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Environmental Issues and Waste Management Technologies in the Ceramic and Nuclear Industries XI

Edited by
Connie C. Herman
Sharon Marra
Dane Spearing
Lou Vance
John Vienna

Proceedings of the 107th Annual Meeting of The American Ceramic Society, Baltimore, Maryland, USA (2005)

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Preface

The eleventh annual symposium on Environmental Issues and Waste Management Technologies in the ceramic and nuclear industry took place in Baltimore, MD, April 10 - 13, 2005. The symposium was held in conjunction with the 107th Annual Meeting of The American Ceramic Society, and was sponsored by the Nuclear and Environmental Technology Division, Legislative and Public Affairs Division, Environmental Stewardship Committee, and the Cements Division. Several sessions with focused topics in the Nuclear and Environmental arena were held, including a panel discussion on nuclear waste form durability. This volume documents a number of papers that were presented at the symposium.

The success of the symposium and the issuance of the proceedings could not have been possible without the support of the staff at The American Ceramic Society and the other organizers of the program. The assistance of the division executive officers is also recognized for helping to solicit speakers, organize the sessions, and review the manuscripts. Their assistance, along with that of the session chair's, was invaluable in ensuring the creation of quality proceedings.

Connie Herman
Sharon Marra
Dane Spearing
Lou Vance
John Vienna

Nuclear and Environmental Technology Applications in the Ceramic Industry

INDOOR AIR POLLUTION CONTROL: FORMALDEHYDE ADSORPTION BY ZEOLITE RICH MATERIALS

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ABSTRACT

Formaldehyde is a carcinogenic byproduct emitted from resins in plywood, hardwood paneling, and carpets. This pollutant is commonly found in indoor environments and as such is purported to be the main causative agent of sick building syndrome. Building materials such as paneling and coating with highly adsorptive properties given by zeolites incorporated into their composition can help curb indoor air pollution. In this research zeolites were synthesized and tested for their ability to adsorb formaldehyde from the air. Class F fly ash, a waste product from coal combustion, and metakaolinite, a clay material, were mixed with sodium hydroxide solutions to produce zeolites. Samples were mixed as pastes and reacted as a function of time and temperature. Zeolite A, faujasite, analcime, and other mixed phases were obtained. Samples were characterized by X-ray diffraction and scanning electron microscopy. To test the ability of materials at cleaning formaldehyde from the air, samples were put in contact with a "polluted" air stream. Compressed air was mixed with the gas phase above a volume of a 10% formalin solution used as permanent source of formaldehyde. Air passed through an adsorption cell consisting of concentric layers coated with zeolite powders. Formaldehyde removal was monitored by observing the change of its infrared spectrum with time by means of Fourier transform infrared spectroscopy. Formaldehyde spectral peaks completely disappeared within few minutes of contact, dropping to "zero" percent formaldehyde. Results obtained from this preliminary study demonstrate the feasibility of using synthesized zeolites to improve indoor air quality.

INTRODUCTION

In order to conserve energy, current practice limits the amount of fresh air that is mixed with recirculated air in tightly sealed buildings. Although energy savings are substantial, the potential risk of pollutant buildup has increased. Some studies show that indoor air can be more polluted than outdoor air[1, 2]. In fact, as a result of energy efficient building designs, a medical condition called sick building syndrome (SBS), has become a major public health concern since it first appeared in the 1970s[3, 4]. In the indoor environment there is a large spectrum of pollutants ranging from carcinogenic volatile organic compounds to combustion products and biological agents[5, 6, 7]. Formaldehyde, emitted from resins in plywood, particleboard, hardwood paneling, and carpets is one of the toxic organic compounds present in indoor air and potential causative agent of symptoms of SBS[8, 9]. Health effects due to formaldehyde exposure range from skin irritation to upper respiratory system cancers[10]. Appropriate ventilation supply as well as the installation of air filters tend to improve air quality, but do not specifically address the problem of the presence of formaldehyde in indoor environments; therefore, novel solutions to clean this

