

CO₂ Capture Utilizing Solid Sorbents

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Goals

- **President Bush's global climatic initiative/NETL carbon sequestration road map plan**
 - CO₂ capture from fossil fuels very important
 - Develop commercial systems that result in less than 10% increase in the cost of energy services by 2012
- **Develop technologies to separate/capture CO₂**
 - **Combustion and gasification gas streams**
 - **Techniques for both low and high temperatures**
 - **Applications at both high and low pressures**
 - **Superior to the existing capture techniques**
 - **Commercialization of the developed techniques**



Technical Challenges

- **Desired sorbent properties**
 - Adsorption capacity
 - Adsorption rate
 - Desorption/recovery rate
 - Recovery of concentrated CO₂ stream
 - Durability
 - Selectivity
 - Sensitivity to moisture and contaminants
- **Suitable for operation with PSA or TSA**
- **Process optimization**
- **Scale up for commercial units**



Experimental Work

- **Volumetric gas adsorption studies – equilibrium adsorption isotherms up to 280 psi**
- **Flow reactor studies at 1 atm and at 20 atm**
 - Competitive sorption of CO₂ from gas mixtures representing coal combustion & gasification
- **Heat of reaction measurements – DSC calorimeter**
- **Thermo gravimetric analysis**
- **Physical and chemical characterization**
- **Spectroscopic characterization of CO₂/sorbent interactions**



Solid Sorbents

- **Zeolites**
 - Ambient temperature and 120 °C
 - Both atmospheric and high pressures
- **NETL liquid impregnated regenerable solid sorbents**
 - Ambient temperature (30 °C) & atmospheric pressure
- **NETL Warm gas alkali based sorbents**
 - 315 °C
 - Both atmospheric and high pressures
- **NETL moderate temperature sorbent**
 - 100 to 150 °C
 - High pressure



Summary of the Results with Zeolites

- **Synthetic alkali alumino silicate zeolites showed excellent CO₂ adsorption at ambient temperature**
- **Alkali alumino silicates with pore diameter of 10 Å showed good adsorption at 120 °C**
- **Presence of water vapor**
 - affected the capacity
 - regeneration at 350 °C is necessary
- **Combination of vacuum and mild temperature regeneration could be suitable**



**NETL Steam Tolerant Low Temperature Sorbent
(NETL –LT) Development
CO₂ Capture Temperature at 25-40 °C**



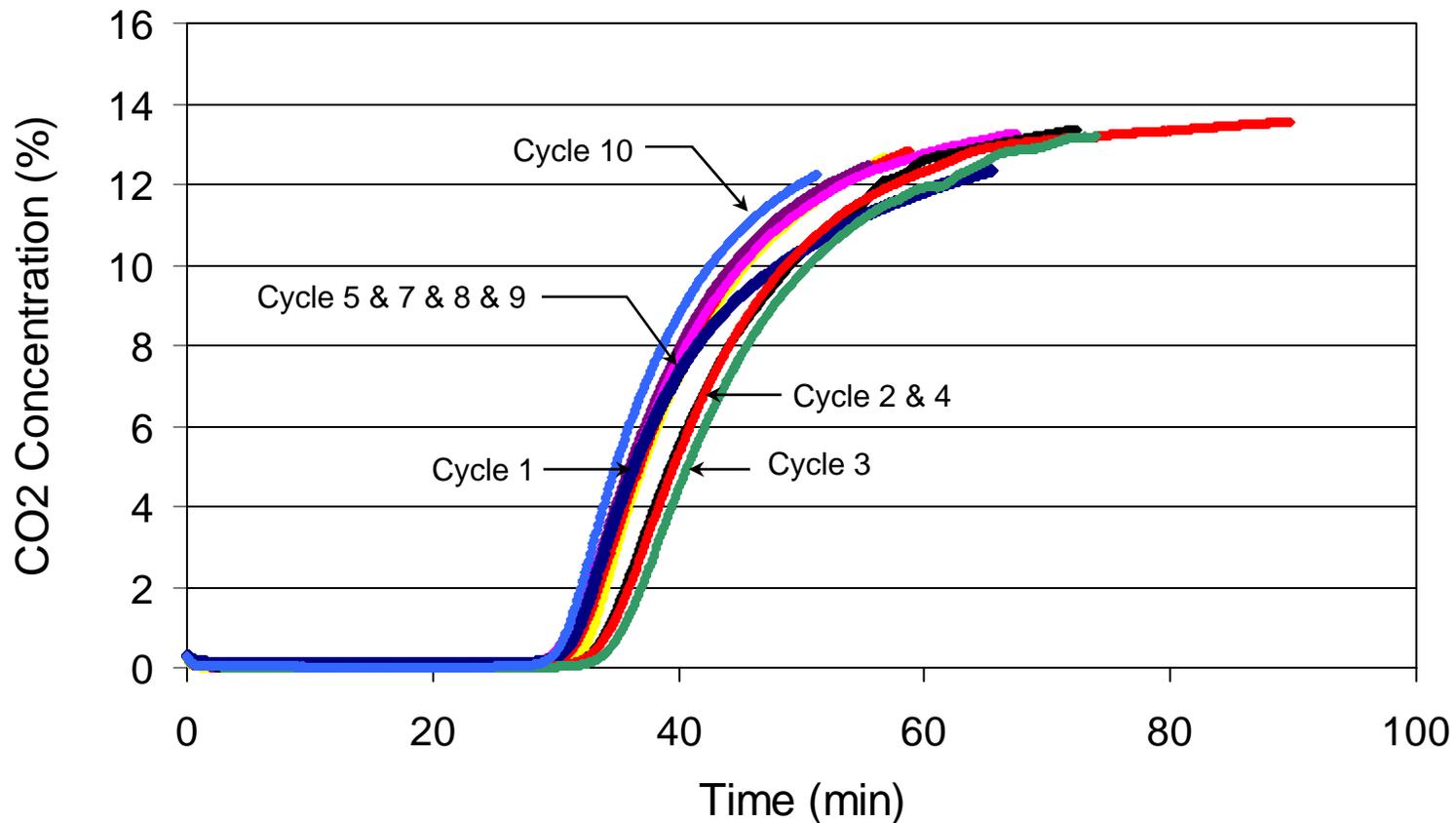
Results with NETL steam tolerant liquid incorporated solid sorbent (NETL-LT)

- **Engineering analysis conducted at NETL**
 - Solid sorbent process has better efficiency than conventional amine technique when operated at
 - 25 °C sorption and 60 °C regeneration
 - High CO₂ sorption capacity during multiple cycles
- **Preparations by incorporating liquids in a solid matrix**
- **No corrosion problems**
- **Very good CO₂ capture capacity and good regenerability**
- **Presence of steam does not affect the performance of the sorbent during multi-cycle tests**
- **Steam could be utilized for regeneration**

