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Advances in Heat Storage(HS) Schemes for Concentrated Solar Power Plants(CSPPs)–A Technical Paper

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Advances in Heat Storage Schemes for Concentrated Solar Power(CSP) Plants

Abstract

Climate change issues, depletiom of the ozone layer has prompted the development of CSP power plants which do not generate greenhouse gas emissions. The source of heat in CSPs is the infinite, abundant and sustainable renewable solar energy. CSPs replace the front end of fossil fueled power plants but retains the tried and tested backend i.e. power engine which is the same as in coal power stations.

Solar energy is only available for a maximum of about 10 hours daily during which there is diurnal and seasonal variability and other factors like cloud cover, rain and humidity levels and hence the need for energy storage to enable 24 hour generation

The paper intends to avail an exhaustive, comprehensive and detailed review of the technologies involved in heat energy storage schemes covered by literature comparing their advantages, disadvantages and economic viabilities. The paper goes on to dimenson and size the storage tanks for the various thermal energy storage technologies.

This paper recommends tricoupled or tribridized energy storage schemes on a single CSP power plant e.g..

(a) Sensible heat for night and day(diurnal storage or short term storage)
(b) Latent heat for solar diurnal variability and cloud cover(medium term thermal energy storage) e.g. for weeks
(c) Thermochemical for long term seasonal variability(seasonal heat storage)-long term storage e.g. months.

all on a single power plant as an effective energy storage scheme! This paper recommends the use of more, stronger and more resliant materials for energy storage tanks such as insulated carbon steel or stainless steel of appropriate thickness to prevent mechanical yield failures due to volumetric expansive forces induced by heat of the storage material therein contained in storage tanks. Engineering material sciences theory and experiemental evidence will assist in the design of storage tanks that has the capacity to withstand stress and tensile forces due to volumetric thermal expansion of storage material.

The technical paper identifies thermal energy storage materials for the three storage technologies.

Keywords: Concentrated Solar Heat Power Plants(CSHPP), Latent Heat Storage(LHS), Sensible Heat Storage(SHS) and Thermochemical Heat Storage(THS).

1.0 Introduction

Energy storage

Energy can be stored in the following different forms i.e. thermal or heat(as in CSPs storage tanks), electrical(batteries), pumped hydro(differential heights-head), chemical reactants(nuclear), biomass, mechanical (kinetic and potential), fuels(Rao & Parulekar, 2009). Flywheels, compressed air, charged springs are also other means of storing energy as potential energy. Water can also be split into oxygen and hydrogen and hydrogen stored as a possible source of future energy. Since potassium nitrate, sodium nitrate combined with appropriate amount of ammonium nitrate are used to ,manufacture gun powder, rocket fuel and explosives,this implies that these materials can also be used as a source of stored energy. Research into copper sulphate combined with manganese and other materials also need to be investigated as a possible way of storing energy. The main and frequently used storage schemes are electrical storage and thermal storage. It is impossible to store electrical energy economically in large quantities of MWh range by conventional means. Among possible energy storage strategies are pumped hydro and compressed air but have to compete with alternatives which include generation expansion which eliminate need for storage, interconnectors with other power utilities e,.g. in other countries. Thermal storage has been found to be ideal for CSPs.

Hot and Cold Systems

This system employs two well insulated storage tanks with necessary pumps, valves and piping. The storage Heat Transfer Fluid is normally molten sodium salt or oil(Singal, 2016). The storage tanks are mainly made of austenitic stainless steel. Steel has a high mechanical withstand strength value given forces that may act on it during storage. These forces may be due to volumetric expansivity of the Heat Transfer Fluid.

The following table shows various materials, their melting points, boiling points and density which are critical dimensions used to determine storage tank materials and thermal energy storage materials including Heat Transfer Fluids.

Table 1.1.

Table showing Mechanical Strength of various materials for making storage tanks

MATERIAL	TENSILE STRENGTH(Megapascals MPa) Value	Sheer STRENGTH
1. Structural steel	400	210 000 Mpa
2. Carbon Steel	841	80 000 PSI
3. Ceramic materials	0.7 upto 7 000 MPa	17.35 UPTO 20.06 MPa
4. Diamond	20 GPa	85 GPa
5. Lithium	4 SI	43 MPa
6. Aluminium	90 MPa	55.2 MPa
7. Mild Steel	400 MPa	345 – 525 MPa

Reliabilty, efficiency, cost and safety of the storage strategy have an outstanding influence on the selection and design of an energy conversion plant and storage subsystem(Rao & Parulekar, 2009)

Where thermal input exists like in Concentrated Solar Power(CSP) plants, enthalpy of the HTF through a heat exchanger to working fliud, heat angines or power blocks are employed to convert heat to electricity. In these schemes thermal storage is ideal.The turn around efficiency of electrical-thermal-electrical cycle is poor i.e. 20% to 30 %. With batteries as a storage tactic, we have electrical input, electrical storage and electrical output.

Conversion efficiencies, cost per kW and storage cost per kWh becomes the prominent economic factors determining choice of a storage strategy.

For CSPs of the Central Receiver Tower, energy losses from the outside of the surfaces of flow tubes and storage tanks need to be minimized, contrained and dimished by thermal insulators such as asbestors, fibre glass cement, porcelain, PVC etc.

Climate change issues, depletiom of ozone layer and toxic substances associated with coal mining like Sulphur which have killed thousands of people historically, coal dust which causes diseases like pneumoconiosis has compelled power planning experts in power utilities to consider shifting from fossil fuels (coal, natural gas and oil) to renewables like solar and wind generation etc. These renewables require to be coupled with energy storage schemes to smoothen the generation profile and hence electricity supply profile of these highly variable, stochastic and intermittent renewables. Renewables are now a symbol of modernity in electricity generation methodologies among the generation mix supplying the grid of a power utility. During the evolution of power generation methods, renewables plays a major, significant and decisive role in ensuring environmental sustainability, decarbonation and raising efficiency and security of supply.

Thermal storage is a vital process in the effective and efficient penetration of renewables into the electricity generation matrix worldwide because of the variability, intermittency and stochastic nature of renewables like solar generation. In order to match intermittent generation or supply with uncertain variable load demand, energy storage schemes are not only necessary but vital for success in the demand and supply matching dynamics. Solar insolation varies according to day and night time cycles, diurnal (morning to afternoon to evening) and seasonal variability. It is also affected by cloud cover conditions sensitive to wind, humidity and atmospheric temperature conditions. Such intermittency makes energy storage schemes necessary, vital and imperative for generation stability, flexibility in power dispatch and load-following capabilities. In addition Thermal Energy Storage(TES) technologies enables competitive and economic viability of CSPs when in operation and may permit maintenance of the heliostat assembly and solar absorber without stopping generation from the CSP if correctly designed. TES systems for high temperature applications are suitable for electricity power generation and operates in the temperature range of 200^0 C up to 1000^0C e.g. 565^OC for the Central Receiver Tower power plants.Thermal Energy storage technologies increases CSP installed capacity levels for power utilities (.Palacios et al., 2020)

These schemes also increases energy management and exploitation capabilities for power utilities(Guruprasad Alva etal., 2018). Thermal energy sources include coal, nuclear and CSPs.