contaminant from air are needed. Studies demonstrate the existence of a "sink" effect of polar and non polar gaseous compounds on building materials, i.e. VOC sorption on wall surfaces[11]. Some configurations of air purifiers have been tested using zeolites as sorptive media[12]. Formaldehyde removal has also been tested with TiO2-zeolite composite materials[13]. The work reported here describes the development of zeolite rich materials to adsorb formaldehyde from indoor air. Zeolites are naturally occurring minerals composed of crystalline aluminosilicates of alkali and alkaline earth elements such as sodium, potassium and calcium. Synthesis of zeolites is possible since geological conditions of high pressure and temperature needed for their formation can be reproduced and accelerated at a laboratory level. Synthesized zeolitic materials could be used as air purifiers to be placed inside air ducts. Finely divided zeolite materials could also be used for sorptive wall and ceiling coatings. Furthermore, these materials could be fabricated as stand alone zeolite rich panels for use in walls and ceilings thus providing both function and air purification, i.e. multitasking building materials. In this study zeolite materials are synthesized from Class F fly ash. Using a waste product to manufacture materials with an environmental application makes the product environmentally friendly. Such characteristic confers an additional level of attractiveness to promote potential products in the marketplace. The study reported below is a preliminary effort to addresses the feasibility of curbing formaldehyde indoor pollution with zeolites, and opens up the door for further research on indoor air quality improvement with highly adsorptive building materials

EXPERIMENTAL

Zeolite Synthesis

Zeolite synthesis from Class F fly ash by hydrothermal alkaline conversion has been studied previously[14, 15, 16, 17] and is relatively straight forward. In the present work, four kinds of zeolite materials were prepared and tested for their ability to adsorb gaseous formaldehyde from air. Class F fly ash from the Fort Martin Power Station (part of Allegheny Power in Maidsville, West Virginia) was dry blended with metakaolinite (thermally treated Troy clay from Troy Idaho) in proportions 1:1 and 5:1 and then mixed to a paste-like consistency with 4M and 8M sodium hydroxide solutions. All mixtures were aged at 40°C for 12 hours, and cured at 185°C for 12 hours in pressurized Teflon lined vessels (Parr bombs). In addition, fly ash was also mixed with an 8M NaOH solution, aged at 40°C for 12 hours, and then cured at 185°C for 12 and 36 hours. Materials characterization was done by scanning electron microscopy (SEM) and X-ray diffractometry (XRD).

Formaldehyde Generation and Detection

Gaseous formaldehyde was generated using a commercial 10% formalin solution as a source. Such solutions contain 3.7 wt% of formaldehyde gas dissolved in water and stabilized with methanol. Formaldehyde is very reactive and tends to polymerize spontaneously in aqueous solution[18]. To promote gaseous formaldehyde release from the liquid phase, the temperature of the generator was set at 40°C. Formaldehyde's presence in the gaseous phase was detected using infrared (IR) spectroscopy. Formaldehyde contains a carbonyl group that undergoes stretching vibrations at 1737.5 cm^{-1} that can be used as characteristic peak for IR data analysis. Change in the intensity of this peak was used as a measure of formaldehyde presence in air, and adsorption efficiencies by materials. Figure 1 shows the experimental set-up, including formaldehyde gas production, the adsorption apparatus and IR detector.

