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Encapsulation of High Temperature Phase Change Materials for Thermal Energy Storage

by

Rupa Nath

A thesis submitted in partial fulfillment
of the requirements for the degree of
Master of Science in Mechanical Engineering
Department of Mechanical Engineering
College of Engineering
University of South Florida

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ABSTRACT

Thermal energy storage is a major contributor to bridge the gap between energy demand (consumption) and energy production (supply) by concentrating solar power. The utilization of high latent heat storage capability of phase change materials is one of the keys to an efficient way to store thermal energy. However, some of the limitations of the existing technology are the high volumetric expansion and low thermal conductivity of phase change materials (PCMs), low energy density, low operation temperatures and high cost. The present work deals with encapsulated PCM system, which operates at temperatures above 500°C and takes advantage of the heat transfer modes at such high temperatures to overcome the aforementioned limitations of PCMs. Encapsulation with sodium silicate coating on preformed PCM pellets were investigated. A low cost, high temperature metal, carbon steel has been used as a capsule for PCMs with a melting point above 500° C. Sodium silicate and high temperature paints were used for oxidation protection of steel at high temperatures. The emissivity of the coatings to enhance heat transfer was investigated.

CHAPTER 1. INTRODUCTION

1.1. Background

There has been a considerable increase in the levels of greenhouse gases due to large scale industrialization, in the last 150 years [Boden et al.,2011]. Carbon dioxide being one of the main components of these gases has had an atmospheric emission of approximately 347 billion tons since 1751 from the consumption of fossil fuels and cement production [Boden et al.,2011]. Fossil fuels are combusted to generate electricity, fuel transportation and for heating and cooling purposes. Fossil fuels are significant energy source, but they are depleting and their combustion is adversely affecting the climate. Experts around the world have warned that greenhouse gas have to be reduced globally, up to 50% in the next 50-100 years. This has generated an increased interest in renewable energy from natural sources, like wind, sunlight, hydropower as well as alternatives like nuclear and geothermal energy. Efforts are being made by scientists, engineers and policy makers worldwide, to develop, commercialize and deploy renewable energy technologies. Solar energy is one of most promising renewable energy sources that is abundantly and freely available. The International Energy Agency has estimated that solar power will produce almost 21% of the world's electricity by 2050 [IEA,2011]. However, there are numerous problems that have to be resolved to successfully utilize solar energy. The intensity of solar radiation varies according to the

time of the day, weather condition such as cloud cover; location and the season. This intermittent nature of the solar energy creates a mismatch between the energy supply and demand. This is where energy storage comes into play. Solar energy can be stored in various forms such as hydrogen energy storage, electrochemical storage and thermal energy storage (TES) [Goswami et al.,1999]. The advantages of energy storage include leveling supply with demand, improving the performance of energy systems and increasing the reliability [Garg et al.,1985]. Without an energy storage system, the annual solar load fraction is low wherein a backup system or auxiliary energy meets the major energy load. This leads to increased consumption of fuels [Garg et al.,1985]. These problems can be overcome by storing thermal energy when solar radiance is available abundantly and used whenever it is required. The excess heat from solar radiation during the daytime can be collected and stored for use during the night time. This is especially useful in the areas of heat recovery systems and electricity generation, where the energy availability and utilization periods are different [Farid et al.,2004]. In the case of electricity consumption, the load varies drastically according to the time of the day. This is a crucial issue in locations which have extremely cold or hot climate, where space heating and cooling (e.g. air conditioning) is the main cause of such variation [Farid et al.,2004]. TES is used to store the energy generated during off-peak hours to meet the demand during peak hours, which leads to a more efficient power distribution [Farid et al.,2004]. Thus, TES is critical to the success of solar energy applications. Apart from utility applications, TES also has its uses in active and passive solar heating, water heating and building heating and cooling. The benefits of TES are:

- Saving of fossil fuels,

- Increasing plant efficiency,
- Load leveling.

There are three types of TES systems, namely, sensible heat storage systems, latent heat storage systems and thermochemical systems. In sensible heat systems, energy is stored in materials as the temperature rises, and this stored energy is utilized when it is released during temperature decrease whereas latent heat storage systems utilize the stored energy during phase change. The most common sensible heat storage materials in use today are rock, concrete etc. However, some of its disadvantages include low energy density, bulky storage system, high range of operating temperature which reduces plant efficiency [Hawlader et al.,2003]. On the other hand, latent heat storage materials can store a large amount of energy in a small volume and can operate at an almost constant or extremely small range of temperature. This can be illustrated when sensible heat capacity of rock which is 2.326 kJ/kg K is compared with the latent heat capacity of calcium chloride hexahydrate which is 193 kJ/kg [Khudhair & Farid,2004]. These latent heat storage materials are known as phase change materials (PCMs). Due to this inherent property of PCMs, they make very promising candidates as storage materials for solar applications and are being researched extensively throughout the world. A few favorable characteristics of PCMs are listed below [Dincer & Dost 1996].

- Heat storage is over a narrow range of temperature. Thus, thermal stratification is not mandatorily considered in the design.
- They make strong candidates in passive storage due to their isothermal nature.
- They store a considerably higher amount of energy per unit volume as compared to sensible heat storage materials.

There are a wide variety of PCMs available which melt and solidify at a broad range of temperatures and are utilized in many applications. One of the most widely used low temperature PCMs is paraffin wax, which is cheap and has moderate thermal conductivity values. Salts are higher temperature materials with higher volumetric energy density and thermal conductivity. Other materials which have been studied in the last several decades are fatty acids and eutectics of organic and inorganic materials. Though these PCMs have properties that make them attractive for storage applications, not all PCMs possess all the properties which would make them ideal for any one application. Different materials have different drawbacks, which includes, low thermal conductivity, high cost, subcooling, phase segregation, volumetric expansion, poor stability at extended temperature cycling and so on [Farid et al.,2004]. Many techniques have been investigated and applied to overcome the limitations. Some of these methods are adding nucleating agents, thickening agents, stabilizers, additives to reduce subcooling and phase segregation; metal and matrix, and fillers, finned tubes to increase the heat transfer rate [Agyenim & Eames et al.,2009;Farid et al.,2004]. A technique through which heat transfer area can be increased, volume change can be accommodated, and the PCM can be protected from the heat transfer fluid is encapsulating the PCM. Microencapsulation and macro-encapsulation [Farid et al.,2004] are methods that are being researched and implemented for a wide range of applications including residential heating.

1.2. Objective of Present Work

The objective of the present work is to investigate low cost methods and materials for encapsulating high temperature (500°C – 1000°C) phase change materials, for thermal energy storage in solar thermal power plants. Steel has been chosen as an encapsulating

material for its high temperature properties and low cost. The properties and behavior of steel at high temperatures have been studied to establish its ability to successfully encapsulate PCMs. High temperature paint and sodium silicate coatings have been incorporated to reduce oxidation of steel and corrosion from molten PCM. The corrosion behavior of steels with and without coatings has been investigated at high temperature and in molten salts. Radiation enhancement coating at high temperatures have been studied and used. A thermal cycle test has been performed, and the temperature profile recorded to verify the steel PCM encapsulated thermal energy storage capacity. The scope of current work encompasses:

- Encapsulation of PCMs using steels,
- Investigating and optimizing coating techniques for oxidation protection of steel,
- Investigating radiation enhancement techniques of steel encapsulation,
- Testing corrosion, emissivity and adherence of steel coatings.

The entire thesis is divided into four chapters, and the essence of each chapter is described below.

- Chapter 1 gives an introduction of the significance of solar energy in the utility sector and importance of thermal energy storage in its commercialization and scope of the present work is described.
- Chapter 2 provides a review of the present technology and ongoing research in thermal energy storage, encapsulation techniques of PCMs, steel properties and corrosion in different media and sodium silicate coating technology.

- Chapter 3 describes techniques adopted for sodium silicate coating, steel corrosion protection, paint application with advantages and disadvantages of each technique.
- Chapter 4 presents summary and conclusion of the current work and recommendations for future work.

CHAPTER 2. LITERATURE SURVEY

The demand of electricity by different users varies during different time of the day and during seasonal changes, which results in a load curve on a daily basis. It can also be seen from the graph that the minimum load is almost half the peak load. For a single power plant to meet the entire load, it has to be designed for the peak load. In this case, the plant has to operate at peak load continuously throughout the day, even when the demand is much lower. There are several disadvantages to the afore-mentioned concept. Firstly, designing the plant for peak load will increase the cost. Secondly, when the plant operates at peak load all the time, there is wastage of energy as the supply is more than demand which results in more fuel consumption then needed. To eliminate this problem, usually auxiliary power plants are added to the grids which supply power during the peak load. In this way, the power plant is designed, not for the peak load but for the minimum load known as the base load. So, for efficient and reliable operation, every electric grid system consists of three types of power plants to supply the varying power demands. They are base load power plants, intermediate power plants and peak power plants.

2.1. Base Load Power Plants

During the 24 hours span of a day, there is always a minimum level of electricity demand by consumers, which has to be met by the power supplier. The power demand by consumers change consistently throughout the day, late evening and early mornings. However, the demand never go below a certain minimum which is known as the base

load. Base load power plants are designed to meet this minimum demand consistently. The base load power plant operates continuously throughout the year and closes down only during repairs. They take a long time to start up and usually operate at 35 to 40 % of the maximum load [Cordaro].

The demand for electricity changes during the time of the day, week and season, by location, population and climate [Cordaro].To meet the peak demand, a peak load power plant is incorporated in the system. They start up quickly and change their output according to the varying demand. They usually operate 10-15 % of the total time. These plants have high operation costs but due to their smaller size they are less expensive [Cordaro].

Intermediate load plants provide power to bridge the gap between base load and peak load. They usually operate between 30 to 60 % of the time and are larger than peak load power plants. Due to their larger size, the construction costs become higher, but they have the advantage of more efficient operation.

2.2. Concentrating Solar Power Plants (CSP)

Concentrating systems use high reflectivity mirrors to concentrate the sun's rays on the receiver pipes that are located on the focal line of the reflectors. The heat is absorbed by the heat transfer fluid (HTF) flowing through the receiver pipes. The HTF which reaches very high temperatures is used to drive a thermodynamic cycle. Concentrating technologies can concentrate the intensity of the sunlight up to 25 to 3000 times through various strategies [EASAC]. Only direct solar radiation can be utilized in these systems and they are suitable for locations with less cloudy days.

