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Equilibrium, kinetics and breakthrough studies for adsorption of hydrogen fluoride on sodium fluoride

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ABSTRACT

In this study, adsorption of hydrogen fluoride on sodium fluoride adsorbent is investigated through an experimental and theoretical study. This process is very important in a section of a total process of producing and making pure fluorine gas in uranium conversion industry. For applying the section of experimental study, experimental sample of differential adsorbed bed was designed and manufactured with necessary side equipment and the required experiments were applied in 22 and 54 °C. By the use of experimental results, Isotherm curve of hydrogen fluoride adsorption on sodium fluoride adsorbent was obtained which is the main tool for designing of adsorption bed. By considering the experimental results and adsorption models applied in this study, it can be concluded that equilibrium data were well represented by a langmuir isotherm equation with maximum adsorption capacities of 1.908 and 0.750 g HF/g NaF in 22 and 54 °C.

1. Introduction

Hydrogen fluoride was the principal impurity to be removed in gas as produced electrolytically such as fluorine (F_2) that is one of the most important and widely used gas in uranium conversion industry. Fluorine is usually used to produce 18,000–21,000 tons of uranium hexafluoride per year which needs 6000–7000 tons of fluorine gas in the world [1].

The production of fluorine in nuclear industries is mainly based on the electrolysis of potassium anhydride difluoride which also leads to the production of hydrogen fluoride gas (HF) as impurity in fluorine. Furthermore the humidity in produced gas reacts with fluorine producing impurity of HF in fluorine gas according to the following reaction [2–4].

$$F_2 + H_2O \rightarrow 2HF + \frac{1}{2}O_2$$

The amount of impurity of HF in the fluorine gas is in the range of 5–10 mol%. In order to use fluorine gas in uranium conversion facilities, it is necessary to purify electrolysis product and decrease the amount of its HF impurity to 0.2 mol% [5].

Various technologies for HF removal had been developed by the above mentioned investigators. One method is the use of condensation process in which a condenser is followed by an adsorption unit. Gas condensation is performed at −78 to −70 °C. In this range of temperature, the HF saturation concentration is of 2–4 mol%.

Cooling is carried out at atmospheric pressure and then the outlet gas of condenser enters to an adsorption bed.

Through an adsorption device, the remaining HF is separated from fluorine gas. Among all the existing methods, the HF adsorption by suitable solid adsorbents seems to offer an interesting and practical alternative. In fact HF adsorption by alkaline metals fluorides such as sodium fluoride and calcium fluoride have been the most popular and effective ones [2,4,6–11]. Sodium fluoride (NaF) is one of the suitable mineral salts which are suggested as HF adsorbent. Calcium fluoride is mainly used to adsorb HF from electrolyte gases like HCl [12].

Adsorption of HF gas on sodium fluoride salt is performed by the following reversible reaction:

$$NaF + HF \Leftrightarrow NaF{\cdot}HF$$

During adsorption process, HF molecules overcome the existing external and internal resistances of mass transfer. And, after reaching the internal and external active surfaces of the adsorbent, they form a complex on the surface of the adsorbent. To break this bond and to separate HF from sodium fluoride salt, temperature should be increased to 280–300 °C [13].

In order to prevent operational problems in uranium conversion facilities, the sodium fluoride salt is used as the pellet instead of using its powder form. This prevents the entering of sodium fluoride powder in next steps of process. To obtain NaF pellets from powder, first powder is mixed with small amount of water then it is

