STATE-OF-THE-ART REPORT

Concrete Admixtures and the Environment

6th Edition, December 2016

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PRELIMINARY REMARKS

This sixth, updated edition of the State-of-the-Art Report „Concrete Admixtures and the Environment“ was prepared by Work Group 2.1 “Concrete and Mortar Admixtures and the Environment” (AK 2.1), discussed and adopted by Special Committee 2 “Concrete Technology” (FA 2). The purpose of this State-of-the-Art Report is to provide information to all member companies as well as the interested public.

All documents submitted by the end of October 2016 and the feedback we received from the 5th edition of this State-of-the-Art Report published in May 2011 have been integrated into this report.

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Deutsche Bauchemie e. V. invites you to share your experience and make comments on this State-of-the-Art Report which should be directed to the main office in Frankfurt am Main

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1 IN GENERAL

Published for the first time more than 20 years ago and meanwhile in its 6th edition, this State-of-the-Art Report "Concrete Admixtures and the Environment" issued by Deutsche Bauchemie e. V. has become a standard reference for all experts and interested readers looking for an overview of this topic or answers to specific questions. Regular updates ensure that the information reflects the latest state in a field that is dynamically evolving. In this edition, various innovations have been added, some of the information revised and new developments laid out.

In the wake of the trend towards sustainability, which encompasses all economic areas and the construction industry in particular, the demand for Environmental Product Declarations (EPD) for construction chemicals has increased. To satisfy the demands of interested parties at a reasonable cost for manufacturers and make this information available to customers and users of concrete admixtures, EDP templates for 6 types of concrete admixtures were prepared by Deutsche Bauchemie in the scope of a project. These EPDs, verified by the German Institute for Construction and Environment e.V. (IBU), were made available to the specialist community the end of 2014.
In a cooperation between Deutsche Bauchemie e.V. and EFCA, the European Federation of Concrete Admixtures Associations, these were transferred to the European level. Since the beginning of 2016, generic EPDs for these 6 concrete admixture types are also available for Europe.

Since June 2015, the changes introduced in the scope of the European Regulation on Classification, Labelling and Packaging of Materials and Mixtures (CLP Regulation) and, in conjunction with this, the "Globally Harmonized System of Classification and Labelling of Chemicals (GHS)", now also apply to mixtures. As a consequence, far reaching changes in classification and labelling have resulted for a number of the raw materials and admixtures dealt with in this State-of-the-Art Report. Particularly affected are the formaldehyde based products which had to be reassessed since formaldehyde was classified carcinogenic, category 1B, as of 01.01.2016.

Due to the numerous changes in classifying and labelling products, it was time to revise the classification scheme for concrete admixtures listed in the Information System for Hazardous Substances maintained by the German construction industry trade association (GISBAU). This information, which is tailored for the concerns of this product group (GISCODES), was updated and the classification catalogue based on this information revised. The responsible work safety specialists now have model operating instructions oriented to the latest regulations.

New market requirements regarding the durability of structures and the performance of concrete, today's most important building material, could be fulfilled in essential ways thanks to continued further development of concrete admixtures. This was made possible through continuous investments in research and development by concrete admixture manufacturers. These investments are also a prerequisite for on-going further development and advancement of existing products as well as for introducing new raw materials and products to the market.

These trends and innovations have been included in this revised edition of the State-of-the-Art Report, ensuring that it will remain an important source of information in the years to come for all professionals who deal with this subject.

2 CRITERIA FOR PRODUCT EVALUATION

A number of different product-specific data and information are used as the basis for assessing the compatibility of products for humans and the environment.

They can be divided into three groups:

- Toxicological criteria
- Ecological criteria
- Physical-chemical criteria

2.1 Toxicological Criteria

Toxicological criteria are of central importance for the assessment of products in regard to their health risk for humans.

Whether products lead to a health risk for humans during production, use or disposal essentially depends on the manner of exposure. The extent and nature of the effect always depend on the quantity taken up. In the case of local effects, e.g. irritation of skin or mucous membranes, the concentration of the active substance also plays a role.

When assessing the effect, a distinction is made between acute effects and long-term effects, depending on whether the observed harm occurs after a single or short-term dose or long-term, repeated doses.

A dose can take place orally (by swallowing), dermally (through the skin) or through inhalation (through the respiratory system). To assess a product, data on acute toxicity, toxicity after repeated dose exposure, skin and mucous membrane tolerance and sensitisation potential are used.

Effects that are carcinogenic (cause cancer), reproduction-toxic or mutagenic (change the genetic code) are of special significance.

2.2 Ecological Criteria

To assess the influence of products on the environment, the criteria listed in the following sections are used:

2.2.1 Ecotoxicological Effects

These are mainly understood as chemical effects that may harm organisms and ecosystems. To assess these effects, tests are carried out which evaluate aquatic and/or terrestrial toxicity, i.e. the harmful effect on organisms and ecosystems in water or soil, e.g. fish, daphnia, algae or bacteria as well as organisms in the soil.

2.2.2 Bioaccumulation

Bioaccumulation is understood as the accumulation of substances in organisms and is the result of interaction between dose and excretion of substances by organisms.

Since the consequences of bioaccumulation are not easy to assess, it is an undesired property on principle.

The distribution coefficient octanol/water (log P_{ow}) is an indicator for the potential of a substance to accumulate.

2.2.3 Biological Degradation

The residence time of products in the environment is decisively determined by their biological degradation.
This is desirable on principle and, in the end, should lead to complete mineralisation or degradation of a substance without forming harmful degradation products.
Biological degradability is determined with the aid of various product group-specific test methods related to the degradation process.
A distinction is made between screening tests, tests for inherent biodegradability, sewage treatment plant simulation tests, tests for anaerobic biodegradability and tests for complete degradability.
These tests are typically carried out according to standardised rules such as DIN, ISO or OECD and are internationally recognised.

- Tests for Ready Biodegradability (OECD 301 Series)

In general, screening tests are the first stage in the assessment of biodegradability and normally take 28 days. The degree of degradation is usually determined by DOC or O_2 reduction or by CO_2 development relative to theoretical maximum values. As a rule, complete biological degradability is deemed given if a degree of degradation of approximately 2/3 can be proved via CO_2/O_2/DOC measurement. It is assumed that the remaining 1/3 of the original quantity of the substance was used to form bacterial biomass.
If a mono-constituent substance is degraded by 2/3 within 10 days, it is deemed “readily biodegradable”; if this degree is achieved within 28 days, it is still deemed “biodegradable”. Substances with less than 20 % degradation are deemed “not easily biodegradable” The use of the 10-day window does not apply to surfactants, i.e. these are still deemed “readily biodegradable” if they have reached the 2/3 level to pass the test at 28 days.

- Tests for Inherent Biodegradability (OECD 302 Series)

Substances that do not fulfil the criteria for “ready biodegradability” can be tested for “inherent biodegradability” to find out whether they are at least inherently biodegradable. In these tests, the test substances are tested under conditions that strongly promote degradation. Conventional test methods for this group are the modified Zahn-Wellens test and the SCAS test.

- Sewage Treatment Plant Simulation Tests (OECD 303, 314)

In addition there are also sewage treatment plant simulation tests such as the OECD Confirmatory Test or the Coupled Unit Test which simulate on a laboratory scale the aerobic degradation conditions found in the biological stage of sewage treatment plants. Depending on regulatory requirements (e.g. biocides, REACH), these tests are either still very important today or no longer have any regulatory significance. The same applies to anaerobic tests or tests for anaerobic degradation.

- Tests for Complete Biological Degradability

To assess the ultimate biological degradation of substances in the environment that are not “readily biodegradable”, higher tier simulation tests are normally used today to prove biodegradation in water (OECD 309), in water sediment (OECD 308) or in soil (OECD 307). In these tests, not only are half-life periods (T1/2) determined for biological degradation of the parent substance, the resulting degradation products (metabolites) are also identified and quantified.
Based on the results of degradation behaviour as well as a metabolite profile, direct statements on degradation behaviour (“persistence behaviour”) of the substance in the environment can be made.

2.3 Water Hazard Classes

To protect aquatic environments from becoming polluted through the release of substances that are hazardous to water, Germany assigns substances to water hazard classes.

There are 3 classes:

WGK 1: Low hazard to waters
WGK 2: Hazard to waters
WGK 3: Severe hazard to waters

Substances assigned to the three water hazard classes are listed in the Annexes of the German “General Administrative Regulation on the Classification of Substances Hazardous to Waters” (VwVwS) and their amendments. Along with the three water hazard classes, VwVwS also has a list of substances that are not hazardous to water (nwg). VwVwS as well as the respective Annexes are published by the German Federal Environment Office (UBA).

To determine the water hazard class of a substance, three main criteria are taken into account:

- acute toxicity to mammals (oral/dermal)
- acute toxicity to water organisms
- biological degradability and bioaccumulation potential

Data on carcinogenic, teratogenic as well as mutagenic effects are also drawn upon when classifying.

The classification of a substance is determined in Germany by the Commission for the Evaluation of Substances Hazardous to Water” (KBwS) upon application. The classification of mixtures can be assigned by the manufacturer based on a rule for mixtures set out in Annex 4 of VwVwS.

Plans have been made to replace VwVwS with the “Administrative Regulation on Facilities for Handling Substances Hazardous to Waters” (AwSV).

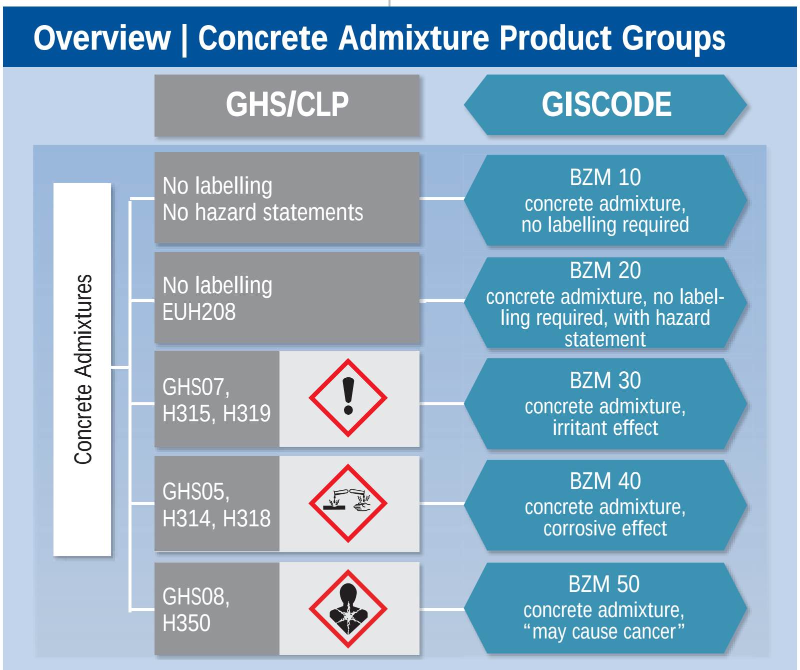
2.4 Physical - Chemical Criteria

A basic requirement for using products safely is a thorough understanding of their physical-chemical properties. As a rule, only a few parameters are of central importance. The most important are water solubility, vapour pressure, flash point and, if applicable, explosive or fire promoting properties. Information on this is given in the Safety Data Sheets for the products.

If necessary, safety rules for handling the products, notes on measures to be taken for transport and storage, limit values for exposure as well as rules for processing and application can be derived from the many evaluation criteria listed here. These are specified according to national and international laws, regulations and directives.

2.5 German Information System for Hazardous Substances (GISBAU)

To support its member companies, the German construction industry trade association (BG Bau) has created an information system that provides comprehensive information on hazardous substances to companies, relieving them of many of their duties to investigate, supervise and instruct. Product information and model operating instructions are at the heart of this system.



In cooperation with the manufacturers of concrete admixtures, product group information that takes the concerns of concrete admixtures into account were revised and brought up to date. Concrete admixtures are divided into five product groups, each with a specific code:

The code is stated in the information provided by the manufacturer and affixed to the packaging label which allows the user to clearly assign products to the respective GISCODE.
With this system, information can be provided on the protective measures to be taken for a number of products based on just a few product groups. The statements refer to the pure product.

Concrete admixture manufacturers provide GISBAU with necessary product information for this.