The solar insolation-to-heat-to-electricity conversion efficiency determines the overall efficiency of a CSP power plant. The heliostat assembly and the solar absorber facilitates the conversion of solar radiation to heat. Energy storage tanks and heat storage technologies facilitates heat storage in large quantities for use when solar radiation is not available. This increases capacity utilization of the CSP power plant and grid and smoothens the supply curve to the grid i.e. continuity of supply. The heat engines or the power block facilitates the conversion of heat to electricity. Coupling Thermal Energy Storage (TES) schemes with CSPs improves grid flexibility. During off peak energy can be stored in TES schemes or technologies for use during peak hours. Storages gives flexibility and commercial profitability resulting from higher efficiencies , cost effectiveess of operations, increased capacity utilization of grid components and supply adequacy resulting in possible power utility customer delight.

Electrical energy cannot be stored economically in large quantities suitable for grid use e.g. in batteries and therefore electricity energy has to be stored in other forms such as thermal energy, hydrogen atoms, pumped hydro, reversible endothermic reactions which can easily later be converted to electrical energy when needed etc. The power industry is grateful to the discoveries made historicaly in energy form convertibility technologies e.g. heat to electricity through heat engines or power blocks.

Solar insolation-to-heat-to-electricity conversion schemes/technologies have to be designed including heat storage tanks as a flexible, superior and modern electricity supply configuration.

As mentioned earlier, the challenge for CSPs is that solar energy is intermittent due to diurnal and seasonal variations of the earth's position relative to the sun, day and night, variable cloud cover, rainy periods and the sun's trajectory during the day from morning to afternoon to evening. This variability means that the energy dispatched from Concentrated Solar Power stations to loads become variable, unstable, unreliable and therefore insecure without storage schemes.

In order to guarantee security and continuity of supply, energy storage schemes are employed. Among these are the following:-

batteries, thermal energy storage schemes e.g. sensible heat, latent heat and thermochemical(or reversible endorthemic reactions), splitting water into hydrogen and oxygen and storing hydrogen as a source of energy, pumped hydro, charged springs, flywheels and compressed air.

For CSPs, thermal energy storage is best implemented in the form of sensible heat storage(SHS), latent heat storage(LHS) and thermochemical energy storage(TCHS) which is a classification pivoted on the principle of storage (Girolama et al.,2020). Sensible heat is the most frequently, abundantly and widely exploited storage scheme among the three in CSPs power plants because of the following reasons (a) reliability (b)cheapness (c) simplicity in implementation (d) huge historical experimental feedback that is available and the technology is past the 'learning curve'. Achkari et al., (2019) posits that Sensible Heat Storage can be achieved when a Thermal Energy Storage material(liquid or solid undergoes a temperature change without any phase change or chemical reaction e.g sand, thermal oil and concrete etc. (Farulla et al., 2020), posits that sensible heat schemes are foundationed on the storing thermal energy which increases temperature linearly in a liquid or solid storing medium without changing its chemical composition or phase..Sensible heat energy stored (Qs)=f(mass of storage material, temperature change, specific heat capacity of storage material), (Girolama, (2020). It is desirable that sensible heat storage materials/systems possess high specific heat capacity like lithium, long term thermal stability under cyclical stress, recyclability, a low carbon footprint, good thermal conductivity,compatibility with its container and recyclability.

The quantified amount of thermal heat energy flow per unit area across a surface is given by using Fourier's law as follows:-

$$q = -k\Delta T = -k(\frac{i\partial T}{\partial x} + \frac{j\partial T}{\partial y} + \frac{k\partial T}{\partial z}) \dots$$

Where *i, j* and *k* are unit vectors in the *x, y* and *z* directions.

If the thermal flow is in a single or one direction, then

$$q = -k\frac{i\partial T}{\partial x}$$

The rate of thermal flow Q= qA

The equation will then translate to Q =$-kA(\frac{i\partial T}{\partial x})$

Note that *Q* is the total thermal energy flow past a point, *q* the thermal energy flow density and *T* is the temperature in degrees Celcius.

Heat flow maybe from the solar insolation to the solar absorber, from solar absorber to heat transfer fluid, from the heat transfer fluid to the heat exchanger and from the heat exchanger to water!(Asadi et al, 2018)

SENSIBLE HEAT STORAGE (SHS)

Materials employed in the sensible heat storages schemes are Concrete,sand, stone.thermal oil, etc. We need to identify their states using the table below in comparison with that state of the storage tank material and solar absorber steel at normal operating temperatures of 565 ^{O}C upto 1000 ^{O}C. Steel will be a solid in this range, potassium nitrate and sodium nitrate will be gases in this range. Lithium will be a liquid and sodium a liquid upto 882 ^{O}C and a gas above 882 ^{O}C. Operation at or above the melting point of steel which makes the storage tank material is not possible.

TABLE 2 PROPERTIES OF MATERIALS-SOME VALUES FROM TABLE BY WOLFRAM RESEARCH INSTITUTE & ALSO FROM REPORT BY METAL SUPERMARKETS (2020)

