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Preparation of Nanofluids of Some Iron Compounds from Industrial Waste $FeSO_4 \cdot 7H_2O$ as Precursor for NOx Reduction

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Keeping in view the reported NOx reduction potential of solid powders of iron containing compounds like FeO, Fe_2O_3 and Fe_3O_4, the new, simpler and cost effective methods for preparation of nanofluids of $Fe(OH)_3$, $Fe(OH)_2$ and Fe_3O_4 in diesel have been developed and presented. $Fe(OH)_3$ and $Fe(OH)_2$ are expected to convert into FeO, Fe_2O_3 at furnace temperature of about 1500 ºC in combustion facilities and than act as NOx reduction agents. These nanofluids shall have advantage due to increased surface area of particles leading to better surface reactions required for NOx reduction. The industrial waste $FeSO_4 \cdot 7H_2O$ has been used for the first time as the starting material for the same for making the methods cost effective. The results of analysis for iron content and particle size determination have also been reported.

Key Words: Fe-Nanofluids, Industrial waste, $FeSO_4 \cdot 7H_2O$, NOx reduction.

INTRODUCTION

Current and near future regulations require 65 to 80 % NOx reduction from coal fired boilers and furnaces[1]. There are several technologies available in literature for NOx reduction. Flameless oxidation and staged combustion significantly reduce thermal NOx in industrial process. Bowin low NOx technology is a hybrid of staged-premixed-radiant combustion technology with a major surface combustion preceded by a minor radiant combustion. Water injection technology, whereby water is introduced into the combustion chamber, is also becoming an important means of NOx reduction through increased efficiency in the overall combustion process. Other technologies, such as selective catalytic reduction (SCR) and selective non-catalytic reduction (SNCR) reduce the post combustion NOx. Introduction of catalytic converters has also been used for reduced emissions from motor vehicles.

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Combination of combustion modification techniques has also been tried for NOx reduction[1]. These include the use of low NOx burners, air staging, fuel staging (burning), AR (advanced reburning - a combination of reburning and N-agent injection in the Reburning zone, along with overfire air or downstream in the burnout zone)[2-5] and injection of metal compounds into combustion and/or reburning zones. Advanced reburning causes 90 % NOx reduction. Injection of metal compounds into combustion and/or reburning zones has been claimed to be comparable with the AR levels NOx reduction[1]. Metallic iron, Fe_2O_3, Fe_3O_4 and iron waste from industry containing about 80 % Fe_2O_3 were co-injected with the reburning fuel, at reburning heat inputs of 18 and 25 %, in amounts needed for 1000 ppm of Fe in the flue gas, in gas and coal fired combustors. Fe metal powder [particles size < 10 μm diameter; 1000 ppm mol fraction in the flue gas or 1000 Fe atoms per 10^6 flue gas molecules], Fe_2O_3 powder [< 5 μm; 0 to 1000 ppm]; Fe_3O_4 ($FeO{\cdot}Fe_2O_3$) [< 50 μm; 0 to 1000 ppm], industrial iron oxide waste (like a byproduct of steel processing industry having 80 % Fe_2O_3 and 20 % impurities mainly $Ca(OH)_2$) [80 % smaller that 50 μm; 0 to 1000 ppm] have been tried as additives for main fuel and the reburning fuel[1,6]. Aqueous solutions of Na_2CO_3, K_2CO_3 and $Ca(CH_3COO)_2$ have also been tried with main fuel and reburning fuel[1]. The heterogeneous NOx reduction on the surface of Fe-containing particles is the most likely explanation of the effect on NOx reduction[6]. NO can be catalytically reduced as follows[7-9]:

