

Effect of composition on thermal stability and microstructural behaviour of non-prototype material (CaO-Fe₂O₃)

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ABSTRACT – The role of simulant materials becomes necessary for the predictive study of the nuclear severe accident phenomena due to its similarity with corium (a liquid form of UO₂ and steel). Since simulant material is eco-friendly and has similar properties to corium, it has been widely used in the research field of severe accident management. In this study, material CaO-Fe₂O₃ a non-eutectic binary mixture is considered for characterization purpose to address the thermophysical properties at different compositional ratios. The CaO-Fe₂O₃ powder mixture was prepared in mortar for 40 minutes manually to form a homogeneous mixture and then cylindrical pellets prepared at five different ratios with the help of the phase diagram. Further, these pellets were heat-treated at 1200°C for three hours soaking time to address its thermal stability in a programmable electric furnace. Finally, pellets ground into powder form manually for further characterization. Initially, the weight loss analysis was reported by measurement of dimensions of pellets before and after heat treatment. The thermal properties, phase analysis, and morphological studies have been carried out through DSC, XRD and FE-SEM in laboratory and results were discussed in the context of the property of ideal simulant materials used for the study of nuclear severe accidents. The melting point of all the samples were found stable (1200°C-1230°C) and values of activation energy and specific heat were well synchronized between with and without heat-treated samples. Dislocation density of samples increases significantly with increasing the proportion value of calcium oxide after heat treatment.

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INTRODUCTION

In the context of public safety, stabilization and termination of debris/molten pool become a necessary issue to a severe accident in a nuclear reactor. Despite the several efforts that have been made to investigate the severe accident phenomena, there is a still need for more such exercise to understand completely the actual phenomena occurred during a severe accident scenario [1]. In nuclear severe accidents, the formation of radioactive, highly corrosive, and high-temperature corium may lead to concrete layer ablation of base material resulting further interact with ground water. Various experiments have been carried with the support of prototype and non-prototype material. Some non-prototype materials are adversely used in the past scenario as a simulant material to study the severe accident [2]. The concept of melt coolability was validated by using up to hundred kilograms of simulant material and corium melt at Forschungszentrum Karlsruhe and Argonne National Laboratory in COMMET experimental series [3–7]. A simulant material CaO-B₂O₃ (30:70 by wt. %) was used in a simulated program named Core Melt Coolability (COMECO) to validate the simulation program MELCOOL for investigation of water ingress [8]. Another simulant material Bi₂O₃-WO₃ used in an experimental program called DEFORE-A test in which an assessment was done to predict the debris bed coolability in different scenarios of melt coolability [9].

The scope of the best simulant materials is still remaining for more comprehensive research to analyse the physical and thermal hydrodynamic phenomena that appeared during severe accidents. In this regard, another simulant material CaO-Fe₂O₃ is considered for the experiment. The application of simulant material depends upon the many factors because it has to be similar properties with corium (a liquid form of UO₂ and steel). Some investigations have been performed by previous researchers are discussed further. The analysis of thermophysical properties of CaO-Fe₂O₃ at different temperature and time have been conducted and found similar to that of corium [10]. Recently, an effect of air quenching of simulant material (CaO-Fe₂O₃ and CaO-B₂O₃) on its properties have been reported that the morphology, phases and thermal properties altered when heat treated at different temperatures [11, 12]. The observation of crystallization and structural behaviour of the molten CaO-Fe₂O₃ system [13, 14] investigated under different chemical composition and cooling rates were found that the iron atoms become more tetrahedral with a concentration of CaO.

The final properties of sintered iron ore and microstructure can be changed by controlling suction pressure, pellet speed, and combustion pattern. Heat-treated powdery material CaO-Fe₂O₃ (22:78 by wt. %) at different temperatures for two hours has been carried to assess the thermophysical properties which reported that the heat of fusion changes remarkably at different temperature although the melting point remains constant. The unit cell volume and crystallite size

increase with increasing temperature [15]. The analysis of crystallization mechanisms of $2\text{CaO-Fe}_2\text{O}_3$ and $\text{CaO-Fe}_2\text{O}_3$ have reported by Avrami [16] and Mo models [17] and the apparent activation energy was evaluated as -464.16 kJ/mole and -172.61 kJ/mole respectively [18]. An investigation of calcium ferrite in molten form has been discussed to analyse the physical properties in the context of structure and found good agreement with previous results [19]. The spinal pigment CaFe_2O_4 is being synthesized and characterized by the polymeric precursor method reported the material remains completely into crystalline at 800°C and further study was done for physical and chemical behaviour [20]. Densities of the melts $\text{FeO-Fe}_2\text{O}_3\text{-CaO}$ system measured under controlled atmosphere by Archimedean principle with an error and also found the molar volume of the ternary system followed by simple additive rule [21]. An assessment has been performed regarding the influential behaviour of CaO on calcium ferrite formation that reported the numerous intermediate unstable and stable phases formed during the solid-state reaction ($< 1200^\circ\text{C}$) which affects the crystallinity and morphological structure of the material. In addition to this, the phases of calcium ferrite like CaFe_2O_5 and CaFe_3O_5 are formed before $\text{Ca}_2\text{Fe}_2\text{O}_5$ [22, 23]. Analysis of particle size and morphology of metal oxides have been carried out and found adversely effected by milling process [24].

