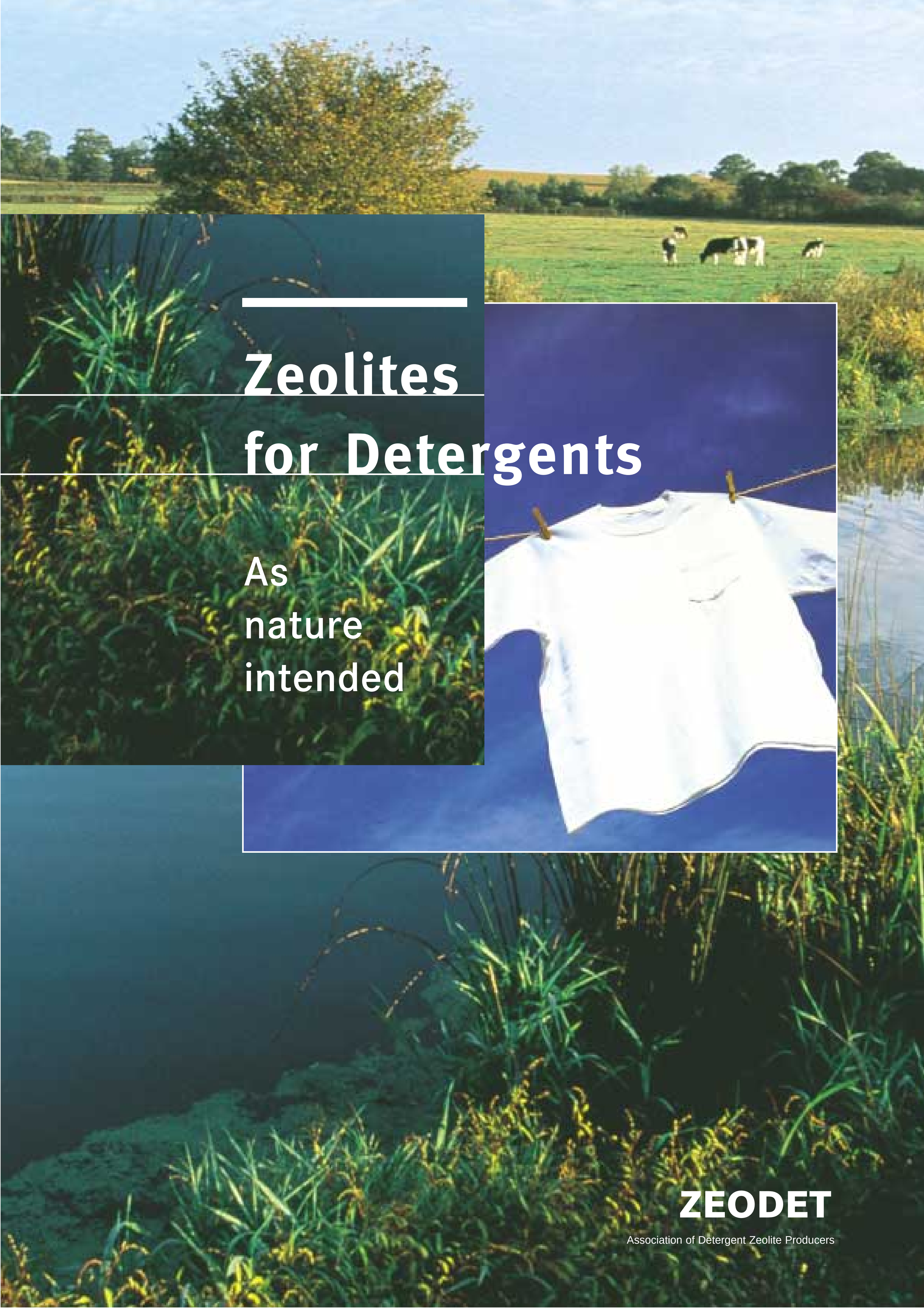

Zeolites for Detergents

As nature intended

ZEODET

Association of Detergent Zeolite Producers

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The challenges for detergent zeolites

On the threshold of the new millennium, the attention of the detergent industry is focused on delivering against four challenges [1]:

Economics
Safety and Environment
Technology
Consumer Requirements

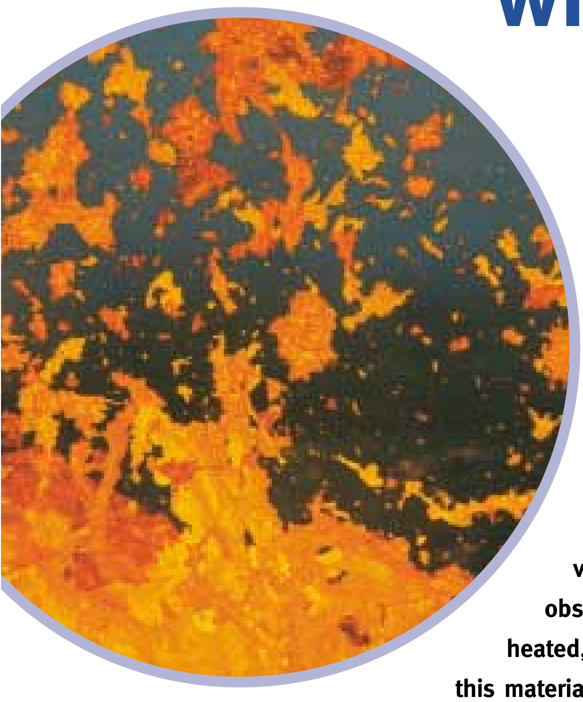
The pressure of increasing costs and competition is forcing manufacturers to seek favourably priced raw materials and production processes. Laws and regulations with respect to environment and safety, as well as voluntary agreements, have already been affecting various detergent ingredients for years (e.g. phosphates and surfactants) and have also impacted upon packaging. New measures include a monitored self-regulation by European detergent manufacturers (AISE: Code of Good Environmental Practice), and the introduction of a European eco-label for detergents. Both measures are having a direct impact on the composition and technology of detergents. In particular, efforts to save energy and to reduce detergent consumption have had an impact on the technological development of both detergents and washing machines.

The crucial factor, however, remains the consumer. Although washing habits differ from country to country, there is a trend towards easier handling (compact powders, tablets). First and foremost, however, the consumer continues to demand a clean wash combined with maximum protection of the items laundered. The resulting requirement to continuously improve the performance of detergents is leading to the use of new or optimised raw materials.

To a large degree, the aforementioned challenges dominated the development of detergents in the 1980s and 90s. Zeolite, originally designed as a phosphate substitute for purely ecological reasons, increasingly had to meet the demands imposed by modified detergent composition and production technologies. In particular, the trend towards compact detergents increased the demand for builder systems with a high adsorption capacity for liquid components, especially for surfactants. Zeolite A, introduced approximately 20 years ago, proved to be a good carrier for surfactants and in the 90s advanced to become the builder leading to compact and supercompact detergents. Nevertheless, the market demanded further improvements.

The manufacturers of detergent zeolites responded to the demand for higher standards of performance and processing by developing new grades of zeolite. These include the zeolites of types P, X and AX, which have all recently been introduced into the market.

Zeolites - special materials with diverse applications



General structural features, properties and areas of application

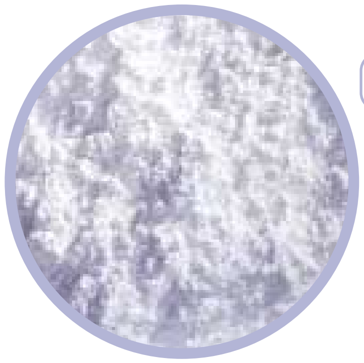
Zeolites are abundant in nature and were first described by the Swedish amateur mineralogist Baron von Cronstedt in 1756. He found these minerals in rocks of volcanic origin and observed that, when rapidly heated, stones containing this material released water and appeared to boil. Therefore he called the mineral "zeolite" which is derived from Greek and translates as "stone that boils".

Today, the term zeolite is used to denote crystalline aluminium silicates of natural or synthetic origin, with the following formula:

$$M_{x/n}[(AlO_2)_x(SiO_2)_y]\cdot zH_2O$$

M is an exchangeable cation with valency n. The primary building unit is composed of SiO_4^- and AlO_4^- tetrahedrons that are linked by so-called secondary building units to form a three-dimensional network. Chemists have classified approximately 50 natural and more than 200 synthetic zeolites [2]. A common property of all zeolites is their ion exchange capability. On the basis of this characteristic, zeolites were first put to industrial use in the sugar industry in 1896. In the 1920s, the adsorptive capacity of zeolites in separation processes led to the name "molecular sieve" being used as a synonym for industrially produced zeolites.

In the 60s, the catalytic properties of zeolites for petrochemical processes, especially the fluid catalytic cracking (FCC) process, were discovered. Today, around 300,000 t of synthetic zeolites are being used annually in catalytic and adsorptive applications. In addition, a further 300,000 t of natural zeolites per annum are being used in the construction materials and paper industries, in waste water treatment, in soil improvement, as an animal feed additive and as cat litter [3].