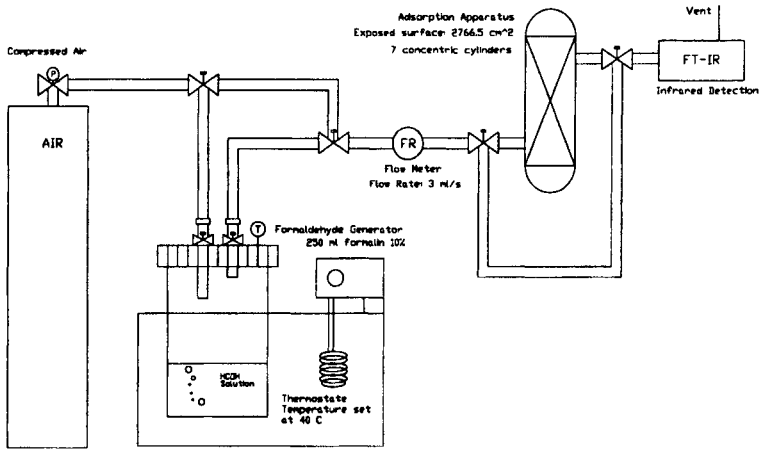


Figure 1. Formaldehyde generator and adsorption apparatus

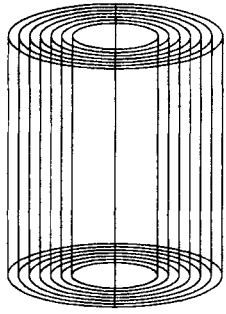


Figure 2. Configuration of adsorption cell

Formaldehyde Adsorption by Zeolite Materials

Solid material was finely ground, dried at 110°C for 1 hour, and then placed in the adsorption cell. To provide with a large contact area for adsorption, powdered zeolites were evenly distributed on the surface of seven concentric cylinders made from one side sticky paper (shelf liner), as shown in Figure 2. The cylinders were 18.5 cm long and had radii starting at 1.9 cm, and ending at 4.9 cm with differences of 0.5 cm. Total surface area was 2766.5 cm^2 (429 in^2). A compressed air cylinder was used as the source of air that continuously flowed into and out of the air space over the formaldehyde solution in the generator. Once the air was "polluted", the air flow was passed through the adsorption cell at a constant rate of 3.2 ml/s. After contact with the zeolite material, IR scans on the exiting gaseous flow were performed over time in a

Fourier Transform Infrared Spectrometer (FTIR). Formaldehyde adsorption was monitored by observing variation of formaldehyde's spectra with time. Spectral peaks completely disappeared within few minutes of initial contact. Time to reach 0% of formaldehyde in air (100% formaldehyde adsorption), total time for 0% formaldehyde in air, and breakthrough times (the time it took for the air to begin to once again show signs of formaldehyde) were recorded.

Formaldehyde concentration in the gas phase was approximated through equilibrium calculations. For all cases, the maximum possible concentration of formaldehyde in air is that corresponding to equilibrium at 40°C. A liquid solution of 10% formalin contains 3.7% (weight) of formaldehyde that corresponds to 1.23 M. Henry's law for solubility of gases in water[19] relates concentration of compounds in the liquid phase with partial pressures in the gaseous phase. The maximum possible concentration of formaldehyde in the system is 665 ppm. A mass balance of formaldehyde, considering steady state and perfect mixing, was applied to estimate formaldehyde generation rate (311 μg/min). This value was used as a reference to calculate formaldehyde uptake by materials.

RESULTS AND DISCUSSION

Synthesized Zeolites

Samples were characterized by X-ray diffraction and SEM. The following crystalline phases were found: Zeolite A (ZA), in the 50:50 sample (50FA50MK) made with 4M NaOH; phillipsite, analcime, AlPO4, and zeolite P-C (Z P-C), in the 5:1 sample (83FA17MK) made with 8M NaOH; and faujasite and analcime in two fly ash samples hydrated for 12 and 36 hours, respectively (FA12h and FA36h). Curing temperature was 185°C for all samples as well as 40°C for 12 hours for precursor aging. Preliminary experimentation was performed to choose the best synthesis conditions (temperatures, solid mixture proportions and caustic solution strengths) for final materials to be tested with formaldehyde. The data here are representative of all of the samples tested, but decidedly better than their counterparts made with different NaOH solutions. Data are summarized in Table I.

Table I. Summary of samples and crystalline phases

Sample ID	Mixture (wt%)		NaOH (M)	Curing Time (h)	Crystalline Phases
	FA	MK			
50FA50MK	50	50	4	12	Zeolite A
83FA17MK	83	17	8	12	Phillipsite, analcime, AlPO4, Z P-C
FA12h	100	-	8	12	Faujasite, analcime
FA36h	100	-	8	36	Faujasite, analcime

Aging at 40°C for 12 hours for all samples. Curing temperature: 185°C
FA=Fly Ash, MK=Metakaolinite

