Prospects of Natural Zeolites in Indonesia for Industrial Separations and Environmental Management

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ABSTRACT

Zeolite as well as molecular sieves are a class of aluminosilicate materials, which have found wide use in industries for separation, purification and pollution control. In the new era of nanomaterials in the 21st century, these nanoporous materials have become more widely used in separation, catalysis and environmental management, even in microelectronic and energy storage sectors. The following briefly shows the great potential of natural zeolites for some important environmental applications: CO_2 removal from landfill gas and coal seam gas using Pressure Swing Adsorption (PSA) with Clinoptilolites: Natural zeolite is not only a cheaper solution to the economical storage system of methane for NGV_s but it also present a safer storage medium as alternative adsorbent such activated carbon is flammable and very costly. There is also an increasing interest in indoor air quality control issues among the building industries and health organizations. It has been demonstrated that clinoptilolite is particularly effective adsorbent for odours and some volatiles in indoor environment. Another area of importantnce of natural zeolites is the solar energy application. Zeolites can adsorb water vapour and create effective cooling with solar heat as the energy to regenerate the zeolite. Systems using zeolites can be designed in such a way that combined cooling and heating can be achieved at about 40-60% efficiency. Adsorption of Nitrogen and Oxygen in zeolites for PSA application Cp zeolite deposit has about 75% of the capacity of a commercial Mordenite zeolite for air separation at 30°C. The dynamics studies showed that Cp zeolite is suitable for N_2 and O_2 separation due to their large difference in adsorption kinetics.

***Keywords**: Cation Exchange, Gas Separation, Natural Zeolites*

INTRODUCTION

Natural zeolites are naturally occurring minerals which have the basic building units of zeolites (TO_4) tetrahedron. The commercial uses of natural zeolites have been expanding over the last decades or so despite the fact that many millions of tons of synthetic zeolites and molecular sieves are produced each year in the world. One of the main drivers for the natural zeolite market is the need for economical solutions to many pollution problems. There have been increasing amounts of natural zeolites mined and sold to the environmental management markets in the USA, Australia, Japan, Hungary, and Mexico. It is estimated that over 20 millions tons of zeolite minerals are at present mined in the world. Indonesia has vast deposits of natural zeolites and clay minerals (over 200 million tons) mainly Clinoptilolite and mordenite.

Traditional applications of natural zeolites as a cheap mineral resource are for fillers in paper manufacturing, in cement and concrete, in fertilizers, and as ion-exchangers. In recent years more and more natural zeolites have found applications in wastewater treatment, air pollution control (for odour removal), and for adsorption separation in drying and gas purification. In the era of high environmental concerns of the public and energy and resource conservation, the attractive physical and chemical properties of natural zeolites will be utilized even more in the years to come.

Mineral compositions of Indonesian zeolite rocks are mostly clinoptilolite, mordenite,

smectite and others. The deposits of natural zeolite in Indonesia is shown on Table 1.

Table 1: Natural zeolites deposits in Indonesia

No.	LOCATION	Deposits (million tones)
1.	Campang, Sidomulyo, Lampung- South Sumatra.	5 (measured) 32 (indicated) 27 (inferred)
2.	Nanggung, West Java	28.843
3.	Cikembar, Sukabumi, West Java	2.5
4.	Cisolok, Sukabumi, West Java	unmeasured
5	Bayah, West Java	12.4 (measured) 34 (inferred)
6.	Cisaat, Sukabumi, West Java	10 (inferred)
7.	Sragen, Banjarnegara, Central Java	2.90
8.	Pule, Karanganyar, East Java	unmeasured
9.	Sukokidul, Trenggalek, East Java	unmeasured
10.	Ngaringan, Blitar, East Java	unmeasured
11.	Ende, Nangapanda, Flores, West Nusatenggara	20

There are more than 150 zeolites, they can be classified into different groups and some types for examples have typical unit cell contents as shown on Table 2.[1,2] The types of zeolites determine specific properties and usage.

PROPERTIES OF NATURAL ZEOLITES

The important structural properties of zeolites concern with the dimensions and arrangements of the crystal pores, the presence of water and metal cations and the ratio of silicon to aluminium atoms which give many unique properties. The loosely bound water can be removed fairly easily by heat or evacuation and replaced reversibility without decomposition of the crystal structure. The cations are partially or fully hydrated and may be bounded weakly to the aluminosilicate framework. If the zeolite is immersed in water containing dissolved salts of others metals, those cations which are within accessible positions in the zeolite may exchange with the cations in the solution.

