CHAPTER I

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1.1 General Introduction

Energy is the basic need of mankind. Energy, in the form of food and fuel, we need. Both these, we get either directly or indirectly from the Sun. There are mainly two types of energy sources. One in conventional and other is non-conventional. The sources which we frequently use, such as coal, oil, gas etc and which are non-renewable are called the conventional sources. Solar energy, wind energy, biomass energy, Ocean-tidal energy which are renewable sources are called the non-conventional energy sources. The conventional energy sources are limited. Their storages are becoming less and less. It is obviously resulting in their rising prices. So since the energy crisis in 1970's all over the world, the research community is thinking over an alternative for these conventional limited sources of energy. While thinking in this manner, such alternative must be inexhaustible, replenishable, non-pollutant and available freely all over the world. Considering these criteria for energy resource for future we find the non-conventional energy sources solar, wind, biomass, ocean energies. Indirectly the Sun causes winds to blow, plants to grow, rain to fall and temperature differences to occur from the surface to bottom of the ocean. Hence the only alternative which can meet the energy needs of future is the solar energy. It is clean, abundant and also free of cost.

It was the first source of energy known to man and it is going to be the last hope of mankind [1]. Only thing we have to do is to use it more and more efficiently.

The power from the Sun intercepted by the Earth is approximately 1.8 x 10" MW [2] which is many thousand times large than present consumption rate on Earth of all energy sources.

1.2 AVAILABILITY OF SOLAR ENERGY [2] :

The Sun is a large sphere of very hot gases. The heat is being generated by various kind of fusion reactions. Its diameter is 1.39×10^6 km, while that of Earth is 1.27×10^4 km. The mean distance between two is 1.5×10^8 km. As viewed from earth, the radiation coming from the Sun appears to be essentially equivalent to that coming from a black surface at 5762 K.

The radiation received without change of direction is called beam radiation while that received after its direction has been changed by scattering and reflection is called diffuse radiation. The sum of beam and diffuse radiation flux is refered to as total radiation or global radiation. The solar radiation flux is usually measured with the help of a pyranometer or a pyrheliometer. A pyranometer

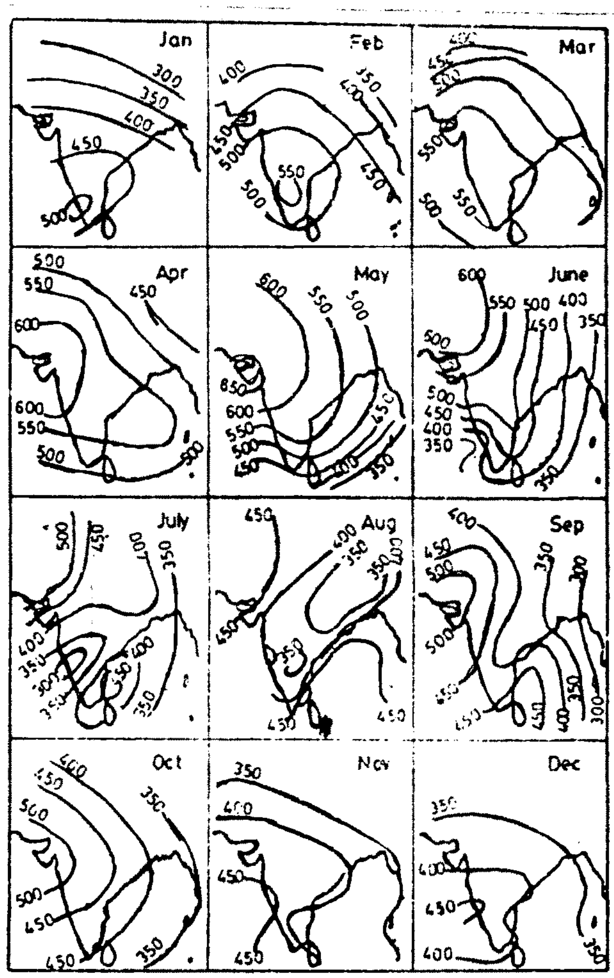

Fig 1.1 Average daily global radiation over India in cal/cm^2- day. (From Mani and Chacko)

