# Experimental Stability and Thermal Characteristics Enhancement Analysis of Water Based Boehmite Nano fluid

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**Mohammed Hussein J. Al –Atia**
Ministry of Science and Technology
E-mail: mohammed57online@yahoo.com
**Sarah A. Abed**
Ministry of Science and Technology

## Abstract

In this work attempt was made to formulate water based boehmite (AlOOH) nanofluid in one and two steps methods. Boehmite is the first born alumina phase as prepared by sol gel route using aluminum isopropoxide precursor, exhibit a combination of excellent consistency and dispersibility in water. Plain nanofluids containing boehmite at different concentrations were investigated for colloidal, suspensions and/or dispersions stability and thermal conductivity enhancement. X-ray diffraction analysis, laser diffraction particle size analysis, viscosity, thermal conductivity measurements, TG/DSC thermal analysis and sedimentation balance were used as characterization tools. The results show promising long-term fluid stability and thermal conductivity enhancement relative to starting based fluid following non-linear dependence on particles concentration. The maximum 2.7 times enhancement in thermal conductivity occurred at narrow boehmite concentration range as a result of achieving optimum nanoparticles aggregation level where neither the case of nanoparticles homogenous dispersion nor the case of fully aggregated clusters could retain these enhancements values. This far beyond behavior from Maxwell's model was explained on the basis of the known mechanisms of thermal conductivity enhancement of nanofluids.

**Keywords**: Boehmite, Sol-gel, Xerogel, Nanofluid, Stability, Thermal conductivity, Alumina, Sedimentation.

## التحليل التجريبي لاستقرارية وتحسن التوصيلية الحرارية لمائع البوهمايت النانوي
### الخلاصة

في هذا العمل تمت محاولة تحضير مائع البوهمايت (AlOOH) المائي الأساس بمرحلة واحدة ومرحلتين ، إذ إن البوهمايت هو الطور الأول للالومينا المحضرة بطريقة المحاليل الجلاتينية باستخدام بادرة ايزوبروبوكسايد الألمنيوم ويمتاز بالثبات والتشتت الممتاز في الماء. تم التحقق من المائع النانوي الحاوي على البوهمايت بتراكيز مختلفة دون إضافات لمدى استقراريته الغروية والعالقية و\ أو التشتت والتحسن في التوصيلية الحرارية. استخدمت تقنية الحيود بالأشعة السينية والحيود الليزرية وفحص اللزوجة والتوصيلية الحرارية والتحليل الحراري والوزني وتوازن الرواسب كأدوات إثبات وتوصيف. بينت النتائج استقرارية واعدة طويلة المدى مع تحسن في التوصيلية الحرارية نسبة إلى المائع المائي الاساس متبعة اعتمادية غير خطية على تركيز الدقائق النانوية. إذ إن أقصى تحسن في التوصيلية الحرارية بلغ 2,7 مرة وقد حصل عند مدى محدود لتركيز دقائق البوهمايت نتيجة بلوغ أفضل مستوى لتكتل الدقائق النانوية والذي لم تبلغه حالة التشتت المتجانس لدقائق البوهمايت النانوية ولا حالة التكتل الكامل لهذه الدقائق. هذا الحيود في السلوك عن نموذج ماكسويل تم مناقشته اعتمادا على الآليات المعروفة لتحسن التوصيلية الحرارية للموائع النانوية .

**الكلمات المفتاحية**: البوهمايت،المحلول الجلاتيني، المائع النانوي، الاستقرارية، التوصيلية الحرارية، الالومينا، الرواسب.

## INTRODUCTION

Nanofluid technology is a field of great importance for advance heat transfer fluid where nanoscience, nanotechnology, and heat transfer engineering meet. The goal of nanofluids since was first discovered in 2001 [1-2] is to achieve the highest possible effective thermal properties at stable suspension and smallest possible concentrations in a base fluid by uniform dispersion of nanoparticles with average size of less than 100nm. Among these nanoparticles, $Al_2O_3$, CuO, $SiO_2$, $TiO_2$, $Fe_2O_3$, C, Cu and ZnO were used in formulation process sought to have wide range of applications in any heat removal involved industrial applications [3]. The dispersions of these particles in based fluid matrix are expected to have a thermal conductivity that obeys the model developed by Maxwell [4]:

$$\frac{K}{K_f} = \frac{k_f + 2k_f + 2\emptyset\,(k_p - k_f)}{k_p + 2k_f - 6\emptyset\,(k_p - k_f)} \qquad \ldots \quad \textbf{(1)}$$

Where

$k/k_f$ is the thermal conductivity *to* the thermal conductivity of the base fluid ratio, $k_p$, is the particle thermal conductivity and $\emptyset$ is the particle volumetric fraction. However, several deviations have been reported by many researchers including a non-linear thermal conductivity enhancement dependence on particle loading beyond that predicted by equation (1) and particle size, shape and fluid temperature [1-4]. Currently, there are two basic methods to formulating nanofluids, the single-step method is a process combining the preparation of nanoparticles with the synthesis of nanofluids, so the agglomeration of nanoparticles is minimized and the stability of the nanofluids is increased [3]. This method is limited to small production scale since is applicable only for low vapour pressure based fluids. In two-step method dry nanoparticles and\or nanotubes are first prepared in a form of powders by physical or chemical methods, e.g. grinding, laser ablation, sol-gel processing, etc. and then they are dispersed in base fluid like Water, toluene, Ethylene glycol or oil. The main disadvantage of this method is the agglomeration and clustering of nanoparticles making the homogenous dispersion by this method very difficult and remains a challenge. However, this method is inexpensive compared to that of single step. Among alumina phases boehmite alumina (AlOOH), which are nano-sized in the dispersed phase, exhibit a unique combination of purity, consistency, and dispersibility that make them excellent materials for use in demanding colloidal applications. In this respect, few attempts have been published yet; the first was an investigation effect of boehmite alumina (AlOOH) nanoparticle in glycol\water cooling system on thermal conductivity enhancement. The output shows the importance of interfacial heat resistance which is proportional to the total surface area of nanoparticles depending on particle sizes and shapes [5]. Later on, inorganic boehmite nanoparticles were synthesized via hydrolysis of aluminum chloride hexa-hydrate and then were peptized to suspend and obtain boehmite nanofluids in a range of 108-372 nm of diameter for optical and thermo-optical properties study [6]. Recently, water-based nanofluids containing three different concentrations of boehmite (AlOOH· xH2O) 0.01, 0.1 and 0.3 wt. % were investigated for cooling performance of channels for the photovoltaic cell. The nanofluids of 0.01% perform

