



Human & Environmental Risk Assessment
on ingredients of household cleaning products

Zeolites A, P and X

CAS No. 1344-00-9 (Sodium Aluminium Silicate)

CAS No.1318-02-1 (Zeolites)

Supplement to the HERA report on the
Environmental Risk Assessment of Zeolite A

Edition 1.0
September 2005

All rights reserved. No part of this publication may be used, reproduced, copied, stored or transmitted in any form or by any means, electronic, mechanical, photocopying, recording or otherwise without the prior written permission of the HERA Substance Team or the involved company.

The content of this document has been prepared and reviewed by experts on behalf of HERA with all possible care and from the available scientific information. It is provided for information only. Much of the original underlying data which has helped to develop the risk assessment is in the ownership of individual companies.

HERA cannot accept any responsibility or liability and does not provide a warranty for any use or interpretation of the material contained in this publication.

1 Executive Summary

The synthetic zeolites A, P and X (sodium aluminium silicate) are used as builders in detergent powders and tablets for water softening in the washing process. In the first phase of the HERA project, an environmental risk assessment was carried out for Zeolite A, which represents, by volume, the most heavily used zeolite type. Based on the calculated PEC/PNEC ratios which are below 1 ($RCR < 1$), no cause of concern was indicated for any of the environmental compartments, i.e. water, sediment, soil and sewage treatment plants (STP). In order to extend the environmental risk assessment to all zeolite types used in detergents, additional studies into the aquatic and terrestrial toxicity of zeolites P and X were commissioned. The data obtained showed that the ecotoxicological profile of all zeolites used in detergent applications is comparable. Based on the enlarged data set a revised environmental risk assessment for the total zeolites used in detergents was carried out. Again, RCR values <1 were obtained for all environmental compartments. The favourable outcome of this environmental risk assessment and the knowledge about the long-term fate of zeolites, which ultimately turn into natural soil constituents (e.g. clays), provide a sound basis for the conclusion that the use of zeolites in detergent products does not pose a risk to the environment.

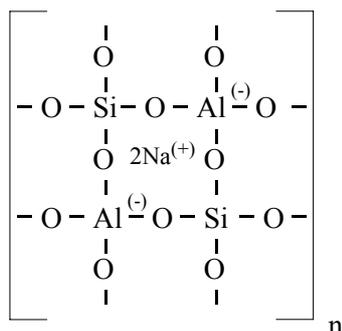
2 Contents

1	<i>Executive Summary</i>	2
2	<i>Contents</i>	2
3	<i>Substance Characterisation</i>	3
3.1	CAS No and Grouping Information	3
3.2	Chemical Structure and Composition	4
3.3	Manufacturing Route and Production/Volume Statistics.....	5
3.4	Use Applications	6
4	<i>Environmental Assessment</i>	6
4.1	Environmental exposure assessment.....	6
4.1.1	Environmental Fate and Removal	6
4.1.2	PEC Calculations.....	6
4.2	Environmental effects assessment.....	7
4.2.1	Toxicity data.....	7
4.2.2	Evaluation of toxicity data for PNEC derivation	10
4.2.3	Derivation of PNEC for detergent zeolites	11
4.3	Environmental Risk Characterisation.....	12
4.4	Conclusions	12
5	<i>References</i>	13
6	<i>Contributors</i>	14

3 Substance Characterisation

3.1 CAS No and Grouping Information

The zeolites used as builders in detergent formulations are synthetic sodium aluminium silicates with the general formula: $\text{Na}_x[(\text{AlO}_2)_x(\text{SiO}_2)_y] \cdot x \text{zH}_2\text{O}$.



Zeolites consist essentially of microporous 3-dimensional aluminosilicate networks with 4-coordinate Si and Al atoms linked by oxygen bridges. These networks are negatively charged and the pores contain cations which compensate this negative charge. The water molecules and cations are able to diffuse through the pore network; the cations can exchange with other cations in the surrounding electrolyte. While the chemical composition and the basic performance properties of the individual detergent zeolites (Zeolite A, Zeolite P, Zeolite X) are almost identical, the individual types have different crystalline structures resulting, for instance, in a firmer binding of calcium ions by Zeolite P and a higher magnesium binding capacity of Zeolite X compared to Zeolite A (Zeodet, 2000 /Ref 1*). Although the more recently developed zeolite types P and X may have improved performance properties, Zeolite A represents the most prominent type of zeolites used in detergents.

