Polish Journal of Environmental Studies Vol. 13, No. 6 (2004), 723-727

Original Research

Fly Ash Zeolites as Sulfur Dioxide Adsorbents

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Received: 29 December 2003
Accepted: 1 June 2004

Abstract

Air protection technologies generate massive amounts of solid wastes, including fly ash (FA). Zeolite synthesis from FA seems to be an effective method for FA utilization. In addition, fly ash zeolites (FAZs) could be used for sulfur dioxide (SO_2) adsorption. Since there is a lack of sufficient information about SO_2 uptake on FAZs, we investigated this phenomenon in detail. Two commercially available zeolites, 3A and SM-27, and two FAZs, one manufactured by the authors and the other obtained from Kimura Chemical Plants, were used for SO_2 adsorption tests. Our experiments confirmed that FAZs could be efficient SO_2 adsorbents. Observed SO_2–zero emission periods varied from 2-3 min for non-activated zeolites to 7-15 min for their thermally activated counterparts. The thermal activation of FAZs increased 2-3 times their SO_2 adsorption capacity, resulting in up to 38 mg of SO_2/g of zeolitic material.

Keywords: fly ash, zeolite, sulfur dioxide, adsorption.

Introduction

At present, fossil fuels are primary sources of energy in global as well as in most of the regional scales. Most air protection problems connected with stationary power generating plants, fueled by hard coal or lignite, are solved by the use of modern air protection technologies. However, these technologies generate massive amounts of solid wastes, *e.g.*, gypsum from wet desulfurization units or fly ash (FA) separated from flue gases. In Poland, for example, every year more than four million tons of FA are produced in power and thermal plants, with 65% of this waste being utilized and 35% being stored in waste disposal sites [1].

There are many possible methods of FA utilization and application. Production of cement or construction materials and civil engineering applications are the traditional fields of FA utilizations. Statistical information and many examples from Europe, USA, and Japan are available at the following websites: *www.ecoba.com/index.html*, *www.acaa-usa.org* and *www.ccuj.or.jp/index-e.htm.* Scheetz and Earle wrote an extensive overview of FA utilization in the aforementioned fields, dividing them into six groups:

a. cement and concrete products,
b. structural fillings and cover materials,
c. waste solidification and stabilization,
d. roadway and pavement constructions,
e. lightweight aggregate materials production, and
f. infiltration barrier construction and underground void filling [2].

Horiuchi *et al.* presented effective ways of FA slurry use in underwater disposal, man-made island construction, and structural fills [3]. Queralt *et al.* summarized the use of FA for ceramics manufacturing [4]. There are also a number of possible FA applications outside of the construction industry. FA can be effectively used for

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Table 1. Properties of employed zeolites.

Name	3A zeolite	SM-27 zeolite	Kimura FAZ	Our FAZ
Manufacturer	POCh S.A., Gliwice, Poland	Alsi-Penta Zeolithe GmbH, Schwandorf, Germany	Kimura Chemical Plants Co., Ltd., Amagasaki, Japan	Authors
Type	Na-A	ZSM-27	Phillipsite	Na-P1 / Na-P[a]
JCPDS No.[b]	39-0222	ND[c]	46-1427	39-0219; 44-0052
Micropore diameter (nm)	0.22 (0.44 after dehydration)	0.53 × 0.56 0.51 × 0.55	0.42 × 0.44 0.28 × 0.48	0.31 × 0.44; 0.28 × 0.49
Structural change temperature (°C)	700	ND	200	250
Chemical formula	$Na_{96}Al_{96}Si_{96}O_{384}·216H_2O$	ND	$(K,Na)_2(Si,Al)_8O_{16}·4H_2O$	$Na_6Al_6Si_{10}O_{32}·12H_2O$; $Na_{3.6}Al_{3.6}Si_{12.4}O_{32}·14H_2O$

[a]High-silica variety. [b]Joint Committee of Powder Diffraction Standard. [c]ND: no data provided by the manufacturer.

the production of different types of zeolites, commercial grade mullite, glass-like materials for industrial applications, plastic and metal composite materials, and sorbents for waste management or waste stabilization and for agriculture purposes [5].