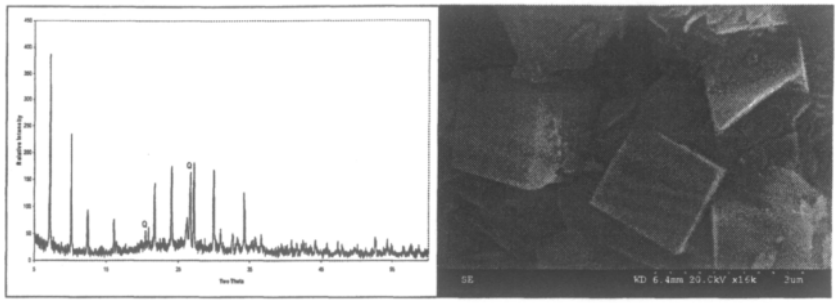


Figure 3. XRD pattern and SEM of sample 50FA50MK. XRD peaks correspond to Zeolite A except for Q=quartz. Morphology shows cubic Zeolite A crystals.

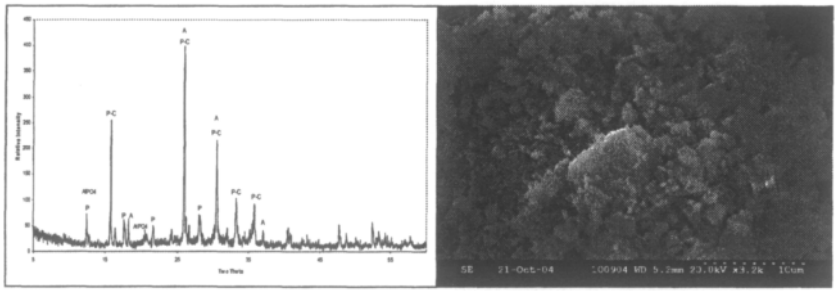


Figure 4. XRD pattern and SEM of sample 83FA17MK. XRD peaks: P=Phillipsite, A=Analcime, P-C=Zeolite P-C, and AlPO4. Morphology suggests mixed crystalline phases and porous surface.

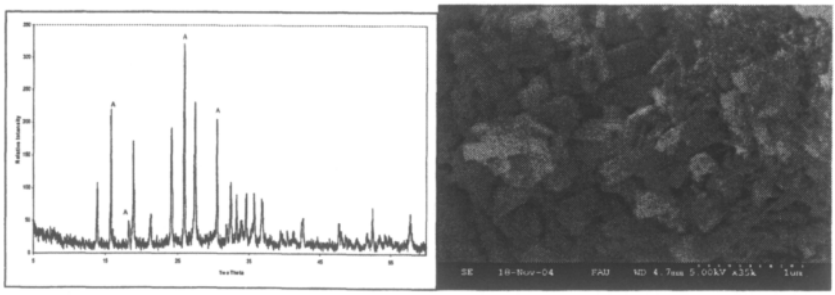


Figure 5. XRD pattern and SEM of sample FA12h. XRD peaks: Faujasite-Na, and A=Analcime-C. Morphology shows needle like crystals for mixed analcime and faujasite phases.

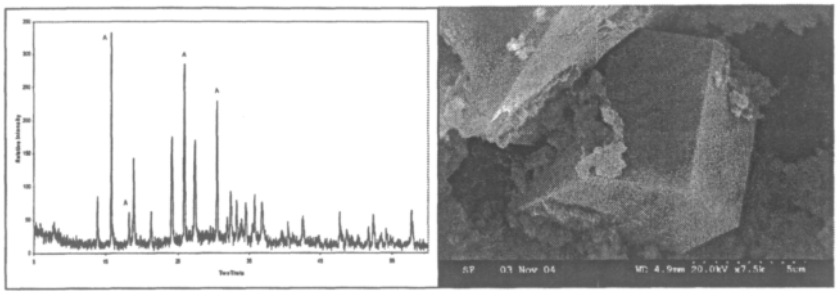
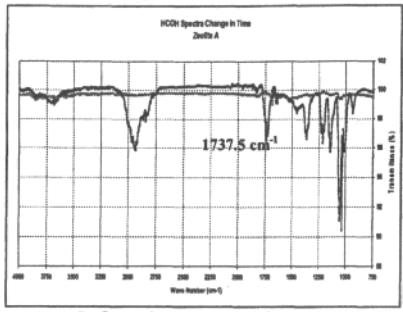


