

Effect of Air-quenching on properties of CaO-Fe₂O₃ and CaO-B₂O₃ simulant materials for nuclear reactor

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Abstract—In present study, the effect of Air-quenching on the properties of CaO-Fe₂O₃ (22:78 by wt. %) powder mixture and CaO-B₂O₃ (30:70 by wt. %) powder mixture was discussed. These materials are used in the nuclear industry as simulant material to study the melt coolability behavior. This study was carried out in order to development of CaO-Fe₂O₃ as a simulant material. The CaO-Fe₂O₃ and CaO-B₂O₃ powder mixture are melted in the Bottom pouring electric furnace then quenched in air. The quenched material have characterized through Field Emission Scanning Electron Microscopy (FE-SEM) with Energy-Dispersive X-Ray Spectroscopy (EDS), X-Ray Diffraction analysis (XRD), and Differential Scanning Calorimetry (DSC) analysis. The FE-SEM was used to study the morphology of the material after air quenching. The particles size analysis of air quenched material was performed macroscopically. The elemental analysis was carried out through the Electron Diffraction Spectroscopy. XRD analysis was carried out to determine the phases after air quenching. The density and porosity of these materials also have been calculated using Archimedes principle.

Keywords—Air-quenching, CaO-Fe₂O₃, CaO-B₂O₃, particle size and porosity.

1. INTRODUCTION

DURING the severe accident, the core is melt down and relocated in the lower head of ex-vessel. After failing the ex-vessel, the melt interacts with the environment. This interaction between the melt and environment is cause of spread radiation, steam explosion and high pressure containment. In the nuclear power plant, it is necessary to ensure the safety against severe accident [1, 2]. To mitigate and stabilization of severe accidents, it is necessary to understand the phenomenon of melt coolability. Many researchers have studied so far with the simulant material on the problem of severe accident to understand actual mechanism behind the melt coolability. The simulant materials (materials have properties similar as the properties of corium) are used in melt coolability experiments to understand quenching behavior. Some simulants materials like NaNO₃-KNO₃ salt, CaO-B₂O₃, Cerreband have been used in RIT experiment [3, 4]. The melt coolability experiment KAPOOL and KAJET have used thermite as simulant materials. The DEFOR test at KTH used CaO-B₂O₃, WO₃-Bi₂O₃, MnO-TiO₂, Bi₂O₃-TiO₂ and Bi₂O₃-CaO as simulant materials [5]. Kulkarni et al. in 2014 have performed some experiments using sodium borosilicate glass as a simulant material [6]. Singh et al. in 2015 also used sodium borosilicate glass as simulant materials. He also used CaO-B₂O₃ and sodium borosilicate glass as simulant material in 2017 [7, 8]. Among them some materials are toxic or some materials are non-toxic. The CaO-B₂O₃ is non-toxic, economical, and user friendly [9]. This work is studied on the thermal and physical properties of CaO-Fe₂O₃ before and after air quenching. This study is performed for confirming that CaO-Fe₂O₃ is simulant material. So, it can be used in the melt coolability experiment. During heating above 1100°C, CaO and Fe₂O₃ completely take place and an unstable phase CaFe₁₂O₁₉ is present [10]. CaO and Fe₂O₃ can be react and form CaO-Fe₂O₃ (CF) and 2CaO.Fe₂O₃ (C2F). If the Fe₂O₃ is excess, the C₂F and Fe₂O₃ form CaO.Fe₂O₃ (CF) by reaction. The ΔG_T^θ of Fe₂O₃-CaO System can be calculate using equation ($\Delta G_T^\theta = A + BT, J/mol$) [11, 12].

In this research work, two powder mixture, one is CaO-Fe₂O₃ (22:78 by wt. %) and CaO-B₂O₃ (30:70 by wt. %) are prepared with the help of is CaO-Fe₂O₃ and CaO-B₂O₃ binary phase diagram [13, 14, 15]. Above materials are melted and quenched at fast cooling rate in air. Both powder mixtures are analyzed through SEM, EDS, XRD, and DSC before and after air quenching. Scanning electron microscopy with energy-dispersive x-ray spectroscopy is used for morphological study as well as for elemental analysis. Phase analysis is carried out through X-Ray powder diffraction analysis. Differential scanning calorimetry (DSC) analysis is used to know the thermal behavior of the material. Archimedes 'principle is used for the calculation of density and porosity of the material after air quenching. This study showed the effect of air quenching on thermal and physical properties (melting



point, activation energy, phases, microstructure, crystal structure, density, porosity and particle size) of materials $\text{CaO-Fe}_2\text{O}_3$ (22:78 by wt. %) and $\text{CaO-B}_2\text{O}_3$ (30:70 by wt. %).