Zeolite A and its basic properties have been discussed in detail in the HERA report on Zeolite A (HERA, 2004). The following information supplements the characterisation of zeolite types used in detergents. All 3 zeolite types are very similar in composition (see formula in Table 1). However, their Si/Al ratio is slightly different: Zeolite A 0.7 – 1.2, zeolite P 1.1 - 2.5, zeolite X 0.7 – 1.1 (Breck, 1974 /Ref 2). Zeolites A and X have a very similar moisture content (20-25%); zeolite P can be manufactured with water content between 10 and 20% (Zeodet, 2003).

While data for zeolite A can be found under two different CAS numbers (CAS 1344-00-9; 1318-02-1), zeolites P and X are subsumed under CAS number 1318-02-1 covering all types of synthetic zeolites.

* The Ref number given in addition to the reference indicated normally is the reference number in the HERA report on Zeolite A (2004)

3.2 Chemical Structure and Composition

Table 1 summarises the relevant information about the chemical properties of detergent-based zeolites.

Table 1: Chemical properties of Zeolites used in detergents

Parameter	Protocol	Results / Remarks		
		Zeolite A (CAS 1344-00-9; 1318-02-1)	Zeolite P (CAS 1318-02-1)	Zeolite X (CAS 1318-02-1)
Macro-molecular description (Physical State/Particle size)		Solid, three-dimensional crystalline structure Particle size: 3-5 um (Zeodet, 2003)	Solid, three-dimensional crystalline structure Particle size: 2-3 um (Zeodet, 2003)	Solid, three-dimensional crystalline structure Particle size: 3-5 um (Zeodet, 2003)
Molecular Weight	calculated	284 [g/mol] $\text{Na}_2\text{O} \times \text{Al}_2\text{O}_3 \times 2 \text{SiO}_2$ (Zeolite A 4 atro) (Breck, 1974 /Ref 2)	284 - 464 [g/mol] $\text{Na}_2\text{O} \times \text{Al}_2\text{O}_3 \times 2.0-5.0 \text{SiO}_2$ (Breck, 1974 /Ref 2)	314 [g/mol] $\text{Na}_2\text{O} \times \text{Al}_2\text{O}_3 \times 2.5 \text{SiO}_2$ (Breck, 1974 /Ref 2)
	calculated	2190 [g/mol] $\text{Na}_{12}[(\text{AlO}_2)_{12}(\text{SiO}_2)_{12}] \times 27 \text{H}_2\text{O}$ (Breck, 1974 /Ref 2)	-	-
Melting Point	other *	1700 [°C] (Degussa 1991 /Ref 3)	No data	No data
Vapour Pressure		not volatile (Zeodet, 2003)	not volatile (Zeodet, 2003)	not volatile (Zeodet, 2003)
Octanol-water Partition Coefficient (Log Pow)		not applicable (inorganic, poorly soluble)	not applicable (inorganic, poorly soluble)	not applicable (inorganic, poorly soluble)
Water Solubility	other *	poorly soluble (< 10 [mg/l]) (Gode, 1983 /Ref 5)	poorly soluble **	poorly soluble **
	other *	about 1.4 [mg/l] (Ca-Zeolite A in river water) (Umweltbundesamt, 1979 /Ref 6)	-	-
	other *	0.25 - 7.2 [mg/l] (depending on water composition) (Henkel /Ref 7)	-	-
	other *	< 1000 [mg/l] (IUCLID /Ref 13)	-	-

