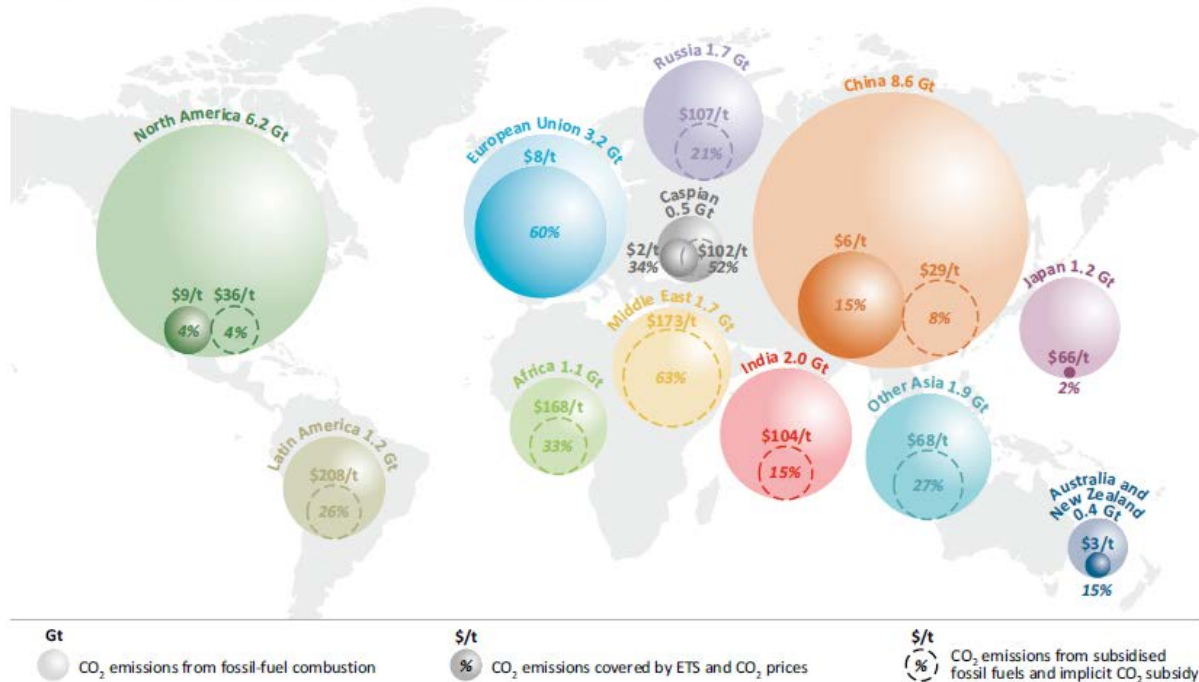
Materials for CO₂ Capture at high temperature

- CCS introduction
- The challenge
- Adsorption
- Pre-combustion IT sorbents
- Post-combustion HT sorbents

Introduction: GHG Emissions Reductions

- Kyoto Protocol (1997) & Doha amendment (2012): Binding targets for 37 countries. USA, Canada, China, India, Brazil, Russia, Japan not included.

Figure 1.2 ▸ Energy-related CO₂ emissions in selected regions, 2014



Notes: The implicit CO₂ subsidy is calculated as the ratio of the economic value of those subsidies to the CO₂ emissions released from subsidised energy consumption. ETS = emissions trading scheme.

- COP21 a step ahead. 195 countries signed a pledging action agreement

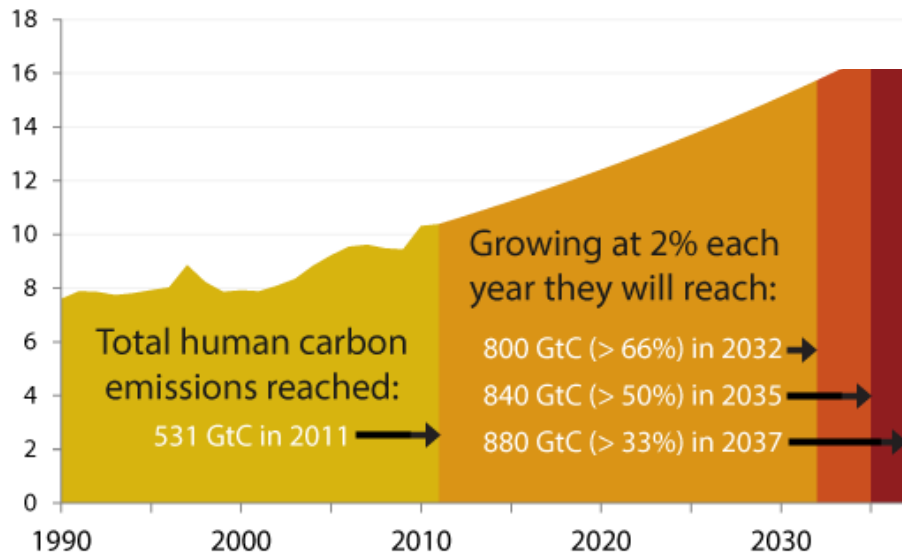
..... Will it be enough??