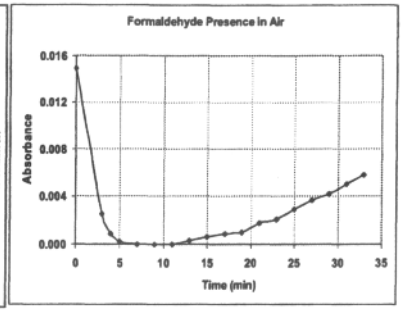
Figure 6. XRD pattern and SEM of sample FA36h. XRD peaks: Faujasite-Na, and A=Analcime-C. Microscopy of sample shows larger hexagonal faujasite crystals.

In terms of synthesis, metakaolinite and fly ash in proportions 1:1 (50FA50MK) resulted into an enhanced solid mixture to produce Zeolite A using a 4M NaOH solution. In fact, SEM picture in Figure 3 shows even formation of Zeolite A cubic crystals. Lower concentration of metakaolinite with stronger NaOH solution (83FA17MK) produced mixed crystalline zeolite phases. Figure 4 shows a very crystalline XRD pattern yet mixed. Morphology suggests a very porous surface for this second sample. Fly ash only mixed with an 8M NaOH solution (FA12h and FA36h) produce faujasite and analcime as it can be observed in XRD patterns in Figures 5 (FA12h) and 6 (FA36h). However, sample cured over 36 hours (FA36h) resulted in larger crystal growth as it can be compared from electron micrographs. In fact, SEM in Figures 5 shows needle like crystals of size approximately 0.2 μ (thickness) versus 6 μ hexagonal crystals shown in Figure 6. Curing temperature was 185°C for all samples as well as 40°C for 12 hours for precursor aging. Preliminary experimentation was performed to choose synthesis conditions (temperatures, solid mixture proportions and caustic solution strengths) for final materials to be tested with formaldehyde.

Formaldehyde Adsorption

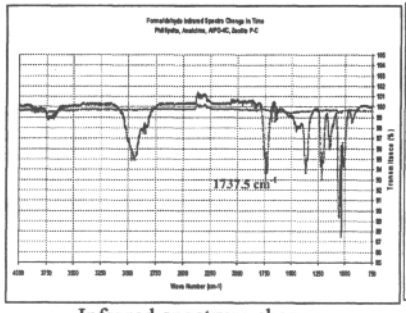
Synthesized materials were tested with an air flow polluted with formaldehyde. Adsorption is evident from change in formaldehyde infrared spectra at the breakthrough point. Infrared spectrum of the gaseous phase was monitored over time. In all cases, after zeolite contact, infrared spectrum of the gaseous phase went from the typical formaldehyde pattern to a more or less flat line as can be observed in spectra in Figures 7 (50FA50MK), 8 (83FA17MK), 9 (FA12h), and 10 (FA36h). Breakthrough curves were generated plotting change of absorbance peak intensity at 1737.5 cm^{-1} (stretching vibration of the carbonyl group) over time. Figures 7 to 10 show breakthrough curves next to infrared spectra for every case.

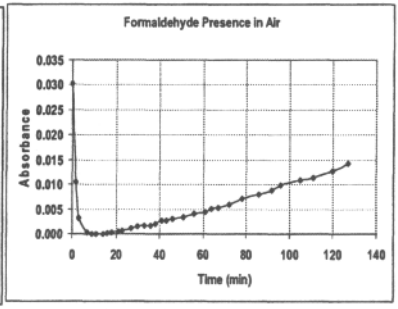




Infrared spectrum change Breakthrough curve

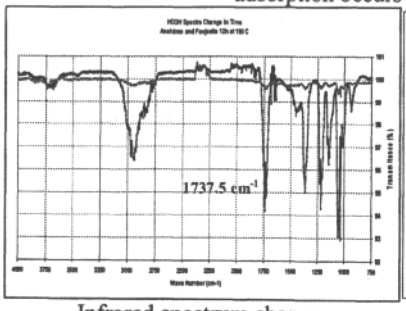
Figure 7. Adsorption of formaldehyde by synthesized zeolite A (50FA50MK). Peak of formaldehyde completely disappears after 5 minutes of contact with sample and total adsorption occurs over 13 minutes.

