

EFFECT OF HIGH DOSES OF GAMMA RADIATION ON THERMOPHYSICAL PROPERTIES OF ZrO₂ NANOFUIDS IN AQUEOUS BASE

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ABSTRACT

This work conducts a general theoretical and experimental study of the physical properties associated with the heat transfer capacity of ZrO₂ nanofluids in aqueous base and the effects of gamma on such properties, with a view to the possibility of applying as heat transfer fluid in future generations of nuclear reactor systems. The effects of concentrations and temperature, before and after the action of ionizing radiation were carried out. Theoretical models, parameters of influence and experimental results available in specialized literature were reviewed. Experimental study of physical properties of nanofluids samples in various concentrations (0.001% vol. 0.01% vol. 0.1% vol.), without the action of gamma radiation was also conducted. The physical properties investigated are the thermal conductivity, electrical conductivity, pH, density, and viscosity. Nanofluid samples were irradiated in the Multipurpose Radiator of IPEN under the doses 1MGy, 2 MGy, and 3 MGy. Analysis using techniques of samples visualization before and after irradiation using scanning electron microscope (SEM) was adopted. The trials will be held to display the verification of the change in distribution of nanoparticles after irradiation of samples. This test aims to check for changes in the structure of the nanoparticles. It is expected with the results from this research project, a contribution to the advancement of knowledge of nanofluids applications in high heat transfer systems.

1. INTRODUCTION

According to many scientific definitions addressing the issue nanofluids and its applications [13-20], it can be set as colloidal fluids composed of chemically stable and nanoparticles dispersed in a base fluid (water, aqueous solutions, refrigerant, oil, and others) at concentrations ranging from 0.01% to 50% by volume. The most widely used and researched nanoparticles are metals (Cu, Ag, Au, Fe, Ti, and others), oxides (Al₂O₃, ZrO₂, FeO, Cu, SiO₂, MgO, TiO₂, ZnO, and others) and the carbon-based compounds (graphite, diamond, carbon nanotubes).

Concerning the new technologies currently developed for heat transfer intensification, nanofluid is a promising one, concerning application in various systems of removal and transport of high heat fluxes. Nanofluids are widely applicable for heat transfer, and, currently, is one of the topics of nanotechnology publications substantially increasing, which demonstrates the importance of this subject has acquired over the last few decades, although the contribution of Brazil is still modest in this area [4].

As demonstrated by the recent works, it has very interesting physical properties regarding its cooling capacity. There are many research groups in the world conducting investigations about nanofluids applications as a cooling fluids in high heat flux systems. Among them, nuclear reactor or nuclear installations and the possibility of it use as working fluid or emergency cooling fluid for nuclear reactors [5-12]. In this context, the influence of ionizing radiation on nanofluid properties are unknown and such behavior must be investigated.

1.1 Nanofluids applications

According to Luke (2008) [20], nanofluids could be applied in a possible crash scenario that leads to the discovery of a nuclear reactor core due to your increased ability of heat transport. In commercial reactors, it is necessary to have emergency core cooling systems (ECCS) operating in case of accidents. The function of this system is to keep the core of the reactor cooled in case of loss of coolant accident (LOCA). This is the first system where nanofluids can potentially be applied.

In a more serious accident scenario, without proper cooling the core eventually will overheat the reactor pressure vessel (RPV). This violates the second barrier to releasing fission products, with only the integrity of containment to prevent atmospheric release of fission products. Similarly, nanofluids there can potentially be applied, this time in conjunction with a cooling system of retention where the pressure vessel.

This system works on the same line as the ECCS however, rather than cooling the core, he floods the reactor cavity and cools the pressure vessel by natural circulation. If this cooling is successful the fission products released inside the pressure vessel will not be exposed to the atmosphere, thus ensuring the safety of the population.

If one consider applications of nanofluids in nuclear reactors, radiation effects on the physical and chemical structure of the nanofluido is the first and most obvious concern apparently. Until now, little effort has been made to evaluate nanofluids under such conditions.

Firstly, there is the impact of the effects of radiation on nanoparticles. The first question that arises is: the energy transmitted by radiation would have any effect on nanoparticles? The second concern is a little less obvious. The means of suspension of colloidal nature through the repulsion of charges on the surface of the particles. This implies there are conditions for this repulsion, and the pH of the fluid is a very important parameter. Radiation can affect the surface charge of nanoparticles through the radiolysis, causing some damage.

Only gamma radiation will be considered in this study, since in cases of applications interest in a nuclear reactor, the same would be turned off. In this condition, the presence of neutron flux quite negligible.