- Lack of immediate action. The agreement come into force in 2020
- Pledges are not strictly binding

Introduction: Solutions for 2050

Reaching the 2°C Carbon Budget (840 GtC by 2100)

Business as Usual carbon emissions in GtC/year



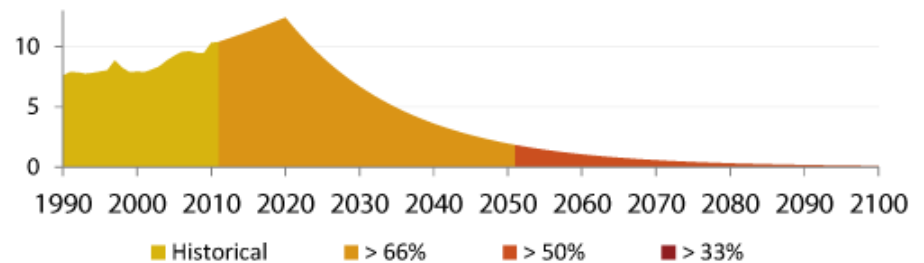
Note: the % in brackets are the chances of limiting warming to 2°C

Data: Budget - IPCC WGI AR5. Historical - Global Carbon Project

Note: assumes limited further non-CO2 forcings as per RCP 2.6 shrinkthatfootprint.com

- One third of oil, half of gas and almost 90% of coal reserves must remain unburned (McGlade and Ekins, *Nature*, 2015:517,187-190)

e) If we wait till 2020 to begin annual reductions of 6%/yr are required



Note: the % is the chances of limiting warming to 2°C

Data: Budget - IPCC WGI AR5. Historical - Global Carbon Project

Note: assumes limited non-CO2 forcing changes (RCP 2.6)

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- Transforming the energy sector is vital, but not the sole solution: the goal can only be achieved provided that CO₂ and GHG emissions in non-energy sectors are also reduced.

- Carbon Capture and Storage: Global CO₂ target of **10-20%**

Introduction: Technical challenge

- Huge scale operations, very large flow rates !!

1000 Megawatt Coal Fired Power Station

Stack gas flow rate = $6 \times 10^6 \text{ m}^3/\text{hr}$
= 1 cubic km per week!
CO₂ flow rate = 1300 tonne/hr
= One tractor trailer load in 4 minutes!



1st Power plant CCS

Location: Boundary Dam Power, Canada

Feedstock: Coal

Size: 139 MW gross (1Mt/yr) Retrofit

Capture Technology: PC amine

CO₂ Fate: EOR in Weyburn field (90% of CO₂).

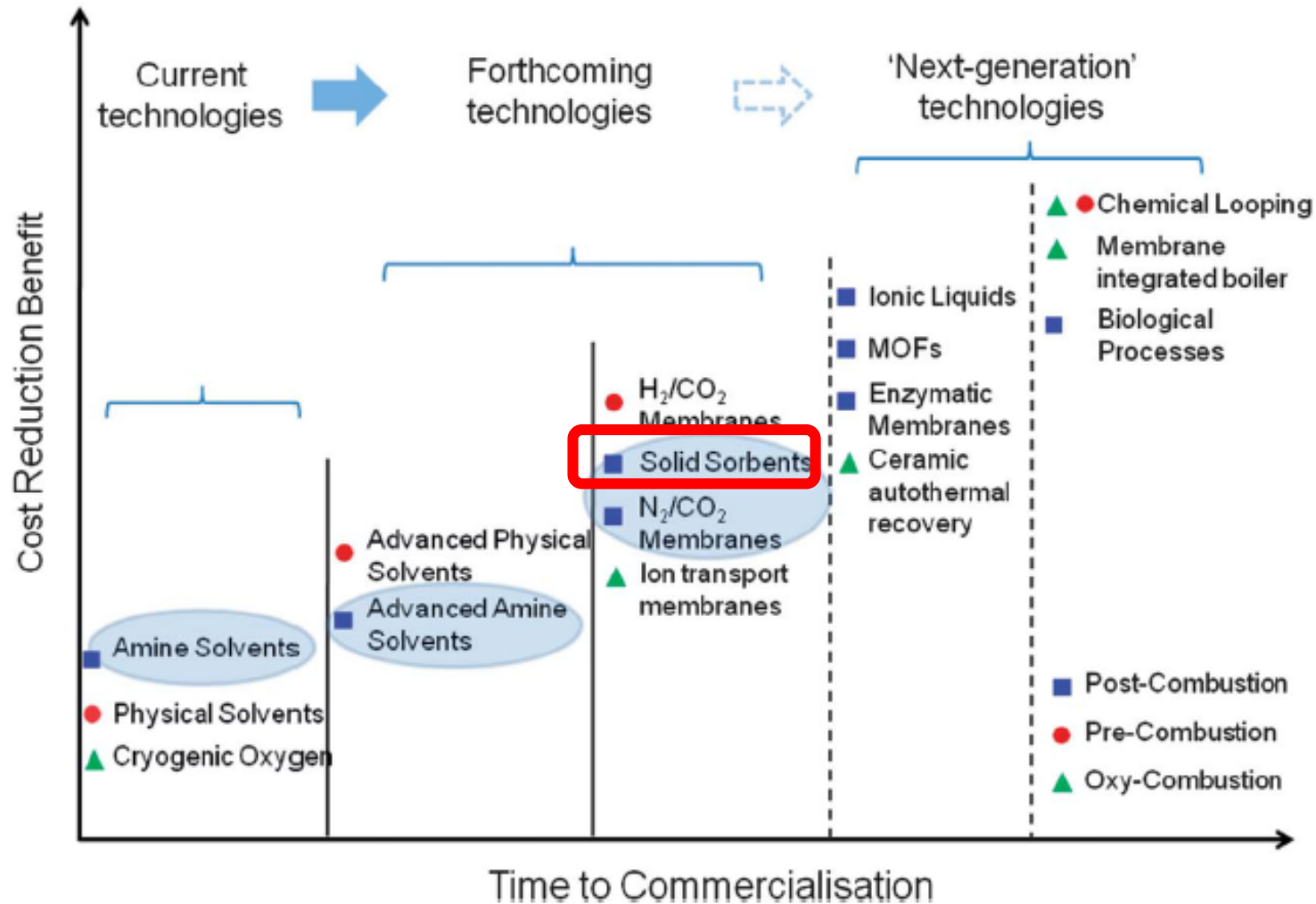
Transportation is via 66 km pipeline.

