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An Innovative Approach in Post Combustion Carbon Capture and Sequestration towards Reduction of Energy Penalty in Regeneration of Solvent

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Abstract

India as a fast growing economy is pursuing strategic knowledge mission for focused research in the area of climate change. Our R&D in Carbon Capture & Sequestration (CCS) will be initially focused on post combustion carbon capture on coal fired power plants. India is 3rd largest emitter of world after China and US with a share of 6.9% in global emission of CO₂, however, India's per capita GHG emission is only 1.6 MT per annum (MTPA) which is well below the world average 7.5 MTPA. National Mission on Strategic Knowledge for Climate Change aims to develop a better understanding of Climate Science impacts and challenges. The planning commission has announced the Government's interest in adding a ninth mission i.e. 'Clean Coal Technologies mission' that would include Carbon Capture & Sequestration. As regards Carbon Capture & Sequestration (CCS) on coal fired power plants in India is concerned, an innovative concept of integrating solar thermal for steam production will pave way for reducing energy penalty in regeneration of solvents from a level of over 15% to around 05%. This chapter deals with an innovative approach of CCS in which the major issues of energy penalty reduction have been taken care of through use of Solar Steam Generation, through concentrated solar plant (CSP) with 24 × 7 thermal energy storage (TES).

Keywords: carbon capture, sequestration, amine solvent, post combustion carbon capture, concentrated solar plant, MEA solvent, energy penalty, oil fired boiler, thermal energy storage (TES), halide salt

1. Introduction: current climate change policies in India and targets

India is rich in coal and is third largest coal producer in the world with estimated coal reserves of the order of 257 billion tons [1]. Coal continues to be the dominating energy source and

meets nearly 58% of total requirement of commercial energy, but accounts for over 50% of the gross emissions. Out of total annual emission of about 2100 million tons per annum (MTPA), CO₂ emitted by the coal based thermal power plants amounts to about over 1000 MTPA. With the developmental activities using fossil fuels on the anvil, the aggregate emission in the country would increase. The coal-based power plants totaling to 192 GW out of total installed capacity of 330 GW would remain main stay of India's power sector for at least 2–3 decades. India, though has lower contribution to the historical GHG accumulation, it holds a large potential for options like cost effective CCS to tackle the adverse effects of climate change [2]. Coal fired power plants in India account for more than half of the energy production in the country annually and about 52% of the total GHG emissions of the country [3, 4]. With a large number of new coal power plants, sub and supercritical, being installed, the problem of GHG emissions is likely to increase.

India has world's largest sedimentary basins. Ganga Basin and adjoining Rajasthan and Vindhya Basins offer a potential site for CO₂ storage [5].

India has made a voluntary commitment at paris agreement; COP-21, that it would decrease its carbon intensity by 30–33% by 2030 from 2005 level. To address the threat of climate change, India has further declared in UNFCCC's Conference of Parties (COP21) at Paris, that it will augment 175 GW of renewable energy, out of which 100 GW would be solar PV and solar thermal. Carbon sequestration of the order of 2.5–3.0 billion tons of CO₂ through additional forest is also aimed at in the perspective five year plans and focus on adaptation in agriculture, forest, water and livelihood would be accelerated [1, 7].

The path chosen makes it imperative that the CO₂, which forms 95% of the GHG emissions be reduced. The reduction of 33% intensity as promised by India at COP-21: Paris; would translate to a decrease of CO₂ emissions from our coal plants from 0.9 kg/kWh to a level of 0.58 kg/kWh by 2030. This decrease is possible by a combination of adaptation and mitigation measures like acceleration of present pace of Low Carbon Technologies (LCT) particularly and Clean Coal Technologies (CCT) and setting up of Carbon Capture & Sequestration (CCS) plants primarily for post combustion carbon capture on our fossil fuel based sub and supercritical thermal power plants.