POSSIBLE HEAT TRANSFER FLUID MATERIAL	**MELTING POINT** (^{O} C)	**BOILING POINT**	**DENSITY** (g/cm3)	**THERMAL CONDUCTIVITY (W/Mk)**	**COMMENTS**
Silver	961	2 162	10.49	430	
Copper	1 084	2 562	8.96	400	
Gold	1 063	2 700	19.32	320	
Aluminum	660	2 470	2.7	235	
Calcium	842	1 484	1.56	200	
Beryllium	1 287	2 469		190	
Magnesium	650	1 091	1.738	160	
Silicon	1 410	2 355	2.32	150	
Carbon	3 550	4 815		140	
Sodium	97.79	882.8	2.26	140	
Stainless Steel	1 375- 1530	Non	7, 500 kg/m^3	15 W/K/m	
Carbon Steel	1 425- 1 540			45 W/K/m	
Lithium	180.5^{O}C	1342 ^{O}C	0.534g/cm^3 as a solid	80 W/Mk	Lightest element of all solids
Liquid Potassium	63.5	758.8	0.862 g/cm^3	102.5 W(m-K	
Potassium Nitrate	334 ^{O}C	400 ^{O}C	2.11 grams per cm^3	0.62 W/K	
Diamond	700 ^{O}C	4 830 ^{O}C	3.5 g/cm^3	2 000 W/m-K	
Zinc	419.5 ^{O}C	907 ^{O}C	7.13 g/cm^3	112.2 W/m-K	
Asbestos	1 482 ^{O}C		0.36 g/cm^3	0.182 W/m-K	
Ceramic	2 000 ^{O}C		6 g/cm^3	1.10 W/m-K	
Concrete	900 ^{O}C		2.4 g/cm^3	2.25 W/m-K	
Sand	1 550 OC	2 230 OC	1 680 kg/m^3	2.05 W/m-K	
Silicon	1 420 OC	2 600 OC	2.329 g/cm^3	2.3 W/m-K	
Germanium	938 OC	2 833 OC	5.323 g/cm^3	1.45 W	
Quartz sand	1 650 OC	2 230 OC	2.65 g/cm^3	7.7 W/m-K	
Cement	1 550		1.44 g/cm,^{3}	0.7 W/m-K	
Silica	1 200 OC		2.65 g/cm^3	1.31 W/m-K	

Granite	1 260 OC		2.65 g/cm^3	7 W/m-K	
Selenium	220 OC	688 OC	4.28 g/cm^3	2.04 W/m-K	
Uranium	1 132 OC	3 818 OC	19 g/cm^3	27 W/m-K	
Plutonium	639.4 OC	3 228 OC	19.84 g/cm^3	0.03 W/cm-K	
Chlorine	-101.5 OC	-34.04 OC	3.214 g/litre	0.00009 W/cm-K	
Fluorine	-219.8 OC	-188.1 OC	1.696 g/litre	0.0279 W/m-K	
Fibreglass	1 135 ^{O}C		2.44 g/cm^3	0.05 W/K m	
Porcelain	1 927 ^{O}C		2.4 g/cm^3	1.5 W/m K	
Polyvinyl chloride(PVC)	100-260 ^{O}C		40 kg/m^3	0.136 W/m K	
Expanded polystyrene	100 ^{O}C		1.05 g/cm^3	0.037 W/m K	
polyurethane	44.1 OC	232 OC	30 kg/m^3	0.025 W/m K	
Alcohol	-114 OC	78.4 OC		0.481 W/m K	
Iron	1 538 OC	2 862 OC	7.87 g/cm^3	80 W/m K	

Sensible heat storages are the frequently and abundantly deployed storage technology involved with CSPs.The amount of energy stored in energy storage tanks through sensible heat storage depends on the (1) mass(m) of the storage material (2) specific heat capacity(c) of the storage material and (3) temperature change involved in the TES material(ΔT) and expressed by the equation

$Q=mc\,\Delta T$ where m is the mass and c is the specific heat capacity and T is the temperature.

(O. Achkari et al., 2019), says that 45.5 % of CSP projects that are either operational or under construction worldwide(45.1% of the total installed capacity) are equipped with TES. 95.6% of them (99.8 % of the total installed capacity) exploited liquid Sensible Heat Storage materials because of their reliability, simplicity of operations and low cost. TES also reduces the levelized cost of electricity. Sensible heat storage is now a highly mature technology vastly used in CSP storage schemes and has almost passed the learning curve for power utilities.

LATENT HEAT STORAGE(LHS)

Latent heat storage (LHS) occurs when heat is absorbed at constant temperature whilst the storage material undergoes phase change normally from liquid to solid or vice versa.. Achkari et al. (2019) says that LHS generally permits higher heat densities than SHS, since heat energy transfer during phase change is normally higher than the energy exchange that occurs during temperature rise of a selected material..Sensible heat materials are potassium nitrate and sodium nitrate. Phase change materials are also inclusive of $MgCl_2$, KCl, NaCl, $NaCo_3$, KCO_3 and $LiCO_3$

PHASE CHANGE MATERIAL	MELTING POINT	LATENT HEAT OF LIQUIFICATION
Magnesium Chloride	714 OC	454 kJ/kg
Aluminum	660 OC	405 Kj/kg
Sodium Carbonate	851 OC	357.8 Kj/kg
Lithium Carbonate	723 OC	44.77 KJ/kg

Latent heat storage is foundationed upon the principle of storing thermal energy into a storage material whilst it simultaneously undergoes a phase change(e.g. liquid to gas, solid to liquid). In this scheme, thermal energy is stored in the absence of a temperature change. The heat quantity stored is given by multiplying the mass of the storage material and the enthalpy change involved in the melting or phase change process (J/kg).

Water-dependent ice storage or micro-encapsulated paraffin based on phase change materials are more ideal for such use (Girolama et al., 2020)).

Advantages of Latent Heat Storage include higher energy density compared to Sensible heat storage schemes(Kuravi et al., 2014).

SORPTION OR THERMOCHEMICAL HEAT ENERGY STORAGE (TCHES)

This technology exploits the principle of reversible endothermic reactions which become exothermic on reversibility. Energy is absorbed and therefore stored whilst the endothermic reaction occurs and emitted whilst the exothermic reaction is occuring. Reaction kinetics determines the speed of energy absorption and energy release. TCHES recovers the reaction heat emitted during the reversible chemical/absoption reaction(Girolama et al, 2020).

According to Scapino et al (2015), the chemical reaction takes place between a sorbent which is a typical liquid or solid and a sorbate which is e.g. a vapor.

During the charging process, a heat source (e.g. solar insolation) is employed to invoke or kickstart an endothermic reaction. Sorbate and sorbent are made to separate. Physical or chemical energy in the 2 components or parts is separately stored.

In the discharging process, the previously stored heat is emitted during the exothermic reaction.

Exothermic

$$CaCO + H_2O \leftrightarrow Ca(OH)_2 \quad \Delta h = -99 Kj/MOL$$

Endothermic

Thermochemical storages involves the forming and breaking of primary bonds whereas latent storages involves the forming and breaking of secondary bonds. Secondary bonds are weaker than primary bonds(ionic and covelant bonds) and have lower bonding energies

Both thermochemical and latent heat storages have greater thermal energy storage density and modularized TES units for intelligent temperature control and higher operating temperatures. A two-tank molten salt system invoving the cold tank and the hot tank is normally preferred for Central Receiver Tower power plants. The TES schemes enables CSPs to meet demand 24/7 i.e. round the clock and hopefully thoughout the year if there is no maintenance scheduled therein. There is continouos supply of heat to the heat exchanger and therefore to the power block or heat engine(i.e. both during the day and during the night, both during clear skies and complete cloud cover conditions). This enhances capacity utilization of the CSP as well as grid components.

