Teesside University

Natural Carbon Capture and Storage through clay minerals

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Freeman Dyson in his book on the **Origins of Life** pointed out that there were three main theories of life, labelled by their most prominent advocates: Oparin (peptides), Eigen (RNA), and Cairns-Smith (Clays). It was on the surfaces of iron minerals (Clays) where the fixation of CO2 and N2 occurred.

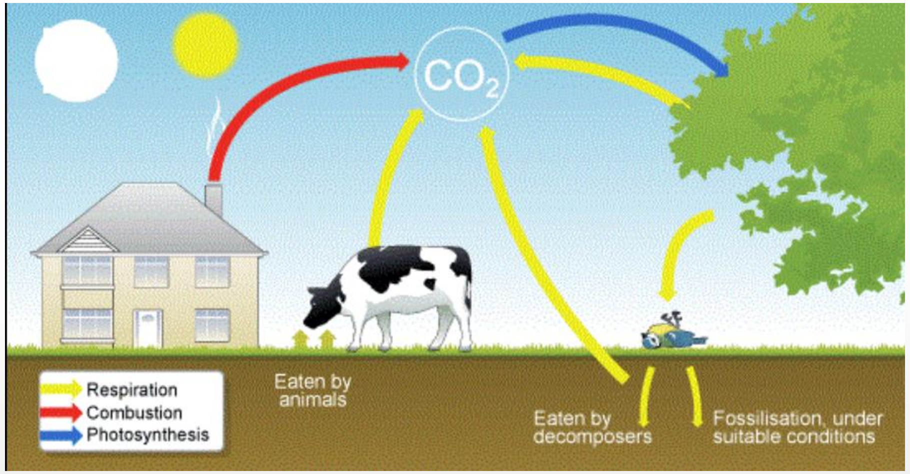
Outline

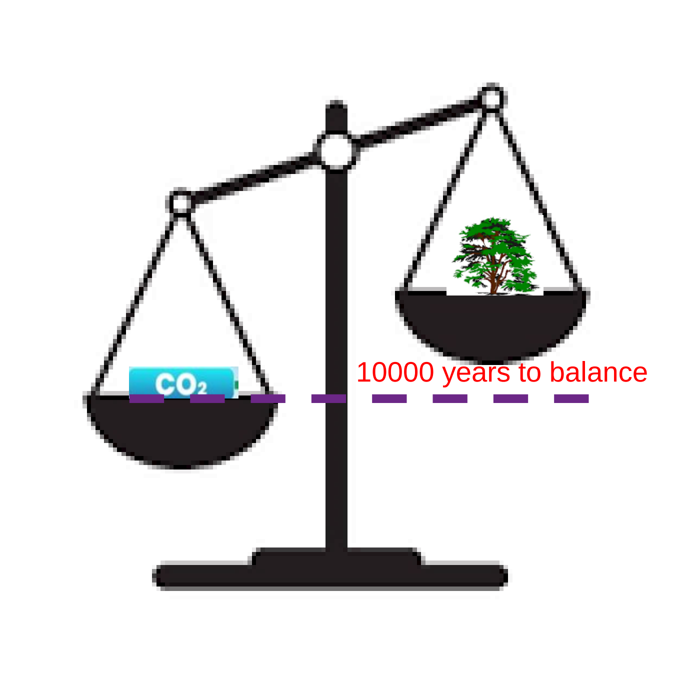
- Acknowledgment
- Greenhouse emission : Global vs UK
- Major decarbonisation techniques – Adsorption and Negative emission techniques
- Clay minerals , Abundance and capture and storage mechanisms
- Land CO2 Capture and Storage monitoring

Acknowledgment:

- Industry support :
- Laboratory and simulations
  - PhD and Master Students

Carbon Cycle





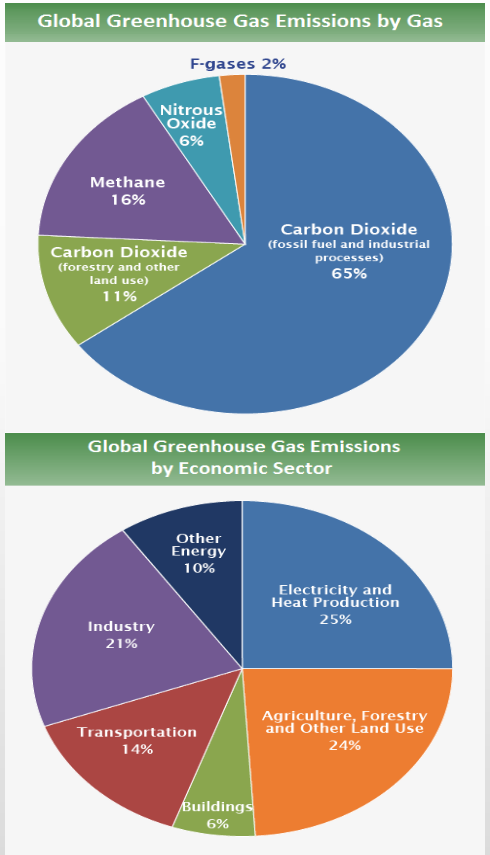
Our planet absorbs and emits about **100 billion tons** of carbon dioxide through this natural cycle **every year,** *Prof Rothman (MIT)* says.

Human CO2 emission through **fossil fuels** is only **a tenth of nature**

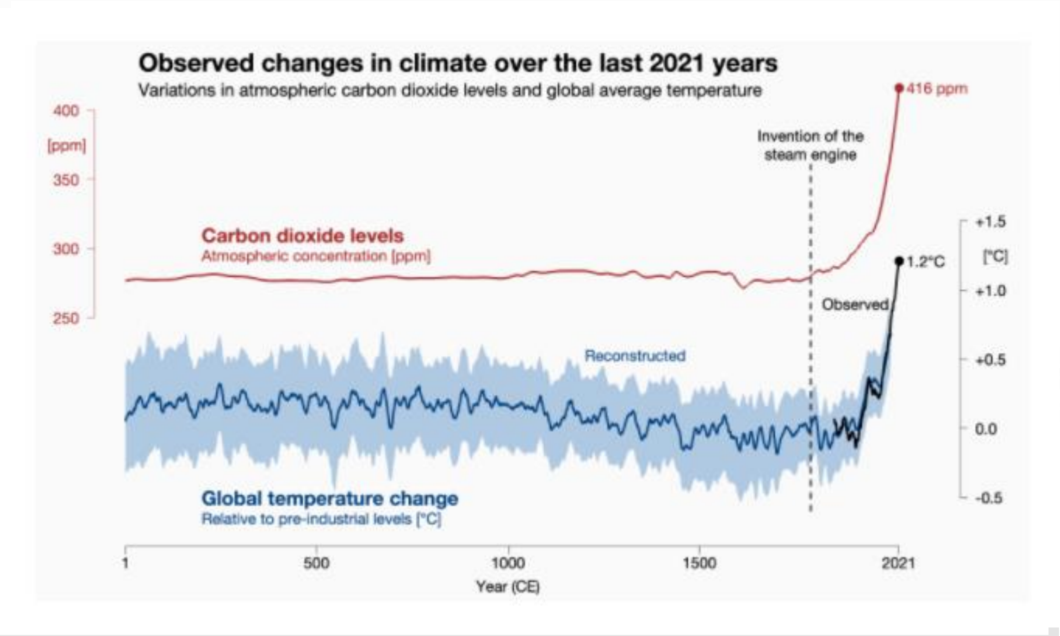
Main Problem : Human activities tip the scales by adding carbon to the air faster than the planet’s sinks can absorb it.

Greenhouse gas emissions

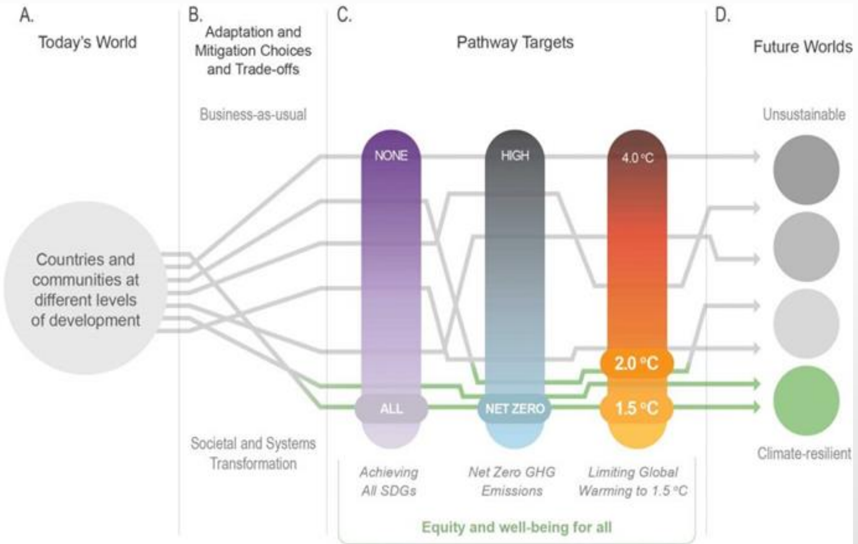
- **Climate change and global warming.**
- **CO_2 concentrations increased from 280ppm to 416 ppm : global temperature increased by 1.2c (Industrial revolution century).**



Global greenhouse gas emissions by gas and economic sector (IPCC, 2018)



Observed change in climate over the last 2021 years (Westbrook,2022)



