CEMENT QUALITY AND DRINKING WATER

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1. Introduction

In recent years cement composition has changed because the industry has to take measures to reduce the high CO2 emission caused by cement production. As drinking water is in contact with cement-based materials like mortar and concrete in reservoirs and pipes, unsuitable substances may potentially be released. Consequently, the question arises, if the use of these new cements poses a problem and which requirements have to be met by cement-based materials to be safely used in contact with drinking water.

In this article, the fundamental interaction between water and cement-based materials is explained. Additionally, the release of harmful substances like heavy metals is discussed. However, faced with the task to build new concrete components and structures in contact with drinking water, recommendations and guidelines are needed to ensure an appropriate selection and application of the material. Based on existing tests and standards, a course of action is recommended by a working group of the Swiss Gas and Water Industry Association (SVGW) that addresses the obligations of both owner and contractor for the issue of cement quality and drinking water.

Einführung

Aufgrund der Maßnahmen, die die Industrie ergreifen musste, um den hohen CO2-Ausstoß bei der Zementherstellung zu reduzieren, hat sich die Zement-Zusammensetzung in den letzten Jahren verändert. Da das Trinkwasser mit Stoffen auf Zementbasis, wie Mörtel und Beton in Speicherbecken und Rohrleitungen in Kontakt kommt, können hier potenziell ungeeignete Substanzen freigesetzt werden. Folglich stellt sich die Frage, ob die Verwendung dieser neuen Zemente ein Problem darstellt und welchen Anforderungen Stoffe auf Zementbasis genügen müssen, um ohne Risiko in Kontakt mit Trinkwasser verwendet werden zu können.

In diesem Artikel wird die grundlegende Interaktion zwischen Wasser und Stoffen auf Zementbasis erläutert. Darüber hinaus wird die Freisetzung von Schadstoffen wie Schwermetallen diskutiert. Allerdings sind für die Herstellung neuer Betonkomponenten und -strukturen, die im Kontakt mit Trinkwasser sind, Richtlinien und Empfehlungen erforderlich, um eine geeignete Auswahl und Anwendung der Stoffe zu gewährleisten. Auf der Grundlage bestehender Tests und Normen wird von einer Arbeitsgruppe des SVGW eine Vorgehensweise empfohlen, die sich sowohl mit den Pflichten der Eigentümer als auch der Auftragnehmer für das Problem von Zementqualität und Trinkwasser befasst.

Introduction

Ces dernières années, la composition du ciment a changé car l'industrie est tenue de prendre des mesures afin de diminuer les importantes émissions de CO2 causées par la production du ciment. Lorsque l'eau potable entre en contact avec des matériaux à base de ciment comme le mortier et le béton dans les réservoirs et les conduites, des substances inappropriées peuvent être libérées. Par conséquent, la question est de savoir si l'utilisation de ces nouveaux ciments pose problème et à quels critères doivent répondre les matériaux à base de ciment pour pouvoir être utilisés en toute sécurité avec de l'eau potable.

Cet article explique l'interaction fondamentale entre l'eau et les matériaux à base de ciment. Le dégagement de substances nocives comme les métaux lourds y est également discuté. Toutefois, face à la nécessité de fabriquer de nouveaux composants et structures en béton en contact avec de l'eau potable, des recommandations et directives sont indispensables pour garantir une sélection et une application appropriées du matériau. Sur la base de tests et de normes existants, un plan d'action qui aborde les obligations du propriétaire comme de l'entrepreneur concernant la qualité du ciment et l'eau potable est recommandé d'une groupe de travail du SVGW.

2. Cement and concrete

Cement is produced by heating a mixture of limestone and clay to about 1450 °C in a rotary kiln. After cooling down and adding gypsum and and five percent of minor additional constituents, the cement clinker is milled resulting in the so-called Portland cement or, according to standard SN EN 197-1 [1], CEM I. A typical concrete is produced by mixing approximately 2000 kg/m^3 of aggregates (natural sand and gravel), 300 kg/m^3 of cement and 150-180 l/m^3 of water. Cement and water react chemically to form intergrowing hydrates that confer concrete its strength. Commonly used components of cement and concrete are given in Tables 1 and 2.

