Long-term leaching of environmentally hazardous substances in admixtures, emitted from concrete

Åse Andersson Lic.Tech.

Department of Building materials. Chalmers University of Technology. SE-412 96 Gothenburg. Sweden. Phone: +46 31 772 2333. Fax: +46 31 772 2296.
E-mail: andersson@bm.chalmers.se

1. INTRODUCTION

Studies on the environmental effects of building materials often focus on manufacturing and destruction processes, with emphasis on energy use and depletion of resources. This study discusses potentially hazardous substances in concrete and the diffuse emission of these substances to surrounding environments during use. Concrete is one of the most widely used construction materials. The use of admixtures in concrete is steadily increasing and as much as 700,000 tons of admixtures were according to Mäder (2000) used in Western Europe in 1999. The growing interest in environmental issues in the building sector has drawn attention to these admixtures, particularly concerning the risk of environmentally hazardous substances released.

Several studies e.g. by Hillier et al (1999) and Andersson (1999) have been carried out on the topic of leaching from concrete, above all on the leaching of heavy metals originating from concrete additives such as fly ash and blast furnace slag. Studies on the release of organic substances have to a great extent focused on water-reducing superplasticizers, which represent the largest volumes used, see Pollet et al (1997). However, the concentration of hazardous substances in superplasticizers are usually very low.

In this study the focus is on elements with proven ecotoxicological effects, present in commonly used concrete admixtures. The studied substances are sodium thiocyanate, resin acids (in tall oil) and nonylphenol ethoxylate. The chronic toxicity to fish and humans, and the genotoxic effects of nonylphenol and resin acids of these elements are well documented but reviewed elsewhere (Lanno et al (1996); Mörck et al (2000); Burggraaf et al (1996); Pacheco et al (1999); Lye et al (1999)

The admixtures concerned improve the concrete in different ways. Thiocyanate accelerates the hydration and increases the strength. Air-entraining admixtures provide an even distribution of air bubbles in hardened concrete, and thereby frost resistance. Natural polymers, such as tall oils, are besides tensides like nonylphenol ethoxylate the main products used. Resin acids in tall oil are diterpenoid carboxylic acids present in most softwood species; dehydroabietic acid and abietic acid being the most abundant, according to Back et al (2000).

In an earlier study, Andersson et al (2001), the diffusion based leaching of thiocyanate and resin acids in concrete admixtures were studied. The time-dependent release were measured during 30 days showing that a diffusion steered leaching is present, and that 6-8% of the studied elements were released from 4*4*16 cm pieces of concrete in water that was changed four times. But still there is a lack of information on the long-term leaching, and about the amount available for leaching, i.e. the amount that is not firmly bound to the cement matrix. The main focus in this report is therefore on the amount of elements that can be leached in a long-term perspective.

2. LEACHING TESTS

2.1 Materials and methods

Materials and admixtures used for the concrete test specimens are presented in Table 1. The abbreviation used for each admixture is later used for the results of the concrete specimens. One accelerating admixture (A) with thiocyanate and two air-entraining products AEA1 and AEA2 were used. The thiocyanate containing concrete (A) and one of the AEA's (AEA 1A) was made at an earlier occasion, and has been stored 3 years in a climate chamber with 20 °C and 85 % relative humidity. This type of concrete was first cured in moulds for one week and then stored in 85% for 20 weeks. The other, newer type was cured in the moulds for 24 hours, then water cured in 25 ° and 100% relative humidity for another 24 hours, and finally water cured in 20 °C for another 72 hours. After two weeks storage at 20 ° C and 50 % RH the specimens were crushed into a size < 2 mm and a size of < 10 mm. This applies to all concretes but four 4*4*16 cm specimens of concrete A, which have been studied in an ongoing diffusion test since 990113 and will also be reported here.

Table 1 Materials and admixtures used for the concrete specimens.