Start Date: Started in October 2014....

Fully operational end 2016

Economics: The total cost of the project was \$1.3 billion.

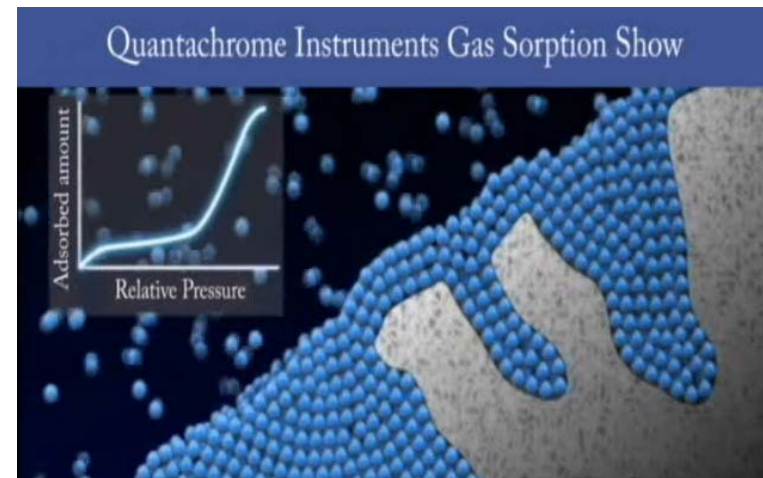
CO₂ capture technologies



- It is a surface phenomenon (the concentration on the surface of adsorbent is different from that in the bulk; its rate is high in the beginning and then decreases till equilibrium is attained).

PHYSICAL ADSORPTION	CHEMICAL-ADSORPTIONS
The forces operating in these are weak vander Waal's forces	The forces operating in these cases are similar to those of a chemical bond
The heat of adsorption are low i.e. about 20 – 40 kJ mol ⁻¹	The heat of adsorption are high i.e. about 40 – 400 kJ mol ⁻¹
No compound formation takes place in these cases	Surface compounds are formed
It does not require any activation energy.	It requires any activation energy.
This type of adsorption decreases with increase of temperature	This type of adsorption first increases with increase of temperature. The effect is called activated adsorption
It forms multimolecular layer	It forms unimolecular layer

Adsorption



- At low relative pressure, a monolayer is adsorbed, which is used to calculate the BET area.
- Increasing relative pressure, additional molecules are adsorbed through multilayer formation
- If the pores are not too large (mesopores), they can be filled completely (capillary condensation)

Desorption

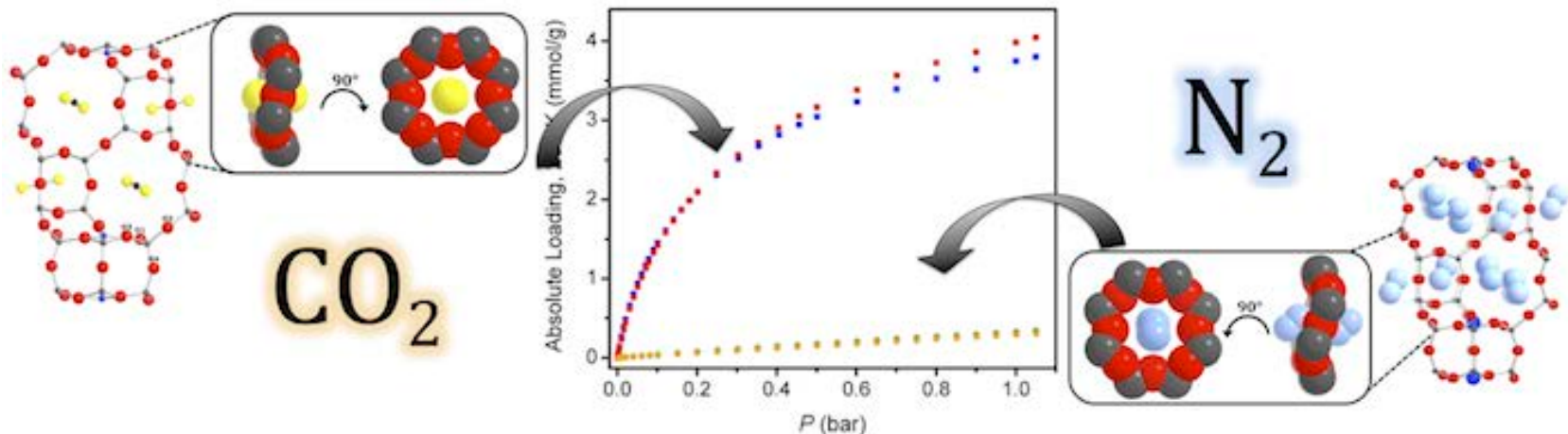


- Adsorbed molecules are desorbed by pressure swing and/or heating

Development of CO₂ sorbents

As an alternative method for CO₂ capture, adsorption can be considered to be one of the more promising methods, offering potential energy savings compared to absorbent systems, especially with respect to compression costs.