$$3CO + Fe_2O_3 \longrightarrow 3CO_2 + 2Fe;$$

$$2Fe + 3NO \longrightarrow 1.5N_2 + Fe_2O_3$$

giving an overall conversion stoichiometry $CO + NO \rightarrow CO_2 + 0.5N_2$. Further FeO is expected to act as $2FeO + NO \rightarrow Fe_2O_3 + 0.5N_2$. These reactions are frequent and most established in a reducing atmosphere like that in combustion units. Fe metal and Fe_3O_4 have been found to be less effective than Fe_2O_3 or iron waste (containing about 80 % Fe_2O_3)[1-6]. It has also been found that the NOx reduction in presence of Fe_2O_3, increases with increase in amount of reburning fuel probably due to increase in CO concentration with an increase in the amount of reburning fuel[1]. Injecting the metal additives (mainly metallic iron, Fe_2O_3, Fe_3O_4) with main fuel caused NOx reduction by 23 % in absence of reburning. In presence of reburning, the NOx reduction was improved by up to 8-10 % when compared with the reburning without additives[1-4,6]. Injecting the metal additives containing Na, K and Ca with main fuel produces upto 30 % NOx reduction while with reburning fuel it improves the NOx reduction by upto 20 % in comparison to conventional reburning[1,5].

Few reports[10-19] are available in literature for preparation of nano size particles of Fe_3O_4 larger than 10 nm diameter in bulk aqueous solution and surfactant systems. The formation of iron oxide vesicles was reported by Mann *et al.*[11]. Reports are available on synthesizing Fe_3O_4 nanoparticles in bulk aqueous solutions without the use of surfactant vesicles[12-14]. Fan *et al.*[20] reported preparation of γ-Fe_2O_3 by a site exchange reaction. Preparation of α-Fe_2O_3 and Fe_3O_4 in mixed media without using different surfactant systems are some of the recent reports[21,22]. Kang *et al.*[10] reported the synthesis of γ-Fe_2O_3 and Fe_3O_4 hydrosols without using surfactant. The resulting particle size was 20-50 nm and 8.5 ± 1.3 nm, respectively. In these methods[10-22], generally the starting materials have been iron oxides or $Fe(OH)_3$ or $FeCl_3$ and $FeCl_2$. Recently, Lissianski *et al.*[6] have suggested that additives containing Fe compounds can be injected as liquid solutions in water or other solvents as components of main fuel, the reburning fuel or products of their pyrolysis or gasification. Injection of additives does not significantly increase the cost of the process as iron containing additives are inexpensive if prepared from industrial wastes containing Fe compounds and do not require a separate injector because additives are injected with main or the reburning fuel.

In the present communication, a new, simple and cost effective method for preparation of $Fe(OH)_2$, $Fe(OH)_3$ and Fe_3O_4 nanofluids in diesel starting from industrial waste containing $FeSO_4 \cdot 7H_2O$ is reported. The aim was to prepare low cost heavy fuel additives for NOx reduction in industrial stationary combustion facilities. An improved efficiency is expected as in combustion furnace, $Fe(OH)_2$ and $Fe(OH)_3$ are expected to convert into FeO and Fe_2O_3, respectively with former finally converting into Fe_3O_4 below the furnace temperature of about 1500 ºC in combustion facilities[23]. These products are already reported to be effective for NOx reduction when injected in solid powder forms as described above and further improvement is expected when these are added in the form of nanofluids as an increase in surface area will felicitate the surface reactions responsible for NOx reduction[1,6]. Preliminary investigations made by us have already shown that some of these fluids have potential in this regard and further studies are required in this direction[24].

EXPERIMENTAL

Samples of $FeSO_4.7H_2O$ with 90.65 % purity were procured from Cosmo Chemical Co. Ltd., Incheon, Republic of Korea which produces it as industrial waste. Doubly distilled water was used for preparation of solutions and washing. All other chemicals used were Sigma Aldrich AR grade. High speed mixer and pH meter used were Gawo tech TLS 250 and Hanna HI-8424 make respectively. The Fe content analysis was done by ICP-AES technique (Jobin-Yvon Ultima -C make). For particle size analysis, Microtrac particle size analyzer model Nanotrac NPA250 was used.