Synthetic zeolite

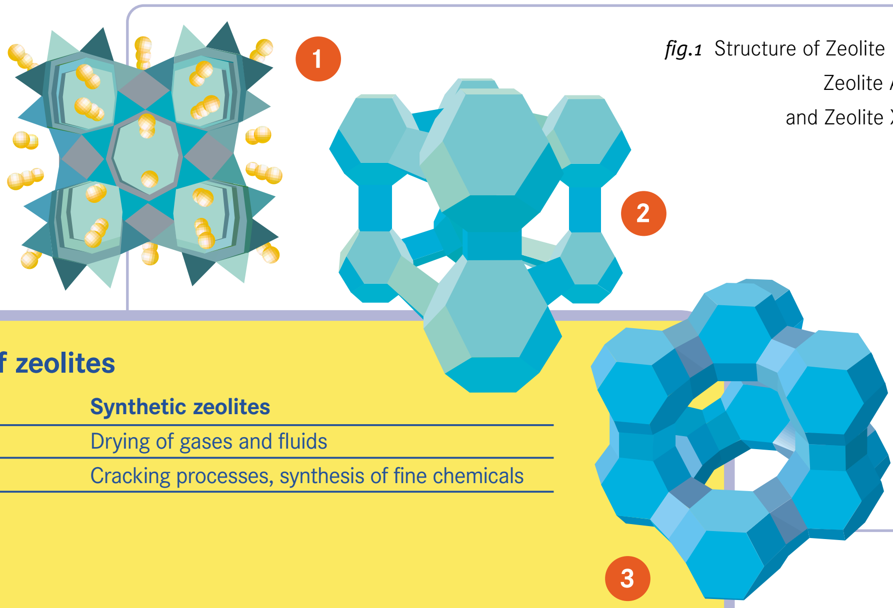


fig.1 Structure of Zeolite P *(1)*
Zeolite A *(2)*
and Zeolite X *(3)*

Properties and applications of zeolites

Property	Natural zeolites	Synthetic zeolites
Adsorbing agent		Drying of gases and fluids
Catalyst		Cracking processes, synthesis of fine chemicals
Filler	Pozzolan cement Paper additive Soil improvement Cat litter	
Ion exchanger	Sewage treatment	Detergent builder

Chemistry and structure of detergent zeolites

In the early 70s, a systematic quest for phosphate substitutes led to research into zeolites as builders for detergents. In principle, sodium aluminium silicates with the following general formula are suitable:

$$Na_x[(AlO_2)_x(SiO_2)_y]\cdot zH_2O$$

All detergent zeolites are characterised by a high aluminium content. According to Löwenstein's rule, not more than half the Si atoms in the crystal lattice can be replaced by Al atoms. In the case of detergent zeolites, a Si/Al ratio of 1 or virtually 1 is achieved. This in turn results in a maximum content of Na^+ ions, which are necessary to neutralise the AlO_2^- units. Since Na^+ ions are able to move in the zeolite pores, they can easily be exchanged for calcium ions, and sometimes other ions.

The zeolites available for detergents today (Zeolite A, Zeolite P, Zeolite X) have significantly different crystalline structures. The basic unit of the zeolite used in detergents since 1976, **Zeolite A** ($x = y = 12$, $z = 27$), often also referred to as Zeolite NaA or Zeolite 4A, comprises 8 cubo-octahedrons linked via 12 cuboids to a cavity which is referred to as the α-cage. The "windows" (pores) of these cages have a diameter of 0.42 nm, and can therefore be permeated only by small molecules or ions. Whilst calcium ions diffuse relatively easily into the interstices, the smaller magnesium ions are impeded by a hydrate shell, and are therefore incorporated more slowly. Only at higher temperatures, when the hydrate shell of the magnesium ion is gradually removed, does the rate of ion exchange increase. Zeolites of the P type with a higher y value in the general structural formula have been known for quite some time, but were unsuitable for detergents due to their inadequate calcium binding. Recently a new type of **Zeolite P** was developed with a y value of nearly 1.0 and a high calcium exchange capacity. The new type, also referred to as zeolite MAP [4, 5], possesses a flexible, layered crystal structure (see figure 1). As a result of the somewhat narrower pores of approximately 0.3 nm, and the more flexible, adaptable crystal structure, the calcium ions are bound more firmly than in the case of Zeolite A.

Following the development of a more economic production process, **Zeolite X** was recently introduced into the market for detergents [6]. Like Zeolite P, the chemical composition of this zeolite is also virtually identical to that of Zeolite A. As with Zeolite A, the basic building blocks of Zeolite X are cubo-octahedrons, which are linked to a faujasite structure via hexagonal prisms (see figure 1). Due to its larger pore diameter of 0.74 nm, Zeolite X is capable of more readily including magnesium ions. The result is a significantly higher magnesium binding capacity compared to Zeolite A and Zeolite P.

A further new development on the market is a co-crystallite comprised of 80% Zeolite X and 20% Zeolite A [7]. This grade, referred to as **Zeolite AX**, displays calcium and magnesium exchange properties which are superior to those of a blend of the pure zeolites.

Zeolites as builders for detergents

The functions and history of builders

The core components of most modern detergents are surfactants, builders (water softeners), bleaching agents and special additives such as enzymes. Surfactants remove the soil from the fibre, but their effectiveness is impaired to a certain degree by hard water. An important task of the builders is to soften the water and thus ensure the effectiveness of the surfactants [8]. Water can be softened either by complexing (e.g. phosphates), ion exchange (e.g. zeolites) or precipitation (e.g. sodium carbonate). In the case of complexing agents and ion exchangers, the water softening additionally prevents the formation of poorly soluble inorganic salts, which are a key factor in the formation of textile incrustations.

Detergent builders also contribute towards the inhibition of greying and the removal of dirt. Beyond these tasks that relate purely to the wash, builders also perform important functions in the production process. In spray-dried detergent powders, they make a key contribution to the structure of the washing powder (hence the name "builder"). In non-tower processes, they serve as a carrier for liquid components.

When the first heavy-duty detergents were marketed at the beginning of this century, the first builders they contained were sodium carbonate and sodium silicate. From the 30s onwards, the more effective phosphates performed the role of builders. The introduction of phosphate-reduced (1976) and later phosphate-free detergents (1983) marked the beginning of the era of builder systems containing zeolites.

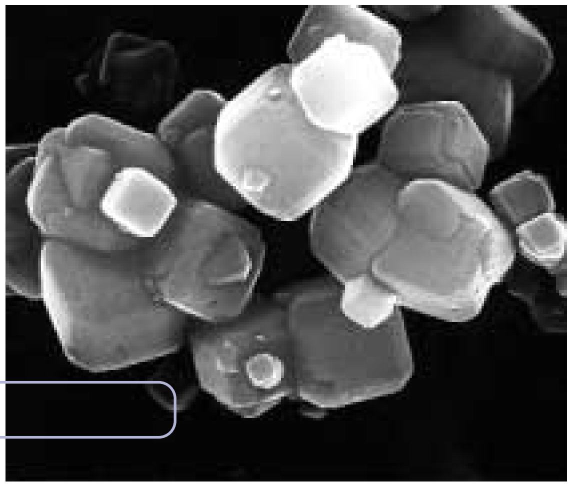
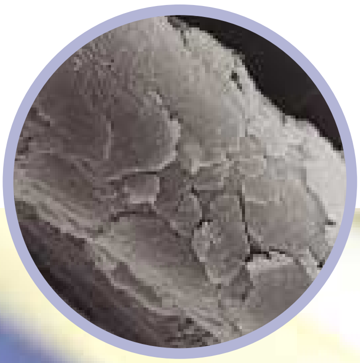


fig.2 Scanning electron micrograph (SEM) of Zeolite A



Incrustation caused by underbuilt non-zeolite detergent powder

Zeolites in the laundering process

Before Zeolite A was first used as a builder in detergents, a number of questions needed to be answered concerning its behaviour in the laundering process. Studies showed that, despite its insolubility, Zeolite A does not lead to excessive incrustation of fibres. This is due to its specific, optimised particle shape (rounded corners and edges) and particle size (mean value 3.5 µm).

Due to the slower kinetics of ion exchange as compared to phosphate, it emerged that Zeolite A was not capable of completely suppressing the precipitation of calcium carbonate, especially at high washing temperatures and elevated water hardness. In view of this fact it was necessary to add a soluble builder. Whilst Zeolite A had first been combined with sodium triphosphate, the addition of polycarboxylate subsequently proved to be significantly more effective. The polycarboxylates are able to delay the formation and precipitation of poorly soluble calcium carbonate, by inhibiting crystal growth even when applied at low concentrations in the substoichiometric range (threshold effect) and through their dispersive action. This finding led to what has since 1983 been the dominant builder system for phosphate-free detergents and which is comprised of Zeolite A, polycarboxylate and sodium carbonate.

Several tests by independent consumer test organisations have demonstrated an excellent performance for these phosphate-free detergents in comparison to phosphate-containing products [9, 10].

Tested under critical conditions, the phosphate-free builder system containing zeolite even proved superior to the earlier sodium triphosphate system. Systems containing phosphates require precise dosage which must be monitored exactly in relation to the water hardness, otherwise significant fibre incrustation will occur caused by phosphate precipitation. By contrast, zeolite-based systems even at low dosages and elevated water hardness tend to cause only low textile incrustation and deposits on washing machine parts [11]. This robust performance under a wide range of conditions and the high degree of flexibility in

Historic development of detergent builders

1907	Silicate (water glass) + carbonate
1933	Diphosphate
1946	Triphosphate
1976	Zeolite A + triphosphate
1983	Zeolite A + carbonate + cobuilders
1994	Zeolite A + special silicates + cobuilders
1994	Zeolite P + carbonate (+ cobuilders)
1997	Zeolite X + carbonate (+ cobuilders)

Cobuilders =
e.g. polycarboxylates, citrate.

Special silicates =
e.g. amorphous or crystalline disilicates.

All builders as sodium salts.

formulation terms facilitated the development of the zeolite-based low dosage compact detergents.

Alongside its main function (that of softening water) zeolite also has other proven effects in the laundering process. Zeolite A for instance promotes the inhibition of greying through heterocoagulation with dirt particles. Furthermore, zeolites can remove dyes from the washing liquor by heterocoagulation and adsorption. In conjunction with the relatively low sodium concentration associated with zeolite as compared with soluble builders, this leads to a reduced risk of dyes discolouring other items. Zeolite is therefore the builder of choice for special products termed "colour detergents".

The new developments – Zeolite P, Zeolite X and Zeolite AX – are superior to Zeolite A in view of their more rapid rate of ion exchange, even at low washing temperatures. In addition, Zeolite X and AX possess an improved magnesium binding capacity. Zeolite P displays better compatibility with sodium percarbonate, which is increasingly replacing sodium perborate in detergents. Thanks to the improved builder properties of the new zeolites, the cobuilder (e.g. polycarboxylate) content of detergents can be reduced considerably [5, 8].