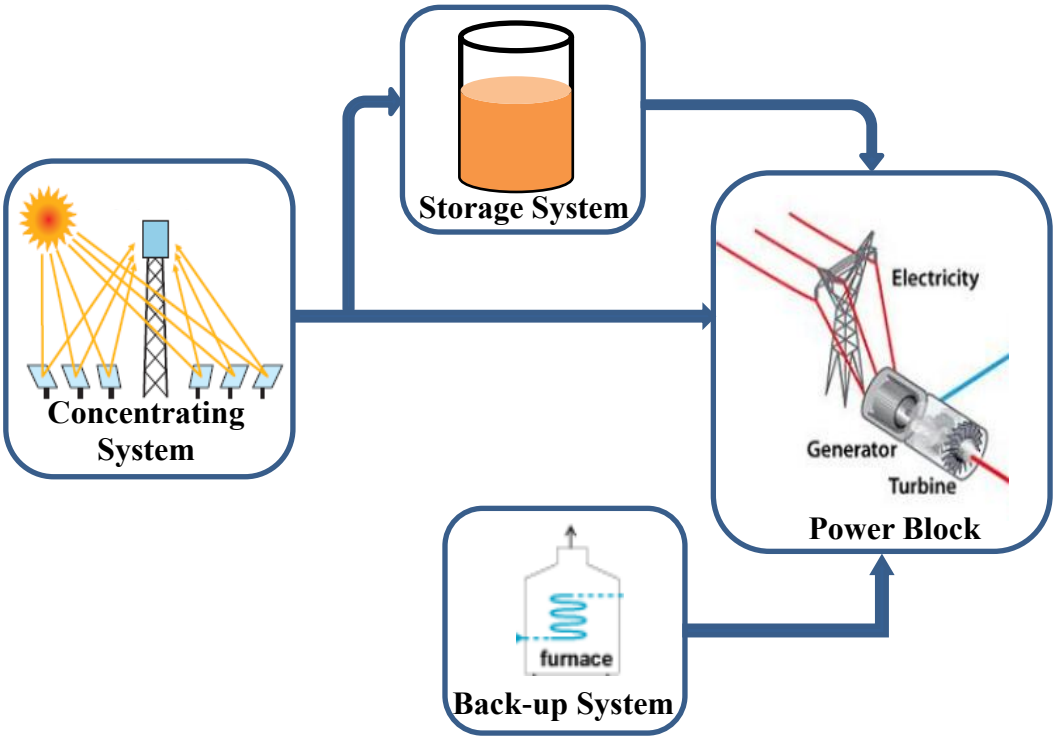


Fig 1. Sub-systems of a CSP Plant

There are mainly four sub-systems: concentrating system, solar receiver, storage or back-up system and power block.

The CSP technology exists in four different types which are categorized according to the type of focus and type of receiver. The four types are described below.

2.2.1. Parabolic Trough

It consists of arrays of linear curved mirrors which focus the sun's rays on a receiver in the form of a pipe. The mirrors are usually 100 m or longer and span 5 to 6 m in width. The pipes are made of stainless steel with a selective coating which can absorb high levels of sun's rays but emit very little infra-red radiation. These pipes are housed inside and evacuated glass tube for insulation. The mirrors and the absorbers track the sun as it moves across the sky. The HTFs used by commercial parabolic trough power plants are

synthetic oils like Dowtherm A (430 °C), which is, a eutectic mixture of biphenyl and diphenyl oxide.

2.2.2. Linear Fresnel Reflectors

These reflectors are in the form a multiple rows of flat or slightly curved mirrors which reflect the sun's rays into a downward facing, fixed linear absorber. Another type is Compact Linear Fresnel Reflectors (CFLRs) in which there are two parallel mirrors in one row. This reduces the total area and therefore, less land for the same output. Due to the simple design and fixed configuration of the receivers, the investment cost is lower, and steam can be generated directly. Cost gets further reduced because the need for HTFs and heat exchangers are eliminated. However, their solar to electricity generation efficiency is less, and incorporation of storage is problematic.

2.2.3. Solar Towers

They are also known as central receiver towers. Hundreds or thousands of mirrors reflect (heliostats) the sun's rays into a central receiver which is mounted on top of a tower. Some plants use molten salts as HTF and storage medium. The concentrating power is much higher which increases the efficiency. Cost of thermal storage is lower.

2.2.4. Parabolic Dish

The mirrors in the form of a dish which concentrate the sun's rays at its focal point. The mirror and the receiver track the sun's movement in the sky. At the focal point, a generator or an engine is placed which eliminates the need of HTF or cooling. Each dish produces electricity independently. Their solar to electricity conversion performance is highest among all CSPs.

2.3. Thermal Energy Storage

In arid and semi-arid areas, when the solar irradiance is maximum the energy demand peaks up due to air-conditioning loads. CSP production is suitable in these places where its peak output matches the peak load. CSP power plants are also used to meet the intermediate load. One disadvantage with solar power production is its intermittent nature, due to cloud cover and weather variations. CSP technology has an advantage over other technologies since the thermal energy produced can be stored and utilized to smooth out the variable energy production. Thermal energy storage has gained a lot of importance for its immense potential for efficient and low cost energy storage capability, which can bridge the gap between energy production and demand in the solar power utility sector.

2.3.1. Forms of Thermal Energy Storage

The various forms in which thermal energy can be stored are sensible heat, latent heat, thermochemical or combinations of these [Sharma & Sagara,2005]. The following sections discuss each of these forms in detail.

2.3.1.1. Sensible Heat Storage

Sensible heat is stored by raising the temperature of a solid or liquid media. Some of the solid mediums used are metals, rock, concrete and liquid medium are oil-based liquids, water, and molten salts. [Farid et al.,2004; Agyenim & Eames et al.,2009; Hasnain,1998].

2.3.1.2. Latent Heat Storage

The advantages of latent heat storage over sensible heat storage are their smaller tank size, lower cost and more efficiency. The phase change from solid to liquid is more

efficient than that of liquid to gas, due to the lower volume change. Latent heat storage systems are also more energy efficient as they operate at a much smaller temperature difference during the charge-discharge process which ultimately increases the plant efficiency and possesses higher energy density.

2.4. Phase Change Materials

Salt hydrates as phase change materials have been studied extensively. The advantages of these materials are their high latent heat, non-flammability, and low cost. However, there are certain disadvantages of inorganic PCMs which have led to the study of organic PCMs. Some of these disadvantages are: their corrosiveness to container materials, instability after repeated melt/freeze cycles, improper re-solidification, and supercooling. Given below is a list of properties of PCMs which make them useful for the present application. [Sharma & Tyagi,2009].

2.4.1. Thermo-physical Properties

- PCMs could be selected with melting temperature in the required temperature range of operation.
- Comparatively higher latent heat per unit volume.
- High specific heat for additional heat storage through sensible heat.
- High thermal conductivity in solid as well as liquid phases to accelerate the charging and discharging time of energy storage systems.
- Small vapor pressure at operating temperatures to reduce the problem of encapsulation.

2.4.2. Kinetic Properties

- Nucleation rate is high which is beneficial for avoiding super cooling of the liquid phase.
- Crystal growth rate is high, which assists the system to meet demands of heat recovery from the storage system.

2.4.3. Chemical Properties

- Chemical stability.
- Complete reversible freeze / melt cycle.
- Almost no degradation after a large number of freeze / melt cycles.

2.5. Heat Transfer Enhancement Techniques

In spite of all the desirable properties of PCMs mentioned earlier, there is one property, which effects, the charge and discharge time drastically. This property is the low thermal conductivity of most of the PCMs. To account for this downside, techniques to enhance the thermal conductivity are employed. Studies conducted in this area are: finned tubes [Horbaniuc et al.,1999; Abdel-Wahed et al.,1979; Ermis,2007; Ismailet al.,2001; Choi & Kim,1992; Agyenim & Hewitt et al,2010; Sparrow et al,1981; Sasaguchi & Takeo,1994], bubble agitation [Velraj et al, 1999], metal matrix in PCM [Trelles & Duffy,2003; Hoogendoorn & Bart,1992], high conductivity particles dispersion in PCM [Mettawee & Assassa,2007], micro-encapsulation of the PCM [Hawlader et al,2003; Griffiths & Eames,2007] or shell and tube [Agyenim & Eames et al,2009; Hendra et al.,2005].

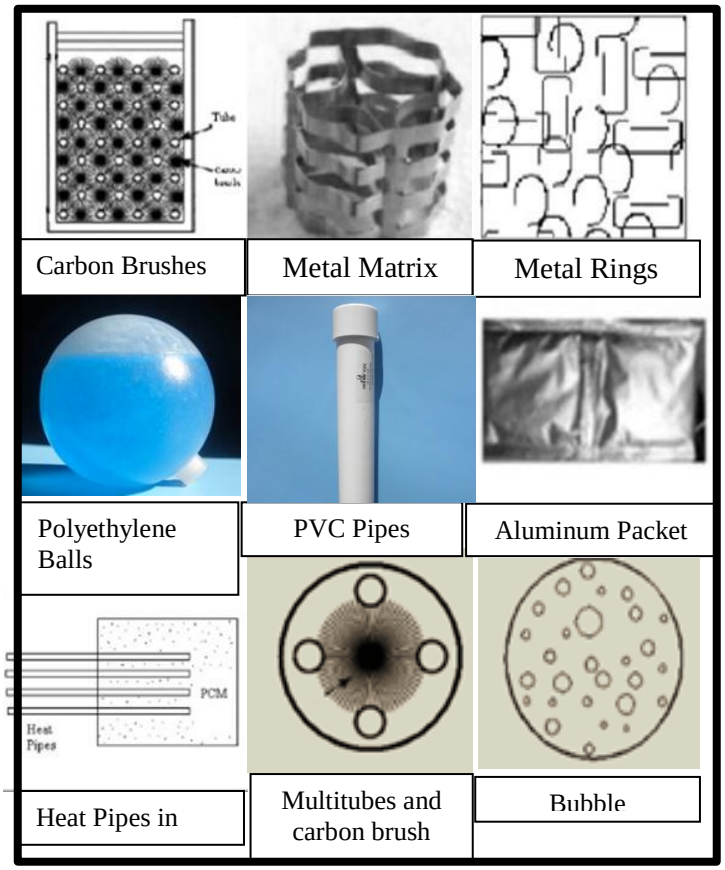


Fig 2. Different Types of Enhancement Techniques of PCM [Adapted from: Agyenim, 2010]

2.6. Encapsulation of PCM

Encapsulation or containment of PCM should:

- meet the requirements of strength, flexibility, corrosion resistance and thermal stability,
- act as a barrier to protect the PCM from harmful interaction with the environment,
- provide sufficient surface for heat transfer; the PCM has a low thermal conductivity so to increase the heat transfer rate, it is encapsulated in conducting materials to increase the heat transfer area to enhance the melting and solidification process,

- provide structural stability and easy handling [Felix et al.,2008],
- "providing large heat transfer area, reduction of the PCMs reactivity towards the outside environment and controlling the changes in volume of the storage materials as phase change occurs" [Farid et al.,2004].