Parameter	Protocol	Results / Remarks		
		Zeolite A (CAS 1344-00-9; 1318-02-1)	Zeolite P (CAS 1318-02-1)	Zeolite X (CAS 1318-02-1)
Sorption coefficients		not applicable	not applicable	not applicable
K _{oc}		not applicable	not applicable	not applicable
Density	other *	1.99 [g/ml] (Breck, 1974 /Ref 2)	2.01 [g/ml] (Breck, 1974 /Ref 2)	1.93 [g/ml] (Breck, 1974 /Ref 2)
Viscosity		not applicable	not applicable	not applicable
pH-Value	other *	10.4 at 50 [g /l] and 20 [°C] (IUCLID /Ref 13)	No data	No data
pK _a		not applicable	not applicable	not applicable
Oxidation		not applicable	not applicable	not applicable
Henry's constant		not applicable	not applicable	not applicable

* method not contained in the IUCLID glossary of standard methods

** no measured data available. However, close comparability to zeolite A is warranted

3.3 Manufacturing Route and Production/Volume Statistics

The annual consumption of all zeolites used in the European detergent market has been relatively constant for a number of years. The figures for the years 1993 - 2000 were in the range 620,000 - 650,000 tons (Zeodet, 2000 /Ref 1). A more recent survey of the use figure of zeolites of the P and X type by the major European detergent producers (2003) yielded a predicted tonnage of about 160,000 tons for the total European use of zeolites P&X in detergents.

As there is presently no more recent and more detailed information available about the production/ consumption figures of the individual zeolite types, the total consumption figure of 650,000 tons/year has been used for the risk assessment of detergent zeolites. This total tonnage has been relatively constant or may have rather decreased during the last years, thus, allowing for a conservative exposure assessment of the entire amount of detergent zeolites.

Synthetic Zeolites are manufactured from SiO₂- and Al₂O₃- containing substances, for instance silicic acid sodium salts, aluminium hydroxides, or aluminates, at temperatures greater than 50 °C and with alkali hydroxides (NaOH) as catalysts (Breck, 1974 /Ref 2). All detergent zeolites are manufactured under similar conditions, being crystallised at high pH from sodium silicate, sodium aluminate and caustic soda. As a result, they exhibit similar pH characteristics when slurried in water and they show essentially the same levels and types of impurity (Zeodet, 2003). They occur as fine white powders or pastes as well as granulates.

3.4 Use Applications

The zeolite types A, P and X are used in household detergents to decrease the water hardness by exchanging the Ca^{++} and/or Mg^{++} -ions for Na-ions. The major part of phosphate-free household detergents is based on the use of Zeolite A as builder. Synthetic zeolites are also used as catalysts or molecular sieves.

4 Environmental Assessment

4.1 Environmental exposure assessment

4.1.1 Environmental Fate and Removal

The major characteristics which are relevant for the environmental exposure assessment of detergent zeolites are common to the zeolites A, P and X. Their main entry to the environment is via water. Due to their water insolubility and their density they will mainly partition into the sludge phase. Based on their identical particle size (Table 1) it is assumed that the sedimentation behaviour of zeolites A and X is comparable. Although zeolite P differs somewhat in terms of the particle size, pertinent studies have shown that zeolites P and A are indistinguishable in sewage settling (Zeodet, 2003). As sedimentation is the main elimination mechanism of zeolites in sewage treatment plants (STP), it can be assumed that the elimination extent of zeolites A, P and X in these conditions is largely comparable. Consequently, the removal by 90% in STP used for the exposure assessment of zeolite A can be applied to all detergent zeolites.

In a long-term range, the stability of zeolites in water is also a determinant in the environmental exposure assessment. For zeolite A a half-life time of 60 days due to its hydrolytical decomposition (Allen et al., 1983 /Ref 9) was taken into account which is equivalent to an in-stream removal rate constant of 0.011 d^{-1} (HERA, 2004). Due to the fact that the local atomic connectivity is identical in all three zeolite types and because pore sizes are similar, hydrolytic stability is assumed to be similar (Zeodet, 2003). Therefore, the hydrolytical parameters used in the zeolite A exposure assessment will also be applicable to zeolites P and X.