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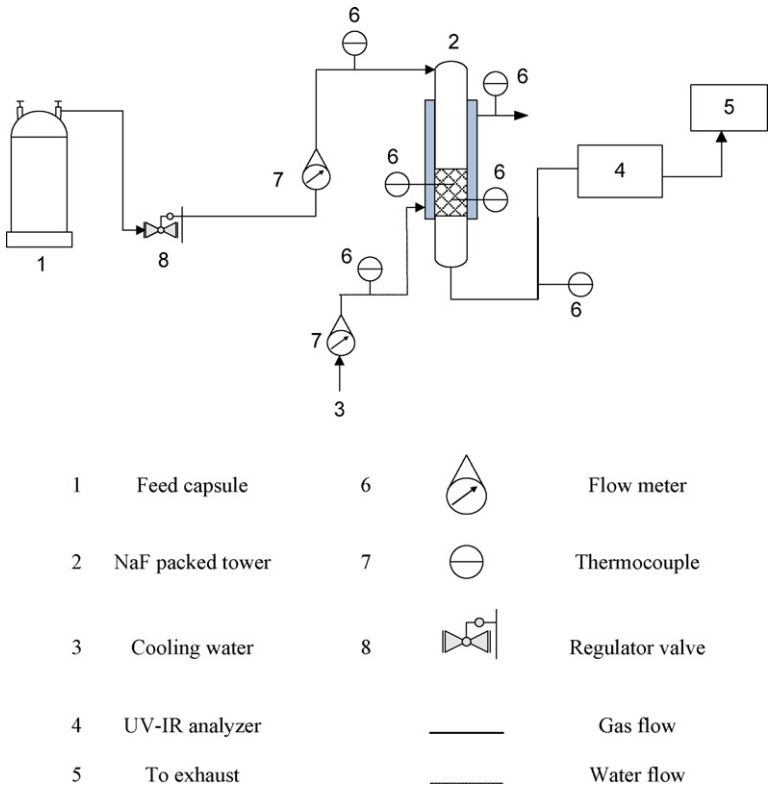

Fig. 1. Schematic diagram of the experimental setup.

pressed to form pellets. Before using the pellets they must be dried in dryers for about 1–2 h in 120 °C.

As a part of a main study, the purpose of the present paper is to investigate the HF adsorption on NaF pellets and to determine the corresponding adsorption isotherm in different operating conditions. Due to the very specific nature and applications of such studies and their results, a very little data have been published in the literature.

2. Methods and materials

A schematic flow diagram of the experimental setup is shown in Fig. 1. Its core is an adsorption column with circular cross-section of 5 cm inner diameter and maximum length of 30 cm. In order to avoid corrosion problems which affects the results, the adsorption column was made from monel[1] and stainless steel. In order to investigate the heat effects, a cylindrical shell with inner diameter of 10 cm was considered around the adsorption column. Water as a cooling or heating fluid with specified temperature and flow rate was passed through the shell during adsorption experiments. The instrumentation provides various measurements of temperature, gas and water flow rates and HF concentration. However, the most important issue was the measurement of HF concentration at outlet gas stream. The HF concentration in gas mixture exiting the adsorption column was measured by a UV–IR analyzer with 0.2 mol% fraction accuracy. Also the inlet and exit temperatures of gas mixture and water temperature at inlet and outlet of the shell were measured by thermocouples (Fig. 1).

In order to produce a vapor-free HF and nitrogen mixture to provide favorite inlet concentration, the necessary amount of HF liquid is weighed and enters a 101-L capsule. The capsule pressure is then increased to 11–14 bar, using nitrogen gas as inert. The diameter of sodium fluoride pellets is 7.03 mm and their height is 5.12 mm. Based on the accurate measurements the pellets actual and apparent densities are 2.29 and 2.03 g/cm^3, respectively. Also porosity and specific surface area of the pellet are 11.4% and 0.11 m^2/g, respectively. Pure and anhydrous HF and nitrogen are used and water is served as the cooling fluid.

In order to obtain the adsorption isotherm, the sodium fluoride pellets were weighed and carefully packed into the column. The height of packed bed was measured. The mixture of nitrogen gas and HF was entering the bed with a constant flow rate. Water passes through the shell as cooling fluid. The analyzer records the outlet concentration continuously. Thermocouples measure the temperatures of inlet and outlet gas and cooling fluid.

The run is continues until the bed is completely saturated and HF concentration at the outlet of the bed is the same as its inlet concentration. The HF inlet concentration is varied between 2 and 15 mol%. The experiments are conducted at 21 °C by regulating the water flow rate and temperature. Fresh pellets were used for each tested inlet concentration.

3. Experimental results and data analysis

The column tests conditions and the isotherms measured are summarized in Table 1. The maximum sorption capacity, q/(mg kg^{-1}), is presented in the last column of Table 1 is calculated by integrating the area above the breakthrough curve for a given inlet HF concentration, operating temperature, mass of adsorbent, and gas flow rate, as it is defined by Eq. (1):

$$q_e = Q_g \frac{y_0 p_t M}{RTm_s} \int_0^{t_e} \left(1 - \frac{y_t}{y_0}\right) dt \quad (1)$$

where y_t, y_0 are the measured mole fraction of HF at the exit and inlet of the bed, at time t, respectively. It must be noted that for

[1] NiCu30 Fe, Monel alloy 400.