- CO₂ loading capacity
- CO₂ adsorption/desorption rate
- Resistance and high activity at high temperature and pressure
- Resistance to moisture, SO₂ etc.
- Cost
- Selectivity



Sorbents for Pre combustion CO₂ capture

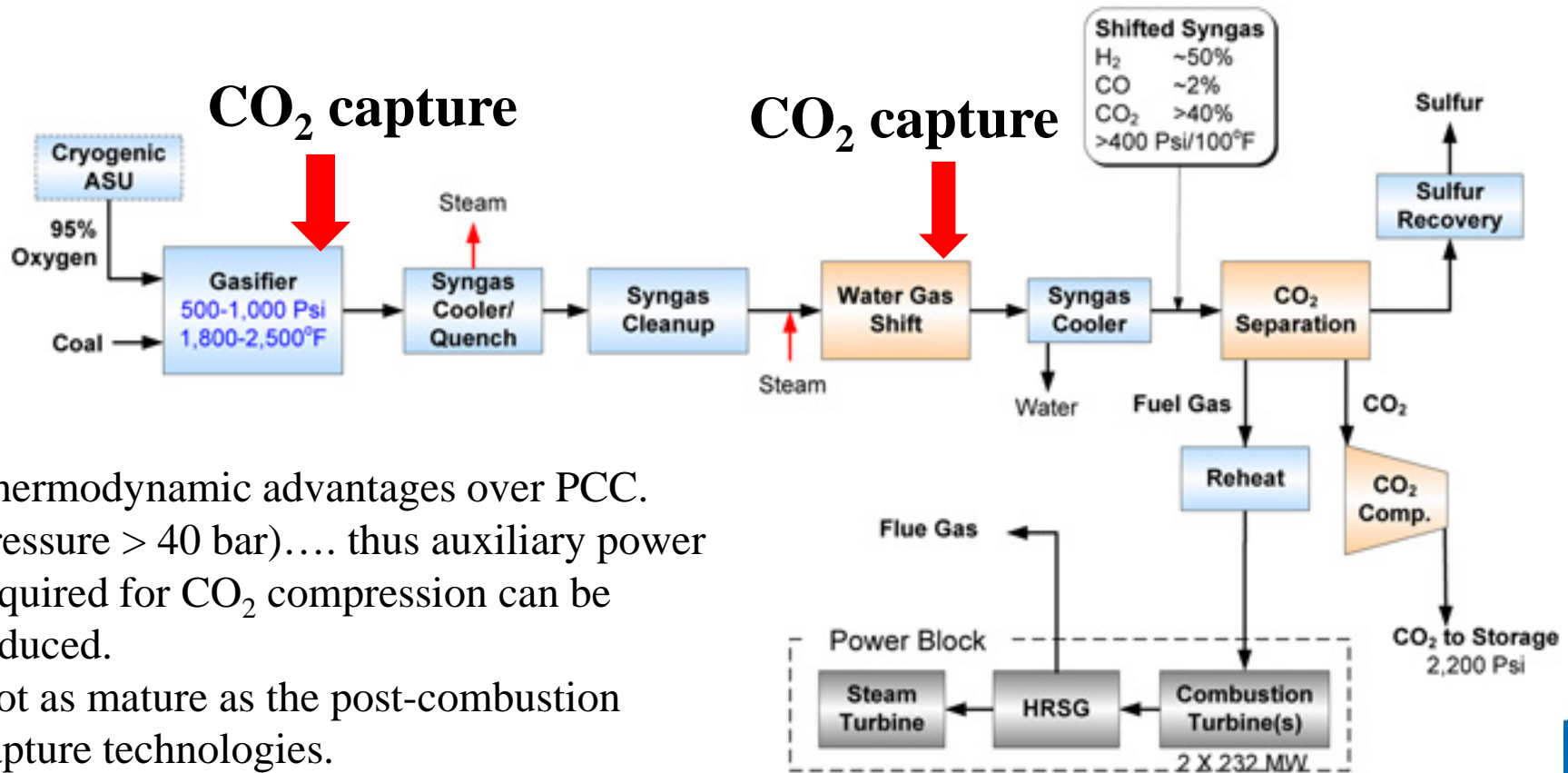
Development of porous solid adsorbents for pre-combustion technologies: (Materials should be able to work at high temperature and pressure). Trial and error, initial screening by TGA

- **Amine modified mesoporous silica sorbents** (e.g. SBA-12/15 mes. silica): Highly selective for CO₂. Capacity \approx ten times zeolites. Suffer thermal degradation at 400-850°C
- **Zeolites**: Capture capacity decreases at high temperature due to degradation of their structure. High affinity for H₂O limit use with humid stack gas. Adsorbent is unstable to acid conditions (SO_x).
- **Calcium and magnesium oxides, Hydrotalcite** (Mg₆Al₂CO₃(OH)₁₆·4(H₂O)): Very good CO₂ capture capacity but sinter at high temperature. To avoid sintering Al₂O₃ can be used as stabiliser for Ca/MgO structure. Hydrotalcite structure collapses at T>550°C.
- **Alkali silicates (e.g. Li₄SiO₄)**: Very good adsorbent at pre-combustion conditions. High CO₂ capture capacity, stable at high temperature, resistant to attrition.