In conclusion, the largely comparable fate-relevant substance characteristics of all detergent zeolite types justifies the adoption of the PEC calculations of the HERA report on zeolite A (HERA, 2004) for the total of zeolites used in detergents. In this previous environmental risk assessment, the total European tonnage of detergent zeolites (650.000 tons per annum) was conservatively attributed to zeolite A.

4.1.2 PEC Calculations

The following table 2 (taken from the HERA report on zeolite A) summarises the output of the exposure calculations based on the modified HERA Scenario as described previously (HERA, 2004).

Table 2: Predicted environmental concentrations of zeolites used in detergents

Zeolite distribution in local compartments	
Concentration in dry sewage sludge [mg/kg]	1,13E5
PEC Water [mg/l]	1,24
PEC Agricultural Soil (total) 30d [mg/kg]	142
PEC Sediment [mg/kg]	0,98
PEC STP [mg/l]	4,94
Zeolite distribution in regional compartments	
PEC Water [mg/l]	0,75
PEC Agricultural Soil 30d [mg/kg]	1,11
PEC Sediment [mg/kg]	0,45

4.2 Environmental effects assessment

4.2.1 Toxicity data

When the HERA report on zeolite A was prepared, no specific information was available about the ecological properties of zeolite P and X. However, this report already mentioned that the chemical and structural comparability of all detergent zeolite types suggests that the environmental behaviour of zeolites P and X be very similar to that of zeolite A. To extend the HERA risk assessment to all zeolite types used in detergents, this comparability should be substantiated by suitable bridging data.

The following tables summarise the ecotoxicological data now available for zeolites P and X. In the subsequent chapter (4.2.2) these specific data are discussed in comparison with the corresponding data of zeolite A which were used in the previous HERA risk assessment (HERA, 2004).

4.2.1.1 Aquatic toxicity of zeolite P and X

The experimental results on chronic toxicity testing towards daphnia and algae are shown in tables 3 and 4.

Table 3: Aquatic tests – Chronic toxicity to invertebrates

	Zeolite P	Zeolite X
Test species	Daphnia magna	Daphnia magna
Test protocol	OECD 202, part 2	OECD 211
Test duration	21 d	21 d
Endpoint	reproduction rate	reproduction rate
Test result	NOEC = 32 mg/l	NOEC = 32 mg/l
Reliability	2	1
Reference	Unilever (1992)	Zeodet 2005a
Remarks	Study was conducted with Ca ⁺⁺ -loaded zeolite P	Study was conducted with Ca ⁺⁺ -loaded zeolite X/A (80/20%). Test result refers to nominal loading of WAF

Table 4: Aquatic tests – Algal toxicity

	Zeolite P	Zeolite X
Test species	Desmodesmus subspicatus	Desmodesmus subspicatus
Test protocol	OECD 201	OECD 201
Test duration	72 h	72 h
Endpoint	cell multiplication	cell multiplication
Test result	E _r C ₅₀ > 100 mg/l NOEC = 100 mg/l	E _r C ₅₀ = 130 mg/l NOEC = 18 mg/l
Reliability	1	1
Reference	Zeodet 2005 b	Zeodet 2005 c
Remarks	Study was conducted with Ca ⁺⁺ -loaded zeolite P. Test result refers to nominal loading of WAF	Study was conducted with Ca ⁺⁺ -loaded zeolite X/A (80/20%). Test result refers to nominal loading of WAF

4.2.1.2 Terrestrial toxicity of zeolite P and X

The experimental results on the plant toxicity of the two zeolites are shown in tables 5 and 6.
Table 5: Terrestrial tests – Plant toxicity of zeolite P

		Zeolite P		
Test protocol	OECD 208			
Test concentrations	0.5 – 15 g/kg			
Test duration	28 d			
Endpoints	Growth (weight per plant), Emergence of plant seeds, phytotoxic effects			
Test species	Avena sativa	Raphanus sativus	Lepidium sativum	
Test results:				
• Growth	EC50 EC10	14 000 mg/kg n.d.*	11 000 mg/kg n.d.*	7 000 mg/kg 2 400
• Emergence	EC50	9 000	9 000	9000
• Phytotoxic effects	NOEC	5 000	5 000	5 000
Reliability	1			
Reference	ZEODET 2001a			
Remarks	Study was conducted with zeolite P, Na- form			