MATERIAL AND METHODOLOGY

Here, two powder mixtures $\text{CaO-Fe}_2\text{O}_3$ (22:78 by wt. %) and $\text{CaO-B}_2\text{O}_3$ (30:70 by wt. %) are formed with the help of phase diagram of $\text{CaO-Fe}_2\text{O}_3$ and $\text{CaO-B}_2\text{O}_3$, respectively. [13, 14, 15] The individual powder of CaO and Fe_2O_3 was taken and mixed in the mortar for 30-40 minutes. Again, CaO and B_2O_3 were taken in the form of powder and mixed in the mortar. Then these powder were prepared.

These powder mixture are poured into the crucible of bottom pouring furnace. Then the material is melted above its melting point. After melting, the melt poured into the crucible in open atmosphere and allowed to quench in air. This procedure followed for both materials $\text{CaO-Fe}_2\text{O}_3$ and $\text{CaO-B}_2\text{O}_3$ powder mixture. The flow diagram of experimental procedure is shown in Fig. 1.

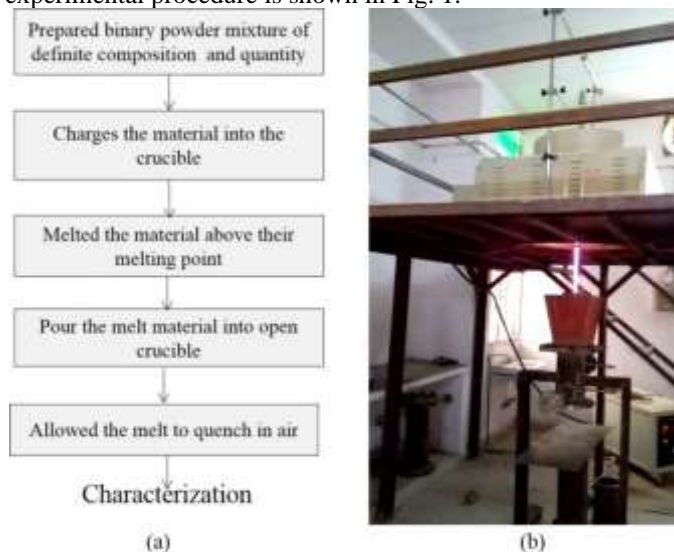
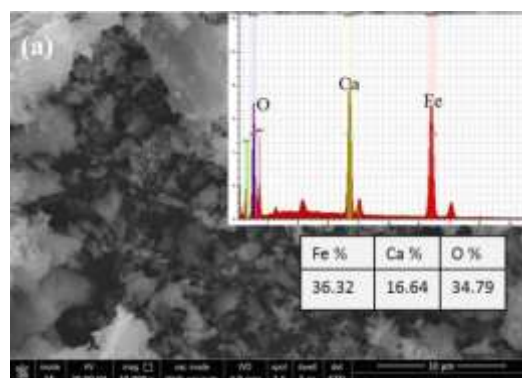


Fig. 1 Flow chart of (a) experimental procedure (b) actual test facility

RESULTS AND DISCUSSION

The morphological studies of $\text{CaO-Fe}_2\text{O}_3$ and $\text{CaO-B}_2\text{O}_3$ before and after air-quenching carried out through FE-SEM. The FE-SEM images of these materials is shown in Fig. 2. The SEM results give the confirmation of transformation of old phases into other new phases. During the process of heating, some unstable phases are formed with increasing temperature like $\text{CaFe}_{12}\text{O}_{19}$ [10]. Elemental analysis is carried through EDS. The results of EDS also attached with SEM image. Fig. 2(a) and 2(c) showed the SEM and EDS analysis for $\text{CaO-Fe}_2\text{O}_3$ and $\text{CaO-B}_2\text{O}_3$ powder mixture, respectively.