1.2 Physical Properties

The cooling capacity of a certain fluid for pool or convective heat transfer process is intrinsically related to it thermal conductivity (k_f) and it dynamic viscosity (ν_f) . So, inthis context, those physical properties were the focus of this investigation.

1.2.1 Thermal conductivity

The thermal conductivity is the physical property associated with the ability of a material to conduct heat and determines the temperature gradient over your geometry.

The most commonly technique for nanofluid's thermal conductivity measurement are the transient hot wire method, the method of temperature oscillation and ω -3 method. According to the literature, the transient hot wire technique is the most used. The hot wire method is based on application of a constant electric current through a wire, dispelling a given amount of heat per unit time and unit of length. This propagation of heat in the middle of infinity rated material generates a transient temperature field. In practice, the ideal heat source (theoretical) is approximated by a slender electrical resistance and the kind of infinity is replaced by a finite sample of high dimensions compared to electrical resistance. Therefore, the heat capacity of the wire, the contact resistance between him and the sample, as well as the finite sample size are factors that will generate a minimum and a maximum time of analysis to be used in the calculation of thermal conductivity. These minimum and maximum times are determined experimentally from the record of the temperature on the surface of the hot wire as a function of time. (Motta, 2012 [39]).

The temperature oscillation method consists in measuring the temperature variation at the ends of a cylinder containing the fluid to be analyzed. These temperature variations at the ends and at some point inside the cylinder give rise to the value of the thermal diffusivity. So, knowing the density and specific heat of the material, the thermal conductivity

Method $3-\omega$ is based on the use of a thin metal strip that acts both as a thermometer as heating source. The resulting warming leads to a variation in temperature. Finally, the product between the chain and the electrical resistance leads to a voltage value. This strain is called $3-\Omega$, used to extract the properties of thermal system. (RAUDZIS et al., 2003).

Linear probe method, based on transient hot wire technique was first proposed by Blackwell, (1954). This is the method adopted for this study on determination of thermal conductivity of nanofluids and this mode is described in detail below.

Second Boer (1980), the mathematical formulation of this method considers the probe an ideal heat source with zero mass and therefore null also heat capacity, infinitely long, diameter, surrounded by an infinite medium whose conductivity to determine thermal.

ASTM D5334-08 (2008) describes the standard procedure for the determination of Thermophysical properties and takes math, the classic method of Linear Probe also known as Transient hot wire method.

Currently four variations of the hot wire method called standard techniques are employed, in parallel, of strength and of two thermocouples. The theoretical model, the basic difference between them is in the temperature measurement procedure. Consequently, the final equation obtained for the calculation of thermal conductivity is distinct for each one of the techniques.

One of the first studies with nanoparticles was developed by Eastman et al. (1997). They produced the following: Al_2O_3 nanofluids in water, CuO in water and Cu in water. Their

nanofluids composed of CuO and Al₂O₃ in water showed satisfactory, while the nanofluid stability of Cu in water showed rapid deposition.

It was observed a significant increase of the effective thermal conductivity, defined as the ratio of the thermal conductivity of nanofluid and your base fluid for solutions of CuO and Al₂O₃, with the first featuring a higher increase. This result is due to a higher thermal conductivity of CuO regarding alumina.

The first model for determination of thermal conductivity of suspensions of solid particles in liquids was proposed by Maxwell (1873 apud CHOI, 1995). It is based on "potential theory" where it is considered that fundamental forces are from potential to satisfy Laplace's equation, (KUMAR et al., 2010). The Maxwell model that's valid for reduced concentrations in that there are no interactions between the particles. The Maxwell equation is given by:

Bruggeman (1935) proposed a model based on Maxwell, from analysis of interactions between spherical particles considered in a solution. According to the author, this model can predict the thermal conductivity for high concentrations. The resulting correlation model of Bruggeman, (1935) presents, for reduced concentrations results close to Maxwell.

Hamilton and Crosser (1962) proposed a model based on Maxwell. They included effects of geometry of the particle as observed by the authors influences substantially on effective thermal conductivity of suspension. Geometry effects were incorporated through a particle sphericity factor, n , defined as $3/\psi$, where ψ is the sphericity of the particle given by the relationship between the surface area of a sphere with similar particle volume and surface area of the particle. So for a cylindrical particle, $\psi = 0.5$ and $n = 6$ in the case of spherical particles $\psi = 1$ and $n = 3$. Note that for spherical particles this model becomes equal to that of Maxwell.

