EUZEPA – European Zeolites Producers Association

Synthetic zeolites

Chemical, toxicological, ecological and legal aspects of production, transport, handling and application

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1. INTRODUCTION

Zeolites are crystalline, hydrated aluminosilicates with a framework structure. The three dimensional, polyanionic networks are constructed of SiO4 and AlO4 trahedra linked by oxygen atoms.
Zeolites became of industrial importance in the 1950s when synthetic zeolites became available on an industrial scale. Since then the world consumption in the fields of ion exchange, adsorption and catalysis has grown continuously. In new zeolites, the aluminium and silicon of the classical zeolites are partly replaced by other elements.

2. CHEMICAL AND PHYSICAL CONSTITUTION

2.1. Chemical compositions

Crystalline aluminosilicates, composed of silica (SiO2) and alumina (Al2O3) in various proportions plus metallic oxides. Produced by hydrothermal treatment of a solid aluminosilicate or of a gel obtained by the reaction of sodium hydroxide, alumina hydrate and sodium silicate. The initially obtained product or a naturally occurring analog, may be partially ion-exchanged to introduce other cations. Specific zeolites are identified by notations indicating crystal structure and predominant cation, e. g. KA, CaX, NaY.

2.2. Physical forms

Most of the chemical and physical properties of the zeolite are essentially determined by the aluminium content of their framework:

Type	Formula	Pore Size [Å]	SiO2 / Al2O3 [mol ratio]
Zeolite A	$Na_{12}[(AlO_2)_{12}(SiO_2)_{12}] \cdot 27\ H_2O$	4.1	2.0 – 2.5
Zeolite X	$Na_{86}[(AlO_2)_{86}(SiO_2)_{106}] \cdot 264\ H_2O$	7.4	2.0 – 3.0
Zeolite Y	$Na_{56}[(AlO_2)_{56}(SiO_2)_{136}] \cdot 250\ H_2O$	7.4	3.0 – 5.5
Zeolite L	$K_9[(AlO_2)_9(SiO_2)_{27}] \cdot 22\ H_2O$	7.1	6.0 – 10.0
Zeolite P	$Na_6[(AlO_2)_6(SiO_2)_6] \cdot 15\ H_2O$	3.1 x 4.5 2.8 x 0.48	2.0 – 5.0
Mordenit	$Na_{8,7}[(AlO_2)_{8,7}(SiO_2)_{39,3}] \cdot 24\ H_2O$	6.7. x 7.0	8.0 – 10.0
ZSM 5	Na0,3H3,8$[(AlO_2)_{4,1}(SiO_2)_{91,9}]$	5.4 x 5.5 5.1 x 5.5	30 -
ZSM 11	$Na_{0,1}H_{1,7}[(AlO2)_{1,8}(SiO_2)_{94,2}]$	5.1 x 5.5 5.1 x 5.5	25 -

Synthetic zeolites containing alkali (sodium) metal are normally colourless crystalline powders. Colours occur if the zeolites contain transition metals by ion exchange or impurities. The primary particle size of synthesized zeolites have an average of 0.1 to 15 µm. The single crystal often forms large aggregates. On heating hydrated zeolites release water. Many zeolites can be almost completely freed of adsorbed water without damaging the crystal structure. This activation is normally done at 400 to 700 °C. The free pore volumes are then available for the adsorption of guest molecules. In spite of their open structure the zeolites have good thermal stability.

3. PRODUCTION AND RAW MATERIALS

3.1. Production routes

The production processes for synthetic zeolites can be divided into the following operations
− raw material storage
− synthesis
− washing solid, liquid filtration
− stabilization
− granulation
− drying and activation
− storage

The synthesis of a single-phase micro-crystalline zeolite powder is normally not the endpoint of the production process. Other properties are also important. For many applications, the assynthesized zeolite must be chemically or physically modified by processes such as ion exchange, de-alumination or acid treatment. Finally, for many applications in adsorption or catalysis, shaped products are required which usually contain binders. The manufacturing of zeolites, therefore, includes more than the actual synthesis which is not a uniformed but a very individual process, depending on type and application of zeolites and consists of a well defined series of individual steps aimed at providing a specific spectrum of tailored processes.

3.2. Raw materials

Raw Materials for the production of synthetic zeolites are aqueous alkali metal silicate solutions (e. g. water glass) and aluminate (e. g. sodium aluminate) or aluminium hydroxide and sodium hydroxide solution. Synthesis with other raw materials are also undertaken but these are of minor importance.

3.3. Synthetic zeolites under REACH, production and raw materials approach

Identification of the synthetic Zeolites which are covered by the registration dossiers submitted by the Consortium is achieved solely by production process and raw materials. Therefore, the Consortium is strictly limiting its registration to the types of synthetic zeolites listed here. These substances are to be registered in subgroups as listed below according to a decision made by ECHA, with possible read-across between these individual registrations.