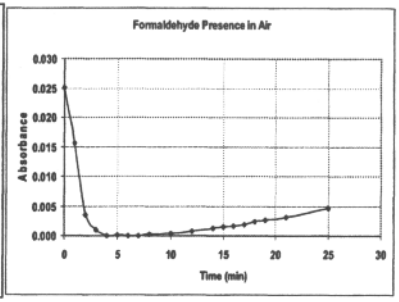




Infrared spectrum change Breakthrough curve

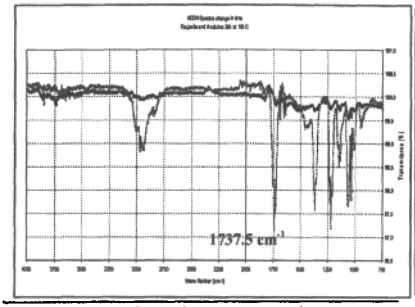
Figure 8. Adsorption of formaldehyde by mixed crystalline phases (83FA17MK). Peak of formaldehyde completely disappears after 7 minutes of contact with sample and total adsorption occurs over 21 minutes.

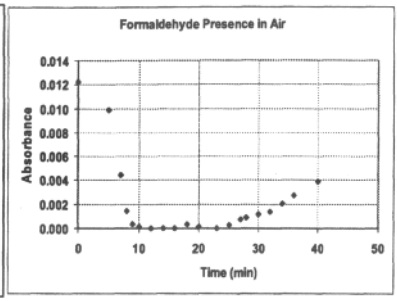




Infrared spectrum change Breakthrough curve

Figure 9. Adsorption of formaldehyde by faujasite and analcime cured over 12 hours. (FA12h). Peak of formaldehyde completely disappears after 4 minutes of contact with sample and total adsorption occurs over 8 minutes.





Infrared spectrum change Breakthrough curve

Figure 10. Adsorption of formaldehyde by faujasite and analcime cured over 36 hours. (FA36h). Peak of formaldehyde completely disappears after 10 minutes of contact with sample and total adsorption occurs over 25 minutes.

For analysis purposes, amount of formaldehyde taken up by materials were calculated as approximate values to compare zeolites' performance. From a mass balance of formaldehyde performed in the system it was theoretically determined that 311 μg/min of pollutant were continuously generated by the formaldehyde source. Using the time of total adsorption by samples, and normalizing by weight of samples used (about 11 grams for all cases), the uptake of formaldehyde by every sample was approximated. Summary of samples adsorption performance is shown in Table II. The percentage of enhancement in formaldehyde adsorption with respect to starting materials was also calculated. Results obtained for samples were compared with uptake of fly ash (109.8 μg formaldehyde/g sample) and metakaolinite (207.3 μg formaldehyde /g sample).

Table II. Synthesized zeolite materials formaldehyde adsorption performance

Sample ID	Time 1 (min)	Time 2 (min)	Time 3 (min)	Uptake μg formaldehyde/g sample	% Enhancement
50FA50MK	5	8	13	270.8	70.8
83FA17MK	7	14	21	414.7	220.8
FA12h	4	4	8	108.2	0.0
FA36h	10	15	25	311.0	183.2

Time 1: Time to reach "zero %" formaldehyde in air (100% adsorption)
Time 2: Time for 100% adsorption.
Time 3: Breakthrough time or time when formaldehyde reappears in air
(*) Uptake of formaldehyde calculated
(**) Enhancement in formaldehyde adsorption with respect to starting materials

Zeolite A (50FA50MK) is fast at adsorbing formaldehyde and enhances reasonably well the adsorption ability of starting materials. If compared to other zeolites, Zeolite A has a void fraction of 0.43 and a window size of 4.2 Å versus, for example, Faujasite that has a void fraction of 0.53 with size of open window of 7.4 Å[20, 21]. These main differences in framework structures seem to be the reason for sample 50FA50MK