2.6.1. Different Types of PCM Containment

The geometry of PCM containment is an important factor in influencing the heat transfer characteristics in the PCM system which includes the melt time and storage performance. Some of the typical containers are in the form of cylinders [Gong & Mujumdar,1997; Papanicolaou & Belesiontis,2001], heat pipes [Horbaniuc et al.,1999], and rectangular containers [Zivkovic & Fuji,2001; Silva et al.,2002]. The cylindrical containment system has been studied by [Butala & Stritih 2009; Castell et al.,2008; Guo & Zhang,2008; Abdel-Wahed et al.,1979]. Some of the container materials used investigated to enhance heat transfer area are Pyrex glass [Choi & Kim,1992], aluminum [Velraj et al.,1999] and acrylic resin [Hamada et al.,2003].

Some of the operating and physical parameters which have considerable impact on the optimization of PCM storage are PCM shell radius [Butala & Stritih,2009], HTF inlet temperature [Butala& Stritih,2009], HTF mass flow rate [Butala& Stritih,2009], and melt time [Abdel-Wahed et al.,1979].

2.7. Metal as an Encapsulation

Metals are one of the best candidates for encapsulation for our application due to their properties such as strength, heat conduction, durability, wear resistance, excellent workability and ductility.

2.7.1. Corrosion of Metals

Corrosion has been derived from the Latin word *corrodere* which means “to gnaw away”. In more technical terms, the gradual destruction of materials as a result of chemical and electrochemical actions with the liquid or gaseous environment is termed as corrosion. In the corrosion phenomenon, metal gets consumed through disintegration and oxidation and undergoes irrecoverable loss. The gradual deterioration of the metal occurs by heterogeneous chemical or electrochemical surface reaction [Tomashov et al.,1966]. Corrosion reactions are generally divided into two types: dry corrosion in which the metal directly combines with non-metallic elements, and wet corrosion in which the metal initially dissolves in an aqueous environment and then forms corrosion products in combination with non-metallic elements in the environment [Burns & Bredley,1967]. Dry corrosion constitutes of oxidation, sulfidation and halogenation reactions.

A corrosion cell functions like an electrolytic cell wherein a cathode and an anode are in contact with each other, in a common electrolyte. The difference in potential or the electromotive force between the cathode and the anode drives the corrosion reaction. In a liquid environment, the oxidation reaction causes the dissolution of the metal as follows:

$$M \rightarrow M^{++} + 2e^{-}$$

In the above reaction, M^{++} ion is formed in the solution, from the atom M, leaving behind two electrons in the metal [Burns & Bredley,1967]. A simultaneous cathodic reaction takes place comprising of the consumption of electrons, to electrically neutralize the metal. In solutions which are nearly neutral, the cathodic reaction is given by,

$$2e^{-} + \frac{1}{2}\,O_2 + HOH \rightarrow 2OH^{-}$$

This represents the formation of hydroxyl ions in an electrolyte, by the combination of oxygen dissolved in electrolyte, with water and electrons from the metal [Burns & Bredley,1967]. Anodic reaction and cathodic reaction form a complete cell reaction as follows:

$$M + \frac{1}{2} O_2 + HOH \rightarrow M^{++} + 2OH^-$$

Discrete areas on the metal act as anode and cathode, where corrosion occurs on the anodic area, and the cathode functions to complete the corrosion cell. When the corrosion is uniform over the metal surface, the anodic and cathodic areas are small in dimension and may keep shifting position with time. Corrosion of mild steel in atmosphere yields a uniform corrosion. Corrosion rate in such cases is expressed as the average penetration per unit time, for example, inches per year. In case of pitting corrosion, the cathodic area covers most of the metal surface and the anodic reaction occurs at few active areas. The corrosion rate is termed as pitting factor.

2.7.2. Classification of Corrosion

According to the corrosion mechanism, corrosion takes place by basically two types namely, chemical corrosion and electrochemical corrosion. The types of corrosion are gaseous corrosion, atmospheric corrosion, contact corrosion, stress corrosion, erosion-corrosion, bi-corrosion, stain corrosion, pitting corrosion, electro corrosion, pinpoint corrosion, subsurface corrosion, inter-crystalline corrosion, corrosion cracking, selective corrosion [Tomashov et al.,1966].

2.7.2.1. High Temperature Oxidation

Oxidation of metals at high temperature occurs when there is a reaction between a metal and oxygen gas to form metal oxides. The chemical equation to explain this phenomenon is as follows [Kofstad,1966]:

$$aM + \frac{b}{2} O_2 \rightarrow M_a O_b$$

where, M is the metal.

The oxidation mechanism may take much more complex paths of reaction than as described above, depending upon a variety of factors. The first step in the oxidation process is the adsorption of gases on a clean surface of metal. This reaction proceeds further where the oxygen dissolves into the metal to form an oxide onto the surface. This oxide may in the form of a film or a separate nucleus. The process described above is a function of factors such as:

- Surface orientation.
- Surface preparation.
- Crystal defects surface.
- Impurities present in the metal as well as the gas.

After the oxide is formed on the surface, it separates the metal from the reactants. For a reaction to occur, the reactants then travel through the oxide film by solid-state diffusion. When the film is thin, this transport of reactants is driven by electric fields across the film. When the film is thick or oxide is in the form of scales, the gradient in chemical potential across the scale drives the reactants. The oxide scales formed, are sometimes

porous in which case the reaction processes occur at the phase boundaries. Oxides also take the form of liquid or become volatile at elevated temperatures.

There is no theory which can describe the oxidation behavior of all metals, as different metals vary largely in their properties. But it can be said that the mechanism of reaction of a metal is a function of the pretreatment and preparation of metal surface, gas pressure, gas composition, temperature and the duration of the reaction.

2.7.3. Corrosion Control

Several methods are employed to protect steel and other metals against corrosion. The main mechanism of corrosion control is by preventing the metal surface and its environment from reacting with each other [Burns & Bredley,1967]. Figure 3 gives a schematic description of the three fundamental approaches used to control corrosion and several methods under each type is used in practice.

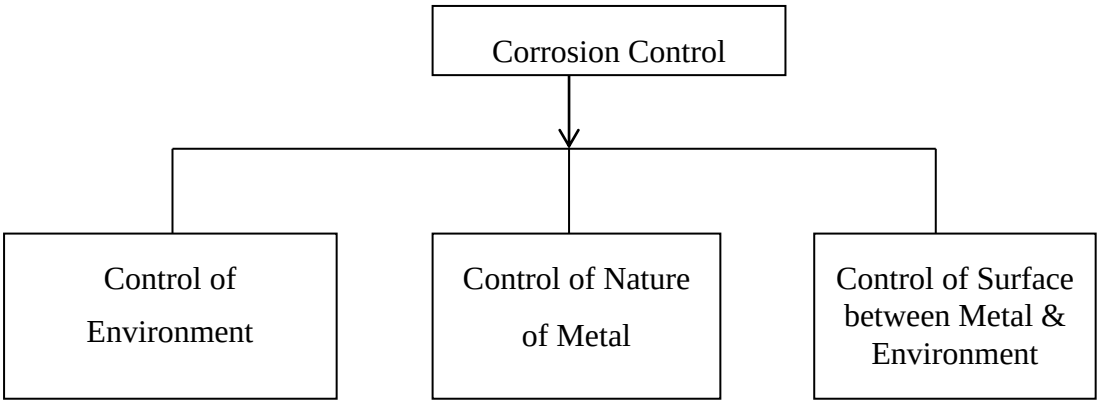


Fig 3. Three Different Approaches to Corrosion Control

- In the case of controlling the environment, factors that cause corrosion like oxygen, dust, sulfurous gases are eliminated or minimized [Burns & Bredley,1967]. For example, useful life of metals is prolonged in boilers and

closed water systems, by deaerating the water and reducing atmospheric pollution with an air-conditioning system [Burns & Bredley,1967].

- Another approach to corrosion control is by altering the nature of the metal. One technique is to select metals with an optimized alloy composition for resistance to corrosion. The alloys are selected by studying in detail their response to the service conditions and exposure to the environment [Burns & Bredley,1967]. Cathodic and anodic protection is also one approach to control corrosion.
- Apart from the methods mentioned above, the other techniques which are adopted to control corrosion are all different types of protective coatings, which separate, the metal from its surroundings.

Depending upon the type of environment the steel will be exposed to, and the extent of coating required, suitable protection method is selected. The types of protection are:

2.7.4. Cathodic Protection

In this method, the potential of the structure is artificially altered to rule out occurrence of any reaction. This method is used to protect steels when it is immersed in water or soil, as in pipelines and submarine applications. It cannot be used to protect steel exposed to the atmosphere. In this method, the steel acts as cathode, there is an auxiliary anode and an electrolyte. Current is passed through this set-up from an external source. After making this set-up two methods can be applied to achieve corrosion protection, namely, impressed current method and sacrificial anode method. In the sacrificial anode method, metals like magnesium, zinc and aluminum are used as anode. These metals have a more

negative potential than steel, due to which the electrons travel from the metal to the steel which acts as a cathode. These metals are sacrificed in this process which gives the process its name. In the impressed current method, current is applied from an external DC (direct current) source through an auxiliary anode. The steel becomes a cathode in this electrochemical cell set-up in which the potential is reduced to a very low level due to which the corrosion does not take place. Some of the auxiliary anodes that have been used are scrap iron and steel, high silicon irons, graphite, lead alloys and platinized anodes. Both the above methods are combined and used during certain circumstances and either of them is used depending on the application. Both of these methods have their pros and cons. While the impressed current method can be controlled efficiently, needs fewer anodes, and is a good for large structures, its disadvantages include more operational supervision, power source requirement, electrical connection errors leading to corrosion instead of protection and so on. The advantages of sacrificial anode method are lower initial cost and easier installation and disadvantages are increase in number of anodes as current availability depends on anode area and problem created due to low conductivity of some soils [Chandler & Bayliss,1985].