The Indian Power Ministry and the Department of Science & Technology have considered CO₂ capture and its sequestration through options like conversion to fuels as a far economical option than storage in sedimentary basins by [6, 7]. As per the Global Assessment Report, there is limited geological storage capacity [8], however a better potential will be found, if the concept of CO₂ storage in Basalt formations can be advanced into a matured option through focused R&D [9, 10].

Expected benefits for the environment and society at large due to the CCS implementation plan are:

- Adoption and implementation of Low Carbon Technologies will pave way for sustainable society prepared to meet the challenges of climate change.

- CO₂ sequestration is a multi-dimensional aspect involving capture of carbon from atmosphere followed by transportation, injection into favorable sites and post-injection monitoring. The favorable sites for storage of CO₂ must be reliable in the sense that CO₂ will be stored there permanently at least for 1000 years and no leakage is preferable. In this backdrop, the most suitable storage sites where CO₂ could be fixed permanently by chemical absorption and reaction respectively are depleted coal beds and saline aquifers [7].
- Carbon Capture & Sequestration would play an important role in reducing GHG emissions at the same time enabling low carbon electricity generation from Power plants. Considering a CCS integrated 500 MW unit, which emits over 3 million tons of CO₂ per annum, would be equivalent to: (a) planting over 60 million trees and maintaining them to grow for 10 years; (b) avoiding energy related emission of about 0.3 million houses [7].

R&D efforts under the aegis of various Ministries of Government of India including Department of Science & Technology, would be required to estimate the economic implications of implementing CCS in the existing coal Fired plants [11]. Nine national missions for managing climate change have been set up by the Planning Commission, which include Clean Coal Technologies and CCS as a prime mitigation measure.

It has been recommended at several forums of Ministry of Power that a better option could be carbon capture and sequestration (CCS) through the technologies of conversion of CO₂ into multipurpose fuels including biodiesel through Algae route. In a post combustion amine based CCS Plant the Energy Penalty in regeneration of solvent has been identified as a main issues in CCS deployment, as such India is taking conscious steps in the area of CCS as under following stage wise program:

- Stage-1 (1–5 years): CO₂ sequestration to selected species of Algae in ash pond in the plant area.
- Stage-2 (5–10 years): sequestration to depleted coal mines for pit-head coal based power stations.
- Stage 3A (10–15 years): sequestration to basalt rocks, saline aquifers & EOR as per site specific options.
- Stage-3B (10–15 years): for costal power stations: CO₂ hydrate formation in seabed sediments.

Innovative concept of energy penalty reduction through integration with the solar thermal could also be an option for India and other countries between tropic of cancer & capricorn viz. under International Solar Alliance launched recently with India in lead role. The CCS option towards sustainability may lead to an opportunity for course-correction in line of thinking of our Planners,

Engineers & Scientists working in the arena of Green Power technology and its development. The time appears to be ripe for implementation of CCS on an actual thermal power plant.

2. Detailed methodology of post combustion CCS on a thermal power plant: a pilot study

A pilot plant of CCS having rated capacity of curbing carbon dioxide of 500 kg/day was installed at RGPV University, Bhopal in Central India in the year 2008. The source of carbon dioxide was a baby boiler of rated capacity of producing 100 kg/h of steam. Desired amount of steam is extracted for catalytic conversion and other heating processes. Another source of flue gases is a biomass gasifier fired engine of capacity 10 kWe, which is also coupled with the system. Scrubbing of flue gas is done using solution of NaHCO_3 , NaOH and lime for removal of SO_x and NO_x ; and for capturing carbon dioxide from flue gas an aqueous solvent of 1–2 M monoethanolamine is used. The strip of CO_2 is sent to the three MEA solvent tanks where the MEA solvent in the three tanks absorb the CO_2 up to their saturation point. The saturated MEA containing CO_2 from the three MEA solvent tanks are sent to the saturated MEA tank. In order to remove CO_2 from the MEA saturated solvent, a stripping tank is provided. The CO_2 is released from the MEA solvent in stripping tank with the help of steam generated from the diesel-fired boiler. Data are recorded by combustion gas analyzer, which was customized to record data as per requirement [12]. The scheme diagram of the plant is shown at **Figure 1**. Catalytic converters/reduction units for methane, hydrogen and CO are installed for this pilot unit.

