Leaching of organic admixtures from concrete

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Despite the small concentrations present in concrete, admixtures are viewed with concern by many authorities. This probably emanates from a lack of hard facts upon which sound judgments can be made. The existent information often has little or no relation to normal admixture use in concrete construction.

The objective of this article is to put the potential for admixture leaching into the context of concrete use according to EN 206-1: 2000 *Concrete: Specification, performance, production and conformity* and to give actual leaching results for the most commonly used admixtures under worst-case migration conditions.

Admixture use in concrete to EN 206-1.

Admixtures must demonstrate established suitability by conforming to the harmonised admixture standard BS EN 934-2: 2001 *Admixtures for concrete, mortar and grout. Concrete admixtures. Definitions, requirements, conformity, marking and labelling* with CE marking to Attestation of Conformity (AoC) level 2+.

EN 206-1: 2000 limits normal admixture use to 5% by weight of cement but, in practice, most admixtures are used at considerably lower dosages. Analysis of sales information(1) from the CAA suggests the types used and normal dosages shown in Figure 1.

Figure 1

Admixture Type to EN 934-2	**Proportion of total admixture sales %**	**Typical dosage range % by weight on cement.**
Superplasticisers	31	0.5 to 2.2*
Normal Plasticisers	45	0.2 to 0.7
Accelerating	2	0.5 to 2.0
Retarding	2	0.2 to 0.8
Air Entraining (AEA)	4	0.2 to 0.5
All other concrete admixtures	16	Up to 5%

(Dosage based on 40% solution, some superplasticisers will be sold at greater dilution with a correspondingly higher dose. In certain specialist applications such as very high strength concrete, these dosages may be exceeded.)*

It is clear from this information that the vast majority (85%) of all admixtures are of the plasticiser / superplasticiser types and that their dosage in most concrete does not exceed 2.2% by weight of cement.
As most concrete will have a cement content of less than 450 kg/m3, the admixture dosage on concrete falls to less than 0.4% by weight.

In the UK, admixtures used in concrete in contact with drinking water have been tested to BS 6920 for compliance with requirements on Taste, Odour, Appearance, Microbial Growth, Cytotoxicity and Extraction of Metals. The CAA reports that it is not aware of any admixture for concrete or mortar failing this test (but not all admixture types have been submitted for test). This article does not consider these parameters further but only considers information on migration of admixtures from concrete in contact with water.

Admixture composition

To aid accurate dispensing and subsequent dispersion, almost all admixtures are sold as solutions in water with a concentration normally less than 40%. This is certainly true for the first five groups listed in Figure 1 and means that the active concentration of admixture on cement is less than 0.8% or on the concrete less than 0.15% by weight.

A wide range of chemicals are used to formulate admixtures but for the plasticiser / superplasticiser types the main components come from one or a combination of the following four substances:

Lignosuphonate
Sulphonated melamine formaldehyde condensate (SMF)
Sulphonated naphthalene formaldehyde condensate (SNF)
Polycarboxylate ether copolymers. (PCE)

These substances will typically constitute 30 to 39% of the formulation in a 40% active admixture solution, sometimes modified with smaller amounts of one or more of the substances given below. None of these substances carry any form of health warning under current EU legislation.

Accelerators (ACC) are usually inorganic salts, such as calcium nitrate, and are rarely more than 30% active. Retarders are based on sugars, hydroxycarboxylic acids and polysaccarides and are normally less than 30% active. Air-entraining admixtures (AEA) are based on surfactants, usually less than 10% active.

The remaining active material (typically less than 1%) will be preservative, air and set control chemicals. At the 1% level, this group are present in the concrete at less than 0.005%.

A committee of experts at the DWI have looked at the toxicology of the substances used in the formulation of admixtures and the results of migration testing of the admixture. As a result, a list of permitted substances has been published that form the basis of permitted admixture formulations, see: http://www.dwi.gov.uk/drinking-water-products/approved-products/soslistcurrent.pdf section 2.4.

Theoretical Leaching of Admixtures from Concrete.