Pre-combustion CO₂ capture

Gasification: $\text{CH}_m\text{O}_n + \text{O}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{CO} + \text{CO}_2 + \text{CH}_4 + \text{C}_2\text{H}_4 + \text{C}_2\text{H}_6 + \text{CH}_m' \text{O}_n'$

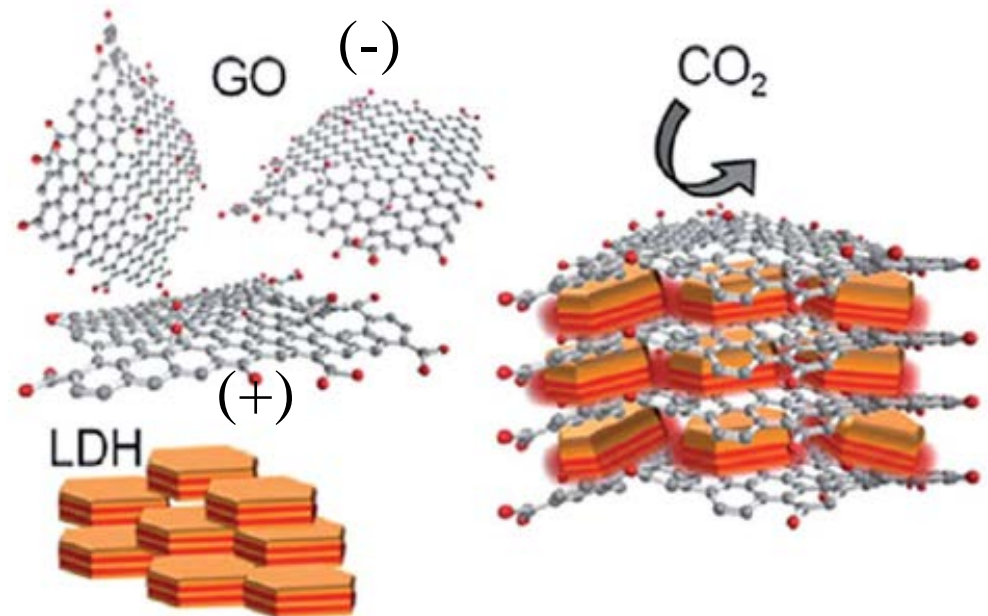
Shift reaction: $\text{CO} + \text{H}_2\text{O}(\text{g}) \rightarrow \text{H}_2 + \text{CO}_2$



- Thermodynamic advantages over PCC. Pressure > 40 bar)... thus auxiliary power required for CO₂ compression can be reduced.
- Not as mature as the post-combustion capture technologies.
- Applicable for new power plants.

- Layered double hydroxides (LDHs) [mainly **Hydrotalcite**, Mg₆Al₂CO₃(OH)₁₆·4(H₂O)] have been heavily investigated as sorbent for intermediate temperatures
- By intercalating long carbon-chain organic anions (e.g. stearate) into LDHs, the CO₂ capture capacity was markedly increased to 1.25 mmol /g, which is 2.5 times higher than that of traditional LDH-based sorbents (0.5 mmol/ g).

Nanohybrids in a “layer-by-layer” fashion

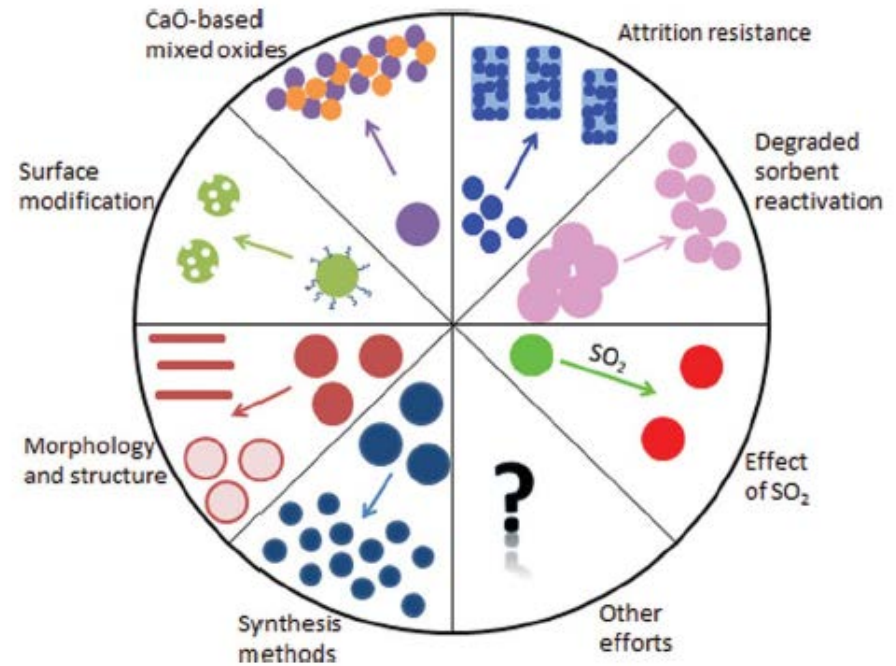
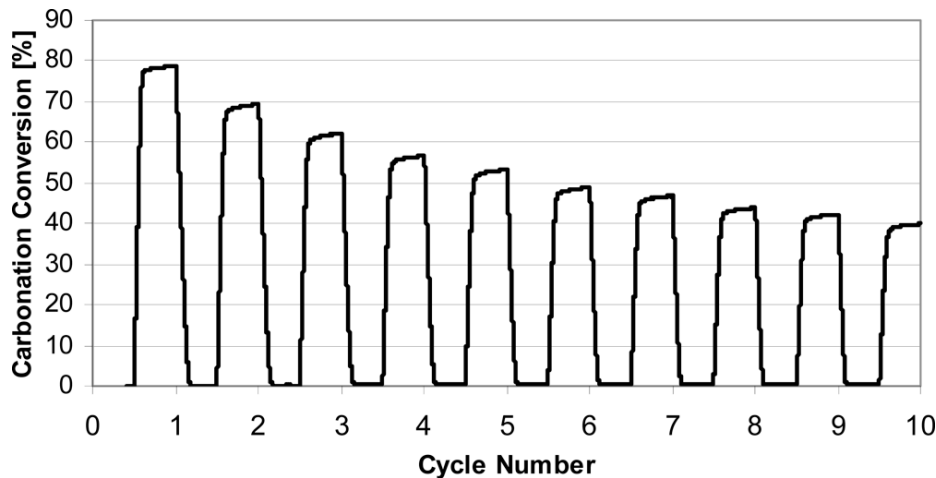