The present research work is discussed about the thermophysical parameters variation with different compositions. The thermal study is analysed using Differential Scanning Calorimetry (DSC) and heat of fusion, melting point, activation energy are reported. Further, structural analysis of $\text{CaO-Fe}_2\text{O}_3$ material is addressed through X-Ray Diffraction (XRD) under which crystalline size, lattice strain, dislocation density are discussed. Finally, morphological studies have been carried out with Field Emission Scanning Electron Microscopy (FE-SEM) to assess the issue of elemental composition, phase formation. All the above thermophysical parameters have been discussed of the sample at the different compositions of heat-treated and non-heat treated samples. The thermal stability of $\text{CaO-Fe}_2\text{O}_3$ material for application as a simulant material is necessary for the context of the predictive study for nuclear severe accident scenario. In present research work, the material $\text{CaO-Fe}_2\text{O}_3$ is taken in powder form (Binary mixture) and characterizations have been carried out before and after heat treatment.

METHODS AND MATERIALS

The sample used in this study is prepared by mixing of two oxides CaO and Fe_2O_3 manually in a mortar up to 40 minutes at five different ratios. All the ratios were considered and verified with the phase diagram of $\text{CaO-Fe}_2\text{O}_3$ in a fixed binary ratio by weight % along the hyper eutectic (non-eutectic) zone as shown in Figure 1 [25]. The individual powders are taken with 99% of purity for investigation purpose. Every sample ratio is assigned with a unique symbol as shown in Table 1 in which the weight percent composition of each sample is given. The samples were pelletized in a hydraulic press under loads of 3.5 tons with five minutes compaction time in cylindrical form with 12 mm diameters and 8mm thicknesses. Further, pellets were kept in a programmable furnace for heating at 1200°C and three hours soaking time. The entire process was carried out in an air atmosphere. Dimensional measurements were carried out with designed apparatus after heat treatment in a furnace and weight loss analysed for every sample. The heated samples were ground into powder form for further characterization.

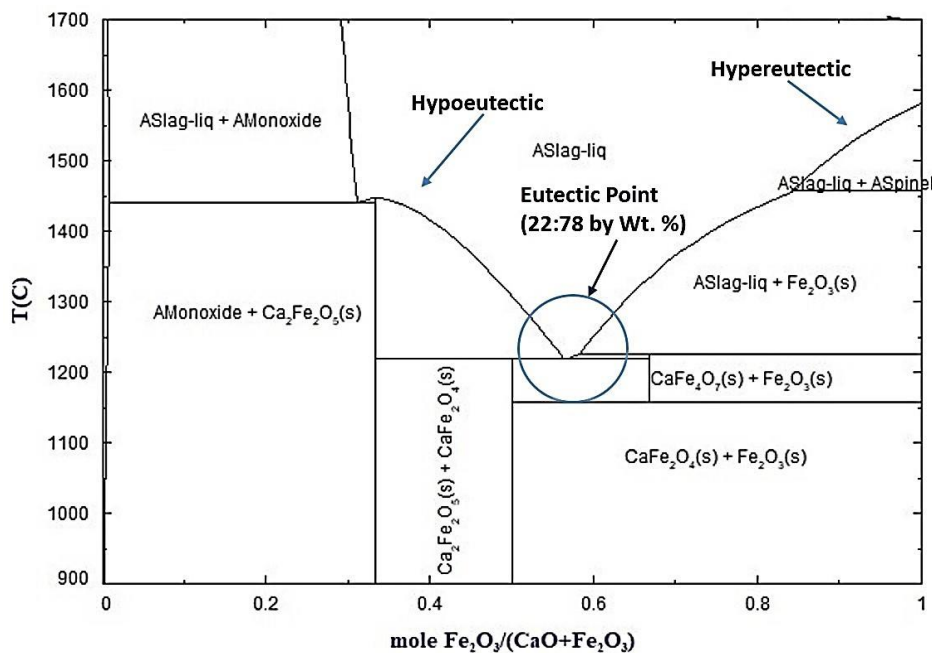


Figure 1. Phase diagram of $\text{CaO-Fe}_2\text{O}_3$ [25]

Table 1. Chemical compositions and symbol of samples

S.no.	Symbol	Chemical Composition (Weight Percent)		Remarks
		CaO	Fe ₂ O ₃	
1.	5C95F	5	95	C refers to CaO and F refers to Fe ₂ O ₃
2.	9C91F	9	91	
3.	13C87F	13	87	
4.	17C83F	17	83	
5.	21C79F	21	79	