The long term “Objectives” behind setting up of a pilot plant are to provide ground for ‘Feasibility study’ on a large thermal units of future having CCS facility with least energy penalty. To this end, the development of Concentrated Solar Power for Steam generation for Regeneration of CO_2 captured MEA Solvent & System optimization studies are on the anvil.

The pilot plant will also provide a study and prove the viability of sequestration of CO_2 to selected species of Algae for getting optimum lipid content from the increased growth of species.

The pilot plant together with the combustion gas analyzer & data acquisition system has been used for 4000 h. Trail run for ‘Uncertainty Analysis’ in the experimentation. CO_2 capture level of 90–93% was achieved for the above post combustion CO_2 sources viz. a boiler and a gasifier. It was seen that H_2 formation to the extent of 21% by volume was also achieved.

The pilot plant (**Figure 2**) was utilized for variety of application during trial run of 4000 h for process stabilization such as: the study of CO_2 capture in mono ethanol amine (MEA) ranging from 1 molar to 5 molar strength; sequestration of CO_2 released from the stripper unit to variety of algae and development of lipid content for bio-diesel production. The pilot plant is also being used for development of low cost catalysts for production of fuel elements like CH_4 [13].

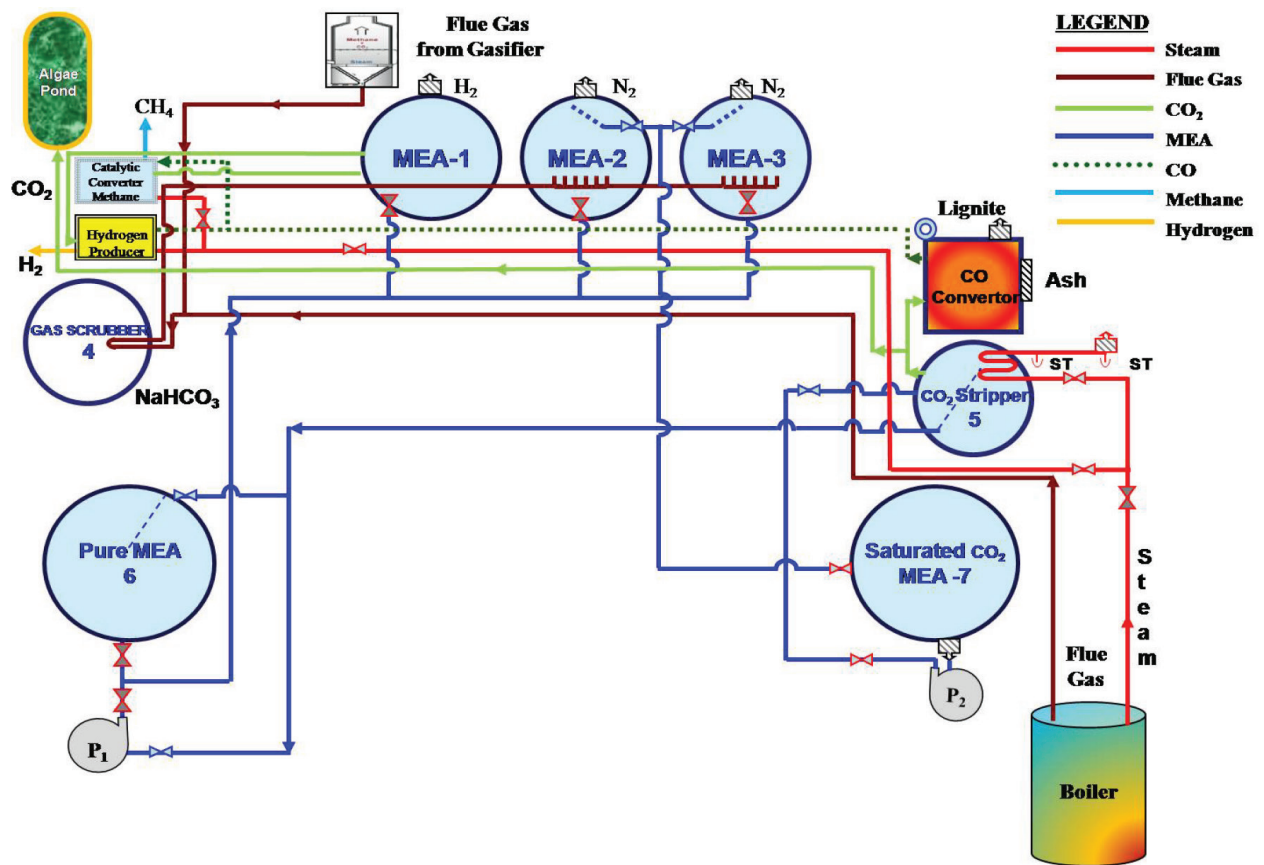


Figure 1. Scheme diagram of CO₂ capture & sequestration pilot plant.



Figure 2. CO₂ capture & sequestration plant (CO₂ & steam source—oil fired baby boiler).

