Applications of Natural Zeolite

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Abstract— **Zeolite crystals have potential applications in the numerous areas of scientific, industrial and agricultural technology has provided impetus for the research and development programmes that have been carried out in several countries. In deccan trap of India, large deposits of zeolites have been found, but studies on these natural zeolites are rarely reported. Taking the advantage of different types of zeolite crystals available in this part of India that is Marathwada (Maharashtra), it was thought worth while to collect different varieties of zeolite crystals, where the occurrence of zeolites have not been reported so far**

INTRODUCTION

Applications of zeolites in different fields depends upon the several physical or chemical properties including (i) ion – exchange (ii) adsorption (iii)dehydration and rehydration and (iv) Siliceous composition.

Some important applications are as follows:-

1 Deactivation of Radioactive Effluents

The nuclear industry and the nuclear energy programm require solution of the problems associated with the developments of effective and cheap methods for the purification of radioactive waste. Approximate calculation shows that the total activity of the radioactive waste products through out the world will be 4 - 6 x 10^{11} Ci (1). At present research is concentrated in three directions. Extractions of radioactive elements from effluent of high activity, deactivation (decontamination) of low and medium activity effluents and the concentration of radioactive effluents for long term storage (2). One of the important methods of purification of the radioactive waste is adsorption deactivation. Zeolite containing rocks are used for these purpose particularly Clinoptilolite containing tuffs are characterized by the high ion exchange selectivity for ^{137}Cs , ^{190}Sr and the other radioactive elements. Clinoptilolite (Hector California, USA) 20 –50 meshes was loaded into column through which the solution containing the radioactive elements was pumped after break through, the Clinoptilolite was removed and buried. Such deactivation was tested and has been established that it can be used in the industry. The removal of Sr2+ and Cs+ from radioactive waste using analcime , chabazite and Phillipsite has been studied. (3, 4)

2 Extraction s of metals from Industrials wastes

Mordenite can be successfully used for the extraction of Cs^+ from Cs^+ solution. (5). Sodium Clinoptilolite is especially selective for the heavy metals (6). It was found that in the presence of lithium, magnesium, aluminum, and yttrium, ion exchange of lead on Clinoptilolite proceeds better. Sodium , calcium and strontium ion decrease sorption as compared with lead and barium , aluminum , cesium and especially potassium ions. In certain cases Clinoptilolite can be used to extract the mercury from effluents (7)

3 Filtration of Drinking Water

New filters for the purification of the drinking water and industrial effluents are very important. Practically water containing suspended particles are purified by percolation through quartz sand 0.5-2 mm grain size. Quartz sand is however rather expensive and has low fine – trapping capacity. Studies have shown that quartz sand can be successfully replaced by natural zeolites, which are superior in several ways (8,9). High porosity is advantageous as this causes high flow rates in Clinoptilolite and Mordenite water filters. Mud trapping capacity of zeolite is higher than with the quartz sand.

4 Gas Purification

Each year some 200 to 250 million tones of ash and up to 160 million tones of sulfur dioxide are ejected into the atmosphere (10). In the USA, thermal power stations burning coal and oil contribute 74% of the sulfur dioxide and about half the nitrogen oxides emitted in that country(11). Some 200 million automobiles contribute 200 million tones of carbon dioxide, 40 million tones of hydrocarbons and 20 million tones of nitrogen oxides (12). This kind of contamination is infact global, especially in the northern hemisphere, i.e. with respect to the industrially developed countries. In certain cases emitted components interact with each other, forming the smog and acids. Developments of technical process for the trapping of emissions concern the solution of two problems: recovery of valuable compounds and their further utilization and the protection of the environment. To overcome this difficulty natural zeolites are used for the purpose.

5 Oxygen Production

Clinoptilolite containing tuffs are also used as adsorbents for the oxygen enrichment of air. Na^+, NH_4^+ , Ca_2^+ and K^+ forms are suitable (13 – 17). Ion exchange was performed by using corresponding salt solutions at room temperature (25°C) for 6 hours with the continuous mixing. Modified samples loaded in to adsorption columns 400 mm long and 12 mm diameters. Air under pressure was supplied to the adsorption column and oxygen – enriched air was collected.