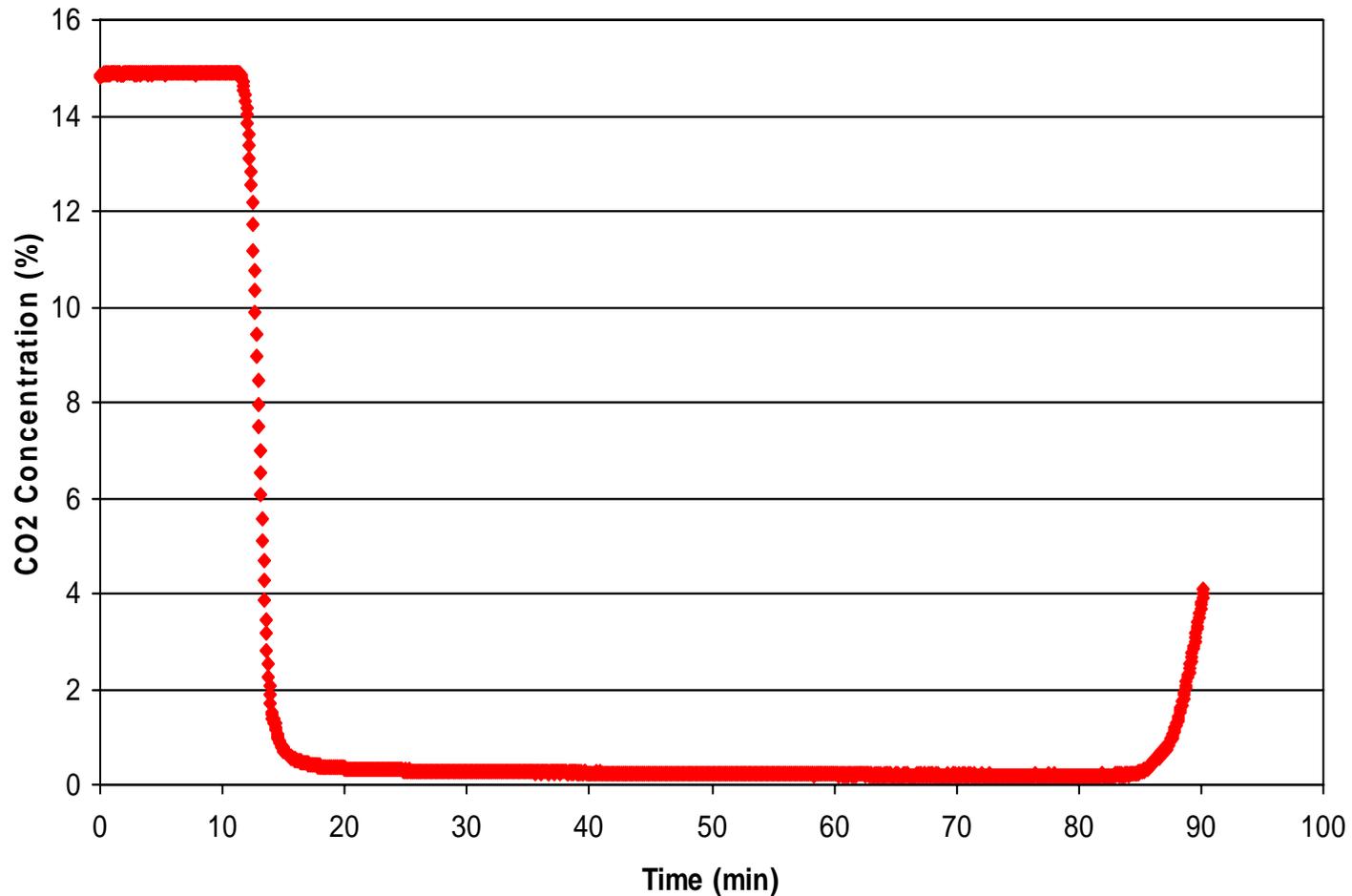


Adsorption of CO₂ on NETL-LT in Atmospheric Lab Scale Reactor

(15% CO₂, 3% O₂, 82% N₂, and Saturated With Water Vapor)



Adsorption of CO₂ on Reformulated NETL-LT to Obtain Better Capacity in Atmospheric Lab Scale Reactor (15% CO₂, 3% O₂, 82% N₂, and Saturated With Water Vapor)