Table 2: Classification of zeolites

Name	Typical Unit Cell Contents
GROUP: S4R	
Analcime	$Na_{16}[(AlO_2)_{16}(SiO_2)_{32}].16H_2O$
Harmotome	$Ba_2[(AlO_2)_4(SiO_2)_{12}].12H_2O$
Phillipsite	$(K,Na)_{10}[(AlO_2)_{10}(SiO_2)_{22}].20H_2O$
Gismondine	$Ca_4[(AlO_2)_8(SiO_2)_8].16H_2O$
P	$Na_6[(AlO_2)_6(SiO_2)_{10}].15H_2O$
Laumontite	$Ca_4[(AlO_2)_8(SiO_2)_{16}].16H_2O$
GROUP: S6R	
Erionite	$Ca_2Mg_{0.5}K_2Na_2[(AlO_2)_9(SiO_2)_{27}].27H_2O$
Offretite	$KCa_2[(AlO_2)_5(SiO_2)_{13}].15H_2O$
Levynite	$NaCa_3[(AlO_2)_7(SiO_2)_{11}].18H_2O$
Sodalite	$Na_6[(AlO_2)_6(SiO_2)_6].8H_2O$
GROUP: D4R	
Zeolite-A	$Na_{12}[(AlO_2)_{12}(SiO_2)_{12}].27H_2O$
ZK-4	$Na_8TMA[(AlO_2)_9(SiO_2)_{15}].28H_2O$
GROUP: D6R	
Faujasite	$(Na_2,Ca,Mg)_{29}[(AlO_2)_{58}(SiO_2)_{134}].240H_2O$
X	$Na_{88}[(AlO_2)_{88}(SiO_2)_{104}].220H_2O$
Y	$Na_{56}[(AlO_2)_{56}(SiO_2)_{136}].250H_2O$
Chabazite	$Ca_2[(AlO_2)_4(SiO_2)_8].13H_2O$
Gmelinite	$Na_{88}[(AlO_2)_{88}(SiO_2)_{104}].220H_2O$
ZK-5	$Na_{30}[(AlO_2)_{30}(SiO_2)_{66}].98H_2O$
GROUP: 4-1 / T_5O_{10}	
Natrolite	$Na_{16}[(AlO_2)_{16}(SiO_2)_{24}].16H_2O$
Mesolite	$Ca_{16}Na_{16}[(AlO_2)_{48}(SiO_2)_{72}].64H_2O$
Thomsonite	$Ca_8Na_4[(AlO_2)_{20}(SiO_2)_{20}].24H_2O$
Edingtonite	$Ba_2[(AlO_2)_4(SiO_2)_6].8H_2O$
GROUP:5-1/ T_8O_{16}	
Mordenite	$Na_8[(AlO_2)_8(SiO_2)_{40}].24H_2O$
Dachiardite	$Na_5[(AlO_2)_5(SiO_2)_{19}].12H_2O$
Epistilbite	$Ca_3[(AlO_2)_6(SiO_2)_{18}].18H_2O$
Bikitaite	$Li_2[(AlO_2)_2(SiO_2)_4].2H_2O$
GROUP : 4-4-1	
Heulandite	$Ca_4[(AlO_2)_8(SiO_2)_{28}].24H_2O$
Clinoptilolite	$Na_6[(AlO_2)_6(SiO_2)_{30}].24H_2O$
Stilbite	$Ca_4Na_2[(AlO_2)_{10}(SiO_2)_{26}].34H_2O$
Barrerite	$Na_8[(AlO_2)_8(SiO_2)_{28}].26H_2O$

The exchangeable cation content varies widely, and is directly related to the aluminium content of zeolite. Table 3 shows typical ion-exchange properties of selected natural zeolites.

The adsorption properties of zeolites are not limited to the external surface of the crystals as they are with many other minerals. The internal structure of many dehydrate zeolites can catalyse many gaseous reactions,

especially when activated with hydrogen ions or particular rare metals. The majority of the sites of adsorption, catalysis and cation exchange in zeolites are within the crystal structure.

Table 3 : Ion exchange properties

Zeolites	Si/Al (exchange capacity)	Original cations	Exchange Selectivities
Analcime	2	Na	Complicated by ion-sieving
Chabazite	1.4 – 2.8	Ca, K	$Tl^+>Cs^+>K^+>Ag^+>Rb^+>NH_4^+>Pb^{2+}>Na^+=Ba^{2+}>Sr^{2+}>Ca^{2+}>Li^+$
Clinoptilolite	2.7 – 5.3	Ca,Na,K	$Cs^+>K^+> Sr^{2+} = Ba^{2+}>Ca^{2+}>>Na^+>Li^+>Pb^{2+}>Ag^+>Cd^{2+}\sim Zn^{2+}>Cu^{2+}>Na^+$
Erionite	3 – 4	Na, K	$Cs^+>Sr^{2+}>K^+>Na^+$
Ferrierite	3.2 – 6.2	K, Mg	Inadequate data
Mordenite	4.4 – 5.5	Ca, Na	$Cs^+>K^+>NH_4^+>Na^+> Ba^{2+}>Li^+.$ $NH_4^+>Na^+>Mn^{2+}>Cu^{2+}> Co^{2+}\sim Zn^{2+}>Ni^{2+}$
Phillipsite	1.3 – 2.9	K,Ca,Na	$Ba^{2+}>Rb^+\sim Cs^+\sim K^+>Na^+>>Li^+$

The trend of ion-exchange affinity are heavy, polarizable, alkali metal ions of large ionic size preferred by zeolites.