6 Solar Energy

Use of natural zeolite in solar energy system, particularly those used for air conditioning (18). Zeolites, unlike other adsorbents, differ by unique adsorptive properties associated with a remarkable nonlinear adsorption isotherm i.e. full adsorption takes place at comparatively low pressure, and the further pressure increase does not affect the process. At the same time when the zeolite is heated, most water is desorbed only at the high partial pressure. Consequently the difference in the adsorption capacity at low and the high temperature is very great, and this allows highly effective use of the solar energy. It was shown that by means of these zeolites systems, one could heat water to 75% and cool to 50% of the

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requirements. Dehydration of the zeolites during day time and adsorption of water at night leads to a temperature change to an extent sufficient for cooling (heating) of small rooms.

According to calculations (19), 1 tone of zeolite exposed on a roof area 19.6 m^2 can cool 1 tone of air. Some hundreds of thousands of tones of natural zeolites would however be required for cooling or heating the buildings by solar energy each year. At present the USA does produce refrigerators designed to use zeolites (20)

7 Zeolites in Cement

Zeolite tuffs are also widely used as silica additives to concrete and cement grouts. Such tuffs are employed in the USA, Japan and Italy (21 , 22) in the production of cements for the manufactures of light agreements.

Introduction of zeolite tuffs into cement grouts increases the longevity of cement stone it's stability in aggressive media and decreases the impact cracking. Studies of the effects of Clinoptilolite tuffs as additive on the properties of cement sand grouts showed that small additions of tuffs increases the activity of the cement but, due to the high hydrophilicity the viscosity of the composite increases as well (23, 24). The use of hydrophobic (very high Si/Al ratio) Clinoptilolite as an additive to the old cement makes it more active. Addition of 1.1% hydrophobic Clinoptilolite increases the strength of old ordinary cement. Thus cement Clinoptilolite grouts can be successfully used for lining drill hole and the construction of the waterproof structure.

8 Zeolites In Paper Industries

Clinoptilolite tuffs is used in Japan as a paper filler. When Clinoptilolite fillers are used, more 'porous' paper is produced and it's weight decreases. The paper is more opaque. At present, Japanese manufacturers use treated Clinoptilolite tuffs as paper fillers in amounts of 250 – 300 tones per month. In Hungery from 1961, 65% zeolite Clinoptilolite tuffs have been used as pulp fillers. The average brightness of the material being 85.9%.

9 Zeolites In Rubber Industries

In order to protect rubber mixtures against premature polymerization during Vulcanization and to recover components of gas in volatile vulcanizing systems, zeolite have been used in the rubber industry. Natural zeolites have been used as the rubber fillers due to the low cost and wide availability. Clinoptilolite and Mordenite tuffs are used various areas in USSR and in particular GSSR deposits can be successfully used as the structuring and modifying agent filters of resin mixtures and to produce special rubbers (49).

10 Zeolite in Fish Pond

Development of fish ponds invokes complex problems associated with creation of optimum conditions for breeding. One of the most important problem is removal of ammonia from the water as ammonia is a cause of mass mortality of fish. The sorption method has proved to be best for removal of ammonium ions. Natural zeolites are widely used for purification of polluted waters in the USA and Japan. Experience regarding the productivity of ponds or fish breeding is of interest. In a 45000-dm3 pond containing some 2000 of breeding fish, the yield increases by about three times when the water is purified of ammonium ion. Removal of NH_4 ions from waste water using natural zeolite was studied in detail earlier (25).

11 Plant Growth

The wide use of fertilizers and the other chemicals in agriculture and their leaching from the soil causes pollution of the environment and increases retention of chemicals in plants and the soil.. In this respect a significant role is played by the natural zeolites which have the high ion exchange retention capacity.

