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Thermo-Physical Properties of CaO-Fe_2O_3 Binary Mixture and its Application in the Field of Nuclear Reactor as Simulant Material

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Abstract: ***The simulant materials play important role in the melt coolability experiments to understand the actual scenarios of core melt accidents in the field of nuclear reactor. Simulant materials are generally oxide/ceramics materials which have the properties similar to the properties of corium (mixture of UO_2, ZrO_2, Zr alloy, Fe, Ni and Cr etc.). This work was carried out to determine the thermo-physical properties of CaO-Fe_2O_3 binary mixtures of different ratio of CaO and Fe_2O_3 (23C77F, 26C74F, 29C71F, 32CF68 and 35C65F; here the ratio is in the wt% and C for CaO and F for Fe_2O_3) and compare the properties of CaO-Fe_2O_3 with the properties of corium. It was observed that the thermo-physical properties of CaO-Fe_2O_3 binary mixture are close to the properties of corium, so it can be said that this material is simulant material. In this research work, thermal behavior of CaO-Fe_2O_3 was also carried out using differential scanning calorimetry (DSC). The simulant material CaO-Fe_2O_3 can be used in the melt coolability experiment to understand the phenomena that happened during the core melt accidents in the nuclear reactor.***

Keywords: ***simulant materials, melt-coolability, corium, CaO-Fe_2O_3 binary mixture, thermo-physical properties.***

I. INTRODUCTION

The nuclear industry plays an important role in the energy production. The nuclear industry adopts advanced techniques to avoid any type of incidents, but the severe accidents is major threat when it happens. The multiple safety system fails and leads to the melting of reactor core during the severe accidents. The reactor core melts and relocated at the lower head of in-vessel. If it is not cooled at time, the molten mass attack the wall of the in-vessel due to the unavailability of coolant. The molten mass released in to ex-vessel with high amount of coolant and lead to the generation of steam that increases the pressure and may lead to steam explosion.

The various techniques are used to mitigate and termination of the severe accident. The melt-coolability experiments are used to understand the phenomena of core melt accidents. The three types of quenching techniques are used in the melt-coolability experiments namely, top flooding, indirect cooling and bottom flooding [1]. In the melt-coolability experiments, simulant materials are used to simulate the phenomena that are occurred in the nuclear reactor during core melt accidents. The ceramics/glass type materials such as sodium borosilicate glass, CaO-B_2O_3, CaO-TiO_2, Bi_2O_3-TiO_2 and CaO-WO_2 etc. were used in the past melt coolabilityexperimets [2-5]. The simulant material is the material which have the thermo-physical properties similar or close to the properties of corium. Corium is the mixtures of materials issued form the molten core at very high temperature. The corium consists of UO_2, ZrO_2, Zr, and in small amounts of Ni, Cr, Ag, Fe, In, Cd [6]. The complex physical and chemical phenomena took placed during the nuclear severe accident. To simulate these phenomena, various types of simulant material has been used in the previous research. Low temperature simulant material used by CORIME [7], Scaled Simulant Spreading Experiments (S3C) [8], and BALI [9-10] due to lower costs and constraints. Some experiment like KATS [11] or COMET facilities [12], used high temperature simulant materials (alumina and thermite) to simulate real corium phenomena. CEA [13] has taken a large program on severe accident with using prototypic corium. The prototypic simulant material has also been used in past research in the experiments like COMAS [14], FARO-KROTOS [15], MACE [16], and COTELS [17]. So, simulant material (non-prototypic and Prototypic) are used to understand the real phenomena by melt coolability experiments during the core melt accidents.