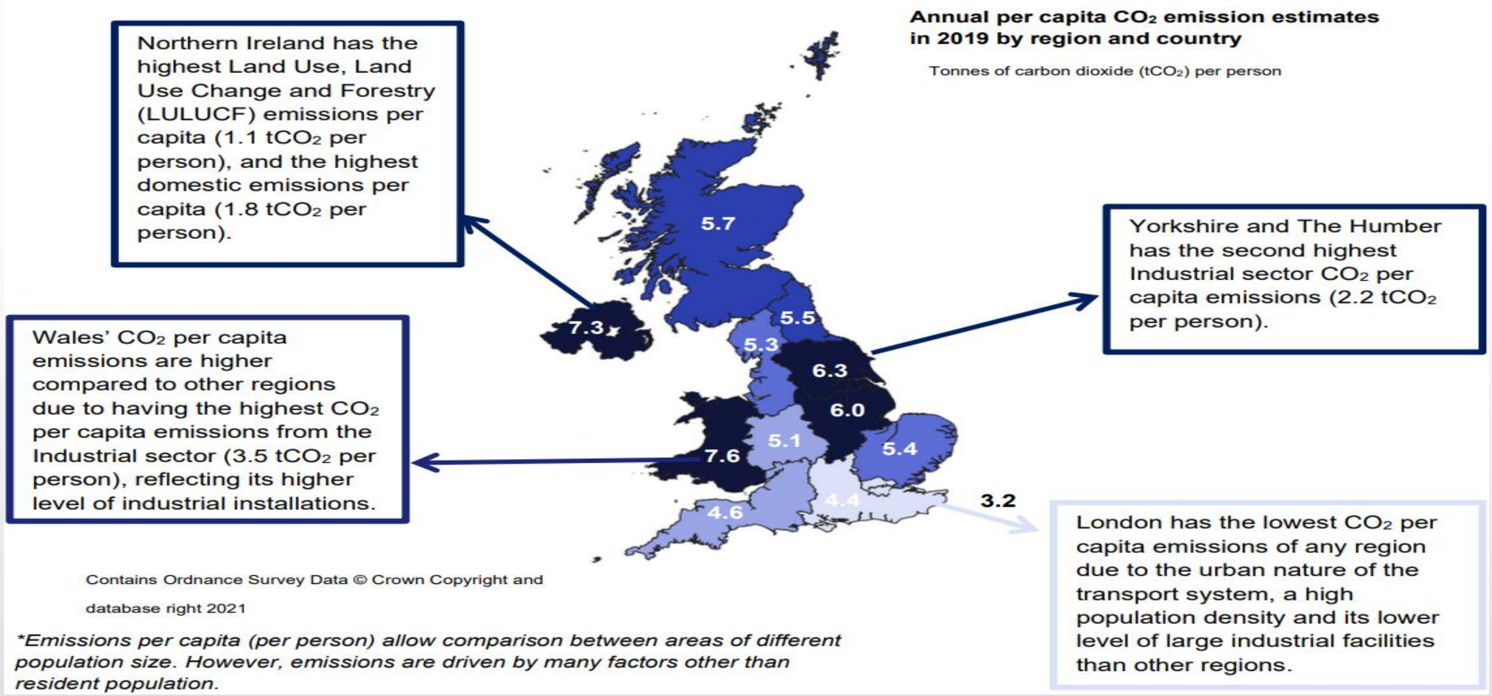
Relation between Greenhouse emission and climate change (IPCC, 2018)

Climate-resilient development pathways (CRDPs) (green arrows)

UK total carbon emissions

- World's total carbon emissions = 40 billion metric tons of CO_2.
- UK's total carbon emissions = 320.245 Million metric tons of CO_2.

The UK is committed to net zero greenhouse gas emissions by 2050 under new governmental plan announced in June 2019 under the national climate change policy.

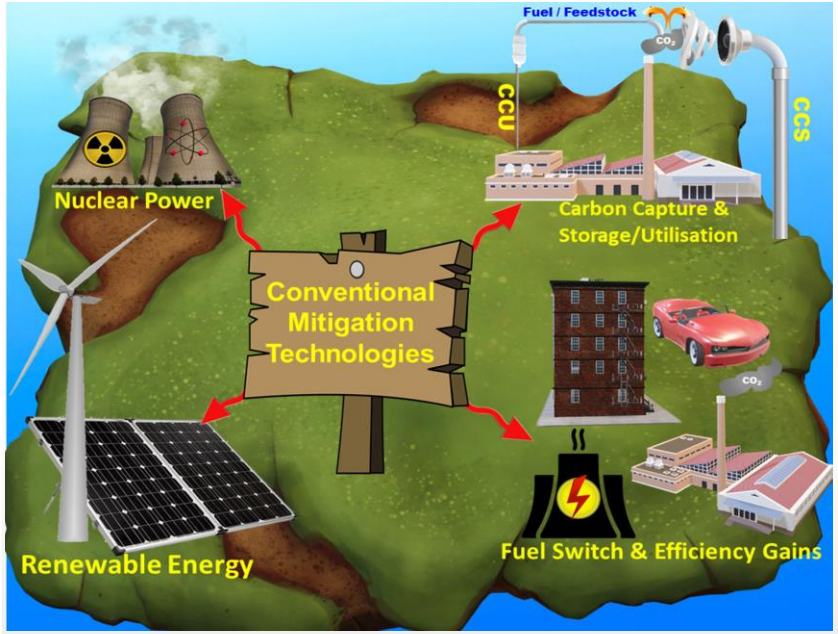


Average CO_2 emissions Per annum (Local CO_2 emissions UK, 2019):

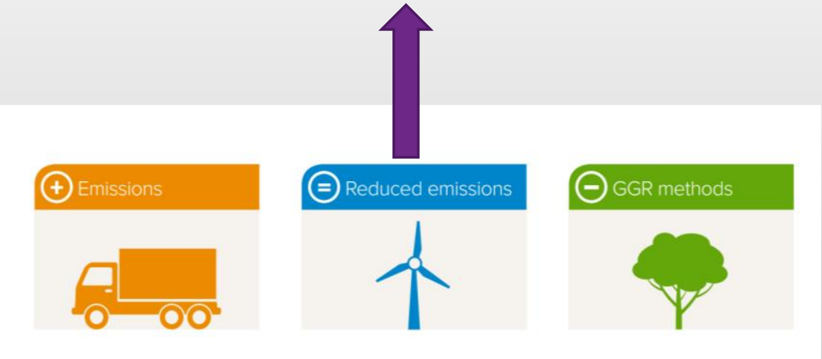
- 1 Person = 4 tons of CO_2
- 1 Car = 24 tons of CO_2
- 1 Refinery = 1.22 million metric tons of CO_2
- 1 Power station = 13-15 million metric tons of CO_2
- 1 Cement factory = 1 ton of cement production releases 622 kg of CO_2
- 1 Fertilizer factory = 1ton of Fertilizer production releases 5.6kg of CO_2

Major decarbonization technologies

Technology	Energy generation (%) –UK (2021)
Nuclear Power	11%
Renewables mixed Wind(15.5%), Bioenergy (6.3%), Solar Power (10.8%) , Hydropower (1%)	33.5%
Fuel Switch (Mainly to gas)	48%
Import	6

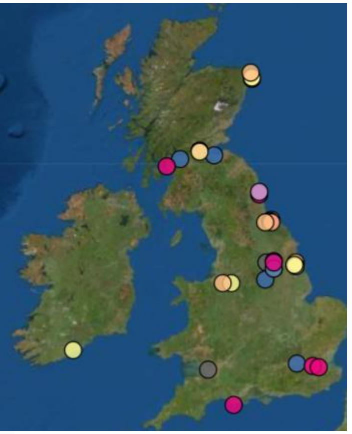


Conventional mitigation technologies (Fawzy et al., 2020)

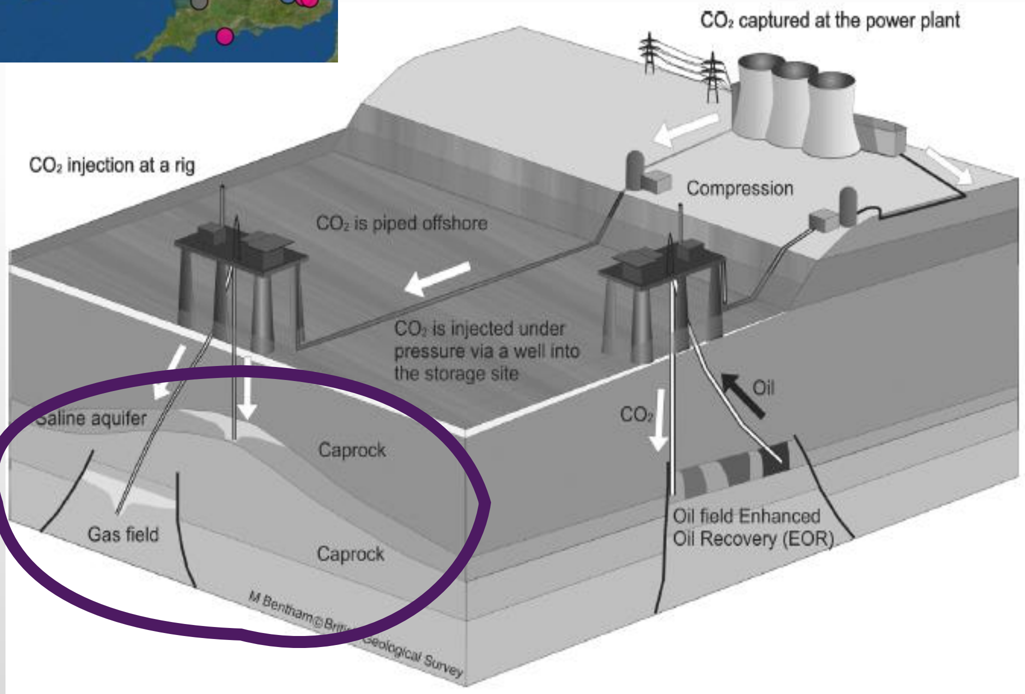


Technology	Energy generation (%) –France (2021)
Nuclear Power	78%
Renewables mixed Wind(12%), Bioenergy (0%), Solar Power (4%) , Hydropower (1%)	17%
Fuel Switch (Mainly to gas)	6.7%
Import	0

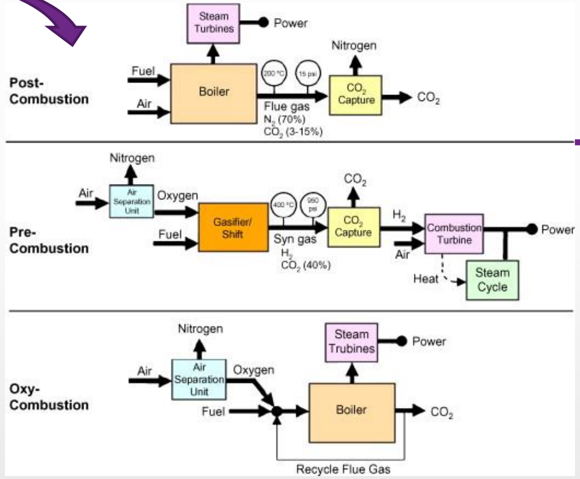
Carbon capture storage



A broad range of post-combustion technologies is used in CO_2 capture technology.