better than water and caused the highest decrease in the average PV cell temperature [7-8].  These attempts were mainly focused on the thermal conductivity enhancement for as received boehmites with no mention to the stability level of these tested nanofluids. Recently a review on how the researchers prepare their nanofluids highlighted that the researchers focused mainly on the enhancement of heat transfer. However, nanofluids preparation also deserves the same attention since the final properties of nanofluids are dependent on the stability of the dispersion as well as different nanoparticles need their own stability method [9-12]. In this work attempt was made to formulate water based boehmite (AlOOH) nanofluid produced in single step by sol gel route using aluminum isopropoxide (AI) as precursor material. Following the two-steps method, boehmite nanofluid was produced based on dispersion of dry boehmite xerogel (AlOOH) in water without any addition of dispersants or stabilizers. Then, these fluids characterized for long term stability and thermal conductivity enhancement in terms of aggregation and settling behaviors at different boehmite loading percents. To the author best knowledge, boehmite nanofluid synthesized via organic sol gel route, is the first in literature and this will interest for many industrial cooling systems where requiring advance coolants with improved performance.

## Experiments

The well known methodology followed to characterize the nanofluids technical performance considered the base fluid type, nanoparticles parameters and nanofluid properties. The interconnection between these variables can be seen in figure (1) [13]. It's clear that no seat for stability measurement within the nanofluid properties block diagram. To bridge this gap for nanofluids engineering application, the urgent work are suggested towered stability evaluation under both stagnant and flow conditions. The current investigation considered the stability at stagnant condition.

**Base fluid:** A local produced soft water of pH 7.2 and maximum total dissolve solid 124 ppm without any additives was the design base fluid used in current work for the preparation of nanofluid.

**Preparation of organic alumina based sol-gel**: The sol was prepared by hydrating aluminum isopropoxide (Al $(OC_3H_7)_3$) [>98% AI Fluka AG] with distilled water (molar ratio 1:90) at about 85°C with stirring for one hour  using magnetic stirrer, and then nitric acid was added into the solution to adjust the Ph value to about 3~5.  A complete hydrolysis process produced hydrated alumina oxide (Boehmite) according to the reaction in the following equation (2) [14]. The concentration of oxide in the final solution was ~0.28 mol\L. This solution denoted as NF-1 in following text.

$$2[(CH_3)_2CHO)]_3Al + (3 + n)H_2O = Al_2O_3 .nH_2O + 6(CH_3)_2CHOH \qquad ... (2)$$
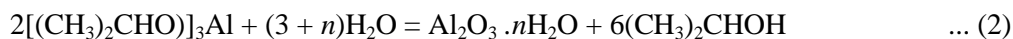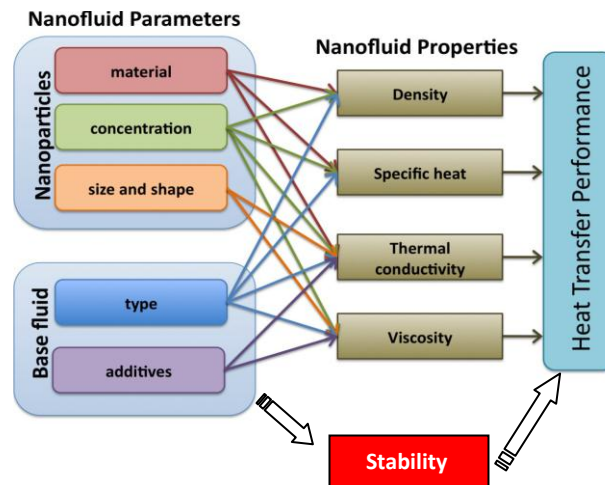
**Figure (1) Methodology illustrated the nanofluid technical performance [13]
The stability adds to integrate the nanofluid properties.**

**Drying of boehmite sol-gel**: To separate the constituents of the sol-gel solution into solid (Xerogel), slow oven drying for 24hr at $80^0$C was applied and then for half an hour at $120^0$C to achieve fully drying of boehmite alumina xerogel.

 **Calcinations of boehmite xerogel**: For dispersion assessments, stability and tracking the phase change limits, the obtained xerogel was calcined in a conventional electrical furnace at different temperatures $175^0$C, $200^0$C, $220^0$C, $250^0$C, $300^0$C , $350^0$C , $600^0$C and $700^0$C for 15min.

**Preparation of nano boehmite alumina / water fluid:** To achieve the function of the resultant fluid characterization in terms of nanoparticles concentration, fluids were formulated by simple stirring technique in two directions:

• Dilution of NF-1 sol by base fluid into six solutions containing different boehmite alumina concentrations 0.1, 0.3, 0.5, 1, 1.5 and 2 wt%.

• Dispersing the obtained xerogel from NF-1 sol in base fluid to form five solutions. The final alumina concentrations were 0.1, 0.5, 1, 2 and 4wt%. These fluids denoted as NF-2 in following text.

In this respect, no dispersants and/or stabilizers were added to these fluids to eliminate their interfacial effects in nanoparticle suspensions within the base fluid matrix. Accordingly, the dispersibility variation of nanoparticles and their effects on possible aggregation into clusters parallel with their impact on the thermal performance of different prepared nanofluids will be supported.
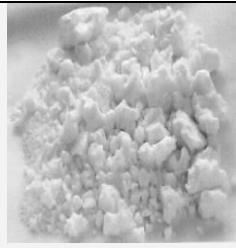
**Characterization**

• The TGA and DTA curves of the boehmite xerogel was carried out by TGA thermal analyzer model 400 Perkin Elmer up to $800^0$C at heating rate $20^0$C/min under helium gas flow rate 20ml/min.

• For large scale sample of boehmite xerogel, weight loss as a function of temperature in range up to $800^0$C was conducted in LAC-L15/12 electrical box furnace.

• Differential scanning calorimetery analysis for alumina xerogel was done by analyzer model Shimadzw DSC-60 up to $300^0$C at heating rate $10^0$C/min in normal atmosphere.

- Laser Diffraction Particle Size analyzer of the type (SALD-2101), measured extent 0.03 and 1000 microns used to measure the sizes and distribution of particles and/or clusters of agglomerated particles in fluids.

- To track the phase's of alumina. XRD curves were obtained in Shimadzu XRD-6000, operating with copper K-gamma radiation at 40 kV and 30 mA, the scanning was conducted for all specimens between ($2\theta$) =20 and ($2\theta$) =60, a speed of 5 degrees per minute.

