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Zeolite synthesis from paper sludge ash at low temperature (90 °C) with addition of diatomite

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Abstract

Paper sludge ash was partially converted into zeolites by reaction with 3 M NaOH solution at 90 °C for 24 h. The paper sludge ash had a low abundance of Si and significant Ca content, due to the presence of calcite that was used as a paper filler. Diatomite was added to the NaOH solution to increase its Si content in order to synthesize zeolites with high cation exchange capacity. Diatomite residue was filtered from solution before addition of ash. The original ash without addition of diatomite yielded hydroxysodalite with a cation exchange capacity ca. 50 cmol/kg. Addition of Si to the solution yielded Na-P1 (zeolite-P) with a higher cation exchange capacity (ca. 130 cmol/kg). The observed concentrations of Si and Al in the solution during the reaction explain the crystallization of these two phases. The reaction products were tested for their capacity for PO_4^{3-} removal from solution as a function of Ca^{2+} content, suggesting the formation of an insoluble Ca-phosphate salt. The product with Na-P1 exhibits the ability to remove NH_4^+ as well as PO_4^{3-} from solution in concentrations sufficient for application in water purification. Both NH_4^+ and PO_4^{3-} removal showed little variation with pH between 5 and 9. Alternative processing methods of zeolite synthesis, including the addition of ash to an unfiltered Si–NaOH solution and addition of a dry ash/diatomite mixture to NaOH solution, were tested. The third process yielded materials with lower cation exchange capacity due to formation of hydroxysodalite. The second process results in a product with relatively high cation exchange capacity, and reduces the number of processing steps necessary for zeolite synthesis.

Keywords: Zeolite; Paper sludge ash; Diatomite; Cation exchange capacity; Hydroxysodalite; Na-P1

1. Introduction

During the manufacture of recycled paper products, paper sludge is generated as an industrial waste. Over 3 million tonnes of sludge is discharged per year in Japan, and approximately 8 and 2 million tonnes in the United States and the United Kingdom, respectively [1,2]. The amount is increasing annually. The sludge consists of organic fibers, inorganic clay-sized materials, and about 60% water, and is incinerated to paper sludge ash by burning out the organic materials, thereby reducing its waste volume. Although some part of the ash is used as cemented fills, lightweight aggregates in the construction industry, and in other minor applications [3,4], the major part is dumped at landfill sites. The large daily output and the limited landfill capacity have caused social and environmental problems. One possible and effective alternative is to convert the ash into zeolite absorbents for environmental applications, such as water purification, and soil conditioning [5–7].

Zeolites are a group of over 40 crystalline, hydrated aluminosilicate minerals with structures based on a three-dimensional network of $(Al, Si)O_4$ tetrahedra that contain exchangeable alkali or alkaline earth cations [8]. Zeolites occur in natural deposits, generally associated with the alteration of glassy volcanic rocks, or are synthesized from a wide variety of high-Si and Al starting materials. Paper sludge ash contains amorphous and crystalline phases formed by incineration, and is compara-

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ble to volcanic ash. Accordingly, the ash can be converted into zeolites [9,10].

In the past, clay minerals such as kaolinite were used for paper filler, but recently calcite has increasingly replaced kaolinite as a filler. Subsequently, incinerated ash has a higher Ca-content, in the form of anorthite ($CaAl_2Si_2O_8$) and gehlenite ($Ca_2Al_2SiO_7$). Furthermore, the decreasing use of silicate minerals as paper fillers has resulted in a lower concentration of Si in the ash. Correspondingly, the Si/Ca ratio is decreased. The low Si content of the ash makes it difficult to convert it into zeolites, or at least into more desirable zeolite phases. Zeolite formation from other ash sources, for example, coal fly ash, has also been investigated [11–14]. It is reported that amorphous SiO_2 particles added to a coal fly ash resulted in the formation of phillipsite, with high cation exchange capacity (CEC), in NaOH solution [15].

Diatomite is a fine-grained, biogenic siliceous sediment, and is available in large quantities at low cost [16]. It consists essentially of amorphous silica derived from opalescent frustules of diatoms, and has a fine porous structure with low density. Diatomite easily dissolves in basic solutions. There are examples of the synthesis of zeolites from diatomite itself [17,18], but the direct synthesis from diatomite lacks Al sources or template agents.