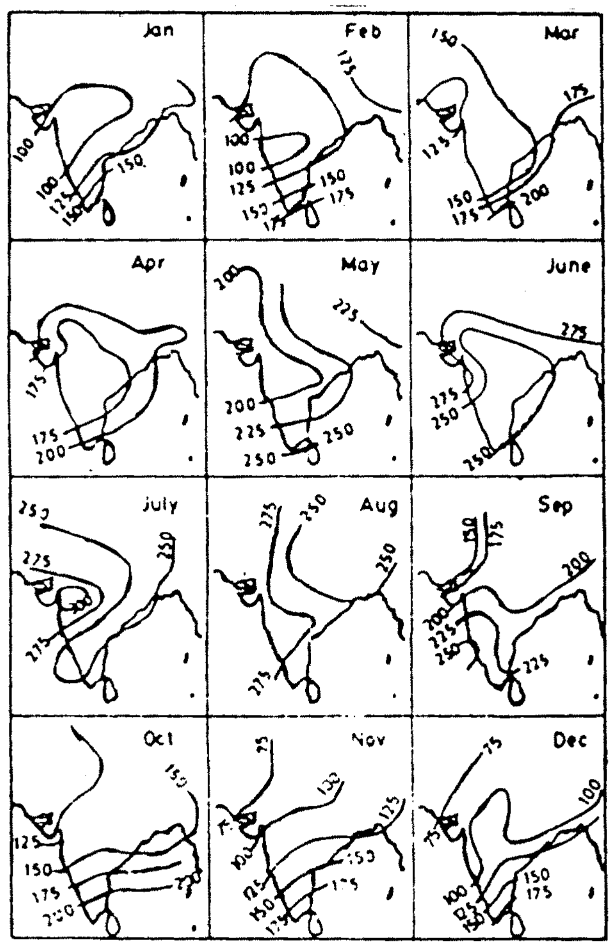

Fig. 1.2 Average daily diffuse radiation over India in cal/cm^2-day. (From Mani and Chacko)

measures either global or diffuse radiation over a hemispherical field of views. While a pyrheliometer measures beam radiation. The duration of bright sunshine in a day is measured by means of a sunshine recorder.

1.2.1 Radiation Data :

Mostly radiation data are measured for horizontal surfaces. The solar radiation flux is often reported in Langleys per hour-day. 1 Langley = 1 Cal/cm^2-day.

A general idea of the availability of solar radiation over different regions can be obtained by constructing solar radiation maps. Such maps have been drawn by Mani and Chako for India [2]. Fig. 1 shows distribution of average daily global radiation while Fig. 2 shows the distribution of average daily diffuse radiation.

From this figure it is seen that the annual average daily global radiation received over the whole country is nearly 450 Langleys. Peak values are generally measured in April or May. The parts of Rajasthan and Gujrat receiving monsoon and winter months, the daily global radiation decreases to about 300 to 400 langleys.

Here it is observed that annual average diffuse radiation received over the whole country is around 175 langleys. The maximum values measured over the whole country is 350 langleys in Gujrat in July.

1.3 VARIOUS CONVERSIONS [2,4] :

Scientists began to think of using this abundent solar energy in day-to-day life. They invented new ways of converting this energy so as to use it for the benefit of mankind. There are different ways of converting the solar energy into various forms as -

Solar Energy Utilization

- Direct Method
  - Thermal
  - Photovoltaic
- Indirect method
  - Water Power
  - Wind
  - Biomass
  - Ocean Temp. Differences

In photovoltaic conversion the solar energy is directly converted to electricity with the help of solar cells. Water storage is used to generate electricity. Wind energy is used to generate electricity as well as to pump water. Biomass is used for combustion and for production of biogas. The temperature differences in ocean are also useful for generation of electricity.

The thermal energy of Sun is very much useful since ancient times. Man is using this energy mainly for drying food products. But there are many uses of this thermal energy from Sun. It is being used for water heating systems, generation of low and high pressure steam etc. Different types of collectors, concentrators are being used for this purpose. Various materials are also being tried to make more efficient use of this thermal energy. The photothermal conversion is nothing but conversion of heat energy from solar radiation into suitable applicable form.