The last TES technology is thermo-chemical heat storage which involves converting thermal energy into chemical energy e.g. when a reversible endothermic reaction absorbs and stores energy which maybe for long periods of time without heat losses. This technology has a huge energy storage potential and a long storage period. It has not been fully investigated and experimented on and therefore has not yet been integrated in CSP plants commercially. Thermochemical systems are gaining more attention due to superior performance compared to sensible heat storages and latent heat storages technologies in terms of storage duration dynamics or quicker reaction kinetics during charging and discharging and energy density(Cellura et al., 2020).Theoretical, experimental as well as possible commercialization studies need to be amplified in literature as part of contribution to world body of knowledge.

Both sensible heat storage and thermochemical heat storages have higher energy storage densities and are modularized.

Thermal energy storage schemes gives additional flexibility, energy supply management capabilities, enhanced power supply quality and continuity of supply compensation for solar intemittecy giving commercial profitability for CSPs(Concentrated Solar Power) Plants (Guarino et al., 2020).

When excess generation exists solar insolation together with electricity heaters converts solar insolation heat and electricity to heat in storage schemes/tanks e.g. thermochemical, latent and sensible heat storage schemes i.e turning both surplus electricity and solar insolation into heat energy stored in heat energy storage schemes resulting in future supply flexibility and system supply stability.The stored heat is released when demand rises and solar insolation is low or non-available.This results in energy conservation, peak shaving and load shifting and enhanced grid components capacity utilization.

The heat storage capacity of the storage tank and storage materials is constrained by the highest temperature of the condenser heat pump coupled thereto.

Many phase change materials(PCM) possess low thermal conductivity that result in slow charging and discharging rates.

USES OR APPLICATION AREAS OF THE STUDY OF KINETICS IN THERMOCHEMICAL HEAT STORAGE SCHEMES

Kinetics can be used to in the optimization of the process involved in the charge and discharge process conditions involved in the thermal storage materials in CSPs of the Central Power Tower type with thermochemical heat storage schemes.

Kinetics can also be employed when required to test (thermal, taste, color, smell equilibria) rate changes theories. It gives the mathematical tools to fully explain changes in speeds and velocities of chemical reactions. The laws of physics which is a pure science will then find applications in chemical reaction where concepts such as chemical reaction momentum and such other concepts begin to apply in chemistry. The integrated application of mathematics and physics in chemistry adds excitement, exhilaration and fun in the design of Concentrated Solar Power(CSP) plants of the Central receiver type where thermochemical energy storage strategies are employed. Kinetics is also used for the measurement of equilibrium constraints and analysis of chemical solutions.

Chemical kinetics can also be used in the analysis of the interactional dynamics of solvents and solutes in thermal energy storage systems of CSPs employing thermochemical heat storage strategy.

TRICOUPLED OR TRIBRIDIZED ENERGY STORAGE SCHEMES FOR CSPs

These storage schemes involves coupling Latent, thermochemical with Sensible heat storage schemes all on the same one particular CSP plant thereby and therefore accumulating all the advantages of all these collective schemes. They get all the advantages of each and every storage scheme i.e. synergy enhancement through tribridization of the three storage methodologies.

The sensible heat storage scheme would be to take care of hours to days storage needs and the latent heat to take care of weeks to months storage needs and thermochemical storage to take care of seasonal and yearly storage needs of that particular CSP power plant.

The tricoupled storage schemes eliminates most disadvantages of each and every disadvantage of each individual storage technology. They enable economics of scale, storage stress sharing and storage burden relief on each and every individual storage technology. The charging and discharging cycles will be lengthened thereby reducing wear and tear of storage components resulting in increased expected service life of each storage portfolio.. There will also be benefits of storage failure risk pooling i.e. risk sharing. Each storage scheme can be serviced or maintained(predictive maintenance, condition-based maintenance, preventive maintenance,periodic maintenance and fault maintenance) without total loss of storage benefits at any point as a function of time from the plant commissioning point.

ATTRIBUTES OR IMPORTANT OPERATIONAL DIMENSIONS OF THERMAL ENERGY STORAGE(TES) TECHNOLOGIES(Ferulla et al., 2020)

- **Storage time span** is defined as the period from the storage time(hours, days, weeks, months or even years) when there is no significant or noticeable loss of stored heat energy or thermal energy to the environment energy in the storage technology. No energy loss enough to significantly compromise the economic and operational storage function
- The rate of charging and discharging i.e speed and response sensitivity to grid energy demand or load following capabilities of the storage technology. This is a critical attribute needed for capacity utilization of grid components, superior service to power utility customers and grid stability.
- Energy storage capacity is the total and maximum amount of energy that can be absorbed by an energy storage technology whilst the charging activity is going on under normal conditions without mechanically, electrically or thermally damaging storage cointainers or any component of the CSP power plant and also without posising danger to utility staff and members of the public e.g. storage tank explosion.
- Heat Energy, volumetric heat capacity or thermal density is the ratio of the stored energy to the volume space of the thermal energy storage system.
- Total charge time is defined as how long in terms of duration in the time dormain is required to fully charge from zero. Total discharge time is the duration in the time dormain to fully discharge from highest charge to zero the energy in the storage unit.
- Self-discharge is defined as the maximum quantity of energy stored initially and lost or dissipated to the environment during a specific non-use time-i.e. during the planned storage horizon.
- Storage Efficiency is taken as the ratio of the thermal enthalpy availed to the grid from the storage unit divided by the heat energy required to fully charge the thermal energy storage system. This explains the thermal energy lost to the environment whilst the storage is occurring or during storage span and the charge and discharge cyclical span.
- Response time of the Storage unit is defined as the rate of response sensitivity or fastness with which the thermal energy is absorbed and emitted or released in response to grid demand or needs of the operational personnel, plant needs, electricity end-user imperatives.

- Discharge Cycle frequency is defined as the number of times the storage system emits the energy after each recharge activity.
- Cyclical life refers to lemgth in the time domain that the storage unit can charge and discharge without being damaged or become nonfunctional due to wear and tear.
- Total costs of a storage unit is capital costs plus operational and maintenance costs during its expected operational life span.
- Cost per usable thermal energy output is the ratio of the cost per unit energy to the efficiency of storage.
- Cycle cost is taken as the cost involved per unit thermal energy to the number of charge/discharge cycles involved.

CLASSIFICATION OF THERMAL ENERGY STORAGE TECHNOLOGIES

Storage schemes are classified according to the time span of useful energy storage.

Short term storage is whereby heat input and output(charge/discharge) happens within several hours or days e.g. sensible heat (Cellura et al., 2020).