adsorb less formaldehyde than, for example, third sample (FA36h). Sample FA12h did not enhance the adsorption uptake of fly ash. However, the same sample cured over 36 hours adsorbs about three times as much formaldehyde compared with fly ash. Both samples, FA12h and FA36h, contain faujasite and analcime according with XRD. In the case of sample FA12h, probably 12 hours were not enough to grow sufficient amount of zeolites and little crystals were rapidly saturated. Longer curing time allowed crystals to grow in larger amount and size to provide with enough internal porosity and better network of cavities and tunnels available for retention of compound. Also it might have happened that sample FA36h was richer in faujasite. In fact, if internal porosity is considered it is clear that faujasite has a void fraction of 0.53 while the value for analcime is 0.18 [20, 21]. Considering uptake of formaldehyde (Table II) and sample composition, the best synthesized materials are samples 83FA17MK and FA36h. Sample 83FA17MK is very effective at adsorbing formaldehyde since probably the mixed crystalline phases offer large internal porosity of crystals distributed in a network of internal cavities suitable for retention of formaldehyde. It is of industrial and environmental interest to produce materials with high content of fly ash in order to divert disposal of this waste product from ordinary landfilling. Furthermore, it is important that samples are rich in fly ash because its pozzolanic properties enhance the mechanical characteristics of synthesized products. In this preliminary study, the concentration of formaldehyde used in air for all the tests was the maximum possible for the system, a calculated value of 665 ppm. However, concentrations found in indoor environments usually range in the order of ppb. Therefore, at low concentrations zeolites synthesized from high concentrations of fly ash would make excellent air cleaners either on wall and ceiling surfaces or in air filters and purifiers. Having obtained results that confirm the potential of zeolites to clean air from formaldehyde, future work will be directed to design zeolite rich air cleaning devices and test them at indoor air conditions.

CONCLUSIONS

Zeolite A was synthesized using a 4M sodium hydroxide solution and a solid mixture containing metakaolinite and 50% fly ash. A second mixture of metakaolinite, 83% fly ash and a sodium hydroxide solution twice as stronger resulted in mixed phases of phillipsite, analcime, zeolite P-C, and AlPO4. Pure fly ash and an 8M NaOH solution cured for 12 and 36 hours resulted in Faujasite-Na, and Analcime-C synthesis. All synthesized zeolites adsorbed formaldehyde from air due to molecular sieve properties and affinity for polar molecules. The best adsorbents are those materials synthesized from high contents of fly ash. Results obtained from this preliminary study demonstrate the technical feasibility of applying zeolites to clean formaldehyde from air.

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MOLYBDENUM-OXIDE BASED SORBANTS FOR TOXIC METALS

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ABSTRACT

The ability of molybdenum trioxide to absorb uranium from water was investigated. It was found that MoO_3 could absorb up to 165 % by weight of uranium via a chemical reaction that produces an insoluble uranium molybdenum oxide mineral oxide called umohoite,$UMoO_6{\cdot}2H_2O$. The rate of reaction between MoO_3 and a slight excess (43 mole %) of 0.100 M uranyl acetate was found to be zero order with a rate constant of 0.42 mmol/hr. A cyclic process was developed whereby MoO_3 adsorbed uranium from aqueous solution and then the uranium and molybdenum trioxide were separated by treatment with aqueous ammonia. Solid ammonium uranate was isolated by filtration and the aqueous ammonium molybdate was converted back to MoO_3 by heating. The recovery of uranium from the separation was 98.9%.

INTRODUCTION

Uranium is a common contaminant of ground water and can arise from natural and anthropogenic sources. Uranium occurs naturally in the earth's crust and in surface and ground water. When bedrock consisting mainly of uranium-rich granitoids and granites comes in contact with soft, slightly alkaline bicarbonate waters under oxidizing conditions uranium will solubilize over a wide pH range. These conditions occur widely throughout the world. For example, in Finland exceptionally high uranium concentrations up to 12,000 ppb are found in wells drilled in bedrock[1]. Concentrations of uranium up to 700 ppb have been found in private wells in Canada[2] while a survey in the United States of drinking water from 978 sites found a mean concentration of 2.55 ppb[3]. However, some sites in the United States have serious contamination with uranium. For example, in the Simpsonville-Greenville area of South Carolina, high amounts of uranium (30 to 9900 ppb) were found in 31 drinking water wells[4]. The contamination with uranium is believed to be the result of veins of pegmatite that occur in the area. Besides entering drinking water from naturally occurring deposits, uranium can also contaminate the water supply as the result of human activity, such as uranium mining, mill tailings, and even agriculture[5,6]. Phosphate fertilizers often contain uranium at an average concentration of 150 ppm and therefore are an important contributor of uranium to groundwater [7]. The Fry Canyon site in Utah is a good example of the dangers of uranium mine tailings. The uranium concentrations measured in groundwater at this site were as high as 16,300 ppb with a median concentration of 840 ppb before remedial actions were taken[8]. Depleted uranium ammunition used in several military conflicts has also been demonstrated as a source of drinking water contamination[9].