One of the most serious environmental problems is the increasing CO_2-concentration in the atmosphere and the related greenhouse effect. Therefore, the reduction or at least the stabilization of the CO_2 emissions is a widely declared political goal. As the cement industry is responsible for about 5 % of the global anthropogenic CO_2 emission [2-4], it takes measures to reduce its share. On the one hand, alternative fuels are used for the rotary kiln (organic waste materials of different origins). On the other hand, the amount of clinker in the cements is reduced by adding mineral additions referred to as main constituents (Table 1). Until about 20 years ago, CEM I was the main cement and is usually still used for drinking water reservoirs in Switzerland. However, today the market is dominated by cements containing main constituents (Figure 1). These main constituents originate from different sources and differ in their composition. In addition to cement clinker, limestone powder is the most commonly used main constituent in Switzerland, but granulated blastfurnace slag, siliceous fly and burnt oil shale are in use as well. This is the reason why concerns about the use of such cements in contact with drinking water have been voiced.

Portland cement clinker	hydraulic material with a defined composition produced from limestone and claystone by sintering at 1450 ℃
minor additional constituent	natural inorganic material or inorganic material originating from clinker production
main constituents	limestone powder, granulated blastfurnace slag, siliceous fly ash, micro silica, burnt oil shale, natural pozzolana
mineral additions	same as main constituents, but not added to the clinker in the cement plant but added to the concrete in the concrete plant
admixtures	material dissolved or suspended in water added to the concrete during mixing in amounts < 5% to alter the concrete properties.
natural aggregates	aggregates produced in quarries from natural stone material solely by mechanical means

Table 1: Definition of the most commonly used cement and concrete components.

	Portland cement clinker	main constituents	minor additional constituent
CEM I	95-100	-	0-5
CEM II/A	80-94	6-20	0-5
CEM II/B	65-79	21-35	0-5
CEM III	5-64	36-95*	0-5

*in CEM lll only granulated blastfurnace slag is permitted

Table 2: Simplified chart of different cement types according to [1].

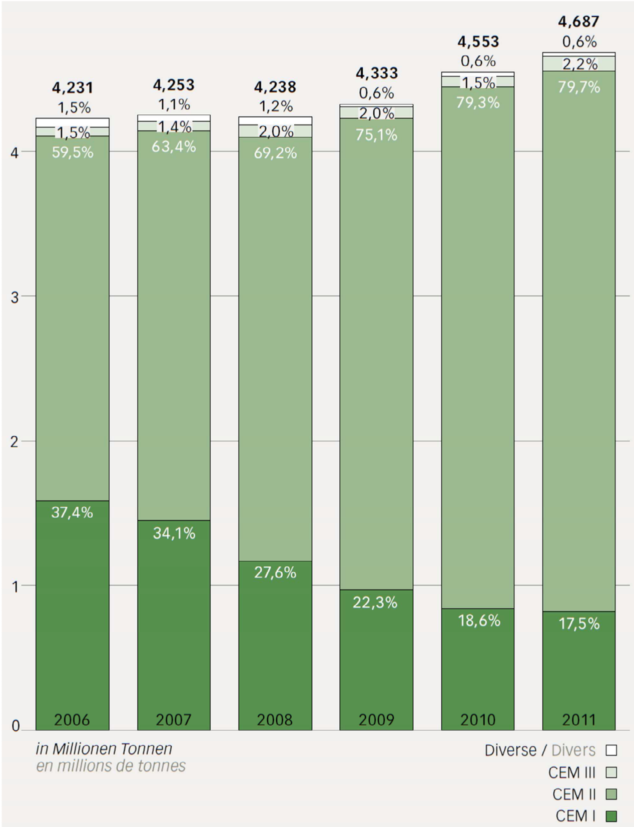

Figure 1: Cement delivered in Switzerland between 2006-2011, showing the subdivisions into different cement types [5]. Content of minor additional constituent and main constituents: CEM I = 0-5%, CEM II = 6-35%, CEM III = 36-95%.