Medium term storage energy storage schemes is whereby the charge and discharge occurs within weeks or months e.g. latent heat

Long term storage- the charge/discharge cycle occurs within seasons or even years e.g. thermochemical energy storage-no or minimal self discharge.

Sensible heat and latent heat storages need insulation systems during the time of storage thus avoiding heat losses. This type of storage cannot store energy for long periods which is its disadvantage..

Thermochemical Energy Storage schemes have greater storage densities of 10 down to 5 times when compared with sensible heat and latent heat storage systems respectively. Thermochemical storage technologies are therefore receiving greater research attention because of this and other advantages.As a result of higher energy storage densities, thermochemical energy storage units are compact thereby reducing the volume space needs of the storage facility.Where space constraints exist, thermochemical storage is the best candidate to be couple with CSPs.

Sensible heat storages(SHS) are less costly than latent heat storages or thermochemical heat storage units. High initial capital costs are the major deterrent to wide deployment of thermochemical energy storage technologies worldwide.

During the commissioning stage of the CSP power plant, the thermochemical storage is first charged to maximum, then the latent heat storage is charged to maximum and then lastly the sensible heat is charged to maximum and then the plant is put into full generation and electricity supply service.

THERMOCHEMICAL PROCESSES AND HEAT ENERGY STORAGE MATERIALS

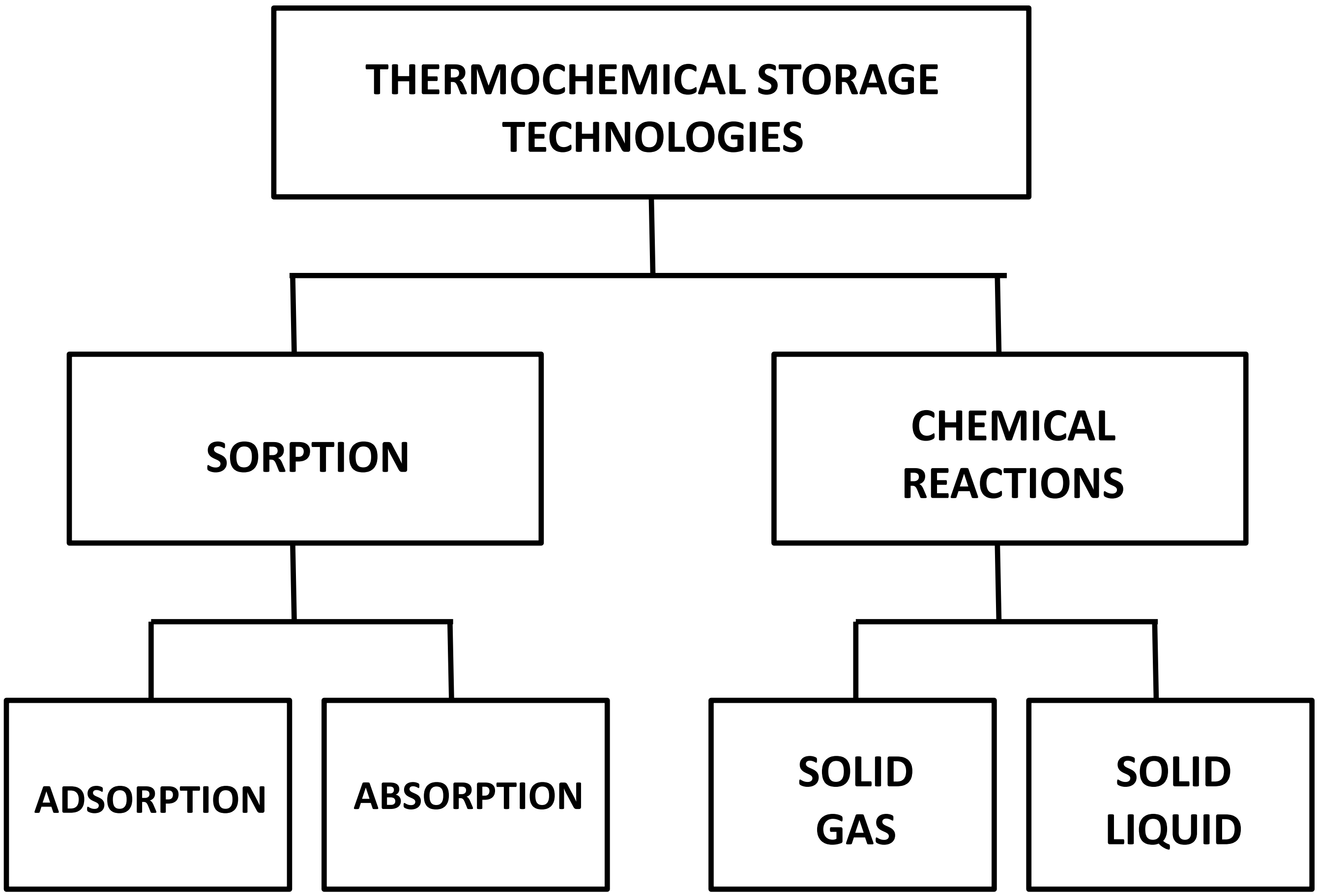

Fig 2 Thermochemical Heat Storage principles-classification from a paper by Girolama et al(2020)

The type of thermochemical reaction fall into two distinct categories namely reversible chemical reactions and sorption(adsorption and absorption) . Chemical reaction (Liquid to gas or solid to liquid) are classified according to alterations involving molecular configuration involving chemical compounds concerned.

Both reversible chemical reactions and also sorption are included in the definition of sorption by (Tu et al., 2014)

Desorption is defined as the charging process during which thermal energy given to the storage compounds or elements is archived in the form of chemical energy potential by dismantling the bonds between the sorbate and sorbent.

Storage is defined as the process whereby the sorbate and sorbent are made seperate. Sorption is defined as the discharging directed at recovering thermal energy by bringing together the sorbate and the sorbent.

Sorption is defined as the process of fixation or trapping of a vapor or gas by a condensed substance.

Nic et al. (2015) posits that adsorption is the process involving adsorbate being retained by absorbent).

Yu et al (2014) defines adsorption as the process taking place at the junction of two phases whereby the cohesive forces behave or reacts with the molecules of all substances notwithstanding their state of aggregation.

Frequently sorption materials are composite sorbents, liquid and solid. Examples are as follows:-

- H_2O /LiBr solution
- H_2O/LiCl solution
- activated alumina/LiCl
- expanded graphite/LiCl
- $H_2O/LiCl_2$ solution
- $H_2O/CaCl_2$ solution
- Binary sales
- Zeolite 5A, Zeolite 13X, Zeolite 4A
- silico-aluminophosphates ($SAPO_5$) and Aluminophosphates($AlPO_5$) and
- Composite materials made by the combination of a salt hydrate and an additive with a porous structure and high thermal conductivity(expanded graphite) metal foam, carbon fiber and activated carbon(Farulla et al., 2020).