1. Zeolite, cuboidal, crystalline, synthetic, non fibrous (EC 930- 915-9)
1.a. Zeolite, cuboidal, crystalline, synthetic, non fibrous, thermally produced (EC 931-125-7)
2. Zeolite, silica rich, crystalline, synthetic, non fibrous (EC 930-985-0)
2.a. Zeolite, silica rich, without aluminium, crystalline, synthetic, non fibrous (EC 930- 986-6)
3. Zeolite, phosphorous containing, crystalline, synthetic, non fibrous (EC 930- 989-2)
3.a. Zeolite, aluminium and iron and phosphor based, crystalline, synthetic, non fibrous (EC 930- 990-8)
4. Zeolite, silica and titanium based, crystalline, synthetic, non fibrous (EC 930-991-3)
4.b. Zeolite, synthetic, crystalline, non fibrous, silica and titanium based (EC 930-993-4)
4.c. Zeolite, silica and sodium and titanium based, crystalline, synthetic, non fibrous (EC 947-741-4)
7. Zeolite, phosphorous and titanium containing, crystalline, synthetic, non fibrous (EC 943.514.9)

3.4. Emissions

3.4.1. Wastes

Due to the production processes employed for the zeolite production only very small amounts of solid wastes are generated. Hazardous waste generation is considered not to be relevant for the production and its related processes. Recycling of process wastes are carried out where practicable. Recycling of raw materials, water and energy are an integrated part of the zeolite production process and are carried out to reduce not only environmental impact but also production costs.

3.4.2. Waste water

The zeolites produced need to be washed to remove soluble salts and used reactants. The waste water from this process is normally recycled or discharged to natural water courses (rivers, sea) after passing through waste water treatment plants.

3.4.3. Emission to water

In the production of zeolite adsorbents, the most important techniques for increasing or decreasing the apparent pore diameters are those involving ion exchange. Zeolite A pore diameters are modified by the exchange of sodium ions with calcium or potassium ions.

Catalytic zeolite Y needs also to be modified by ion exchange. Therefore, the emission to water during the production process of synthetic zeolite A or Y are besides solids, pH, temperature and salts from the ion exchange process. In most cases mother liquors are recycled due to economic reasons. The use of template compounds in the production of speciality zeolites presents greater problems. The organic compounds are difficult to destroy by oxidation in the mother liquid. Therefore, a two-step programme has been considered. The first step is to minimize the amount of the compounds in the synthesis and special waste water treatment is required for the second step.

3.4.4. Emission to air

Dust emission mainly occurs during the drying and activation process, but also during the handling of the powders including natural binders. Emission volumes and the amount of particulates released to the environment are dependent on the drying and activation technology used. Direct drying/activation processes fired with natural gas additionally emit CO2, CO, NOx and in case of other combustibles (oil or coal) also SO2.

4. MAIN APPLICATIONS AND USES OF SYNTHETIC ZEOLITES

Zeolites have three main properties which are the basis for its many applications:

Pore structure and chemical composition: due to its homogeneous pores with well defined sizes, zeolites can be very effectively used as so called molecular sieves (e.g. by removing CO2 from air or purification of O2). The unique pore size also makes it extremely suitable for all kind of chemical reactions.

Ion exchange: the ions in the pores of zeolites can be exchanged with other ions. This property is amongst others used in applications as water softening (in detergents or in filters of coffee machines) or water treatment (for instance binding of ammonium in fishponds or heavy metals in water purification).

Adsorption: fully dried zeolites (activated zeolites) have the ability to quickly adsorb e.g. water. They are therefore used in a range of drying applications, both static (e.g. in double glazing) or dynamic (as in industrial gas drying processes).

- **Air applications**: Mobile emission catalysts contribute to cleaner air. Among other applications, specialty zeolites are used as key raw materials in diesel automotive emissions catalysts. Increasingly stringent automotive emissions regulations are leading to an ever rising demand for advanced exhaust-gas treatment catalysts. Specialty zeolites contribute to meeting these regulations and thus contribute to cleaner air.

- **Water applications**: Due to the ion exchange properties of Zeolites, their applications in water treatment are numerous. The best known example of the Zeolites use is water softening, mainly in detergents and soaps. The strong ion exchange properties even allow Zeolites to remove radioactive ions from contaminated water (a recent example is Fukushima, Japan) or nuclear waste. Zeolites can also be used for water filtration, heavy metal (such as arsenic) removal or ammonia removal from fish pond.