2.6 Hygiene, Health and Environmental Protection

In the European Union, the Construction Product Regulation forms the basis for general assessment of fitness for use of construction products. It defines a number of "basic requirements for construction works" to which the product assessment must be oriented as the basis for placing construction products on the market. Along with structural stability, safety in use, fire protection and several other requirements, "hygiene, health and environmental protection" are also set out as an essential basic requirement for buildings.

In 2005, the European Commission gave the European Committee for Standardization (CEN) mandate M/366 to harmonise the test standards for hazardous substances. By autumn 2016, the harmonisation project had produced three technical specifications. CEN/TS 16637-2:2014 describes the leaching procedure for evaluating the release of hazardous substances from monolithic, plate formed or sheet-like construction products. CEN/TS 16637-3:2016 is the "Horizontal Up-flow Percolation Test" for evaluating the release of hazardous substances from granular construction products. CEN/TS 16516:2013 deals with the release of volatile organic compounds (VOC) from construction products into indoor air.

In Germany, the Institute for Construction Technology (DIBt) has drawn up principles for evaluating the effects of construction products on soil and ground water as well as their effects on indoor air and living quality. DIBt has used these evaluation schemes so far when issuing National Technical Approvals for construction products.

However, the German approval system will change decisively in the future because the European Court of Justice adjudicated on October 16, 2014, Case C-100/13, that the additional requirements Germany places on CE marked construction products constitute a violation against the Construction Product Directive.

So authorities plan to completely abolish part 1 of the Construction Product List and other additional requirements on harmonised construction products in other regulations. Requirements still deemed necessary at the national level are to be specified at the construction works level (construction-related requirements). To achieve this, requirements set out in § 3 Model Building Code (MBO), including those in regard to environmental protection, are to be specified in a new, administrative rule “Technical Building Rules (VV TB). In regard to the environmental compatibility of construction products, DIBt has presented two drafts, one titled “Requirements on Construction Works Regarding Effects on Soil and Water (ABuG)” and the other “Requirements on Construction Works Regarding Health Protection (ABG)”.

2.6.1 Soil and Ground Water

Quite a while ago, under the auspices of the Institute for Construction Technology (DIBt), “Principles for Assessing the Effects of Construction Products on Soil and Ground Water” (May 2009) was compiled in an interdepartmental project group in cooperation with a number of interested parties, including Deutsche Bauchemie.

Up until now, these principles have been applied by DIBt when issuing National Technical Approvals. When the intended, new administrative rule “Technical Building Rules” (VV TB), “Requirements on Construction Works Regarding Effects on Soil and Water (ABuG)” is introduced, it will replace these old principles.

In Germany, no test is required for the assessment of effects of concrete on soil and ground water when standardised raw materials are used which are deemed a priori safe or for which environmental compatibility has already been proved by a National Technical Approval (e.g. according to “Principles for Assessing the Effects of Construction Products on Soil and Ground Water” (May 2009). Concrete admixtures according to EN 934 are deemed a priori safe. This was clearly explained by the German Committee for Structural Concrete (DAfStb). This explanation can be downloaded in German from DAfStb’s website.

2.6.2 Indoor Air

Increased awareness among the population regarding environmental and health issues during the past years has increasingly directed the attention of specialists to emission behaviour of construction products.

To assess the emission behaviour of construction products in regard to volatile organic compounds (VOC), DIBt has presented a draft titled “Requirements on Construction Works Regarding Health Protection (ABG)” in which the test and assessment of emission behaviour is governed in general. Further information on the AgBB concept [German Committee for Health-Related Evaluation of Emissions of Volatile Organic Compounds] used so far and other rules on which the drafts are based are found in Deutsche Bauchemie’s State-of-the-Art Report “Gesunde Innenraumluft mit modernen Bauprodukten”.

2.7 REACH

REACH is the European legislation on chemicals and has been in force since June 1, 2007. It governs the registration, evaluation (assessment), authorisation (approval and restriction) of chemical substances. The regulation has the goal of ensuring a high level of protection for human health and the environment. At the heart of REACH lies the obligation to register all chemical substances produced in or imported into the EU in a quantity as of 1 tonne/year with the European Chemicals Agency, ECHA.

To register, the manufacturer/importer must present an extensive dossier that contains basic data for assessing environment and health relevant properties of the substances. What is new is that the substances are not seen isolated; instead, an assessment in regard to the use of the substances takes place – and that over their entire life cycle. This takes place in steps within the scope of registering the substances. Since December 1, 2009, all chemicals that are produced in the EU or are imported into the EU that fall under REACH must be pre-registered with ECHA; otherwise they may no longer be used. Full registration of relevant substances then takes place between 2010 and 2018, depending on hazard potential and the quantities produced or imported. Preparations or mixtures (concrete admixtures) themselves are not registered, only the chemical substances they contain. The main responsibility and the central tasks lie with the manufacturers and importers of these (basic) chemical substances.

Under REACH the Safety Data Sheet is still the central instrument for information. New is that after final registration the Safety Data Sheet may contain an annex – a so-called exposure scenario. These exposure scenarios contain the basic conditions for safe use and, if applicable, protective measures. During the period until 2018, the Safety Data Sheets will be successively revised, if required, and the latest version passed on to customers.

The use of a chemical product (concrete/mortar admixtures) is then safe if the user observes the conditions (which, if applicable, are stated in an exposure scenario) given in the Safety Data Sheet. If the commercial user observes the protective measures and conditions for use stated in the Safety Data Sheet and, if applicable, in the enclosed exposure scenario, he has no further obligations under REACH.

If a customer in the construction chemical industry (user, downstream user) discovers that the protective measures and conditions for use stipulated in the Safety Data Sheet cannot be implemented in practice, this must be discussed with the manufacturer of the product and together they must find a solution. The same applies if the customer's use deviates from the stated use. The manufacturer of the product must then examine whether the deviating use can be authorised by observing further conditions, if applicable, or must be prohibited.

2.8 Environmental Product Declarations for Construction Products

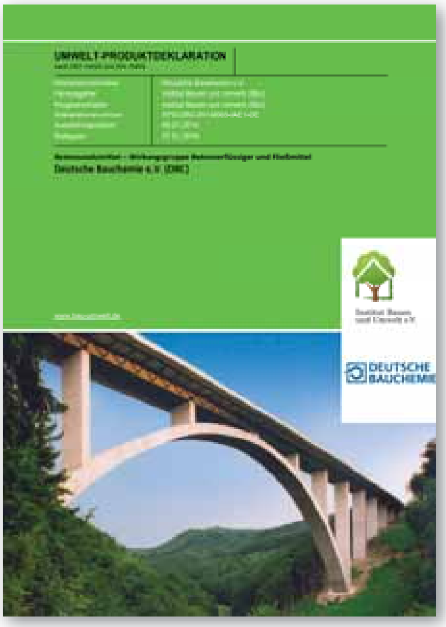
Most construction products are used together with many other products to produce a building or structure. Environmental Product Declarations (EPD) for individual construction products are useful for ecological evaluation as well as for assessment and evaluation of their sustainability.

The Construction Product Regulation, which has been in force since July 2013, contains an additional basic requirement, No. 7 “Sustainable Use of Natural Resources”. An option for implementing these requirements is to use the EPDs according to EN 15804 as an element in a harmonised procedure for evaluating sustainable construction.

In an extensive, overall project, a number of model environmental product declarations for types of concrete admixtures were prepared by Deutsche Bauchemie which have been certified by Institut für Bauen und Umwelt [German Institute for Construction and Environment] (IBU). These model environmental product declarations can be downloaded from the DBC website.
(http://bauchemie.vci.de/wiki/DBC_Muster-EPDs/Seiten/Betonzusatzmittel.aspx)

As a result of a joint project between the European Federation of Concrete Admixtures (EFCA) and Deutsche Bauchemie, there are now also European model environmental product declarations for concrete admixture types that have been certified by the Institut für Bauen und Umwelt (IBU). These model EPDs can be downloaded from the EFCA homepage. (http://www.efca.info/efcapublications/environmental/)

You will also find further information on this subject in Deutsche Bauchemie’s Information Script “Environmental Product Declarations for Construction Chemicals” (1st Edition, June 2015).



3 CONCRETE PLASTICIZERS AND SUPER PLASTICIZERS

Concrete plasticizers (BV) must correspond to the common requirements set out in EN 934-1 and the specific requirements in EN 934-2, Table 2.

A concrete plasticizer is defined in EN 934-2 as:

„An admixture that allows the water content of a specific concrete mixture to be reduced without impairing its consistence or to increase its slump without changing the water content or to achieve both effects at the same time.“

Super plasticizers (FM) must correspond to the common requirements set out in EN 934-1 and the specific requirements in EN 934-2, Table 3.1/3.2.

A super plasticizer is defined in EN 934-2 as:

„An admixture that allows the water content of a specific concrete mixture to be considerably reduced without impairing its consistence or to considerably increase its slump/flow without changing the water content or to achieve both effects at the same time.“

There are also super plasticizers that are tested according to Tables 11.1/11.2 in EN 934-2 which are defined as:

„An admixture that has the combined effects of a super plasticizer (primary function) and a retarder (secondary function).“

These are the product groups that may be used in Germany as concrete plasticizers and super plasticizers. However, EN 934-2 also recognises two further multi-functional type admixtures.

Admixtures according to Table 10, “admixtures that have the combined effects of a concrete plasticizer (primary function) and a retarder (secondary function)” may only be used in Germany if they have received an approval for use issued by the German Institute for Construction Technology (DIBt). Concrete admixtures according to Table 12, “admixtures that have the combined effects of a concrete plasticizer (primary function) and a set accelerator (secondary function)” are found on the market in other countries but their use in Germany is presently not approved.

3.1 Raw Materials for Concrete Plasticizers and Super Plasticizers

The raw materials essentially used in Germany for concrete plasticizers (BV) and super plasticizers (FM) are:

- Lignosulphonates, Na, Ca, Mg salts
- Melamine sulphonates, Na salts
- Naphthalene sulphonates, Na, Ca salts
- Polycarboxylate(s)/polycarboxylether, Na salts

These raw materials are used either in the form of aqueous solutions or powders and they are free of organic solvents. According to GHS criteria, classification or labelling of lignosulphonates and polycarboxylate(s)/polycarboxylether as such is not mandatory.

Polycondensation products of melamine and naphthalene normally contain slight amounts of free formaldehyde due to production processes.

According to GHS criteria, classification or labelling of products with a free formaldehyde content < 0.1 % is not mandatory.

Due to the hazardous substance classification of formaldehyde as of 01.01.2016, products with a free formaldehyde content ≥ 0.1 and < 0.2 % must be labelled with the hazard statement H 350 “May cause cancer” as well as EUH 208 “May cause allergic reactions. Contains: FORMALDEHYDE” in accordance with GHS (Regulation (EC) No 1272/2008).

To ensure safe handling of these products, the applicable rules for health protection at the workplace should be observed.

Products that contain ≥ 0.2 % of free formaldehyde are normally no longer on the market.

3.1.1 Lignosulphonates

Lignin is a complex, highly polymeric, natural substance which, along with cellulose, is the main constituent of wood. It is separated from cellulose by hydrolysis and sulphonation. The resulting lignosulphonates can therefore be considered a modified natural product. Very uniform qualities are available for concrete technology today.

Lignosulphonates are deemed safe from a toxicological standpoint. This has been verified by the results from acute and sub-acute toxicity studies on different species, administered orally.

Irritating effects on the skin and eyes of rabbits have not been observed. Genetic code changing properties were not determined in short-term tests (AMES test: negative).

In eco-toxicological studies on different species of fish and aquatic organisms, lignosulphonates do not cause any harm.

Lignosulphonates are inherently biodegradable. The material may neither be directly led into sewage outfall drains nor directly discharged into aquatic environments or the sewer system. Lignosulphonates are classified Water Hazard Class 1: low hazard to waters (Annex 4 of VwVwS).

Because lignosulphonate is easily soluble in water and has a low n-octanol/water distribution coefficient, bioaccumulation can be ruled out.

Lignosulphonates are also used as a pelletizing aid in the feed industry. Because of their physiological properties, lignosulphonates are officially approved for feed (EEC-No.: E 565) according to the [German] Feed Law from July 2, 1975 (German Law Gazette I, pp 1745-1753) – amended by the first act on the Amendment of the Feed Law from January 12, 1987 – German Law Gazette I pp. 138-140.