*The EC10 value was calculated for the most sensitive endpoint of the study only

Table 6: Terrestrial tests – Plant toxicity of zeolite X

		Zeolite X		
Test protocol	OECD 208			
Test concentrations	0.5 – 15 g/kg			
Test duration	28 d			
Endpoints	Growth (weight per plant), Emergence of plant seeds, phytotoxic effects			
Test species	Avena sativa	Raphanus sativus	Lepidium sativum	
Test results:				
• Growth	EC50 EC10	9 000 mg/kg n.d.*	6 000 mg/kg 2 400	7 000 mg/kg n.d.*
• Emergence	EC50	9 000	9 000	9000
• Phytotoxic effects	NOEC	5 000	5 000	5 000
Reliability	1			
Reference	ZEODET 2001b			
Remarks	Study was conducted with zeolite X, Na- form			

*The EC10 value was calculated for the most sensitive endpoint of the study only

4.2.2 Evaluation of toxicity data for PNEC derivation

It has been the main objective of this supplemental study on the environmental properties of zeolites P and X to find out if the conclusions of the HERA environmental risk assessment of zeolite A are also applicable to these zeolite types. If so, this would allow a general conclusion on the environmental safety of zeolites used in detergents to be drawn.

As fish toxicity was shown to be the least sensitive aquatic toxicity endpoint of zeolite A (HERA, 2004), and also for animal protection reasons, no fish toxicity tests on zeolites P and X were conducted. Instead, it was considered sufficient to assess the aquatic toxicity of these two zeolite types on the basis of their chronic toxicity towards daphnia and algae. In addition, their terrestrial toxicity was investigated because soil represents a major sink for zeolites due to the potential agricultural use of zeolite-containing sewage sludges. The toxicity of zeolites P and X to microorganisms in sewage treatment plants was not tested specifically considering the pertinent low toxicity of zeolite A (HERA, 2004) and the general view of a high degree of comparability in terms of the ecotoxicological potential of the 3 zeolite types.

4.2.2.1 Algal toxicity

The algal NOEC determined for Ca^{++} -loaded zeolite P was 100 mg/l while the corresponding value for zeolite X/A (80/20%) was 18 mg/l. The corresponding EC50 values were > 100 mg/l in both cases. Deliberately, the Ca^{++} -loaded zeolite types were used in the tests as previous investigations with zeolite A have shown (HERA, 2004) that the environmentally more relevant Ca-form should preferably be tested to avoid artificial inhibitory effects caused by nutrient depletion due to ion exchange. For testing zeolite X only a 80/20% mixture with zeolite A was available from supplier companies. However, this has not been considered a real problem as the pertaining data on zeolite A are known and any significantly increased toxicity of the zeolite X component would be easily recognisable.

The corresponding algal toxicity value of Ca^{++} -zeolite A reported in the HERA risk assessment is NOEC = 50 mg/l (no EC50 values available) while an EC50 = 18-34 mg/l was reported for the Na-form (HERA, 2004). Taking the measured algal NOECs of zeolite A and zeolite X/A (80/20%) into account and assuming additive toxicity of the two zeolite types, a NOEC = 15.5 mg/l can be calculated for the pure zeolite X. This confirms that the chronic algal toxicity of the zeolites is in the same order of magnitude although zeolite X appears to be slightly more toxic.

4.2.2.2 Chronic daphnia toxicity

Testing the long-term toxicity of zeolite P and zeolite X/A (80/20%) in the 21-day daphnia reproduction test revealed a NOEC = 32 mg/l for both of the chemical compounds. Again, Ca^{++} -loaded zeolites were used in the test, as these are the most environmentally relevant form of these chemicals, and are also suitable for a direct comparison with the pertinent test result on zeolite A. The HERA environmental risk assessment of zeolite A used the Daphnia NOEC = 37 mg/l as the most sensitive endpoint determining the PNEC (HERA, 2004). The comparison of the now available NOEC values shows that the zeolite types used in detergents exhibit a virtually identical chronic toxicity to invertebrates.