Leaching results are often expressed as TOC (Total Organic Carbon) as this is relatively easy to measure on a sample with unknown leachate using a carbon analyser.
Leaching results are usually related to a surface to volume ratio (s/v). This is the area of concrete in contact with a unit volume of water. One such ratio that is commonly quoted is 1.33dm^2 / litre. This is the s/v that is obtained in a water filled 300 mm diameter pipe. It is unlikely that concrete would be used in any smaller application and usually it would be much bigger, leading to a correspondingly lower s/v. The main exception to this is mortar lined steel pipes.

If the total admixture in the concrete is known, then a worst case leaching situation can be calculated and predictions made about the probable leaching in normal concrete.

If we assume that as a worst case:

The active admixture concentration is 0.15% on concrete weight as calculated above.
The entire admixture in the top 20 mm of the concrete is leached out over the first contact period.

The admixture concentration leached into the water will be less than 1g /litre.
TOC will depend on the chemical composition of the admixture but will be about 650mg/litre. *(1g = 1000 mg)*

It is unlikely that such rapid leaching of admixture would ever occur from concrete. Most admixtures become chemically bonded to the cement and for those that are free, concrete has a very low permeability. On a theoretical basis one would expect that, after the first few cycles, the TOC due to admixture leaching would be several orders of magnitude lower than the theoretical maximum of 650mg/litre and practical leaching tests confirm that this is the case.

Practical Leaching tests on Admixtures.

For approvals purposes, the UK Drinking Water Inspectorate (DWI) required information on the leaching of admixtures from concrete in contact with drinking water[(2)]. To this end a project was initiated with the Cement Admixture Association (CAA) and water research specialists WRc-NSF Ltd. This project considered factors affecting leaching as determined by TOC analysis. Gas chromatography & Mass spectrometry (GCMS) was also undertaken on the leachates to detect minor admixture components and unexpected reaction/degradation products.

A synopsis of the test method is given below:

Concrete to EN 480-1
Washed gravel aggregates (max 20 mm)
Admixture dosage 110% of the maximum recommended by the manufacturer.

Test concrete is water reduced to give a target consistence of 125 mm slump
Control mixes without admixture carried out at the start and finish of each test series.

Cured in 1 litre HDPE (high density polyethylene) cube moulds for 7 days at 20^{o}C and >90% RH
Demoulded and cured for 3 days at 20^{o}C and >90% RH
Rinsed with tap then deionised water.
Sprayed with 100 mg/lit aqueous solution of free chlorine
Allowed to stand for 30 min
Rinsed with tap then deionised water.

Leaching commenced at 10 days after mixing
Surface to volume ratio s/v 1.3 dm^{2}/lit
Deionised water with 5 mg/lit sodium hypochlorite used as test water
3 day leaching periods followed by water change up to 48 days (16 x 3 day leaching periods)

This test regime is stringent and was regarded as simulating a worst case situation. It is more stringent that that currently being proposed for the EAS[3] (European Acceptance Scheme for construction products in contact with drinking water) The high dosage and short curing period, the lack of water curing and limited washing/aqueous preconditioning prior to the leaching test will all maximise the probability of admixture leaching occurring.

The Tests
Eight admixtures were tested in this programme, covering all the types in Figure 1 except retarders.
One admixture type selected from the 'other admixtures group' was designed to migrate within the concrete and also had a high dosage (4%). It was selected as being an absolute worst case situation expected to show maximum leaching. It did exhibit the highest leaching and its results have been separated out.

The results for 7 of the 8 admixtures are given in Figure 2. They are the mean of two sets of tests carried out 4 weeks apart and include the means of the controls mixes without admixture. Control 1 was carried out at the start of each days test series and control 2 at the end of the day.
The leaching is shown as TOC (Total Organic Carbon) after each 3 day period of leaching.