3.1.2 Melamine Sulphonates

These are sulphite-modified, melamine-formaldehyde condensation products. These raw materials are especially suitable for flowing concrete and are distinguished by their good compatibility with cement.

According to GHS criteria, classification or labelling of products with a free formaldehyde content < 0.1 % is not mandatory.

Due to the hazardous substance classification of formaldehyde as of 01.01.2016, products with a free formaldehyde content ≥ 0.1 and < 0.2 % must be labelled with the hazard statement H 350 "May cause cancer" as well as EUH 208 "May cause allergic reactions. Contains: FORMALDEHYDE" in accordance with GHS (Regulation (EC) No 1272/2008).

To ensure safe handling of these products, the applicable rules for health protection at the workplace should be observed.

Products that contain ≥ 0.2 % of free formaldehyde are normally no longer on the market.

On the basis of presently available data on acute toxicity, melamine sulphonates are considered virtually non-toxic after a single oral intake. Even with longer term oral administration (28 days), melamine sulphonates have proved to be only slightly toxic.

Person-related measurements have shown that when melamine sulphonates subject to labelling are used for the intended purpose and properly handled, the formaldehyde concentration is generally clearly below the workplace exposure limit value. However, this should always be verified by measuring in regular intervals.

The chemical structure of melamine sulphonates does not give any indication that they may have a toxic effect on reproduction or development.

In all probability, melamine sulphonates are not acutely harmful for aquatic organisms.

They do not fulfil the criteria for being readily biodegradable and may neither be directly led into sewage outfall drains nor discharged directly into aquatic environments or the sewer system.

Melamine sulphonates are classified Water Hazard Class 1: low hazard to waters (Annex 4 VwVwS).

Melamine sulphonates does not fulfil the criteria for PBT (persistent/bioaccumulative/toxic) or vPvB (very persistent/very bioaccumulative).

Water soluble melamine sulphonates are predominately used for mineral building materials.

3.1.3 Naphthalene Sulphonates

Naphthalene is produced during dry distillation of bituminous coal due to a decomposition reaction. Through sulphonation of naphthalene and conversion with formaldehyde, a sulphonated naphthalene condensation product results. In concrete technology, naphthalene sulphonates have been used since approximately 1930 to plasticize concrete. Today, especially medium and high molecular naphthalene sulphonates are used as super plasticizers.

Due to the hazardous substance classification of formaldehyde as of 01.01.2016, products with a free formaldehyde content ≥ 0.1 and < 0.2 % must be labelled with hazard statement H 350 "May cause cancer" as well as EUH 208 "May cause allergic reactions. Contains: FORMALDEHYDE" in accordance with GHS (Regulation (EC) No 1272/2008).

To ensure safe handling of these products, the applicable rules for health protection at the workplace should be observed.

Only products with a free formaldehyde content < 0.1 % are found on the German market. According to GHS (Regulation (EC) No 1272/2008), classification and labelling of these products is not mandatory.

As far as acute toxicity is concerned, naphthalene sulphonates are deemed safe.

Irritating effects on the skin and eyes of rabbits have not been observed.

Previous studies have shown that acute toxicity for bacteria and fish is so low that classification and/or labelling according to GHS criteria is not mandatory. Genetic code changing properties were not determined in short-term tests (AMES test: negative).

Naphthalene sulphonates do not fulfil criteria for being readily biodegradable. They may neither be directly led into sewage outfall drains nor discharged directly into aquatic environments or the sewer system.

Naphthalene sulphonates are classified Water Hazard Class 1: low hazard to waters (Annex 4 VwVwS). Because naphthalene sulphonates are easily soluble in water and have a low n-octanol / water distribution coefficient, bioaccumulation can be ruled out.

Naphthalene sulphonates are used as accompanying and auxiliary agents in the textile and leather goods industry. They are also used on a large scale for dispersing solid matter sludge (flotation processes).

3.1.4 Polycarboxylate(s) / Polycarboxylether (PCE)

As a rule, water soluble polycarboxylate(s) / polycarboxylic ether are used in their sodium salt form as a raw material for concrete plasticizers and super plasticizers. They are derived from unsaturated organic carboxylic acids.

Normally, polymerisation products from acrylates and maleinates as well as different derivatives of these with polyalkylene glycol ethers are used in concrete admixtures.

Experiments on rats and rabbits (oral and dermal administration) have proved that the polycarboxylate / polycarboxylic ether normally used for the production of concrete admixtures is not acutely toxic. Skin and mucous membrane irritation may occur with acrylates; maleinates and polycarboxylic ether are described as „non-irritant“. Classification or labelling of these raw materials is not mandatory according to GHS criteria.

The biodegradability of polycarboxylate/polycarboxylic ethers ranges from not readily biodegradable to poorly biodegradable. They may neither be directly led into sewage outfall drains nor discharged directly into aquatic environments or the sewer system. Polycarboxylate/polycarboxylic ether is classified Water Hazard Class 1: low hazard to waters (Annex 4 VwVwS).

Polycarboxylates have been used as dispersing agents in the paint industry for decades. For many years now, they have also been widely used as an aid in the detergent area as a so-called “builder“.

3.2 Auxiliary Agents and Additives for Plasticizers and Super Plasticizers

Concrete admixtures may also contain preservatives and de-foaming agents, usually in a range of up to 0.5 %.

The main task of de-foaming agents is to limit the introduction/stabilisation of air voids in concrete while being mixed. This is necessary, not only in regard to the desired strength of the concrete but also in regard to the surface quality of the concrete elements. De-foaming agents also prevent excessive foam formation when admixtures are filled into containers and when the admixture is added to the concrete.

Preservatives protect an admixture from biological infestation. Under normal conditions they ensure that the admixture remains stable during storage and has a shelf-life of months to years.

When assessing the concrete admixture from a toxicological and eco-toxicological standpoint, the low concentration of these additives must also be taken into account.

An example: a super plasticizer that contains 0.5 % by mass de-foaming agent.
If this super plasticizer is added to concrete of strength class C 30/37 with 300 kg cement/m³ in a quantity of 1.0 % by mass relative to the cement, the hardened concrete then contains 6 ppm de-foaming agent.

3.2.1 De-Foaming Agents

Tri-iso-butylphosphate and other surface-active, organic compounds are used as de-foaming agents. Tri-n-butylphosphate is no longer used in concrete admixtures because of its hazard classification.

Based on the toxicological findings presently available on acute toxicity for animals, tri-iso-butylphosphate is slightly toxic (LD50 rat oral > 5000 mg/kg body weight; LD50 rabbit dermal > 5000 mg/kg body weight). Tri-iso-butylphosphate is not or only moderately irritant to the skin and eyes of rabbits. A neuro-toxic effect was not observed in animals.

Tri-iso-butylphosphate is classified as skin sensitising (Skin Sens. 1B) according to regulation (EC) No. 1272/2008 [CLP] and must be labelled H317 "May cause allergic skin reactions". Eco-toxicologically, tri-iso-butylphosphate is classified Water Hazard Class 1: low hazard to waters (self-assessment according to VwVwS). According to regulation (EC) No. 1272/2008 [CLP], labels of concrete admixtures with a content of 0.1 to < 1 % tri-iso-butylphosphate must contain the statement "EUH 208: May cause allergic reactions. Contains: TRIISOBUTYL PHOSPHATE".

Other types of de-foaming agents are based, for example, on EO/PO – block polymers, ethoxylated alcohols or aliphatic fatty acids. Experiments on rats (oral administration) have proved that these types of de-foaming agents are generally not acutely toxic. Irritation of skin and mucous membranes may occur.

Polydimethyl siloxane has a slightly irritant effect on mucous membranes; a teratogenic effect could not be completely ruled out. It has no influence on the immune system. Skin resorption does not take place. Due to the diversity of de-foaming agents, a generally valid statement regarding water hazard class cannot be given.

3.2.2 Preservatives

Preservatives are added to concrete admixtures to protect them from infection with micro-organisms (bacteria, mould, yeast) during storage and transport.

This ensures the quality and functionality of liquid additives until their final use in concrete.

Because of the low concentration in which they are used and their degradation to harmless daughter products in fresh concrete, the content of biocide substances in hardened concrete is negligible or not detectable by analytical means.

The placement of preservatives on the market today is governed by Regulation EU No. 528/2012 (Biocidal Product Regulation, BPR), which has been in force since September1, 2013, replacing the Biocidal Products Directive (BPD, RL 98/8/EC).

Preservatives and their active substances are subject to a strict approval procedure based on a harmonised evaluation of health related and eco-toxicological properties. Comprehensive testing of the biocide substances found on the market is presently being carried out at EU level in accordance with the Biocidal Product Regulation (BPR). If the evaluation by the Biocidal Products Committee (BPC) is positive, the substances will be added to the so-called Union list of approved active substances (formerly Annex II of the BPD) which can be viewed on the ECHA website. Once an active substance has successfully gone through the evaluation procedure, biocidal products (formulations, preparations) that contain the registered active substances must be approved within a period of 2 years. The approval of the biocidal products can take place at the national level by the designated authorities – in Germany e.g. by the Federal Institute for Occupational Safety and Health (BAuA, Dortmund) – or, more recently, directly at EU level through the newly introduced Union approval procedure.

To preserve concrete admixtures, preparations based on the following groups of substances are mainly used:

- Compounds that give off formaldehyde
- Isothiazolinones
- Bronopol
- Phenolic compounds

In terms of quantity, the market is dominated by preservatives based on compounds that split off formaldehyde. Since January 2016, these effective and proved preservatives must be classified and labelled carcinogenic (Category 1B) and mutagenic (Category 2) when used. Labelling is not mandatory for biocidal products that split off formaldehyde if the quantity of free formaldehyde in the formulated products is below 0.1 % (1000 ppm).

As long as this limit value is observed, it will be possible to use biocidal products that split off formaldehyde in the future as well.

Concentrations for use are approximately 0.1 to 0.2 % by mass of the preservative that contains the formaldehyde depot substance relative to the concrete admixture to be protected.

Certain formaldehyde splitters (e.g. benzylhemiformal, tetramethylol acetylenediurea, (ethylendioxy) dimethanol) have already been evaluated in Germany or at EU level in regard to their toxicity and use for certain purposes. They have, for example, a positive assessment from the Federal Institute for Risk Assessment (BfR) for use as a preservative for raw materials that are suitable for the production of paper that comes in contact with food (Recommendation List XXXVI) and some have also been approved for preserving cosmetics. However, the final evaluation of formaldehyde splitters according to the Biocidal Product Regulation (BPR) has not yet been concluded and a statement on the future usability of individual representatives from this product group is currently not possible.

Preservatives based on isothiazolinones are another important active substance group used for the production of biocidal products to preserve liquid concrete admixtures.

Important representatives of this substance class are methylchloroisothiazolinone / methylisothiazolinone (CMIT/MIT) mixtures, benzisothiazolinone (BIT), methylisothiazolione (MIT) as well as N-octylisothiazolinone (OIT) which is sometimes added as a fungicidal component.

As a rule, commercially available preservatives on a methylchloroisothiazolinone / methylisothiazolinone base have an active substance content of 0.5 to 1.5 %. Only small quantities of these highly effective products, ranging between 0.02 to 0.2 % by mass, are needed to preserve concrete admixtures.

The content of the pure active substance in the concrete admixture is thus just a few ppm.

When products are used that have been formulated with methylchloroisothiazolinone / methylisothiazolinone, they must be labelled “May cause allergic skin reactions” (H 317) if the concentration of the effective substance is 15 ppm or higher. Up to this maximum amount, preservatives on a CMIT/MIT base have also been approved for preserving cosmetics. Methylchlorothiazolinone / methylisothiazolinone mixtures are also listed in BfR Recommendations XIV (plastic dispersions) and XXXVI (paper, paperboard and cardboard for contact with food).

When preservatives on a benzisothiazolinone (BIT) base are used, the labelling threshold for “May cause allergic skin reactions” (H 317) begins as of a content of 500 ppm active substance in the product to be preserved. With a commercially available, 20 % benzisothiazolinone preparation, for example, the maximum possible quantity that can be used without labelling is thus 0.249 %.

In recent years, a mixture of benzisothiazolinone/methylisothiazolinone has been widely used for in-can preservation. Compared with a conventional methylchlorothiazolinone/methylisothiazolinone preparation, this new combination has the advantage of having a less sensitising effect and therefore greater possibilities for use without labelling.