Specifically for cylindrical particles, Yamada and Ota (1980) proposed the unit cell model to predict the thermal conductivity of a mixture. The concept of unit cell is used to represent the symmetry of a given crystal structure.

Yu and Choi (2003, 2004) extended the Maxwell model and Hamilton and Crosser, respectively, in order to provide for the effective thermal conductivity of nanofluids. This model assumes spherical and non-spherical particles in suspension in a liquid base. The spherical particulate model assumes the presence of a nanometer thick layer around the particles, called nanolayers. This layer would be responsible for the increased volume concentration and thermal conductivity of nanofluids, mainly for particle diameters below 10 nm. The authors suggest that the nanolayer acts as a bridge linking the nanoparticles to the fluid base, justifying the increase in thermal conductivity. As there are no experimental data for thermal conductivity of nanolayers, they suggested four empirical values for the thickness of the nanolayer and verified effective thermal conductivity values higher in nanofluids when they take the nanolayer.

Main theoretical models for prediction of effective thermal conductivity (k_{eff}) for nanofluids, according to the papers presented in specialized literature, are:

Bruggeman model (1935):

$$\phi_v \left(\frac{k_p - k_{eff}}{k_p + 2k_{eff}} \right) + (1 - \phi_v) \left(\frac{k_b - k_{eff}}{k_b + 2k_{eff}} \right) = 0 \quad (1)$$

Hamilton and model Crosser (1962):

$$\frac{[k_p + (n-1)k_f - (n-1)\phi_v(k_f - k_p)]}{[k_p + (n-1)k_f + \phi_v(k_f - k_p)]} \quad (2)$$

Yamada and Ota model (1980):

$$\frac{\frac{k_p + k - k\phi_v \left(1 - \frac{k_p}{k_b}\right)}{k_b}}{\frac{k_p + k + \phi_v \left(1 - \frac{k_p}{k_b}\right)}{k_b}} \quad (3)$$

Model of Yu and Choi (2003, 2004):

$$\frac{k_{pe} + 2k_b + 2(k_{pe} - k_b)(1-\beta)^3 \theta_v}{k_{pe} + 2k_b + (k_{pe} - k_b)(1-\beta)^3 \theta_v}; \quad \left(1 + \frac{n\phi_{eff}A}{1 - \phi_{eff}A}\right) \quad (4)$$

1.2.2 Dynamic viscosity

Viscosity is related to the rate of deformation of a fluid, and may further be characterized as the resistance to flow (flow) movement of a material. It is relevant in several applications in engineering, among which are lubrication processes, heat transfer and the power required to pump a fluid related to pressure loss by dissipative effects. Researches carried out in this specific field show that there is linearity of obtained data for Newtonian fluid behavior for nanofluids analyzed; other researchers have reported non-linearity with variations of concentrations. A particle size is a factor that also need to be considered. Results show, for example, that the viscosity of Al₂O₃ based nanofluids not only increases non-linear with the concentration, but also depends on the size of the nanoparticles relative to the size of the tube. There are findings that show viscous shear stresses nanofluids-based zero CuO/ethylene glycol and that changes abruptly when the volume fraction of particles becomes greater than 0.2%. Therefore, this volume fraction is considered as the dilution limit. Substantial improvement on thermal conductivity is achievable only when the particle concentration is lower than the dilution limit. For concentrations above this threshold, where both rotation and translation Brownian movements are restricted, there is no further increase in conductivity beyond the predictions of the theory effective means. For some nanofluids how the particles aggregate has a strong effect on both the viscosity and on the thermal conductivity of nanofluido.

Their nanofluids have higher viscosity than their base fluids and require greater pumping power to achieve the same thermal performance. They have flow properties similar to those of a single base and have little or modest increase in load loss. The increase in thermal conductivity can be offset by the increase in viscosity, the decrease in the effective specific heat or variation of wettability [13,14].

This flow behavior is attractive for applications in engineering. To obtain good results in practical applications of heat transfer processes, the fluids should be designed to increase the heat transfer coefficient without penalizing the load loss. This requires a precise selection of

the particle shape, size, materials, and concentrations. In the case of applications with presence of ionizing radiation also have to design the nanofluido of way no activation effects of its components generating high doses of radiation in the environment.