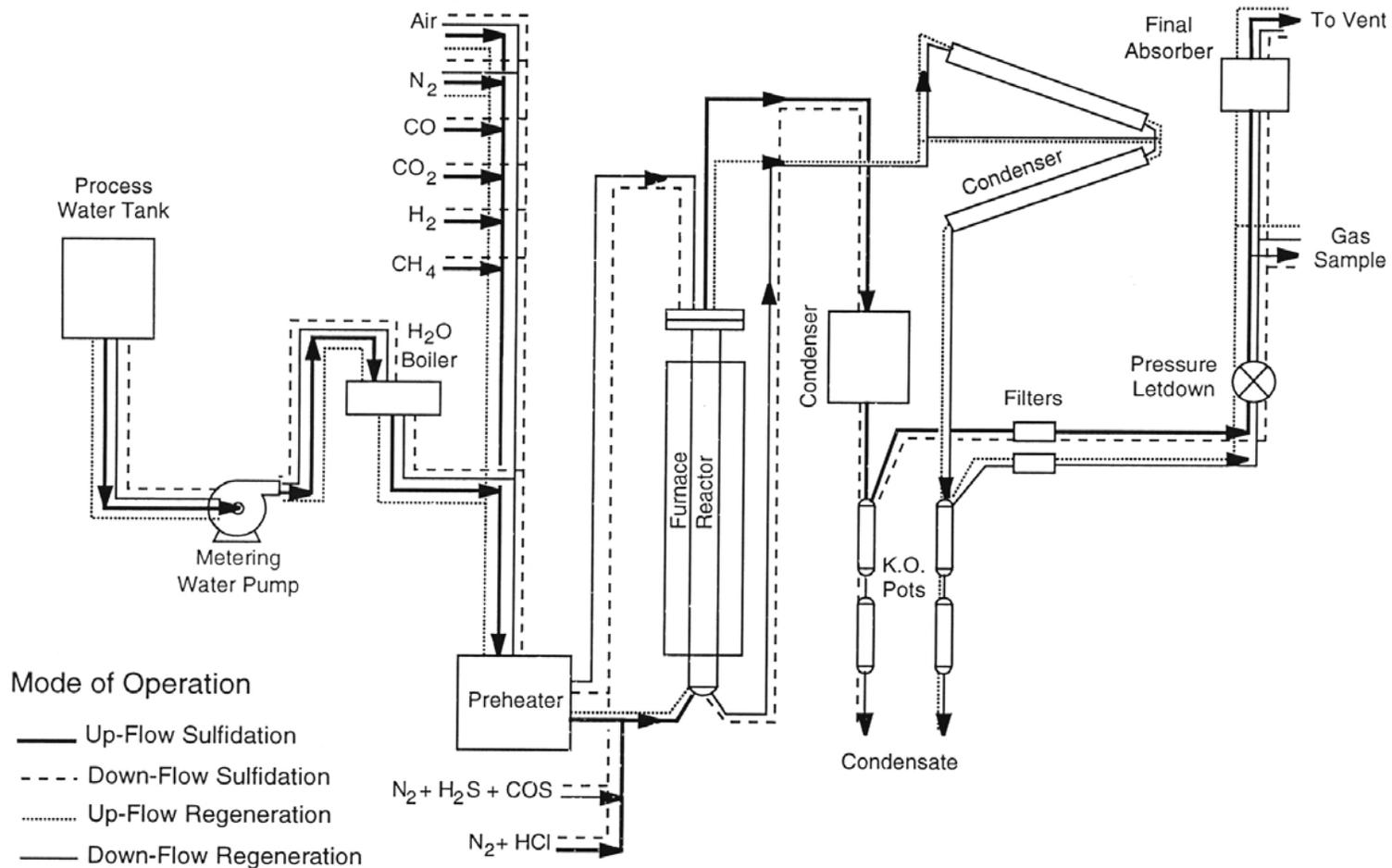


Bench Scale Flow Reactor Tests with Large Scale Preparation of NETL-LT

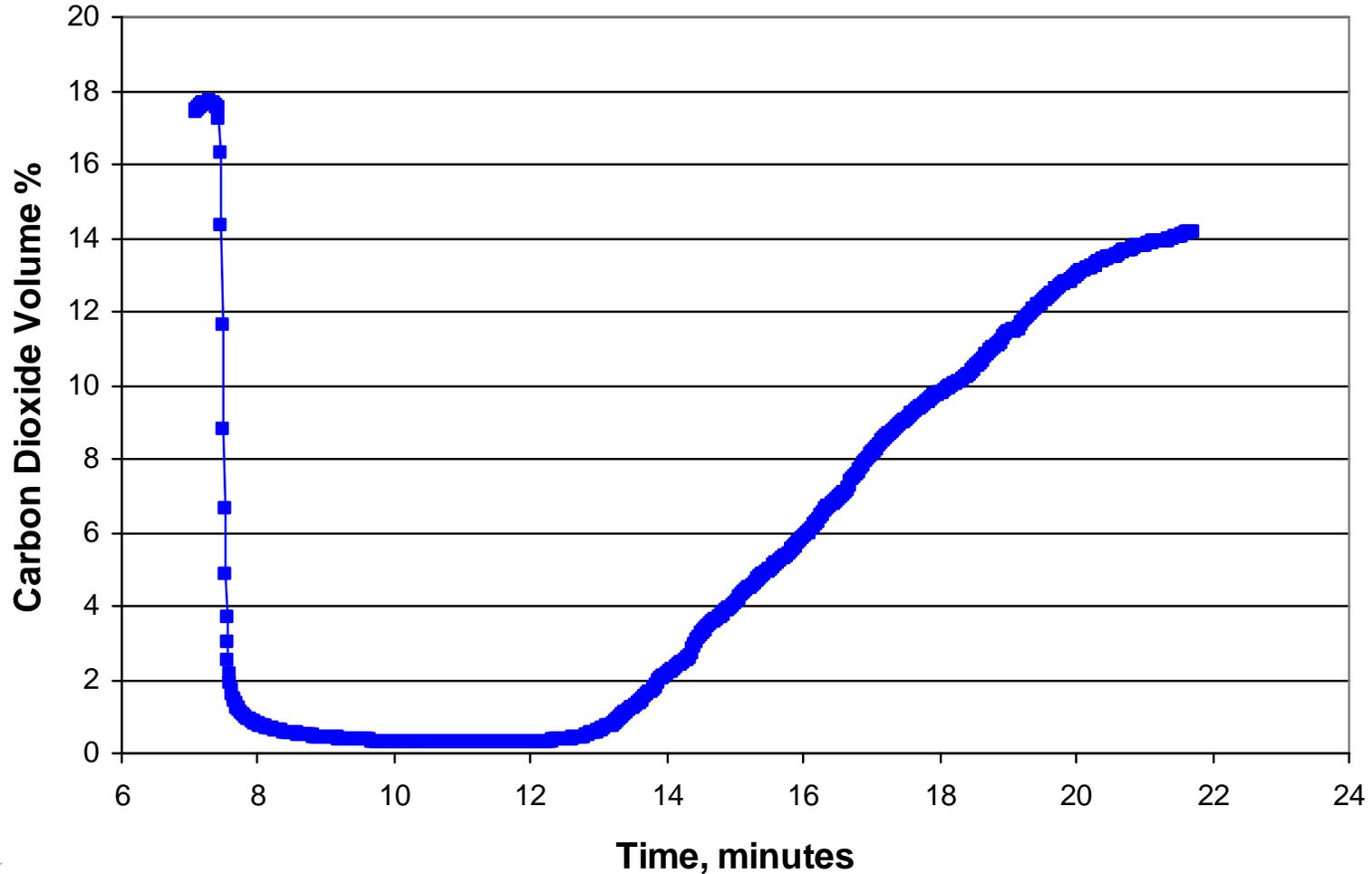
- Industrial level preparation
- Mixer –Pelletizer
- Bench scale reactor tests – two inch diameter reactor with six inch bed height
- ~350 grams of sorbent
- Tests conducted at both 500 hr⁻¹ and 1000 hr⁻¹ space velocity
- Temperature of the CO₂ sorption – 25-30 °C
- Temperature of regeneration – 80 °C