Overview summary of CCS process (IPCC,2018)



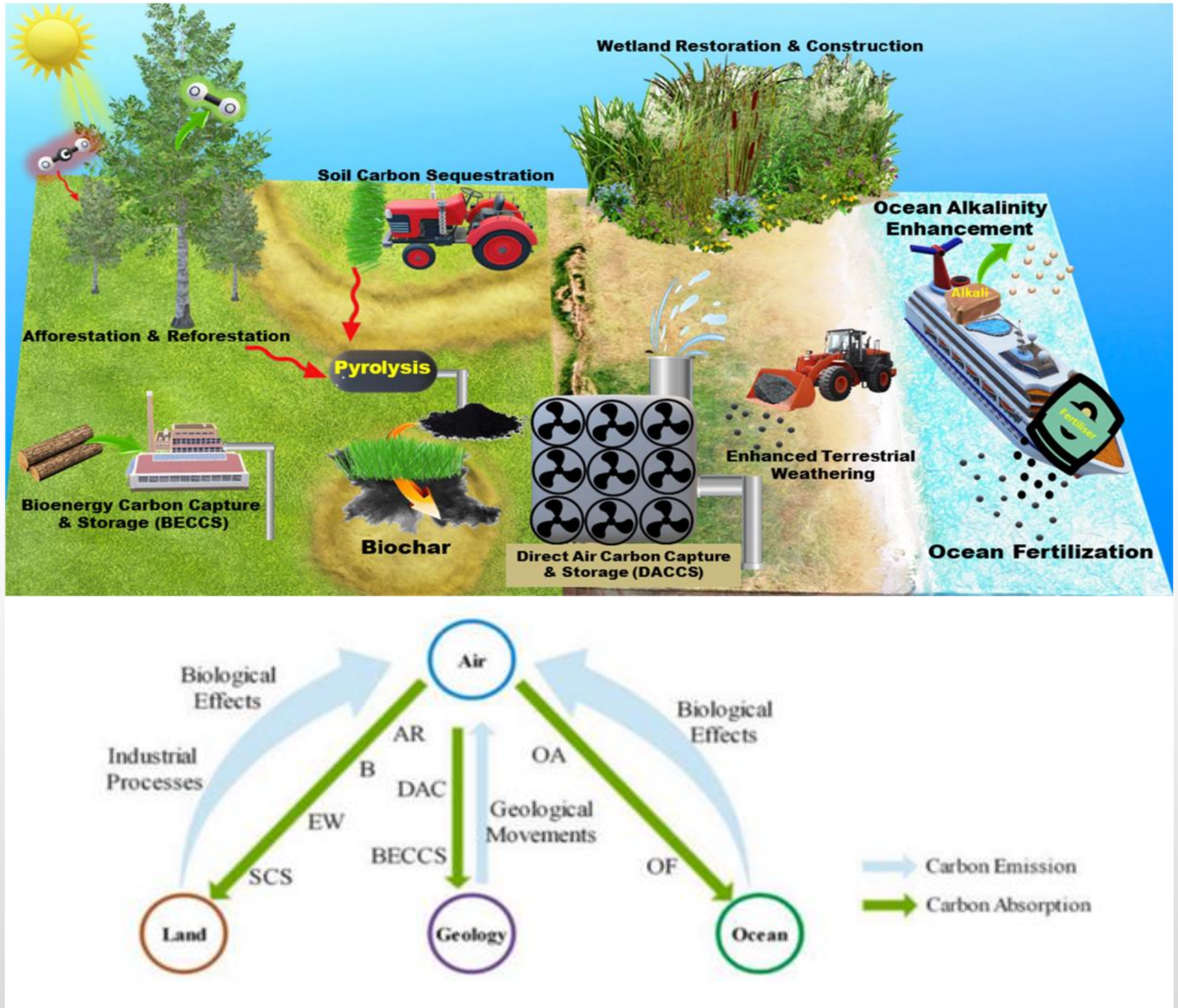
Block diagrams illustrating post-combustion, pre-combustion, and oxy-combustion systems (Figueroa *et al.*, 2008)

- Membranes
- Cryogenic separation
- Absorption
- Adsorption

In CCS systems, adsorption technology is becoming more popular due to its minimal energy requirement, practicability and versatility.

Zeolite from waste materials/clay

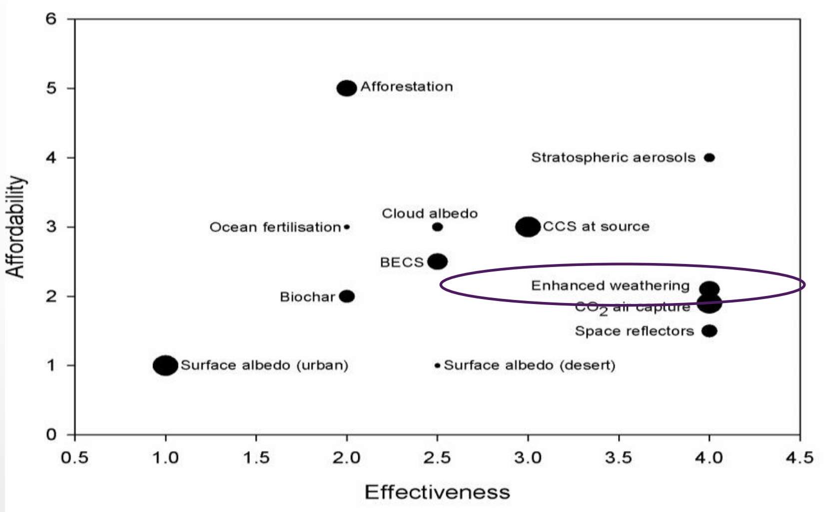
Negative emission technology



Negative emission technologies (Fawzy et al., 2020)

Best case scenario: Negative emissions of 0.5–3Gt C year−1 and 50–250 Gt C of storage capacity are required.

Worst case scenario: Negative emissions of 7–11 Gt C year−1 and 1000–1600 Gt C of storage capacity are required.



Economic and technical assessment of various geoengineering technologies (Royal Society, 2009)

GGR Technology Comparison

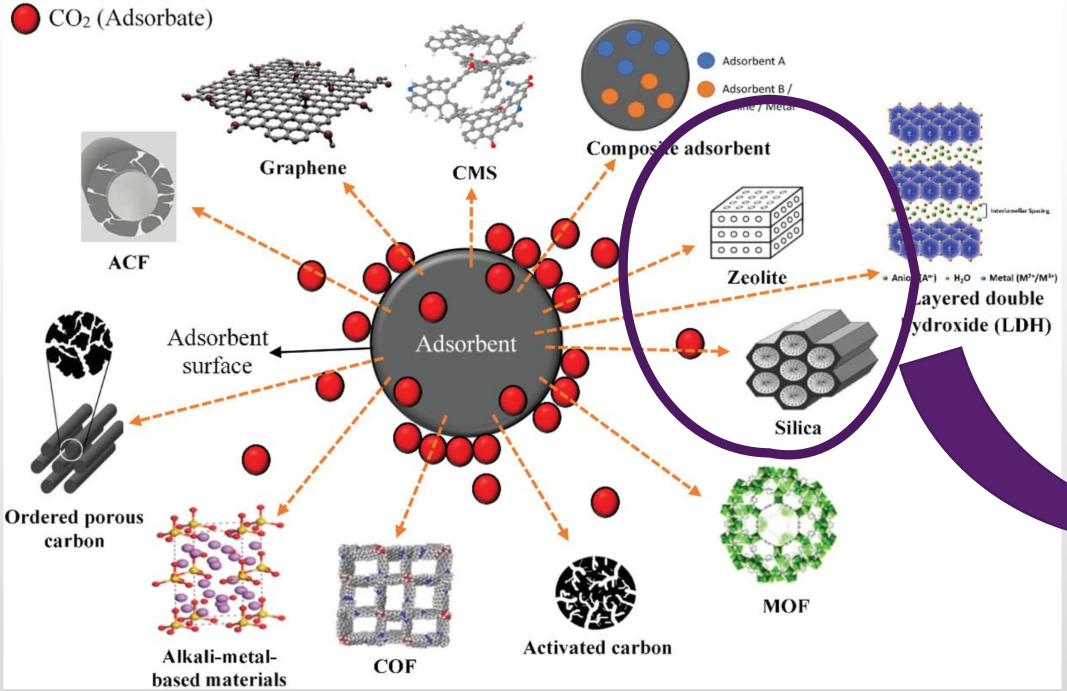
Type of technology	GGR capacity GtCO2/year	Cost $/tCO2
BECCS	0.5-5	100-200
Afforestation and reforestation	0.5-3.6	5-50
Biochar	0.3-2	90-120
Soil carbon sequestration	2.3-5.3	0-100
Direct air carbon capture and storage	0.5-5	100-300
Ocean fertilization	Up to 3.7	2-457
Enhanced weathering	2-4	50-200

(Royal Society and Samer Fawzy et al, 2022)

Adsorption Technology

- The viability of an adsorption process is highly dependent on the nature of adsorbents hence it is an area of research to find the ideal adsorbent for CO2 capture.