A need was established soon after the 4000 h trail runs of this pilot plant to explore:

- i. Optimum value of molar strength of MEA solvent for highest efficiency of capture with minimum cost penalty of regeneration.
- ii. Optimum value of carbon dioxide recycling for conversion to CO to attain heat gain up to the calculated theoretical limit of 21.88%.

Simulation studies were carried out and a 1.5 molar strength was found to be optimum for CO₂ capture to the level over 90%. Further, using lignite Gasifier the carbon monoxide of the order of 20% was produced for recycling to the boiler using short-flame burners, which is close to the theoretical limit of 21.88%. The pilot plant was also used for the feasibility study of installation of CCS plant on a 500 MW thermal power plant as discussed further.

The objective of this pilot project is also to carry out feasibility study, prototype design & development of a 30% CO₂ capture & sequestration unit for installation on a 500 MW coal-fired thermal power plant as per the broad scheme given below (**Figure 3**). The project proposal also provides details of plant modification to be done by plant engineers for steam tapping from turbine extractions, as well as design and consultancy scope, etc. A full-scale plant on a 500 MW Pulverized Coal Fired Unit would require a plant of 510 tonnes/h capacity. This interdisciplinary project is expected to resolve certain frontline issues in CO₂ sequestration such as energy intensive process optimization in terms of cost of generation and development of effective catalyst for methane, hydrogen and biodiesel recovery through Algae route. This