- **Detergent applications**: Detergent powders comprise a water softening agent (so called builder) to ensure optimum performance of its other ingredients. Due to their excellent ion exchange properties in combination with its favorable environmental and consumer safety profile, zeolites are nowadays the builder of choice in laundry detergent powders. Additionally due to their large external surface area, zeolites have the ability to absorb larger quantities of liquids (such as surfactants). This not only results in improved free-flow properties of the final detergent powders, but also enables uses of cheaper and more environmentally friendly production processes as dry granulation to produce the final detergent powder.

- **Window isolation applications**: The function of the zeolite in double or multiple glassed windows is to capture moisture through adsorption to keep the space between the glasses dry. The use of zeolites as desiccants in numerous fields is widespread. The application in windows meets its analogues for instance in drug container caps (see chapter health), air brakes of trucks or the abundant small bags and boxes in food packages or technical equipment, containing zeolite beads as desiccants.

- **Health applications**: Non fibrous synthetic zeolites have no known toxic, carcinogenic, mutagenic, teratogenic or hormone-like effects. This makes them a safe and sustainable material for numerous applications. Most of these applications have an indirect beneficial effect on human and animal health through their positive environmental effects. For instance catalysts reduce air pollution and zeolites can be used to remove contaminants from waste water.
  A more direct impact on our health have zeolites as desiccants in drug container caps to keep the drugs dry or as a component of dental cements. As the main acting principle in health related treatments, zeolites are used as feed additive to reduce the risk of milk fever in cattle. In humans, zeolites can be used for heavy metal detoxification, including radioactive isotopes, or as an aid to stop bleeding. Due to the strictly physical mode of action, zeolites are not considered as active pharmaceutical ingredients (API) in these applications.
  The medical potential of synthetic zeolites has not yet been exploited to a significant extent, though in the life science literature articles have been published where zeolites have been used as API carriers.

- **Chemical industry**: Synthetic zeolites have a well-defined pore structure and adjustable hydrophobicity making them highly suitable for a large variety of separation and purification processes. Therefore, zeolites are widely used as adsorbents in the chemical industry.
  Synthetic zeolites have the potential of specifically separating molecules which makes them powerful adsorbents. In the chemical industry synthetic zeolites adsorbents are used for instance to remove carbon dioxide from air, sulfur dioxide or water from natural gas streams. An example of a liquid phase process would be separation of xylene isomers.

- **Industrial Catalysis**: Synthetic zeolites have a well-defined pore structure and adjustable acidity making them highly suitable for a large variety of chemical reactions. Therefore, zeolites are widely used as catalysts.
  One important application of synthetic zeolites in the petrochemical industry is as catalysts, e.g. in fluid catalytic cracking (FCC) and hydrocracking. Zeolites confine molecules in small spaces, which causes changes in their structure and reactivity. The hydrogen forms of zeolites - which are synthesized by ion-exchange - are powerful solid-state acids, and can facilitate acid-catalyzed reactions, such as isomerisation, alkylation, and cracking.

- **Personal care applications**: In cosmetics and personal care products, synthetic zeolites are used in a wide variety of product types. In facial masks zeolites control the rheology and tactile qualities of facial makeup and masks. In powders zeolites have an anti-caking and deodorizing function. When hydrated, zeolites produce a warming effect that promotes deep cleansing in facial and body scrubs. Zeolites also deodorize other odorous ingredients, e.g. in lotions, creams and pastes. Once activated with water, they produce smoothing, soothing and warming effects.

- **Other applications**: Next to the previously mentioned applications there are many other areas zeolites are being used in today. Although the below list will not be complete, it will demonstrate the wide range of applications where zeolites play a role.
  - It is used in combination with zinc-salts as stabilizer in PVC (to replace the much less environmentally friendly lead based systems).
  - It finds application as opacifier and titanium dioxide extender in paints, coatings and paper.
  - In agricultural applications it is not only used as flow aid to keep fertilizer free flowing, but it also finds applications as foliant (treatment on leaves to protect them from drying).
  - In soil improvement, zeolites bind nutrients and are lowly releasing them as needed by the soil and plants thus preventing nutrient loss by leaching.
  - In the newest types of dishwashers, especially the most energy efficient ones, it is used to assist with drying.
  - In construction applications it can be found as extender to cement.
  - In animal feed it is used as an additive to reduce smell of manure.
  - It can be used in cat litter to absorb odour.
  - In biotechnology, zeolites have been experimentally used as an immobilization matrix for bacteria.