- Viscosity measurements at $40^0$Cwere obtained in Ubbelohde viscometer model HVU481.

- Thermal conductivity measurements for different formulated fluids were done in thermo-calories device set, model KD2 Pro, consisting of hand held controller and single needle sensors.

## Results and discussion

**Sol and xerogel analysis**: The well known hydrolysis reaction of aluminum isoprppoxide according to equation (2), producing alumina boehmite of chemical formula $Al_2O_3$. $n$$H_2O$ or $2n$AlOOH. Figure (2-a) shows the x-ray diffraction analysis of the alumina boehmite xerogel granular obtained after drying the sol-gel at $120^oC$ . The patterns match those of standard spectra   files JCPDS- 21-1307 for hydrated aluminum oxides as boehmite AlOOH. This type of boehmites are commonly referred pseudo-boehmite, gelatinous boehmite or boehmite aluminas, to make a clear distinction with naturally found well-crystallized boehmite[15].The stoichiometric calculation for equation (2) based on mole balance indicate that the hydrolysis of 240gm [(CH3)2CHO]3Al (Mwt=204), 98% purity, produce 81 gm boehmite $Al_2O_3$ .$n$$H_2O$, namely at ratio ~3:1. However in current experiment, the obtained ratio was ~1.74:1 and when the xerogel has been densified at $600^0C$ the ratio increased almost to the stoichiometric value of 3:1, then the value of $n$ is estimated 1.98 and the crystalline water percent included in obtained boehmite is 25.9%. This result came in good agreement with the range of values given to account for expected hydration range of alumina boehmite where $n$=1 to 2 and in most boehmites there is 70–82 wt % $Al_2O_3$ per gram of powder [16]. The above stoichiometric results also indicate that both of boehmite and part of the by-product.

**Table (1): Stoichiometric values for the hydrolysis reaction in equation (2) practiced for producing hydrated boehmite xerogel as raw material for preparation the nanofluid.**

| Constituents | Weight (gm) | | | | |
|---|---|---|---|---|---|
| | Reactants (gm) | Products (gm) | Xerogel dried at $120^0$C(gm) | Xerogel treated at $600^0$C(gm) | |
| [(CH₃)₂CHO)]₃ Al | 240 | -- | -- | -- | |
| H₂O | 52.92 | -- | -- | -- | |
| H₂O (excess) | 1852.8 | 1852.8 | -- | -- | |
| Al₂O₃. 2H₂O | -- | 81.14 | 81.14 | 32.4 | **Xerogel Products dried at  $120^0$C** |
| (CH₃)₂CHOH | -- | 211.68 | 56.6 | -- | |
| Xerogel | -- | -- | 138 | 32.4 | |

((CH₃)₂CHOH) in a ratio of ~1.43:1 formed a structure of high dispersibility and long term stability in water. Table (1) summarize the over all stoichiometric calculation for the hydrolysis reaction in equation(1) which considered as mainstay

mass balance for process formulation of the alumina boehmite nanofluid in single and two stages.
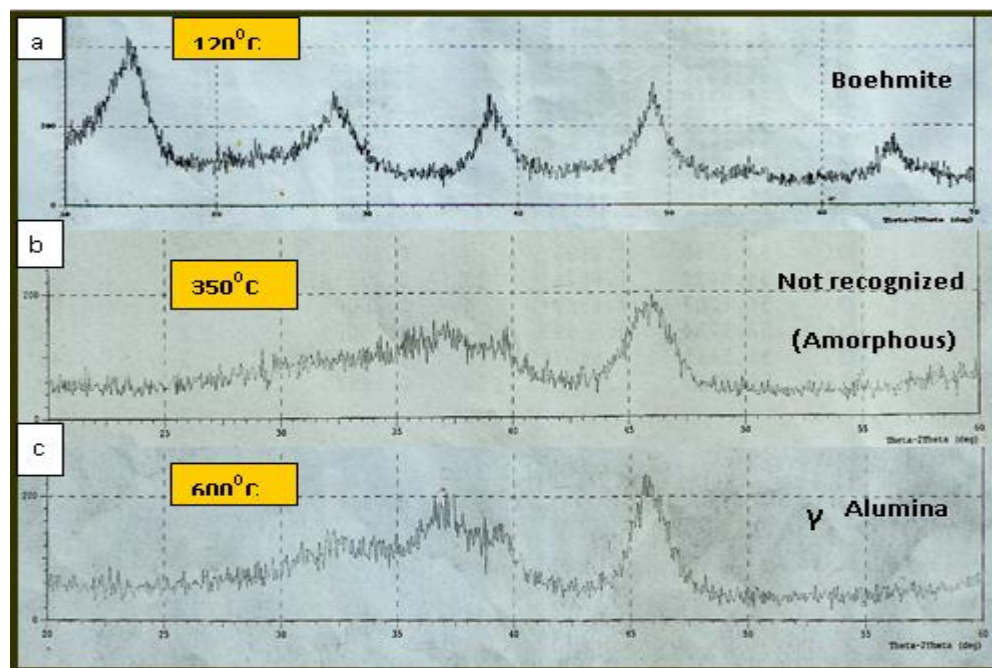


**Figure (2): X-ray diffraction patterns curves for the xerogel granules at different heat treatment temperatures up to 600$^{0}$C showing the recognized phases.**

## Characterization behavior of the starting xerogel powders by XRD

The rystallization behavior of the phase's transformation at different heat treatment temperature was investigated. Figure (2-b, c) revealed the XRD patterns for the xerogel obtained from the hydrolysis reaction in equation (1) after half hour treatment at 120$^{0}$C, 350$^{0}$C and 600$^{0}$C. The obtained patterns match those of boehmite standard spectra file JCPDS- 21-1307, amorphous alumina and γ-alumina of standard spectra files JCPDS-11-0517 respectively. These results came in good agreementwith the thermal transformations sequence of aluminum hydroxide to form different standard transition aluminas phases [17-18], however, these transformations make the evaluation of the stability of boehmite phase AlOOH upon heating and their impact on forming stable colloidal suspensions or slurry dispersions nanofluid with water interesting field as can be seen later.