RESULTS AND DISCUSSION

Preparation and analysis of nanofluid of $Fe(OH)_3$: In 3 L stainless steel beaker, 80 g of $FeSO_4 \cdot 7H_2O$ was mixed with 500 g water and 20 g of 30 % H_2O_2 solution was added and stirred for 45 min. Exothermic reaction takes place

$$FeSO_4 \cdot 7H_2O \xrightarrow{H_2O_2} Fe_2(SO_4)_3$$

20 g NaOH was dissolved in 2 L water separately (pH to be maintained at about 13-14) and mixed slowly with $Fe_2(SO_4)_3$ solution and stirred at about 450 rpm for 0.5 h so that the pH remains between 10-12.

$$Fe_2(SO_4)_3 + 6NaOH \longrightarrow 2\ Fe(OH)_3\downarrow + 3Na_2SO_4$$

The solution was kept for about 12 h for allowing the brown coloured precipitates to set down. The precipitates were washed with 2 L water. 1 L water was added to precipitates and stirred with 30 mL of oleic acid for 45 min at 20-30 ºC for chemisorption of oleic acid molecules on $Fe(OH)_3$ particles. Now, 1 L diesel was added and stirring continued for further 0.5 h. The contents were transferred to separating funnel and the sedimentation was allowed for 2-3 d. Lower layer was removed and upper reddish layer was separated and placed for 1 more day for allowing sedimentation, if any. This transparent reddish brown coloured sol of $Fe(OH)_3$ in diesel was stable for over 8 months and its analysis revealed that it contained an average particle size of 22.48 nm (Fig. 1) and 1.69 % Fe.

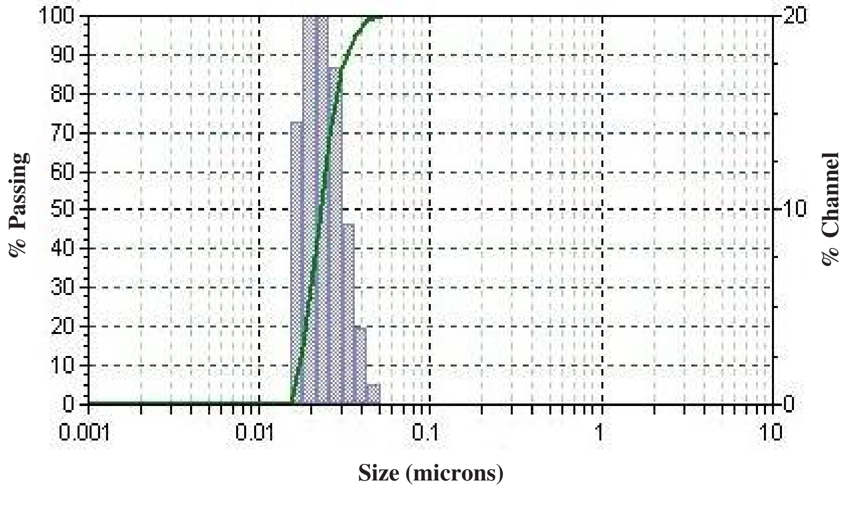

Fig. 1. Particle size analysis for $Fe(OH)_3$ nanofluid

Preparation and analysis of nanofluid of $Fe(OH)_2$: In 3 L stainless steel beaker, 80 g of $FeSO_4 \cdot 7H_2O$ was mixed with 500 g water. 20 g NaOH was dissolved in 2 L water separately (pH to be maintained at about 13-14) and mixed slowly with $FeSO_4 \cdot 7H_2O$ solution and stirred at about 450 rpm for 0.5 h so that the pH remains between 10-12. The reaction involved may be given as:

$$FeSO_4 + 2NaOH \longrightarrow Fe(OH)_2\downarrow + Na_2SO_4$$

The solution was kept for about 12 h for allowing the greenish precipitates to set down. The precipitates were washed with 2 L water. 1 L water was added to precipitates and stirred with 30 mL of oleic acid for 45 min at 20-30 ºC for chemisorption of oleic acid molecules on Fe $(OH)_2$ particles. Now, 1 L diesel was added and stirring continued for further 0.5 h. The contents were transferred to separating funnel and the sedimentation was allowed for 2-3 d. Lower layer was removed and upper greenish layer was separated and placed for 1 more day for allowing sedimentation, if any. This transparent dirty green coloured sol of $Fe(OH)_2$ in diesel was stable for over 8 months and was found to have an average particle size of 31.3 nm (Fig. 2) and Fe content 1.48 %.