- CO₂ capture capacity of the Layered double hydroxides (LDHs) increased by 60% using 7 wt% GO as support.

High Temperature CO₂ sorbents (> 400°C): CaO

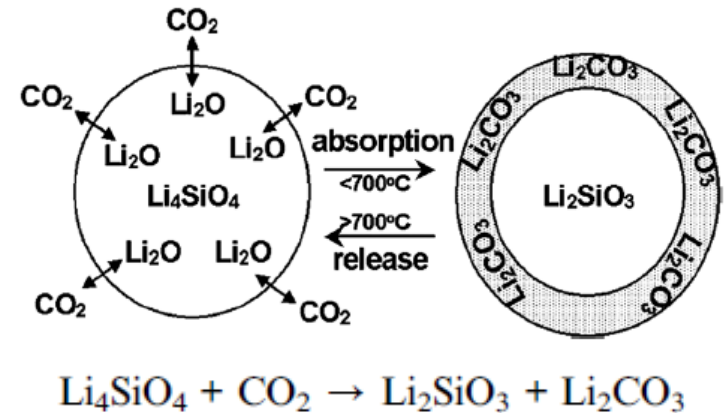
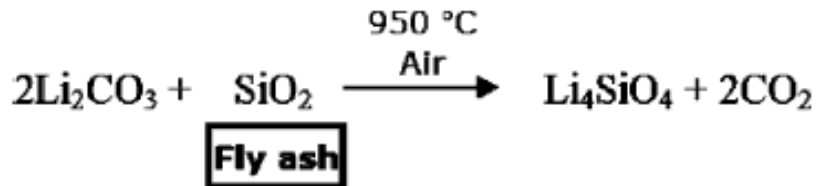
Abundant and cost-effective Ca-based sorbents have high sorption capacity (10-16 mmol CO₂/g sorbent at 700°C) but present important limitations such as:

- rapid loss of activity during the capture cycles
- sintering and attrition (fragile material)
- desorption at 850-900°C
- SO₂ irreversibly forms CaSO₄



High Temperature CO₂ sorbents (> 400°C): alkali-metals from fly ash

- Alkali metal based sorbents advantages are: high CO₂ capture capacity, lower regeneration temperatures (<750°C) and excellent stability.
- Pure lithium silicates have shown the largest CO₂ sorption capacity and the fastest CO₂ sorption.
- Fly ash (FA) from the combustion of ground or powdered coal in power plants can be used as a cheap source of SiO₂



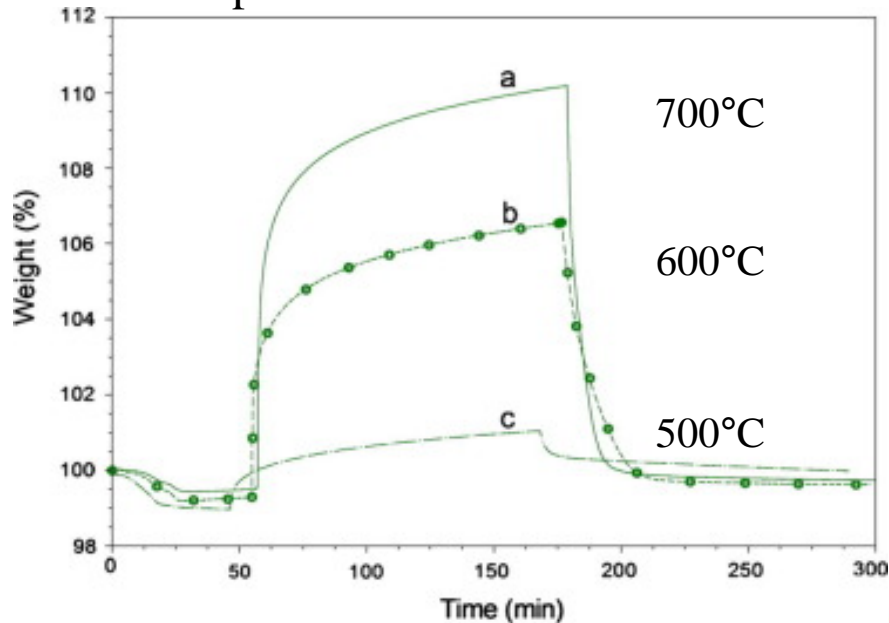
- At 600°C and 40 mol% K₂CO₃, the maximum CO₂ sorption capacity for the sorbent derived from fly ash was 2.4 mmol CO₂/g sorbent.