($AlPO_5$) and ($SAPO_3$) are among promising materials of sorption which may be used for low temperature thermal storage.

Zeolite 13X is the most frequently researched on thermochemical material as a result of its non-corrosive nature, mechanical and hydrothermal stability.

$MgSO_4$-$MgCl_2$-H_2O, LiBr-silica gel/$H_2O$$CaCl_2$-silica gel/$H_2O$, $CaCl_2$-FeKII_2/H_2O, , $MgSO_4$-Zeolite/H_2O, are examples of composite materials..

Heat(e.g. 100 to 400^{0}C) and higher (greater than 400^{O}C) can be stored in chemical reactions. Below are examples of chemical reactions:-

- Deammoniation of ammonium chlorides
- Dehydration of metal hydrides
- Dehydration of metal hydroxides
- Dehydration of salt hydrates
- Metal oxide redox
- Catalytic dissociation
- Methane steam reforming
- Decarboxylation of metal carbonates

(Cerulla et al., 2020)

Extensive studies of the hydration of MgO was carried out as far back as 1960. As early as 1988, the hydration of Ca(OH)2 received wide attention.

The National Energy Administration and American Pacific Northwest National Laboratories supported investigations on $CaO/Ca(OH)_2$ as a thermal storage scheme.

Chemical processes frequently use Ca(OH)2/CaO systems which has numerous advantages such as (a)efficient reaction kinetics and (b) high reaction enthalpy. They are vastly useful materials in heat energy storage schemes particularly for systems involving high temperatures (400-600 ^{O}C) in industrial plants..

Use of Ca(OH)2/CaO thermochemical schemes in power-to-thermal applications has aroused huge investigations with focus on the heat and mass transfer process.

Metal hydrides thermochemical storage schemes were investigated since mid 1970s. Mg-based schemes are giving encouraging results among all metal hydrides as a result of their high reaction enthalpy. Mg-based schemes show cyclic stability(from 250^{O}C to 550^{O}C) with high thermal energy densities reaching up to 2 257Kj/KG. Metal hydrides exhibit excellent cyclical stability together with reversibility as well as high enthalpies.

Salt hydrates exhibit high energy density and desorption temperatures which makes them fit for use in power-to-heat technologies and waste heat sources.

Several advantages are exhibited by metal carbonates such as low cost, nontoxicity, high energy density and are abundantly available. These advantages make metal carbonates appropriate for thermochemical heat storage applications. Alternatives include CaO/$CaCO_3$(with density 0.49 kWh/kg). CaCO3 being one of the vastly available materials in nature.

Fermandez et al employed CaO/$CaCO_3$ as the working pair in order to create a system called 'Photovoltaic-calcium looping (PV-CaL)' to construct a huge heat energy storage scheme. This pair demonstrates that high turning temperatures of the exothermic carbonate reaction permits the use of high efficient power cycles.

Storage schemes need high heat storage capacity and excellent good heat transfer to perform their duties excellently.

We have open loop and closed loop thermochemical heat storage schemes.

Open systems operate exposed to the atmospheric pressure and are always in interfacing with the outside environment and closed loop systems operate with water vapor, doing rounds in hermetically closed loops in the presence of vacuum pressure.

An open system is simpler in its design.

Reversible Reactions

$$CaCO_3 \rightleftharpoons CaO + CO_2 \quad (950^{o}C) \quad 39\% \text{ efficiency}$$

$$2CuCO_2 \rightleftharpoons 2CuO + O_2 \quad (1200^{o}C)$$

The discharge process begins when the energy demand from the grid increases. The exothermic process begins during this period in order to provide extra heat for the heat engine and therefore more electricity to the grid. In this exothermic reaction stored molten CuO_2/CuO stored is then oxidized and its temperature lowered into an oxidation reactor utilizing air.

Thermal heat storage density is taken as the thermal energy perr unit mass of the CuO raw material,

The round trip efficiency is defined as the quantity of electricity that can be recovered per given energy input.

The main setbacks for the above method is high heat sources and high operating temperature, complexity, high equipment investment costs, high operational and maintenance costs.

NH_3/$LiNO_3$ where NH_3 is the solute whereas LiNO3 is the sorbent.

CHEMICAL KINETICS AND REACTION DYNAMICS IN THERMOCHEMICAL HEAT STORAGE

We can split the study of chemistry into three major clusters of study namely structures, equilibria and rates (K.A. Connors., 1990). Methods of quantum mechanics describe the chemical structure of an atom or molecule of a substance. Statistical mechanics enables study of equilibrium and thermodynamics facilitates the study of rates of reactions and the study of rates of chemical reactions constitute kinetics.

Kinetics is the study of the quantification, interpretation or measurement of the rates of a chemical reaction. It is important to select thermochemical heat storage materials or reactants with a high rate of reaction in order for fast charge and fast discharge and hence quick response to grid demand by the Concentrated Solar Power Station of the Central receiver Tower type. When the storage materials or reactants are receiving or absorbing heat i.e endothermic we say its charging. When the storage materials are releasing heat to the power block or heat engine we say that its discharging.

Kinetics can be classified into two major classes namely physical kinetics and chemical kinetics (Houston, 2000). Physical kinetics covers physical phenomena like diffusion and viscosity. Chemical kinetics covers the chemical rates of reactions (involving both covalent bonds and noncovalent bond alterations) (Connors, 1990)

The study of thermodynamics in an energy storage scheme i.e. is the solar absorber and storage tanks) of a thermochemical heat storage scheme is limited only to the analysis of the initial state of the reactants and the final state of the system when an equilibrium is reached.

Chemical kinetics concentrates on all the processes in the intermediate stage or intervening processes overlooked by thermodynamic analysis. What transpires between the initial state and the ultimate or final state of a chemical reaction and precisely how and how fast the transition from one state to the other transpires in the province of chemical kinetics.

In thermochemical heat storages i.e. reversible endothermic which become exothermic or reversibility or just simple reversible reactions which generate heat, we are also interested in the heat of reaction. Enthalpy limits and specific heat capacities of various thermal storage materials is of critical interest in the design of the Central Receiver Tower CSPs.

Kinetics attempts to describe the behavioral dynamics of the molecules during molecular collisions and the resulting transformation into new species and separate or move apart again.

Changes in thermodynamic quantities such as enthalpy and entropy depend only on the initial and final state of e.g. thermochemical heat storage reactants and or materials. Thermodynamics is constrained by the fact that it does not give essential, critical and vital information concerning intervening states of the thermal energy storage materials in the solar absorber, heat storage tanks or HTF transport pipes. It is exactly, precisely and definitely these intermediate states which becomes the premise and subject material of chemical kinetics which is a very interesting subject in the study of Concentrated Solar Power Plants of the Central receiver Tower types with thermochemical storage schemes.