Cement:	Swedish Portland cement (PC1) complying with ENV 197 (Skövde)
Aggregates:	Crushed rock in 8-12 mm, gravel in 0-8 mm, sand in 0.068 - 0.354 mm and 0.125 - 0.707 mm, fine quartz sand (as filler)
Added was one of following three admixtures:	
1,25% of cement content:	Accelerator (A), containing 7% sodium thiocyanate (CAS 540-72-7)
0,4% of cement content:	Air-entraining agent (AEA1), containing 5% tall oil resin (CAS 8050-09-7)
0,2% of cement content:	Air-entraining agent (AEA2), containing 18% tall oil (CAS 8002 26-4), 5-10% alkyl ethoxylate sulphate (CAS 68585-34-2) and 0,2 % nonylphenol ethoxylate (CAS 9016-45-9)

The existing standard leaching test for concrete, NEN 7341, is an availability test that aims at determining the fraction that is available for leaching, by stirring finely ground (<125 μm) concrete specimens in demineralised water at pH=7 for three hours, and at pH=4 for another three hours. The test gives information about the long-term leaching — but not the time-dependency. In that extremely aggressive environment very little of the function of the material is left. The ambition here has been to test the concrete during conditions which are aggressive, i.e. small size of the concrete particles, a high liquid/solid ratio and a duration of 24 hours, but with no added acid and a much larger size of the grounded particles than in the standard. The test is still very much an acceleration of the leaching in reality for concrete that is still functioning as a construction material. For concrete as a filler material in road banks etc the test is more realistic. We used 30 mg of material to 1 litre of nano-pure water, covered the beaker and let the water circulate rather slowly, without moving the concrete around. After 24 hours the water was filtered and analysed.

The diffusion test with concrete type A that has been ongoing since 990113 has been part of a larger diffusion leaching test with concretes containing tall oil (AEA 1A), thiocyanate (A) or different types of slag and fly ashes (containing heavy metals). The test is to a great extent completed and has been reported earlier, see Andersson (1999), Andersson et al (2001), but the thiocyanate test was proceeded to see what will happen at a longer perspective. When the test started in 1999, the concrete specimens were placed in containers filled with nano-pure water so that all sides were covered. The liquid/solid ratio was 5 [m^3/m^3] and the leached water was renewed and analysed four times during 30 days. The thiocyanate containing concrete was then left for over three years until now when the final analysis of the water was made.

3 RESULTS AND DISCUSSION

3.1 Availibility test

The availability test showed quite a few interesting results, displayed in Figure 1 and Figure 2. One of the admixtures, AEA 1, has been bought at two occasions (1A and 1B). It seems as the content of the product has been changed rather much, if comparing the results from the old product, AEA 1A and the new product AEA 1B in Figure 1. The old concrete showed a much higher leaching than the newer, both in absolute figures and if compared to the amount that was added from the start. The leached amount is remarkably low for the newly bought product, which can imply that the content of resin acids in this product is lower, giving a too low estimation of the percentage of the original content that is leached. Further, almost only one acid was detected – the toxic dehydroabietic acid. Also compared to the earlier diffusion tests, where 6-8 % were leached during a month in a much slower leaching test, the figure of 2-3% leaching must be regarded as uncertain. However, the absolute value of the leaching is definitively lower than for AEA 1A.