Animal testing and studies of occupationally-exposed people, have shown that the major health effect of uranium is chemical kidney toxicity, rather than a radiation hazard[10]. Both functional and histologic damage to the proximal tubulus of the kidney have been demonstrated [11]. Little is known about the effects of long-term environmental uranium exposure in humans but there is an association of uranium exposure with increased urinary glucose, alkaline phosphatase, and ß-microglobulin excretion[12], as well as increased urinary albumin levels[13]. As a result of

such studies, the World Health Organization has proposed a guideline value of 2 ppb for uranium in drinking water while the US EPA has specified a limit of 30 ppb.

Current municipal treatment practices are not effective in removing uranium. However, experimentation indicates, that uranium removal can be accomplished by a variety of processes such as modification of pH or chemical treatment (often with alum) or a combination of the two [14]. Several sorbants have been shown to be useful for removal of uranium from water. Activated carbon, iron powder, magnetite, anion exchange resin and cation exchange resin were shown to be capable of adsorbing more than 90% of the uranium and radium from drinking water. However, two common household treatment devices were found not to be totally effective for uranium removal [4].

Besides treatment of well water, there is also a strong need for prevention of the spread of uranium contamination from concentrated source such as uranium mine tailings. Commonly used above-ground water treatment processes are not cost-effective and do not provide an adequate solution to this problem. However, permeable reactive barriers (Figure 1) have been demonstrated to be a financially-viable and elegant alternatives to active pump and treat remediation systems. Such barriers composed of metallic iron, ferric oxyhydroxide, and bone char phosphate have been designed and proven effective for uranium[8]. Iron metal performed the best and consistently lowered the input uranium concentration by more than 99.9 percent after the contaminated groundwater had traveled 1.5 ft into the permeable reactive barrier.

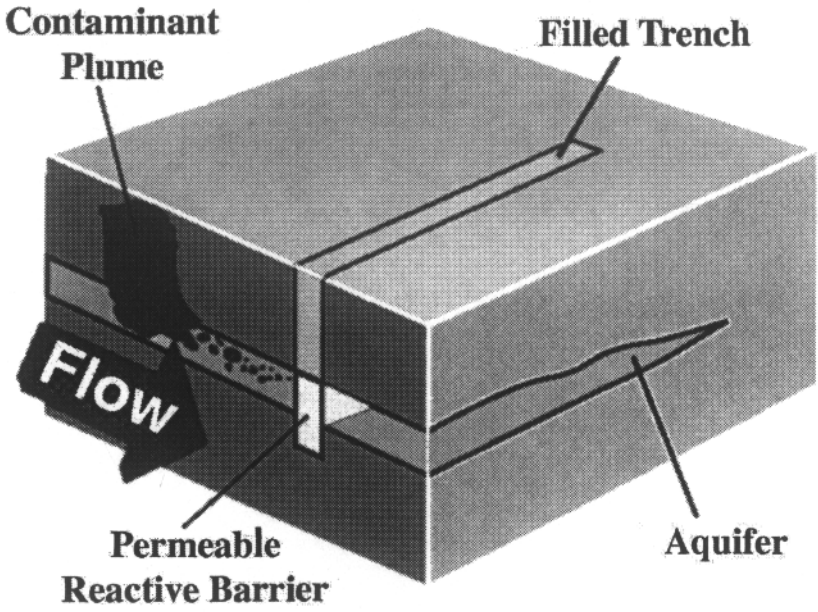

Figure 1. Operation of a Permeable Reactive Barrier