## Furnace thermal analysis:

The TGA and DTA curves of the boehmite aluminas xerogel was investigated for different thermal analysis up to 800$^{0}$C as shown in figure (3).There is an initial weight loss ~18 % up 200$^{0}$C due to the partial release of the alkoxid and crystallization water, followed by a major weight loss ~ 27% between 200$^{0}$C and 300$^{0}$C attributed to the full release of the alkoxid and decomposition of the boehmite, nitrate ions and release of the major crystallization water. At higher temperatures, decomposition of boehmite is complete at 480$^{0}$C which in good agreement with the normal range 275$^{0}$C-475$^{0}$C [17]. The maximum rate of water removal occurs at 222.65$^{0}$C as revealed by DSC thermal analysis shown in figure (4). These tests

normally use very small sample (< 25mg).  To clear more practical laboratory results in a higher sample scale, furnace thermo-gravimetric test was conducted on 46 gm of dried boehmite xerogel powder of different size (< 50μm).  Figure (5) shows good agreement with that obtained in the TGA curves. Between $300^{o}$C and $500^{o}$C decomposition of boehmite is complete and the weight loss was 8% with no sign of weight change upon heating between $500^{o}$C and $600^{o}$C. Based on these results, there are quite structural changes for initially obtained xerogel. Therefore, from practical point of view, close investigation for the boehmite phase AlOOH upon heating is require to clear the function of dispersibility variation in base fluid on the fluid stability in terms of both phase change and the loss of alkoxid and crystalline water.
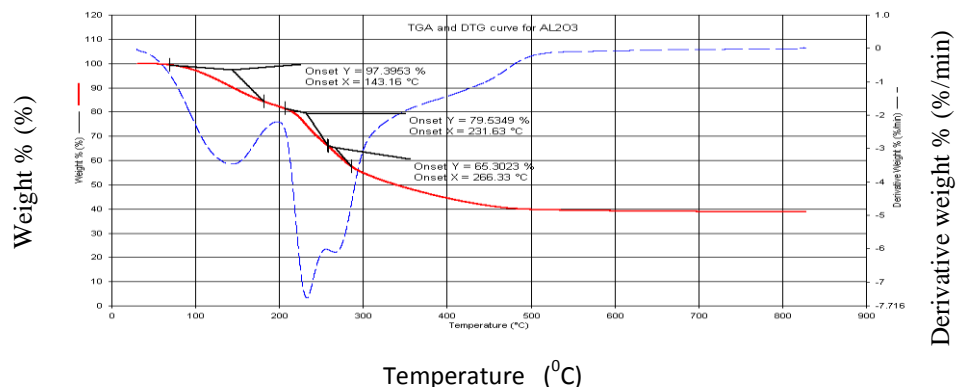


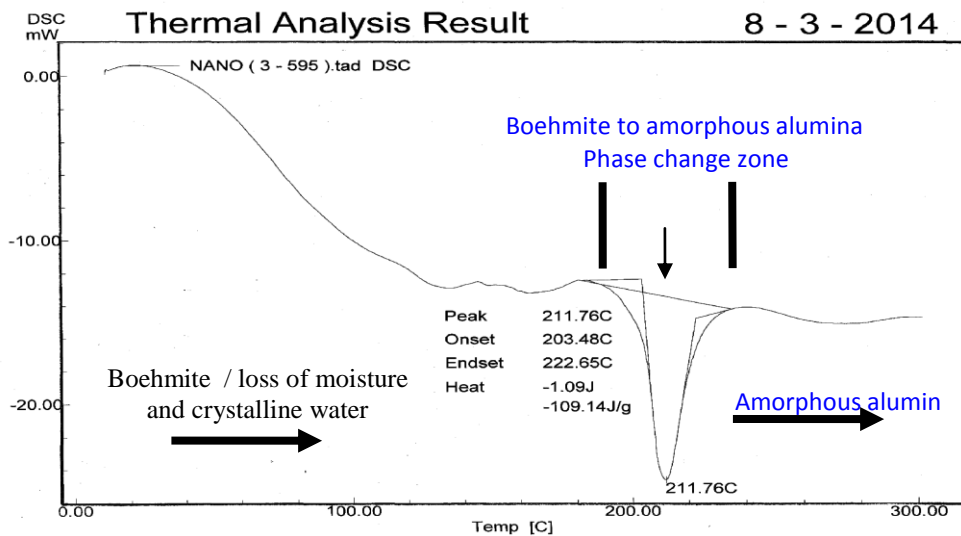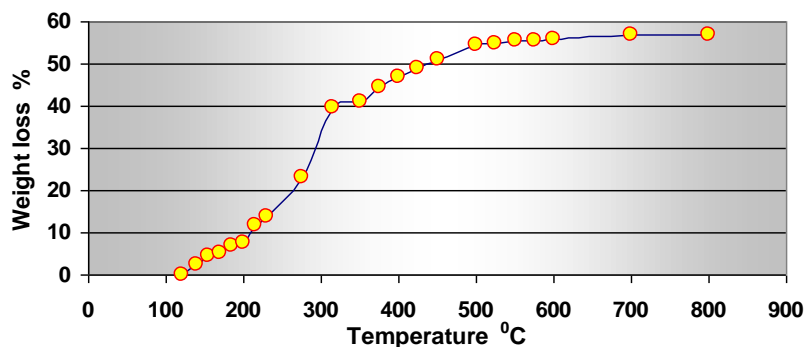**Figure (3): TGA and DTA analysis curve of boehmite alumina xerogel**



**Figure (4): DSC thermal analysis curve of boehmite alumina up to $300^{0}$C**

**Figure (5): Thermal analysis of boehmite AlOOH.$2H_2O$ xerogel produced by the reaction in equation (2), presenting the variation of weight loss in terms of temperature increase**

## Nanofluid stability assessment: Sedimentation tendency

There are many inspection instruments and method that can verified the stability of nanofluid suspension well defined recently. In this work, sedimentation balance was used for fluids relative stability ranking. The weight of sediment settling during 48 hours time was measured. The suspension fraction (SF) for each case was calculated by the formula FS = $(W_0 — W)/W_0$ in which $W_0$ is the weight of xerogel loaded in base fluid and W is the weight of the sediment. Then, the sediments% was calculated as 100(1-SF) [12].