Zeolites in detergent production

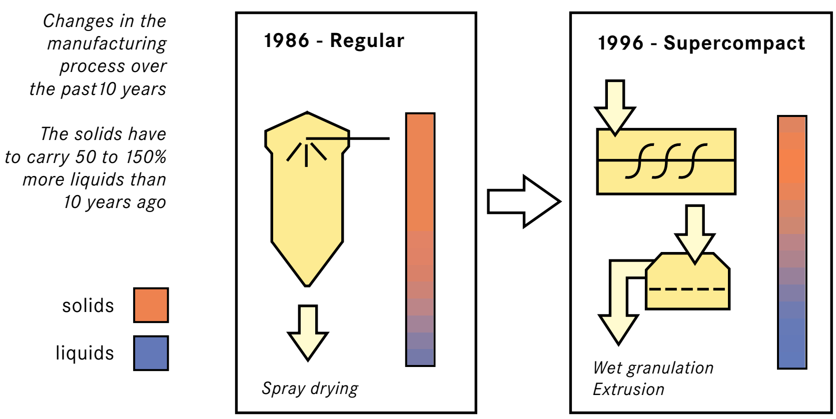
Generally, zeolites possess a number of advantages over other builders during the production of detergents. For example, zeolites display a very high product stability, regardless of the particular process employed (spray drying, granulation, extrusion etc.). They prove inert when exposed to elevated temperatures, mechanical influences or alkalinity. Partial decomposition or chemical conversion, as can occur with sodium triphosphate or specific layered silicates depending on the process design, have not been reported with zeolites. This makes zeolites particularly flexible materials for the production of detergents. Additionally, zeolites are used as an effective flow aid for powder handling.

A further salient feature of zeolites is their high adsorptive capacity for liquid components, e.g. surfactants. This property facilitated the development of the surfactant-rich compact detergents which have now been on the market since the late 80s. In Europe (1998), the market share of compact powders accounted for about 30% in value which corresponds to 37% of the whole powder segment [12]. In the U.S. (1998), over 90% of the powders market was already represented by compact detergents [12].

The compact detergents of the most recent generation, often also called supercompact detergents, are characterised not only by particularly low dosage and thus high surfactant content, but also by an increase in bulk densities to approximately 700-900 g/l. To achieve these bulk densities, special technologies such as roller compacting, extrusion or wet granulation are required [13].

By contrast, conventional spray-drying processes are increasingly being displaced. Regardless of the compacting method, zeolites prove to be particularly suitable builders for achieving the desired bulk densities and powder properties. Today's compact and super-

fig.3 **Modifications to production processes for detergents**



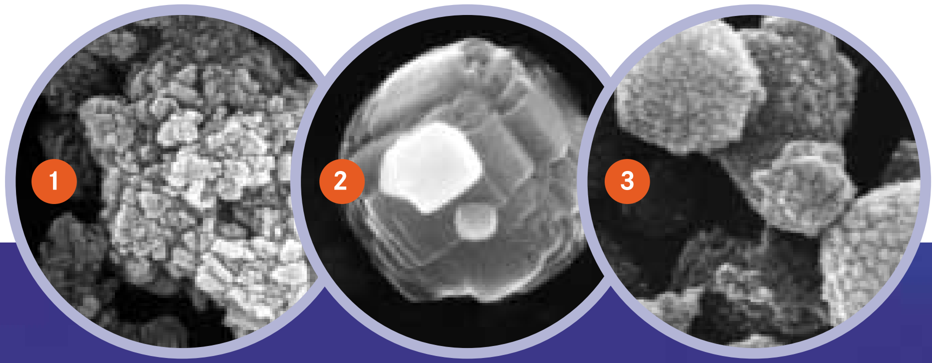


fig.4 SEM of Zeolite X *(1)*, AX *(2)* and P *(3)*

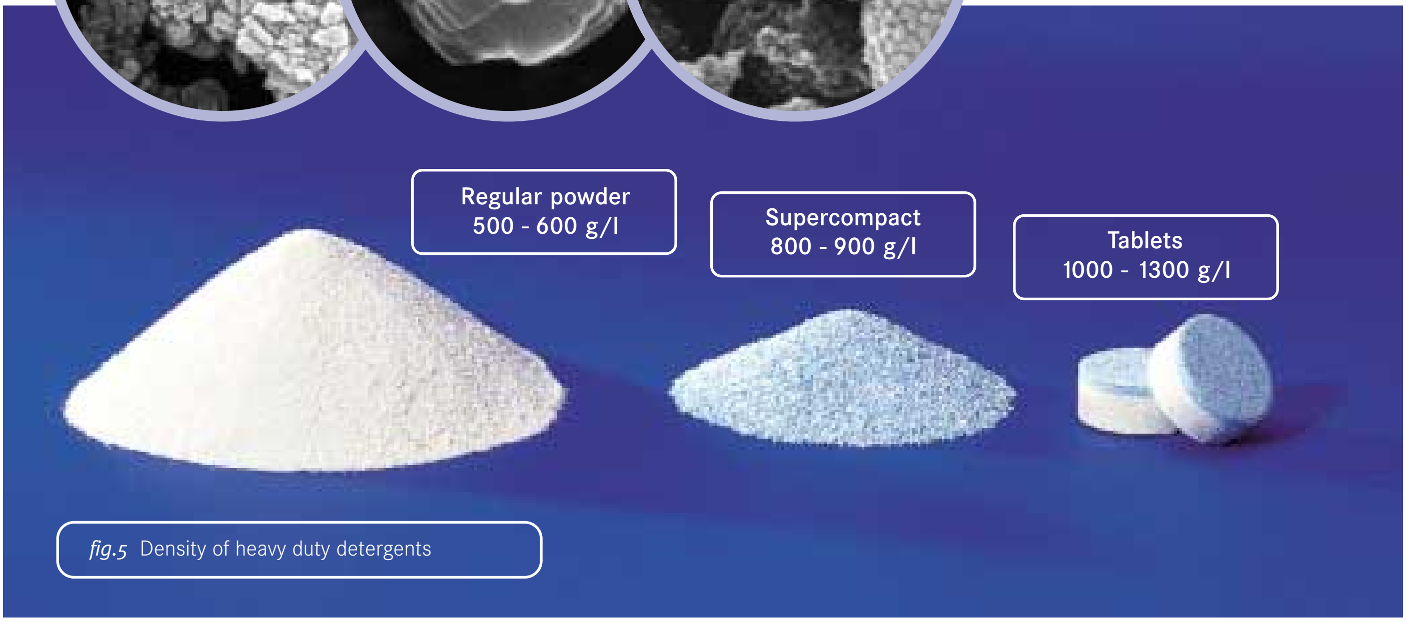


fig.5 Density of heavy duty detergents

compact detergents are therefore predominantly zeolite-based. This is also true for tablets which need highly adsorptive builders like zeolites. Tablets represent the latest development in laundry detergents. Only one year after their launch in 1998, they have already gained a market share of about 8 % in Western Europe [12]. It is predicted that tablets will reach a market share of 15 to 20 % in this region during the year 2000 [1].

The adsorptive capacity for liquid components was significantly increased yet again when the new zeolites of type X, P and AX were developed. In some cases the adsorptive capacity achieved with these zeolites is more than twice that achieved with Zeolite A. The high flexibility of zeolites with respect to formulation and ease of processing together with the economic advantage of the raw material have led to it becoming an extremely attractive builder.

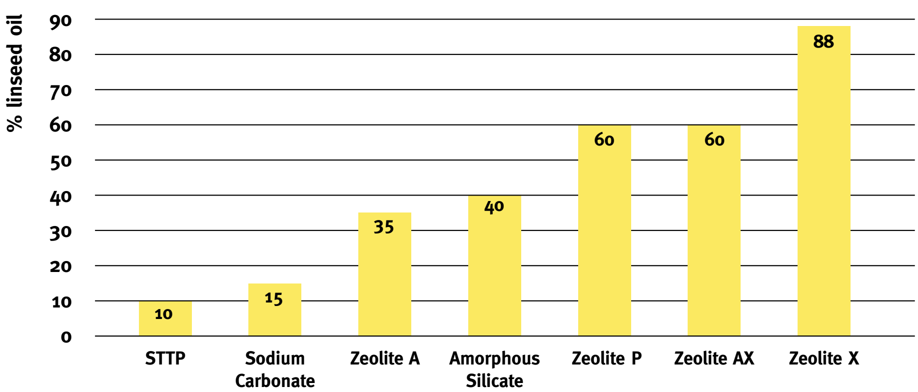
Properties of detergent zeolites in the laundering process

- minimised fibre damage via special particle morphology
- minimised incrustations due to optimised particle size distribution
- high water softening capacity
- robust performance under a wide range of conditions
- inhibition of greying
- inibition of dye transfer

... in detergent production and storage

- high adsorption capacity for liquid components
- high stability during processing
- effective flow aid for powder handling

fig.6 Adsorptive capacity of various builders



Testing based on ISO Standard 787/150

Zeolites - safe for humans and the environment

Detergents and the environment

It has long been shown that detergents constitute a burden to the environment [14]. Triggered by high levels of foam covering some European rivers in the late 50s which were caused by poorly degradable surfactants, legal restrictions on the substances contained in detergents and cleansing agents were introduced for the first time in the early 60s. In Germany for example, the Law on Surfactants in Detergents and Cleaning Products of 1961 imposed a ban on poorly biodegradable surfactants. This law led to the poorly degradable surfactant tetrapropylene benzene sulphonate (TPS) being substituted by the more easily degradable linear alkyl benzene sulphonate (LAS). It was the first time that legislative action had impacted upon the ingredients used in detergents.

In the 70s and 80s, further laws and ordinances on detergents and cleansers followed in Europe which affected both surfactants and other detergent ingredients. Attention was focused in particular on phosphates, due to the eutrophication of bodies of water. Between 1970 and 1991, regulations were introduced in Europe, the USA and in some Asian countries to limit the phosphate content of detergents and cleansers or to ban the use of phosphates entirely.