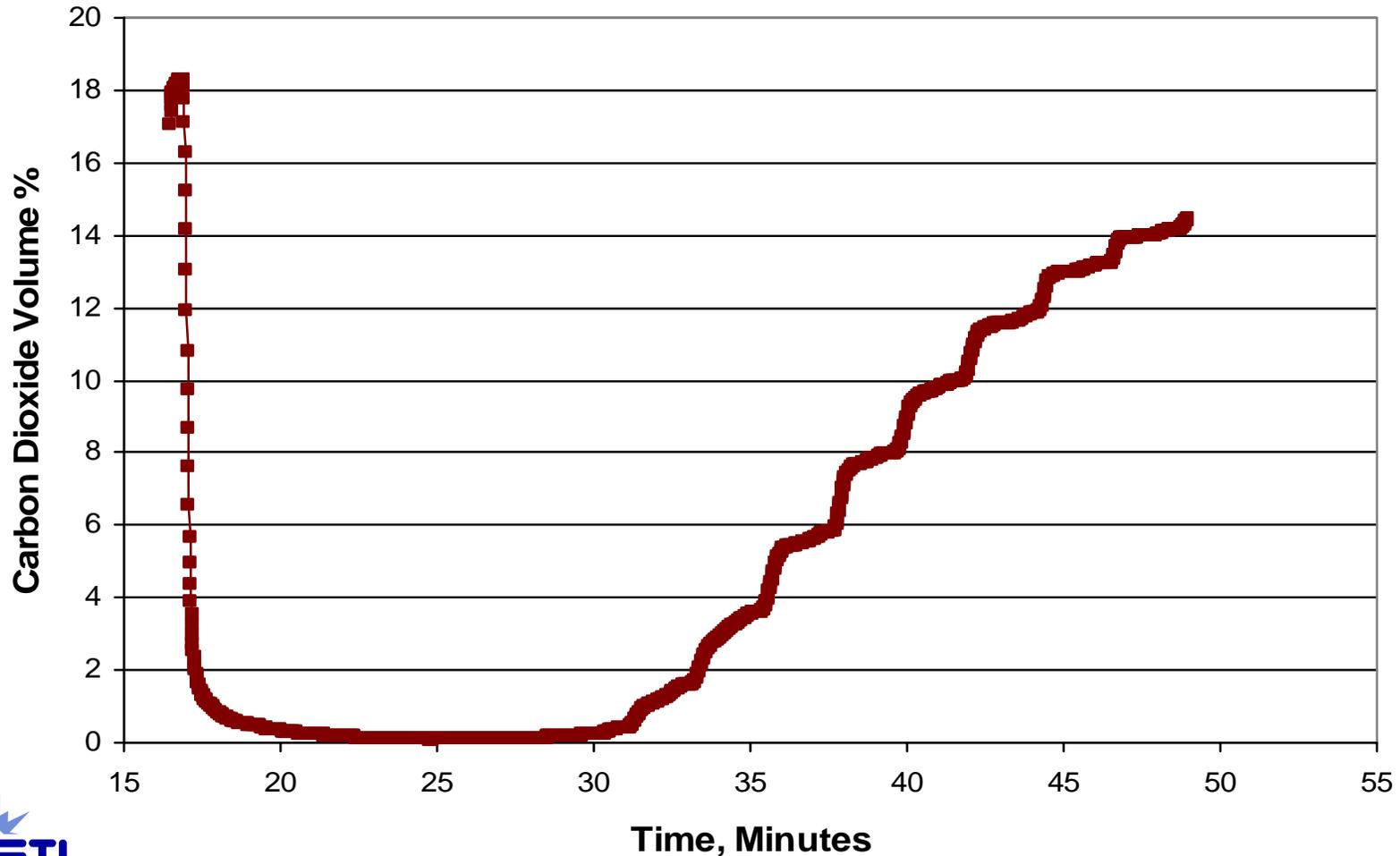
Flow Diagram of the High Pressure Bench Scale Flow reactor



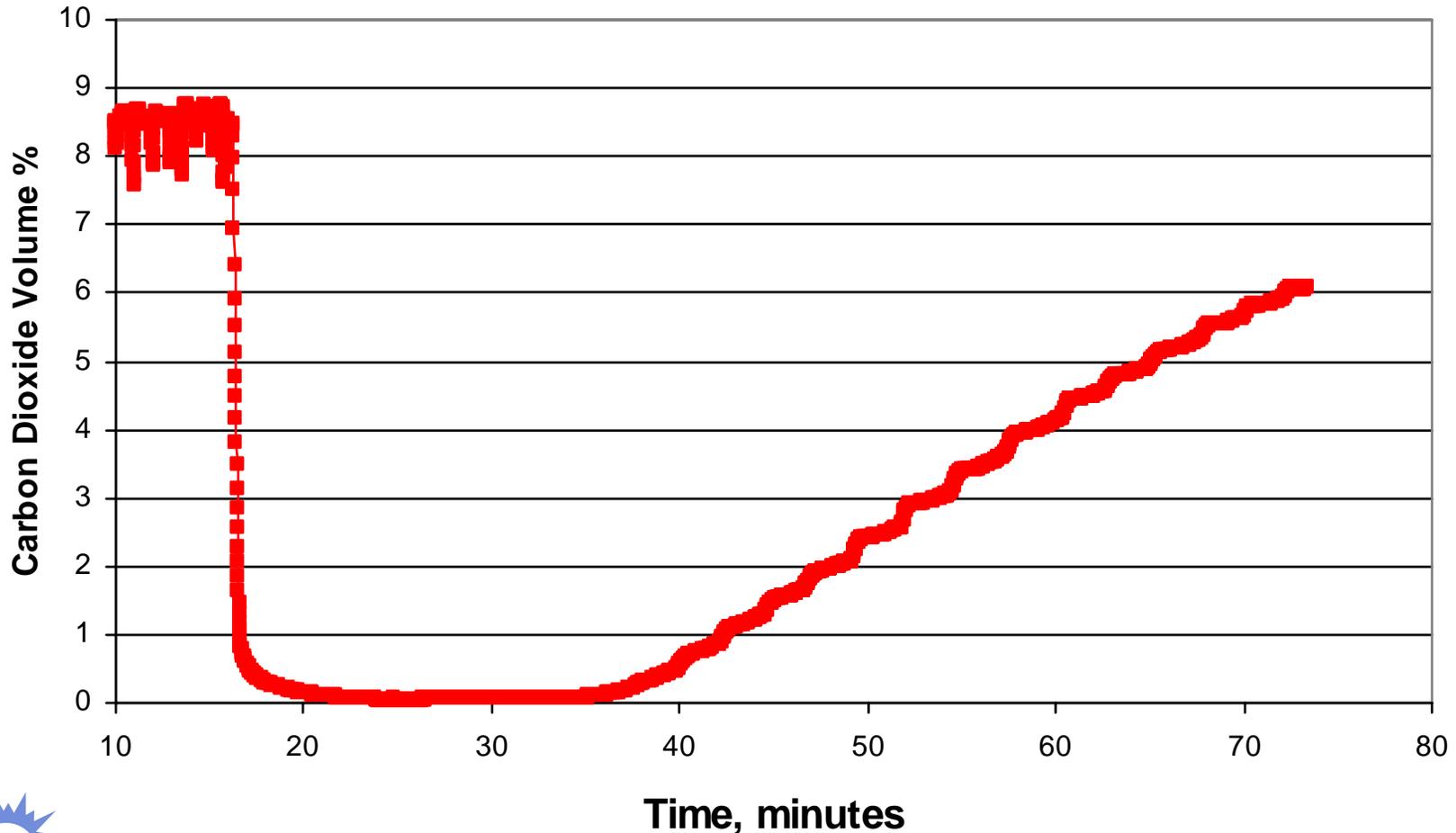
Adsorption of CO₂ on NETL-LT in Atmospheric Bench Scale Reactor- 1000 hr⁻¹space velocity, 25-30 °C (17% CO₂, 3%O₂, 80% N₂)



Adsorption of CO₂ on NETL-LT in Atmospheric Bench Scale Reactor- 500 hr⁻¹space velocity, 25-30 °C (17% CO₂, 3%O₂, 80% N₂)