The use of BIT/MIT based biocidal products was released for BfR Recommendations XIV (plastic dispersions) and XXXVI (paper, paperboard and cardboard for contact with food).

When recommended concentrations for use are observed, n-octylisothiazolinone, which is used as a fungicidal component, is normally clearly below the labelling limit of 500 ppm for this substance in regard to skin sensitization (H 317).

A new regulatory rule in force since June 1, 2015 concerning the use of all isothiazolinones is the EUH 208 statement ("Contains: >substance<. May cause allergic reactions"). This is to inform persons who are especially sensitive that the contents contain substances with a sensitising effect.

The following limit values apply for isothiazolinones in regard to the EUH 208 statement:

- CMIT/MIT as of 1.5 ppm
- BIT as of 50 ppm
- MIT as of 100 ppm
- OIT as of 50 ppm

The EUH 208 statement must be affixed to the containers if the specified limit value is exceeded.

Bronopol, which was originally developed for preserving cosmetics, has increasingly been used in recent years to preserve technical products because it can be easily combined with isothiazolinones (particularly CMIT/MIT).

Along with use in cosmetics, Bronopol is also listed in the BfR Recommendations XIV and XXXVI mentioned above.

Bronopol has been awarded the „Blue Angel" environmental sign according to RAL UZ 102 for coatings and paints that are used in indoor areas.

Phenolic compounds are another group of active substances that are of interest. This class of products has little oral or dermal toxicity as a rule and the compounds are not mutagenic. A risk of sensitisation by these products is not given in the recommended concentrations for use or, at the most, is rated very low.

Important representatives of this class of substances are o-phenylphenol and p-chloro-m-cresol.

Both of these active substances are listed in BfR Recommendation XIV (plastic dispersions) and o-phenylphenol is also listed in BfR Recommendation XXXVI (paper, paperboard and cardboard for contact with food). Within certain concentration limits, both products are also approved for preserving cosmetics.

To optimise the efficacy of biocidal products, products are often produced that use combinations of the basic substances listed here.

3.3 Concrete Plasticizers and Super Plasticizers as Concrete Admixtures

Concrete plasticizers and super plasticizers mainly contain lignosulphonates, naphthalene sulphonates, melamine sulphonates or polycarboxylates / polycarboxylic ether or mixtures of these. De-foaming agents and preservatives are added as accompanying and auxiliary agents.

The concrete plasticizers and super plasticizers on the market are in liquid form as a rule. The active substance concentration ranges between 10 and 40 % by mass. The quantity of concrete plasticizer added usually ranges between 0.2 and 0.5 % by mass and for super plasticizers between 0.4 and 2.0 % by mass relative to cement.

The preparations of concrete plasticizers and super plasticizers normally found on the German market with a free formaldehyde content < 0.1 % do not need to be classified or labelled according to GHS criteria.

Formulations with free formaldehyde contents ≥ 0.1 and < 0.2 % must be labelled with hazard statement H 350 “May cause cancer” as well as EUH 208 “May cause allergic reactions. Contains: FORMALDEHYDE” in accordance with GHS (Regulation (EC) No. 1272/2008). Applicable regulations on safety and health at the workplace should be observed when handling these products.

Concrete plasticizers and super plasticizers do not fulfil the criteria for ready biodegradability.

These admixtures may neither be directly led into sewer outfall drains nor discharged directly into aquatic environments or the sewer system. They are classified Water Hazard Class 1: low hazard to waters (Annex 4 of VwVwS).

3.4 Concrete Plasticizers and Super Plasticizers in Concrete

As previously stated above, concrete plasticizers are usually added to concrete in quantities of 0.2 to 0.5 % by mass and super plasticizers in quantities of 0.4 to 2.0 % by mass. This means that the admixture content in concrete is very low. Here an example: When a super plasticizer in a 40 % solution is added in a quantity of 2.0 % by mass relative to cement, the hardened concrete contains only 0.1 % of the active substance.

According to the state of our knowledge today, the raw materials normally used for concrete plasticizers and super plasticizers are adsorbed at the cement particle/water interface shortly after the admixture is added to the concrete. As a result, the concentration of the active substances is quickly reduced in the aqueous phase.

Adsorption studies with calcium lignosulphonate, sodium melamine sulphonate and sodium naphthalene sulphonate have shown that these active substances are bound into the cement paste matrix to more than 90 % within seven days.

Analyses of pore water pressed out of 28 day old cement paste under high pressure (up to 5000 bar) confirm the results of the adsorption studies. After a hydration period of 28 days, the concentration determined in the pore water shows that for calcium lignosulphonate, for example, 95 % of the active substance is adsorbed by the cement.

When evaluating the environmental compatibility of concrete that has been produced with admixtures and its ability to be recycled, what is important is not its adsorption behaviour but whether substances in the admixture could possibly be released. Since concrete admixtures are substances that are less volatile in general, it can be assumed that substances which, due to chemical equilibrium, are present in small quantities dissolved in the pore water of the cement paste will essentially only be given off into the environment through diffusion processes in the liquid phase.

Elution studies on uncrushed cement paste cylinders (w/c = 0.40, diameter and height 100 mm) in a trough test have shown that only less than 0.5 % of the active substance quantities used were leached out within 24 hours. With further progress of time, the release rate decreased even more. Consequently, diffusion processes in exterior building elements with a normal moisture content only lead to very low leaching rates. According to newer studies, only monomer compounds are essentially leached out in the case of naphthalene sulphonates. The higher condensed compounds, which represent the greater part of concrete admixtures, remain immobilised. Leaching is not possible on dry, interior building elements.

Accordingly, tests for the suitability of concrete plasticizers and super plasticizers for the construction of drinking water facilities have produced the following results:

a) The United States Environmental Protection Agency (EPA) states that the addition of 4.5 % by mass Melment L 10/20 % of cement weight in concrete that comes in contact with drinking water is safe.

b) Tests according to Belgian standard NBNS 29.004 on mortar prisms with 2 % by mass Melment L 10/20 % showed that cement, fly ash and the super plasticizer Melment L 10/20 % fulfil the requirements of the standard and can be used for lining reservoirs that are used for long-term storage of drinking water since the amounts of leached formaldehyde and melamine sulphonate lie clearly below the limit values of this standard.

c) Tests on melamine sulphonate, naphthalene sulphonate and sodium lignosulphonate solutions according to DVGW [German Gas and Water Trade Association] Worksheet W270 and W 347 showed that they fulfil the requirements for use in drinking water reservoirs and for reservoir linings.

To assess the question concerning possible emissions of substances in gas form from concrete that contains concrete admixtures, there are a good number of examination results related to practice:

a) In the examination of a composite slab produced with a bonding layer that contained Melment and a repair mortar containing Melment, a formaldehyde concentration of 0.01 ppm was determined in the 1 m³ chamber which corresponds to the blank value of the chamber. Therefore, the examined composite slab can be designated as practically free of formaldehyde emissions.

b) When examining 28 day old concrete slabs that were produced with the maximum permissible quantity of 32 ml/kg cement Melment L 10/20 %, a formaldehyde concentration of 0.03 ppm was determined in the 1 m³ chamber after a testing period of 120 hours. The emission of ammonia from this concrete slab in the 1 m³ chamber was measured at 0.02 ppm. To evaluate the emission of ammonia, 1/20 of the MAK value is recommended as a guide value, i.e. 2.5 ppm (recommendation by experts, special expert opinion 1987). The determined emission of ammonia lies clearly below this evaluation standard.
   Two year old concrete slabs with a comparable Melment content showed a formaldehyde concentration of 0.01 ppm after testing for 192 hours. After 28 days under the same conditions, naphthalene sulphonate (40 % solution) in a quantity of 14 ml/kg cement showed a formaldehyde concentration of 0.01 ppm.
   These formaldehyde concentrations lie clearly below the guide value recommended by BfR for interior spaces with a room air formaldehyde concentration of 0.1 ppm and also the value specified for wood materials of 0.1 ppm according to the [German] Chemical Prohibition Regulation (ChemVerbotsV) § 9 (3).

c) In addition to testing hardened concrete slabs in the 1 m³ test chamber, formaldehyde emission from fresh concrete with super plasticizers that contained naphthalene and melamine sulphonates was measured under practical conditions at building sites, in ready-mix concrete works, pre-cast concrete works and in a concrete engineering laboratory according to TRGS 402 [Technical Regulations for Hazardous Substances].

   In summary, these examinations show formaldehyde emissions in a range from non-measurable to 0.0245 mg/m³ air. They were therefore clearly below the occupatioal exposure limit value of 0.3 ppm or 0.37 mg/m³ in all cases.

Based on these results, it can be assumed from our state of knowledge today that concrete made with plasticizers or super plasticizers does not present a hazard to humans or the environment through the release of volatile substances.

4 RETARDERS

Retarders (VZ) must correspond to the common requirements set out in EN 934-1 and the specific requirements in EN 934-2, Table 8.

A retarder is defined in EN 943-2 as follows:

„An admixture that increases the time of a concrete mixture's transition from the plastic to the solid state".

4.1 Raw Materials for Retarders

The raw materials most often used in Germany for retarders are:

- Sucrose
- Gluconates
- Phosphates
- Lignosulphonates
- Dextrins
- Vinasse/molasses

All of these raw materials are used either in powder form or as aqueous solutions.

4.1.1 Sucrose

Depending on origin, sucrose is normal cane or beet sugar that is used to sweeten foods in households and therefore not regarded as a hazardous substance. However, from an eco-toxicological point of view, the situation is somewhat different. Sucrose is readily biodegradable but, because of its high biological oxygen demand during degradation, its impact on aquatic environments is negative. For this reason, products that contain sucrose are classified Water Hazard Class 1: low hazard to waters (self-assessment according to VwVwS).
That is why products that contain sucrose should neither be directly led into sewer outfall drains nor discharged into aquatic environments or the sewer system.

4.1.2 Organic Acids

4.1.2.1 Gluconates

Gluconates are a modified sugar and are often used in the form of sodium gluconate (sodium salt of gluconic acid).

Data found in literature indicate only little acute toxicity. An irritant effect on skin and eyes could not be proved.

Labelling is not mandatory. This product is also readily biodegradable but because of its high biological oxygen demand during degradation, it is classified Water Hazard Class 1: low hazard to waters (self-assessment according to VwVwS). Therefore, products that contain gluconates should not be led directly into sewer outfall drains or directly discharged directly into aquatic environments or the sewer system.

Gluconates are used as an additive in dietary foods. Apart from that, they are also intermediate products of human metabolism.

In the Unites States, sodium gluconate has „GRAS" status (generally recognised as safe), so from a toxicological as well as an eco-toxicological point of view, this raw material can be deemed safe.

4.1.2.2 Fruit Acids

Fruit acids are organic acids that are often found in fruits. They contribute to their aroma and have an anti-microbial effect. Well-known representatives are citric acid, tartaric acid, gluconic acid, lactic acid and malic acid. These are hydroxycarboxylic acids and in concrete they have a retarding effect.

The citric acid that is preferably used for the production of recycling aids is safe as far as acute toxicity is concerned and has no know chronic-toxic effects. When handled properly, adverse health effects for humans are not known nor are they to be expected. In concentrated form, citric acid irritates skin and eyes. It is readily biodegradable. Bioaccumulation does not take place and citric acid is classified as not hazardous to water (nwg) (VwVwS).

Since pure citric acid is readily soluble in water and has an acidic reaction in an aqueous solution, it must be labelled GHS07 and H319 according to the CLP Regulation. Contact with skin and eyes should be avoided.

Citric acid is approved as a food additive (E 330) and has „GRAS“ status (generally recognised as safe) in the USA. It is thus deemed safe as a raw material from a toxicological as well as an eco-toxicological standpoint.

4.1.3 Inorganic Retarders

4.1.3.1 Phosphates

The main phosphates used are:

- tetrapotassium pyrophosphate
- sodium tripolyphosphate
- sodium hexametaphosphate

It is known that the phosphates used in retarders are not acutely toxic. These are inorganic substances for which the term biodegradability does not apply.

Tetrapotassium pyrophosphate shows an alkaline reaction in aqueous solution and must therefore be labelled GHS07 (Warning). The substance is classified irritant to eyes (H319). Phosphates are classified Water Hazard Class 1: low hazard to waters (self-assessment according to VwVwS) and may not be led directly into sewer outfall drains or discharged directly into aquatic environments or the sewer system. These phosphates are also often used in foods.