However, detergent laws in Austria, Germany, Italy and The Netherlands were designed not only to regulate the use of certain ingredients but were also of an increasingly precautionary nature for the detergent product itself. For instance, one aim was to minimise the quantities of product consumed (Germany, 1987). Recommended dosages and labels were designed to help consumers use detergents responsibly. Further steps in this direction included the European Commission Recommendation for the Labelling of Detergents and Cleaning Products (1989) and the introduction of a European eco-label for detergents (1995). The criteria for this eco-label are revised regularly and currently include both ecological measures (e.g. on biodegradation and eutrophication) and performance requirements. This labelling procedure is designed not only to raise consumer awareness but also to help manufacturers develop strategies to optimise detergent performance and to stimulate the use of more ecologically-compatible raw materials.

Water quality, a challenge for a growing society

Recommended dosages and labels help consumers use detergents responsibly

Another move in the direction of conservation is the initiative of the European detergent manufacturers (AISE) which was presented under the banner of "Code of Good Environmental Practice" and has been in force as an official European Commission Recommendation since 1998. Within the framework of this monitored, self-imposed obligation, detergent manufacturers aim to achieve the following targets by 2002:

- **5% of energy saved per wash**
- **10% of product saved per capita**
- **10% of packaging saved per capita**
- **10% reduction in poorly degradable organic ingredients per capita**

Laws and regulations impacting on detergents

	Law/regulation	Theme/comments
1961	Germany, Law on Surfactants in Detergents and Cleaning Products *[15]*	Primary degradation of surfactants
1973	European Council Directive on the Biodegradability of Anionic Surfactants *[16]*	General requirements for biodegradability
1975/87	Germany, Law on Detergents and Cleaning Products *[17]*	Quantitative regulations*
1970-91	Europe, regulations to limit phosphates in various countries	Laws or voluntary agreements
1972-88	USA, regulations on the use of phosphates in various states	Bans or limitations
1989	European Commission Recommendation for the Labelling of Detergents *[18]*	Quantitative data on ingredients of more than 0.2%
1991/98	Germany, Packaging Ordinance *[19]*	Prevention of waste, recycling
1995	European Commission Decision on the Eco-Label for Laundry Detergents *[20]*	Establishing ecological and performance criteria
1998	European Commission Recommendation on Good Environmental Practice for Household Laundry Detergents *[21]*	Conservation targets

** (Control of the release of detergent ingredients e.g phosphates).*

Zeolites – behaviour towards aquatic organisms

With the growing focus on eutrophication issues an intensive search for detergent phosphate substitutes was undertaken which led to zeolites emerging as particularly promising materials. Alongside the technical developments in the field of detergent formulation and production processes which were taking place, from 1974 to 1979 a comprehensive programme was implemented in Germany to establish the ecological and toxicological safety of Zeolite A. This programme was conducted through co-operation between the industry and a total of 15 governmental and independent research institutions and public authorities. The results of the programme were published in a comprehensive study in 1979, issued by the German Federal Environmental Agency [22]. According to this study, Zeolite A displays no harmful influence on aquatic organisms, nor does it promote the growth of algae. These results have since been corroborated by a number of more recent investigations [23].

Furthermore, different studies revealed no relevant impact on the growth of diatoms [22]. This is also in line with model calculations which show that the contribution from the use of zeolite-containing detergents to the total environmental silicon burden is almost negligible [24].

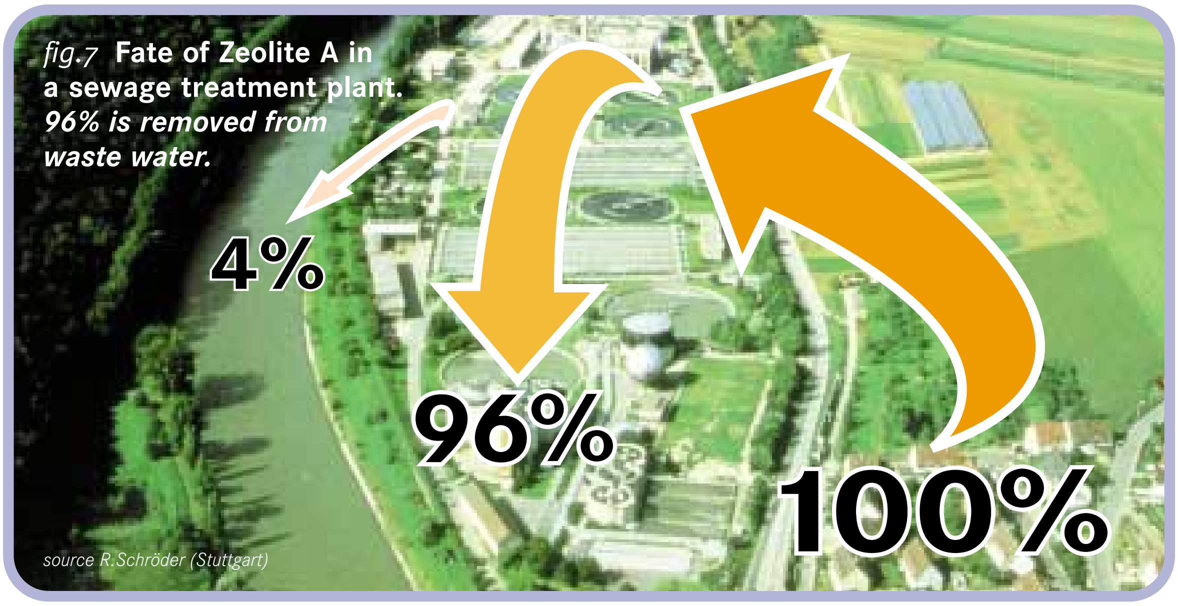
Some years ago, zeolites were suspected to have an influence on the occurrence of mucilages in the Italian Adriatic (summer 1988/89). However, comprehensive studies conducted by the Trieste Institute "Laboratorio di Biologia Marina" found no evidence for the involvement of zeolite in this phenomenon [25].

In lakes and rivers too, for instance the lakes of Switzerland, no harmful effects on phytoplankton, zooplankton or fish have been observed after 10 years' experience with phosphate-free, zeolite-based detergents [26]. The independent Swiss researchers have found that to the contrary the substitution of phosphates in detergents has led to a reduction in water burdens and progress towards desired water protection targets.

Zeolites in waste water

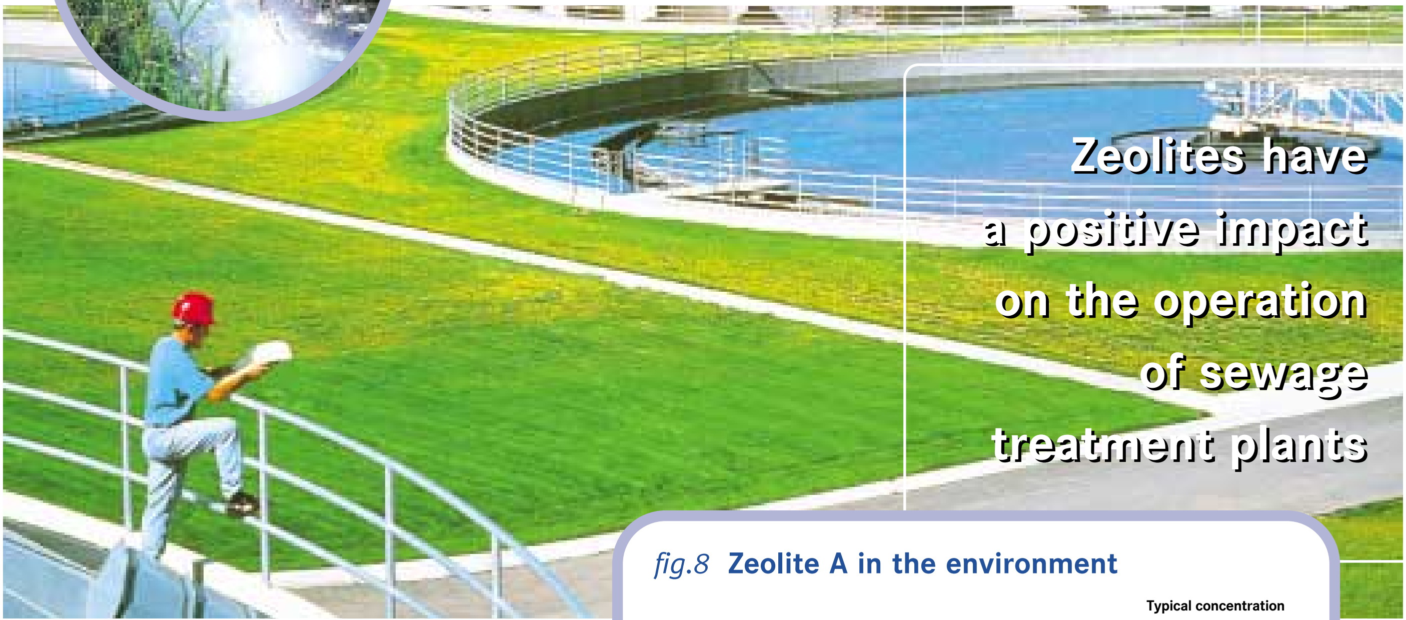
The sedimentation behaviour of Zeolite A under laboratory and actual use conditions has been investigated extensively [2, 22, 23]. In particular, the question has been addressed as to whether zeolite causes sediment deposits and hence clogging in domestic and municipal sewerage systems. In a large-scale study conducted in the residential area of Stuttgart-Büsnau from February 1976 to March 1977, approximately 900 households were given exclusively zeolite-based detergents. Neither in the domestic sewers nor in the main drains were sludge deposits accumulated or solidified over a prolonged usage period. The same result was achieved in a study involving approximately 180 households in the residential area of Düsseldorf-Holthausen [27] and in a trial conducted in 75 Belgian households where zeolite-based detergents were used for four months [28].

fig.7 **Fate of Zeolite A in a sewage treatment plant.** ***96% is removed from waste water.***



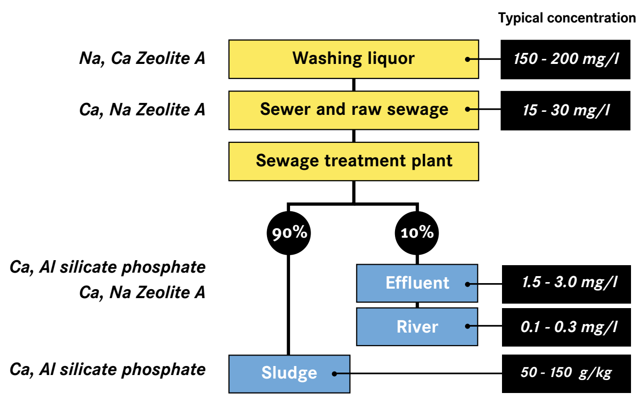
source R.Schröder (Stuttgart)

Zeolites aid progress towards water protection targets



Zeolites have a positive impact on the operation of sewage treatment plants

fig.8 **Zeolite A in the environment**



Zeolites in sewage treatment plants

Generally, zeolites have a positive impact on the operation of sewage treatment plants (STPs) especially with respect to sedimentation performance. In the large-scale study in Stuttgart-Büsnau it was found that approximately 96% of the incoming Zeolite A was removed in the sewage treatment plant and only around 4% was discharged.