Clay minerals and Zeolite have good behaviour in catalysis and adsorption in CO2 capture processes with **high stability and availability.**



CO2 capture application by various types of solid adsorbents ((Lai et al., 2021)

Enhanced weathering

- Weathering of silicate minerals is a natural process that removes CO2 from the atmosphere, helping to regulate atmospheric CO2 on geological timescales.
- Ex: weathering reaction of feldspar to kaolinite, and this process takes around 103–104 years.

$$CaAl_2Si_2O_8 + CO_2 + 2H_2O \rightarrow CaCO_3 + Al_2Si_2O_5(OH)_4 \quad \Delta G = -281 kJ/mol$$

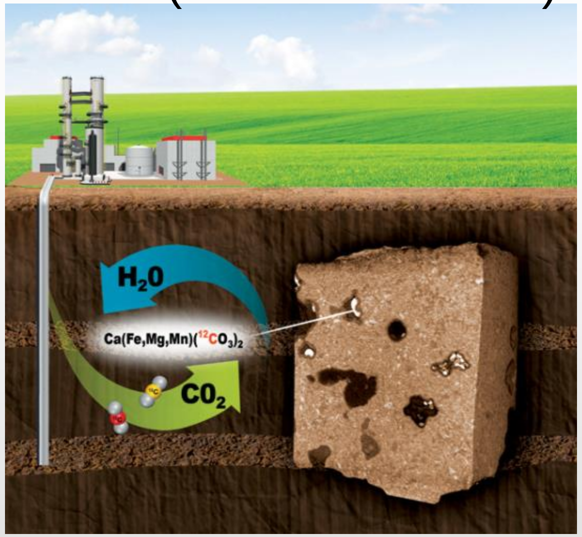
- What is Enhance weathering ?
- Enhanced weathering involves the dissolution of silicate minerals so that calcium and magnesium are leached out, and react with dissolved carbon dioxide (HCO3−, CO32−). Precipitation of carbonate minerals (e.g. calcite; CaCO3, magnesite;MgCO3, dolomite; CaMg(CO3)2) out of solution is possible.
- **Source of silicate**:
- Silicate minerals occur naturally at the surface in igneous rock formations which are chemically classified as acidic, intermediate, basic and ultrabasic depending on their silica content.
- Artificial silicates are produced as a by-product of some human activities (mine waste, cements, ashes, slags, demolition waste)

Different methods of silicate dissolution

Number of methods have been suggested to promote the dissolution of silicates on human relevant time scales including:

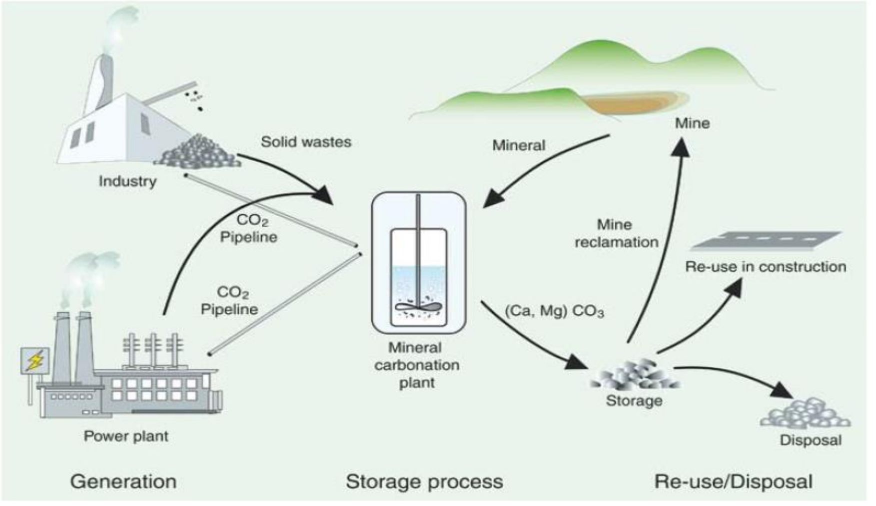
- In Situ mineral carbonation: underground injection into silicate rock formations.
- Ex situ mineral carbonation: high temperature/pressure reactor methods.
- Enhanced weathering on the land surface.

In situ (Basalt formation)



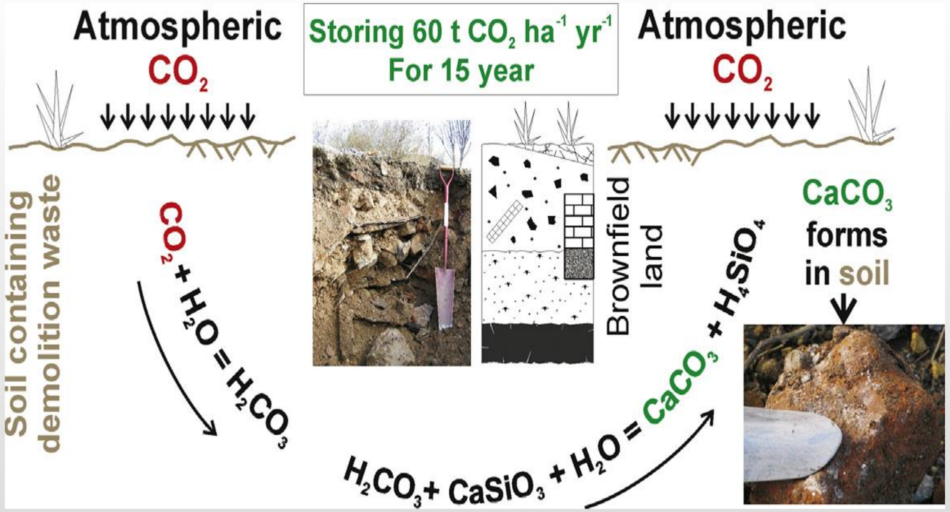
$17/tCO2

Ex situ (Carbonator reactor)



$50-300 /tCO2

Enhance weathering on the land surface

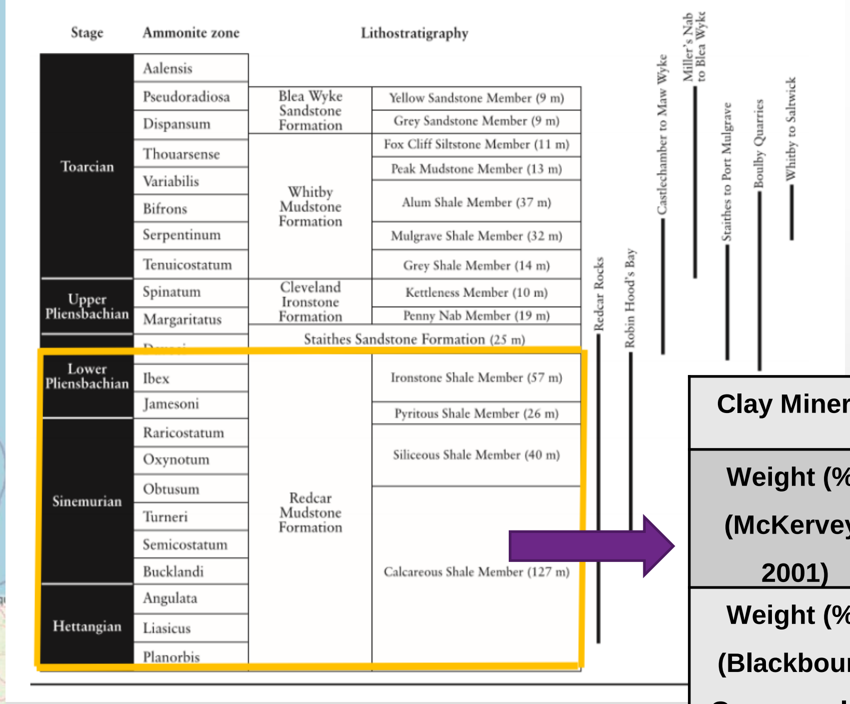


$0-100/tCO2

Clay minerals availability in UK

- Approximately, there are 86 - 90 clay reserves in different parts of the UK .
- Surrounding Tees valley and Durham region mostly consists of clay & shale, fire clay, silica sand and Igneous rocks.