In this research work, the thermo-physical properties (melting point, density, specific heat capacity, thermal conductivity, thermal diffusivity and heat of fusion) of CaO-Fe_2O_3 binary mixture with various ratio by wt.% (23C77F, 26C74F, 29C71F, 32C68F and 35C65F) was calculated. The powder of CaO and Fe_2O_3 was mixed in mortar and pestle for 35-40 minutes. Then, the mixed material was characterized with differential scanning calorimetry. The melting point, heat of fusion and specific heat capacity of CaO-Fe_2O_3 binary mixture was determined using the DSC data. The thermal conductivity and density were calculated byusing the mixture rule. The thermal diffusivity was calculated using the thermal conductivity, density and specific heat capacity values of CaO-Fe_2O_3.

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All the thermo-physical properties of CaO-Fe_2O_3 binary mixture were observed close to the properties of corium. So, the CaO-Fe_2O_3 binary mixture can be used in the melt coolability experiments to simulate the scenario of severe accident.

II. MATERIALS AND METHODOLOGY

The CaO and Fe_2O_3 powders were mixed in the mortar and pestle and prepared five sample using various ratio of CaO and Fe_2O_3 (by wt.%) (23C77F, 26C74F, 29C71F, 32C68F and 35C65F; here, C for CaO and F for Fe_2O_3). Thermal behavior was determined of these powder mixtures by using differential scanning calorimetry.The DSC experiments was performed in the temperature range from room temperature to 1350°C with 10°C/minute heating rate in the nitrogen atmosphere. The weight of samples was taken 10 mg (for each sample) in the DSC experiments. The melting point, heat of fusion and specific heat capacity was determined using the DSC data. The formula [18] was used to calculate the specific heat capacity (Cp) was given below as

$$C_p = \frac{Q}{m.\Delta T} \quad \text{…. (1)}$$

Where, Q is the amount of heat required to increase the temperature the material, m is amount of material and ΔT is the temperature difference.

The density of CaO-Fe_2O_3 was calculated using following formulae (Gross et al. and Hirai formulae) [19].

$$\rho = \frac{x_{CaO}.M_{CaO}+(1-x_{CaO}).M_{Fe_2O_3}}{\left(\frac{x_{CaO}.M_{CaO}}{\rho_{CaO}}\right)+\left(\frac{(1-x_{CaO}).M_{Fe_2O_3}}{\rho_{Fe_2O_3}}\right)} \quad \text{….(2)}$$

Where, ρ = density of CaO-Fe_2O_3, kg/m^3,
x_{CaO} = mole fraction of CaO,
$x_{Fe_2O_3}$= mole fraction of Fe_2O_3,
ρ_{CaO} = density of CaO, kg/m^3,
$\rho_{Fe_2O_3}$ = density of Fe_2O_3, kg/m^3,
M_{CaO} = molecular mass of CaO,
$M_{Fe_2O_3}$ = molecular mass of Fe_2O_3

El-Fakharany et al., (2012) has reported the thermal conductivity of CaO approximate 1.5 W/mK [20] and Takeda et al., (2009) has reported the thermal conductivity of Fe_2O_3 approximate 3 W/mK [21]. the thermal conductivity of CaO-Fe_2O_3 was calculated using Gross et al. and Hirai formulae that is given below [19].

$$Thermal\ conductivity, k = x_{CaO}.k_{CaO} + x_{Fe_2O_3}.k_{Fe_2O_3} - 0.72(x_{CaO}.x_{Fe_2O_3})$$

Where, k = thermal conductivity, W/mK,
k_{CaO} = thermal conductivity of CaO, W/mK,
$k_{Fe_2O_3}$ = thermal conductivity of Fe_2O_3, W/mK,
x_{CaO} = mole fraction of CaO,
$x_{Fe_2O_3}$ = mole fraction of Fe_2O_3,
The thermal diffusivity of CaO-Fe_2O_3 (26:74 by wt.%) was calculated using the following equation. [20]

$$\alpha = k/(\rho.Cp)$$

Where, α = thermal diffusivity, m2/s,
ρ = density, kg/m3,
C_p= Specific heat capacity, J/kg.K,

$$Thermal\ conductivity, k = x_{CaO}.k_{CaO} + x_{Fe_2O_3}.k_{Fe_2O_3} - 0.72(x_{CaO}.x_{Fe_2O_3})\left|k_{CaO} - k_{Fe_2O_3}\right|$$