It should be noted that when transporting retarders on a phosphate base as of a quantity of 1,000 kg, they must be classified as dangerous goods in compliance with the European Agreement concerning the international carriage of dangerous goods by road (ADR).

4.1.3.2 Phosphonic Acids

Organic derivatives of phosphonic acids are also used as retarders. These are compounds that have a phosphorous-carbon bond.

An example of this is 2-phosphonobutane-1,2,4-tricarboxylic acid (PBTC).

According to the current data available, an approx. 50 % aqueous solution of PBTC is deemed safe from a toxicological point of view. Irritating effects on the skin of rabbits were not determined and PBTC is only mildly irritant to rabbit eyes.

No indications of teratogenic properties (rat) or a mutagenic effect (AMES test, micronucleus test) were found.

In eco-toxicological tests on bacteria and fish, PBTC showed no harmful effects even in high concentrations. PBTC is classified Water Hazard Class 1: low hazard to waters (VwVwS). When used properly it does not cause disturbances in biological clarification plants. According to the CLP Regulation, labelling of PBTC is not obligatory. PBTC is used for treating cooling and process water to prevent crusts from forming, e.g. on heat exchangers, as well as in liquid cleaners for the food industry.

4.1.3.3 Lignosulfonates
Further information on lignosulphonates is found in section 3.1.1.

4.2 Auxiliary Agents and Additives for Retarders

Since sucrose and gluconates are readily biodegradable, the types of retarders that contain these raw materials must also be preserved.

Preservatives protect the admixture from biological infestation, ensuring stability during storage as well as a long shelf-life. It is only possible to produce durable concrete in the desired quality if the retarder retains its effect, even after longer storage periods. (Preservatives are dealt with in section 3.2.2).

Depending on auxiliary agent or additive used, appropriate labelling may become mandatory (Contains <substance>: May cause allergic reactions.).

4.3 Retarders as Concrete Admixtures

Retarders are aqueous solutions of the raw materials described above or aqueous solutions made of mixtures of these raw materials. The active substance concentration normally ranges between 10 and 30 % by mass.

Based on the data available for these raw materials, the retarders found on the German market are deemed practically non-toxic. From an ecological standpoint, retarders on a sucrose or gluconate base are readily biodegradable but have a high biological and chemical oxygen demand during this process.

The term biodegradability does not apply to retarders on a phosphate base. Lignosulphonates are inherently biodegradable.

Retarders are classified Water Hazard Class 1: low hazard to waters (self-assessment according to VwVwS).

4.4 Retarders in Concrete

Retarders are added to concrete or mortar in quantities that range between 0.2 and 2.0 % by mass relative to cement, depending on the working time desired.

According to present knowledge, retarders – similar to concrete plasticizers and super plasticizers – are also tightly bound into the cement paste matrix.

5 SET/HARDENING ACCELERATORS AND SPRAYED CONCRETE ACCELERATORS

Set/hardening accelerators and set accelerators for sprayed concrete must correspond to the common requirements set out in EN 934-1 and the specific requirements in EN 934-2 or EN 934-5. They are defined here as:

Set accelerators (BE) according to EN 934-2:
„An admixture that reduces the time of a concrete mixture's transition from the plastic to the solid state"

Hardening accelerators (BE) according to EN 934-2:
„An admixture that accelerates initial strength with or without an influence on setting time".

Hardening accelerators for sprayed concrete as well as non-alkaline hardening accelerators for sprayed concrete are specified in DIN EN 934-5.

Set accelerators for sprayed concrete EN 934-5:
„An admixture that allows sprayed concrete to set very early, distinguishing them from the set accelerators defined and specified in EN 934-2."

Non-alkaline set accelerators for sprayed concrete according to EN 934-5:
„Set accelerators for sprayed concrete with an alkali content (given as an Na_2 equivalent) of maximum 1.0 % relative to the mass of the admixture".

5.1 Raw Materials for Accelerators

The raw materials mainly used in Germany for hardening, set and sprayed concrete accelerators are:

- Aluminium sulphate
- Formiates
- Fluorides
- Aluminates
- Amorphous aluminium hydroxides
- Carbonates
- Silicates
- Ethanolamines

These raw materials are used alone or in combination, in powder form or in aqueous solutions as well as in the form of dispersions or suspensions.

Along with the above named raw materials, nitrates, nitrites and thiocyanates are also used. These substances are listed in EN 934-1, Annex A.2 („substances to be declared") but according to DIN 1045-2, section 5.2.6, they may not be used in reinforced concrete in Germany because of their possible corrosion promoting effect on steel. Sulphides and formiates are exempt from this prohibition, however, their use in prestressed concrete is prohibited in Germany.

5.1.1 Aluminium Sulphate

Aluminium sulphate is a powder that dissolves in water at different speeds, depending on its water of crystallization content. It is used as a powder, solution or as an aqueous suspension.

Solid aluminium sulphate is labelled GHS05 (Warning) and H318 (Causes serious eye damage). Concentrated, aqueous aluminium sulphate solutions are labelled GHS05 (Danger), H290 (May be corrosive to metals) and H319 (Causes serious eye irritation).

Aluminium sulphate is classified Water Hazard Class 1: low hazard to waters. As a pure, inorganic substance, the term biodegradability does not apply to aluminium sulphate. However, since the aluminium ions hydrolyse to aluminium hydroxide in water, the substance can be easily eliminated. Aluminium sulphate may not be led directly to sewage outfall drains nor to aquatic environments or the sewer system.

Aluminium sulphates are used, e.g. for treating sewage and for the treatment of drinking water.

5.1.2 Formiates

Calcium formiate

To comply with the CLP Regulation, calcium formiate must be labelled GHS05 (Danger) and H318 (Causes serious eye damage). Calcium formiate did not show any indication of mutagenic activity in an AMES test. In long-term studies on rats, nothing conspicuous in regard to chronic or carcinogenic effects was observed with the treated animals compared to an untreated control group.

Reproduction studies on rats showed unchanged growth and unchanged fertility over two and five generations. Neither maternal-toxic nor embryo-toxic or teratogenic effects were observed under the experimental conditions in any of the dosage groups.

The product is assigned to Water Hazard Class 1: low hazard to waters (self-assessment according to VwVwS). Calcium formiate may not be led directly to sewage outfall drains nor aquatic environments or the sewer system.

Calcium formiate is used, e.g. as a preservative for food, for silaging green fodder and in animal feed.

Aluminium formiate

Aluminium triformiate is labelled H318 (Causes serious eye damage) and GHS05 (Danger). Aluminium formiate is classified Water Hazard Class 1: low hazard to waters.

According to our knowledge today, aluminium formiate is only used in combination with other aluminium compounds such as aluminium sulphate and aluminium hydroxide. Depending on composition and concentration of the individual components, labelling of these set accelerators may or may not be mandatory. Labelling is found in the respective data sheets for the products.

5.1.3 Fluorides

As a rule, only aluminium fluorides are used.

Aluminium fluoride trihydrate is a powder and labelled H302 (Harmful if swallowed), H315 (Causes skin irritation), H319 (Causes serious eye irritation) and H335 (May cause respiratory irritation) as well as GHS07 (Warning).

Aluminium fluoride trihydrate is classified Water Hazard Class 1: low hazard to waters. According to our knowledge today, just like aluminium formiate, aluminium fluoride is only used in combination with other aluminium compounds such as aluminium sulphate and aluminium hydroxide. Labelling is found in the respective data sheets for the products.

5.1.4 Aluminates

Sodium aluminates or potassium aluminates as well as mixtures of these are predominately used as raw materials. Because of their high pH value they can burn skin and mucous membranes. According to the CLP Regulation, they must be labelled with the hazard pictogram GHS05 (Danger) and hazard statement H314 (Causes serious burns on skin and serious eye damage).

Concentrated solutions are toxic to aquatic organisms.

Aluminates and their solutions are classified Water Hazard Class 1: low hazard to waters (VwVwS). This classification is based primarily on the shift in the pH value of an aqueous solution to the alkaline range. They may neither be directly led into sewage outfall drains nor discharged directly into aquatic environments or the sewer system.

Aluminates are used, for example, to treat sewage and for the treatment of drinking water.

5.1.5 Amorphous Aluminium Hydroxides

Amorphous aluminium hydroxides are used in powder form or as an aqueous suspension. These products are not hazardous substances according to the CLP Regulation and labelling is not required.

If the general limit value for dust of 3 mg/m³ (alveoli penetration fraction) or 10 mg/m³ (fraction that can be inhaled) according to TRGS 900 is observed, $Al(OH)_3$ causes no harm if inhaled.

Amorphous aluminium hydroxides are not water soluble and therefore classified as substances not hazardous to water (VwVwS).

5.1.6 Silicates

So-called „water glass“ is used as a silicate, normally in the form of sodium or potassium salts. These are water soluble and consist of a silicic acid component (SiO_2) and an alkali component (Me_2O). The lower the molar ratio SiO_2 : Me_2O, the more alkaline the corresponding alkali silicates are.

From a toxicological point of view, the alkali component is of primary relevance and, depending on concentration and alkalinity, no classification or classification as irritant or corrosive may be necessary.

A comparison of the classifications of soluble silicates and powder according to the CLP Regulation and Directive 67/548/EEG was carried out by CEES. According to this, the soluble silicates either do not need to be labelled or must be labelled GHS07 (Warning) or GHS05 (Danger), depending on the molar ratio of SiO_2 : Me_2O.

According to presently available studies, water glass is neither mutagenic nor carcinogenic. However, an influence on reproduction has been indicated. Water glass is not teratogenic.

Acute oral toxicity is low. In long-term studies (rats) with relatively high doses, treated animals showed no significant changes compared with the untreated control group.

Eco-toxicological data on water glass is available, according to which acute toxicity to fish, daphnia and bacteria is rated as low. Since alkali silicates are inorganic substances, the term biodegradability does not apply to them. They occur in nature as weathering products of certain rocks.

Silicates are classified Water Hazard Class 1: low hazard to waters (self-assessment according to VwVwS). This classification is mainly based on the shift in the pH value of an aqueous solution to the alkaline range. They may neither be directly led into sewage outfall drains nor discharged directly into aquatic environments or the sewer system.

Silicates are used in different daily applications, e.g. for the treatment of drinking water, as a stabiliser in soil to bind heavy metals and in detergents and cleaning agents.

5.1.7 Carbonates

Carbonates in the form of soda (sodium carbonate) or potash (potassium carbonate) are used. Both substances have an irritant effect and according to the CLP Regulation they must be labelled GHS07 (Warning) and H319 (Causes serious eye damage). Potassium carbonate must be additionally labelled H315 and H335. They are not acutely toxic orally. Soda has no teratogenic effect.

Aquatic organisms (daphnia, fish) are relatively insensitive to alkali carbonates according to the results of available studies. Effects may eventually be caused by a shift in pH. The term biodegradability does not apply to inorganic substances. In the catalogue of substances hazardous to water, sodium and potassium carbonate are classified Water Hazard Class 1: low hazard to waters (VwVwS). They may neither be directly led into sewage outfall drains nor discharged directly into aquatic environments or the sewer system.

Soda has been used for producing glass for more than 3,000 years.

5.1.8 Ethanolamines

The ethanolamines used in practice are mainly diethanolamine (DEA) and triethanolamine (TEA). Both substances are used in combination with the raw materials named above. In set accelerators for sprayed concrete, for example, DEA may be used in concentrations of several % by mass.

Diethanolamine is a very readily water soluble compound and labelled GHS08, GHS07, GHS05 (Danger), H315, H373, H302, H318. According to VwVwS, DEA is classified Water Hazard Class 1: low hazard to waters, readily biodegradable and slightly toxic to aquatic organisms (LC50 - Pimephales promelas - 1460 mg/l - 96 h, EC50 - Daphnia magna - 55 mg/l - 48 h).

Triethanolamine is also very readily soluble in water and not classified according to the CLP Regulation. According to VwVwS, triethanolamine is classified Water Hazard Class: 1 low hazard to waters, readily biodegradable and only negligibly toxic to aquatic organisms.