1.4 THERMAL APPLICATIONS OF SOLAR ENERGY :

The various applications of thermal energy of Sun are briefly summerise below [2,4].

1.4.1 Water Heating :

Water heating is one of the most attractive applications from an economic stand point. Two main components of such system are the liquid flat plate collector and the storage tank. The tank is located above the level of the collector. Here natural circulations of water occurs. Small capacity domestic solar water heaters are also available in simpler designs in which the functions of collector and storage tank are combined in one unit.

When large amounts of hot water are required, a natural circulation system is not suitable. Large arrays of flat plate collectors are then used and forced circulation is maintained with a water pump. Also a provision is made for auxiliary heater. System of this type are well suited for places like hospital, hostels, hotels, offices and factories.

1.4.2 Space Heating :

In such systems the energy is transferred to air circulating in the house by means of water to air heat exchanger. Here two pumps provide forced circulation between the collectors and the tank and between the tank and heat exchanger. Here also provision is made for auxiliary heater. We have active direct heating and also passive indirect heating systems.

1.4.3 Power Generation :

Solar thermal energy can also be used to generate electrical power. Solar thermal power cycles can be broadly classified as low, medium and high temperature cycles. Low temperature cycles generally use flat plate collectors so that maximum temperature are limited to 100°C. Medium temperature cycles work at maximum temperature ranging from 150°C to 300°C. While high temperature cycles work at maximum temperature above 300°C. Here for low and medium temperature ranges, thermodynamic cycle preffered in the Rankine cycle for the high temperature range the Bryton and the Stirling cycle are also being considered.

1.4.4 Space Cooling and Refrigeration :

It is also one of the most promising thermal application of solar energy. Since the energy of the Sun is being received as heat, the obvious choice is a system working on the absorption refrigeration cycle which requires most of its energy outputs as heat. We require cooling mostly in summer. Hence in this case, there is seasonal matching between the energy needs of refrigeration system and availability of solar radiation.

1.4.5 Distillation :

In many small communities the natural supply of fresh water is inadequate, but brackish or saline water is available. Solar distillation is an effective way of supplying drinking water to such communities. Here the store basin of water is lined with black impervious material.

1.4.6 Drying :

One of the traditional uses of solar energy has been for drying of agricultural products. It removes moisture and helps in preservation of the product. The drying process on open ground is slow and that insects and dust get mixed with the product. Thus use of solar dryers helps to eliminate these disadvantages. Drying can be done faster and in a controlled fashion. Also a better quality of product is obtained.

1.4.7 Cooking :

It is an important domestic thermal application of solar energy. Different types of solar cookers are being designed and used all over the world.

From above discussion it is clear that the solar thermal energy has a treamendous value.The economic and efficient utilization of thermal energy derived from solar radiations require an efficient and low cost solar `selective coating' or `selective surface' as an absorber. An efficient selective surface is defined as a surface having a high absorptance 'α' over the solar spectrum (0.3 µm to 2 µm) and in addition also having a low emittance `ϵ' to reduce thermal radiative heat losses. A parameter that has been used to characterize a solar selective surface is the ratio of solar absorptance 'α' to the thermal emittance 'ϵ' i.e. α/ϵ. We can increase the efficiency either by increasing α or by decreasing ϵ. But here an increase in α is more effective in improving the operating efficiency than a corresponding derease in ϵ.

Hence if a surface is to be used as an absorber for the solar thermal energy, is coated with a suitable coating called selective coating then the efficiency of that absorber increases. Thus a selective coating plays an important role in photothermal conversion of solar energy.

1.5 SELECTIVE COATING [3,4] :

The key requirement of an efficient solar absorbing coating is the spectral selectivity. A surface whose optical properties of absorptance, reflectance and emittance vary in the solar and thermal Infra Red regions, is termed a spectrally selective surface. It should have an abrupt transition between low and high reflectance regions around 2 μm, which is approximately the limit of solar spectrum. A practical selective surface should be stable at the operating temperature and must have a long life and low fabrication cost. The various types of absorber surfaces are intrinsic absorbers, absorber reflector tanelems, multilayer interference stacks, powdered semiconductor reflector combinations, optical trapping system, composite material films and quantum size effects.