5. REGULATORY STATUS OF SYNTHETIC ZEOLITES

5.1. Product registration

Zeolites are Existing Chemical Substances according to EU regulations. The joint submissions (i.e., registration dossiers) prepared by the Consortium cover exclusively the following substances under the general CAS No. 1318-02-1:

Registration in EU (REACH) – Synthetic Zeolite groups	Formula	EC No.
1. Zeolite, cuboidal, crystalline, synthetic, non fibrous	M*2/nO Al2O3 ySiO2 • wH2O	930-915-9
1.a. Zeolite, cuboidal, crystalline, synthetic, non fibrous, thermally produced	M*2/nO Al2O3 ySiO2 • wH2O	931-125-7
2. Zeolite, silica rich, crystalline, synthetic, non fibrous	M*2/nO Al2O3 ySiO2 • wH2O	930-985-0
2.a. Zeolite, silica rich, without aluminium, crystalline, synthetic, non fibrous	M*2/nO [SiO4/2]y [AlO4/2] • wH2O	930-986-6
3. Zeolite, phosphorous containing, crystalline, synthetic, non fibrous	M*2x/n[SiO2]x [AlO2]y [PO2]z • wH2O	930-989-2
4. Zeolite, silica and titanium based, crystalline, synthetic, non fibrous	[SiO4/2]x [TiO4/2]y • wH2O	930-991-3
4.b. Zeolite, synthetic, crystalline, non fibrous, silica and titanium based	xTiO2 ySiO2	930-993-4
4.c. Zeolite, silica and sodium and titanium based, crystalline, synthetic, non fibrous	(0.6-1.0) Na20 TiO2 (2.5-3.0) SiO2 • H2O	947-741-4
7. Zeolite, phosphorous and titanium containing, crystalline, synthetic, non fibrous	M*2/nO [TiO4/2]t [SiO4/2]x [AlO4/2]y [PO4/2]z • wH2O	943-514-9

* Cation M, predominantly sodium

In accordance with REACH Regulation (EC) No. 1907/2006 the compiled International Uniform Chemicals Information Data Base (IUCLID) data sets are all published or internal data covering the physico-chemical, eco-, and toxicological properties of the synthetic zeolites non fibrous.
Further to in-depth discussions with ECHA, the general CAS No. 1318-02-1 and EINECS No. 215-283-8 are not valid identifiers for synthetic zeolites but are merely used for information as related numbers and as a pre-registration identifier.

It is important to note that commercially produced ***synthetic zeolites are not nanomaterials***. They do not fulfill the definition given in “Commission Recommendation 2011/696/EU”. The zeolite crystals are larger than 100 nm. Using modified synthesis procedures, it is possible to manufacture zeolite crystals smaller than 100 nm. These zeolite crystals are stable in diluted suspensions only and are a niche product, not covered by the above stated REACH registrations.

Synthetic zeolites are also registered or pre-registered in REACH-like legislations outside of EU. It is noted that registration in these countries may be done in a different manner than the groups registered in Europe.

Global registration - REACH-like legislations	
Korea, REACH	Act on the Registration and Evaluation of Chemicals (ARECs)
Turkey, KKDIK	Turkey Registration, Evaluation, Authorisation and Restriction of Chemicals
UK, REACH	UK Registration, Evaluation, Authorisation and Restriction of Chemicals

Synthetic zeolites are also listed in other national inventories:

Global Chemical Inventories	
Australia, AICS	Australian Inventory of Chemical Substances
Canada, N/DSL	Non/ Domestic Substance List
China, IECSC	Inventory of Existing Chemical Substances Produced or Imported in China
Japan, ENCS	Japanese Inventory
Japan, ISHL	Japan's Industrial Safety and Health Law
Korea, KECI (ECL)	Korean Existing Chemicals Inventory
Korea, ISHL	Korea's Industrial Safety and Health Law
New Zealand, NZIoC	New Zealand Inventory of Chemicals
Philippines, PICCS	Philippine Inventory of Chemicals and Chemical Substances
Russia, RPOHV	Russian Register of Potentially Hazardous Chemical and Biological Substances
Switzerland (Produktregister Chemikalien)	Not applicable
Taiwan, CSNN	Chemical Substance Nomination and Notification
Thailand, DIW	Department of Industrial Works
USA, TSCA	The Toxic Substances Control Act (Zeolites are considered to be mixtures of the substances used to manufacture them. The individual reactant materials used to produce zeolites are listed separately on the Inventory.)

5.2. Classification according to EU Regulations

As a consequence of the REACH dossier preparation, all available data on synthetic zeolites have been thoroughly reviewed by the respective Lead Registrants. Based on this evaluation the members of the

European Zeolites Producer Association have concluded that typical zeolites covered by the Synthetic Zeolites Consortium can be classified as harmless and non-hazardous for all end-points. Yet some specific grades are classified but do not come into contact with consumers.

Since classic synthetic zeolites are not classified as hazardous or assessed to be PBT or vPvB, no exposure assessment is required for this substance. Moreover, there is no obligation to communicate along the supply chain about uses and exposures according to the REACH-Regulation and to the Regulation 1272/2008/EC on classification, labelling and packaging of substances and mixtures (CLP).