In this work, we synthesize zeolites at low temperature (90 °C) from paper sludge ash, with addition of diatomite. To our knowledge, no previous effort has been made to use diatomite as an additive Si source in synthesizing zeolite from the paper sludge ash. The resulting zeolites exhibit cation exchange properties, and selectively sorb certain cations, such as NH_4^+. Also, it has been reported that Ca^{2+} contained in the original paper sludge ash reacts with phosphoric acid to form apatite-like materials, which removed PO_4^{3-} from solution [6]. Therefore, we aim to obtain a material suitable for water purification, which contains zeolite phases and soluble Ca in the product. We present here the chemical reaction of paper sludge ash with diatomite, the CEC of the end product, and demonstrate the removal capacity for NH_4^+ and PO_4^{3-} from aqueous solution by sorption and precipitation with Ca, respectively.

2. Experimental methods and results

2.1. Raw materials

Paper sludge ash was obtained from a paper company in Fuji, Japan. The composition of the ash, determined by scanning electron microscopy (SEM) (Hitachi, S-2600 H) equipped with energy dispersive spectrometry (EDS) (Horiba, EX-200), is listed in Table 1. The ash is mainly composed of SiO_2, Al_2O_3 and CaO in the form of amorphous matter and the minerals gehlenite ($Ca_2Al_2SiO_7$) and anorthite ($CaAl_2Si_2O_8$), determined by X-ray diffraction (XRD) (Rigaku, Rint-2200U/PC-LH) (Fig. 1). The ash has a low SiO_2 and a high CaO content compared to other similar materials. Such a composition is not favorable for the synthesis of zeolites [19].

Diatomite occurs in nature in two types of geological environments, marine and lacustrine. The sample used in this study has a seawater origin, and was obtained from the deposits located in Takanosu, Akita prefecture in Japan. The diatomite was ground to a size smaller than 30 mesh and dried at 60 °C. The chemical composition of the diatomite determined by SEM-EDS is listed in Table 1. The original sample contains 50–75% water. The dried sample is composed of diatom frustules that precipitate in an amorphous silica form, but it also contains some rock fragments. The fragments are mainly made of feldspar and quartz (Fig. 1) derived from surrounding rocks. Diatomite readily dissolves in a basic solution. Fig. 2 shows Si concentrations in solution as a function of reaction time during the dissolution of diatomite in 3 M NaOH solution at 90 °C. In all cases, dissolution of the amorphous silica of diatomite is nearly complete within 1 h. Hence, the dissolution time for diatomite is taken as 1 h hereafter.

Table 1
Chemical composition of paper sludge ash and diatomite

Oxide (wt.%)	Paper sludge ash	Diatomite
SiO_2	35.9	92.8
Al_2O_3	22.8	3.4
CaO	33.2	0.3
Na_2O	0.6	0.5
K_2O	–	0.5
MgO	4.5	0.5
Fe_2O_3	0.9	2.0
TiO_2	2.2	–
Total	100.1	100.0

These data were analyzed by EMAX ENERGY package. The analytic errors are <5%.

2.2. Zeolite synthesis from the ash in diatomite solution

We prepared 3 M NaOH solution with Si concentrations of 0, 5, 10 and 20 g/L by addition of 0, 16, 32 and 64 g of diatomite respectively, at 90 °C for 1 h. The solutions were filtered and cooled to room temperature. Paper sludge ash (100 g) was then

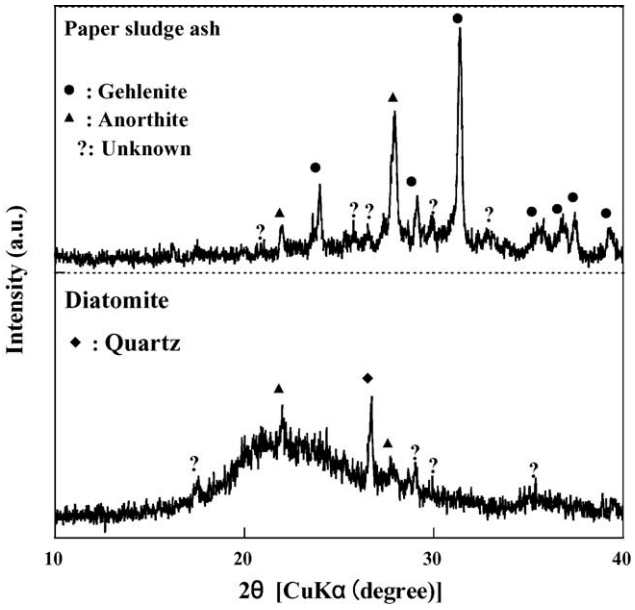

Fig. 1. Powder X-ray diffraction patterns of paper sludge ash and diatomite.