… (3)

Where, k = thermal conductivity, W/mK, k_{CaO} = thermal conductivity of CaO, W/mK, $k_{Fe_2O_3}$ = thermal conductivity of Fe_2O_3, W/mK, x_{CaO} = mole fraction of CaO, $x_{Fe_2O_3}$ = mole fraction of Fe_2O_3.
The thermal diffusivity of CaO-Fe_2O_3 was calculated using the following equation [22].

$$\alpha = k/(\rho.C\_p) \quad \text{….. (4)}$$

Where, α = thermal diffusivity, m_2/s,
ρ = density, kg/m3,
C_p= Specific heat capacity, J/kg.K,

III. RESULTS AND DISCUSSION

The study of thermal behavior of CaO-Fe_2O_3 with different composition was carried by using the differential scanning calorimetry as shown in figure 1. The five sample of CaO-Fe_2O_3 of different composition was study using the differential scanning calorimetry. the melting point of CaO-Fe_2O_3 mixture was increased with increasing the ratio of CaO and decreasing the ratio of Fe_2O_3. The sample 23CaO-77Fe_2O_3 (by wt.%) have shown the melting point around the 1212°C and the melting point of 35CaO-65Fe_2O_3 (by wt.%) was observed around 1218°C. The melting point of 29CaO-71Fe_2O_3(by wt.%) was observed around 1214°C. The variation in the melting point was observed more or less same. There is not much difference in the melting point peak. These peaks are peak where melting of material was started. The material was taken much heat to complete melting with increasing the amount of CaO and decreasing the amount of Fe_2O_3.

The heat of fusion was increased with increasing the ratio of CaO in the CaO-Fe_2O_3 binary mixture. The heat of fusion of the material is area under the melting peak in the DSC curve. It is confirmed from the figure 1 that the area under the melting peak was increased with increasing the ratio of CaO powder, so heat of fusion of the material was increased. The heat of fusion of 23CaO-77Fe_2O_3 (by wt.%), 26CaO-74Fe_2O_3 (by wt.%), 29CaO-71Fe_2O_3 (by wt.%), 32CaO-68Fe_2O_3 (by wt.%) and 35CaO-65Fe_2O_3 (by wt.%) was found around 101 J/g, 104 J/g, 119 J/g, 133 J/g, and 157 J/g, respectively, as shown in the table 1.

The specific heat capacity of 23CaO-77Fe_2O_3 (by wt.%), 26CaO-74Fe_2O_3 (by wt.%), 29CaO-71Fe_2O_3 (by wt.%), 32CaO-68Fe_2O_3 (by wt.%) and 35CaO-65Fe_2O_3 (by wt.%) was also calculated by using equation (1) and DSC results and specific heat capacity was found around 974 J/kg.K, 1565 J/kg.K, 956 J/kg.K, 1460 J/kg.K, and 821 J/kg.K, respectively, as shown in the table 1. The specific heat capacity is heat that was absorbed by the material to increase 1°C temperature of 1 gram of material.

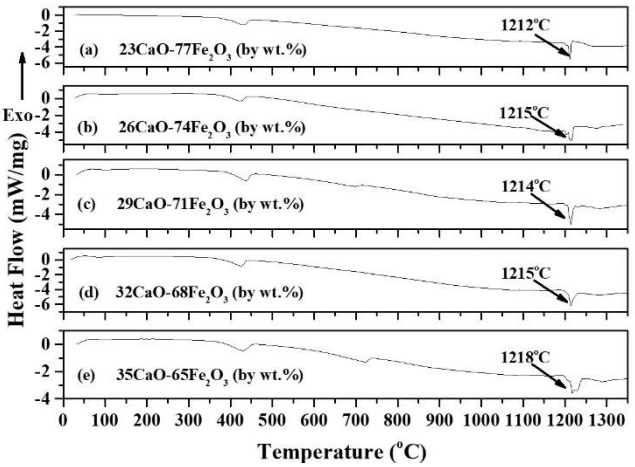

Figure 1. DSC curves for various composition of CaO-Fe_2O_3 binary mixture.