2.7.5. Protective Coating

The primary function of the protective coating is to create a barrier between the metal and the oxidizing environment. It should stop the diffusion of any oxygen into the metal. The coating forms either metal, refractory oxides or other compounds, forms a protective oxide scale to protect the metal [Kofstad,1966].

2.7.5.1. Metal Coatings

The metals used for corrosion protection are zinc, aluminum and cadmium. Zinc is the most common type of coating used. The application methods of these coatings are:

- Hot Dipping is one application method. Zinc, tin, lead and aluminum coatings are used in this process. The surface preparation of steel before coating application includes degreasing with caustic soda, blast cleaning and pickling with dilute hydrochloric acid solution for removing scales.
- Spraying is another mode of application. Metals like aluminum are used for coatings. This process does not require and binder as molten aluminum is sprayed on the steel. This coating does cover the substrate entirely and is porous. High standard of cleaning is required for the metal coating to bond with substrate as there is no metallurgical bond.
- Electro deposition is also another method. Zinc and cadmium coating are the most commonly applied coating through this technique. The steel must be cleaned thoroughly and pickled before application of coating. The coating is applied through an electrolytic method or by chemical or electro less plating.

Several other coating application methods used are diffusion, plasma spraying, vacuum evaporation. Metal coatings are abrasion resistant, do not require drying and have easier application methods. However, they do not provide protection for a long time and requires additional paint coating [Chandler & Bayliss,1985].

2.7.5.2. Paint Coating

Paints are made up of pigments dispersed in liquid binders. Application of paints with several methods are brush or roller manual application, air spray and airless, dip coating, flow coating, roller coating, electrostatic and powder coating. The nature of the surface of the steel to be coated determines the quality of paint and its longevity. Surface preparation is an important factor for adhesion of paints. The steel surface should be free of rust, mill scale, oil, grease and other foreign particles. Surface preparation methods are described below.

- Hand and power tool cleaning is one method. Hand tools like wire-brushes, scrapers and hammers are used to clean heavy deposits on the surface. A variety of tools with grinding tools is also used. It is usually done before blast cleaning [Chandler & Bayliss,1985].
- Dry abrasive blast cleaning is one of the most common surface preparation methods for paint coatings. Abrasives are blown onto a surface in a stream of compressed air through a hose or nozzle.
- Air blast cleaning uses pressure of about 90-100 psi. This technique is used to remove rust or scales and also to roughen up the surface for better adhesion of coatings. The surface roughness is also termed as etching, profile or anchor pattern. Abrasives used are metallic abrasives like shot and grit, sand abrasives, zinc coated abrasives.
- In flame cleaning, an oxyacetylene flame is passed on the surface of steel to flake off rust and mill scale. This method does clean the steel to a high level

and is usually employed for maintenance purposes [Chandler & Bayliss,1985].

- Pickling- is a method in which rust or mill scale is dissolved in dilute acids. Acids like sulphuric, hydrochloric and phosphoric are used.

The Steel Structure Painting Council of America gives standards and specifications of cleaning in different applications.

CHAPTER 3. ENCAPSULATION METHODS

Several methods to encapsulate PCM were investigated. The objective here was to develop an encapsulation or storage system which would:

- Have enough strength to hold the PCM inside during melting and solidification.
- Be non-porous to prevent any molten PCM leakage.
- Be stable at high temperatures and continual thermal cycling.
- Be a good thermal conductor to effectively transfer heat from the heat transfer fluid (HTF) to the PCM.
- Be non-reactive to the molten PCM.
- Be non-reactive to the HTF.
- Be a low cost material.
- Have low fabrication cost.

In order to develop an encapsulation with the above characteristics, two different approaches were adopted to form a PCM encapsulation system. One was to make a PCM pellet of desired shape, either spherical or cylindrical and then apply a coating or a series of coatings which would act as a shell to hold the PCM inside. The other approach was to fabricate a shell (cylindrical or spherical) and then fill the PCM inside it.

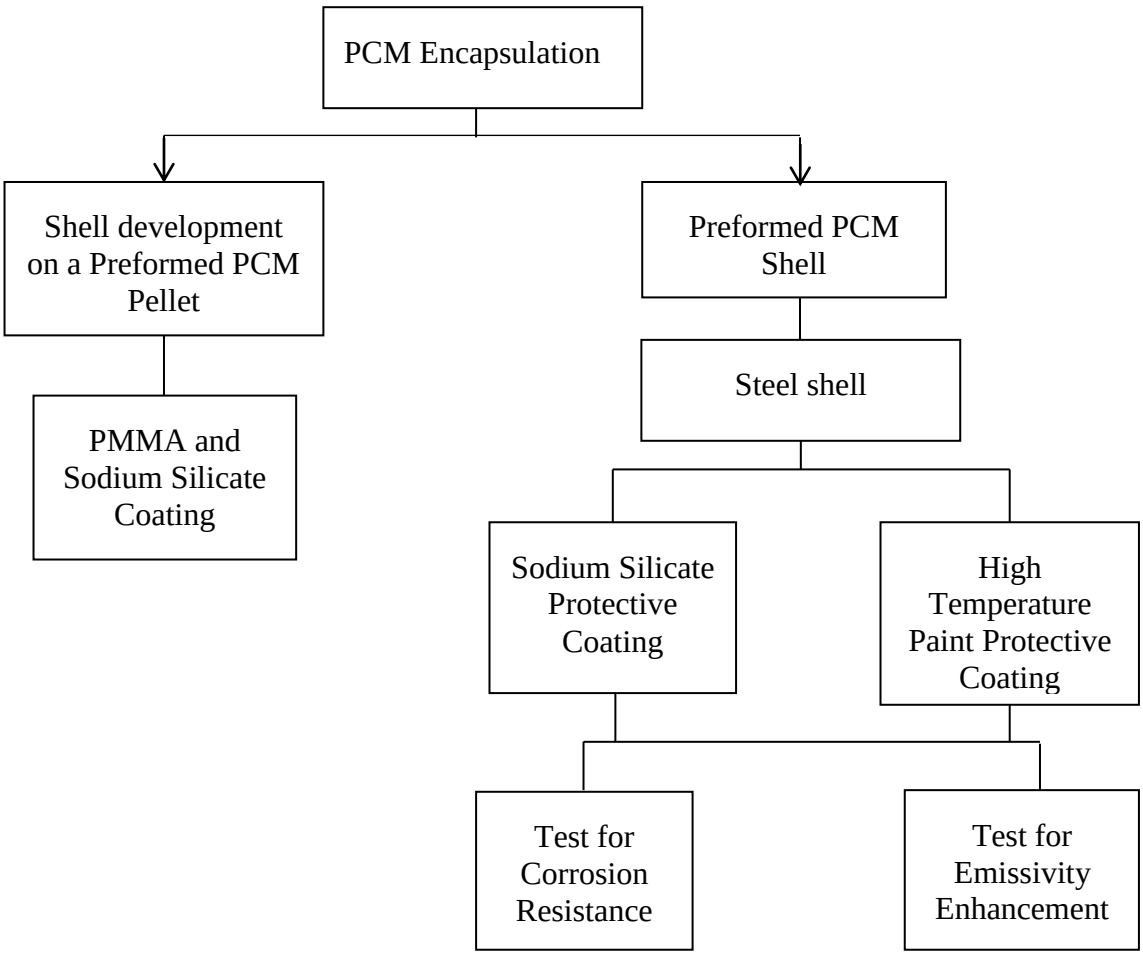


Fig 4. Schematic of Steps to Develop PCM Encapsulation

The above diagram divides the work done in the present study into different sections. In the section of preformed PCM pellet, the method of application of coating and the curing of the coating was studied. In the section of preformed PCM shell, the shell material, its compatibility with PCM and HTF, protective coating, high emissive coating and charging and discharging time of encapsulated PCM were investigated.

3.1. Shell Development on a Preformed PCM Pellet

In this method, PCM pellets of cylindrical and spherical shapes were fabricated and layers of different coatings were deposited on them.

3.1.1. Material Selection

Sodium silicate was chosen as a coating material due to its inherent properties of stability at high temperatures, high strength and rigidity, low cost, non-flammability and bonding with metals, glass and ceramics. Sodium silicate is also known as water glass, soluble glass, liquid glass, sodium met silicate and silicate of soda. In dry form it is available as white powder or lumps and in liquid form it is available as solution in water with different ratio of silica to soda. The powder form is soluble in water and alkali, but is insoluble in acids and alcohol [Owusu,1982]. One of its applications is as high temperature adhesive bonds in pelletizing, briquetting, refractory cements and coatings [Horikawa et al]. It is also used in wood, paper, abrasives, cleaners (detergents), deflocculants and so on [Owusu,1982]. When the solution of sodium silicate is used, different methods of drying and curing are used according to the application, which have been studied by Glasser et al, Horikawa et al, and Matveev & Guzhavina.

Table 1 lists three commercially available sodium silicate solutions with varying silica to sodium oxide ratios. The viscosity increases from the N type to the RU type due to the decrease in water content. The N type was used in most of the experiments because of its ease of forming a thin and uniform coating due to its relatively low viscosity. The sodium

Table 1 Types of Sodium Silicate

Type	SiO_2 %	Na_2O %	H_2O %	Weight Ratio SiO_2/Na_2O
N	28.70	8.90	62.4	3.22
K	31.70	11.00	57.3	2.88
RU	33.20	13.85	52.95	2.40

silicate solution used in all the experiments, unless otherwise mentioned, was the 'N' type from PQ Corporation.

The PMMA used was Norland 72 which is an adhesive which adhered well with glass. This was chosen to bond the sodium silicate with the PCM. The curing is in UV light and is be done in few minutes.