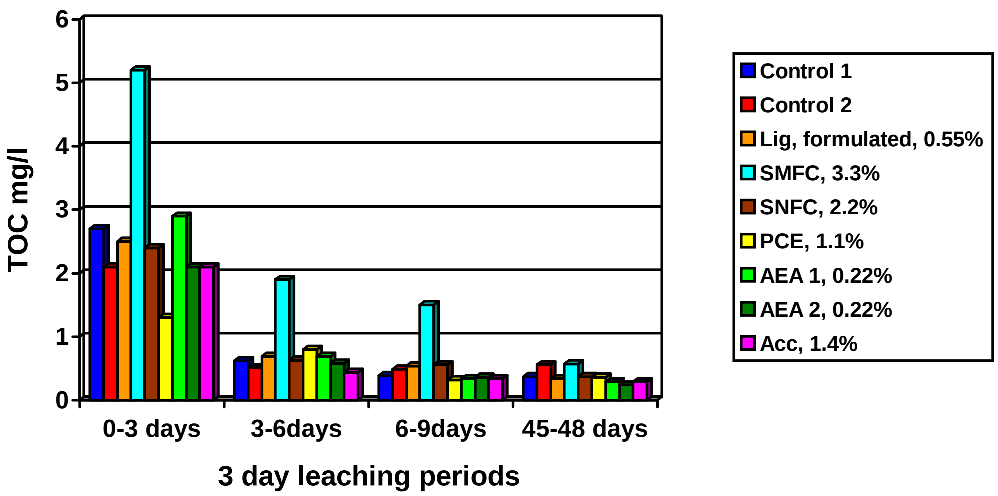

Figure 2

The rate of leaching falls off very quickly and is generally less than 500 micrograms (μg) per litre after the third 3 day leaching period. (1g = 1,000,000 μg)
The admixture leaching is generally insignificant when compared to the background leaching from the control mixes.
From Figure 2, the only admixture to show leaching that is significantly above that of the control mixes is the Sulphonated melamine formaldehyde condensate and even here the level has dropped back close to that of the controls by the sixteenth 3 day leaching period at 45 to 48 days.

The eighth admixture was tested at a high dose of 4.4% on cement weight and it was a type designed to be migratory within the concrete. It was therefore expected to show significant leaching and the results confirmed this, see Figure 3.

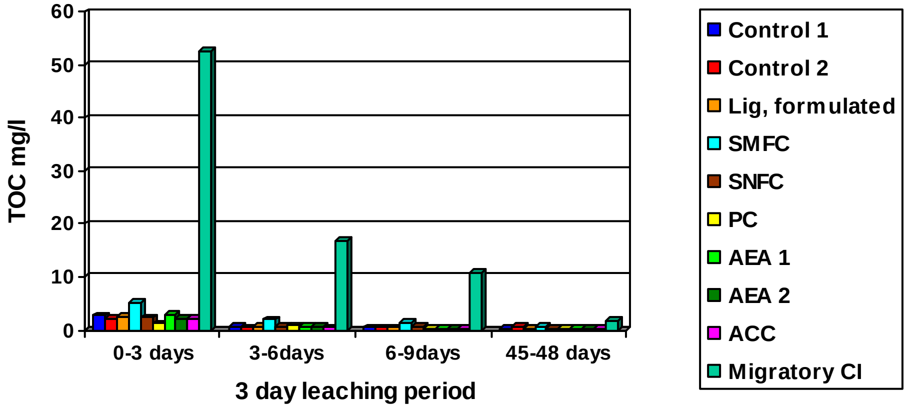

Figure 3

The TOC leaching results are summarised in Figure 4 as a difference on the mean TOC of the control mixes in micrograms μg (thousandths of a milligram) per litre over the third and sixteenth, 3 day leaching periods.

Leaching Period	**6-9 days**	**45 – 48 days**
Average Control	440 µg	465 µg
	Change on control	Change on control
Lig, formulated	+ 100 µg	- 125 µg
SMFC	+ 1 060 µg	+ 105 µg
SNFC	+ 120 µg	- 95 µg
PCE	- 100 µg	- 175 µg
AEA 1	- 100 µg	- 175 µg
AEA 2	- 120 µg	- 225 µg
ACC	- 100 µg	- 175 µg
Migratory CI	+ 10 460 µg	+ 1 335 µg

Figure 4

After 16 leaching cycles, only two of the admixtures are still giving TOC values above those of the control and the remainder are all lower, suggesting that the admixture may have helped to reduce the permeability of the concrete.

The migratory admixture has shown leaching over 10 milligrams per litre above control after 3 cycles but by 16 cycles, the maximum leaching has fallen to below 2 milligrams per litre.