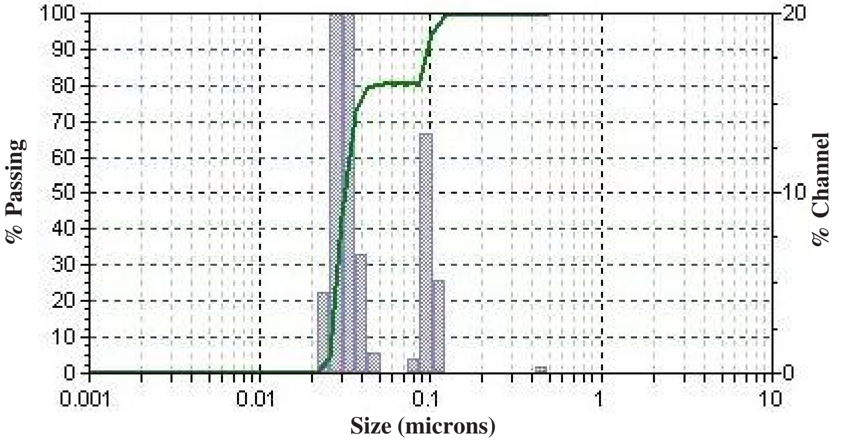

Fig. 2. Particle size analysis for $Fe(OH)_2$ nanofluid

Preparation and analysis of nanofluid of Fe_3O_4: Solution X was prepared by mixing 160 g of $FeSO_4 \cdot 7H_2O$ with 500 g water and adding 40 g of 30 % H_2O_2 solution to it and then stirring in 3 L stainless steel beaker, for 45 min. Exothermic reaction takes place and $Fe_2(SO_4)_3$ is formed. Solution Y was of 80 g of $FeSO_4 \cdot 7H_2O$ in 400 g water. For preparation of solution Z, 60 g NaOH was dissolved in 2 L water maintaining pH at about 13-14.

Solution X and Y were mixed and solution Z was added slowly to it and stirred at about 450 rpm for 0.5 h. The pH should remain between 10-12. The involved main reaction is as follows:

$$FeSO_4 + Fe_2(SO_4)_3 + 6NaOH \longrightarrow 2Fe_3O_4\downarrow + 3Na_2SO_4$$

The paramagneticity was tested *in situ* by placing a magnet near the black precipitate of Fe_3O_4. The precipitate was isolated in the magnetic field by taking the contents in a glass beaker and placing it on a magnet for 2 h. The supernatant was removed by decantation. The precipitate was washed with 5 L water. 1 L water was added to precipitate and stirred with 90 mL of oleic acid for 1 h at 20-30 ºC for chemisorption of oleic acid molecules on Fe_3O_4 particles. Now, 1 L diesel was added and stirring continued for further 40 min. The contents were transferred to separating funnel and the sedimentation was allowed for 10 d. Lower layer was removed and upper black layer was separated and placed for 1 more day for allowing sedimentation, if any. This transparent black coloured sol of Fe_3O_4 in diesel was stable for over 8 months and was found to have an average particle size of 18.05 nm (Fig. 3) and 3.53 % Fe content.

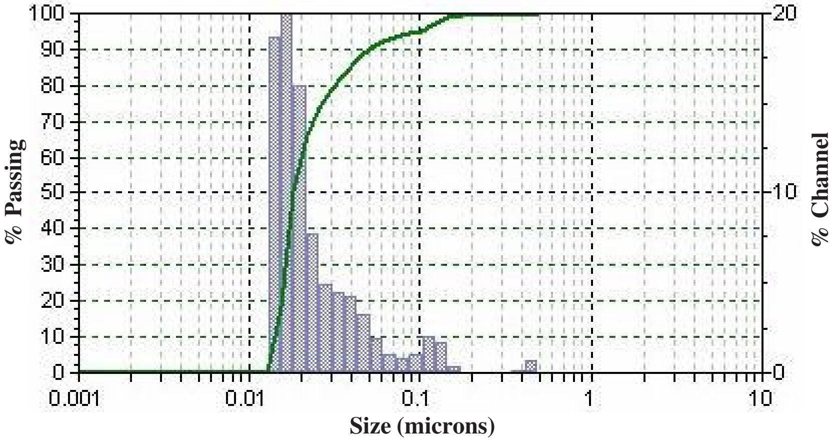

Fig. 3. Particle size analysis for Fe_3O_4 nanofluid

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