Figure 2 shows the entire methodology with a conceptual workflow diagram. Phase analysis, Thermal properties, and morphological studies of all the samples were carried out through XRD (X-Ray Diffraction Method), DSC (Differential Scanning Microscopy), and FE-SEM (Field Emission Scanning Electron Microscope) respectively. The characterizations were carried out for sample powders and heat-treated powder. Further, a comparative analysis of thermophysical properties has been carried over-treated (heated) and untreated materials. As the density of material reduced by contraction of pellets due to heat treatment, the weight losses were measured dimensionally by measurements of pellets before and after heating for different samples. The maximum weight loss was found in 5C95F and the remaining samples were found thermally stable. Figure 3 shows the variation of weight losses of different samples before and after heat treatment. It demonstrated that all the samples were stable (1.4%-1.8%) except 5C95F (6%) due to minor percentage of carbon when subjected to 1200°C and out of these all the samples, 17C83F found minimum weight loss.

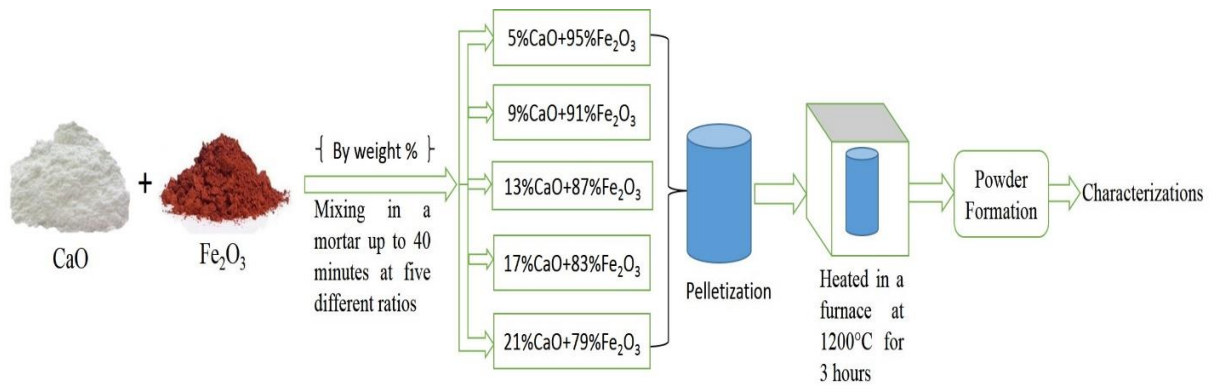


Figure 2. Conceptual work flow diagram

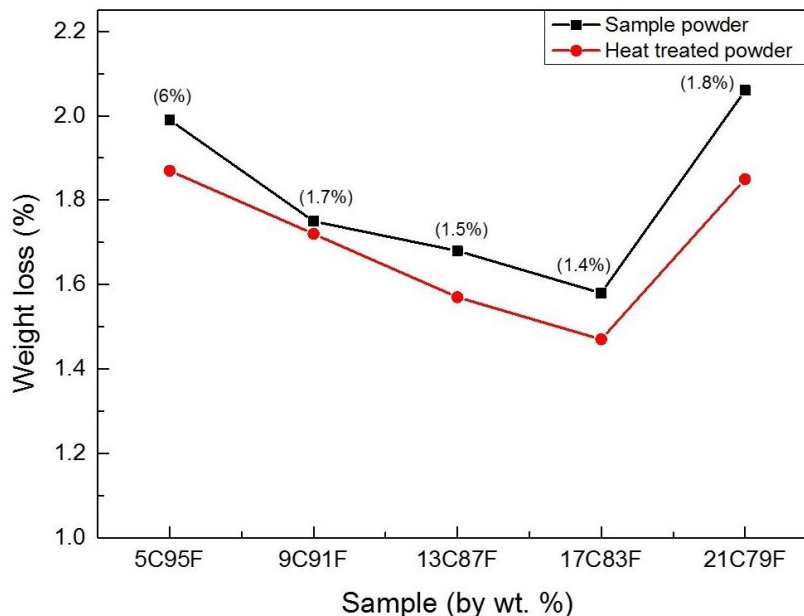


Figure 3. Weight loss analysis of samples before and after heat treatment

RESULTS AND DISCUSSION

Phase Analysis of CaO-Fe₂O₃ before and after Heat Treatment

The XRD patterns of CaO-Fe₂O₃ powder are shown in Figure 4. Generally, ceramics materials are amorphous but the powder mixture shows the semi-crystalline behaviour. Only two phases appeared as CaO and Fe₂O₃ in all the samples. Figure 4(e) represents more than one phase due to a higher percentage of CaO in the powder mixture. When samples were heat-treated at 1200°C for three hours soaking time, different phases were noticed during heating. Figure 5 shows the XRD pattern of different heat-treated samples. The major phases like CaFe₃O₄ and CaFe₄O₇ were reported after heat treatment and well-matched with standard JCPD files. Apart from these stable phases, some unstable phases were also reported during analysis and found that intermediate phases of calcium ferrite like CaFe₂O₄, CaFe₃O₅ and many more were formed and finally they disappeared during heating of material. This shows the behaviour of a stable crystalline structure of the material used at different ratios as all the samples reported the majority of stable phases because unstable phases were disappeared at high temperature but after air quenching, converted into CaFe₂O₄ and CaFe₄O₇ having orthorhombic and monoclinic crystal structure, respectively. The value of crystallite size, crystalline structure, lattice strain, and dislocation density have been determined by the Hall-Williamson method of crystallinity [26].