Availability of clay in the UK (Mindat,1993)



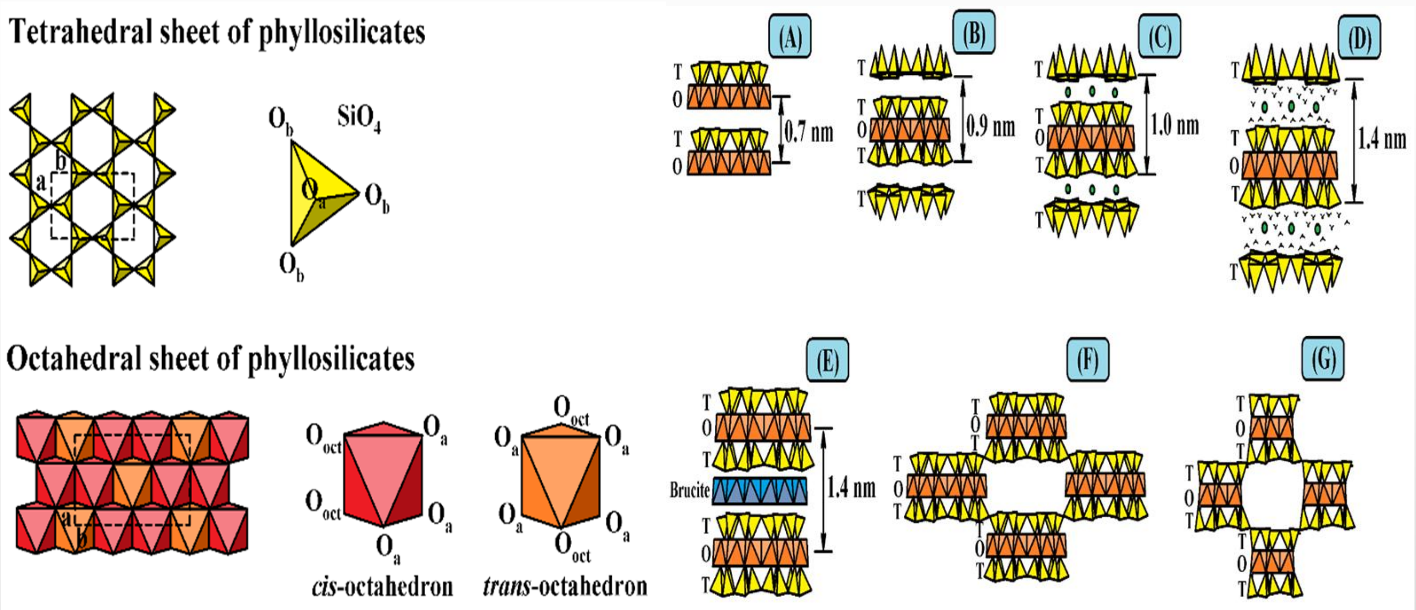
Lithostratigraphy formation (Simms, 2004)

Clay percentage minerology of Redcar Mudstone

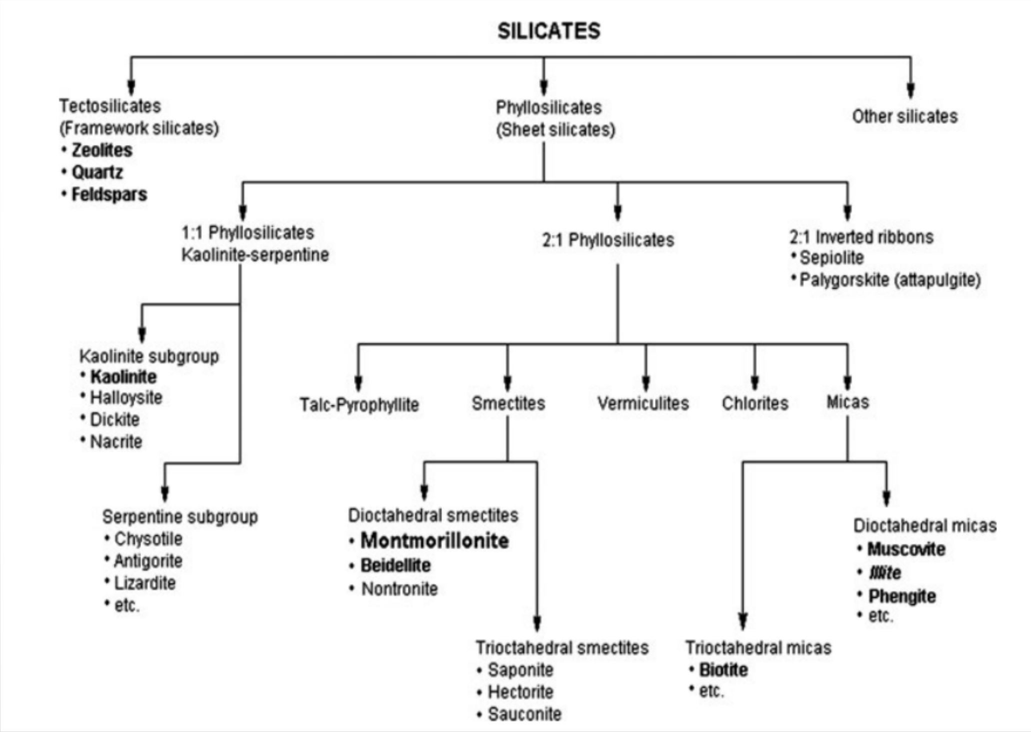
Clay Mineral	Illite	Illite/Smectite	Kaolinite	Chlorite	Quartz	Calcite
Weight (%) (McKervey, 2001)	42-58	20-35	5-14	15-22	0	0
Weight (%) (Blackbourn Geoconsulting, 2018)	35	23	20	15	2	1

Clay mineral

- Clay minerals are fine ground hydrous phyllosilicates that are composed of small microcrystalline particles.
- Phyllosilicate clay materials are characterised by faceted order of their intrinsic atoms in interlinked planes forming a sheet-like structure (Tetrahedral and octahedral).
- Based on the arrangement of sheets and extent of isomorphous substitution, clays can be classified into various groups.



Chemical structures of phyllosilicate minerals (Chouikhi *et al.*, 2019)



Classification of silicates (Khalid et al., 2016) .

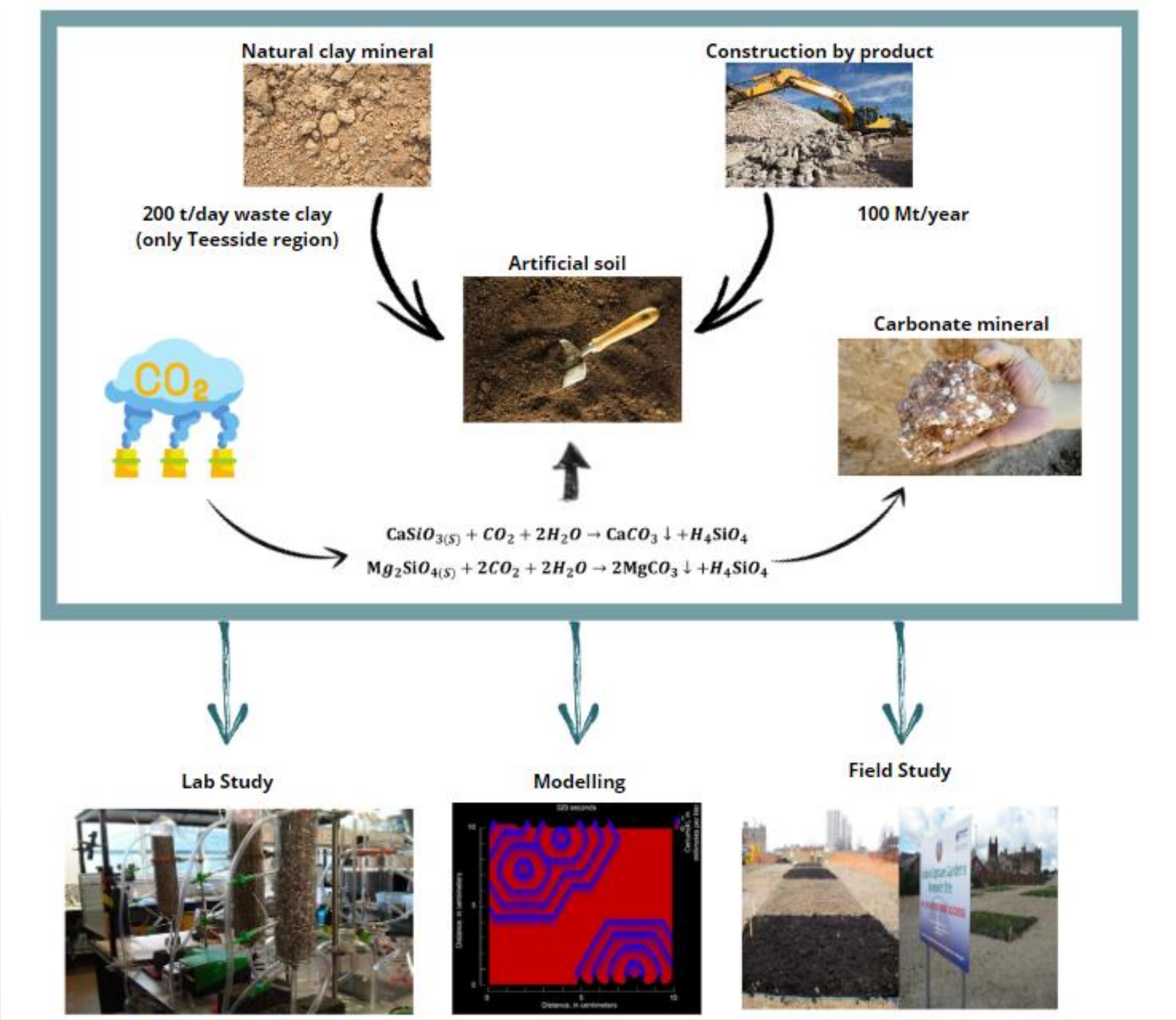
CO2 adsorption capacity of raw clay minerals

In general clay minerals has low CO2 adsorption capacity. Therefore, modified clay minerals were studied for various adsorption of gases such as CO2, N2, CH4 and O2 to increase the adsorption capacity for this cost efficient material.

CO2 adsorption capacity of raw clay minerals (Chouikhi et al., 2019).