We are going to study the photothermal applications so we require a good absorbing material.

In absorber reflector tendems, a coating having high absorptance at solar wavelengths i.e. it is black but it is transparent to long wavelengths radiations, is deposited onto a highly Infra Red reflecting metal substrate like aluminum, copper, silver, steel etc. Therefore the system has high solar absorptance due to black exterior deposits and low thermal emittance due to the metallic reflector substrate.

For high solar absorptance, a material with as low refractive index as possible is required. This requirement is easily met out by a semiconductor for which the fundamental absorption edge is located in the proper spectral range.

We can have a number of such black selective coating e.g. black nickel, black chrome, black copper, black iron, cobalt oxide, tungsten oxide etc.

Many more workers [5-45] have studied different selective surfaces such as Black nickel, Black chrome, Black copper, Black iron, Cobalt oxide, Tungstan oxide etc. They have used different methods to prepare the layers or films of these materials. All these are reffered. The methods used were sparying, chemical conversion, electroplating, electrolyte bath, etching etc.

The various types of selective coatings are summerised below in brief.

1.5.1 Intrinsic Materials

There is no material occuring in nature which exhibits ideal solar selective proportional. There are of course some having approximate selective properties. The intrinsic solar selective properties can be found in two types of materials, i) Transition metals and ii) semiconductors for each one to serve as an intrinsic absorber would mean that it would have to be greatly modified. In general metals exhibit a plasma reflection edge at abount 0.3 micrometer, which can be shifted towards the Infra Red by creation of internal scattering centers e.g. MoO_3, HfC, lanthanum hexaboride LaB_6 etc. Hafusum Carbida (HfC) has different reflections in different parts of spectrum. It has high reflectance in the thermal Infra Red region and high absorptance in solar regions. For HfC thermal emittance is about 0.10 and solar absorptance of about 0.65. For successful and efficient use in photothermal conversion of the solar radiations, absorptance should be more than this and the transition from low reflectance to high reflectance should be steep. Perhaps these characteristics can be achieved either by some structural or compositional changes in the lattice of HfC or by coating it with a quarter wave of dielectric material. HfC selective surface is useful as an absorbing surface at elevated temperatures, because of its high melting point.

1.5.2 Absorber Reflector Tandems

In absorber reflection tandems a coating having high absorptance at solar wavelengths (i.e. the coating is black but is transperent to long wavelength radiations) is deposited on to a highly Infra Red reflecting substrate e.g. aluminium, copper, silver, steel etc. Therefore the system has high solar absorptance due to black exterior deposits and low thermal emittance due to the metallic reflector substrate. High absorption of the exterior coating may be either intrinsic in nature or geometrically enhanced or may be combination of two. Generally these black coatings are semiconductor in nature and their absoption is a result of interaction of photons having energies greater than band gap. Therefore the coatings absorb the photon as a result of raising the materials valence electron into the conduction band and the photons of less than band gap energy are transmitted through the material unaffected.

In brief a good absorber reflector tandem should meet the following requirements -

Solar Range	Absorber	$Kd > 1$ and $n < 2$
	Reflector	$0.1 < R < 0.6$
Thermal Range	Absorber	$Kd \approx 0$ and n can have any value
	Reflector	$R \approx 0$

where d is absorber thickness, n and k are optical constants, R is reflectance. The examples of such tandems are Black nickel, black chrome, black copper, black iron, cobalt oxide, tungston oxide etc.

1.5.3 Conversion Coatings

Chemically converted coatings are generally used for the decorative purposes. They are easy to produce, low in cost and have wide availability. Several researchers investigated solar selective properties of coloured stainless steel, copper oxide, copper sulphide, chromate and chloride conversion of zinc and ALCOA 655 coating. The chemical conversions were made by the same standard solutions available in the market e.g. copper sulphide, coloured stainless steel, selective coatings. ALCOA 655 selective surface etc.