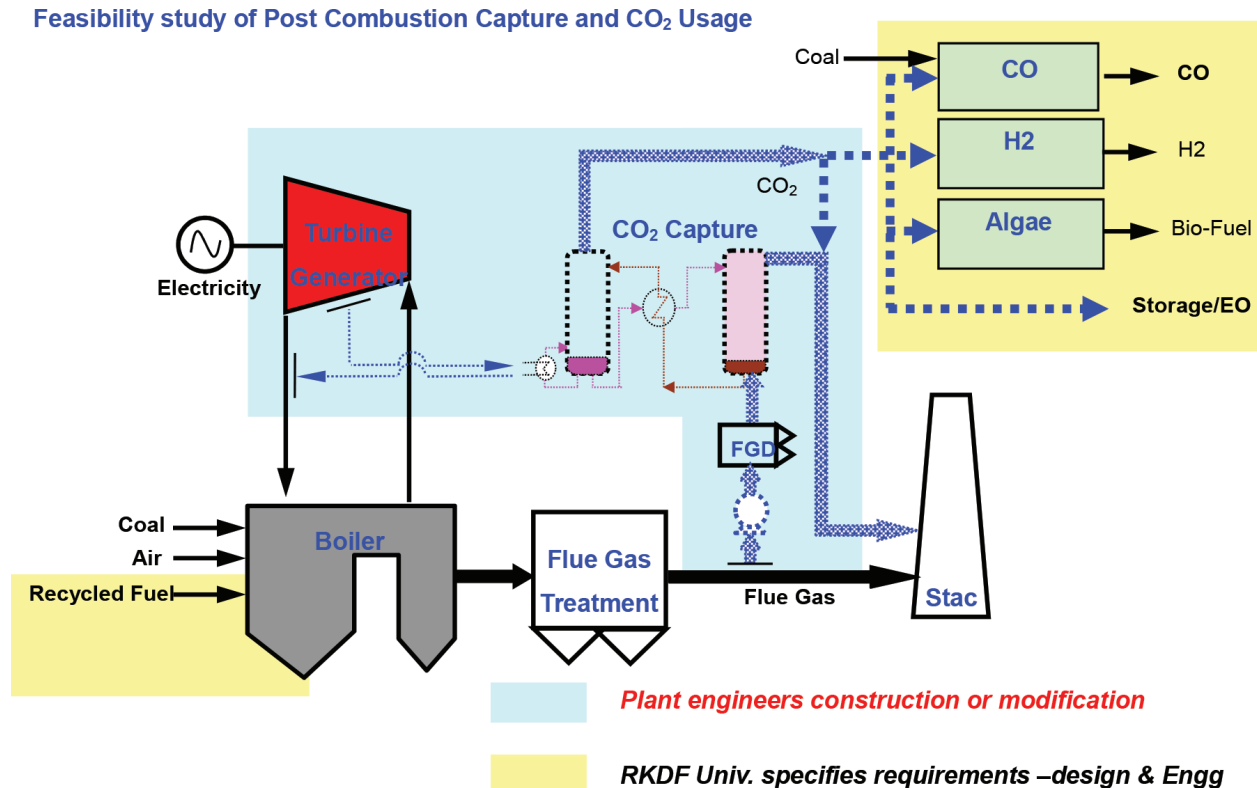


Figure 3. Conceptual diagram of a power project with CCS.