5.3. Transport regulations

Since classic synthetic zeolites are not classified, they are not subjects to the UN dangerous goods transport recommendations. Synthetic zeolites are not classified in any of those regulations: land transport (ADR/RID/I), inland waterway transport (AND(R)), marine transport (IMDG) and air transport (ICAO/IATA).

However, it is recommended to consult section 14 of the relevant SDS.

6. HANDLING, STORAGE & GUIDANCE ON SAFE USE

6.1. General information and advice

- **Handling:**
    - Information for safe handling: Prevent formation of dust. Keep receptacles tightly sealed. Provide suction extractors if dust is formed.
    - Any unavoidable deposit of dust must be regularly removed. Prevent static electric sparks.
    - Information about fire - and explosion protection: Protect against electrostatic charges. Earth container to avoid electric sparks, especially in contact with flammable substances.

- **Storage:**
    - Requirements to be met by storerooms and receptacles: No special requirements.
    - Information about storage in one common storage facility: Store away from foodstuffs.

- Further information about storage conditions: Keep container tightly sealed. Store in dry conditions. This product is hygroscopic.
- Storage class: 13

6.2. First-aid measures

- General information: Take note of the following instructions.
- After inhalation: Supply fresh air; consult doctor in case of complaints.
- After skin contact: Generally the product does not irritate the skin.Wash with water.
- After eye contact: Rinse opened eye for several minutes under running water. If symptoms persist, consult a doctor.
- After swallowing: If symptoms persist consult doctor.

6.3. Accidental release measures

- Person-related safety precautions: Wear protective clothing.
- Measures for environmental protection: No special measures required.
- Measures for cleaning/collecting: Sweep the spill area; avoid raising dust.
- Additional information: No dangerous substances are released.

6.4. Fire precautions

- Suitable extinguishing agents: Use fire extinguishing methods suitable to surrounding conditions.
- For safety reasons unsuitable extinguishing agents: Water with full jet.
- Protective equipment: Wear protective equipment.
- Additional information: Dispose of fire debris and contaminated fire fighting water in accordance with official regulations. Collect contaminated fire fighting water separately. It must not enter the sewage system.

6.5. Exposure controls & personal protection

- Additional information about design of technical facilities: No further data
- Control parameters: Occupational Exposure limit values (OEL)

Country/Authority	Value / Form of exposure: **inhalable inert dust** OEL, 8 h [mg/m³]	Value / Form of exposure: **respirable inert dust** OEL, 8 h [mg/m³]	**OEL** name (if specific)	Adopted by/Law denomination
Austria	10	5	MAK (Maximale ArbeitsplatzKonzentration)	Verordnungen BGBl. II 382/2020
Belgium	10	3	-	Ministère de l'Emploi et du Travail
Czech Republic			Přípustný expoziční limit (PEL) (=Permissible exposure limit)	Governmental Directive
Denmark	10	5	TLV (Threshold Limit Value)	Direktoratet fot Arbeidstilsynet
France	10	5	VME (Valeur limite de Moyenne d'Exposition)	Ministère du Travail
Germany	10	0,5	AGW (Arbeitsplatzgrenzwert)	Bundesministerium für Arbeit und Soziales (BMAS)
Italy	10	3	-	Decreto Legislativo 1 giugno 2020 n. 44
Luxemburg	10	6	MAK (Maximale ArbeitsplatzKonzentration)	Bundesministerium für Arbeit
Netherlands	10	5	TGG (Totstandkoming grenswaarden)	Ministerie van Sociale Zaken en Werkgelegenheid
Norway	10	5	Administrative Normer (8hTWA) for Forurensing I ArbeidsmiljØet	Direktoratet for Arbeidstilsynet
Portugal	10	5	VLE (Valores Limite de Exposição)	Instituto Portuges da Qualidade, Hygiene & Safety at Workplace
Spain	10	3	VL (Valores Limites)	Instrucciones de Técnicas Complementarias (ITC)
Sweden	5	2,5	Yrkeshygieniska Gränsvärden	National Board of Occupational Safety and Health
Slovenia	10 (20*)	1,25 (2,5)	MV (zavezujoča mejna vrednost = occupational exposure limits occupational exposure limit) KTV (kratkotrajna vrednost = Short-term exposure Limit Value)	Ministry of Labour, Family, Social Affairs and Equal Opportunities
UK	10	4	WEL (Workplace Exposure Limits)	Health & Safety Executive
US OSHA PEL	15	5	TWA (time-weighted average)	PELs from OSHA in 29 CFR 1910.1000

https://ima-europe.eu/wp-content/uploads/2022/12/OEL-FULL-TABLE-January-2022-Europe.pdf