Recently, many studies have been published about employing FA as a raw material for zeolite synthesis, although this process was demonstrated for the first time almost twenty years ago. Zeolites are manufactured in the process of hydrothermal treatment of FA. A class F power plant FA contains large quantities of silica oxide (~50%) and aluminum oxide (~25%). The zeolite synthesis occurs in the presence of sodium or potassium hydroxide at an appropriate time and temperature. The crystallization of various types of fly ash zeolites (FAZs) is a function of reaction time, temperature, pH, and concentrations of FA and the respective hydroxide. Usually, FA zeolitic process efficiency is 50-60%, but much lower values have also been reported. A literature search on FAZ syntheses indicates that the following types of zeolites have been identified thus far: faujasite [6, 7], Na-A [8], Na-P [9], Na-P1 [8-10], Na-X [11], P [7, 12], and phillipsite [8]. In addition, mixtures of two different zeolites, analcime and sodalite [11], gobbinsite and Na-P1 [13], K-L and K-W [14], Na-A and Na-X [8], Na-P1 and analcime [9], Na-P1 and hydroxy-sodalite [15], Na-P1 and Na-X [16], and P and hydroxy-sodalite [12], or mixtures of three different zeolites, analcime, hydroxy-sodalite and tobermosite [8]; analcime, Na-P and gmelinite [9]; kalsilite, linde-F and tobermorite [8]; and Na-P1, analcime and gmelinite [9], were also reported. The aforementioned syntheses were conducted under batch regime in a laboratory scale.

According to data provided by Donald W. Breck in his fundamental textbook on zeolites published in 1974, zeolites' (KL, Na-A, Ca-A, and Na-X) adsorption of sulfur dioxide (SO_2) at low concentrations (several hundreds ppm) at 25°C ranges from 130 to 170 mg/g of zeolitic material [17]. Since then, more experimental SO_2 adsorption data for other types of zeolites have been published, *e.g.*, approximately 38 mg SO_2/g of sillicalite [18], 128 and 19.2 mg SO_2/g of sillicalite S-115 and DAY, respectively [19], 267 mg SO_2/g of Na-Y [20].

Few papers, however, have dealt with SO_2 adsorption on FAZ. Srinivasan and Grutzeck demonstrated a relationship between drying condition of FAZ and SO_2 adsorption [11]. Their zeolites, dried in the air at 110°C, adsorb three times smaller amounts of SO_2 than those dried in a microwave, *i.e.*, 6-7 mg SO_2/g of analcime or sodalite zeolite. Querol *et al.* reported that KM and Na-P1 zeolites adsorb up to 20 mg of SO_2/g of zeolite, but much higher values were found for the following FAZs: Na-chabazite – 100, 4A – 300, and X – 380 mg of SO_2/g [21]. It should be noted that these researchers employed thermally activated zeolites.

FAZs could be cost-effective sorbents for controlling SO_2 emissions from industrial sources. The lack of information about SO_2 uptake on FAZs, both thermally activated and not activated, encouraged us to further investigate this phenomenon.

Experimental Procedures

Zeolites

Two commercially available zeolites, 3A and SM-27, and two FAZs, one manufactured by us and the other obtained from Kimura Chemical Plants Co., Ltd. (Amagasaki, Japan), were used for SO_2 adsorption tests (Table 1).

A detailed procedure of our FAZ manufacturing process have been described [22]. Briefly, FA samples were collected from a dust chamber of an electrostatic precipitator of the 6th boiler of Łagisza Power Plant (Będzin, Poland) fueled by pulverized hard coal. FA (100 g/L of base solution) was added to 2.0 M NaOH solution. This reaction slurry was continuously mixed and kept at 80°C for 24 h. The zeolitic material produced was filtered, washed four times with distilled water, and then dried at 100°C for 6 h. A FAZ produced this way is referred in this paper as "non-activated". In addition, activated forms of FAZs were generated by keeping the necessary amounts of samples at 400°C for 10 h. The commercial zeolites were thermally activated using the same method. Both forms of zeolites were used for SO_2 adsorption tests.

Laboratory Set-Up

The experimental set-up, shown in Fig. 1, consists of the following elements: SO_2 and nitrogen gas cylinders, mass flow controllers (BETA-ERG, Sp. z o.o., Warsaw, Poland), a gas mixing chamber, a fixed-bed glass adsorber (~20 cm in length, 2.5 cm in diameter), and an infrared non-dispersive SO_2 analyzer Rosemount 880 (Rosemount Analytical Inc., USA) with on-line recording. A desired gas mixture was directed to the upper part of the adsorber and flowed through the zeolite sample placed on a sintered glass shelf in the bottom part of the adsorber. The gases used, SO_2 (100%) and nitrogen (99.99%), were purchased from MG Polska (Chorzów, Poland).