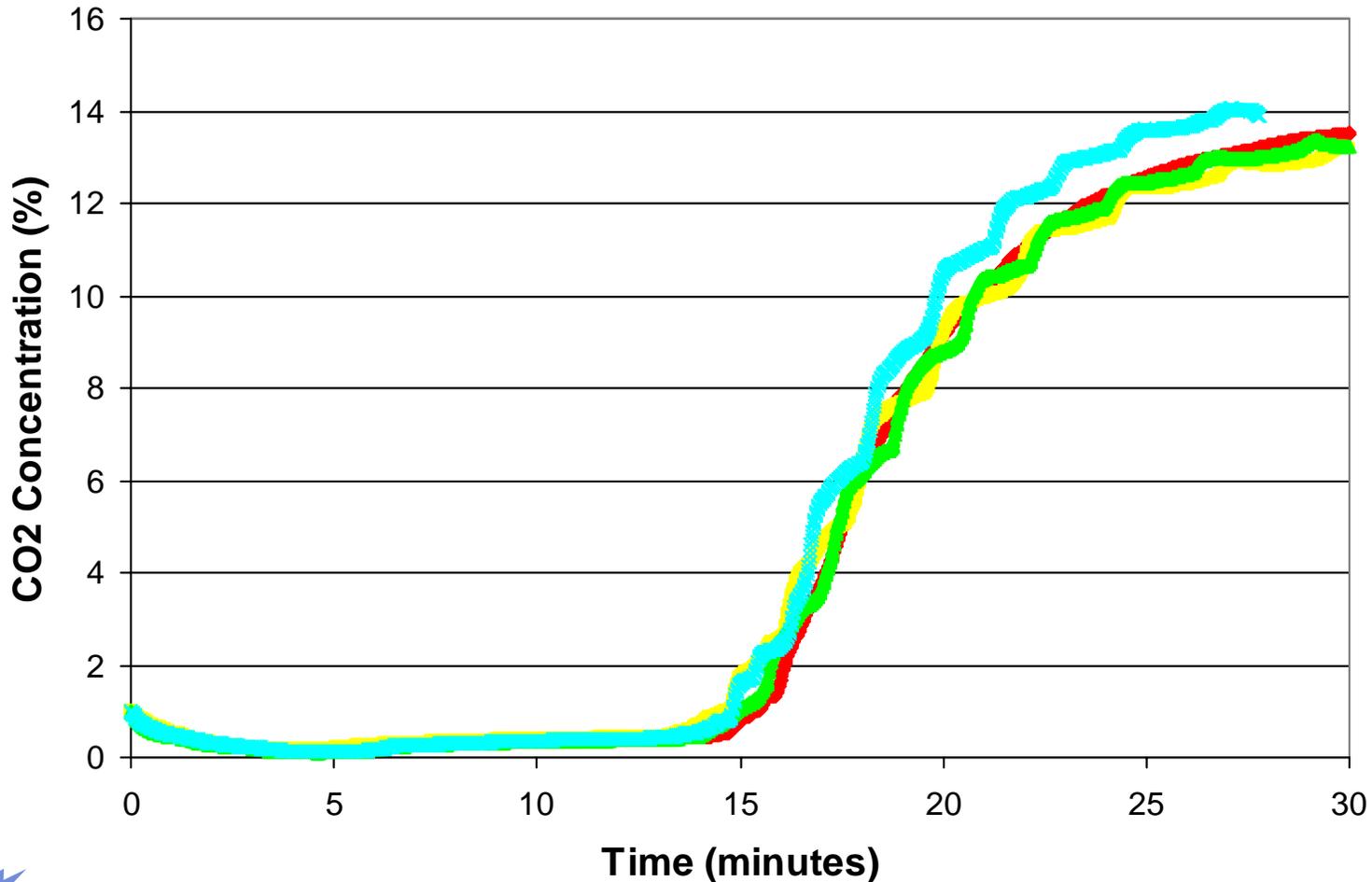


Adsorption of CO₂ on NETL-LT in Atmospheric Bench Scale Reactor- 500 hr⁻¹space velocity, 25-30 °C (8% CO₂, 3%O₂, 89% N₂)



Multi cycle sorption of CO₂ on NETL-LT in Atmospheric Bench Scale Reactor

17% CO₂, 3% O₂, 80% N₂, 500 hr⁻¹ space velocity, 25-30 °C



Summary of the Bench Scale Multi Cycle Tests with NETL-LT

- **Stable performance during multi cycle tests after regenerating at 80 °C for one hour**
 - Regeneration did not affect the capacity and efficiency
- **CO₂ capture capacity of 2 – 2.5 moles/liter**
 - Twice the capacity that of liquid amine process
- **99% CO₂ removal during multi cycle tests**
- **Temperature increase due to exothermic reaction**
 - No temperature control in the flow reactor
 - Better capacities may be obtained with proper temperature control
 - Exothermic heat may be utilized for regeneration



**NETL Warm Gas Temperature Sorbent
(NETL-WT) Development
CO₂ Capture Temperature at 315 -500 °C**



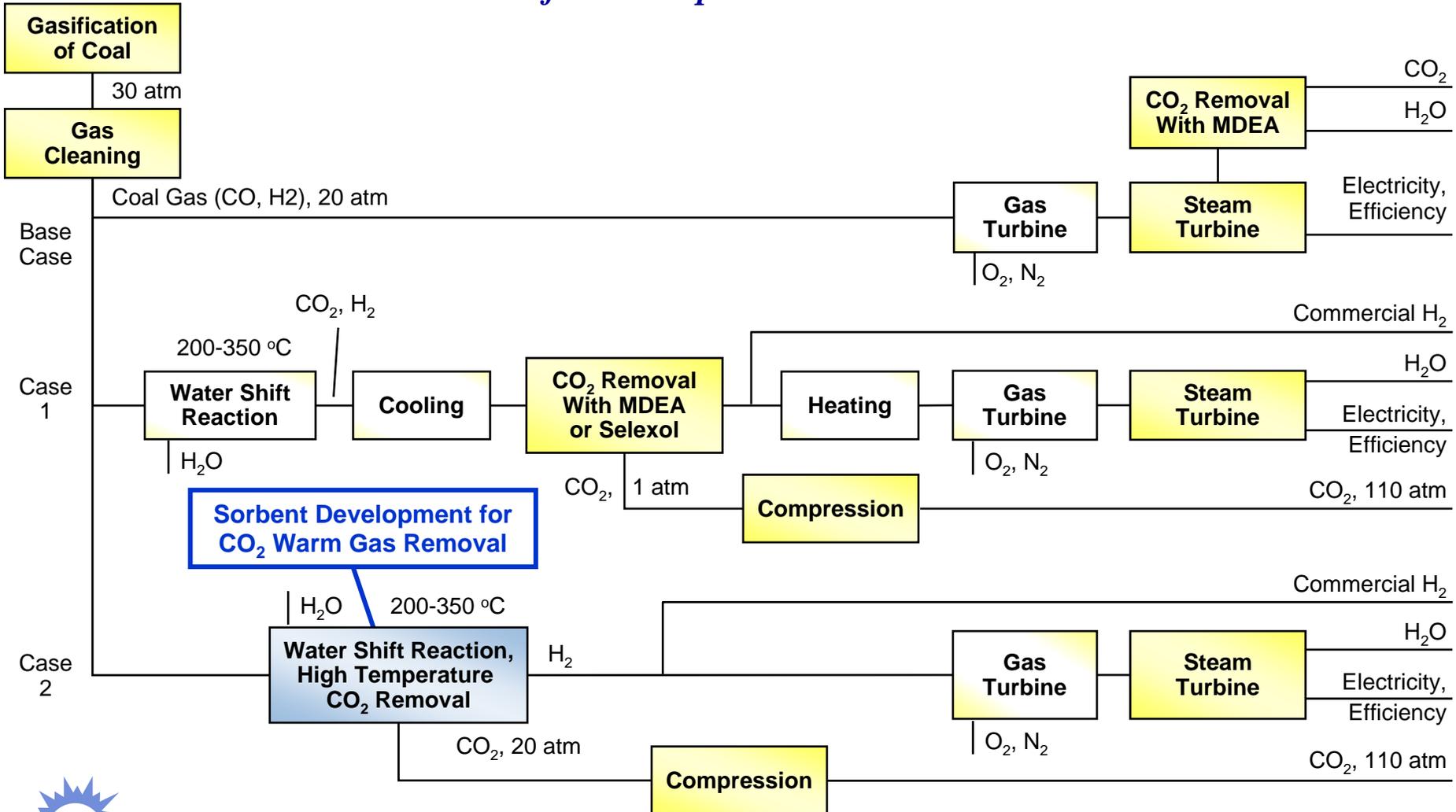
Importance of the Sorbent Development at Warm Gas Temperatures