**Fluid NF-1:** Figure (6) shows photographic images for NF-1 nanofluids at different boehmite loading. No sediments and/or suspension settling under gravity with time over three months were observed with all of these fluids. This observation reflected the highly dispersion stability of these fluids. However, the pH values were measured 5.9, 5.2, 4.2, 3.8 and 3.6 as the boehmite concentrations were 0.1, 0.5, 1, 1.5 and 2 wt% respectively. To explain this long term stability, it was claimed that the hydration the precursor in acidic environments (pH<4) according to equation (1) leads to stable polynuclear cataions of boehmite alumina with a structure formula of: $[AlO_4Al_{12}(OH)_{24}(OH2)_{12}]^{7+}$ and 3~5nm size [19]. These cataions are highlydispersible due to the high positive surface charge and embody themselves in polymeric chains and as the fluid's pH increased as a result of dilution by base fluid of pH =7.4, a basic catalyst acts over middle of these chains allowing the formation of highly interconnected polymer clusters structure these clusters are in some cases non-continuous and non- uniform in the matrix of solution.
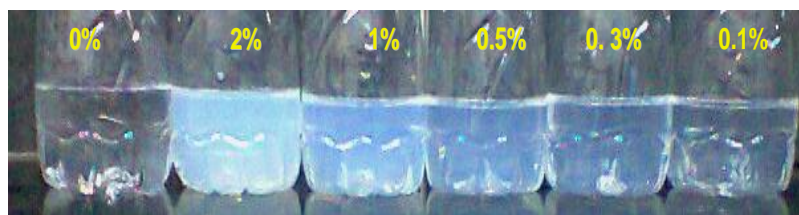


**Figure (6): Photographic images for NS-1 nanofluids at different boehmite loading under gravity with time over a three months period.**
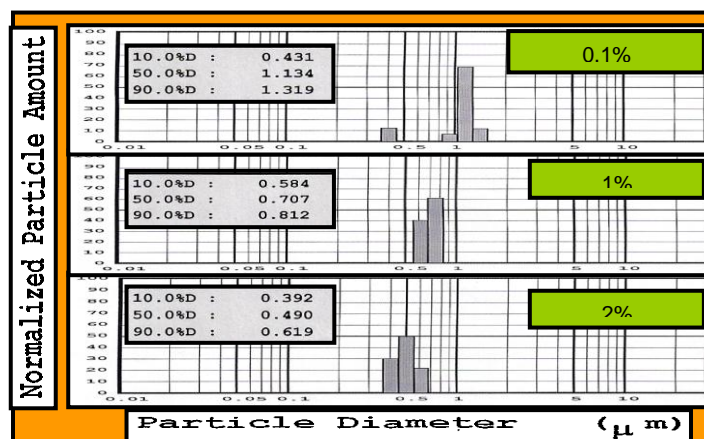
**Figure (7): The laser diffraction particles size analysis for three selected fluids prepared  from fluid NF-1 treated at 175$^0$C at different  boehmite loading percent 0.1, 1and 2 wt%.**

At the higher pH up to 5.9,  the stability of dispersion and/or suspension was almost found not changed, reflecting the presence of enough positive surface charges on the boehmite particles to maintain the high stability degree. However, the case of null particles surface charge (iso-electric pH) was not reached for all practiced fluids, which is reported to be around pH 9.2 for alumina fluid in general cases [20]. In another words there is considerable relation between fluid boehmite concentrations and boehmite chains aggregation degree into cluster structure. To clear this behavior for Fluid NS-1, three concentrations were analyzed by laser diffraction technique for cluster size change observation. The results are shown in figure (7) indicate that:

- The cluster size at D$_{50}$% increased from 490nm at 2% boehmite alumina to 707nm and 1134nm at 1% and 0.1% respectively.
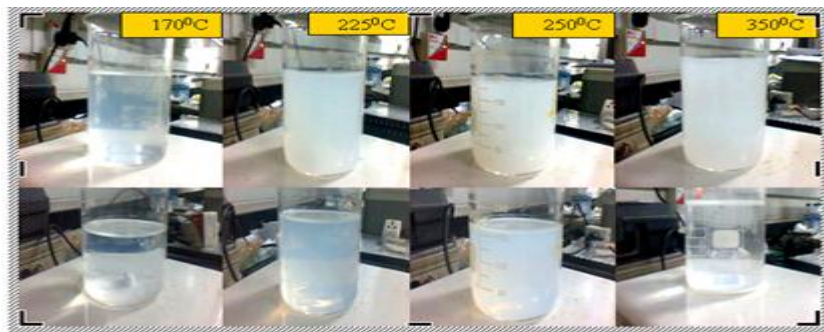


- The particles were stacked on narrow size range of two column at fluid of 1% loading while at 2% and 0.1 loading the size range expand to three and four columns respectively, reflecting the cases of dispersion uniformity and continuity changes according to the agglomeration degree.

This mean that, in current case the aggregation and /or agglomeration of these clusters in fluids matrix are highly effected by concentration and pH variations.

**Figure(8): Visual observation for four fluids prepared by addition same amount of different thermal treated xerogels of boehmite. The lower raw was   after 48 hours settling time**

In this respect, based on general definition [21], The characterization of these fluid were changed from solution at boehmite born time by equation (2) to colloidal dispersion then to suspension with no observable effect on the suspension stability and accordingly the particles movement within the fluids are also changed from kinetic to Brownian to convection movement according to the common solutions characterizations. The effect of all these behaviors on the fluids thermal characterization is an interesting observation as can be seen later.

**Fluid NF-2:**
Fluids stability vs. boehmite treating temperature: Different thermal treated xerogels up to $700^0$C were studied in terms of obtaining colloidal and/or slurry suspensions nanofluids properties as a function of stability at same concentration. The following results were obtained at the end of preparation stages of the fluid NF-2:
Figure (8) illustrate the visual observation for four fluids prepared by addition same amount of different thermal treated xerogels of boehmite and after 48 hours settling time. These fluids reveal different colors ranging from clear light blue , turbid light blue to colorless as the dispersed xerogel was heated to $170^0$C,$225^0$C, $250^0$C and $350^0$C respectively indicating different fluid characterizations of colloidal dispersions and suspensions resulting in different amount of structural water include these phases, hence producing different fluid stability levels.