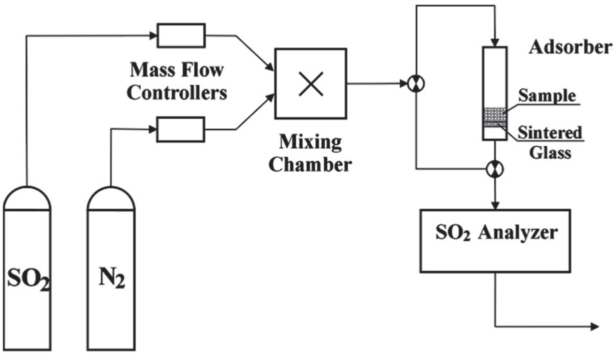

Fig. 1. Schematic diagram of the experimental set-up.

Procedure

Gas flow rate and SO_2 concentration were maintained at 60 L/h and 1050 ppm, respectively. The relative proportions of SO_2 and nitrogen were controlled with the mass flow controllers. First, gas was run through the adsorber bypass. Next, a zeolite sample (2.0 g) was placed into the adsorber. After the recording system of the SO_2 analyzer was turned on, gas flow was switched from the bypass to the adsorber. After a run, gas was again directed to the bypass, the adsorber was opened, and the sample was collected. All experiments were conducted at room temperature.

Results and Discussion

Typical experimental results for the raw FA and our FAZ are shown in Fig. 2. SO_2 was completely adsorbed on the zeolite bed in beginning periods of all runs. This period of SO_2–zero emission time, called also the breakthrough time (tb), depends on employed adsorption material. It varied from 1 to 10 min for the raw FA and our FAZ, respectively. Next, outlet SO_2 concentrations gradually increased up to the level of the inlet SO_2 concentration. When the outlet SO_2 concentration reached the inlet concentration, the bed became completely saturated with SO_2. The period between the beginning of the run and the bed saturation is called filling up time (tf). For calculations we used tf values that correspond to the time-point when the SO_2 outlet concentration reached 95% of inlet concentration. The amount of SO_2 adsorbed during the tb and the tf period is Ab and Af (mg of SO_2/g of zeolitic material), respectively. Results presented in Fig. 2 clearly show that our FAZ adsorbed several times more SO_2 than the raw FA.

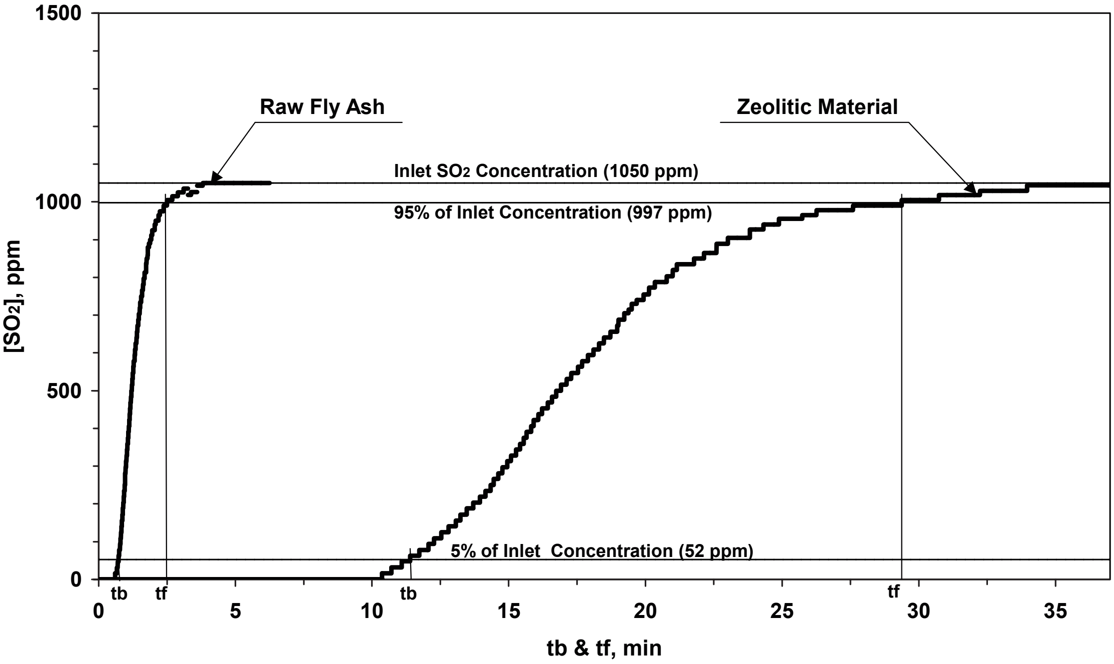

Fig. 2. Breakthrough curves for the raw FA and our FAZ.