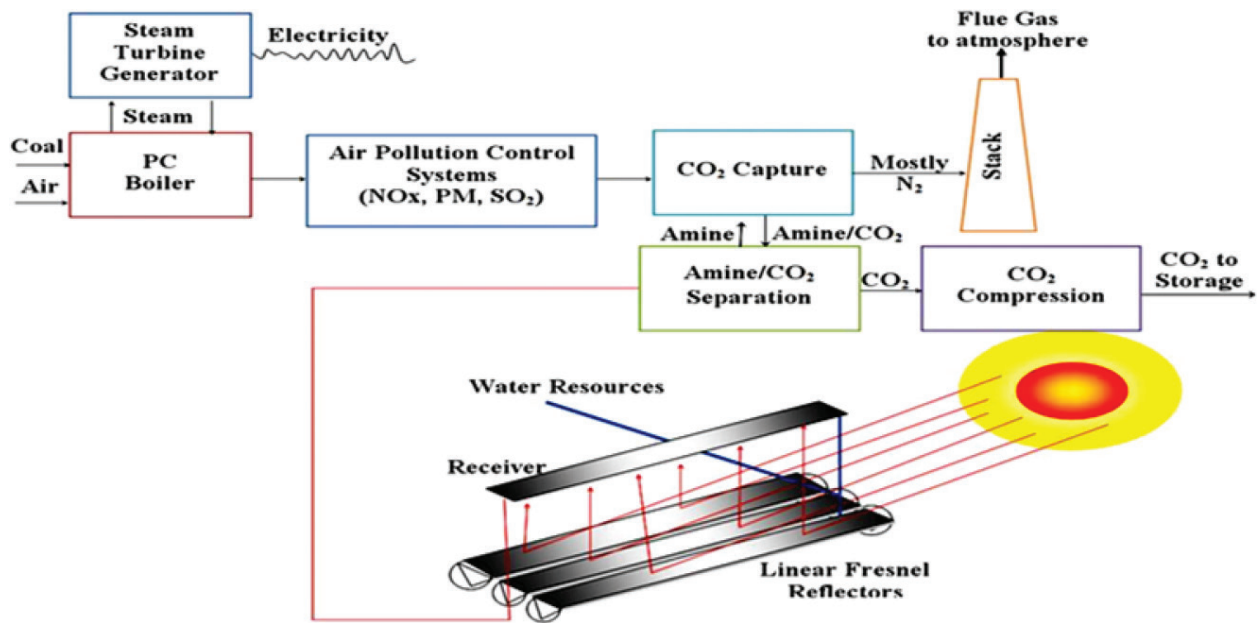


Figure 4. Scheme of implementation of CCS plant through integration with solar thermal.

scheme of retrofitting of existing 500 MW unit with CO₂ capture & recycling of CO is being discussed with power utilities like NTPC, TOSHIBA and BHEL and the broad outline of the same are given at **Figure 3**.

The methodology of implementation of CCS plant on a 500 MW unit is broadly shown in this figure. The scheme also shows steam turbine extractions for providing steam for regeneration of solvent which will cause energy penalty of the order of 15%. The same can be reduced to 4–5% level by combination of solar thermal generated steam coupled with thermal energy storage using a concentrated solar plant (CSP) as shown below in the conceptual **Figure 4**. The incorporation of solar thermal with CCS will pave way for reduction of energy penalty in regeneration of solvents [1, 7].

An amine solvent based plant with 30% CO₂ capture would mean an energy penalty of about 25% including about 15% for sequestration to mineral rocks, gas hydrates and ocean. In any case the energy penalty in our case when we are going for CO₂ conversion to multipurpose fuels the energy penalty still remains at level of 12–15% [1, 7]. The reduction to about 10% has been calculated using MATLAB simulation and shall be verified after establishment of pilot scale CO₂ capture and sequestration plant integrated with Concentrated Solar Power (CSP) for carrying out system optimization studies (**Figure 4**).

3. Solar thermal technology application in post combustion CCS on a thermal power plant

Concentrated Solar Plant (CSP) is presently a matured technology in which several thermal energy storage options are being deployed. Energy storage in form of heat offers a

potential pathway for small (local) and large (utility power plants) scale applications. Thermal storage systems provide a unique opportunity to store energy locally in the form of heat that cannot be transported over long distances. Current thermal storage systems are still in its infancy. The most common ones are large, water-heating storage tanks and molten salt-based systems at solar power plants. These systems have been designed based on the economics of water and salt, the heat capacity of water, and the latent heat of salts. Research on a large host of sensible heat storage and phase-change materials have been conducted over the past two decades. The materials parameters that are relevant for this application are: melting point, boiling point, vapor pressure, density, heat capacity, thermal conductivity, latent heat of fusion and chemical reactivity. While it is intuitive that increasing the temperature of storage could pack in more energy, barriers to the development and deployment of high energy density storage remain, including handling materials at high temperatures, associated systems costs, and operating costs. Thus sensible thermal storage systems are cost prohibitive. Phase change materials (PCM) do provide a viable economical solution for higher energy storage density. However, operation temperatures limit current PCM systems; higher temperatures cause chemical instability and reactivity with containers. Development of affordable high-density thermal storage system will only be possible by utilizing low cost earth abundant thermal storage materials in conjunction with suitable thermally insulating container materials. Current heat storage systems utilize either sensible heat storage (i.e. water in storage tanks) or latent heat storage (i.e. phase-change materials such as molten salts). The relatively low operating temperatures of these systems limit their capacity to store thermal energy; storage systems with higher temperatures would be more economical.

The technologies which hold promise for achieving temperatures in the range of 150–600°C and beyond can be categorized by the phases of matter of the materials used: liquid, gaseous, solid, as under:

- A liquid pathway is considered to look much like today's molten salt two tank tower configuration, but using a suitable high temperature and cost effective HTF/TES.
- Gaseous pathways use an inert gas flowing through a receiver to absorb the solar energy and then transfer the thermal energy to a storage system and/or the turbine working fluid.
- Solid pathways involve solid inert media which absorbs solar radiation and stores that energy as heat. When electric power is needed, the turbine working fluid is heated by the solid media.