5.2 Accelerators as Concrete Admixtures

Accelerators are used as powders, aqueous suspensions or solutions of the raw materials described or mixtures of these. Active substance concentration normally ranges between 10 and 100 % by mass.

The quantity of accelerators usually used for concrete in Germany ranges between 1 and 3 % by mass relative to cement. Sprayed concrete accelerators are used in Germany (according to DIN 18551) in quantities up to 10 % by mass relative to cement.

Depending on their pH value, both aqueous as well as powder formed preparations of silicate, aluminate and carbonate based accelerators must be labelled corrosive or irritant according to the CLP Regulation with GHS05 (Danger) or GHS07 (Warning).

Accelerators on a calcium formiate base can cause serious eye damage and must be labelled GHS05 (Danger) and H318 according to the CLP Regulation.

Set accelerators for sprayed concrete are predominately water based solutions or suspensions. Their active substances are mainly aluminium sulphate, aluminium formiate, aluminium fluoride and aluminium hydroxide or mixtures of these. Aluminium formiate and aluminium fluoride, on the other hand, are only used in a mixture with the other components. Depending on their composition, concentration and pH value, these accelerators are mainly labelled GHS05 (Danger). Labelling is found in the respective Safety Data Sheets.

Aluminates increase the pH value of aqueous solutions very strongly, the reason why accelerators on an aluminate base are toxic to aquatic organisms in concentrated form.

Set accelerators with an alkali content (given as an Na_2O equivalent) of max. 1.0 % relative to the mass of the admixture are deemed alkali-free.

They are found on the market in powder form, mixed with inert fillers such as calcium carbonate as well as in the form of water based solutions or suspensions.

When handling these concrete admixtures, the necessary job safety measures stated on the label must be taken.

When handling accelerators in powder form, the dust limit value for fine dust concentrations according to the MAK value list as well as the normal job safety rules for handling powders should be observed.

5.3 Accelerators in Concrete

Silicates, carbonates, fluorides and aluminates, which are calcium salts, are poorly soluble in water and, just like formiates, they are bound into the cement paste matrix.

Aluminium sulphates as well as most other aluminium compounds mainly react to ettringites.

With the high dosages that are normal for sprayed concrete, leaching experiments have shown that when alkali based accelerators are used, a part of the sodium and potassium ions can be leached out by water. Alkali-free set accelerators are predominately used in the sprayed concrete area in Europe because of their advantages when it comes to industrial hygiene, concrete technology and ecology.

6 AIR ENTRAINING AGENTS

Air-entraining agents (LP) must correspond to the common requirements set out in EN 934-1 and the specific requirements in EN 934-2, Table 5, where they are defined as:

„An admixture that introduces a certain quantity of small, evenly distributed air bubbles during the mixing process which remain in the concrete after it hardens".

For the safe use of air-entraining agents and their mode of action in concrete, Deutsche Bauchemie has published an information script on the production of air-entrained concrete titled "Informationsschrift Herstellen von LP-Beton".

6.1 Raw Materials for Air Entraining Agents

There are a number of surface active substances called surfactants that are used to create air bubbles.

The term surfactant covers all chemical compounds that are capable of concentrating on interfaces and reducing interfacial tension between two immiscible phases.

To improve resistance to frost and de-icing agents, it is necessary to introduce air bubbles into the concrete in a defined quantity, size and distribution.

The addition of small quantities of soaps made from natural resins or synthetic, non-ionic or ionic surfactants (e.g. alkylpolyglycol ether, alkylsulphates and alklysulphonates) have proved to be suitable for this purpose.

6.1.1 Soaps Made of Natural Resins

For the production of resin soaps, root resins, tall resins, gum resins (colophony) and derivatives of these natural resins are mainly used which are then converted with sodium or potassium hydroxide or soda into corresponding resin soaps.

Root resins are extracted from roots and gum resins from the gum that flows from artificially wounded pine trees (resin tapping).

Tall resins are by-products that are formed during the production of cellulose when a sulphate process is used. These resins are deemed safe as far as acute toxicity is concerned; however, since they can irritate skin, eyes and the respiratory system, they are classified „irritant“. Especially in the case of colophony in the oxidised form, there may be sensitising effects which is the reason they must be labelled GHS08 as well as H334 and H 317. Preparations with a colophony content as of 1 % must also be classified sensitising.

Natural resins are available as powders in saponified and unsaponified form. Varying concentrations of readily soluble sodium or potassium salts are offered as aqueous solutions.

Due to their alkalinity, which can irritate skin, eyes and the respiratory system, resin soaps in powder form are classified „irritant“ and must be labelled GHS07 as well as H315, H319 and H335. According to the CLP Regulation; saponified resins in the form of aqueous solutions either do not have to be labelled or must be labelled „irritant“ or „corrosive“, depending on their alkali content.

These resins are biodegradable. Unsaponified resins are insoluble in water and classified Water Hazard Class 1: low hazard to waters. Resin soaps are classified Water Hazard Class 2: hazardous to waters (self-assessment according to VwVwS) and may neither be led directly into sewer outfall drains nor discharged directly into aquatic environments or the sewer system.

Esters of natural resins are used as an ingredient in chewing gum. In the form of sodium salts, also in dissolved form, they are used in adhesives, floor covers (linoleum), natural colouring agents, plastics and rubber (e.g. automobile tyres). Certain resin derivatives are used for hydrophobizing paper and cardboard and have been approved by BfR (German Institute for Risk Assessment) and the FDA (Food and Drug Administration) for use in direct contact with foods.

6.1.2 Synthetic Surfactants

Alkyl polygylcol ether, alkylsulphates and alkylsulphonates are the main raw materials used. Studies on rats in which these substances were administered orally have proved that they are safe from a toxicological point of view.

As a rule, the raw materials named above do irritate skin, mucous membranes and eyes and must therefore be labelled GHS05 as well as H315, H 319 and H335. However, irritation normally only occurs with high concentrations. Because they are extremely effective, products based on synthetic surfactants are usually strongly diluted.

The surfactants usually used as concrete admixtures are readily biodegradable according to requirements set out in §4 of the [German] Washing and Cleaning Agent Law (WRMG) (last revised on July 17, 2013).

On a long-term basis, surfactants do have a harmful effect on aquatic organisms. Surfactants are classified Water Hazard Class 2: hazardous to waters (self-assessment according to VwVwS) and may neither be led directly into sewer outfall drains nor discharged directly into aquatic environments or the sewer system.

Surfactants are also used in cosmetics, detergents and cleaning agents.

6.2 Air Entraining Agents as Concrete Admixtures

The active substance content in the air-entraining agents normally used in Germany ranges between 1 and 5 % by mass (concentrates up to 20 % by mass) which means quantities of 0.05 to 1.0 % by mass relative to cement.

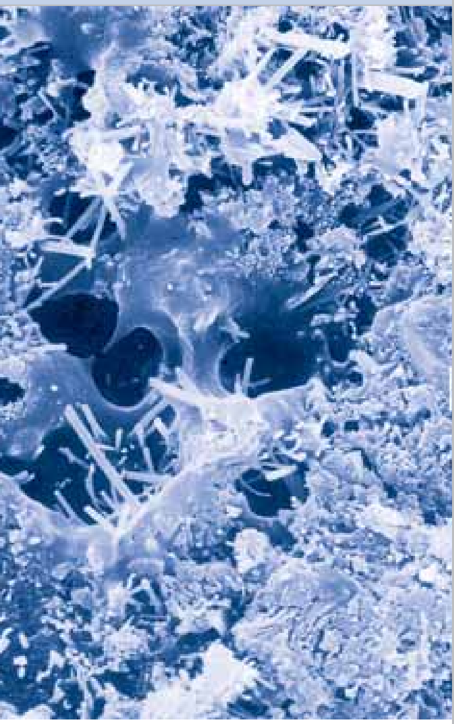
Since synthetic surfactants are readily biodegradable, air-entraining agents formulated with these raw materials must be preserved. (Preservatives are dealt with in section 3.2.2).

Stored properly (according to the Technical Data Sheet provided by the manufacturer), they ensure that the product remains stable in storage and has a long shelf-life of months or even years. Concretes that are resistant to frost and de-icing salt can only be produced in the desired quality if the air-entraining agent retains its effect, even when stored for longer periods.

6.3 Air Entraining Agents in Concrete

Due to the structure of air-entraining agents which consists of a hydrophobic and a hydrophilic group, the surfactant concentrates at the edge of the air bubble and the hydrophilic part anchors soundly to the cement paste matrix.

Because they are highly effective, surfactants are only added to concrete in small quantities and the quantity of surfactants in hardened concrete is correspondingly low. Here an example: An air-entraining agent contains 5 % by mass surfactant. If this air-entraining agent is added to C 30/37 concrete with 320 kg cement/m³ in a quantity of 0.3 % by mass, the hardened concrete contains 20 ppm of this surfactant.



7 OTHER ADMIXTURES

7.1 Waterproofing Agents

Waterproofing agents (DM) must correspond to the common requirements set out in EN 934-1 and the specific requirements in EN 934-2, Table 9, where they are defined as follows:

„An admixture that reduces capillary water absorption in hardened concrete“.

In Germany, however, only waterproofing agents proved to be effective according to EN 934-2, Table 9, with the same water-cement ratio may be used for concrete according to DIN 1045-2.

7.1.1 Raw Materials for Waterproofing Agents

Salts of higher fatty acids are mainly used as raw materials. In general, this is calcium stearate which is used as a powder or in the form of an aqueous dispersion. In both cases, the product is free of solvents. From today‘s point of view, calcium stearate is neither toxic or harmful to health, nor is it irritant or corrosive and therefore labelling according to the CLP Regulation is not mandatory. Calcium stearate is readily biodegradable and classified either Water Hazard Class 1: low hazard to waters (self-assessment according to VwVwS) or not hazardous to water (nwg), depending on manufacturer.

7.1.2 Auxiliary Agents and Additives for Waterproofing Agents

Waterproofing agents may also contain small quantities of de-foaming agents or preservatives. (De-foaming agents and preservatives are dealt with in sections 3.2.1 and 3.2.2 respectively.)

7.1.3 Waterproofing Agents as Concrete Admixtures

The active substance content of waterproofing agents normally used in Germany ranges between 20 and 50 % by mass, using quantities of 1 to 5 % by mass relative to cement.

7.1.4 Waterproofing Agents in Concrete

Because waterproofing agents have a water repelling effect, the risk of their being leached out of the concrete is very low.

7.2 Admixtures for Intrusion Grout for Prestressing Tendons (Grout Aids)

Admixtures for intrusion grout in prestressing tendons (grouting aids (EH)) must correspond to common requirements set out in EN 934-1 and the specific requirements in EN 934-4.

The purpose of grouting aids (EH) is to improve flowing capacity, reduce water demand, reduce settlement or achieve moderate swelling of the grout. In Germany, only powder form grouting aids are used.

7.2.1 Raw Materials for Grouting Aids

Grouting aids may contains plasticizers, super plasticizers and retarders. For more information on these admixtures, see sections 3 and 4.

The desired swelling effect is achieved through small quantities of metallic aluminium in powder form which completely convert by generating hydrogen in the alkaline environment of the grouting aid before setting begins. This reaction begins with what is called aluminium stabilisation during which a thin, protective film of paraffin encapsulates the powder after approx. 30 minutes.

No toxic properties are known for aluminium powder. It is used as an ingredient in paints and fulfils purity criteria for paints that come in contact with foods. Aluminium powder is classified not hazardous to water (nwg).

7.2.2 Grouting Aids as Admixtures

Since they have a strong swelling effect, the content of active substances in conventional grouting aids is very low.

In general, they range between 0.1 and 1.0 % by mass and are used in quantities of 0.2 to 1.0 % by mass relative to cement.

In fresh intrusion grout, metallic aluminium reacts before setting begins, converting to hydration products that cannot be distinguished from those of the cement. They become an integral part of the hydrated cement.

7.3 Water Retaining Admixtures and Viscosity Modifiers

Water retaining admixtures (ST) must correspond to common requirements set out in EN 934-1 as well as the specific requirements in EN 934-2, Table 4.

A water retaining admixture is defined here as an admixture which reduces the loss of water by a reduction of bleeding.

Viscosity modifiers must correspond to the common requirements set out in EN 934-1 and the specific requirements found in EN 934-2, Table 13.

A viscosity modifier is defined in EN 934-2 as an "admixture that is used to limit segregation by improving cohesion in the concrete."