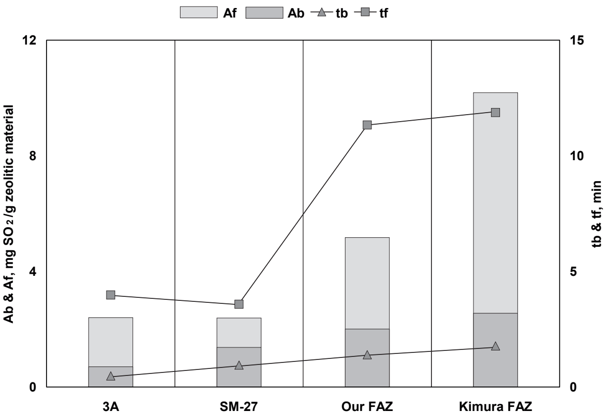

Fig. 3. Amounts of adsorbed SO_2 (Ab and Af) on non-activated zeolites and their corresponding breakthrough (tb) and filling up (tf) times.

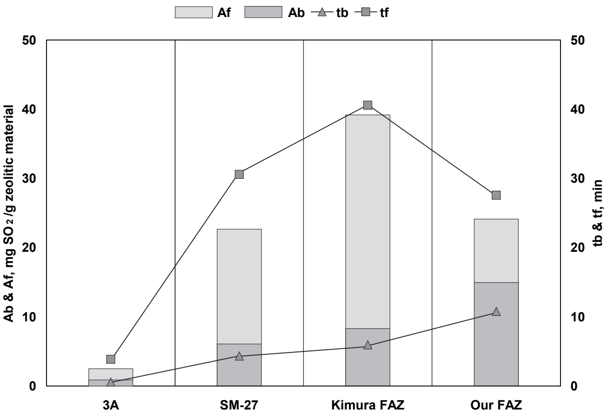

Fig. 4. Amounts of adsorbed SO_2 (Ab and Af) on activated zeolites and their corresponding breakthrough (tb) and filling up (tf) times.

The observed relatively long SO_2-zero emission times of tested FAZs have important implications for technological applications of FA in flue gas control systems. FAZ as SO_2 sorbent should have contact with flue gases for longer periods of time to be fully saturated by SO_2. This limitation means that a fluidized bed contactor should be employed; a fixed bed apparatus can also be considered. But any contact method of FAZ and flue gases needs more process and economic analysis.

Two commercially available zeolites and two FAZs were employed for SO_2 adsorption kinetic tests. In addition, necessary amounts of these zeolites were thermally activated and also used for SO_2 adsorption experiments. The SO_2 adsorption uptakes obtained from the breakthrough curves are shown in Figs. 3 and 4.

Results of SO_2 adsorption on non-activated zeolites are presented in Fig. 3. Ab values for investigated zeolites ranged from 0.5 to 2.0 mg of SO_2/g of zeolitic material, the latter value being for the FAZs. The tb values for SO_2 increased in the following order: 3A < SM-27 < our FAZ < Kimura FAZ. The commercial zeolites, 3A and SM-27, exhibited similar Af values, approximately 2.5 mg of SO_2/g of zeolite. But marked differences in Af values existed among FAZs.

Results of SO_2 adsorption on activated zeolites are shown in Fig. 4. The activation process did not change the adsorption property of the 3A zeolite. For other zeolites substantial changes in adsorption properties were observed. Ab values were approximately three times higher for the FAZs and approximately two times bigger for the SM-27 as compared to their non-activated counterparts. The tb values for SO_2 increased in the following order: 3A < SM-27 < Kimura FAZ < our FAZ (~ 15 min.). A similar trend was observed for Af values (except that the Af value for Kimura FAZ was much higher than that for our FAZ).

Both FA and FAZs are very hydrophobic materials. The thermal activation of zeolites removes adsorbed water molecules at lower temperatures and structural water at higher temperatures as well. But structural changes of zeolites at higher temperatures can also extend their internal surface areas and, therefore, affect their adsorption properties. Our experimental data confirmed this. The 3A zeolite has a very stable structure up to 700°C (Table 1). Therefore, no significant differences in SO_2 uptake were observed for its non-activated or thermally activated type. A different behavior was observed for the tested FAZs and SM-27. Their structural changes occurred at 200°C (Kimura) and 250°C (our FAZ) as shown in Table 1. This phenomenon is responsible for the dramatic rise in SO_2 uptakes with thermally activated FAZs.

In conclusion, the results confirmed that FAZs could be used for SO_2 adsorption. Observed SO_2–zero emission periods varied from 2-3 min for non-activated zeolites, and from 7-15 min for thermally activated ones. Furthermore, the thermal activation of FAZs increased SO_2 adsorption capacity 2-3 times (up to 38 mg of SO_2/g of FAZ).

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