Any thorough, exhaustive and comprehensive study of chemical reactions in a thermochemical energy storage scheme must as a result fully cover (a) structural (b) equilibrium and (c) kinetic research, analysis and investigations.

The chemical properties of any system at equilibrium do not alter, change or modify with time and consequently is definitely not a thermodynamic variable. An unrestricted, unconstrained and free system which is not in equilibrium state, spontaneously changes with time and hence theoretical and experimental studies of such changes involving time, time becomes a variable of interest. Curiosity, interest and difficulties becomes engrained in this branch of chemistry because of the presence of time in chemical reactions as a variable to be accounted for in the study and analysis of chemical kinetics. The speed of a chemical reaction being a scalar quantity as in physics. As contribution to the world body of knowledge, this paper introduces the concept of the velocity of a chemical reaction which takes care of both the rate of the chemical reaction and trajectory of color change (from white, cream, yellow, orange, red, pink, brown, green, grey, black). The paper introduces the concept of one-dimensional kinetics (only rate, two dimensional kinetics (rate, color)). Three dimensional kinetics (rate, color, taste (from sweet, sour, bitter and toxic)). In future when reaction kinetics is just mentioned without mentioning dimensions it is assumed that we are talking about the one dimensional kinetics as has always been the case.

Within chemical kinetics we have areas of study namely structural, equilibrium, kinetic investigations and finally time. The first three areas of study are spatial and time is a linear variable in chemical kinetics (Connors, 1990).

Reaction Mechanisms (structural, equilibrium, kinetic investigations & time) (rate, color, taste)

Reactants $\longrightarrow$ Final Product

During a chemical reaction of two products there may be changes in heat content (enthalpy), color, taste or smell changes involving the materials and therefore a four quadrant, four dimensional analysis and description of the kinetics would be more complete description and exhaustively informative assessment of reaction kinetics.

Complete color transformation / time taken which ischromatic kinetics.

Complete taste change/time=deliciomic kinetics

The word deliciomic being derived from the word, ‘delicious’

The chromatic spectrum range

White=1; Cream=2, Yellow=3; Orange=4; Red=5; pink=6; green=8; grey=9; black=10

The deliciomic spectrum Range

Sweet=1; tasteless=2; sour=3 bitter=4; toxic=5

Smellionic Spectrum Range

SWEET SCENT=1, neutral smell like air=2, smelly=3, very uncomfortably odorous=4

Chromatic kinetics: rates of change of color as the reaction proceeds from intial reactants to final products

Tastiomic kinetics: rates of change of tastes or toxicity from initial reactants upto final product

Smellionic kinetics: rate of change of smell of reactants in the process of a chemical reaction.

The word Smellionic being derived from the word,'smell'.

Masionic kinetics for nuclear power stations which is change of mass in unit time.

Thermionic kinetics is charge discharge rates of heat

Equilibria kinetics- rate from one chemically stable state to another chemically stable state (with regard to reversible endothermic and reversible exothermic reactions)

Reaction momentum is mass of thermal energy storage material in reaction tank x kinetic velocity (chromatic, deliciomic etc).

Chromatic kinetical momentumis mass of thermal energy storage materials in reaction tank or solar absorber x speed of color change.

Tastiomic kinetical momentum is mass of thermal energy storage materials in reaction tank or boiler x velocity of change of taste of the same material.

Smellionic kinetical momentum is mass of thermal energy storage materials in the reaction tank x smell change velocity

4 QUADRANT ANALYSIS OF CHEMICAL KINETICS AND REACTION DYNAMICS (CONTRIBUTION TO WORLD BODY OF KNOWLWDGE)

Chromatic kinetics=$\frac{(final\ color - initial\ color)}{time\ taken\ for\ the\ change}$

Tastionic kinetics=$\frac{(final\ taste - initial\ taste)}{time\ taken\ for\ the\ change}$

Smellionic kinetics=$\frac{final\ smell - intial\ smell)}{time\ taken\ for\ the\ change!}$

Enthalpic kinetics= $\frac{final\ enthlpy - intial\ enthalpy}{time\ taken\ for\ the\ change!}$

Total chemical kinetics=chromatic kinetics x tastionic kinetics x Smellionic kinetics x enthalpic kinetics Four quadrant analysis of chemical kinetics and reaction dynamics

SIZING OF ENERGY STORAGE TANKS

SENSIBLE HEAT

MATERIAL	SPECIFIC HEAT CAPACITY(J/kg/K)
Iron	0.451
Saturated Sand	1 632
Concrete	880
Stones	1 000
Thermal Oil	2 000
Sodium Nitrate	1 094
Potasium Nitrate	1 118

MATERIAL	THERMAL CONDUCTIVITY(W/m-K)
Steel	45
Saturated Sand	2.56
Concrete	1.6
Stones	3

Sunshine is available for 10 hrs a day on average in Zimbabwe which means the storage has to supply 500 MW for(24-10)=14 Hrs.

14x500MWh has to be stored during the daylight 10 hrs=7 000

7 000x60x60 J storage required=25 200 000 J

Given specific heat capacity in J/kg/K and density of storage material, we can calculate the volume required to store25 200 000 J for Sensible heat material. For latent heat we require latent heat of liquification to calculate the volumes. For Thermochemical we require heat of reaction per mole to calculate the volumes of storage tanks.

STORAGE FACILITY SIZING

LATENT HEAT OF VAPORIZATION

Material	Latent Heat of Vaporization(Kj/kg)
Ammonia	1 369
Water	2 256
Methanol	1 100

THERMOCHEMICAL STORAGE

Mix the following materials to release heat

(1) Water and LiBr
(2) Water and LiCl
(3) Water and LiCl2
(4) Water and CaCl
(5) Water and Zeolite 5A, water and Zeolite 13X, WATER and Zeolite 4A
(6) Water and Silico Alumino Phosphate

Heat or evaporate water from the above mixtures using concentrated solar energy to store heat energy.