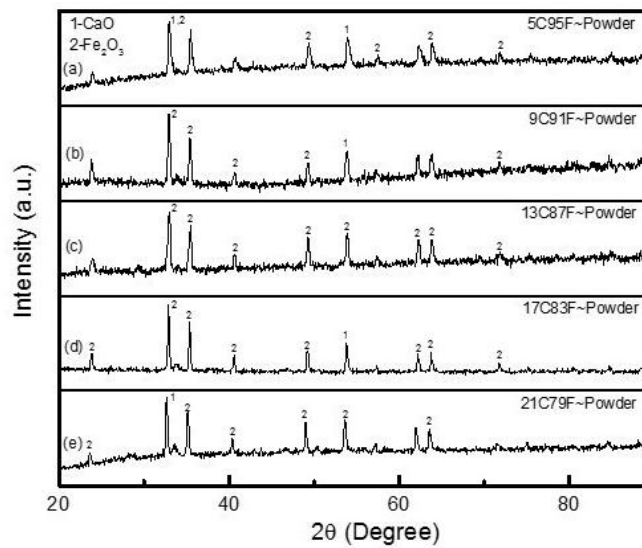


Figure 4. XRD Image of CaOFe₂O₃ powder at different composition

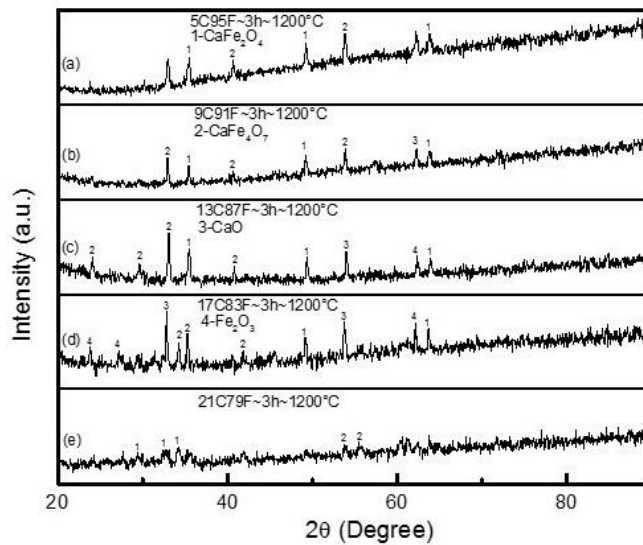


Figure 5. XRD Image of heat treated CaOFe₂O₃ at different composition for 3 hours

Effect of Composition on Lattice Strain, Crystallite Size, Dislocation Density before and after Heat Treatment

The compositional effect of the material's properties is shown in Figure 6. The analysis was carried out of the material CaO-Fe₂O₃ at various compositions based on before and after heat treatment. Figure 6(a) shows the behavioural changes in lattice strain after heat treatment which indicates that the value decreases continuously with increasing the CaO in the mixture even the sample 21C79F shows negative strain as it has the highest amount of Fe₂O₃ in the binary mixture. Figure 6(b) shows the same pattern of variation in crystallite size before and after heat treatment which leads to the stability of crystallinity structure during heating at 1200°C for three hours of soaking time. But the value of the dislocation density of samples increases significantly with increasing the proportion value of calcium oxide after heat treatment is compared with and without heat treatment samples which further indicates the stability of the molecular structure.