According to the literature, the main theoretical models for predicting the dynamic viscosity of nanofluids can be summarized by the following models:

Einstein (1956):

$$\mu_{nf} = (1 - 2,5\phi_v)\mu_f \quad (12)$$

Brinkman (1952):

$$\mu_{nf} = \frac{1}{(1-\phi_v)^{2,5}}\mu_f \quad (13)$$

Batchelor (1977):

$$\mu_{nf} = (1 + 2,5\phi_v + 6,5\phi_v^2)\mu_f \quad (14)$$

Wang et al. (1999):

$$\mu_{nf} = (1 + 7,3\phi_v + 123\phi_v^2)\mu_f \quad (15)$$

Maiga et al (2004):

$$\mu_{nf} = (1 + 0,19\phi_v + 306\phi_v^2)\mu_f \quad (16)$$

Corcione (2011):

$$\mu_{nf} = \left[\frac{1}{\left(1 - 34,87 \left(\frac{d_p}{d_f}\right)^{-0,3} + \phi_v^{1,05}\right)} \right] \mu_f \quad (17)$$

Where, μ_{nf} is the dynamic viscosity of nanofluid, μ_f is the dynamic viscosity of the base fluid, ϕ_v is the volumetric fraction of the particle, d_p is given by the ratio $d_p/d_f = 0,1 (M/N\pi\rho_{f0})^{1/3}$ with M being the molecular weight of the particle or fluid and ρ_{f0} is the density of the base fluid.

2. METHODS

In this work the measurements of thermophysical properties, viscosity and visualization technic were carried out in order to evaluate the effect of high doses gamma radiation on such properties for ZrO₂ nanofluids.

Nanofluid samples were prepared by mixing nanoparticles of ZrO₂ (~40 nm, Sigma-Aldich Co) and demineralized and deionized water, using a sonicator until it became homogeneous (~40 min). Nanofluid samples volumetric concentrations were 0,001% wt and 0.01% wt. The volumetric concentrations were obtained according to the following expression:

$$\phi_v = \frac{\phi_m \rho_f}{\rho_p + \phi_m \rho_f - \phi_m \rho_p} \quad (18)$$

Where ϕ_m is the mass concentration of the particles dispersed in the fluid and ϕ_f and ϕ_p are the specific masses of the base fluid and the particles, respectively. The ρ_p and ρ_f are the particle and base fluid densities, respectively.

The KD2 PRO thermal properties meter were used to measure resistivity, thermal conductivity and diffusivity of nanofluids samples by monitoring the heat dissipation of a linear heat source given a known voltage.

Nanofluid sample's viscosity was determined in the laboratory using the equipment Brookfield DV-I Prime.

Nanofluid samples of ZrO_2 were irradiated in a Co-60 source at IPEN Multipurpose Irradiator. Samples were prepared and arranged in 50 ml borosilicate tubes and irradiated at a different time depending on the desired dose. Gamma radiation doses studied was 1 MGy and 2 MGy.



Figure 1. Nanofluid samples prepared for irradiation.

Nanofluid samples were prepared and visualized in a scanning electron microscope of Jeol, model JSM 6701F, operating at 5 kV at a distance of 3.0 mm work (SEM-FEG), in the Laboratory of Microscopy and Microanalysis Center of Science and Technology of Materials - CCTM / IPEN. The results of the visualizations of the ZrO_2 nanofluid can be seen in Fig. 1.

3. RESULTS

After eight measurements in the same condition we had that for nanofluid ZrO_2 before being irradiated a decrease in electrical conductivity as there was a decrease in concentration 0.1% (156 $\mu S/cm$) against 0.001% (12 $\mu S/cm$) and also the thermal conductivity 0.1% (0.722 W/mK) against 0.001% (0.354 W/mK).

The thermal conductivity, thermal resistivity and the dynamic viscosity of ZrO_2 nanofluids in volumetric concentrations of 0.01%, and 0.1% for ambient temperature (20 °C) are showed in Table 1.

Table1 – Thermal conductivity and dynamic viscosity of ZrO₂ nanofluids.

Volumetric concentration [%]	Thermal conductivity [W/mK]			Dynamic viscosity [cP]		
	Non-irradiated	Irradiated [kGy]		Non-irradiated	Irradiated [kGy]	
		500	1500		500	1500
0.0		-	-		-	-
0.01	0.724	0.609	0.601	1.340	1.310	-
0.1	0.772	-	-	1.360	1.324	-

In Table 1 it is possible to verify some effect of reduction of thermal conductivity of ZrO₂ nanofluids as a function of the irradiation doses. A reduction of 16% in thermal conductivity is observed for irradiation doses of 500 kGy and 17% for 1500 kGy. Data for volumetric concentration of 0.1% are still being obtained. For non-irradiated samples, an increasing of 7% is observed when changing the volumetric concentration from 0.001% to .01%.