- **Reported system studies**
 - CO₂ removal at warm gas temperatures (200 -350 °C) is the most energy efficient for IGCC systems
- **Existing commercial cold gas technologies**
 - Loss of thermal efficiency due to cooling of gas
- **Warm gas temperature sorbent**
 - Utilize gas without cooling after shift reactor and pure hydrogen stream can be obtained
 - No commercial processes
- **No regenerable sorbents for CO₂ removal at 250-350 °C reported in the literature**



Comparison of Different Options for CO₂ Removal and H₂ Production from IGCC Power Plants

Ref: TNO report R 1997/363b



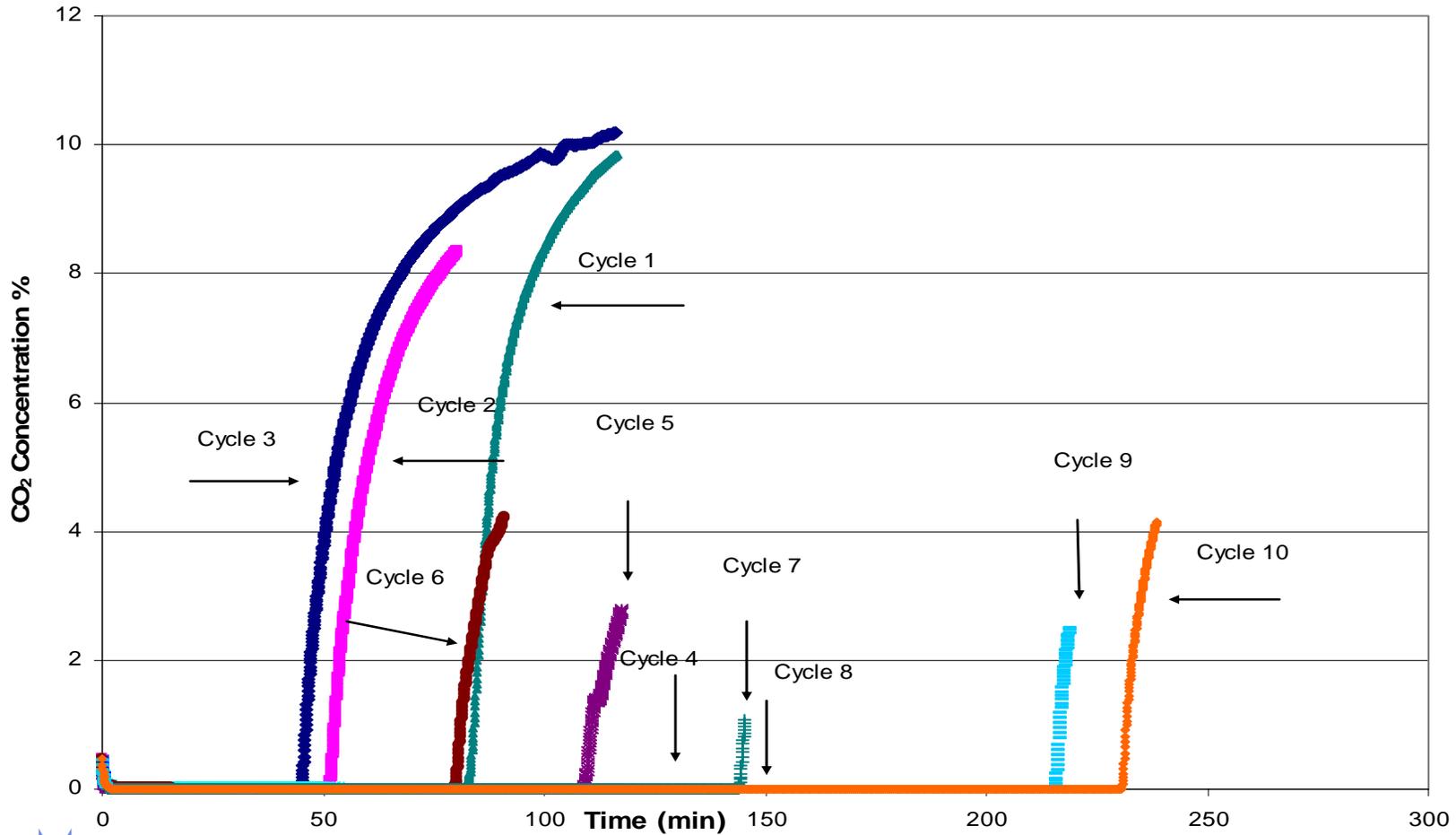
Experimental work

- **New sorbent for warm gas temperatures - Sodium based compounds**
- **Involves chemical reaction – “Sorption”**
- **Tests were conducted at 315 °C – both with simulated IGCC fuel gas and simulated post shift gas reactor gas**
- **Both low pressure and high pressure flow reactor tests**
- **Regeneration at 700 °C during ten cycle test**



Ten Cycle Test of CO₂ with Warm Gas Sorbent at 315 °C

(Simulated IGCC Gas Stream :12% CO₂, 35.9% CO, 27.1% H₂, 25% He, sat. with H₂O, 5cc/min, 1 atm)