3.1.2. PCM Pellets Compaction Technique

A stainless steel pellet press die and hydraulic press was used to fabricate pellets of spherical and cylindrical shapes of 10 mm diameters. Pressures ranging from 1 ton to 5 ton were applied for about 3 to 5 minutes.



Fig 5. Pellet Press Die Components

3.1.3. Coating Materials and Techniques

In the present work, two layers of coating were applied. A coating of PMMA (Para-methoxymethamphetamine) was applied on the pellet and a coating of sodium silicate above the PMMA.

A coating of PMMA was applied with a brush to cover the pellet completely. The pellet was then cured in UV light for approximately 15 minutes. A second coating of sodium silicate was applied. Various applications techniques for sodium silicate are described below.

- Rotating-drum Coating
- Brush Coating
- Dip Coating

In rotating-drum coating, sodium silicate solution is applied on a bed of pellets through a spray atomizer nozzle. The pellets cascade in the drum which rotates at a controlled speed. This method yields reduced process time since many pellets are coated in one run.

In brush coating, sodium silicate was applied using a brush to acquire as uniform a coating as was possible manually. This method was better than the earlier drum coating procedure as the uniformity and thickness of the coating could be controlled.

In dip coating process, the substrate to be coated is dipped in the sodium silicate solution, removed and suspended for some time, to let the extra solution drip off. This method was used to get a relatively uniform coating.

3.1.4. Curing of Sodium Silicate

The main mechanism of curing a sodium silicate coating is by moisture loss. Several methods which have been studied are: drying at room temperatures from several days to weeks [Dent &Lee,1971], drying at varying relative humidity [Horikawa et al], using additives like clay [Horikawa et al], microwave heating [Grant et al.,2009], adding pigments like cuprous oxide, titanium oxide and zinc oxide [Glasser et al.,1982], spray drying [Balfanz & Steinreich,1971].

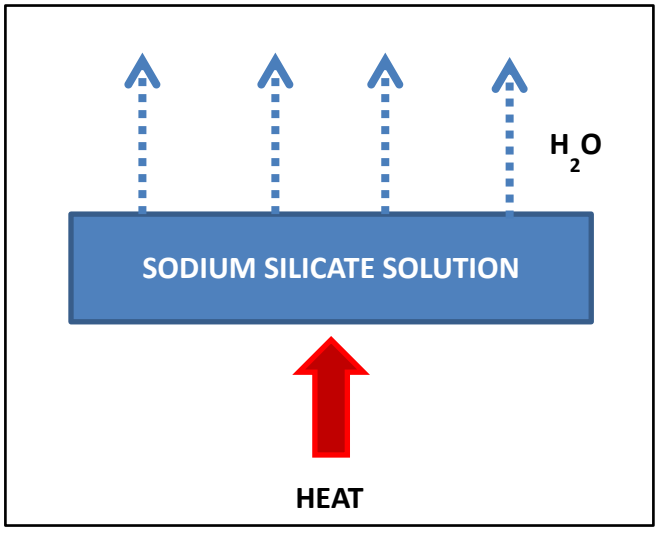


Fig 6. Sodium Silicate Coating Curing Mechanism

The curing techniques of sodium silicate coating investigated are described in the following sections.

3.1.4.1. Rotating-drum Drying

A coating of sodium silicate was applied by an atomizer spray as explained in the drum coating section. Instead of sodium silicate as described earlier, hot air flow is circulated through the front opening of the drum while the drum is rotated at a certain speed. In this process a batch of pellets are coated at a time.

The steps of the process are described below:

- The drum is loaded with adequate number of pellets and rotated at a controlled speed.
- Baffles in the drum facilitate adequate circulation of pellets.
- The coating solution is sprayed through an opening at the front of the drum.
- The pellets cascade downwards while the drum rotates and pass through the spraying zone.
- The coated pellets are dried with a hot air blower while the drum is still rotating.

During the process, sodium silicate was deposited not only on the pellets but also on the drum surface and the baffles. The pellets adhered to each other during the drying of the sodium silicate deposited on them. This hindered the adequate movement of the pellets inside the drum. As a result, a non-uniform, non-continuous coating on the pellets was formed. Also, continuous tumbling of the pellets in the drum and the mutual rubbing of the pellets within the drum caused erosion of the pellets. The drum was coated with Teflon to reduce the adherence of the coated pellets to it. This did not reduce the problem of pellet-drum adherence. Sodium silicate due to its adhesive characteristic adheres to the drum and so this process was deemed unsuitable for the curing of sodium silicate.

3.1.4.2. Curing at Room Temperature in Ambient Air

A thin layer of sodium silicate was applied on the PMMA coating and allowed to dry overnight in the ambient air.

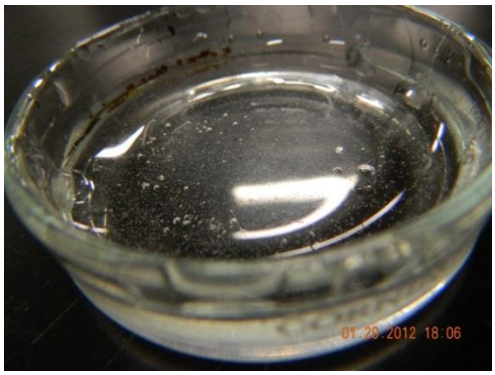


Fig 7. Sodium Silicate Solution Cured in Ambient Air in a Petri Dish

After the curing a transparent and hard coating was observed. To test the ability of this coating to hold molten salt inside it, this pellet was heated to higher temperatures. Though a glassy uniform coating was formed after the curing at room temperature, on further heating at temperatures up to 300°C, it lost its uniformity and formed a porous voluminous layer. This layer did not possess much strength and lost adhesion easily. One reason for such behavior of the coating was the moisture loss from the PCM at high temperatures, which penetrated the silicate layer, making it porous. The PMMA layer did not serve its purpose to act as a barrier layer between the sodium silicate layer and PCM. This indicated that the PMMA layer was porous. It decomposed at temperatures above 200°C. The combined effect of the PMMA decomposition, sodium silicate efflorescence and water vapor escape produced a sodium silicate coating as described above.

Also, any curing method in case of sodium silicate on preformed shell was limited by the properties (i.e. melting point) of the salt PCM and polymer layer.

3.2. Preformed PCM Shell

Instead of developing a shell on a pellet, using a preformed shell was the other approach investigated. This method would require less fabrication time as opposed to the earlier

method which had curing time for each coating of few hours to days. Also, in this case the shell would be of a single material unlike the earlier method which had several coating materials. Both of the advantages mentioned, will assist in reduction of the cost. Also, when using a preformed shell, the choice of material, material properties and processing techniques are much wider than that of a coating.

3.2.1. Carbon Steel Shell

Carbon steel was selected as a shell material for its high conductivity, strength and low cost.



Fig 8. Steel Canister with End-caps Sealed with Sodium Silicate and Filled with PCM, after 10 Thermal Cycles.

A cylindrical capsule was fabricated to test the thermal cycling ability of such a system and the compatibility of the steel with molten salt and air. A carbon steel tubing of 1” OD was filled with sodium chloride and potassium chloride eutectic. Both the ends were sealed with end caps and molten sodium silicate. The container was filled with above salt. This system was then thermally cycled in a vacuum furnace for 10 cycles. The table below gives a detailed temperature profile for each thermal cycle.

Table 2 Temperature Profile of Thermal Cycling

Start Temperature (℃)	End Temperature (℃)	Time	Cycle
25	690	120	1st Cycle
690	690	360	
690	620	70	
620	690	70	2nd & 3rd Cycle
690	690	360	
690	620	70	
620	690	70	4th Cycle
690	690	360	
690	620	120	
620	690	70	5th Cycle
690	690	360	
690	620	100	
25	690	690	6th Cycle
690	690	600	
690	25	360	
25	690	120	7th – 10th Cycle
690	690	720	
690	25	120	

Scaling of the steel on the outer surface of the capsule was observed due to contact with air at high temperatures. The inside of the canister, which was in contact with molten salt displayed pitting corrosion. Thus the need to protect the steel shell against corrosion arose. The development of a protective coating was investigated hereafter.



Fig 9. Pitting Corrosion on the Inner Surface and FeO (the layer adjacent to iron), Fe3O4 (middle layer) and Fe2O3 (surface layer), on the Outer Surface.

3.3. Sodium Silicate as Protective Coating

Sodium silicate as a coating was investigated earlier in this study. The coating defects in the earlier experiments were not eliminated primarily due to three reasons. These reasons were: water content in the substrate, properties of sodium silicate and the curing procedure. However, if the defects could be eliminated, sodium silicate would be a good prospective coating because of its high temperature properties and low cost. To investigate potential of sodium silicate as a protective coating for steel, further experiments were performed wherein the curing procedure was improved. Given below, are different curing procedures implemented.

3.3.1. Curing at Elevated Temperatures in Air

Preliminary experiments were performed using glass as the substrate. Glass slides were used as substrate to cure sodium silicate coating to temperatures up to 200˚C. The slides were carefully cleaned with 10 N sodium hydroxide solution, nitric acid and DI water. A thin layer of sodium silicate was spread on a glass slide and allowed to dry in the vacuum furnace by slowly increasing the temperature till 155˚C. Another method employed was to dip the slide in the silicate solution and suspend it to drip off the extra solution. The

resulting layer in both the cases was observed to have bubbles or blistering on the thicker areas and a powdery crust on others. The sodium silicate increased in volume and formed a powdery crust with increased volume which is known as efflorescence. Coating on this substrate formed less efflorescence, as opposed to coating on a sodium nitrate pellet though this problem was not completely eliminated. This crust is brittle and affects the adhesion of the coating on the surface. Veinot et al has indicated the powdery crust is a carbonate. The problem of efflorescence was augmented by the reaction between carbon dioxide from the atmosphere and sodium silicate [Veinot et al,1999].