Concerning the dynamic viscosity, a increasing of 1.5% is observed when changing volumetric concentration. Irradiated samples showed a drop of about 2.5% for irradiation doses of 500 kGy for both concentrations.

Visualization by SEM technique of the nanofluid samples before and after irradiation are shown in Fig 2.

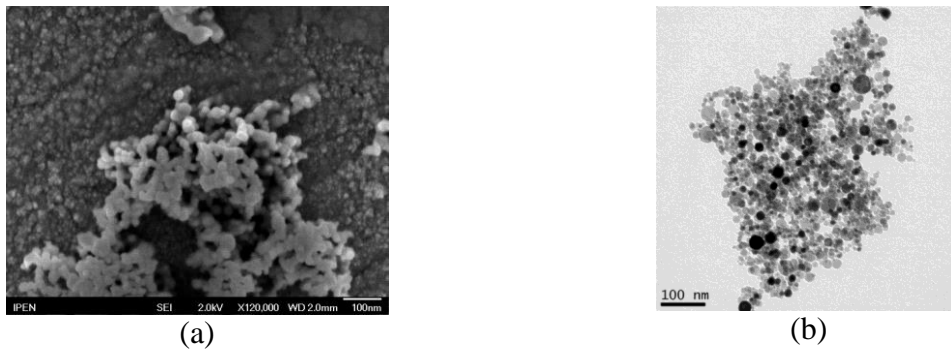


Figure 2. ZrO₂ nanofluid samples SEM images before (a) and after (b) irradiation.

4. CONCLUSIONS

It is concluded that the variation of volumetric concentrations of nanofluids implies an increase in densities, although quite small.

Tests of determination of the thermal conductivities as a function of volumetric concentrations and temperatures were also carried out successfully. It was observed a considerable reduction when doses where irradiated. Concerning the volumetric concentration, an increasing was observed.

Tests for the determination of the nanofluid's viscosity as a function of the volumetric concentration of nanofluids were also conducted. Viscosity has an decreasing of 2,5% in

relation to irradiation effect (500 kGy), and an increasing concerning volumetric concentration.

The research project contributed to the emergence of a new group of interdisciplinary research in the institution, with contribution of researchers from other institutions and with potential for human resources training.

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REFERENCES

1. Choi, S. U. S., Developments and Applications of non-Newtonian Flows”, ASME FED, vol.66, (1995). p. 99–105
2. S.K. Das, S.U.S. Choi, H.E. Patel, Heat transfer in nanofluids: a review, Heat Transfer Engineering, 27 (2006) 3-19.
3. W. Daungthongsuk, S. Wongwises, A critical review of convective heat transfer of nanofluids, Renewable and Sustainable Energy Reviews, 11 (2007) 797-817.
4. Web of Knowledge SM Database , < <http://m.webofknowledge.com> >
5. Rocha, M.S., Estudo da influência da radiação ionizante sobre os nanofluidos visando aplicações em novas gerações de reatores nucleares, Relatório Científico de Progresso (2016).
6. J. Buongiorno, Convective transport in nanofluids, Transactions of ASME, 128 (2006) 240-250.
7. I.C. Bang, G. Heo, Y.H. Jeong, S. Heo, An axiomatic design approach of nanofluid-engineered nuclear safety features for generation III+ reactors, Nuclear Engineering and Technology, 41 (2009) 1157-1170.
8. Gandra, [A. Com](#) crise hídrica em São Paulo, Aben defende uso de energia nuclear. EBC, São Paulo, 05 de dez. 2014. Economia. Disponível em: < www.ebc.com.br > Acesso em: jun, 2015.
9. Pop, M. G. M., Lockamon, B. G., Nuclear power plant using nanoparticles in emergency systems and related method, Areva NP, 2008.

10. Base de dados Periódicos Capes , em < <http://www.periodicos.capes.gov.br> >
11. J. Bouré, Conférences de thermique appliquee aux reacteurs (IEA), Instituto de Pesquisas Energéticas e Nucleares IPEN/CNEN-SP, 2 (1964) C3/SF 3-20.
12. Lucas, T. R., Study of Chemistry and Irradiation Effects on Nanofluids to be used Light Water Reactor Accident Cooling, B.S.A.S.T Nuclear Engineering Tecnology Thomas Edison State College, 2004.
13. Glasstone S., Sesonske A., "Nuclear Reactor Engineering, Volume I" Springer, 1994.
14. Motta, F. C. Caracterização da condutividade térmica, viscosidade dinâmica e ângulo de contato de nanofluidos baseados em partículas de alumina-gama em água, 2012. 107f. Tese.