 Figure (9) shows the sediment percent changes for all prepared fluids showing different values after 48 hours settling time. The plotted function shows that the boehmite heated at $150^0$C was the most stable forming fluid with no observed sediment and as the treatment temperature increased gradually up to $225^0$C the sediment percent reached a maximum value of 12 %. At $225-275^0$C the percent was increased dramatically to 81% and being 94% at $350^0$C. This mean that the starting solution has stable boehmite colloidal properties while the solutions obtained from xerogels treated for higher temperature shows partly unstable suspension properties below $350^0$C and fully slurry suspension properties above $350^0$C. These changes in dispersibility attributed to the gradual transformation of boehmite to amorphous alumina and then to γ-alumina as recognized by the x-ray diffraction analysis shown in figure (2).  These transformations can represent in equation (3):

$$2AlOOH.H_2O(Al_2O_3.2H_2O) \rightarrow Al_2O_3(amorphous)+2H_2O \rightarrow \gamma\text{-}Al_2O_3 \qquad \text{... (3)}$$

This process is key issue to consider during selection the treatment temperatures before using the boehmite xerogel in fluid preparation.
To stand on the qualitative analysis of these sediments, x-ray analysis shows no crystalline spectral existence before thermal treatment of these sediments up to 600-$700^0$C where γ-alumina phases was tracked. In this respect, it is clear that these phases are not excellent materials for use in demanding colloidal and/or suspension applications like boehmite xerogel, which is nano-sized in the dispersed phase (as seen later) and exhibit a unique combination of consistency and dispersibility. However, many researchers also mentioned for unsatisfying results that is very difficult to suspend even 10nm γ-$Al_2O_3$ particles in stable fluids [22-23].
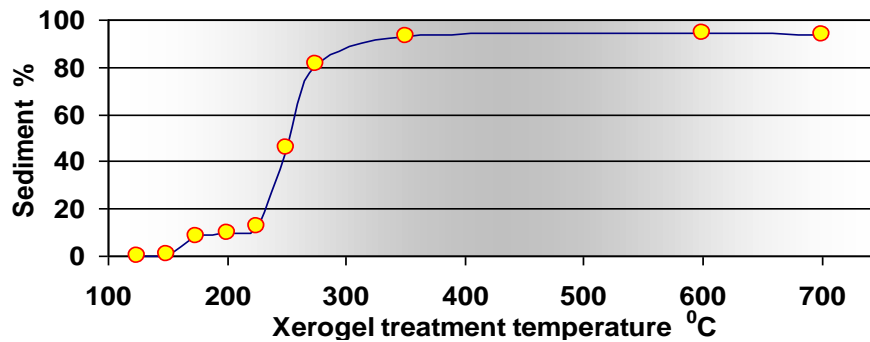
**Figure (9): Sediment percent after dispersion of boehmite xerogel treatment at different temperatures in water base fluids measured after 48h settlement.**

Based on above results, the boehmite treated at no more $175^0$C was used in fluids formulation at different loading percents for farther stability and thermal characterization studies.
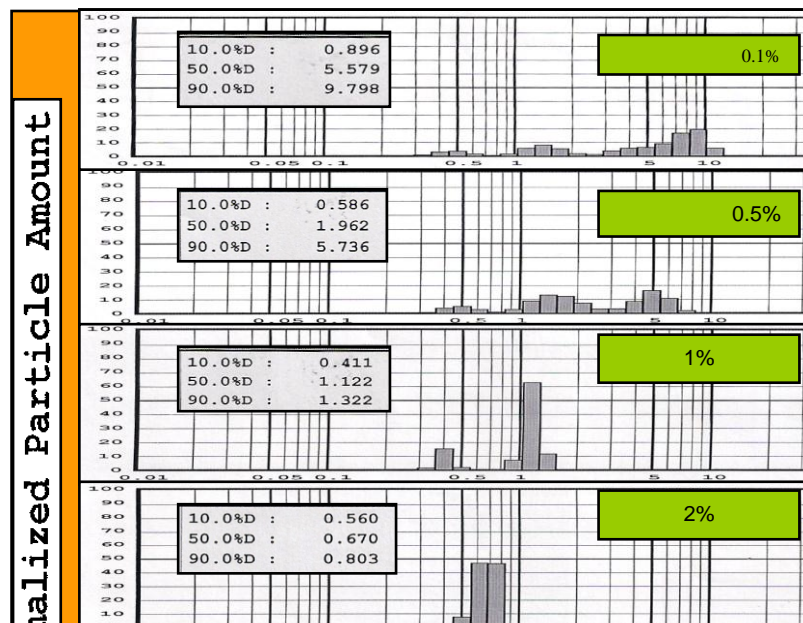
Fluid stability vs. boehmite concentration**:** Figure (10) presented the laser diffraction particles size analysis for five selected fluids prepared from xerogels treated at $175^0$C at different boehmite loading percent 0.1, 0.5, 1, 2 and 4wt%.

In this respect the pH values for all fluids samples were 3.65±< 0.3%. The variation of particles and/or clusters size at $D_{10\%}$, $D_{50\%}$, $D_{90\%}$ is plotted in figure (11) as a function of boehmite loadings. It is clear that the sizes remain at less than 100nm for fluid loading by 4% boehmite while these sizes increased rapidly in a non linear function as the loading percent decreased to<1%. The continuous observation within 24hours shows no sediments and/or suspension settling under gravity, but with time over two months, settling under gravity were observed with fluids of 0.1% and 0.5% boehmite concentration at suspension fraction almost at twice values for the fluid of 0.1% concentration. This means that the agglomeration degree is inversely related to concentration changes which explained that the nanofluids are not a simple mixture of liquid and the solid particles tend to aggregate and/or agglomerate at certain concentration to form unstable suspension fluid.

This will reflect a disagreement with the current thought that agglomeration and concentration is directly related. Once again, the effect of these obtained behaviors on the fluids thermal characterization is an interesting observation as can be seen later.

**Thermal conductivity assessment:**

The measurements of thermal conductivity for different formulated fluids of the sets NF-1 and NF-2 were done in thermo - calories device set, model KD2 Pro. The relative comparison in thermal conductivity enhancement was made with the base fluid.

**Figure (10): The laser diffraction particles size analysis for five selected fluids prepared from xerogels treated at 175$^{0}$C at different boehmite loading percent 0.1, 0.5, 1, 2 and 4wt%.**
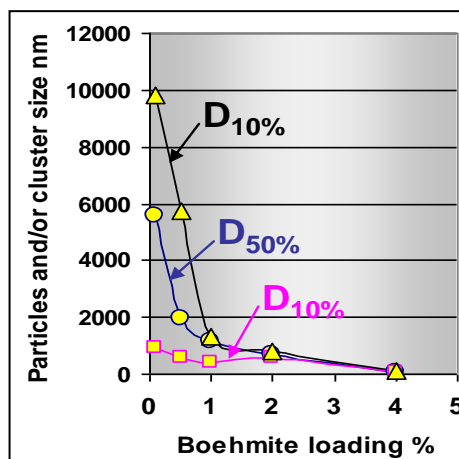


**Figure (11): Particles and/or clusters size variations at D$_{10\%}$ , D$_{50\%}$, D$_{90\%}$ as a function of boehmite concentration (data were adopted from results in figure (10)).**

**The goal of nanofluids is to achieve the highest possible effective thermal properties at stable suspension and smallest possible concentrations in a base fluid by uniform dispersion of nanoparticles [3]**