In terms of the operation and performance of the biological treatment stage of STPs, no detrimental effects from Zeolite A were observed [22]. In a number of other field studies, figures of between 80 and 95% for the elimination of Zeolite A were recorded depending upon the mode of operation of the STP [2]. As a rule, the rate of elimination is greater than 90% for STPs equipped with mechanical and biological treatment stages. According to laboratory tests using municipal waste water, in STPs with a tertiary treatment stage (phosphate elimination) Zeolite A does not impair phosphate removal [28].

Experimental measurements and model calculations show that Zeolite A typically accounts for an increase of approximately 10% in the dry mass of the sewage sludge. However, sludge volume is more important with respect to sludge handling and disposal. Field studies indicate that zeolite-based detergents do not cause any increase in the volume of sewage sludge [2, 22]. On the contrary, in the presence of Zeolite A the sedimentation and dehydration properties of the sludge are improved, such that a lower volume index results which can facilitate the operation of the STP.

Fate of zeolites in the environment

As already indicated, by far the largest proportion of Zeolite A remains in the sewage sludge. Amongst the range of options for the further treatment or utilisation of the sewage sludge three processes dominate [29]:

- **cropland application**
- **landfill**
- **incineration**

During combustion the zeolite structure is completely destroyed, resulting in a mixture of other harmless aluminosilicates. No formation of quartz or christobalite has been detected [30]. Consequently, the subsequent disposal of the ash of zeolite containing sludges poses no hazard. With regard to the direct application of sludges containing zeolites to arable soil, the key issue of concern was the scope of possible impact on plant growth. Studies indicate however that the effect on plants is determined less by zeolite and more by the remaining composition of the sludges [22, 23]. No significant changes in yields were observed in crops exposed to sewage sludges containing Zeolite A.

Also investigated was the fate of the minor amounts of Zeolite A which pass through the STPs and end in surface waters. Results from various laboratory studies are as follows [2, 31]:

- **In neutral, phosphate-free water the half-life of Zeolite A was approximately 1-2 months.**
- **In water containing phosphate and calcium the half-life was 12-30 days depending on the pH value.**
- **In phosphate-free systems, the degradation products formed are amorphous minerals (i.e. gibbsite and halloysite).**
- **In the presence of calcium and phosphate at concentrations that are typical of natural waters the final products formed are poorly soluble calcium aluminium silicate phosphates.**

These calcium aluminium silicate phosphates are amorphous and have no ion exchange properties. Consequently, they cannot contribute to the remobilization of heavy metals. By forming these poorly soluble hydrolysis products Zeolite A does not lead to an increase in the level of soluble aluminium compounds and it even contributes towards phosphate immobilisation.

Phosphate reduction overall has been linked to a decrease in heavy metal concentrations in ground water. Following a twelve years study, Swiss scientists concluded that an observed decrease in concentrations of manganese and cadmium could be attributed to lower phosphate levels in rivers and aquifers [32].

Zeolites have no negative effects on plant growth

Life cycle assessment and production of zeolites

The environmental impacts caused by a product can be determined by carrying out a Life Cycle Assessment (LCA) or Life Cycle Inventory Analysis (LCI) [14]. The life cycle study of a detergent ingredient is the basis for an LCA of a detergent (including production and packaging), which ultimately leads to an LCA of the washing process including consumer habits. In 1993 the Association of Detergent Zeolite Producers (ZEODET) commissioned the Swiss institute EMPA in St. Gallen to prepare an LCI study on the production of Zeolite A. This LCI study was conducted as a "cradle to factory gate" study in accordance with recognised standards (as now defined by ISO 14040, 1997; ISO 14041, 1998). In line with these standards, the LCI study was critically reviewed and approved by a commission of independent experts (peer review) [6, 33]. The LCI study represents the average situation for Zeolite A production in Europe in 1993.

Apart from the crystallisation of calcined kaolin clay practised in Asia, world-wide Zeolite A is produced predominantly using the "aluminium silicate hydrogel route" (see fig. 9).

The initial substances required for production using the hydrogel route are the readily accessible raw materials of water glass and sodium aluminate. In aqueous solution a gel-like, amorphous sodium aluminium silicate is produced which under special conditions, is then hydrothermally crystallised and further processed to produce either a slurry or a spray-dried powder. The LCI study includes information on the consumption of energy and raw materials, on emissions into the atmosphere and water, and on the production of solid waste. On the basis of these data, further LCAs/LCIs can then be carried out on builder systems or on complete detergents containing zeolites. In 1994, Landbank Environmental Research & Consulting in London [34] published a "Life Cycle Study" on phosphate- and zeolite-based builder systems. The report came to more or less the same outcome for both phosphate and zeolite builders. However, the study was criticised because it did not comply with the standardised requirements for LCAs (e.g. clear functional unit, incorporation of precombustion energy, peer review) and in the case of Zeolite A used only estimated data based on the literature and patents [6, 33].

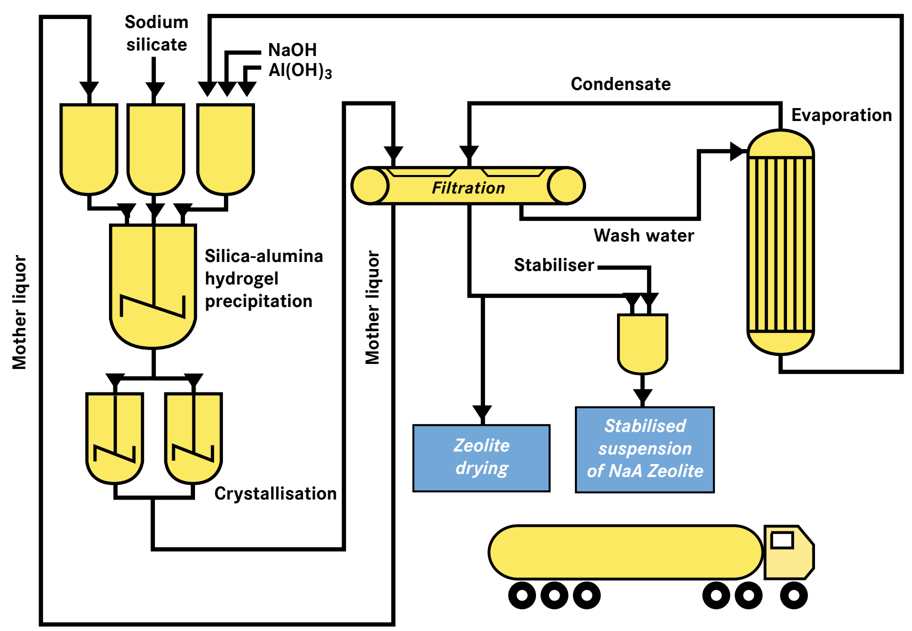
Zeolite-based detergents contribute to the reduction of detergent consumption

Environmental impact of zeolite has been fully characterised by life cycle analysis

Impact of zeolite based builder systems on detergent consumption

In a study commissioned by the Swedish Association of Cosmetics, Toiletries and Household Products Manufacturers (KTF), the Danish environmental research group MFG reviewed the technical and environmental aspects of various builders [29]. The study surveyed the advantages and drawbacks of phosphate- and zeolite-based detergents and made comparable overall conclusions. With respect to controlling detergent usage which is important for the environment, this study confirmed that the introduction of zeolite-based detergents did not lead to an increase in detergent consumption.

fig.9 **Production of Zeolite A (hydrogel route)**



An analysis of changes in the composition and dosage of a leading detergent brand [6] demonstrated that the switch to phosphate-free builder systems was accompanied by a significant reduction in the detergent dosage used per wash (see fig. 10). This is clearly related to the introduction of zeolites in detergents.

This reduction in the recommended detergent dosage is also reflected by a significant decrease of the per capita consumption of detergents (see for example Germany, fig. 11).

Toxicological and dermatological safety of zeolites

Zeolite A has undergone intensive toxicological studies and has been shown to be non-toxic in living organisms [23, 35]. In particular, no allergenic or irritancy potential was identified upon skin contact or inhalation. Furthermore, Zeolite A has no acute systemic toxic properties if swallowed, after dermal contact or upon inhalation. Potential residues on textile fibres which might contain zeolite therefore pose no hazard to the consumer. This has also been demonstrated in controlled exposure tests with zeolite-based detergents [36].

Detailed studies have also been carried out on the long-term behaviour of Zeolite A, including investigations into fibrogenic properties. In contrast to natural zeolites, which in rare cases can also be fibrous such as the erionite found in Turkey, the structure of synthetic zeolites such as Zeolite A is isomorphically cubic, with rounded corners and edges. This structure, coupled with high purity (there is no detectable quartz content), makes synthetic zeolites inert, as demonstrated in the long-term studies. In contrast to quartz, inhalation tests revealed no evidence of silicosis caused by Zeolite A. This has been confirmed by factory medical officers observing operators working in plants manufacturing and processing zeolites over a prolonged period of many years.

Zeolite A has been shown to be devoid of any mutagenic potential. Long-term inhalation studies produced no evidence of chronic toxicity or carcinogenicity [23, 35]. From development toxicity studies both in rats and rabbits there are no indications for any teratogenic potential.