➤ Lithium is expensive, toxic and rare.....

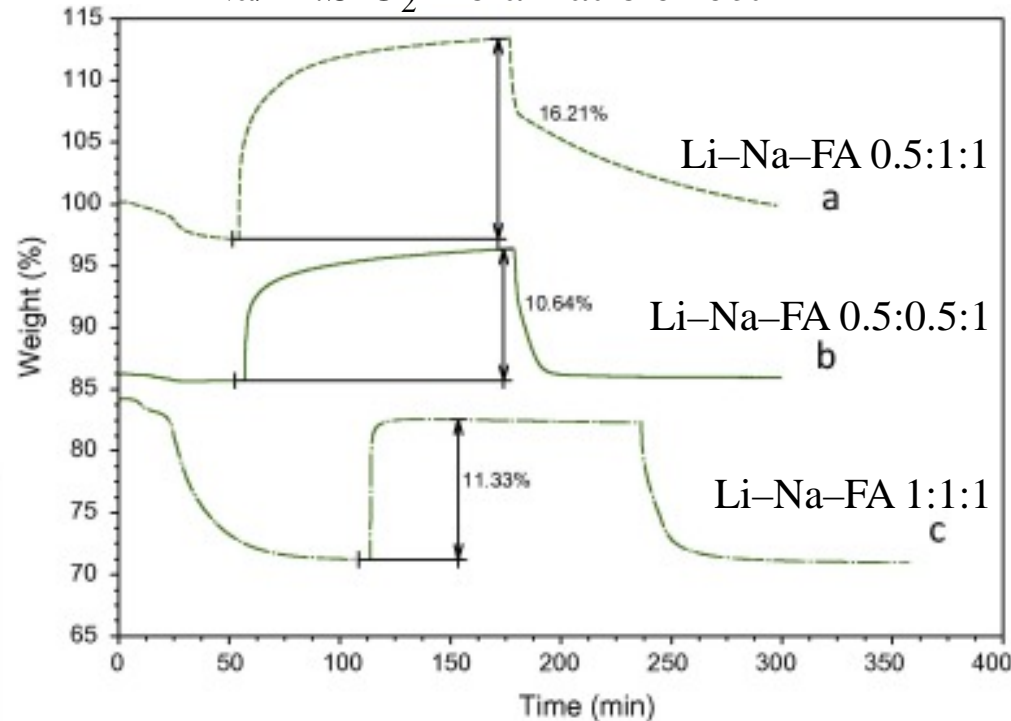
Development of materials with limited amount of lithium:

- $\text{Li}_4\text{SiO}_4 + \text{CO}_2 \rightarrow \text{Li}_2\text{CO}_3 + \text{Li}_2\text{SiO}_2$
- $\text{Na}_2\text{SiO}_3 + \text{CO}_2 \rightarrow \text{Na}_2\text{CO}_3 + \text{SiO}_2$