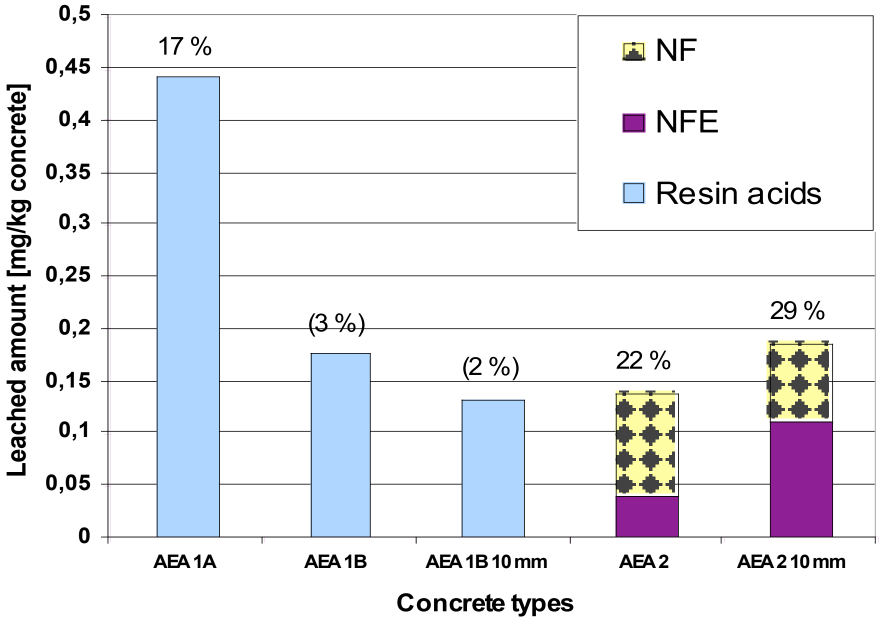

Figure 1 Leached amount of resin acids, NF and NFE in 24 hours availability test.

The other air-entraining agent, AEA 2, was only tested for its content of nonylphenol ethoxylate (NFE), even though it also contains 18 % of tall oil. The whole water volume was needed for the NF-ethoxylate analysis and its is very likely that this tall oil product would behave similarly to AEA 1. The result shows that 22 % of the NF- elements in the small-sized concrete and 29 % of the NF –elements in the concrete with particles < 10 mm were leached. More surprising is the detection of nonylphenol in the water. The product is said to contain a small dosage of NF-ethoxylate, but the results show a big fraction of nonylphenol as well. Nonylphenol is a very toxic substance and also very stable in the nature. One possible explanation is that the nonylphenol ethoxylate has been transformed to nonylphenol, an ordinary process in nature but still surprising here, as the time between concrete casting, leaching process and chemical analysis was very fast. Interesting is also the fact that as much – in fact even more – is leached from the concrete with large particles. Moreover, the relation between the nonylphenol ethoxylate and the nonylphenol is very different, with a higher content of NFE in the concrete with large particles. It seems as it has been easier to degrade the NFE in the concrete with small particles. The phenomena can not easily be explain by uncertainties in the chemical analysis, which had very good accuracy.

The availability was also tested for concrete with thiocyanate. In earlier tests we have received very high leaching levels, and wanted to see if this was repeated yet again. In Figure 2 the fraction of the added amount that was detected in the water is displayed, showing that the percentage of leached thiocyanate is very high: 71 % of the added amount. In addition, the leaching of thiocyanate is also very high in absolute figures: 141,6 mg/ kg concrete.

Thiocyanate seems to be very easily soluble in water, which can be the reason behind this behaviour. It is also very clear that thiocyanate is not firmly bound to the cement matrix.