3. Interaction between concrete and drinking water

The main chemical components of cement are calcium oxide (~ 60 %) and silicon oxide (~ 20%) with aluminum, iron and sulfur oxides as minor components. Additionally, traces of other elements including heavy metals are present. They end up in the cement as part of the raw material, mainly the clay, and as residue of the fuel used for the rotary kiln. Due to variations in the composition of the raw material and of the fuel, the composition of the cement exhibits certain variations. The mix design of concrete itself is adapted to requirements it has to meet. Now, what happens when concrete is contact with drinking water?

The cement hydrates in concrete are stable in a highly alkaline environment (pH 12.5-13.5). However, they are partially soluble when in contact with liquids of pH < 8. Depending on its source and on seasonal variations, drinking water has a pH between 6.5 and 8.0. Therefore, it is able to dissolve components of the cement hydrates. Firstly, the alkalis and calcium hydroxide go into solution and then the main hydrate phase calcium-silicate-hydrate (C-S-H) is partially dissolved. In this leaching process, mainly calcium goes into solution. This leads to an increased porosity of the concrete and to a weakening of the surface. This process is fairly complicated in detail, as calcium is not only dissolved but precipitated again as calcite close to the concrete surface. This calcite precipitation can occur either as a thin and dense calcite layer or as linings of pore walls in the leached area of the concrete (Figures 2 and 3). However, the effect on the concrete is the same: the surface of the concrete weakened by leaching is reinforced even when the initial strength is not reached anymore. The diffusion-governed leaching process is time dependent. At the first contact with drinking water, it progresses relatively fast but than slows down considerably, because the leached concrete surface provides a protection for the deeper-lying, not affected areas of the concrete. The pace with which leaching progresses is dependent on pH and water hardness. Soft water is relatively aggressive, hard water less so. Water from Lake Zürich, for example, exhibits an average water hardness of 18 French degrees (°F) an d can be classified as medium hard. During the condition assessment of a pre-ozonization chamber of a drinking water plant located at Lake Zürich, the concrete exhibited leaching phenomena up to a maximum depth of 12 mm after an exposure of 40 years. In the majority of the chamber, the original concrete surface was still present. Because leaching progresses very slowly after such long duration of exposure, no repair was needed. But this example clearly shows that drinking water is able to dissolve the cement paste of the concrete.