The density of the material was calculated using the equation (2). The density of CaO and Fe_2O_3 are 3.34 g/cm3 and 5.24 g/cm3, respectively. These values of density of CaO and Fe_2O_3 was used in the equation (2) to calculate the density of CaO-Fe_2O_3. The density of CaO-Fe2O3 was increased with increasing the amount of CaO, as shown in the table 1.

The thermal conductivity of CaO-Fe_2O_3 was calculated using the equation (3). Values of thermal conductivity of CaO and Fe_2O_3 was used to calculate the thermal conductivity of CaO-Fe_2O_3 mixture. The thermal conductivity of CaO-Fe_2O_3 was varied with the variation in composition of CaO and Fe_2O_3. The thermal conductivity of CaO-Fe_2O_3 was shown in the table 1. The thermal conductivity of this material decreased with increasing the ratio of CaO. The thermal conductivity of this material is very close to the thermal conductivity of corium.

The thermal diffusivity of CaO-Fe_2O_3 was also calculated theoretically using the equation (4). For the calculation of thermal diffusivity, values of density, specific heat capacity and thermal conductivity was used. The thermal diffusivity of CaO-Fe_2O_3 was observed close to thermal diffusivity of corium as shown in the table 1.

All the thermo-physical properties (melting point, density, specific heat capacity, thermal conductivity and thermal diffusivity) of CaO-Fe_2O_3 with different composition of CaO and Fe_2O_3 are close the properties of Corium [4, 23] and other simulant material CaO-B_2O_3 [4], sodium borosilicate glass [24] that were used in the past research of melt coolability. These thermo-physical properties of CaO-Fe_2O_3 was shown in table 1. The properties of CaO-Fe_2O_3 are more or less same for all the composition of CaO-Fe_2O_3 binary mixute. The material CaO-Fe_2O_3 is non-toxic, easily available, economical and easy to use at laboratory basis, so it can be used in the melt coolability experiments to simulate the actual melt coolability phenomena that occurs in the nuclear reactor during the core melt accidents or nuclear severe accidents.

IV. CONCLUSONS

The thermo-physical properties of CaO-Fe_2O_3 with different composition was carried out in this research work. The melting point, heat of fusion, and specific heat capacity of CaO-Fe_2O_3 were determined using differential scanning calorimetry. The density, thermal conductivity and thermal diffusivity were determined theoretically using mixture rule. All these thermo-physical properties were altered with increasing the ratio of CaO in the mixture of CaO and Fe_2O_3. These thermo-physical properties of CaO-Fe_2O_3 for all the composition that was used in present research work was observed more or less same and close to the properties of corium and other simulant material that was used in past research work. The material CaO-Fe_2O_3 binary mixture is also very useful to simulate the actual melt coolability phenomena of core melt accidents that were occurred in the nuclear reactor and it is a simulant material as corium.

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Table- I: Thermo-physical properties of $CaO-Fe_2O_3$ with respect to the properties of corium.

Properties	**23C77F**	**26C74F**	**29C71F**	**32C68F**	**35C65F**	**Corium (UO_2 + ZrO_3 mixture) (80:20 by weight)**
Density (kg/m^3)	4639	4571	4499	4424	4365	7450
Melting Point (^oC)	1212	1215	1214	1215	1218	2577
Specific heat capacity (J/kg.K)	974	1565	956	1460	821	410
Heat of fusion (J/g)	101	104	119	133	157	----
Thermal conductivity (W/m.K)	2.04	1.98	1.92	1.87	1.82	2.5
Thermal diffusity (m^2/s)	4.51×10^{-7}	2.77×10^{-7}	4.46×10^{-7}	2.89×10^{-7}	5.10×10^{-7}	8.18×10^{-7}