Clay mineral	CO_2 Adsorption capacity (mg CO_2/g)	Adsorption Condition	
Kaolinite	3	25C, 1 bar	
Kaolinite	0	25C, 1 bar	
Bentonite	6	25C, 1 bar	
Bentonite	5	25C, 1 bar	
Bentonite	14	45C, 1 bar	
Montmorillonite	10	45C, 1 bar	
Montmorillonite	7	25C, 1 bar	
Montmorillonite	22	10C, 1 bar,	
Sepiolite	15	45C, 1 bar	
Sepiolite	41	45C, 1 bar	
Sepiolite	65	25C, 1 bar	
Sepiolite	137	25C, **120 bar**	P effect
Playgroskite	12	45C, 1 bar	
Playgroskite	18	**25C**, 1 bar	T effect

Overview about project



Waste materials

Natural/waste clay

- Clay 1/ Scott Bros
- Clay 2/ Scott Bros
- Clay 3/ Scott Bros
- Redcar mudstone/Anglo American Plc

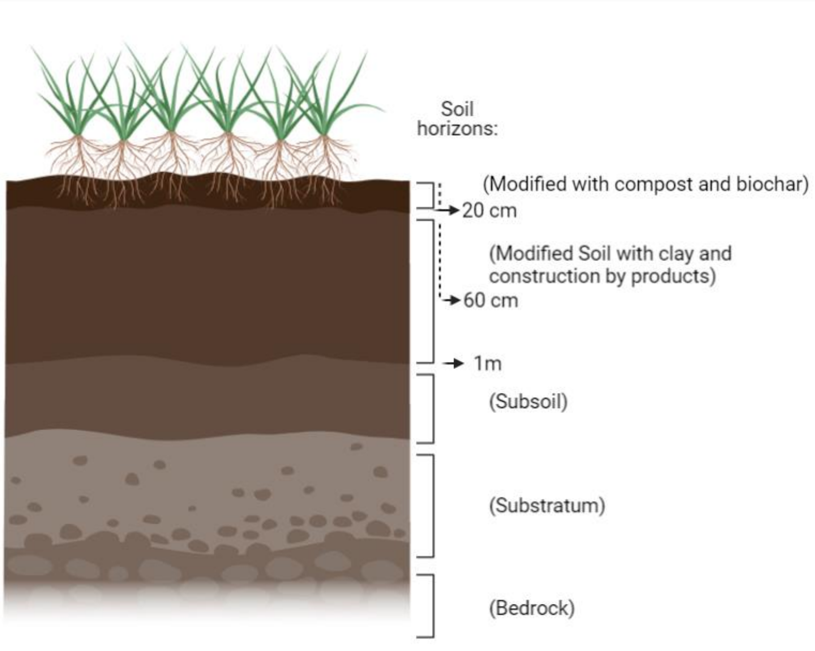
Construction by-products

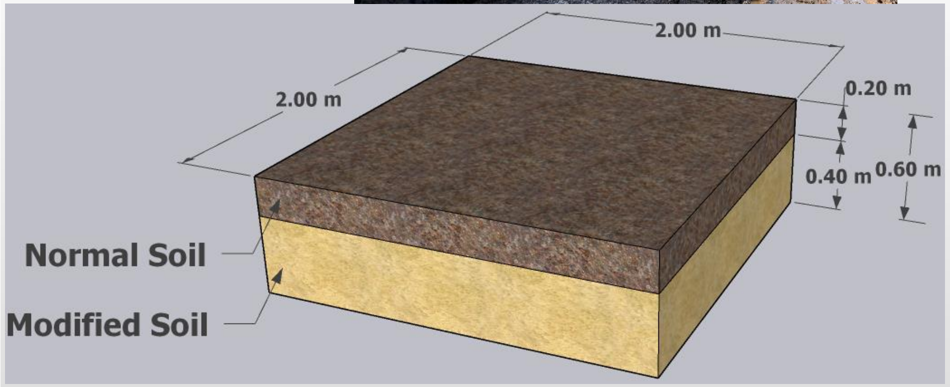
- Demolition Waste/ Scott Bros
- Fly Ash/ Tarmac
- IBM Ash/ Waste to Energy Teesside
- Ground Granulated Blast-Furnace Slag (GGBFS)

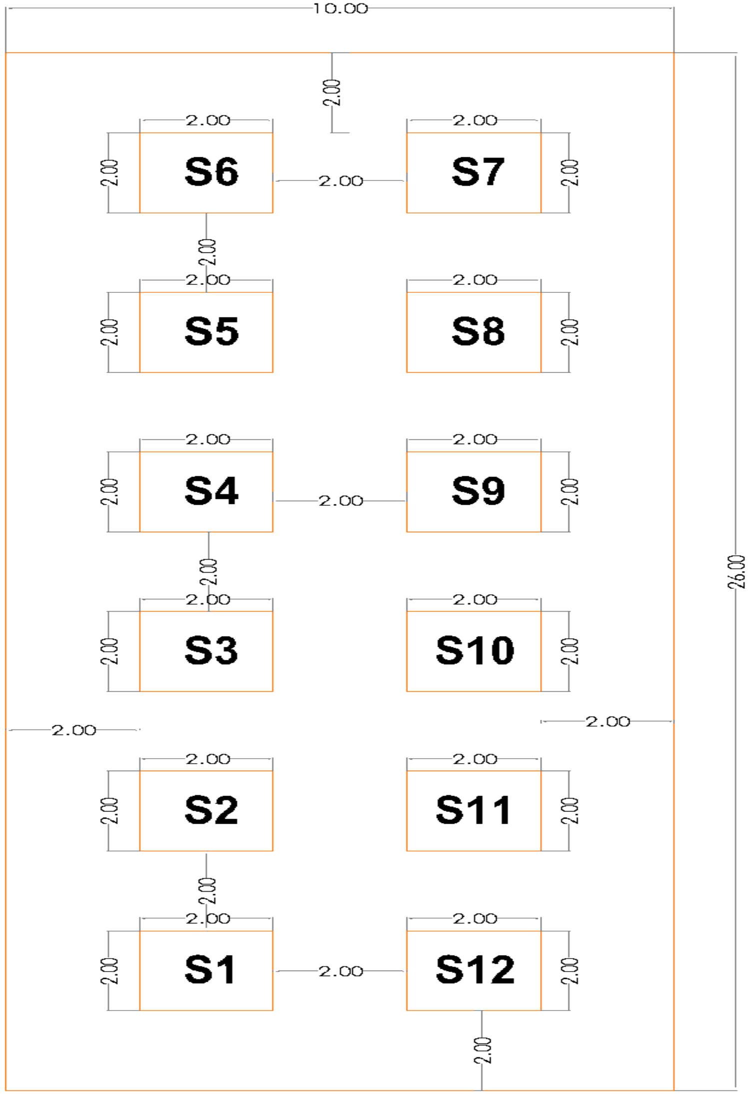
Field preparation

Field Study

- Different trail pits can be used at the selected site of Scot Bros Company. A proportion of the materials (natural/waste clays and construction by-products) will be crushed and spread on the site as a layer of made ground from 0.2 to 0.6 m in thickness with a width and length of 2m to 2m, respectively.
- Soil types at the location of each trial pit will be recorded up to 1 m depth since the first 1 m of the profile is where the major carbonation occurs depending on soil type and precipitation for three years.
- The land will be monitored for three years, and soil samples will be tested every three months.





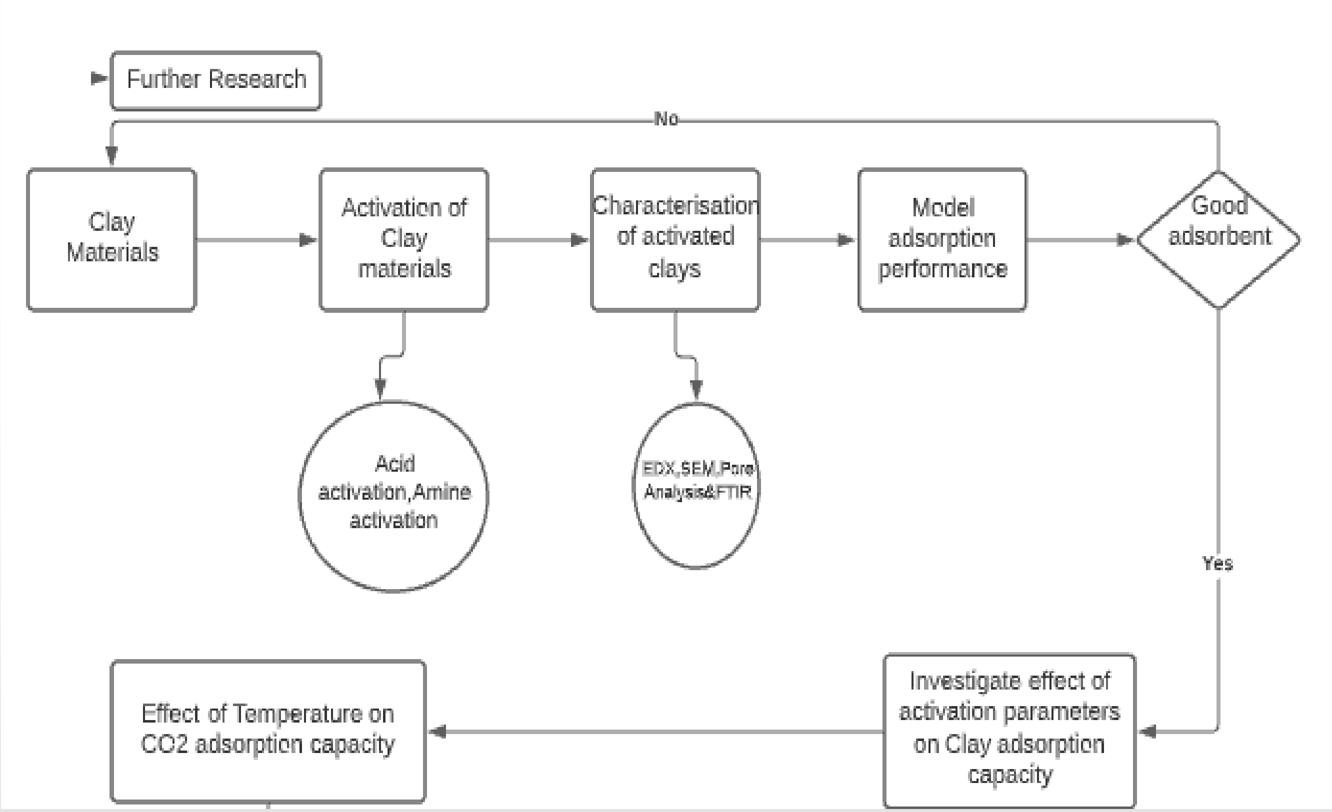


Ongoing Lab work/ Clay surface activation

- **Acid treatment**

Improve hydrophilic nature of surface by breakdown of pore walls and increase surface area.