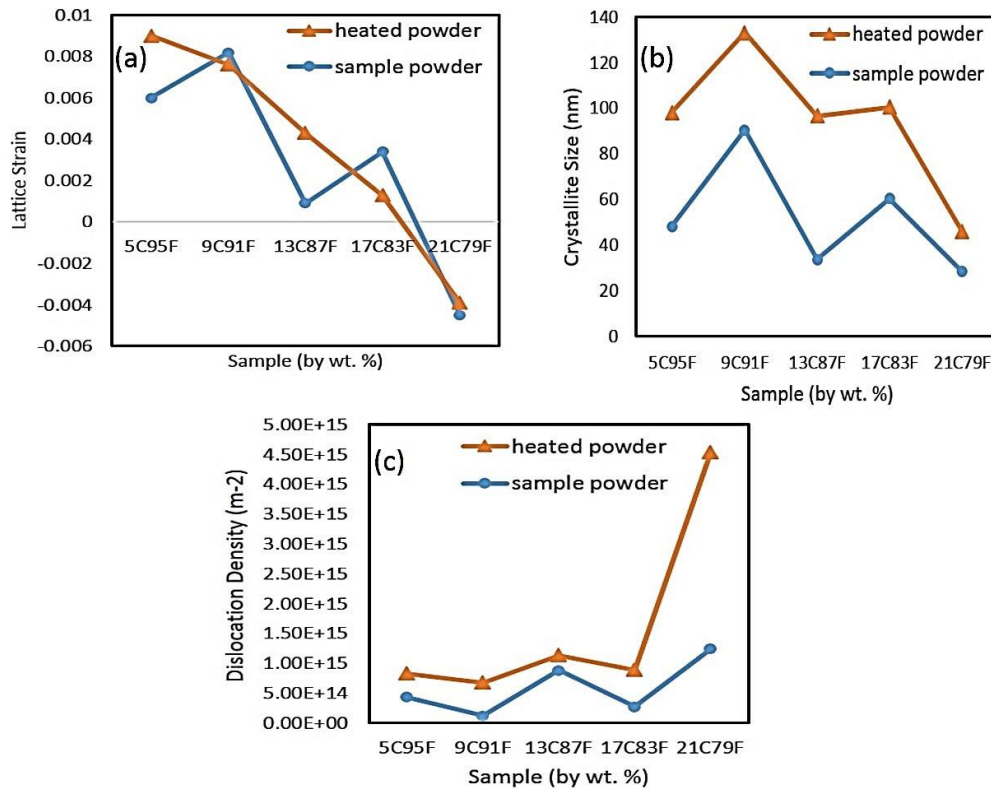


Figure 6. Compositional effect of material on: (a) lattice strain, (b) crystallite size and (c) dislocation density

Thermal Analysis of CaO-Fe₂O₃

Figure 7 shows the DSC image of all samples powder before heat treatment and confirm the melting point of material is in the range of 1212°C to 1238°C as sample 21C79F shows the melting point is 1212°C which is stable since it is taken near to the eutectic ratio and validated through the phase diagram [25]. The first endothermic peak of every sample was appeared near to 400°C due to evaporation of volatile material present and these peaks were little bit shifted towards right due to the increase of iron oxide in the mixture. Figure 8 shows the images of CaO-Fe₂O₃ of different compositions which are being heat treated at 1200°C for three hours soaking time. As the sample was heated at 1200°C for three hours, there were no any significant changes occurred in melting point because the transition of material into liquid phase starts from 1200°C which was found good agreement with the literature [5] and completely turned into liquid up to 1220°C. Figure 9 (a) and 9 (b) shows the behavioural change of Heat of Fusion (HOF) and Melting Point (MP) before and after heat treatment of CaO-Fe₂O₃ due to different composition of CaO and Fe₂O₃. The variation of the heat of fusion and melting point of heat-treated samples were found almost proportional to untreated powders. The results of Specific Heat (SH) and Activation Energy (AE) were found in good agreement with the initial powder which shows the thermal stability of the material. The activation energy of samples has been determined by the Arrhenius equation [27]. The maximum specific heat has appeared in the 21C79F sample as shown in Figure 9 (b). This is because of the highest amount of Fe₂O₃ contain in the mixture at this ratio.