APPLICATIONS

(1) CO_2 removal from landfill gas and coal seam gas using Pressure Swing Adsorption (PSA) with Clinoptilolites: Cp has been found to be effective to separate CO_2 from methane (CH_4) because of the molecular sieving effect. This can be an excellent candidate to be used in PSA units to upgrade biogas or coal seam gas into high value-adding methane for industrial pipeline or energy generation.

(2) Natural zeolite is not only a cheaper solution to the economical storage system of methane for NGV_s but in also present a safer storage medium as alternative adsorbent such activated carbon is flammable and very costly. It has been demonstrated that natural zeolites are highly efficient for methane storage at moderately low pressure (0.5-1 Mpa). Further enhancement on the adsorption capacity of Cp at low pressure range (below 0.5 Mpa) can lead to a more viable, cost-effective means of fuelling for NGVs.

(3) There is also an increasing interest in indoor air quality control issues among the building industries and health organizations. It has been demonstrated that clinoptilolite is particularly effective adsorbent for odours and some volatile in indoor environment. In fact, room air cleaners using natural zeolite filters have been developed in the US and Japan for the removal of urine odours and other volatile gases in houses and similar facilities.

(4) Another area of important of natural zeolites is the solar energy application. Zeolites can adsorb water vapour and create effective cooling with solar heat as the energy to regenerate the zeolite. Systems using zeolites can be designed in such a way that combined cooling and heating can be achieved about 40-60% efficiency.

(5) Adsorption of Nitrogen and Oxygen in zeolites for PSA application Cp zeolite deposit has about 75% of the capacity of a commercial Mordenite zeolite for air separation at 30 ^{0}C. The dynamic studies showed that Cp zeolite is suitable for N_2 and O_2 separation due to their large difference in adsorption kinetics.

Natural zeolites are minerals that can do many things. The Russians dropped tons of a zeolite called clinoptilolite on the Chernobyl Reactors, filtered milk produced in the area and even put it in candy bars to feed the children. Zeolite eliminate odours,, clean up chemical pollutants and heavy metals and even stops pain from bee stings, coral stings and muscle strains. Yet, zeolites are classified as a GRAS substance (Generally Recognized As Safe) by the Food and Drug Administration.

Hundreds of other uses of zeolites

Zeolite work by ion exchange, gas adsorption and as a catalyst. There hundreds of zeolites usages in the daily life and in industry for examples: zeolites can eliminate animal odors from urine, eliminate animal odors from feaces; eliminate odors from dead animals; eliminate heat and hormonal odors in animals; eliminate bad breath in animals;

save animals (cattle) that have consumed lead; reduces morbidity rates in farm animals, cattle, swine and chickens; eliminate cigarette odors in automobiles, dead rat odors in automobiles, eliminate sour milk odors in cars, eliminate locker room odors, eliminates beauty shop odors, eliminates bilge odors, eliminates cat box odors, soak eliminates leg ulcer odors, eliminates pollutants from building materials, removes formaldehyde from carpets and glues, removes odors from flooded basements. It can also cleans up pesticides, eliminates mold and mildew odors, eliminates burned pop corn odors from microwave, cleans burned beans from pan without scrubbing, eliminates fish odors from fish market, eliminates spoiled food odors from freezers, including fish, shrimp and chicken. It can also picks up glue odors, eliminates cancer odors, eliminates chemotherapy odors, odors in dental office, odors from gangrene, picks up lead, cleans air from gases from cigarette smoke in buildings and filter smoke stack pollutants also filter food odors.

In addition, it can help skin rash, removes chemical poisions, safely chelate heavy metals, removes radioactive cesium from people and animals, cleans up fish waste from pond and tanks, removes heavy metals from soils, cleans up contaminated soils, hold water in soils for farming and irrigation, improve cation exchange in soil for crops, grow crops in-zeoponics, and use to improve fertilizers. In relating with water, it can be used in fish farming, filter waste from water, filter heavy metals from water, filter radioactive materials from humans.

Also it makes great humidifier for humidor, preserve food under refrigeration, use as food additive, use to adsorp chemicals from the skin, remove chemicals and pesticides from food stuffs. Some are use as insulation, and locks up chemicals for safe disposal. All zeolites are not created equal. The type of erionite is known can cause cancer, however zeolites are the mineral for the next century.

CONCLUSION

Natural zeolites are versatile and highly effective adsorbents, ion-exchangers, and good catalyst carriers. The attractive properties of zeolites plus the modification are more and more realized and utilized by increasing applications. The environmental management industries, especially promising for the expanding the market of natural zeolites, and it is a prospect on 21st century will see growth in the mining and utilization of natural zeolites.

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