The reaction mechanism as stated by Cotton and Wilkinson [Cotton & Wilkinson,1972] is as follows:

$$CO_2 + OH^- = HCO_3$$

$$HCO_3^- + OH^- = CO_3^{-2} + H_2O$$

The above reactions indicate that efflorescence, which is a carbonate, is formed when OH- in the silicate solution reacts with CO_2 in the environment and is catalyzed by water vapor. It was observed by Veinot et al that the degree of efflorescence was dependent on the presence of water vapor and carbon dioxide in the environment and the alkalinity of the silicate solution (i.e. silica to sodium oxide molar ratio). At room temperature, the sodium silicate solution is present in different forms which is illustrated by the equation below.

$$Na_2SiO_3 + H_2O \leftrightarrow H_2SiO_3 + Na_2O$$

$$Na_2O + H_2O \rightarrow 2NaOH$$

$$NaOH + CO_2 \rightarrow NaHCO_3$$

The sodium oxide reacts with water molecules to form sodium hydroxide, which absorbs carbon dioxide, when it is exposed to atmosphere and releases it when heated forming efflorescence.

To eliminate the problem of efflorescence, the curing was carried out in a vacuum environment where water vapor and carbon dioxide would be absent.



Fig 10. Sodium Silicate Cured on Glass at 300˚C, Forms Efflorescence

3.3.2. Curing using Additives

Additives such as titanium oxide (TiO2) and calcium aluminate (CaAl), zinc oxide (ZnO) were used in the ratio of 1:5, 1:20 and 1:10 respectively. They were mixed with sodium silicate solution diluted with methanol, using a magnetic stirrer. These solutions were used on a glass substrate and cured in a vacuum furnace up to a temperature of 210˚C. The coatings did not form any bubbles or efflorescence till 150˚C, but they started to form at different temperatures above 200˚C for different additives. The above mixtures were also used on aluminum substrate to check if the aforementioned defects were dependent on the nature of the substrate, but they did not yield any different results**.** Also, calcium carbonate (5%) was added to the silicate solution before application, but it did not yield any different result. As seen earlier, carbonates are not desirable for a smooth coating formation with a sodium silicate solution, and this method was not pursued further.

3.3.3. Curing at Elevated Temperatures in Vacuum

As explained earlier, curing in the vacuum up to temperatures of 200˚C yielded reduced efflorescence but did not eliminate it completely. A slightly different coating was done this time where a very thin layer of sodium silicate solution was spread with a glass slide on the substrate. The coating was then heated in vacuum up to 200˚C. Due to the very thin coating efflorescence was not observed but formation of bubbles were observed.

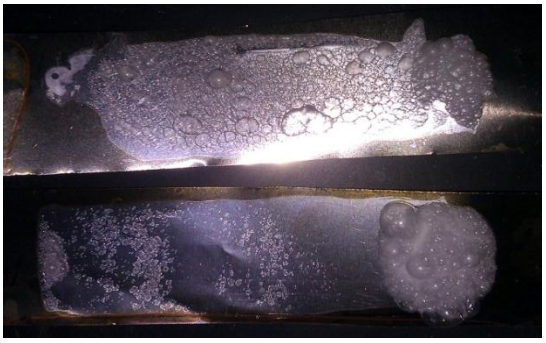


Fig 11. Sodium Silicate Coating on Steel Substrate, Cured at 200 ° C in Vacuum

This is a phenomenon where a layer of sodium silicate formed bubbles/blisters during the curing process. It was observed that the primary reason of bubbling was the drying of the uppermost layer of the silicate coating before the underlying layers. As the uppermost layer got rid of all the water content and dried, the water in the underlying layers was still intact. On increasing the temperature, this water content tries to escape through the solidified layer forcibly, causing bubbles. Thus, to eliminate the above problems, the experiments were hereafter performed in a vacuum furnace to reduce the presence of air as much as possible.

Other defects which were observed were cracking and flaking. The layer of sodium silicate formed cracks after curing at high temperatures. This was mainly observed when

the heating rate was higher than 10˚C/min and also when the coating was cured on a hot plate. When the heating rate was high, the difference in thermal expansion of the coating and the substrate caused the coating to crack. This was avoided by following a slow heating rate. In case of a hot plate, since the coating was in contact with the ambient air while the substrate was with the hot plate, a thermal gradient was created which caused the coating to crack. This defect was eliminated by curing at a slow heating rate and making a very thin coating.



Fig 12. Sodium Silicate Coating on Glass Cured at 200^{o} C on a Hot-plate Displays Cracking

Another defect which was observed was flaking. The coating forms flakes and loses adhesion after curing. This was observed when the substrate was not cleaned adequately and also when the substrate was very smooth. This problem was observed in very few cases and is not a major drawback. To eliminate this problem, substrates were carefully cleaned and the surface was made rough by acid pickling, sand blasting or with sand paper.

3.3.4. Curing in Vacuum and Humid Environment

From all the earlier experiments, it was observed that, in order to obtain a good coating of sodium silicate, two conditions were necessary, which are vacuum environment and a thin coating. However, a very thin coating would not provide a complete coverage of the

substrate. In order to get a good coating without having to make it very thin, a new method was used. In this method, a temperature gradient was created from the substrate to the outermost layer of the coating.

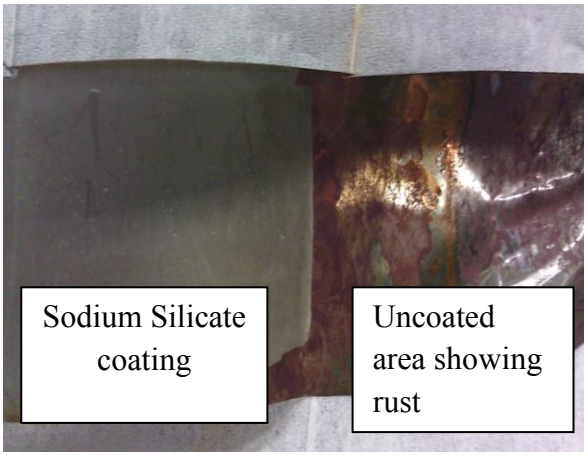


Fig 13. Sodium Silicate Coating on Steel Substrate Cured at 200 ° C in Vacuum and Water Vapor Environment

The bottom surface of the substrate was heated to a high temperature while the topmost layer of the coating was in water vapor environment which had a lower temperature. This was obtained by making a setup where a beaker was filled with water and the coated sample was placed on the rim of the beaker, with the coating facing downwards. The figure 3.5 illustrates the set-up in detail. This setup was kept in a vacuum furnace and slowly heated to 200°C. As the temperature increased, the water from the sodium silicate solution evaporated and escaped the coating layer. When a thermal gradient in this set-up was maintained, the substrate was always at a higher temperature than the outermost layer of the coating. Due to this the bottom most layer which was in contact with the substrate heated up faster, lost water and solidified before the layers on top. The adjacent

layers cured from substrate to periphery which eliminated the trapping of bubbles, thereby forming a uniform smooth coating.

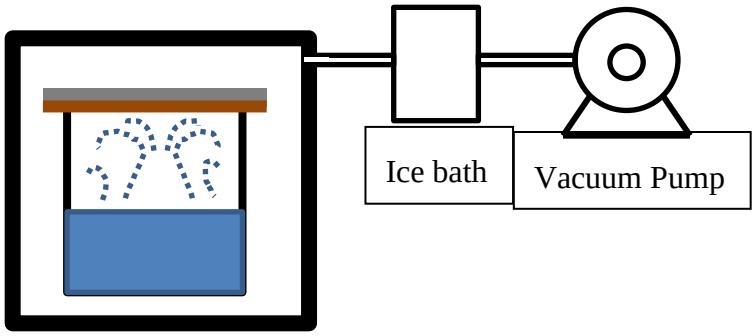


Fig 14. Schematic of Vapor Environment Test Set-up

This experiment was done by applying a thin layer of sodium silicate on a steel substrate. The layer was spread with a glass slide and placed in the vacuum furnace as explained above. The temperature was slowly increased to 200℃. After the curing a smooth coating was observed which was free of bubbles and efflorescence. This coating protected the steel from rust which was observed after the sample was kept in ambient air for almost a year. Then the sample was heated up to 800°C and no oxidation was observed on the areas of the sample where there was a sodium silicate coating. However this process was slow .Thus, forming a good coating rapidly on substrates posed a problem.

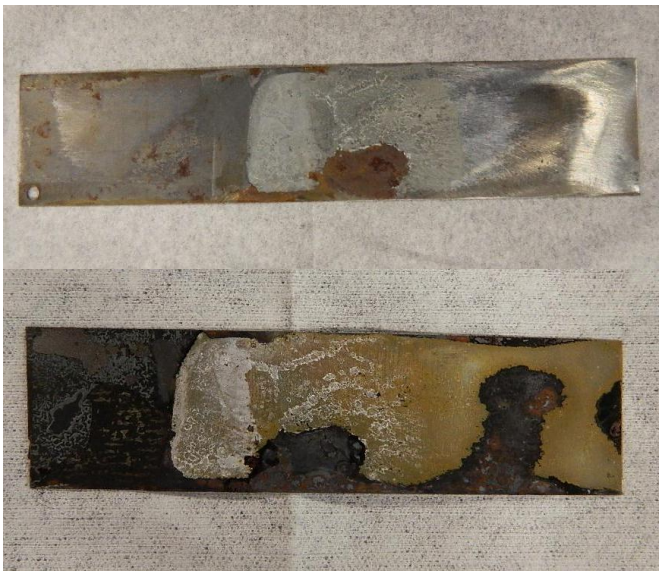


Fig 15. Top: Steel Sample Partially Coated with Sodium Silicate and Cured Bottom: Sample Heated to 800°C with Coated Area Showing No Oxidation

3.3.5. Curing at Melting Point in Vacuum

Sodium silicate coating displayed varied behavior at different elevated temperatures. At room temperature, a very smooth glassy coating would bubble up at 100°C, and then form efflorescence as the temperature was increased. To study this behavior, the temperature was increased till the melting point of sodium silicate. Thus several experiments were performed to optimize the curing procedure to acquire a good coating. It was observed that as the melting point approached, the efflorescence slowly disappeared. Initial experiment was carried by coating a steel strip with the N type sodium silicate, and heated in a vacuum furnace till 1080°C. At the melting point, coating free of bubbling, flaking, cracking, efflorescence and adhered well with the substrate. A very hard glassy coating was formed but it was not uniform and formed bluish green droplets.