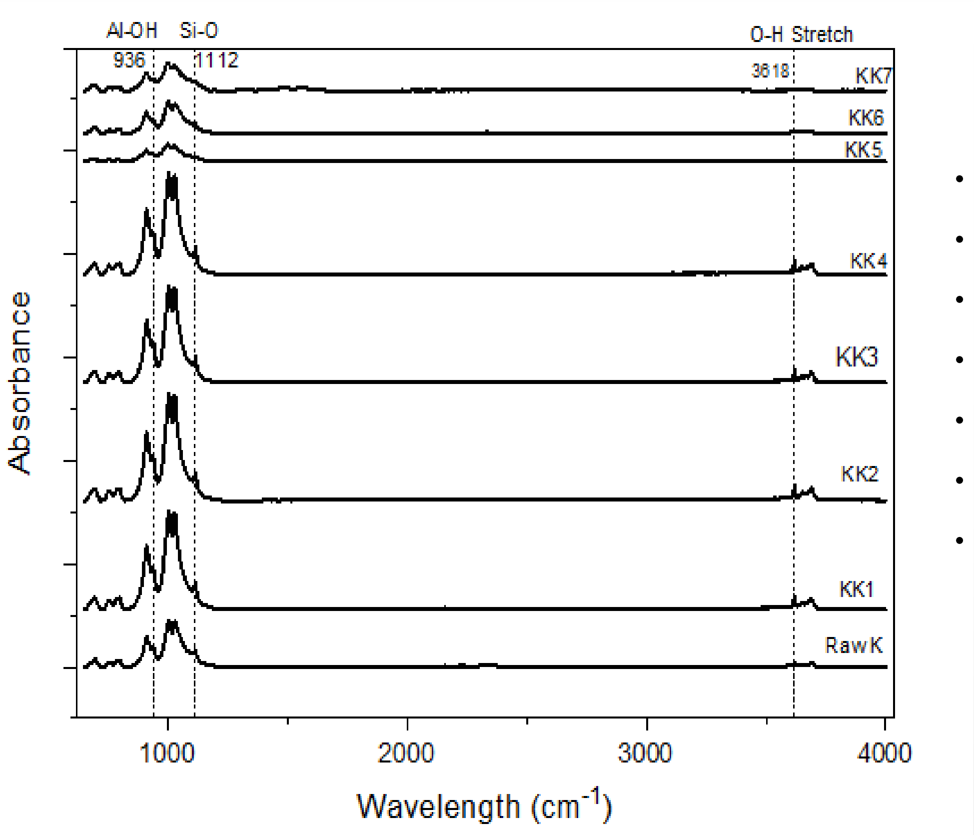
- **Microwave treatments** selected as alternative of oven to reduce time reaction and energy consumption.



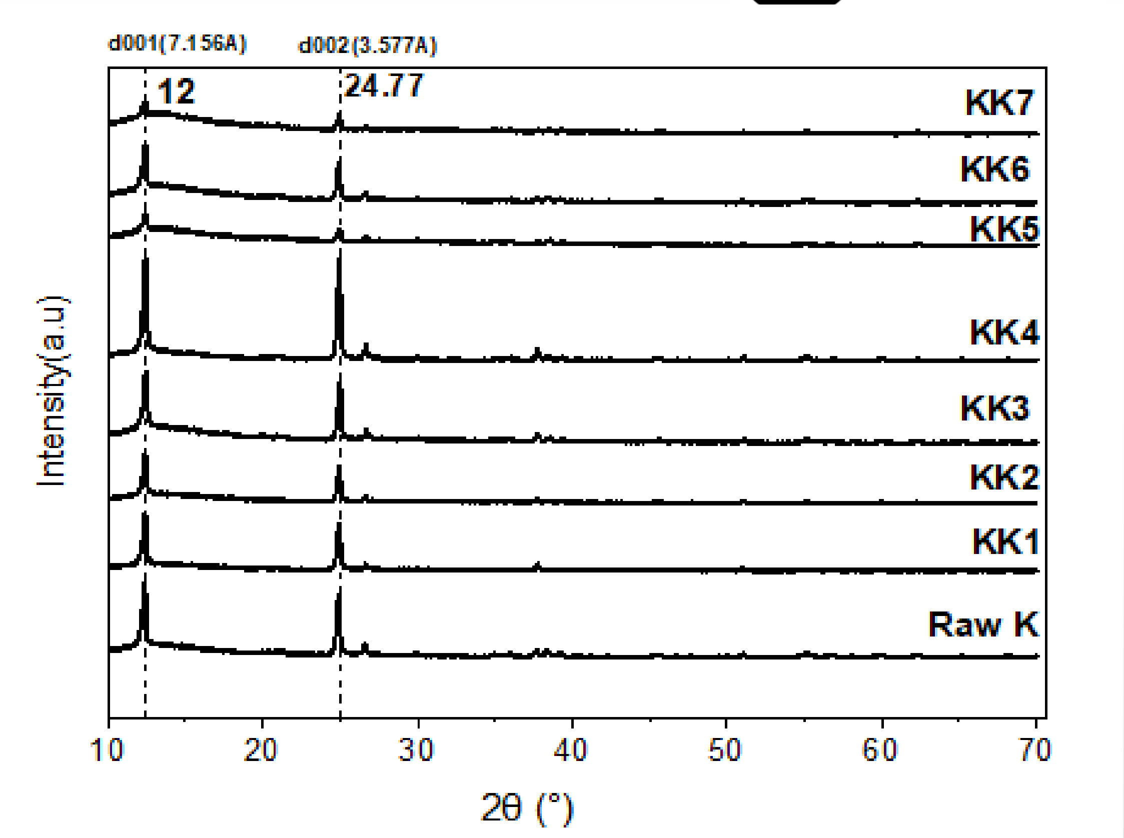
- **Amine treatments**

Involves the formation of zwitter ion through the interaction of CO_2 with an amine followed by deprotonation of zwitterion by the base to produce carbamate.