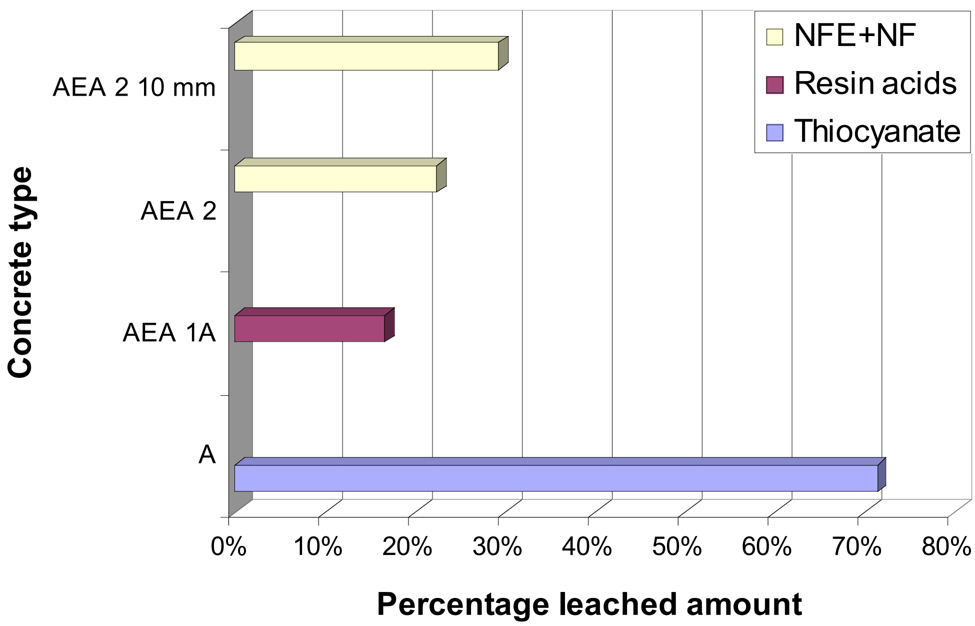

Figure 2 Percentage of originally added substance that is leached in the availability test.

Diffusion test

Also the leaching pattern for the diffusion tests that have been carried out earlier, shows a different leaching behaviour between the thiocyanate and the resin acids. Where the resin acids shows a continuous diffusion curve from the start to the last water renewals, the thiocyanate is emitted very fast in the beginning and very slowly already after 30 days, see Andersson (2001). To see whether the thiocyanate is still leached, but with a slower rate, the test was prolonged for over three years. The result is viewed in Figure 3, where the new figures are added to the old leaching pattern. The chart clearly shows that the diffusion of thiocyanate goes from a very high rate in the beginning, to a slow but still ongoing release after the third water renewal, which was after 15 days. This particular leaching pattern is intensified by the fact that all four specimens show exactly the same curve.

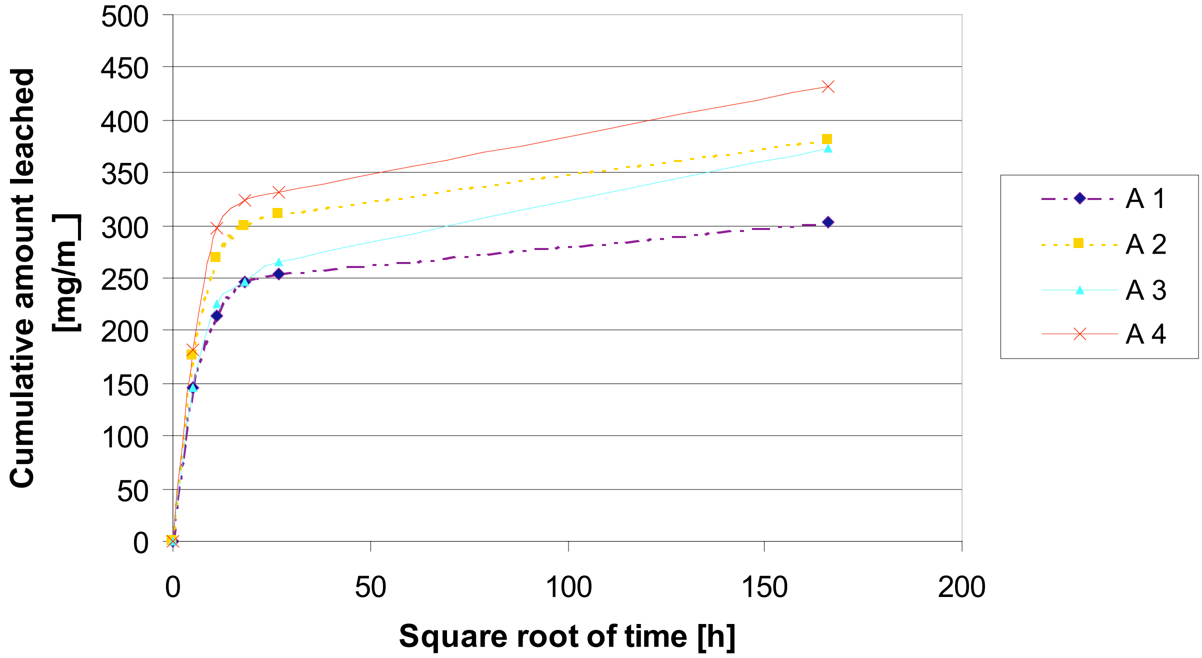

Figure 3 Cumulative leaching of thiocyanate from concrete specimens with accelerator A added. A1-A4 represent each specimen. Diffusion test with L/S ratio=5, renewed 5 times during 1146 days; after 1 day, 5 days, 14 days , 30 days and finally 1146 days.