- Personal protective equipment:
    - General protective and hygienic measures: The usual precautionary measures are to be adhered to when handling chemicals.
    - Respiratory protection: dust masks or respirators, if the WEL value is exceeded. Filter P2

- Protection of hands: protective gloves. Wear gloves for protection against mechanical hazards according to EN 388. Use gloves of stable material (e.g. Nitrile) - if necessary tricoted to improve the wearability. Preventive skin protection by use of skin-protecting agents is recommended. After use of gloves apply skin-cleaning agents and skin cosmetics.
- Material of gloves EN 388: Minimum requirements for efficiency level 1 for all groups. The selection of the suitable gloves does not only depend on the material, but also on furthermarks of quality and varies from manufacturer to manufacturer. Butyl rubber, BRNitrile rubber, NBR.
- Recommended thickness of the material: ≥ 0.11 mm.
- Penetration time of glove material EN 420: Minimum requirements for efficiency level 1 for all groups. For the mixture of chemicals mentioned below the penetration time has to be at least 480 minutes (Permeation according to EN 374 Part 3: Level 6).·For the permanent contact gloves made of the following materials are suitable: Butyl rubber, BRNitrilerubber, NBR
- Eye protection: safety glasses.
- Body protection: Protective work clothing.

7. WASTE DISPOSAL & END OF LIFE

- Recommendation: Disposal must be made according to official regulations.
- Waste disposal key: The disposal of the product has to be carried out in accordance with the legal requirements. EWC waste codes are strictly industry-oriented, therefore waste classification has to be done by the waste producer.
- Uncleaned packaging: Recommendation: Disposal must be made according to official regulations.
- End of life could not be exact determined, because it depends by the application, where zeolites are using for. Zeolites are stable under recommended storage and handling conditions. The product is hygroscopic and should be keep in dry place (protect from moisture and water). Under normal use conditions, no hazardous decomposition products expected and there is no shelf life defined if zeolites are using in detergent industry. On the other hand, when using zeolites as the adsorbents or ion-exchanging materials, it is recommendation to analyze the capacity for the exact values and function before using (approximately) after one year from its production. Due to the effect of moisture on the properties and related storage, the zeolite manufacturer cannot guarantee an exact shelf life.

8. HAZARDS TO THE ENVIRONMENT AND HUMAN HEALTH

Under the OECD High Production Volume Chemicals Programme, a comprehensive hazard and initial risk assessment was performed for synthetic zeolites. Some important aspects of the OECD assessment are described under this section. For further detail it is referred to the published document on the website of the United Nations Environmental Programme (UNEP Chemicals 2006).

8.1. Ecological issues

8.1.1. pH value/water solubility

Untreated synthetic zeolites are generally alkaline in aqueous solutions (pH value > 10) and therefore neutralization should be carried out before discharging to water/effluent systems. However, no adverse effects on aquatic biosystems are to be expected. There are some exceptions e.g., Silica rich zeolites which are much more acidic (pH 3) due to the high silica content.

The water solubility for zeolite is pH dependent, at neutral conditions (pH 7) the ionic components slightly dissolve in water without affecting the stable zeolite structure itself. The water solubility for synthetic zeolites is stated to be < 0.1 g/L.

8.1.2. Partition coefficient/bioaccumulation potential

The calculation of partition coefficient (normally determined with n-octanol/water) is not suitable for inorganic substances which are not soluble in organic solvents and can therefore not be adequately assessed for synthetic zeolites.

Due to its inherent chemico-physical properties, the uptake of synthetic zeolites isalow and no potential risk for bioaccumulation is to be expected.

8.1.3. Biodegradability, chemical or biochemical oxygen demand (COD, BOD)

As Zeolite is an inorganic substance, no risk for adsorption potential neither for water, sediment nor soil is expected. Phototransformation, due to the absence of UV-Vis adsorption, is not a relevant process for synthetic zeolites.

The substances have no COD or BOD impact on effluents. As a constituent of the wastewater stream, synthetic zeolites are being removed by 90% in sewage treatment plants as the dominant fate process and are efficiently transferred from the wastewater stream to the sludge.

8.1.4. Behaviour in natural aquatic systems

The relative contributions of anthropogenic zeolites to the existing natural pools of aluminum and silicates in soils and sediments is very small. Therefore, the contribution is not relevant either in terms of added amounts or in terms of toxicity as the comparison of the transformation/dissolution tests of artificial soil/sediments and synthetic zeolite demonstrates, with concentrations below 10 µg/L (< LOQ) for the ionic constituents. Thus, even though bioaccumulation/- concentration cannot be excluded there is no associated potential risk.