Some years ago, it was speculated that there may be a link between Zeolite A and Alzheimer's disease. Due to the accumulation of aluminium in diseased areas of

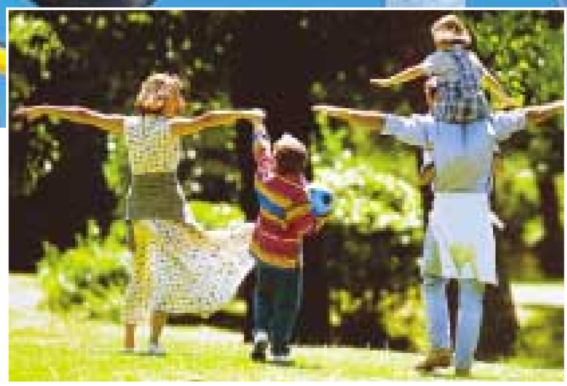
fig.10 **Changes in detergent ingredients and dosages (1979 - 2000)**

(values in % ; values in parentheses = g ingredient per wash)

Main ingredients	Heavy duty detergent type (Germany)				
	Regular 1979	Regular 1991	Compact 1991	Supercompact 1996	Tablet 2000
Anionic surfactants	5.9 (16.2)	7.5 (11.0)	8.0 (7.8)	14.9 (11.3)	15.2 (11.4)
Nonionic surfactants	4.0 (11.0)	5.2 (7.6)	6.0 (5.9)	4.4 (3.3)	3.7 (2.8)
Soap	3.0 (8.3)	1.5 (2.2)	0.8 (0.8)	0.9 (0.7)	0.7 (0.5)
Pentasodium triphosphate	39.0 (107.3)	•	•	•	•
Zeolite NaA	•	25.0 (36.5)	23.5 (23.0)	20.6 (15.7)	25.1 (18.8)
Sodium carbonate	•	12.1 (17.7)	12.6 (12.3)	9.0 (6.8)	2.6 (2.0
Sodium polycarboxylate	•	3.8 (5.5)	5.5 (5.4)	5.2 (4.0	3.2 (2.4)
Silicates	4.9 (13.5)	4.3 (6.3)	3.0 (2.9)	1.6 (1.2)	1.8 (1.4)
Sodium perborate (4 H_2O)	24.9 (68.5)	24.0 (35.0)	9.0 (8.8)	•	•
Sodium perborate (1 H_2O)	•	•	10.0 (9.8)	12.2 (9.3)	•
Sodium percarbonate	•	•	•	•	15.0 (11.2)
TAED	•	2.0 (2.9)	5.5 (5.4)	7.0 (5.3)	7.0 (5.3)
Disintegrant	•	•	•	•	6.0 (4.5)
Recommended dosage (normally soiled laundry, 14-21 °d)	**275**	**146**	**98**	**76**	**75 [g]**

Other ingredients (mainly water and additives) up to 100%.

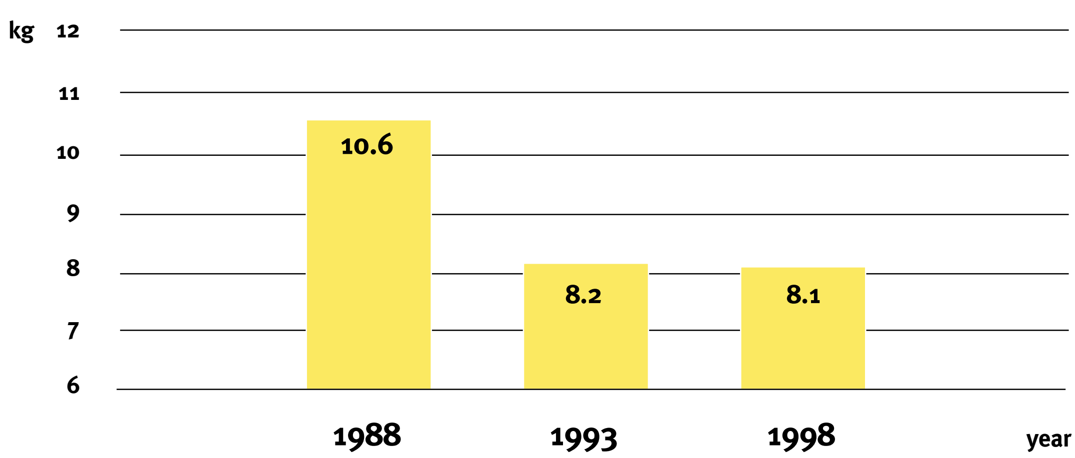
Detergent zeolites - safe for humans



the brain, a debate arose concerning a link between the elevation in aluminium concentrations in drinking water and Alzheimer's disease. Disregarding the fact that the aluminium theory is no longer considered the most promising line of enquiry in the debate surrounding Alzheimer's, the evaluation of the fate of Zeolite A has – as already indicated – clearly demonstrated that Zeolite A does not increase the level of soluble aluminium compounds in surface waters and aquifers [31].

Due to their lack of hazardous properties, zeolites are not classified as "dangerous substances" under chemicals, dangerous substances or transport regulations.

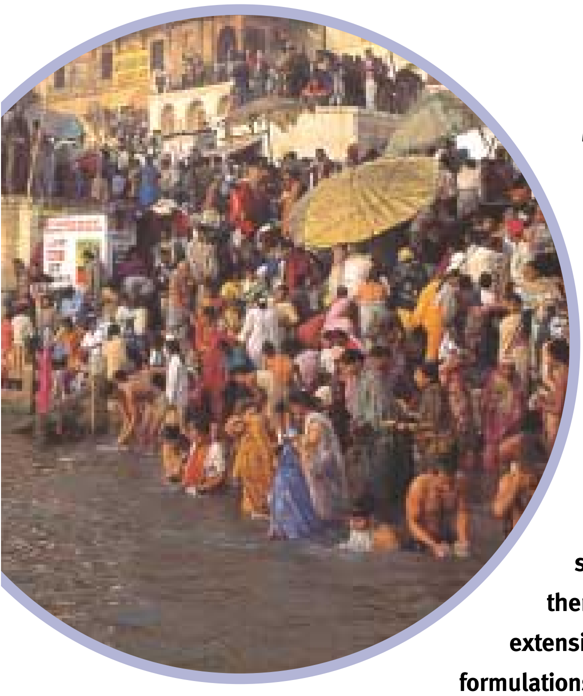
fig.11 **Per capita consumption of detergents (Germany 1988 - 1998)**



Source: IKW, Germany

5

The success of zeolites



Market trend

In the 20 years since zeolites were first introduced, their advantageous builder properties combined with their excellent human and environmental safety standards have led to them being included in an extensive range of detergent formulations world-wide. In Western Europe, the USA, Japan and several regions of East Asia, they have replaced phosphates to a large extent [13]. In Spain, Portugal and a number of Eastern European countries phosphate-based detergents predominate (see fig. 12) but even in these areas, there is a growing move towards zeolite built detergents.

What is striking is the use of zeolites not only in countries where phosphate regulations are in place, but also in regions that are not yet subject to limitations on phosphates. This development can be explained by both the technical and economic benefits of zeolites. A key factor in the overall success of zeolites, however, has been the high level of consumer acceptance demonstrated for phosphate-free detergents. At present, more than 1,000,000 metric tons of zeolites are used per annum in detergents and cleaning products world-wide. In Europe, the usage of zeolites has been steadily growing over a number of years with consumption now forecast at a level of 650,000 tons p.a. for the year 2000 [see fig. 13].

Outlook

The ongoing increase in detergent compacting resulting in innovative products such as tablets and supercompacts and the increasing use of non-tower processes will continue to boost the trend towards builder systems with a high adsorption capacity for liquid components. Eminently well suited for this are Zeolite A and especially the innovative Zeolite P, Zeolite X and Zeolite AX. **Therefore, zeolites have the potential to remain the detergent builders of choice from technical as well as environmental and economic considerations.**

Tablet detergents offering easy and controlled usage

fig.13 **European market: zeolite as a builder for detergents** **(thousand metric tons p.a)**