4.2.2.3 Terrestrial toxicity

Experimental data on the terrestrial toxicity of zeolites P and X are available from a previous study in which these compounds and zeolite A as well were tested in the OECD 208 plant growth test using the commercial Na-form (Zeodet 2001a, 2001b, 2001c/Ref 20). Growth of the seedlings of 3 different plant species was the most sensitive endpoint in all tests. In the case of zeolite P, *Lepidium sativum* proved to be the most sensitive species with an EC50 = 7000 mg/kg and an EC10 = 2400 mg/kg. *Raphanus sativus* was the most sensitive species in the test of zeolite X exhibiting an EC50 = 6000 mg/kg and an EC10 = 2400 mg/kg. These data can be compared with the previously reported results on zeolite A (HERA, 2004) with *Raphanus sativus* as the most sensitive species and an EC50 = 4000 mg/kg and EC10 = 900 mg/kg. Therefore it is evident that the zeolite A data and the PNEC derivation based upon it form the most conservative basis for the terrestrial risk assessment of zeolites used in detergents. The data basis for the terrestrial PNEC of zeolite A has been discussed in detail previously (HERA, 2004).

4.2.3 Derivation of PNEC for detergent zeolites

As already pointed out in the HERA report on zeolite A, it should be noted that all of the determined NOEC values for zeolites are in a concentration range which is already above the solubility limit. Therefore, it can be concluded that the effects measured above the NOEC may not be attributable to systemic toxic effects but rather due to physical effects of the undissolved material or due to nutrient depletion effects. Such effects will be of low relevance in practice considering the predicted environmental concentrations of the detergent zeolites.

Table 7 summarises the data base for PNEC derivation of detergent zeolites.

Table 7: PNEC derivation for detergent-based zeolites

	NOEC	Relevant zeolite type	Assessment factor	PNEC
Aquatic Organisms	15.5 mg/l	Zeolite X	10	1.55 mg/l
Terrestrial Organisms	60 000 mg/kg	Zeolite A	100	600 mg/kg
Microorganisms	330 mg/l	Zeolite A	10	33 mg/l
Sediment Organisms	PNEC derived from aquatic NOEC			1.1 mg/kg

According to the available and discussed data on zeolites A, P and X (4.2.2), the most sensitive aquatic toxicity endpoint is the algae NOEC = 15.5 mg/l calculated for zeolite X. While this data does not differ strongly from the daphnia NOEC forming the basis for the aquatic PNEC in the HERA risk assessment of zeolite A (HERA, 2004), a revision of the corresponding risk assessment calculation was appropriate for covering all detergent-relevant zeolite species. As NOEC data are available for fish, daphnia and algae, an assessment factor of 10 is to be applied for the PNEC derivation. Consequently, for the aquatic risk assessment of zeolites used in detergents a PNEC = 1.55 mg/l is being used.

The terrestrial PNEC representative for the detergent-relevant zeolites is based on the available data for zeolite A (see 4.2.2.3) by using an application factor of 100. The PNEC for micro-organisms in sewage treatment plants was derived from the EC10 of a test of zeolite A

with a specific bacterial population (HERA, 2004) using (conservatively) an application factor of 10.

4.3 Environmental Risk Characterisation

Based on the PEC calculations (Chapter 4.1.2) and on the revised overview of PNEC data (Chapter 4.2.3) risk characterisation ratios for the individual environmental compartments were calculated. The RCR values shown in the following table represent the summary of the environmental risk characterisation of zeolites used in detergents.