In this CCS integrated with CSP project we examined several options of 'Solid Pathway' such as cast iron core of Mount Abu 1 MW solar plant used for steam generation, CL-CSP plant at the State technological University of MP, RGPV, in Central India in which pebbles/rock storage has been proposed for energy storage for heating air in primary cycle and steam in secondary cycle.

In this CSP to CCS integration project, we are developing an affordable high energy density (in excess of 300 kWh/m³) thermal storage system, that can store heat at temperature around

1000°C [14, 15]. The unique aspects of this system are the selection of an alkali halide salt with high melting temperature and a corrosion resistant cheap ceramic container material. The thermal storage unit will be coupled with a high solar concentrator system (1000–10,000×). As a part of an on-going project at RKDF University in near vicinity of RGPV, funded by MNRE, the project collaborator in Solar thermal, the Rensselaer Polytechnic Institute of USA has developed flux grown crystals of high melting temperature (700–1500°C) mixed alkali halide compounds doped with metallic impurities to enhance thermal conductivity. The trade-off between material density, specific heat capacity, thermal conductivity and cost of raw material has been evaluated to develop a material system that could meet the system's specification at cost of energy storage lower than current electrochemical systems (batteries). In addition, a SiC based composite polymeric coating solution has been developed to avoid corrosion of steel containers used for the thermal storage unit [16]. These materials have been shipped to RKDF University and incorporated into the field unit (test-bed). The test-bed at RKDF comprises of a thermal storage unit, Fresnel lens based solar tracking unit to focus sunlight into the thermal storage media and a steam generation unit (for future electricity generation using a steam turbine). **Figure 5** shows the installation and initial evaluation activities of the solar thermal storage unit at RKDF University.

The expected physical outcomes of the project of CSP integration with CCS as discussed above are in terms of establishment of the pilot plant of CO₂ capture and sequestration on an actual thermal power station for future development of technology of CCS in India and countries between tropic of cancer & capricorn bestowed with high solar DNI [1, 7].

Test results have shown that the innovative halide salt used as thermal storage material stores heat to such an extent that it retains heat for over 5 days to be able to produce steam (**Figure 6**). This innovative halide salt was also tested in the pilot plant shown at **Figure 5**. The biggest challenge in this project is, however, the development of Alkali Halide Salt indigenously for which efforts are under way at RKDF University to procure some of the key components for growing crystals with high energy density, capable of retaining heat. Also efforts are underway towards indigenous development of Heliostats, Fresnel lens and low cost trackers.



Figure 5. Solar thermal storage unit at RKDF University.