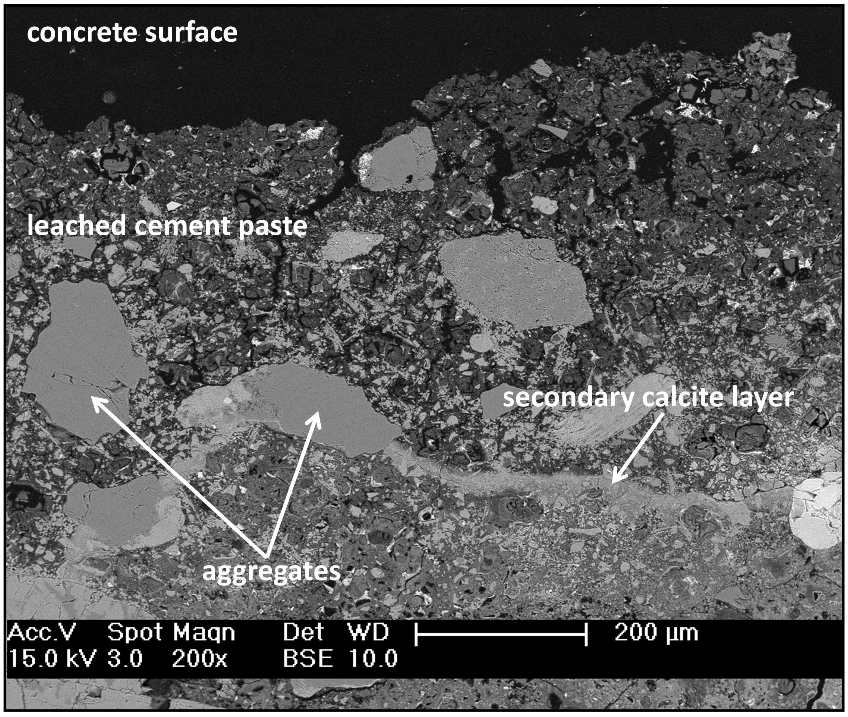

Figure 2: Leached area directly at the concrete surface and ensuing dense calcite layer. Image acquisition with scanning electron microscope.

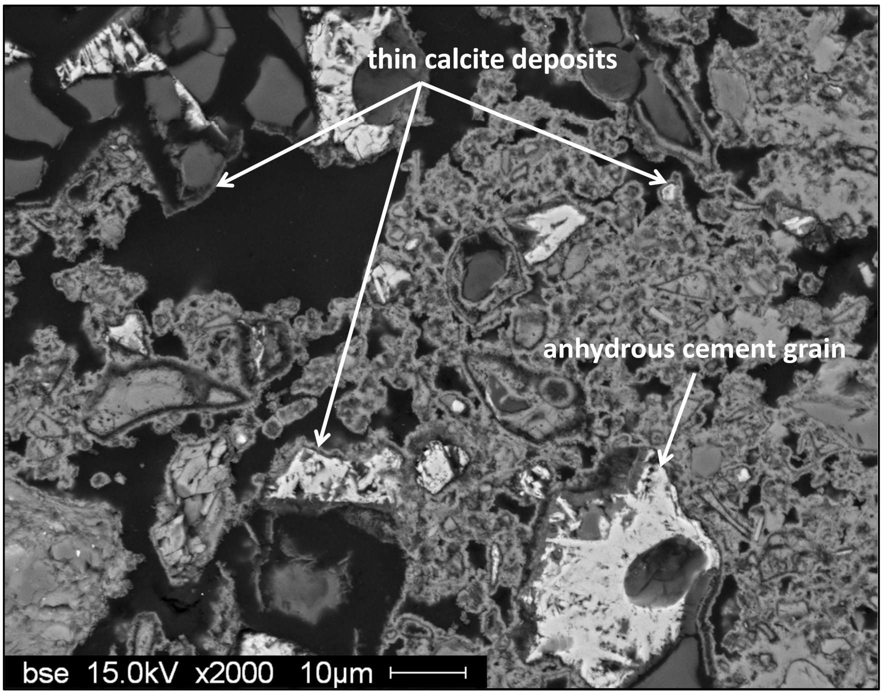

Figure 3: Precipitation of secondary calcite (bright layers) on pore walls in a previously leached area close to the concrete surface. Image acquisition with scanning electron microscope.

