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Fluidized bed reactor for treatment of gaseous pollutant: Flourides a case study

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ABSTRACT

Gaseous effluent from Aluminium industry is treated under different operating conditions. Air and industrial gaseous effluent are used as fluidizing medium and secondary gas in the FBR respectively. The fluoride component from the effluent gas reacts with different metallic groups present in the bed materials. The exit gas was allowed to circulate back to the fluidizer for certain time period to allow proper contact among gaseous effluent and bed materials. Different bed materials are used at high temperatures to check the maximum reduction of fluorides from industrial gaseous effluent. The phase composition and structural transition of bed materials at different temperatures are analysed. Characterisation of bed materials before and after the experiments are carried out by several types of analysis like FT-IR, ICP-MS, FESEM, EDX, PSA, BET and XRD analysis. After the experiments, the presence of fluoride was confirmed through all characterisation techniques. Presences of NaF, AlF_3, FeF_2, and FeF_3 in the bed material were confirmed by above mentioned analysis techniques. From these analysis reports, it can be concluded that abatement of fluorides from industrial effluents by FBR is confirmed, thereby implying the fluidized bed technique to be the most efficient technique for abatement of fluorides from gaseous effluents.

1. Introduction

It is desirable to minimise the release of harmful gases and by-products into the atmosphere to protect vegetation and grazing animals and there of human health. People are exposed to airborne fluorides because of air pollution caused by aluminium smelting, coal burning and nuclear power plants, glass etching, petroleum refining, plastic manufacturing, phosphatic fertilizer production, silicon chip manufacturing and uranium enrichment facilities. Exposure to fluoride gas either in the form of direct contact with the skin or inhalation leads to serious health hazards even at very low concentrations. Therefore it is required for all those industries which emit effluents containing fluorides to adopt certain modern abatement techniques to reduce their emissions and to meet the Government regulations. That is why treatment of gaseous fluoride needs serious attention. The fluorides coming out from process industries need to be treated before venting to the atmosphere. Researchers have used bag filters for the abetment of fluorides (Alary et al., 1982).

Several other methods have been developed by the researchers for the treatment of gaseous effluents containing fluorides. Different methods being used by different researchers (Arno, 2004; Cady, 1935; Tonnis et al., 1998, 2000) for abatement of fluorides are dilution treatment, conventional treatment, dry abatement, wet abatement, thermal abatement, point-of-use method, adsorption method and fluidized bed method. The most recent abatement technique for treatment of gaseous effluents containing fluorides is the fluidization technique which uses fluidized bed reactor (FBR). The FBR has many advantages over other reactors. Proper design of FBR can treat industrial gaseous effluents efficiently. Efficiency of a reactor depends upon the extent of conversion of the reactants which in turn depends upon many factors. Thus degree of gas–solid contact is one of the factors which affects the reaction kinetics in turn the efficiency of the reactor.

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Jia et al. (2013) have used fluidized bed method to treat wastewater for abatement of fluorides. Holmes et al. (1967) have described the abatement of fluorides from gaseous effluents using a fluidized bed of activated alumina particles. High fluoride removal efficiency (>99%) has been observed at a reaction temperature between 300 °C and 400 °C with the flow rate limited to 1.25–1.65 times minimum fluidization velocities. Other methods of fluoride abatement are also reported Netzer (1997). By the use of zirconium alloys in fluidized beds, it is also possible to abate NF_3 by contacting with the alloys (Iwata and Hatakeyama, 1995). Fluoride species from the gas mixture (groups consisting of fluoride, chloride, trifluoride and mixture containing fluoride species) is destroyed or reduced by contacting the gas with the bed materials which is capable of reacting with fluoride species (Hsiung and Withers, 1999). It is further observed that the studies on abetment of fluorides at higher temperatures in a FBR are very much limited as it is not economical to have high temperature. Therefore it is felt that if the gaseous fluoride can react with bed materials at optimum temperature or use of any catalyst can accelerate the reaction at lower temperature, the process can be made economical. It is seen that effluent gas from Aluminium industry emits fluoride to atmosphere and produces huge amount of solid waste, Red Mud causing environmental problem. This is a major problem in the authors' home state. That is why it is thought of abating Fluoride in an economical way. With this thought attempt is made to carry out studies on the abetment of fluorides from Aluminium industry effluent gas using a FBR in the present work.