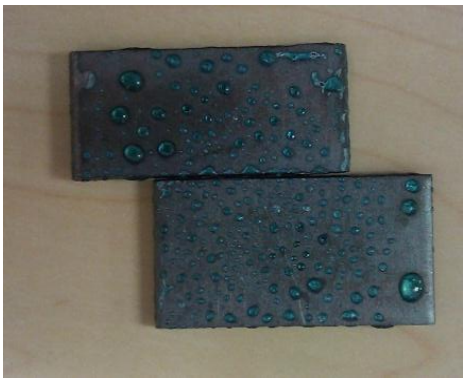


Fig 16. Sodium Silicate Cured at 1080 °C in Vacuum, on a Steel Substrate

It was suspected that the bluish color was possibly due to the formation of phosphates or met silicates due to the phosphoric acid treatment of the steel substrate prior to the application of the coating. So, the surface treatment of the steel substrate was altered to eliminate formation of any residue after the treatment. To check if the formation of droplets was due to the type of the sodium silicate used, K type was used for later experiments but it cured the same way as the N type. The surface was prepared by rinsing with toluene, hydrochloric acid and acetone, and the experiments were repeated. The same problem persisted with the changed surface preparation.

3.4. Sodium Silicate as High Emissivity Coating

Sodium Silicate itself is not a very good absorber in the IR range. Carbon being a good emitter (emissivity) and a good thermal conductor is a potential candidate to enhance the emissivity of the sodium silicate coating. Carbon lampblack and graphite were used with sodium silicate to make a coating on steel substrate. The adherence of these materials was weak after the coating was cured. The adhesive characteristic of the sodium silicate was not adequate to adhere the carbon particles to the steel.

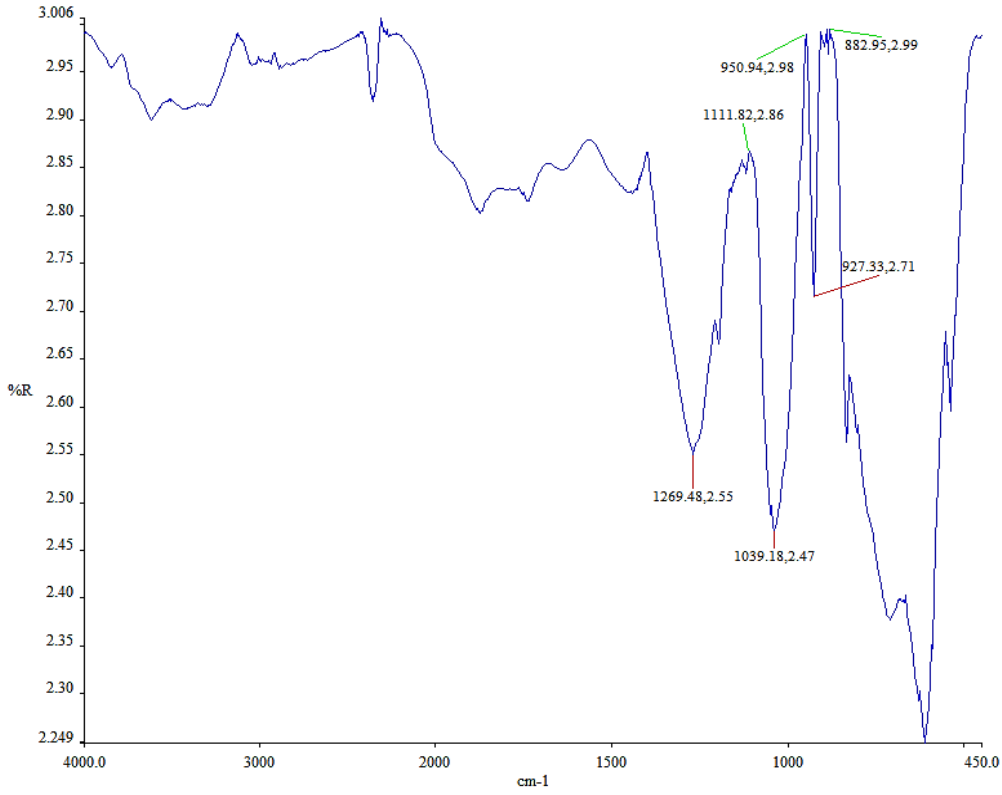


Fig 17. Measured Reflectance Spectra of Sodium Silicate

3.5. High Temperature Paint as Protective Coating

Commercially available high temperature paints for steel were investigated to check for their potential to protect steel from corrosion. The application of these paint coatings would serve several purposes. They will be applied on the outer surface of the encapsulation to protect from the heat transfer fluid and on the inside to protect from molten salts and also to enhance the emissivity to increase the heat transfer.

Two different commercial paints Sealmet and Aremco CP-3015BL were used to investigate their protection capability. These paints have metal and ceramic oxide pigments which indicate that they form protective oxide layer at high temperature to form an impervious layer to stop any diffusion of oxygen into the metal. Sealmet paint

contains aluminum oxide and cobalt oxide and CP-3015BL has copper chromite black spinel. Protective oxides which contain these elements display maximum stability [Kofstad]. Sealmet is specifically made to protect steel at high temperatures and thermal cycling. CP-3015BL is a high emissivity coating which resisted thermal shock. Due to aforementioned properties of these paints, they were selected for further investigation.

For good adherence of paints at high temperatures and thermal cycling a rough surface is required either by sandblasting (recommended for sealmet and CP-3015BL) or etching (recommended for CP-3015BL). Removal of any residues after aforementioned surface treatment is necessary which can be done by MEK or trichloroethylene. In the present work, steel was sandblasted and then cleaned with trichloroethylene.

Brush and spray painting was suggested by the manufacturer. Three methods were then used to apply the paints. Application of paints with a brush could not yield a uniform coating. The layer was uneven coating with some areas of it being very thick and others very thin. Also, a thin layer of coating could not be achieved with this method of application. This resulted in flaking and peeling of the paint after extended heating at high temperatures. To obtain a thin coating, these paints were then applied with an atomizer spray gun. A complete coverage of the substrate could not be attained in a laboratory scale but industrial automated spraying with optimized spray angle, spray area and atomizing size may yield smooth complete coverage. Painting with a foam brush ensured a complete coverage of substrate and very thin layers could be created. Flaking and peeling were not observed with this paint application method.

The following steps were adopted to cure the paint.

- The paint coating was allowed to dry in air.
- It was then heated in a furnace up to 80 C and dwelled at that temperature for few hours.
- The temperature of the furnace was then increased to 700 C to make it insoluble to water (manufacturer specification). It also ensured outgassing at higher temperatures.
- The coating which was greyish in color turned black at high temperatures which indicated that the coating had formed into an oxide protective layer.

3.5.1. Protection from Oxidation

Steel strips were sandblasted and degreased with trichloroethylene. Then the paint was applied with a brush and allowed to set. These coated steel strips were then heated in the furnace in air to check formation scaling had formed.



Fig 18. Steel Sample Heated to 700 ° C
Top: With Sealmet Coating No Scaling, Bottom: No Coating Forms Scales

No scaling was observed as compared to uncoated steel strips. Paint sealmet protected the steel at temperatures up to 900°C and the corr-paint protected up to 700°C, in isothermal heating. Sealmet showed less peeling and flaking at high temperatures, as compared to corr-paint.

Sealmet was coated on a mild steel sample with aforementioned procedure. It was then heated in a furnace to 700° C and dwelled at that temperature for six hours. Another sample of same material without any coating was also heated as above. It was observed that no scaling had formed on the coated steel but the uncoated steel showed heavy scaling. This indicated that this paint prevented the formation of oxidizing layers at that temperature. However, peeling was observed at places where the paint was thick.

The above sample displayed formation of rust in areas where the coating was thin, after a span of six months. This indicated that thin layer of coating was permeable due to which oxygen from the atmosphere diffused into the steel. This corrosion had also spread underneath the coating forming reddish black color. This throws light on the fact that any discontinuity in the coating initiates corrosion which can also spread to protected areas. Thus, it is important to coat every exposed areas and sharp edges.

For thermal cycling tests, mild steel was coated with sealmet and cured as earlier procedure. It was thermally cycled in a furnace from 650 to 680°C for 20 cycles. No scaling was observed on the coated steel. The uncoated steel displayed heavy scaling. The weight gain in the coated was 0.1 % as compared to 1.3% ($\pm$0.001%) in uncoated steel. The weight gain could have been due to diffusion of oxygen through permeable portions of the coating.

The paint could be used to prevent the formation of oxidation layers on steel at high temperatures. The adherence of the paint after repeated thermal cycling as is required in the present application was of concern. To investigate this, several methods of paint application were implemented. Paint was applied using a brush, spray gun and a foam brush. Furthermore, adhesion tests were performed after heating the coated samples, to check the flaking and peeling of the paint.

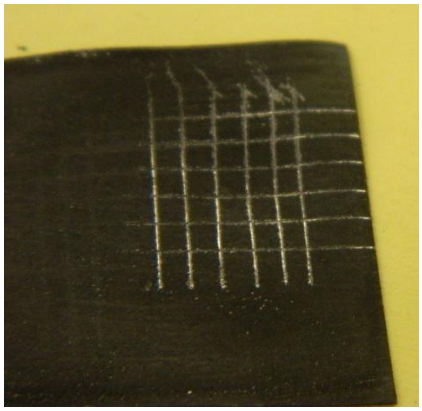


Fig 19. Steel Coated with Sealmet Paint and Adhesion Test Performed on it

Coated steel samples were heated up to 900°C and horizontal and vertical lines were cut on the coating. An adhesive tape (duct tape) was pressed and pulled off. The remaining squares of paint that were intact were checked. Most parts of the pant showed good adhesion except for the edges and paint particles had adhered to the duct tape. This indicated that flaking and peeling was not observed but erosion of this paint needs to be eliminated.

3.6. High Temperature Paint as High Emissivity Coating

Two types of paint as mentioned earlier were investigated for their emissive properties. Their reflectance in the range of 2.5 µm to 22.5 µm was measured in an FTIR with a

capability to measure spectral reflectance. It was found that these paints had about 10 % specular reflectance in the above mentioned range. The diffuse reflectance was not accounted in this measurement but it indicated that the paints attenuates IR radiation, and are potential candidates to enhance emissivity.