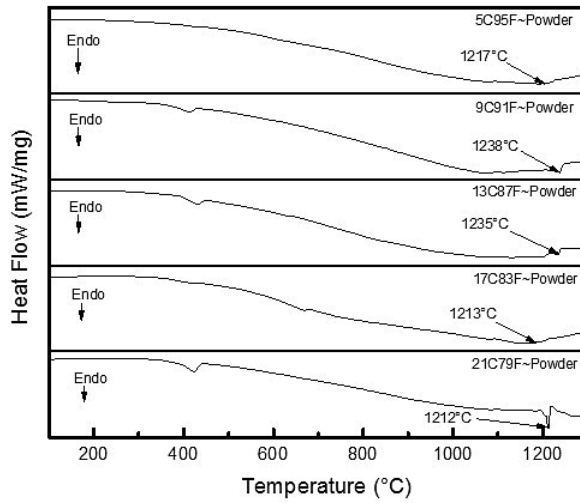


Figure 7. DSC image of CaO-Fe₂O₃ powder with various composition

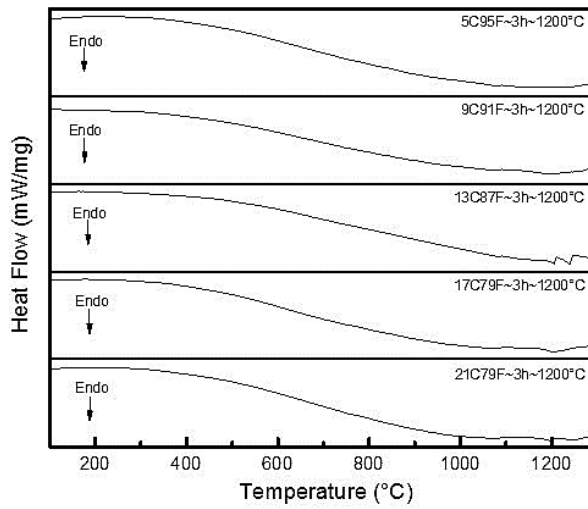


Figure 8. DSC image of heat treated CaO-Fe₂O₃ powder with various composition

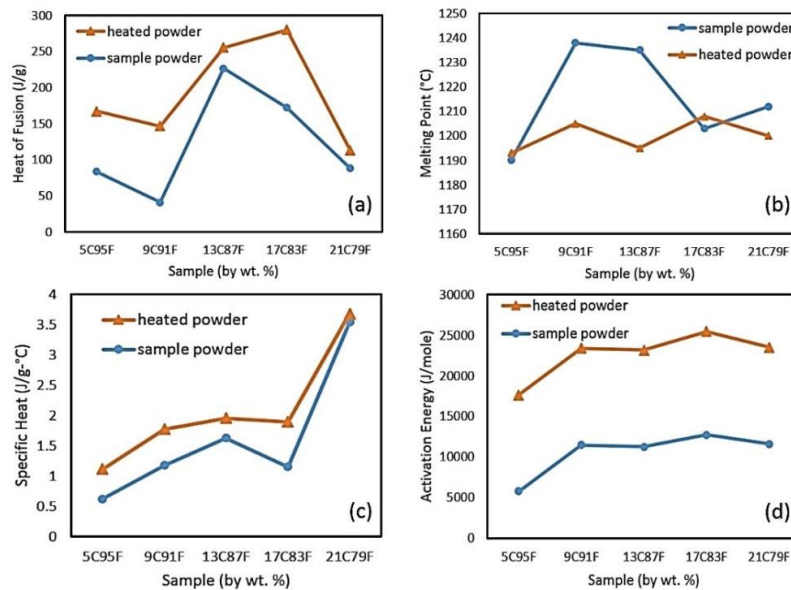


Figure 9. Effect of composition before and after heat treatment on: (a) heat of fusion, (b) melting point, (c) specific heat and (d) activation energy

Morphological Analysis of CaO-Fe₂O₃

The SEM (Scanning Electron Microscopy, FE-SEM 450 FEI) was used to determine the morphological behaviour of material before and after heat treatment. Figure 10 shows the image of sample CaO-Fe₂O₃ at different compositions which reports about the size of grain structure and elemental analysis. All the images were taken at the same magnification level so that the variation can be easily detected. The average sizes of the particles of heat treated samples measured from ImageJ software were found in the range of 1.2 to 2.9 microns. Elemental analysis of samples assessed by SEM and reported that the percentage of Ca increases with increasing the CaO components in the mixture. But Fe and O are varied randomly due to the non-homogeneous mixture as it was prepared manually in mortar. Figure 11 shows the morphology of heat-treated samples of different compositions at 1200°C for three hours of soaking time. Every sample shows the diffused boundary of grain structure as it was heated near to the melting point i.e 1215°C. The particles of heat-treated samples enlarged due to the high diffusion rate. The diffusion of particles was high due to three hours of soaking time because the material gets recrystallized during this time and some new unstable phases were formed which might be disappeared at high temperatures. The elemental composition of constituents is found almost equal except few elements due to weight loss after heat treatments.