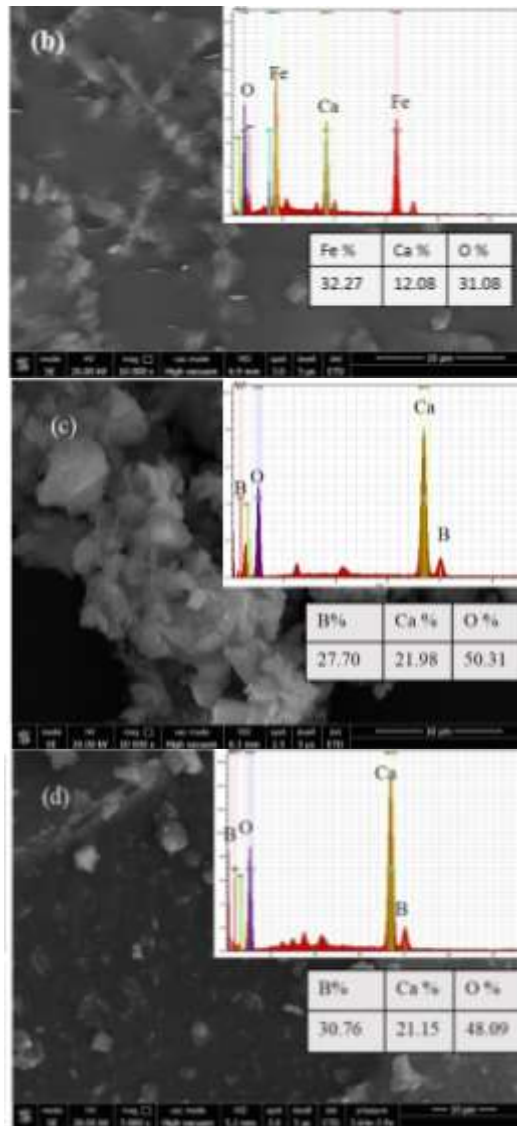


Fig. 2 SEM images for (a) CaO-Fe₂O₃ powder mixture (b) Air quenched CaO-Fe₂O₃ (c) CaO-B₂O₃ powder mixture (d) Air quenched CaO-B₂O₃

In the case of CaO-Fe₂O₃ powder mixture, the particles of two phases CaO and Fe₂O₃ are uniformly present [Fig. 2(a)], but after air quenching, these phases are changed in to new phases like CaFe₂O₄ and CaFe₄O₇ shown in Fig. 2(b). The particles of these new phases arranged in the form of 'plus sign' which is shown in Fig. 2(b). In the case of CaO-B₂O₃, The CaO and B₂O₃ changed in to new phases CaB₂O₄ and CaB₄O₇ after air quenching. These phases are shown in Fig. 2(d).

The macroscopically particles size measurement of air quenched CaO-Fe₂O₃ and air quenched CaO-B₂O₃ was shown in Fig. 3. The particles size range of CaO-Fe₂O₃ is from 1cm to 4.5cm. The particles of CaO-Fe₂O₃ are black with slightly yellow shining in color. The particle size range of CaO-B₂O₃ is from 0.5cm to 4.5cm. The particles of CaO-B₂O₃ are gray in color.





Fig.3 The particles size for both Air quenched (a) $\text{CaO-Fe}_2\text{O}_3$ and (b) $\text{CaO-B}_2\text{O}_3$

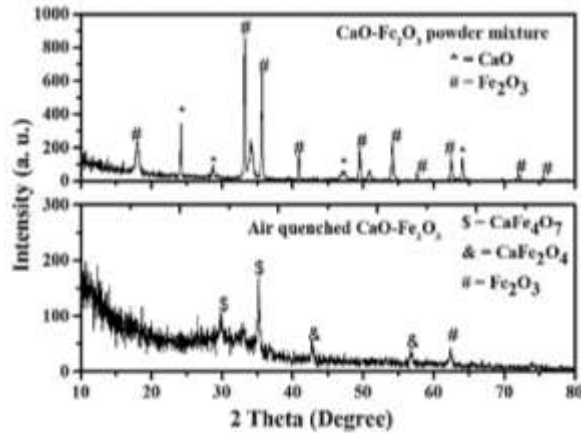


Fig. 4The XRD result of $\text{CaO-Fe}_2\text{O}_3$ for air quenched and powder mixture samples.

The formation of new phases was confirmed by XRD analysis which is shown in Fig. 4. In the case of $\text{CaO-Fe}_2\text{O}_3$ powder mixture, only two phases CaO and Fe_2O_3 were present which have cubic and rhombohedral crystal structure, respectively, but after air quenching, these phases were changed into two new phases CaFe_2O_4 and CaFe_4O_7 having orthorhombic and monoclinic crystal structure, respectively. Mohammad et al. also reported the formation of CaFe_2O_4 from the mixture of CaO and Fe_2O_3 [16]. In the case of $\text{CaO-B}_2\text{O}_3$ powder mixture, two phases CaO and B_2O_3 were present having cubic and hexagonal crystal structure. After air quenching, these phases were completely changed into new phases CaB_2O_4 and CaB_4O_7 as shown in Fig. 5. These phases also have orthorhombic and monoclinic crystal structure, respectively. The formation of new phases take placed due to the rearrangement of atoms and changed in the value of d-spacing of materials.