Advantages and disadvantages of the warm gas temperature sorbent

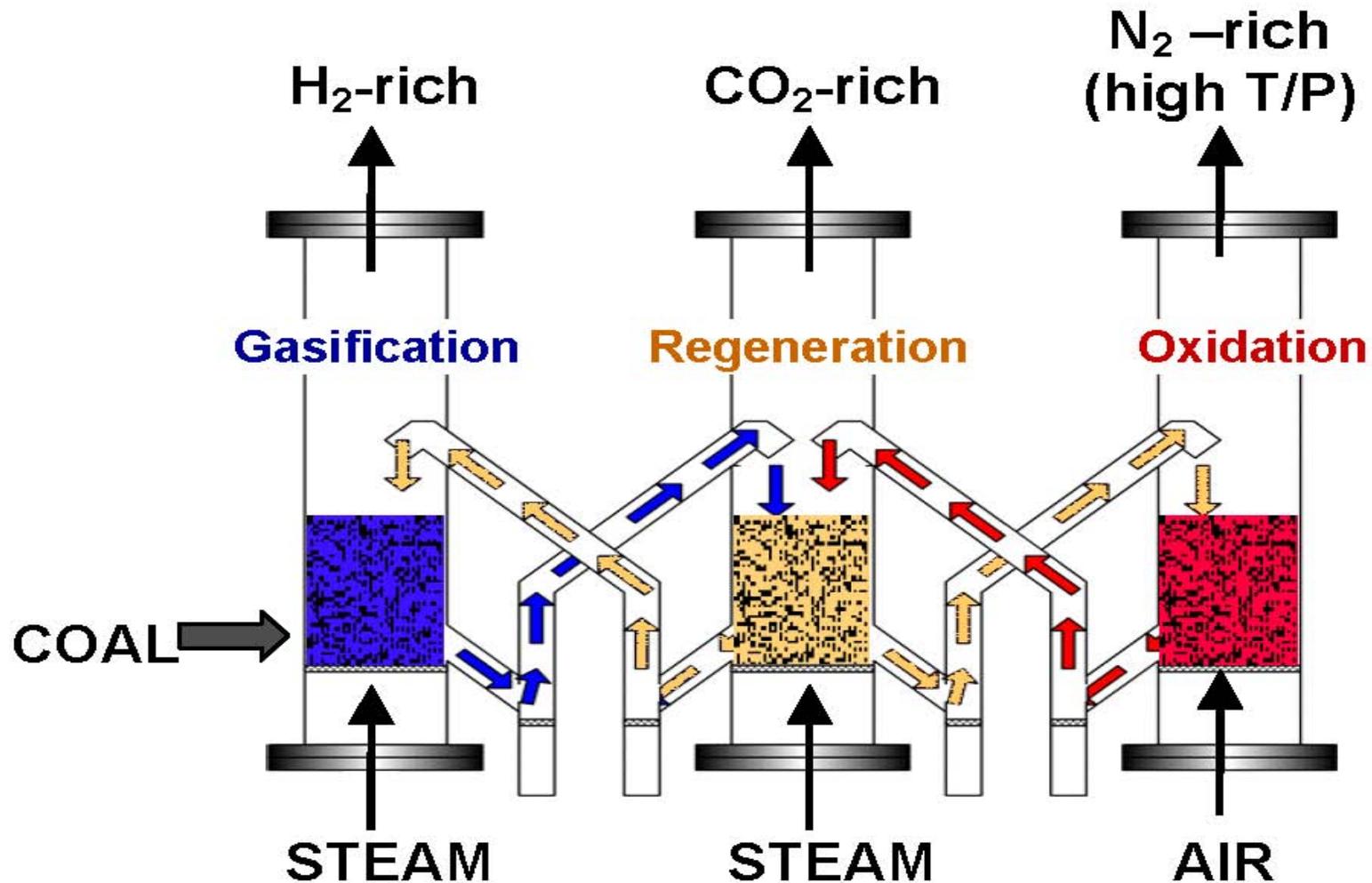
- **CO₂ removal efficiency is >99% at 315 °C**
- **CO₂ capacities improved during 10 cycle test**
 - Cycle 10 : 6.0 moles/kg (38 times that of selexol)
 - low regeneration cost and small vessel size
- **System studies at NETL**
 - Regeneration at 700 °C is not optimum for direct IGCC
- **Additives/conditions for lowering regen.T investigated –TPD/XPS studies**
 - Additives can lower the decomposition temperature
 - Decomposition can take place at 400 °C in vacuum
- **Applications in GE Fuel Flexible Gasification-Combustion system**



Application of Warm/High Temperature Sorbents

Fuel Flexible Gasification-Combustion Technology for Production of H_2 and Sequestration-Ready CO_2 by GE Global Research