8.2. ECOTOXICOLOGICAL DATA

The acute and long-term toxicity testing on fish, invertebrates, plants, micro- and macro-organisms in their respective compartments (aquatic, sediment, soil) on synthetic zeolites (non fibrous) do not meet the criteria for classification as hazardous (according to Directives 67/548/EEC and 1272/2008/ EC) nor is it considered to be a PBT/vPvB. No PNEC is derived.
However, the low toxicity observed especially in the aquatic compartment can be attributed towards zeolites complexing and ion-exchange activity, leading to nutrient-poor culture-media of ecotoxicological standard tests, rather than an effect of its intrinsic properties.

Fish	
Freshwater fish	LC0 (96h) >= 680 mg/l
Pimephales promelas	NOEC (30d) >= 86.7 mg/L
Aquatic invertebrates	
Daphnia magna	EC50 (24h) = 2,808 mg/L
Daphnia magna	NOEC (21d) = 130.8 mg/L
Algae and aquatic plants	
Desmodesmus subspicatus (green algae)	EC10 (72h) > 100 mg/L
Micro-organisms	
Pseudomonas putida	EC50 (16h) = 0.095 g/L
Terrestrial plants	
Lolium perenne & Lolium italicum	NOEC (12mo) >= 4 g/kg dw
Macro-organisms (sediment)	
Caenorhabditis elegans	NOEC repro (96h) >= 1563 mg/kg dw
Caenorhabditis elegans	NOEC growth (96h) >= 12500 mg/kg dw
Macro-organisms (soil)	
Eisenia andrei (Annelida)	NOEC repro (56d) >= 1000 mg/kg dw
Eisenia andrei (Annelida)	LC50 (28d) > 1000 mg/kg dw

8.3. Toxicological data

The toxicological data retrieved through either published or internal data do not meet the criteria for classification as hazardous (according to Directives 67/548/EEC and 1272/2008/EC) for synthetic zeolites (non fibrous). No DNEL is derived.

8.3.1. Acute toxicity

In reliable oral toxicity tests (acc. OECD 401) in rats neither mortality nor any signs of clinical poisoning were observed with a respective LD50 > 5110 mg/kg body weight (bw).

A study on acute toxicity after inhalation exposure with crystalline aluminosilicate (zeolite) no signs of toxicity were observed, leading to a LC0 >= 18.3 mg/L air.

For the dermal administration route, an acute toxicity study on rabbits showed no mortality nor any signs of clinical poisoning up to > 2000 mg/kg bw (LD50).

8.3.2. Skin Irritation

Reliable studies in both in-vitro and in-vivo assessed synthetic zeolites as non-irritant. In the in-vivo study only very slight erythema was observed, only at the day of substance application. The slight irritation can be attributed to the more alkaline test solution of zeolites dissolved in water.

8.3.3. Eye Irritation

In in vivo eye irritations studies, no adverse effect is observed. However, following administration of 60 mg (0.1 ml) of a type X zeolite, based on 24-hour findings and by FHSA definition, 4 eyes were positive for corneal injury, iritis and conjunctival irritation. Therefore, the substance was an FHSA irritant. The irritation was attributed to high molar concentration. All eyes were healed after 72 hours. After instillation of 10 mg, no eyes developed corneal opacity or iritis. According to table 3.3.2 of the GHS (2019) this does not fulfill the criteria for classification.
In conclusion, all reliable studies did not fulfill the criteria for classification of synthetic zeolites.

8.3.4. Sensitisation

A skin sensitisation study in guinea pigs (Buehler test) concluded that no reaction resembling hypersensitivity was observed. Therefore, it is presumed that synthetic zeolites have no skin sensitisation potential.

8.3.5. Repeated dose toxicity

Multiple number of repeated dose toxicity studies were performed on rats, ranging from 80 to 200-day testing period. Based on the lowest most representative No Observed Adverse Effect Levels (NOAELs) of zeolites, a low toxicity is determined with a value of 292 mg/kg bw/d (NOAEL 12w).

For repeated dose toxicity via inhalation, there are reliable studies available in a type A zeolite. In both studies, in hamsters and rats, a NOAEL of equal or greater than 20 mg/m^3 was assessed. There was no evidence of fibrotic disease or silicosis changes of or carcinogenic effects to the internal organs after inhalation of the type A zeolite. It was also examined whether that substance reached the lower respiratory system of the experimental animals. According to this study, the presence of silicon in the lungs of rats after inhalation could be considered as evident. But macroscopically no changes in the internal organs nor deviations from the controls were observed.