1.5.4 Pure Semiconductors

The spectral selectivity can be obtained from an absorber reflector tandem by overcoating an opaque metal having thermal Infra Red reflectance with a thin film of semiconductor having an energy band gap from about 0.5 eV (25 μm) to 1.26 eV (1.0 μm) which would absorb solar radiations but is transperent to Infra Red radiations. Such materials include Si (1.1 eV), Ge (0.7 eV) and PbS (0.4 eV) semiconductor materials. They have high refractive indices 'n' which give high reflectivities at air or semiconductor interface e.g. PbS (n=4.1) in vacuum has a normal reflectance about 40%. The reflection coefficient can also be reduced by proper thickness control to get destructive interference at solar maxima. The reflection coefficient can also be reduced by making a thin film of high porosity or by the application of antireflection coating. In the gas evaporation technique, for the porous deposits, the material is deposited in a gas atmosphere (0.1-1.0 torr) sufficient to cause vapour phase nucleation of very fine particles (100-500 Å) e.g. silicon and germanium, PbS-Lead sulphide.

1.5.5 Metal Silicide and Carbide Solar Selective Surfaces

Harding studied in detail the solar selective properties of D.C. relatively sputtered metal carbide and metal silicide film on metals. Similarly Blickensderfor et al studied RF reactively sputtered metal carbide and metal nitride surfaces. The refractory nature and low vapour pressure of metal carbides and metal silicides enhances the stability at high temperature of these selective surfaces. The iron, steel, tungston, chromium etc. by D.C. reaches sputtering of pure metals or metal mixture in a gas mixture containing 2% methane or silane in argon. The films were sputtered under a pressure of 35 Pa with cathode voltage 1 kV current density 20 A/m^2 and a deposition rate 0.04 m/min on bulk copper substrate.

1.5.6 Powdered Semiconductor Reflector Combinations

This category is a subclass of absorber reflector tandems described in previous section. In this type the particular semiconductor coating is dispersed or deposited onto a highly reflecting substrate. The feasibility of this type of coatings was first demonstrated by Williams, Lappin and Duffic in 1963. They prepared PbS coating consisting of semiconducting particles suspended in an appropriate vehicle. These coatings have various advantages such as ease of application of fabrication, low cost, large area availability and environmental durability. Several authors have investigated solar selective properties of semiconductor, inorganic metal oxides, organic blacks and metal dust pigmented selective paints. Extensive research was carried out at Honeywell Corporation USA on paint coatings e.g. semiconductor pigmented selective coating paints, Inorganic metal oxides pigmented selective paints, organic black pigmented selective paints, metal dust pigmented selective paints.

1.5.7 Multilayer Interference Stacks

In absorber reflector tandems the selective effect is caused by single pass through the optically active medium or the return pass after reflection by underlying mirror surface respectively. However in case of multilayer interference stack the dielectric layer of the stack sandwiched between semitransperent and totally reflecting surface. Saraphin prepared such an interference stack. It depicts a four layer interference stack comprised of two quarterwave dielectric layers separated by thin semitransperent film. In this case it is not necessary for dielectric layer to have intrinsic absorption for the stands to be an effective absorber. The first layer corresponds to the reflectivity of metal layer which has high reflectance in Infra Red region and slightly less reflectance in visible region. By the addition of second layer of dielectric material, the reflectance in the visible region is found to be reduced and the shape and the position is dependent on the thickness of dielectric layer. The further addition of third semitransperent metal layer reduces the reflectance in the visible region. The final fourth dielectric layer increases the absorption in the visible region and broadens the region of high absoption.

1.5.8 Optical Trapping Systems

Surface texturing is a common technique to obtain wavelength descrimination optical trapping of solar energy. Properly textured surfaces appear rough and absorbing to solar energy, while appearing mirror like and highly reflective to thermal energy. Tabor in 1957 proposed a method of enhancing the solar absoptance almost to unity by corrugating the surface into series of 'Vs'. The surface would consists of a dense forest of aligned needles whose diameters are of the order of visible wavelengths and the spacing between which is several wavelengths. This surface would absorb solar radiations with high efficiency because of multiple reflections as the incident photons penetrate the needle maze. In the corrugated surface reaction whose projection on the plane of the paper is normal to the folded surface suffers various interreflections. The radiations whose projected angle of incidence is 90° suffers only one reflection.