Final Technical report –DE FC26 00FT40974 –Nov. 2004



**NETL Moderate Temperature Sorbent
(NETL –MT) Development
CO₂ Capture Temperature at 100–150 °C**



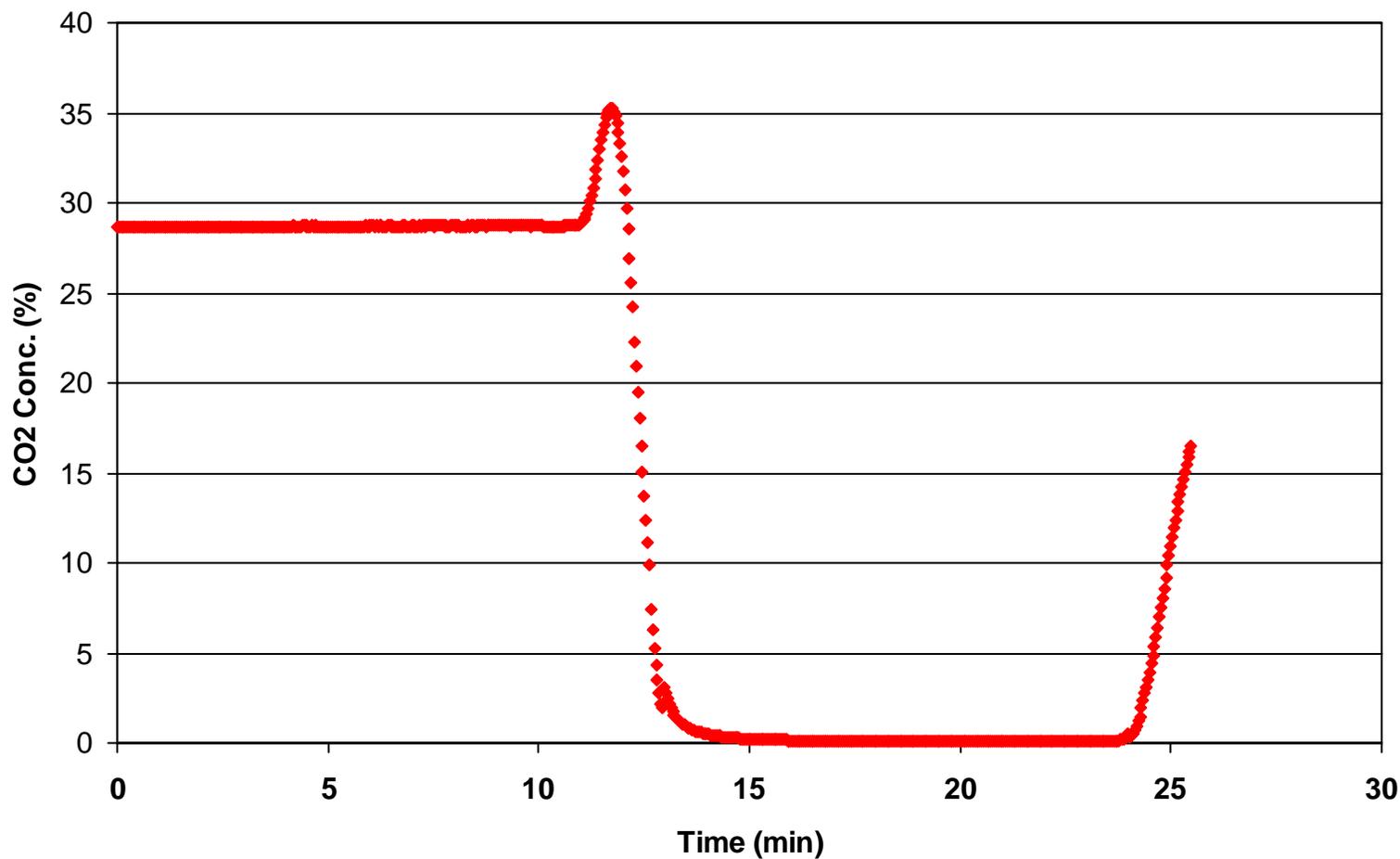
Sorbents for CO₂ Sorption at 100-150 °C

- Alkali/alkali earth based sorbent
- Performance best at high pressure according to the reaction mechanism
- Performs best in the presence of steam
- CO₂ capture at 100-150 °C and Regenerates at 350 °C
- Conducted micro reactor tests with post shift reactor CO₂ composition (28% CO₂ in He) at atmospheric reactor
- High pressure reactor studies planned
- System studies is currently being conducted

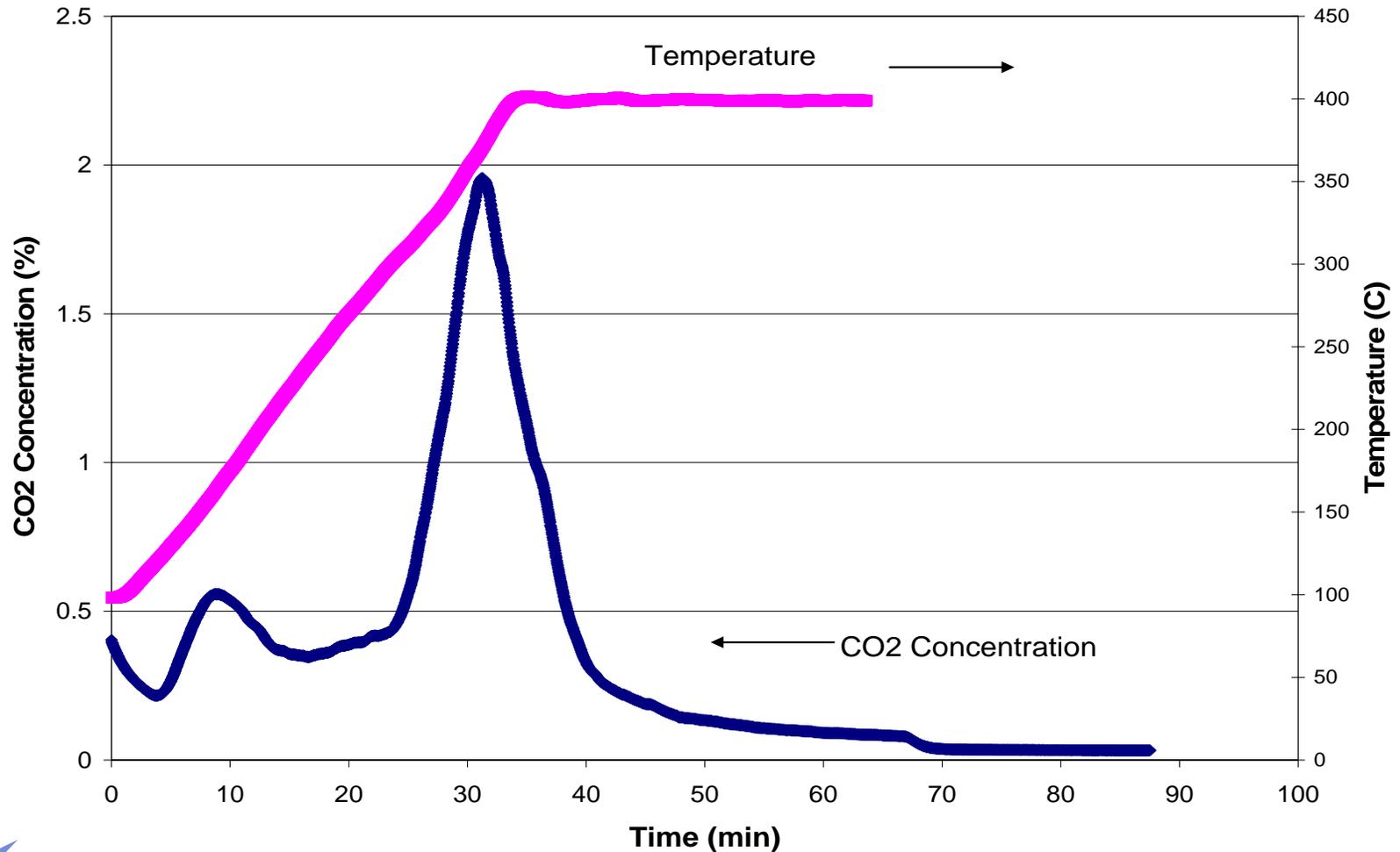


Adsorption of CO₂ on NETL-MT sorbent in Atmospheric Lab Scale Reactor at 100 °C

(28% CO₂ in He, and Saturated With Water Vapor)



Temperature Programmed Desorption of NETL-MT Sorbent after CO₂ Sorption at 100 °C



Conclusions

- **Performance of zeolites affected by water vapor**
- **NETL-LT sorbent at 30 °C abs./ 60-80 °C reg.**
 - Resistance to water vapor
 - Achieved 99% removal at industrial approved space velocity
 - Capture capacity is about 2.5-3 moles/liter
 - Better capacities with proper temperature control
 - Utilize exothermic heat for regeneration
- **NETL-WT sorbent at 315 °C abs./700 °C reg.**
 - Promising results during multi-cycle tests.
 - Additives can lower regeneration temperature
 - Other applications
- **NETL moderate T sorbent at 100 °C abs./350 °C reg,**
 - 99% removal efficiency from 28% CO₂ with steam.
 - System studies currently being conducted