For satisfactory performance of FBR it is necessary to study different aspects of FBR. It is also essential to study the effects of different parameters on the yield of the FBR. Bed expansion depends on the reaction of the metal particles with the gaseous effluents (Hsiung and Withers, 1999). In the fluidized bed method gaseous fluorides are converted to solid fluorides. The industrial gaseous effluent containing fluorides is allowed to pass through the fluidized bed of metal particles which are capable of reacting with gaseous fluorides. Therefore the characteristic of the bed materials in FBR is one of the most important aspects to determine the efficiency of FBR. Metal particles which are capable of reacting with fluorides are considered as bed materials for FBR.

Huge amounts of Red Mud (nearly 1.5 tons per 1 ton of Alumina) are produced as solid waste from Aluminium plant. The composition of Red Mud shows six major constituents viz. silicon, aluminium, iron, calcium, titanium, sodium to be present in it (Chaddha et al., 2007; Reddy and Chandra, 2014; Liu and Zhang, 2011; Vangelatos et al., 2009; Agrawal et al., 2004; Wang et al., 2008). Chemical analysis shows that Red Mud also contains an array of minor elements namely K, Cr, V, Ba, Cu, Mn, Pb, Zn, P, F, S, As, etc. It is observed that Al_2O_3 and Fe_2O_3 are the major components of Red Mud along with many other metals in traces (Table 1). This implies use of Red Mud to be a better choice as bed material for abatement of gaseous fluorides. In the present work Red Mud and Sand are used as bed materials for FBR to study on the abatement of gaseous fluorides.

Table 1 – Composition of bed materials gas.

Typical composition of Red Mud		Typical composition of Sand	
Composition	Weight, %	Composition	Weight, %
Fe_2O_3	30–60	SiO_2	60–65
Al_2O_3	10–20	Na_2O	20–25
SiO_2	3–50	Al_2O_3	3–5
Na_2O	2–10	MgO	6
CaO	2–8	B_2O_3	3
TiO_2	25	K_2O	0.5

2. Experimentation

At first some preliminary experiments are carried out using a perspex column to study the bed hydrodynamic where different bed materials (viz. Sand, Red Mud and Red Mud–Aluminium mixture) are allowed to fluidize by air under ambient conditions. Experimental conditions required for proper fluidization are noted down. Main experiments are then carried out in a stainless steel reactor having dimension of 10 cm ID and 70 cm height. Schematic diagram and laboratory view of experimental set up are shown in Figs. 1 and 2 respectively. Initially bed materials are taken in the FBR up to certain height. The bed materials within FBR are then fluidized by air. Temperature within the FBR is then increased. When the desired temperature is attained within FBR, the effluent gas obtained from the Aluminium industry is used as a secondary gas. As soon as secondary gas comes in contact with hot bed materials reaction starts taking place. For the first set of experiment, Sand (77 μm) is used as the bed material which is fluidized with the mixture of air and effluent gas at 250 °C within the FBR. In the second set of experiment, Red Mud (77 μm) is fluidized with the mixture of air and the effluent gas. The bed material is made to fluidize at the temperature of 250 °C with the contact time of 30 min by which the effluent gas is allowed to come in contact with the bed materials properly. The bed material samples are then collected and analysed. For the third set of experiment, Red Mud (77 μm) and Aluminium powder (82.5 μm) mixture is used as the bed material (in 9:1 weight ratio). The bed materials are fluidized with the mixture of air and effluent gas at temperature of 250 °C. The bed materials in each case are characterised by several analysis techniques before and after the experiment to check the presence of fluorides in them.

The XRD pattern of the material and the material composition are analysed using PHILIPS X'Pert X-ray diffractometer. The FT-IR spectra of the samples are obtained by using Perkin Elmer FT-IR Spectrometer (Spectrum RX-I). The TGA and DTA analysis are carried out using SHIMADZU DTG – 60H. In this analysis 17.361 mg of the sample is used at room temperature. The sample is heated from 28 °C to 500 °C at a heating rate of 10 °C min^{-1} in N_2 atmosphere where the gas flow rate is maintained at 35 ml min^{-1}. FESEM and EDX analysis using NOVA NANO SEM 450 are carried out to study the surface morphology and elemental composition of the samples respectively. ICP-MS analysis is carried out to find the elemental composition of the samples. The particle sizes of the samples are measured using MALVERN MASTERSIZER (Hydro 2000MU and Range: 0.02–2000 μ). The surface area of the samples is also measured by BET apparatus (QUANTACHROME AUTOSORB-1). List of instruments used for characterisation of samples is shown in Table 2.

3. Results and discussion

3.1. *Hydrodynamic studies for different bed materials*

As the reactor made up of stainless steel is used to carry out high temperature reactions among hazardous chemicals like