This trend will eliminate the error arise from measuring the absolute value since the device and measuring procedure were applied for all fluid samples. The role of interfacial layers and the effect of nanoparticles aggregation on the effective thermal conductivity enhancements for both nanofluids NF-1 and NF-2 will be analyze and discuss as follow:

**Fluid NF-1:**

Figure (12) shows non-linear relation between the fluids relative thermal conductivity enhancement and boehmite loading percent. As it can be seen, a narrow boehmite loading range at around 1-0.9% was observed for achieving maximum relative thermal conductivity enhancement of about 2.7. Figure (12) also, related the boehmite loading percents with particles aggregation degree. The optimum particles aggregation degree was 770 nm at $D_{50\%}$ where the optimum boehmite loading 0.9%.
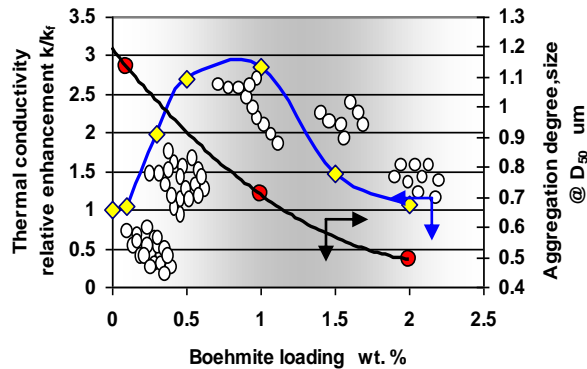


**Figure (12): Thermal conductivity relative enhancement of fluid NF-1 as a function of boehmite loading percents and the particles aggregation degree**
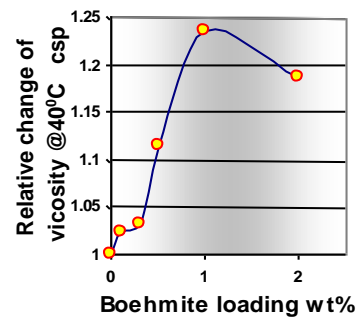


**Figure (13): Function of relative change in NF-1 fluids viscosity in terms of boehmite loading %**

These results clearly reflect the case of deviation from the predictions of Maxwell's model for linear dependence effect of particles loading on the fluids thermal conductivity enhancement, where neither the dispersion at 2% boehmite loading with 490nm cluster aggregation size at $D_{50\%}$ nor the case of highly aggregated at 0.1% boehmite loading with1134nm aggregation size at $D_{50\%}$ could retain the optimum enhancement. In chemistry standard [21], the fluids retain their suspension characterizations at particles size >200nm, this limit was found equivalent to practical particles aggregation degree between 490nm and 1134nm at $D_{50\%}$, producing the non-linear dependence presented in figure (12). Therefore, this fluid should be characterized as stable suspension with convection movement of particles and/or cluster within the based fluid matrix. This movement is due mainly to electrostatic repulsion between particles and/or clusters and in general is highly dependent on their effective volume since the base fluid normally formed a highly ordered immobilized fluid layer around these particles [11] which considered as high thermal conductivity layer. Therefore the heat transfer along such clusters should go through these layers which their volume is known to be inversely related to particles volume size.

**Effective volume of particles = volume of particles + volume of immobilized fluid layer**
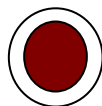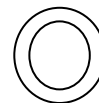
**and/or cluster**          **and/or cluster**          **around particles and/or cluster**

On the basis of these findings, the impacts of both immobilized fluid Interfacial layer and clusters or aggregation of particles will discuss in the following text to set the most effective one in producing the obtained unusual behaviors:

**Interfacial layers impact:** To include the immobilized fluid layer effect, a nanoparticle in liquid suspension with monosized spherical particles of radius r and particle volume concentration φ was considered. Hence, assuming that the solid-like immobilized layer of thickness h around the particles is more ordered than that of the bulk liquid and that the thermal conductivity of this ordered layer is higher than that of the bulk liquid and could be combined with the particle to form an equivalent particle. This assumptions result in an equivalent particle radius     r +h and an increased volume concentration. Based on effective medium theory, the equivalent thermal conductivity $k_{pe}$ of the equivalent particles can be calculated, then Maxwell equation (1) can be modified into equation (4) [25]:

$$k_e \quad \frac{k_{pe} + 2k_l + 2(k_{pe} - k_l)(1 + \beta)^3 \varphi}{k_{pe} + 2k_l - (k_{pe} - k_l)(1 + \beta)^3 \varphi} \quad k_l \qquad \dots (4)$$

Where

$K_e$ is nanofluid final thermal conductivity $K_{pe}$ is the equivalent thermal conductivity of the equivalent particles, $\beta = h/r$ is the ratio of the nanolayer thickness to the original particle radius. $K_l$ is the thermal conductivity of the based fluid. It can be seen in equation (4), the nanolayer impact is significant for small particles (r << h). However, for large particles (r >>h, $\beta \rightarrow 0$), the immobilized layer impact is small and any enhancement in the thermal conductivity will be degraded hence the modified Maxwell equation reduces to the original Maxwell equation; however, this degradation can be limited by large aggregate sizes where it was practiced with current fluid NF-1 as presented in figures (7).

**Effect of clusters and aggregation of particles:** The optimum enhancement of thermal conductivity relative to base fluid obtained for NF-1 fluid can be explained on the basis of aggregated cluster morphology. In combining with the explanation for long term stability of this fluid and the obtained results presented in figure (7), there are three possible configurations for the particles and/or clusters suspension in the current fluid matrix:

- As born from hydrolysis reaction (2), polynuclear nano-cataions of boehmite alumina of 3~5nm size.
- At 2% boehmite loading, cluster of nano-cataions suggested with no and/or low-aspect-ratio of 490nm at $D_{50\%}$.
- At 1% loading, polymeric linear chain-like aggregates of nano-cataions with high-aspect-ratio up to 707nm at $D_{50\%}$.
- Interconnected polymeric linear chains forming large clusters structure with lower-aspect-ratio at 0.1% boehmite loading.