8.3.6. Mutagenicity

Multiple tests were performed on genotoxicity with synthetic zeolites. In all the available genotoxicity studies, neither gene mutations nor chromosomal aberrations or dominant lethal mutations were induced. Only one ion exchanged zeolite with silver showed positive cytotoxic effects (OECD 473). But this is disproved by an in vivo study in cytotoxicity (OECD 474) with the same test item which did not show any mutagenic effects. Therefore, synthetic zeolites should not be considered as genotoxic.

8.3.7. Carcinogenicity

A combined chronic toxicity and carcinogenicity study in rats via oral route with synthetic zeolite type A showed no dose-dependent accumulation of tumorous changes. Therefore, synthetic zeolite was in the dosage of 10 – 1000 ppm for rats under the experimental conditions neither carcinogenic nor did it induce hyperplastic reactions, stated with a NOAEL (104w) >= 1000 ppm.

Similar findings are seen in a rat chronic inhalation study with only one dose and one control group. No tumorous changes were found pathologically or histologically in the respiratory tract or in other associated locations observed. The quality of those tumors observed, and their temporal occurrence gave no indications of a carcinogenic activity of the synthetic zeolite test item, leading to a NOAEL (22mo) >= 20 mg/m^3.

There are additional reliable studies via the intraperitoneal route. One study tested in the peritoneum of 586 BALBlC male mice after a single intraperitoneal or intraabdominal wall injection. After single application the test substance did not show carcinogenicity within 23 months. In another study which allowed rats to live out their lives until they showed signs of distress at which point they were sacrificed, the synthetic zeolite tests item was not carcinogenic in the rat and did not induce mesotheliomas.

8.3.8. Reproduction/developmental toxicity

There are two reliable studies in developmental toxicity with type A zeolite available. No maternal or developmental toxicity was seen with oral doses up to 1600 mg/kg bw/d administered in both studies (NOAEL >= 1600 mg/kg bw/d). There are also four oral supporting studies with the read-across substance sodium silicoaluminate in four different species. In none of these maternal or developmental toxicity was seen with doses up to 1600 mg/kg bw/d administered in all studies, too. Developmental toxicity was only assessed via the oral route.

Although there is no study in fertility available, it was assessed that an extended one-generation reproductive and toxicity study was not required for synthetic zeolites since all relevant endpoints in this study design were already covered in the database on the synthetic zeolites constituents $Si(OH)_4$ and Al^{3+}.

9. REGISTRATION FOR SPECIAL APPLICATIONS

Synthetic zeolites have been registered for REACH with a wide variety of industrial, professional and consumer uses. A comprehensive list of identified uses can be found on the ECHA webpage.

The list below indicates specific application areas for synthetic zeolites. It is not exhaustive and is based on the current knowledge of the members. There may be additional specific national/regional requirements which should also be considered. In any case, it is recommended to any downstream user of synthetic zeolites to contact its suppliers for advice.

9.1. Use in plastics intended for foods/beverage applications

Synthetic zeolites are authorized under the term of silicic acid which includes corresponding salts of aluminium, sodium and potassium. They are as such in compliance with the PIM, Commission Regulation (EU) No 10/2011 on plastic materials and articles intended to come into contact with food.

Annex I (Substances)

PM/Ref. No	FCM Substance No	Substance name	SML [mg/kg]	Restrictions and specifications
85680	417	Silicic acid	-	-

10. SUMMARY

EUZEPA member companies are committed to provide users of synthetic zeolites with technical data and information as required in order to ensure the safe handling, application and disposal of this environmentally acceptable group of industrial materials.

Disclaimer

The information contained in this document is intended for guidance only and whilst the information is provided in utmost good faith and has been based on the best information currently available, it is to be relied upon at the user's own risk. No representations or warranties are made with regards to its completeness or accuracy and no liability will be accepted by EUZEPA or any of its members for damages of any nature whatsoever resulting from the use of this information.

About EUZEPA
EUZEPA is a sector group of the European Chemical Industry Council (Cefic) and represents the leading synthetic zeolites producers in Europe. EUZEPA is a non-profit organisation dedicated to promoting the safe use and benefits of synthetic zeolites. More info available on www.euzepa.eu

LITERATURE

ECHA, Dissemination webpage, BRIEF profile : https://echa.europa.eu/brief-profile/-/briefprofile/100.110.564

EUZEPA, European Zeolites Producers Association, website, www.euzepa.eu

GUIDANCE ON SAFE USE related to Synthetic non-fibrous and non-classified Zeolites grades, *EUZEPA and Synthetic Zeolites Consortium, www.zeolites.be* (2010)

HERA, Human & Environmental Risk Assessment on ingredients of European household cleaning products. Zeolite A (represented by CAS Number 1344-00-9 (Sodium aluminium silicate) and by CAS Number 1318-02-1 (Zeolites). *A.I.S.E. & Cefic* (2004)

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