Natural zeolites can absorb ammonium and potassium ions and then release them gradually into the soil solution. Thus zeolites in the soil can prolong the effects of mineral fertilizers. The great affinity of natural zeolites for the water and their capacity to retain it can also affect the soil water regime. Natural zeolites can increase the pH of the medium as well effects of Clinoptilolite tuffs on soil productivity are well known. According to Japanese workers (26) the cropping capacity of carrot, apples and wheat increases with introduction of the Clinoptilolite (15 – 63%). Natural Japanese zeolites for use as soil conditioners are exported to Taiwan. Introduction of ammonium and potassium Clinoptilolite increased the cropping capacity by 26%. Good results have been obtained for wheat when Clinoptilolite tuffs are introduced into the soil. The soil retains the water better when 5 to 10 tones of Clinoptilolite are added per hector (27)

12 Protection of Environment

Zeolites can be used for fixation of tetraethyl lead . A car using the leaded petrol emits about 80 mg of lead per kilometers traveled. In order to find out the rate of the penetration of lead into plants, the content of lead into stalks , roots and fruits of maize was studied (28).Lead and Clinoptilolite (0.29 of lead as nitrate per kg of soil) were introduced in the soil and lead nitrate alone in another. The lead migrates actively from the soil into plants. At the last stages of growth the content of lead in plants is higher by an order of magnitude than in the sample containing the zeolite. This means that Clinoptilolite tuffs can adsorb lead from the soil and decreases the content of lead in plants.

Zeolite dense substrates are used in biotechnology to cultivate microorganisms. In organic materials it can serve as substrates in particular natural zeolites (29).

13 Zeolite as catalysts

Zeolites are extremely useful as catalysis for several important reactions involving organic molecules. The most important are cracking isomerization and hydrocarbon synthesis. Zeolite can promote a diverse range of catalytic reactions including acid – base and metal induced reactions. Zeolites can also be acid catalysts and can be used for the supports for active metals or reagents. Zeolites can be shape – selective catalysts either by the transition state selectivity or by the exclusion of competing reactants on the basis of molecular diameter. They have also been used as oxidation catalysts. The reactions can take place within the pores of the zeolite, which allows a greater degree of the product control. The main industrial application areas are Petroleum refining and petrochemical production. The consumption of zeolite catalysts was over 2,20,000 tons annually. Natural zeolites and their modified forms can catalyze many chemical reactions.

14 Zeolites In Detergents:

For detergents, synthetic zeolites have been developed to fulfill the role of the product 'builder'. The main function of a builder in the detergents products is to soften the water by extracting water hardness components (presents as the calcium and the magnesium compounds). Additionally in the detergent powders builders can also absorb liquid components of the formulation so as to maintain dry, free – flowing powder characteristics .In view of their high

functionality and their favorable safety and ecological properties, synthetic zeolites have become widely employed by the detergent industry. It has been shown (55) that Clinoptilolite tuff can be introduced into detergents to replace sodium tripoly phosphate, an ecologically undesirable compound.

15 Zeolite In Soil Erosion

Synthetic zeolite, made of coal fly ash, a waste product of the electrical power plants increased soil aggregation and permeability therefore soil erosion was reduced .It was assumed that sodium cations where substituted by calcium cations from the synthetic zeolite as a result, dispersion of the soil was retained and soil permeability increased (30).