1.6 PURPOSE OF DISSERTATION :

Nowadays we are facing a problem of off supply, load shedding etc. more or less frequently because of shortage in production of electricity. Sometime the reason is given of less supply of coal to power stations. There are limitations on the supply from hydro electric power stations. Nuclear power stations are also facing the fuel problem. Also there is problem of its hazzardous waste. So it is need of the time to have environmentally clean and long lasting power stations which require low cost fuel input moreover free of charge input for them.

Solar thermal power stations can fulfill the above criteria. It is therefore required to develope Indegeneous technology for such power stations. For the efficient conversion of solar thermal energy some sort of good absorber is needed. We can have black nickel, black chrome, black copper, black iron, cobalt oxide, thugston oxide etc. as the selective absorber coatings. Out of these we have chosen cobalt oxide as it is cheap and stable even at high temperatures.

There are three well defined oxides of cobalt [46], namely cobaltous oxide CoO, Cobaltosic oxide CO_3O_4

and cobaltic oxide CO_2O_3. Cobaltous oxide is obtained when cobalt is burnt in oxygen or when oxygen is blown through the molten metal. It is also obtained by roasting the powder metal in air, by heating cobaltous hydroxide below 350°C in a current of hydrogen or by heating the hydroxide or carbonate in air. It varies in colour from greenish gray, red, brown to black according to method of preparation and size of grain. Cobaltous hydroxide $Co(OH)_2$ is precipitated when potassium hydroxide is added to a solution of cobaltous salt out of contact with air as blue is considered to be $CoOH_2O$ and the rose $Co(OH)_2$, the latter gradually turns brown in contact with air forming cobaltic hydroxide $Co(OH)_3$. Cobaltosic oxide is formed superficially when metallic cobalt is heated in air or by heating cobaltic oxide or hydroxide in air; when the product is heated in hydrogen it is reduced first to cobaltous oxide and then to metal. Cobaltic oxide is formed when a concentrated solution of cobaltous chloride mixed with potassium chlorate is evaporated to dryness, heated to a temperature of about 250°C and then extracted with water. On heating to 265°C it decomposes leaving Co_3O_4 and at a high temperature yields CoO. Impure forms of hydrated cobatic oxide are found in various minerals and the oxidation of cobaltous salts in acid or alkaline solutions yields these compounds, the composition of the hydrate depending on the concentration and temperature of the solution and nature of the oxidising agent used. The preparation of a number of definatre hydrates has been reported including $3Co_2O_3$ $2H_2O$; Co_2O_3 H_2O; $2Co_2O_3$ $3H_2O$; $3Co_2O_3$ $5H_2O$; Co_2O_3 $2H_2O$; Co_2O_3 $3H_2O$.

Cobaltous oxide is used for the preparation of the salts of cobalt and also smart the glass obtained by heating the oxide with certain fluxes such as sand. It is also used by enamellers and porcelain manufacturers for the production of finest blue glaze and colour or porcelain glass and other vitrifiable substances. The presence of 1/2000 of oxide imparts a bluish tinge to clear glass. The presence of other oxides has an injurious effect on the colour produced by this substance, it is therefore necessary for the more delicate work, to ensure its complete freedom from such impurities.

When heated with magnesia it produces a pink mass; with alumina a fine blue (Thenard's blue) and with zink oxide a green (Rinmann's Green). Zaffre is obtained by heating a mixture of roasted cobalt ore with sand to a temperature below the melting point.

Some aspects of effects of Co_3O_4 and Sb_2O_3 influence on $ZnO-Bi_2O_3$ sintering behaviour, which are important for the characterization of ZnO varistors were studied by M.S. Castro et al. [47]. Cobalt oxide can form alloys with strontium, iron. A thermogravimetric study of the phase diagram of strontium cobalt iron oxide $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$ were studied by L.M. Liu, T.H. Lee etc. [48].

In the present investigations it is planned to develope cobalt oxide coating in the form of thin film on Cu, Al, St.Steel substrates by spray pyrolysis technique. The different preparative parameters will be optimised. The films will be studied for structural and optical properties. It's applications as solar thermal absorber will be studied.