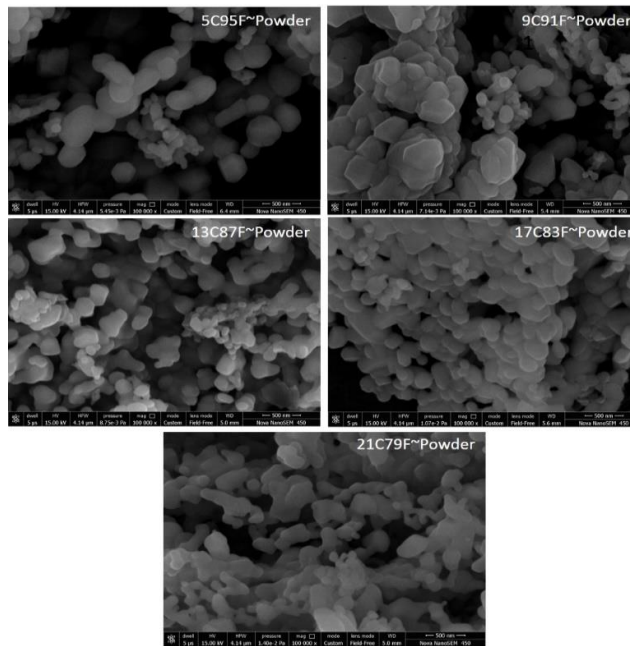


Figure 10. SEM image of CaOFe₂O₃ powder with various composition

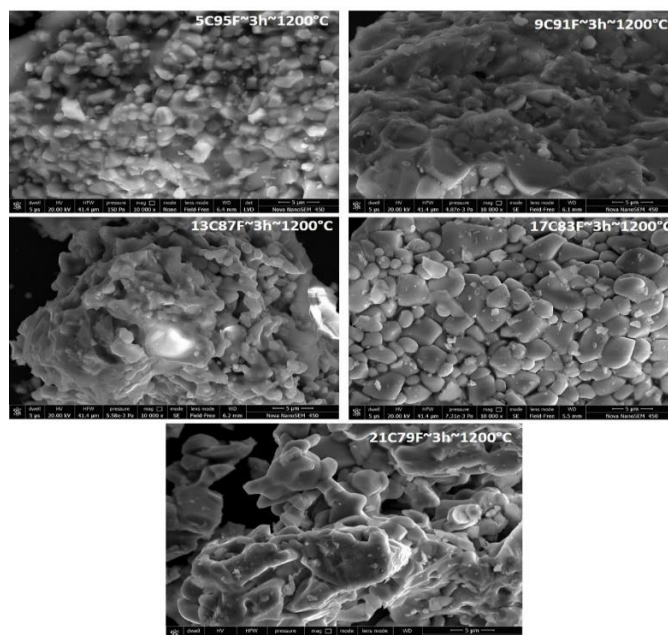


Figure 11. SEM image of heat treated CaOFe₂O₃ powder with various composition

CONCLUSIONS

The material CaO-Fe₂O₃ was prepared in the form of a non-eutectic binary mixture of different compositional ratios which were aimed to investigate and analyse the thermophysical properties and compared with and without heat treatment. All the parameters were found through the characterization of samples via DSC, XRD, and FE-SEM and concluded that the melting point of all the samples were found stable (1200°C-1230°C). The values of activation energy and specific heat were well synchronized between with and without heat-treated samples. Weight loss was maximum for 5C95F sample and minimum for 13C87F which indicates the thermal stability of the material near eutectic. Further, the dislocation density of samples increases significantly with increasing the proportion value of calcium oxide after heat treatment which were compared with and without heat treatment samples. With the effect of this studies, the samples can be further used and tested in the molten form for viscosity and thermal conductivity analysis at different ratios so that this material can be used as a simulant material in the study of a nuclear severe accident by melt coolability technique.