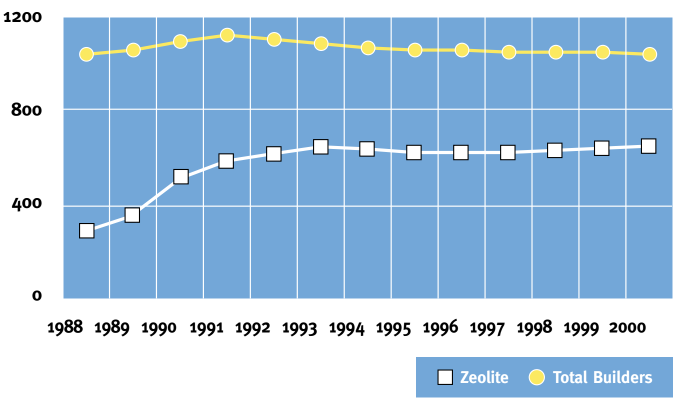
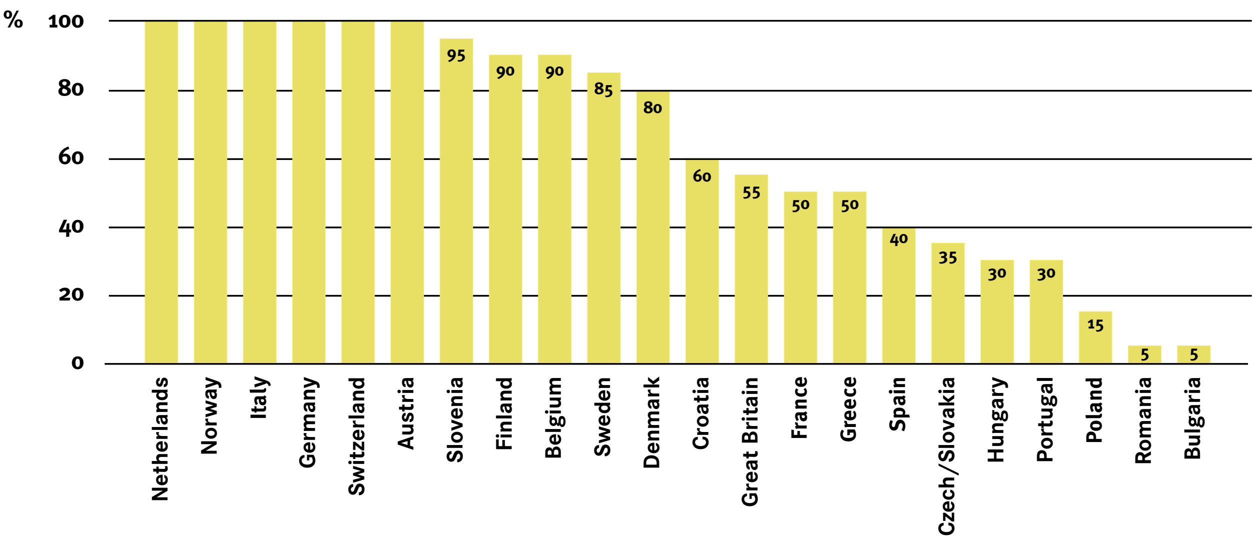
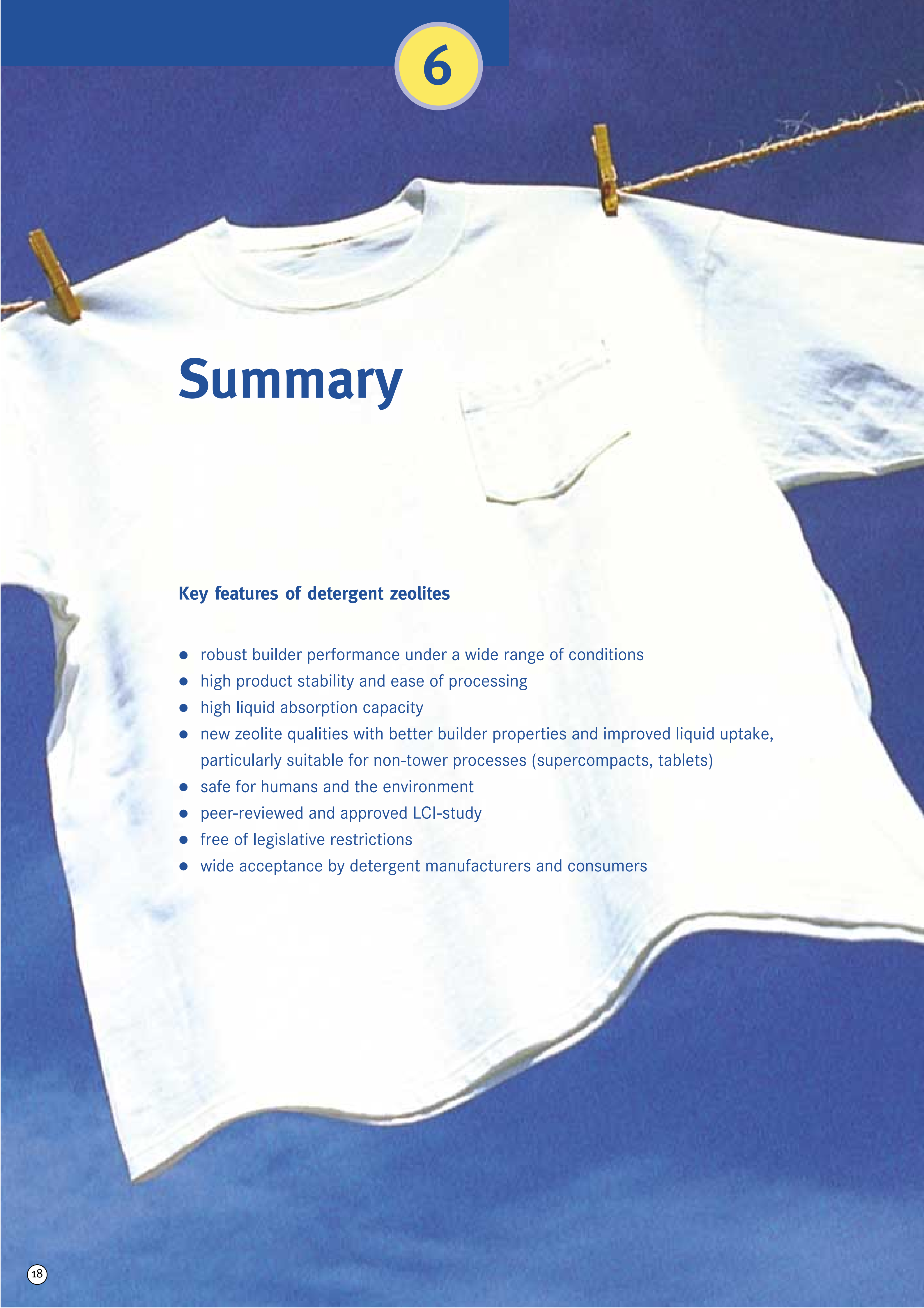


fig.12 **Market shares of phosphate-free powder detergents in Europe (1998)**



Source: E.J. Smulders



6

Summary

Key features of detergent zeolites

- robust builder performance under a wide range of conditions
- high product stability and ease of processing
- high liquid absorption capacity
- new zeolite qualities with better builder properties and improved liquid uptake, particularly suitable for non-tower processes (supercompacts, tablets)
- safe for humans and the environment
- peer-reviewed and approved LCI-study
- free of legislative restrictions
- wide acceptance by detergent manufacturers and consumers

Glossary

Note: all words in italics refer to particular titles within the glossary

AISE

"Association Internationale de la Savonnerie, de la Détergence et des Produits d'Entretien" (European Association of Soap and Detergent Manufacturers), Brussels.

Alzheimer's disease

Degenerative brain disorder that develops in mid - to late adult life and results in a progressive and irreversible decline in memory and various other cognitive functions.

Aquifer

Water-saturated soil layer. The aquifer can either be fed from percolating surface water (e.g. rain) or from rock (crystal) water of the deeper earth crust. The ground water contained in aquifers is important as a drinking-water reservoir.

Biodegradation

Biochemical process effecting the break-down of organic matter mainly due to the metabolic action of microorganisms. The initial degradation step of a molecule is called primary degradation. The complete break-down of an organic molecule to CO_2, H_2O, and the concomitant formation of microbial biomass is called ultimate biodegradation.

Bleaching agents

Detergent ingredients which generate oxidising compounds (usually active oxygen containing compounds like sodium perborate or sodium percarbonate, optionally together with bleach activators like TAED) and which help to remove stains like coffee, tea, juice from the fabric.

Builder

The substance in detergents which exerts a key influence on the structure and performance of the washing powder and especially on ***water softening***.

Cobuilder

A substance which is used in small quantities in detergents alongside zeolite or phosphate to support the builder effect. Today, these are usually ***polycarboxylates*** whose main task is to inhibit the precipitation of poorly soluble inorganic salts which contribute towards ***incrustation***.

Colour detergents

Detergents designed primarily for washing coloured textiles. They usually do not contain brightener or bleaching agents.

Compact detergents

A class of very efficient detergents with a high degree of compaction (bulk density higher than 600 g/l). This makes low dosages and small packages possible.

Complexing agents

Substances which bind metal ions in soluble complexes.

Diatoms

A specific taxonomic group of algae which form shells of amorphous silica in their cell membranes.

Dye transfer

Undesirable colouration of textiles caused by dyes from other items running in the wash. Can be inhibited by special formulations (e.g. ***colour detergents***)

EMPA

"Eidgenössische Materialprüfungs- und Forschungsanstalt" (Swiss Federal Laboratories for Materials Testing and Research), St. Gallen, Switzerland.

Eutrophication

Surplus of nutrients - especially in aquatic systems - leading to unbalanced growth of certain organism groups, like algae. Well known is the phosphate eutrophication of lakes. Eutrophication can lead to environmental problems because the increased floral biomass reduces directly (by dark respiration) or indirectly (by aerobic biodegradation of decaying plants) the concentration of vital dissolved oxygen in surface waters.

Greying

Undesirable effect, especially evident on white textiles, caused by the redeposition of dirt particles already removed. Occurs after multiple washing cycles if the soil is not sufficiently dispersed in the wash liquor.

Incrustation

Inorganic and organic deposits on laundry items and on the heating coils in washing machines. Occurs after multiple washing cycles.

Life Cycle Assessment/ Life Cycle Inventory Analysis (LCA/LCI)

Methodology by which the various stages of the life cycle of a product can be described, analysed and measured. In an LCA/LCI the energy balance, resource consumption, emissions and wastes generated in the manufacture, utilisation and disposal of a product can be quantified and evaluated.

Löwenstein's rule

A rule that defines the proportion of aluminium in the lattice of zeolites. It states that the Si/Al ratio cannot fall below 1 if the tetrahedral structure is to be maintained.

Mucilages

Gelatinous macroaggregates which may cover large areas of the surface of the sea. They are mainly constituted by detritus, living organisms and inorganic matter (e.g. soil particles) held together via mucous excretion produced by marine organisms.

Non-tower processes
Processes for the manufacture in particular of ***supercompact detergents*** which do not focus on product drying via a spray tower (spray drying), e.g. granulation, extrusion, roller compacting, pelleting, blending and tableting processes.

Oxygen demand
Oxygen consumption for the biological or chemical oxidation of substances in aqueous media.

Phosphate elimination
Removal of phosphates in sewage treatment plants using additional chemicals (e.g. iron/aluminium salts) or through an extra biological process step.

Phosphates
Salts of phosphoric acid, containing PO_4^{3-} as a basic unit. Used as ***builders for detergents***, commonly in the form of sodium triphosphate.

Phytoplankton
Photosynthetic (chlorophyll-containing) free-living microorganisms, mainly algae. Phytoplankton is the primary producer of fixed organic carbon (from CO_2) and thus represents the lowest (but very important) trophic level of the aquatic food chain.