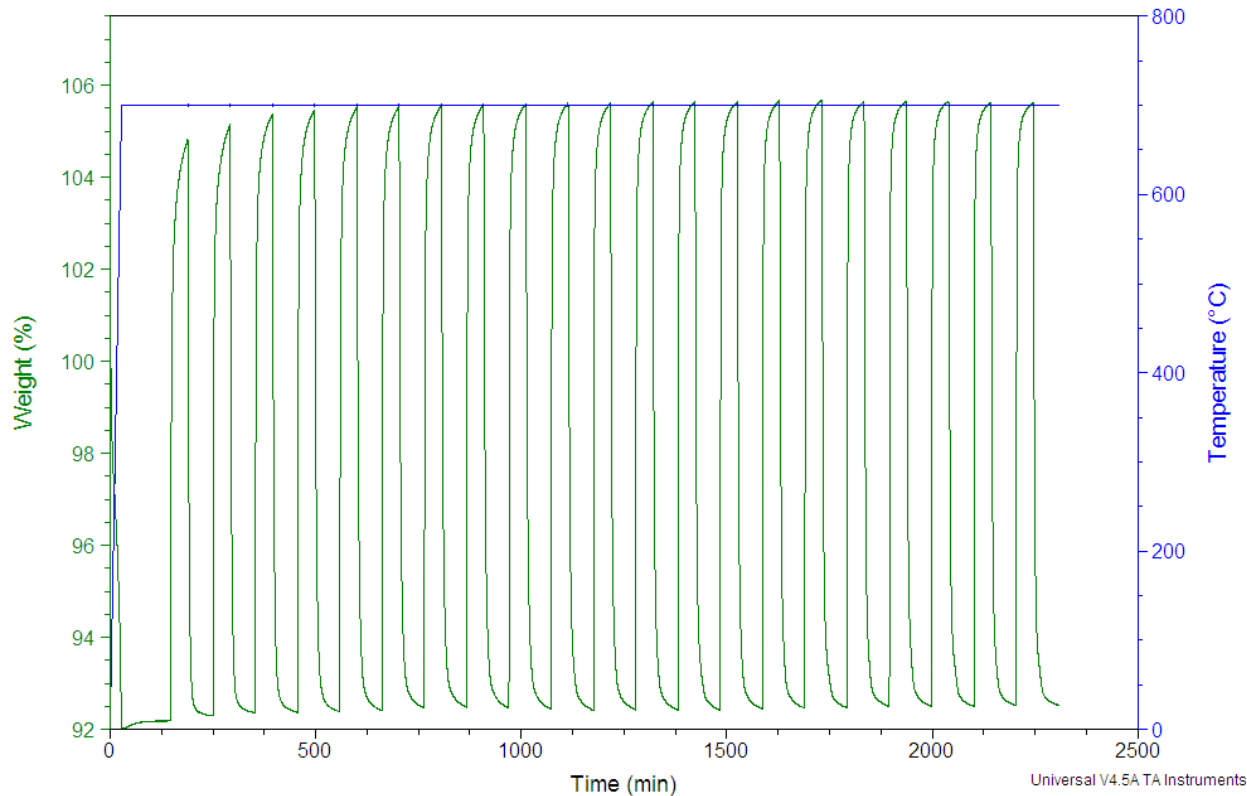
Temperature effect



Na/Li:SiO₂ molar ratio effect

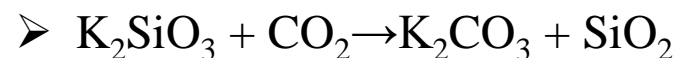


- Li–Na–FA molar ratios and calcination temperature determined the sorbents CO₂ uptake
- CO₂ uptake capacity was **2.54 mol CO₂/kg sorbent** with 12% H₂O and 14% CO₂ at 700°C



- Na/Li–FA sorbents stability maintained after **21 cycles**

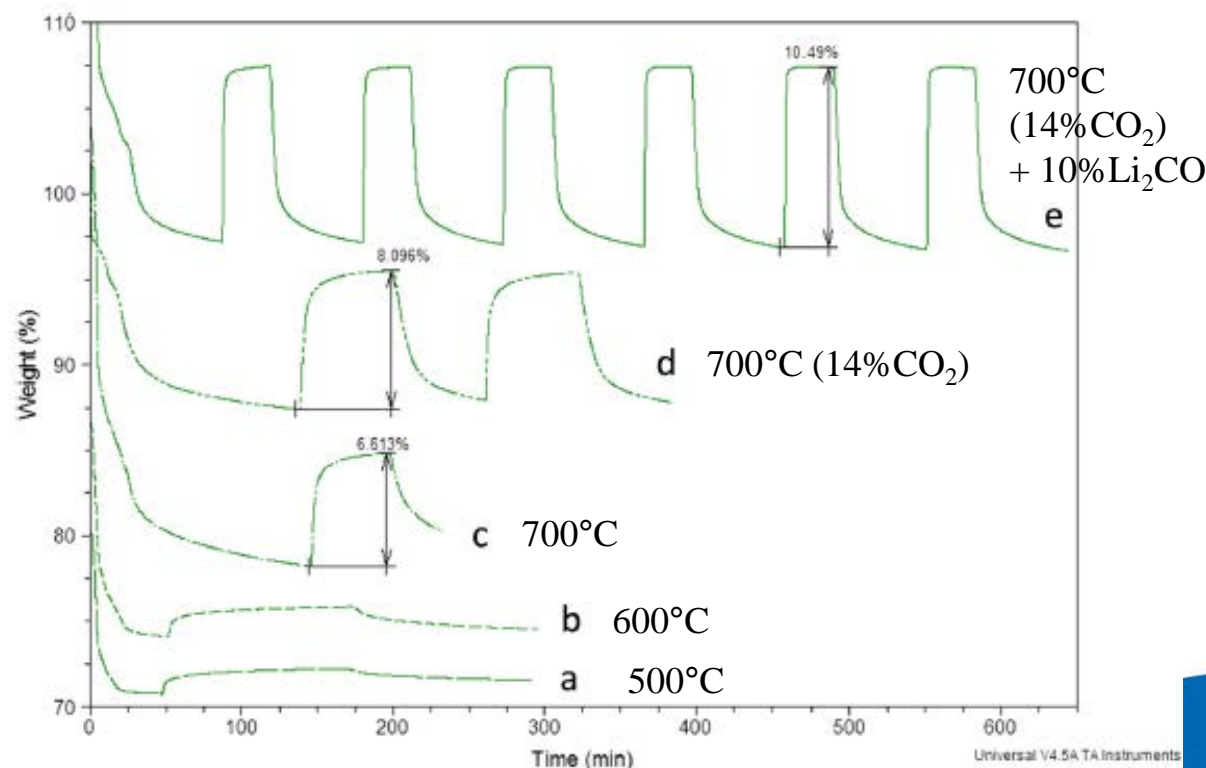
- A maximum loading of 2.38 mmol CO₂/g K-FA at 700°C (similar to Li-Na and Li-FA sorbents)



- CO₂ chemisorption follows a double layer mechanism with formation of carbonate layer on the surface

- Presence of additives (e.g. Li₂CO₃) favour the diffusion of cations and CO₂ in the material matrix

K-FA 1:1



Conclusions

- For intermediate temperature CO₂ sorbents, LDH derived mixed oxides are very promising but remaining issue is how to maintain their mechanical strength in the presence of steam and at high temperatures
- For high temperature CO₂ sorbents, CaO has a high CO₂ uptake capacity, but suffers severely from sintering during regeneration and degraded sorbent reactivation and effect of SO₂ must be addressed
- Alkali-silicates (e.g. Li₄SiO₄) are emerging high temperature sorbents, which have shown high CO₂ capture capacity and lower regeneration temperatures compared to CaO

Thank You!