Table 8: Environmental Risk Characterisation ratios of detergent zeolites

Environmental compartment		PEC	PNEC	RCR
Water	regional	0.75 mg/l	1.55 mg/l	0.48
	local	1.24		0.80
Soil	regional	1.11 mg/kg	600 mg/kg	0.002
	local	142		0.24
Sediment	regional	0.45 mg/kg	1.1 mg/kg	0.41
	local	0.98		0.89
STP	local	4.94 mg/l	33 mg/l	0.15

4.4 Conclusions

The environmental exposure assessments for detergent-based zeolites were conducted using the HERA detergent scenario (HERA, 2004). The PNEC values used in the risk assessment were derived from the most conservative reliable NOEC values available from either of the concerned zeolite types A, P and X. These long-term ecotoxicity data have confirmed the anticipation that the ecological behaviour of the zeolite types used in detergents is very similar. The risk characterisation ratios based upon the discussed exposure and effects data show RCR values < 1 and, hence, do not indicate a risk for any of the environmental compartments, i.e. water, sediment, soil and sewage treatment plants (STP).

The favourable outcome of this environmental risk assessment provides a sound basis for the conclusion that the use of zeolites in detergent products does not pose a risk to the environment.

5 References

Allen, H.E., Cho S.H., Neubecker T.A., 1983. Ion exchange and hydrolysis of type A zeolite in natural waters. *Water Res.* 17, 1871-1879

Breck D.W., 1974. *Zeolite Molecular Sieves - Structure, Chemistry and Use.* WileyInterscience, New York

Degussa AG, 1991. DIN Safety Data Sheet: Aluminiumsilikat P820 (25.11.91)

Gode P., 1983. Sodium aluminium silicates in detergents – investigation of the influence of algal growth. *Z. Wasser – Abwasser- Forschung* 16, 210 – 219

Henkel KGaA, Düsseldorf. unpublished data

HERA, 2004. Report on Zeolite A, version 3.0 (January 2004). Available on website: <http://www.heraproject.com>

IUCLID Dataset for CAS 1344-00-9, CAS 1318-02-1

Umweltbundesamt , 1979. Die Prüfung des Umweltverhaltens von Natrium – Aluminium – Silikat. Zeolite A als Phosphatersatzstoff in Wasch- u. Reinigungsmitteln. *Materialien* 4/79, Erich Schmidt-Verlag, Berlin.

Unilever, 1992. The comparative chronic toxicities of Zeolite MAP (Ca exchanged) and Zeolite 4A (Ca exchanged) to *Daphnia magna*. Report No. CT/539/03 (unpublished)

Zeodet, 2000. *Zeolites for detergents (Broschüre).* ZEODET / CEFIC , Brussels

Zeodet, 2001a: Determination of toxic effects of a soil-incorporated chemical substance (Doucil A24) on emergence and growth of terrestrial plants. LAUS GmbH, Report No. AB01 021905J01 (Dec 18, 2001) (unpublished)

Zeodet, 2001b: Determination of the acute toxicity of soil-incorporated chemical substance (Vegobond AX) on emergence and growth of terrestrial plants. LAUS GmbH, Report No. AE01021906J01 (Dec 19, 2001) (unpublished)

Zeodet, 2001c: Determination of toxic effects of a soil-incorporated chemical substance (Wessalith 4000) on emergence and growth of terrestrial plants. LAUS GmbH, Report No. AB01021907J01 (Dec 19, 2001) (unpublished)

HERA – Zeolite A, P and X – September 2005

Zeodet, 2003: Structural and chemical relationships between zeolite types A, X and P. Unpublished document prepared by Ineos Silicas (October 2003)

Zeodet, 2005a: Determination of the effects of Ca⁺⁺-loaded Zeolite X/A (80/20%) on the reproduction of *Daphnia magna* according to OECD 211 resp. EU C.20. LAUS GmbH, Report No. AB04112902G205 (Febr 5, 2005) (unpublished)

Zeodet, 2005b: Determination of 72h-EC50 of Ca⁺⁺-loaded Zeolite P against *Desmodesmus subspicatus*. LAUS GmbH, Report No. AB04112901G301 (Jan 26, 2005) (unpublished)

Zeodet, 2005c: Determination of 72h-EC50 of Ca⁺⁺-loaded Zeolite X/A (80/20%) against *Desmodesmus subspicatus*. LAUS GmbH, Report No. AB04112902G301 (Jan 27, 2005) (unpublished)

6 Contributors

This report has been prepared by Henkel KGaA, Düsseldorf on behalf of ZEODET, the Association of Detergent Zeolite Producers.