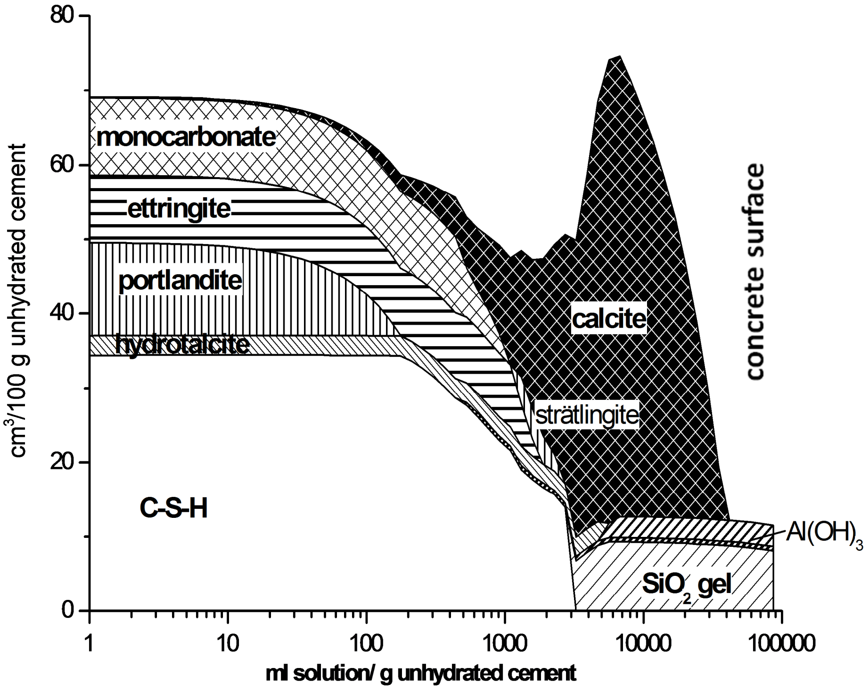

Figure 4: Phase composition determined with thermodynamic modeling at the concrete surface exposed to leaching by water with a hardness of 32 °F. On the left the original phase composition is shown and on the right the one formed by leaching and secondary calcite precipitation [6].

But what is the dissolution behavior of heavy metals? In the year 2000 the results of an in-depth Dutch study were published [7]. The subject was the leaching behavior of mortar produced with different cement types. The mortar bars were crushed before the start of the experiments to increase the surface area and to simulate a "worst case" scenario. The amount of dissolved zinc, vanadium, molybdenum, lead and chromium projected on the service life of the structure were clearly below the required limit values. Furthermore, the use of granulated blastfurnace slag as main constituent did not increase the amount of dissolved heavy metals. In an English investigation, leaching from concrete surfaces was determined during 250 days [8]. None of the used concrete specimens exposed 28 days after casting gave off heavy metals above the detection limit. In a Belgian project [9] heavy metals were dissolved in concentrations above the detection limit, however the values were well below the requirement of the European Directive 98/93/EC relating to the quality of water intended for human consumption [10] (Table 3). The amount of dissolved heavy metals decreased when granulated blastfurnace slag was used as main constituent. Furthermore, the leached heavy metals decreased from the start of the experiments by a factor of 5 to 30 within 64 days.

Element	Concrete produced with CEM I	Concrete produced with CEM III/A	Parametric values 98/83/EC
	[µg/l]		
Nickel	0.19-0.45	0.10-0.28	20
Chromium	0.31-0.71	0.13-0.29	50
Antimony	0.011-0.028	0.010-0.068	5
Selenium	<0.06	<0.06	10
Manganese	<0.006	<0.006	50
Mercury	<0.002	<0.002	1
Arsenic	<0.002-0.006	<0.002-0.007	10
Lead	<0.001-0.027	<0.001	10
Cadmium	<0.001-0.002	<0.001	2
Copper	<0.004-0.015	<0.004	2000

Table 3: Concentrations (minimum-maximum) of heavy metals leached from concrete compared to the parametric values of the European Directive 98/83/EC [Marion, 2005]. Concentrations <x are below the detection limit. CEM III/A = 36-65% granulated blast furnace slag.

In Switzerland the hygienic requirements for cement, mortar and concrete in contact with drinking water are tested and assessed according to the guideline DVGW W 347 (hygienic requirements for cementitious materials in contact with drinking water [11]). The guideline demands to test the amount of hazardous substances like arsenic, cadmium, nickel and lead in the components of mortar and concrete. Additionally, leaching of organic carbon and heavy metals from mortar and concrete specimens is determined. A spoiling of the drinking water in contact with the specimens is assessed in regard to color, clouding, foam formation and smell.