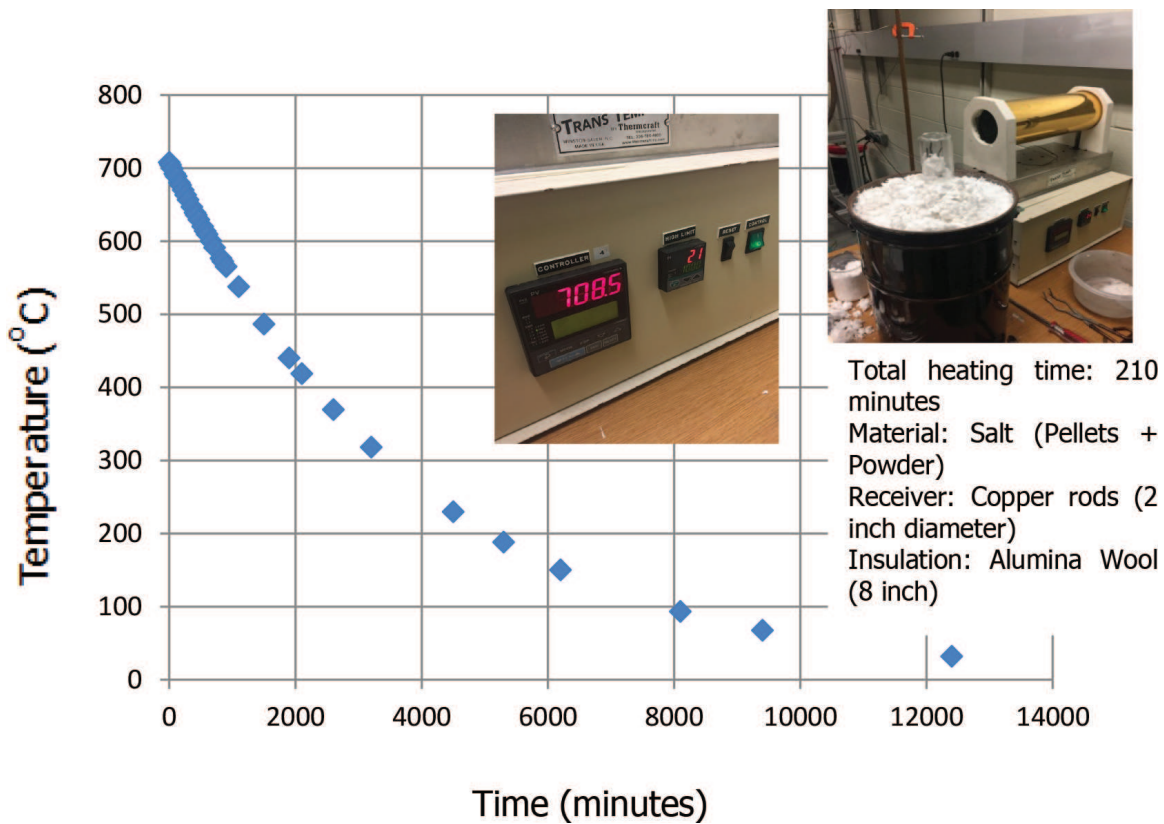


Figure 6. Thermal cooling profile testing of the halide salt at RPI, USA.

4. Conclusion & way forward

Low Carbon Technology Vision for India together with strategies, challenges & opportunities in Green Power for energy security environmental sustainability are put forward in this paper covering Carbon Capture & Sequestration as a key factor. While there is growing trend of carbon dioxide emissions by energy sector since coal continue to play role in primary energy consumption, the urgency of CCS deployment in countries where coal is the main stay is very important. A pilot plant has been developed at RGPV University, for capture of CO_2 and converting the same into useful fuel like hydrogen for fuel cell application, methane for multiple applications and bio-diesel production through algae route. MATLAB simulations have shown that the recycling of CO back to the boiler will provide heat gain up to theoretical limit of 21.88%. Further, the energy penalty in regeneration of solvent using steam produced by solar thermal plant with an innovative Halide salt as thermal energy storage material will reduce by about 10%.

Climate change has already been experienced in many parts of the world therefore state policies need to support practices that successfully keep carbon in the ground, prevent deforestation, support agricultural practice that sequesters carbon and promote sustainable land use practices that reduce emissions. Policies should push especially the more prosperous communities towards less carbon intensive lifestyles, either through taxes or incentives or both. In

addition, the path to zero-emissions must be progressive and in line with the progress of new and renewable technologies of hydro, solar and wind. The first step towards in this progressive path should be CCS.

Indigenous development of critical components of solar thermal plants for integration with CCS is nevertheless important. The following is a list of identified components that will be necessary to be developed within India at ultra-low cost by technology licensing and manufacturing technology transfer approaches by commercial entities (from abroad) to translate the existing technology for large scale adoption:

1. Large area high optical quality Fresnel lens/Heliostats/Fresnel Reflectors manufacturing with low cost.
2. High thermal storage density material development for 24×7 heat storage.
3. Corrosion resistance nano-coating process.
4. Ultra-low cost solar trackers.
5. Energy efficient, low maintenance cost thermal transport systems for heat exchange.

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