The GCMS detected large numbers of substances, known and unknown but almost all were also present in the control mixes without admixture. Where substances were found only in the admixture lechates, they were mostly present in only one of the two samples and at levels below 5 micrograms per litre.
GCMS did detect the defoaming agent from the modified lignosulphonate in the first leaching cycle and formaldehyde from the SMFC superplasticiser even after 48 days.

Other testing within the project looked at the effect of water hardness, admixture dosage and cement type. These tests were more limited but suggested that these factors did not have a very significant effect on the result.

German Leaching tests.

In Germany, all admixtures are subject to a leaching test if they are to be approved for use in concrete in contact with drinking water. The test conditions appear to be less stringent than those detailed above with a lower admixture dosage, curing for a longer period and curing in water so that some leaching will have occurred before the TOC leaching test starts. The basis of the assessment is also different so direct comparison with the UK results is not possible but the trend is generally similar as shown in Figure 5.

In these test results[4] it appears that the control value has been subtracted from the admixture leaching result in order to show that the leaching of the admixture is in compliance with German regulations of 10 milligrams per metre squared per day (mg/m^2/day).

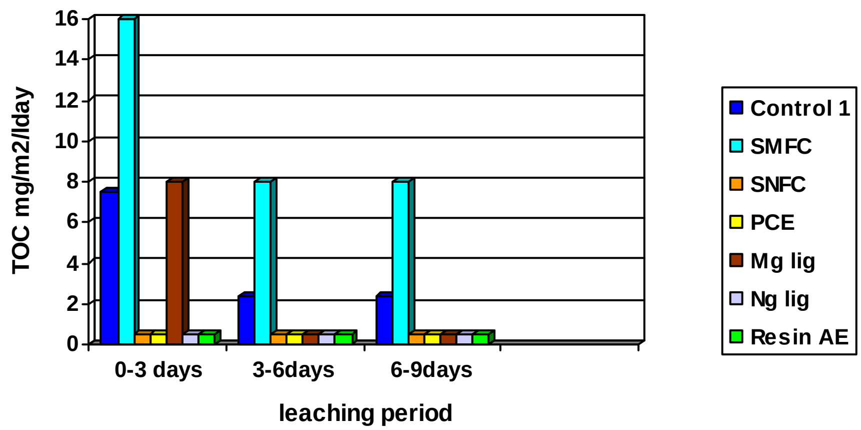

Figure 5

Conclusions

Concrete is an essential construction material and admixtures play a key part in ensuring performance and durability. However, health and environmental effects associated with admixture use must be considered. Leaching of admixtures from the hardened concrete would be of importance where concrete is in contact with drinking water and in normal structures where leaching could affect the environment in which it is placed.

Concrete production and admixture use are normally controlled by European Standard EN 206-1 and within the constraints of this standard it is clear that the quantity of admixture available to leach is very small. Concrete is a dense low permeability material where movement of dissolved substances is very slow. It is inconceivable that all of the admixture could leach out in one or two contacts with water. Theoretical consideration of the total available admixture in concrete, even when added at maximum dose, suggest that TOC in the leachate will be measured in micrograms per litre.

Leaching tests on concrete containing high dosages of admixture and under aggressive leaching conditions confirm that there is minimal leaching of the admixture. After 3 leaching cycles, the total TOC leached from a control concrete without admixture is generally less than 0.0005grams per litre per 3 day leaching period. The tests with admixture are similar or in many cases lower than the control suggesting that admixtures may actually reduce the total leaching by reducing permeability in the concrete.

The testing conditions used were more extreme that those currently being proposed by the EAS (European Acceptance Scheme for construction products in contact with drinking water). The evidence shows that for the commonly used admixtures conforming to EN 934 and used in accordance with concrete standard EN 206-1, there is no significant risk of leaching of admixtures from the concrete, even when used at maximum recommended dosage.

References

(1) CAA sales statistics 2007 (private communication).
(2) DETR/DWI report number 4869 (private communication).

(3) European Acceptance Scheme for construction products in contact with drinking water (EAS). http://europa.eu.int/comm/enterprise/construction/internal/essreq/eas/easrep.htm.
(4) Admixture manufacturer test reports (private communication).