STORAGE TANK SIZING

Assumptions

(1) The solar absorber raises the temperature of Heat Transfer Fluid from 600 ^{O}C to 1000 ^{O}C
(2) We want to supply the grid with 500 MW for 14 hours (2.25 x 10^{13}J of storage required

From specific heat capacities of thermal energy storage materials we can calculate the mass required to generate 500 MW. From this and the material density, we can calculate the volume required for the storage tank. Assuming a 10m high tank, we can calculate the radius of the needed tanks as follows:-

SALT	SPECIFIC HEAT CAPACITY	MASS	DENSITY	VOLUME	DIAMETER (10M HEIGHT)
Sodium Nitrate	1371 J/kg K	42 254 583 kg	2260 kg/m^3	18 790 m^3	50 m(MODULARIZE)
Potassium nitrate	1118.5 J/kg K	51 793 504 kg	2110 kg/ m^3	24 546 m^3	60m (Modularize)
Saturated sand	1 632 J/kg K	38 602 941 Kg	1 980 kg/m^3	19 497 m^3	50m

If we modularize the tanks to 7 tanks instead of one big tank we have the following

SALT	DIAMETER
SODIUM NITRATE	1 tank 25m radius(too risky), or 7 tanks 10m radius or 30 tanks 5m radius
POTASIUM NITRATE	1 tank 30m radius, 9 tanks 10m radius or 40 tanks 5 m radius
SATURATED SAND	1 tank 25m radius(too risky), or 7 tanks 10 m radius or 30 tanks 5m radius

Sodium Nitrate/Saturated Sand		Potasium Nitrate	
NUMBER OF TANKS	RADIUS	NUMBER OF TANKS	RADIUS
1	25	1	30
7	10	9	10
30	5	40	5

LATENT HEAT

From the latent heat of vaporization, we can calculate the mass required to generate 500 MW. From the material density, we can calculate the volume and therefore size the storage tanks

MATERIAL	ENERGY PER KILOGRAM	KILOGRAMS REQUIRED	DENSITY	VOLUME	RADIUS assuming 10m high tank
$MgCl_2$	1338 Kj/kg	2 072 000kg	2 320kg/m3	894 m3	5.35 m
KCl	5 960 000 Kj/kg	4 229kg	1 980 kg/m3	2.1m3	0.26m
NaCl					
NaCO3					

LiCO3					
KCO3					
KCL	31.31 kJ/kg	804 854 680 kg	1980 kg/m3	406 493m3	360m(not practical)

MATERIAL	MELTING POINT	LATENT HEAT (Kj/kg)	SOLID SENSIBLE(Kj/kg)	LIQUID SENSIBLE(Kj/kg)	TOTAL HEAT(Kj/kg
Magnesium Chloride	714 ^{O}C	454	0.1356	0.34023	454.48
Aluminum	660 ^{O}C	405	0.053	0.000055	405
Sodium Carbonate	851 ^{O}C	357	0.3396	0.2017	357
Lithium Carbonate	723 ^{O}C	45	0.1733	0.3902	45

VOLUME OF TANKS REQUIRED FOR LATENT HEAT

PHASE CHANGE MATERIAL	Kg Required	Density	Volume	Diameter of Tank Assuming a 10 m high tank
Magnesium Chloride	55 506 608	2 320 kg/m3	23 926 m3	55m
Aluminum	62 359 276	2 700 kg/m3	23 096 m3	55m
Sodium Carbonate	70 743 716	2 540 kg/m3	27 852 m3	60 m
Lithium Carbonate	561 233 480	2 110kg/m3	265 988 m3	185m(not practical & lithium is very expensive)

THERMOCHEMICAL

From the heat of reaction per mole, we can calculate the mass required to generate 500 MW. From the density of the material, we can calculate the volume of the needed tank as follows:-

SALT	ENERGY PER KILOGRAM	KILOGRAMS REQUIRED	DENSITY	VOLUME	RADIUS(assuming 10m high)
CaCO	14.52 kJ/kg	1 735 537 190.08	2 710 kg/m3	640 419.63	142m(not practical)
LiBr plus H_2O	578.3 Kj/kg	43 575 999	3 460 kg/m3	12 595m3	21m
LiCl	-91.994 Kj/kg	2 739 310	2 160 kg/m3	1 270m3	6.4 m
CaCl2 plus water	656.8 Kj/kg-K	88 202	2 150 kg/m3	17 845 m3	24m

In practice a combination e.g. of sensible heat and latent heat exists at the same time.

Thermochemical heat storage strategy requires a deeper understanding of chemical kinetics and reaction dynamics.Chemical kinetics was split into four components namely chromatic kinetics, tastionic kinetics, Smellionic kinetics and enthalpic kinetics. Chromatic kinetics being observed rate of change of color of reactants from white=1, cream=2, yellow=3, pink=4, red=5, brown=6, green=7, purple=8, grey=9, black=10-the chromatic spectrum. Tastionic kinetics being the rate of change of taste of the reactants from sweet=1, neutral=2 through bitter=3 to poisonous=4. Smellionic kinetics is the rate of change of smell from sweet scent=1, neutral=2 smell, ordorous=3 to stinking=4. Enthalpic kinetics is the rate of change of heat content within the energy storage tanks or solar absorber. These constitute the four dimensions for analysis of chemical reaction kinetics

Chemical kinetics can be analysed by a 4 quadrant analysis as follows:-.

Chromatic kinetics=$\frac{(final\ color-initial\ color)}{time\ taken}$

Tastionic kinetics=$\frac{(final\ taste-initial\ taste)}{time\ taken}$

Smellionic kinetics= $\frac{final\ smell - intial\ smell)}{time\ taken\ for\ the\ change!}$

Enthalpic kinetics= $\frac{final\ enthlpy - intial\ enthalpy}{time\ taken\ for\ the\ change!}$

Total chemical kinetics=chromatic kinetics x tastionic kinetics x Smellionic kinetics x enthalpic kinetics

Four quadrant analysis of chemical kinetics and reaction dynamics

The working temperatures in the turbine is between 566 ^{O}C and 800 ^{O}C. Our observation is that solids have lower specific heat capacities than liquids. Within the above temperature range some materials like sodium nitrate and potassium nitrate will melt and evaporate meaning the latent heats of liquification and evaporation are over and above the sensible heat. This explains why they are the most widely used thermal storage materials.

CONCLUSIONS

There are basically three energy storage technologies considered so far for Concentrated Solar Power plants of the Central Receiver Tower type namely Sensible heat schemes, Latent heat technologies and Thermochemical heat storage technologies. This paper recommends that in future the tricoupled or tribridized heat storage stategy be adopted which involves installing all the three storage schemes on one single CSP power plant to take care of short-term, medium term and long term storage needs of the power plant. A tricoupled storage scheme harnesses all the benefits of all the storage technologies for the benefit of a single CSP power plant. In addition,.the sensible heat storage system can be maintained for days whilst the thermochemical and latent heat storages supplies needed heat energy needed for generation during the night and cloud cover conditions. Similarly the Latent heat and thermochemical storage systems can be maintained without loosing night and cloud cover conditions generation. This brings and enhances flexibility in maintenance activities as well as dispatchability of the power plant.

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