CONCLUSIONS

From the laboratory results presented here, some main conclusions can be made:

- The long-term leaching behavior for elements in concrete admixtures is not uniform, but vary with the solubility of the element, and with the way the element is bound to the cement matrix.

- The long-term leaching for nonylphenol elements is ~20-30% of the added amount. The concrete emits not only nonylphenol ethoxylate but also nonylphenol – a more toxic, genotoxic and low-degradable substance.

- The long term leaching varied for the resin acids, which may be caused by an alteration of the tall oil mix used, to a lower content of resin acids. This possible modification of the product is very positive from an environmental point of view.

- The leached amount of thiocyanate in the availability test was very high, both in concentration and in percentage of added product.

The main reflections that can be made from the results of this study, is that hazardous substances in concrete admixtures can be released, slowly when functioning as a construction material, but faster when being crushed and reused in road banks etc. The results show the necessity of knowing what is being added to concrete, as the market for reuse of materials is growing and will continue to grow, with regard to other important environmental aspects.

6. REFERENCES

Andersson, Å. 1999. Hazardous substances emitted from concrete – first study on leaching properties. In *Utilizing Ready-Mixed Concrete and Mortar*; (Dhir, R.K., Limbachiya, M.C., editors). Proc. Dundee, pp. 345-355.

Andersson, Å. and Strömvall, A.-M. 2001. Leaching of concrete admixtures containing thiocyanate and resin acids. *Environ. Sci. Technol*. Vol. 35, no. 4, pp. 788-793.

Burggraaf, S., Langdon, A.G., Wilkins, A.L. and Roper, D.S. 1996. Accumulation and depuration of resin acids and fichelite by the freshwater mussel hyridella menziesi. *Environ. Toxicol. Chem.,* 1996, Vol.15, pp. 369-375.

Hillier, S.R., Sangha, C.M., Plunkett, B.A. and Walden, P.J. 1999**.** Long-term leaching of toxic trace metals from Portland cement concrete. *Cem. Conc. Res*.,Vol 29, pp. 515-521.

Lanno, R.P. and Dixon D.G. 1996. Chronic toxicity of waterborne thiocyanate to rainbow trout (Oncorhynchus mykiss), *Can. J. Fish. Aquat. Sci.*, Vol. 53, pp. 2137-2146 .

Lye, C.M., Frid, C.L.J., Cooper, D.W. and Jones, D.M. 1999. Estrogenic alkylphenols in fish tissues, sediments, and waters from the UK Tyne and Tees estuaries. *Environ. Sci. Technol.* Vol. 33, pp. 1009-1014.

Mäder, U. 2000. European Dederation of Concrete Admixtures Associations (EFCA). Personal communication.

Mörck, R., Björklund Jansson, M. and Dahlman, O. 2000. Resinous compounds in effluent from pulp mills. *Pitch Control, Wood Resin and Deresination*, (Back E.L., Allen L.H., editors). pp. 245-263. Tappi Press, Technology Park, Atlanta.

Pacheco, M. and Santos, M.A. 1999. Biochemical and genotoxic responses of adult eel (*Anguilla anguillla* L.) to resin acids and pulp mill effluent: laboratory and field experiments. *Ecotoxicol. Environ. Saf.*, Vol. 42, pp. 81-93.

Pollet, B. Germanneau, B. and Defossé, C. 1997. Fixation des adjuvants de type polynaphtalène ou polymélamine sulfonate dans les mortiers et bétons. *Mat. Struct.* Vol 30, pp. 627-630.