REFERENCES

[1] Gradev, G.D. , Thesis Moscow Univ. (1978)
[2] Mercer, B.W. and Ames L.L. Nuclear Application Technology 451 462
[3] Kuznetsov , Yu. V. ,Schebetkovskii V.N. and Trusov A.G. Bases of water purification against radioactive impurities (Atomizdat Moscow,1974)
[4] Lepez. Mencrero, E In: Practices in the treatment of low and intermidiate level Radioactive wastes (IAEA), Vienna , 1966) P. 869 – 900.
[5] Mercer B.W. Ames L.L. and Smith P.W. Nuclear Application Technology, 8, 62 (1970).
[6] Semmens, M.I. and Sayfarth ,M.Natural zeolites occurrence properties used (Pargoman Oxford 1978) – P. 517 – 526
[7] Mamedova I.A. Ibragimov Ch. Sh. And Muradova N.M. Az. Chem J, 2, 135 (1985).
[8] Babaev I.S. Rajbabli S.B. and Aliev T.B. Technical progress 6, 45 (1976)
[9] Tarasevich ,Y.I. , Rudenko, G.G., Kravchents, V.A. and Polyakov V.E. chemical technology,1, 66 (1979)
[10] Detri G. The Atmosphere should be clean (Progress , Moscow, 1973)
[11] Detri G. The Atmosphere should be clean (Progress, Moscow , 1974)
[12] Nikitin D.P. and Novikov Yu. V. : Environment and Man (High School Moscow , 1980).
[13] Haralampiev Glebova I, chaika I and Girupsev G. Proc session /kinetics and Mechanism, sofia (1975) P. 281 – 286).
[14] Calabova I and Haralam Piev , G. Proc Symp. Kinetics and Mechanism , Sofia (1975) P. 287
[15] Galabova I, Proc. Chem. Techn. Inst. Sofia 23 , 257 (1977)
[16] Galabova, I.M. Haralampiev, G.A. & Alexiev, B. Natural zeolites occurrence Properties, use (Pargamon Oxford 1978) pp 431 – 437
[17] Galabova ,I.M. Haralampiev, G. A. Natural zeolites (Tbilisis 1979 p – 239 – 246.
[18] Tchernev, D.I. Natural Zeolites Occurrence, Properties & Use (Pargamon Oxford 1978) P 479 , 85.
[19] Techernev, D.I. Proc Fifth Intern. Conf. On zeolites , 788 (1980)
[20] Mchedlishvili, O.P. Likhacheva, V.A. Usherov Marshak, Tara sevich A.V. Polyakov, Y. I., Wegnar, V.E., Rudenko, G.R. Prima V. I. Chemical Technology (Naukova , Dumka, Kiev 1980) P. 11 15.
[21] Wegnar G. K., Physio Chemistry of Activation processes of cement Dispersions (Naukova Dumka , Kiev. 1980).
[22] Wegner G. K., Detkov , V.P. Kruglitski N.N., Ovcharenko F.D. , Prima E.I. and Tarasevich Y. I. , J. Abstracts , Ministry of Petroleum Industry of the USSR , No. 2 P. 26 – 7 (1979).
[23] Rapchinskaya S.E. Bloch G.A., Tsitsishvili , G.V. , Chumicheva, N. P., Ovcharov, V.I. and Andronikashvili T.G. Natural ZeolitesOccurrence, Properties & Use (Pargamon Oxford 1978)pp.227 – 33
[24] B. T. Bhoskar , S. D. Ghan, Asian Journal of Chem Vol. 17 (2005) P 634
[25] Torii K In: L.B. Sand and E.A. Mumption (Eds.) Natural Zeolites Occurrence, Properties & Use(Pergamon , Oxford , 1978) P. 441 – 450
[26] Aliev S. A., Iskenderov I.S., Verdiev K.Z. and Mamedova S.N. Natural zeolites Occurrence Properties & Use (Pargamon Oxford 1978 P. 109 , 115.
[27] Tsitsishvili G.V. Andronikashvili T.G., Kvantaliani A.S., Maisuradze G.V. , Mudvani A.L., Machavariani M. Sh. GvakhariaV.G. Natural Zeolites Occurrence Properties & Use (Pargamon Oxford 1978) P. 159, 163 .
[28] Korolev S.G., Chebakov S.I. , Tsitsishvili G.V. Andronikashvili T.G., Zurabashvili Z.A. and Kvashali N.F. (Eds) Use of Natural Zeolites in Animal Husbandry and Plant Growing .
[29] Pope. A. Popovici E., Vasile A., Alexandrose I. M. and cruce and Siozeo M., 84 , 288 (1984).
[30] Tahel Yamamoto , Aritune Yuya , Akl Saton , Hidetomo Takashi, Musae – Sumikoshi , Hossein Deghanisanij , Mehahem Agassi , ASEA Annual Meeting (2004) P. No. 42081.