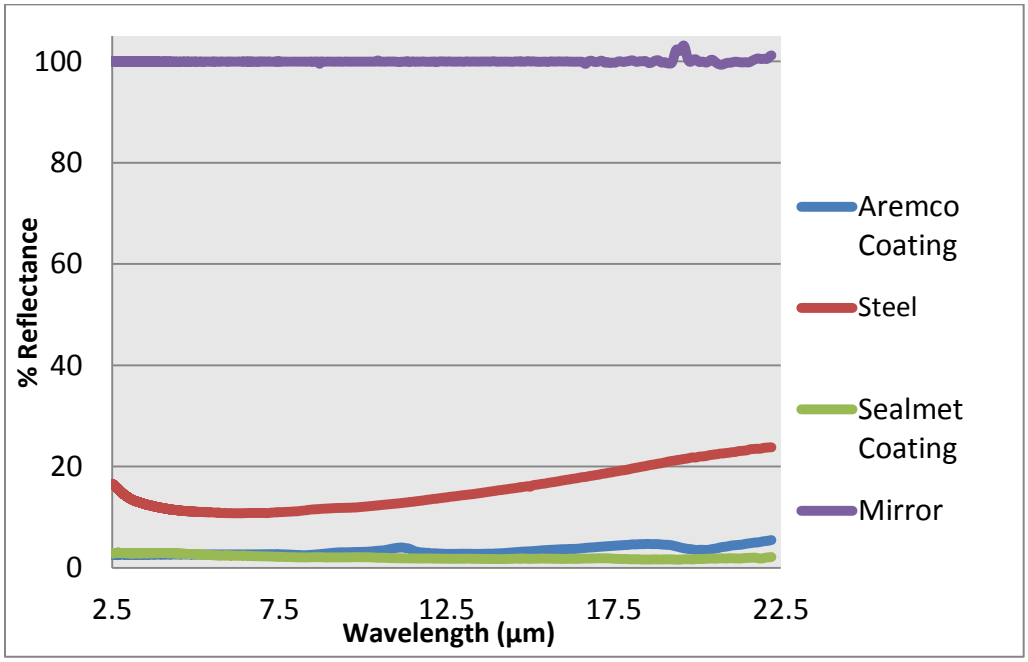


Fig 20. A Comparison of Reflectance Spectra of Paints, Mirror and Steel

3.7. Melting Rate Test

To test the capability of steel encapsulation of efficient thermal energy storage, tests were performed by encapsulating PCMs in steel cylinder.

3.7.1. Experimental Set-up

A test set-up was fabricated where an encapsulated PCM was heated up to 680°C and the temperature was monitored for melting process. The PCM used was a mixture of sodium chloride (44% by weight) and potassium chloride (NaCl-KCl) and the encapsulation was

a carbon steel tube of 2” diameter and 3” length. The tube was coated with high temperature paint on the outside and the inside. The tube was sealed on both the ends with a commercially available high temperature sealant (Resbond 907GF). Thermocouples were inserted inside the canister, on the outer surface of the canister and in the surrounding air. The thermocouples were attached to a data acquisition system which recorded the temperature every minute. The canister was heated inside a muffle furnace.

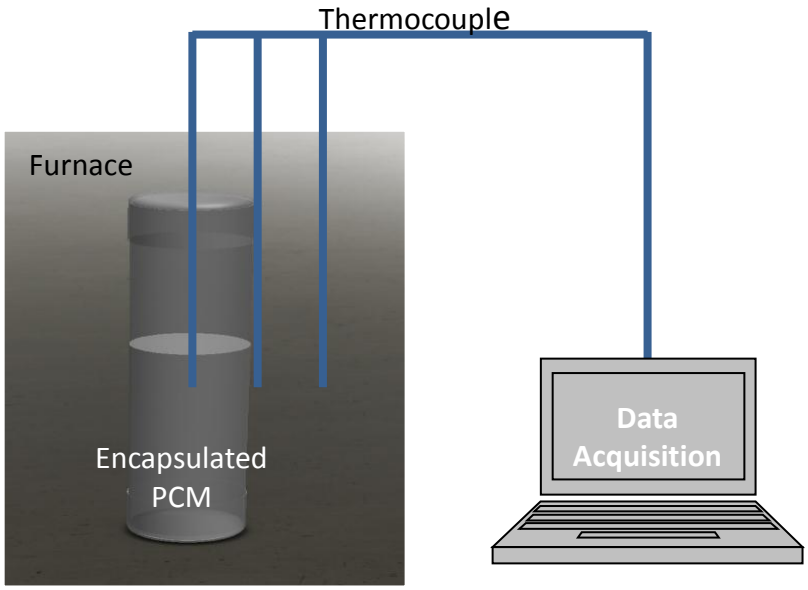


Fig 21. Experimental Test Set-up of PCM Encapsulation Thermal Cycling

3.7.2. Observations

No scaling was observed on the outside of the canister. The melt time at the center of the canister was recorded which was approximately 50 minutes. This was a preliminary estimate of the charging time for 100g of NaCl-KCl eutectic in a cylindrical steel canister with protective coating.

Heavy pitting and crevice corrosion were observed at places where the sealant had failed and salt had leaked. Further experiment was done wherein steel with and without coating was immersed in molten NaCl for 72 hours. Both the steel samples had dissolved indicating that carbon steel, sealmet paint and sodium chloride were not compatible at high temperatures in air. Impurities in the salt might also have augmented the corrosion process. Further investigation needs to be done to check their compatibility in non-oxidizing environment (i.e. inert atmosphere or vacuum and pure salt).

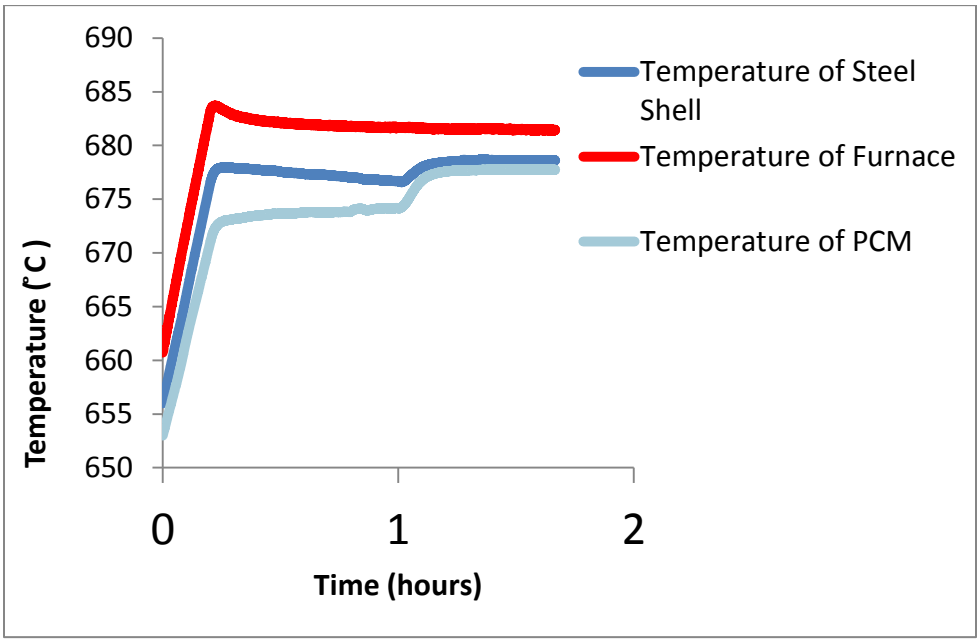


Fig 22. Temperature Profile of the PCM, Steel Shell and the Furnace During Thermal Cycling

CHAPTER 4. DISCUSSION AND CONCLUSION

4.1. Discussion

Sodium silicate as a coating on preformed pellets and steel shell was investigated. For sodium silicate to form a good coating on a preformed PCM pellet, the need to coat an intermediate impervious layer has to be identified, since the polymer coating which was applied to address this need decomposes and reactive to sodium silicate.

Steel was identified as a candidate for preformed shell for PCMs and its behavior at high temperature in air and in molten salt was studied. It was found that in order for steel to withstand high temperature thermal cycling a durable corrosion resistant coating is required. Corrosion inhibition by developing a protective coating was investigated. Sodium silicate and high temperature paint were two kinds of coating studied. Defects of sodium silicate coating which arose during the initial curing procedures were identified and several techniques developed to eliminate them. When using sodium silicate coating on steel, the thinnest possible layer of sodium silicate with complete coverage would eliminate the problems of bubbling, efflorescence and cracking to form a clear coating. A curing procedure which consisted of heating in vacuum and water vapor environment was developed which successfully cured sodium silicate coating on steel. This coating demonstrated protection capability of steel against oxidation in air up to 800 C, but the coating process was slow. Also, oxidation protection at high temperature thermal cycling

needs to be investigated further. High temperature paint coating was effectively used to protect steel from oxidizing at high temperatures in air. The flaking and peeling of paint on the steel after repeated thermal cycling, which initially posed a challenge was carefully eliminated by optimizing the surface preparation of steel and the method of paint application. It was found that a coating of a very uniform, thin and see through layer was needed to eliminate the problems of flaking and peeling. This could be attained by applying the paint with a foam brush which eliminated the problem of paint run-off and accumulation at the edges forming thick uneven coating.

Emissivity of the protective coatings was investigated. The high temperature paints showed more promise as a means to enhance emissivity. As these paints showed a good potential of dual functionality of corrosion protection and emissivity enhancement, further tests were executed to confirm their performance. Sealmet displayed adequate protection against formation of scales, during thermal cycling op to 700 C. Adhesion tests threw light on the erosion of paint, which indicates that the paint may erode during actual extended thermal cycling. Further investigation needs to be done to check permeability of paint at higher thickness.

4.2. Recommendations

Sodium silicate is a good candidate to protect the PCM from the heat transfer fluid. However, a stand-alone coating of sodium silicate would not suffice. A non-porous intermediate layer has to be identified. Also if sodium silicate is used as a coating, another material to add strength is required.

Sodium silicate as a protective coating on steel is promising and a large scale industrial method for obtaining a thin defect-free coating has to be identified. Adherence and corrosion optimization will throw more light on its coating potential. Metal coatings and thermal spray coatings for oxidation protection could also be investigated and compared with above technologies.

Sealmet paint pigments like aluminum oxide and cobalt oxide can be further investigated. A new composite coating material can be formed by adding these pigments to sodium silicate, which would act as a bonding agent.

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