FTIR/XRD analysis of Kaolinite

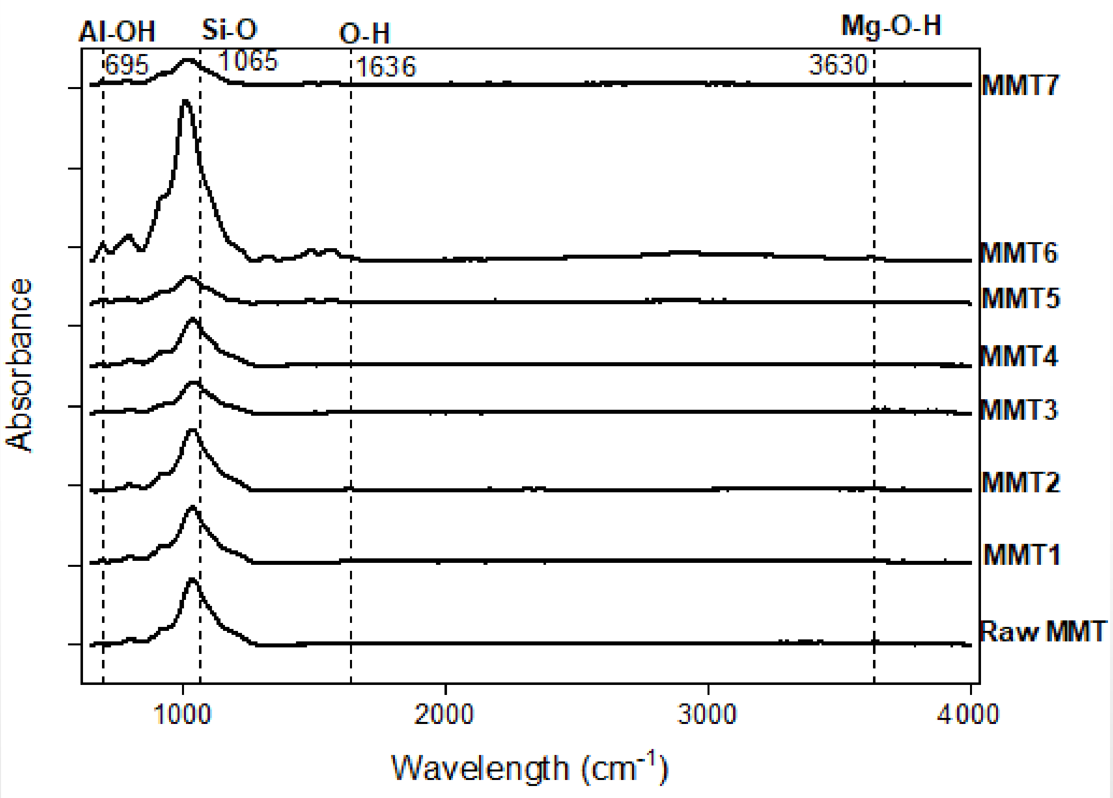


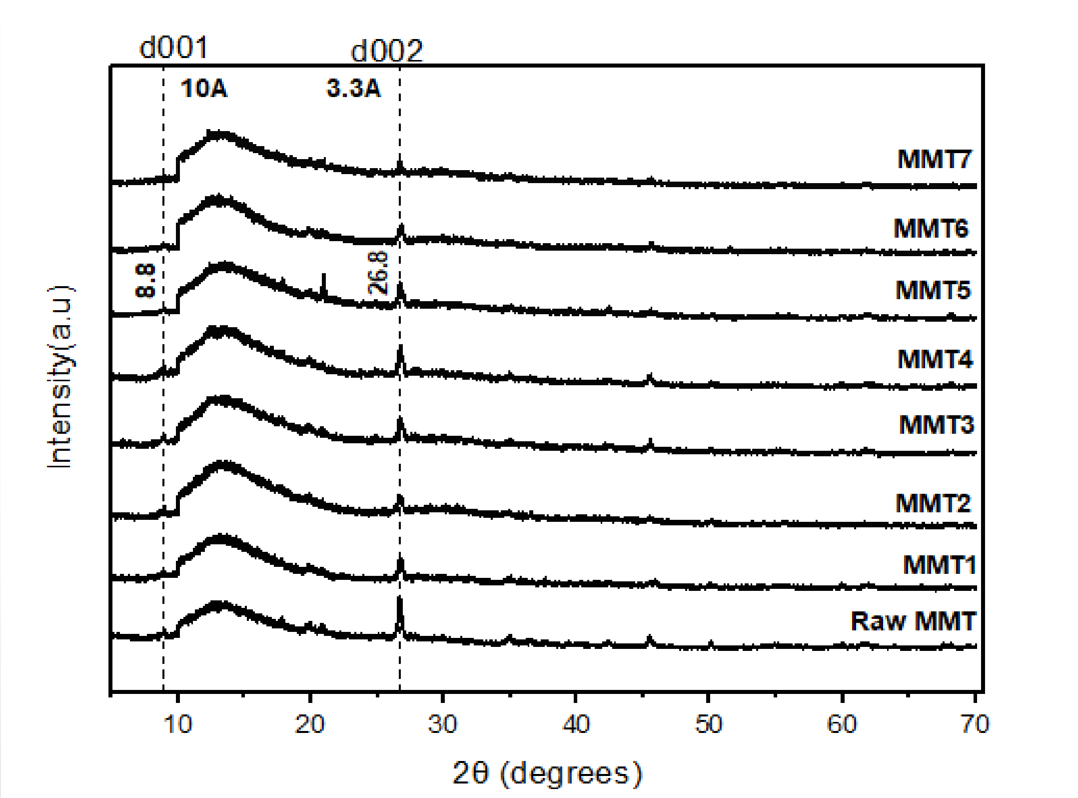
- 1 aa room temp
- 2 aa oven
- 3 aa micro wave 30 s
- 4 aa micro wave 1 min
- 5 amine ac room temp
- 6 amine ac oven
- 7 amine micro wave (30 s)



Best method is amine activation using microwave

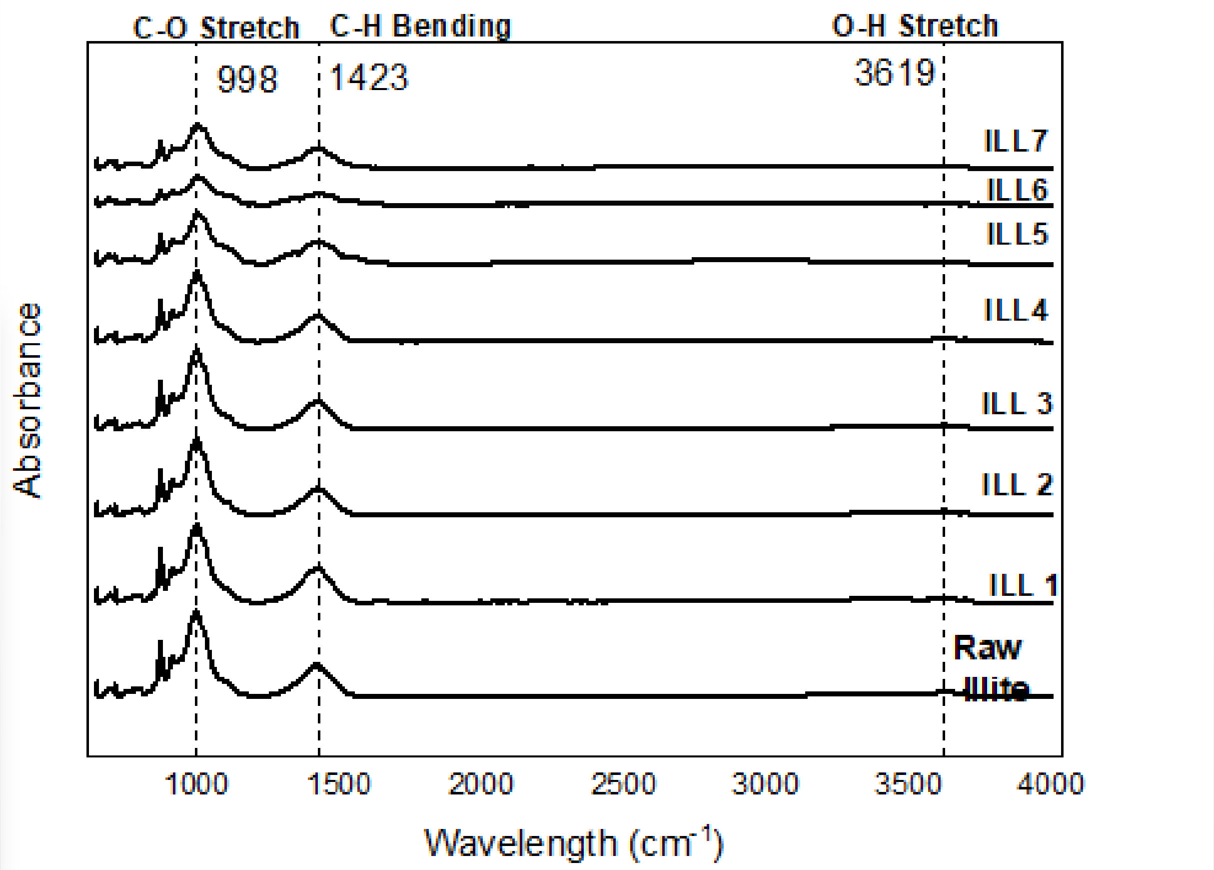
FTIR/XRD analysis of Montmorillonite

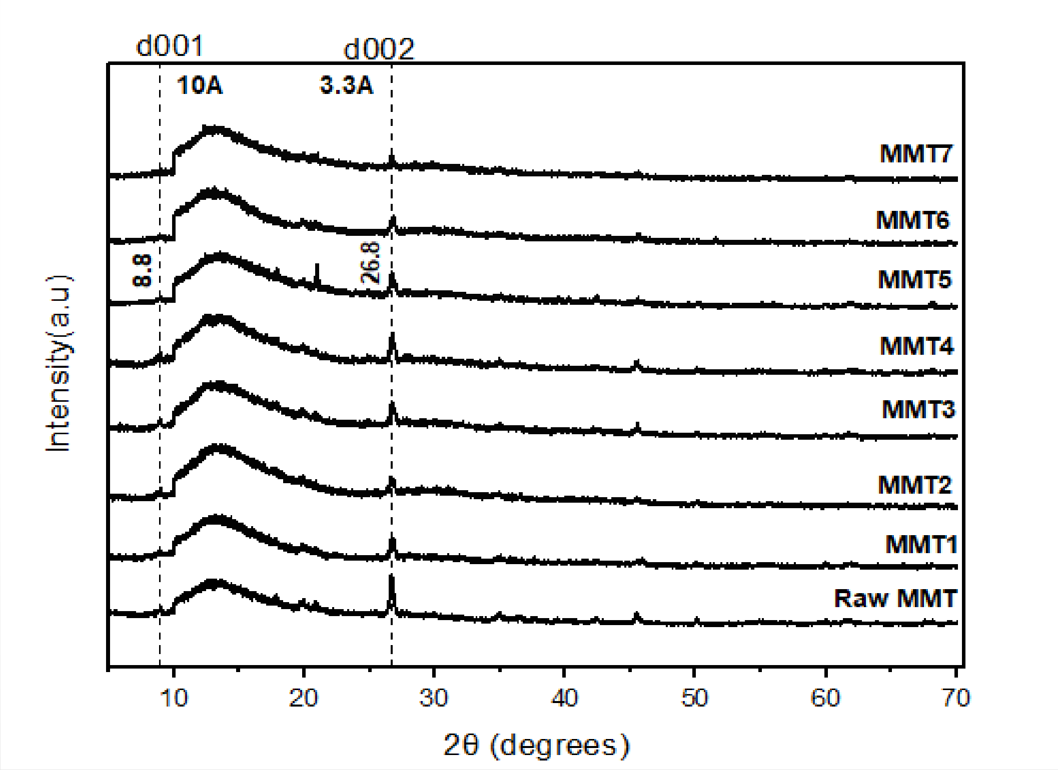




Best method is amine activation using microwave

FTIR /XRD analysis of Illite





Best method is amine activation using micro-wave

Surface area, pore volume and CO_2 adsorption of acid and amine activation of different clay minerals

Raw Clay minerals/ Acid and amine activation clay minerals using microwave	SBET(m2/g)	Adsorption capacity (mg/g)	Pore volume cm3/g
Untreated kaolinite	29	3	0.02
Acid activated Kaolinite	86	9	0.12
Amine activated Kaolinite	145	23	0.05
Untreated montmorillonite	72	15	0.16
Acid activated montmorillonite	120	30	0.54
Amine activated montmorillonite	183	33	0.24
Untreated illite	54	8	0.09
Acid activated illite	92	14	0.14
Amine activated illite	161	26	0.11

Conclusion

- Surface modification of clays conveys a possible increase in adsorption capacity.
- Montmorillonite is the best adsorbent compared to Kaolinite and Illite clays as it has a greater surface area and pore volume.
- Microwave-assisted acid activation improves the surface properties of kaolinite, making it more susceptible to acid attack.
- Treatment temperature affects acid and amine activation of clays.