As described in the short literature overview, the concentrations of heavy metals leached from cementitious materials are well below the one detrimental to health. In addition to this situation, corresponding test for the concrete and its components are available.

4. Recommendations for the call for tenders of concrete in contact with drinking water

4.1 Introduction

The following information can be used calling for tenders of concrete in contact with drinking water. The recommendations are mainly based on the SN EN 206-1 [12] including national appendices and the SIA 262 [13]. These standards can be purchased at www.sia.ch.

4.2 Definition of the concrete (call for tender) and responsibilities

The concrete has to be defined in the project planning of a structure. By doing so, the owner or his representative has to ensure that all relevant requirements for the concrete properties are either defined as "designed concrete" or as "prescribed concrete". The definition that has to be passed to the concrete producer includes the concrete properties relevant for transport, casting and further treatment.

"Designed concrete" is defined in a way that the owner prescribes the properties and the concrete producer delivers a concrete meeting these properties. In the case of "prescribed concrete" the concrete producer delivers a concrete with the composition demanded by the owner. A decisive point is that the concrete producer is responsible for the concrete in the first case and the owner in the second case. If the owner demands "prescribed concrete", he is taking an unnecessary risk and is obliged to cover the costs for testing the properties of the concrete. Therefore, the national appendix of the SN EN 206-1 recommends calling for "designed concrete".

4.3 Designed concrete

If designed concrete is called for, all fundamental requirements and, if necessary, additional requirements have to be defined.

The specification of concrete shall contain:

- *requirement to conform to EN 206*
- *compressive strength class*
- *exposure classes (see clause 11 for the abbreviated format);*
- *D_{upper} and D_{lower} (grain size aggregates)*
- *chloride content class*

(SN EN 206-1:2000, clause 6.2.2)

In addition, for ready-mixed concrete and site-mixed concrete:

- *consistence class or a target value for consistence*

(SN EN 206-1:2000, clause 6.2.2)

Additional requirements can be called for (s. SN EN 206-1:2000, clause 6.2.3). Within these additional requirements it is possible to demand to test the concrete or the components of the concrete (excluding the aggregates) according to [11]:

- the concrete has to be tested according to DVGW W347

or

- cement and mineral additions have to be tested according to DVGW W347

If a producer of concrete components plans to use them for concrete in contact with drinking water, it is advantageous if he has already tested them according to DVGW W347. In such a case, he can immediately deliver his products for such a project.
A concrete producer cannot test all his mix designs in advance as the investment would be too large. Therefore, he will test the concrete only with a specific project at hand. As the test duration is three months, the concrete has to be tested already during the planning stage. The cost for the test has to be listed in the call for tenders as a separate position.

The testing of the concrete components is recommended for smaller projects. For larger projects the testing of concrete should be considered, if there is enough time during the planning stage.

The association of cantonal chemists (VKCS) and the association of the Swiss producers of admixtures (FSHBZ) have set up a guideline of requirements that have to be met by admixtures used in concrete in contact with drinking water. These requirements are judged by the SVGW. If approved, the product will be published in a "positive list" of admixtures permitted to be used for concrete in contact with drinking water. Consequently, the following can be demanded as an additional requirement in the call for tender:

- the used admixtures have to be present on the "positive list" of the SVGW

It has to be mentioned that all producers of cement, aggregates and admixtures as well as the majority of concrete producers are part of quality management systems and are additionally certified according to ISO 9001:2000 [14] and ISO 14001:2000 [15]. Concrete and its components are subjected to regular production controls that are conducted and assessed according to a variety of standards.