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REFERENCES

- [1] B. R. Sehgal, "Stabilization and termination of severe accidents in LWRs," *Nucl. Eng. Des.*, vol. 236, no. 19–21, pp. 1941–1952, 2006.
- [2] N. Singh, A. K. Nayak, and P. P. Kulkarni, "Experimental Investigation of Melt Coolability Under Bottom Injection : Effects of Melt Volume , Melt Composition , Nozzle Diameter , and Inlet Pressure Experimental Investigation of Melt Coolability Under Bottom Injection : Effects of Melt Volume , Melt ," *Nucl. Technol.*, vol. 198, no. 3, pp. 306–318, 2017.
- [3] S. H. Tromm W, Alsmeyer H, "Fragmentation of melts by water inlet from below," in *Proc. Int. Topl. Mtg. Nuclear Reactor Thermal-Hydraulics (NURETH-6)*, 1993, pp. 99–106.
- [4] W. Tromm, "Nuclear Engineering and Design addition from below," *Nucl. Eng. Des.*, vol. 157, pp. 437–445, 1995.
- [5] T. E. Note and H. Alsmeyer, "Concept of a core cooling system and experiments performed," *Nucl. Eng. Des.*, vol. 154, pp. 69–72, 1995.
- [6] T. W. Alsmeyer H, Spencer B, "The COMET-concept for cooling of ex-vessel corium melts," in *CD-ROM Proc. of ICON-6*, 1998, pp. 437–445.
- [7] J. J. Foit, M. Bürger, C. Journeau, H. Alsmeyer, and W. Tromm, "Quenching of Melt Layers by Bottom Injection of Water in the COMET Core-Catcher Concept," in *The 3rd European Review Meeting on Severe Accident Research (ERMSAR-2008)*, 2008, no. September, pp. 23–25.
- [8] A. Kumar, R. Kumar, P. P. Kulkarni, and B. Raj, "A numerical and experimental study of water ingression phenomena in melt pool coolability," *Nucl. Eng. Des. J.*, vol. 239, pp. 1285–1293, 2009.
- [9] P. Kudinov, A. Karbojian, C. Tran, and W. Villanueva, "Agglomeration and size distribution of debris in DEFOR-A experiments with Bi 2 O 3 – WO 3 corium simulant melt," *Nucl. Eng. Des.*, vol. 263, pp. 284–295, 2013.
- [10] V. K. Pandey, S. K. Jatav, U. Pandel, and R. K. Duchaniya, "Effect of soaking time on properties of non-prototype material (CaO-Fe₂O₃; 21:79 by wt. %)," in *Materials Today: Proceedings*, 2020.
- [11] S. K. Jatav, V. K. Pandey, U. Pandel, A. K. Nayak, and R. K. Duchaniya, "Thermo-physical Properties of CaO-Fe₂O₃ (26:74 by wt.%) Binary Mixture and Its Application in the Field of Nuclear Severe Accident Management," *Int. J. Sci. Technol. Res.*, vol. 9, no. 03, pp. 5773–5778, 2020.
- [12] S. K. Jatav, V. K. Pandey, U. Pandel, A. K. Nayak, and R. K. Duchaniya, "Thermo-Physical Properties of CaO-Fe₂O₃ Binary Mixture and its Application in the Field of Nuclear Reactor as Simulant Material," *Int. J. Eng. Adv. Technol.*, vol. 9, no. 3, pp. 1706–1709, 2020.
- [13] T. J. Suh IK, Sugiyama K, Waseda Y, "Structural Study of the Molten CaO - Fe₂O₃ System by X-ray Diffraction," *Zeitschrift für Naturforsch.*, vol. 44, no. 6, pp. 580–584, 1989.
- [14] M. D. Park TJ, Choi JS, "Communication In Situ Observation of Crystallization Cooling Rates and Chemical Scanning Microscope," *Metall. Mater. Trans. B*, vol. 49, no. 5, pp. 2174–81, 2018.
- [15] V. K. Pandey, R. K. Duchaniya, U. Pandel, and S. Yadav, "Behavior of thermophysical properties of heat treated CaO-Fe₂O₃ at different temperature," in *AIP Conference Proceedings*, 2019, vol. 2148.
- [16] M. Avrami, "Kinetics of Phase Change. I General Theory," *J. Chem. Phys.*, vol. 1103, 1939.
- [17] T. Liu, Z. Mo, and S. Wang, "Nonisothermal Melt and Cold Crystallization Kinetics of Poly (Aryl Ether Ether Ketone Ketone)," *Polym. Eng. Sci.*, vol. 37, no. 3, 1997.
- [18] C. Ding, X. Lv, Y. Chen, and C. Bai, "Crystallization Kinetics of 2CaO - Fe₂O₃ and CaO - Fe₂O₃ in the CaO – Fe₂O₃ System," vol. 56, no. 7, pp. 1157–1163, 2016.

- [19] Y. T. Sumita S, Morinaga K, "Physical Properties and Structure of Binary Ferrite Melts," *Transactions of the Japan Institute of Metals*, vol. 24, no. 1. pp. 35–41, 1983.
- [20] R. A. Candeia, M. I. B. Bernardi, E. Longo, I. M. G. Santos, and A. G. Souza, "Synthesis and characterization of spinel pigment CaFe_2O_4 obtained by the polymeric precursor method," vol. 58, pp. 569–572, 2004.
- [21] O. K. Hara S, Irie K, "Densities of Melts in the $\text{FeO-FeO}_3\text{-CaO}$ and $\text{FeO-Fe}_2\text{O}_3\text{-SiO}_2$," *Trans. Japan Inst. Met.*, vol. 29, no. 12, pp. 977–989, 1988.
- [22] J. Jeon, S. Jung, and Y. Sasaki, "Formation of Calcium Ferrites under Controlled Oxygen Potentials at 1 273 K," vol. 50, no. 8, pp. 1064–1070, 2010.
- [23] J. Yin, X. Lv, S. Xiang, C. Bai, and B. Yu, "Influence of CaO Source on the Formation Behavior of Calcium Ferrite in Solid State," vol. 53, no. 9, pp. 1571–1579, 2013.
- [24] J.-L. J. Vera-Serna P, Martínez-Sánchez MA, Kusy M, Bolarín-Miró AM, Tenorio-González FN, "Effect of milling process on particle size, morphology and magnetization in non-stoichiometric $\text{Fe}_2\text{O}_3\text{-MnO}_2$," *J. Mech. Eng. Sci.*, vol. 13, no. 1, pp. 4613–4622, 2019.
- [25] B. S. Boyanov, "SOLID STATE INTERACTIONS IN THE SYSTEMS $\text{CaO}(\text{CaCO}_3)\text{-Fe}_2\text{O}_3$ and $\text{CuFe}_2\text{O}_4\text{-CaO}$," *J. Min. Metall.*, vol. 41B, pp. 67–77, 2005.
- [26] V. D. Mote, Y. Purushotham, and B. N. Dole, "Williamson-Hall analysis in estimation of lattice strain in nanometer-sized ZnO particles," pp. 2–9, 2012.
- [27] R. Pilawka and S. Paszkiewicz, "Thermal degradation kinetics of PET / SWCNTs nanocomposites prepared by the in situ polymerization," pp. 451–460, 2014.