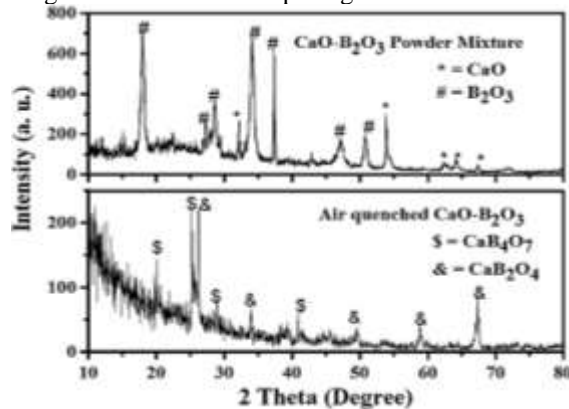


Fig. 5 The XRD result of $\text{CaO-B}_2\text{O}_3$ for air quenched and powder mixture samples

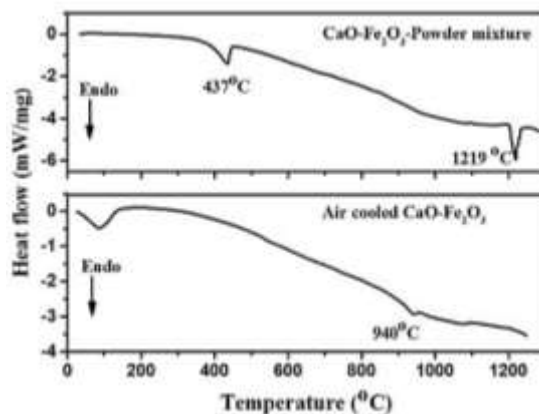


Fig. 6 DSC analysis of $\text{CaO-Fe}_2\text{O}_3$ for air quenched and powder mixture samples.

Thermal analysis of CaO-Fe₂O₃ powder mixture, air quenched CaO-Fe₂O₃, CaO-B₂O₃ powder mixture and air quenched CaO-B₂O₃ is carried out through DSC is shown in Fig. 6 and Fig. 7. The thermal scanning of these samples are carried with the help of instrument NETZSCH DSC 404F3, heating rate 10 K/minute, weight 10-15 mg, temperature range up to 1250°C for CaO-Fe₂O₃, and temperature range up to 1050°C for CaO-B₂O₃. Here, we observed that the melting peaks and activation energies are changed after air quenched for both material CaO-Fe₂O₃ and CaO-B₂O₃. These changes have come due to the formation of new phases after air quenching. The activation energies of CaO-Fe₂O₃ powder mixture, air quenched CaO-Fe₂O₃, CaO-B₂O₃ powder mixture and air quenched CaO-B₂O₃ were calculated 15.710 KJ/mol, 14.275 KJ/mol, 13.385 KJ/mol and 13.377 KJ/mol respectively.

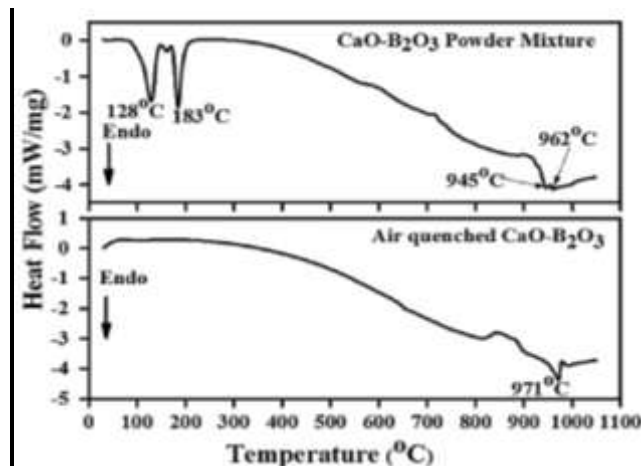


Fig. 7 DSC analysis of CaO-Fe₂O₃ and CaO-B₂O₃ for air quenched and powder mixture samples.

The density of powder mixture for CaO-Fe₂O₃ and CaO-B₂O₃ was calculated using mixture rule. The values of density for these material were found 4.825g/cm³ and 2.724g/cm³, respectively. After the air quenching, the material was reformed into irregular shape and size. The Archimedes principle was used for the calculation of density of these particles of irregular shape and size. The Archimedes principle states that the buoyant force on a submerged object is equal to the weight of the fluid that is displaced by the object. The average density of CaO-Fe₂O₃ and CaO-B₂O₃ after air quenching was calculated approximate 3.198g/cm³ and 2.075 g/cm³, respectively. Here, we observed that the density of both materials after air quenching have decreased. This was happened due to the ingression of air inside the material. It means that some pores are available inside the material. So materials have porosity or materials became porous after air quenching.