These morphologies have different chemical dimension and radius of paths to aggregate. At high boehmite loading ~2%, where the fluid pH was low ~3.6 , the aggregation of polynuclear cataions of boehmite alumina was limited to higher size dispersed cluster. As the loading decrease and the pH gradually increase between 4 and 5, polymeric chains like aggregates of these cluster with high-aspect-ratio stared to form in fluid matrix producing gradual enhancement in thermal conductivity up to optimum point where the morphology of these cluster changed gradually again to

interconnected polymeric chains with low -aspect-ratio as the loading has farther decease with more increasing in pH>5. Therefore four morphologies of different configurations were play significant role in producing the optimum enhancement as presented in figure (12) these results suggest that nanofluids without chain-like aggregates do not exhibit significant enhancement of thermal conductivity. In this respect, this aggregation morphology provides direct evidence for efficient transport of heat within the clusters matrix through percolating paths. These results came in good agreement with other study suggested that the optimum design for thermal conductivity enhancement of nanofluids would involve the use of high-aspect-ratio single wall carbon nanotubes, rather than spherical or ellipsoidal particles [26]. Figure (13) presents a function of relative change in fluids viscosity in terms of boehmite loading increase up to 2%. It is clear that the function is non-linear and similar in trend to that obtained for thermal conductivity enhancement shown in figure (12). The maximum relative viscosity recorded was at ~1% boehmite loading. This result strongly supports the formation of high-aspect-ratio aggregates. It is, however, important to notice that the use of high-aspect-ratio fillers in fluids will lead to dramatic increases in fluid viscosity [24, 26].

**Fluid NF-2:**

This fluid represents the case of two steps method for boehmite nanofluid formulation which shows quite different from the case of single step NF-1 fluid in term of thermal conductivity enhancement trend. It is clear from results presented in figure (14) that no considerable enhancement in thermal conductivity before ~1% boehmite loading at particles aggregation size of 1122nm with non-linear dependence on boehmite loading increasing. The optimum relative enhancement in thermal conductivity was about ~ 1.7 at 2% boehmite loading and particles aggregation degree of 670nm at $D_{50\%}$. The particles and/or clusters were stacked on a narrow size range reflecting the case of ultimate dispersion uniformity and continuity. In comparison with fluid NF-1, the obtained enhancement of NF-2 fluid was lower and occurred at higher boehmite loading, but at near particles aggregation degree value where this value for fluid NF-1was 707nm.  As already discussed, these results clearly reflect the case of deviation from the predictions of Maxwell's model for linear dependence effect of particles loading on the fluids thermal conductivity enhancement, where neither the dispersion at 4% boehmite loading with 76nm cluster aggregation size at $D_{50\%}$ nor the case of highly aggregated at 0.1% boehmite loading with5579nm aggregation size at $D_{50\%}$ could retain the obtained optimum enhancement. It is seen that the boehmite loading amount play only part of the role in enhancing the thermal conductivity since the obtained enhancement trend shown in figure (14) was a non-linear dependence function. The other part of the role in enhancement process may attribute to the lower aspect ratio of aggregated clusters. This behavior may explain on the basis of the variation in fluid viscosity values in terms of increasing boehmite loading percent. Figure (15) presents the trend of this function which seems similar to that obtained for fluid NF-1 but at lower relative viscosity value.  In this respect, no significant change in fluids pH (3.65±<0.3%) were observed. This parameter found play significant role with fluid NF-1 at certain optimum value as in embodying the particles and/or clusters in linear chain with higher aspect ratio. On other hand, we found that the trying of increasing the clusters aspect ratio by increasing the fluid pH value lead practically to affect the stability and

cause more sedimentations which should be avoided. Therefore it is important to subject both of fluid stability and conductivity enhancement to one optimization goal. However, the following explanations for the enhancement function trend practiced for currently investigated fluid NF-2 as illustrated in figure (14):

- At 4% boehmite loading, fully clusters of nanoboehmite particles 76nm size at $D_{50\%}$ with very low aspect ratio.

- Aggregation of the nano-clusters to form polymeric linear chains of low aspect ratio comparing with that obtained for NF-1. This aggregation behavior occurred at 2% boehmite loading and clusters size 670nm at $D_{50\%}$.

- Interconnection of the nano-clusters to form higher size clusters of low aspect ratio 670nm-1122nm.

- Fully particles aggregation in large size 1122nm-5579nm with very low aspect-ratio. This case observed at <1% boehmite loading.
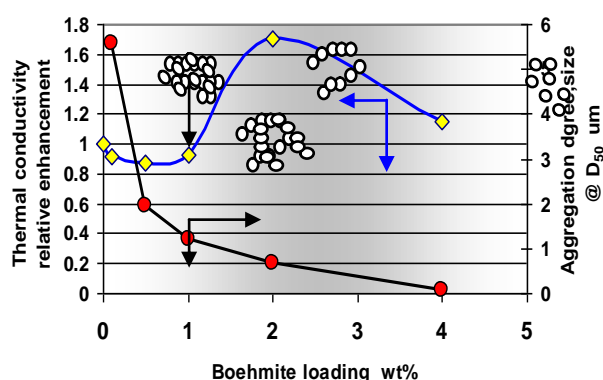


**Figure (14): Thermal conductivity relative enhancementof fluid NF-2 as a function of boehmite loading percents and the particles aggregation degree.**
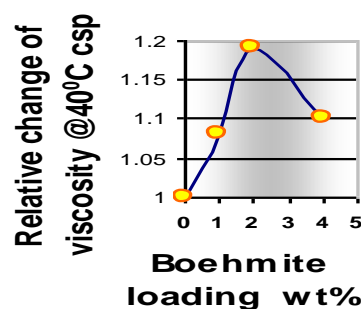
**Figure (15): Function of relative change in NF-2 fluids viscosity in terms of boehmite loading %**

## Conclusions

The experimental analysis to investigate the suspension stability and thermal conductivity enhancement of nano boehmite alumina were done for fluids formulated from boehmite alumina prepared by organic sol gel route. It was found that, in addition to boehmite loading percent, other parameters including particles aggregation degree, viscosity, aggregation configuration with high-aspect-ratio value have significant impact on the suspension stability and thermal conductivity enhancements especially for the fluid formulated by single step method (NF-1).

This study also demonstrated the feasibility of the single step method in formulating a highly stable boehmite nanofluid with thermal conductivity enhancement up to 2.8 times by controlling the particles and/or clusters aggregation in certain linear chains configuration with optimum aspect ratio.

Finding from this study imply that, although the dominate fluids system characterization are suspension with convection particles movement, as the aggregation of boehmite nanoparticles were measured between 76nm and 5579nm, both of the fluids NF-1 and NF-2, shows anomalous self abilities of boehmite nanoparticles to embody themselves in several configurations producing clusters with

different aspect-ratio affecting the fluids viscosity in similar non-linear function trend that practiced by boehmite loading change.

   This means that there is away to create and control a high aspect-ratio configurations for the aggregated clusters inside the base fluids matrix.

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