7.3.1 Raw Materials for Water Retaining Admixtures and Viscosity Modifiers

The following classes of substances are mainly used as raw materials for water retaining admixtures / viscosity modifiers:

- starch/cellulose derivatives (e.g. starch ether, cellulose ether)
- polysaccharides, either natural or won by fermentation (e.g. xanthan gum, welan gum)
- synthetic, high molecular polymers (e.g. poly(ethylene) oxides and polyacrylates)
- fine grained, inorganic substances with large specific surfaces (e.g. silica dust and silica suspension, silica sol)

Starch derivatives are won by digestion and modification of plants that contain starch such as potatoes and grain. Starch ethers are modifications of natural starches. Cellulose ethers are won through etherification of natural cellulose, e.g. from cotton and wood. Polysaccharides are isolated from suitable micro-organisms in fermentation processes.

Starch/cellulose derivatives and polysaccharides are neither acutely toxic nor do they irritate skin or mucous membranes.

Labelling according to the CLP Regulation is not required. Starch/cellulose derivatives and polysaccharides are not hazardous to aquatic organisms.

Because they are readily biodegradable and have a high oxygen demand, these substances are classified Water Hazard Class 1: low hazard to waters (self-assessment according to VwVwS). They may neither be directly led into sewage outfall drains nor discharged directly into aquatic environments or the sewer system.

Synthetic, high molecular polymers are produced through polymerisation of ethylene oxide and/or acrylates.

The polyethylene oxides normally used for producing water retaining admixtures are in powder form and labelling according to the CLP Regulation is not required. They are not acutely toxic, there is no proof that they impair the ability to reproduce, studies on gene toxicity have not shown any effect and they have not proved to be carcinogenic in animal experiments.

These products are not readily biodegradable and classified Water Hazard Class 1: low hazard to waters (self-assessment according to VwVwS).

Polyalkylene glycols are used in many ways in technical applications, e.g. the production of packaging materials, in the food and personal care product area as well as in pesticides.

As a rule, polyacrylates are used in the form of aqueous dispersions. They are not hazardous substances and labelling is not mandatory. They are not acutely toxic, no impairment of the ability to reproduce has been determined, studies on gene toxicity showed no effect in this respect and they have not proved to be carcinogenic in animal experiments.

The products are not readily biodegradable and classified Water Hazard Class 1: low hazard to waters (self-assessment according to VwVwS).

Fine grained, inorganic substances with large specific surfaces are used, e.g. in the form of silica dust and silica suspension or silica sols. These are not acutely toxic and they neither impair the ability to reproduce nor do they have a toxic effect on genes.

Since they are inorganic substances, the term biodegradability does not apply. They are classified Water Hazard Class 1: low hazard to waters.

7.3.2 Auxiliary Agents and Additives for Water Retaining Admixtures and Viscosity Modifiers

With the exception of products produced with inorganic substances, water retaining admixtures / viscosity modifiers contain small quantities of preservatives and sometimes de-foaming agents. (De-foaming agents and preservatives are dealt with in sections 3.2.1 and 3.2.2, respectively.)

7.3.3 Water Retaining Admixtures and Viscosity Modifiers as Concrete Admixtures

Water retaining admixtures / viscosity modifiers are added to concrete in liquid or powder form. Standard quantities cannot be stated but the quantity of active substance in the concrete from products on an organic substance base is extremely low and, as a rule, clearly less than 1 % by mass relative to cement.

Water retaining admixtures / viscosity modifiers made of inorganic substances must be added in clearly higher quantities as a rule. A quantity of up to 5 % by mass may be necessary.

To assess the water retaining admixtures and viscosity modifiers described here, the underlying types of pure raw materials can be taken into account since mixtures are not commonly used.

7.3.4 Water Retaining Admixtures and Viscosity Modifiers in Concrete

Water retaining admixtures and viscosity modifiers are increasingly being used in easily consolidated and self-consolidating concretes. Examination results prove that the water retaining admixture / viscosity modifiers become an integral part of the cement matrix.

7.4 Chromate Reducers

Chromate reducers are used to keep the content of water soluble chromium (VI) in cement paste below the limit value of 2 ppm by reducing this substance to water insoluble chromium (III).
The chromate that goes into solution after the cement is mixed with water (cement paste) is deemed responsible for „chromate contact dermatitis“, commonly called „mason‘s itch“.

7.4.1 Raw Materials for Chromate Reducers

The main raw material presently used is iron (II) sulphate which is a by-product in the production of titanium dioxide.

Tin (II) sulphate preparations are also still used as highly effective, stable chromate reducers.

Iron (II) sulphate must be labelled GHS07 as well as H302, H315 and H 319. It is harmful if swallowed (H203) and may irritate skin (H315) and eyes (H319).

Tin (II) sulphate must be labelled GHS05, GHS07 as well as H315, H317, H318, H332, H335, H341, H361, H373 and H412. Iron (II) sulphate and tin (II) sulphate are classified as Water Hazard Class 1: „low hazard to waters”. They may neither be directly led into sewage outfall drains nor discharged directly into aquatic environments or the sewer system.

Iron (II) sulphates are often used in hydrochemistry (precipitation agents and coagulants used to eliminate phosphate and hydrogen sulphide in sewage plants), in special agricultural fertilisers, as a trace element medium in feed mixtures and for the desulphurisation of bio-gas.

Tin (II) sulphates are also used in electroplating techniques (anodising) and for treating the surface of sheet metals (tin cans for food).

7.4.2 Chromate Reducers as Concrete Admixtures

Chromate reducers on an iron (II) sulphate base are offered in powder, granulate and liquid form. When quantities of 0.2 to 0.5 % by mass relative to the active substance and relative to cement are added, a sufficient chromate reducing effect can be presumed. When handling these substances, the information given in section 7.4.1 should be observed.

Chromate reducers on a tin (II) sulphate base are offered in powder and liquid form that have a long shelf-life. Quantities of 0.02 to 0.07 % by mass relative to the active substance and relative to cement reduce chromate without causing stains.

7.4.3 Chromate Reducers in Concrete

In the alkaline environment of concrete, most of the iron (II) sulphate used is converted by oxidation through the chromate as well as oxygen in the air into poorly soluble hydrated iron (III) oxide. An environmental hazard through elution is not to be expected.

Tin (II) sulphate is converted into water insoluble compounds in the highly alkaline concrete matrix. An environmental hazard through elution is not given.

7.5 Foaming Agents

According to the approval principles for concrete admixtures issued by the Institute for Construction Technology (DIBt), foaming agents are defined as follows:

„Foaming agents [are used to] introduce air pores to produce foamed concrete or concrete with porous cement paste.“

7.5.1 Raw Materials for Foaming Agents

Foaming agents mainly consist of synthetic, anionic and zwitterionic surfactants. Among these are, for example, alkyl sulphates, polygylcol sulphates and amine oxides or betaines.

These substances irritate skin and mucous membranes and cause serious eye damage. They are thus classified H315 and H318 and labelled with the signal word „Danger” and the hazard pictogram GHS 05 (corrosive).

The products are assigned to Water Hazard Class 2: Hazard to waters (self-assessment according to VwVwS). They may neither be directly led into sewage outfall drains nor discharged directly into aquatic environments or the sewer system.

Surfactants do harm aquatic organisms over the very long term, so depending on concentration, foaming agents that contain these substances must be labelled H412 “Harmful to aquatic life with long-lasting effects”. That is why foaming agents should not be allowed to enter the ground or reach surface or ground water.

The synthetic surfactants used in foaming agents are predominately readily biodegradable and meet the requirements for detergents and cleaning agents.

Because of the concentration of active substances in foaming agents, the use of a preservative is often not necessary.

7.5.2 Foaming Agents as Concrete Admixtures

Foam is normally produced with the aid of a foaming agent and a foam generator. The quantity added is calculated according to the volume of foam to be produced. To produce 100 litres of foam, 0.1 to 0.2 litres of foaming agent are needed. The foam is then mixed into the mortar or concrete.

Foamed concrete or light-weight aerated concrete has an air pore content of more than 30 % by volume as a rule.

7.5.3 Foaming Agents in Concrete

The structure of surfactant molecules, consisting of a polar and a non-polar group, causes them to attach to the interface of cement paste and air in the concrete with the polar group acting as an anchor group and the non-polar group projecting into the air pore.

7.6 Shrinkage Reducers

Shrinkage reducers are presently not governed by the building inspectorate in Germany. They are used for the most part to significantly reduce shrinkage without changing the water content while the concrete dries.

7.6.1 Raw Materials for Shrinkage Reducers

Higher molecular glycols are the raw materials most often used for shrinkage reducers.

This group of substances is included in the list of approved substances for concrete admixtures found in EN 934-1, Annex A.1.

A typical representative of higher molecular glycols is dipropylene glycol. According to the CLP Regulation, dipropylene glycol does not need to be labelled.

Dipropylene glycol is used as an inactive carrier in cosmetics and is also found, for example, in more than 900 medicines that are approved in Germany.

Acute toxicity of dipropylene glycol is very low. The LD50 value, determined on rats, is 13,300 mg/kg. Skin resorption of harmful quantities is not likely, even with longer exposure. The LD50 value determined on rabbits is greater than 5,000 mg/kg.

No sensitisation, carcinogenic effect or disturbance of the ability to reproduce could be proved in studies on this substance.

Dipropylene glycol is readily biodegradable according to OECD and not harmful to aquatic organisms.

7.6.2 Shrinkage Reducers as Concrete Admixtures

Glycols or mixtures of glycols with a 100 % active substance content are used as shrinkage reducers and added to concrete in quantities between 3 and 7 l/m³. Plasticizing concrete admixtures that contain glycol are also on the market and are added in quantities between 1 and 2 % by mass relative to cement.

7.6.3 Shrinkage Reducers in Concrete

Glycols are dissolved or dispersed in the pore water of fresh concrete and, through adsorption, become an integral part of the cement matrix and pore system of hardened concrete.

The development of an indoor air concentration, which can occur due to the glycols in concrete, strongly depends on the composition of the glycol based shrinkage reducer, the composition of the concrete and the concentration of the active substance used.

The development of VOC concentration in indoor air over time after release from construction products can be examined according to the AgBB Evaluation Scheme (Committee for Health-Related Evaluation of Building Products). A concrete produced with a shrinkage reducer fulfils criteria if the TVOC value is ≤ 10 mg/m³ after 3 days. To assess the long-term behaviour of VOC emissions from a construction product, the TVOC content is tested again after 28 days. The concrete fulfils the criteria if a value of ≤ 1.0 mg/m³ is determined. Only shrinkage reducers that have been tested accordingly should be used in interior spaces of buildings.

The mobilisation of glycols through evaporation from the concrete also depends on the type of glycols used and normally decrease rapidly within a short period of time. After buildings are taken into service, there should be no emission of glycols from the concrete in quantities worth mentioning.

7.7 Hollow Microspheres

Hollow microspheres are presently governed in Germany by European Technical Approvals (ETA) or National Technical Approvals. They are used as so-called “prefabricated air bubbles” instead of an air entraining agent to produce concrete with high frost and frost/de-icing agent resistance.

7.7.1 Raw Materials for Hollow Microspheres

Hollow microspheres are small, spherical, plastic balls that consist of an elastic polymer hull (e.g. polyacrylonitrile) in which a hydrocarbon gas (e.g. isopentane) is encapsulated as a propellant. By heating the spheres, the pressure of the gas inside the hull increases and, at the same time, the hull softens. The volume of the hollow microspheres can be controlled through this process. The normal diameter of hollow microspheres for applications in concrete ranges between 5 and 100 µm. Microspheres are available in dry as well as moist form. They must be labelled with hazard statement H228 “Flammable solid” and must be kept away from heat, sparks, open flames as well as hot surfaces.

Hollow microspheres are not readily biodegradable and there is no potential for bioaccumulation. They are insoluble in water, may not be led to surface water or the sewer system and are classified Water Hazard Class 1: low hazard to waters.

Hollow microspheres are often also a component in thermoplastic materials, thermosetting plastics, coatings (lacquers, printing inks, leather), paper, adhesives, sealants, technical textiles as well as products that come in contact with food.