Another point has to be taken into account in the call for tender. There is a new guideline dealing with the prevention of the alkali-aggregate reaction (AAR) in concrete structures (SIA guideline 2042 [16]). The chemical reaction mainly occurs in massive structural members with high relative humidity and can lead to cracking of the concrete. Based on the environmental and risk class of a planned structure, a prevention class including a specific course of actions is defined. Depending on the conditions a specific drinking water reservoir is exposed to, it will be classified either in prevention class P1 or P2. In the first case, no actions are required. In the second case, the AAR resistance has to be proven (see Figure 1 of the guideline). This can be added to the call for tender as additional requirement (see Table 4).

4.4 Recommendation for the definition of "designed concrete"

A concrete meeting the requirements of exposure class XC4 is recommended for the use in structures or building components in contact with drinking water (Table 4). According to the national appendix of the SN EN 206-1:2000, the carbonation resistance of this concrete has to be tested. Many years of experience have shown that this concrete is always waterproof. A corresponding test can be demanded, but this is not necessary from a technological point of view.

requirement	meaning	
concrete according to SN EN 206-1	The concrete is subjected to a systematic production control that has to be certified regularly.	All concrete components need to have a corresponding certified production control, e.g. aggregates according to SN EN 12620 [17]
C30/37	strength class	Characteristic minimal compressive strength of cylinders $f_{ck,cyl}$ = 30 N/mm^2 and characteristic minimal compressive strength of cubes $f_{ck,cube}$ = 37 N/mm^2, respectively
XC4(CH)	exposure class	Cyclic wetting and drying of the concrete surface. In this exposure class, the minimum cement content has to be 300 kg of cement per m^3 of concrete and the w/c-ratio has to be ≤ 0.50.
Dmax32	Diameter of the maximum grain size of the aggregates	The maximum aggregate size has to be defined based on the distance between the reinforcement bars. The maximum grain size has an influence on the minimal cement content (see SN EN 206-1:2000).
Cl 0,10	chloride content class	In the current example 0.10 % for pre-stressed building components
C3	consistence class	Compaction value of 1.10 -1.04 (represents a concrete with good workability)
AAR-P2	AAR prevention class	Based on the risk class and the environmental class, a structure or building component is classified as AAR prevention class P2 according to SIA MB 2042 [16].

Table 4: Recommendations for the basic requirements of a designed concrete used for structures or building components in contact with drinking water.

Recommendation for the additional requirements:

- cement and mineral additions have to be tested according to DVGW W347
- admixtures have to be on the positive-list of the SVGW

Based on SN EN 206-1:2000 a concrete with the properties defined above will be defined using abbreviations as:

- **C30/37 XC4(CH) Dmax32 Cl 0.10 C3**
- cement and mineral additions have to be tested according to DVGW W347
- admixtures have to be on the positive-list of the SVGW
- AAR-P2

4.5 Curing of the concrete

Apart of choosing a suitable concrete for the structures in contact with drinking water, an appropriate curing is decisive for achieving a dense and durable concrete surface. Therefore, guidelines are given in the SIA 262 ([13] / chapter 6.4.6). Already in the call for tender, the curing class 4 should be defined for drinking water reservoirs as it is standard for structures with a service life of 50 or more years. For a planned service life below 50 years, curing class 3 is sufficient.

5. Summary

Drinking water mainly leaches calcium from the concrete. Heavy metals are only dissolved in amounts that are significantly below concentrations detrimental for health. The currently available data do not indicate an increase in the soluble heavy metals when mineral additions are used in the concrete. The diffusion governed leaching of concrete slows down considerably with time and the amount of dissolved ions decreases to a few percent of the initial one after a couple of weeks. In Switzerland, the concentration and the solubility of hazardous substances in concerte and its components are tested according to the DVGW guideline W 347 [11].

In the call for tender, concrete is defined according to SN EN 206-1 including national appendix and SIA 262. For drinking water reservoirs it is recommended to call for "designed concrete" with additional requirements demanding tests for concrete and its components according to DVGW guideline W 347 and demanding the use of admixtures present on the" positive-list" of the SVGW.

6. References

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