The percentage porosity also calculated using the Archimedes principle. The formula for the calculation of percentage porosity is given below. [17]

$$\text{Percentage Porosity} = \frac{\text{SG} - \text{BD}}{\text{SG}} \times 100$$

Where, SG = Specific gravity or real density is mass divided by solid volume

BD = Bulk density is mass divided by bulk volume

So, the percentage porosity of air quenched CaO-Fe₂O₃ and CaO-B₂O₃ were calculated using above formula around 38% and 42%, respectively. Here, we observed that air quenched CaO-B₂O₃ have higher porosity than CaO-Fe₂O₃. The water ingression capacity of CaO-B₂O₃ is higher than the CaO-Fe₂O₃. So, CaO-B₂O₃ is cooled faster than CaO-Fe₂O₃. [18] The properties of air quenched CaO-Fe₂O₃ and air quenched CaO-B₂O₃ have shown in table 1.

Table 1. Properties of Air quenched CaO-Fe₂O₃ and CaO-B₂O₃.

Properties	CaO-Fe ₂ O ₃ powder mixture	CaO-B ₂ O ₃ powder mixture	Air cooled CaO-Fe ₂ O ₃	Air cooled CaO-B ₂ O ₃
Activation Energy (kJ/mol)	15.710	13.385	14.275	13.377
Melting point (°C)	1219°C	~950°C	Above 1219°C	~971°C
Phases	CaO, Fe ₂ O ₃	CaO, B ₂ O ₃	CaFe ₂ O ₄ , CaFe ₄ O ₇	CaB ₂ O ₄ , CaB ₄ O ₇
Crystal Structure	Cubic, Rhombohedral	Hexagonal	Orthorhombic, Monoclinic	Orthorhombic, Monoclinic
Particles Sizes (cm)	powder	Powder	1 – 4.5	0.5 – 4.5
Average density (g/cm ³)	4.825	2.724	3.198	2.075
Porosity (%)	-----	-----	38	42

CONCLUSION

The study was carried out on the effect of air-quenching on the properties of powder mixture $\text{CaO-Fe}_2\text{O}_3$ (22:78 by wt. %) and $\text{CaO-B}_2\text{O}_3$ (30:70 by wt. %). In this research work, these material were quenched from the higher temperature above their melting point and new phases were formed after air-quenching. The formation of new phases confirmed from SEM analysis because the morphology of material altered. The macroscopically particle size analysis was carried out. After air-quenching, the particles size of $\text{CaO-Fe}_2\text{O}_3$ (22:78 by wt. %) and $\text{CaO-B}_2\text{O}_3$ (30:70 by wt. %) was found in the range 1-4.5 μm and 0.5-4.5 μm , respectively. CaO and Fe_2O_3 were changed into the new phases, namely CaFe_2O_4 and CaFe_4O_7 . The structure of initial phases also altered. CaO and B_2O_3 were also changed into CaB_2O_4 and CaB_4O_7 after air quenching. So the formation of new phases was also confirmed from the XRD results. Here, effect of air quenching is also found on density of the material. The melting point and activation energy of these materials were also changed after air-quenching that was confirmed through DSC analysis. The values of density of powder mixture $\text{CaO-Fe}_2\text{O}_3$ (22:78 by wt. %) and $\text{CaO-B}_2\text{O}_3$ (30:70 by wt. %) are 4.825 g/cm^3 and 2.724 g/cm^3 , respectively. These values of density were decreased to 3.198 g/cm^3 and 2.075 g/cm^3 after air-quenching, respectively. $\text{CaO-Fe}_2\text{O}_3$ have shown 38% porosity while $\text{CaO-B}_2\text{O}_3$ has shown 42% porosity after air-quenching. The quenching rate of $\text{CaO-B}_2\text{O}_3$ may be higher than the quenching rate of $\text{CaO-Fe}_2\text{O}_3$ because material have higher number of pores, so it can absorb more water. These binary system show the different thermal and physical properties after air quenching. These materials are very useful in the field of nuclear reactor to analysis the melt coolability phenomena as simulant materials.

ACKNOWLEDGMENT

I am very grateful of Bhabha Atomic Research Centre, Mumbai because the experimental facility is established of its help in the Department of Metallurgical and Materials Engineering, Malaviya National Institute of Technology Jaipur. I am working on the BARC funded project entitled "Quenching Behavior of Bottom Flooded Molten Pool" as a SRF. The fellowship is provided for me by Bhabha Atomic Research Centre, Mumbai

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