7.7.2 Hollow Microspheres as Concrete Admixtures

Due to the process used, hollow microspheres are expanded in water which can be removed afterwards by drying. In principle, not only “wet” but also dry hollow microspheres can be used as a concrete admixture, however, it is generally more advantageous to use “wet” (paste-like) hollow microspheres since they are not only easier to handle (no dust formation) but also because moist hollow microspheres are more easily dispersed in the concrete mixture. The dry content of hollow microspheres in paste-like products ranges from 10 to 20 % by mass. These products are added to concrete in quantities between 1.5 and 7 kg/m³.

7.7.3 Hollow Microspheres in Concrete

Since the surface of hollow microspheres is hydrophobic, they do not bond well to the cement matrix. Water can collect at the interface between the hollow microspheres and the hardened cement paste and freeze at respectively low temperatures. Since the polymer hull is elastic, the ice that forms can expand in the direction of the hollow microsphere which is then deformed or damaged. The entire space originally filled by the hollow microsphere basically remains available as an “air pore” for the expansion of ice. Just as when air entraining agents are used, water from adjacent pores can reach these “compensation spaces” where they freeze. This prevents pressure from increasing through crystallization which increases the resistance of the concrete to frost and frost/de-icing agents.

Since the polymer hull of hollow microspheres is water insoluble, it can be ruled out that the material will be released by leaching. Even though they are only weakly bonded to the cement matrix, the hollow microspheres are mechanically fixated by the surrounding, hardened cement paste. This also applies to smaller particles which may detach when the hollow microspheres are damaged while freezing.

8 CONCRETE ADMIXTURES WHEN RECYCLING CONCRETE

Old concrete is now being recycled more and more often. It is crushed and used as a road building material or as a mineral aggregate for producing concrete. Due to the immobility of all the firmly bonded active concrete admixture substances, it can be concluded that there is no reason why old concrete should not be recycled. Fundamental research in this area has confirmed the good results that have been achieved in practice.

ANNEX 1: TOXICOLOGICAL AND ECO-TOXICOLOGICAL TERMS

ABG [Anforderungen an baulichen Anlagen bezüglich des Gesundheitsschutzes]
[German] Requirements on construction works regarding health protection

ABuG [Anforderungen an bauliche Anlagen bezüglich der Auswirkungen auf Boden und Gewässer]
[German] Requirements on construction works regarding their effects of soil and water

Additive
A substance that is added to other substances or products in small quantities to alter their properties in a certain way

ADR
European Agreement concerning the International Carriage of Dangerous Goods by Road

AgBB [Ausschuss zur gesundheitlichen Bewertung von Bauprodukten]
[German] Committee for Health-Related Evaluation of Building Products

alveoli-penetrating dust fraction
Dust fractions which, due to their very small particle size, can be not only inhaled but also reach the pulmonary alveoli (air cells) where they may be deposited

AMES test
A test on bacteria to determine the mutagenic properties of a chemical compound

aquatic
Pertaining to water; originating in water; found in water; living in water

BfR [Bundesinstitut für Risikobewertung]
Federal Institute for Risk Assessment: German federal authority within the scope of the Federal Ministry of Food, Agriculture and Consumer Protection (BMEL); responsible for scientific risk assessment of food and animal feed as well as substances and products as a basis for consumer protection in regard to health run by the Federal Government

biodegradable
The property of chemicals to convert (degrade) into simple, natural compounds (H_2O, CO_2, etc.) through naturally occurring enzymes of micro-organisms

carcinogen
Causes cancer

[German] Chemicals Act
German law on protection against hazardous substances (ChemG)

[German] Chemicals Prohibition Ordinance
Ordinance on the prohibition and restriction of marketing hazardous substances, preparations and products under the German Chemicals Act (ChemVerbotsV)

CLP Regulation
European Regulation (EC) No. 1272/2008 on classification, labelling and packaging of substances and mixtures with which the „Globally Harmonized System (GHS) of Classification, Labelling and Packaging of Chemicals“ issued by the United Nations has been implemented into European law

depot substance
Substance with a long-term effect

dermal
The intake of substances through skin that is intact

DVGW [Deutscher Verein des Gas- und Wasserfaches]
[German] Gas and Water Trade Association e.V., Bonn

EC_0
Highest tested concentration without an effect (EC = effective concentration)

EC_{50}
Concentration at which 50 % of the examined individuals show the observed effects

EC, EU
Abbreviations for European Community/European Union

eco-toxicology
Science concerned with the distribution and effects of chemical substances on organisms when direct or indirect harm to the environment and humans is involved

embryo-toxic
Harmful, toxic effect during the embryonal period

FDA
Food and Drug Administration

gene-toxic
A generic term for damage to the genome, i.e. the sum of genes in a cell

GHS
Globally Harmonized System

H-Codes (excerpt from GHS)
H302 Harmful if swallowed.
H311 Toxic in contact with skin.
H314 Causes severe skin burns and eye damage.
H315 Causes skin irritation.
H317 May cause allergic skin reaction.
H318 Causes serious eye damage.
H319 Causes serious eye irritation.
H335 May cause respiratory irritation.
H350 May cause cancer.
H373 Causes damage to organs through prolonged or repeated exposure.
H412 Harmful to aquatic life with long lasting effects.

Hazard statements (excerpt from GHS)
GHS05 Danger Corrosive
GHS07 Warning Health risk
GHS08 Danger Harmful to health

GISBAU [Gefahrstoffinformationssystem der BG BAU]
Hazardous substance information system maintained by the German construction industry trade association (BG Bau)

GISCODE
A classification system used in GISBAU in which product groups are classified according to their potential risk

GRAS status
Abbreviation for "generally recognized as safe"

hazardous substance
A substance that shows at least one of the so-called hazardous characteristics (e.g. toxic, harmful, corrosive, carcinogenic, genetic code altering, risk of explosion, fire-promoting, flammable)

[German] Hazardous Substances Ordinance
Ordinance on protection against hazardous substances (GefStoffV)

IC
Abbreviation for "inhibition concentration"

immobilisation
The binding of a substance or a small particle to a solid matrix

inhalation
Intake of substances, particles, etc. through the respiratory tract

KBwS
[German] Commission for Evaluation of Water Hazardous Substances

LC_0
Highest tested concentration without a lethal effect (LC = lethal concentration)

LD_{50} value
The lethal dose at which 50 % of the experiment organisms die within a certain period of time

maternal toxic
Toxic effect on the mother animal

matrix
In a chemical sense, the (rigid or highly viscous) sheathing material that encloses another (dissolved) material

mutagenic
Property of an agent to cause irreversible changes to the genetic code

NOEL
Abbreviation for „no observable effect level"; quantity of a substance which, when administered to an experiment animal, does not cause either functional or structural changes

OECD
Abbreviation for "Organization of Economic Cooperation and Development"

oral
Intake of substances, particles, etc. through the mouth

pH value
The negative decimal logarithm of hydrogen ion concentration in an aqueous medium. pH 7 indicates a neutral reaction, pH values <7 stand for acidic, pH values >7 for alkaline reactions

polymers
Synthetic products that result through polymerisation, i.e. through a chemical process in which many small molecules of one or more substances assemble into large molecules with new properties

raw materials
Basic materials that are plant, animal, mineral or chemical in origin for the purpose of further processing

reproduction toxic
Influence of harmful chemical and physical effects on reproduction

sensitisation
Administration of an exogenic substance to an organism which then shows a specific, changed reaction if the substance is repeatedly administered or is brought in contact with the organism. Sensitisation precedes an allergy.

sewage outfall drain
Flowing water that may be used to take up water from drainage systems, from industry and households or from sewage treatment plants.

solvents
Substances that are used to dissolve, dilute, emulsify or suspend other substances so that these substances can be worked or removed. Solvents are liquid under normal conditions.

sub-acute
A characterisation of the toxicity of a chemical substance within a testing period of a max. of 28 days.

teratogenic
The ability of an agent, through the effect of a sufficient dose, to cause congenital deformity.

toxicology
The science of disturbances in living systems caused by substances, i.e. toxic effects

TRGS [Technische Regeln für Gefahrstoffe]
[German] Technical Regulations for Hazardous Substances

VwVwS [Verwaltungsvorschrift wassergefährdende Stoffe]
[German] Administration rules for substances hazardous to waters

[German] Water Hazard Class
Abbreviated WGK. Designation for a system consisting of three classes to characterise the degree of hazardousness of substances

WGK 1: Low hazard to waters
WGK 2: Hazard to waters
WGK 3: Severe hazard to waters

In Germany, substances that are not deemed hazardous to water are designated „not hazardous to water“ („nwg“) and are found in a „List of Substances Not Hazardous to Water“ issued by the German Federal Environment Office.

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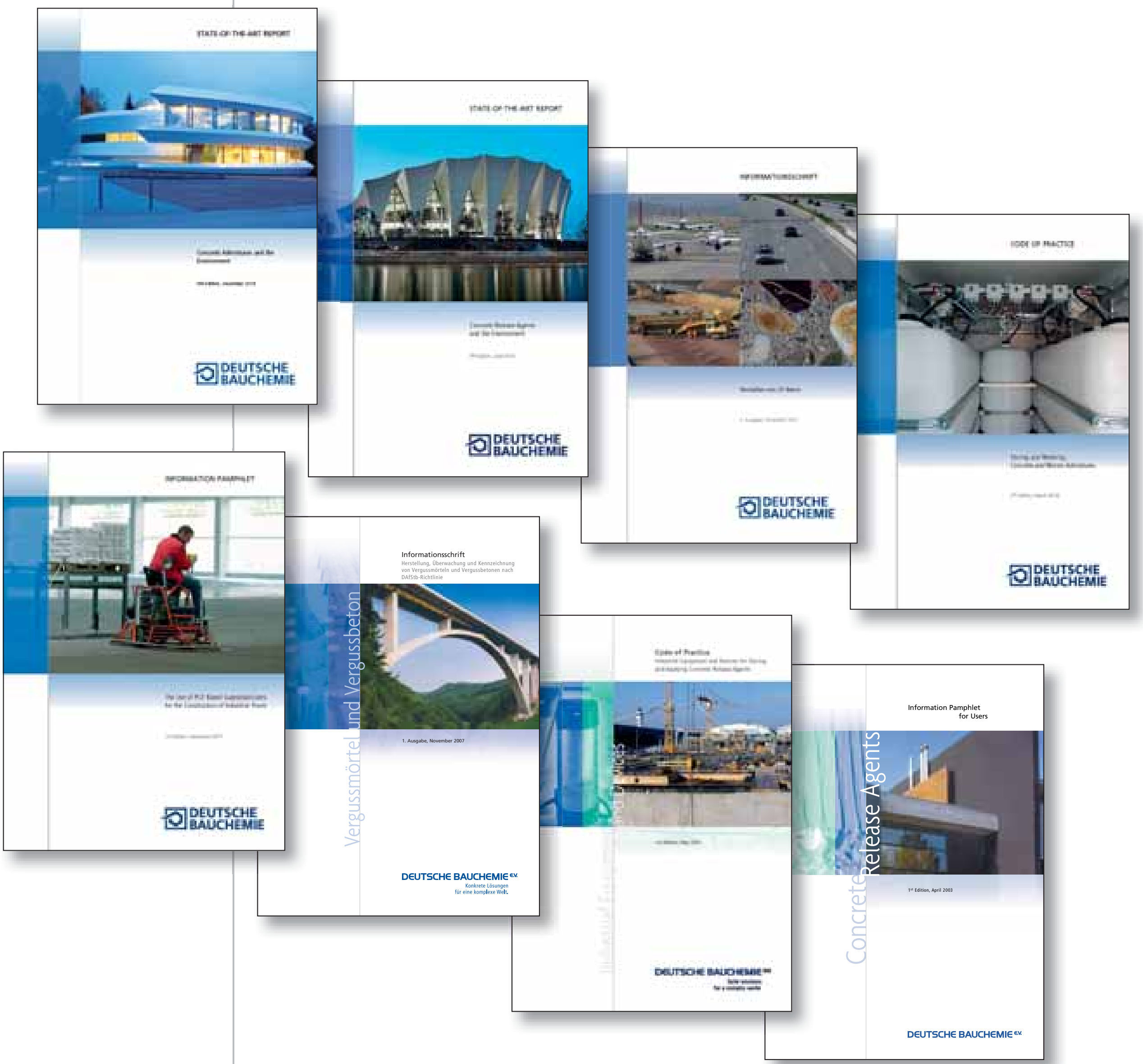

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