Polycarboxylates
Predominantly maleic acid and acrylic acid based copolymers used in zeolite- and phosphate-based detergents as ***cobuilder***.

Silicates
Amorphous or crystalline substances mainly used as sodium salts for anti-corrosion and as ***builders***.

Silicosis
Progressive fibrosis of the lungs caused by inhalation of dust containing quartz.

Sodium carbonate (soda ash)
Inorganic substance used in detergents in combination with zeolites and designed to serve as source of alkalinity.

Supercompact detergent
Second generation of ***compact detergents*** with an even higher degree of compaction (bulk densities up to approx. 900 g/l).

Surfactants
Organic compounds which lower the surface tension of water (surface active agents) and which are used as key ingredients in all detergents. They are instrumental in removing soils, both fatty and particulate, and in keeping them emulsified, suspended or dispersed. Corresponding to the electric charges, categories of surfactants are called anionic (for example, LAS), nonionic (for example, ethoxylated alcohols), cationic or amphoteric.

Tablet detergents
New generation of supercompact detergents manufactured in tablet form offering easy and controlled dosage for the consumer.

Water softening
Binding of hardness ions (calcium and magnesium) through ion exchange, complexing or precipitation.

Zooplankton
Mobile aquatic microanimals (e.g. daphnia) that feed on ***phytoplankton*** and thus represent the next higher trophic level of the aquatic food chain.

References

[1] T.H. Müller-Kirschbaum, E.J. Smulders, "Facing Future's Challenges - European Laundry Products on the Threshold of the 21st Century", Lecture at the 4th World Conference and Exhibition on Detergents, Montreux (Switzerland), 4-8 October, 1998.

[2] C.P. Kurzendörfer, P. Kuhm, J. Steber, "Zeolites in the Environment", in "Detergents in the Environment" (Ed.: M.J. Schwuger), Marcel Dekker, New York 1997, p. 127.

[3] E. Roland, P. Kleinschmit in Ullmann's Encyclopedia of Industrial Chemistry, Vol. A 28, VCH, Weinheim 1996, p. 475.

[4] C.J. Adams et al., "Zeolite MAP: The New Detergent Zeolite", in "Progress in Zeolite and Microporous Materials", Studies in Surface Science and Catalysis, Vol. 105, Elsevier 1997, p. 1667.

[5] T.J. Osinga, Journal of the 45th SEPAWA-Congress, Bad Dürkheim, 1998, p. 78.

[6] H.G. Hauthal, SÖFW-Journal 122 (1996) 13, 899.

[7] A. Zatta et al., "Zeolite AX - A New Zeolite Builder for Detergents", XXVII. Journadas del Comite Español de la Detergencia, 1997, p. 71.

[8] H. Upadek, B. Kottwitz, B. Schreck, Tenside Surf. Det. 33 (1996) 5, 385.

[9] test (Berlin, Germany) 1989, No. 2, p. 65; ibid. 1989, No. 7, p. 74.

[10] Test Achats magazine (Brussels, Belgium) 1996, No. 386, p.34.

[11] H. Upadek, P. Krings, Seifen-Öle-Fette-Wachse 117 (1991) 15, 554.

[12] Leading international market research institute; information by Henkel KGaA, Düsseldorf, October 1999.

[13] P. Krings, E.J. Smulders, Journal of the 45th SEPAWA-Congress, Bad Dürkheim 1998, p. 70.

[14] G. Wagner, Waschmittel - Chemie und Ökologie, Ernst Klett Verlag, Stuttgart, 2nd Edition, 1997.

[15] "Gesetz über Detergentien in Wasch- und Reinigungsmitteln", BGBl Teil I (1961) S.1653, 5 September 1961.

[16] Council Directive 73/405/EEC of 22 November 1973 on the approximation of the laws of the Member States relating to methods of testing the biodegradability of anionic surfactants.

[17] "Gesetz über die Umweltverträglichkeit von Wasch - und Reinigungsmitteln", BGBl I S.876, new version of 5 March 1987 (first version 1975).

[18] Commission Recommendation 89/542/EEC of 13 September 1989 for the labelling of detergents and cleaning products.

[19] "Verordnung über die Vermeidung und Verwertung von Verpackungsabfällen", new version of 21 August 1998 (first version 1991).

[20] Commission Decision 95/365/EC of 25 July 1995 establishing the ecological criteria for the award of the Community eco-label to laundry detergents.

[21] Commission Recommendation 98/480/EC of 22 July 1998 concerning good environmental practice for household laundry detergents.

[22] Umweltbundesamt (Ed.), Materialien 4/79, "Die Prüfung des Umweltverhaltens von Natrium-Aluminium-Silikat Zeolith A als Phosphatersatzstoff in Wasch- und Reinigungsmitteln", E.Schmidt Verlag, Berlin 1979.

[23] P. Christophliemk, P. Gerike, M. Potokar, "Zeolites", in "Handbook of Environmental Chemistry", Vol. 3, Part F "Detergents" (Ed.: N.T. de Oude), Springer Verlag, Berlin 1992, p. 205.

[24] A. Willing, J. Steber, internal report of Henkel KGaA (Düsseldorf), 16 April 1999.

[25] M. Monti, C. Welker, S.F. Umani, Chemosphere 32 (1996), 1741.

[26] EAWAG (Dübendorf, Switzerland), EAWAG news 42 D, 1996.

[27] W.A. Roland, W. Graupner, W. Holtmann, GWF Wasser/ Abwasser 120 (1979), 55 [cf. also reference 22].

[28] J.E. King, W.D. Hopping, W.F. Holman, J. Water Poll. Control Fed. 52 (1980), 2875.

[29] J. Folke, "Phosphate, Zeolite and Citrate in Detergents - Technical and Environmental Aspects of Detergent Builder Systems", Report No. 95002/06, MFG, Environmental Research Group, Gillelje, Denmark 1996 (commissioned by Kemisk-Tekniska Leverantörförbundet, Stockholm, Sweden).

[30] T.J Osinga, E. Alink, internal report of Crosfield B.V. (Eijsden), 9 March 1994.

[31] P. Kuhm, W. Lortz, in "Zeolites and related Microporous Materials: State of the Art 1992" (Ed.: J. Weitkamp, H.G. Karge, H. Pfeifer, W.Hölderich), Stud. Surf. Sci. Catal. 84 (1994), 2303.

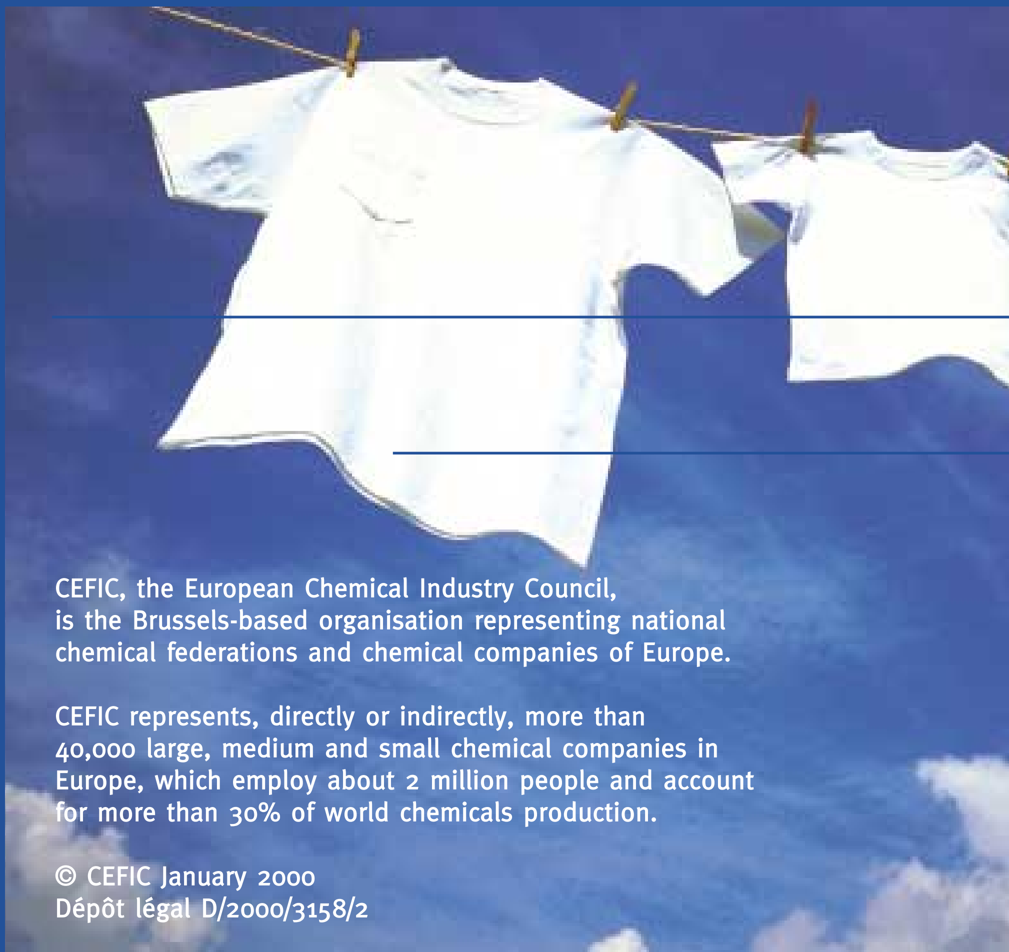
[32] H.R. von Gunten, Ch. Lienert, Nature 364 (1993) 220-222.

[33] M. Fawer, D. Postlethwaite, H.-J. Klüppel, Int. J. LCA 3 (1998) 2, 71.

[34] B. Wilson, B. Jones, The Phosphate Report, Landbank Environmental Research & Consulting, London, 1994.

[35] Ch. Gloxhuber et al., Fd. Chem. Toxic. 21 (1983) 2, 209.

[36] W. Matthies, A. Löhr, H. Ippen, Dermatosen 38 (1990) 6, 184.



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CEFIC

Avenue E. Van Nieuwenhuyse 4, bte 1
B - 1160 Bruxelles
telephone +32 2 676 72 11
fax +32 2 676 73 01
http://www.cefic.org

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